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THÈSE présentée par :

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Tailor-made heterofunctional poly(ethylene oxide)s *via* living anionic polymerization as building blocks in macromolecular engineering

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Gladys Pozza

A ma maman,
A ma famille.

This PhD research project has been effected in the under Cotutelle between two universities: The University of Jena, Germany and the University of Strasbourg.

I was member of European Doctoral College of the University of Strasbourg during the preparation of my PhD, from 2011 to 2014, class Immanuel Kant. I benefited from specific financial support offered by the EDC. I have followed a special course on topics of general European interests presented by international experts.

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I want to clarify, I wrote myself the acknowledgments and nobody has corrected my English or my French!

Table of content

Documentation of authorship

This section contains a list of the individual authors' contribution to the publications reprinted in this thesis.

1 "Macromonomers as well-defined building blocks in the synthesis of hybrid octafunctional star-shaped poly(ethylene oxide)s"

Gladys M.-E. Pozza, Hassan Harris, Markus J. Barthel, Jürgen Vitz, Ulrich S. Schubert, Pierre J. Lutz

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Gladys M.-E. Pozza:	Conceptual development, synthesis and characterization of the polymers, preparation of the manuscript
Hassan Harris:	Conceptual development, synthesis and characterization of the polymers
Markus J. Barthel:	Conceptual development, synthesis and characterization of the polymers, preparation of the manuscript
Jürgen Vitz:	Conceptual development, synthesis and characterization of the polymers
Ulrich S. Schubert:	Correction of the manuscript, supervision
Pierre J. Lutz:	Conceptual development, correction of the manuscript, supervision

2 "Precise synthesis of undecenyl poly(ethylene oxide) macromonomers as heterofunctional building blocks for the synthesis of linear diblocks or of branched materials"

Gladys M.-E. Pozza, Markus J. Barthel, Sarah Crotty, Jürgen Vitz, Felix H. Schacher, Pierre J. Lutz, Ulrich S. Schubert

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Markus J. Barthel:	Conceptual development, synthesis and characterization of the polymers, preparation of the manuscript
Sarah Crotty:	MALDI-ToF MS measurements
Jürgen Vitz:	Conceptual development, synthesis and characterization of the polymers, preparation of the manuscript
Felix H. Schacher:	Correction of the manuscript
Pierre J. Lutz:	Conceptual development, correction of the manuscript, supervision
Ulrich S. Schubert:	Correction of the manuscript, supervision

3. “SAXS studies of the molecular and structural parameters of hybrid PEO/POSS star-shaped materials”

   Gladys M.-E. Pozza, Sarah Crotty, Michel Rawiso, Ulrich S. Schubert, Pierre J. Lutz

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Gladys M.-E. Pozza:	Conceptual development, synthesis and characterization of the polymers, preparation of the manuscript
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4. “End-group functionalized polyisoprene-*b*-poly(ethylene oxide) prepared by combining anionic polymerization and click chemistry”

   Gladys M.-E. Pozza, Jürgen Vitz, Pierre J. Lutz, Ulrich S. Schubert

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5. “Hybrid polystyrene star-shaped polymers with octafunctional silsesquioxane cores”

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Jean-Michel Guenet: Correction of the manuscript

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Declaration of the supervisors:

Dr. Pierre J. Lutz

Prof. Dr. Ulrich S. Schubert

List of abbreviations

AIBN: Azobisisobutyronitrile

AROP: Anionic ring-opening polymerization

ATRP: Atom transfer radical polymerization

Bipy: 2,2’Bipyridine

$CDCl_3$: Deuterated chloroform

CH_2Cl_2: Dichloromethane

cmc: Critical micelle concentration

CuBr: Copper(I) bromide

DABCO: 1,4-Diazabicyclo[2.2.2]octan

DLS: Dynamic light scattering

DMF: *N,N*-Dimethylformamide

DMPA: 2,2-Dimethoxy-2-phenylacetophenone

DMSO: Dimethylsulfoxide

DPMK: Diphenylmethyl potassium

DSC: Differential scanning calorimetry

EO: Ethylene oxide

EXPTFE: Expanded polytetrafluoroethylene

FTIR: Fourier transform infrared spectroscopy

FRP: Free radical polymerization

LS: Light scattering

MA: Methacrylic anhydride

MALDI-ToF MS: Matrix assisted laser desorption ionization – time of flight mass spectrometry

MMA: Methyl methacrylate

NaH: Sodium hydride

NaOH: Sodium hydroxide

M_n: Number average molar mass

M_w: Mass average molar mass

NMR: Nuclear magnetic resonance

OEGMA: Oligo(ethylene glycol) methyl ether methacrylate

PDI: Polydispersity index

PEG: Poly(ethylene glycol)

PEGMA: Poly(ethylene glycol) methyl ether methacrylate

PEO: Poly(ethylene oxide)

PHBP: Propargyl 2-hydroxylmethyl-2-(α-bromoisobutyraloxymethyl)-propionate

PI: Polyisoprene

PI-*b*-PEO: Polyisopene-*b*-poly(ethylene oxide)

PI-N_3: ω-Azido polyisoprene

PI-OH: ω-Hydroxy polyisoprene

PI-Ts: ω-Tosyl polyisoprene

PMDETA: *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine

PMMA: Poly(methyl methacrylate)

POSS: Polyhedral oligomeric silesquioxanes

PS: Polystyrene

RT: Room temperature

$Q_8M_8^H$: Octakis(dimethylsilyloxy)silsesquioxane

$Q_8M_8^{PEO}$: PEO star-shaped polymer with octakis(dimethylsilyloxy)silsesquioxane core

SAXS: Small angle X-ray scattering

sec-BuLi: *Sec*-butyllithium

SEC: Size exclusion chromatography

SLS: Static light scattering

*t*Bu-P_4: Phosphazene base

TEA: Triethylamine

TEM: Transmission electron microscopy

TGA: Thermogravimetric analysis

THF: Tetrahydrofuran

TsCl: Toluenesulfonyl chloride

Résumé

1.1. Introduction générale

Le poly(oxyde d’éthylène) (POE) est un polymère hydrosoluble largement utilisé, tel quel ou associé à d’autres polymères, dans de nombreuses applications. Il peut être modifié facilement. Il n’est pas toxique et n’est pas reconnu par le système immunitaire. Il se caractérise par une bonne hémo et biocompatibilité. Incorporé dans les structures de réseau ou greffé sur des surfaces, le POE et les matériaux à base de POE se prêtent bien à des applications biomédicales très diverses. Le POE constitue également une brique élémentaire de choix pour l’élaboration d’architectures macromoléculaires complexes.

Le premier chapitre de la thèse sera consacré à une discussion très générale, à partir de données bibliographiques, sur l’oxyde d’éthylène, sa polymérisation et les principales caractéristiques du POE. Dans le même chapitre, les différentes méthodes de polymérisation seront rappelées brièvement. Une attention particulière sera portée à la méthode de polymérisation anionique et plus particulièrement à la polymérisation anionique par ouverture de cycle (PAOC) de l’oxyde d’éthylène. Les différents amorceurs permettant d’accéder par PAOC à des POEs linéaires de masse molaire parfaitement contrôlée et caractérisés par une distribution de masse molaire étroite seront présentés. La PAOC de l’oxyde d’éthylène fait en général appel à un alcoolate potassique obtenu par réaction entre un alcool avec une base forte. L’utilisation de cryptants, d’une base phosphazène ou de complexes d’aluminium lors de la PAOC de l’oxyde d’éthylène sera aussi discutée. La présence de ces additifs permet en effet de polymériser l’oxyde d’éthylène y compris lorsque l’on fait appel à un amorceur ou macroamorceur lithié.

Une partie conséquente de ce premier chapitre sera consacrée à une discussion approfondie sur la synthèse de macromonomères de POE. Les deux principales approches de synthèse permettant d’accéder à des macromonomères de POE seront discutées dans une deuxième partie du premier chapitre. L'insaturation peut être introduite soit au cours de l'amorçage, soit lors de la désactivation induite des sites actifs à l'aide d'un composé électrophile insaturé.

Les macromonomères constituent en effet de précieux intermédiaires pour la synthèse de copolymères greffés ou de copolymères à structure en peigne bien définis. Ils peuvent aussi bien se prêter, comme on le verra dans notre travail, à la synthèse de copolymères à blocs, de polymères à structure en étoile, voire de réseaux macromoléculaires. Les POEs décorés d'insaturations en extrémité de chaîne sont de plus en plus utilisés dans des réactions de post-polymérisation, par exemple, par thiol-ène « click » réaction pour introduire des composés bioactifs (unités de sucre).

Les POEs ramifiés représentent une autre classe de composés à base de POE auxquels de nombreux travaux ont été consacrés aux cours des années. Des polymères ramifiés à base de POE très divers ont été synthétisés et étudiés : polymères à structure en étoile, en peigne, hyperramifiés ou à structure dendritique. La synthèse de ces POEs ramifiés est dictée non seulement par l'intérêt pour l'élaboration d'architectures macromoléculaires bien définies ou par le désir de disposer de modèles pour des études physico-chimiques, mais aussi par leur utilisation particulièrement dans le domaine des applications biomédicales. Les architectures à structure en étoile à base de POE peuvent être préparées, soit en faisant appel à des amorceurs multifonctionnels, soit par réaction des extrémités de chaîne de POE monofonctionnels avec des composés multifonctionnels dotés de fonctions antagonistes. Ce point sera rediscuté plus loin dans le texte. De nombreux travaux ont été également consacrés à la synthèse de POE à structure en peigne par polymérisation radicalaire (contrôlée) de macromonomères de POE monfonctionnels. Les espèces ramifiées ainsi obtenues se caractérisent par une densité en segment très élevée, puisque chaque unité monomère de la chaîne principale porte un greffon. Quelques exemples de ces diverses structures ramifiées à base de POE seront discutés dans le premier chapitre

Les travaux déjà réalisés sur la synthèse de copolymères à blocs linéaires dotés d'une séquence (ou de deux séquences POE) associée(s) à une ou plusieurs séquences polyisoprène y seront également relatés brièvement. Les copolymères à blocs poly(isoprène-*b*-poly(oxyde d'éthylène) (PI-*b*-POE) sont d'un grand intérêt en raison de leur aptitude à s'auto-organiser sous forme d' agrégats micellaires dans des solvants sélectifs. Ils sont utilisés dans diverses applications, par exemple comme support organique de catalyseur pour la polymérisation d'éthylène ou pour la synthèse de polymères dendritiques. La synthèse de PI-*b*-POE peut être réalisée selon deux approches. On peut soit préparer d’abord un PI ω-carbanionique par polymérisation anionique en faisant appel à un amorceur comme le *sec*-butyl lithium (*sec*-BuLi). Les extrémités de chaîne du PI sont ensuite désactivées par l'addition d’oxyde d’éthylène pour introduire des fonctions alcools. Ces dernières sont ensuite activées par addition, en général, de diphénylméthyl potassium (DPMK). L’alcoolate potassique ainsi créé sera ensuite utilisé pour amorcer la polymérisation anionique d’oxyde d’éthylène. La deuxième approche repose sur l’utilisation d'une base phosphazène de type *tert*-butyle (t-BuP$_4$) lors de la polymérisation de l’oxyde d’éthylène, amorcée par l’alcoolate créé en extrémité de chaîne du PI.

Une dernière partie de ce premier chapitre sera consacrée à des remarques très générales sur les étoiles de POE, les Polyhedral Oligomeric SilSesquioxane (POSS) et les matériaux organique-inorganiques hybrides obtenus en associant le POE et les POSS.

Les POEs à structure en étoile constituent une classe de matériaux particulièrement prometteurs. Ils représentent des modèles de choix pour les études physico-chimiques et peuvent servir des briques élémentaires bien définies pour la synthèse d’hydrogels fonctionnels. Ils sont d'un grand intérêt également dans un large nombre d'applications biomédicales et pharmaceutiques. Ils peuvent également servir d'agents de modification de surface pour améliorer la biocompatibilité de surfaces. Plusieurs approches, basées sur la polymérisation anionique de l’oxyde d’éthylène, ont été développés pour accéder à des étoiles de POE. La méthode « core-first » et la méthode « arm-first » sont les plus utilisées.

Peu de travaux ont cependant été consacrés à des étoiles de POE hybride inorganiques / organiques. Des étoiles de POE dotés de cœur silesquioxanes pourraient constituer de nouveaux matériaux caractérisés d’une part par une plus grande stabilité thermique et thermomécanique et d’autre part par une meilleure résistance mécanique. La synthèse de ce type d’étoile de POE constituait un des objectifs principaux de cette thèse

Quelques exemples représentatifs d’architectures à base de POE préparées dans le cadre de ma thèse sont illustrés ci-dessous :

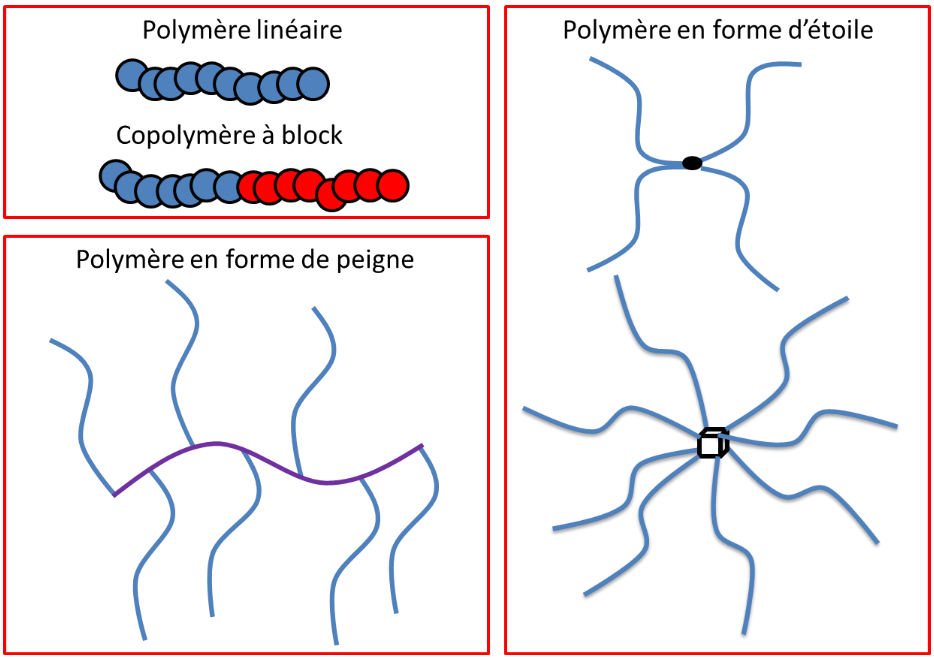


Schéma 1 Représentation schématique d'architectures à base de POE

1.2. Préparation de POE et de macromonomère de POE

Les chapitres suivants de la thèse porteront sur la synthèse et la caractérisation de macromonomères de POE α-méthoxy-ω-allyle, α-méthoxy-ω-undécènyle, α-undécènyle-ω-hydroxy, α-undécènyle-ω-méthacrylate et α-undécènyle-ω-acétylène. La synthèse de macromonomères de POE peut être réalisée soit par modification des extrémités de chaînes de POE à l'aide d'un composé hétérofonctionnel doté d'une insaturation, soit par PAOC de l'oxyde d'éthylène en faisant appel à un amorceur porteur d'une insaturation.

1.2.1. POE α-méthoxy-ω-allyle

Pour réaliser la synthèse de POE α-méthoxy-ω-allyle, j'ai fait appel à la réaction de modification des extrémités de chaîne de POE α-méthoxy-ω-hydroxy commerciaux préalablement purifiés. L'addition d'une quantité stœchiométrique de DPMK agissant comme une base forte permet de transformer quantitativement les groupements hydroxyles terminaux en alcoolates. Dans une deuxième étape, l'addition de bromure d'allyle, en léger excès, conduit au macromonomère de POE recherché. Une caractérisation approfondie, des

POEs ainsi obtenus par SEC, par RMN du proton et du carbone, par diffusion de la lumière et par MALDI-ToF MS a permis de déterminer leur masse molaire, de confirmer l'absence de produits de couplages et de démontrer le caractère quantitatif de la fonctionnalisation.

1.2.2. POE α-méthoxy-ω-undécènyle

La même approche a été testée pour essayer de doter les extrémités de chaînes de POE mono ou di-OH de groupements undécènes en faisant appel cette fois-ci au 1-bromo-11-undécène comme agent désactivant insaturé. Les macromonomères de POE ainsi obtenus devraient porter en extrémité de chaîne, entre la chaîne de POE et la double liaison, un espaceur hydrophobe «flexible» dont le rôle serait d'améliorer l'accessibilité de la double liaison et d'accentuer le caractère amphiphile du macromonomère de POE. Il ressort des études de caractérisation des produits de réaction que les taux de fonctionnalisation ne sont pas très élevés. Lorsque cette réaction est effectuée à 110 °C, en masse et en présence d'hydrure de sodium introduit en large excès, les résultats sont bien meilleurs. Comme le démontre, l'analyse par RMN du proton, la fonctionnalisation est pratiquement quantitative dans ces conditions. Ce résultat a été confirmé par MALDI-Tof MS et par SEC. Ces mesures ont également montré que la chaîne de POE n'avait pas été dégradée lors de la réaction en masse à 110 °C

1.2.3. POE α-undécènyle-ω-hydroxy

Peu de travaux ont porté jusqu'à présent sur la synthèse de macromonomères POE par amorçage, à partir d'undécènolate de potassium comme amorceur. Des telles structures à base de macromonomères de POE amphiphiles pourraient être utiles pour de nombreuses applications par exemple, pour la modification de surfaces fonctionnelles destinées à des applications biomédicales. Dans le troisième chapitre, une autre approche par PAOC de l'oxyde d'éthylène a donc été développée en faisant appel à un amorceur hétérofonctionnel insaturé, obtenu par réaction entre le 10-undécène-1-ol et une quantité stœchiométrique de DPMK. Le principal avantage de cette approche qui conduit à des POEs α-undécènyle-ω-hydroxy réside dans le fait que l'on obtient des POEs caractérisés par un taux de fonctionnalisation proche de 100 %. Lors de la préparation de cet amorceur, la formation d'un précipité dans le milieu réactionnel a été observée. L'utilisation d'un amorceur partiellement précipité n'affecte cependant pas les caractéristiques moléculaires des POEs: les valeurs des masses molaires sont conformes aux valeurs calculées et la distribution des masses molaires demeure étroite. Ce résultat peut s'expliquer par la lenteur de la réaction de propagation. Cette observation m'a amené à envisager la préparation d'un amorceur sous forme de poudre. Un amorceur sous forme de poudre présenterait plusieurs avantages par rapport à celui préparé en solution juste avant emploi. Ainsi la « poudre active » peut être facilement pesée dans des conditions inertes, après dispersion dans le solvant, et introduite directement dans le réacteur. La disponibilité d'un tel amorceur sous forme de poudre faciliterait donc le déroulement de la réaction. Un tel amorceur a effectivement pu être obtenu, isolé et purifié. Il a été utilisé avec succès pour la préparation de macromonomères de POE α-undécènyle-ω-hydroxy. Ces POEs ont été caractérisés par SEC, RMN du proton et par MALDI-Tof MS. Leur masse molaire absolue a été déterminée par diffusion de la lumière. Ces macromonomères sont effectivement bien définis en masses molaires et quantitativement dotés à une extrémité de chaîne d'une double liaison et à l'autre d'un groupement hydroxyle. Le comportement en solution de ces POEs a été étudié dans le méthanol et dans l'eau par diffusion de la lumière statique. L'influence du groupement undécène sur le comportement en solution a été aussi étudiée par viscosimétrie et par des mesures de concentration micellaire critique.

1.2.4. POE α-undécènyle-ω-méthacrylate

La présence de ce groupement hydroxyle en extrémité de chaîne du POE permet de greffer, par exemple, une double liaison méthacrylique par réaction avec l'anhydride méthacrylique en présence de triéthylamine (TEA) selon une méthode décrite dans la littérature (cf. aussi chapitre trois). Les caractéristiques moléculaires, déterminées par RMN du proton, MALDI-ToF MS, de ces POEs α-undécènyle-ω-méthacrylate sont parfaitement conformes à celles attendues. Des macromonomères de POE originaux porteurs à une extrémité d'un groupement undécène et à l'autre extrémité d'un groupement méthacrylique ont donc pu être obtenus. Ces POEs seront utilisés pour la préparation d'architectures macromoléculaires à structure en peigne ou en étoile.

1.2.5. POE α-undécènyle-ω-acétylène

Dans le troisième chapitre, la synthèse de macromonomères de POE avec, en extrémité de chaîne, une triple liaison est présentée et discutée. Pour la synthèse de ces POEs, le DPMK (en quantité stœchiométrique) a été ajouté d'abord sur les POEs α-undécènyle-ω-hydroxy puis suivi de l'addition de bromure de propargyle. Les POEs α-undécènyle-ω-acétylène, ainsi obtenus, ont été caractérisés par SEC, RMN du proton et MALDI-Tof MS. Leurs caractéristiques sont conformes à celles attendues. Ces POEs seront utilisés pour la préparation des copolymères PI-*b*-POE dont la synthèse et la caractérisation seront détaillées dans le chapitre quatre.

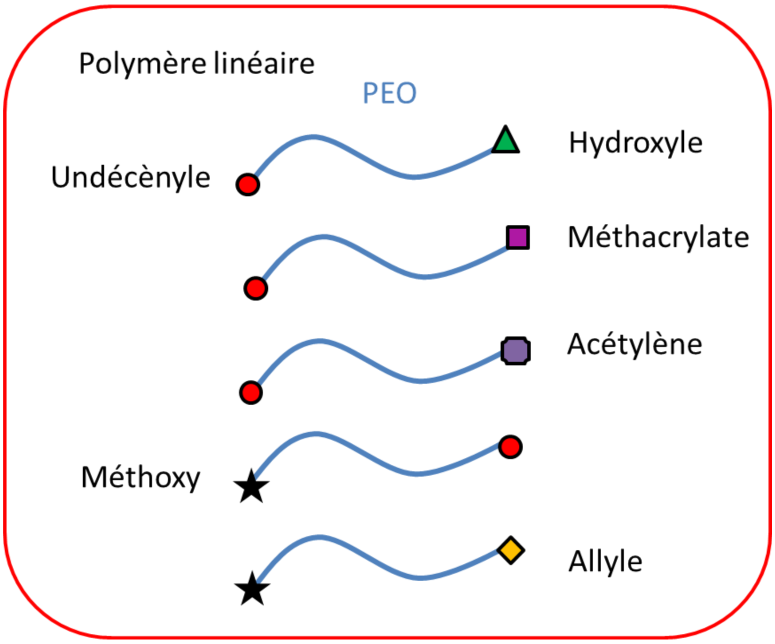


Schéma 2 Représentation schématique des différents POEs linéaires synthétisés

1.3. Préparation de diverses architectures macromoléculaires à base de POE

1.3.1. A partir de POE α-undécènyle-ω-méthacrylate

Nous avons montré que l'on pouvait accéder à des macromonomères de POE α-undécène-ω-méthacrylate originaux, porteurs en extrémité de chaîne d'insaturations de réactivités très différentes. Cette différence de réactivité permet d'élaborer des architectures macromoléculaires ramifiées à base de POE contenant encore des doubles liaisons undécènes, utilisables pour des réactions ultérieures.

Deux approches ont été utilisées pour accéder à ces architectures ramifiées, la polymérisation radicalaire de la double liaison terminale méthacrylique du POE et la réaction thiol-ène entre le macromonomère de POE et des mercaptopropionates tétrafonctionnels. Dans le premier cas, la réaction devrait conduire à la formation de POEs à structure en peigne alors que des POEs à structure en étoile devraient résulter de la réaction thiol-ène.

1.3.1.1. POE à structure en peigne

L'homopolymérisation des macromonomères de POE α-undécènyle-ω-méthacrylate a d'abord été étudiée par voie radicalaire en présence de l'azobisisobutyronitrile (AIBN) dans le toluène puis par ATRP (atom transfer radical polymerization) dans l'eau (CuBr/bipyridine). L'homopolymérisation s'avère effectivement possible. Ces conclusions résultent des analyses par SEC réalisées sur les produits de réaction. Les rendements de la réaction d'homopolymérisation ne sont cependant pas quantitatifs. La purification du produit brut de réaction par fractionnement a permis cependant d'isoler le polymère en forme de peigne de son précurseur.

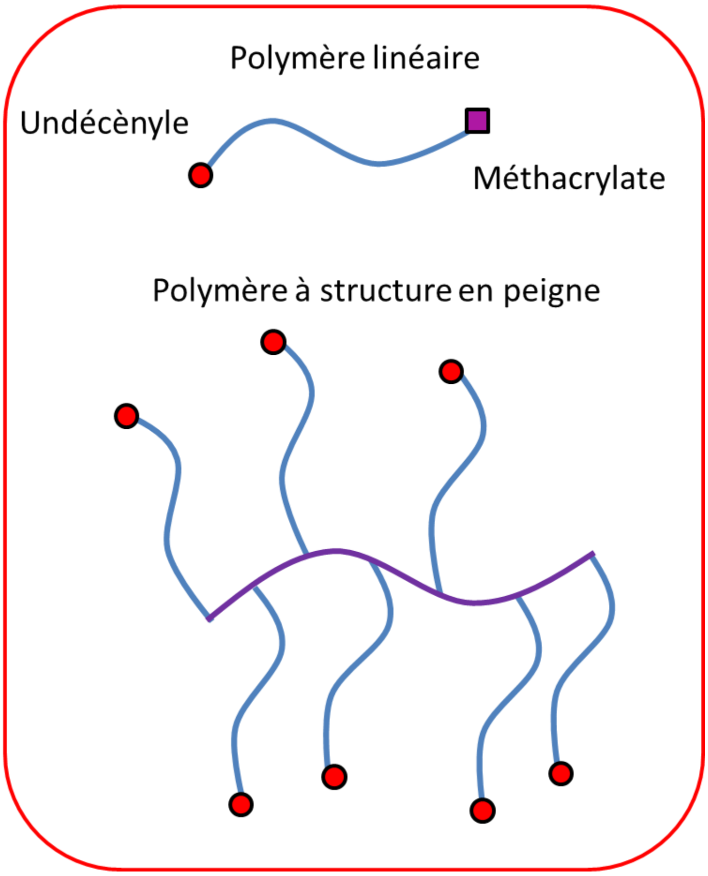


Schéma 3 Représentation schématique de POE à structure en peigne

1.3.1.2. POE à structure en étoile à quatre branches

La réaction de greffage par chimie « click » des macromonomères de POE α-undécène-ω-méthacrylate sur des mercaptopropionates tétrafonctionnels conduit effectivement à la formation d'étoiles de POE tétrafonctionnelles. Il faut cependant souligner que plusieurs étapes de purification sont nécessaires pour isoler ces étoiles. Les mesures par RMN du proton réalisées sur le produit après purification confirment la présence des doubles liaisons undécènes. Les pics caractéristiques des protons de la double liaison méthacrylique ont par contre disparu.

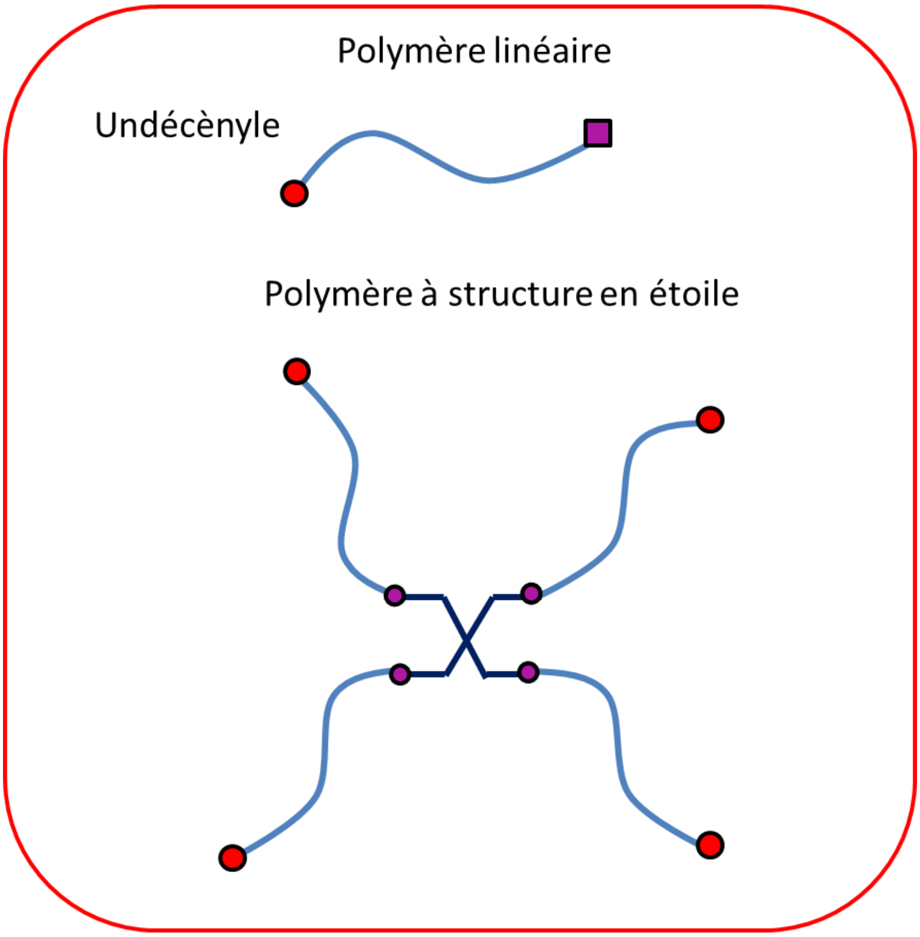


Schéma 4 Représentation schématique de POE à structure en étoile à quatre branches

1.3.2. Copolymère à block PI-*b*-POE

Les troisièmes et quatrièmes chapitres de la thèse seront consacrés à la synthèse de copolymères à blocs dotés d'une séquence hydrophile (POE) et d'une séquence hydrophobe polyisoprène (PI). Ces copolymères suscitent un intérêt croissant non seulement en raison de leur aptitude à s'auto-organiser mais aussi de leurs applications très diverses, par exemple en tant que support de catalyseur pour la réaction de polymérisation de l'éthylène ou encore dans la synthèse de polymères dendritiques. La synthèse de copolymères à bloc PI-*b*-POE peut en principe être réalisée selon deux approches : le PI est préparé d'abord par polymérisation anionique en milieu non-polaire en utilisant le *sec*-BuLi comme amorceur. En fin de réaction de polymérisation on peut rajouter directement l'oxyde d'éthylène et conduire ensuite la réaction de polymérisation en présence d'une base phosphazène pour accéder ainsi au copolymère à bloc. On peut aussi désactiver l'extrémité de chaîne par addition d'oxyde d'éthylène. L'extrémité de chaîne du PI-OH peut ensuite être activée par une base, comme le DPMK, pour être utilisée comme macroamorceur pour la polymérisation anionique de l’oxyde d’éthylène.

Une autre approche a été proposée et qui pourrait permettre d’accéder à ces copolymères par chimie « click ». En faisant réagir un POE porteur en extrémité de chaîne d’une triple liaison avec le PI-N_3 on devrait aussi obtenir le copolymère recherché. Nous avons montré que l’on peut assez facilement modifier l’extrémité de chaîne de POE α-méthoxy-ω-hydroxy ou de POE α-undécènyle-ω-hydroxy par des triples liaisons. Parallèlement à ces réactions de fonctionnalisation de POE, du PI-N_3 a été préparé. Pour ce faire, un PI ω-hydroxy a été synthétisé par voie anionique, le *sec*-BuLi a été utilisé comme amorceur et la réaction a été terminée par l’addition d’oxyde d’éthylène. Après purification, l’extrémité de chaîne du PI ω-hydroxy a été modifiée d’abord par réaction avec du chlorure de tosyle, puis après une nouvelle purification sur colonne bio-beads®, par de l’azoture de sodium afin d’accéder au PI azoture. Par la suite, la réaction de chimie « click » a été réalisée entre le PI-N_3 et le POE porteur en extrémité de chaîne d’une triple liaison en présence de N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (PMDETA) et du bromure de cuivre. L’analyse par SEC des produits de réaction a permis de confirmer le bon déroulement de la réaction. Le copolymère PI-*b*-POE a pu être séparé du produit brut de réaction par passage sur colonne bio-beads®. Par RMN du proton et du carbone, la structure chimique et la présence groupements introduits sur les polymères ainsi que les taux de fonctionnalité à chaque étape ont pu être déterminés. L’infra-rouge a permis de déterminer la présence puis l’absence des groupements tosyle et azoture sur les différents polymères.

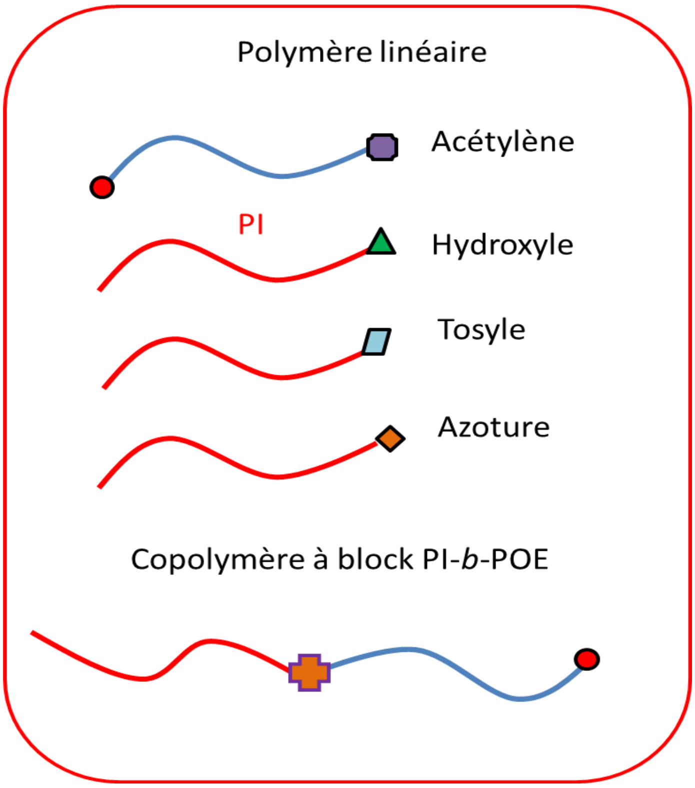


Schéma 5 Représentation schématique de PI-b-POE

1.3.3. POE à structure en étoile à huit branches

Les deuxièmes et cinquièmes chapitres de la thèse porteront sur les POEs à structure en étoile. La synthèse de polymères à structures en étoile à base de POE a fait l'objet de nombreux travaux et diverses stratégies ont été développées pour accéder à des POEs à structure en étoile, caractérisées par des branches de masse molaire bien définie et de fonctionnalité bien contrôlée. Les étoiles de POE caractérisées par des cœurs organiques de nature chimique variée et de fonctionnalité bien contrôlée sont maintenant facilement accessibles. Peu d'études ont porté sur la synthèse de matériaux hybrides ramifiés à base de POE notamment sur des polymères inorganiques / organiques à structure en étoile. La présence dans ces matériaux de cœur inorganiques devrait leur conférer une meilleure stabilité thermique et mécanique.

Cela nous a amené à consacrer des études approfondies à la synthèse contrôlée de polymères en forme d'étoile (POE / POSS). Pour se faire, le greffage par hydrosilylation des extrémités terminales (allyle ou undécènyle) de POEs sur les groupements Si-H d'octakis(dimethylsilyloxy)silsesquioxane (Q_8M_8H) a été étudié. Les différents polymères ainsi obtenus ont été caractérisés systématiquement par SEC, IR et RMN du proton.

1.3.3.1. A partir de POE α-méthoxy-ω-allyle

Un premier exemple d'étoile de POE à cœur POSS a été discuté dans le chapitre deux. Ces étoiles de POE ont été synthétisées par couplage par hydrosilylation de macromonomères de POE α-méthoxy-ω-allyle avec une cage octafonctionnelle, Q_8M_8H, décorée de huit fonctions Si-H en présence d'un catalyseur de « Speier ». Des POEs α-méthoxy-ω-allyle de masse molaire respectivement de 1 900 et 4 600 g / mol ont été choisis. La mesure SEC, réalisée après réaction de greffage, met en évidence la présence de deux pics. Le premier pic, aux faibles volumes d'élutions, peut être attribué à un polymère de masse molaire élevée (a priori l'étoile), alors que le deuxième, aux volumes d'élutions élevés, correspond au macromonomère, non incorporé, ajouté en léger excès. La cinétique de la réaction a été suivie par RMN du proton. Les expériences de greffage préliminaires ont démontré que la réaction doit être effectuée avec un rapport molaire [α-méthoxy-ω-allyle POE] / [Q_8M_8H] d'au moins 10, pour éviter la présence des fonctions Si-H résiduelles. Dans ces conditions, des étoiles de POE, caractérisées par des branches des masses molaires jusqu'à 4 600 g / mol ont pu être. Une précipitation fractionnée a permis d'isoler le polymère à structure en étoile du produit brut de réaction. La diffusion de la lumière, réalisée sur le polymère purifié, donne accès à la valeur de leur masse molaire absolue et de permet de déterminer le nombre de branches greffées sur la cage, Q_8M_8H. Les études par RMN du proton et du carbone ainsi que l'infra-rouge ont confirmé le greffage quantitatif des branches et l'absence de fonctions Si-H. Une fonctionnalité moyenne de huit a été mesurée. Une étude approfondie de ces étoiles a été effectuée par MALDI-ToF MS et a confirmé la masse molaire et la fonctionnalité de ces étoiles de POE hybride. Les valeurs sont en bon accord avec celles mesurées par diffusion de la lumière.

1.3.3.2. A partir de POE α-méthoxy-ω-undécènyle

L'utilisation du POE α-méthoxy-ω-undécènyle dans l'élaboration des étoiles de POE / POSS aurait plusieurs avantages. La présence d'un espaceur hydrophobe entre le POSS et les chaînes de POE peut améliorer la réactivité lors de la réaction d'hydrosilylation.

Le dernier chapitre de la thèse est consacré à la synthèse et la caractérisation physico-chimique détaillée des étoiles de POE avec un cœur silsesquioxane. Le greffage par hydrosilylation des extrémités de chaîne des POEs α-méthoxy-ω-undécènyle sur les groupes Si-H de la cage Q_8M_8H, en présence du catalyseur de « Karstedt » a été étudié. Les conditions optimales de réaction ont pu être établies. L'influence des divers paramètres expérimentaux sur le rendement de greffage tels que la température, le temps de réaction et la concentration du catalyseur de « Karstedt » utilisée, a été étudiée par SEC. Une fois purifié par précipitation fractionnée, les étoiles de POE ont été caractérisées par diffusion de la lumière afin de déterminer leurs masses molaires absolues. Une fonctionnalité moyenne de huit a pu être calculée. L'absence de fonctions Si-H résiduels a été confirmée par IR et par RMN du proton. La RMN du silicium a permis de confirmer que la « cage » Q_8M_8H n'avait pas été modifiée lors de la réaction et la formation de la liaison Si-C entre le cœur et les chaînes de POE. Les mesures par MALDI-ToF MS ont fourni des informations sur la masse molaire et la fonctionnalité de l'étoile. Des mesures de calorimétrie à balayage différentiel (DSC) et de diffusion des rayons X aux petits angles (SAXS) ont été effectuées sur les mêmes échantillons. Avec les résultats de SAXS, différents courbes ont pu être tracés et permettent de confirmer la fonctionnalité de huit. Ces mesures ont aussi donné accès au rayon de l'étoile ainsi qu'au rayon de giration. La cristallisation des étoiles de POE a été étudiée par microscopie optique.

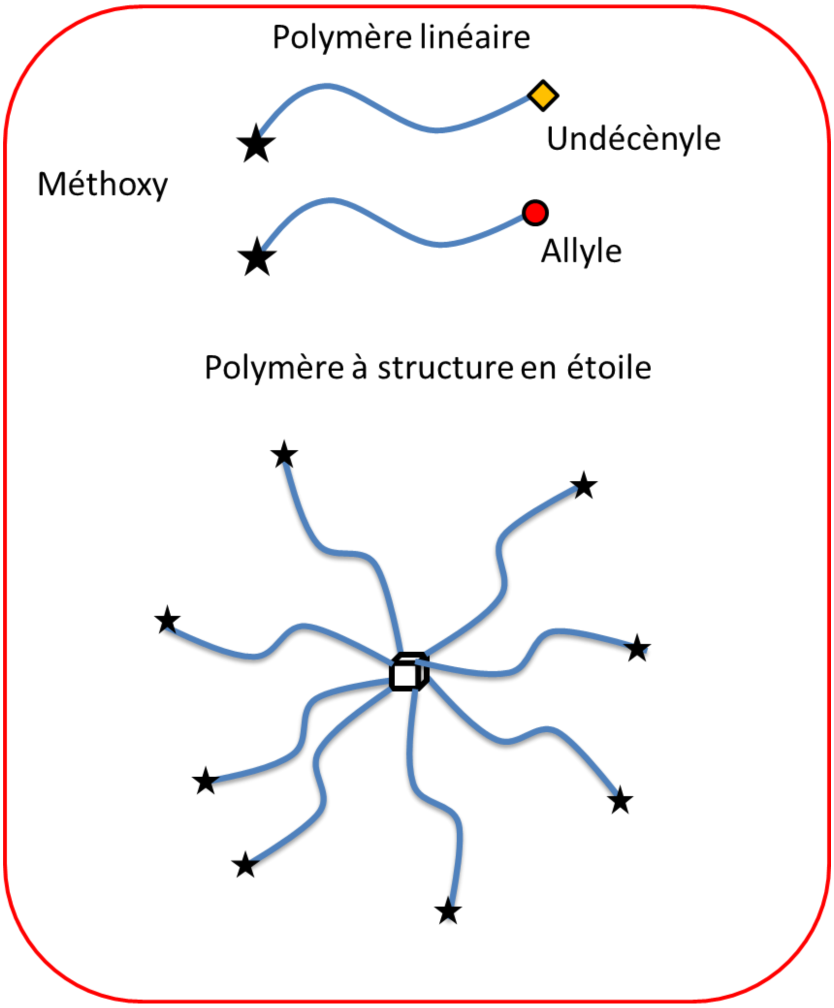


Schéma 6 Représentation schématique de POE à structure en étoile à 8 branches

1.4. Conclusion

L'objectif principal de ma thèse portait sur la synthèse contrôlée et la caractérisation d’architectures macromoléculaires complexes originales à base de POE: POE hétérofonctionnels dotés quantitativement en extrémité de chaînes de groupements undécènyle, méthacrylate ou acétylène, copolymères à blocs PI-*b*-POE, POE à structures en peignes fonctionnels et matériaux hybrides à structure en étoile à base de POE.

Pour la synthèse de POE α-undécènyle-ω-hydroxy, j’ai fait appel à la PAOC de l’oxyde d’éthylène en utilisant l’undécènolate de potassium comme amorceur. J’ai ainsi pu accéder à des POEs α-undécènyle-ω-hydroxy bien définis couvrant un large domaine de masse molaire. Les caractéristiques structurales des polymères ainsi obtenus sont en tous points conformes à celles attendues. L’aspect le plus original de cette partie de ma thèse porte sur la mise au point d’un amorceur sous forme de poudre qui présente plusieurs avantages par rapport à l’undécènolate de potassium préparé *in-situ*. Ainsi la « poudre active » peut être facilement pesée dans des conditions inertes, après dispersion dans le solvant, et introduite directement dans le réacteur. La synthèse automatisée par PAOC de l'oxyde d'éthylène de POE α-undécènyle-ω-hydroxy est donc parfaitement envisageable, et constitue une perspective intéressante de cette thèse. Le comportement en solution de ces macromonomères de POE a été étudié dans le méthanol et dans l'eau par diffusion de la lumière statique. L'influence du groupe undécènyle sur leur comportement en solution a également été étudiée par viscosimétrie. Ces structures à base de macromonomères de POE amphiphiles pourraient être utiles pour de nombreuses applications, par exemple, pour la modification de surfaces fonctionnelles destinées à des applications biomédicales. Comme décrit dans la thèse, le groupement hydroxyle peut être facilement modifié. Des macromonomères de POE hétérobifonctionnels α-undécènyle-ω-méthacrylate décorés aux extrémités de chaîne par des doubles liaisons de réactivités différentes ont ainsi pu être obtenus. Cette différence de réactivité entre le groupement undécènyle et le groupement méthacrylate m’a permis de préparer, par ATRP dans l'eau, des POEs hydrosolubles à structure en peigne. Ces polymères ramifiés portent aux extrémités de branches des fonctions réactives, susceptibles d’être engagées dans des réactions chimiques ultérieures.

J'ai également tiré parti des fonctions terminales méthacryliques de ces mêmes POEs pour essayer de synthétiser, par l'intermédiaire de réaction "click", des POEs à structure en étoile tétrafonctionnelles décorées avec des groupements undécènyle en extrémité de branche en faisant appel au tétrakis (3-mercaptopropionate) comme précurseur du cœur de l'étoile. La réaction avec des groupements méthacrylates conduit effectivement à la formation d'étoiles à quatre branches de POE. Il a également été montré que les doubles liaisons undécènyle ne sont pas affectées lors de la réaction. Ces doubles liaisons sont donc disponibles pour d'autres réactions.

Les groupements hydroxyles des POEs α-undécènyle-ω-hydroxy ont aussi été utilisés pour préparer des macromonomères de POE α-undécènyle-ω-acétylène hétérobifonctionnels décorés à une extrémité par un groupement undécènyle et à l'autre par un groupement acétylène. En faisant réagir ces macromonomères, par réaction « click » avec le polyisoprène ω-azoture, on devrait pouvoir obtenir des copolymères à blocs PI-*b*-POE. De tels copolymères suscitent un intérêt croissant non seulement en raison de leur aptitude à s'auto-organiser mais aussi de par leurs applications très diverses. J'ai effectivement réussi à accéder à de tels copolymères comme le confirment les résultats des caractérisations moléculaires et structurales réalisées par SEC, RMN et IR sur ces échantillons. Les étapes de purification de ces copolymères sont toutefois longues et délicates. Il s'agit probablement du premier exemple de copolymères à blocs PI-*b*-POE obtenus par chimie « click ». L'approche que j'ai sélectionnée présente l'avantage, par rapport à la méthode classique, d'être applicable dans un large domaine de masse molaire. Son principal intérêt réside cependant dans la présence des doubles liaisons undécènyles en extrémité de la séquence POE utilisables pour des réactions ultérieures, comme par exemple, pour la fixation de colorants ou d'unités de sucre permettant des applications intéressantes en sciences de la vie.

Une autre approche a également été utilisée avec succès pour la préparation de macromonomères de POE. Elle fait appel à la réaction des extrémités de chaîne de POE α-méthoxy-ω-hydroxy avec du bromure d'allyle ou du 1-bromo-11-undécène soit après métallation par le DMPK, soit en présence d'un large excès de NaH. Après purification et caractérisation, ces POEs ont servi à la synthèse d'architectures macromoléculaires à structure en étoile par réaction d'hydrosilylation entre la double liaison terminale du POE et les fonctions Si-H de la cage, Q_8M_8H. Le POE α-méthoxy-ω-undécènyle, contrairement au POE α-méthoxy-ω-allyle, porte un espaceur flexible hydrophobe entre la séquence POE et la double liaison. La présence de cet espaceur facilite l'accès à la double liaison et augmente probablement sa réactivité par rapport à celle du POE ω-allyle. L'influence des divers paramètres expérimentaux tels que la température, le temps de réaction et la concentration en catalyseur sur le rendement de la réaction de greffage a été étudiée par SEC et RMN du proton. Ces études ont permis d'établir les conditions de réaction optimales de réaction. Une fois isolée du produit brut de réaction par précipitation fractionnée, les étoiles de POE ont été caractérisées par diffusion de la lumière afin de déterminer leur masse molaire absolue et leur fonctionnalité. L'absence de fonctions Si-H résiduels a été confirmée par IR et par RMN du proton. La RMN du silicium a permis de confirmer le greffage. Les mesures par MALDI-ToF MS ont fourni des informations sur la masse molaire et la fonctionnalité de l'étoile. Des mesures de calorimétrie à balayage différentiel (DSC) et de diffusion des rayons X aux petits angles (SAXS) ont été effectuées sur les mêmes échantillons. La cristallisation des étoiles de POE a été étudiée par microscopie optique. Ces étoiles de POE dotées de cœur silesquioxanes constituent de nouveaux matériaux aux caractéristiques thermiques et thermomécaniques améliorées.

General introduction

Poly(ethylene oxide) (PEO) is used in various applications and as building block for the design of complex macromolecular architectures. The attractive properties of PEO can be ascribed to the distance between the alternating oxygen atoms in the chains that is in agreement with the hydrogen distances in liquid water allowing the formation of intensive hydrogen bonding networks with water. PEO is often used in health care applications since it is known to exhibit stealth properties, i.e. it is not recognized by the immune system.

The synthesis of well-defined PEO can be performed *via* an anionic ring-opening polymerization (AROP). This mechanism is preferred (compared to a cationic ring-opening polymerization) since it proceeds without side-reactions if stringent purification methods are applied for the used reagents. The living AROP of ethylene oxide is based on an alcohol in combination with a strong base to create the anionic initiator species. Several heterofunctional initiators were developed to synthesize PEO macromonomers decorated at one or both chain-ends with a polymerizable group.

Another approach has been developed to prepare PEO macromonomers by chain-end modification of already existing (commercial) PEOs. End-group functionalization of PEOs has gained more and more importance to access a large number of water soluble heterofunctional PEOs. PEO macromonomers are accessible by reaction of an alkoxide function, located at one chain-end, with an appropriate unsaturated electrophile.

The living polymerization technique enables the preparation of well-defined macromolecular architectures. The synthesis of such complex architectures containing PEO chains is developed to access amphiphilic graft, comb and star-shaped polymers or copolymers.

These architectures can be prepared using multifunctional initiators for the AROP of ethylene oxide or by reaction of the chain-ends of PEO macromonomers. Several PEO macromonomers have been extensively used to design graft or comb-shaped polymers by free or controlled radical polymerization procedures. PEOs are more and more used in post-polymerization reactions, e.g., the thiol-ene click reaction to introduce bioactive compounds (sugar units, cell-penetrating peptides), for a specific tuning of the polymer or the surface properties of hydrogels and other systems.

Polyisopene-*b*-poly(ethylene oxide) block copolymers (PI-*b*-PEO) are of broad interest for their micellization behavior and their ability to self-organize in selective solvents into a wide variety of micellar aggregates. They are composed of two polymers with different behavior in solution, a hydrophilic PEO sequence and a hydrophobic polyisoprene (PI) sequence. These copolymers have the ability to self-organize and are used in several applications, such as organic supports for ethylene polymerization or in the synthesis of dendritic polymers. The synthesis of PI-*b*-PEO can be carried out using two approaches. Firstly, PIs were prepared by anionic polymerization with an initiator. Living chain-ends were deactivated by addition of EO / acetic acid to introduce hydroxyl functions at the PI chain-ends. Hydroxyl PI chain-ends were also activated by a base and EO was added for the AROP. The reaction was deactivated with acetic acid. The second method is based on the addition of *tert*-butyl phosphazene base (*t*-BuP$_4$) onto living polyisoprenyllithium chains.

PEO star-shaped polymers are regarded as a particularly promising class of materials since they represent interesting models for physicochemical studies, variable building blocks for hydrogels, or for amphiphilic networks that are of great interest for a wide range of biomedical and pharmaceutical applications. They can also serve as surface-modifying agents to improve the biocompatibility of surfaces designed for biomedical applications. Several approaches based on the living anionic polymerization of EO have been developed to provide access to PEO stars. Hybrid inorganic-organic materials have attracted increasing interest in recent years. Polyhedral oligomeric silesquioxanes (POSS) can be used to create a large variety of hybrid macromolecular architectures. Star-shaped PEOs with POSS cores were established as an emerging class of new materials characterized by enhanced thermal and thermomechanical stability, mechanical toughness, or optical transparency.

The main aim of the thesis will be to take advantage of the anionic polymerization method for accessing linear heterofunctional PEO macromonomers. More complex macromolecular objects will be prepared from these heterofunctional PEOs: Block copolymers, comb and star-shaped polymers.

The first chapter of the thesis is devoted to a general discussion of PEO. A substantial part of this section will focus on the AROP of ethylene oxide and various initiators. The different approaches for accessing heterofunctional PEOs and, more particularly, to PEO macromonomers with polymerizable end-groups at one or both PEO chain-ends will be discussed in a second part. These macromonomers are valuable intermediates for the synthesis of branched polymers or graft copolymers. A variety of branched polymers based on PEO have been synthesized and studied over the years: Comb, star, hyperbranched and dendritic structures. The synthesis of these branched PEOs is dictated not only by the interest in the development of well-defined macromolecular architectures or the desire to have models for physico-chemical studies, but also by their use particularly in the field of biomedical applications. The last part of this chapter will develop general remarks on organic-inorganic hybrid material, POSS. These materials are attracting growing interest. The incorporation of POSS into polymers improves their thermal stability and their mechanical behavior.

The second chapter of the manuscript will focus on the synthesis and characterization of a series of α-methoxy-ω-allyl PEOs obtained by deactivation *via* diphenylmethyl potassium (DPMK) following by addition of allyl bromide on commercial α-methoxy-ω-hydroxy PEOs. The same approach has been tested to provide the undecenyl chain-ends on PEO with 11-bromo-1-undecene. The interest for the undecene end-group arises from the presence of a flexible hydrophobic spacer between the double bond and the PEO which may enhance the reactivity and could affect the solubility in water. The second part concerns the coupling, *via* hydrosilylation, of ω-allyl PEO macromonomers with silsesquioxanes cores ($Q_8M_8^H$) decorated with eight antagonist Si-H functions to yield star-shaped structures in the presence of a “Speier” catalyst.

Less attention was given to the synthesis of PEO macromonomers *via* AROP based on undecenol as initiator although amphiphilic PEO macromonomer-based structures could be useful for several applications, e.g., as building block in precise macromolecular engineering or for the design of biomaterials. The third chapter will focus on synthesis of α-undecenyl-ω-hydroxy PEO macromonomers by AROP of EO in the presence of the appropriate undecenolate potassium initiator, prepared *in-situ* and extended to an alcoholate in the powder form. Well-defined α-undecenyl-ω-hydroxy PEO macromonomers could be obtained and correspond to heterofunctional PEO macromonomers decorated with an undecenyl group at one chain-end and a hydroxyl function at the other chain-end covering a wide range of molar masses.

An important part of the thesis will be devoted to the synthesis of complex architectures containing PEO, such as comb and star-shaped polymers. The presence of the hydroxyl group at the chain-end of PEOs represents an advantage to graft methacrylic double bonds. An approach was developed for accessing the original macromonomer carriers to one chain-end of an undecenyl group and at the other chain-end a methacrylic group with a different reactivity between both chain-ends. This difference permits to develop branched macromolecular architectures based on PEOs containing free double bonds. Two approaches are used, a controlled radical polymerization, atom transfer radical polymerization (ATRP), of the methacrylic double bond to design comb-shaped PEOs and the thiol-ene reaction between PEO macromonomers and tetrafunctional mercaptopropionates to access star-shaped PEO with four arms. α-undecenyl-ω-propargyl PEOs can be used for the synthesis of PI-*b*-PEO block copolymers These PEOs were obtained by addition of propargyl bromide after modification of the chain-end of α-undecenyl-ω-hydroxy PEOs with DPMK. The synthesis of PI-*b*-PEO block copolymers was prepared by reaction of α-undecenyl-ω-propargyl PEOs and ω-azido PIs *via* click chemistry. In the next chapter, this approach will be discussed more in details. ω-Hydroxy PIs were obtained by anionic polymerization of isoprene and the hydroxy chain-ends were modified to azide groups. The classical click chemistry was performed between α-undecenyl-ω-propargyl PEOs and ω-azido PIs.

The last chapter of the thesis will focus on the design of complex hybrid architectures based on PEO. An approach will deal with the design of α-methoxy-ω-undecenyl PEO macromonomers *via* deactivation in the presence of sodium hydride and 11-bromo-1-undecene. The second part concerns with the coupling, *via* hydrosilylation, of ω-undecenyl PEO macromonomers with silsesquioxanes cores ($Q_8M_8^H$) decorated with eight antagonist Si-H functions to yield star-shaped structures in the presence of a “Karstedt” catalyst.

Chapter 1.

Bibliography

1.1. Polymers and polymerization process

1.1.1. History of polymers

Polymers or materials based on polymers are the most commonly man-made matters used in a wide range of applications. They are present more and more in daily life in the modern societies. In this part, some important aspects are discussed.

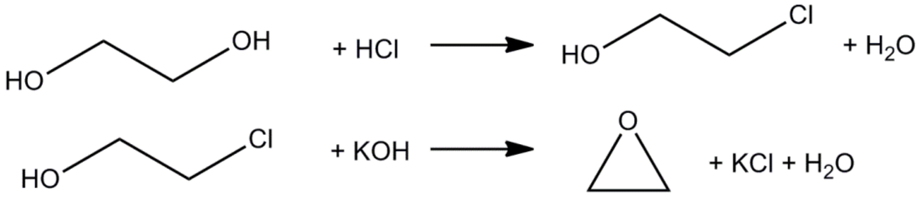
The term polymer was described for the first time by J. Berzelius.[1] This definition was modified with the years for a giant or macromolecule constructed by multiple repeating units joined together by covalent bonds.[2]

Polyisoprene (PI) is one of the first known polymers, a natural example, discovered by C. M. de La Condamine and F. Fresneau de la Gataudière. The authors described the properties of rubber in 1755.[3] This polymer was cross-linked by addition of sulfur (vulcanization) by C. Goodyear and T. Hancock, in 1844.[4,5] Polystyrene (PS) was discovered in 1839 by E. Simon[6] and the structure was confirmed by H. Staudinger.

Ethylene oxide (EO) was discovered in 1835 by A. Wurtz. More explanations on this discovery will be given in the next section. During the nineteenth century, H. Staudinger has classified macromolecules:[7] A large covalently bonded organic chain molecule containing more than 10^3 atoms.

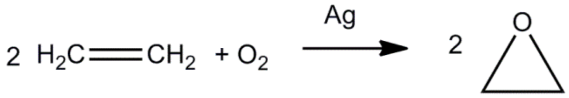
1.1.1.1. Ethylene oxide

EO was first prepared by A. Wurtz by treating ethylene glycol with hydrochloric acid to obtain ethylene chlorohydrine followed by reaction of potassium hydroxide (Scheme 1).[8]



Scheme 1: Schematical representation of the reaction of ethylene glycol with hydrochloric acid and ethylene chlorohydrin with potassium hydroxide.

In 1931 T. Lefort synthesized EO from ethylene and oxygen in the presence of a silver base catalyst (Scheme 2).[9]



Scheme 2: Schematical representation of the reaction between ethylene and oxygen (taken from ref.[9]).

This method was used in industry.[8] Another possibility to prepare EO is the reaction of a mixture of a chlorohydrin solution with calcium hydroxide. In this process, ethylene chlorohydrin was heated to temperatures between 70 and 250 °C in the presence of an alkali under pressure for a period of time sufficient to cause substantial reaction. Thereafter EO could be removed from the reacted mixture.[10] S. Lenher studied the direct reaction between oxygen and ethylene to form EO.[11]

EO can be used in other applications. Examples are the sterilization of spices by EO (1938 by L. Hall[12]) or the sterilization of medical equipment (objects sensitive to temperatures greater than 60 °C) such as bandages, sutures, implants, etc. …

1.1.2. Principle of polymerization

Two major classes of polymerization are known: Step-growth polymerization and chain polymerization. The chain polymerization is in general based on three steps: Initiation, propagation and termination. The nature of the solvent, the temperature and the reaction medium are very different depending of the type of polymerization process.

1.1.2.1. Step-growth polymerization

In the step-growth polymerization, monomers or organic molecules (mono-functionalized, bi-functionalized or multifunctionalized) react with a second monomer to form a dimer, then the dimer reacts with a new monomer to form a trimer or with another dimer to form a tetramer and this process continues and provides access to polymers. Step-growth polymerization is extensively used in industry for the synthesis of polyesters, polyurethanes, polyamides and others. There are two types of step-growth polymerizations, the condensation polymerizations and the addition polymerizations. In the condensation polymerization, the molecules join together with an elimination of small molecules such as water. In the second polymerization method, each step is an addition reaction without small molecules evacuated. W. H. Carothers described this difference in 1929.[13] He developed the polyester synthesis[14] by linear condensation and introduced a series of mathematic equations to describe the behavior of step polymerization system (Carothers Equation[15]). In 1953, P. Flory discussed the differences between step-growth polymerization and chain polymerization. The first polymerization uses a functional group and the second requires of the presence of a radical or an ion at the chain-end.[16]

1.1.2.2. Chain polymerization

In chain polymerizations, the growth of a polymer chain results exclusively from reactions between monomers and the reactive site. The principal steps are the initiation and the propagation. It is necessary to create an active center during the initiation. The active center can be a radical or an ionic species or a metal center. An active center adds a monomer to yield a new active center. To stop the reaction, an active center is deactivated by addition of water, methanol or acid. By this process, polystyrene, polyisoprene, polypropylene, polyvinyl chloride or polyethylene can be prepared.

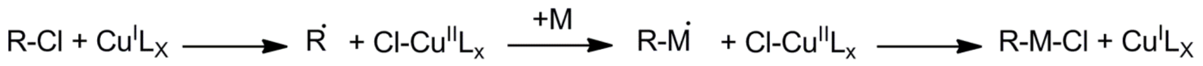
1.1.2.2.1 Radical polymerization

During the radical polymerization process, active radical species exist. The radical polymerization is characterized by a short life time. For the initiation, an active center is created. Several types of initiation are possible: By photolysis, thermal heating, electrochemical reactions or redox processes. The main step is the propagation. The macromolecular chain is formed by successive additions of monomer units on growing "macro-radicals". The termination can take place either by combination between two active chain-ends or by disproportionation (a hydrogen atom is taken from one active chain-end and reacts on the second chain-end to form two non-active chains) or by combination with an initiator radical. The controlled radical polymerization allows the control of molar mass, narrow PDI values and different end-groups. Examples are the atom transfer radical polymerization and the reversible addition−fragmentation chain-transfer polymerization.

1.1.2.2.2 Atom transfer radical polymerization ATRP

This process was described by K. Matyjaszewski and M. Sawamoto simultaneously in 1995.[17,18] The reaction uses a catalytic transition metal/ligand complex. The catalytic complex controls the polymerization reaction by mediating a dynamic equilibrium between the radicals and the inactive form of the polymer, called the dormant species. The dormant form is stabilized and only a few monomer unit are added at a time. This method is effective for the synthesis of copolymers, for example based on methacrylic monomers.

The process is initiated by an alkyl halide (R-X) and mediated by a transition metal complex. Copper(I) halides (Cu(I)Cl or Cu(I)Br) are the most frequently metal salts used in conjunction with nitrogenbased ligands (L) such as 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) and 2,2’bipyridine.[19,20] The catalytic complex extracts the halogen atom from the initiator (R-X) by a redox process. The radical $R^\bullet$ is created that propagates adding monomers. The growing chain then fixes a halogen atom from the catalytic complex to form a dormant species. The chain is further reactivated when the catalytic complex traps the chain-end halogen atom to be oxidized (Scheme 3).[20]



$$\text{R-Cl} + \text{Cu}^{\text{I}}\text{L}_\text{X} \longrightarrow \dot{\text{R}} + \text{Cl-Cu}^{\text{II}}\text{L}_\text{x} \xrightarrow{+\text{M}} \text{R-}\dot{\text{M}} + \text{Cl-Cu}^{\text{II}}\text{L}_\text{x} \longrightarrow \text{R-M-Cl} + \text{Cu}^{\text{I}}\text{L}_\text{X}$$

Scheme 3: Schematical representation of the ATRP process (taken from ref [17]).

J.-S. Wang *et al.* synthesized PS by repetitive atom transfer radical additions in the presence of an alkyl chloride, 1-phenylethyl chloride as an initiator and a transition-metal halide, copper chloride, complexed by 2,2'-bipyridine as a catalyst and produced a well-defined high molar mass polymers with narrow molar mass distributions.[17]

M. Kato *et al.* studied the controlled polymerization of methyl methacrylate with a ternary initiating system consisting of carbon tetrachloride CCl_4, dichlorotris(triphenylphosphine)ruthenium(II) $RuCl_2(PPh_3)_3$, and methylaluminum bis-(2,6-di-*tert*-butylphenoxi) $MeAl(ODBP)_2$.[18]

The first ATRP with PEO macromonomers was studied by X.-S. Wang and S. P. Armes on oligo(ethylene glycol) methyl ether methacrylate (OEGMA) (seven and eight EO units) in aqueous solution in the presence of initiator (several types were tested) and CuCl/bipy. The examples led to the formation of homopolymer OEGMA with a narrow molar mass distribution.[21,22] The authors tested also poly(ethylene glycol) methyl ether methacrylate PEGMA (45 EO units). S.-I. Yamamoto *et al.* used the ATRP of di(ethylene glycol) methyl ether methacrylate and tri(ethylene glycol) methyl ether methacrylate (two and three EO units) for the synthesis of copolymers in the presence of CuBr/bipy in acetone.[23] S. Buathong *et al.* prepared comb-shaped PEOs *via* ATRP of ω-methacryloyloxy PEO macromonomers or hydrogel PEOs *via* ATRP of α,ω-methacryloyloxy PEO macromonomers. First the synthesis and the characterization of these macromonomers was performed. Secondly, the comb-shaped PEOs were synthetized by ATRP with an initiator ratio of 0.02; the average homopolymerization degree values were rather low (from four to five). In contrast, when an initiator/polymerizable entities ratio of 0.06 was used, the homopolymerization yield was significantly higher, up to 85 wt.%, and the molar mass distribution of the resulting comb-shaped PEO was rather sharp. The influence of several experimental parameters, including the solvent (water or toluene), or the initiating conditions, on the physicochemical properties of hydrogels obtained by ATRP was studied.[24]

1.1.2.3. Ionic polymerization

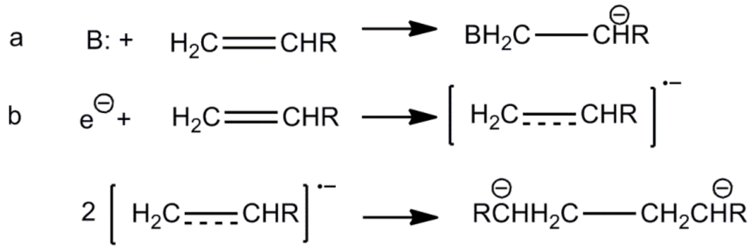
Contrary to radical polymerization, in ionic polymerization the active site is anion or cation. These cations or anions play, associated by counter ions, an important role in the polymerization mechanism. No termination reaction occurs (if no termination agents are present) and after complete consumption of the monomer, the active ends are still present.

1.1.3. Anionic polymerization

The first living anionic polymerization was demonstrated with styrene and dienes by M. Szwarc in 1956.[25] He started the reaction with a sodium naphthalide complex. A wide range of polymers can be obtained by opening the double bond (olefins and vinyl monomers, styrene and isoprene) or by ring opening polymerization (EO or lactone). M.

Szwarc defined the term "living polymers".[26] The polymerization process, in the ideal cases, does not involve a termination step and spontaneous transfer (in the absence of water and oxygen). He explained: "Any growth requires food, the monomer is the food for a growing polymer. If the supply of monomer is exhausted the growth is interrupted. If an additional amount of monomer is available, the living chain-ends are able to grow further".[26]

The first step, initiation, is the reaction between a strong base, like an organometallic species or an alcoholate and the monomer. The monomer obtained has a negative charge. The initiation can be started by attack of an anion or a base (B:) to form a carbanion (a) or by transfer of one electron from one active donor at the double bond of the monomer to form a radical anion and can be dimerized to give a dianion able to grow at both extremities (b) (Scheme 4).[27]



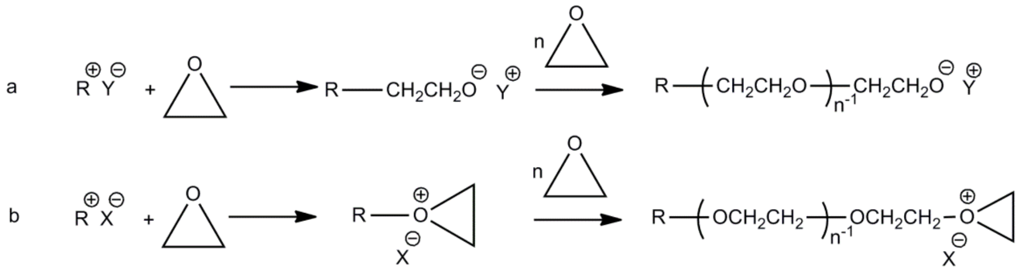
Scheme 4: Schematical representation of the initiation step (the counter ions are omitted) (taken from ref.[27]).

