UNIVERSITÉ DE STRASBOURG

*ÉCOLE DOCTORALE DE PHYSIQUE, CHIMIE PHYSIQUE*

**Institut Charles Sadron**

**THÈSE** présentée par :

**Georgiy SMOLYAKOV**

soutenue le : **25 septembre 2012**

pour obtenir le grade de : **Docteur de l'université de Strasbourg**

Discipline/ Spécialité : Physique/ Physico-chimie

# POLYELECTROLYTES ET LIQUIDES IONIQUES

| | |
|---|---|
| **THÈSE dirigée par :** | |
| **M. RAWISO Michel** | Directeur de recherches, Université de Strasbourg |
| **RAPPORTEURS :** | |
| **M. BUHLER Eric** | Professeur, Université Paris VII |
| **Mme DUCHET-RUMEAU Jannick** | Professeur, INSA de Lyon |
| **AUTRES MEMBRES DU JURY :** | |
| **Mme COSTA GOMES Margarida** | Professeur, Université Clermont-Ferrand II |
| **M. SCHAAF Pierre** | Professeur, Université de Strasbourg |

## Acknowledgments

A number of people have contributed to the present work and supported my activity, both professionally and personally. Without their collaboration and help this study obviously could not be realized. I would like to thank these persons as well as some participated organizations for their specific contributions to the present project and to my daily life during the last three years.

First of all I am grateful to my scientific supervisor Michel Rawiso. He has actively participated in my scientific formation during these three years. Discussions with Michel were very important to get knowledges about new science field in which I had to work, as well as to learn new technique which I had to apply. His advices and critics during these discussions were important and constructive for me. Collaboration with Michel helped me to enter world of science after student life and to understand key principles of scientific activity. His kind relation to me and help in daily life was important for me to adapt in a new country, which I enjoy now. Even simple conversations with Michel were interesting and useful due to his life experience and new important ideas which he brings. Michel's contribution to my formation is an important basis for my scientific career and interesting experience for my personal life.

I am sincerely thankful to my colleagues and friends Guillaume Fleith, Philippe Lorchat and Laure Herrmann. They kindly helped me in numerous questions related to working activity and daily life. Specifically I should note Guillaume's regular help and participation in technical problems.

I thank Jérôme Combet for his frequent support in different questions. Jérôme is a symphatic person and was an important part of our group. I was regretting when he has left us to go at ILL in Grenoble.

I thank a lot Jean-Marie Catala and Jean-Philippe Lamps for their help in PSS synthesis. They have synthesized a number of the samples which always had excellent quality.

I want to thank all members of our team for constructive discussions. I am thankful in particular to Pierre Petit, Diana Salem and François Schosseler as they accepted me in discussion of their subject, resulted in publication with me among co-authors.

I thank Catherine Foussat for technical support in numerous SEC experiments, as well as Yves Guilbert for his help in questions concerning NMR and TGA measurements.

I would like to thank my neighbors in office in different periods of my PhD formation: Sergei Obukhov, Manuel Durand, Julie Quillé and Volodymyr Savenko. They provided not only good

assistance for interesting discussions, but appropriate conditions for concentrated working in the office too.

I am thankful to Jean-François Legrand and Jean-Michel Guenet, former and present heads of our lab, for their kind participation in official events, as well as for short but constructive scientific discussions, which also took place.

I am really grateful to all collective of ICS. I should note that good conditions with quiet and friendly atmosphere are created in our lab, and this promotes pleasant and productive work.

I thank a lot University of Strasbourg and CNRS, as well as French state in general for opportunity to work and to live here. These three years are very important for my professional formation, being a nice period of my life too.

Specifically I want to thank Doctoral School of our university for offered interesting lectures, both scientific and humanitarian.

I would like to thank external scientists participated in realization of present thesis.

Bruno Demé from ILL has helped us two times for neutron scattering measurements and for our stay at ILL in general.

Benoît Heinrich from IPCMS (Strasbourg) provided an opportunity to use wide-angle X-ray scattering for the first time for our systems. A useful discussion about applied diffractometers was carried out as well.

Sergei Obukhov has kindly supported me during my first time in Strasbourg. His advises and help in my daily problems were quite important at that time.

During PhD formation I have participated in three conferences, in which given presentations and carried out discussions enriched me with new ideas and experience. I should specifically thank Charlotte Drappier met in Arcachon. She is not only amazing girl, but has also presented me to large number of experienced and especially young persons, providing active and useful communication.

I am very thankful to my former professors from Taras Shevchenko National University of Kyiv, in particular to L.A. Vretik, V.V. Zagnyi, V.G. Syromyatnikov and A.U. Kolendo. They have given me necessary knowledges and skills for further scientific formation. Specifically I thank a lot N.V. Kutsevol for large contribution in obtained grant for present PhD research, as well as for further support.

I thank my first teacher of Chemistry, N.V. Stolbtsova, for given great interest in this science and solid basis for further progress.

I thank a lot my parents, relatives and friends for their regular support and fine minutes spent together.

I thank Sveta for inspiration and offered great moments.

All personally mentioned people have made in a some way their contribution in the present study. I highly appreciate this help and participation, which supported me along all this complicated way within three years.

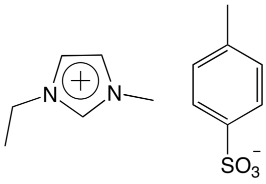
## French summary

Les liquides ioniques (LIs) sont des sels de point de fusion inférieur à 100 °C. Ils forment une nouvelle classe de solvants, notamment à cause de leurs propriétés d'ininflammabilité, de volatilité négligeable (faible tension de vapeur) et de conduction ionique élevée. Leur stabilité chimique, électrochimique ou thermique est, de surcroît, exceptionnelle. La communauté scientifique s'intéresse aujourd'hui, plus particulièrement, aux systèmes binaires constitués de polymères, ou de copolymères, et de LIs parce qu'elle s'efforce d'associer aux propriétés de conduction des LIs la tenue mécanique des polymères ou des gels, voire de créer de nouveaux matériaux intelligents. Ces systèmes binaires ont un autre intérêt pratique évident. Les LIs sont en effet des solvants de certaines polymérisations, ou copolymérisations, et de macromolécules réputées insolubles, comme la cellulose ou certains biopolymères. Ce pouvoir de solubilité des LIs n'est toutefois pas encore bien compris et les scientifiques y portent un intérêt croissant. L'étude des solutions de polyélectrolytes (PEs) dans les LIs vise à réaliser des progrès dans ce domaine. Ces solutions représentent aussi des systèmes binaires originaux. Parce que les LIs présentent des fluctuations de densité et de densité de charge électrique sur une échelle de distance plus grande que les liquides simples, on peut s'attendre à ce que le comportement d'un PE dans de tels solvants soit différent aussi bien de celui d'un polymère neutre en solvant organique que de celui d'un PE en solution aqueuse, en absence de sel ajouté. Dans ce domaine en émergence, tout reste à découvrir.

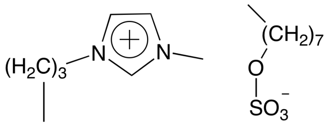
Notre projet de recherche avait deux buts principaux :

- Étudier la structure des solutions de PEs dans les LIs et la comparer à celle des solutions aqueuses de PEs et plus généralement à celle des solutions plus classiques de polymères neutres. La question était évidemment de savoir si les interactions électrostatiques restent cardinales dans de tels solvants. La structure est en fait la structure statique qui recouvre la conformation moyenne et l'état de dispersion des PEs dans les solvants. Elle s'étudie en utilisant principalement les techniques de diffusion de rayonnement (lumière, rayons X et neutrons) aux petits angles
- Étudier la structure locale des LIs ainsi que l'influence de la présence de PEs sur celle-ci. Cette structure locale s'étudie en utilisant la diffraction de rayons X ou de neutrons aux grands angles.

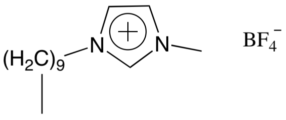
Les LIs offrent une grande flexibilité. Parmi tous les LIs qui pouvaient être abordés, nous en avons considéré trois (IL1, IL2 et IL3):



LI1



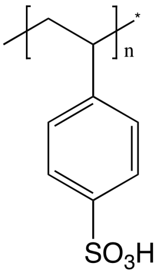
LI2



LI3

Les formules chimiques semi développées de ces LIs sont semblables, mais leurs natures sont fondamentalement différentes. Cela se traduit en particulier par des structures locales distinctes. Ainsi, les trois LIs présentent un phénomène d'agrégation à l'échelle nanoscopique, mais il est différent pour chacun d'eux. Dans le LI1, l'existence de «clusters» résulte d'une interaction entre groupes polaires; dans les LI2 et LI3, elle provient de la ségrégation de chaînes aliphatiques non-polaires. L'existence et la structure de ces «clusters» ont été étudiées en observant l'évolution des profils de diffraction de rayons X ou de neutrons lorsque l'on ajoute un PE, ou un solvant, et lorsque l'on augmente la température.

Le PE que nous avons utilisé dans cette étude est le polystyrène sulfonate (PSS), principalement sous forme acide.