There is a correlation between polymerizability of the monomer, its electronic affinity, and the base. These three factors are related at the substituent nature of the double bond. If the substituent has a high electroactivity, the double bond will have a high electronic affinity. If the monomer has a substituent highly electroattrative, a relatively weak base can be used for the polymerization.[27] The initiation should be fast and quantitative and the nucleophilicity of the initiator should match to the electron affinity of the monomer. If it is too small, initiation may be slow (and/or incomplete), which implies broadening of the molar mass distribution and possibly loss of the molar mass control. Side reactions may occur if the nucleophilicity of the initiator is too high. For each monomer the most adequate initiator has to be selected to attain fast initiation and to avoid side reactions.[28]

The propagation corresponds to the addition of one monomer to the negative charge of the first monomer. The propagation continues as long as monomer is present.

At the end of the reaction, addition of an alcohol, acid or water is necessary to deactivate the active chain-end of the polymer. Spontaneous transfer or termination reactions do not take place, if proper systems and adequate reaction conditions are used. At the chain-ends a metal-organic site is present which enables further reactions. This active site is used to prepare block copolymers or functionalized oligomers or polymers.[28]

P. Sigwalt described the developments of ring opening polymerization using organometallic initiators in the case of epoxides. He explained the difference between anionic (a) and cationic (b) polymerization such as the difficulties of initiation taking the example of EO (Scheme 5).



Scheme 5: Schematical representation of the reaction between anionic or cationic initiators with EO (taken from ref.[29]).

The formation of living sites in equilibrium with monomers has been demonstrated in anionic and cationic polymerization processes of heterocyclic monomers. However, the cationic polymerizations are disturbed by the reactions between the active centers present at the chain-end and the oxygen functions of polymer chains leading to cyclic products and by various types of termination reactions.[29] Consequently, for the EO polymerization, the anionic mechanism is preferred.

However, some authors prepared PEOs by cationic polymerization. The polymerization of ethylene oxide by stannic chloride in ethylene chloride solution was developed by D. J. Worsfold and A. M. Eastham.[30,31] The polymerization with boron fluoride was also studied.[32-34] More recently A. Yahiaoui *et al.* prepared PEO with a dihydroxylated terminal structure by cationic ring-opening polymerization of EO in conjunction with ethylene glycol as a cocatalyst in the presence of an acid-exchanged montmorillonite clay, Maghnite-H^+, as a catalyst.[35]

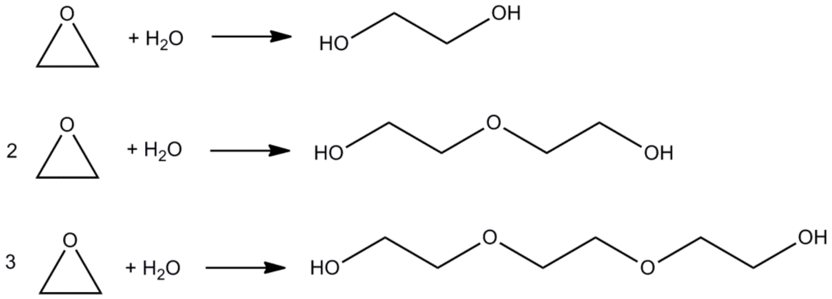
1.1.4. Polymerization of ethylene oxide

PEO is an uncharged polymer, it is the simplest structure of a water-soluble polymer. PEO is a neutral, non-toxic polymer and water soluble at room temperature. PEO has a strong tendency to form hydrogen bonds with water molecules *via* –O– groups. The water solubility of PEO is unlimited, at least up to temperatures slightly below 100 °C. The presence of $-CH_2-CH_2-$ groups generates some degree of hydrophobicity allowing PEO to be soluble in some organic solvents. This provides the possibility to perform synthetic procedures, including polymerization and phase transfer catalysis, in a broad range of polar and non-polar solvents.[36,37]

PEO is commercially available in an extraordinarily wide range of molar masses from 200 g/mol to several millions and more. PEO, according to Harris[38] and others[39], is also called poly(ethylene glycol) (PEG) for molar masses below 20000 g/mol and PEO refers to higher molar masses polymers.[38] PEO is used in a variety of applications, such as in cosmetics, building materials, papermaking, drug delivery, tablet binders, hydrogels, and polymer electrolytes due to properties such as thickening, lubricity and film formation.[37] As PEO is not recognized by the immune system, materials constituted of PEO incorporated in network structures or grafted onto surface are often used in health care applications. They exhibit a good hemo and biocompatibility.

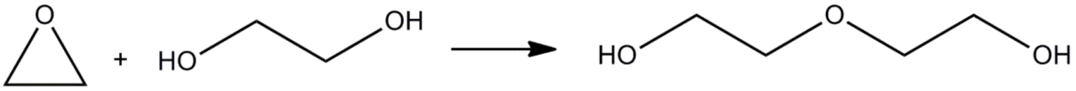
1.1.4.1. First synthesis

In the works of A. Wurtz, glycol ethylenic alcohol is obtained by reactions with EO and water. With two molecules of EO he obtained diethylenic alcohol and with three the triethylenic alcohol was created (Scheme 6).[40]



Scheme 6: Schematical representation of the reaction between EO and water.

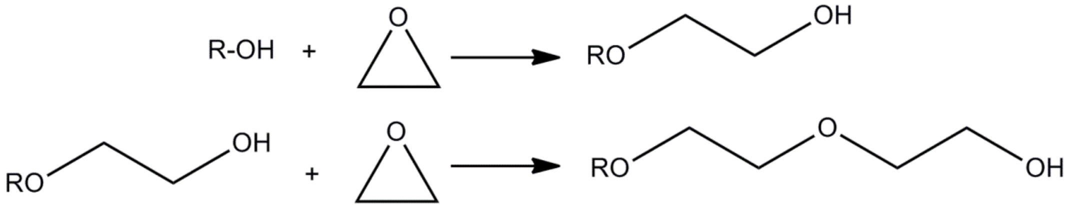
Another possibility was proposed by A. Wurtz heating EO with glycol (Scheme 7).[41]



Scheme 7: Schematical representation of the reaction between EO and glycol.

In 1940, P. Flory described the different methods to obtain PEO and predicted a narrow Poisson distribution.[42]

P. Flory explained also that EO polymerization may be initiated by alcohols, amines or mercaptant capable of generating a hydroxyl group through reaction with the monomer. In the presence of strong acidic or basic catalysts, the polymerization of EO proceeds rapidly in the following manner (Scheme 8).[16]



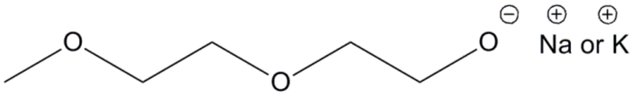
Scheme 8: Schematical representation of the reaction of an alcohol and EO (taken from ref.[16]).

M. M. Cohen proposed to react EO with alcohols with an alkyl chain (butyl alcohol $CH_3(CH_2)_3OH$, amyl alcohol $CH_3(CH_2)_4CH_2OH$, hexylic alcohol $CH_3(CH_2)_5OH$ and heptylic alcohol $CH_3(CH_2)_6OH$) in the presence of KOH.[43] The resulting products represent excellent intermediates for the synthesis of detergents and other surface active agents. Nonionic agents are becoming more and more useful as time goes on, because they are not affected by the presence of salts that might decrease their activity.[8] Nonionic wetting and surface-active agents can be obtained with mercaptans[44] or with HCN to obtain ethylene cyanohydrins.[45]

The kinetics studies of the EO polymerization were investigated in the presence of sodium alkoxides. Several initiators based on the reaction of alcohol and sodium were tested.[46] These authors focused also on the EO polymerization in dioxane with sodium or potassium as initiator and several alcohols.[47]

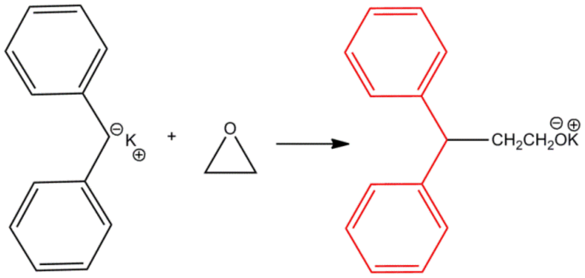
1.1.4.2. Initiators

As it will be extensively discussed in the following part, EO polymerization can be initiated under good conditions with alkoxides. EO polymerizations can be performed in hexamethyl phosphoramide solution using sodium and potassium alcoholates of monomethylether of diethylene glycol as initiators (Scheme 9).[48]



Scheme 9: Schematical representation of the reaction between monomethylether of diethylene glycol and sodium or potassium.

Potassium *tert*-butoxide can be used in dimethyl sulfoxide or hexamethyl-phosphoric triamide for the EO polymerization.[49] DPMK proved also very efficient as initiator for the EO polymerization. H. Normant and B. Angelo prepared this initiator by addition of diphenylmethane to a solution of naphthalene potassium in THF.[50] F. Candau *et al.* performed the AROP of EO in the presence of DPMK. The living chain-ends are deactivated with acid to introduce hydroxyl functions at one chain-end. Diphenylmethyl groups at the other chain-ends allow to determine the molar mass of PEOs by UV spectroscopy. These PEO samples are characterized by low polydispersity index values (Scheme 10).[51]



Scheme 10: Schematical representation of the reaction between DPMK and EO.

Not only this type of initiators can be used for the EO polymerization. M. J. Bruce and F. M. Rabagliati polymerized EO in benzene with diphenylzinc, phenylzinc *t*-butoxide and zinc *t*-butoxide as initiators.[52] J. Furukawa *et al*. proposed dialkylzine-Lewis base system as active catalyst for the EO polymerization in toluene with dimethyl sulfoxide as cocatalyst. The diphenylzinc-dimethyl sulfoxide system is efficient for the preparation of high molar mass PEOs. However the obtained PEOs are characterized by high polydispersity index values.[53] Moreover, also calcium amide or calcium hexa-ammoniate as catalyst were utilized for the preparation of PEOs.[54] In another example, a trifunctional initiator for random copolymerization of ethylene oxide and glycidol has been employed by D. Wilms *et al.* to prepare hyperbranched PEOs in one step.[55]

1.1.4.3. Some remarks on the AROP of EO

Living ring-opening polymerizations of heterocyclic monomers were discussed in several articles.[37,56,57] The AROP of EO requires the use of nucleophilic initiators and involves mostly alkali metal compounds, which are characterized by a high nucleophilicity of the monomer-attacking agent and by a low Lewis acidity of the positive counterion.[37,56] Thus, nucleophilic initiation of the anionic polymerization does not require any monomer coordination to the metal. Sodium, potassium, or cesium-based initiators in an ether solvent, such as THF or hexamethylphosphortriamide (HMPTA), afford a living polymerization allowing the synthesis of end-functional PEO. The propagation rate depends on the counter ion; low in case of lithium and high in case of the cesium. The polymerization with K^+ as counter ion in THF as solvent proceeds with auto acceleration. This is because the polyether chains can solvate the K^+ counter ion increasing in this way the propagation rate constant of the ion pairs by shifting the corresponding equilibrium from contact to separated species and increasing the degree of dissociation of the ion pairs into ions with monomer conversion. The degrees of aggregation as well as the corresponding rate constants of propagation were determined.

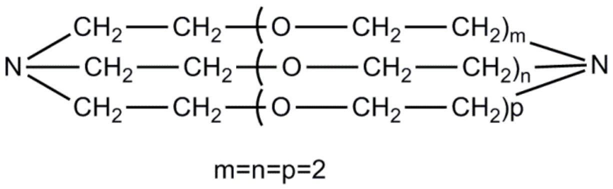
The solution behavior of PEO in water or in organic solvents and the precise determination of the molecular and structural parameters of PEOs have been the subject of extensive discussions since many years. This is directly connected to the fact that PEO may aggregate in solution. V. Elias *et al.*[58] have shown many years ago by vapor pressure osmometry and light scattering (LS) that PEO chains aggregate in acetonitrile, dioxane, benzene and carbon tetrachloride. However, no aggregation was observed in water, methanol and dimethylformamide. Many studies were also conducted on the determination of the structural parameters of PEOs by measuring intrinsic viscosity values in water.[59] The evolution of the instrinsic viscosity of PEO with molar mass was established for water, methanol and DMF. C. Strazielle[60,61] demonstrated by LS measurements that the PEO solutions in water or in methanol, $M_n < 10000$ g/mol, do not contain aggregates. On the contrary W. F. Polik and W. Burchard[62] observed that aggregates are formed with M_n > 20000 g/mol. Many other studies were conducted on the solution behavior of PEO in water or methanol. From all these studies it could be concluded that methanol constitutes one of the best solvents for PEO. The problem of aggregation of PEO has been investigated systematically by M. Duval.[63] SEC, based on calibration with linear PEOs, is presently the method of choice to be used for the determination of the molar mass of linear PEOs. However molar mass determinations in THF are limited to $M_n < 10000$ g/mol. For higher molar masses the measurements have to be conducted in water or mixtures of water and acetonitrile. If the PEO chains are decorated at one or both chain-ends with hydrophobic sequence the characterization can be even more complex. Some examples will be given in the present thesis. For branched or star-shaped PEOs, as the hydrodynamic volume of the star-shaped is lower than that of the linear PEO of identical molar mass, LS measurements have to be performed.

1.1.4.4. Cryptands

As describe before, the EO polymerization requires the use of initiators activated by a metal. However, the type of metal determines the propagation of the polymerization. The propagation during the anionic polymerization occurs through active centers. For the EO polymerization, the reactivity of the active chain-ends increases strongly with increasing the size of the counter-ion. Ion pair association causes a complex reaction kinetics. The rate of polymerization depends on the association and formation of ion pairs. In the medium, inactive aggregates and active species coexist. For the EO polymerization with Li^+, the initiation is possible but no propagation has been observed. One explanation is that the comparatively high charge density of the lithium cation induces a strong aggregation between species after insertion of the first EO units because of their tendency to form covalent bonds with the EO^-. As a consequence, no propagation reaction is possible for the EO polymerization.

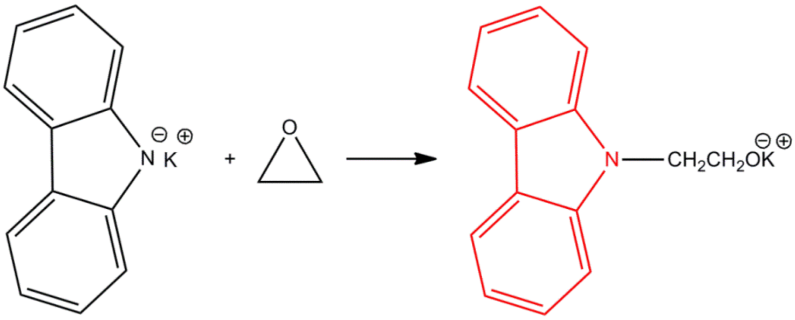
A possibility to improve the propagation is the encapsulation of the cations by addition of cryptands. This molecule surrounds the cation and hides it inside the molecular cavity.[56] AROP of EO with carbazylpotassium complexed by cryptands [222] in THF was performed by

A. Deffieux and S. Boileau.[64] Viscosity, conductance and kinetics measurements were also studied (Scheme 11).



Scheme 11: Schematical representation of the cryptand [222].

C. Eisenbach and M. Peuscher prepared PEOs of high molar masses with narrow molar mass distributions. The authors used cryptands and carbazylpotassium as initiator system. SEC, high pressure liquid chromatography and viscosity measurement were used to determine the molar masses (Scheme 12).[65]



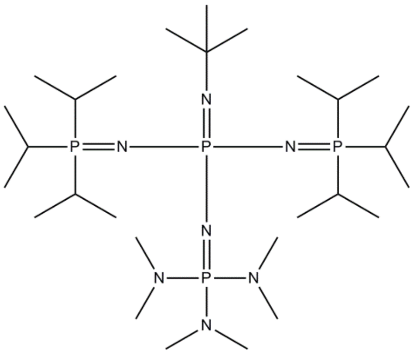
Scheme 12: Schematical representation of polymerization of EO initiated by carbazylpotassium (taken from ref.[65]).

1.1.4.5. Phosphazene bases

A new kind of base, polyiminophosphazene, is of great interest for the EO polymerization. This base plays the role of a cryptand. The polar anion groups are located inside the globular molecule and the outer shell is formed by the alkyl substituents. The free volume inside the molecule might be sufficient to host the rather compact Li^+ ion. The phosphazene base can complex the Li^+ counter-ion and enable EO polymerization.[66]

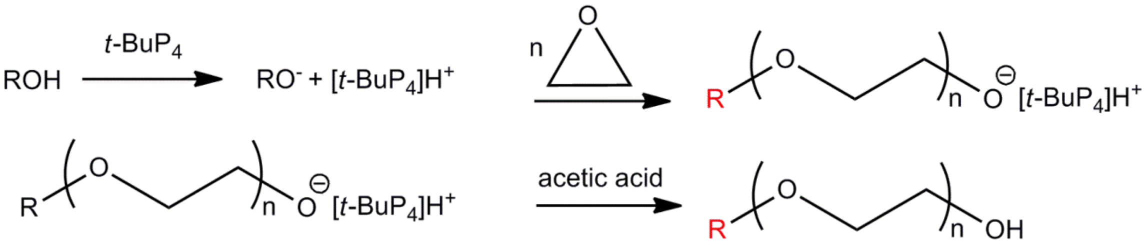
Phosphazene bases are extremely strong uncharged Brönsted bases, which contain at least a phosphorus atom P(V) bonded to four nitrogen functions of three amines and one imine substituents. *t*-BuP_2 and *t*-BuP_4 bases (commercially available phosphazene bases) have attracted interest in the field of anionic polymerization and are intensively studied.[67]

Several types of base exist with lit0hium, protonated and non-protonated phosphazenium base.



Scheme 13: Schematical representation of phosphazene base t-BuP$_4$.

Esswein *et al*. synthesized PEO with *t*-BuP$_4$ in the presence of an alcohol, methanol or 1-octanol and with or without organolithium (BuLi) in THF or in toluene (Scheme 14).[68]

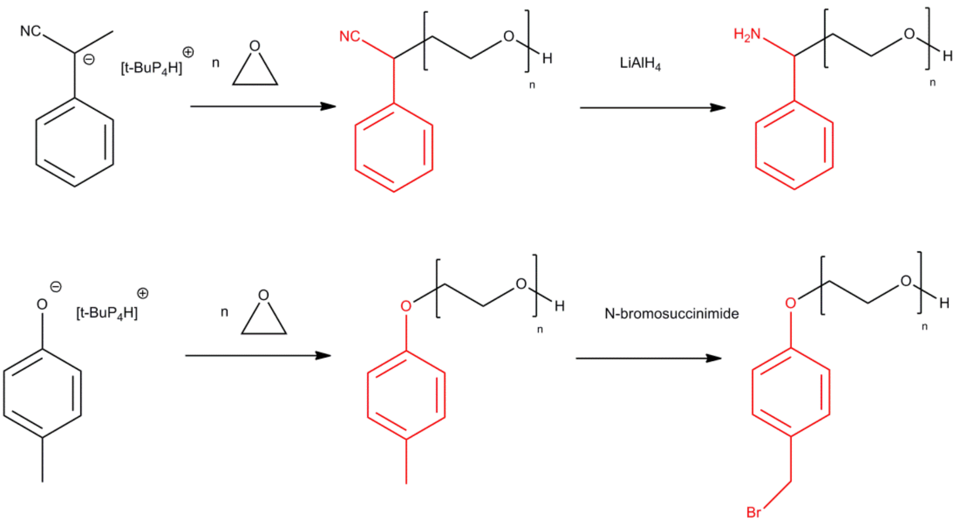


Scheme 14: Schematical representation of polymerization of EO in the presence of phosphazene base t-BuP$_4$ (taken from ref.[69]).

The authors used *t*-BuP$_4$ and BuLi as initiator system. The alkyl substituents form the outer shell and the polar anion groups are located inside the globular molecule. Li$^+$ ion is sufficiently compact to enter into the free volume inside the molecule. The authors concluded that the phosphazene base can form a [Li-*t*-BuP$_4$]$^+$ complex that suppresses ion pair association. The activation of lithium alkoxides such as BuLi, by *t*-BuP$_4$, for the EO polymerization was performed. The base can complex lithium ions and facilitate the EO polymerization by the formation of reactive lithium alkoxides and a good agreement was observed between theoretical and experimental molar mass values.[66]

In another contribution the authors performed the EO polymerization in the presence of *t*-BuP$_4$ initiated with 1-octanol or methanol.[66] Poly[ethylene-*co*-(vinyl alcohol)]-*graft*-poly(ethylene oxide) copolymers were obtained.

The protonated *t*-BuP$_4$ base was studied to access a well-defined α,ω-heterobifunctional PEOs. The system is based on a conjugated acid and a monofunctional initiator, α-methylbenzyl cyanide or *p*-cresol, in THF (Scheme 15).[70]

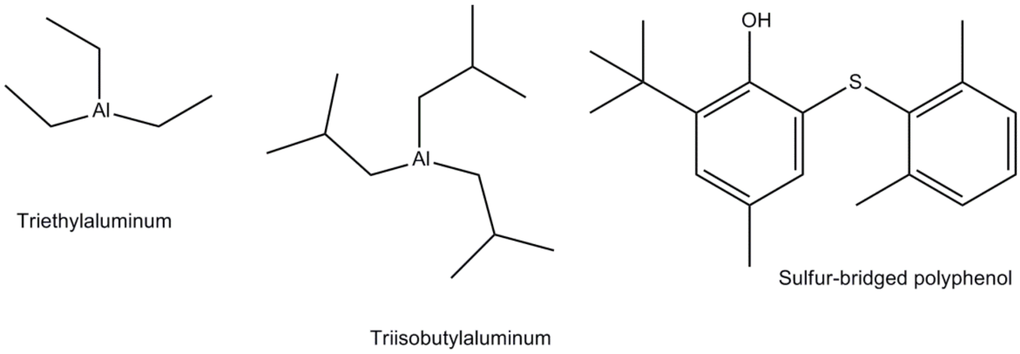


Scheme 15: Schematical representation of polymerization of EO initiated by α-methylbenzyl cyanide or p-cresol (taken from ref.[70]).

H. Schmalz *et al*. worked with several initiators and [Li/*t*-BuP$_4$] counterions under different reaction conditions and followed the reaction by IR.[71] The influence of different initiators, *sec*-BuLi, Bu^{t}OH, Bu^{t}OLi and diphenylhexyl lithium on the EO polymerization, was investigated.

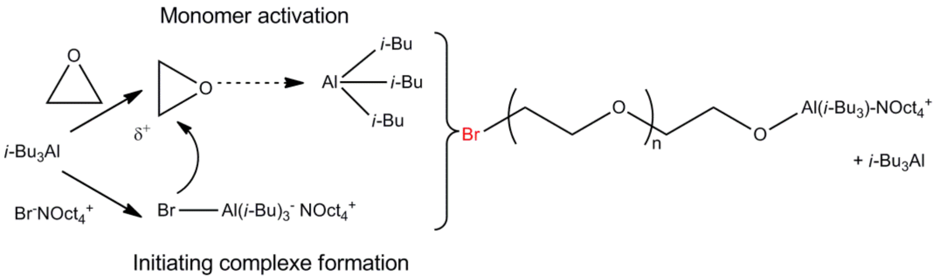
1.1.4.6. Aluminum complexes

Aluminum complexes can be also used for the EO polymerization.[72] In this case, the active sites are obtained by reaction of trialkylaluminium on porous silica in order to convert the silanol functions (Si-OH) to Si-O-AlR$_2$ groups. The remaining Al-C bonds are hydrolyzed by an excess of alcohol to provide the desired aluminium alcoholate for the EO polymerization. E. P. Wasserman *et al*. proposed the EO polymerization catalyzed by aluminum complexes, triethylaluminum and triisobutyllaluminum, of sterically hindered sulfur-bridged bisphenols. Three important aspects of catalysis can be pointed out: The structure of the catalyst precursors in the solid state and in solution, the changes in structure effected by the introduction of monomer and the initiation of polymerization. The authors noticed that the sulfur atom of the ligand appears to play an important role in each of these three phases of catalyst formation. The reaction of sulfur-bridged bis(phenol) compounds with trialkylaluminum species yields highly active catalysts for EO polymerization (Scheme 16).[73]



Scheme 16: Schematical representation of triethyllaluminum, triisobutylaluminium and one example of a sulfur-bridged polyphenol.

V. Rejsek *et al*. proposed to use triisobutylaluminum as an activator and sodium alkoxide (*i*-PrONa) or tetraalkylammonium salts (NBu_4Cl tetrabutylammonium chloride and $NOct_4Br$ tetraoctylammonium bromide) as initiators in dichloromethane for the AROP of EO and copolymerization with propylene oxide(Scheme 17).[74]



Scheme 17: Schematical representation of the EO polymerization with triisobutylaluminum (taken from ref.[74]).

L. Tang *et al*. used the same process but with triethylamine as initiator. The authors showed that aluminum tetraphenoxides in the presence of Lewis bases can represent a highly active catalysts during ring-opening polymerization of EO and that triethylamine is likely to be the predominant initiator in this family of catalysts.[75]

Recently, A.-L. Brocas *et al*. discussed of ring-opening polymerization of ethylene oxide utilizing alkali metal derivatives or other initiating systems in conjunction or not with activating systems.[76]

1.2. Macromonomers

1.2.1. General introduction

Macromonomers are usually linear polymers of rather low M_n (from 1000 to 20000 g/mol) decorated at one or both chain-end with a polymerizable group. They are valuable intermediates in macromolecular engineering.[20,77,78] Typically PS, PI and PEO macromonomers are extensively used for the synthesis of macromolecular architectures such as graft copolymers[79] by copolymerization of the macromonomer with a low molar mass polymerizable compound for comb-shaped polymers[80] by homopolymerization of ω-functional macromonomers or even for hydrogels[81,82] by homo or copolymerization of water-soluble α-ω-bifunctional macromonomers. Until recently ionic polymerization, characterized by the absence of spontaneous termination and transfer reactions, was the method of choice to design well-defined macromonomers. Recently controlled radical polymerization processes increasingly contribute to the synthesis of macromonomers of precise molar mass and functionality.[20]

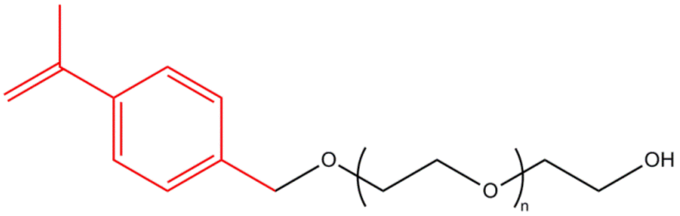
Macromonomers can be prepared by ionic polymerization essentially by two different ways. Either a heterofunctional unsaturated initiator is used to initiate the ionic polymerization or the active chain-end is deactivated by means of a heterofunctional polymerizable compound. This approach is limited to a few examples of monomers as the growing chain-end has not to react with the terminal polymerizable group. The second approach can be applied more generally just after polymerization or on already existing polymers.[20] These methods can be used to decorate polymeric chain-ends at one or the both chain-ends with vinyl benzyl, allyl, undecenyl, norbornenyl, methacrylate groups or polymerizable heterocycles.

1.2.2. Poly(ethylene oxide) macromonomers

Since many years extensive research has been devoted to PEO macromonomers as they represent interesting buildings blocks for the synthesis of complex branched or cross-linked materials.[83-85] Two approaches have been developed to design PEO macromonomers by initiation or by deactivation.[20] The first method refers to a heterofunctional unsaturated alcohol used as initiator, after appropriate modifications, for the AROP of oxirane. In the second method, a heterofunctional polymerizable compound is reacted with the PEO chain-ends. These different approaches will be briefly presented and discussed below.

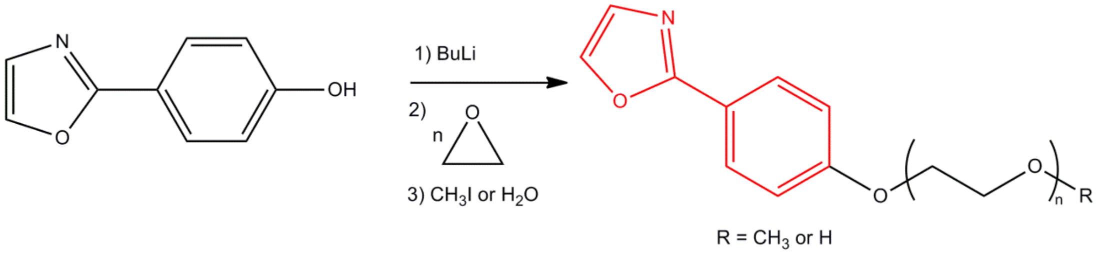
1.2.2.1. PEO macromonomers prepared by initiation

Ethylene oxide is only polymerizable by ionic polymerization methods. However anionic polymerization was shown to be much more efficient for the synthesis of PEO macromonomers than cationic polymerization.[37] DPMK or potassium methoxyethanolate have been extensively used for the preparation of ω-methoxy PEOs. The former initiator has the advantage to be well soluble in THF, efficient, and leads to PEO chains decorated with diphenyl groups in α-position. For the synthesis of PEO macromonomers by initiation an alcoholate is prepared by addition of a stoichiometric amount of DPMK, acting as metallating agent, to a polymerizable heterofunctional alcohol. As expected the resulting alcoholate is only partially soluble in THF. This does not affect the polydispersity index of the resulting PEOs as the medium becomes homogeneous after addition of a few oxirane units. The relatively low nucleophilicity of this compound prevents the attack of the double bond under the conditions used. Masson *et al.* were among the first to use potassium *p*-isopropenylbenzyl alcoholate (obtained by reaction of the corresponding alcohol with DPMK) for the synthesis by AROP of EO. Well-defined α-*p*-isopropenylbenzy-ω-hydroxy PEO macromonomers could be obtained.[86] The molar masses are those expected from the monomer consumed to initiator molar ratio, and the polydispersity index is low (Scheme 18).



Scheme 18: Schematical representation of α-p-isopropenylbenzy-ω-hydroxy PEO macromonomer (taken from ref.[86]).

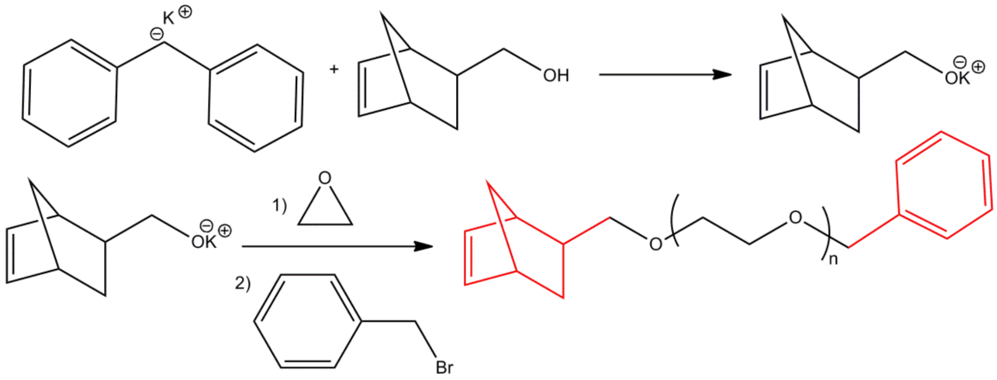
Many years ago oligomeric 2-oxazoline PEO macromonomers could be prepared by AROP of EO starting from 2-(*p*-hydroxy-phenyl)-2-oxazoline in the presence of BuLi. The living chain-ends can be deactivated by methyl iodide to access the methoxy terminal groups or by water to introduce hydroxyl terminal groups. Their homopolymerization or copolymerization with 2-phenyl-2-oxazoline was investigated (Scheme 19).[87]



Scheme 19: Schematical representation of the AROP of EO to access to 2-oxazoline PEO macromonomers (taken from ref.[87]).

PEO-*b*-(2-methyl-2-oxazoline) block copolymers were prepared *via* polymerization of 2-methyl-2-oxazoline with α-methoxy-ω-4-(chloromethyl)-benzoate PEO and α-methoxy-ω-4-toluene-sulphonate PEO macromonomers, based on ω-hydroxy PEO macromonomers.[88,89]

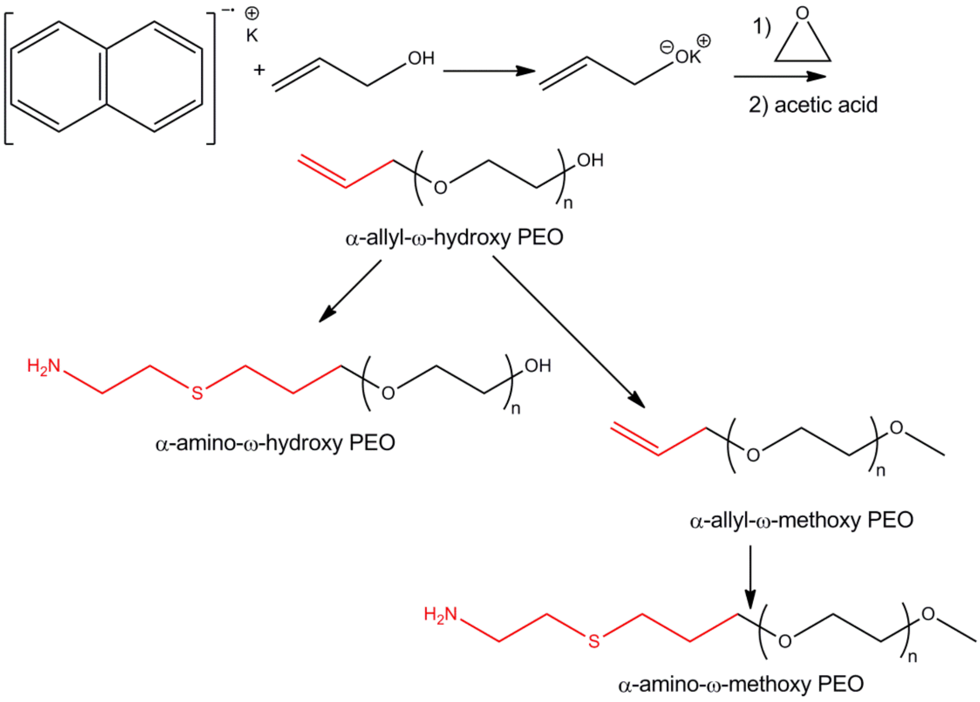
α-Norbornenyl PEO macromonomers could be obtained by V. Heroguez *et al. via* AROP of EO in the presence of a potassium alcoholate obtained by reaction with hydroxymethyl-5-bicyclo[2.2.1]heptane deprotonated by DPMK. The living chain-ends were deactivated with benzyl bromide.[90] The ring-opening metathesis polymerization of these macromonomers was studied in the presence of a Schrock-type catalyst (Scheme 20).



Scheme 20: Schematical representation of the synthesis of α-norbornenyl PEO macromonomers (taken from ref.[90]).

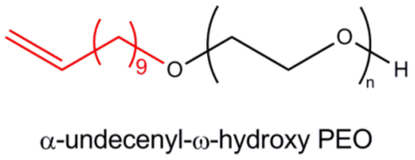
Heterobifunctional α-hydroxy-ω-amino and α-methoxy-ω-amino PEOs were obtained by S. Cammas *et al.* in the presence allyl alcoholate acting as initiator for the AROP of EO.

The living chain-ends were deactivated by addition of acetic acid to introduce hydroxyl groups. After purification, the hydroxy groups of α-hydroxy-ω-allyl PEOs were modified to yield α-hydroxy-ω-amino or α-methoxy-ω-amino PEO macromonomers (Scheme 21).[91]



Scheme 21: Schematical representation of the synthesis of α-hydroxy-ω-amino or α-methoxy-ω-amino PEO macromonomers (taken from ref.[91]).

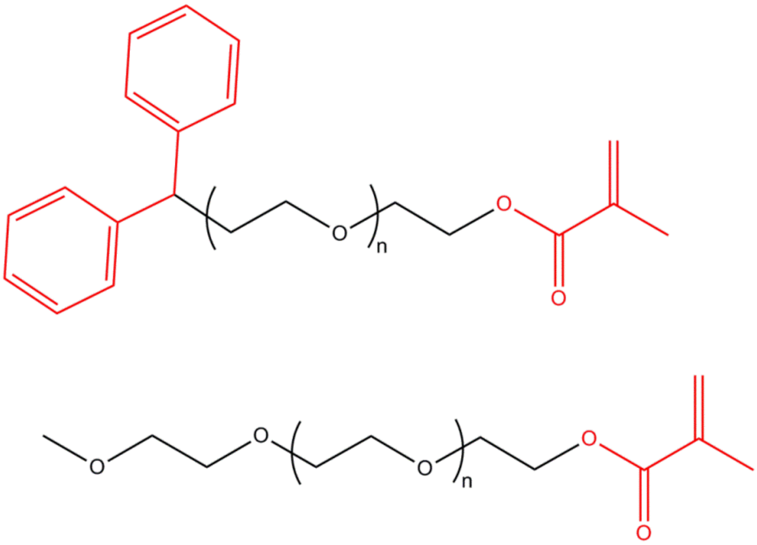
H. Harris *et al.* described the synthesis of α-undecenyl-ω-hydroxy PEO macromonomers *via* AROP of EO initiated by the alcoholate obtained by reaction of 10-undecen-1-ol with DPMK (Scheme 22).[92]



Scheme 22: Schematical representation of an α-undecenyl-ω-hydroxy PEO macromonomer.

1.2.2.2. PEO macromonomers prepared by deactivation

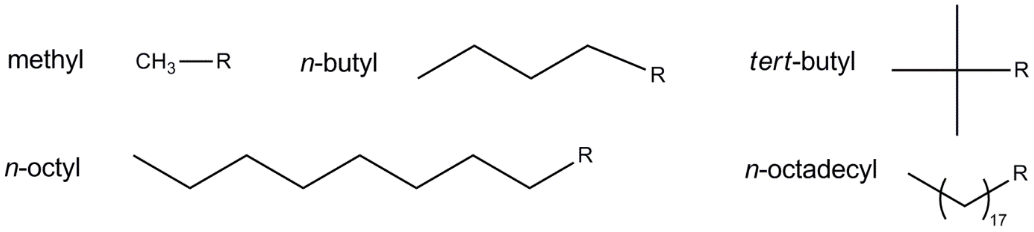
The introduction of the polymerizable entity at the PEO chain-end can also be performed by deactivation with a heterofunctional polymerizable compound. This alternative way to prepare PEO macromonomers involves deactivation of the alkoxide function of a monofunctional PEO by means of an unsaturated electrophile. The addition can be performed either after the AROP of EO to deactivate the living chain-ends of PEO or after the chain-end modification of an existing PEO. In the first case, potassium 2-methoxyethanolate or DMPK was used for the AROP of EO and the chain-ends were deactivated by methacryloyl chloride (Scheme 23).[86]



Scheme 23: Schematical representation of the α-diphenylmethyl or α-methoxy-ω- methacryloyl PEO macromonomers (taken from ref.[86]).

Similarly K. Ito *et al.* prepared *p*-vinylbenzyl (or methacryloyl) PEO macromonomers. Potassium 2-methoxyethanolate was used for the AROP of EO and the living chain-ends were deactivated by *p*-vinylbenzyl chloride.[84]

The same authors extended this approach to the synthesis of different α-alkyl-ω-*p*-vinylbenzyl or α-alkyl-ω-methacryloyl PEO macromonomers by AROP of EO with the corresponding potassium alkoxides as the initiators (methyl, *n*-butyl, *tert*-butyl or *n*-octyl) followed by end capping with *p*-vinylbenzyl chloride or methacryloyl chloride. The homopolymerization or copolymerization by free radical in water was investigated, their organization in micelles was observed. The influence of the lengths of the alkyl spacer on the micelle formation could be demonstrated (Scheme 24).[93]



Scheme 24: Schematical representation of the different initiator groups.

PEO macromonomers with hydroxyl groups at one chain-end can be prepared. The potassium alkoxide of *tert*-butyldimethylsilyl ether of ethylene glycol was used as initiator for the AROP of EO.[94] The homopolymerization and copolymerization of the result ω-hydroxy PEO macromonomers with styrene were studied.

p-Styrylalkyl PEO macromonomers could be obtained either by initiation or by deactivation and were used in the radical homopolymerization in water or in benzene to design comb-shaped PEOs. The influence of the chemical nature on the kinetics of the free radical polymerization was demonstrated.[95]

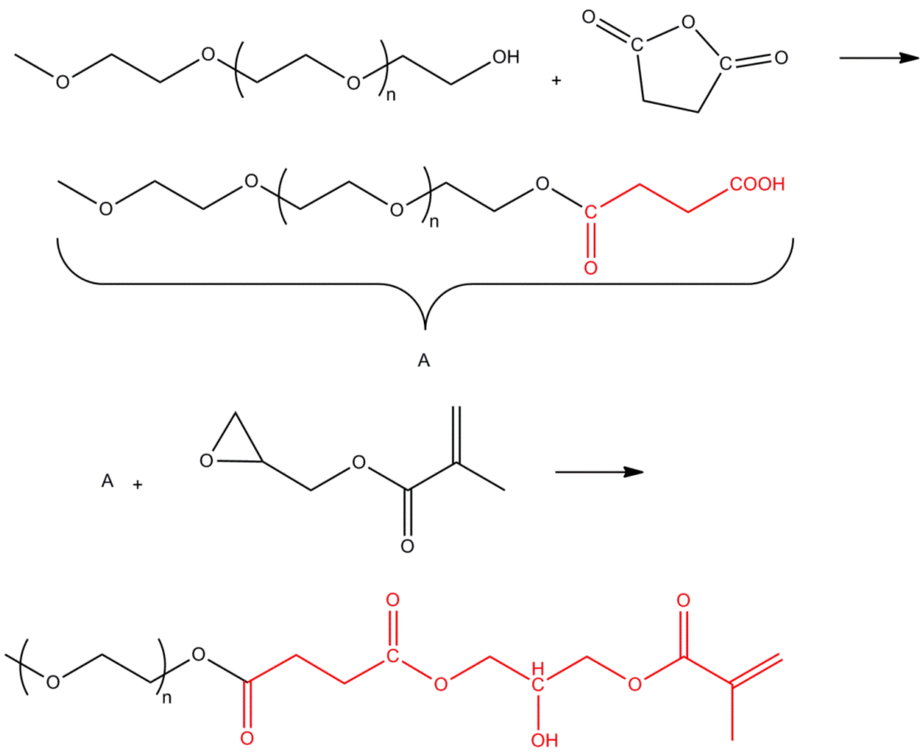
The synthesis, characterizations and applications of several other types of PEO macromonomers are described.[96]

Many examples of the synthesis of macromonomers based on the chain-end modification of ω-hydroxy or α-hydro-ω-hydroxy PEOs have been presented in the literature. It is impossible to discuss all these examples in this thesis. The modification of commercial PEOs does not require the use of EO to access PEO macromonomers. However the contamination of some commercials ω-hydroxy PEOs by α-hydro-ω-hydroxy bifunctional PEOs pose some problems.

A. Revillon and T. Hamaide prepared, starting from commercial PEO, ω-functional PEO macromonomers design for the free radical copolymerization with styrene. To achieve that aim the chain-ends ω-hydroxy PEO were reacted with *p*-vinylbenzyl chloride in the presence of sodium hydroxide.[97] The kinetics of the radical copolymerization of these PEO macromonomers with styrene was systematically investigated and the authors concluded that the chemical structure of the bond between the macromonomer chain and the polymerizable chain-end determines the reactivity of the reaction.[83]

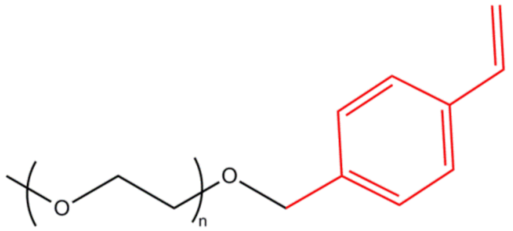
Typically ω-allyl PEO macromonomers were prepared *via* deactivation on the chain-end of commercial ω-hydroxy PEOs with allyl bromide. PEO was dissolved in THF following by the addition of DPMK to obtain an alcoholate, following by the addition of allyl bromide. These macromonomers were used for the preparation of hybrid star-shaped PEO polymer.[92]

Cyclic anhydride can be used as unsaturated compound and subsequently modified with glycidyl methacrylate (Scheme 25).[96]



Scheme 25: Schematical representation of the glycidyl methacryloyl PEO macromonomer (taken from ref.[96]).

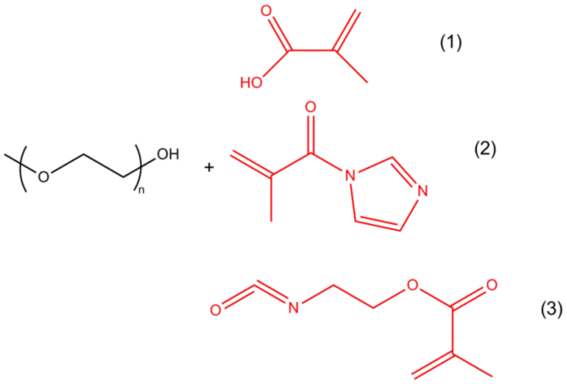
In another example, ω-hydroxy PEO in alkaline medium was reacted with *p*-vinylbenzyl chloride to access to terminal *p*-vinylbenzyl groups (Scheme 26).[96]



Scheme 26: Schematical representation of the p-vinylbenzyl PEO macromonomers.

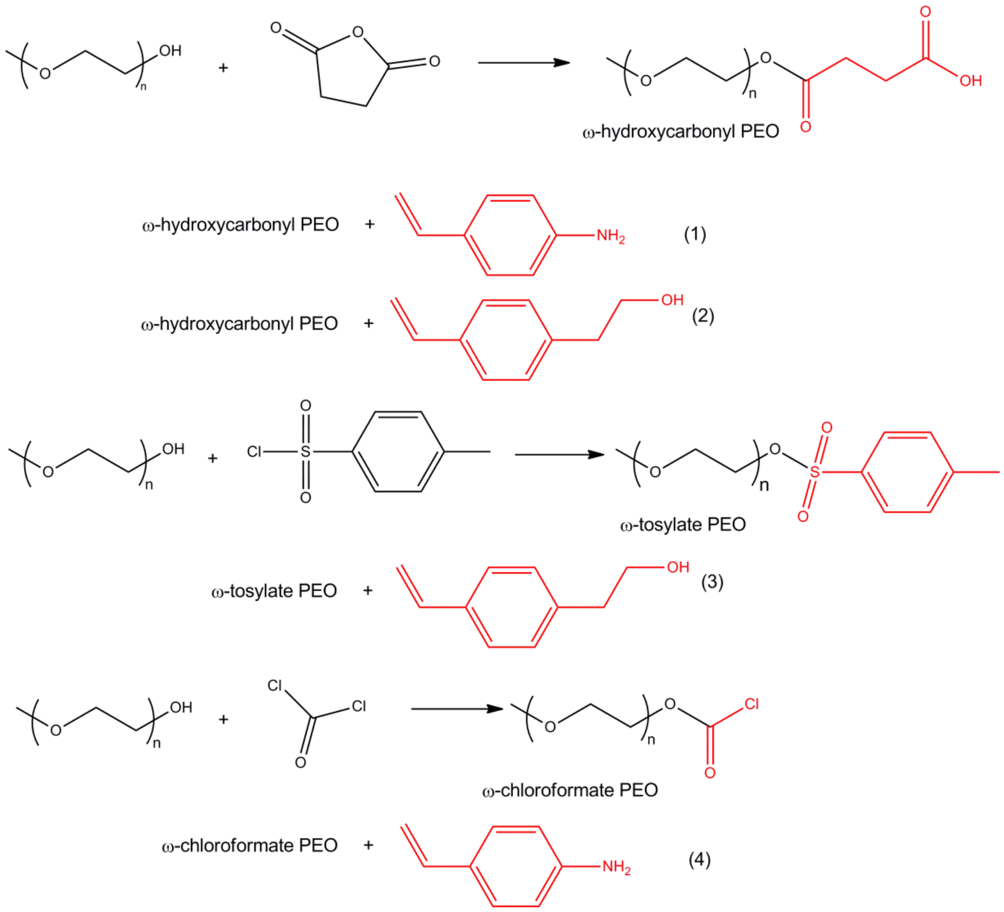
K. Ito prepared α-dodecyl-ω-methacryloyl PEO macromonomers *via* deactivation with methacryloyl chloride of α-dodecyl-ω-hydroxy PEO in the presence sodium hydride. The macromonomers were used to study on the radical copolymerization of styrene or benzyl methacrylate.[84]

Methacrylic acid (1), 1-methacryloylimidazole in the presence of triethylamine (2) and 2-isocyanatoethyl methacrylate (3) were used for the synthesis of ω-methacryloyl PEO macromonomers (Scheme 27).



Scheme 27: Schematical representation of the compounds for preparation of methoxy methacryloyl PEO macromonomers.

PEO macromonomers with 4-vinylphenyl end-group were prepared by Y. Gnanou and P. Rempp. The authors reacted ω-hydroxycarbonyl PEO macromonomers with 4-vinylaniline (1), with 2-(4-vinylphenyl)ethanol (2), ω-tosylate PEO macromonomers with 2-(4-vinylphenyl)ethanol or ω-chloroformate PEO macromonomers with 4-vinylaniline (Scheme 28).[98]

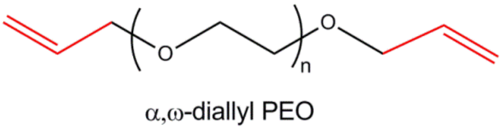


Scheme 28: Schematical representation of the compounds for preparation of 4-vinylphenyl PEO macromonomers.

α-*n*-Octadecyl-ω-*p*-vinylbenzyl PEO macromonomers were prepared by deactivation of mono stearyl ether PEO in the presence of sodium hydride followed by end capping with *p*-vinylbenzyl chloride.[93]

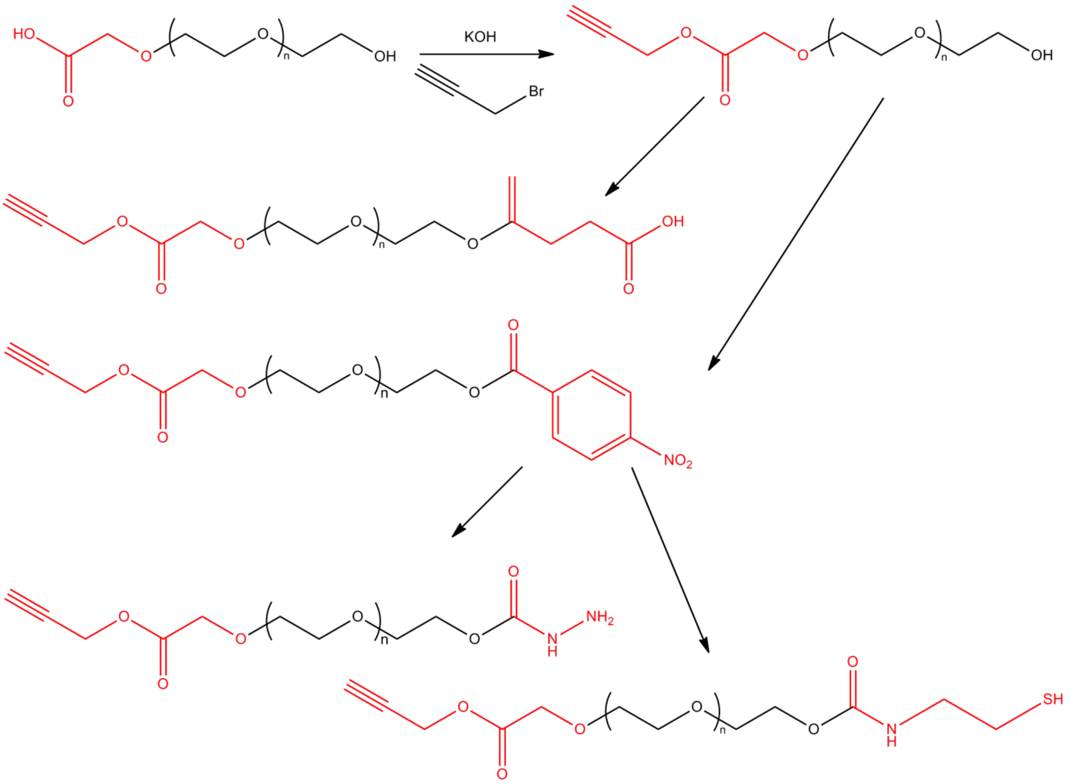
α-Hydro-ω-hydroxy PEOs were modified at the chain-end by reaction of the hydroxy end-groups with a large excess of allyl bromide in bulk in the presence of a sodium hydroxide. Well-defined α,ω-diallyl PEOs were obtained. They were subsequently used in the synthesis of hydrogels by reacting them *via* hydrosilylation 2,4,6,8-tetramethyltetrahydrocyclosiloxane acting as the cross-linking agent. Hydrogels characterized by a low percentage of extractible material and exhibiting good mechanical properties could be obtained.[99]

H. Harris *et al*. prepared also α,ω-diallyl PEO macromonomers by the addition of allyl bromide to metallated bifunctional PEOs.[85] PEO hydrogels were synthesized in toluene by coupling these PEO macromonomers with octafunctional silsesquioxanes *via* hydrosilylation in the presence of a ''Speier'' catalyst (Scheme 29).



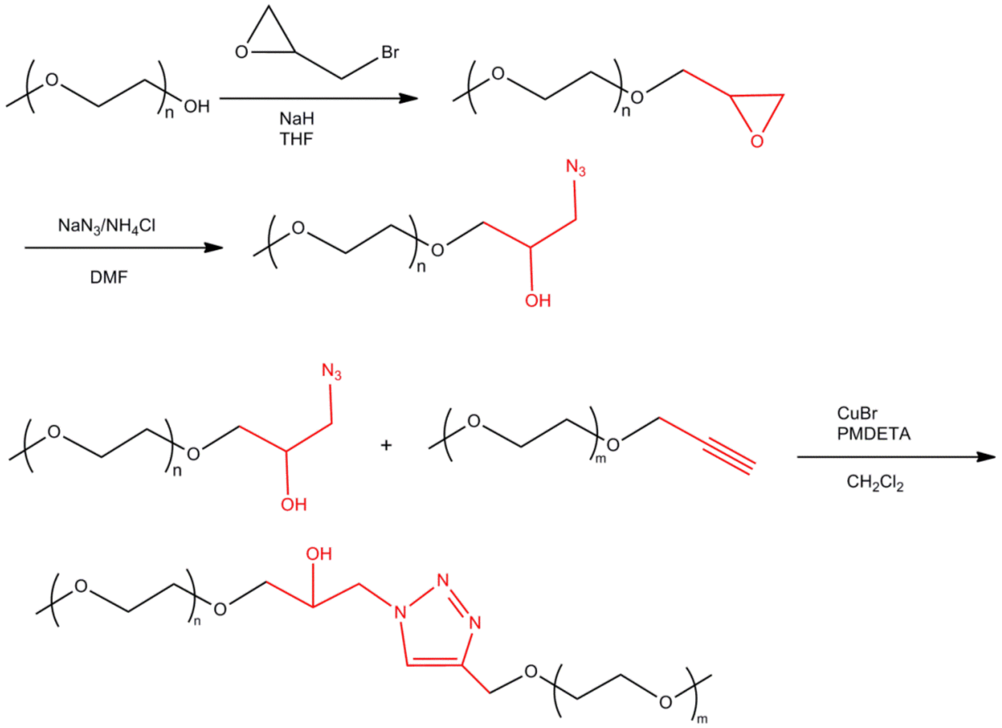
Scheme 29: Schematical representation of an α,ω-allyl PEO macromonomer.

Recently many studies discussed of the synthesis of heterobifunctional PEO. α-Hydroxy-ω-carboxyl PEO was used as the starting polymer and transformed in α-hydroxy-ω-propargyl PEO. Subsequently this PEO was modified to α-carboxyl-ω-propargyl PEO, α-mercapto-ω-propargyl PEO or α-hydrazide-ω-propargyl PEO (Scheme 30).[100]



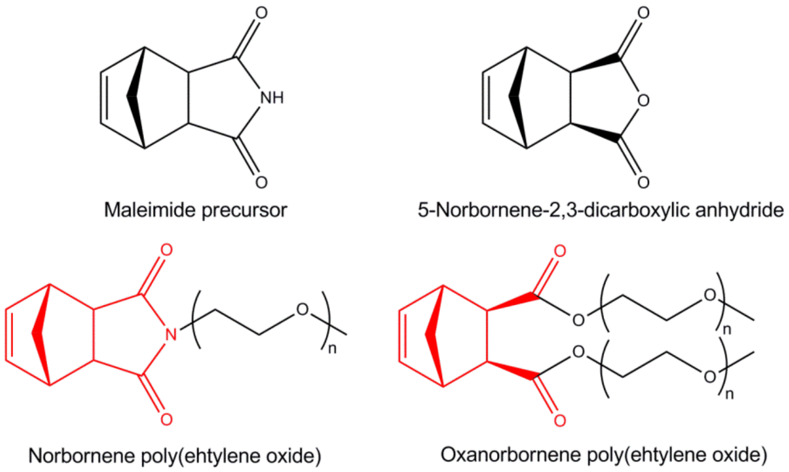
Scheme 30: Schematical representation of the synthesis of different PEO macromonomers (taken from ref.[100]).

α-Propargyl PEO and mono-epoxide-functionalized PEO were prepared and click reaction was performed between the both PEO macromonomers to yield heterobifunctional PEOs (Scheme 31).[101]



Scheme 31: Schematical representation of the synthesis of homo arm PEO star (taken from ref.[101]).

S. F. Alfred *et al*. proposed the preparation of new end-functionalized PEOs with norbornene and oxanorbornene end-groups from commercial hydroxy PEOs.[102] These macromonomers were polymerized to comb-polymers by ring-opening metathesis polymerization as described already by Heroguez *et al.* (Scheme 32).*[90]*

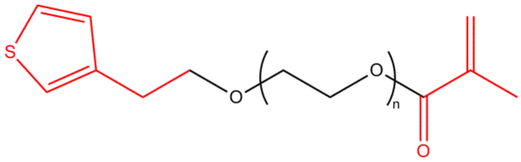

Maleimide precursor
5-Norbornene-2,3-dicarboxylic anhydride
Norbornene poly(ehtylene oxide)
Oxanorbornene poly(ehtylene oxide)

Scheme 32: Schematical representation of the norbornene and oxanorbornene PEO macromonomers (taken from ref.[102]).

K. Naraghi *et al*. prepared degradable hydrogels constituted of hydrophobic PEO chains containing a short central degradable poly(1.3-dioxolane) block from the α,ω-methacryloyl PEO-*b*-poly(1.3-dioxolane)-*b*-PEO macromonomers.[103]

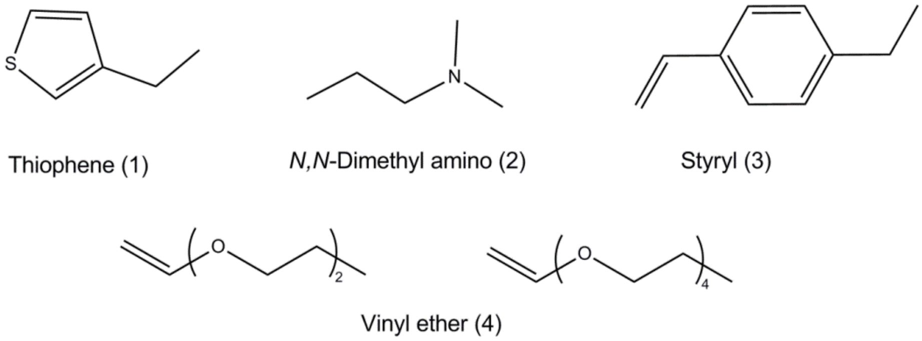
1.2.2.3. Heterobifunctional PEO macromonomers

F. Yilmaz *et al*. synthetized α-thienyl-ω-methacryloyl PEOs macromonomers *via* AROP of EO initiated by potassium thienylethoxide. The living chain-ends were deactivated by methacryloyl chloride. This macromonomer can be used for free radical and oxidative polymerization (Scheme 33).[104]



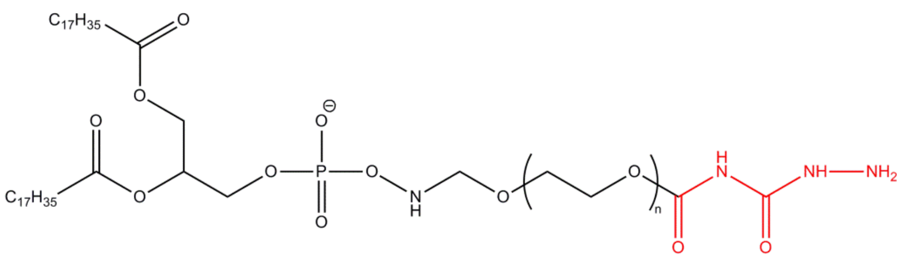
Scheme 33: Schematical representation of a PEO macromonomer with methacryloyl and thienyl end groups (taken from ref.[104]).

Y. Yagci and K. Ito synthesized new heterobifunctional PEO macromonomers by AROP of EO initiated by thiophene (1), *N,N*-dimethyl amino (2), styryl (3) or vinyl ether (4) activated by potassium naphthalide The ω-end standing polymerizable methacryloyl groups were introduced by reaction of the activated chain-ends with methacryloyl chloride. The macromonomers were used in the elaboration of various PEO based macromolecular architectures (Scheme 34).[105]



Scheme 34: Schematical representation of the different chain-end groups (taken from ref.[105]).

In a review article, M. S. Thompson *et al*. discussed the synthesis and some applications of a series of heterobifunctional poly(ethylene oxide) oligomers and macromonomers.[106] Several types of efficient heterofunctional initiators were developed to design these PEO macromonomers fitted at the chain-end with carboxyl, amine, thiol or maleimide groups (Scheme 35).



Scheme 35: Schematical representation of an amine-terminated lipid-PEO copolymer (taken from ref.[106]).

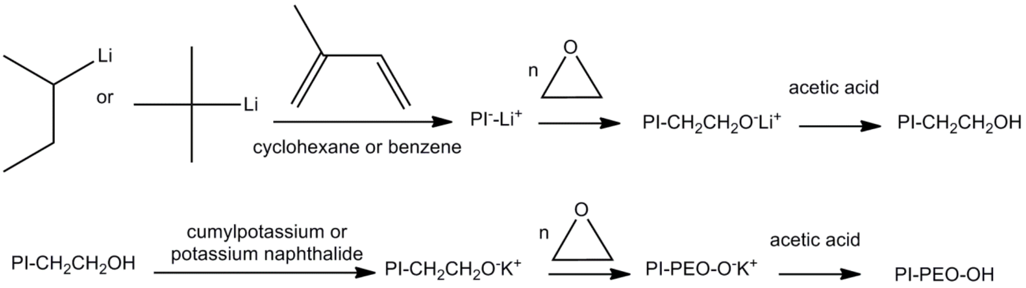
D. Neugebauer discussed in a review article the application of the macromonomer strategy for the preparation of graft copolymers. The author examined the influence of the polymerization process (living polymerization, ring-opening metathesis polymerization, reversible addition-fragmentation chain transfer, atom transfer radical polymerization etc. …) on the grafting yield and on the structure of the graft copolymers. Some properties and applications of these graft polymers were discussed in the same articles.[36]

1.3. Polyisoprene-*b*-poly(ethylene oxide)

Self-assembly of amphiphilic diblock copolymers in solution has attracted increasing interest due to the possibility to aggregate in selective solvents. They can form micelles in water and in non-polar solvents. The micelle morphology has been shown to depend strongly from the molecular parameters such the overall degree of polymerization and the composition of the copolymer.[107-109] Numerous potential applications were found for these materials such as tunable delivery vehicles, as templates for biomineralization, as nanoreactors or scaffolds for biological conjugation.[110] Among the different types of amphiphilic diblock copolymers, copolymers of PI and PEO constitute one of the emerging class of polymeric amphiphiles. The synthesis of PS-*b*-PEO, PB-*b*-PEO or PI-*b*-PEO refers essentially to sequential living anionic polymerization of the unsaturated monomer (butadiene, isoprene or styrene) with EO. In the following section the two main approaches to design PI-*b*-PEO diblock polymers *via* anionic copolymerization will be briefly discussed. A more recent method based on a combination of AROP of EO and nitroxide-mediated polymerization will also be presented.

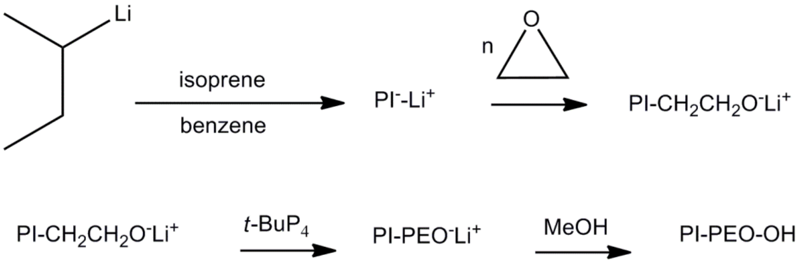
1.3.1. Synthesis

As mentioned above two approaches have been developed over the past 20 years to access PI-*b*-PEOs. In the first case an ω-living PI is prepared by anionic polymerization, in cyclohexane or benzene, with *sec*-BuLi or *tert*-butyllithium as initiator. After polymerization, the living chain-ends are deactivated by addition of EO / acetic acid to introduce hydroxyl functions at the chain-ends. In a second step, the hydroxyl chain-ends are deprotonated with cumylpotassium[111] or potassium naphthalide[96,97] EO was added for the AROP. The chain-ends of the resulting diblock copolymers were deactivated with acetic acid (Scheme 36).[112,113]



Scheme 36: Schematical representation of the copolymerization of isoprene and EO.

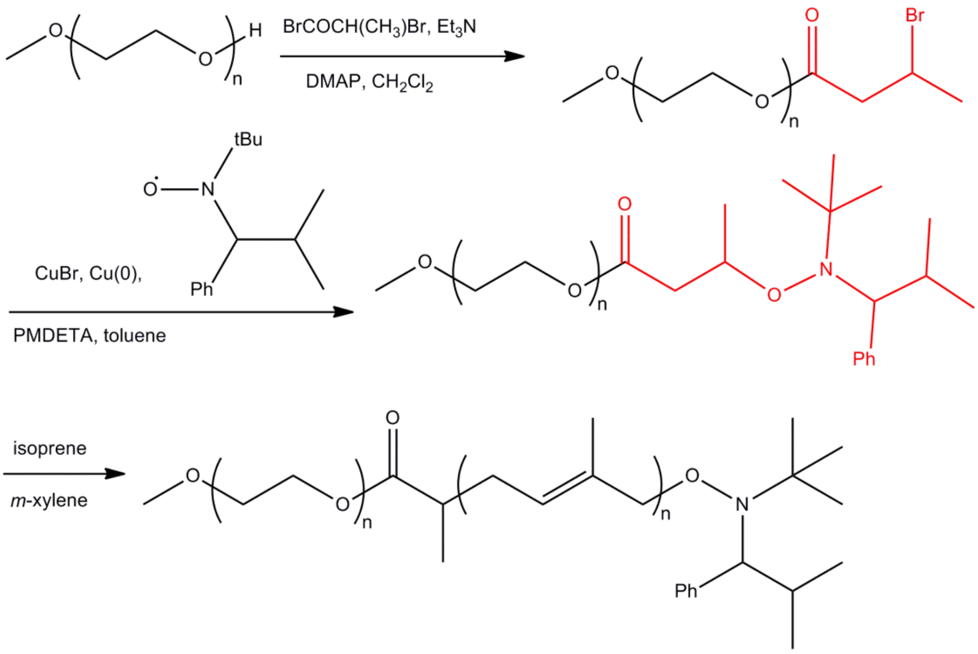
The second method is based on addition of *tert*-butyl phosphazene base.[114,115] As described before, this strong base not only disrupts the O-Li aggregates but also creates free anions, which are able to initiate the polymerization of EO. Typically, the isoprene polymerization was initiated with *sec*-BuLi in benzene. The living chain-ends were modified by addition of EO to introduce O-Li$^+$ functions at the PI chain-ends, *t*-BuP$_4$ and EO were added (Scheme 37).



Scheme 37: Schematical representation of the isoprene and EO copolymerization with addition of t-BuP$_4$ (taken from ref.[114]).

V. Rejsek *et al.* prepared in a one step process PS-*b*-EPO or PI-*b*-PEO by direct polymerization of EO initiated by ω-living polystyrenyllithium or polyisoprenyllithium in the presence of triisobutylaluminum.[69,116]

J. K. Wegrzyn *et al.* proposed another method based on the nitroxide-mediated free radical polymerization from PEO macroinitiators. This macroinitiator, PEO α-bromo ester, was prepared first by reaction of ω-hydroxy PEOs with 2-bromopropionyl bromide in the presence of 4-(dimethylamino)-pyridine and triethylamine. PEO α-bromo ester PEO macromonomers were reacted with CuBr, PMDETA and nitroxide in toluene to access PEO alkoxyamine macroinitiators. The polymerization of isoprene was performed in *m*-xylene with a PEO alkoxyamine macroinitiator.[117] The microstructure of the PI block, approximately 90% 1,4-, 5% 1,2-, and 5% 3,4 repeat units, is typical for a free radical polymerization process (Scheme 38).

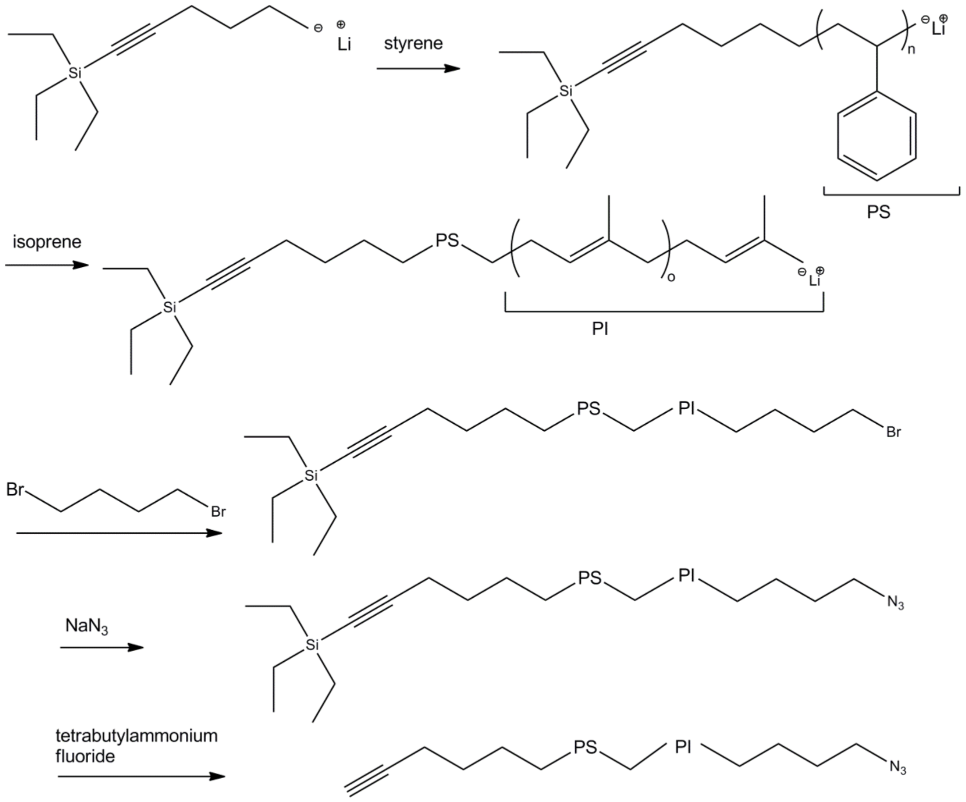


Scheme 38: Schematical representation of the synthesis of PI-b-PEO via nitroxide-mediated free radical polymerization (taken from ref.[117]*).*

1.3.2. Synthesis *via* click chemistry

Click chemistry was used in many cases to prepare block copolymers. For example the synthesis of cyclic PS-*b*-PI copolymers was performed *via* click chemistry of α-acetylene-ω-azido-PS-*b*-PI.[118] PS were prepared by anionic polymerization using 5-triethylsilyl-4-

pentynyllithium (TESPLi) as initiator. Isoprene was added on the living PS chain-ends and the living chain-ends of PS-*b*-PI were deactivated with 1,4-dibromo butane. The bromo chain-ends of α-(TES-acetylene)-ω-bromo-PS-*b*-PI were modified to azide functions. TES-acetylene chain-end was unprotected with tetrabutylammonium fluoride to obtain acetylene functions. Finally, the click chemistry reaction was performed on the final product to access cyclic block copolymers (Scheme 39).



Scheme 39: Schematical representation of the synthesis of α-acetylene-ω-azido-PS-b-PI (taken from ref.[118]).

Isotactic PS-*block*-PEO was synthesized *via* a thiol-ene click coupling reaction of vinyl-terminated isotactic PS with thiol-terminated PEO.[119] These PEO were synthesized by the direct esterification of ω-hydroxy PEO with 3-mercaptopropionic acid using hafnium(IV) chloride tetrahydrofuran complex. iPS was prepared by the extremely highly isospecific polymerization of styrene with 1,4-dithiabutandiyl-2,20-bis(6-*tert*-butyl-4-methylphenoxy) titanium dichloride and methylaluminoxane in the presence of 1,7-octadiene as a chain transfer agent.[120] The behavior and micelle morphology of the crystallization-driven self-assembly of these blocks in *N,N*-dimethylformamide were investigated in detail.

1.4. PEO star-shaped polymers and silsesquioxanes

One of the previous sections of this chapter is devoted to the synthesis *via* AROP of EO of various heterofunctional or heterobifunctional macromonomers of precise molar mass and functionality. Among these, ω-allyl PEO macromonomers could be used successfully to design star-shaped polymers by coupling *via* hydrosilylation with multifunctional cores decorated with antogonist Si-H functions. Star-shaped PEOs are not only model materials for physicochemical studies, they can also be used for many applications. This stimulated the search for efficient ways to design star-shaped systems characterized by cores of controlled topology, and if possible of controlled functionality, controlled arm-length and eventually functionalizable at the outer-end of the branches. The first part of the present section concerns a discussion on the synthesis of selected examples of star-shaped PEOs. These PEO stars are characterized in most cases by organic cores. Only a few examples of hybrid star-shaped polymers exist. Most of these hybrid stars are constituted of POSS cores and organic polymers. The already existing few examples of POSS / stars will be presented in the final part of this section.

1.4.1. PEO star-shaped polymers

Star-shaped polymers are characterized as branched species where all the chains of one molecule are connected to a central unit which can also be a more extended core. The interest for star-shaped polymers arises from their compactness and enhanced segment density as compared to that of their linear counterparts of same molar mass. In the past 40 years intensive work has been devoted to star-shaped PEOs.[121,122] They represent interesting models for physicochemical studies and can also be used as building blocks for the synthesis of hydrogels[123] or serve as surface-modifying agents[124,125] to improve the biocompatibility of surfaces designed for biomedical applications.

Two main approaches were developed to design star-shaped polymers PEO: The so-called "core-first" method[121] in which a living polyfunctional core is used to initiate the AROP of EO. In the "arm-first" approach monofunctional PEOs[126,127] are reacted with low molar mass multifunctional compounds with antagonist functions. The major progress in the synthesis of star-shaped PEO polymers is based on the development of “core-first” strategies giving access to star-shaped species with functionalizable end-groups[122,128] at the outer end of the branches. The existence of these functionalizable star-shaped polymers opened new perspectives in the domain of macromolecular engineering. Below some typical examples of star-shaped PEO polymers will be presented and discussed.

1.4.1.1. “Core-first” method

Gnanou *et al*. used the “core-first” method for the preparation of star-shaped PEO. A polyfunctional initiator based on the reaction between potassium naphthalide and divinylbenzene was applied for the AROP of EO. The authors also described the possibility to access three-arms star PEOs *via* AROP of EO initiated by DPMK on trimethylolpropane.[121]

Well-defined PEO multiarm stars[129] characterized by high functionality were also prepared by R. Knischka *et al*. in a “core-first” strategy. Hyperbranched polyglycerol as well as polyglycerol modified with short oligo(propylene oxide) segments were deprotonated with DPMK and used as polyfunctional initiators for the AROP of EO to prepare functionalizable PEO stars.

Based on the same idea, multiarm PEO-star polymers, with a purely aliphatic polyether structure have been synthesized with different molar masses in a direct “grafting from” polymerization of EO from a multifunctional initiator. Hyperbranched poly(glycerol) precursor systems were partially deprotonated using CsOH H_2O or potassium naphthalide to initiate AROP of EO was performed. The PEO arms were characterized by MALDI–ToF MS.[130]

Eight-arm EPO stars can be prepared by the “core-first” method in the presence of octahydroxylated precursors.[131] This precursor is based on an modified *tert*-butylcalix[8]arene and the AROP was performed by addition of DPMK.

B. Comanita *et al.* described the synthesis of 4-arm, 8-arm, and 16-arm star PEOs starting from hydroxy multifunctionalized carbosilane dendrimers in the presence of potassium naphthalene as initiator and cryptand [222].[132] The PEO arms are grown anionically from the multifunctional cores. The number of arms and the M_n value of each PEO arm are strictly controlled.

The synthesis of dendrimer-like polymers is based on the combination of the AROP of EO with three alcoholate functions as initiator.[133] 1,1,1-Tris(hydroxymethyl)ethane with DPMK was used as initiator for the AROP of EO. Three arm PEOs are obtained and the hydroxy chain-ends are modified with allyl chloride, in the presence of tetrabutylammonium bromide and sodium hydroxide, yielding a three-arm PEO star with allylic end-groups. This compound was, in turn, submitted to a bis-hydroxylation reaction using OsO_4 and *N*-methylmorpholine-*N*-oxide and *tert*-butyl alcohol. The reiteration of these steps yielded dendrimer-like PEOs up to the eighth generation, carrying 384 hydroxyl end groups.

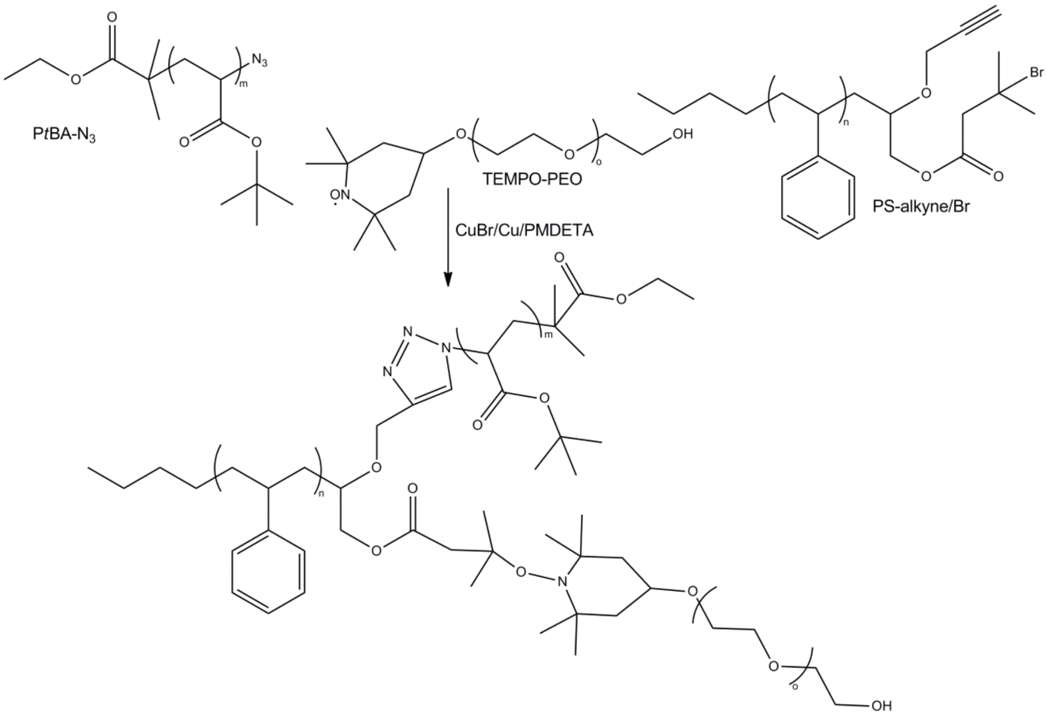
Another type of star-shaped PEOs was synthesized based on a modified cyclodextrins core able to form channels in lipid bilayers. The per-2,3-heptyl-*b*-cyclodextrins was used as EO polymerization initiator. Addition of DPMK to a solution of this molecule leads to formation of alkoxide functions, subsequently the EO polymerization was performed.[134]

1.4.1.2. “Arm-first” method

S. Hou *et al*. developed another possibility to access multiarm PEO stars. The authors prepared six arm PEO stars with six pyridyl or twelve hydroxyl end-groups. Heterodifunctional PEOs were synthetized using hydroxymethyl pyridine or 5,5-dimethyl-2-hydroxymethyl-1,3-dioxane as initiators with DPMK for the AROP of EO. α-Pyridyl-ω-hydroxy PEOs were obtained in the first case and α-ketal-ω-hydroxy PEOs in the second case. The hydroxyl functions of these PEO were deprotonated with DPMK and hexacyclophosphazene was introduced. 6-Armed pyridiniumum-ended PEO were elaborated in the first case and 6-armed dodecahydroxy-ended PEOs in the second case. The last six arm PEO star was used for the synthesis of dendrimer-like PEO.[127]

1.4.2. Controlled polymerization process and click chemistry

More recently, "click chemistry" was used in combination with controlled polymerization processes to access PEO based branched architectures.[135-137] A new approach was described for the synthesis of ABC 3-miktoarm star polymers with poly(ethylene oxide)-*block*-polystyrene-*block*-poly(ε-caprolactone)s *via* combination of click chemistry, atom transfer radical polymerization and ring opening polymerization.[135] Q. Fu *et al.* developed an original strategy for the synthesis of 3-miktoarm star terpolymers to obtain star-shaped terpolymers. The ABC 3-miktoarm star terpolymers are a type of nonlinear polymers, which consists of three chemically different polymeric chains emanating from a central junction point. The three precursors poly(*tert*-butyl acrylate) with azide end group, TEMPO-PEO and ω-propargyl and ω'-(2-bromoiso butyryl) PS were prepared separately. The star terpolymer constituted of poly(*tert*-butyl acrylate), PS and PEO could be obtained *via* a combination of click chemistry and atom transfer nitroxide radical coupling reaction (Scheme 41).[136]

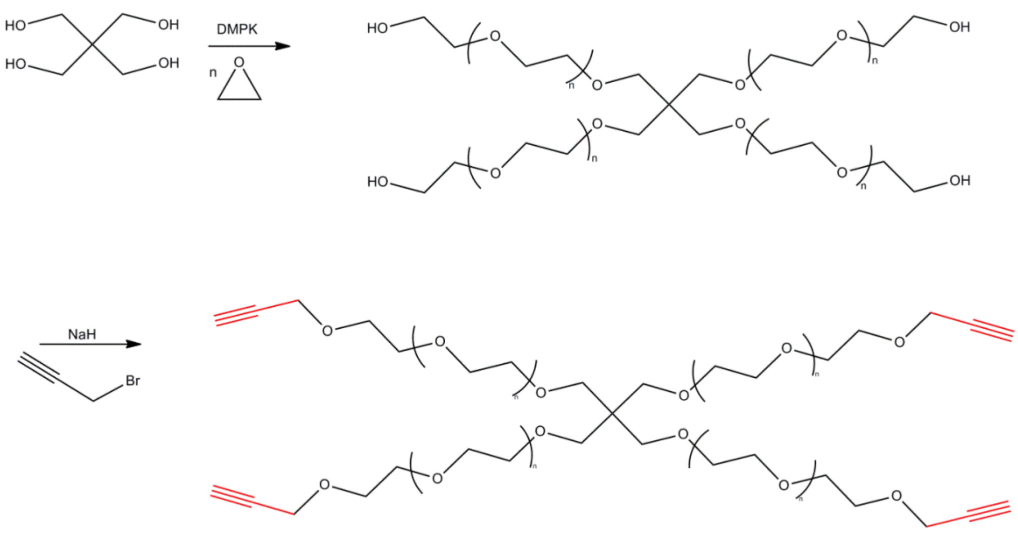


Scheme 40: Schematical representation of the synthesis of 3-miktoarm star terpolymer star(PtBA-PS-PEO) (taken from ref.[136]*).*

Dendrimer-like [PEEGE-(PS/PEO)]$_2$ was synthesized in one step by coupling *via* click chemistry star[polystyrene-poly(ethylene oxide)-poly(ethoxyethyl glycidyl ether)] [star(PS-PEO-(PEEGE-OH))] terpolymers modified with propargyle bromide.[137]

The combinatorial chemistry was used to design a novel star-shaped block copolymer, consisting of a PEG core and a poly(ε-caprolactone) shell with a unique potential for a range of applications.[138]

Star-shaped PEOs were synthesized by AROP of EO using pentaerythriol as initiator and DPMK. The EO polymerization was terminated by addition of acidic methanol to introduce hydroxyl functions at the outer end of the PEO arms. These chain-ends were transformed in acetylene functions. Finally eight-shaped PEOs were obtained by Glaser coupling reaction (Scheme 42).[139]

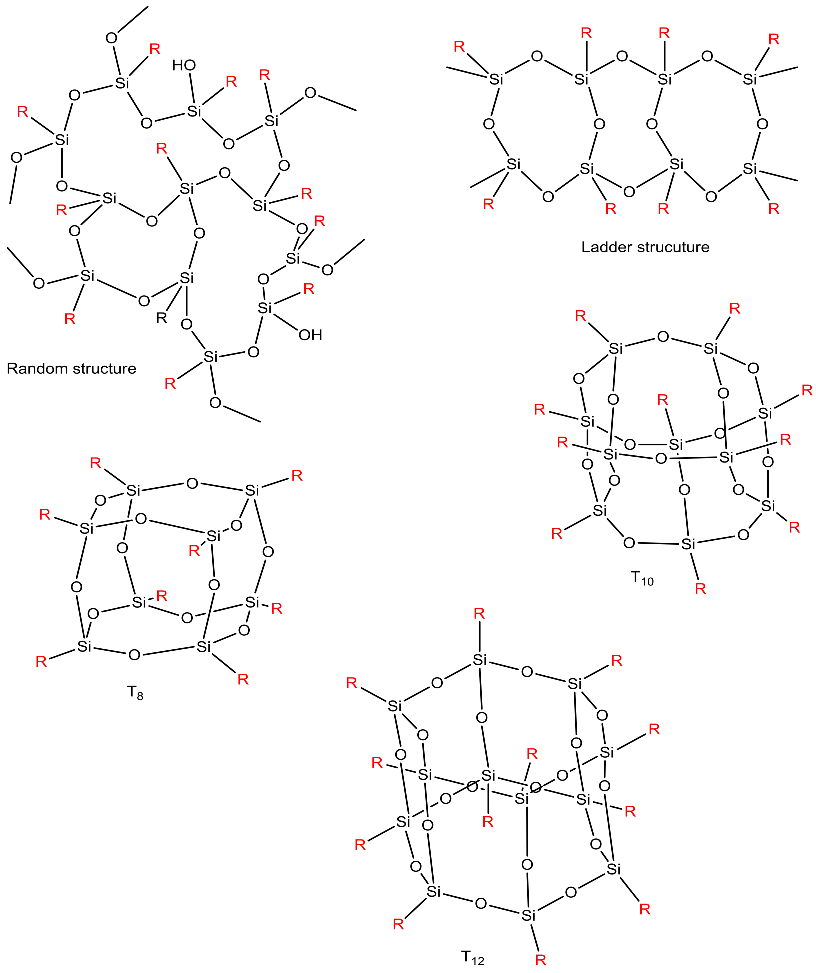


Scheme 41: Schematical representation of the synthesis star-shaped PEO with alkyne group (taken from ref.[139]).

1.4.3. Polyhedral oligomeric silsesquioxanes

The term silsesquioxanes refers to all structures with the empirical formulas $RSi0_{3/2}$ where R is hydrogen or any alkyl, alkylene, aryl, arylene. …[140] The first oligomeric organosilsesquioxanes, $(CH_3SiO_{3/2})_n$, were isolated by D. W. Scott in 1946.[141] The structures of silsesquioxanes have been reported as random structure, ladder structure, cage structures, and partial cage structure (Scheme 43).[140,142]

POSS are unique three dimensional nanometer-sized building blocks that can be used for the construction of a large variety of organic-inorganic hybrid macromolecular architectures.[140-145] R. H. Baney *et al.* described the structure, preparation, properties, and applications of silsesquioxanes. A variety of structures can be prepared with the general formula $(RSiO_{3/2})_n$, where n is commonly 6, 8, or 10. Various substituents can be introduced on the inorganic cores. Non-reactive substituents improve the solubility and ensure the compatibility of POSS with an organic medium. Functional groups, polymerizable or not, linked to inorganic cores are used to incorporate POSS in polymers. The combination between POSS and organic polymers has attracted increasing interest in recent years. The Si-O-Si fragments are chemically inert and thermally stable. The incorporation and effects of POSS on polymeric material properties have been published.



Scheme 42: Schematical representation of different silsesquioxanes.

Octasilsesquioxanes POSS with the $(RSiO_3/_2)_8$ formula are the most studied. These POSS are constituted of the siloxane cage and with up to eight reactive functions.[142] Many types of POSS structures, $R'R_7Si_8O_{12}$, where R' and R are two different substituents or functions, such as organic, organometallic groups or single atoms (H, Cl), have been prepared in the last twenty years.[144] The different ways, by copolymerization or grafting, to incorporate these POSS structures in polymers and the properties of the resulting hybrid materials, have been discussed recently by S.-W. Kuo *et al.*.[145]

1.4.4. PEO / POSS

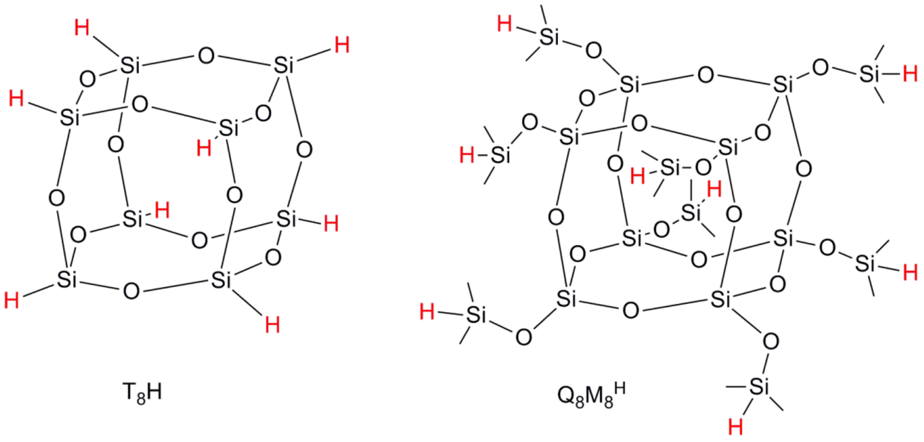
Most of the materials based on POSS and polymers are constituted of hydrophobic polymers.[146] Only few studies were conducted on the grafting of PEO chains onto POSS entities.[126,147] PEO / POSS combinations would provide access to new hybrid materials, eventually water-soluble, characterized by enhanced thermal and thermomechanical stability, mechanical toughness or optical transparency. Such materials are already applied in lithium ion batteries.[148]

A novel type of amphiphilic spherosilsesquioxane derivative with POSS was developed by R. Knischka *et al.*.[147] Monosubstituted cube-shaped spherosilsesquioxanes were synthesized with amphiphilic properties *via* hydrosilylation between the hydrophobic spherosilsesquioxane core, $(HSiO_{3/2})_8$ (T_8H), a hydrophilic PEO segments, an ω-allyl PEO of M_n = 750 g/mol, in the presence of a H_2PtCl_6 catalyst (Speier catalyst). The surface tension of the water-soluble PEO base amphiphile was measured. Self-organization of the amphiphiles in solution leads to micellar and vesicular structures.[147]

The ω-allyl PEO could also be used to prepare octafunctional PEO star-shaped polymers, $Q_8M_8^{PEO}$.[149] The hydrosilylation was preformed between $Q_8M_8^{H}$ and ω-allyl PEO (n= 2, 4, 8, 12) with platinum divinyltetramethyl disiloxane, Pt(dvs) (Karstedt catalyst). The reaction was carried out under anhydrous conditions until the Si-H signal (4.7 ppm) disappeared in the ^1H NMR spectrum. The properties of $Q_8M_8^{PEO}$ were studied in TGA and DSC measurements.

E. Markovic *et al.* proposed to study the properties of the ω-allyl PEO (n = 2, 3, 4, 6) and $Q_8M_8^{PEO}$ by DSC and TGA.[150] The authors expanded the hydrosilylation reaction with T_8H. The products were chemically characterized by FTIR, ^1H, ^{13}C, and ^{29}Si NMR spectroscopy.

K. Y. Mya *et al*. prepared $Q_8M_8^{PEO}$ with an ω-allyl PEO of M_n = 2000 g/mol. Star-shaped PEO were prepared by hydrosilylation reaction between ω-allyl PEO and $Q_8M_8^{H}$ with the Karstedt catalyst. The amphiphilic properties and aggregation of $Q_8M_8^{PEO}$ in aqueous solution were carried out by fluorescence, DLS, SLS, and TEM. A core-corona structure of unimolecular and aggregated $Q_8M_8^{PEO}$ was found in aqueous solution probably due by the presence of very short chains of PEO with the protective effect of the core would be ineffective or defective functionalization (f = 5) (Scheme 44).[126]



T_8H

$Q_8M_8^H$

Scheme 43: Schematical representation of the structures of silsesquioxanes T_8H and Q_8M_8H.

Conclusion

This bibliographic study provides some state of art information on the different methods to prepare linear hydroxy PEOs, PEO macromonomers, block copolymers and star-shaped PEOs.

AROP is the best method to prepare PEOs. Initiation can be performed by an alcoholate or a functional initiator (generally by a metal initiated with sodium or potassium) to introduce functionalities at the α-chain-end. The living chain-ends are deactivated with alcohol or acid to introduce hydroxyl functions at the ω-chain-end. The introduction of functionalities at the ω-chain-end can also be performed by deactivation with an unsaturated compound. This function can be used for the preparation of block copolymers, graft copolymers and star-shaped polymers. However, this method requires the use of EO. Commercial ω-hydroxy or α-hydro-ω-hydroxy functionalized PEOs can be utilized to access PEO macromonomers by chain-end modification with an unsaturated compound. By these both methods, well-defined PEO macromonomers can be obtained, heterofunctional, heterobifunctional or bifunctional.

Usually anionic polymerization of isoprene and EO is applied for the preparation of PI-*b*-PEO. ω-Hydroxyl PIs are prepared by addition of some EO units at the end of the isoprene polymerization. The hydroxyl chain-ends were activated by an initiator to perform the EO polymerization and to access PI-*b*-PEO. However the addition of a phosphazene base after the end of the isoprene polymerization enables the preparation of an EO polymerization in the same medium. Click chemistry is another option to synthesize such blocks copolymers.

The preparation of PEO star-shaped polymers is elaborated by the “core-first” or the “arm-first” approaches. The “core-first” method requires the use of EO and a polyfunctional initiator. In the “arm-first” method, heterofunctional PEOs or POSS compounds can be used as core. Click chemistry is another possibility for the synthesis of ABC 3-miktoarm, star terpolymers, star-shaped block copolymers and eight-shaped PEOs.

PEO chains grafted on POSS allows to access hybrid organic/inorganic nano-object. PEO star-shaped with one or eight PEO branches can be elaborated *via* hydrosilylation on POSS compound.

This discussion has oriented the work of the presented thesis to the synthesis of PEO macromonomers. The first approach (undecenolate initiator) is employed *in situ* or in powder form, for the EO polymerization. α-Undecene-ω-hydroxy heterobifunctional PEO macromonomers can be obtained with high molar masses and low polydispersity index values. The advantage of the hydroxy groups is the possible modification of the PEO chain-ends in α-undecene-ω-methacryloyl or α-undecene-ω-acetylene PEO macromonomers. Methacryloyl groups can be reacted to form star or comb-shaped PEOs with free terminal undecenyl double bonds *via* thiol-ene click reaction or ATRP in water. α-Undecene-ω-acetylene PEO macromonomers can be coupled *via* click chemistry with ω-azido PI to obtain PI-*b*-PEO. ω-Azido PI can be prepared by chain-end modification of ω-hydroxy PI. The second approach allows the preparation of ω-allyl and ω-undecenyl PEO macromonomers starting from commercial ω-hydroxy terminated PEOs. The grafting of these PEOs on the $Q_8M_8^H$ *via* hydrosilylation will be discussed.

List of schemes

List of references

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Chapter 2

ω-Allyl poly(ethylene oxide)s and hybrid star-shaped polymers

Gladys M.-E. Pozza, Hassan Harris, Markus J. Barthel, Jürgen Vitz, Ulrich S. Schubert*, Pierre J. Lutz*

"Macromonomers as well-defined building blocks in the synthesis of hybrid octafunctional star-shaped poly(ethylene oxide)s"

Macromol. Chem. Phys. **2013**, *20*, 2181-2191

2.1. Summary

The second chapter of the thesis is devoted to the controlled synthesis of new branched hybrid inorganic-organic water soluble materials. These PEO based materials should combine the unique behavior of organic polymers with the good physical properties of POSS. They should be characterized by enhanced thermal and thermomechanical stability as well as mechanical toughness.

The synthesis and characterization of a series of PEO macromonomers decorated at one or both chain ends either with allyl or with undecenyl end-groups is described first. The second part concerns the coupling, *via* hydrosilylation, of ω-allyl PEO macromonomers with octafunctionalized silsesquioxanes to yield star-shaped polymers.

A series of α-methoxy-ω-allyl PEO macromonomers were obtained upon addition of allyl bromide to commercial α-methoxy-ω-hydroxy PEOs after modification of the chain-end with DPMK. The resulting functional PEOs were characterized by SEC to verify the absence of coupling products. The functionalization yields are almost quantitative as revealed by ^{1}H NMR. MALDI-ToF MS measurements attested also the presence of the allyl group at the chain-end of the mono or bifunctionalized PEOs. A similar approach was investigated to try to decorate PEO chain-ends with undecenyl end-groups. The interest for such PEOs arises from the presence of a flexible hydrophobic spacer between the double bond and the PEO who may enhance the reactivity and could affect the solubility in water. These attempts were not successful as under the chosen experimental conditions almost identical to those used for the synthesis of α-methoxy-ω-allyl PEOs no quantitative functionalization could be achieved. This point will be addressed again in Chapter 3 as PEOs quantitatively decorated with undecenyl end-groups may be of interest for a range of potential applications.

The second part discusses the coupling of these ω-allyl PEOs *via* hydrosilylation with silsesquioxanes cores ($Q_8M_8^H$) decorated with eight antagonist Si-H functions. The former becomes the branch and the latter the core of the star-shaped PEO named $Q_8M_8^{PEO}$. For these reactions, a platinum catalyst (Speier catalyst) was selected. Two ω-allyl functional PEOs of M_n 1900 and 4600 g/mol were chosen. The different reaction products were characterized by three independent methods: SEC, IR and ^1H NMR. SEC with RI detection was used to evaluate the amount of ω-allyl PEO grafted. The kinetics of the reaction was followed by ^1H NMR. Preliminary grafting experiments demonstrated that the reaction has to be carried with a molar ratio [ω-allyl PEO] / [$Q_8M_8^H$] of at least 10, to avoid the presence of residual Si-H functions. Under these conditions hybrid PEO stars (Figure 2.1a) characterized by branches of M_n up to 10000 g/mol could be obtained. The absence of Si-H functions was confirmed by IR and ^1H NMR. Once purified by fractional precipitation, the absolute molar mass of the star molecules was determined by light scattering. An average functionality of eight was measured.

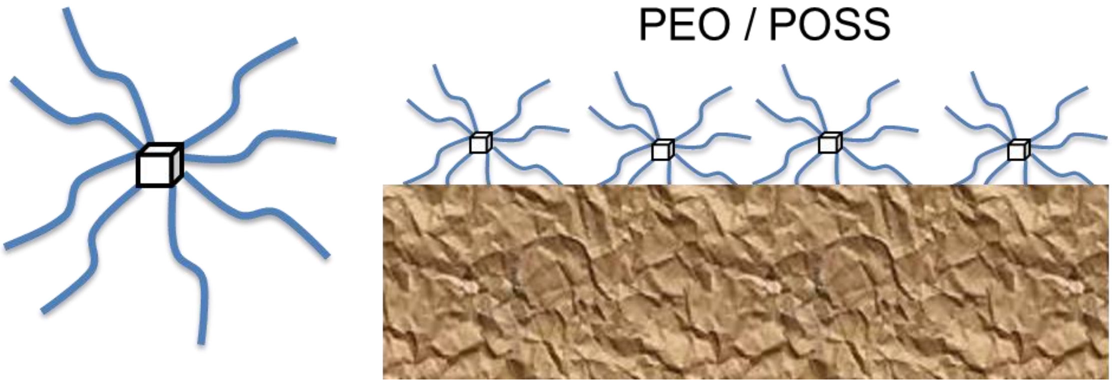

Figure 2.1 a) Left typical representation of a PEO / POSS star. b) Schematical representation of a block surface modified by PEO / POSS stars.

Molar mass and functionality of the PEO stars were also determined by MALDI-ToF MS. The values are in good agreement with those measured by LS.

A potential application of these PEO / POSS stars as surface modifying agent is presented in Figure 2.1. These PEO / POSS could by linked to hydrophobic surfaces to enhance their hydrophilicity as well as their biocompatibility. In addition the presence of the POSS entity should also improve the mechanical properties of the surface coating.

The extension of this reaction to ω-undecenyl PEO macromonomers will be discussed in Chapter 5 of the thesis.

2.2. Article 1

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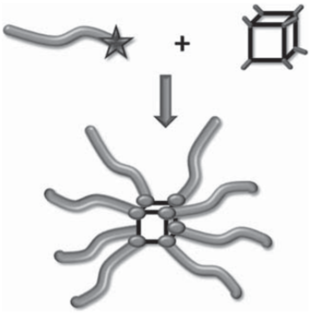
Macromonomers as Well-Defined Building Blocks in the Synthesis of Hybrid Octafunctional Star-Shaped Poly(ethylene oxide)s

Gladys M.-E. Pozza, Hassan Harris, Markus J. Barthel, Jürgen Vitz, Ulrich S. Schubert,* Pierre J. Lutz*

The present work addresses the synthesis and the molecular and structural characterization of soluble macromolecular architectures based on functional poly(ethylene oxide) (PEO)s and octafunctional silsesquioxanes. The synthesis of a series of functional PEOs by deactivation, decorated with allyl groups at one chain-end, was considered first. PEO star-shaped polymers were prepared by coupling via hydrosilylation of ω-allyl PEOs with octakis(hydridodimethylsiloxy)octasilsesquioxane $(HMe_2SiOSiO_{1.5})_8$ ($Q_8M_8^H$), in the presence of a "Speier" catalyst. The products were characterized by SEC, ^{1}H NMR spectroscopy, light scattering, and MALDI–TOF MS to determine the molar masses and degree of functionalization. The star-shaped PEOs ($Q_8M_8^{PEO}$) could be isolated from the raw reaction product and characterized. A functionalization close to the theoretical value was obtained.



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1. Introduction

Poly(ethylene oxide) (PEO) star-shaped polymers[1–3] are regarded as a particularly promising class of materials since they represent interesting models for physicochemical studies, variable building blocks for hydrogels,[4,5] or for amphiphilic networks that are of great interest for a wide range of biomedical and pharmaceutical applications. They can also serve as surface-modifying agents to improve the biocompatibility of surfaces designed for biomedical applications.[6,7] Several approaches based on the living anionic polymerization of oxirane have been developed to provide access to PEO stars covering a large range of molar masses and constituted of cores of different

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chemical nature and functionalities.[1–3,8,9] Strategies based on the polymerization of well-defined monofunctional PEO macromonomers represent an interesting alternative to design PEO branched architectures.[10–12] Such polymers behave as branched or star-shaped polymers depending on the length of the backbone.[13,14] More recently, "click chemistry" was used in combination with controlled polymerization processes to enable access to PEO-based branched architectures.[15–18] The advantage of combinatorial chemistry was used to design a novel class of PEO-based branched amphiphilic materials with a unique potential of applications.[19]

Hybrid inorganic–organic materials, combining the behavior of organic polymers with physical properties of ceramics, have attracted increasing interest in recent years.[20–24] In the past two decades, polyoctahedral silsesquioxanes (POSS) constituted unique three dimensional nanometer-sized building blocks that can be used to create a large variety of hybrid macromolecular architectures.[23–26] Much interest has been devoted to hybrid materials based on POSS and PEO. PEOs, fitted at one chain with POSS[27] or star-shaped PEOs with a central octafunctional POSS core,[28] represent typical examples. Monosubstituted cube-shaped spherosilsesquioxanes with amphiphilic properties, combining the hydrophobic spherosilsesquioxane core with the hydrophilic oligo (ethylene oxide), were synthesized. Aggregation of the uncondensed amphiphile leads to micellar and vesicular structures.[27] Along the same line, new amphiphilic PEOs modified at the chain-ends with POSS entities[29] could be obtained and their dilute solution behavior examined. As mentioned above, octafunctionalized cubic silsesquioxanes were also used as nanosized reactive building blocks to yield PEO star-shaped polymers[28,30] or cross-linked PEO-based materials.[31] Star-shaped PEOs with silsesquioxane cores were established as an emerging class of new water-soluble materials characterized by enhanced thermal and thermomechanical stability, mechanical toughness, or optical transparency.[28] Their structural parameters and behavior were systematically investigated. However, most of the studies were limited to PEO chains of molar masses ($\overline{M}_n$) of 2000 g mol^{-1} or below. Therefore, the protection exerted by the PEO chain is not efficient and the solubility of the resulting star-shaped polymers poses problems. The main goal of the present work is to design new complex hybrid architectures based on PEO and to extend the domain of molar masses covered by the ω-functional PEO precursors. The first part of the manuscript will be devoted to the synthesis and the characterization of a series of ω-allyl PEOs to be used in hydrosilylation reactions. The second part discusses the coupling of these ω-allyl PEOs by hydrosilylation with octafunctionalized silsesquioxanes ($Q_8M_8^H$) with the aim to access well-defined hybrid star-shaped PEO.

2. Experimental Section

The purification of the different products and the synthesis of ω-allyl or ω-undecenyl PEOs obtained by deactivation of the chain-end with allyl bromide or 11-bromo-1-undecene after modification with diphenylmethyl potassium (DPMK) as well as the synthesis of the octafunctional star-shaped poly(ethylene oxide)s ($Q_8M_8^{PEO}$) from ω-allyl PEOs via hydrosilylation with $Q_8M_8^H$ in the presence of a "Speier" catalyst are discussed in Supporting Information (s.i.).

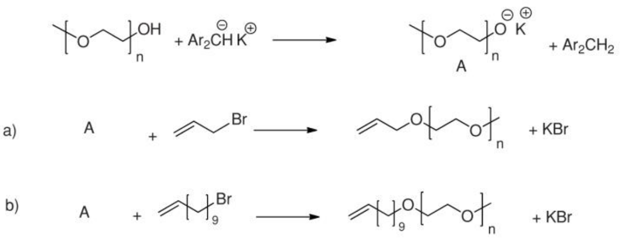
3. Results and Discussions

3.1. Synthesis of the PEO Macromonomers

A great variety of methods have been developed over the years to synthesize PEO macromonomers.[32–35] A detailed discussion of the different approaches to design PEO macromonomers is out of the scope of the present work. Briefly, two main approaches have been considered, either the initiator contains a polymerizable group, which is not affected by the polymerization reaction, or the living chain is capped with an electrophile containing a polymerizable group.

3.1.1. ω-Allyl PEOs

In the present work, we selected an approach derived from the "chain-end functionalization" method to prepare the ω-allyl PEOs starting from commercial PEOs after modification of the chain-ends with DPMK[36] followed by the addition of ally bromide (Scheme 1a). The metalation can also be performed with potassium naphthalene.[27] This



Scheme 1. Schematical representation of the functionalization of α-methoxy-ω-hydroxy PEOs with allyl bromide (a) or 11-bromo-1-undecene (b) after modification of the chain-end by reaction with a stoichiometric amount of DPMK.

Table 1. Molecular characteristics of the ω-allyl PEOs obtained by deactivation with allyl bromide after modification of the chain-end with DPMK.

Reference	$\overline{M}_{\mathrm{w}}$ [a)] [g mol^{-1}]	$\overline{M}_{\mathrm{n}}$ [b)] [g mol^{-1}]	PDI [c)]	$\overline{M}_{\mathrm{w}}$ [d)] [g mol^{-1}]	$\overline{M}_{\mathrm{n}}$ [e)] [g mol^{-1}]	PDI [f)]	f [g)] [%]
PEOallyl1	1800	1750	1.03	1900	1800	1.05	92
PEOallyl2	1800	1750	1.03	1900	1800	1.05	93
PEOallyl3	1800	1750	1.03	1900	1800	1.05	93
PEOallyl4	5350	4900	1.09	5600	5100	1.10	95
PEOallyl5	11 100	10 000	1.11	11 300	10 200	1.11	96
EOallyl1*	–	–	–	9800	9050	1.08	96
EOallyl2	–	–	–	11 100	10 500	1.06	92
EOallyl3*	–	–	–	14 300	12 900	1.11	97

*These sample were prepared by living anionic polymerization of ethylene oxide followed by direct deactivation of the alcoholate with allyl bromide as described in ref. [40]; [a)]Weight - average molar mass of the α-methoxy-ω-hydroxy PEOs, measured by SEC, calibration with linear PEOs; [b)]Number - average molar mass of the α-methoxy-ω-hydroxy PEOs, measured by SEC, calibration with linear PEOs; [c)]Poly dispersity index (PDI) of the α-methoxy-ω-hydroxy PEOs ($\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$) determined by SEC; [d)]Number - average molar mass of the ω-allyl PEOs, measured by SEC, calibration with linear PEOs; [e)]Weight - average molar mass of the ω-allyl PEOs, measured by SEC, calibration with linear PEOs; [f)]PDI of the ω-allyl PEOs ($\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$) determined by SEC; [g)]Yield of functionalization of the ω-allyl PEOs measured by ^{1}H NMR (400 MHz) in $CDCl_3$ using an external standard ($C_2H_2Cl_2$); All the SEC measurements were conducted in THF ($dn/dc_{PEO} = 0.062$ mL g^{-1}).

procedure is preferable over the NaOH method because potassium initiators are much more efficient for the metalation and can be used at room temperature.[37]

PEO samples were obtained using DPMK for initiating the anionic polymerization of ethylene oxide, according to a well-established procedure,[38] followed by induced deactivation with allyl bromide. These syntheses are aimed to provide access to well-defined PEOs with molar masses higher than those of the commercial ones. The synthesis of such PEOs is also possible starting from allyl alcoholate as a initiator.[39]

After purification, the different reaction products were submitted to detailed characterization. It has to be established if every single molecule is modified with an end-standing double bond. The resulting functional PEOs were first characterized by size-exclusion chromatography (SEC) to verify the absence of the PEO precursor and of coupling products. Small PDI values, close to the precursor PEOs, were obtained by SEC (see Figure s.i.1, Supporting Information; and Table 1). In most cases the M_n values determined by SEC, and based on calibration with linear α-hydro-ω-hydroxy PEOs, are in good agreement with the expected values. The slight increase in molar mass with respect to the PEO precursor is attributed to the presence of the unsaturation at one chain-end.

For the same samples, ^{1}H NMR measurements were performed in $CDCl_3$ or DMSO-d_6. A typical ^{1}H NMR spectrum measured in DMSO-d_6 is presented in Figure s.i.2 (Supporting Information). In addition to the signals of the methylene protons [CH_2 (4n -2H), $\delta = 3.65$ ppm, PEO chain except the first methylene group], the spectrum is characterized by peaks assignable to the methoxy protons (initiator potassium methoxyethanolate). New peaks corresponding to the $CH_2 = CH$–protons appear ($CH_2 = CH$: $\delta = 5.20$ ppm, $CH_2 = CH$: $\delta = 5.90$ ppm) and the corresponding peak of the hydroxyl function (in the precursor polymer at 4.70 ppm) disappeared. By integrating the signals of the ^{1}H NMR spectra of the chain-end modified PEOs, the double bond content could be determined. The values are in good agreement with the expectation. The $\overline{M}_{\mathrm{n}}$ values of the ω-allyl PEOs could also obtained from ^{1}H NMR measurements and are close to the $\overline{M}_{\mathrm{n}}$ values measured by SEC. However, one has to be aware about the fact that, in particular for the 10 000 g mol^{-1} molar mass sample, the accuracy of the determination of the functionality by ^{1}H NMR is questionable. This could be a possible explanation for the apparent lower functionalization yield in some cases.

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI–TOF MS) has also been applied to analyze the different PEOs. Figure s.i.3a and 3b (Supporting Information) depict the MALDI–TOF MS spectra of an ω-allyl PEO, $\overline{M}_{\mathrm{n,SEC,}}$ 1900 g mol^{-1} and of its precursor, respectively. The signals between a m/z value of 1 772 and 1 816 with a characteristic shift of m/z 44 are unambiguously due to the PEO chain. The values calculated for the molar masses are in good agreement with the theoretical values. The difference in molar mass (of 40.18 g mol^{-1}) corresponds exactly to the value of the allyl end group. Furthermore, no α-methoxy-ω-hydroxy PEO is detectable. These different characterization results confirm that induced deactivation of metalated PEOs with allyl bromide indeed led to the expected ω-allyl compound.

3.1.2. ω-Undecenyl PEO Macromonomers

ω-Undecenyl PEO macromonomers characterized by the presence of a hydrophobic spacer between the double bond and the PEO chain exhibit an enhanced amphiphilic character. They are therefore of great interest as versatile amphiphilic building blocks. The first attempt to synthesize ω-undecenyl PEO macromonomers refers to an approach similar to that used for the synthesis of ω-allyl functional PEOs (see also Scheme 1b and Supporting Information). This choice was motivated by the fact that these PEO macromonomers are fitted at one chain-end with a methoxy group (and not an OH function, which is always present at the chain-end of α-undecene, ω-hydroxy PEO macromonomers obtained by initiation). We must remember, that the main interests of these ω-undecene PEO macromonomers lie in their use in coordination copolymerization with ethylene and, as well-defined build block, in the synthesis of star-shaped polymers by grafting via hydrosilylation onto POSS cores. In both cases, the OH function that is present at the PEO chain-end of macromonomers obtained by initiation may lead to side reactions. Two series of monofunctional PEO macromonomers were prepared with molar masses of 1750 and 4900 g mol^{-1}, respectively. Their structural characteristics were determined by SEC, ^{1}H NMR spectroscopy, and MALDI–TOF MS to determine the molar masses and the degree of functionalization. The results are presented in Table 2 together with the experimental conditions.

It appears that for the PEO species prepared at room temperature, the functionalization yields are far from being quantitative. This is probably due to the occurrence of side reactions during the functionalization process. This prompted us to perform a series of functionalization tests at lower temperatures. Decreasing the temperature from 25 to 10°C should limit the appearance of side reactions. It could be observed that the yield of functionalization is indeed higher, close to 65% for a PEO macromonomer with a molar mass of 4900 g mol^{-1}. As PEO is well known to crystallize in THF at a temperature below 0°C, functionalization reactions at lower temperatures are not possible. It also seems that an increase in the molar mass of the PEO chain corresponds to an increase of the yield of functionalization. That can be explained by the increasing solvation effect of PEO chains as the molar mass increases. The characterization by MALDI–TOF MS confirms the presence of several distributions corresponding to the precursor polymer, the functionalized polymer, and side products (Figure 1).

Therefore, this approach should not be considered for the synthesis of well-functionalized PEO macromonomers decorated at one or at both chain-ends with undecene groups. Such polymers are, however, of significant interest for a wide range of applications. This stimulated the search for more efficient ways to design PEO macromonomers quantitatively fitted at least at one chain-end with undecene end groups (to be reported in a future manuscript).[40]

3.1.3. PEO Star-Shaped Polymers by Coupling of ω-allyl PEOs with $Q_8M_8^H$

As indicated in "Section 1," there is a growing interest for star-shaped PEOs. The present work proposes to study well-defined hybrid star-shaped PEOs, covering a much larger

Table 2. Molecular characteristics of the ω-undecenyl PEO macromonomers obtained by deactivation with 11-bromo-1-undecene after modification of the chain-end with DPMK.

Reference	$\overline{M}_{\mathrm{w}}$ a) [g mol^{-1}]	$\overline{M}_{\mathrm{n}}$ b) [g mol^{-1}]	**PDI** c)	$\overline{M}_{\mathrm{w}}$ d) [g mol^{-1}]	$\overline{M}_{\mathrm{n}}$ e) [g mol^{-1}]	**PDI** f)	**Temp** [°C]	f g) [%]
PEOund1	1800	1750	1.03	2000	1900	1.05	25	25
PEOund2	1800	1750	1.03	2000	1900	1.05	25	45
PEOund3**	1800	1750	1.03	1950	1900	1.03	25	48
PEOund4	5350	4900	1.09	5750	5050	1.14	25	38
PEOund5*	5350	4900	1.09	5050	4800	1.05	25	30
PEOund6**	5350	4900	1.09	5150	4900	1.05	25	45
PEOund7	5350	4900	1.09	5800	5100	1.13	13	65

These samples were prepared by deactivated with 11-bromo-1-undecene after modification of the chain-end with: * Naphthalene Na or ** DPMNa; a)Weight - average molar mass of the α-methoxy-ω-hydroxy PEOs, measured by SEC, calibration with linear PEOs; b)Number - average molar mass of the α-methoxy-ω-hydroxy PEOs, measured by SEC, calibration with linear PEOs; c)PDI of the α-methoxy-ω-hydroxy PEOs ($\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$) determined by SEC; d)Weight - average molar mass of the ω-undecenyl PEO macromonomers, measured by SEC, calibration with linear PEOs; e) Number average molar mass of the ω-undecenyl PEO macromonomers, measured by SEC, calibration with linear PEOs; f)PDI of the ω-undecenyl PEO macromonomers ($\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$) determined by SEC; g)Yield of functionalization of the ω-undecenyll PEO macromonomer measured by ^{1}H NMR (400 MHz) in $CDCl_3$ using an external standard ($C_2H_2Cl_2$); All the SEC measurements were conducted in THF ($dn/dc_{PEO} = 0.062$ mL g^{-1}).

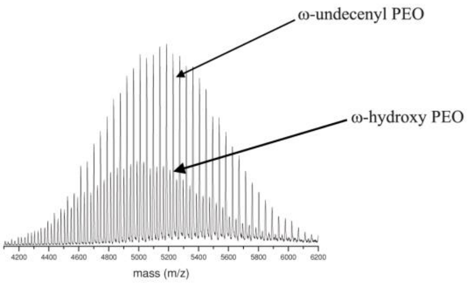


Figure 1. MALDI–TOF MS of an ω-undecenyl PEO macromonomer obtained by deactivation of the chain-end with 11-bromo-1-undecene after modification with DPMK.

domain of molar masses than existing PEO/silsesquioxane star-shaped PEOs. The synthesis is based on the coupling via hydrosilylation of ω-allyl functional PEOs with $Q_8M_8{}^H$ fitted with 8 antagonist Si–H functions. The hydrosilylation was selected because this reaction is well known to provide a convenient route for the synthesis of functional materials.[41]

3.1.3.1. Premiary Studies

It has been shown, that if an ω-allyl PEO is reacted by hydrosilylation with $Q_8M_8{}^H$, chemical bonds are formed between the precursor chains and the silsesquioxane compound (Scheme 2).[28,42] The former becomes the branch and the latter the core of the star-shaped PEO named $Q_8M_8{}^{PEO}$.

For these reactions, a platinum catalyst ($H_2PtCl_6 \bullet 6H_2O$/*iso*PrOH) was selected whose efficiency

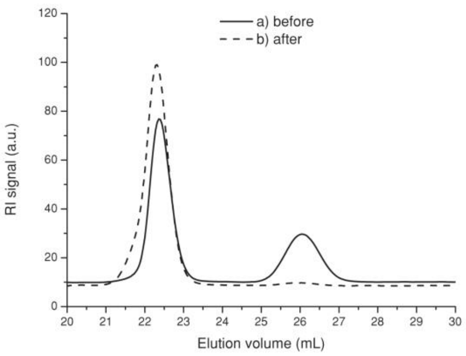
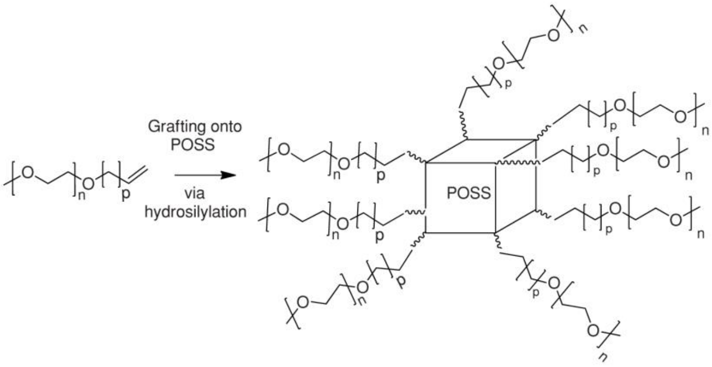


Figure 2. SEC traces (RI detector) of $Q_8M_8{}^{PEO}$, (a) before fractionation and (b) after fractionation.

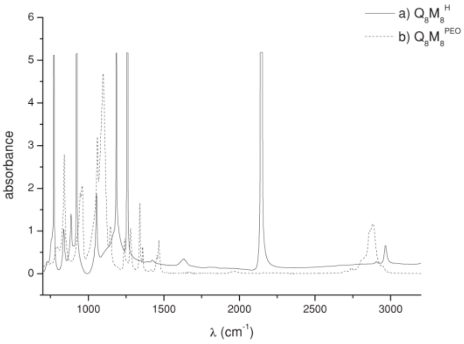
in hydrosilylation reactions is well established. This so-called "Speier" catalyst[43] is generally assumed to proceed by the Chalk-Harrod mechanism.[44] It is clear that side reactions cannot be entirely excluded.[37] Some attempts with the Karstedt catalyst are now under progress.[40]

A series of preliminary grafting experiments was carried out starting for ω-allyl functional PEOs of molar masses ($\overline{M}_n$) around 2000 and 5000 g mol^{-1}, respectively, for a ratio with [ω-allyl PEO]/[$Q_8M_8{}^H$] of **8** as described in Section 2 (see Supporting Information). The reaction was conducted at 75 °C for 15 h at a PEO concentration of 30 wt% and a platinum concentration of 10^{-5} mol L^{-1}. The reaction products were characterized by three independent methods: SEC, IR, and ^{1}H NMR. SEC with RI detection was used to evaluate the amount of PEO grafted onto the octafunctionalized silsesquioxane core. SEC with multi-angle light scattering was used to determine the absolute molar mass of the reaction products. It has to be established whether or not all the ω-allyl PEO chains have reacted with the antagonist functions of the octafunctionalized silsesquioxane core. A typical SEC trace is given in Figure 2a. This SEC reveals the presence of two peaks: a major one (attributed to the star-shaped PEO) and a second one corresponding to the unreacted ω-allyl PEO.

In this experiment, an ω-allyl PEO of an average



Scheme 2. Schematical representation of the synthesis of $Q_8M_8{}^{PEO}$ stars by coupling via hydrosilylation monofunctional ω-allyl (p = 1) or ω-undecenlyl (p = 9) PEO with $Q_8M_8{}^H$ in the presence of a "Speier" catalyst.



■ *Figure 3.* Infrared spectrum: (a) $Q_8M_8^H$, (b) $Q_8M_8^{PEO}$.

molar mass ($\overline{M}_n$) of 1900 g mol^{-1} was selected. Considering a core functionalization value of 8, the number-average molar mass of the PEO star should be 16 200 g mol^{-1}. Based on the calibration with linear PEOs, an apparent molar mass of 11 300 g mol^{-1} is obtained for the former, which is lower than expected. It is well established that star-shaped polymers, owing to their higher segment density, which implies a smaller hydrodynamic volume, exhibit higher elution volumes than the linear equivalent. It appears for the SEC results that the reaction product contains between 10 to 20 wt% of unreacted ω-allyl PEOs. However, from the IR measurements made on the same samples (after the same reaction time), it can be concluded that most of the Si–H functions (2150 cm^{-1}) disappeared (Figure 3).

This result is in contradiction with the ^{1}H NMR measurements, where the specific peak corresponding to unreacted Si–H (at 4.70 ppm) functions is still present in small amounts. A possible explanation for this phenomenon can be given by the characteristics of the IR-probe. Due to a self-absorbance of the diamond crystal in the Si–H region, the sensitivity of the measurements is significantly decreased.

3.1.3.2. Kinetic Studies of the Addition of the ω-allyl PEOs

This contradiction found in the studies mentioned above prompted us to investigate in more detail the grafting process with the help of ^{1}H NMR spectroscopy to establish the influence of the [ω-allyl PEO]/[$Q_8M_8^H$] ratio on the efficiency of the grafting process. We examined also the influence of the macromonomer and Pt concentration of the grafting yields for an [ω-allyl PEO]/[$Q_8M_8^H$] ratio of 10. Initially, we performed a series of grafting experiments with different [ω-allyl PEOs]/[$Q_8M_8^H$] ratios: 4, 8, and 10 at an ω-allyl PEO concentration of 30 wt% and a platinum concentration of 1 × 10^{-5} mol L^{-1}. The results of these studies are presented in Table 3.

Table 3. Molecular characteristics of the PEO star-shaped polymers obtained by grafting via hydrosilylation of ω-allyl PEOs onto octafunctional silsesquioxanes ($Q_8M_8^{PEO}$).

Reference	$\overline{M}_n$[a] [g mol^{-1}]	$\overline{M}_{n,th}$[b] [g mol^{-1}]	**Macro**[c]	$\overline{M}_{w,Star}$[d] [g mol^{-1}]	$\overline{M}_{n,Star}$[e] [g mol^{-1}]	**PDI**[f]	$\overline{M}_{w,\,Star}$[g] [g mol^{-1}]	f[h]
SSPEO1	1900	16 200	22	13 600[i]	12 400[i]	1.08[i]	17 000	–
SSPEO2[j]	1900	16 200	23/25	13 500	12 500	1.08	17 000	8.9
SSPEO3[j]	1900	16 200	18/4	12 200	11 300	1.08	–	–
SSPEO4	1900	16 200	22/3	13 400	12 300	1.09	15 500	8.2
SSPEO5	1900	16 200	29/3.7	12 900	11 800	1.09	– *	–
SSPEO6	1900	16 200	21/1	13 000	12 300	1.06	–	–
SSPEO7	4600	37 000	38/4	28 000	25 000	1.12	32 000	9.3
SSPEO8	4600	37 000	32	26 000	22 700	1.14	– **	–

Experimental conditions: solvent toluene, polymer concentration (30 wt%), Pt concentration: 10^{-5} mol L^{-1}, reaction temperature 75 °C, reaction time 15 h; *This sample is characterized by the presence in the raw samples of three peaks in RI detection (PEO macromonomer, the star-shaped PEO, and the coupling product corresponding probably to the reaction between Si–H groups of two stars). The main product could be isolated by repeated fractionation from raw reaction product; **Fractionation of this sample was not efficient, this sample contained low concentrations of high molar mass PEO star resulting probably form coupling of two stars during the reaction (detected by SEC online light scattering); [a]Number - average molar mass of the ω-allyl PEOs, measured by SEC, calibration with linear PEOs; [b]Number - average molecular mass of the PEO stars calculated taking into account the molar mass of the branch, the core and assuming a functionality of 8; [c]wt% of the residual PEOs in the raw reaction product/after purification; [d]Weight - average molar mass of the PEO stars, measured by SEC, calibration with linear PEOs; [e]Number - average molar mass of the PEO stars, measured by SEC, calibration with linear PEOs; [f]PDI determined by SEC in THF; [g]Weight - average molar mass determined by LS in methanol after fractional precipitation; [h]Functionality of the PEO star calculated from the ratio between the mass - average molar mass of the PEO star (measured by LS in methanol, after fractionation) and the molar mass of the precursor measured by SEC (RI); [i]Values determined on the raw sample by SEC based on calibration with linear PEOs; [j]These samples were purified by dialysis.

Samples SSPEO9 and SSPEO10 (not mentioned in Table 3) were prepared at an ω-allyl PEO concentration of 15 wt% and a Pt concentration of 2×10^{-4} and 1×10^{-5} mol L^{-1}, respectively. SEC studies performed with these samples revealed that the grafting reaction is not quantitative. The content of residual ω-allyl PEO is higher than 60 wt%. The studies confirmed the influence of the polymer concentration in the reaction medium on the overall functionalization yield, already observed by other authors.[45,46] As a consequence, we decided to perform all the grafting reactions at much higher concentrations. These conditions were used to study the influence of the ratio [ω-allyl PEO]/ [$Q_8M_8^H$] on the grafting yield. The reaction products obtained in these reactions were systematically investigated by IR, ^{1}H NMR, and SEC. It was found, that regardless the ratio [ω-allyl PEO]/[$Q_8M_8^H$], the characteristic peak at 2150 cm^{-1} for the Si–H function disappeared (Figure 3). After reaction of the ω-allyl PEO with the Si-H functions of $Q_8M_8^H$, the characteristic peaks of the double bond at 5.20 and 5.80 ppm disappeared as well as the peak at 4.70 ppm, characteristic for the Si–H functions. The peak of the methyl group on the $Q_8M_8^H$ entity at 0.25 ppm is shifted to higher fields (0.13 ppm). The ^{1}H NMR spectra of the different reaction products are presented in Figure 4.

The peak associated to the Si–H functions is totally absent in the ^{1}H NMR spectrum when the reaction is conducted with a ratio [ω-allyl PEO]/[$Q_8M_8^H$] of 10 (Figure 4c). However, double bonds of ω-allyl PEO could not be detected. This is not the case when the reaction is performed with a ratio of 8 (Figure 4b). The characteristic peak for the methyl group ($Si(CH_3)_2$) is still present at 0.25 ppm, however, only in very small amounts. This peak is, as expected, more significant when the reaction is performed at a ratio [ω-allyl PEO]/[$Q_8M_8^H$] of 4 (Figure 4a). From these results, it can be concluded that the NMR technique seems much more suited than FTIR to monitor the grafting reaction of ω-allyl PEOs onto octafunctionalized silsesquioxane cores. These results led us to conduct all grafting reactions of ω-allyl PEOs onto silsesquioxanes with a molar ratio [ω-allyl PEO]/[$Q_8M_8^H$] of at least 10. However, this implies that, even when all the Si–H functions have been coupled with the ω-allyl PEOs, unreacted ω-allyl PEO is still present in all grafting reaction products, which has to be removed from raw reaction products. The results of the reaction of a series of ω-allyl PEOs, under the above-mentioned conditions, are reported in Table 3. A typical SEC trace of such a reaction product is given in Figure 2a. The efficiency of grafting was also evaluated by IR and ^{1}H NMR. However, such measurements are of limited interest as they were performed on raw samples. Nevertheless, they can be helpful for preliminary experiments to define rapidly the optimal experimental conditions. The first major peak, present at a low elution volume, corresponds to the star-shaped PEO. The second peak, present in a small quantity at higher elution volume, corresponds to the ω-allyl PEO, which was on purpose introduced in excess. Thus, the raw reaction product contains both the star-shaped PEO and the ω-allyl PEO, which has to be removed. This is important as the presence of a linear PEO would affect the behavior of the star-shaped PEO. The above discussed results stimulated us to investigate different approaches to isolate the PEO star from the raw reaction

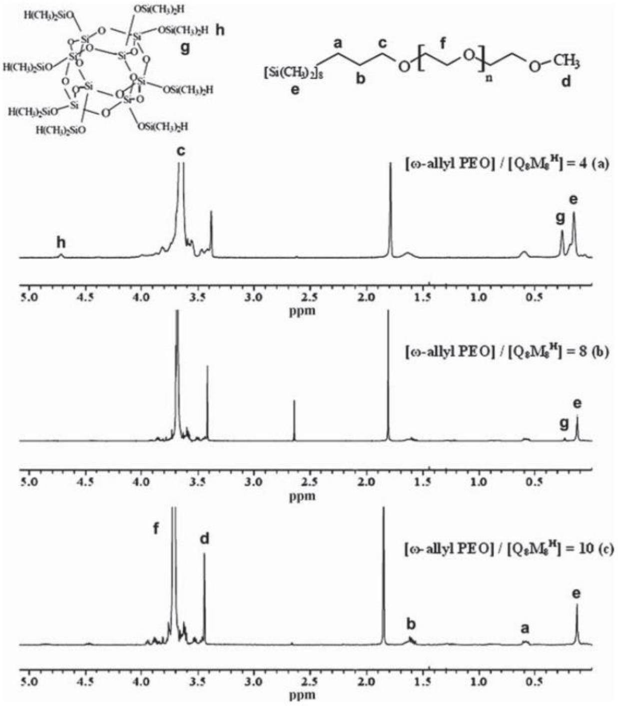


Figure 4. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the kinetics of the addition reaction of ω-allyl PEOs onto $Q_8M_8^H$ conducted at different [ω-allyl PEO]/[$Q_8M_8^H$] ratios (4, 8, and 10).

product. Classical fractionation methods imply temperature manipulation. These methods revealed to be very efficient for the fractionation of noncrystalline polymers such as the isolation of cyclic polymers from raw reaction products.[47] However, it has been established that the fractionation of PEOs does not work if the θ temperature is much below the crystalline melting point. However, advantage has been taken from the existence of a lower critical solution temperature (LCST) of PEOs to fractionate the raw products efficiently. It is also well known that the addition of salts lowers the LCST. By performing fractional precipitation in an aqueous solution of sodium carbonate, Merrill and co-workers[48] were able to isolate star-shaped PEOs obtained by the called "core-first" method,[49] characterized by bulky hydrophobic poly(divinylbenzene) "cores" from the raw reaction product. Some years ago, Gnanou and co-workers[50] prompted the development of the use of supercritical fluids for the fractionation of PEOs since this technique already constitutes an important method to fractionate broadly distributed polymers to quite narrowly distributed fractions. This procedure of fractionation proved to be particularly efficient compared with dialysis or SEC techniques. The first method takes much time and the latter provides access only to rather small amounts of fractionated PEO. Recently, Trimpin et al.[51] were able to achieve fractionation of mixtures of low molar mass PEOs (functionalized or not) using liquid adsorption chromatography at critical conditions combined with a MALDI–TOF MS characterization. Dialysis is known since many years as a possible separation method to remove undesired compounds from raw polymers in water by selective and passive diffusion through a semipermeable membrane. This technique has been used successfully to remove unreacted homopolymers in block copolymers or PEO branches in star-shaped PEOs. We tested this approach to isolate our "POSS" stars from raw reaction product. The details concerning the fractionation are given in Supporting Information. As mentioned in that section, the main product, kept behind the membrane, was concentrated, recovered by precipitation, and characterized by SEC. From these measurements, it can be concluded that not all the ω-allyl PEO could be removed even when the process was conducted over several weeks. The stability of the POSS/PEO stars in water over long periods may also be questionable. In some cases, we detected a shift of the reaction product peak toward higher elution volumes in the SEC curves after dialysis, that is, lower molar masses. A possible explanation may be the cleavage of the covalent bonds between the POSS core and the PEO chain in the presence of H_3O^+. This stimulated us to test other methods to isolate the star-shaped PEO from the raw reaction product. Although the efficiency of classical fractionation methods based on solvent/nonsolvent methods is questionable, we submitted our raw samples to fractionation using toluene as a solvent and cyclohexane as precipitant as described in "Section 2" (see Supporting Information). Each fraction was allowed to settle for at least 24 h to provide adequate sedimentation of the precipitate. The samples were characterized independently by SEC (and online LS) to investigate the efficiency of the fractionation and grafting process and by IR and ^{1}H NMR to verify the absence of Si–H functions. The successful isolation of the star-shaped PEO by fractional precipitation from the crude mixture was confirmed by SEC analysis. The efficiency of the fractionation procedure is illustrated in Figure 2a and b. The amount of "ungrafted" ω-allyl PEO is vanishingly small. However, the star-shaped nature of the polymer characterized by a low elution volume has to be established, and its functionality determined. As star-shaped PEOs are known to exhibit a more compact structure in solution than the linear equivalent of the same absolute molar mass, the apparent molar mass values we obtained by SEC based on calibration with linear PEO are underestimated (Table 3). As a consequence, attempts were made to access the absolute molar masses of the PEO stars by SEC with online light scattering. These measurements showed significantly higher values than those obtained by SEC with RI detection. However, in most cases, they were much higher than the calculated values under the assumption of 8 chains grafted onto one silsesquioxane core. A possible explanation for this may be the formation of aggregates or covalent coupling reactions between two PEO star-shaped molecules due to the presence of unreacted Si–H functions. To overcome these problems, ethylene can be added at the end of the grafting reaction to transform the remaining unreacted Si–H functions into short alkanes following a procedure described in a previous publication.[27] Therefore, we did not pursue the studies on the molar determination of the PEO stars by SEC with online light scattering. The determination of the mass-average molar mass of PEO stars by classical light-scattering in methanol[52] revealed to be much more efficient to access the absolute molar mass of the PEO stars with a silsesquioxane core (Figure 5).

Selected values are provided in Table 3. In principle, the average number of branches of a star-shaped polymer is obtained from the ratio of the absolute weight-average molar mass, determined by light scattering, to the molar mass of the branch. It can be concluded from the data presented on Table 3 that, in most cases, the value of the functionality (f) is close to its theoretical one, taking into account the limits of characterization techniques. The efficiency of the grafting of the ω-allyl PEOs on the silsesquioxane cores was also verified by IR and ^{1}H NMR spectroscopy. The intense peak of Si–H group at 2 150 cm^{-1} completely disappeared in the spectrum of the star. The ^{1}H NMR spectrum shows the absence of the characteristic peaks for the double bond of the ω-allyl PEO

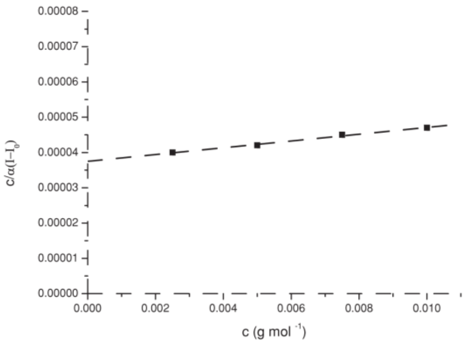


Figure 5. Light-scattering data of $Q_8M_8^{PEO}$ measured in methanol.