Il a été préparé au laboratoire en sulfonant totalement des chaînes de polystyrène (PS) de différentes masses molaires M, ou différents degrés de polymérisation N, préalablement caractérisées par chromatographie d'exclusion stérique. C'est un PE fortement chargé (polyacide fort de fraction de charge chimique $f = 1$ dans les solvants polaires comme l'eau) dont la distribution de charge le long de la séquence chimique est statique (on parle de PE « quenched » en anglais). En solution dans l'eau, à cause du phénomène de condensation des contreions de Manning-Oosawa, la fraction de charge effective des macroions, définie par la relation $f_{eff} = b/l_B$, lorsque les contreions sont monovalents, où $b$ est la taille des monomères et $l_B$ la longueur de Bjerrum, est inférieure à 1 (de l'ordre de $2.5/7.1 = 0.36$). Nous avons étudié la structure des solutions aqueuses des formes acide (PSSH) et sel (PSSNa) de ce PE, en absence de sel ajouté. Nous avons ainsi montré que le PSSNa et le PSSH ont des fractions de charge effective $f_{eff}$ distinctes. Les protons $H^+$ sont en effet des contreions plus condensés que les contreions $Na^+$, ce qui conduit à une valeur de $f_{eff}$ plus faible pour le PSSH. Ce résultat provient de la nature particulière du cation $H^+$, qui ne contient pas d'électrons et a une taille extrêmement petite par rapport aux autres cations monovalents. Leur densité de charge étant plus grande, le phénomène de condensation est accentué et probablement favorisé également par l'établissement de liaisons hydrogène entre les protons $H^+$ et le macroion $PSS^-$. La forme acide permet toutefois de solubiliser le PSS dans quelques solvants organiques et dans les LIs. Nous avons ainsi pu étudier les solutions de PSSH dans l'éthanol et le DMSO. Le comportement du PSS dans ces solvants est celui d'un PE solvophobe. On peut aussi remarquer que la forme acide du PSS, en plus d'être soluble dans quelques solvants organiques et les LIs, présente l'avantage d'être bien adaptée aux expériences de diffusion de rayons X puisque les contreions $H^+$ ne donnent alors pratiquement aucun signal. Les fonctions de diffusion des macroions peuvent ainsi être déterminées directement, sans aucun marquage particulier. On peut également remarquer que le monomère des macroions $PSS^-$ a une formule chimique semi-développée quasi-identique à celle de l'anion du LI1. Cela conduit en particulier à des densités de longueur de diffusion et longueurs de contraste voisines.

Les principales caractéristiques structurales des macroions $PSS^-$, comme le rayon de giration $R_g$ et le second coefficient du viriel $A_2$, ont été mesurées dans l'eau et l'éthanol en présence d'électrolytes de faible masse molaire (LMEs) ajoutés. Pour cela, les expériences de diffusion ont été réalisées à température ambiante et en régime dilué ($c < c^*$; $c^*$ étant la concentration critique de recouvrement des chaînes). L'eau est un bon solvant du PSSH, comme elle l'est pour le PSSNa. L'éthanol est un solvant du PSSH plus pauvre puisque la conformation moyenne des chaînes de PSS est plus compacte. Ces comportements des macroions dans quelques solvants moléculaires, sous condition d'écrantage des interactions électrostatiques, ont ensuite été comparés à ceux du PSSH dans les LIs 1, 2 et 3.

Les solutions de PSSH dans les LIs 1 et 2 ont été étudiées, en utilisant également les techniques de diffusion de rayonnement. Les intensités diffusées, aussi bien dans le régime dilué que dans le régime semi-dilué ($c > c^*$), ne présentent alors aucun pic électrostatique caractéristique du comportement des PEs en solution aqueuse, en absence de sel ajouté. Le comportement du PSSH, et des PEs en général, dans les LIs est donc celui d'une macromolécule neutre. Cela résulte de deux effets : le premier est relié à la faible polarité des LIs, ou la faible valeur de leur constante diélectrique ($\varepsilon \cong 20$), qui conduit forcément à une fraction de charge effective des macroions plus faible (en accord avec l'augmentation de la longueur de Bjerrum); le second, à l'écrantage électrostatique important des ions des LIs. Les caractéristiques structurales des macroions PSS peuvent ainsi être déterminées par extrapolation des données à concentration nulle, comme pour les macromolécules neutres. De cette façon, nous avons démontré que le LI1 pouvait être considéré comme un bon solvant du PSS. L'interaction du PE avec le LI inclut certainement une faible contribution électrostatique, au moins locale, mais elle implique également d'autres interactions comme les interactions π-π (π-stacking) et les liaisons hydrogène qui peuvent jouer un rôle cardinal. Ce caractère bon solvant du LI1 est démontré par les valeurs mesurées pour les paramètres structuraux $R_g$ et $A_2$, ainsi que par la décroissance du facteur de forme $P(q)$, au delà du domaine de Guinier ($qR_g > 1$), en $q^{-1/\nu}$, où $\nu$ est l'exposant de volume exclu ($\nu = 3/5$, ou $0.588$ d'après le Groupe de Renormalisation) (Figure 1).

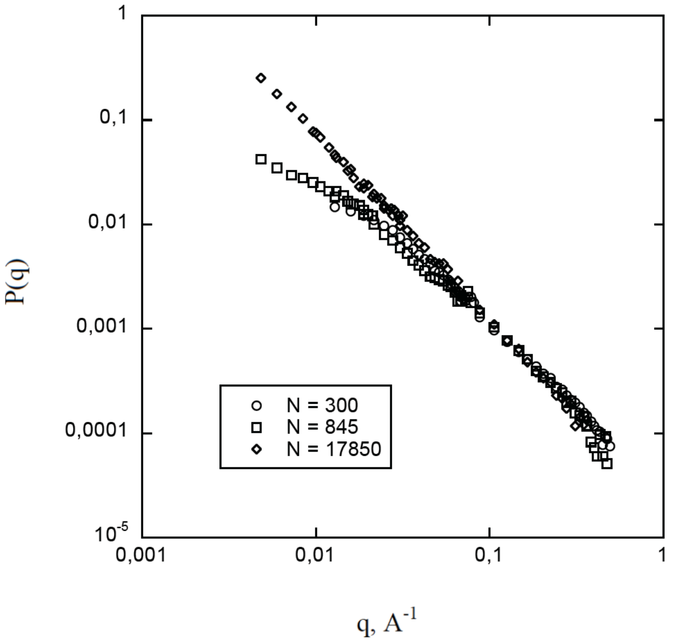
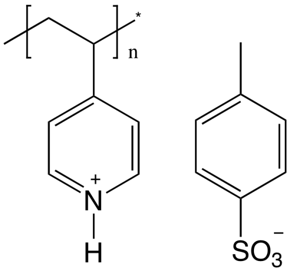


Figure 1. $P(q)$ pour PSS de différentes valeurs de $N$ dans le LI1.

Les valeurs de $R_g$ et $A_2$ pour le PSSH dans le LI2 sont plus faibles. Ce résultat peut être interprété comme une baisse de la qualité du solvant associée à une diminution de la polarité du LI et une interaction plus faible du PSS avec le LI. On peut aussi conjecturer qu'il est dû à l'existence de «clusters» hydrophobes de taille plus grande avec le LI2. Ces «clusters» sont alors responsables d'une conformation moyenne plus compacte du PSS, résultant de leur décoration par les chaînes de PSS. Finalement, le LI3 est un mauvais solvant du PSS à température ambiante puisqu'il ne le dissout pas à cette température. Le cation imidazolium du LI3 contient un radical alkyle apolaire, ou fortement hydrophobe, responsable de l'interaction avec PSS. De surcroît, le phénomène d'association en «clusters» s'intensifie avec le LI3, en particulier par comparaison avec le LI2. Cela joue certainement un rôle essentiel dans la perte de solubilité du PSS dans le LI3 à température ambiante.

En conclusion, à la différence des solvants organiques usuels, les LIs peuvent être de bons solvants du PSS, malgré leur faible polarité. C'est en fait leurs propriétés structurales, et en particulier leur capacité à former des «clusters» hydrophobes, ou non-polaires, qui règle leur caractère bon ou mauvais solvant. La notion de qualité de solvant est donc d'origine distincte de celle qui prévaut pour les solvants usuels et qui est reliée aux seules polarisabilités des molécules et des monomères.

Nous avons aussi montré que le PSS, classiquement considéré comme un PE fort, peut devenir un PE faible lorsqu'il est dans certains solvants. Ce comportement est dû à la possibilité de formation de liaisons entre les protons et les macroions. On peut ainsi supposer que dans un milieu LI, peu polaire et peu basique, les monomères du PSSH ne sont que partiellement dissociés. Pour étudier des effets électrostatiques dans les systèmes binaires composés de PEs et de LIs il faut pourtant arriver à une dissociation complète des monomères des PEs. Pour l'atteindre, nous avons considéré le p-toluènesulfonate de poly(4-vinylpyridinium) (P4VP-Tos). Ce PE est en effet a priori complètement ionisé.



Nous avons pu observer la présence d'un faible pic électrostatique dans les intensités diffusées par les solutions de P4VP-Tos dans le LI1 et une augmentation de la rigidité locale des macroions conduisant à une conformation plus étirée. L'écrantage des interactions électrostatiques par les ions du LI1 n'est donc pas total dans ce système binaire composé du

P4VP-Tos et du LI1. De ce point de vue, il faut remarquer que, bien que constitués principalement d'ions, les LIs étant souvent associés sont moins efficaces pour l'écrantage des interactions électrostatiques. Le comportement structural d'une véritable macromolécule neutre, la poly(vinylpyrrolidone) (PVP), dans le LI1 a aussi été étudié. Les chaînes de PVP sont fortement agrégées. La dissolution de la PVP dans le LI1 n'est donc pas réalisée à l'échelle moléculaire.

Le PSSH occupe donc une position intermédiaire entre les PEs complètement dissociés et les polymères neutres, sa fraction de charge chimique pouvant varier de façon importante, suivant la nature du solvant. La présence de protons acides augmente la solubilité du PSSH dans les milieux modérément polaires, et en particulier dans les LIs. Simultanément, l'existence d'une forme non dissociée du PSSH peut éliminer les effets électrostatiques lorsqu'il se trouve en solution dans un LI. Le PSSH dans les LIs a le même type de comportement que lorsqu'il est solubilisé dans les solvants moléculaires en présence d'électrolytes de faible masse molaire (LMEs). De façon générale, les PEs dans les LIs ont des comportements distincts suivant la nature chimique des deux constituants PE et LI, et l'existence de «clusters» dans le LI joue un rôle important.

*Summary*

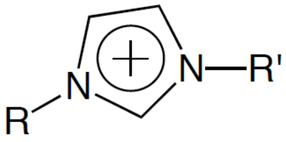
# *General introduction*

## Ionic liquids

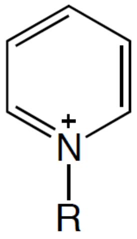
Ionic liquids (ILs) are salts with melting point $T_m < 100^{o}C$[1-3]. Those of them, which are liquid at room temperature, are called room-temperature ionic liquids (RTILs). Although ILs were discovered in the end of 19th century, their intensive study began in the 90th years of 20th century. At present ILs have diverse applications in science and technology. They are used like electrolytes for batteries[4,5], drugs in pharmaceutics[6], dispersants[7], gas storage agents[8] etc. But probably the most important application of ILs for the moment is their use like solvents[9,10]. They have a high dissolving ability with respect to a number of inorganic and organic compounds, including polymers[11,12]. In addition ILs in a role of solvents possess another important properties: low vapour pressure, large liquid range, noninflammability, wide electrochemical window etc. Numerous ILs are characterized by nontoxicity and ability to biodegradation as well. Thus ILs are related to green solvents[13]. Another important feature of ILs is a diversity of their chemical structures and a flexibility in their synthesis, which gives possibility to create a IL for a some specific application. Due to this, ILs are often called designer solvents[14].