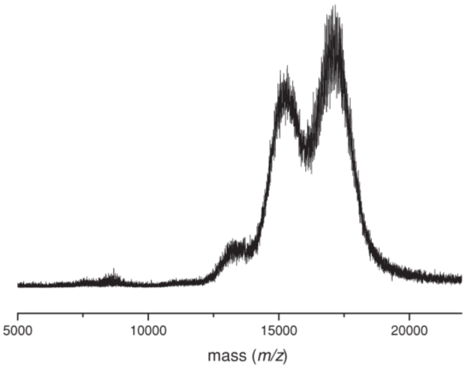


Figure 6. MALDI–TOF MS of $Q_8M_8^{PEO}$.

(peak at 5.80 and 5.20 ppm), which confirms the grafting onto the cage. In addition, the peak of the Si–H function (at 4.70 ppm) disappeared from the ^{1}H NMR spectrum. ^{1}H NMR spectroscopy was also used to determine the number of PEO chains attached to $Q_8M_8^H$ average value of the functionality. By considering the ratio between the integrals of the peak of the methyl group at 0.13 ppm ($Si(CH_3)_2$) (on the core) and the methylene group at 0.56 ppm ($Si–CH_2–CH_2$) (originating from the ω-allyl PEO), a functionality value close to 8 was calculated. In the first part of the present work, we have demonstrated the effectiveness of MALDI–TOF MS techniques to determine the molar mass and the functionality of ω-allyl PEOs. MALDI–TOF MS was also used for the detailed investigation of the star-shaped PEO on both the raw sample (characterized by residual ω-allyl PEO) and the star-shaped PEO after purification. Only few investigations were made on the determination of structural parameters of branched PEOs by that technique. The works on dendrimer-like PEOs[53] and Janus-Type dendrimer-like PEOs[54] constitute nice examples. More recently, Doycheva et al.[55] reported a detailed characterization by MALDI–TOF MS of PEO multiarm star-shaped polymers with a purely polyether structure. These samples were obtained by the so-called "core-first" method[1] using a hyperbranched polyglycerol-modified core as a multifunctional initiator for the anionic ring-opening polymerization of oxirane.[2] These MALDI–TOF MS measurements confirmed the performance of that technique to determine the molecular and structural characteristics of star-shaped PEOs. As a consequence, a detailed investigation by MALDI–TOF MS on sample SSPOE4 was performed on the raw grafting product and the purified one. The MALDI–TOF MS spectrum of the "pure" PEO star is presented in Figure 6.

These MALDI–TOF MS measurements corroborate the results obtained by SEC, ^{1}H NMR analysis, and light-scattering measurements. As expected, the raw sample (not presented) is characterized by the presence of two peaks: a first one present at a m/z value of 2049 with a peak-to-peak mass increment of 44 (calculated 44.053 corresponding to the molar mass of one EO unit) and another peak of m/z value of 17 217 (with a shoulder at a maximum of 15 447). By taking into account the molar mass of the methoxy group and of the chain end (allyl-end group), the distribution of chains reflected in the MALDI–TOF MS spectrum could be perfectly assigned. The first peak appeared at m/z (44.053n ($n = 45$ (CH_2CH_2O) + 31.034 (CH_3O) + 41.072 (CH_2CHCH_2) + 22.990 (Na) (where n is the degree of polymerization) and is attributed to the ω-allyl PEO. The major peak corresponds to the star-shaped PEO with a molar mass value close to the value measured by light scattering in methanol, taking into account the accuracy of experimental techniques. This peak is characterized by a shoulder ($m/z = 15\ 447$). This peak is related to a star-shaped PEO with only seven PEO branches. However, it is unclear whether this seven-armed PEO has been formed during the synthesis or results from a cleavage of the octafunctionalized star-shaped PEO. It is worth to note that the ω-allyl PEO peak is absent in the purified product. This was already observed by SEC on the same sample. The peak corresponding to the star-shaped PEOs, in the purified grafting product, looks quite similar to the one observed for the raw product.

4. Conclusion

The reaction of well-defined ω-allyl PEOs via hydrosilylation with octakis(hydrido-dimethylsiloxy)octasilsesquioxane has been investigated in detail. This reaction was used successfully for the synthesis of PEO star-shaped polymers, and the functional PEO precursors and the star-shaped samples were characterized accurately. They have been shown to exhibit, after fractional precipitation (for the star-shaped species), rather well-defined structures. The molar distribution is unimodal and quite narrow. The molar mass calculated under the assumption of a functionality of 8 for the core is close to the experimental value measured by light scattering in methanol. Hybrid PEO star-shaped polymers characterized by branches of molar masses up to 10 000 g mol^{-1} could be obtained. The thermal properties of these hybrid PEO stars are currently under investigation using differential scanning calorimetry (DSC). Precise measurements concerning the dependence of the crystal structure (SAXS, WAXS) on the arm length as well as the nature of the core will also be made in the future. Further studies are now under progress to extend the hydrosilylation reaction to ω-undecenyl PEO macromonomers. The synthesis of such macromonomers via chain-end modification of ω-methoxy PEOs poses, however, some problems. The different approaches to design such well-defined ω-undecenyl PEO macromonomers, based either on PEO chain-end modification or on living anionic polymerization of ethylene oxide, in the presence of the appropriate heterofunctional initiator will be presented and discussed in a forthcoming publication.[40]

Supporting Information

Supporting Information is available from the Wiley online Library or from the author.

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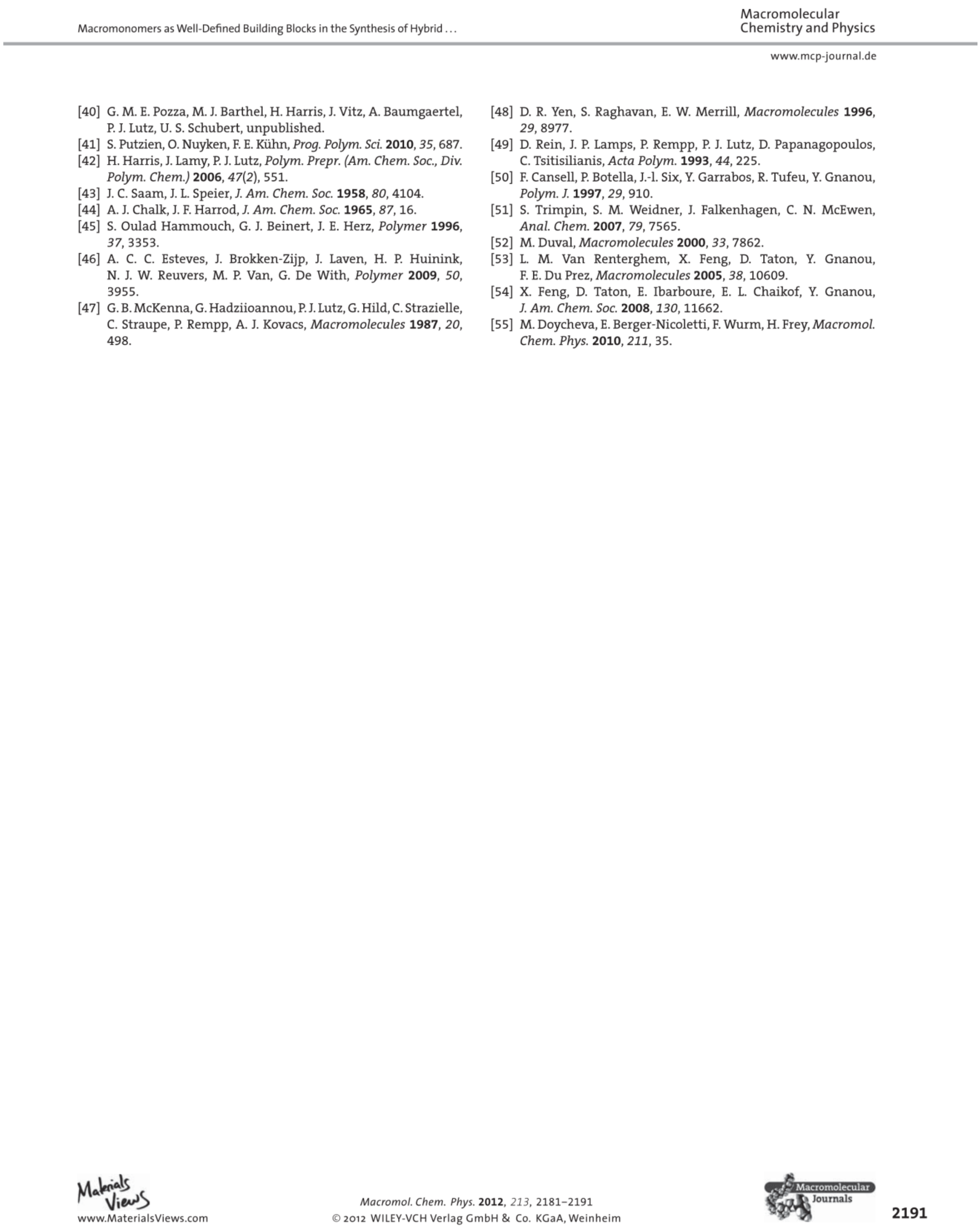

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Chapter 3

ω-Undecenyl poly(ethylene oxide)s and potential heterofunctional building blocks

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"Precise synthesis of undecenyl poly(ethylene oxide) macromonomers as heterofunctional building blocks for the synthesis of linear diblocks or of branched materials"

In press, *Eur. Polym. J.*

3.1. Summary

In the previous chapter we discussed the synthesis of well-defined ω-allyl PEO macromonomers and their use in the synthesis of hybrid PEO / POSS star-shaped polymers of precise molar mass and functionality.

The first part of this chapter is focused on the synthesis *via* AROP and the characterization of PEO macromonomers decorated at one chain-end with undecenyl end-groups and at the other chain-end with hydroxyl groups. The second part concerns the synthesis of branched PEOs based on the ATRP of α-undecenyl-ω-methacryloyl PEO macromonomers or on coupling *via* click chemistry.

ω-Undecenyl PEO macromonomers are characterized by the presence of a flexible hydrophobic spacer between the terminal double bond and the PEO chain-end. The attempts to synthesize ω-undecenyl PEO macromonomers by chain-end modification using an approach similar to ω-allyl PEO were not successful. Therefore we decided to prepare undecenyl-PEO macromonomers *via* AROP in the presence of a heterofunctional initiator based on 10-undecen-1-ol. Two strategies for the preparation of the initiator were considered: Either the potassium undecenolate initiator was prepared *in situ* or the previously prepared initiator was added. The potassium undecenolate initiator prepared *in situ* is obtained by reaction of DPMK with 10-undecen-1-ol. The reaction with the previously prepared initiator is obtained by directly adding the potassium undecenolate in a powder form. The initiator in powder form would have several advantages as compared to the one prepared in solution just before use. The availability of such a powder initiator would facilitate the processing and the reaction procedure. Due to the active powder, which can easily be weighed under inert conditions, a subsequent time consuming titration in the reactor can be avoided. The resulting α-undecenyl-ω-hydroxy PEOs were characterized by SEC, ^{1}H NMR and MALDI-ToF MS to determine the molar masses and the functionality. Well-defined α-undecenyl-ω-hydroxy PEO macromonomers could be obtained in both cases. The solution behavior of these PEO macromonomers was investigated in methanol and in water by DLS. The influence of the undecenyl group on their solution behavior was also studied by viscosimetry and critical micelle concentration (cmc) measurements.

The hydroxy function of the α-undecenyl-ω-hydroxy PEOs could be selectively and quantitatively modified with a methacryloyl group providing access to a new class of heterobifunctional PEO macromonomers decorated at the chain-ends with double bonds of different reactivity. We took advantage of the different reactivity between undecenyl and methacryloyl group to prepare comb-shaped PEOs *via* ATRP in water of the α-undecenyl-ω-methacryloyl PEO macromonomers. The same macromonomers were used to try to design *via* "click reaction", tetrafunctional PEO star-shaped polymers decorated with undecenyl groups at the other end of the branches.

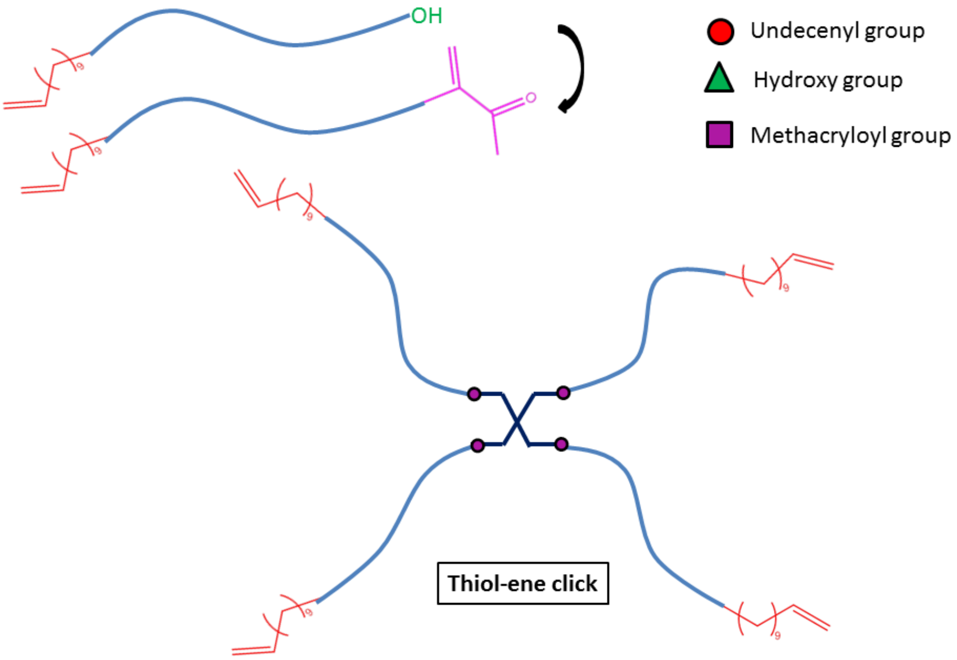

Figure 3.1 Schematical representation of PEO macromonomers and star-shaped PEO with four branches.

3.2. Article 2

Precise Synthesis of Undecenyl Poly(ethylene oxide) Macromonomers as Heterofunctional Building Blocks for the Synthesis of Linear Diblocks or of Branched Materials

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ABSTRACT: Heterofunctional α-undecenyl-ω-hydroxy poly(ethylene oxide) (PEO) macromonomers could be designed by initiation. For their synthesis *via* Anionic Ring-Opening Polymerization (AROP) of ethylene oxide, a potassium alcoholate, prepared *in-situ* by reaction of 10-undecene-1-ol with a stoichiometric amount of diphenylmethyl potassium (DPMK), was used. The applicability of the same initiator but in powder form was evaluated for the polymerization of ethylene oxide. This initiator is well-suited for, e.g., automated high-throughput screening approaches by simply weighing in the amount of initiator needed. The macromonomers were characterized by SEC, ^{1}H NMR, MALDI-TOF MS and light scattering. Independent from the applied approach, well-defined heterobifunctional PEO macromonomers could be obtained. Their solution behavior was investigated in water and methanol by Dynamic Light Scattering (DLS) and in water by critical micelle concentration (cmc) measurements. Chemical modification of the hydroxyl end-group by methyl methacrylate or by propargyl bromide could be achieved leading to heterobifunctional PEO macromonomers. These PEOs offer a great potential as building blocks in macromolecular engineering. PI-*b*-PEO diblocks or comb-shaped PEOs represent typical examples.

1. Introduction

Poly(ethylene oxide) (PEO) is a water soluble polymer with outstanding biocompatibility. PEOs are used as building blocks for a large number of complex macromolecular architectures designed for various applications [1-6]. Due to the chemically inert backbone of the PEO chain containing ether units, controlled modification of that backbone to insert functional groups is difficult. However, end-group functionalization of PEOs has gained more and more importance to access a wide range of water soluble heterofunctional PEOs. Over the last years, several approaches have been developed to prepare PEO macromonomers *via* Anionic Ring Opening Polymerization (AROP) of ethylene oxide in the presence of a heterofunctional initiator or by chain-end modification of PEOs [7]. Potassium *p*-vinyl or *p*-isopropenyl benzylates belong to the first generation of initiators providing access to well-defined PEO macromonomers [7-11]. In the mentioned example, advantage is taken from the very large difference in electroaffinity between the vinyl group and the oxirane ring. Several other heterofunctional initiators were developed to synthesize PEO macromonomers fitted at the chain-end with a polymerizable heterocycle [12, 13]. The synthesis of monofunctional ω-allyl PEOs based on the alcoholate derived from allyl alcohol has also been described in the literature [14]. An alternative method using acetals as protecting group has been proposed recently to decorate PEOs at one chain-end with an allyl group [15]. α-Hydroxy-ω-allyl PEOs were successfully prepared by deprotection of the hydroxyl ends of these heterofunctional PEOs.

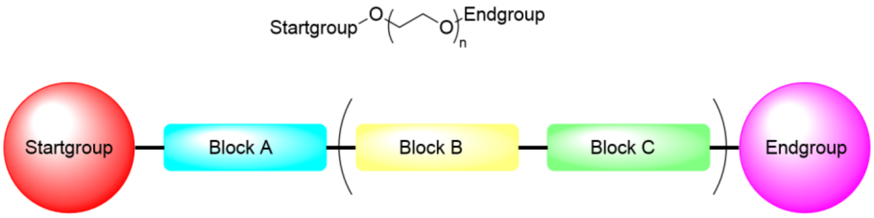
Less attention was given to α-undecenyl-ω-hydroxy PEOs characterized by a flexible hydrophobic spacer between the PEO chain and the unsaturated unit in spite of the potential interest of such macromonomers. Besides our preliminary studies on the synthesis of α-undecenyl-ω-hydroxy PEOs, covering a limited range of PEO molar masses, [16], Herrwerth *et al.* [17] reported in 2003 the synthesis of α-(carboxymethyl)-ω-[11-

mercapto(undecenyloxy)-poly(ethylene oxides) *via* AROP in the presence of 10-undecene-1-ol activated with NaH. Such heterofunctional PEOs could be useful for various applications, *e.g.*, as building block in precise macromolecular engineering *via* hydrosilylation [18] or to create surfaces with specific antigen binding capacity [17].

Functional PEOs including macromonomers are also accessible by reaction of the alkoxide function, located at one chain-end, with an appropriate unsaturated electrophile. Such a strategy was used successfully with allyl bromide [19, 20], methacryloyl choride [8, 21], *p*-vinyl benzyl bromide [10, 21-23] or norbornene carbonyl chloride [24, 25]. The extension of the approach to the synthesis of ω-undecenyl PEOs will be discussed in a forthcoming article [18]. Decisive progress in the functionalization reactions with alkyl halides was made with the introduction of phase transfer catalysts [26-28].

ω-Methacryloyl or ω-styrenyl PEOs macromonomers have been extensively used to design graft or comb-shaped polymers by free or controlled radical polymerizations. No examples of FRP or CRP polymerization or copolymerization with low molar monomers of ω-allyl or undecenyl PEOs could be found in the accessible literature. This can be explained by the low reactivity of the allyl or undecenyl group in radical polymerization process. Few literature references exist discussing the metallocene-catalysed ethylene copolymerization with *N,N*-bis(trimethysilyl)-1-amino-10-undecene [29] or the synthesis of allyl-terminated polar monomers by coordination polymerization of 10-undecene-1-ol [28]. ω-Allyl or ω-undecenyl polystyrene could also be incorporated by coordination polymerization in polyethylenes [30].

However, PEO macromonomers decorated with allyl-end groups are well-suited for coupling reactions *via* hydrosilylation. Typically the synthesis of PEO / poly(dimethylsiloxanes) block or graft copolymers covering a large number of applications including surface modification could be achieved by hydrosilylation [31, 32]. They served also in the synthesis of monosubstituted cube-shaped spherosilsesquioxanes with amphiphilic properties, combining the relatively hydrophobic spherosilsesquioxane core with hydrophilic PEO segments [33], in star-shaped PEOs with spherosilsesquioxane cores [16, 20, 34] or in cross-linked materials [35, 36]. These PEOs are increasingly used in post-polymerization reactions, e.g., thiol-ene click reaction to introduce bioactive compounds (sugars, cell-penetrating peptides), for a specific tuning of the polymer or surface properties [37-42]. This stimulated us to investigate the precise synthesis *via* AROP of ethylene oxide and the characterization of a series of heterofunctional amphiphilic PEOs, decorated with an undecenyl group at one chain-end and a hydroxyl function at the other end (Scheme 1), covering a large domain of molar masses. The synthesis in the presence of an initiator prepared *in-situ* will be considered first and extended to an alcoholate in the powder form. Next some preliminary studies of the solution behavior of these α-undecenyl-ω-hydroxy PEO macromonomers will be presented. The modification of the hydroxyl chain-end with a polymerizable methyl methacrylate (MMA) group or with an acetylene group will be attempted. The coupling *via* “click reaction” of an α-undecenyl-ω-acetylene PEO with an ω-azido PI will be discussed in the further section. The application of the α-undecenyl-ω-methacryloyl heterobifunctional PEO macromonomers in the design of PEO based functional branched architectures will be discussed in the last part.



SCHEME 1. Representation of a PEO heterofunctional macromonomer with start and end group.

Additional Supporting Information may be found in the online version of this article.

2. Experimental

2.1. Materials

Cyclohexane, ethylbenzene and tetrahydrofuran (THF) (Aldrich) were purified by conventional methods and kept under argon atmosphere (THF was first treated with a solvent purification system (PureSolv, Innovative Technology)). Dichloromethane (Carlo Erba), dimethyl sulfoxide DMSO (Aldrich) and diethyl ether (Carlo Erba) were used as received. Ethylene oxide (Linde or Aldrich) was purified over sodium and distilled before use. 10-undecene-1-ol (Aldrich, 98%) was purified by distillation over CaH_2 under reduced pressure and kept under argon atmosphere. Methacrylic anhydride (Aldrich, 94%) and triethylamine (Aldrich, 99.5%) were used as received. 2,2'-Azobis(2-methyl propionitrile) (AIBN) (Acros) was purified by crystallization. Copper I bromide (Aldrich, 98%) was stirred 5 hours in acetic acid, filtered, washed with ethanol and dried in vacuum. 2,2′-Bipyridine (bipy) (Aldrich), 2,2-dimethoxy-2-phenylacetophenone (DMPA) (Aldrich, 99%) and pentaerythritol tetrakis(3-mercaptopropionate) (Aldrich, 95%) were used as received. *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylene triamine (PMDETA) (Aldrich, 99%) and propargyl bromide (Aldrich, 80 wt.% in toluene) were used as received. Diphenylmethyl potassium (DPMK) was synthesized in the laboratory according to a well-established procedure [43]. The functionalization reactions were conducted in classical glass vessels under a slight argon pressure. The ethylene oxide polymerization was conducted in a classic glass apparatus or in a BüchiGlasUster “PicoClave” pressure reactor.

2.2. Measurements

2.2.1 Size exclusion chromatography (SEC)

Number average molar mass (M_n), weight average molar mass (M_w) and the polydispersity index (PDI) value of the different PEO samples were determined by SEC at RT on a Shimadzu SIL-20A system controller with a LC-20AD pump, a RID-10A refractive index detector and a Shimadzu SPD 10 Avp UV detector. THF with a flow rate of 1 mL/min was used as solvent. Calibration was made with PEO standards from Polymer Laboratories with molar masses from 194 to 22,800 g/mol. SEC measurements were also performed on a SEC Shimadzu SCL-10A system controller with LC-10AD pump, a RID-10A refractive index detector and a PL gel 5 μm Mixed-D column at 25 °C. A mixture of chloroform:triethylamine:*iso*-propanol (94:4:2) with a flow rate of 1 mL/min was used as solvent. Calibration was made with linear monodisperse PEO standards from PSS (Polymer Standards Service GmbH, Mainz, Germany) with molar masses from 1,470 to 23,600 g/mol. Preparative SEC with fraction collector was used. The system was calibrated with PEO standards from PSS with molar masses from 1,470 to 42,000 g/mol.

2.2.2. Static and dynamic light scattering

The static light scattering (SLS) measurements were carried out with a red He-Ne laser with a wavelength of λ_0 = 632.8 nm, a discrete-angle goniometer acting within the range from 20° to 155°, a Hamamatsu type photomultiplier as the detector, a photo-counting device and a toluene index matching bath [44]. DLS measurements are run with an ALV/DLS/SLS-5020F experimental setup (ALV-Laser Vertriebsgesellshaft mbH, Langen, Germany) equipped with a vertically polarized light of a 22 mW He−Ne laser of 632.8 nm as an incident beam, a compact ALV/CGS-8 goniometer system and an ALV-5000 autocorrelator. The measurements are performed at 60, 90 and 120° at 25 °C. Polymer solutions with a concentration from 1 to 5 g/L were prepared by direct dissolution in water or in methanol. The CONTIN algorithm was applied to analyze the obtained correlation functions. Apparent hydrodynamic radii were calculated from the Stokes-Einstein equation. All CONTIN plots are unweighted.

2.2.3. MALDI-TOF MS

For the measurement of the matrix-assisted laser desorption/ionization (MALDI) spectra, an Ultraflex III TOF/TOF instrument (Bruker Daltonics, Bremen, Germany) was used. The instrument was calibrated prior to each measurement with poly(methyl methacrylate) (PMMA) as the external standard (PSS). Samples were mixed with either 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB), or 2,5-dihydroxybenzoic acid (DHB) as matrix in reflector as well as in linear mode and the doping agent NaI (dried droplet method).

2.2.4. ^{1}H NMR

Solution ^{1}H NMR spectra were recorded on a Bruker AC 300 MHz or a Bruker DRX 400 MHz in deuterated chloroform ($CDCl_3$) or dimethylsulfoxide (DMSO-d_6).

2.2.5. Fourier Transform Infrared (FTIR)

IR spectroscopy was performed in the Attenuated Total Reflection Mode (ATR-FTIR) using a Vertex 70 spectrometer (Bruker, Germany) equipped with a DTGS detector and a single reflection diamond ATR accessory (A225/Q Platinum ATR, Bruker, Germany). Reference (air) and sample spectra were taken by collecting 20 interferograms between 500 and 3500 cm^{-1} using a Blackman-Harris three-term apodization and the standard Bruker OPUS/IR software (version 5.0).

2.2.6. Critical micelle concentration determination (cmc)

Fluorescence spectra were measured on a Hitachi F-4010 spectrofluorometer between 350 and 500 nm. Pyrene was used as a fluorescent probe, usually with an excitation wavelength at 335 nm. The vibronic fluorescence spectrum of pyrene exhibits five peaks denoted 1–5 [45]. It is well known that the ratio I_1 / I_3 of the intensities of the first to the third peak correlates with the polarity of the immediate environment of pyrene. It is equal to 1.8–1.9 in water and reaches 0.9 in non-polar solvents. In these experiments, I_1 / I_3 was measured as a function of the polymer concentration in order to follow the association process and to determine the order of magnitude of the cmc. A series of PEO macromonomer solutions were prepared over a concentration range from 5×10^{-6} to 5×10^{-4} mol/L using a (stock) solution of pyrene in water (5×10^{-7} mol/L).

2.2.7. Viscosimetry

An automatic capillary viscosimeter of Schott AVS 360 equipped with Ubbelohde capillary of 0.53 mm diameter was used. The apparatus was tempered at 25 °C (± 0.02 °C). The measurements were conducted in methanol. The viscosimeter was used according to the range of associative polymer concentration.

2.3. Synthesis

2.3.1. Synthesis of the α-undecenyl-ω-hydroxy PEO by initiation

10-Undecene-1-ol (1×10^{-3} mol, 0.17 g, 0.2 mL) was introduced directly into the reactor, then dry THF (100 mL) was added and the hydroxyl functions were transformed into alcoholates by addition of a stoichiometric amount of DPMK (0.58 M, 1×10^{-3} mol, 1.7 mL) at room temperature (the stoichiometry was determined by colorimetry). Subsequently, the reaction medium was cooled to −20 °C and the calculated amount of ethylene oxide (1×10^{-3} mol, 10 g, 11.36 mL) was added. The solution was heated to 40 °C in one hour and was stirred for 1 to 2 days at 30 to 50 °C (depending on the molar mass of the PEO sample, see Table 1). In one case, for purpose of comparison, the hydroxyl functions were only partially transformed into alcoholates by addition of DPMK (around 20 mol. % of the theoretical amount). Then, the ethylene oxide polymerization procedure described above was carried out. Methanol (containing a few drops of acetic acid) was added to deactivate the alcoholates. The resulting polymer was precipitated in diethyl ether, filtered, dried and characterized by SEC and ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, δ , ppm): 5.8 (m, 1H, $-CH{=}CH_2$), 5.1 (m, 2H, $-CH{=}CH_2$), 3.6–3.8 (m, 4H*n, $-O-CH_2-CH_2-$), 2.0 (m, 2H, $-CH_2-CH{=}CH_2$), 1.5 (m, 2H, $-CH_2-(CH_2)_7-CH_2-CH{=}CH_2$), 1.1–1.3 (m, 2H*7, $-CH_2-(CH_2)_7-CH_2-CH{=}CH_2$).

2.3.2. Synthesis of α-undecenyl-ω-hydroxy PEO by initiation starting from an initiator in powder form

2.3.2.1 Preparation of the initiator

DPMK (41.25 mL, 0.76 M) was added dropwise to a solution of 10-undecene-1-ol (5 mL, 2.5 × 10^{-2} mol in 40 mL of dry THF) at RT until the red color of DPMK persists, which is an indication that all alcohol functions have been transformed into alcoholates. The reaction mixture was kept stirring at RT for at least 20 h. Yellow particles were formed which could not be entirely precipitated by the addition of cyclohexane (70 mL). After removal of the cyclohexane under vacuum, a yellow pasty product was recovered and dispersed again in cyclohexane. This operation was repeated at least two times in order to remove the side products (e.g., diphenylmethane). The solid product was transferred into the glove box, filtered and washed several times with cyclohexane. The final product was recovered, dried and characterized by ^{1}H NMR in order to evaluate its purity. A white powder was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.8 (m, 1H, $-CH{=}CH_2$), 4.9 (m, 2H, $-CH{=}CH_2$), 3.6 (m, 2H, $-CH_2-O^-K^+$), 2.0 (m, 2H, $-CH_2-CH{=}CH_2$), 1.5 (m, 2H, $-CH_2-CH_2-O^-K^+$), 1.2–1.4 (m, 2H*6, $-(CH_2)_6-CH_2-CH{=}CH_2$).

2.3.2.2 Polymerization of ethylene oxide

The undecenol-based alcoholate was tested for the AROP of ethylene oxide. The desired amount of the powder initiator was determined by weighing (in the glove box), dispersed in dry THF (or ethylbenzene in some cases) and introduced directly into the reactor. Then, the polymerization procedure described above was carried out. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.8 (m, 1H, $-CH{=}CH_2$), 5.1 (m, 2H, $-CH{=}CH_2$), 3.6–3.8 (m, 4H*n, $-O-CH_2-CH_2-$), 2.0 (m, 2H, $-CH_2-CH{=}CH_2$), 1.5 (m, 2H, $-CH_2-(CH_2)_7-CH_2-CH{=}CH_2$), 1.1–1.3 (m, 2H*7, $-CH_2-(CH_2)_7-CH_2-CH{=}CH_2$)

2.3.3 Synthesis of α-undecenyl-ω-methacryloyl PEO macromonomers by chain-end modification with methacrylic anhydride in the presence of triethylamine

The sample EOp-und3 (see Table 2) (M_n = 3,300 g/mol, 1 g, 3.03×10^{-4} mol) was dissolved in dry CH_2Cl_2 then triethylamine (1.5 eq, 0.06 mL, 4.55×10^{-4} mol,) and methacrylic anhydride (1.5 eq, 0.07 mL, 4.55×10^{-4} mol) were added. The reaction was kept at RT for 4 days. The solvent was evaporated, the PEO was dissolved in DMSO then precipitated in diethyl ether and filtered. This procedure was repeated but the polymer was dissolved in THF. The functionalized PEOs were characterized by SEC, ^{1}H NMR and MALDI-TOF MS. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.1 (s, 1H, $CH_3–C=CH_2$), 5.8 (m, 1H, $–CH=CH_2$), 5.5 (s, 1H, $CH_3–C=CH_2$), 4.9 (m, 2H, $–CH=CH_2$), 4.3 (t, 2H, $CH_2–O–C=O$), 3.6–3.8 (m, 4H*n, $–O–CH_2–CH_2–$), 2.0 (m, 2H, $–CH_2–CH=CH_2$), 1.9 (s, 3H, $CH_3–C=CH_2$), 1.5 (m, 2H, $–CH_2–(CH_2)_7–CH_2–CH=CH_2$), 1.1–1.3 (m, 2H*7, $–CH_2–(CH_2)_7–CH_2–CH=CH_2$)

2.3.4 Synthesis of α-undecenyl-ω-acetylene PEO

The hydroxyl functions of the α-undecenyl-ω-hydroxy PEO (2,000 g/mol, 4.5 g, 2.15×10^{-3} mol) were transformed into alcoholates by addition of a stoichiometric amount of DPMK (around 2.59 mL, DMPK concentration 0.85×10^{-3} mol/L) at room temperature (stoichiometry determined by colorimetry). In the next step, propargyl bromide (2 eq., 0.38 mL, 5×10^{-3} mol) was added to the PEO solution. The slight yellow coloration disappeared rapidly. The reaction medium was kept at room temperature overnight. The polymer solutions were centrifuged in toluene. The solvent was evaporated. The resulting polymer was dissolved in THF, precipitated in diethyl ether, filtered, dried and characterized by SEC and ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.8 (m, 1H, $–CH=CH_2$), 5.1 (m, 2H, $–CH=CH_2$), 4.3 (s, 2H, $–CH_2–C≡CH$), 3.6–3.8 (m, 4H*n, $–O–CH_2–CH_2–$), 2.4 (s, 1H, $–C≡CH$) 2.0 (m, 2H, $–CH_2–CH=CH_2$), 1.5 (m, 2H, $–CH_2–(CH_2)_7–CH_2–CH=CH_2$), 1.1–1.3

(m, 2H*7, $-CH-(CH_2)_7-CH_2-CH=CH_2$). FTIR ($cm^{-1}$): 3260 ($C\equiv CH$, stretching), (2880 (CH, stretching), 1467 (CH_2, deformation), 1100 (CO, stretching).

2.3.5 Synthesis of (PI-*b*-PEO) *via* click chemistry

$PI-N_3$ (7,700 g/mol, 1 g, 1.29×10^{-4} mol) was dissolved in 20 mL of THF. PEO (5,800 g/mol, 0.75 g, 1.29×10^{-4} mol) and CuBr (5 eq., 6.49×10^{-4} mol, 0.093 g) were added. Oxygen was removed from the solution by three freeze-pump-thaw cycles. PMDETA was added. (5 eq., 6.49×10^{-4} mol, 0.135 mL). The reaction was stirred for 24 hours at room temperature. Afterwards, the solvent was evaporated. The resulting polymer was dissolved in THF, precipitated in cold acetone and dried. This operation was repeated three times. The resulting polymer was investigated by SEC and purified by preparative SEC using Bio-Beads® in THF. The polymer fraction was characterized by ^1H NMR. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.8 (m, 1H, $-CH=CH_2$), 5.2 (m, 1H, trans-1,4-PI and cis-1,4-PI), 5.1 (m, 2H, $-CH=CH_2$), 4.7 (m, 2H, 1,2 PI), 4.6 (m, 2H, 3,4 PI), 3.6–3.8 (m, 4H*n, $-O-CH_2-CH_2-$), 2.0 (m, 2H, $-CH_2-CH=CH_2$), 1.8–2.1 (m, 2H, trans-1,4-PI, cis-1,4-PI, 3,4 PI), 1.5–1.7 (m, 2H trans-1,4-PI and 1,2 PI, 3H, cis-1,4-PI and 3,4 PI), 1.5 (m, 2H, $-CH_2-(CH_2)_7-CH_2-CH=CH_2$),1.4 (m, 3H, trans-1,4-PI), 1.1–1.3 (m, 2H*7, $-CH-(CH_2)_7-CH_2-CH=CH_2$), 0.8–0.9 (m, 6H, $CH_3-CH_2-CH(CH_3)-$). FTIR (cm^{-1}): 2930 (CH_2, stretching, PI), 2880 (CH, stretching, PEO), 2860 (CH_2, stretching, PI), 1778–1728 (N=N, stretching) 1645 (C=C, stretching, PI), 1467 (CH_2, deformation, PEO), 1450 (CH_2, deformation, PI), 1375 (CH_3, deformation, PI), 1100 (CO, stretching).

2.3.6 Homopolymerization of α-undecenyl-ω-methacryloyl PEO macromonomers by (controlled) free-radical polymerization (FRP)

2.3.6.1 Homopolymerization by FRP of α-undecenyl-ω-methacryloyl PEO macromonomers

The sample PEOund-MA5 (see Table 3) (M_n = 3,500 g/mol, 0.3 g, 8.57×10^{-5} mol) was dissolved in dry toluene and AIBN (0.28 mg, 1.71×10^{-6} mol, 2% in mol per methacryloyl entity) was added. The system was degassed three times using freeze pump thaw cycles. The reaction was kept at 70 °C for 1 day. The solvent was evaporated. This reaction was also conducted in THF at 50 °C. The sample PEOund-MA5 (M_n = 3,500 g/mol, 0.25 g, 7.14×10^{-5} mol) was dissolved in dry THF and AIBN (0.23 mg, 1.43×10^{-6} mol, 2% in mol per methacryloyl entity) was added. The reaction was kept at 50 °C during 6 hours. The solvent was evaporated. Both reaction products were characterized by SEC (without purification).

2.3.6.2 Homopolymerization by ATRP of α-undecenyl-ω- methacryloyl PEO macromonomers

The sample PEOund-MA6 (M_n = 3,500 g/mol, 0.3 g, 8.57×10^{-5} mol) was dissolved in 1 mL degassed Milli-Q water. A solution of CuBr/bipyridine was prepared by mixing bipyridine. (0.12 eq., 16.1 mg, 1.03×10^{-5} mol) and CuBr (0.18 eq., 22.0 mg, 1.54×10^{-5} mol) in 10 mL degassed Milli-Q water under Argon. This solution was stirred vigorously during 15 min to obtain a brown solution. 1 mL of this solution was added to the PEO solution. The PEO bromide macro-initiator [46] (0.18 eq., 27.7 mg, 1.54×10^{-5} mol dissolved in 0.5 mL degassed Milli-Q water) was added. The reaction was kept at 60 °C during 1 day. The solvent was evaporated. The final product was passed through alumina column to remove Cu derivatives and characterized by SEC.

2.3.7 Synthesis of α-undecenyl-ω-methacryloyl PEO star-shaped polymers *via* pentaerythritol tetrakis(3-mercaptopropionate)

In an air-tight microwave glass vial 167 mg (M_n = 3,900 g/mol, 4.9×10^{-5} mol) of PEOund-MA5 were dissolved in 4 mL of THF. To the solution 5.23 mg (1.1×10^{-5} mol, ratio 1/4) pentaerythritol tetrakis (3-mercaptopropionate) and 2.2 mg DMPA (8.6×10^{-6} mol, ratio 1/5) were added and the reaction mixture was degassed with argon for 30 min. Afterwards the mixture was irradiated for 24 h under UV-light (366 nm) to ensure a maximum conversion of the functional PEO precursor. The purification of the reaction mixture was performed on a preparative SEC system with automated fraction collector. The identified 4 arm star-shaped PEO was further characterized by ^{1}H NMR and MALDI-TOF MS.

2.4 Isolation of the comb-shaped PEO

2.4.1 Dialysis

The raw reaction product (0.5 g) was dissolved in de-ionized water (100 mL). This solution was introduced into a dialysis membrane constituted of regenerated cellulose and characterized by pores of controlled size (molar mass cut-off at 7,500 g/mol). This membrane was placed into a great excess of de-ionized water. PEO comb-shaped molecules should be retained, whereas α-undecenyl-ω-methacryloyl PEOs should pass freely through the membrane. After one day, water was replaced, this operation was repeated several times during four days. The water solutions were concentrated, the remaining product was dissolved in THF, precipitated in diethyl ether and characterized by SEC.

2.4.2 Fractional precipitation

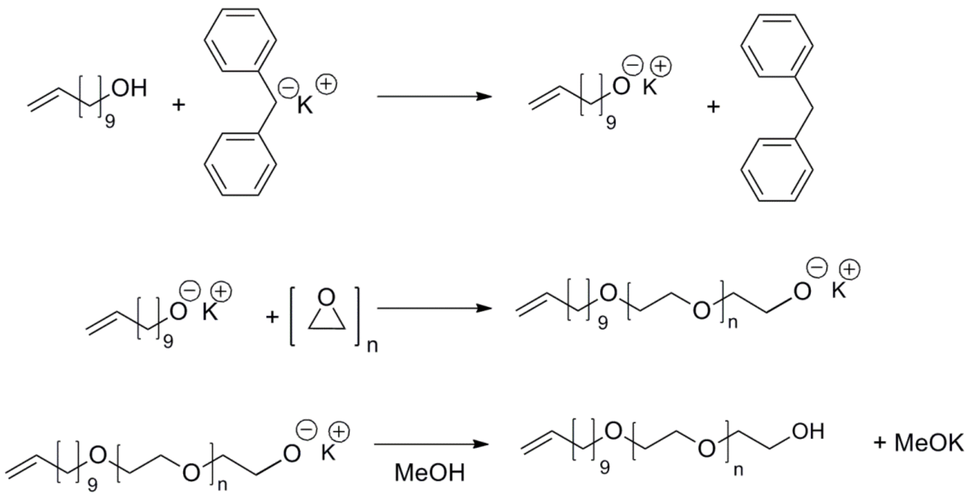
Fractional precipitation was carried out in a tempered water circulating bath. The raw reaction product (0.95 g) was dissolved in toluene (60 mL) in a conventional pear-like vessel at 25 °C. Cyclohexane was added drop by drop until the medium had become turbid. Thus the solution is heated up until the turbidity had vanished. The temperature is decreased to 25 °C, and the solution was kept at that temperature during 24 hours. The lower phase should contain the comb-shaped PEO and the upper one the unreacted macromonomer. The fractions were recovered and analyzed by SEC.

3. Results and discussion

The development of efficient approaches based on AROP of ethylene oxide to decorate PEO chain-ends with an undecenyl end-group constitutes the main aim of the present work. For undecenyl end-functionalized polymers, the flexible aliphatic alkyl spacer may enhance the reactivity of the terminal double bond and also influence the properties of the polymer at least for the PEO chains with lower molar masses.

3.1. Synthesis of α-undecenyl-ω-hydroxy PEOs by initiation

As mentioned in the introduction, preliminary studies [16, 17], have shown that α-undecenyl-ω-hydroxy-PEO macromonomers can be obtained starting from 10-undecene-1-ol (Scheme 2). Compared to the approach that uses the chain-end modification of existing monofunctional PEOs [47], AROP of ethylene oxide in the presence of an unsaturated initiator such as potassium undecenolate presents several advantages. The molar mass of the PEO macromonomer can be tailored by controlling the ratio of monomer to initiator. The hydroxyl function present at one chain-end of the heterofunctional α-undecenyl-ω-hydroxy PEO macromonomer can be selectively modified. This can be made without affecting the unsaturation, which remains present for further reactions. On the other hand, the double bond at the chain-end can also be chemically transformed, provided the hydroxyl function is protected. This stimulated us to perform a systematic investigation of the AROP of ethylene oxide initiated by the alcoholate derived from undecenol.



SCHEME 2. Schematic representation of the synthesis of an α-undecenyl-ω-hydroxy PEO macromonomer by initiation.

At first, we used classical conditions for the preparation of a series of α-undecenyl PEO macromonomers starting from undecenol. The preparation of the initiator and the polymerization procedure are described in detail in the experimental section. THF was selected as solvent instead of non-polar solvents, like toluene, to limit the aggregation of the potassium undecenolate. Dimethyl sulfoxide (DMSO) would have been an interesting alternative to prevent strong aggregation of propagating aggregates due to its higher dissociating power and higher propagating rates [27]. However, this solvent poses some problems due to the fact that the dimethylsulfinyl carbanions, formed by transfer of propagating alkoxides to DMSO, may also act as initiators [27, 48].

After addition of a stoichiometric amount of DPMK to 10-undecene-1-ol in THF, a potassium alcoholate is formed, which subsequently serves as an initiator for the AROP of ethylene oxide. Once DPMK is added, the reaction medium becomes gradually heterogeneous due to the association and aggregation of the alcoholates. This should have no consequences on the characteristics of the resulting PEOs as the exchange of protons between active alkoxides and hydroxylated species is rapid and much faster than the propagation rate. This was applied for the synthesis of star- or dendrimer like PEOs [27, 49-53]. Therefore, we decided to proceed to partial deprotonation of undecenol followed by AROP of ethylene oxide. This experience was not convincing. As a consequence, all our attempts to design the α-undecenyl-ω-hydroxy PEOs by initiation were performed in the presence of an initiator obtained by addition of a stoichiometric amount of DPMK to 10-undecene-1-ol in THF, which forms a potassium alcoholate. As mentioned above, partial precipitation of the initiator was observed, too.

However, when the PEO chains reach a sufficient length, they contribute to solvate the potassium and the reaction medium becomes homogeneous. The relatively low nucleophilicity of the active chain-end should prevent the attack of the undecene double bond. After given reaction times, depending on the concentration of active sites and the desired molar mass, the living chain-ends are deactivated with acidified methanol (MeOH). The molecular characteristics of the resulting α-undecenyl-ω-hydroxy PEOs obtained by SEC are given in Table 1 together with the experimental conditions.

TABLE 1

Molecular characteristics of the α-undecenyl-ω-hydroxy PEO macromonomers synthesized by AROP of oxirane, potassium undecenolate being used as initiator (polymerization solvent THF).

Sample	Time (h)	Temp. (°C)	[EO] (mol)	$M_{n\ th.}$[a] (g/mol)	$M_{n\ calc.}$[b] (g/mol)	M_n[c] (g/mol)	M_w[d] (g/mol)	PDI[e]	M_n[f] (g/mol)
						SEC	SEC		MALDI
EO-und1	48	35	0.45	2,000	1,760	1,750	1,800	1.05	1,800
EO-und2	48	35	0.45	2,000	1,800	1,800	1,900	1.05	-
EO-und3	48	35	0.45	2,000	1,800	1,800	1,900	1.05	1,900
EO-und4	48	35	0.45	5,000	3,600	3,600	3,900	1.08	-
EO-und5	48	35	0.45	5,000	4,500	4,500	5,100	1.14	-
EO-und6	48	35	0.45	5,000	4,900	5,400	5,800	1.08	-
EO-und7*	24	45	0.11	5,000	2,300	2,700	3,000	1.11	-
EO-und8	48	45	0.45	10,000	9,500	10,200	11,200	1.10	11,200
EO-und9	24	50	0.22	10,000	8,100	8,800	9,200	1.15	10,500
EO-und10	48	50	0.22	10,000	7,600	8,900	9,700	1.09	9,500
EO-und11	48	40	0.27	10,000	7,700	9,300	9,500	1.04	10,300
EO-und12	48	40	0.58	25,000	22,000	23,000	25,000	1.11	26,000

[a] Theoretical number average molar mass of the α-undecenyl-ω-hydroxy PEOs, assuming total conversion;

[b] Theoretical number average molar mass of the α-undecenyl-ω-hydroxy PEOs calculated taking into account the polymerization yield;

[c] Number average molar mass of the α-undecenyl-ω-hydroxy PEOs, measured by SEC in THF, calibration with linear PEOs;

[d] Weight average molar mass of the α-undecenyl-ω-hydroxy PEOs, measured by SEC in THF, calibration with linear PEOs;

[e] PDI of the α-undecenyl-ω-hydroxy PEOs (M_W/M_n) determined by SEC;

[f] Number average molar mass of the α-undecenyl-ω-hydroxy PEOs, measured MALDI-TOF MS.

* This sample was obtained by AROP of oxirane, a mixture of undecenol and potassium undecenolate being used as initiator (20 mol % of DPMK).

α-Undecenyl-ω-hydroxy PEO macromonomers covering a range of molar mass from 2,000 g/mol to 23,000 g/mol could be obtained. The SEC curves (Fig. S1) are sharp in most cases, demonstrating a good control of the polymerization process although the reaction took place in a partially heterogeneous medium. This can be explained by the fact that the reaction medium becomes homogeneous after addition of a few ethylene oxide units and the propagation reaction is a slow process. The molar masses are close to those expected from the ratio of monomer to initiator concentration, taking the polymerization yield into account. The degree of functionalization, determined by ^{1}H NMR (Fig. S2), is in agreement with the theoretical calculations.

3.2. Synthesis of α-undecenyl-ω-hydroxy PEO by initiation starting from an initiator in the powder form

3.2.1 Preliminary remarks

As we noticed that the potassium initiator based on 10-undecen-1-ol may precipitate in the reaction medium during its formation, we tried to take advantage of this phenomenon to design this initiator in powder form. Such an initiator would have several advantages as compared to classical initiators prepared in solution just before use. The availability of such a powder initiator would facilitate the processing and the reaction procedure. Due to the active powder, which can easily be weighed under inert conditions, a subsequent time consuming titration in the reactor can be avoided. Beyond that, a possible automation of the ethylene oxide polymerization in robot systems would benefit from the application of initiators in powder form.

3.2.2. Preparation of the initiator

In classical strategies, the transformation of the hydroxyl group into potassium alcoholates with DPMK leads to the formation of diphenylmethane as a side-product. These products may contaminate the final PEO and it has been shown that traces of these contaminants are difficult to remove (e.g., twofold reprecipitation to remove diphenyl methane) [20]. The absence of contaminations is in particular important for PEOs designed for biological applications.

As described in the experimental section we were able to prepare and purify such a powder initiator based on undecenol following a strategy close to that used for potassium methoxy ethanolate [54]. In Figure S3, the ^{1}H NMR spectrum of a carefully purified product is presented where no contamination in the powder is visible. Another outstanding feature is the long term stability of the powder of undecenol initiators. We stored them up to 6 months in the glove box and no deactivation could be observed in later polymerization reactions.

3.2.3. Polymerization of ethylene oxide

The powder initiator, whose synthesis has been described above, was used for the preparation, in THF or in ethylbenzene, of a series of α-undecenyl-ω-hydroxy PEOs by AROP of ethylene oxide. The different characterization results of the PEO macromonomers are collected in Table 2 together with the experimental conditions. PEOs covering a range of molar masses from 2,400 up to 44,800 g/mol could be obtained. No significant differences were observed between the samples whether they are prepared in THF or in ethylbenzene.

TABLE 2

Molecular characteristics of the α-undecenyl-ω-hydroxy PEO macromonomers synthesized by initiation with a powder initiator.

Sample	Time (h)	Temp. (°C)	[EO] (mol)	$M_{n\ th.}$ [a] (g/mol)	$M_{n\ calc.}$ [b] (g/mol)	M_n [c] (g/mol)	M_w [d] (g/mol)	PDI [e]	M_n [f] (g/mol)	M_n [g] (g/mol)
						SEC	SEC		MALDI	^{1}H NMR
EOp-und1	24	45	0.34	2,000	1,800	2,100	2,200	1.04	-	2,500
EOp-und2	24	45	0.11	3,000	3,500	3,000	3,200	1.06	3,100	2,900
EOp-und3	24	45	0.22	5,000	2,700	3,300	3,500	1.06	3,700	3,700
EOp-und4	72	40	0.22	5,000	3,700	4,100	4,300	1.06	3,500	4,700
EOp-und5	96	45	0.34	10,000	10,800	7,500	7,900	1.05	7,500	7,800
EOp-und6	24	40	0.45	15,000	13,700	14,000	15,300	1.09	13,700	13,600
EOp-und7	24	40	0.22	20,000	14,600	14,000	15,000	1.09	14,600	17,200
EOp-und8	24	40	0.34	20,000	17,800	19,300	21,700	1.13	19,600	-
EOp-und9*	48	50	0.22	30,000	28,100	35,400	37,700	1.06	31,700	-
EOp-und10*	144	40	0.59	50,000	36,600	38,000	41,000	1.1	32,600	-
EOp-und11*	72	45	0.22	50,000	39,400	44,000	47,000	1.07	39,500	-
EOp-und12	72	45	0.22	50,000	43,400	44,800	47,600	1.06	43,000	-

[a] Theoretical number average molar mass of the α-undecenyl-ω-hydroxy PEOs assuming total conversion;
[b] Theoretical number average molar mass of the α-undecenyl-ω-hydroxy PEOs calculated taking into account the polymerization yield;
[c] Number average molar mass of the α-undecenyl-ω-hydroxy PEOs, measured by SEC in THF, calibration with linear PEOs;
[d] Weight average molar mass of the α-undecenyl-ω-hydroxy PEOs, measured by SEC in THF, calibration with linear PEOs;
[e] PDI of the α-undecenyl-ω-hydroxy PEOs (M_W/M_n) determined by SEC;
[f] Number average molar mass of the α-undecenyl-ω-hydroxy PEOs, measured MALDI-TOF MS;
[g] Number average molar mass of the α-undecenyl-ω-hydroxy PEOs, measured by ^{1}H NMR. These determinations were not possible for samples of higher molar masses.
* Solvent: ethylbenzene

On the Figure 1, the presence of the hydroxyl group (at 4.58 ppm) at the chain-end has been demonstrated unambiguously by ^{1}H NMR performed in DMSO-d_6.

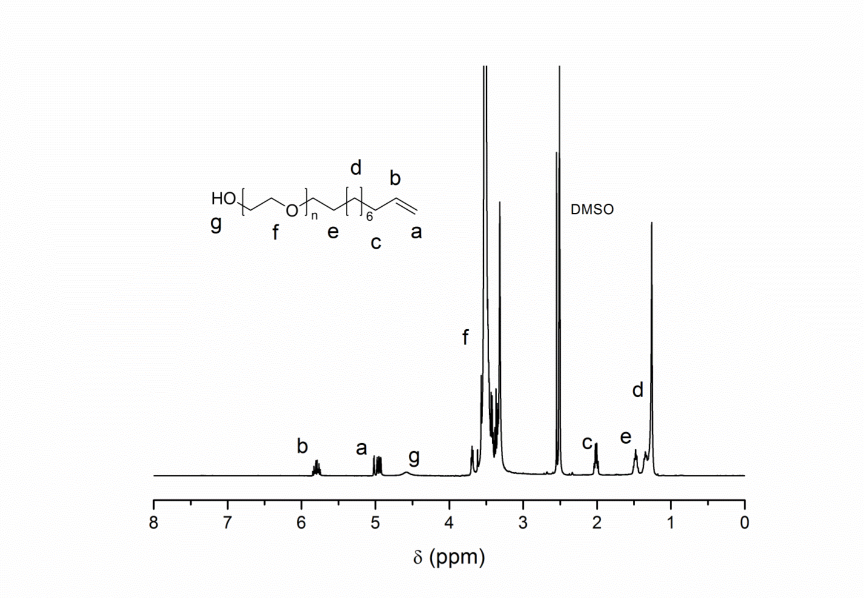
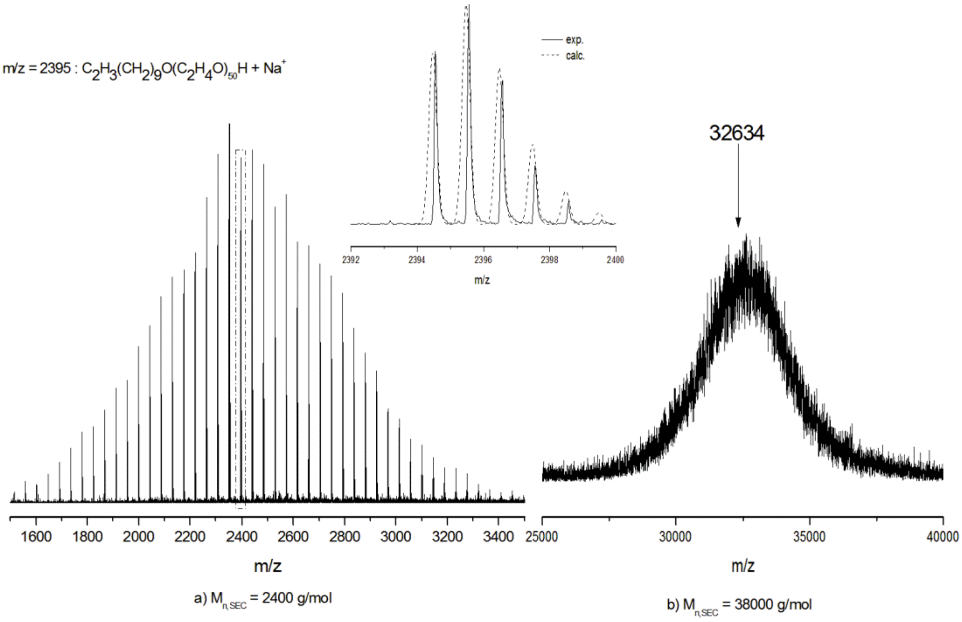


Fig. 1. ^{1}H NMR spectrum of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation (initiator in the powder form) (400 MHz, DMSO-d_6).

For most of the samples, the M_n values are in good agreement with the expected values taking the polymerization yield into account, the PDI values of the samples are below 1.1. As done before, the molecular parameters of the different α-undecenyl-ω-hydroxy PEOs were systematically determined by MALDI-TOF MS. Typical MALDI-TOF MS measurements are presented in the Figure 2. The M_n values calculated by MALDI-TOF MS are in good agreement with the M_n values determined by SEC (based on a calibration with linear PEOs).

The peak at *m/z* 2395 is attributed to the α-undecenyl-ω-hydroxy PEO (169.284 ($CH_2CH(CH_2)_9O$) + 44.053n (n = 50) (CH_2CH_2O) + 1.008 (H) + 22.990 (Na)) (where n is the degree of polymerization). Figure 2 depicts the MALDI-TOF MS spectra of an α-undecenyl-ω-hydroxy PEO, $M_{n,SEC}$ = 2,400 g/mol. The shift of *m/z* 44 is caused by the PEO chain. The values calculated for the molar masses are in good agreement with the theoretical values. This is the case even for PEO sample (EOp-und10) of a molar mass (M_W) of 41,000 g/mol, determined by SEC (see Table 2). To proof this molar mass, we additionally characterized this sample by SEC with an online multi angle light scattering detector (MALS) in THF and by classical light scattering (LS) in methanol. For the online LS a value of M_w 38,700 g/mol was obtained whereas the LS study in methanol showed a value of M_W 35,700 g/mol. These results are confirming the efficiency of the powder initiator.



a) $M_{n,SEC}$ = 2400 g/mol

b) $M_{n,SEC}$ = 38000 g/mol

Fig. 2. MALDI-TOF MS of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by AROP of oxirane **a)** $M_{n,SEC}$ = 2,400 g/mol **b)** $M_{n,SEC}$ = 38,000 g/mol (initiator in the powder form) (Matrix: DCTB, NaI).

3.3. Solution behavior of the undecenyl PEO macromonomers

Aqueous solutions of end-modified PEOs have attracted considerable attention over the past decades. Most of the studies which were already published are based on end-capped PEOs with short hydrophobic entities. These groups can be short alkanes [55, 56] or hydrophobic polymerizable entities [3, 57, 58]. They can be located at one or both chain-ends. The influence of the different terminal groups (including hydroxyl or methyl), the length of the PEO block and the hydrophilic/hydrophobic balance on the properties and the solution behavior in water has been investigated systematically from both a fundamental [59] and an experimental [60-64] point of view. These polymers found many applications, as viscosity modifiers [63],[65], in cosmetics [66], in inks [67], in paints, as building blocks for biomedical applications [68]. Extensive studies by light scattering [69, 70], X-ray [71] and neutron scattering [72], viscometry [56] or even by ^{1}H NMR [73] were performed to characterize these systems. However, almost no work was published on amphiphilic PEO macromonomers constituted of a hydrophilic PEO chain decorated at one chain-end with a hydrophobic undecenyl entity. To investigate this in detail, DLS measurements were performed on PEO macromonomers characterized by the presence of an undecene entity at one chain end. Therefore, methanol or water solutions with a concentration from 1 to 5 g/L of two und-PEO-OH samples (sample EOp-und8, M_n = 19,300 g/mol and sample EOp-und1 2,100 g/mol respectively) were prepared. The different PEO solutions were analyzed by DLS. The measurements were made at three different angles: 60, 90 and 120 °. No angular dependence was observed.

For the measurements made in methanol on sample EOp-und8, at 1 or 5 g/L, only one peak is visible (Fig. S4). The hydrodynamic radius values are around 3 nm for both concentrations. These values are in good agreement with those measured for PEO samples of almost identical molar masses [64]. For the measurement made on sample EOp-und1 (Fig. S5), at a concentration of 2.5 g/L we obtained a hydrodynamic radius around 2 nm. For these two samples we did not observe aggregates in methanol or an influence on the M_n. These conclusions were confirmed by *intrinsic viscosity* measurements performed in methanol on the samples EOp-und1 and EOp-und10. The evolution of η_r (reduced viscosity) with the concentration remains strictly linear over the same range of concentration studied. The presence of the undecene group at the PEO chain-end does not affect the solution behavior at least in domain of concentration studied in this work.

However, for the DLS measurements made on the same samples (EOp-und8, 4.2 g/L) in water, we can clearly identify two peaks (Fig. S6). For the measurement made on sample

EOp-und1 (Fig. S7). At 1.4 g/L or 5.7 g/L we can draw the same conclusion. In water, it could clearly be shown that the undecene parts affects the solubility of the PEO chain as some aggregates are present for all the samples. Therefore, we submitted also our samples to fluorescence probe experiments. The details concerning the preparation of the samples are given in the experimental section. The variation of the I_1 / I_3 ratio of the first and third vibronic peaks in the fluorescence spectrum of pyrene solubilized in water containing the amphiphilic polymers constitutes a good evaluation of the polarity of the probe microenvironment. Pyrene is not very soluble in water, it prefers hydrophobic domains. The evolution of the I_1 / I_3 ratio was measured for two α-undecenyl-ω-hydroxy PEO macromonomers. The results are presented in Figure 3. The I_1 / I_3 ratio decreases with increasing concentration. It seems clear that an increase in the length of the PEO block corresponds to better solubility in water (Fig. 3). In conclusion, the presence of the hydrophobic block clearly influences more the behavior in water than in methanol.

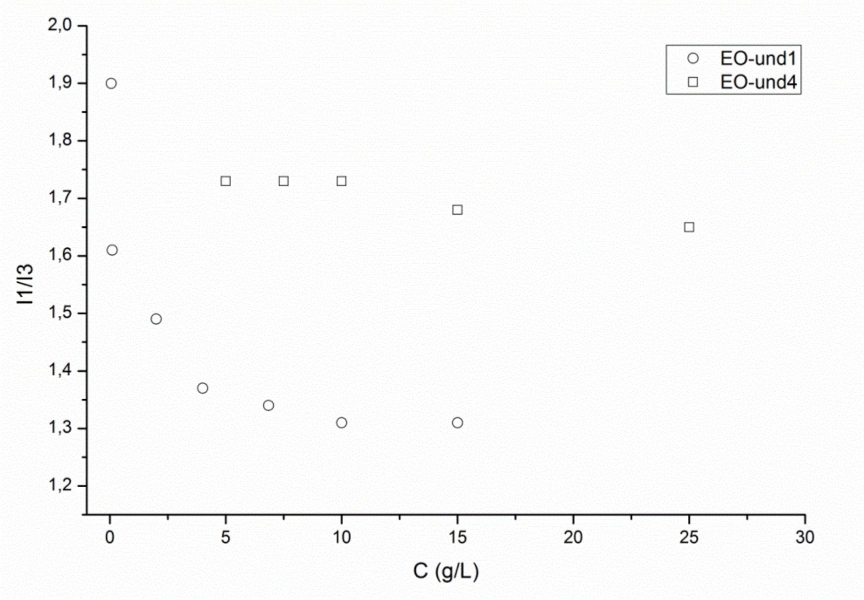
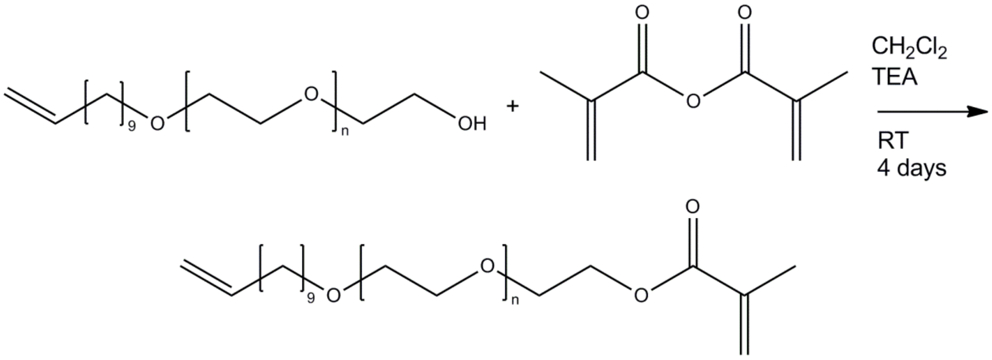


Fig. 3. Variation of the ratio I_1 / I_3 versus concentration for three PEO samples: EO-und1 (PEO α-undecenyl-ω-hydroxy, M_n = 1,750 g/mol), EO-und4 (PEO α-undecenyl-ω-hydroxy, M_n = 3,600 g/mol) (Some values have been taken from Hassan Harris thesis, Strasbourg, 2009).

3.4. Synthesis of α-undecenyl-ω-methacryloyl PEO macromonomers by chain-end modification with methacrylic anhydride in the presence of triethylamine

As discussed in the introduction, PEO macromonomers are characterized by a high degree of synthetic flexibility that enables the introduction of a large number of functions at one or both chain-ends. Their homopolymerization or copolymerization with a low molar mass polymerizable entity, and the properties and behavior of the resulting comb-shaped, graft-shaped or crosslinking materials have attracted considerable attention [13, 21, 39, 74-76]. PEO based materials covering a large number of applications have been developed over the years. Typically PEOs can serve in the design for polymeric drug nano carriers as soluble polymers [77] or in the form of micro or nanogels [78]. The modification of surfaces with PEO macromonomers or with PEO brushes is increasingly used to confer hydrophilicity and to improve biocompatibility [47, 79, 80].

If the hydroxyl group of α-undecenyl-ω-hydroxy PEO is modified with polymerizable groups of a different chemical nature, further possibilities could be granted to design new PEO based materials. Since the pioneering work of Ito *et al.* [81] increasing interest was devoted to heterofunctional PEO macromonomers decorated with two chemically different polymerizable entities. Yagci *et al.* [82] designed a few years ago PEO macromonomers with a styryl group on one end and a methacryloyl on the other. They extended the approach to α-vinyl ether ω-methacryloyl PEO macromonomers [82, 83]. However almost no work was made on the modification of the hydroxyl end of α-undecenyl-ω-hydroxy PEO macromonomers. To achieve that aim, the hydroxyl functions of a series of α-undecenyl-ω-hydroxy PEO macromonomers were acetylated with methacrylic anhydride in the presence of triethylamine as shown by Lin-Gibson [84] (Scheme 3). The molecular characteristics of the PEO precursor samples and of the resulting PEO macromonomers, determined by SEC and ^{1}H NMR, are collected in Table 3. A typical SEC diagram is also presented in Figure S8.



SCHEME 3. Schematic representation of the α-undecenyl-ω-methacryloyl PEO macromonomer by chain-end modification of an α-undecenyl-ω-hydroxy PEO macromonomer with methacrylic anhydride in the presence of triethylamine.

TABLE 3

Molecular characteristics of the α-undecenyl-ω-methacryloyl PEO macromonomers obtained by chain-end modification with methacrylic anhydride in the presence of triethylamine.

Sample	M_n[a] (g/mol)	M_n[b] (g/mol)	M_w[c] (g/mol)	M_n[d] (g/mol)	PDI[e]	*f* [f] (%)
	SEC	SEC	SEC	MALDI		^{1}H NMR
PEOund-MA1	2,100	2,300	2,500	-	1.05	90
PEOund-MA2	3,000	3,100	3,200	-	1.03	100
PEOund-MA3	3,300	3,400	3,600	3,900	1.06	100
PEOund-MA4	3,300	3,400	3,600	-	1.06	90
PEOund-MA5	3,300	3,500	3,700	-	1.06	100
PEOund-MA6	3,300	3,500	3,700	-	1.06	100

a) Number average molar mass of the α-undecenyl-ω-hydroxy PEOs, measured by SEC in THF, calibration with linear PEOs;
[b] Number average molar mass of the ω-undecenyl-α-methacryloyl PEOs, measured by SEC in THF, calibration with linear PEOs;
[c] Weight average molar mass of the ω-undecenyl-α-methacryloyl PEOs, measured by SEC in THF, calibration with linear PEOs;
[d] Number average molar mass M_n of the ω-undecenyl-α-methacryloyl PEOs, measured by MALDI-TOF MS;
[e] PDI of the ω-undecenyl PEOs (M_W/M_n) determined by SEC;
[f] Yield of functionalization of the ω-undecenyl-α-methacryloyl PEOs, measured by ^{1}H NMR (400 MHz) in $CDCl_3$.

The ^{1}H NMR spectrum is presented in Figure S9 which unambiguously shows the presence of peaks characteristic of the undecene ($CH_2=CH$) $\delta = 5.8$ ppm) and of the methacryloyl groups ($CH_3–C=CH_2$: $\delta = 6.1$ and 5.5 ppm and $CH_3–C=CH_2$: $\delta = 1.9$ ppm). The average functionality of the PEO macromonomers was determined by integrating the signals of the ^{1}H NMR spectra, i.e. the peaks at 6.1 ppm (methacryloyl double bond, 1H) and the peak at 5.8 ppm

(CH_2=C*H*) (ω-undecene). The different values are provided in Table 3. In most cases, the functionalization yield is close to 100%. The M_n values obtained by SEC and determined by ^{1}H NMR spectroscopy are in good agreement.

The presence of the methacryloyl entity at the chain-end was confirmed by MALDI-TOF MS (Fig. S10). As expected, the molar mass of the α-undecenyl-ω-methacryloyl PEO is higher than that of the α-undecenyl-ω-hydroxy PEO. A difference of m/z of 69 could be noted, which is attributed to the methacryloyl group. For the MALDI-TOF MS spectrum presented in Figure S10, a "minor" distribution is visible. The distribution corresponds to the "sodiated" but not to the "potassiumed" α-undecenyl-ω-methacryloyl PEO. As discussed later in the text, these α-undecenyl-ω-methacryloyl PEOs were used as well-defined building blocks for the synthesis of comb- or star-shaped PEOs.

3.5 Synthesis of α-undecenyl-ω-acetylene PEO macromonomers by chain-end modification with propargyl bromide

The possibility to access modified ω-hydroxy chain-ends by acetylene groups in the presence of DPMK or sodium hydride was already demonstrated [85, 86]. As a consequence α-undecenyl-ω-acetylene PEO can be obtained. We selected an approach derived from the "chain-end functionalization" method to prepare the α-undecenyl-ω-acetylene PEOs starting from α-undecenyl-ω-hydroxy PEOs after modification of the chain-ends with DPMK followed by the addition of propargyl bromide (Scheme S1). After purification, the different α-undecenyl-ω-acetylene PEOs were submitted to a detailed characterization. It must be ensured that every single polymer chain is modified with a terminated triple bond. The resulting functional PEOs were characterized by SEC to prove the absence of the PEO precursor and of any coupling products (Figure 4). In most cases, the M_n values determined by SEC (based on a calibration with linear α-hydro-ω-hydroxy PEOs) are in good agreement with the expected values. The slight increase in molar mass with respect to the PEO precursor is attributed to the presence of the unsaturation at one chain-end.

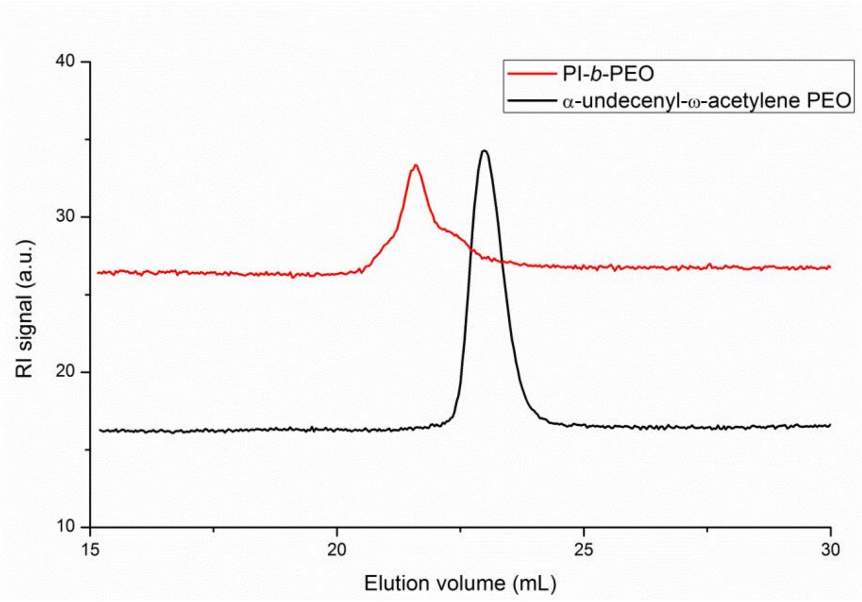


Fig. 4. Typical SEC trace of an α-undecenyl-ω-acetylene PEO macromonomer and a PI-*b*-PEO block copolymer (SEC in THF based on calibration with linear PEOs).

For the same samples, ^{1}H NMR measurements were performed in $CDCl_3$. A typical ^{1}H NMR spectrum is presented in Figure S13. In addition to the signals of the undecenyl protons [$CH_2{=}C\mathit{H}$–: $\delta = 5.8$ ppm, $C\mathit{H}_2{=}CH$–: $\delta = 5.1$ ppm], new peaks corresponding to the –C≡C*H* protons appeared at 4.3 ppm and to $–C\mathit{H}_2–C{\equiv}CH$ protons at 2.4 ppm, respectively. By integrating the signals of the ^{1}H NMR spectra of the chain-end modified PEOs, the triple bond content could be determined (>95%).

MALDI-ToF MS has also been applied to analyze the different α-undecenyl-ω-acetylene PEOs. Figure S14 depicts the MALDI-ToF MS spectrum of an α-undecenyl-ω-acetylene PEO ($M_{n,SEC}$ = 2,200 g/mol). The signals between *m/z* values with a characteristic shift of *m/z* 44 are unambiguously caused by the PEO chain. These different characterization results confirm that induced deactivation of metalated PEOs with propargyl bromide indeed led to the expected α-undecenyl-ω-acetylene compound. The M_n values calculated by MALDI-TOF MS are in good agreement with the M_n values determined by SEC. The peak at m/z 1756 is attributed to the α-undecenyl-ω-acetylene PEO (153.284 ($CH_2CH(CH_2)_9$) + 44.053n (n = 35) (CH_2CH_2O) + 54.047 (OCH_2CCH)+ 6.941 (Li)) (where n is the degree of polymerization).

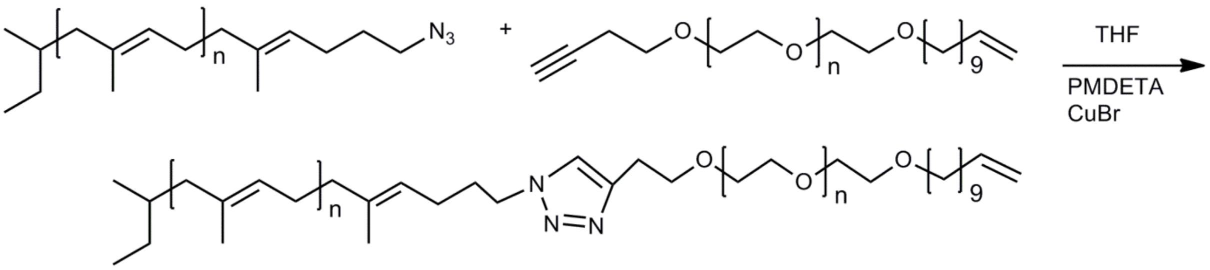
3.6. Synthesis of PI-b-PEO diblock copolymers via a combination of living anionic polymerization and azide/alkyne cycloadditon

PI-*b*-PEO diblock copolymers are utilized in many applications and are of broad interest due to their high potential in micellization and their ability to self-organize in selective solvents into a wide variety of micellar aggregates [87, 88]. Two approaches, based on the sequential living anionic polymerization of isoprene and ethylene oxide, have been developed over the past 20 years to access PI-*b*-PEOs [87, 89]. In the first case an ω-living PI was prepared by anionic polymerization, in cyclohexane or benzene, with *sec*-butyllithium or *tert*-butyllithium as initiator. In a second step, the hydroxyl chain-ends were deprotonated with cumyl potassium [90] or potassium naphthalide [91, 92] followed by addition of EO for the AROP. Increasing efforts have been made to design efficient approaches providing access to PI-*b*-PEO diblock copolymers in an one step process. In non-polar solvents, if excess EO is added to ω-living PIs only an end-group functionalization takes place without oligomerization or polymerization. This is not the case when additives such as cryptates or phosphazene bases are used [93, 94]. Typically, isoprene polymerization was initiated with *sec*-butyllithium in benzene. After the isoprene polymerization, the carbanionic chain-ends are reacted with EO, whereupon $O\text{-}Li^+$ alcoholates are generated, then $t\text{-}BuP_4$ was added followed by a new addition of a controlled amount of EO. V. Rejsek *et al.* prepared in a one step process PI-*b*-PEO by direct polymerization of EO on initiated ω-living polystyrenyllithium or polyisoprenyllithium in the presence of triisobutylaluminum [95]. We developed a new approach to access PI-*b*-PEO diblock copolymers *via* a combination of living anionic polymerization and azide/alkyne cycloadditon.

PI-N_3 were prepared as described in reference [96]. Briefly, carbanionic PIs were synthesized by anionic polymerization in toluene with *sec*-butyllithium as initiator. Quenching with EO and subsequently acidified methanol provided access to ω-hydroxy PIs characterized by a high content of 1,4-cis units and exhibiting low polydispersity index values. In a second step, the tosylation of the hydroxy functions of the PI chain-ends and the conversion of the tosylated chain-ends into azide functional groups was achieved. PI-N_3 were characterized by SEC to verify the absence of coupling products (not presented here). The molar mass values obtained by SEC / LS are in good agreement with the expected data.

By ^{13}C NMR measurements, the characteristic peak of carbon atoms ($–CH_2–N_3$) at 50 ppm could be observed. The proton and the carbon peaks characteristic of the methyl group in the tosyl functions disappeared at 2.4 (^{1}H NMR) and 22 ppm (^{13}C NMR) as well as the peaks characteristic of tosyl functions in the aromatic region at 7.8 and 7.3 ppm (^{1}H NMR) and 147, 129.8 and 127.8 ppm, respectively (^{13}C NMR) (Fig. S11 and S12).

The click chemistry reaction was performed between ω-azido PI and α-undecenyl-ω-acetylene PEO in the presence of PMDETA and CuBr (Scheme 4).



SCHEME 4. Schematic representation of the synthesis of PI-*b*-PEO *via* click reaction between α-undecenyl-ω-acetylene PEOs and ω-azido PIs.

PI-*b*-PEO was characterized by SEC (calibration with linear PEOs). The SEC trace of the resulting product shows two peaks, one at low elution volume corresponding to PI-*b*-PEO ($M_{n,SEC,}$ 13,700 g/mol) and the second one at higher elution volume attributed to unreacted PI. This PI-*b*-PEO was purified by preparative SEC using Bio-Beads® in THF. Fraction 1 was characterized by SEC and a M_n value of 11,000 g/mol could be obtained (Figure 5). α-

Undecenyl-ω-acetylene PEO is not present in the SEC trace of the fractionated PI-*b*-PEO (this PEO has an elution volume of 23.5 mL and in the SEC trace of PI-*b*-PEO no distribution is visible at this elution volume). However, despite of the delicate purifications, ω-azido PIs are also present.

The structure of the PI-*b*-PEO was characterized by ^{1}H and ^{13}C NMR (Fig. 5 and S15). A peak at 8 ppm appeared and corresponds to the proton in the triazol group. The peak characteristic of undecenyl bond is present (5.8 and 5.1 ppm). The signal at 4.3 ppm of $–CH_2–C≡CH$ disappeared confirming the absence of α-undecenyl-ω-acetylene PEO (already shown in the SEC trace). At 50 ppm the peak characteristic for $CH_2–N_3$ disappeared.

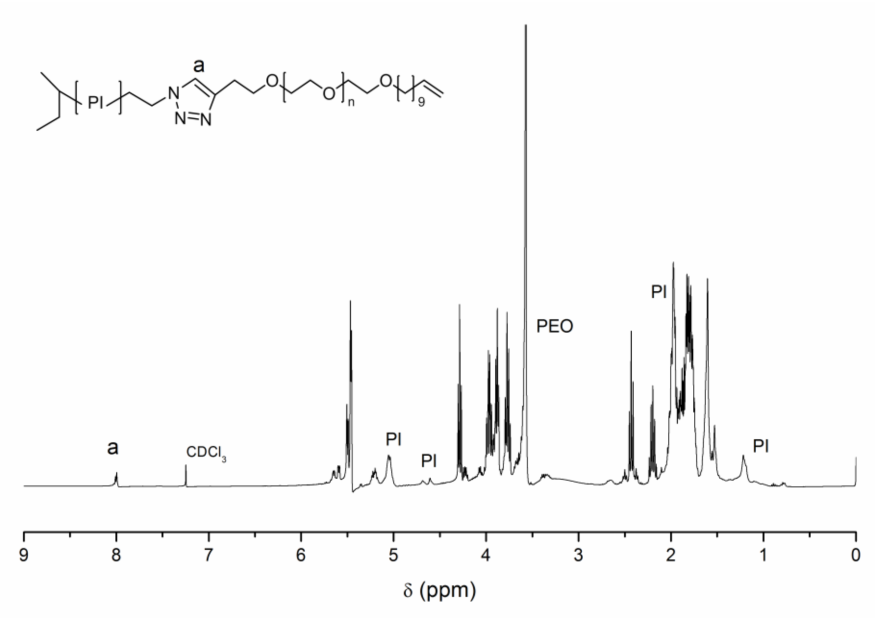


Fig. 5. ^{1}H NMR spectrum of a PI-*b*-PEO (400 MHz, $CDCl_3$).

FTIR spectra of PI-N_3, α-undecenyl-ω-acetylene PEOs and PI-*b*-PEO are shown in Figure 6. The peak of the N_3 groups (2110 cm^{-1}) and –C≡CH (3260 cm^{-1}) disappeared in the spectrum of PI-*b*-PEO block copolymer. However, at 1778 and 1728 cm^{-1} the peaks corresponding to N=N became visible.

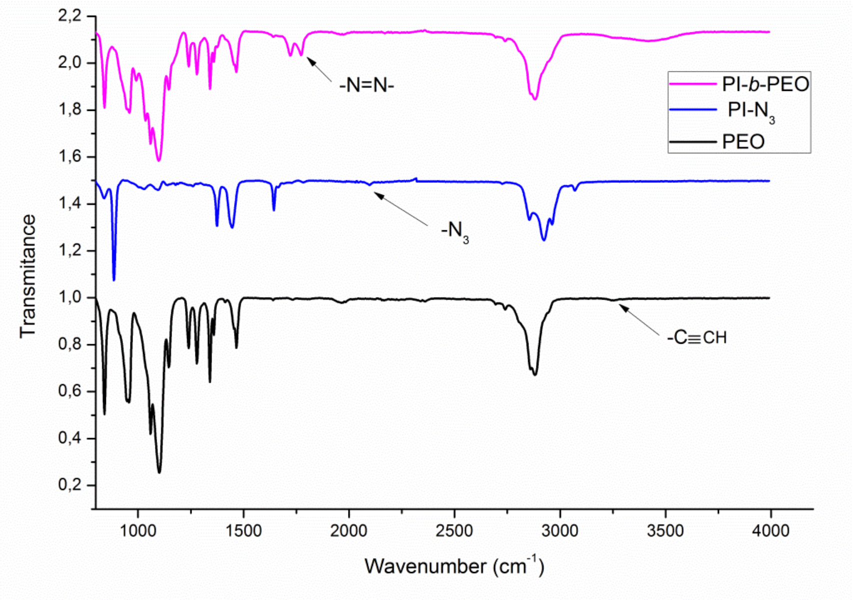


Fig. 6. FTIR spectrum of an ω-azido PI, an α-undecenyl-ω-acetylene PEO and a PI-*b*-PEO.

3.7. Homopolymerization of α-undecenyl-ω-methacryloyl PEO macromonomers by Free-Radical Polymerization (FRP) or Atom-Transfer Radical-Polymerization (ATRP)

As mentioned in the introduction, FRP of PEO macromonomers carrying a methacryloyl group at one chain-end has been extensively used to design comb-shaped polymers characterized by a hydrophobic PMMA backbone and water soluble grafts. In FRP homopolymerization yields are far from being quantitative and the PDI values are rather high. Significant progress was made with the development of ATRP, which made it possible to synthesize comb-shaped PEOs with controlled molar mass and narrow molar mass distributions. Polymerization yields were high, up to 95 % and molar mass distributions by 1.2. In addition the presence of water has been shown to have no deleterious effects on the ATRP process [46, 97-99].

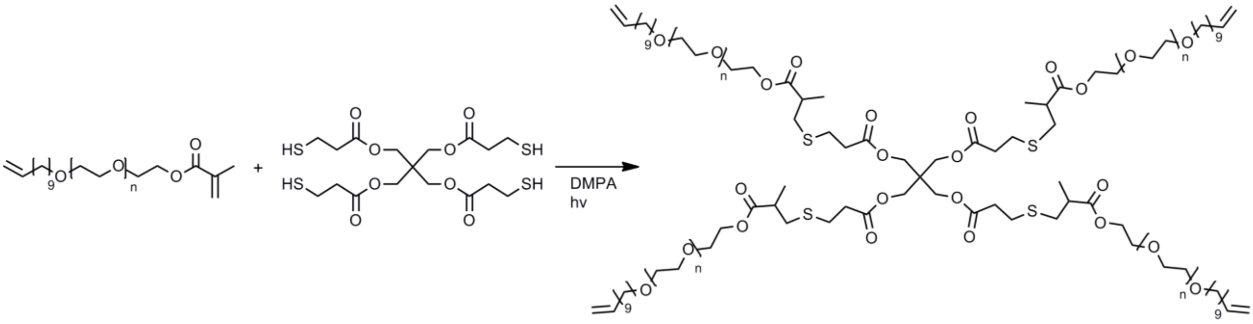
If a α-undecenyl-ω-methacryloyl PEO macromonomer is submitted to free or controlled radical polymerization, the methacryloyl group alone should be involved in the polymerization process whereas the undecenyl group should not react. We submitted our α-undecenyl-ω-methacryloyl PEO macromonomers to a series of homopolymerization tests either by FRP or by ATRP as indicated in the experimental section. Typical SEC curves of the reaction products obtained by FRP are presented on Figure S16. These SEC curves are characterized by the presence of two peaks: a first one corresponding to the precursor, the α-undecenyl-ω-methacryloyl PEO macromonomer and the second one attributed to the comb-shaped PEO. The PDI of the comb-polymer is very large. Similar observations were made for the samples prepared in THF (Fig. S17).

Far better results were obtained by ATRP in water. The details concerning the preparation of the samples are given in the experimental section. On the SEC curve of the reaction product (Fig. S18) we can again see two distributions. The first one at high elution volumes corresponds to the α-undecenyl-ω-methacryloyl PEO macromonomer and the second peak to the comb-shaped PEO. In order to remove the linear PEO chain from the raw reaction product we initially made some attempts by dialysis. The comb-shaped PEOs that are larger than the pores of the dialysis membrane should be retained on the sample side of the membrane, but the linear PEO macromonomer should pass through the membrane. This technique has been already used successfully to remove unreacted PEO branches in star-shaped PEOs [100]. The SEC trace (not presented) of the dialysed raw comb-shaped PEO retained on the sample side of the membrane is almost identical to the SEC of the starting product. Several other approaches were explored to fractionate PEOs of various structures or functionalities. Cansell *et al*. [101] used supercritical fluids to isolate star-shaped PEO from the raw reaction. Trimpin *et al*. [102] fractionated mixtures of low molar mass PEOs with liquid adsorption chromatography at critical conditions combined with a MALDI-TOF MS characterization. Classical fractionation methods based on solvent / non solvent methods using toluene as a solvent and cyclohexane as precipitant revealed to be very efficient to isolate star-shaped PEOs obtained by grafting of PEO macromonomers onto POSS from the raw reaction product [20]. We finally decided to test also this fractionation method to isolate the comb-shaped PEOs obtained by ATRP of α-undecenyl-ω-methacryloyl PEO macromonomers. A typical

SEC trace of a fractioned product is presented in Figure S19. Compared to the raw reaction product containing 60 wt.% of unreacted macromonomer, the amount of residual macromonomer could be reduced to 30 wt.%

3.8. Synthesis of ω-undecenyl-PEO star-shaped polymers via pentaerythritol tetrakis(3-mercaptopropionate).

PEOs star-shaped polymers have gained increasing interest over the past thirty years. The main approaches to design star-shaped PEOs are based on "arm-first" or "core-first" strategies and have been extensively discussed in a recent review article published by Lapienis *et al.* [53]. In an "arm-first" strategy, star-shaped polymers are obtained upon grafting of ω-functional linear polymers onto plurifunctional compounds decorated with antagonist functions. In the following, some preliminary results on the extension of the "arm-first" strategy to the grafting of α-undecenyl PEO macromonomers onto pentaerythritol tetrakis(3-mercaptopropionate) core molecules (named as tetra-thiol) *via* thiol-ene chemistry [103] will be presented. We tested first the thiol-ene click reaction of an α-undecenyl-ω-hydroxy PEO macromonomer with a tetra-thiol core molecule to access 4 arm star-shaped PEO molecules (Scheme S2). AIBN and DMPA were tested as initiators for the reaction. The SEC trace (not presented here) of the reaction product (after 36 h reaction time) corresponds exactly to that of the α-undecenyl-ω-hydroxy PEO macromonomer. This seems to indicate that the undecenyl end-group of the α-undecenyl-ω-hydroxy PEO is not involved in the grafting reaction. Loubat *et al.* [104-107] have shown that tetrafunctional star-shaped polymers of acrylic acid can be obtained based on tetra-thiols. This stimulated us to test the grafting of our α-undecenyl-ω-methacryloyl PEO macromonomers with the tetra-thiol core molecules (Scheme 5). This reaction should lead to the formation of a functional 4-arm PEO star-shaped molecule with free undecenyl double bonds at the outer-end of the branches. These double bonds are thus available for further reactions such as coupling *via* hydrosilylation of Si-H end-functionalized micro or macromolecular species.



SCHEME 5. Schematic representation of 4 arm PEO star molecules obtained *via* thiol-ene click reaction of α-undecenyl-ω-methacryloyl PEO macromonomer with pentaerythritol tetrakis(3-mercaptopropionate).

As shown in the SEC trace (Fig. 7,) the raw reaction product contains different distributions corresponding probably to the different functionalities of the PEO star. To try to isolate a pure fraction, a preparative size exclusion chromatography with automated sample collection was performed (Fig. 8). We focused in this case on fraction 1 (pointed line) due to its narrow molar mass distribution, the high molar mass and the absence of side product with lower functionality.

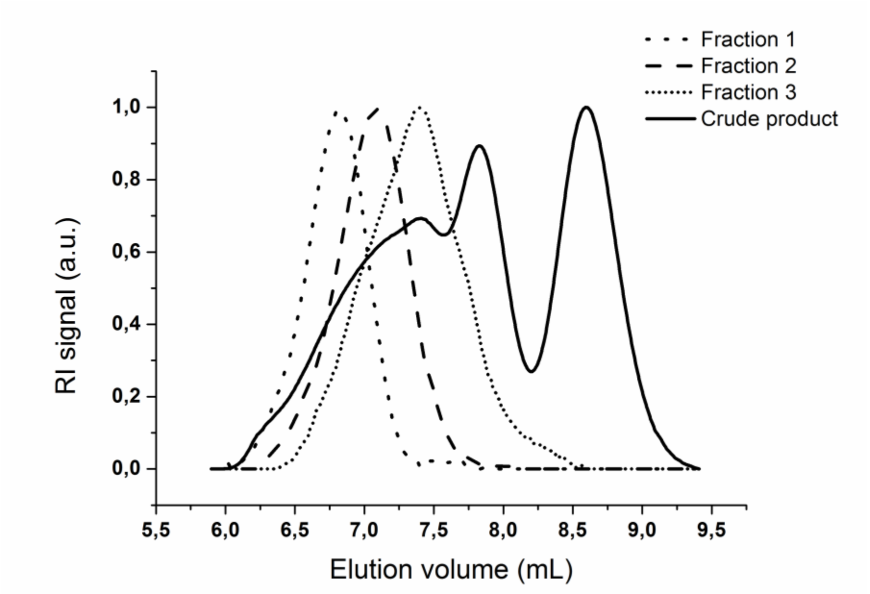


Fig. 7. Typical SEC trace of 4 arm PEO star molecules obtained *via* thiol-ene click reaction of α-undecenyl-ω-methacryloyl PEO macromonomer with pentaerythritol tetrakis(3-mercaptopropionate).

To prove the complete conversion of the MMA double bond and the presence of the core molecule as well as the unreacted undecenyl double bond in the PEO star, ^{1}H NMR spectroscopy of the isolated fraction 1 was performed (Fig. S20). The spectrum of the PEO precursor shows clearly the signals of the MMA double bond (signal a), the CH_2 group of the methacryloyl entity next to the PEO chain and the undecenyl double bond (signals b and c). As characteristic signal for the tetra-thiol the peak for the CH_2 group of the pentaerythritol core (signal e) was chosen. The ^{1}H NMR spectrum of the pure 4 arm fraction shows the complete disappearance of the methacryloyl double bond signals and the presence of the signal characteristic of the core molecule. Furthermore, the signal of the undecenyl double bond is still visible. Therefore, the reaction can be regarded successful.

Additionally, the product was characterized by MALDI-TOF MS (Fig. S21). Due to the difficult ionization of the 4 arm product a high laser intensity must be used, resulting in a fragmentation of the star molecule. Therefore, in each measurement all species are visible.

Conclusions

The first aim of the present work was to design undecenyl PEO macromonomers of precise molar mass and functionality, and characterized by very low PDIs. AROP of ethylene oxide was achieved in the presence of an unsaturated heterofunctional initiator. The most innovative part of the work concerns the development of a new unsaturated heterofunctional initiator in powder form to be used for the AROP of ethylene oxide. The availability of a powder initiator facilitates the processing and the reaction procedure. Such an initiator would be well-suited for the synthesis of libraries of end-functional PEOs, of copolymers based on PEO by AROP combined with ATRP or of various types of branched PEOs. Based on a long-term stable powder initiator obtained by reaction of undecenol with a stoichiometric amount of DPMK, and thereafter carefully purified, a series of α-undecenyl-ω-hydroxy PEO macromonomers could be obtained. Their molecular characteristics met the expectations. These heterofunctional PEO macromonomers are decorated at one chain-end with a double bond and at the other chain-end with a hydroxyl function. This hydroxyl function could be selectively and quantitatively modified with a methacryloyl group providing access to a new class of heterobifunctional PEO macromonomers decorated at the chain-ends with double bonds of different reactivity well-suited for the synthesis of branched PEOs. ATRP in water made it possible to prepare comb-shaped PEOs characterized by the presence of branches with undecenyl groups at the outer-end. The same macromonomers were successfully used to synthesize *via* “click reaction” tetrafunctional PEO star-shaped polymers decorated with undecenyl groups. If the hydroxyl function is transformed in an acetylene group, PI-*b*-PEO diblocks could be obtained by coupling the resulting α-undecenyl-ω-acetylene PEO with ω-azido functionalized PI *via* “click reaction”. The special property of these PI-*b*-PEO block copolymers is the presence of undecene groups at the chain-end of PEO block. This double bond can be utilized for subsequent reactions, e.g. for the attachment of dyes, cell penetrating peptides or sugar units enabling interesting applications in life sciences.

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Chapter 4

Functionalized PI-*b*-PEO

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“End-group functionalized polyisoprene-*b*-poly(ethylene oxide) prepared by combining anionic polymerization and click chemistry”

In preparation

4.1. Summary

In the previous chapter, we discussed the synthesis of well-defined α-undecenyl-ω-hydroxy PEO macromonomers and their use in the synthesis of comb- and star-shaped polymers. These PEO macromonomers could also be used for the preparation of PI-*b*-PEO *via* click reaction.

The fourth chapter of the thesis is devoted to the synthesis of PI-*b*-PEO. These diblock copolymers are characterized by hydrophilic and hydrophobic blocks, their chains may aggregate in aqueous solution to form spherical, cylindrical or vesicular assemblies.

The first part of this chapter is focused on the synthesis *via* anionic polymerization and the characterization of ω-hydroxy PI. ω-Tosyl PIs were obtained after chain-end modification of hydroxy groups in the presence of *p*-toluenesulfonyl chloride and triethylamine. These ω-tosyl PIs were also modified in ω-azido PI by sodium azide.

The second part concerns the synthesis of α-undecenyl-ω-acetylene PEO macromonomers based on the chain-end modification of α-undecenyl-ω-hydroxy PEO macromonomers *via* deactivation with DPMK and propargyle bromide.

Finally, a classical click reaction was performed between α-undecenyl-ω-acetylene PEO and ω-azido PI in the presence of *N,N,N',N'',N''*-pentamethyldiethylenetriamine and copper(I) bromide. The resulting functional PI-*b*-PEOs were characterized by SEC, ^{1}H NMR and MALDI-ToF MS.

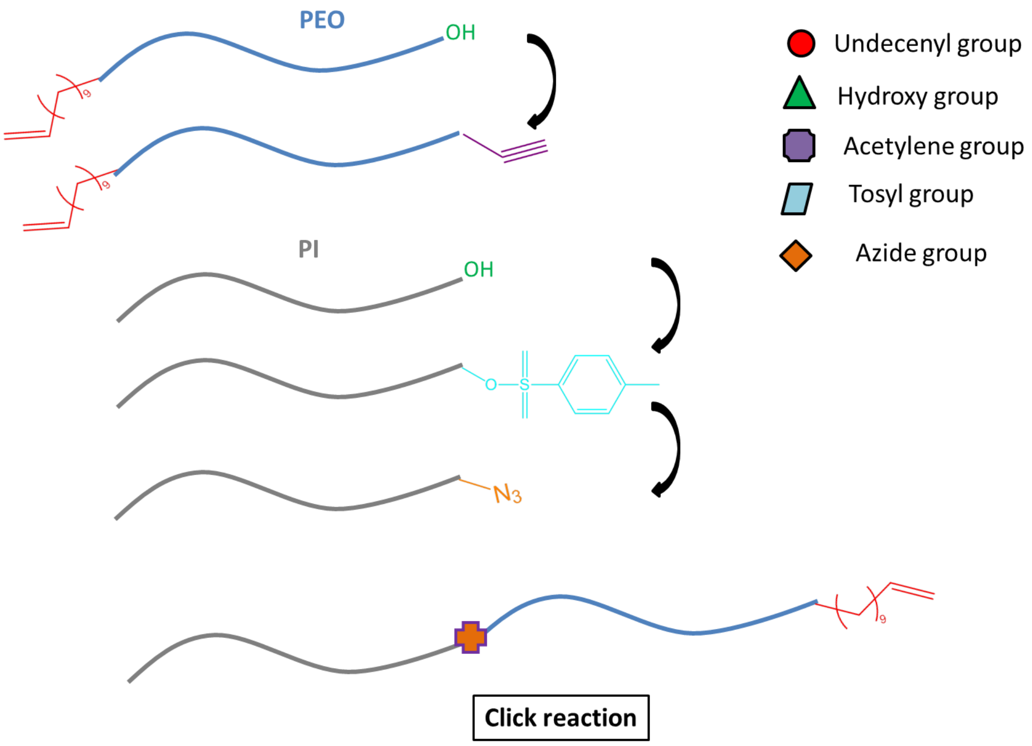

Figure 4.1 Schematical representation of functional PI-b-PEO.

4.2. Article 3

End-group functionalized polyisoprene-*b*-poly(ethylene oxide) prepared by combining anionic polymerization and click chemistry

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In preparation

Abstract

Polyisoprene-*b*-poly(ethylene oxide) (PI-*b*-PEO) diblock copolymers were designed *via* a combination of living anionic polymerization and azide/alkyne cycloadditon. ω-Carbanionic PIs were prepared by anionic polymerization in toluene with *sec*-butyllithium as initiator. Quenching with EO and subsequently acidified methanol provided access to ω-hydroxy PIs characterized by a high content of 1,4-cis units and exhibiting low polydispersity index values. In a second step, the tosylation of the hydroxy functions of the PI chain-ends and the conversion of the tosylated chain-ends into azide functional groups was achieved. The α-undecenyl-ω-hydroxy-PEOs were synthesized by anionic ring opening polymerization of ethylene oxide in THF, with potassium undecenolate as initiator. α-Undecenyl-ω-acetylene PEO macromonomers were obtained upon reaction with propargyl bromide after modification of the hydroxyl chain-ends by an intermediate addition of a stoichiometric amount of diphenylmethyl potassium. The click reaction was performed between the ω-azido PI and the α-undecenyl-ω-acetylene PEO in the presence of *N,N,N',N'',N''*-pentamethyldiethylene triamine and copper(I) bromide. The α-undecenyl-ω-acetylene PEOs, the ω-azido PIs and the coupling products were characterized by SEC, ^{1}H and ^{13}C NMR, FTIR and MALDI-ToF MS to obtain information about the molar mass, chemical-composition and functionality. The successful coupling of the ω-azido PI and the α-undecenyl-ω-acetylene PEO could be confirmed.

INTRODUCTION

Self-assembly of amphiphilic diblock copolymers, characterized by hydrophilic and hydrophobic blocks, has attracted increasing interest due to their possibility to aggregate in selective solvents.[1,2] In aqueous solution, they may aggregate to form spherical, cylindrical or vesicular assemblies. These morphologies have been shown to depend strongly on the molecular parameters such as the overall degree of polymerization and the composition of the copolymer.[3-5] Numerous applications were found for these materials, e.g. as tunable delivery vehicles, as templates for biomineralization, as nanoreactors or scaffolds for biological conjugation.[6] Copolymers of PEO and poly(diene)s form an important class of polymeric amphiphiles where the backbone unsaturation in the hydrophobic block enable further chemical modification after polymerization.[2,3] Poly(ethylene oxide)-*b*-poly(butadiene)[7] can form giant wormlike micelles that can be chemically cross-linked by treatment with radical sources in aqueous solution. These blocks can be crosslinked in aqueous solution by γ-irradiation to yield copolymer vesicles.[8] PI-*b*-PEO copolymers constituted of a hydrophobic polyisoprene (PI) sequence and a hydrophilic poly(ethylene oxide) PEO block represent one of the emerging classes of polymeric amphiphiles. They are of broad interest due to their high potential in micellization and their ability to self-organize in selective solvents into a wide variety of micellar aggregates. These copolymers were utilized in many applications.[5,9,10]

The phase behavior and viscoelasticity of the PEO-PI-PEO mixed with AOT (sodium bis(2-ethylhexyl) sulfosuccinate)/water/decane microemulsions was studied.[11] The water-in-oil microemulsions, in particular dispersions of water droplets coated with a monolayer of the anionic surfactant AOT, in *n*-decane with addition of these amphiphilic triblocks, form a transient network.[12] The phase state and dynamics of structure formation for a series of PI-*b*-PEO blocks copolymers using SAXS and rheology was investigated,[13] the phase diagram of binary blends of PI-*b*-PEO was experimentally determined[14] and the thermal and thermodynamic properties were investigated.[15]

Gournis *et al*. investigated the structure of laponite/PEO and laponite/PEO-PI clay/block copolymer nanocomposites.[16] Core-double-shell systems characterized by complex onion-type architecture were synthesized by “grafting-onto” of block copolymers, PI-*b*-PEO or PS-*b*-PEO, on polyphenylene dendrimers.[17] Heurtefeu *et al*. reported how micellar structures obtained by the self-assembly of PI-*b*-PMMA and PI-*b*-PEO block copolymers can be effectively used as organic supports for ethylene polymerization catalyzed by metallocene and post-metallocene catalysts.[18]

Two approaches, based on sequential living anionic polymerization of isoprene and ethylene oxide, have been developed over the past 20 years to access PI-*b*-PEOs.[1,19] In the first case an ω-living PI was prepared by anionic polymerization, in cyclohexane or benzene, with *sec*-butyllithium or *tert*-butyllithium as initiator. After polymerization, the living chain-ends were deactivated by addition of EO / acetic acid to introduce hydroxyl functions at the chain-ends. In a second step, the hydroxyl chain-ends were deprotonated with cumyl potassium[9] or potassium naphthalide[13,14] followed by addition of EO for the AROP. The chain-ends of the resulting diblock copolymers were deactivated with acidic (HCl) methanol.[13,14] Block copolymers characterized by a narrow molar mass distribution and of a controlled chemical composition could be obtained.[9]

Besides the two-step procedure described above, increasing efforts have been made to design efficient approaches providing access to PI-*b*-PEO diblock copolymers in one step process. However the fact that the synthesis of PI chains characterized by high a 1,4-cis content has to be conducted in non-polar solvents with lithium as counter-ion poses some problems. If excess EO is added to ω-living PIs only an end-group functionalization takes place without oligomerization or polymerization. This approach is based on the addition of additives such as cryptates or phosphazene bases.[20,21] If a *tert*-butyl phosphazene base (t-BuP$_4$) is added to a solution of ω-living polyisoprenyllithium chains[15,19] not only the O-Li aggregates are disrupted but free alcoholates are created. These free alcoholates are able to polymerize EO in THF even at room temperature. Typically, isoprene polymerization was initiated with *sec*-butyllithium in benzene. After the isoprene polymerization, the carbanionic chain-ends are reacted with EO, whereupon O-Li$^+$ alcohaltes are generated, then t-BuP$_4$ was added followed by a new addition of a controlled amount of EO. V. Rejsek *et al*. prepared in a one step process PS-*b*-PEO or PI-*b*-PEO by direct polymerization of EO on initiated ω-living polystyrenyllithium or polyisoprenyllithium in the presence of triisobutylaluminum.[22] K. Wegrzyn *et al*. introduced an alternate route. Starting from commercially available ω-hydroxy PEO, the authors prepared macroinitiators suitable for the nitroxide-mediated free radical polymerization of isoprene.[2] Click chemistry was used in many cases to prepare block copolymers, e.g. the synthesis of cyclic PS-*b*-PI copolymers was performed *via* click chemistry of α-acetylene-ω-azido-PS-*b*-PI.[23] Isotactic PS-*block*-PEO (iPS-*b*-PEO) was synthesized *via* a thiol-ene click coupling reaction of vinyl-terminated isotactic PS with thiol-terminated PEO.[24] Triblock copolymers of PS-*b*-PEO-*b*-poly(tert-butyl acrylate) were obtained *via* combination single electron transfer living radical polymerization (SET-LRP) with "click" chemistry.[25]

In this contribution, we propose a new approach to access PI-*b*-PEO diblock copolymers *via* a combination of living anionic polymerization and azide/alkyne cycloadditon. The synthesis *via* anionic polymerization, the end-functionalization and the detailed characterization of the ω-azido PIs will be discussed in the first part. The preparation of α-undecenyl-ω-acetylene PEO macromonomers by chain-end modification of α-hydroxy-ω-undecenyl PEOs will be presented in the same section. The click reaction between α-undecenyl-ω-acetylene PEO macromonomers and ω-azido PIs in the presence of *N,N,N′,N″,N″*-pentamethyldiethylene triamine and copper(I) bromide will be discussed in the final section. This reaction should lead to functional PI-*b*-PEO diblock copolymers decorated at the outer-end of the PEO block with a double bond which can be utilized for subsequent thio-click reactions, e.g., introducing sugar units or dyes. Almost no examples of such structures with a double bond at PEO chain-ends have been reported in the literature.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) (Aldrich), cyclohexane (Aldrich) and dichloromethane (Aldrich) were purified by conventional methods and kept under argon atmosphere. Dichloromethane (Carlo Erba), methanol (Carlo Erba), toluene (VWR), THF (Carlo Erba), THF without stabilizer (Aldrich), *N,N*-dimethylformamide (DMF) (Aldrich, ACS Spectrophotometric Grade, 99.8%) and acetone (Carlo Erba) were used as received. Isoprene was distilled over sodium and kept under nitrogen atmosphere. *sec*-Buthyllithium (*sec*-buLi) (1.4 M in cyclohexane) (Aldrich), *p*-toluenesulfonyl chloride (TsCl) (Aldrich 99%), triethylamine (TEA) (Aldrich, 99.5%), sodium azide (NaN_3) (Aldrich, 99%), *N,N,N',N',N''*-pentamethyldiethylene triamine (PMDETA) (Aldrich, 99%) and propargyl bromide (Aldrich, 80 wt.% in toluene) were used as received. Copper(I) bromide (CuBr) (Aldrich, 98%) was stirred 5 hours in acetic acid, filtered, washed with ethanol and dried in vacuum. Diphenylmethyl potassium (DPMK) was synthesized in the laboratory according to a well-established procedure.[26]

Characterization

Size exclusion chromatography (SEC)

The absolute weight average molar mass (M_w) of the different PI samples was determined by SEC / online light scattering (SEC / LS) at room temperature (RT) on a Waters apparatus equipped with five PL gel columns (Polymer Laboratories Ltd), an autosampler Waters WISP 717, a differential refractometer Shimadzu RID 6A and a multi-angle laser light scattering (LS) detector Wyatt DAWN DSP (laser: λ = 632.8 nm). The apparent number average molar mass (M_n), M_w and the polydispersity index (PDI) value of the different PI samples were determined by SEC based on calibration with linear PS. THF with a flow rate of 1 mL min^{-1} was used as solvent. Calibration was made with PS standards from Polymer Laboratories with molar masses (M_n) from 1 350 to 32 100 g mol^{-1}.

The apparent M_n, M_w and the PDI value of the different PEO and PI-*b*-PEO samples were determined by SEC at RT on a Shimadzu SIL-20A system controller with a LC-20AD pump, a RID-10A refractive index detector and a Shimadzu SPD 10 Avp UV detector. THF with a flow rate of 1 mL min^{-1} was used as solvent. Calibration was made with PEO standards from Polymer Laboratories with molar masses (M_n) from 7 190 to 22 800 g mol^{-1}.

^{1}H and ^{13}C NMR

Solution NMR spectra were recorded on a Bruker DRX 400 MHz in deuterated chloroform ($CDCl_3$).

Fourier Transform Infrared (FTIR)

Spectroscopy was performed in the Attenuated Total Reflection Mode (ATR-FTIR) using a Vertex 70 spectrometer (Bruker, Germany) equipped with a DTGS detector and a single reflection diamond ATR accessory (A225/Q Platinum ATR, Bruker, Germany). Reference (air) and sample spectra were taken by collecting 20 interferograms between 500 and 3500 cm^{-1} using a Blackman-Harris three-term apodization and the standard Bruker OPUS/IR software (version 5.0).

MALDI-ToF MS

For the measurement of the matrix-assisted laser desorption/ionization (MALDI) spectra, an Ultraflex III ToF/ToF instrument (Bruker Daltonics, Bemen, Germany) was used. The instrument was calibrated prior to each measurement with polymethyl methacrylate (PMMA) as the external standard (PSS, Polymer Standards Service GmbH, Mainz, Germany). Samples were mixed with either 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB), or 2,5-dihydroxybenzoic acid (DHB) as matrix and the doping agent NaI (dried droplet method).

Synthesis

Synthesis of ω-hydroxy PI (PI-OH)

The polymerization of isoprene was carried out in a glass reactor (BüchiGlasUster “PicoClave” pressure reactor). Cyclohexane (100 mL) was introduced in the reactor and the *sec*-BuLi solution was added (2.8 mmol, 2 mL). The temperature was decreased to 10 °C and isoprene (2.8 mmol, 14 g, 20.58 mL) was added. The reactor was heated at 40 °C for 2 hours. PI-OH was formed by reaction of ethylene oxide (in excess over the initiator concentration) on the living PI chain-ends The reaction was stirred over night at 20 °C and the living PI-CH_2CH_2OLi chain-ends were deactivated with methanol (containing a few drops of acetic acid). The solvent was evaporated and the polymer was dissolved in toluene to be centrifuged to remove the salts. Subsequently the toluene was evaporated. The resulting polymer was dissolved in THF, precipitated in methanol, filtered, dried and characterized by SEC, ^{1}H and ^{13}C NMR, FTIR and MALDI-ToF MS. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.2 (m, 1H, trans-1,4-PI and cis-1,4-PI), 4.7 (m, 2H, 1,2 PI), 4.6 (m, 2H, 3,4 PI), 1.8–2.1 (m, 2H, trans-1,4-PI, cis-1,4-PI, 3,4 PI), 1.5–1.7 (m, 2H trans-1,4-PI and 1,2 PI, 3H, cis-1,4-PI and 3,4 PI), 1.4 (m, 3H, trans-1,4-PI), 0.8–0.9 (m, 6H, CH_3–CH_2–CH–CH_3). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 147.5 (–CH–, 3,4 PI), 135.2 (–C–, trans-1,4-PI, cis-1,4-PI, –CH–, 1,2 PI), 125.1 (–CH–, trans-1,4-PI, cis-1,4-PI), 111.1 (CH_2=, 3,4 PI), 61.1 (–CH_2–CH_2–OH), 47.8 (–CH–, 3,4 PI), 40.1 (=C(CH_3)–CH_2–), 36 (–CH_2–CH_2–OH), 23.4 (–CH_3, cis-1,4-PI, 3,4 PI and 1,2 PI), 18.6 (CH_3–CH_2–CH(CH_3)–), 15.9 (–CH_3, trans-1,4-PI), 11.6 (CH_3–CH_2–CH(CH_3)–). FTIR (cm^{-1}): 3078 (=CH, stretching), 2966 (CH_3, stretching), 2930 (CH_2, stretching), 2860 (CH_2, stretching), 1645 (C=C, stretching), 1450 (CH_2, deformation), 1375 (CH_3, deformation).

Synthesis of ω-tosyl PI *(PI-Ts)*

PI_3-OH (7 100 g mol^{-1}, 2 g, 2.81 × 10^{-4} mol) was dissolved in 5 mL of anhydrous CH_2Cl_2 under argon and TEA (10 eq., 0.39 mL, 2.81 × 10^{-3} mol) was added. The solution was cooled to 0 °C and TsCl (10 eq., 0.537 g, 2.81 × 10^{-3} mol) was added. The solution was left to stir overnight at RT. The polymer was purified as before and by preparative SEC using Bio-Beads® in CH_2Cl_2 and was characterized by ^{1}H NMR and ^{13}C NMR. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.8 and 7.3 (m, 2H, aromatic), 5.2 (m, 1H, trans-1,4-PI and cis-1,4-PI), 4.7 (m, 2H, 1,2 PI), 4.6 (m, 2H, 3,4 PI), 4.0 (m, 2H, –CH_2–O–S), 2.4 (s, 3H, CH_3–C–), 1.8–2.1 (m, 2H, trans-1,4-PI, cis-1,4-PI, 3,4 PI), 1.5–1.7 (m, 2H trans-1,4-PI and 1,2 PI, 3H, cis-1,4-PI and 3,4 PI), 1.4 (m, 3H, trans-1,4-PI), 0.8–0.9 (m, 6H, CH_3–CH_2–CH(CH_3)–). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 147.5 (CH, 3,4 PI), 147 (C, aromatic), 135.2 (C, trans-1,4-PI, cis-1,4-PI, CH, 1,2 PI), 129.8 and 127.8 (CH_2, aromatic), 125.1 (CH, trans-1,4-PI, cis-1,4-PI), 111.1

(CH_2=, 3,4 PI), 70 (2H, –CH_2–O–S), 47.8 (–CH–, 3,4 PI), 40.1 (=C(CH_3)–CH_2–), 23.4 (–CH_3, cis-1,4-PI, 3,4 PI and 1,2 PI), 22 (C*H*$_3$–C–), 18.6 (CH_3–CH_2–CH(C*H*$_3$)–), 15.9 (–CH_3, trans-1,4-PI),11.6 (*C*H_3–CH_2–CH(CH_3)–). FTIR (cm^{-1}): 3078 (=CH, stretching), 2966 (CH_3, stretching), 2930 (CH_2, stretching), 2860 (CH_2, stretching), 1645 (C=C, stretching), 1450 (CH_2, deformation), 1375 (CH_3, deformation), 1180 (S=O).

Synthesis of ω-azido PI (PI-N_3)

PI3-Ts (7 700 g mol^{-1}, 0.7 g, 9.09×10^{-5} mol) was dissolved in a mixture dry THF / dry DMF (7 and 3 mL) and NaN_3 (5 eq., 0.029 g, 4.54×10^{-4} mol) was added. The solution was stirred vigorously at 35 °C for 24 hours and subsequently for 3 days at RT. Afterwards, the solvent was evaporated. An extraction with dichloromethane / water was performed to remove the salts. Then the solvent was evaporated under vacuum. The resulting polymer was dissolved in THF, precipitated in methanol, dried and characterized by ^1H NMR and ^{13}C NMR. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.2 (m, 1H, 1 trans-1,4-PI and cis-1,4-PI), 4.7 (m, 2H, 1,2 PI), 4.6 (m, 2H, 3,4 PI), 3.2 (m, 2H, –CH_2–N_3), 1.8–2.1 (m, 2H, trans-1,4-PI, cis-1,4-PI, 3,4 PI), 1.5–1.7 (m, 2H trans-1,4-PI and 1,2 PI, 3H, cis-1,4-PI and 3,4 PI), 1.4 (m, 3H, trans-1,4-PI), 0.8–0.9 (m, 6H, C*H*$_3$–CH_2–CH(C*H*$_3$)–). ^{13}C NMR (400 MHz, $CDCl_3$, δ, ppm): 147.5 (–CH–, 3,4 PI), 135.2 (–C–, trans-1,4-PI, cis-1,4-PI, –CH–, 1,2 PI), 125.1 (–CH–, trans-1,4-PI, cis-1,4-PI), 111.1 (CH_2=, 3,4 PI), 50 (–CH_2–N_3), 47.8 (CH, 3,4 PI), 40.1 (=C(CH_3)–*C*H_2–), 23.4 (–CH_3, cis-1,4-PI, 3,4 PI and 1,2 PI), 18.6 (CH_3–CH_2–CH(*C*H_3)–), 15.9 (–CH_3, trans-1,4-PI),11.6 (*C*H_3–CH_2–CH(CH_3)–). FTIR (cm^{-1}): 3078 (=CH, stretching), 2966 (CH_3, stretching), 2930 (CH_2, stretching), 2860 (CH_2, stretching), 2110 (N_3), 1645 (C=C, stretching), 1450 (CH_2, deformation), 1375 (CH_3, deformation).

Synthesis of α-undecenyl-ω-acetylene PEO

The hydroxyl functions of the α-hydroxy-ω-undecenyl PEO (2 000 g mol^{-1}, 4.5 g, 2.15×10^{-3} mol) were transformed into alcoholates by addition of a stoichiometric amount of DPMK (around 2.59 mL, DMPK concentration 0.85×10^{-3} mol L^{-1}) at RT (stoichiometry determined by colorimetry). In the next step, propargyl bromide (2 eq., 0.38 mL, 5×10^{-3} mol) was added to the PEO solution. The slight yellow coloration disappeared rapidly. The reaction medium was kept at RT overnight. The resulting polymer solutions were centrifuged in toluene. The solvent was evaporated. The resulting polymer was dissolved in THF, precipitated in diethyl ether, filtered, dried and characterized by SEC and ^{1}H NMR. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 5.8 (m, 1H, $-\mathrm{C}H{=}\mathrm{CH_2}$), 5.1 (m, 2H, $-\mathrm{CH{=}C}H_2$), 4.3 (s, 2H, $-\mathrm{C}H_2-\mathrm{C{\equiv}CH}$), 3.6–3.8 (m, 4H*n, $-\mathrm{O}-\mathrm{C}H_2-\mathrm{C}H_2-$), 2.4 (s, 1H, $-\mathrm{C{\equiv}C}H$), 2.0 (m, 2H, $-\mathrm{C}H_2-\mathrm{C}H{=}\mathrm{CH_2}$), 1.5 (m, 2H, $-\mathrm{C}H_2-(\mathrm{CH_2})_7-\mathrm{CH_2}-\mathrm{CH{=}CH_2}$), 1.1–1.3 (m, 2H*7, $-\mathrm{CH}-(\mathrm{C}H_2)_7-\mathrm{CH_2}-\mathrm{CH{=}CH_2}$). FTIR (cm^{-1}): 3260 (C≡CH, stretching), (2880 (CH, stretching), 1467 (CH$_2$, deformation), 1100 (CO, stretching).

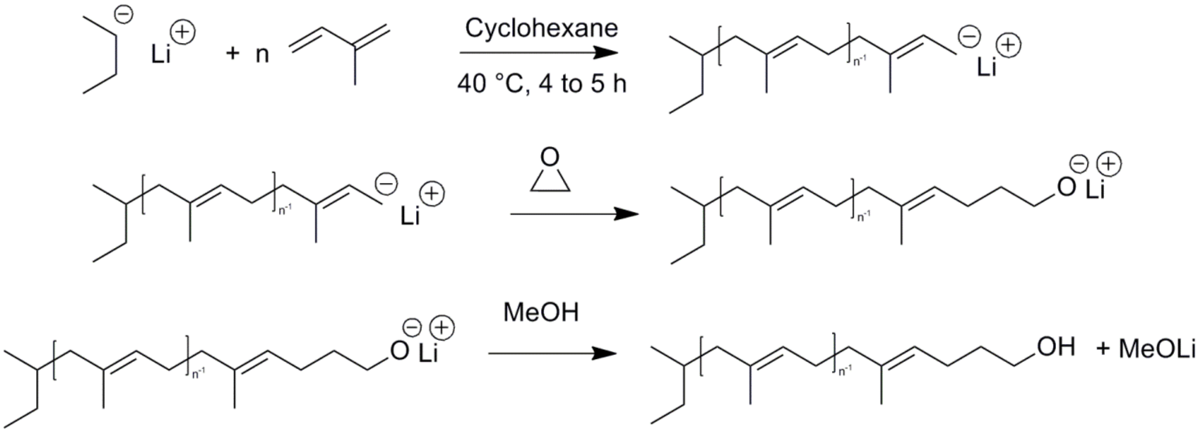
Synthesis of (PI-b-PEO) via click chemistry

PI-N$_3$ (7 700 g mol^{-1}, 1 g, 1.29×10^{-4} mol) was dissolved in 20 mL of THF. PEO (5 800 g mol^{-1}, 0.75 g, 1.29×10^{-4} mol) and CuBr (5 eq., 6.49×10^{-4} mol, 0.093 g) were added. Oxygen was removed from the solution by three freeze-pump-thaw cycles. PMDETA was added. (5 eq., 6.49×10^{-4} mol, 0.135 mL). The reaction was stirred for 24 hours at RT. Afterwards, the solvent was evaporated. The resulting polymer was dissolved in THF, precipitated in cold acetone and dried. This operation was repeated 3 times. The resulting polymer was characterized by SEC and purified by preparative SEC using Bio-Beads® in THF. The polymer fraction was characterized by ^{1}H NMR. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 5.8 (m, 1H, $-\mathrm{C}H{=}\mathrm{CH_2}$),5.2 (m, 1H, trans-1,4-PI and cis-1,4-PI), 5.1 (m, 2H, $-\mathrm{CH{=}C}H_2$), 4.7 (m, 2H, 1,2 PI), 4.6 (m, 2H, 3,4 PI), 3.6–3.8 (m, 4H*n, $-\mathrm{O}-\mathrm{C}H_2-\mathrm{C}H_2-$),2.0 (m, 2H, $-\mathrm{C}H_2-\mathrm{CH{=}CH_2}$), 1.8–2.1 (m, 2H, trans-1,4-PI, cis-1,4-PI, 3,4 PI), 1.5–1.7 (m, 2H trans-1,4-PI and 1,2 PI, 3H, cis-1,4-PI and 3,4 PI), 1.5 (m, 2H, $-\mathrm{C}H_2-(\mathrm{CH_2})_7-\mathrm{CH_2}-\mathrm{CH{=}CH_2}$),1.4 (m, 3H, trans-1,4-PI), 1.1–1.3 (m, 2H*7, $-\mathrm{CH}-(\mathrm{C}H_2)_7-\mathrm{CH_2}-\mathrm{CH{=}CH_2}$), 0.8–0.9 (m, 6H, $\mathrm{C}H_3-\mathrm{CH_2}-\mathrm{CH}(\mathrm{C}H_3)-$). FTIR (cm^{-1}): 2930 (CH$_2$, stretching, PI), 2880 (CH, stretching, PEO), 2860 (CH$_2$, stretching, PI), 1778□1728 (N=N, stretching) 1645 (C=C, stretching, PI), 1467 (CH$_2$, deformation, PEO), 1450 (CH$_2$, deformation, PI), 1375 (CH$_3$, deformation, PI), 1100 (CO, stretching).

RESULTS AND DISCUSSSION

Synthesis of ω-azido PI (PI-N_3)

The preparation of PI, requires the use of organolithium initiators and hydrocarbon solvents whereas the anionic ring-opening polymerization of ethylene oxide proceeds in the presence of potassium organic initiators and polar solvents. The reaction of organolithium initiators in nonpolar media with EO does not permit the polymerization of EO.[27] The reason for the two-step procedure for the preparation of PI-*b*-PEO is the tendency of living PEO chain-ends to strongly aggregate with Li^+, forming ion pairs that terminate chain propagation. This prevents polymerization of the second block by addition of ethylene oxide to the living PI block.[19] This method is used for the preparation of ω-hydroxy PI. Several PI-OH were prepared by anionic polymerization of isoprene (Scheme 1). The molar masses and PDI values of the PI samples determined by SEC / LS and ^{1}H NMR are collected in Table 1.



Scheme 1. Schematic representation of the synthesis of ω-hydroxyl PIs *via* anionic polymerization.

Table 1. Molecular characteristics of hydroxy terminated PIs synthesized by anionic polymerization.

Sample	Time (h)	Temp. (°C)	[I] (mol)	$M_{n\ th.}$ [a] (g mol^{-1})	$M_{n\ calc.}$ [b] (g mol^{-1})	M_n [c] (SEC / LS; g mol^{-1})	M_w [d] (SEL / LS; g mol^{-1})	PDI [e)]	M_n [f] (^{1}H NMR; g mol^{-1})
PI_2OH	24	40	0.10	2 000	1 891	2 220	2 440	1.09	2 100
PI_1OH	24	40	0.15	5 000	4 750	5 840	5 850	1.01	4 600
PI_3OH	24	40	0.20	5 000	4 821	7 180	7 220	1.01	6 500
PI_6OH	24	40	0.30	6 000	5 757	6 700	6 970	1.04	6 800
PI_5OH	24	40	0.15	7 000	9 200	12 520	12 990	1.03	10 700
PI_4OH	24	40	0.20	10 000	9 285	14 740	14 860	1.01	12 600

a Theoretical number average molar mass of the hydroxy PIs assuming total conversion.
b Theoretical number average molar mass of the hydroxy PIs calculated taking into account the polymerization yield.
c Number average molar mass of the hydroxy PIs, measured by SEC in THF, with online light scattering.
d Weight average molar mass of the hydroxy PIs, measured by SEC in THF, with online light scattering.
e PDI values of the hydroxy PIs (M_w / M_n) determined by SEC in THF, with online light scattering.
f Number average molar mass of the hydroxy PIs, measured by ^{1}H NMR.

The M_n and M_w values by SEC / LS are in good agreements with the theoretical values. The polydispersity is around 1.05. The microstructure of the PI-OH was studied by ^{1}H and ^{13}C NMR in $CDCl_3$. Typical spectra are presented in Figure 1 and 2. As expected, for isoprene polymerization conducted in non-polar solvent, the sample is characterized by the presence of a majority of 1,4-isomers and, in small quantity, of 3,4- and 1,2-isomers (less than 10%, determined by ^{1}H NMR).[28,29]

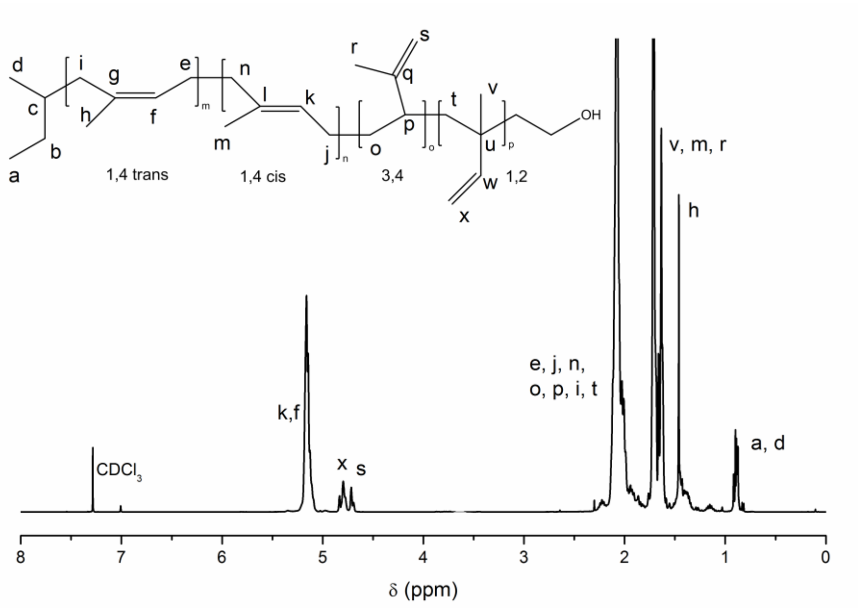


Fig. 1. ^{1}H NMR spectrum of an ω-hydroxy PI obtained by anionic polymerization (400 MHz, $CDCl_3$).

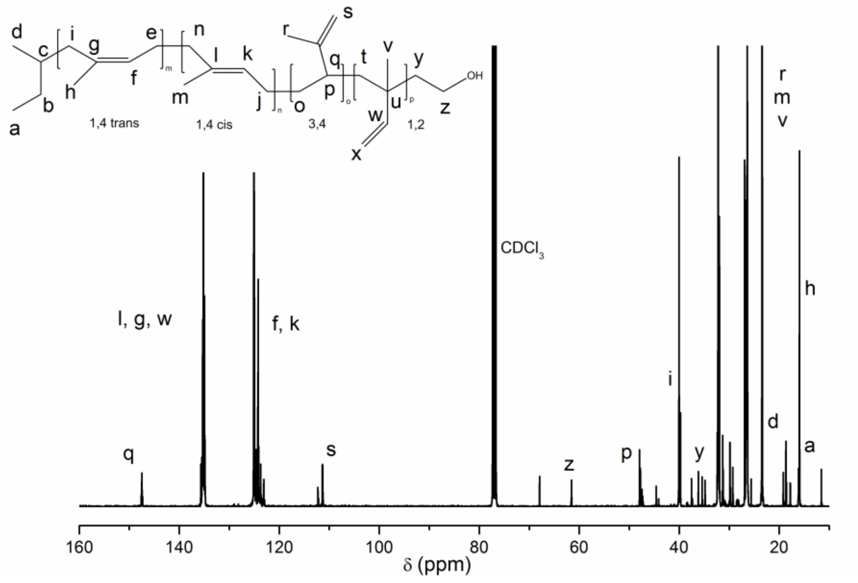


Fig. 2. ^{13}C NMR spectrum of an ω-hydroxy PI obtained by anionic polymerization (400 MHz, $CDCl_3$).

FTIR measurements of PIs were discussed by several authors.[30-33] Detailed assignments of the observed fundamental bands of trans-1,4-PI have been analyzed as the peak positions and relative intensities. The shift of absorption peaks caused by microstructure content's variation was also discussed. The recorded FTIR spectra of PI-OH, PI-Ts and PI-N_3 are shown in Figure 3. The =C–H stretching frequency is placed between 3100 and 3000 cm^{-1}. The CH_2 and CH_3 stretching typically appears in the region 3000 to 2800 cm^{-1}. The deformation vibration of the –(CH_2) groups absorbs in the region from 1500 to 1400 cm^{-1}. The –C=C stretching frequency appears between 1680 and 1665 cm^{-1}. The methyl deformation mode, $-CH_3$, is observed at 1375 cm^{-1}.

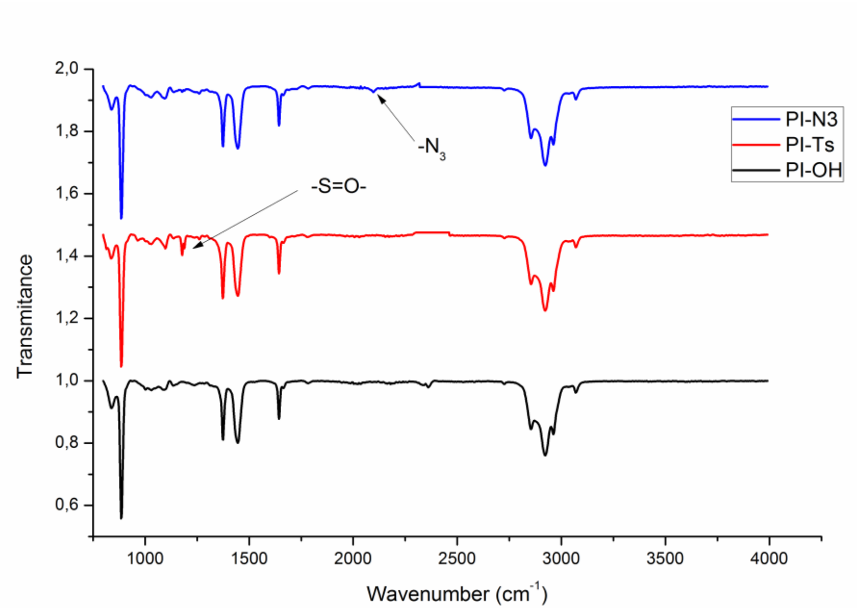


Fig. 3. FTIR spectra of an ω-hydroxy, ω-tosyl and ω-azido PI.

MALDI-ToF MS measurements confirm the functionality of PI macromonomers. Figure 4 depicts the MALDI-ToF MS spectra of an ω-hydroxy PI, ($M_{n,SEC / LS}$ = 2 200 g mol^{-1}). The peak at m/z 1912 is attributed to the ω-hydroxy PI (57.114 (C_4H_9) + 68.117n (n =25) (C_5H_8) + 45.060 (CH_2CH_2OH) + 107.868 (Ag)) (where n is the degree of polymerization). The shift of m/z 68 is caused by the PI chain. The values calculated for the molar masses are in good agreement with the theoretical values.

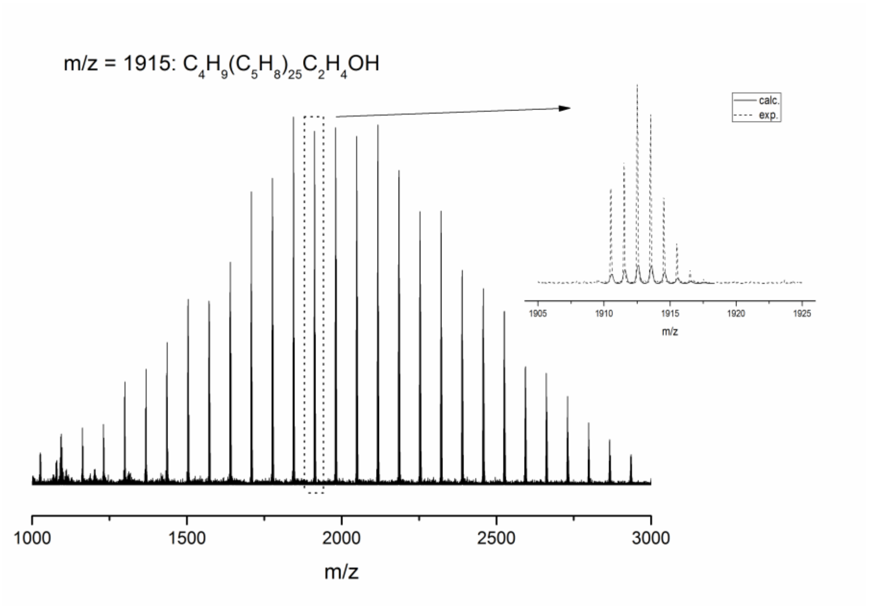
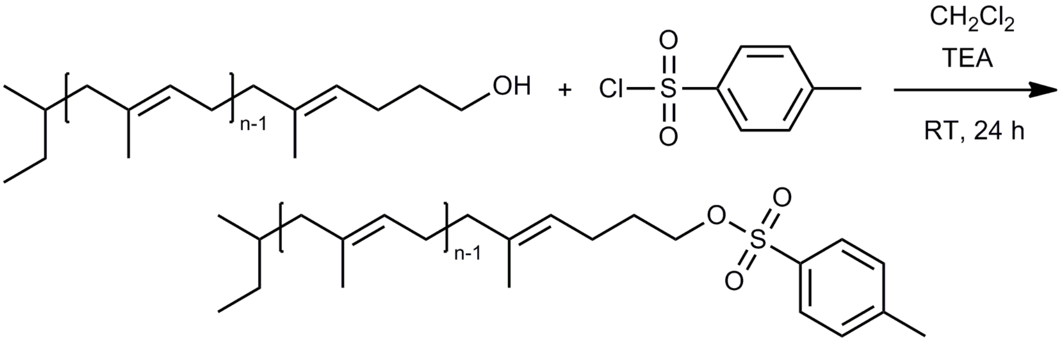


Fig. 4. MALDI-TOF MS of an ω-hydroxy PI obtained by anionic polymerization ($M_{n,SEC / LS}$ = 2 200 g mol^{-1}) (Matrix: dithranol, AgTFA).

The hydroxyl groups are transformed into tosyl groups (Scheme 2) as described in the experimental section.



Scheme 2. Schematic representation of the synthesis of ω-tosyl PIs.