For the moment the most important fields of ILs application like solvents are organic synthesis and cellulose processing. In the first case ILs often act not only like a solvent, but like a catalyst as well. In the second case ILs is one of a few types of solvents, able to dissolve the cellulose. This dissolution happens mainly due to the hydrogen bonds formation. Although ILs are built up from ions, rather often the electrostatic interaction with solute is not a dominant one for this type of solvents. Hydrogen bonding, dipole-dipole forces, π-π stacking, C-H···π and Van der Waals interactions largely contribute to solvent properties of ILs. A reason for that is a usually big size of ions along with delocalization of a charge, which doesn't promote strong electrostatic interaction. Instead a presence of different functional groups in complex ILs structure provides another types of interaction. Thus, a description of these solvents from purely electrostatic point of view, like for usual molten salts, is not correct. Even an introduction of some integral characteristics like the dielectric constant is not completely correct as well, because ILs properties depend on local effects at molecular level. That is ILs can't be considered like continuous dielectric medium. Every IL should be regarded taking into account its particular complex structure.

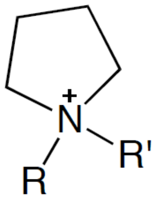
By their structure ILs are commonly divided into several classes. The structure of the cation of almost all used ILs corresponds to one of the following types:



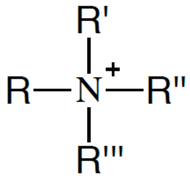
Imidazolium



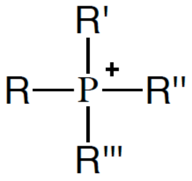
Pyridinium



Pyrrolidinium



Ammonium



Phosphonium

The most of commercially available ILs are imidazolium-based, followed by ammonium-based. Classical imidazolium-based ILs are 1,3-disubstituted. But there are examples of 1-monosubstituted, which are much more acidic, and 1,2,3-threesubstituted, which usually have lower $T_m$ due to disappearance of a hydrogen bond between anion and proton of C2 atom of imidazolium ring. This proton is the most acidic one between those linked to carbon atoms of the aromatic ring. Properties of ammonium cations and corresponding ILs mainly depend on a nature of substituents and can be largely modified by varying a structure of the latter. For example these substituents can be rather long alkyl chains, giving hydrophobicity to the corresponding cation, or contain some polar functional groups, providing the cation with a hydrophilic character.

Anions for ILs are more diverse by their chemical nature and more classical from chemical point of view. The most often used anions are the next ones: $Cl^-$, $Br^-$, $BF_4^-$, $PF_6^-$, $CH_3COO^-$, $CF_3SO_3^-$, $(CF_3SO_3)_2N^-$ etc. With respect to a type of anion ILs can be divided into halogen-containing and halogen-free ones. A majority of ILs contains a halogen like a simple anion or like a part of a complex one. In particular, the use of an IL with $Cl^-$ or $Br^-$ increases its dissolving ability due to a tendency of these anions to form hydrogen bonds. For example, for dissolution of the cellulose this type of ILs is used. But the presence of halogen can cause the formation of dangerous HX (X = F, Cl, Br) via hydrolysis or thermal decomposition. Thus halogen-free ILs are usually less toxic and less corrosive.

## Polyelectrolytes

Polyelectrolytes (PEs) are polymers carrying ionizable groups[15-18]. The latter are able to dissociation in a polar media. The dissociation leads to a formation of polyions, which can be charged either negatively (polyanions), either positively (polycations), and oppositely charged counterions. The latter can be dispersed in the solution (free counterions) or condensed around the polyions (condensed counterions). Thus, for strongly charged polyelectrolytes, due to the Manning-Oosawa counterion condensation process[19,20], part of counterions are condensed and the effective charge fraction $f_{eff}$ becomes less than the chemical charge fraction $f$. $f_{eff}$ mainly depends on the valence as well as on the nature of counterions. According to the Manning-Oosawa approach and concerning monovalent counterions, $f_{eff}=b/l_B$, where $b$ is the monomer contour length and $l_B$ is the so-called Bjerrum length (Eq. 3). $f_{eff}$-value is also the fraction of free counterions.

In order to study the conformational characteristics of a single polymer chain in a solution, one can investigate the dilute regime in which intermolecular correlations are negligible. This regime corresponds to a concentration range $c < c^*$, $c^*$ being the critical overlap polymer concentration. For neutral polymer, it is usually defined by

$$c^* = 1/[\eta] \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity.

But in dilute PE solution charged groups interact with each other through the unscreened Coulomb potential, as distance between them is smaller than the Debye screening length $r_D$

$$r_D^{-2} = k^2 = 4\pi l_B I, \text{ with } I = \sum_i c_i z_i^2 \qquad (2)$$

$c_i$ is the concentration of $i$-ion, $z_i$ being its valence; $l_B$, the Bjerrum length

$$l_B = e^2/(4p\varepsilon k_B T) \qquad (3)$$

The latter is the distance at which the electrostatic interaction between two elementary charges $e$ in the medium of dielectric constant $\varepsilon$ is equal to the thermal energy $k_BT$. Thus $l_B$ is a constant for the used solvent at a certain temperature (in water at room temperature $l_B=7.1$ Å, but it is increased, about 4 times, in a IL).

The electrostatic interaction is exponentially screened on the length scales larger than $r_D$. At distances below $r_D$ this interaction leads to a correlation between chains in solution. This correlation is characterized by the so-called electrostatic correlation length $\xi$. In the dilute regime it is the average distance between chains and scales like $\xi \sim c^{-1/3}$. Another consequence of the electrostatic repulsion between charged groups is a large increase in the chain stiffness, or persistent length. In the semidilute regime PE chains begin to overlap and $\xi$ represents the mesh size of the temporary network formed by the chains, or macroions, according to the isotropic model initially proposed by de Gennes. $\xi$ then scales like $\xi \sim c^{-1/2}$. The crossover between dilute and semidilute regimes, or the change in the exponent of the scaling law $\xi(c)$, allows to determine $c^*$ for salt-free PE solutions. Thus, it has been demonstrated that $c^*$ scales as $c^* \sim N^{-2}$ with the degree of polymerization $N$, in agreement with an elongated conformation for PE chains.

In order to achieve a conformational behavior similar to that of a neutral polymer in a good solvent, the electrostatic interaction should be screened. A way to this is the addition of a low-molecular electrolyte (LME) in the PE solution, which provokes the decrease of $r_D$-value following Eq. 2.

## Characterization of polymer solutions in the dilute regime using scattering techniques: determination of molar mass, average size and solvent quality

After screening of electrostatic interactions between charged groups of a PE, its macromolecular characteristics can be determined by means of a scattering technique[21-25]. These characteristics include the average degree of polymerization $N$ (which is the weight-average one in this case) and the z-average of the mean-square radius of gyration $<R_g^2>^{1/2}$ (further denoted as $R_g$ for simplicity). The second virial coefficient $A_2$, which characterizes the dispersion state, or the solvent quality, can also be measured.

An illustration of a radiation scattering experiment is shown in Figure 1.

Static scattering measurements give the dependence of the scattered intensity $I$ on the scattering vector $q$. The latter is defined as follows (X-ray and neutron scattering):

$$q = 4\pi/\lambda \sin(\theta/2) \qquad (4)$$

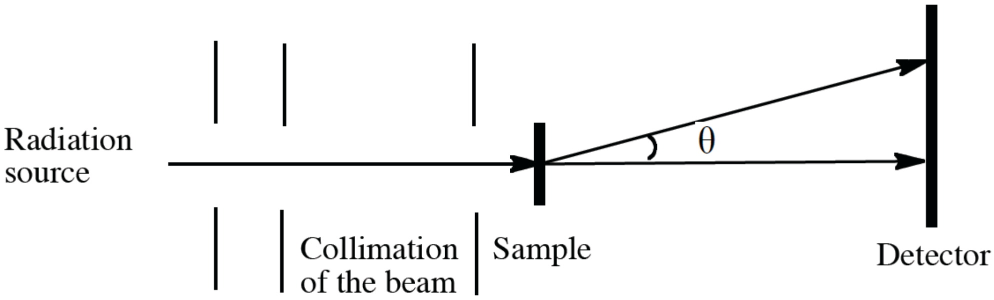


Figure 1. Basic sketch of a radiation scattering experiment (static scattering).

$\lambda$ is the wavelength of the incident beam, $\theta$ is the scattering angle.

For $I$ $(cm^{-1})$ one has the relationship[26]

$$I(q,c) = K^2 c g(q,c) \qquad (5)$$

where $K$ $(cm)$ is the contrast length, $K^2$ $(cm^2)$ is the contrast factor between polymer and solvent, $c$ $(cm^{-3})$ is the polymer concentration and the term $g(q,c)$ (unitless) represents the total correlation function

$$g(q,c) = \frac{1}{N} \sum_{\alpha,\beta} \sum_{i,j} < \exp[-i\vec{q}(\vec{r}_i^{\,\alpha} - \vec{r}_j^{\,\beta})] > \qquad (6)$$

where $\alpha$ and $\beta$, the chain indexes; $i$ and $j$, the monomer indexes.

By regrouping the intramolecular and intermolecular pairs, we have:

$$g(q,c) = g_1(q) + c g_2(q) \qquad (7)$$

$g_1(q)$ and $g_2(q)$ represent the intra- (form factor) and intermolecular correlations respectively. Here, we assume that both don't depend on $c$. If the solution is diluted, $g(q,c) \cong g_1(q)$. In its turn

$$g_1(q) = N{*}P(q) \qquad (8)$$

$P(q)$ being the form factor normalized to unity at $q = 0$. When intermolecular correlations are negligible, we have also:

$$P(q) = I(q)/I(0) \qquad (9)$$

$P(q)$, as well as $g_1(q)$ decribes the average shape of the macromolecules. However, at small $q$-values or more precisely in the so-called Guinier-range ($qR_g < 1$), $P(q)$ doesn't any more depend on the shape of the macromolecules and is only determined by their average size:

$$P(q)^{-1} = 1 + q^2R_g^2/3 \qquad (10)$$

Thus $R_g$ can be measured from the variation of $P(q)$, or $1/P(q)$, with $q^2$. That can be done in a following way, which allows determination of $N$ and $A_2$ as well. At finite concentration in a real solution one has:

$$K^2c/I(q,c) = 1/N(1 + R_g^2q^2/3) + 2A_2c \qquad (11)$$

Obviously a value of $N$ can be found by double extrapolation at $c \rightarrow 0$ and $q \rightarrow 0$. The best way to perform this extrapolation is by drawing a Zimm plot $K^2c/I(q,c)$ vs. $(q^2 + k'c)$, with $k'$ being an arbitrary constant. Two series of straight lines should be drawn from experimental points, one corresponding to the same angle and another one to the same concentration. Their extrapolation to $c = 0$ and to $q = 0$ gives a value of $1/N$. In the same time, the slope of the line extrapolated to $c = 0$ gives a $R_g$-value, and the one of the line extrapolated to $q = 0$ yields a $A_2$-value.

As mentioned above, the extraction of a $R_g$-value in this way is correct at $qR_g < 1$. Sometimes proper measurements at this condition are impossible. In this case one can explore a $q$-range with a condition $q < 3/R_g$ and then calculate $R_g$-value by using a fit of $g_1(q)$ with a Debye function $g_D(q)$

$$g_D(q) = N[2(x - 1 + exp(-x))/x^2], \text{ with } x = q^2R_g^2 \qquad (12)$$

$g_1(q)$ is then obtained by extrapolation to $c = 0$ of Eq. 7.

So, by performing scattering measurements for several different polymer concentrations in dilute regime, one can determine average molar mass, average size and solvent quality for a polymer in a specific solvent. For the case of a PE, LME should be added to the solution for such a determination, as discussed above.

## Small-angle X-ray and neutron scattering

In the present work small-angle X-ray and neutron scattering (SAXS and SANS respectively) were applied[27,28]. Description of these methods is in complete agreement with general description of scattering technique, given above. Nevertheless SAXS and SANS possess their own features, that should be briefly discussed here. These features are mainly linked with a special nature of X-ray and neutron radiation. Practically this affects the calculation of the contrast factor $K^2$, carried out in a different way for different scattering methods.

X-rays are electromagnetic waves, which are scattered by electrons. $K^2$ $(cm^2)$ for X-ray scattering is expressed as follows:

$$K_x^2 = \gamma_e^2(\rho_{e,u} - \rho_{e,s})^2 V_u^2/M_u^2 N_a^2 \qquad (13)$$

Here $\rho_{e,u}$ and $\rho_{e,s}$ are the electron densities of the repetitive unit (monomer) and the solvent molecule respectively, which may be considered as elementary scatterers for the small-angle domain; $V_u^2$ and $M_u$ are respectively molar volume and molar mass of the repetitive unit; $\gamma_e$ is the electron gyromagnetic ratio; $N_a$, Avogadro's number. Thus $K_x^2$ depends on the difference between electron densities of the repetitive unit and the solvent. Some heavy atoms in the repetitive units obviously lead to an increase in the scattered intensity. In the same time, high content of heavy atoms in the solvent significantly increases absorption of X-rays, leading to a low transmission.

Neutrons are matter waves, which are mainly scattered by atomic nuclei. $K^2$ $(cm^2)$ for neutron scattering is expressed in the following way:

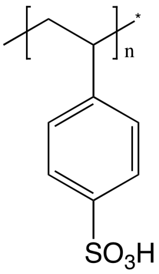
$$K_n^2 = (\sum b_i - (Vs/Vu)\sum b_j)^2 \qquad (14)$$

Here $b_i$ and $b_j$ are the coherent scattering lengths related to the repetitive unit and the solvent molecule respectively. $b$-value is a particular characteristic of the considered isotope of an element, and measures the strength of its coherent scattering. If a taken isotope has nonzero nuclear spin, an incoherent scattering is provided too. The latter adds a flat background noise, which is rather undesirable and has to be subtracted to obtain the coherent signal that contains all the information about the structure. One way to eliminate the incoherent scattering is an isotopic exchange, for example often used exchange of protons by deuterium[29].

To get X-rays in a laboratory, $K_\alpha$ radiation of Cu with $\lambda = 0.154\ nm$ is used. Neutrons are produced by nuclear reactors in specialized research centers (as ILL at Grenoble and LLB at Saclay, France). A detailed description of instruments used for scattering studies in the present work is given in annex.

## PEs and ILs chosen for the present study

The problem of the choice of particular PEs and ILs was treated with a special care. Poly(4-styrenesulfonic acid), that is polystyrene sulfonate in the acid form (PSSH) was taken as the first PE:



PSS is a classical example of a strong PE, well studied in aqueous solutions by a number of researchers[30,31], as well as by our team[32,33].

Different salt forms of PSS were usually taken for the previous studies, the most often PSSNa. But the latter appeared insoluble in most ILs, thus the acid form of PSS (PSSH) was tested in order to increase the PE solubility. Indeed, the use of protons like counterions provided required solubility of PSS in our ILs. Higher solubility of acids in comparison with their salts in polar organic solvents is typical. This is usually related to the possibility of hydrogen bonds formation in the case of the acids, as well as to the fact, that organic solvents have lower solvating ability with respect to ions in comparison with that of water. In the same time, neutral polar compounds can be easily solvated by polar organic solvents. Thus the acids, which can exist in a form of nondissociated molecules, are better soluble in moderately polar solvents than salts, which have ionic structure at any conditions. Most of ILs, by their chemical structure, can be also related to organic solvents. Moreover by their polarity they are close to short-chains alcohols. So higher solubility of PSSH in taken ILs with respect to that of PSSNa was expectable.

As mentioned above, only aqueous solutions of PSS in the salt forms were studied in details. Some attention was paid to behavior of PSSH in aqueous solutions[34]. That is a point of interest for us, because behavior of a PE in an IL is reasonable to study in parallel with that in water for comparison. Thus before experiments with the PE solutions in ILs we investigated corresponding aqueous solutions for the case of not enough studied PSSH. Small differences with respect to PSSNa have been found.

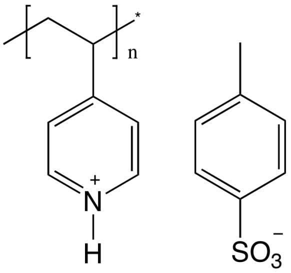
Taken for the present work ILs by their chemical structure belong to organic compounds. Thus, a comparison between a PE behavior in these ILs and in usual organic solvents is reasonable too. As PSSH behavior in organic solvents was also not yet enough explored, we have performed related scattering experiments, using classical polar organic solvents: protic one, ethanol, and aprotic one, DMSO. This study was possible due to solubility of PSSH in these organic solvents, which is not the case for PSSNa.

By these comparisons we can see, how special ionic structure of an IL influences a PE behavior in this new type of solvents with respect to its behavior in common solvents, water and organic ones.

Also, as ILs are ionic medium, one can suppose that PE charge screening takes place in these solvents. Thus a comparison with PE solutions in water and organic solvents suggest an added LME in two last cases. So PSS solutions in water and organic solvents were studied at two different conditions: first, in absence of LME, to see the influence of protons as counterions and the nature of solvent on the electrostatic peak position and the effective charge fraction $f_{eff}$ of PSS; second, in presence of LME, to provide PSS charge screening for correct comparison with PSS behavior in ILs. HCl was used as LME, because it has the same cation like PSSH.

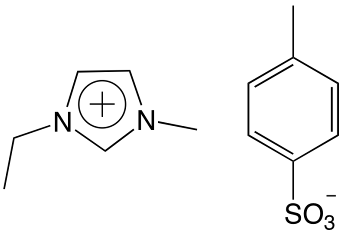
When PSSH is used as PE, one should remember the next important remark. PSSH is a strong PE, like PSSNa, and is fully dissociated from chemical point of view in water[26]. That means an absence of covalent linking between ionized groups and counterions, thus the PE chemical charge fraction in aqueous solutions equals to one. Although the counterion condensation process can lead to a lower $f_{eff}$-value. But there is a basic possibility in PSSH for covalent linking between sulfo groups and protons, which can be realized in a solvent, less polar than water. Thus PSSH can exist in the neutral form. This should be kept in mind for the analysis of our results. Further for simplicity let’s call PSSH as PSS.

The second PE chosen for the study is poly(4-vinylpyridinium p-toluenesulfonate) (P4VP-Tos):



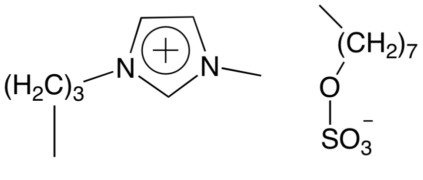
It’s composed of polycation of aromatic type (like polyanion of PSS is) and anion almost identical to PSS-unit. P4VP-Tos is a true PE in any kind of solution, that is it’s chemical charge always equals to 1, because covalent linking between macroion and counterions is impossible for P4VP-Tos. This PE was studied in the IL1 (see below). It appeared soluble in the IL, probably due to large size of ions and their complex organic structure, which provides efficient interaction with components of IL1. The chemical structure of P4VP-Tos allows supposing that corresponding monomer should be an IL.

Concerning chosen ILs, the first one is 1-ethyl-3-methylimidazolium tosilate (EMIM-Tos), denoted as IL1:



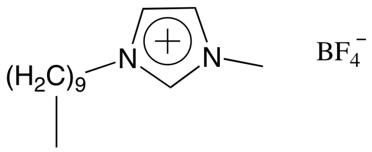
EMIM-Tos has typical for an IL cation of imidazolium type with short alkyl chains and anion almost identical to PSS-unit. The latter provides a decrease in the number of components in the system, which is important for studying the local structure of the IL in presence of the PE. This study could be also interesting in order to explore different aspects of mutual influence of ILs and PEs, which both are charged systems.