The resulting functional PIs were characterized by SEC to verify the absence of coupling products. In most cases, M_n values determined by SEC / LS are in good agreement with the expected values. The slight increase in molar mass with respect to the PI precursor is attributed to the presence of the tosyl group at one chain-end. By NMR measurements, at 7.8 and 7.3 ppm (^{1}H NMR) and at 147, 129.8 and 127.8 ppm (^{13}C NMR), the characteristic peaks of the aromatic groups could be observed. Protons and carbon peaks characteristic for the methyl group in the tosyl functions appear at 2.4 and 22 ppm, respectively. At 61.1 and 36 ppm, the peaks characteristics of carbons ($–CH_2–CH_2–OH$) are absent. The average functionality of

PI-Ts was determined by integrating the signals of the ^{1}H NMR spectra, i.e. the peaks at 0.8 ppm (CH_3 at the star-end) and the peak at 2.4 ppm (CH_3) of the PI-Ts chain. In most cases, the functionalization yield is close to 100% independent of the molar mass of the precursor PI.

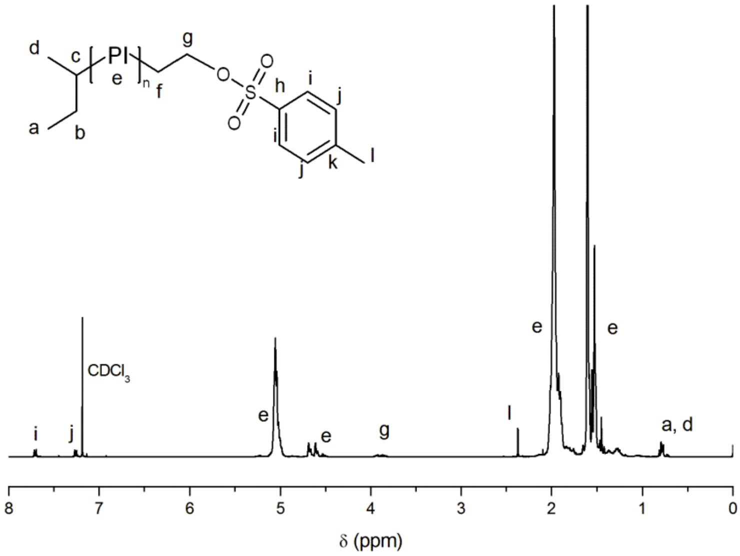


Fig. 5. ^{1}H NMR spectrum of an ω-tosyl PI obtained by chain-end modification of an ω-hydroxy PI with TsCl in the presence of TEA (400 MHz, $CDCl_3$).

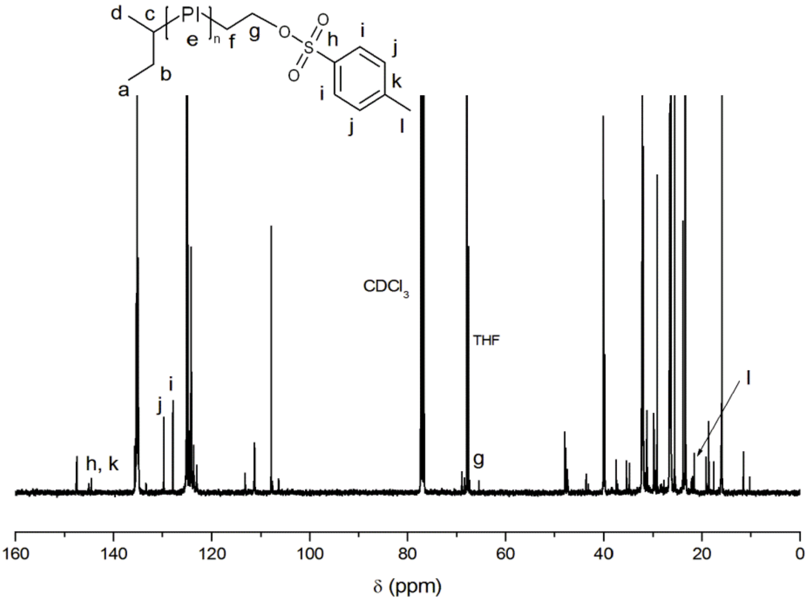
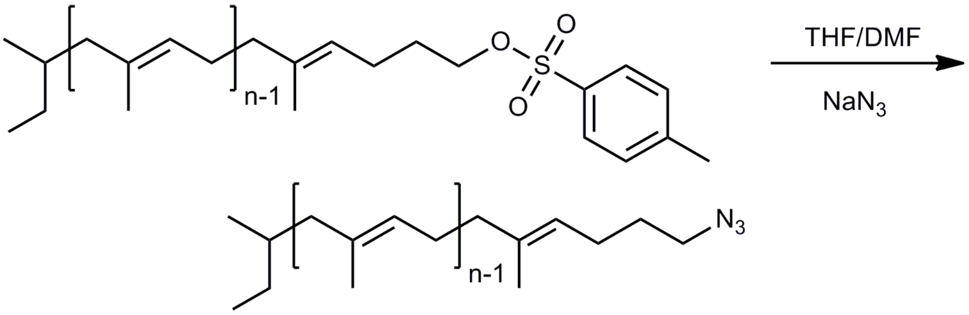


Fig. 6. ^{13}C NMR spectrum of an ω-tosyl PI obtained by chain-end modification of an ω-hydroxy PI with TsCl in the presence of TEA (400 MHz, $CDCl_3$).

In the FTIR spectra, characteristic peaks of the –S=O– groups are present at 1180 cm^{-1} (Figure 3, PI-Ts).

For further functionalization, the tosyl groups were transformed in azide groups (Scheme 3) as described in experimental section.



Scheme 3. Schematic representation of the synthesis of ω-azido PIs.

The resulting functional PIs were characterized by SEC to verify the absence of coupling products (not presented here). In most cases, the M_n values obtained by SEC / LS are in good agreement with the expected data.

By ^{13}C NMR measurements, the characteristic peak of carbons ($–CH_2–N_3$) at 50 ppm could be observed. The proton and the carbon peaks characteristic of the methyl group in tosyl functions disappeared at 2.4 (^{1}H NMR) and 22 ppm (^{13}C NMR) as well as the peaks characteristic of tosyl functions in the aromatic region at 7.8 and 7.3 ppm (^{1}H NMR) and 147, 129.8 and 127.8 ppm (^{13}C NMR).

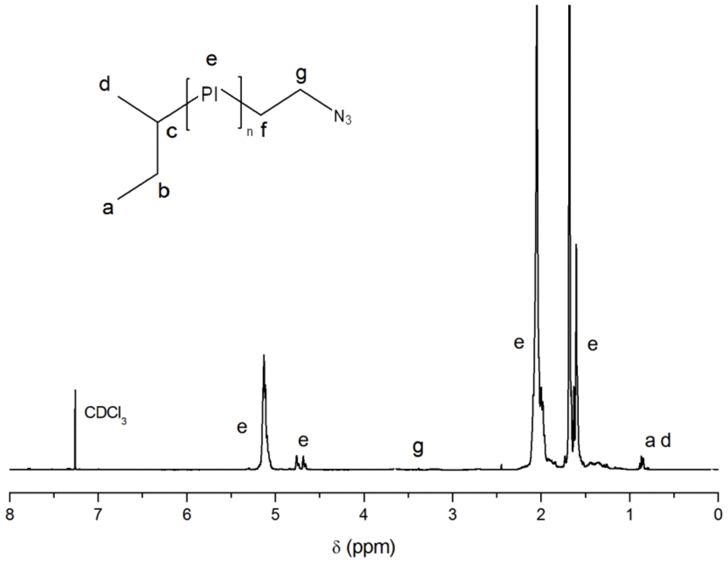


Fig. 7. ^{1}H NMR spectrum of an ω-azido PI obtained by chain-end modification of an ω-tosyl PI in the presence of NaN_3 (400 MHz, $CDCl_3$) (g not well visible).

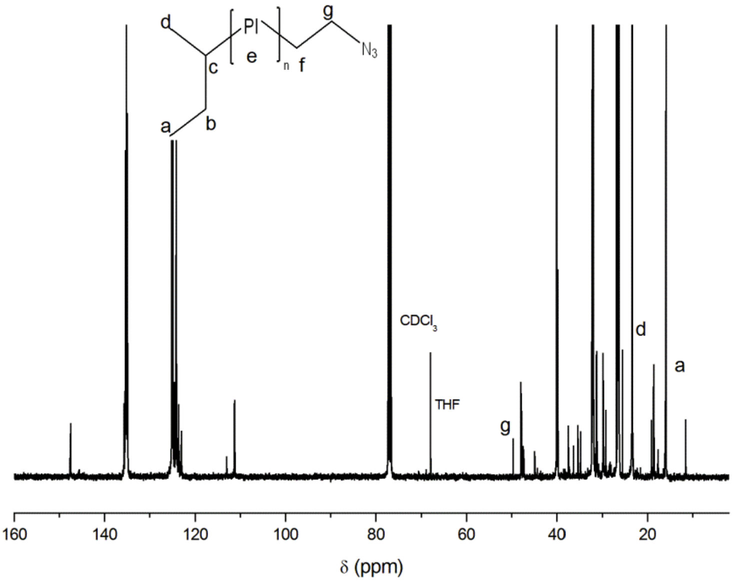


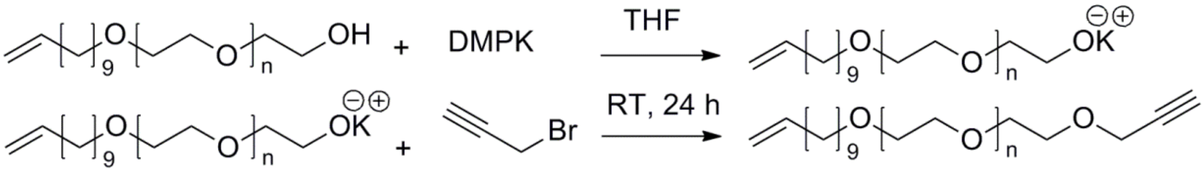
Fig. 8. ^{13}C NMR spectrum of an ω-azido PI obtained by chain-end modification of an ω-tosyl PI in the presence of NaN_3 (400 MHz, $CDCl_3$).

PI_6, PI_6-Ts and PI_6-N_3 were analyzed by SEC / LS. The absolute M_w value of PI_6-Ts ($M_{w,SEC / LS}$ = 7 500 g mol^{-1}) increases compared to the value of PI_6 ($M_{w,SEC / LS}$ = 7 200 g mol^{-1}), confirming the presence of a tosyl group at the PI chain-end. The same observation is made in case of the PI_6-N_3. The absolute M_w value of PI_6-N_3 ($M_{w,SEC / LS}$ = 7 300 g mol^{-1}) decreases compared to the value of PI_6-Ts ($M_{w,SEC / LS}$ = 7 500 g mol^{-1}), indicating the presence of an azide group at the PI chain-end.

In the FTIR spectra, characteristic peaks of the –S=O– groups disappear at 1180 cm^{-1} (Figure 3, PI-Ts) and at 2110 cm^{-1}, the peak of the N_3 groups appears (Figure 3, PI-N_3).

Synthesis of α-undecenyl-ω-acetylene PEO

PEO is a hydrophilic polymer with outstanding biocompatibility. PEOs are used as building blocks for a large number of complex macromolecular architectures designed for various applications.[34] α-Hydroxy-ω-undecenyl PEOs were obtained by AROP of ethylene oxide using potassium undecenolate initiator according to a well-established procedure.[34] The possibility to access modified ω-hydroxy chain-ends[25,35] by acetylene groups in the presence of sodium hydride or DPMK was already demonstrated. As a consequence α-undecenyl-ω-acetylene PEO can be obtained. We selected an approach derived from the “chain-end functionalization” method[36] to prepare the α-undecenyl-ω-acetylene PEOs starting from α-undecenyl-ω-hydroxy PEOs after modification of the chain-ends with DPMK followed by the addition of propargyl bromide (Scheme 4).



Scheme 4. Schematic representation of the synthesis of α-undecenyl-ω-acetylene PEO macromonomers.

After purification, the different α-undecenyl-ω-acetylene PEOs were submitted to a detailed characterization. It must be ensured that every single polymer chain is modified with a terminated triple bond. The resulting functional PEOs were characterized by SEC to prove the absence of the PEO precursor and of any coupling products (Figure 9). In most cases, the M_n values determined by SEC (based on a calibration with linear α-hydro-ω-hydroxy PEOs) are in good agreement with the expected values. The slight increase in molar mass with respect to the PEO precursor is attributed to the presence of the unsaturation at one chain-end.

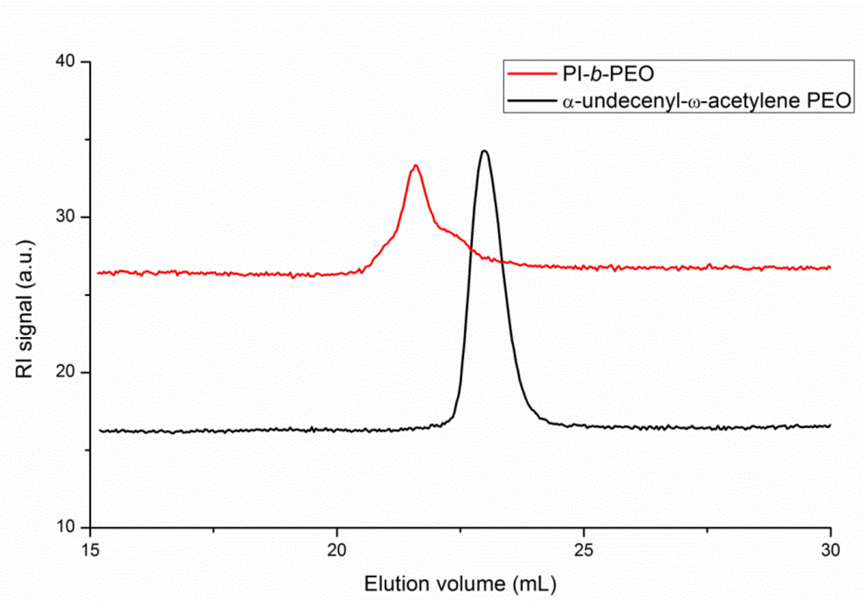


Fig. 9. Typical SEC trace of an α-undecenyl-ω-acetylene PEO macromonomer obtained by chain-end modification of an α-undecenyl-ω-hydroxy PEO macromonomer with propargyl bromide in the presence of DPMK and a PI-*b*-PEO obtained by click reaction between α-undecenyl-ω-acetylene PEO and ω-azido PI (SEC based linear PEO in THF).

For the same samples, ^1H NMR measurements were performed in $CDCl_3$. A typical ^1H NMR spectrum is presented in Figure 10. In addition to the signals of the undecenyl protons [$CH_2{=}CH$–: δ = 5.8 ppm, $CH_2{=}CH$–: δ = 5.1 ppm], new peaks corresponding to –C≡C*H* protons appear at 4.3 ppm and to –CH_2–C≡CH protons at 2.4 ppm, respectively. By integrating the signals of the ^1H NMR spectra of the chain-end modified PEOs, the triple bond content could be determined (closed to >95%).

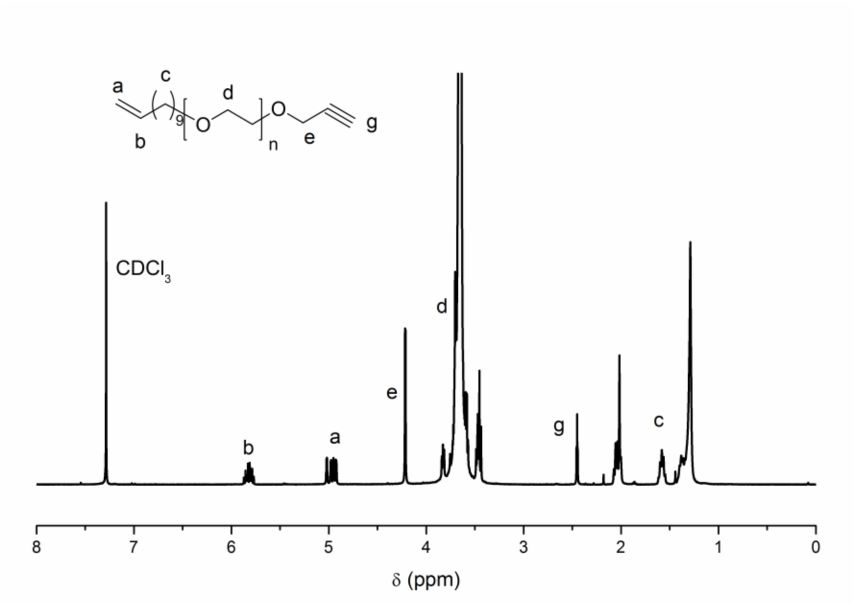


Fig. 10. ^{1}H NMR spectrum of an α-undecenyl-ω-acetylene PEO macromonomer obtained by chain-end modification of an α-undecenyl-ω-hydroxy PEO macromonomer with propargyl bromide in the presence of DPMK (400 MHz, $CDCl_3$).

MALDI-ToF MS has also been applied to analyze the different PEOs. Figure 11 depict the MALDI-ToF MS spectra of an α-undecenyl-ω-acetylene PEO ($M_{n,SEC}$ = 2 200 mol^{-1}). The signals between *m/z* values with a characteristic shift of *m/z* 44 are unambiguously due to the PEO chain. These different characterization results confirm that induced deactivation of metalated PEOs with propargyle bromide indeed led to the expected α-undecenyl-ω-acetylene compound. The M_n values calculated by MALDI-TOF MS are in good agreement with the M_n values determined by SEC. The peak at m/z 1756 is attributed to the α-undecenyl-ω-acetylene PEO (153.284 ($CH_2CH(CH_2)_9$) + 44.053n (n = 35) (CH_2CH_2O) + 54.047 (OCH_2CCH) + 6.941 (Li)) (where n is the degree of polymerization).

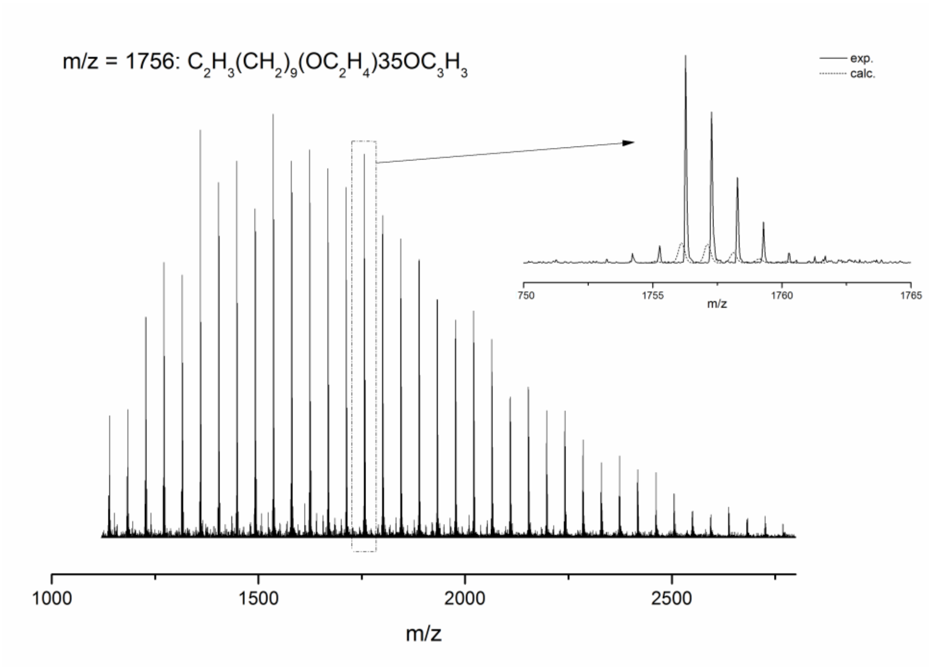
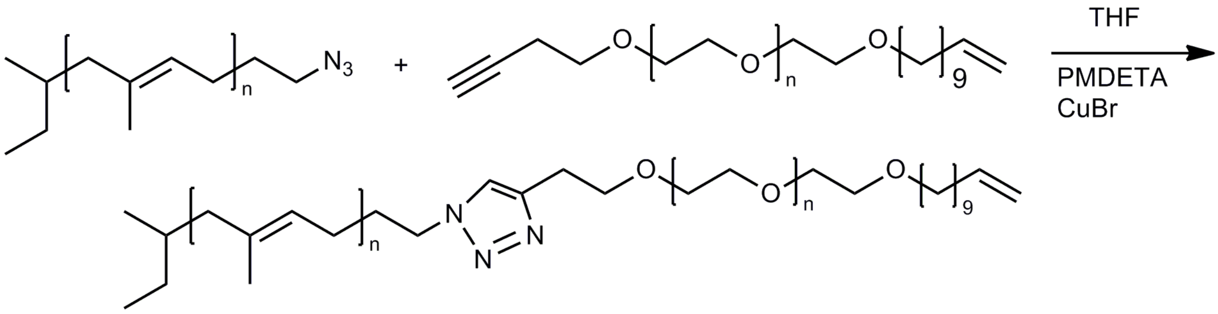


Fig. 11. MALDI-TOF MS of an α-undecenyl-ω-acetylene PEO macromonomer obtained by chain-end modification of an α-undecenyl-ω-hydroxy PEO macromonomer with propargyl bromide in the presence of DPMK (Matrix: dithranol, AgTFA).

Synthesis of PI-b-PEO via click chemistry PI-b-PEO

The click chemistry reaction was performed between ω-azido PI and α-undecenyl-ω-acetylene PEO in the presence of PMDETA and CuBr (Scheme 5).



Scheme 5. Schematic representation of the synthesis of PI-*b*-PEO *via* click reaction between α-undecenyl-ω-acetylene PEOs and ω-azido PIs.

PI-*b*-PEO was characterized by SEC (calibration with linear PEO). The SEC trace of the resulting product shows two peaks, one at a low elution volume corresponding to PI-*b*-PEO ($M_{n,SEC,}$ 13 700 g mol^{-1}) and the second one at a higher elution volume attributed to unreacted PI. This PI-*b*-PEO was purified by preparative SEC using Bio-Beads® in THF. Fraction one was characterized by SEC and a M_n value of 11 000 g mol^{-1} could be obtained (Figure 10). α-Undecenyl-ω-acetylene PEO is not present in the SEC trace of the fractionated PI-*b*-PEO (this PEO has an elution volume of 23.5 mL and in the SEC trace of PI-*b*-PEO no distribution is visible at this elution volume). However, despite of the delicate purifications, ω-azido PIs are also present.

The structure of the PI-*b*-PEO was characterized by ^{1}H and ^{13}C NMR. A peak at 8 ppm appears and corresponds to the proton in the triazol group. The peak characteristic of undecenyl bond is present (5.8 and 5.1 ppm). The peak at 4.3 ppm of $-CH_2-C\equiv CH$ disappeared to confirm the absence of α-undecenyl-ω-acetylene PEO (already show in the SEC trace). At 50 ppm the peak characteristic of CH_2-N_3 disappeared.

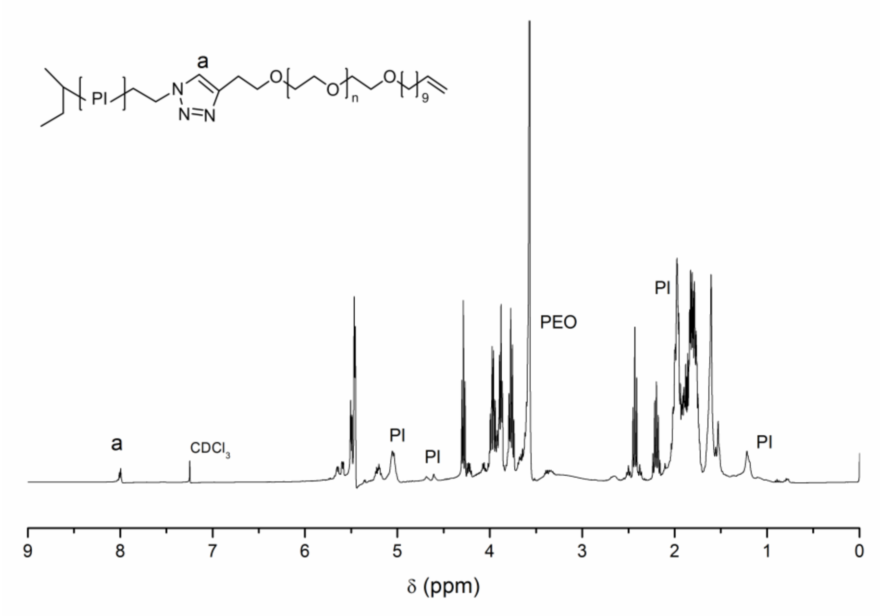


Fig. 12. ^{1}H NMR spectrum of a PI-*b*-PEO obtained by click reaction between α-undecenyl-ω-acetylene PEO and ω-azido PI (400 MHz, $CDCl_3$).

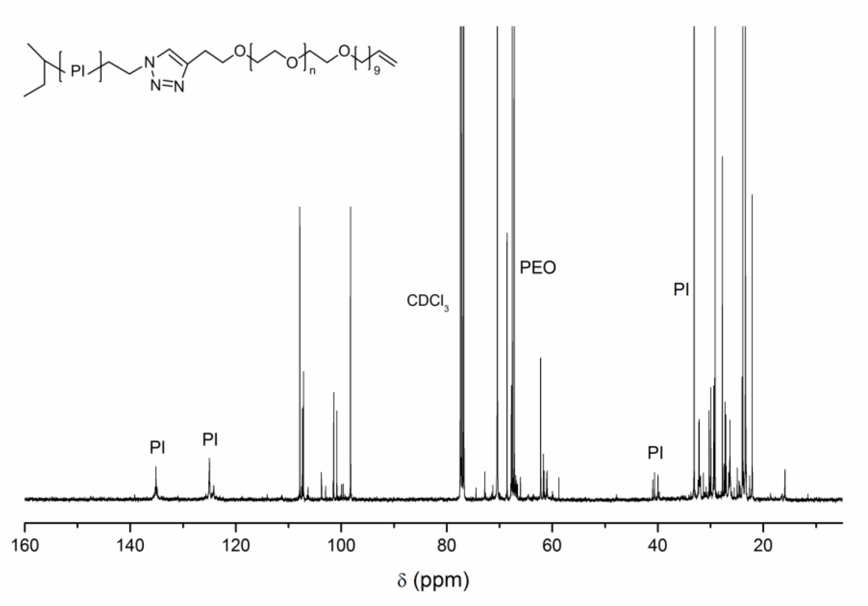


Fig. 13. ^{13}C NMR spectrum of a PI-*b*-PEO obtained by click reaction between α-undecenyl-ω-acetylene PEO and ω-azido PI (400 MHz, $CDCl_3$).

FTIR spectra of PI-N_3, α-undecenyl-ω-acetylene PEOs and PI-*b*-PEO are shown in Figure 14. The peak of N_3 groups (2110 cm^{-1}) and –C≡CH (3260 cm^{-1}) disappeared in the spectrum of PI-*b*-PEO block copolymer. However, at 1778 and 1728 cm^{-1} the peaks corresponding to N=N appeared.

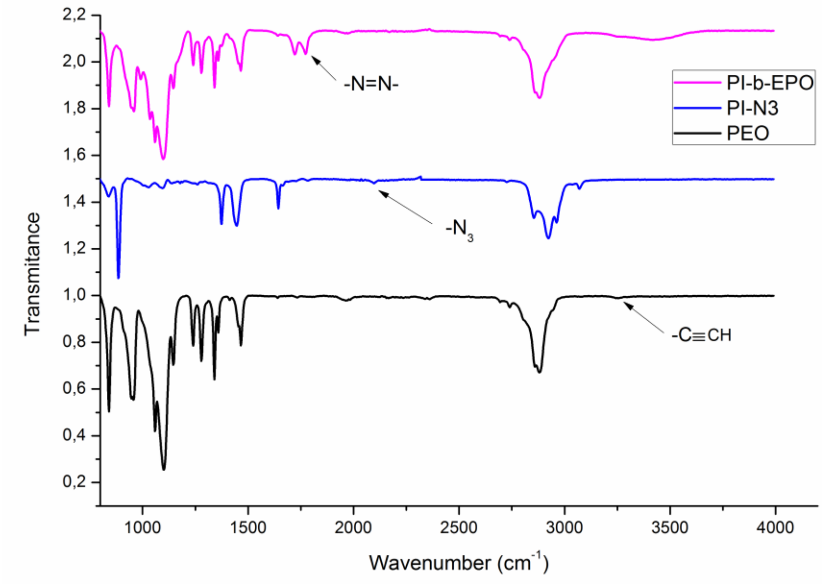


Fig. 14. FTIR spectrum of an ω-azido PI, an α-undecenyl-ω-acetylene PEO and a PI-*b*-PEO.

Conclusions

The aim of the present work was to design functional PI-*b*-PEO block copolymers. Anionic polymerization of isoprene was achieved in the presence of *sec*-BuLi as initiator. After several chain-end modifications, ω-azido functionalized PI was obtained. α-Undecenyl-ω-acetylene PEOs were prepared *via* chain-end modification of α-undecenyl-ω-hydroxy PEOs. ω-Azido PI and α-undecenyl-ω-acetylene PEOs can be react *via* “click reaction” to access PI-*b*-PEO. The originality of these PI-*b*-PEO block copolymers is the presence of undecene groups at the chain-end of PEO block. This double bond can be utilized for subsequent reactions, e.g. for the attachment of dyes, cell penetrating peptides or sugar units enabling interesting applications in life sciences.

Acknowledgements

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Chapter 5

ω-Undecenyl poly(ethylene oxide)s and hybrid star-shaped polymers

Gladys M.-E. Pozza, Sarah Crotty, Michel Rawiso, Ulrich S. Schubert*, Pierre J. Lutz*

"SAXS studies of the molecular and structural parameters of hybrid PEO/POSS star-shaped materials"

Submitted to *J. Phys. Chem. B*

5.1. Summary

Many strategies have been developed to access PEOs or PEO based star-shaped polymers of precise molar mass of the arms and controlled functionality. PEO stars characterized by organic cores of various chemical nature, functionality and structure are now easily accessible. However, only little work has been devoted to inorganic / organic PEO star-shaped polymers. This stimulated us to devote extensive research to the controlled synthesis of PEO / POSS based star-shaped polymers.

A first example of PEO / POSS stars has been discussed in Chapter 2 of the thesis. These PEO / stars could be synthesized by coupling *via* hydrosilylation ω-allyl PEO macromonomers with octafunctional POSS decorated with eight Si-H functions. Well-defined octafunctional PEO / POSS stars could be obtained.

The use of α-methoxy-ω-undecenyl PEOs or of α-undecenyl-ω-hydroxy PEOs as intermediate in the elaboration of such PEO / POSS star-shaped structures would have several advantages. The presence of a hydrophobic spacer between the POSS and the PEO chains may enhance the reactivity. For the α-undecenyl-ω-hydroxy-PEOs the possibility would be opened to decorate the PEO / POSS stars with reactive functions at the outer end of the arms. These functions would be well-suited for subsequent reactions.

The last chapter of the thesis is devoted to the synthesis and the detailed physicochemical characterization of PEO star-shaped polymers with a silsesquioxane core. The first part of the chapter deals with the preparation and the detailed characterization of α-methoxy-ω-undecenyl PEOs *via* deactivation with 11-bromo-1-undecene in the presence of NaH. The resulting functional PEOs were characterized by SEC to verify the absence of coupling products. The functionalization yields are almost quantitative as revealed by ^{1}H NMR. MALDI-ToF MS measurements confirmed the presence of the undecenyl group at the chain-end of the mono or bifunctionalized PEOs.

The second part of the chapter concerns the grafting *via* hydrosilylation of the chain-ends of the α-methoxy-ω-undecenyl PEO macromonomers on the Si-H groups of octafunctionalized silsesquioxanes, $Q_8M_8^H$ in the presence of a platinum catalyst. Grafting experiments were carried out utilizing ω-undecenyl functional PEOs with a M_n of 1800 g/mol. The influence of several experimental parameters such as the temperature, the reaction time and the concentration of the used Karstedt catalyst on the grafting yield was investigated by SEC. Once purified by fractional precipitation, these PEO / POSS star molecules were characterized by light scattering to determine their absolute molar mass. An average functionality of eight could be calculated. The absence of residual Si-H functions was confirmed by IR and ^{1}H NMR. MALDI-ToF MS measurements provided information on the molar mass and the functionality of the $Q_8M_8^{PEO}$. DSC and SAXS measurements were conducted on the same samples. The crystallization of the PEO / POSS stars was investigated by optical microscopy.

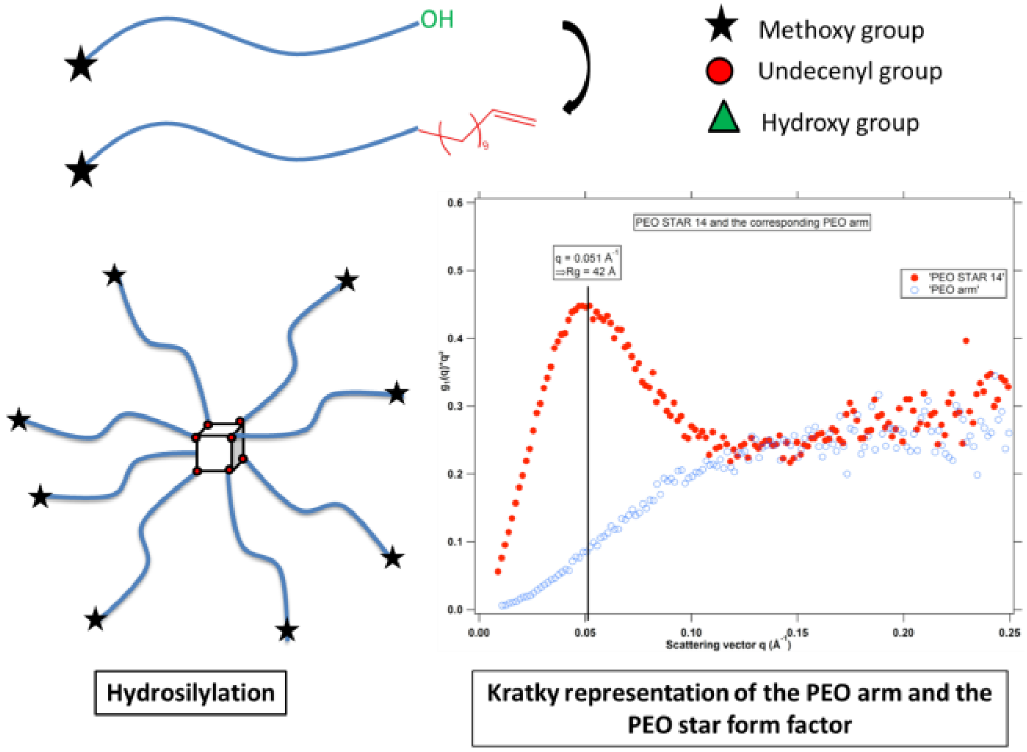

Figure 5.1 Schematical representation of a PEO star-shaped polymer with eight branches.

5.2. Article 4

SAXS Studies of the Molecular and Structural Parameters of Hybrid PEO/POSS Star-shaped Materials

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KEYWORDS Heterofunctional macromonomers; MALDI-ToF MS; poly(ethylene oxide); silsesquioxanes; SAXS

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ABSTRACT

α-Methoxy-ω-undecenyl poly(ethylene oxide) (PEO) macromonomers of precise molar mass and functionality could be prepared by chain-end modification of commercial α-methoxy-ω-hydroxy PEOs with 11-bromo-1-undecene in the presence of sodium hydride. These α-methoxy-ω-undecenyl PEO macromonomers were reacted *via* hydrosilylation with octakis(dimethylsilyloxy)silsesquioxanes ($Q_8M_8^H$) in the presence of Karstedt catalyst. PEO star-shaped polymers ($Q_8M_8^{PEO}$) could be obtained. The molecular and structural characteristics of the $Q_8M_8^{PEO}$ were determined by SEC, ^{1}H, ^{13}C and ^{29}Si NMR, static light scattering, MALDI-ToF MS and small-angle X-ray scattering. The absence of residual Si-H functions was verified by Fourier Transform Infrared. The thermal properties were evaluated by differential scanning calorimetry. The crystallization of PEO precursor and $Q_8M_8^{PEO}$ was shown by microscopy

INTRODUCTION

Poly(ethylene oxide) (PEO) is a water soluble polymer with outstanding properties and is the building block for a large number of macromolecular architectures designed for various applications.[1-3] PEO macromonomers are accessible either *via* anionic ring opening polymerization (AROP) of ethylene oxide in the presence of a heterofunctional unsaturated initiator or by chain-end modification of already existing PEOs.[4-6] Typically ω-allyl PEO or α,ω-diallyl PEO macromonomers are obtained upon reaction of hydroxyl PEOs with allyl-bromide after transformation of the end-standing hydroxyl function into an alcoholate by reaction with a stoichiometric amount of diphenylmethyl potassium (DPMK),[7] sodium hydroxide (NaOH)[8, 9] or sodium.[10] The interest for PEO macromonomers characterized by the presence of a flexible hydrophobic spacer between the terminal double bond and the PEO chain-end can be explained by the increased accessibility of the terminal double bonds. This would, in addition, enhance the amphiphilic character of the end-modified PEO. Preliminary attempts to synthesize ω-undecenyl PEO macromonomers by chain-end modification of existing PEOs based on the DPMK approach[11] failed. An explanation might be the occurrence of side reactions occurring during the metallation process. This stimulated us to search for more efficient ways to design PEO macromonomers, quantitatively fitted at least at one chain-end with undecenyl end-groups. The use of NaH has proven to be efficient for the chain-end functionalization of PEOs.[2, 12]

PEOs or PEO-based star-shaped polymers covering a large range of molar masses and constituted of cores of different chemical nature and functionalities are accessible with a range of approaches.[13] PEOs stars are of great interest as surface-modifying agents to improve the biocompatibility of surfaces designed for biomedical applications[13-15] or as building block for the synthesis of functional PEO hydrogels.[16]

Living anionic polymerization of ethylene oxide has been used for the preparation of a series of 4-arm, 8-arm, and 16-arm PEO stars starting from carbosilane dendrimers after appropriate modification of the hydroxy functions into alcoholate.[17] Eight-arm PEO stars can be also obtained *via* AROP of ethylene oxide in the presence of other octahydroxylated precursors.[18] Multiarm PEO-star polymers,[19] with a purely aliphatic polyether structure have been synthesized in a direct 'grafting from' polymerization of ethylene oxide using hyperbranched polyglycerol with different molar masses as a multifunctional initiator. The PEO arms were characterized by MALDI-ToF MS and the measurements confirmed that the arms of the star-shaped polymers possess homogeneous lengths.

Another possibility to access multiarm PEO stars based on the "arm-first" method was developed by S. Hou *et al.* The authors prepared six arm PEO stars with 6 pyridyl or 12 hydroxyl end-groups.[20] The synthesis of dendrimer-like polymers is based on the combination of the AROP of ethylene oxide with three alcoholate functions as initiator and by branching reactions of PEO chain-ends that were repeated several times.[21]

Only a few examples of hybrid materials based on PEO and Polyhedral Oligomeric Silesquioxanes (POSS) have been presented and discussed in the literature. POSS are three dimensional nanometer-sized species and represent interesting reactive building block for the elaboration of organic-inorganic materials including hybrid macromolecular architectures.[22-28] The different ways, by copolymerization or grafting, to incorporate these POSS structures in polymers and the properties of the resulting hybrid materials have been discussed recently by S.-W. Kuo *et al.*.[26]

PEOs based on POSS may represent new water-soluble materials characterized by enhanced thermal and thermomechanical stability, mechanical toughness or optical transparency.[11, 29] A few years ago monosubstituted cube-shaped spherosilsesquioxanes with amphiphilic properties, combining the relatively hydrophobic spherosilsesquioxane core with hydrophilic PEO segments[30] could be prepared.

In this contribution, we discuss first the synthesis and the characterization of a series of heterofunctional α-methoxy-ω-undecenyl PEO macromonomers, decorated with undecenyl end-groups by chain-end modification of commercial α-methoxy-ω-hydroxy PEOs with 11-bromo-1-undecene in the presence of NaH. The second section will focus on the coupling of the α-methoxy-ω-undecenyl PEOs with octafunctional silsesquioxanes $Q_8M_8^H$ *via* hydrosilylation to yield star-shaped PEOs. The PEO star-shaped polymers will be investigated in detail by different physico-chemical characterization methods.

EXPERIMENTAL SECTION

Solvents, monomers, initiators, deactivating agents.

Toluene (Aldrich) was purified by conventional methods and kept under argon atmosphere. Dichloromethane (Aldrich), tetrahydrofurane (THF) (Carbo Erba) and diethyl ether (Carbo Erba) were used as received. 11-Bromo-1-undecene (Aldrich, 95%) was purified by distillation over CaH_2 under reduced pressure and kept under argon atmosphere. Sodium hydride (NaH) (Aldrich, 95%) was used as received and stored in the glove box. 1-Naphthyl isocyanate (Aldrich, 98%), 1,4-diazabicyclo[2.2.2]octan (DABCO) (Aldrich, 98%) and 1-undecene (Aldrich, 97%) were used without purification. The platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane Pt(dvs) catalyst (Aldrich) (Karstedt catalyst)[31] was used either as so (0.05 M in poly(dimethylsiloxane), vinyl terminate) or diluted to 5×10^{-4} M or 2×10^{-3} M solution with anhydrous toluene. Octakis(dimethylsilyloxy)silsesquioxane ($Q_8M_8^H$) (Aldrich) was utilized without further purification. Commercial PEOs were received as a gift from Clariant (molar masses of 1000, 1700, 4700 and 10900 g mol^{-1} for the α-methoxy-ω-hydroxy and 6000 g mol^{-1} for the α,ω-dihydroxy PEO). The functionalization and hydrosilylation reactions were conducted in classical glass vessels under a slight argon pressure.

Characterization techniques.

Number average molar mass (M_n), weight average molar mass (M_w) and the polydispersity index (PDI) value of the different PEO samples were determined by SEC at RT on a Shimadzu SIL-20A system controller with a LC-20AD pump, a RID-10A refractive index detector and a Shimadzu SPD 10 Avp UV detector. THF with a flow rate of 1 mL min^{-1} was used as solvent. Calibration was made with PEO standards from Polymer Laboratories with molar masses from 194 to 22800 g mol^{-1}).

The static light scattering (SLS) measurements were carried out with a red He-Ne laser with a wavelength of $\lambda_0 = 632.8$ nm, a discrete-angle goniometer acting within the range from 20°

to 155°, a Hamamatsu type photomultiplier as the detector, a photo-counting device and a toluene matching bath. [32]

To determine the absolute molar mass of a polymer by static light scattering, the exact value of dn/dc is a prerequisite an essential parameter. The dn/dc of α-methoxy-ω-undecenyl PEO in methanol solutions was measured by using a Wyatt Optilab Rex refractometer at a wavelength of 670 nm. Dn/dc of α-methoxy-ω-undecenyl PEO solution in methanol is equal to 0.150 mL g^{-1} at 25 °C.

Nuclear magnetic resonance (NMR) spectroscopy: Solution ^{1}H NMR, ^{13}C NMR and ^{29}Si NMR spectra were recorded on a Bruker DRX 400 MHz in deuterated chloroform ($CDCl_3$).

Fourier Transform Infrared (FTIR) Spectroscopy was performed in the Attenuated Total Reflection Mode (ATR-FTIR) using a Vertex 70 spectrometer (Bruker, Germany) equipped with a DTGS detector and a single reflection diamond ATR accessory (A225/Q Platinum ATR, Bruker, Germany). Reference (air) and sample spectra were taken by collecting 20 interferograms between 500 and 3000 cm^{-1} using a Blackman-Harris three-term apodization and the standard Bruker OPUS/IR software (version 5.0).

Matrix-assisted laser desorption/ionization time-of-flight m*ass* spectrometry (MALDI-ToF MS): For the measurement of the matrix-assisted laser desorption/ionization (MALDI) spectra, an Ultraflex III TOF/TOF instrument (Bruker Daltonics, Bremen, Germany) was used. The instrument was calibrated prior to each measurement with polymethyl methacrylate (PMMA) as the external standard (PSS, Polymer Standards Service GmbH, Mainz, Germany). Samples were mixed with either 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB), or 2,5-dihydroxybenzoic acid (DHB) as matrix and the doping agent NaI (dried droplet method).

UV-visible spectroscopy was achieved on a VARIAN CARY 500 SCAN SPECTROPHOTOMETER with ethanol as solvent. Low concentrations of PEO were chosen

(7×10^{-2} to 2×10^{-1} g L^{-1}) to ensure the validity of the Beer's law. The optical path-length of the cell was 1 cm. A calibration curve was established using 1-naphthyl carbamate with an absorption-maximum (λ max) observed at 291 nm and an extinction coefficient of 7060 mol^{-1} cm^{-1}.

Small-Angle X-ray Scattering (SAXS) experiments were performed with a diffractometer developed by Molecular Metrology (Elexience in France) that uses a Rigaku Micromax 007HF generator with a copper-rotating anode. The wavelength of the incident X-ray beam is $\lambda = 0.154$ nm. This diffractometer operates with a pinhole collimation of the X-ray beam focused by a multilayer optic designed by Osmic and a two-dimensional gas-filled multiwire detector. The sample-detector distance was set at $D = 0.7$ m, leading to a range of scattering vectors covered by the experiment $0.001 < q < 0.032$ nm^{-1}. The scattering vector q is defined by $q = (4\pi/\lambda) \times \sin(\theta/2)$, where λ is the wavelength of the incident beam and θ, the scattering angle. Cells of 1 mm thickness and calibrated Mica windows were used as sample holders. Measurements were performed at room temperature.

A Perkin Elmer Diamond Differential Scanning Calorimetry (DSC) using stainless steel capsules under nitrogen atmosphere was used to determine thermal transitions. All the samples were dried under vacuum overnight before measurement. To remove any previous thermal history, all samples were heated up to 100 °C with a fast heating rate of 20 °C min^{-1} and held for 1 min, and then quenched to 0 or –60 °C. A heating rate of 10 °C min^{-1} was used in the both first cases then a heating rate of 5 °C min^{-1}.

The microscopy pictures were taken with a crossed polarized optical microscopy (Leica DMR-X microscope).

Synthesis of ω-undecenyl PEO macromonomers by deactivation with 11-bromo-1-undecene in the presence of NaH.

The commercial α-methoxy-ω-hydroxy PEO ($M_{n,SEC}$ = 1700 g mol^{-1}, 10 g, 5.88 mmol) was heated at 110 °C and NaH (0.71 g, 29.41 mmol,) ([PEO]/[NaH] = 1/5 or 1/10) was added. After 20 min, 11-bromo-1-undecene (4 eq, 5.16 mL, 23 mmol) was introduced and the reaction was kept at 110 °C for 24 h. The PEO solution was then passed through alumina columns in dichloromethane (8 g / 10 mL). After evaporation of dichloromethane and addition of THF, the PEO was precipitated in diethyl ether and filtered. The functionalized PEOs were characterized by SEC, ^{1}H NMR and MALDI-ToF MS. The same experimental procedure was used for the synthesis of the α,ω-diundecenyl PEOs. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.8 (m, 1H, $-CH{=}CH_2$), 5.1 (m, 2H, $-CH{=}CH_2$), 3.6-3.8 (m, 4H*n, $-O-CH_2-CH_2-$), 3.3 (s, 3H, $-O-CH_3$), 2.0 (m, 2H, $-CH_2-CH{=}CH_2$), 1.5 (m, 2H, $-CH_2-(CH_2)_7-CH_2-CH{=}CH_2$), 1.1-1.3 (m, 2H*7, $-CH_2-(CH_2)_7-CH_2-CH{=}CH_2$).

PEO star-shaped polymer ($Q_8M_8^{PEO}$).

Several conditions experimental conditions were tested for the grafting reactions. The Karstedt catalyst (0.05 M) was used either as so or diluted to 5 × 10^{-4} M or 2 × 10^{-3} M solution in anhydrous toluene. The reaction was conducted either at 40 or 80 °C for reaction times of 2 or 24 h, under air or inert atmosphere.

56.5 mg of $Q_8M_8^H$ (0.05 mmol) and 1 g of an α-methoxy-ω-undecenyl PEO macromonomer ($M_{n,SEC}$ = 1800 g mol^{-1}, 0.55 mmol) were dissolved in 0.7 mL of toluene (1 g for a total volume of 2.2 mL). 0.5 mL of a 5 × 10^{-4} M Karstedt catalyst solution in toluene was added under atmosphere. The reaction mixture was kept at 40 °C for 2 h (see star 1 in Table 2). If not specified 1 g PEO was used. The reaction was repeated under argon first with 0.5 mL (star 3) and then 1 mL (star 4) of a 5 × 10^{-4} M Karstedt catalyst solution. The influence of the concentration of catalyst was further investigated. 1 drop of the Karstedt catalyst (0.05 M) in 1 mL of polymer solution in toluene was used in the reaction 2 (star 2). Then a 2 × 10^{-3} M Karstedt catalyst solution in toluene was used (0.15 mL) with 1 mL of polymer solution in toluene (star 5) and the reaction time was increased to 24 h (star 6). This reaction was also made at a lower polymer concentration (1g for a total volume of 6.3 mL) (star 7 and 8) with 0.3 mL of a 2×10^{-3} M Karstedt catalyst toluene solution at 40 °C. The reaction was made at higher temperatures 80 °C (1 g for a total volume of 6.15 mL) (star 9 at 12) with 0.15 mL of a 2×10^{-3} M Karstedt catalyst toluene solution.

At the end of the reaction, undecene (same quantity that PEO mol number) was added to react with the Si-H functions of $Q_8M_8^H$ (star 10 at 12). This addition prevents the coupling between two Si-H functions. All the reaction products were treated as follows. They were precipitated directly in diethyl ether, filtered, dried under vacuum to constant weight and characterized. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.6-3.8 (m, 4H*n, $-O-CH_2-CH_2-$), 3.3 (s, 3H, $-O-CH_3$), 2.1 (m, 2H, $-CH_2-CH_2-CH_2-Si-$), 1.5 (m, 2H, $-CH_2-(CH_2)_7-CH_2-CH_2-CH_2-Si-$), 1.1-1.3 (m, 2H*7, $-CH_2-(CH_2)_7-CH_2-CH_2-CH_2-Si-$), 0.5 (m, 2H, $-Si(CH_3)_2-CH_2-$), 0 (t, 6H, $-Si(CH_3)_2-$). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 70.2-70.4 ($-O-CH_2-CH_2-$), 58.7 ($-O-CH_3$), 25.8-29.3-33.2 ($-(CH_2)_7-$), 22.7 ($-Si(CH_3)_2-CH_2-CH_2-$), 17.4 ($-Si(CH_3)_2-CH_2-$), 0.6 ($-Si(CH_3)_2-$).–). ^{29}Si NMR ($CDCl_3$, 400 MHz): δ 12.55 (PEO-*Si*-), -108 (*Si*-O_4). IFTIR spectrum (ATR, cm^{-1}): 2880 (υ C–H), 1467 (δ CH_2), 1100 (υ C–O).

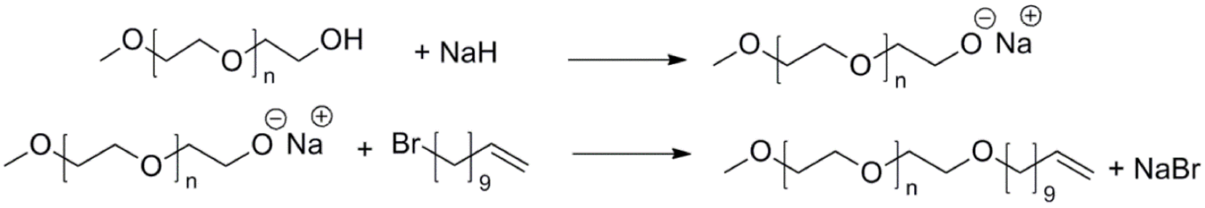
Fractionation of PEO star-shaped polymers.

Fractional precipitation was carried out in a tempered water circulating bath. The raw reaction product was dissolved in toluene in a conventional pear-like vessel (example 0.95 g in 60 mL of toluene at T = 25 °C). Cyclohexane was added drop by drop from a burette until the medium becomes turbid. At that point the turbid solution is heated until the turbidity had vanished. The temperature is decreased to 25 °C, and the solution was kept at that temperature during 24 hours. The lower phase should contain the $Q_8H_8^{PEO}$ and the upper one the unreacted macromonomer. The fractions were recovered and analyzed by SEC to investigate the efficiency of the fractionation and grafting process.

RESULTS AND DISCUSSIONS

Synthesis of ω-undecenyl PEO macromonomers by deactivation with 11-bromo-1-undecene in the presence of NaH.

As described in the experimental section, a series of ω-undecenyl PEO macromonomers were prepared by chain-end modification of commercial α-methoxy-ω-hydroxy PEOs ($M_{n,SEC}$ = 1000-1700-4600-10900 g mol^{-1}) or α-hydro-ω-hydroxy PEOs ($M_{n,SEC}$ = 6000 g mol^{-1}) with 11-bromo-1-undecene in the presence of NaH (Scheme 1).[2] The molecular characteristics of the precursor samples and of the resulting PEO macromonomers, determined by SEC and ^{1}H NMR, are collected in Table 1. A typical SEC diagram is also presented in Figure S5 (link to Supporting Information section).



Scheme 1. Schematical representation of the synthesis of an ω-undecenyl PEO macromonomer by deactivation with 11-bromo-1-undecene in the presence of NaH

Table 1. Molecular characteristics of the ω-undecenyl PEO macromonomers obtained by deactivation with 11-bromo-1-undecene in the presence of NaH

Sample	M_n [a)] (g mol^{-1}) SEC	M_n [b)] (g mol^{-1}) SEC	M_w [c)] (g mol^{-1}) SEC	M_n [d)] (g mol^{-1}) MALDI	PDI [e)]	*f* [f)] (%) ^{1}H NMR
PEO1	1000	1200	1300	1300	1.04	100
PEO2	1700	1800	1900	2100	1.05	100
PEO3	1700	1800	1900	2000	1.05	95
PEO4*	1700	1800	1900	2000	1.05	100
PEO5*	1700	1800	1900	-	1.05	95
PEO6*	4600	5100	5500	5100	1.08	90
PEO7*	4600	5000	5300	-	1.06	99
PEO8	10900	7600	10400	10400	1.36	89
PEO9 (di OH)	6000	6500	7100	6500	1.09	100

[a)] Number average molar mass of the precursor PEOs, measured by SEC in THF, calibration with linear PEOs;

[b)] Number average molar mass of the ω-undecenyl PEOs, measured by SEC in THF, calibration with linear PEOs;

[c)] Weight average molar mass of the ω-undecenyl PEOs, measured by SEC in THF, calibration with linear PEOs;

[d)] Number average molar mass M_n of the ω-undecenyl PEOs, measured by MALDI-ToF MS;

[e)] PDI of the ω-undecenyl PEOs (M_w /M_n) determined by SEC;

[f)] Yield of functionalization of the ω-undecenyl PEOs, measured by ^{1}H NMR (400 MHz) in $CDCl_3$.

*PEO/NaH = 1/5

From SEC it can be concluded that the sample is almost free of precursor polymer. The small shift in the elution volume reflects the addition of the undecenyl end-group. To confirm the absence of a degradation of the PEO chain during the functionalization process at 110 °C, we kept an α-methoxy-ω-hydroxy PEO at this temperature for 24 h. The sample was characterized by SEC and MALDI-ToF MS. The SEC curve is identical to that of the same

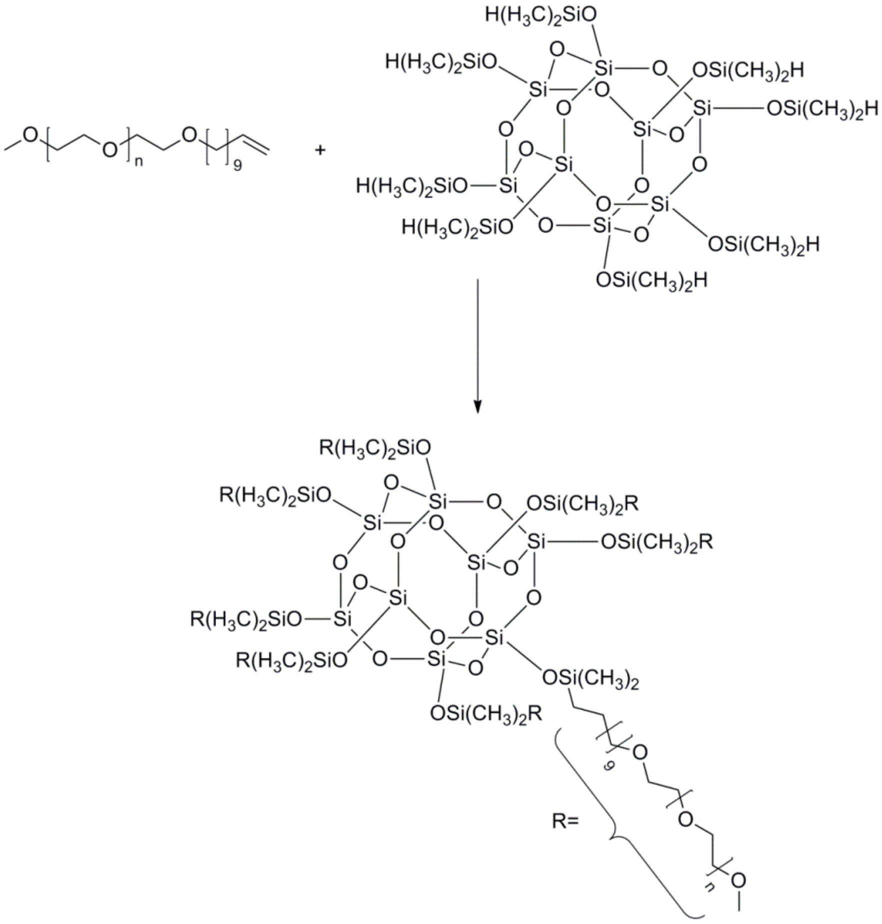
PEO before heating. Hence, no degradation occurs during the chain-end modification of PEOs with 11-bromo-1-undecene in the presence of NaH. Moreover, also the MALDI-ToF MS spectrum remains unchanged. ^{1}H NMR spectroscopy (Figure S6) was also used for end-group titration and to calculate the functionality of the different reaction products. In addition to the peaks characteristic for the precursor PEO, new peaks corresponding to the CH_2=CH– protons appear (CH_2=CH–: δ = 5.1 ppm, CH_2=C*H*–: δ = 5.8 ppm). The average functionality of the PEO macromonomers was determined by integrating the signals of the ^{1}H NMR spectra, i.e. the peaks at 5.1 ppm (double bond) and the peak at 3.3 ppm (CH_3O–) of the PEO chain. The different values are provided in Table 1. In most cases, the functionalization yield is close to 100% independent of the molar mass of the precursor PEO. The M_n values obtained by SEC and determined by ^{1}H NMR are in good agreement. The presence of the undecenyl entity at the chain-end was confirmed by MALDI-ToF MS (Figure S7). As expected, the molar mass of the ω-undecenyl PEO is higher compared to that of the precursor PEO. A difference of m/z of 152 could be noted, which confirms the presence of the undecenyl group and the almost quantitative functionalization of the PEOs. For the bifunctional PEO, a difference of m/z of 304 is observed. For the MALDI-ToF MS in Figure S7, a "minor" distribution is visible. The distribution corresponds to the "protonated" but neither to the "sodiated" ω-undecenyl PEO, nor the unfunctionalized PEOs.

To determine the detection limit of α-methoxy-ω-hydroxy PEOs by MALDI-ToF MS, 5, 10, 20 or 30 wt % of an α-methoxy-ω-hydroxy PEO were added to a selected α-methoxy-ω-undecenyl PEO ($M_{n,SEC}$ = of 1800 g mol^{-1}). The presence of the α-methoxy-ω-hydroxy PEO in all contaminated samples could be confirmed by the clearly detected second distribution. Two typical MALDI-ToF MS spectra of the samples (M_n = 1800 g mol^{-1}) containing 5 and 20 wt % of α-methoxy-ω-hydroxy PEO are presented in Figure S8. To determine the amount of contamination by ^{1}H NMR, we used the ratio of the integrals for the peak at 5.1 ppm (double bond) and the peak at 3.3 ppm (CH_3). These measurements attested the presence of α-methoxy-ω-hydroxy PEO for the samples contaminated with 10, 20 and 30 wt %. This is not the case for the 5 wt % sample. As a result, contaminations less than 10 wt % are not detectable by ^{1}H NMR spectroscopy. In conclusion, the chain-end modification of α-methoxy-ω-hydroxy PEOs or α-hydro-ω-hydroxy PEOs with 11-bromo-1-undecene in the presence of NaH represents a simple and efficient approach to decorate almost quantitatively PEOs with undecenyl end-groups. The reaction can be conducted in the absence of solvent. No degradation of the PEO chain takes places during the functionalization process as demonstrated by SEC and MALDI-ToF MS

PEO star-shaped polymers prepared with ω-undecenyl PEO macromonomers ($Q_8M_8^{PEO}$).

Branched PEOs such as comb-shaped polymers,[33] star-shaped polymers,[13, 34] hyperbranched polymers,[35] and dendrimers[13] have attracted much attention in the past thirty years since they constitute interesting species for physicochemical studies and can serve as building blocks for materials designed for many applications. A precise control of the functionality and the arm-length constitutes in most cases a prerequisite. In addition, the higher the functionality of the star-shaped polymers the better the solubility in water provided the molar masses of the water-soluble PEO branches are sufficiently high. This can be explained by the protecting effect exerted in water by the PEO chains. Recently we[11] and others[10] prepared PEO stars containing a central core by coupling *via* hydrosilylation of ω-allyl PEOs with $Q_8M_8^H$ in the presence of a hydrosilylation catalyst. The products $Q_8M_8^{PEO}$ could be characterized after purification by fractional precipitation as well-defined octafunctional PEO stars.

We propose in this contribution the use of ω-undecenyl PEO macromonomers. The undecenyl group should facilitate the accessibility of the double bond for subsequent applications. The reaction between these ω-undecenyl PEO macromonomers and $Q_8M_8^H$ is described in Scheme 2. The reaction products were systematically characterized by independent methods: SEC, ^{1}H, ^{13}C and ^{29}Si NMR, Infrared spectroscopy, MALDI-ToF MS and SAXS. SEC with RI detection was used to evaluate the amount of PEO grafted onto the octafunctionalized silsesquioxane core. It has to be established whether or not all the ω-undecenyl PEO chains have reacted with the antagonist functions of the octafunctionalized silsesquioxane core. The results are presented in the Table 2.



Scheme 2. Schematical representation of the synthesis of a $Q_8M_8^{PEO}$ star by coupling *via* hydrosilylation monofunctional α-methoxy-ω-undecenyl PEO macromonomers with $Q_8M_8^{H}$ in the presence of a Karstedt catalyst

Table 2. Molecular characteristics of the PEO star-shaped polymers obtained by grafting *via* hydrosilylation of ω-undecenyl PEOs onto $Q_8M_8^H$

Sample	PEO (g)	Time (h)	Temp. (°C)	Toluene (mL)	Catalyst (5 × 10^{-4} M) (mL)	M_na) (g mol^{-1}) SEC	M_nb) (g mol^{-1}) SEC	PDIc)	% star SEC
Star1	1	2	40	0.7	0.5	14300	16100	1.12	33
Star2	1	2	40	1	1 drop	1900	2000	1.05	0
Star3	1	2	40	0.7	0.5	10800	13500	1.25	13
Star4	1	2	40	0.7	1	11600	13600	1.17	20
Star5	1	2	40	1	0.15*	14300	21100	1.48	50
Star6	1	24	40	1	0.15*	10700	12200	1.14	54
Star7	1	2	40	5	0.3*	10080	11700	1.16	65
Star8	1	2	40	5	0.3*	14300	16200	1.13	52
Star9	1	24	80	5	0.15*	12700	13600	1.07	83
Star10	1	24	80	5	0.15*	11300	12100	1.06	83
Star11	1.4	24	80	7	0.2*	11700	12500	1.07	83
Star12	1.7	24	80	9	0.25*	11700	12700	1.08	83

* Catalyst at 2 × 10^{-3} M

Number average molar mass of the ω-undecenyl PEO precursor measured by SEC in THF, calibration with linear PEOs: $M_n = 1800$ g mol^{-1}

Number average molar mass of the PEO stars calculated taking into account the molar mass of the branch, the core and assuming a functionality of 8: 15417 g mol^{-1}

a) Weight average molar mass of the PEO stars, measured by SEC, calibration with linear PEOs.

b) Number average molar mass of the PEO stars, measured by SEC, calibration with linear PEOs.

c) PDI of the PEO stars (M_W/M_n) determined by SEC in THF.

For the hydrosilylation reaction (star 1) carried out in the presence of oxygen, the SEC trace of the resulting product shows two well separated peaks (Figure 1), one at low volume elution corresponding to the $Q_8M_8^{PEO}$ and second at higher volume elution attributed to unreacted macromonomer introduced. 30 wt % of $Q_8M_8^{PEO}$ were obtained.

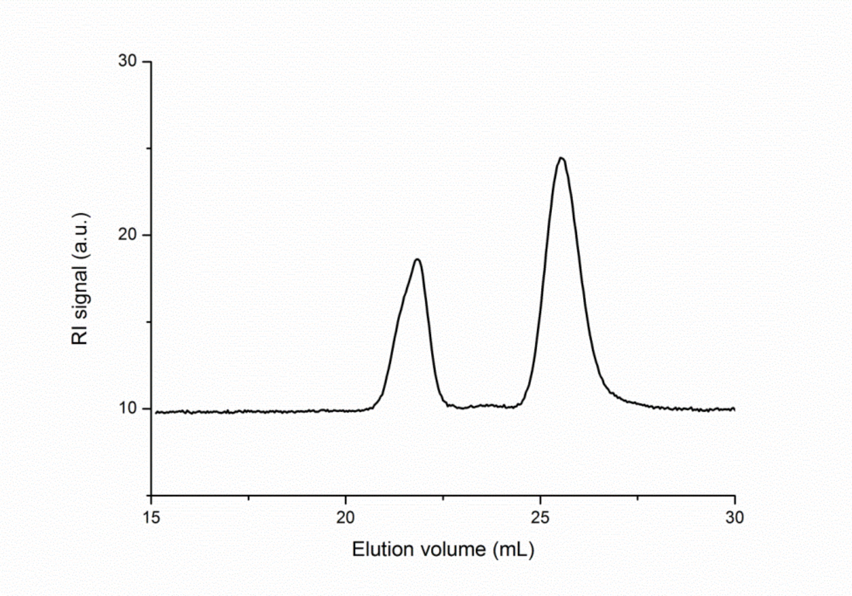


Figure 1. Typical SEC trace of $Q_8M_8^{PEO}$ ($M_{n,SEC,Macro} = 1800$ g mol^{-1}).

One drop of pure Karstedt catalyst (0.05 M) was added into a solution of ω-undecenyl PEO in 1 mL of toluene as discussed in the experimental part (40 °C for 2 h). The SEC trace of the resulting reaction product is characterized by the presence of only one peak which can be easily attributed to the unreacted PEO macromonomer (see in the Table 2, star 2). We tested also a diluted solution of the Karstedt catalyst (0.5 mL or 1 mL at 5×10^{-4} M). The SEC result confirmed the presence of two peaks corresponding, respectively, to the unreacted macromonomer and to the star-shaped PEO. 30 wt % of $Q_8M_8^{PEO}$ were obtained (star 3 and 4). If one increases the catalyst concentration from 5×10^{-4} M to 2×10^{-3} M (0.15 mL) even better results are obtained. In this case 50 wt % of $Q_8M_8^{PEO}$ were obtained (star 5). However, increasing the reaction time for the same catalyst concentration does not yield to high grafting yields (star 6). We decided then to increase the reaction temperature from 40 to 80 °C. Under these conditions (1 g PEO in 5 mL of toluene, 0.15 mL of a solution of the Karstedt catalyst

(2×10^{-3} M)) we obtained far better results, around 80 wt % of $Q_8M_8^{PEO}$ (star 9 at 12). The reaction was repeated several times and the results are approximately the same.

Several methods can be used to remove undesired compounds from raw polymers.

Dialysis is known as a possible separation method in water by selective and passive diffusion through a semi-permeable membrane. This technique has been used successfully to remove unreacted PEO in star-shaped PEOs.[34] D. R. Yen *et al.*[36] isolated pure star-shaped PEOs in aqueous solution of sodium carbonate, F. Cansell *et al.*[37] used supercritical fluids for the fractionation of PEOs. S. Trimpin *et al.*[38] utilized liquid adsorption chromatography at critical conditions combined with a MALDI-ToF MS characterization to achieve fractionation of mixtures of low molar mass PEOs (functionalized or not).

However for $Q_8M_8^{PEO}$, the fractional precipitation is the best method to isolate the star-shaped product in a very effective way.[11] For this purpose toluene as solvent and cyclohexane as precipitant were utilized. The SEC curve shows (Figure 2) the successful isolation of the star-shaped PEOs. One peak is visible and the elution volume peak corresponding to a maximum of 22.5 mL can be attributed to a M_n of 11700 g mol^{-1}.