The second IL taken for the study (IL2) is 1-butyl-3-methylimidazolium octylsulfate (BMIM-OS):



This IL2 has a gross formula close to the one of IL1, but another chemical structure of anion. Instead of aromatic one, present in IL1, aliphatic one is taken for IL2. Normally aliphatic anion should be more inert in sense of interaction with rather polar solute. Indeed PSS has lower solubility in IL2, than in IL1. In the latter 0.5M PSS solution could be prepared, while in IL2 0.2M PSS concentration is the highest one, which could be achieved.

The third IL applied for the study (IL3) is 1-decyl-3-methylimidazolium tetrafluoroborate (DMIM-TFB):



Again the gross formula is rather close to the ones of IL1 and IL2, but chemical structure is basically changed. A long aliphatic tail belongs now to the cation, so the anion represents just a small group bearing the charge. A solubility of PSS in IL3 appeared even lower than in IL2. At room temperature PSS concentration equal to 0.05M was achieved, while at 70°C 0.10M PSS solution can exist as well. Such a decrease of PSS solubility in IL3 compared to IL2 is probably related to the fact that the aliphatic tail belongs now to the cation, which is mainly responsible for interaction with PSS. Another reason can be a low tendency of $BF_4^-$ anion to hydrogen bonding with acidic protons of PSS[35]. IL3 on the contrary to IL1 and IL2 is not miscible with water, thus belonging to a class of hydrophobic ILs[36,37]. That is a consequence of a hydrophobic nature of both cation and anion in IL3[38]. The latter was finally used in the present work only to study a ILs nanoscale structure.

Except direct way via solute-solvent interaction, ILs influence on PE behavior in a solution can be varied via modification of nanostructure of these solvents.

Thus, the use of these ILs gives the possibility to follow an influence of the basic changes of ILs chemical structure on their solvent properties. First, general properties are an object of study, that is the PE average conformation in ILs and the solvent quality of the latter with respect to the PE. This was studied by using PSS as a classical PE, soluble in a wide range of solvents. Second, specific solvent properties of ILs provided by their ionic structure are a point of interest too. For this P4VP-Tos was taken, being less common, but true PE in all types of solvents. Thus electrostatic effects of ILs on charged solute could be displayed.

So, the present work was performed in the following steps. Nanoscale structure of the neat ILs was investigated in order to see an influence of the IL chemical structure on heterogeneities formation. An evolution of these heterogeneities under action of different factors was studied too, in particular under addition of water, a low-polar solvent and a PE, as well as at heating. Then LME-free solutions of PSS were studied in water and organic solvents to see an influence of the nature of counterions and the solvent on the $f_{eff}$-value of PSS. After that a detailed comparison of PSS behavior in IL1, IL2, water and ethanol (with added LME in two last cases) was performed in order to characterize the PE conformation and solvent quality for different ILs compared to that for water and organic solvent. Found changes of $R_g$ and $A_2$ were explained taking into account specific chemical structure of the solvents and their interaction with PSS. Finally a difference in P4VP-Tos behavior in water and IL1 was found, displaying electrostatic influence of the IL on persistent length and conformation of the PE charged chains.

## References

[1]C. Chiappe and D. Pieraccini, *J. Phys. Org. Chem.*, **18** (2005), 275–297
Ionic liquids: solvent properties and organic reactivity

[2]P. Wasserscheid and M. Keim, *Angew. Chem. Int. Ed.*, **39** (2000), 3772–3789
Ionic Liquids – New « Solutions» for Transition Metal Catalysis

[3]T. Welton, *Chem. Rev.*, **99** (1999), 2071-2083
Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis

[4]J.-K. Kima, A. Matica, J.-H. Ahnb and P. Jacobssona, *Journal of Power Sources*, **195** (2010), 7639–7643
An imidazolium based ionic liquid electrolyte for lithium batteries

[5]M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, R. Scrosati, *Nature Materials*, **8** (8) (2009), 621-629
Ionic-liquid materials for the electrochemical challenges of the future

[6]R. Ferraz, L. C. Branco, C. Prudencio, J. P. Noronha, and Z. Petrovski, *ChemMedChem*, **6** (2011), 975 – 985
Ionic Liquids as Active Pharmaceutical Ingredients

[7]M. Boukherissa, F. Mutelet, A. Modarressi, A. Dicko, D. Dafri and M. Rogalski, *Energy & Fuels*, **23** (2009)**,** 2557–2564
Ionic Liquids as Dispersants of Petroleum Asphaltenes

[8]D. J. Tempel, P. B. Henderson, J. R. Brzozowski, R. M. Pearlstein and H. Cheng, *J. Am. Chem. Soc.*, **130** (2008), 400-401
High Gas Storage Capacities for Ionic Liquids through Chemical Complexation

[9]M. Mora-Pale, L. Meli, T. V. Doherty, R. J. Linhardt, J. S. Dordick, *Biotechnology and Bioengineering*, **108** (2011), 1229-1245
Room Temperature Ionic Liquids as Emerging Solvents for the Pretreatment of Lignocellulosic Biomass

[10]D. W. Morrison, D. C. Forbesa and J. H. Davis, *Jr. Tetrahedron Letters*, **42** (2001), 6053–6055
Base-promoted reactions in ionic liquid solvents. The Knoevenagel and Robinson annulation reactions

[11]T. Ueki, M. Watanabe, *Macromolecules*, **41** (2008), 3739-3749
Macromolecules in ionic liquids: progress, challenges, and opportunities

[12]Y. He, T.P. Lodge, *Chem. Commun.*, (2007), 2732-2734
A thermoreversible ion gel by triblock copolymer self-assembly in an ionic liquid

[13]M. J. Earle and K. R. Seddon, *Pure Appl. Chem.*, **72** (2000), 1391–1398
Ionic liquids. Green solvents for the future

[14]M. Freemantle, *Chem. Eng. News*, **76** (1998), 13, 32-37

Designer solvents - Ionic liquids may boost clean technology development

[15]A. V. Dobrynin, M. Rubinstein, *Prog. Polym. Sci.*, **30** (2005), 1049–1118
Theory of polyelectrolytes in solutions and at surfaces

[16]J. L. Barrat, J. F. Joanny, *Adv Chem Phys*, **94** (1996), 1–66
Theory of polyelectrolyte solutions

[17]P.G. De Gennes, P. Pincus, R.M. Velasco, F. Brochard, *J. Phys. France*, **37** (1976), 1461-1473
Remarks on polyelectrolyte conformation

[18]M. Hara (Ed.), *Marcel Dekker*, New York 1993
Polyelectrolytes: Science and Technology

[19]G. S. Manning, J. Ray, *J Biomol Struct Dyn*, **16** (1998), 461–76
Counterion condensation revisited

[20]M. Muthukumar, *J Chem Phys*, **120** (2004), 9343–9350
Theory of counter-ion condensation on flexible polyelectrolytes: adsorption mechanism

[21]B.H. Zimm, *J. Chem. Phys.*, **16** (1948), 1093-1099
The Scattering of Light and the Radial Distribution Function of High Polymer Solutions

[22]B. Hammouda, D. L. Ho, *Journal of Polymer Science: Part B: Polymer Physics*, **45** (2007), 2196–2200
Insight Into Chain Dimensions in PEO/Water Solutions

[23]E. C. Lee and S. J. Muller, *Macromolecules*, **32** (1999), 3295-3305
Flow Light Scattering Studies of Polymer Coil Conformation in Solutions in Extensional Flow

[24]O. Glatter, O. Kratky, *Eds. Academic Press*, (1982)
Small Angle X-Ray Scattering

[25]J. S. Higgins, H. C. Benoît, *Oxford U. Press*, (1994)
Polymers and Neutron Scattering

[26]M. Rawiso, *J. Phys. IV France*, **09** (1999), Pr1-147-Pr1-195
De l'intensité à la structure en physico-chimie des polymères

[27]C. D. Putnam, M. Hammel, G. L. Hura and J. A. Tainer, *Quarterly Reviews of Biophysics*, **40**, 3 (2007), 191–285
X-ray solution scattering (SAXS) combined with crystallography and computation: defining accurate macromolecular structures, conformations and assemblies in solution

[28]G. Cheng, Y. B. Melnichenko, G. D. Wignall, F. Hua, K. Hong and J. W. Mays, *Macromolecules*, **41** (2008) 9831-9836
Small Angle Neutron Scattering Study of Conformation of Oligo(ethylene glycol)-Grafted Polystyrene in Dilute Solutions: Effect of the Backbone Length

[29]A. Brulet, D. Lairez, A. Lapp and J.-P. Cotton, *J. Appl. Cryst.*, **40** (2007), 165–177

Improvement of data treatment in small-angle neutron scattering

[30] M. Nierlich, F. Boué, A. Lapp, R. Oberthur, *J. Phys. France*, **46** (1985), 649-655
Radius of gyration of a polyion in salt free polyelectrolyte solutions measured by S. A. N. S.

[31] F. Boué, J-P. Cotton, A. Lapp, G. Jannink, *J. Chem. Phys.*, **101** (1994), 2562-2568
A direct measurement of the polyion conformation in aqueous solutions at different temperatures. Small angle neutron scattering of PSSNa using zero average and full contrast

[32] J. Combet, F. Isel and M. Rawiso, *Macromolecules*, **38** (2005), 7456-7469
Scattering Functions of Flexible Polyelectrolytes in the Presence of Mixed Valence Counterions: Condensation and Scaling

[33] J. Combet, M. Rawiso, C. Rochas, S. Hoffmann, F. Boué, *Macromolecules*, **44** (2011), 8925-8935
Structure of polyelectrolytes with mixed monovalent and divalent counterions : Poisson-Botzmann analysis and SAXS measurements

[34] L. Kotin and M. Nagasawa, *J. Am. Chem. Soc.*, **83**, 5 (1961) 1026–1028
A Study of the Ionization of Polystyrene Sulfonic Acid by Proton Magnetic Resonance

[35] R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, **124** (2002), 4974-4975
Dissolution of Cellose with Ionic Liquids

[36] Z. Samec, J. Langmaier and T. Kakiuchi, *Pure Appl. Chem.*, **81**, 8 (2009), 1473–1488
Charge-transfer processes at the interface between hydrophobic ionic liquid and water

[37] L. Zhang and X. Wang, *J. Sep. Sci.*, **33** (2010), 2035–2038
Hydrophobic ionic liquid-based ultrasound assisted extraction of magnolol and honokiol from cortex Magnoliae officinalis

[38] J. Ranke, A. Othman, P. Fan and A. Muller, *Int. J. Mol. Sci.*, **10** (2009), 1271-1289
Explaining Ionic Liquid Water Solubility in Terms of Cation and Anion Hydrophobicity

# *CHAPTER 1*

# *Nanostructure of the ionic liquids*

# Introduction

The diversity of IL chemical structures provides different types of nanoscale organization. IL can be either structurally homogeneous, either display some aggregations at nanoscale length. In recent years special attention was paid to nanostructure of IL.

Usually an existence of structural heterogeneities is related to asymmetrical structure of ionic liquids and to a presence of a long aliphatic tails (with a number of carbon atoms $n > 10$)[1,2]. The latter possess a tendency to segregation. Thus a microphase separation of the hydrophilic ionic head groups and hydrophobic alkyl chains occurs. In the resulted layered structure ionic head groups are separated by nonpolar regions. That gives rise to structural correlations, which induce an occurrence of a peak at scattering profile. A position of the peak depends on a number of carbon atoms in the aliphatic tail. Correlation distance increases at around 2Å for every additional methylene difference.

Short-range order is also typical for IL formed by rather small and symmetrical ions. It's the case for [C1mim]-based IL[3] and for alkylammonium-based IL (with Alk = Et and Pr)[4]. An order is provided in this case by electrostatic and hydrogen bond interactions between polar groups, as well as by hydrophobic interaction between short alkyl chains ($n < 4$).

IL with intermediate alkyl chain length ($4 \leq n \leq 10$) was considered during long time like structurally homogeneous. Only recently a number of molecular dynamics (MD) simulation studies shown an existence of segregation due to interaction between alkyl chains[5,6]. Later this segregation was observed by means of X-ray[7] and neutron[8] diffraction. A size of heterogeneities appeared linearly dependent on alkyl chain length, thus proving that polar groups are separated by aggregates of nonpolar chains.

A position of an anion with respect to a cation in IL is another interesting question, related to IL structure. A preferencial configuration of a single ion pair for [C4mim][$BF_4$] was found, using a gas phase *ab initio* calculation[9]. In this configuration the anion interact with the hydrogen bonded to the C2 carbon atom between the two nitrogen atoms, as this hydrogen is the most acidic one. In this anion position negatively charged fluorine atoms are associated with hydrogens of alkyl chains as well. For [C4mim][$PF_6$] such a preferential anion location was proven by liquid phase MD simulation[10]. A probability distribution of the anion around the cation was calculated as well. Except C2 carbon atom, $BF_4$ anion can be found near C4 and C5 carbon atoms. Much lower probability corresponds to location near methyl group, and the region near the butyl chain is devoid of anion density. Anions, considered in available studies, are small inorganic ones, which interact with cations electrostatically and via hydrogen bonding. It's reasonable to suppose, that more complex anion, in particular organic ones with aromatic rings, could have another orientation with respect to a cation. For example the one with parallel orientation of aromatic rings of cation and anion to provide the $\pi$-$\pi$ stacking.

Ability to aggregation of IL in water was tested too[11,12]. A micelle formation and an action as surfactant were observed for a number of IL with intermediate and long alkyl chains. In the same time an influence of gradual water addition on IL nanostructure was not yet well studied, as well as an influence of low-polar organic solvents, which is a point of interest too.

Some attention was paid to temperature dependence of X-ray diffraction patterns, in particular for [C8mim][$BF_4$] (the IL, almost identical to our IL3)[7]. A shift of a position of the peak can be attributed to density changes only below $T_g$, whereas between $T_g$ and room temperature peak was shifting to higher $q$-values at heating, that is in disagreement with density changes. Thus thermal behavior of the IL is rather complex, showing a significant role of diffusive processes at $T > T_g$. In the same time a lack of studies was performed on thermal stability of aggregates, that is a study of evolution of X-ray diffraction patterns at high temperature.

An effect of the presence of a PE on nanoscale structure of IL is another problem with a lack of studies for the moment. Although this question is related to PE solutions in IL, we treat it in this chapter as a question about IL nanostructure.

Another interesting point is a possible existence of aggregation in IL due to other types of interaction, except above-described Van der Waals one. In particular there is an indication on strong interaction between EMIM and Tos, which form our IL1[13]. This interaction can have different contributions: coulombic, hydrogen bonding, dipole-dipole, aromatic $\pi$-$\pi$ and weak aliphatic Van der Waals ones. Thus one can suppose, that such an interaction between cation and anion can also lead to the formation of structural heterogeneities. The latter should be of another type, being induced by aggregation between charged groups. In results given below we treat this problem.

## 1.1 Nanostructure of IL2 and IL3

### 1.1.1. Nanostructure of neat IL2 and IL3

IL2 and IL3 belong to IL with intermediate alkyl chain length, and normally should display segregation due to hydrophobic interaction between aliphatic chains. To verify that, scattering measurements were performed for both IL, SANS for IL2 and SAXS for IL3. Results are shown at Figure 1.

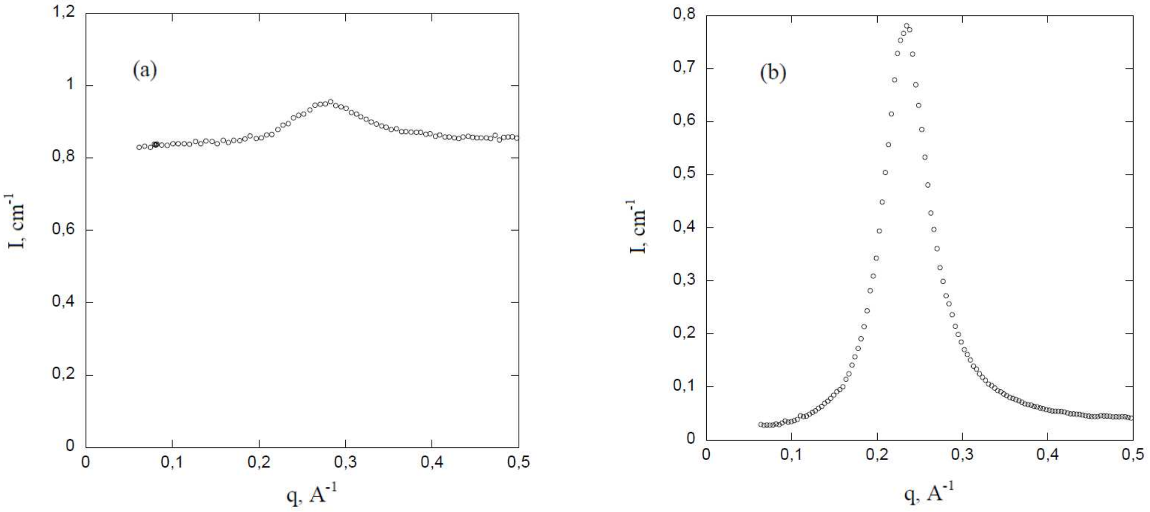


Figure 1. Scattering profiles of IL2 (a) and IL3 (b).

Indeed the peak, related to correlation in positions of polar groups via formation of nonpolar domains is present in both cases. The size of heterogeneities is higher a little in IL3, than in IL2, obviously due to increased length of alkyl chains. A sharpness of the peak has also increased for IL3, and this is another feature of increased length scale of structural correlations. Note a high level of scattering for IL2 in SANS experiment, which is due to use of protonated samples. The latter give high incoherent scattering, although it’s still lower, than the one of $H_2O$, as volume fraction of hydrogen is lower in IL2 compared to that in water.

### 1.1.2. Influence of solvents on nanostructure of IL2 and IL3

An evolution of scattering profile of IL2 under water (in $D_2O$ form) addition was studied as well. As water was gradually added, the peak was shifted to smaller q-values and increased in intensity, showing an increasing of size of aggregates. As the latter are formed due to hydrophobic interaction, a presence of polar molecules of water provokes stronger tendency to aggregation. Although we study a nanostructure of IL at small water content, obviously we have the influence of water, similar to that in the case of micelles formation in aqueous solutions of IL. A change of IL3 scattering profile at water addition was not explored, as this IL is hydrophobic one.

An influence of a low-polar organic solvent on heterogeneities in IL2 and IL3 was investigated too. As such solvent chloroform was used (in deuterated form for SANS and protonated one for SAXS). This solvent is a classical low-polar one, miscible with studied ILs and easily available in the deuterated form. Its high absorbance with respect to X-ray (due to a high content of relatively heavy atoms of Cl) was not a significant problem, as volume fraction of chloroform in studied systems was far away from 100%. Nevertheless a long time of counting was required in corresponding SAXS experiments. So, a gradual addition of chloroform to IL2 and IL3 resulted in gradual disappearance of the peak, related to nanoscale structural correlations. Thus the low-polar solvent destroys aggregates, formed by the alkyl chains. Obviously this happens due to hydrophobic interaction of added chloroform with the nonpolar chains, which is competitive with respect to the one between alkyl groups of IL. So, as we have shown, an effect of a presence of the low-polar solvent is opposite to the one of water presence.

### 1.1.3. Influence of PSS on nanostructure of an amphiphilic IL

Especially interesting for us was the question about influence of a PE on the nanostructure of IL, in particular amphiphilic one, IL2. SANS patterns were obtained for different PSS concentration in this IL. In Figure 2 we compare interference peaks for the PSS solutions and neat IL2. For convenience a flat scattering from hypothetic non-aggregated IL2 is removed.

There is a clear shift of the interference peak position to smaller q-values when PSS is added to IL2 and when the PE concentration further increases. So there is a structuring effect of PSS on heterogeneities in IL2. Another interesting point to note is a fact, that at PSS addition the peak becomes bimodal. Probably this is related to a formation of two types of heterogeneities, the ones, formed only by low-molecular ions, and another ones, in which formation PSS chains participate. But a confident conclusion about the bimodal structure of the peak can’t be made, as resolution of the scattering curves is not enough high.