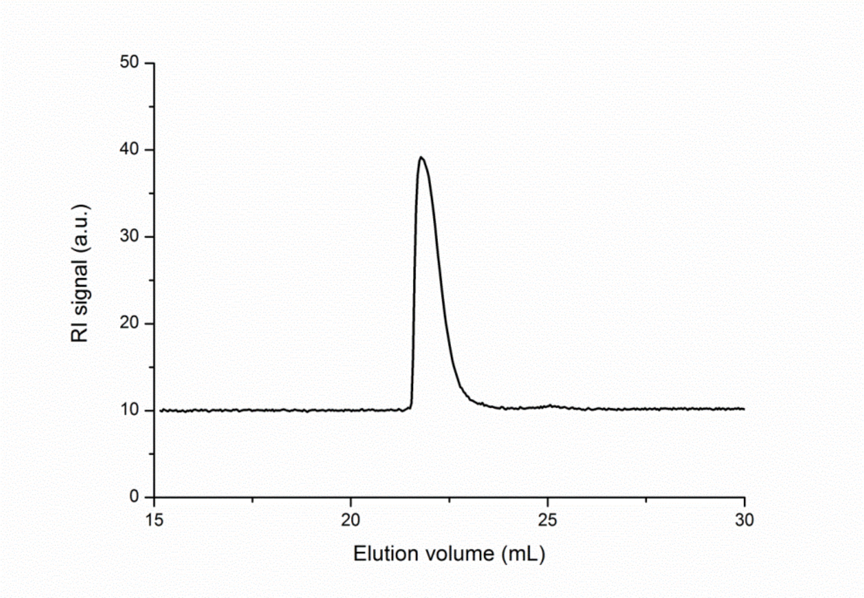


Figure 2. Typical SEC trace of fractionated $Q_8M_8^{PEO}$ ($M_{n,SEC,Macro}$ = 1800 g mol^{-1}).

However, by SEC based on calibration with linear PEO the apparent molar mass values is underestimated, in fact, star-shaped PEOs are known to exhibit a more compact structure in solution than the linear equivalent of the same molar mass. The determination of the absolute molar mass of $Q_8M_8^{PEO}$ by classical light-scattering (LS) in methanol revealed to be much more efficient. Star 10 was characterized by LS in methanol.[39-41] A typical LS diagram of a star-shaped PEO sample constituted of PEO chains ($M_{n,\ SEC}$ = 1800 g mol^{-1}) is presented in Figure S9. From these measurements a M_w value of 17000 g mol^{-1} was obtained. From the ratio of the latter molar mass to the molar mass of the branch determined by SEC, an average functionality of 9.71 could be estimated. A functionality value of 8.5 is obtained from the ratio of the $M_{w,LS}$ of $Q_8M_8^{PEO}$ to the M_n of the branch determined by MALDI-ToF MS ($M_{n,MALDI\text{-}ToF\ MS}$ = 2000 g mol^{-1}). This value is in close agreement with the theoretical value taking into account the limits of characterization techniques.

The efficiency of the grafting of the ω-undecenyl PEOs on the silsesquioxane cores was also verified by ^{1}H NMR. The methyl group signals of $Q_8M_8^H$ appear at 0.23 ppm, and Si-H proton signals appear at 4.7 ppm. In the spectrum of the pure $Q_8M_8^{PEO}$ (Figure 3), the methyl proton signals are slightly shifted to low ppm values, the characteristic peaks of the double bond of the ω-undecenyl PEO macromonomer (at 5.7 and 4.9 ppm) disappeared. The peak at 4.7 ppm belonging to the Si-H function of the cage is absent. However a new peak at 0.5 ppm appeared confirming the formation of the bond between the cage and the PEO chain. The signals at 1.5 and 1.2 ppm characteristic of the 9 CH_2 entities are present which confirms the grafting onto the cage. The new peak at 0.84 ppm corresponds to the protons of CH_3 of the undecene molecule grafted to the residual Si-H functions. ^{1}H NMR was also used to determine the number of PEO chains attached to $Q_8M_8^H$. A functionality of 7.2 could be calculated by considering the ratio between the integrals of the peak of the methyl group at 0.09 ppm ($-Si(\mathit{CH_3})_2$) (on the core) and the methylene group at 0.56 ppm ($-Si-\mathit{CH_2}-CH_2$) (originating from the ω-undecenyl PEO) (star 11).

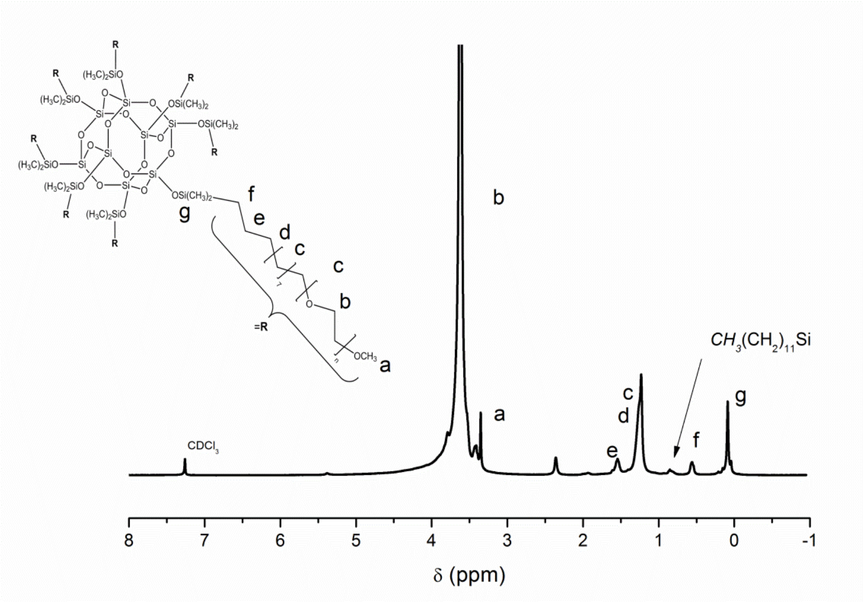


Figure 3. ^{1}H NMR spectrum of $Q_8M_8^{PEO}$ (400 MHz, $CDCl_3$).

The ^{13}C NMR measurement shows the absence of the characteristic peaks for the double bond of the ω-undecenyl PEO. In the Figure S10, the carbon peaks of the double bond of ω-undecenyl PEO have disappeared (at 138.8 and 113.9 ppm). The peak at 0.6 ppm represents the methyl carbon of Si-CH_3 and the appearance of two carbon signals at 17.4 and 22.7 ppm in alpha and beta of Si respectively due at the unsaturated carbons of the undecenyl group on the silsesquioxane core.

The ^{13}Si NMR allows the detection of the peak of Si groups. In Figure 4, at –1.42 ppm the peak characteristic of the *Si*-H and at –108 ppm the *Si*-O_4 group of the POSS are observed. On the spectrum of the $Q_8M_8^{PEO}$, the peak at –1.42 ppm is shifted to 12.55 ppm and corresponds to the bond between Si and PEO. The presence at 108 ppm of the *Si*-O_4 group confirms that the POSS core is not affected by the reaction. No signals characteristic of side products were detected.

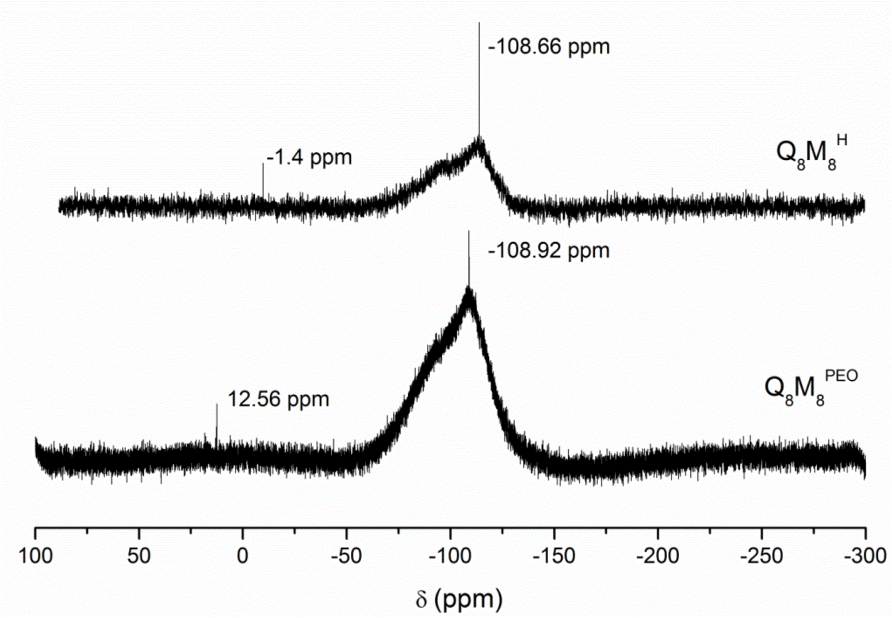


Figure 4. ^{29}Si NMR spectrum of $Q_8M_8^H$ and $Q_8M_8^{PEO}$ (400 MHz, $CDCl_3$).

The intense peak characteristics of the Si–H bond of $Q_8M_8^H$ is not present on the FTIR spectrum of $Q_8M_8^{PEO}$ (Figure 5). However, the characteristic peaks of PEO can be observed in the spectrum. The $Q_8M_8^H$ is completely surrounded by PEO chains. This is partially due to the shielding of PEO and POSS represents only 6 wt % in weight in the star-shaped PEO.

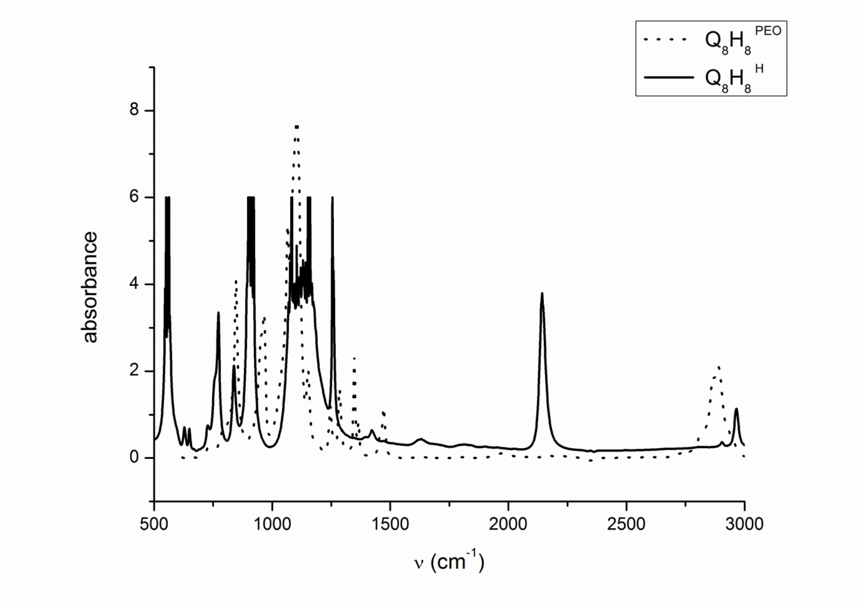


Figure 5. FTIR spectrum: (a) $Q_8M_8^H$ (b) $Q_8M_8^{PEO}$.

An investigation by MALDI-ToF MS was performed on the pure star 12 (Figure 6). These MALDI-ToF MS measurements corroborate the results obtained by SEC and ^{1}H NMR. The sample is characterized by the presence of three peaks: A first one (peak A) present at *m/z* value of 2234 and a second peak (peak B_1) at *m/z* value of 15974 (with one shoulder at 14040 (peak B_2)) and a last distribution, C at 7773. This latter is the doubly charged species of the singly charged PEO (m/z 15974). In MALDI-ToF MS mostly singly charged species are observed making the spectra much easier to analyze; however, doubly charged species are observed too and have been reported earlier.

In the MALDI-ToF MS spectrum, the distribution of chains corresponding to the PEO are visible. The peak A corresponds to a calculated value 153.284 ($(CH_2)_9CHCH_2$) + 44.053 n (n = 46) (CH_2CH_2O) + 31.034 (CH_3O) + 22.990 (Na) (where n is the degree of polymerization) and can be assigned to the PEO macromonomer. A peak-to-peak mass increment of 44 corresponding to the molar mass of one ethylene oxide unit can be observed. However, the SEC and NMR measurements show the absence of PEO precursor. We assume that due to the difficult ionization of the $Q_8M_8^{PEO}$ a high laser intensity must be used, resulting in a fragmentation of the star molecule. However, it is unclear whether the seven-armed PEO (peak B_2), which was detected by MALDI-ToF MS, has been formed during the synthesis or results from a cleavage of the $Q_8M_8^{PEO}$ PEO under the MALDI conditions.

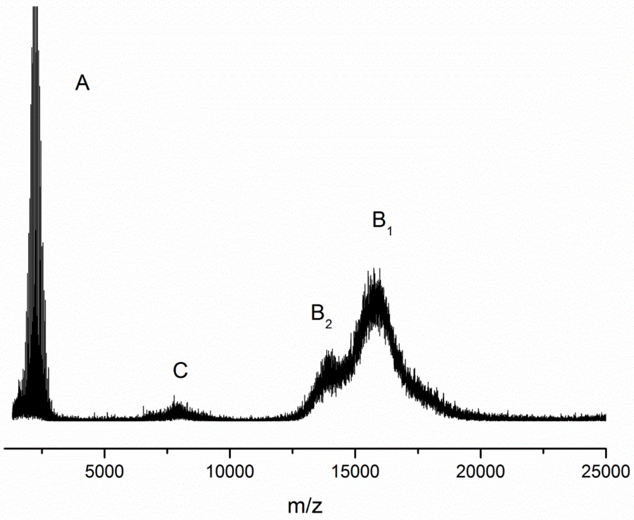


Figure 6. MALDI-ToF MS of $Q_8M_8^{PEO}$ (Matrix: DCTB, NaI).

SAXS measurements are used in reference[42] to obtain information about the structure of polystyrene stars as well as PMMA dendritic branched polymers. Specifically, they yield the average size and shape, or the internal structure, of these macromolecules. SAXS measurements also allowed to study the average structure of the styrene-butadiene-styrene triblock copolymers modified with POSS.[43] Here, we present their use for characterizing the average conformation of the prepared PEO star-branched macromolecules.

Data were treated according to a standard procedure for isotropic SAXS. After radial averaging, spectra were corrected from the electronic noise of the detector, empty cell, absorption and sample thickness. A ^{55}Ir source was used for the corrections of geometrical factors and detector cells efficiency. A Silver Behenate sample allowed the q-calibration and the normalization to the unit incident flux was obtained using Lupolen as standard sample. Finally, the scattered intensities were corrected from the scattering of the solvent. According to such a procedure, a scattered intensity per unit volume I(q) (cm^{-1}) containing all the structural information is obtained for each polymer solution in methanol. Actually, I(q) is the sum of an intramolecular term and an intermolecular one.[44-46]

$$I(q) = K^2 c \mathcal{N} [g_1(q) + c g_2(q)] \quad (1)$$

K (cm) is the contrast length of the ethylene oxide monomers with respect to the solvent; K^2 (cm^2), the contrast factor; c (mol cm^{-3}), the concentration of the polymer solution; $\mathcal{N}$, Avogadro's number (mol^{-1}). $g_1(q)$ is the form factor; $g_2(q)$, the intermolecular correlation function.

The scattered intensities measured from several solutions of distinct concentrations (as $c = 2.043 \times 10^{-4}$, 4.086×10^{-4} and 6.129×10^{-4} mol cm^{-3} for the PEO stars $Q_8M_8^{PEO}$), in the dilute regime ($c < c^*$; c^* being the critical overlap concentration of the macromolecules), allow separating out the intra- and intermolecular terms. Specifically, as suggested by Eq. (1), the extrapolation to c = 0 of $I(q)/K^2c\mathcal{N}$ yields the form factor $g_1(q) = NP(q)$. N is the degree of polymerization of macromolecules, P(q) their form factor normalized in such a way as P(0) = 1. Accounting for polydispersity, it is actually the weight average of the form factor, $<g_1(q)>_w$ that is determined.

$$<g_1(q)>_w = N_w<P(q)>_z \quad (2)$$

Where N_w is the weight average of the polymerization degree; $<P(q)>_z$, the z-average of the form factor P(q).

At small q values, in the Guinier range $qR_g < 1$ where R_g is the radius of gyration of the macromolecules, a series expansion of the form factor leads to:

$$1/g_1(q) = (1/N_w) [1 + q^2<R_g^2>_z/3 + o(q2)] \quad (3)$$

The form factors of both the PEO stars $Q_8M_8^{PEO}$ and the PEO linear macromolecules corresponding to their arms are shown in Figure 7. The form factor of PEO arms is characteristic of that of a linear polymer.[44-46] At small q values, we observe a plateau and its height corresponds to the average degree of polymerization $N_w = 38$. Beyond the Guinier range, the form factor can be described by a scaling law ($g_1(q) \propto q^{-1.55}$) close to the one characterizing the internal structure of a linear macromolecule in a good solvent ($g_1(q) \propto q^{-1.7}$). In contrast, the form factor of PEO stars displays two successive scaling laws beyond the Guinier range. This scattering behavior is characteristic of a star-branched polymer. At high q-values the form factor is superimposed to that of PEO arms, displaying a similar scaling law. In the intermediate q-range, it is described by another scaling law ($g_1(q) \propto q^{-3.02}$) with an exponent that is close to the double of the one of the scaling law observed at high q-values. The crossover in between these scaling laws occurs at $q = 1/\xi(R)$, where $\xi(R)$ is the size of the largest blob in the Daoud-Cotton model of star-branched macromolecules of geometric radius R. [45, 47-51] With the relationship $\xi(R) = Rf^{1/2}$, we obtain R = 1.2 nm since the number of arms of PEO stars is f = 8. In the Guinier range, we observe a plateau which leads to $N_w = 450$.

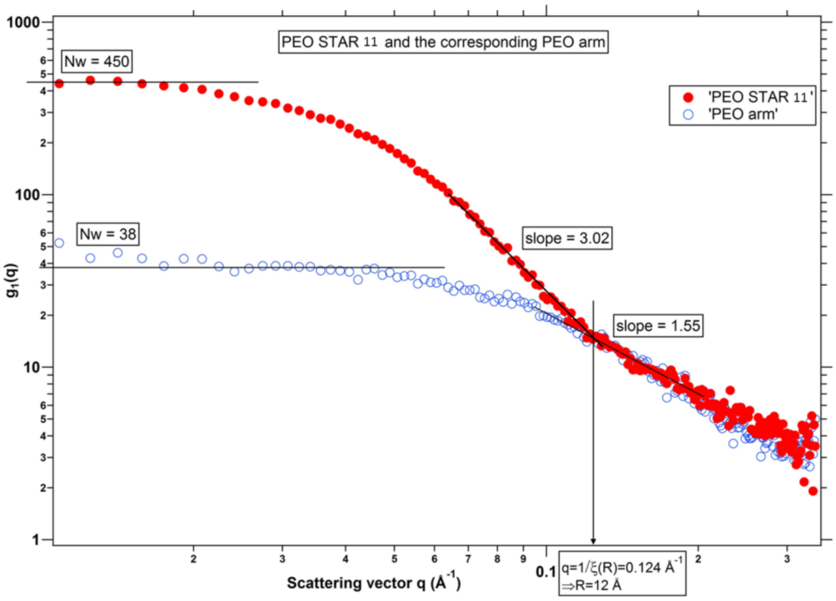


Figure 7. Form factors of PEO arms (ω-undecenyl PEO) and related PEO stars (star 11) in methanol.

The polymerization degrees and radii of gyration of both PEO arms and PEO stars were also determined by fitting the form factors to the Debye function $g_D(q)$ and the Benoît function $g_B(q)$, respectively, in the q-range $qR_g < 3$. These fits are shown in Figure 8. They provide N = 42.8 and R_g = 1.71 nm for PEO arms; N = 489.3 and R_g = 3.78 nm for PEO stars.

The Debye function, which describes the form factor of a Gaussian chain of radius of gyration R_g, is:

$$g_D(q) = (2N/x^2)\,[x - 1 + \exp(-x)] \qquad (4)$$

Where N is the degree of polymerization and $x = q^2R_g^2$.

The Benoît function, which describes the form factor of a Gaussian star-branched polymer of radius of gyration R_g, is:

$$g_B(q) = (2N/x^2)\,[(f/2)(f-1)\exp(-2x/f) - f(f-2)\exp(-x/f) + x + (f/2)(f-3)] \qquad (5)$$

N and f are the degree of polymerization and the number of arms of the star, respectively; $x = (q^2R_g^2)[f^2/(3f-2)]$ this time.

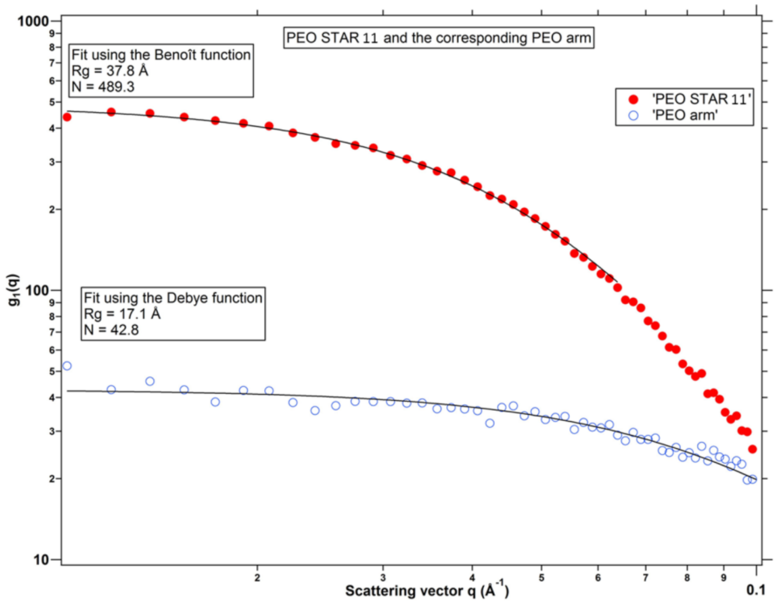


Figure 8. Fits of the PEO arm and star form factors to the Debye and Benoît functions, respectively.

Similar results were obtained using the Zimm representation of the data ($1/g_1(q)$ versus q^2) and Eq. (3), in the Guinier range $qR_g < 1$.

Finally, the Kratky representation of the PEO arm and star form factors are presented in Figure 9. It emphasizes the increase in the internal density for star-branched polymers with respect to linear ones.[51] In this representation, a maximum thus appears for the PEO star form factor at a q value, which depends on the radius of gyration R_g and the functionality f. With f = 8, it appears at $qR_g = 2.13$.[45] This leads to $R_g = 4.2$ nm, in agreement with the R_g values previously determined for PEO stars using either a fit to the Benoît function in the q-range $qR_g < 3$, or the Zimm representation with Eq. (9) in the Guinier range $qR_g < 1$.

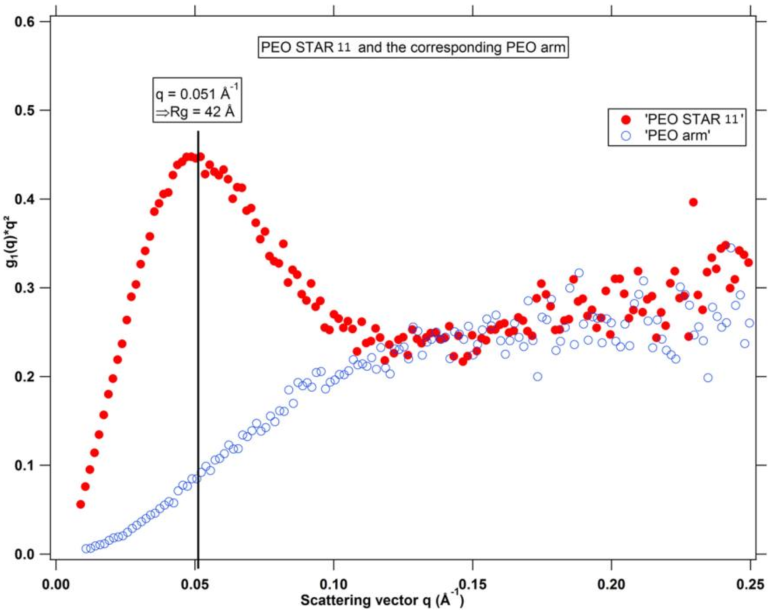


Figure 9. Kratky representation of the PEO arm and PEO star form factor.

The incorporation of the POSS should improve into polymers the thermal stability compared to unmodified PEO polymers.[10] POSS are known for their thermal stability.[25]

We investigated first the thermal properties by DSC. The thermal properties of the ω-allyl and ω-undecenyl-functional PEOs and $Q_8M_8^{PEO}$ were studied by DSC. The crystallization temperatures (T_c) and the melting temperatures (T_m) were taken as the temperatures of the minima and the maxima of both exothermic and endothermic peaks, respectively and the values are noted in the Table 3. Data were gathered on the second heating runs with scan rates of 10 °C min^{-1}. Linear PEOs were characterized by DSC measurements; the T_m values increased with the molar mass. In the literature, the T_m value of 53.8 °C is obtained for the α,ω-dihydroxy PEO (2000 g mol^{-1}) [52] For α-methoxy-ω-hydroxy PEO precursors, the T_m value is 56.3 °C. Compared with ω-allyl PEO, no variations could be observed due at the short chain-end. With ω-undecenyl PEO a second peak during the heating is visible, maybe caused by the hydrophobic part of undecenyl groups of the PEO.

For $Q_8M_8^{PEO}$ (based allyl or undecenyl PEO) a shoulder is present and most probably corresponding to the low crystallization of the $Q_8M_8^{PEO}$. The T_m value of $Q_8M_8^{PEO}$ based allyl PEO is at 56.3 °C and at 54.3 °C for $Q_8M_8^{PEO}$ based undecenyl PEO, compared to ω-allyl PEO (58.5 °C) or ω-undecenyl PEO (55.9 °C).

For the T_c values, the temperature of α-methoxy-ω-hydroxy PEO precursor are 37.6 °C, 34.4 °C for ω-allyl PEO and 27.9 °C for ω-undecenyl PEO, respectively. This difference can be explained by the presence of a flexible spacer between the double bond and the PEO chain. This spacer requires more times to organize during the crystallization. Concerning the star compounds, the spacer has the same effect, the T_c value of allyl $Q_8M_8^{PEO}$ is 28.8 °C and 38.2 °C for undecenyl $Q_8M_8^{PEO}$.

Table 3. Thermal properties of the ω-undecenyl or ω-allyl PEO macromonomers and $Q_8M_8^{PEO}$ prepared with allyl or undecenyl PEO

Sample	T_m (°C)	T_c (°C)
α-methoxy-ω-hydroxy PEO (1700 g mol^{-1})	56.3	35.8
ω-allyl PEO (1800 g mol^{-1})	58.5	34.4
ω-undecenyl PEO (1800 g mol^{-1})	55.9	27.9
$Q_8M_8^{PEO}$ prepared with ω-allyl PEO	56.3	28.8
$Q_8M_8^{PEO}$ prepared with ω-undecenyl PEO	54.3	38.2

The crystallization is observed in crossed polarized optical microscopy. The Figure 10 represents the crystallization of different compounds: ω-Undecenyl PEO and $Q_8M_8^{PEO}$.

Compared to the ω-undecenyl PEO, on the image of the $Q_8M_8^{PEO}$ the existence of spherulites can be observed. The ω-undecenyl PEO to crystallize at 39.8 °C after 4.33 min cooling. For $Q_8M_8^{PEO}$ this value is decreased to 38.5 °C after 4 min. $Q_8M_8^{PEO}$ takes more time to organize in crystals, this difference is caused by the structure of the star and by the presence of $(CH_2)_9$ spacer. The total crystallization of ω-undecenyl PEO is observed after T = 5.4 min at 36 °C and for $Q_8M_8^{PEO}$ after T = 6.2 min at 33 °C.

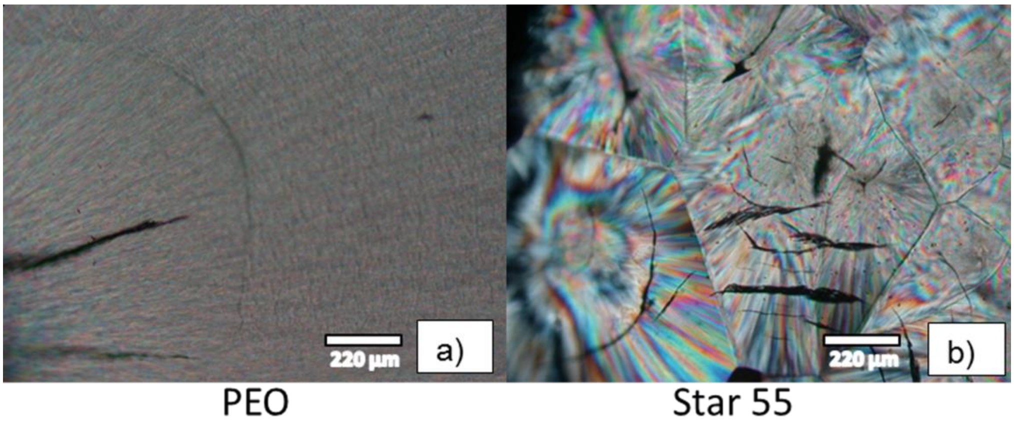


Figure 10. Sequences of micrographs obtained by optical microscopy with polarized light at distinct temperatures, during a scanning melting process. The first crystallization point of ω-undecenyl PEO is observed at 39.8 °C (T = 4.33 min), and total crystallization is observed 36°C (T = 5.4 min) (a). The first crystallization point of $Q_8M_8^{PEO}$ is observed 38.5 °C (T = 4 min), and total crystallization is obtained 33°C (T = 6.2 min) (b).

CONCLUSION

The aim of the present work was to design well-defined monofunctional amphiphilic α-methoxy-ω-undecenyl PEO macromonomers. The chain-end of commercial PEOs was functionalized with 11-bromo-1-undecene in the presence of NaH. These PEOs could be used successfully to design octakis(dimethylsilyloxy)silsesquioxane octafunctional PEO star-shaped *via* hydrosilylation. After fractional precipitation, well-defined star-shaped species were obtained. The molar distribution is unimodal and quite narrow. The molar mass calculated under the assumption of a functionality of 8 is close to the experimental value measured by light scattering in methanol and by MALDI-ToF MS. The star-shaped structure was characterized by ^{1}H, ^{13}C and ^{29}Si NMR and FTIR. Precise measurements concerning the dependence of the crystal structure (SAXS) are presented. The thermal properties of these hybrid PEO stars are also studied using DSC. The star-shaped crystallization was investigated by microscopy.

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General conclusion

Since many years extensive research has been devoted to PEO macromonomers. They represent valuable intermediates in macromolecular engineering, used for the synthesis of macromolecular architectures such as graft copolymers or cross-linked materials, and they can used in a wide range of applications. PEO is a water soluble, uncharged polymer, neutral, non-toxic. The presence of $–CH_2–CH_2–$ groups generates some degree of hydrophobicity allowing PEO to be soluble in some organic solvents. This provides the possibility to perform synthetic reactions, including polymerizations and phase transfer catalysis, in a broad range of polar and non-polar solvents. As PEO is not recognized by the immune system, materials constituted of PEO incorporated in network structures or grafted onto surface are often used in health care applications, for body care (cream, shampoos), building materials, drug delivery as well as tablet binders.

The aim of the thesis was the controlled synthesis and the characterization of complex macromolecular architectures based on PEO: Linear functional PEOs including macromonomers, graft, comb and hybrid star-shaped materials based on PEO.

PEO macromonomers decorated with undecenyl end-goups were prepared *via* living anionic ring-opening polymerization (AROP) of ethylene oxide starting from undecenolate potassium as initiator. Characterizations by SEC, NMR, LS and MALDI-ToF MS of these macromonomers were conducted to determine the structure and the molar masses. Well-defined α-undecenyl-ω-hydroxy PEO macromonomers can be obtained with large variations in molar masses. The presence of a flexible hydrophobic spacer between the terminal double bond and the PEO chain-end may enhance the reactivity and could affect the solubility in water. The solution behavior of these PEO macromonomers was investigated in methanol as well as in water by DLS. The influence of undecenyl group, i.e. the hydrophobic spacer, on their solution behavior was also studied by viscosimetry and CMC measurements.

The interest of this structure, with at one chain-end undecenyl groups and at in other one a hydroxy group, is the possible modification of the hydroxy group to methacryloyl groups providing access to a new class of heterobifunctional PEO macromonomers decorated at the chain-ends with double bonds of different reactivity. We take advantage of the different reactivity between the undecenyl and the methacryloyl group to prepare comb-shaped PEOs via ATRP in water of the α-undecenyl-ω-methacryloyl PEO macromonomers. Comb-shaped PEOs can be obtained with the presence of free undecenyl double bond at the chain-end. The same macromonomers were used to design, *via* “click reaction”, tetrafunctional PEO star-shaped polymers decorated with undecenyl groups at the other end of the branches starting from pentaerythritol tetrakis(3-mercaptopropionate). We demonstrated first that undecenyl double bonds do not react with the pentaerythritol core. The reaction with methacryloyl groups should lead to the formation of a functional 4-arm star-shaped PEO. Characterization by SEC, NMR and MALDI-ToF MS confirms also the structure of these star-shaped PEO. These double bonds are, thus, available for further reactions such as coupling *via* hydrosilylation of Si-H end-functionalized micro or macromolecular species.

Secondly, we take advantage of the hydroxy groups on α-undecenyl-ω-hydroxy PEO to prepare heterobifunctional PEO macromonomers decorated with at one chain-end undecenyl groups and at the other one acetylene groups, α-undecenyl-ω-acetylene PEOs. These PEO macromonomers can serve for the preparation of diblock copolymers such as PI-*b*-PEO. These diblock copolymers are characterized by hydrophilic and hydrophobic blocks, their chains may aggregate in aqueous solution to form spherical, cylindrical or vesicular assemblies. ω-Hydroxy PIs were obtained *via* anionic polymerization. The hydroxy groups were transformed in ω-azido PI. Classical click reaction was performed between α-undecenyl-ω-acetylene PEO and ω-azido PI. The resulting functional PI-*b*-PEOs were characterized by SEC, ^{1}H NMR, infra-red and the MALDI-ToF MS. The first interest of this method is the choice of the M_n values for PI and PEO macromonomers to prepare PI-*b*-PEO diblock copolymers. The possibility to use a short or longer polymer chain is conceivable. Second interest is the presence of undecenyl double bonds on the PEO chain-ends for subsequent reactions.

Another method can be used for the preparation of PEO macromonomers: The deactivation of living chain-ends of commercials hydroxy PEO by an unsaturated compound. This approach was used for the preparation of α-methoxy-ω-allyl or α-methoxy-ω-undecenyl PEO macromonomers starting from α-methoxy-ω-hydroxy PEOs initiated by DMPK or NaH and deactivated with allyl bromide or 1-bromo-11-undecene was performed. Both types of macromonomers permit access to macromolecular architectures at the silsesquioxane core. This architecture was prepared by hydrosilylation of PEO macromonomers on Si-H functions of octafunctionalized silsesquioxanes, $Q_8M_8^H$, in the presence of a catalyst. It is essential to establish the optimal reaction conditions for quantitative grafting. The influence of several experimental parameters such as the temperature, the reaction time and the concentration of Karstedt catalyst on the grafting yield was investigated by SEC. With the optimal reaction conditions established, well-defined star-shaped PEO with eight branches can be obtained, characterized by SEC, NMR, MALDI-ToF MS, infrared, LS and SAXS.

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Publication list

Publication

1. *G. M.-E. Pozza,* H. Harris, M. J. Barthel, J. Vitz, U. S. Schubert, P. J. Lutz

Macromol. Chem. Phys. **2012**, *213*, 2181-21091.
“Macromonomers as well-defined building blocks in the synthesis of hybrid octafunctional star-shaped poly(ethylene oxide)s”

Accepted publication

1. *G. M.-E. Pozza*, M. J. Barthel, S. Crotty, J. Vitz, F. H. Schacher, P. J. Lutz, U. S. Schubert

“Precise synthesis of undecenyl poly(ethylene oxide) macromonomers as heterofunctional building blocks for the synthesis of linear diblocks or of branched materials”, *Eur. Polym. J.*

Submitted publications

1. *G. M.-E. Pozza*, S. Crotty, M. Rawiso, U. S. Schubert, P. J. Lutz

“SAXS studies of the molecular and structural parameters of hybrid PEO/POSS star-shaped materials”, *J. Phys. Chem. B*

Manuscripts in preparation

1. *G. M.-E. Pozza, Jürgen Vitz, Pierre J. Lutz, Ulrich S. Schubert*

“End-group functionalized polyisoprene-*b*-poly(ethylene oxide) prepared by combining anionic polymerization and click chemistry”

2. H. Harris, *G. M.-E. Pozza*, Ouidade L. Ouanaïm, J.-M. Guenet, R. Schweins, U. S. Schubert, P. J. Lutz

“Hybrid polystyrene star-shaped polymers with octafunctional silsesquioxane cores”

Oral presentations

G. M.-E. Pozza, *"Functional poly(ethylene oxide)s"*, High-throughput Experimentation, Review Meeting of the Dutch Polymer Institute (DPI), Arnhem, The Netherlands, 05.11.2013

G. M.-E. Pozza, "*Poly(ethylene oxide): From the origin to usual applications"*, Precision Macromolecular Chemistry group meeting, Institut Charles Sadron, Strasbourg, France, 18.10.2013

G. M.-E. Pozza, "*Water soluble polymers"* High-throughput Experimentation, Review Meeting of the Dutch Polymer Institute (DPI), Schlossgartenstr. 6, D-64289 Darmstadt, Germany, 04.07.2013

G. M.-E. Pozza, "*Matériaux hybrides à base de POE hétérofonctionnels"*, 13ème Journée Scientifique du Groupe Français des Polymères (GFP) Grand-Est, Institut de Science des Matériaux de Mulhouse, Mulhouse, France, 06.06.2013

G. M.-E. Pozza, "*Precise synthesis of undecenyl poly(ethylene oxide)s and hybrid star-shaped polymers"* High-throughput Experimentation, Review Meeting of the Dutch Polymer Institute (DPI), Friedrich-Schiller-Universität, Jena, Germany, 03.12.2012

G. M.-E. Pozza, "*Synthesis and characterizations of poly(ethylene oxide) macromonomers and PEO compounds"*, Precision Macromolecular Chemistry group meeting, Institut Charles Sadron, Strasbourg, France, 19.10.2012

G. M.-E. Pozza, "*New hybrid materials based on poly(ethylene-oxide) macromonomers"*, Precision Macromolecular Chemistry group meeting, Institut Charles Sadron, Strasbourg, France, 15.04.2011

G. M.-E. Pozza, "*New hybrid materials based on PEO macromonomers"*, High-throughput Experimentation, Review Meeting of the Dutch Polymer Institute (DPI), Friedrich-Schiller-Universität, Jena, Germany, 06.12.2010

Poster presentations

G. M.-E. Pozza, L. O. Ouianaïm, U. S. Schubert, P. J. Lutz, “*POSS containing polystyrene star-shaped polymers”,* Annual Seminar of Group Français des Polymères, ENSAIT 2 allée Louise et Victor Champier Roubaix, France, 18-21.11.2013

G. M.-E. Pozza, F. Badique, P. J. Lutz, U. S. Schubert, K. Anselme, “*Poly(ethylene oxide) hydrogels and SaOs-2 cells”*, Summer School “Polymers at interfaces” SoMaS School soft matter research of the Freiburg institute for advanced studies, Mittelwihr, France, 07-12.07.2013

G. M.-E. Pozza, H. Harris, P. J. Lutz, “*ω-Allyl poly(ethylene oxide)s and hybrid star-shaped polymers”*, European Research Council (ERC) Grantees Conference, Conseil de l’Europe, Strasbourg, 22-24.11.2012

G. M-E. Pozza, H. Harris, M. J. Barthel, J. Vitz, P. J. Lutz, U. S. Schubert, “*Poly(ethylene oxide) in Branching Reactions”*, 5ème journée Scientifique du Pôle Matériaux et Nanosciences Alsace (PMNA), Amphithéâtre Forestier de L’Ecole Chimie, Polymères et Matériaux (ECPM), Strasbourg 16.10.2012

G. M-E. Pozza, H. Harris, M. J. Barthel, J. Vitz, P. J. Lutz, U. S. Schubert, “*Poly(ethylene oxide) in branching reactions”*, Summer School “Self-assembly” SoMaS School soft matter research of the Freiburg institute for advanced studies, Mittelwihr, France, 08-13.07.2012

G. M-E. Pozza, M. Bennoui, A. Condé, P. J. Lutz, U. S. Schubert, “*Polystyrene macromonomers in branching reactions”*, Summer School “Concepts for the design” SoMaS School soft matter research of the Freiburg institute for advanced studies, Mittelwihr, France 10-12.07.2011

Declaration of authorship

I certify that the work present here is, to be best of my knowledge and belief, original and the result of my own investigations, except as acknowledged, and has not been submitted, either in part or whole, for a degree at this or any other university.

Strasbourg, 15.07.2014

Pozza Gladys

Annexes

Annex 1: Supporting information of article 1

ω-Allyl poly(ethylene oxide)s and hybrid star-shaped polymers

Macromol. Chem. Phys. **2013**, *20*, 2181-2191

Supporting Information

Macromonomers as Well-defined Building Blocks in the Synthesis of Hybrid Octafunctional Star-Shaped Poly(ethylene oxide)s

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Materials and Methods

1. Solvents, monomer initiators, deactivating agents

Cyclohexane, tetrahydrofuran (THF) and toluene and were made free of protonic impurities by conventional methods and kept under argon atmosphere. Allyl bromide and 11-bromo-1-undecene were purchased from Aldrich, distilled over CaH_2 before use and kept under argon atmosphere. Octa(hydridodimethylsiloxy) octasilsesquioxane $(HMe_2SiOSiO_{1.5})_8$, $(Q_8M_8^H)$[1] (Aldrich) was used without further purification. α-Methoxy-ω-hydroxy PEOs were received as a gift from Clariant. Diphenylmethyl potassium (DPMK) and diphenylmethyl sodium (DPMNa) were synthesized according to well-established procedures.[2] DPMK was titrated according to the acetanilide method before use. The "Speier" catalyst[3] $(H_2PtCl_6{\cdot}6H_2O)$ (Aldrich) was used in isopropanol at a 13.6 wt.-% of Pt. Ethylene oxide (EO) (Linde, Aldrich) was degassed, distilled over sodium wire and stored in graduated ampoules. The functionalization reactions were conducted under inert atmosphere in an airtight reactor with argon inlet, magnetic stirrer, and temperature control and connected to ampoules containing the solvent and the different reagents. For the synthesis of the PEOs via anionic polymerization of EO a Büchi Glas Uster reactor was used. The hydrosilylation reactions were performed in Schlenk tubes under argon.

2. Synthesis of ω-allyl PEOs

The commercial PEOs were dissolved in dry dimethylsulfoxide (DMSO) (or THF / DMSO) (10 wt.-%) filtered, precipitated in diethyl ether (500 mL diethylether for 50 mL THF) and dried. Just before use, they were again dried under vacuum over 24 h and dissolved in dry and oxygen free THF (around 5 g PEO (5 000 g mol^{-1}) for 50 mL THF, 10^{-3} moles). The hydroxyl functions of the α-methoxy-ω-hydroxy PEO, were transformed into alcoholates by addition of a stoichiometric amount of DPMK (around 2 mL, DMPK concentration 5×10^{-3} moles of potassium per 1 mL) at room temperature (RT), (stoichiometry determined by colorimetry). In the next step, allyl bromide (0.140 g mL^{-1} (1.1 × 10^{-3} moles)), 10% molar excess with respect to stoichiometry) was added to the PEO solution. The slight yellow coloration disappeared rapidly. The reaction medium was kept at RT overnight. The resulting polymer solutions were centrifuged, filtered, precipitated twice from their THF solution into diethyl ether and characterized by SEC, MALDI-TOF MS and ^{1}H NMR.

3. Synthesis of ω-undecenyl PEO macromonomers by deactivation

To modify the PEO chain-ends with undecene or allyl groups, similar experimental conditions were used. In some cases, the reaction was conducted at different temperatures for the purpose of comparison. This is discussed in detail in the main text. It has to be mentioned that the recovery and the treatment of the ω-undecenyl PEO macromonomers is much more difficult, resulting in purification problems. This can be explained by their enhanced amphiphilic character of the ω-undecenyl PEO macromonomer. The different functionalization products were characterized by SEC, MALDI-TOF MS and ^{1}H NMR.

4. Synthesis of octafunctional star-shaped poly(ethylene oxide)s ($Q_8M_8^{PEO}$) from ω-allyl PEOs

Typical conditions are given in the following procedure: 50 mg of $Q_8M_8^H$ (0.049 mmol) and 876 mg of an ω-allyl PEO (M_n = 1 900 g mol^{-1}) (0.451 mmol) were dissolved in 2.5 mL of dry toluene under an argon atmosphere. The mixture was heated to 75 °C and 2 µL of a 13.6 wt.-% solution of the $H_2PtCl_6 \cdot 6H_2O$ catalyst in isopropanol was added. The mixture was stirred for 15 h at 75 °C. The toluene was removed by evaporation and the resulting product was dissolved in DMSO (15 mL), precipitated in diethyl ether (100 mL), filtered, and dried under vacuum. Finally, the product was characterized by SEC, MALDI-TOF MS, IR and ^{1}H NMR.

5. Isolation of the PEO stars from the raw reaction product

5.1. Dialysis:

To achieve that aim we dissolved the raw reaction product in de-ionized water at a weight concentration of 1 or 2 wt.-%. This solution was introduced into a dialysis membrane of regenerated cellulose characterized by pores of controlled size (with a molar mass cut-off at 3 500 g mol^{-1}). This membrane was placed in a great excess of de-ionized water (on the opposite side of the membrane) for several days. PEO star-shaped molecules that are larger than the pores of the membrane-pores are retained on the "raw sample" side of the membrane, but the ω-allyl PEOs should pass freely through the membrane, reducing the amount of PEO in the raw reaction product. After 3 or 4 days the water was replaced. This operation was repeated several times until no more ω-allyl PEO could be detected in the water solution. The main product, kept behind the membrane, was concentrated, recovered by precipitation and characterized by SEC (See comments main text).

5. 2. Fractional precipitation

Fractional precipitation was carried out for several PEO samples. Typically, a 1-2 wt.-% toluene solution of the raw PEO sample was kept in a thermostat at a constant temperature of 25 °C. Cyclohexane was slowly added from a burette until the solution had become turbid. Thereafter the temperature was increased until the turbidity had vanished (around 45 °C). The solution was cooled again to the initial temperature (25 °C). The coacervate was allowed to settle overnight. The same operation was repeated several times. Fractionation yields were close to quantitative. The different fractions were characterized by SEC, MALDI-TOF MS, IR, ^{1}H NMR and by static light-scattering (LS) for selected samples.

6. Characterizations

6.1. Size exclusion chromatography (SEC)

The different soluble PEOs were characterized by SEC to determine their molar masses and to ascertain the absence of coupling during deactivation. For the "star-shaped PEOs", SEC was also used to determine the extent of coupling reactions. Number average molar mass (M_n), weight average molar mass (M_w) and polydispersity index (PDI) were determined by SEC at RT on a Waters apparatus fitted with five PL gel columns, an auto sampler Waters WISP 717, a differential refractometer Shimadzu RID 6A, a UV spectrometer Beckman 147 ($\lambda = 254$ nm) and a multi-angle laser light scattering detector Wyatt DAWN DSP (laser: $\lambda = 632.8$ nm). The measurements were conducted in THF at a flow rate of 1 mL min^{-1}. The system was calibrated with monodisperse PEO standards (dn/dc = 0.066 mL g^{-1}, in THF). That technique provides access to the concentration of the different polymeric species and the real molar mass of the macromonomer precursor and of the star-shaped polymer in one experiment. Light scattering experiments were also carried on the star-shaped PEOs dissolved in methanol with a modified FICA instrument. The dn/dc of the star-shaped PEOs was measured in methanol (dn/dc = 0.141 mL g^{-1}). This value is close to the value measured for the PEO precursor.

6.2. MALDI-TOF MS

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) spectra were obtained using a REFLEX II time-of-flight mass spectrometer (Bruker Daltonics, Bremen, Germany) operated at 20 kV accelerating voltage in reflector mode with positive ionization. α-Cyano-4-hydroxycinnamic acid (HCCA) and Dithranol (DIT), 1,8,9-anthratriol, 1,8,9-trihydroxyanthracene were used as matrixes: NaCl or silver trifluoroacetate, respectively, was added for cationization (solvent: THF). Data were externally calibrated by means of PEO standards.

6.3. ^{1}H NMR

Solution ^{1}H NMR spectra were obtained using a Bruker DRX 400 MHz NMR spectrometer in deuterated chloroform ($CDCl_3$) or deuterated dimethylsulfoxide (DMSO-*d*$_6$). **6.4. Infra Red**

IR spectra were measured on a FTIR Perkin Elmer 1 600 spectrometer or Bomen MB 155 spectrometer (with KBr pellets).

Caption of figures

Figure s.i.1. Typical SEC traces of ω-allyl PEOs, (a) obtained by deactivation of the chain-end with allyl bromide after modification with DPMK, (b) obtained by initiation with DPMK followed by deactivation with allyl bromide.

Figure s.i.2. ^{1}H NMR spectrum of a functional PEO with an allyl chain-end measured in DMSO-d_6.

Figure s.i.3. MALDI-TOF MS of an ω-allyl PEO obtained by deactivation of the chain-end with allyl bromide after modification with DPMK. The spectrum was measured using dithranol as a matrix and sodium trifluoroacetate as cationizing agent.

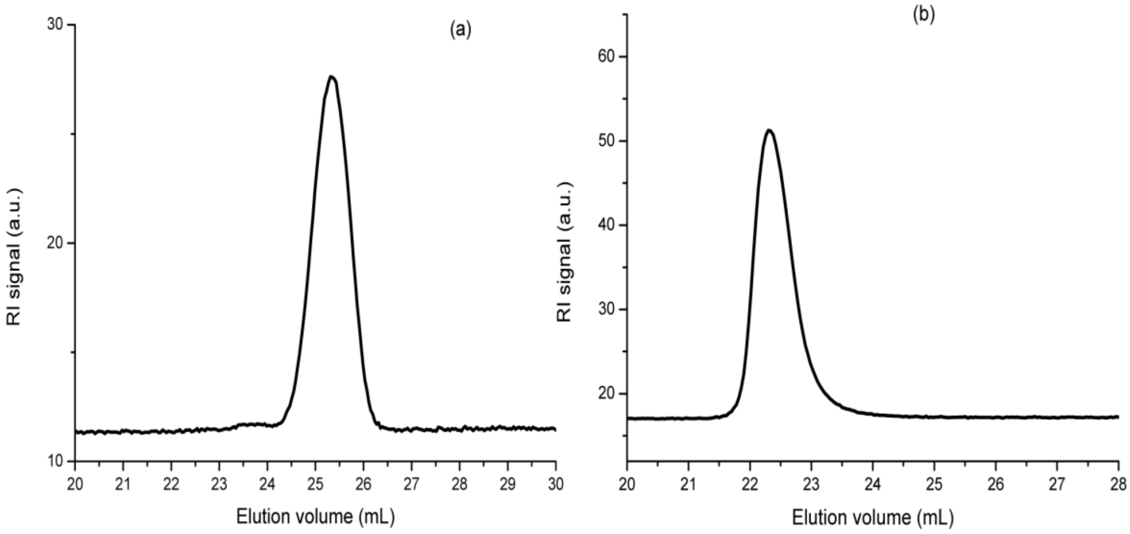

Figure s.i.1. Typical SEC traces of ω-allyl PEOs (a) obtained by deactivation of the chain-end with allyl bromide after modification with DPMK, (b) obtained by initiation with DPMK followed by deactivation with allyl bromide.

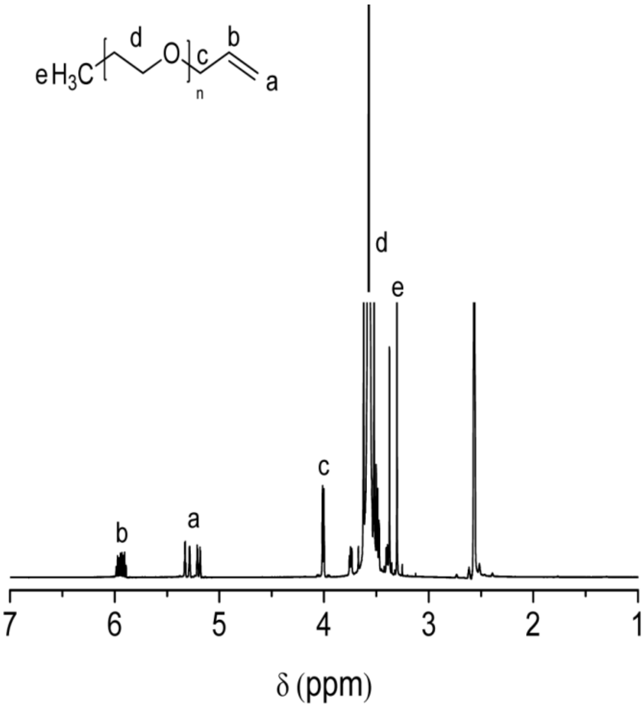

Figure s.i.2. ^{1}H NMR spectrum of an ω-allyl PEO with an allyl chain-end measured (in DMSO-*d*$_6$).

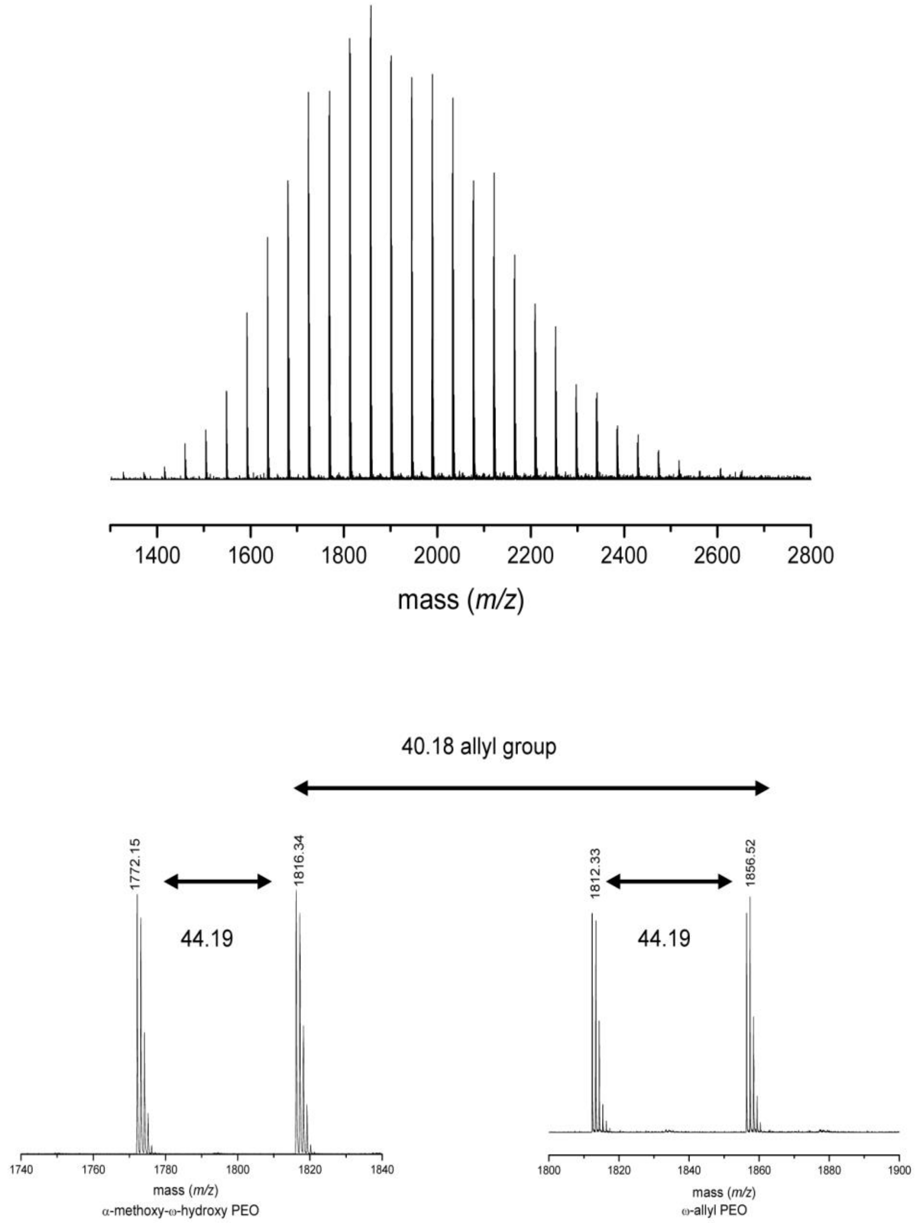

Figure s.i.3. MALDI-TOF MS of an ω-allyl PEO obtained by deactivation of the chain-end with ally bromide after modification with DPMK. The spectrum was measured using dithranol as a matrix and sodium trifluoroacetate as cationizing agent.

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Annex 2: Supporting information of article 2

ω-Undecenyl poly(ethylene oxide)s and potential heterofunctional building blocks

Accepted *Eur. Polym. J.*

Supporting Information

Precise Synthesis of Undecenyl Poly(ethylene oxide) Macromonomers as Heterofunctional Building Blocks for the Synthesis of Linear Diblocks or of Branched Materials

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Caption of Figures

Fig. S1. Typical SEC trace of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation (initiator undecenol/DMPK) ($M_{n,SEC}$ = 1,750 g mol^{-1}).

Fig. S2. ^{1}H NMR spectrum of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation (initiator undecenol/DMPK) (400 MHz, DMSO-d_6).

Fig. S3. ^{1}H NMR spectrum of a powder potassium undecenolate initiator (400 MHz, DMSO-d_6).

Fig. S4. Determination of the hydrodynamic radius by DLS in methanol of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation ($M_{n,SEC}$ = 38,000 g mol^{-1}).

Fig. S5. Determination of the hydrodynamic radius by DLS in methanol of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation ($M_{n,SEC}$ = 2,100 g mol^{-1}).

Fig. S6. Determination of the hydrodynamic radius by DLS in water of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation ($M_{n,SEC}$ = 3,8000 g mol^{-1}).

Fig. S7. Determination of the hydrodynamic radius by DLS in water of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation ($M_{n,SEC}$ = 2,100 g mol^{-1}).

Fig. S8. Typical SEC trace of an α-undecenyl-ω-methacryloyl PEO macromonomer obtained by chain-end modification of an α-undecenyl-ω-hydroxy PEO macromonomer with methacrylic anhydride in the presence of triethylamine ($M_{n,SEC}$ = 3,400 g mol^{-1}).

Fig. S9. ^{1}H NMR spectrum of an α-undecenyl-ω-methacryloyl PEO macromonomer obtained by chain-end modification of an α-undecenyl-ω-hydroxy PEO macromonomer with methacrylic anhydride in the presence of triethylamine (400 MHz, $CDCl_3$).

Fig. S10. MALDI-TOF MS spectrum of an α-undecenyl-ω-methacryloyl PEO obtained by chain-end modification of an α-undecenyl-ω-hydroxy PEO macromonomer with methacrylic anhydride in the presence of triethylamine ($M_{n,SEC}$ = 3,300 g mol^{-1}) (Matrix: DCTB, NaI).

Fig. S11. ^{1}H NMR spectrum of an ω-azido PI 400 MHz, $CDCl_3$).

Fig. S12. ^{13}C NMR spectrum of an ω-azido PI (400 MHz, $CDCl_3$).

Fig. S13. ^{1}H NMR spectrum of an α-undecenyl-ω-acetylene PEO macromonomer (400 MHz, $CDCl_3$).

Fig. S14. MALDI-TOF MS spectrum of an α-undecenyl-ω-acetylene PEO macromonomer (Matrix: dithranol, AgTFA).

Fig. S15. ^{13}C NMR spectrum of a PI-*b*-PEO (400 MHz, $CDCl_3$).

Fig. S16. Typical SEC trace of the raw reaction product obtained by FRP of sample PEOMA5 in toluene (50 °C, 24 hours).

Fig. S17. Typical SEC trace of the raw reaction product obtained by FRP of sample PEOMA5 in THF (50 °C, 6 hours).

Fig. S18. Typical SEC trace of the raw reaction product obtained by ATRP of sample PEOMA6 in water (60 °C, 24 hours).

Fig. S19. Typical SEC trace of fractionated product obtained by ATRP of sample PEOMA6 in water (60 °C, 24 hours).

Fig. S20. ^{1}H NMR spectrum of 4 arm PEO star molecules obtained via thiol-ene click reaction of α-undecenyl-ω-methacryloyl PEO macromonomer with pentaerythritol tetrakis(3-mercaptopropionate) (400 MHz, $CDCl_3$).

Fig. S21. MALDI-TOF MS spectrum of 4 arm PEO star molecules obtained via thiol-ene click reaction of α-undecenyl-ω-methacryloyl PEO macromonomer with pentaerythritol tetrakis(3-mercaptopropionate) (Matrix: DCTB, NaI).

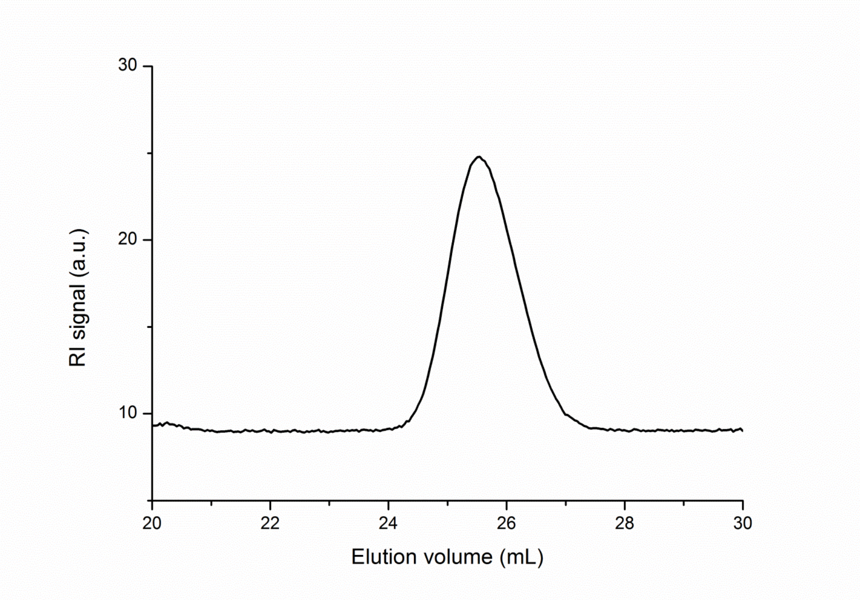


Fig. S1. Typical SEC trace of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation (initiator undecenol/DMPK) ($M_{n,SEC} = 1{,}750$ g mol^{-1}).

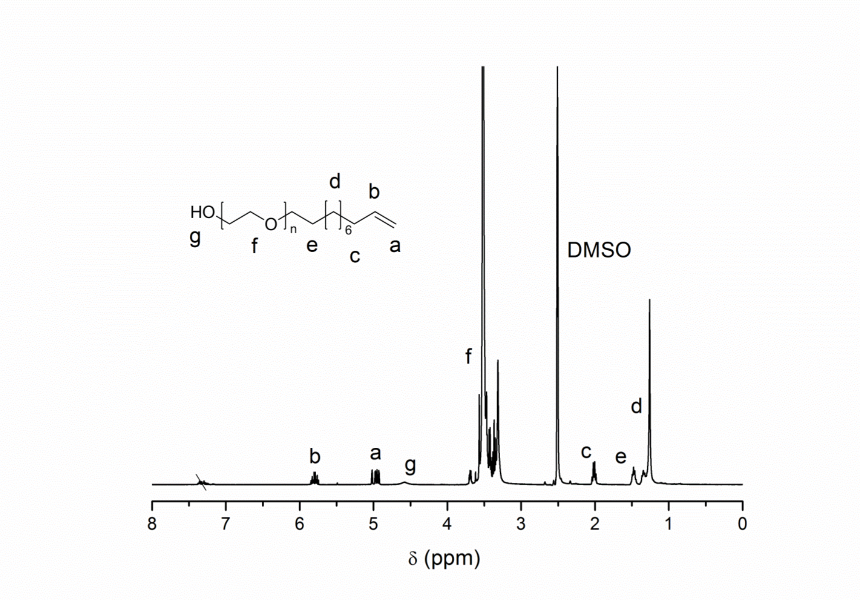


Fig. S2. ^{1}H NMR spectrum of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation (initiator undecenol/DMPK) (400 MHz, DMSO-d_6).

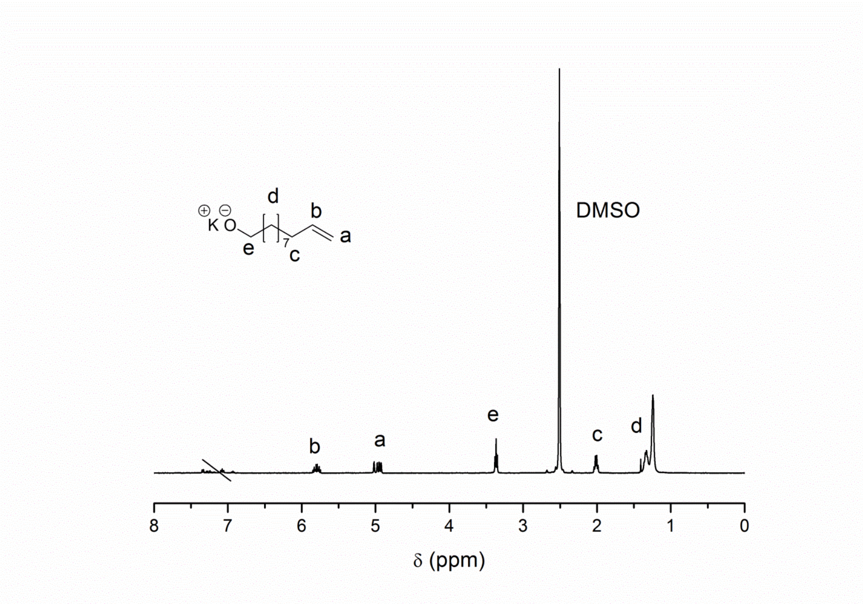


Fig. S3. ^{1}H NMR spectrum of a powder potassium undecenolate initiator (400 MHz, DMSO-*d*$_6$).

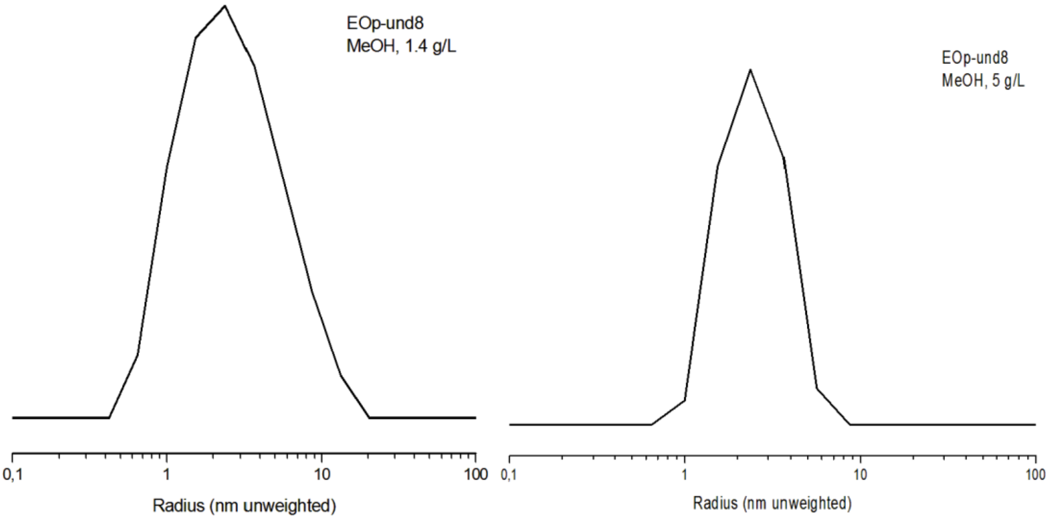


Fig. S4. Determination of the hydrodynamic radius by DLS in methanol of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation ($M_{n,SEC}$ = 38,000 g mol^{-1}).

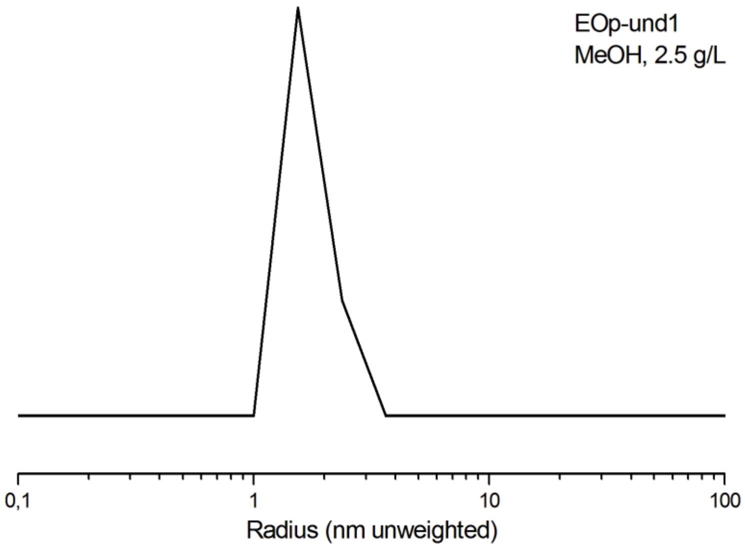


Fig. S5. Determination of the hydrodynamic radius by DLS in methanol of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation ($M_{n,SEC}$ = 2,100 g mol^{-1}).