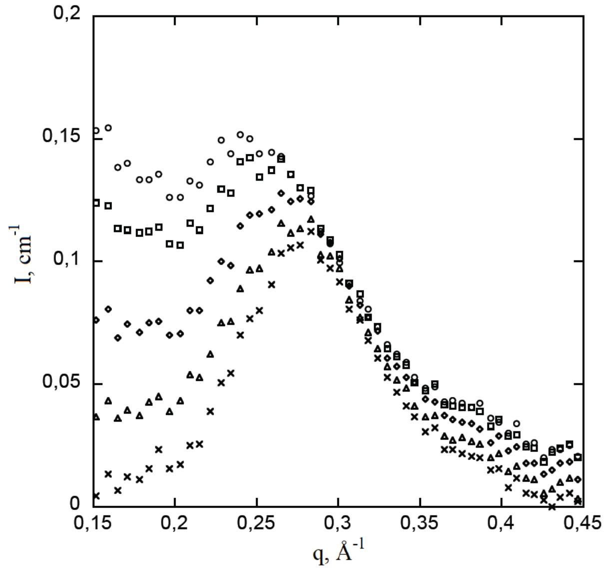


Figure 2. The peak, related to heterogeneities in IL2, for PSS solutions at concentration 0.20M (circles), 0.15M (squares), 0.10M (rhombus), 0.05M (triangles) and for the neat IL2 (crosses) (corresponding region of $q = 0.15 \div 0.45$ A$^{-1}$ is represented).

## 1.2. Nanostructure of IL1

### 1.2.1. Nanostructure of neat IL1

The structure of IL1 is not really amphiphilic, because it doesn't contain enough big nonpolar fragment. The phenylene group of tosylate anion is polarized by substituents and cannot be considered as nonpolar. In addition this phenylene group can interact with charged imidazolium aromatic ring of EMIM in a way different from the London dispersion interaction, the only possible for nonpolar alkyl chains. Thus there are no reasons for microphase separation, and instead there is a possibility for strong cation-anion interaction, that perhaps can lead to some kind of structural organization in IL1.

SAXS on IL1 was done in order to check a possible formation of structural heterogeneities in this IL. A corresponding profile is shown in Figure 3.

As we can see, there is a peak at around 0.4Å$^{-1}$ that is broad and has rather low intensity. Using a relation

$$L = 2\pi/q^* \qquad (1)$$

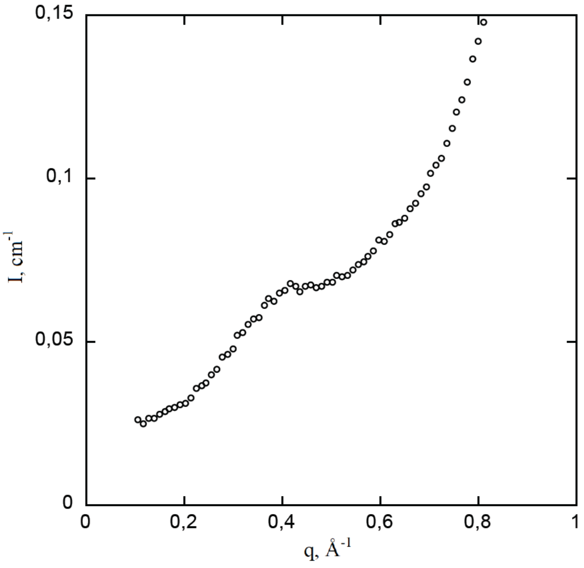


Figure 3. Scattering profile of IL1.

with *L* being the spatial correlation and *q** being the peak position, we find that *L* is around 16Å. To what kind of spatial correlation this distance refers is not completely clear for the moment, but a formation of structural heterogeneities in IL1 is evident. Probably there is an association between cations and anions due to strong interaction between them. Thus the peak is broad and has rather low intensity due to a fact, that degree of this association is not constant, so correlations characterized by different *L*-values take place. The heterogeneities can include not only a different number of ions, but a mutual orientation of the latter can be different as well. This orientation can be governed either by hydrogen bonding, like in the case of small symmetrical anions, either by π-π interaction. In the latter case imidazolium ring should be an acceptor of π-electron density, and phenylene ring should be a donor of the latter. Thus a sandwich configuration will be formed with parallel orientation of the two rings.

### 1.2.2. Influence of water on nanostructure of IL1

To check our hypothesis about oppositely charged ion association, we studied an effect of water addition on heterogeneities formation in IL1. If this formation is due to the interaction between polar groups of the cation and the anion, it should disappear under water addition[12]. Water hydrates the ions, thus disturbing the interaction between them and breaking their association. The SAXS patterns for IL1 in presence of water are shown in Figure 4.

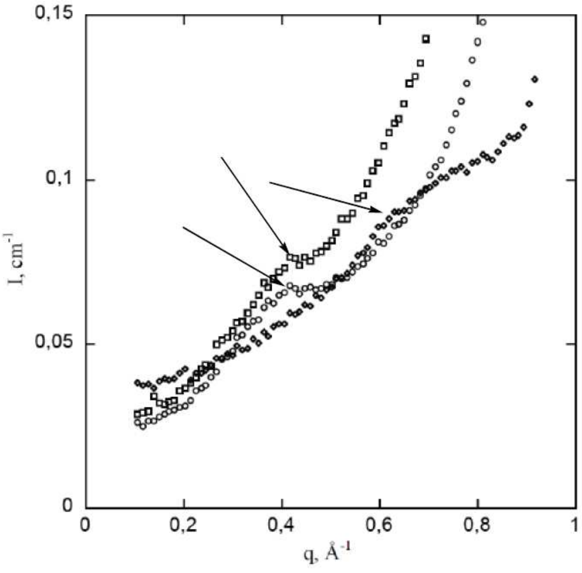


Figure 4. Scattering profiles of neat IL1 (circle), IL1 with water at 1:1 by mol composition (square) and IL1 with water at 1:1 by weight composition (rhombus); the peaks are noted by arrows.

We see that after the equimolar water addition (that is one molecule of water per two ions of IL) the intensity of the peak slightly decreases. After an increasing of water content in order to achieve a composition 1:1 by weight for the binary IL-water system (that equals about 1:16 by mol) the peak completely disappears. Instead for the last composition a peak at around 0.6Å$^{-1}$ appears, that can correspond to spatial correlations between formed hydrated ions of IL. These ions are rather large, although smaller, than ion aggregates. Thus water provokes a disappearance of ion aggregates, formed due to interaction between hydrophilic chemical groups. For the resulted hydrated ions in concentrated aqueous solution an existence of spatial correlation is observable too.

### 1.2.3. Thermostability of ion aggregates in IL1

The thermostability of the ion aggregation in IL1 was tested by comparison of SAXS profiles, obtained at different temperature. The SAXS curves are represented in Figure 5.

As the intensity and position of the peak are not affected by heating until 150$^{o}$C, the aggregates are thermostable at studied temperature region. An increasing of the intensity of scattering at heating is probably related to an increasing of compressibility.

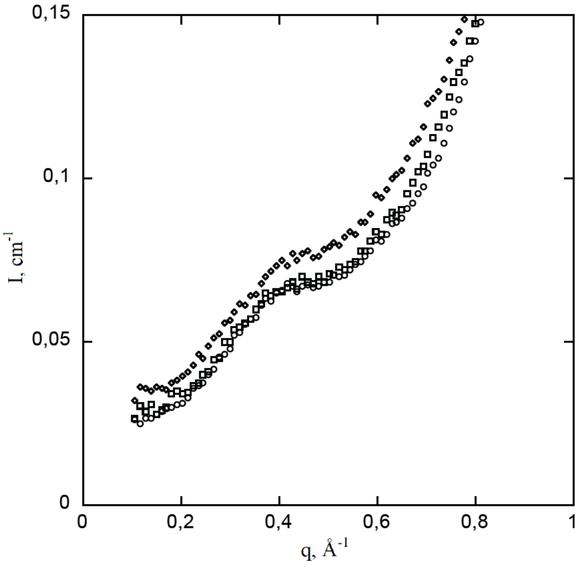


Figure 5. Scattering profiles of IL1 at room temperature (circle), 80°C (square) and 150°C (rhombus).

### 1.2.4. Influence of PSS on nanostructure of IL1

An effect of PSS addition on heterogeneities in IL1 was explored as well. In the case of this IL no changes of scattering profile were observed, when PSS was added in a concentration until 0.2M. Thus for IL1, which has the anions almost identical to the PE units, there is a partial replacement of low-molecular anion by the macroion units without changing the IL nanostructure. We can consider this replacement like a covalent linking between some of the anions, which in viscous media doesn't significantly affect aggregates size and structure.

The last important note about IL structure is an absence of long-range spatial correlations. Thus IL scattering profile doesn't display any peaks at $q < 0.2$ *Å*$^{-1}$, allowing to study concentration fluctuations in corresponding PE solutions.

## Conclusions

All ILs taken for the study display an existence of heterogeneities at nanoscale length.

IL2 and IL3, being amphiphilic ones, are characterized by spatial correlation between polar groups, which are separated by nonpolar regions. The latter are formed by alkyl chains, aggregated due to Van der Waals interaction. This type of heterogeneities is sensitive to both polar water and low-polar chloroform, but an effect of these solvents is opposite. While water causes a formation of heterogeneities of larger size, chloroform destroys them. Concerning an action of PSS, an addition of the latter to IL2 provides a shift of the interference peak to smaller $q$-values, thus the PE has a structuring effect on nanoscale order in the IL.

IL1 doesn't contain large nonpolar fragments, nevertheless it forms aggregates, obviously due to different types of interaction between polar groups. The effect of water on these heterogeneities is opposite to the one in the cases of IL2 and IL3, due to another nature of heterogeneities in IL1. An addition of PSS, that can be described like a covalent linking between some of the anions, has no influence on aggregates in IL1. These aggregates are also rather thermostable.

All three studied ILs don't have a long-range order, thus a study of PE solutions in these ILs is possible.