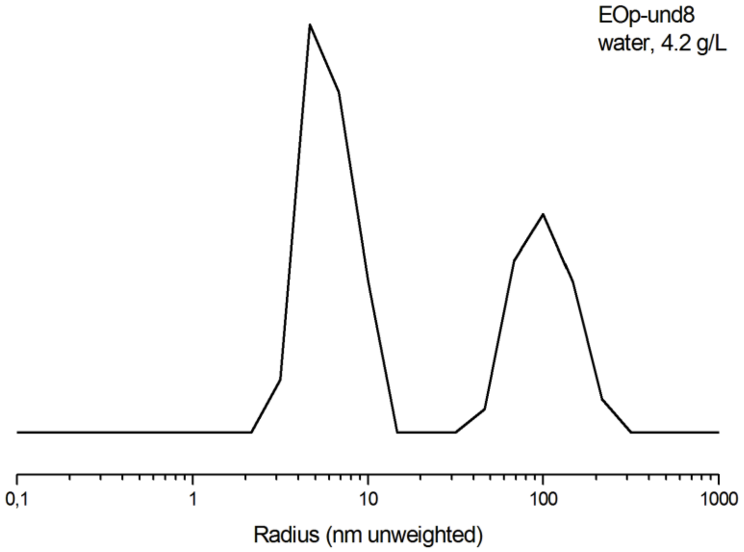


Fig. S6. Determination of the hydrodynamic radius by DLS in water of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation ($M_{n,SEC}$ = 38,000 g mol^{-1}).

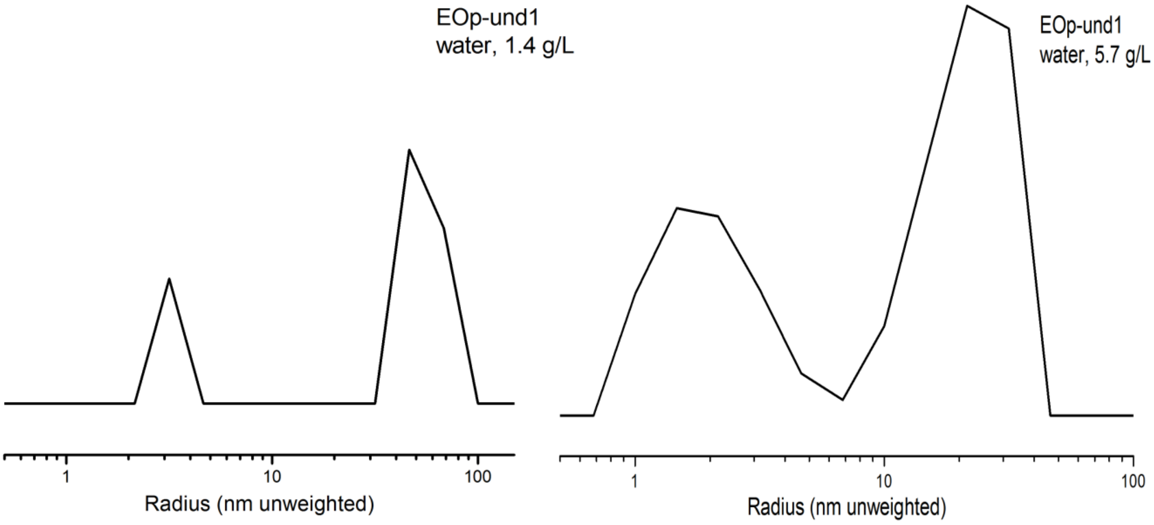


Fig. S7. Determination of the hydrodynamic radius by DLS in water of an α-undecenyl-ω-hydroxy PEO macromonomer obtained by initiation ($M_{n,SEC}$ = 2,100 g mol^{-1}).

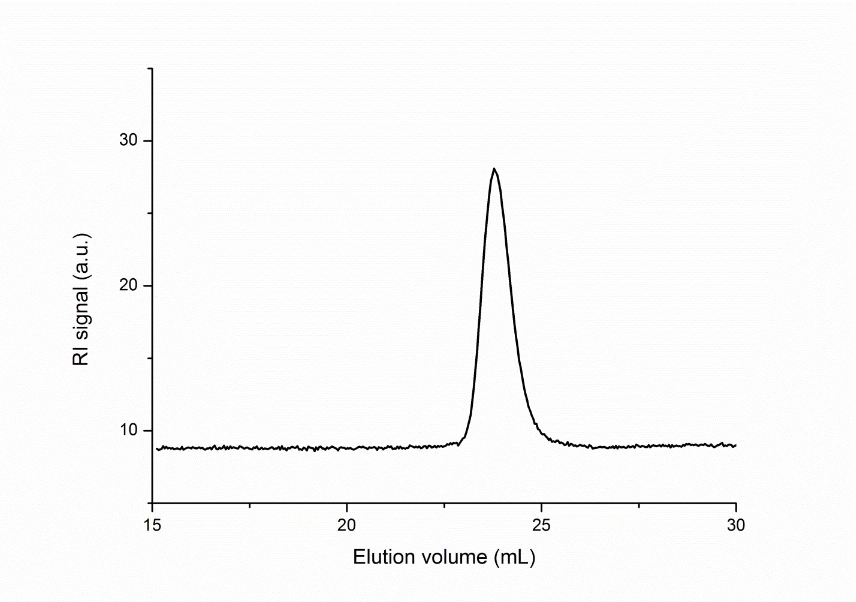


Fig. S8. Typical SEC trace of an α-undecenyl-ω-methacryloyl PEO macromonomer obtained by chain-end modification of an α-undecenyl-ω-hydroxy PEO macromonomer with methacrylic anhydride in the presence of triethylamine ($M_{n,SEC}$ = 3,400 g mol^{-1}).

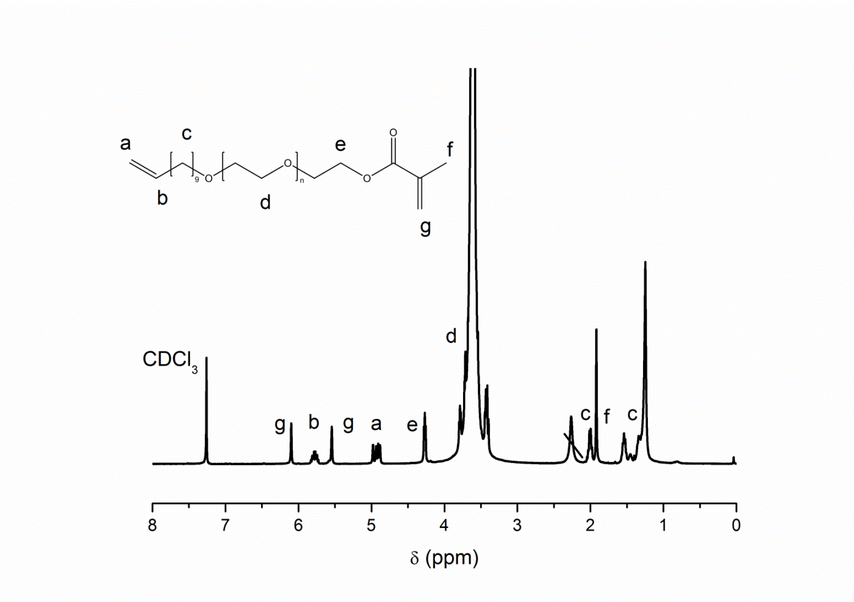


Fig. S9. ^{1}H NMR spectrum of an α-undecenyl-ω-methacryloyl PEO macromonomer obtained by chain-end modification of an α-undecenyl-ω-hydroxy PEO macromonomer with methacrylic anhydride in the presence of triethylamine (400 MHz, CDCl$_3$).

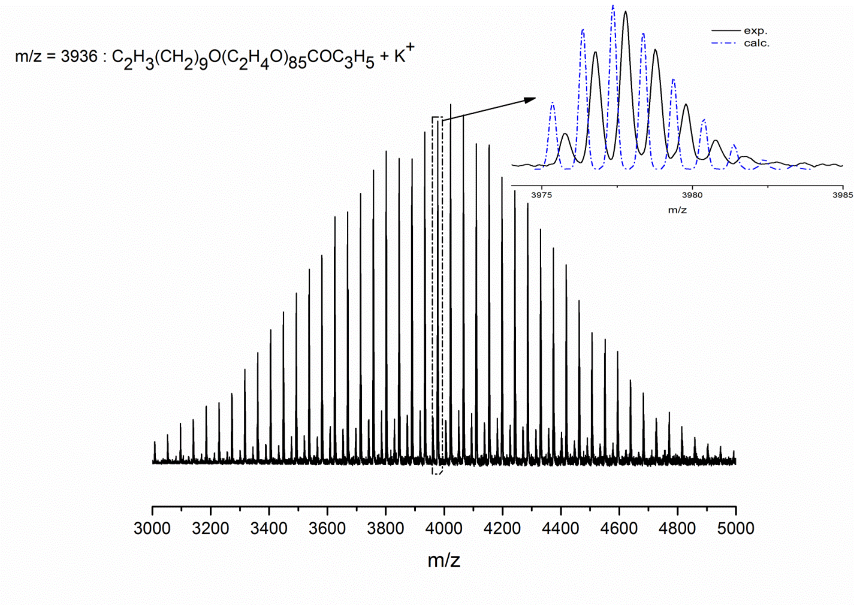


Fig. S10. MALDI-TOF MS spectrum of an α-undecenyl-ω-methacryloyl PEO obtained by chain-end modification of an α-undecenyl-ω-hydroxy PEO macromonomer with methacrylic anhydride in the presence of triethylamine ($M_{n,SEC}$ = 3,300 g mol^{-1}) (Matrix: DCTB, NaI).

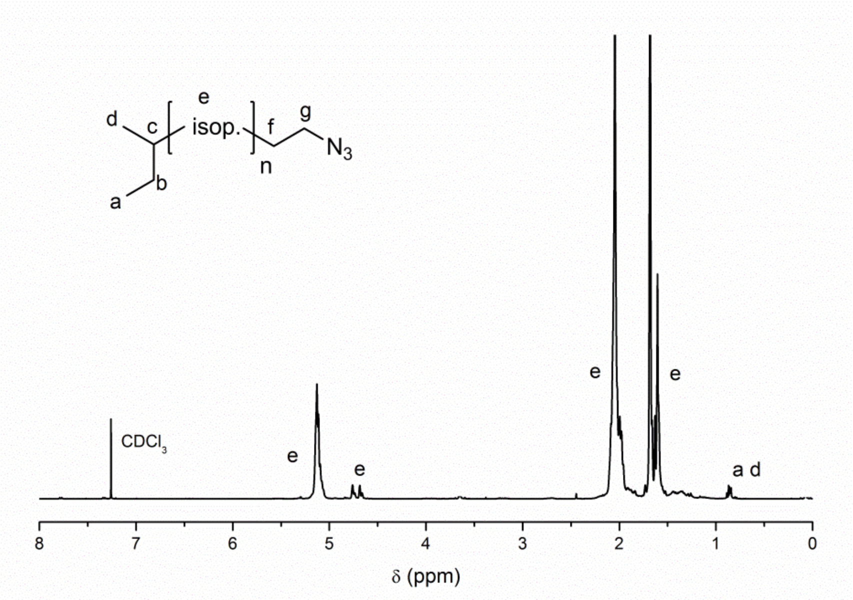


Fig. S11. ^{1}H NMR spectrum of an ω-azido PI 400 MHz, $CDCl_3$).

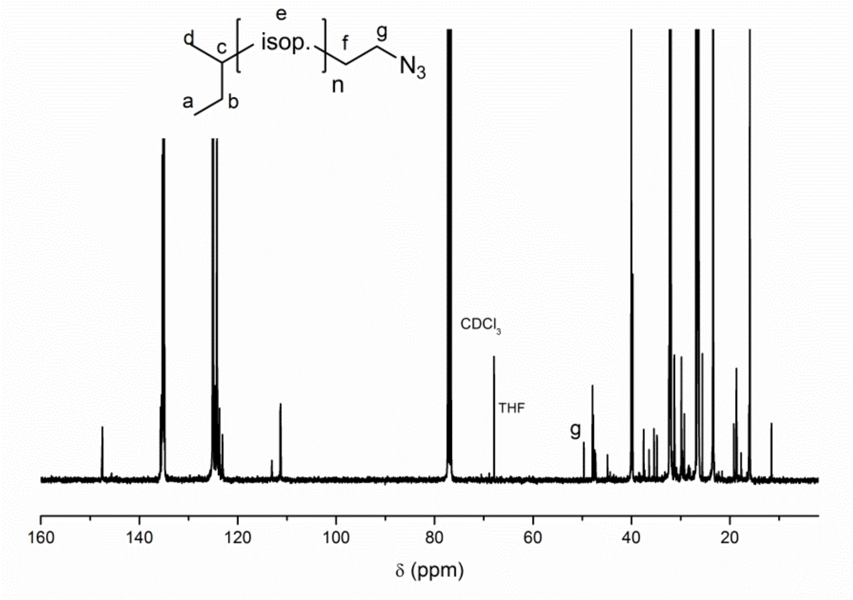


Fig. S12. ^{13}C NMR spectrum of an ω-azido PI (400 MHz, $CDCl_3$).

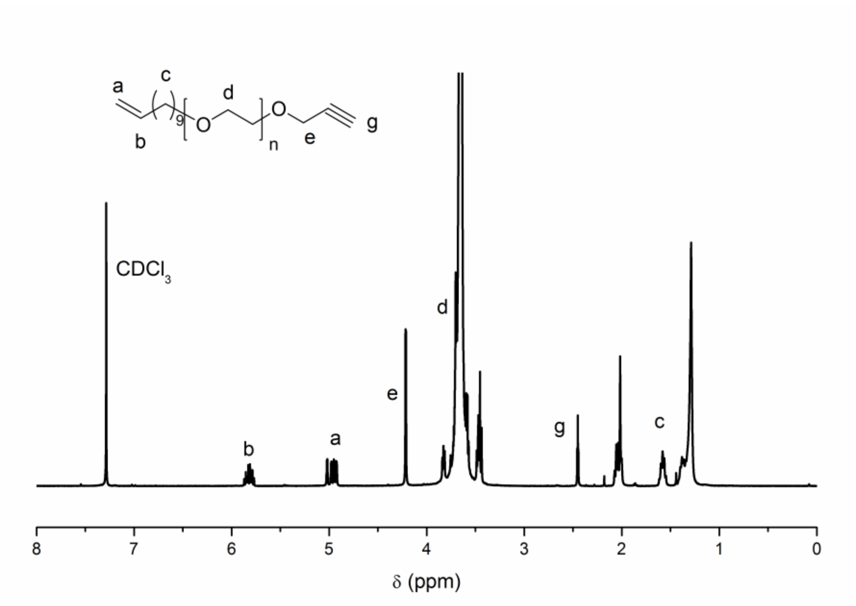


Fig. S13. ^{1}H NMR spectrum of an α-undecenyl-ω-acetylene PEO macromonomer (400 MHz, CDCl$_3$).

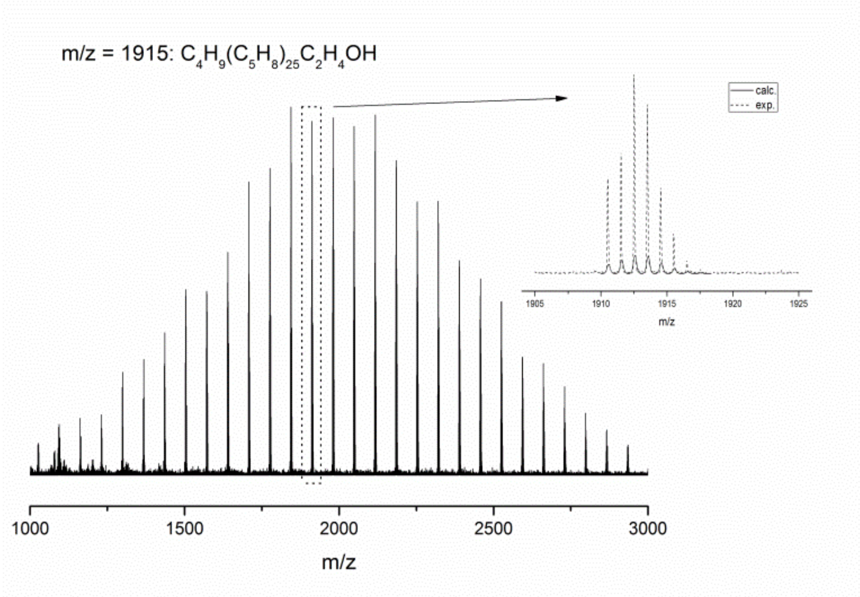


Fig. S14. MALDI-TOF MS spectrum of an α-undecenyl-ω-acetylene PEO macromonomer (Matrix: dithranol, AgTFA).

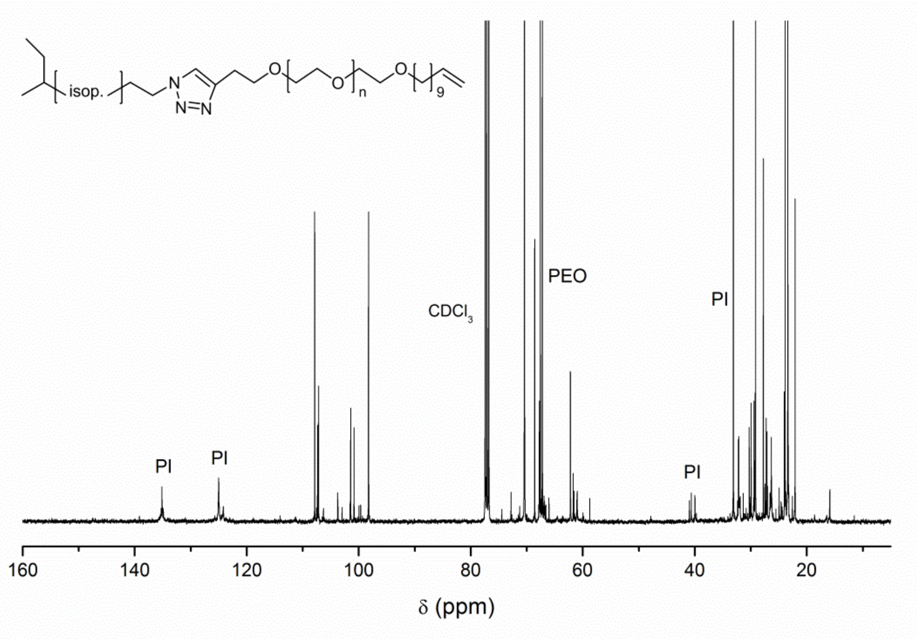


Fig. S15. ^{13}C NMR spectrum of a PI-*b*-PEO (400 MHz, CDCl$_3$).

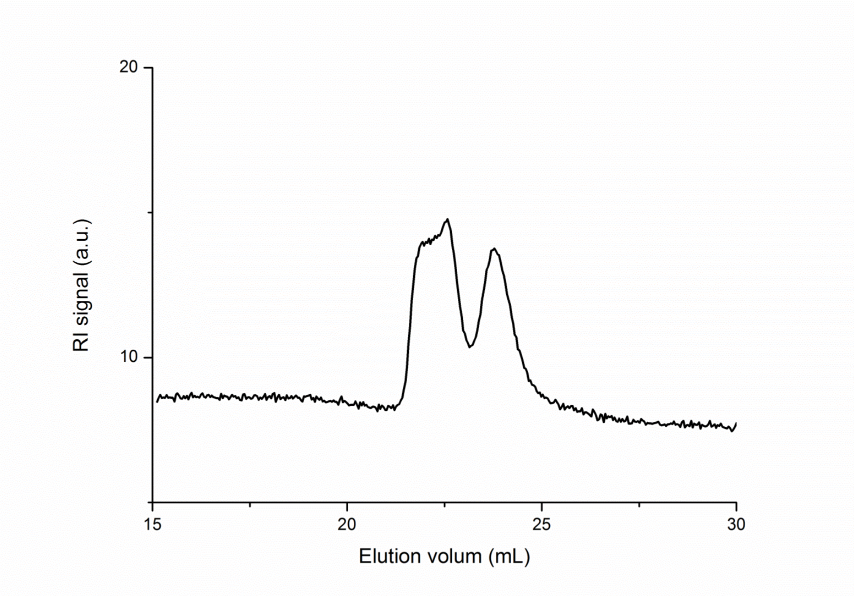


Fig. S16. Typical SEC trace of the raw reaction product obtained by FRP of sample PEOMA5 in toluene (50 °C, 24 hours).

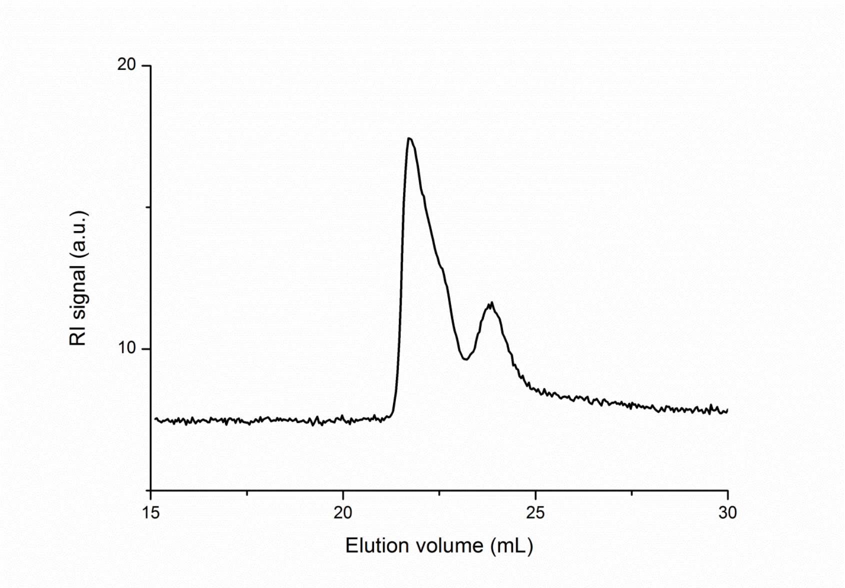


Fig. S17. Typical SEC trace of the raw reaction product obtained by FRP of sample PEOMA5 in THF (50 °C, 6 hours).

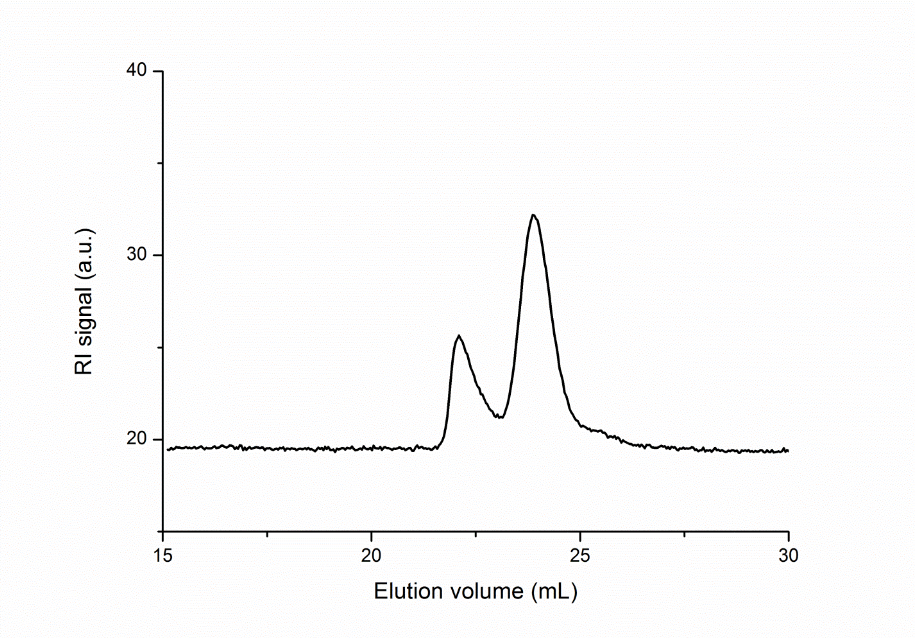


Fig. S18. Typical SEC trace of the raw reaction product obtained by ATRP of sample PEOMA6 in water (60 °C, 24 hours).

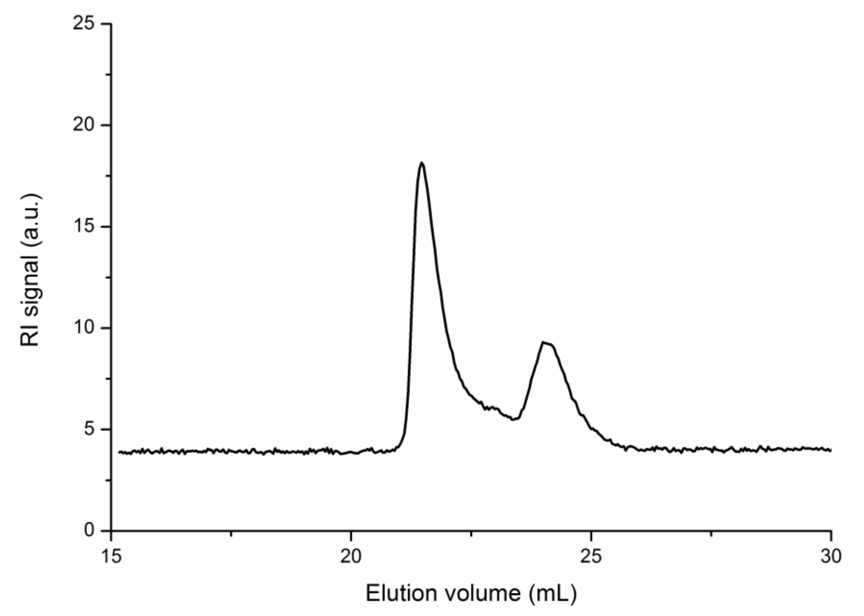


Fig. S19. Typical SEC trace of fractionated product obtained by ATRP of sample PEOMA1 in water (60 °C, 24 hours).

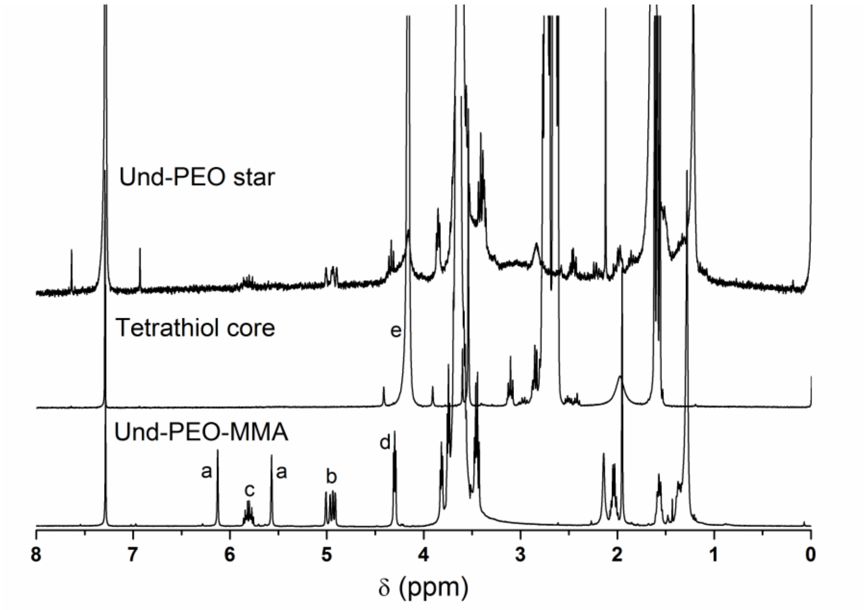


Fig. S20. ^{1}H NMR spectrum of 4 arm PEO star molecules obtained via thiol-ene click reaction of α-undecenyl-ω-methacryloyl PEO macromonomer with pentaerythritol tetrakis(3-mercaptopropionate) (400 MHz, $CDCl_3$).

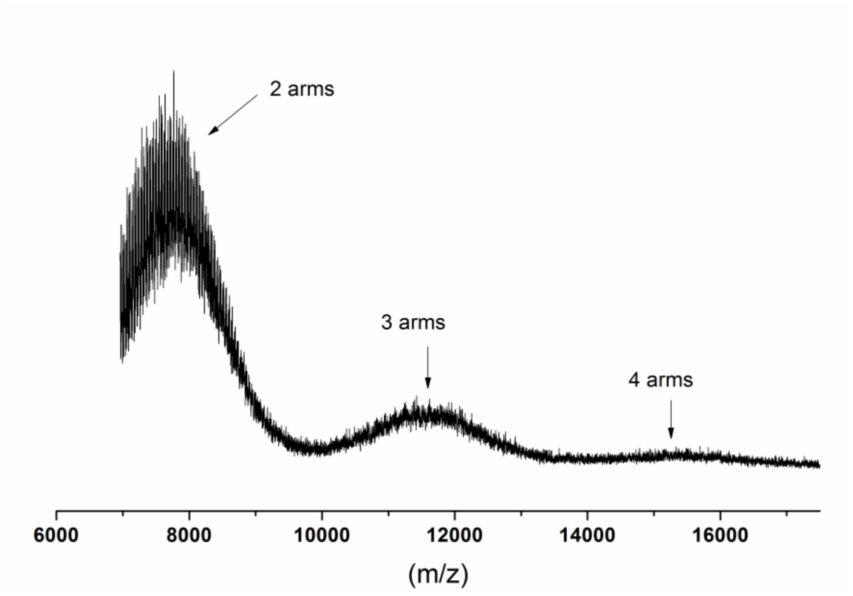
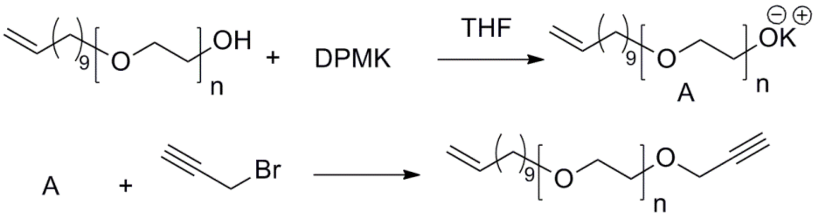
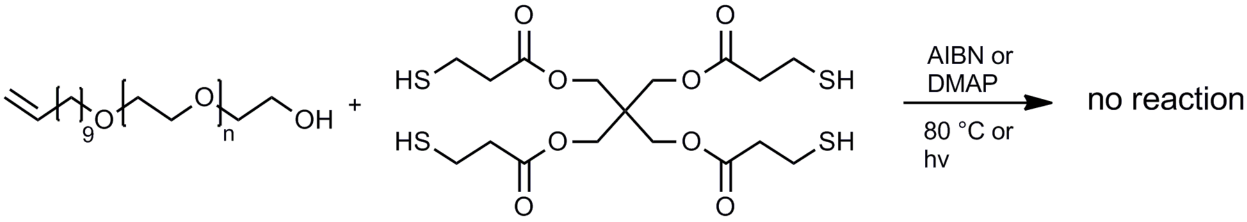


Fig. S21. MALDI-TOF MS spectrum of 4 arm PEO star molecules obtained via thiol-ene click reaction of α-undecenyl-ω-methacryloyl PEO macromonomer with pentaerythritol tetrakis(3-mercaptopropionate) (Matrix: DCTB, NaI).



SCHEME S1. Schematic representation of the synthesis of α-undecenyl-ω-acetylene PEO macromonomers.



SCHEME S2. Schematical representation of the synthesis 4 arm PEO star molecules with the α-undecenyl-ω-hydroxyl PEO macromonomer by thiol-ene click reaction.

Annex 3: Supporting information of article 4

ω-Undecenyl poly(ethylene oxide)s and hybrid star-shaped polymers

Submitted to *J. Phys. Chem. B*

Supporting Information

SAXS Studies of the Molecular and Structural Parameters of Hybrid PEO/POSS Star-shaped Materials

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KEYWORDS Heterofunctional macromonomers; MALDI-ToF MS; poly(ethylene oxide); silsesquioxanes; SAXS

Experimental section for the determination of the functionality of commercial PEOs via chemical modification of the chain-ends with 1-naphthyl isocyanate

Table S1. Molecular characteristics of the ω-naphthyl carbamate PEOs

Figure S1. Typical SEC traces of an ω-naphthyl carbamate PEO ($M_{n,SEC}$ = 1800 g mol^{-1}).

Figure S2. UV spectrum of an ω-naphthyl carbamate PEO measured in ethanol.

Figure S3. ^{1}H NMR spectrum of an ω-naphthyl carbamate PEO (400 MHz, $CDCl_3$).

Figure S4. MALDI-ToF MS of an ω-naphthyl carbamate PEO ($M_{n,SEC}$ = 1200 g mol^{-1}) (Matrix: DCTB, NaI).

Figure S5.Typical SEC trace of an ω-undecenyl PEO macromonomer obtained by deactivation with 11-bromo-1-undecene in the presence of NaH ($M_{n,SEC}$ = 1800 g mol^{-1}).

Figure S6. ^{1}H NMR spectrum of an ω-undecenyl PEO macromonomer obtained by deactivation with 11-bromo-1-undecene in the presence of NaH (400 MHz, $CDCl_3$).

Figure S7. MALDI-ToF MS of an ω-undecenyl PEO macromonomer obtained by deactivation with 11-bromo-1-undecene in the presence of NaH ($M_{n,SEC}$ = 1900 g mol^{-1}) (Matrix: DCTB, NaI).

Figure S8. MALDI-ToF MS of an ω-undecenyl PEO macromonomer with contamination of α-methoxy-ω-hydroxy PEO at 5 and 20 wt % ($M_{n,SEC,\ Macro}$ = 1900 g mol^{-1}) (Matrix: DCTB, NaI).

Figure S9. Light scattering data of $Q_8M_8^{PEO}$ measured in methanol.

Figure S10. ^{13}C NMR spectrum of $Q_8M_8^{PEO}$ (400 MHz, $CDCl_3$).

Figure S11. Sequences of micrographs obtained by optical microscopy with polarized light at distinct temperatures, during a scanning melting process. The first point of the spherulite $Q_8M_8^{PEO}$ is observed at 38.5 °C after 4 min cooling (a) and the total crystallization is after 6.2 min at 33 °C (f).

Scheme S1. Schematic representation of the synthesis of an ω-naphthyl carbamate PEO

Determination of the functionality of commercial PEOs via chemical modification of the chain-ends with 1-naphthyl isocyanate.

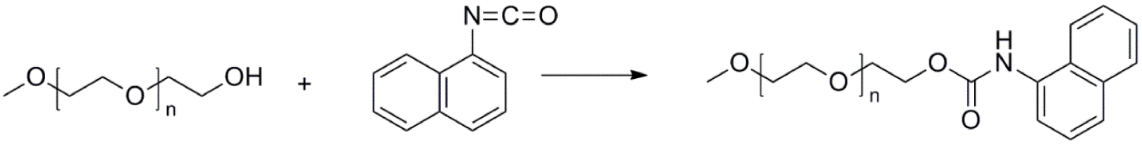
Experimental section: Preparation of the samples.

The commercial α-methoxy-ω-hydroxy PEO (M_n = 1700 g mol^{-1}, 2 g, 1.18 μmol) was dissolved in 60 mL of dry THF under argon (T = 50 °C). One spatula of 1,4-diazabicyclo[2.2.2]octan (DABCO) was added, then 1-naphthyl isocyanate (20% molar excess, 0.202 mL, 1.41×10^{-3} mol) was introduced. The reaction was kept at 50 °C for 5 h. Afterwards, the THF was removed by evaporation under vacuum. The ω-naphthyl carbamate PEO was dissolved in THF:DMSO (50/50, v/v) and precipitated twice into cold diethyl ether (M_n < 4000 g mol^{-1}) and diethyl ether at room temperature for all the PEOs of higher molar masses. The resulting end-modified PEOs were characterized by SEC with RI and UV detection. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.2–8 (m, 7H, Ar), 4.4 (m, 2H, $-CO-O-CH_2-$), 3.6–3.8 (m, 4H*n, $-O-CH_2-CH_2-$), 3.3 (s, 3H, $-O-CH_3$). The same experimental procedure was used for the modification of the bifunctional PEOs.

Discussion of the results.

The analysis of the hydroxyl content of commercial monofunctional PEOs revealed that they can be contaminated with critical amounts of bifunctional PEOs. Bifunctional PEOs are characterized by molar masses twice as high as the monofunctional PEO.

Their formation is attributed to the presence of water during the AROP process. They increase the PDI value of the supposedly “monofunctional” PEOs and further increase the average functionality. Moreover, the existence of bifunctional species may lead to undesired cross-linking during the copolymerization of the PEO macromonomers with low molar mass polymerizable species. Hence, unexpected properties may be obtained. To overcome such difficulties, high osmotic pressure chromatography was used successfully to isolate the monofunctional PEO.[1] However, this strategy is time consuming and cannot be envisaged for the purification of large PEO quantities. As a consequence, it was important to determine the content of hydroxyl functions in the monofunctional PEOs used in the present study. Several approaches have been proposed in the literature to identify the chain-ends and to quantify the hydroxyl content of commercial monofunctional PEOs. This can be achieved directly by means of ^{1}H NMR[2] or after chain-end modification with trichloroacetyl isocyanate,[3] hexafluoroacetone,[4] or 1-naphthyl isocyanate.[5] Among the different possible approaches, we selected the method based on the modification of the hydroxyl chain-ends for a series of commercial PEOs with 1-naphthyl isocyanate. Naphthyl isocyanates are much more reactive than alkyl isocyanates. If appropriate experimental conditions are selected, the conversion of the hydroxyl functions into naphthyl carbamate groups is quantitative.[5] This reaction was applied to a series of commercial monofunctional PEOs covering a range of molar masses (M_n) from 1000 to 10900 g mol^{-1} and to a bifunctional sample with a M_n of 6000 g mol^{-1} (Scheme S1).



Scheme S1. Schematic representation of the synthesis of an ω-naphthyl carbamate PEO

The functionalization reaction and the treatment of the end-modified PEOs are described below. It should be noted that the different samples had to be submitted to several precipitations to eliminate eventual traces of unreacted labeling agent leading to an overestimation of the functionalization rates. The different samples were characterized by three independent methods (SEC in THF with RI and UV detection, UV spectroscopic analysis and ^{1}H NMR) to assess the molar masses and polydispersity index values, and to confirm the presence of the naphthyl carbamate entity at the chain-end. MALDI-ToF MS measurements were also performed for all the chain-end modified PEOs. The characterization data of the different naphthyl carbamate chain-end modified PEOs are presented in Table S1 together with the experimental conditions for the preparation of the samples. A typical SEC curve is presented in the supporting information section (Figure S1).

Table S1. Molecular characteristics of the ω-naphthyl carbamate PEOs

Sample	[napht]/ [PEO]$^{a)}$	$M_n$$^{b)}$ (g mol^{-1}) SEC	$M_n$$^{c)}$ (g mol^{-1}) SEC	$M_w$$^{c)}$ (g mol^{-1}) SEC	$M_n$$^{d)}$ (g mol^{-1}) MALDI	$M_n$$^{e)}$ (g mol^{-1}) UV	f$^{f)}$ (%) ^{1}H NMR
PEONC1	1.2	1000	1100	1100	1200	1200	102
PEONC2	1.2	1700	1800	1900	2000	2000	101
PEONC3	1.2	4550	4700	5000	4900	4800	101
PEONC4	1.2	10900	11100	12400	10700	10600	105
PEONC5*	2.4	6000	5900	6400	6500	6100	103

[a)] Molar ratio 1-naphthyl isocyanate / PEO.

[b)] Number average molar mass of the precursor PEOs, measured by SEC in THF, calibration with linear PEOs.

[c)] Number average molar mass of the ω-naphthyl carbamate PEOs, measured by SEC in THF, calibration with linear PEOs.

[d)] Weight average molar mass of the ω-naphthyl carbamate PEOs, measured by SEC in THF, calibration with linear PEOs.

[e)] Number average molar mass of the ω-naphthyl carbamate PEOs, measured by MALDI ToF MS.

[f)] Yield of functionalization of the ω-naphthyl carbamate PEOs, measured by ^{1}H NMR (400 MHz) in $CDCl_3$.

*PEO di OH.

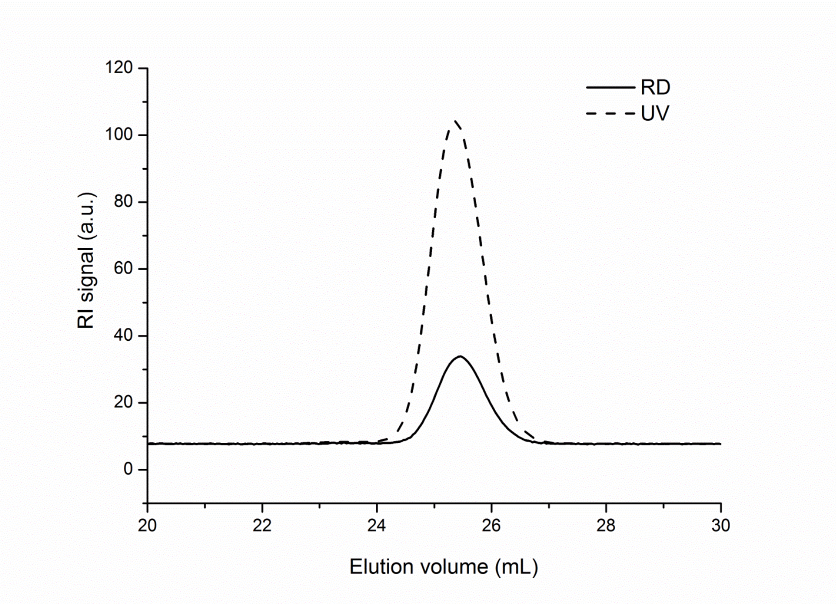


Figure S1. Typical SEC traces of an ω-naphthyl carbamate PEO ($M_{n,SEC}$ = 1800 g mol^{-1}).

Low PDI values, close to the precursor PEOs, were obtained by SEC (Figure S1 and Table S1). In most cases, the M_n values determined by SEC and based on calibration with linear α-hydro-ω-hydroxy PEOs, are in good agreement with the expected values. The slight increase in the molar mass with respect to the precursor PEO is attributed to the presence of the naphthyl carbamate entity at the chain-end. The results of the SEC with online UV detection (Figure S1) attested the presence of the naphthyl carbamate entity at the chain-end: A strong UV adsorption is observed at the elution volume corresponding to the PEO chain. Classical UV spectroscopy was also used to quantify the functionalization yield. The measurements were conducted in ethanol (Figure S2). This method allows the determination of the M_n values taking into account the chain-modified PEO concentration, the extinction coefficient (7060 mol^{-1} cm^{-1}) and the optical density. These values are presented in Table S1 and are consistent with the M_n values measured by SEC based on calibration with linear PEOs. The same remark is valid for the commercial bifunctional PEO sample with a molar mass (M_n) of 6000 g mol^{-1} and modified at the chain-end with 1-naphthyl isocyanate (Table S1).

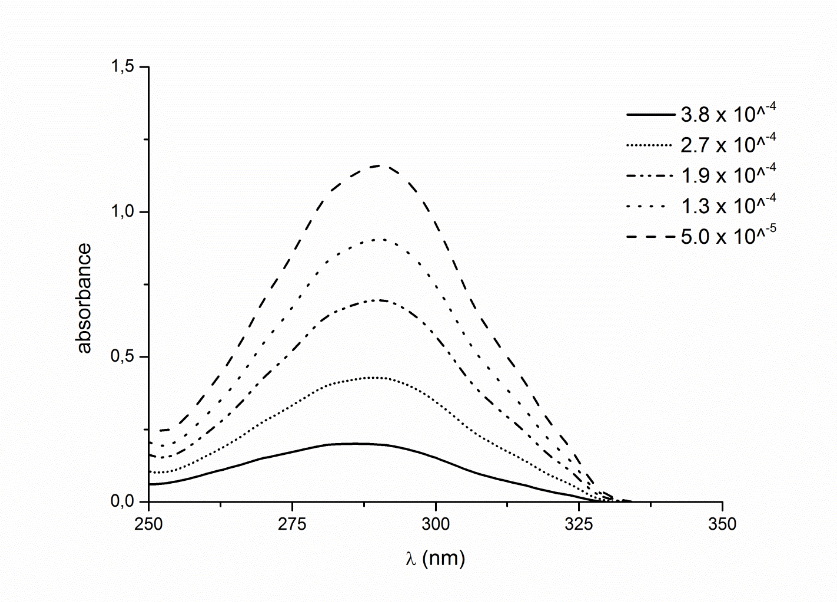


Figure S2. UV spectrum of an ω-naphthyl carbamate PEO measured in ethanol.

For the same samples, the functionality was determined by ^{1}H NMR measurements in $CDCl_3$. A typical ^{1}H NMR spectrum is presented in Figure S3. In addition to the signals of the methylene protons [–O–C*H*2–C*H*2 (4H*n), δ = 3.6 to 3.8 ppm, PEO chain except the first methylene group], the spectrum is characterized by peaks assignable to the methoxy protons (initiator potassium methoxyethanolate). The corresponding peak of the hydroxyl function (in the precursor polymer at 4.70 ppm) disappeared. A new peak at 4.4 ppm appeared, corresponding to the bond-formation between the naphthyl carbamate group and the PEO chain ($-CH_2-CH_2-O-CO-N-$). ^{1}H NMR was also used to determine the functionalization yield. Considering the ratio between the integrals of the peak of the methyl group at 3.3 ppm (CH_3–O–PEO, outer chain) and the methylene group at 4.4 ppm (originating from the other end the PEO chain), a functionality value close to 1 was calculated.

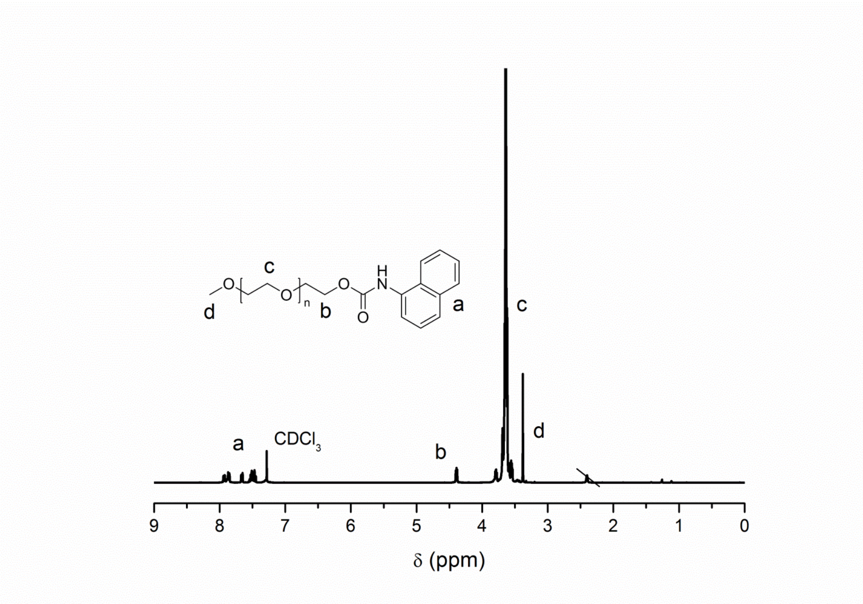


Figure S3. ^{1}H NMR spectrum of an ω-naphthyl carbamate PEO (400 MHz, $CDCl_3$).

The same PEO samples were additionally analyzed by MALDI-ToF MS to verify the molar mass and to confirm the presence of the naphthyl carbamate entity at the chain-end (Figure S4). The measurements were systematically performed on the chain-end modified PEOs as well as on their precursors for comparison. The M_n values resulting from MALDI-ToF MS are shown in Table 1 together with the values determined by SEC and UV. A typical MALDI-ToF MS spectrum of a low molar mass naphthyl carbamate chain-end modified PEO ($M_{n,SEC}$ = 1200 g mol^{-1}) is presented in Figure S4. The M_n values determined for both, the precursor α-methoxy-ω-hydroxyl PEO and the α-methoxy-ω-naphthyl carbamate PEO, are in good agreement with the theoretical values. The signals between *m/z* 1236 and 1280 with a characteristic shift of *m/z* 44 are caused by the monofunctional PEO chain. The difference in the molar mass between the precursor PEO and the chain-end modified PEO (170 g mol^{-1}) corresponds exactly to the value of the naphthyl carbamate entity. However, besides these major peaks, a “minor” distribution is observed (see peaks at 1258 and 1303 g mol^{-1}). This distribution fits well with a monofunctional “protonated” naphthyl carbamate for the same number n, and not with a difunctional “protonated” or “sodiated” naphthyl carbamate PEO.

The resulting mass spectrometrical signal appeared at *m/z* 1303: $CONHC_{10}H_7O(CH_2CH_2O)_{25}CH_3H$ (186.187 ($OC_{10}H_7NHCO$) + 44.053n (n = 25) (CH_2CH_2O) + 15.035 (CH_3) + 1.008 (H) (where n is the degree of polymerization)). The same “minor” distribution is observed for the PEO of molar mass 1700 g mol^{-1}. This “minor” distribution is not present in the chain-end modified PEO samples prepared from precursors of higher molar masses or from the bifunctional precursor of a molar mass of 6000 g mol^{-1}. These results confirm a nearly quantitative functionalization of the PEO chain-ends.

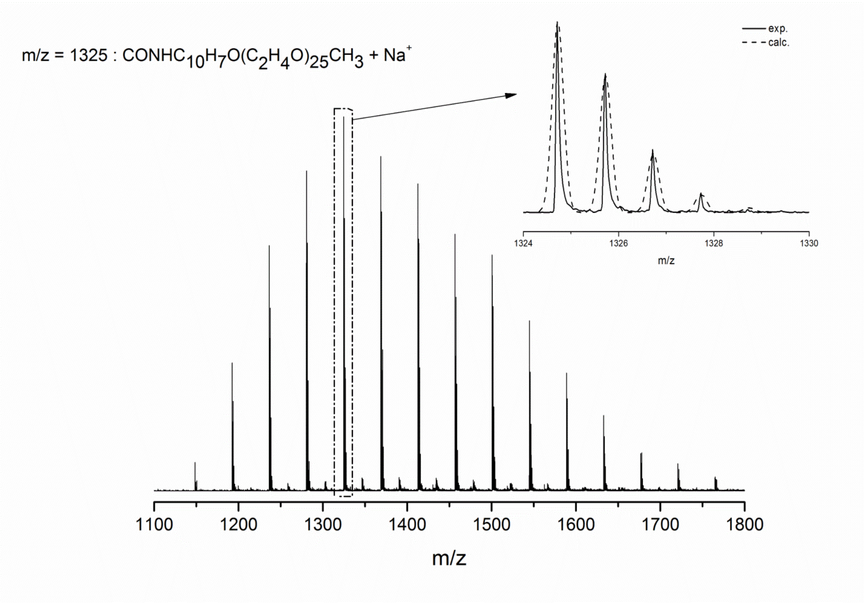


Figure S4. MALDI-ToF MS of an ω-naphthyl carbamate PEO ($M_{n,SEC}$ = 1200 g mol^{-1}) (Matrix: DCTB, NaI).

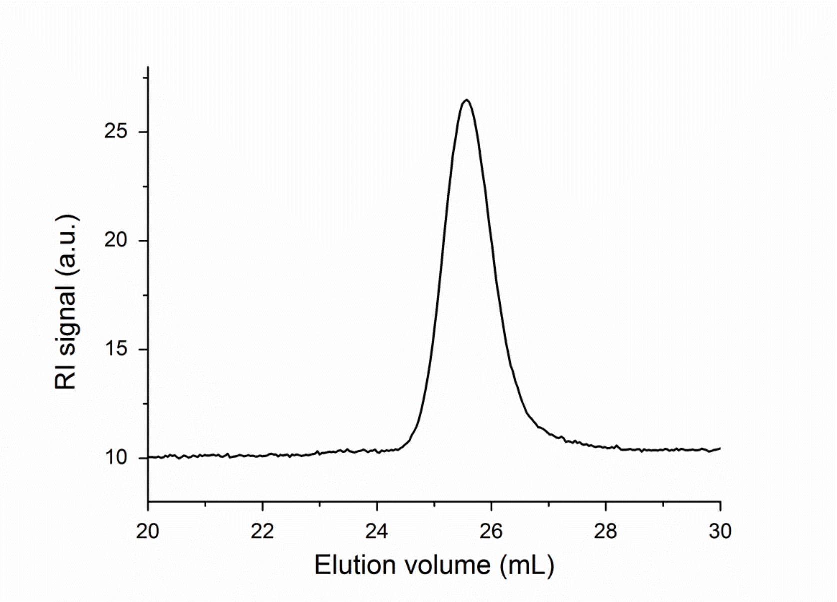


Figure S5.Typical SEC trace of an ω-undecenyl PEO macromonomer obtained by deactivation with 11-bromo-1-undecene in the presence of NaH ($M_{n,SEC}$ = 1800 g mol^{-1}).

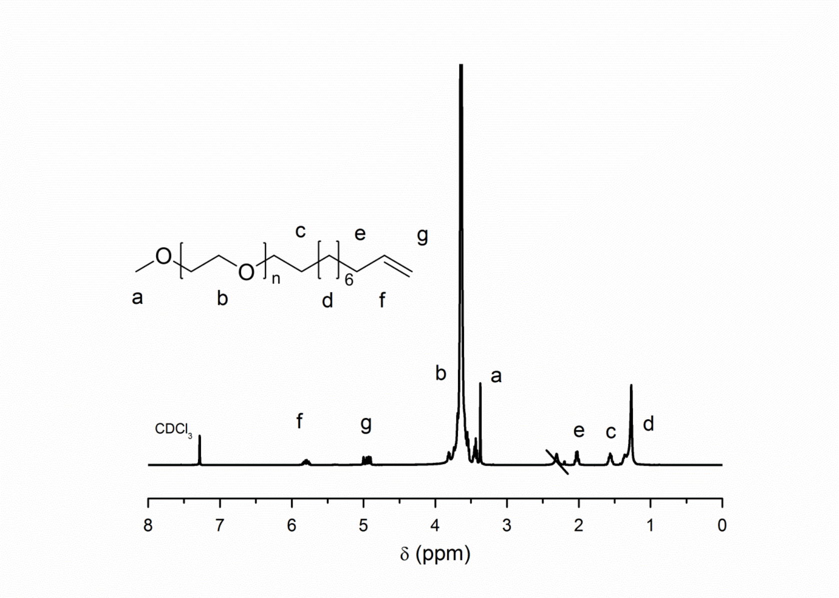


Figure S6. ^{1}H NMR spectrum of an ω-undecenyl PEO macromonomer obtained by deactivation with 11-bromo-1-undecene in the presence of NaH (400 MHz, $CDCl_3$).

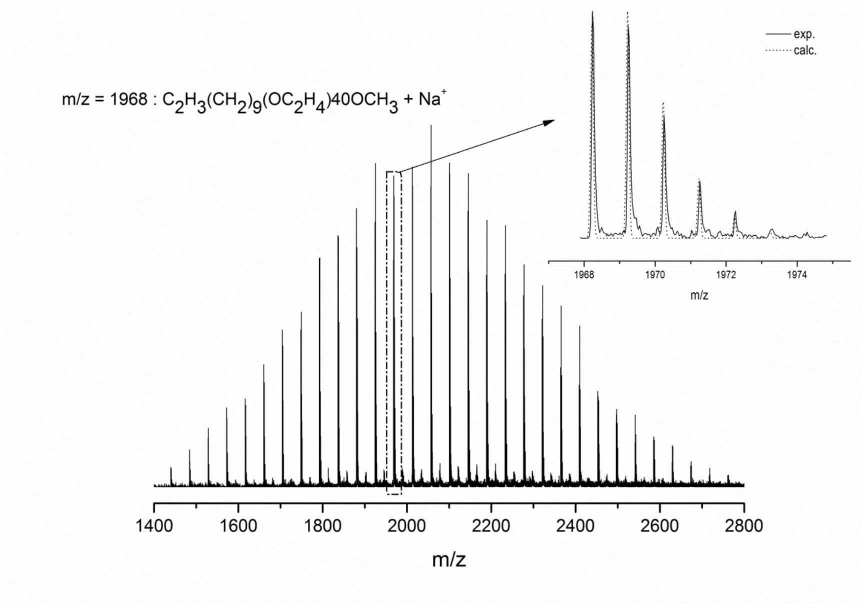
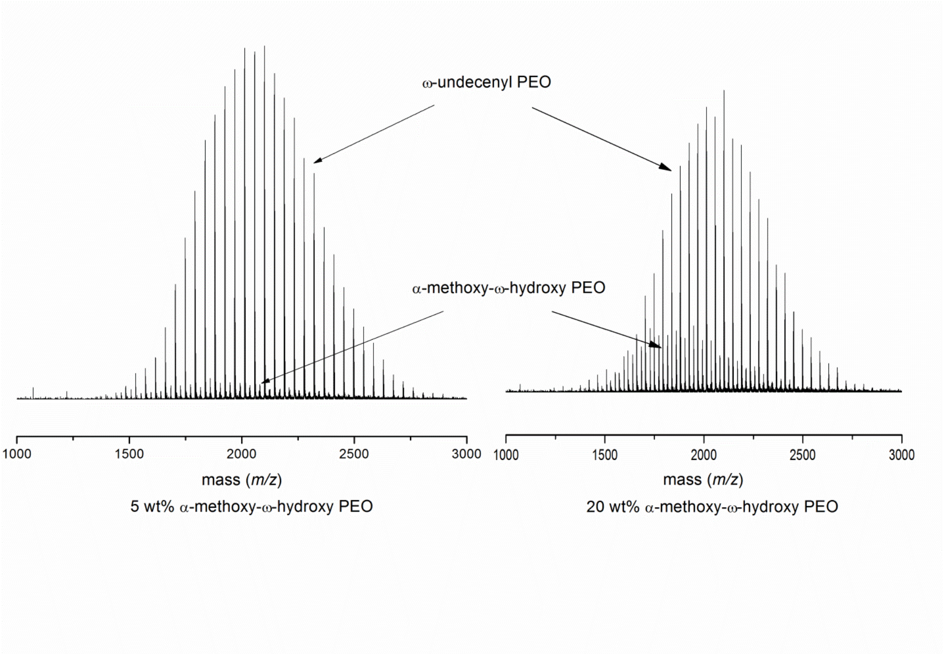


Figure S7. MALDI-ToF MS of an ω-undecenyl PEO macromonomer obtained by deactivation with 11-bromo-1-undecene in the presence of NaH ($M_{n,SEC}$ = 1900 g mol^{-1}) (Matrix: DCTB, NaI).



5 wt% α-methoxy-ω-hydroxy PEO

20 wt% α-methoxy-ω-hydroxy PEO

Figure S8. MALDI-ToF MS of an ω-undecenyl PEO macromonomer with contamination of α-methoxy-ω-hydroxy PEO at 5 and 20 wt % ($M_{n,SEC,\ Macro}$ = 1900 g mol^{-1}) (Matrix: DCTB, NaI).

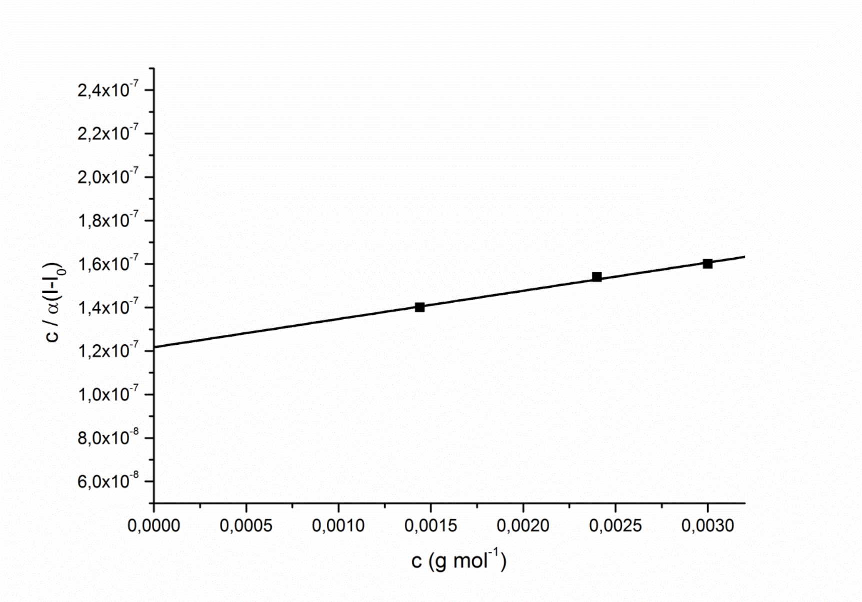


Figure S9. Light scattering data of $Q_8M_8^{PEO}$ measured in methanol.

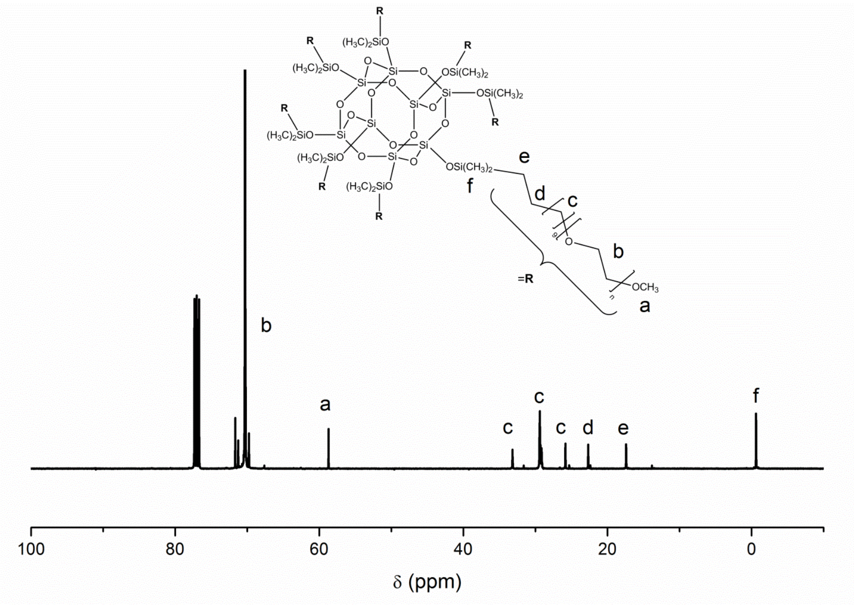


Figure S10. ^{13}C NMR spectrum of $Q_8M_8^{PEO}$ (400 MHz, $CDCl_3$).

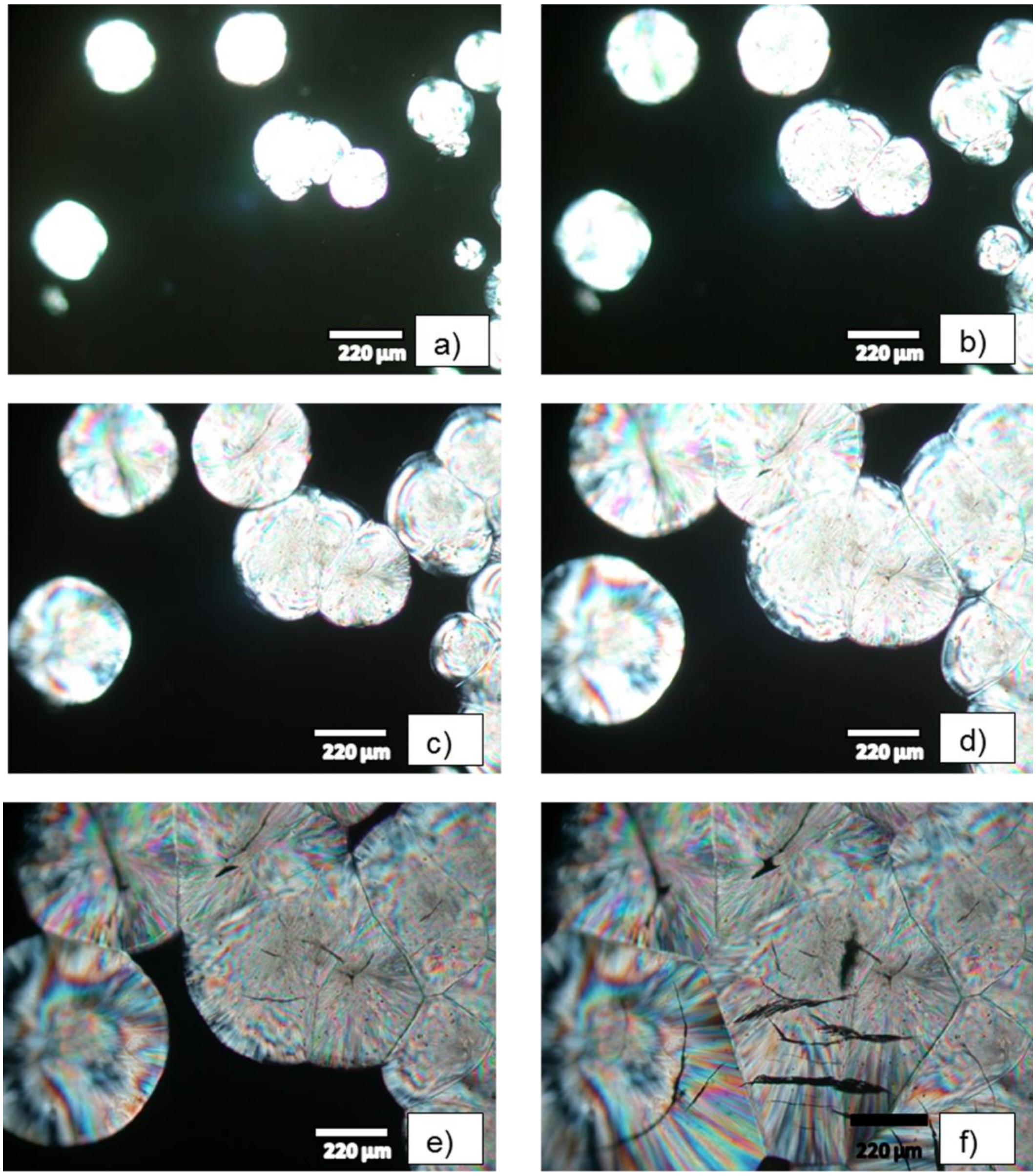


Figure S11. Sequences of micrographs obtained by optical microscopy with polarized light at distinct temperatures, during a scanning melting process. The first point of the spherulite $Q_8M_8^{PEO}$ is observed at 38.5 °C after 4 min cooling (a) and the total crystallization is after 6.2 min at 33 °C (f).

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Gladys POZZA

Tailor-made heterofunctional poly(ethylene oxide) *via* living anionic polymerization as building blocks in macromolecular engineering

L'objectif principal de la thèse porte sur la synthèse contrôlée et la caractérisation d'architectures macromoléculaires complexes originales à base de POE. Les POEs α-undécènyle-ω-hydroxy sont obtenus par polymérisation anionique par ouverture de cycle de l'oxyde d'éthylène. Le groupement hydroxyle est modifié pour accéder à des POEs α-undécènyle-ω-méthacrylate et des POEs α-undécènyle-ω-acétylène. Ces premiers POEs sont ensuite utilisés pour préparer soit des POEs à structure en peigne par ATRP dans l'eau soit par l'intermédiaire de réaction « click », des POEs à structure en étoile tétrafonctionnelles, tandis qu'avec les seconds permettent d'obtenir des PI-*b*-POE par réaction « click » avec le polyisoprène ω-azoture. Les extrémités de chaîne de POE commerciaux α-méthoxy-ω-hydroxy sont modifiées en POEs α-méthoxy-ω-allyle ou en POEs α-méthoxy-ω-undécènyle pour synthétiser par réaction d'hydrosilylation des étoiles de POE à structures en étoile octafonctionnelles.

Mots clé:

Architecture macromoléculaire, copolymère à block PI-*b*-POE, macromonomère hétérobifonctionnel, macromonomère hétérofonctionnel, polymère à structure en étoile, polymérisation anionique par ouverture de cycle, poly(oxyde d'éthylène).

The main objective of the thesis focuses on the controlled synthesis and the characterization of original and complex macromolecular architectures based on PEO. α-Undecenyl-ω-hydroxy PEOs are obtained by anionic ring opening polymerization of ethylene oxide. The hydroxyl group is modified to access to α-undecenyl-ω-methacrylate PEOs and α-undecenyl-ω-acetylene PEOs. These first PEOs are used to prepare either comb-shaped PEOs by ATRP in water or through by click reaction of tetrafunctional star-shaped PEOs. Whereas the second PEOs allow obtaining block copolymers PI-*b*-PEO *via* click reaction with ω-azide polyisoprene. The chain-ends of commercial α-methoxy-ω-hydroxy PEO are modified in α-methoxy-ω-allyl PEOs or in α-methoxy-ω-undecenyl PEOs to synthesize by hydrosilylation reaction octafunctional star-shaped PEOs.

Keywords:

Anionic ring opening polymerization, block copolymer PI-*b*-PEO, heterobifunctional macromonomer, heterofunctional macromonomer, macromolecular architecture, poly(ethylene oxide), star-shaped PEO.