## References

[1] J. D. Holbrey and K. R. Seddon, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2133–2139
The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals

[2] A. E. Bradley, C. Hardacre, J. D. Holbrey, S. Johnston, S. E. J. McMath and M. Nieuwenhuyzen, *Chem. Mater.*, **14** (2002), 629-635
Small-Angle X-ray Scattering Studies of Liquid Crystalline 1-Alkyl-3-methylimidazolium Salts

[3] Y. Wang and G. A. Voth, *J. Phys. Chem. B*, **110** (2006), 18601-18608
Tail Aggregation and Domain Diffusion in Ionic Liquids

[4] R. Atkin and G. G. Warr, *J. Phys. Chem. B*, **112** (2008), 4164-4166
The Smallest Amphiphiles: Nanostructure in Protic Room-Temperature Ionic Liquids with Short Alkyl Groups

[5] J. N. A. C. Lopes and A. A. H. Padua, *J. Phys. Chem. B*, **110** (2006), 3330-3335
Nanostructural Organization in Ionic Liquids

[6] Y. Wang and G. A. Voth, *J. Am. Chem. Soc.*, **127** (2005), 12192-12193
Unique Spatial Heterogeneity in Ionic Liquids

[7] A. Triolo, O. Russina, H.-J. Bleif and E. Di Cola, *J. Phys. Chem. B*, **111** (2007), 4641-4644
Nanoscale Segregation in Room Temperature Ionic Liquids

[8] C. Hardacre, J. D. Holbrey, C. L. Mullan, T. G. A. Youngs and D. T. Bowron, *J. Chem. Phys.*, **133** (2010), 074510
Small angle neutron scattering from 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids ($[C_n\text{mim}][PF_6]$, $n$=4, 6, and 8)

[9] Morrow T. I. and Maginn E. J., 2003, Molecular structure of various ionic liquids from gas phase *ab initio* calculations *Ionic Liquids as Green Solvents: Progress and Prospects* (*ACS Symposium Series* vol 856) ed R. D. Rogers and K. R. Seddon, 162–173

[10] Z. Liu, S. Huang and W. Wang, *J. Phys. Chem. B*, **108** (2004), 12978-12989
A Refined Force Field for Molecular Simulation of Imidazolium-Based Ionic Liquids

[11] Z. Miskolczy, K. Sebok-Nagy, L. Biczok, S. Gokturk, *Chemical Physics Letters*, **400** (2004), 296–300
Aggregation and micelle formation of ionic liquids in aqueous solution

[12] Y. Zhao, S. Gao, J. Wang and J. Tang, *J. Phys. Chem. B*, **112** (2008), 2031-2039
Aggregation of Ionic Liquids $[C_n\text{mim}]\text{Br}$ ($n$ = 4, 6, 8, 10, 12) in $D_2O$: A NMR Study

[13] I. F. Pierola and I. E. Pacios, *J Fluoresc,* **22** (2012), 145–150
Fluorescence Study on the Structure of Ionic Liquid Aggregates in Aqueous Solutions

# *CHAPTER 2*

# *Influence of the nature of counterions and solvent on the PSS behavior in solution*

## Introduction

Strong PEs, in particular PSS in the acid and salt forms are fully dissociated from chemical point of view in water[1,2]. In the same time the counterions condensation process leads to a decrease of $f_{eff}$-value. Nevertheless PE chains remain charged, thus an electrostatic interaction between them causes a correlation between their positions in a solution and an appearance of an electrostatic peak[3,4]. The position of the latter $q^*$ is related to $\xi$ as $q^* = 1/\xi$. For the case of a solvophilic behavior of the PE, in particular for fully sulfonated PSS in water, one has[5]

$$q^* = f_{eff}^{2/7}(l_B/b)^{1/7}(bc)^{1/2} \qquad (1)$$

The Bjerrum length $l_B$ for water at 25°C is equal to 7.14 Å; the monomer size $b$ for PSS is equal to 2.56 Å. Thus $q^*$ scales like $q^* \sim f_{eff}^{2/7}$. So small-angle scattering is one of the ways to determine $f_{eff}$-value. Other methods for that include viscosimetry, osmotic pressure measurements, electrophoresis, NMR etc[6].

Most of counterions applied for previous studies of PSS in aqueous solutions are cations of alkali metals or small ammonium ones[7]. These counterions interact with PSS in electrostatic way and their condensation could be described according to the Manning-Oosawa approach[8,9]. Thus the nature of counterions didn't play an apparent role and could be neglected in the first approximation. But this is not always the case[10]. As was shown by Hofmeister, each counterion provides its own effect on the PE behavior in solution[11]. Such a specific effect is caused either by a big change of magnitude of electrostatic interaction, either by an existence of another types of interaction between a counterion and a PE. Actually the influence of a certain counterion is always specific, but a difference between counterions could be apparent only if their chemical nature is essentially different.

If protons as counterions for PSS are taken and compared with usually used $Na^+$-counterions, an observable difference in $f_{eff}$-values of PSS should be expectable. Indeed $H^+$-cations are extremely small and don’t contain electrons. So they can approach closer the sulfo groups of PSS, increasing the energy of electrostatic interaction. Even a penetration of protons in electronic layers of oxygen atoms of sulfo groups should happen in some extent, being typical for interaction between proton and an electronegative atom. Such a partial penetration takes place due to an absence of electrons in $H^+$-cations and consequently an absence of repulsion between electron layers of interacting atoms. This proton penetration provides a partially covalent character of a linking between $H^+$ and electronegative atoms. This special feature of protons is responsible for the nature of hydrogen bonding, which is realized in described way due to partial covalent linking[12,13]. That's why hydrogen bond has higher energy compared to other types of intermolecular interaction. So the use of $H^+$-counterions for PSS is expected to increase the electrostatic interaction and to provide hydrogen bonding between considered counterions and PSS. This theoretically should lead to higher degree of counterion condensation and to lower $f_{eff}$-value in comparison with the case of PSSNa.

For the moment this problem is not yet treated in the literature, although PSSH was used in some studies and even compared to PSSNa. But the difference between monovalent cations has not received an attention and was considered as insignificant compared to that between cations of different valence. Indeed due to the scaling law $q^* \sim f_{eff}^{2/7}$ $q^*$-values for any monovalent counterions fall in the same narrow $q$-region. Nevertheless a difference can be clearly detected.

A question about the preferential use of PSSNa by most of the scientists can be asked. Actually PSSNa is more stable and less hydrophilic, thus more convenient for work compared to PSSH. Higher stability of PSSNa is attributed both to its higher thermostability and stability during conservation. But thermostability of PSSH is sufficiently high too: its decomposition begins at around 200°C, as we have determined by using TGA. Concerning conservation, PSSH can be kept during several month at ambient conditions without decomposition. The problem of high hydrophility of PSSH was easily solved in a way described below in this chapter. Thus PSSH is enough stable and convenient at conditions and timescales of our experiments. The use of PSSH helped us to achieve PSS solubility in some organic solvents and ILs, where usual salt forms of PSS are insoluble.

Second main topic discussed in this chapter is the influence of solvent on the PSS behavior and its $f_{eff}$-value in solution. Contrary to the explored in details PSS behavior in water, the one in organic solvents remains not enough studied, mainly due to insolubility of usual salt forms of PSS in this kind of solvents. In the same time these solvents have a number of known advantages, making them widely used in science and industry. They have been applied for dissolution of some PEs as well[14,15]. Achieving the PSS solubility in the organic solvents could open new challenges for the study and application of this PE. One work in this direction should be mentioned. Authors prepared and explored solutions of $Na^+$-form of partially sulfonated polystyrene in DMSO[16]. They observed an absence of solvophobic effects, which this PE displays in aqueous solutions. But to achieve a complete dissolution of $Na^+$-form of fully sulfonated polystyrene in DMSO appeared impossible.

We have found that the use of PSSH instead of PSSNa provides a solubility of the PE at molecular level in some organic solvents. The latter should be polar and able to hydrogen bonding. In particular aprotic one DMSO and protic one ethanol dissolve PSSH. While another tested organic solvents didn't provide the PSSH solubility, in particular acetone, acetonitrile, ethyl acetate and toluene. Indeed these solvents are either not enough polar, either they are too bad acceptors of acidic protons.

Thus PSSH solutions at different concentration could be prepared in DMSO and ethanol. A dependence $q^*$ *vs.* $c$ was found in both cases, allowing to make a conclusion about character of PSSH behavior in the organic solvents.

## 2.1. Taken samples and preparation of solutions

### 2.1.1. Features of the samples

PSS in the salt and acid forms was prepared from polystyrene following Makowski et al. procedure[17]. The description of the latter is given in annex. A final product of the applied procedure is PSSNa, which was used as the PSS salt form for our investigations, as well as transformed to PSSH in order to get the acid form. The latter was taken to perform a characterization of obtained PSS by means of SEC. $N_w$-value appeared equal to *780*, and $N_w/N_n$-value is equal to *1.06*.

As mentioned above, PSSH is very hydrophilic and quickly absorbs water during the sample conservation and preparation of solutions. The presence of water in PSSH sample is not a significant problem for the preparation of aqueous solutions at definite PE concentrations, as the water content can be taken into account. A problem is consistent in uncertainty of this content. To eliminate the last problem PSSH samples were kept at ambient conditions every time before a solution preparation. In such a case taken samples were saturated by water, that is a content of the latter was constant. This content was determined by TGA and appeared equal to *22%* by weight. Of course the maximum water content is sensitive to temperature and humidity in the lab at a particular moment, but in a first approximation it can be considered as a constant. To achieve the saturation of a PSSH sample by water we waited during one hour, as sample weight stopped to change. The TGA curve is illustrated in Figure 1. Along with water evaporation a beginning of PSSH decomposition at around $200^oC$ can be seen.

Demineralized water was taken for preparation of PSS aqueous solutions. A low salts content in water was important to avoid an influence of the low-molecular ions on electrostatic interaction between PSS chains.

Anhydrous DMSO and ethanol were taken for preparation of PSSH solutions in the organic solvents. For this systems water present in the PE samples became an impurity in resulted solutions. But the water content introduced by PSSH samples in the solutions is rather low, as the PE concentration is low. This water content is comparable with that introduced during a use of the taken bottle with a solvent, as well as during solutions preparation. Thus water is anyway present in the final systems, but its concentration is low and probably not significant for interpretation of obtained results. This assumption is supported by the fact that taken organic solvents are also polar, thus low water content should not strongly change their solvent properties.

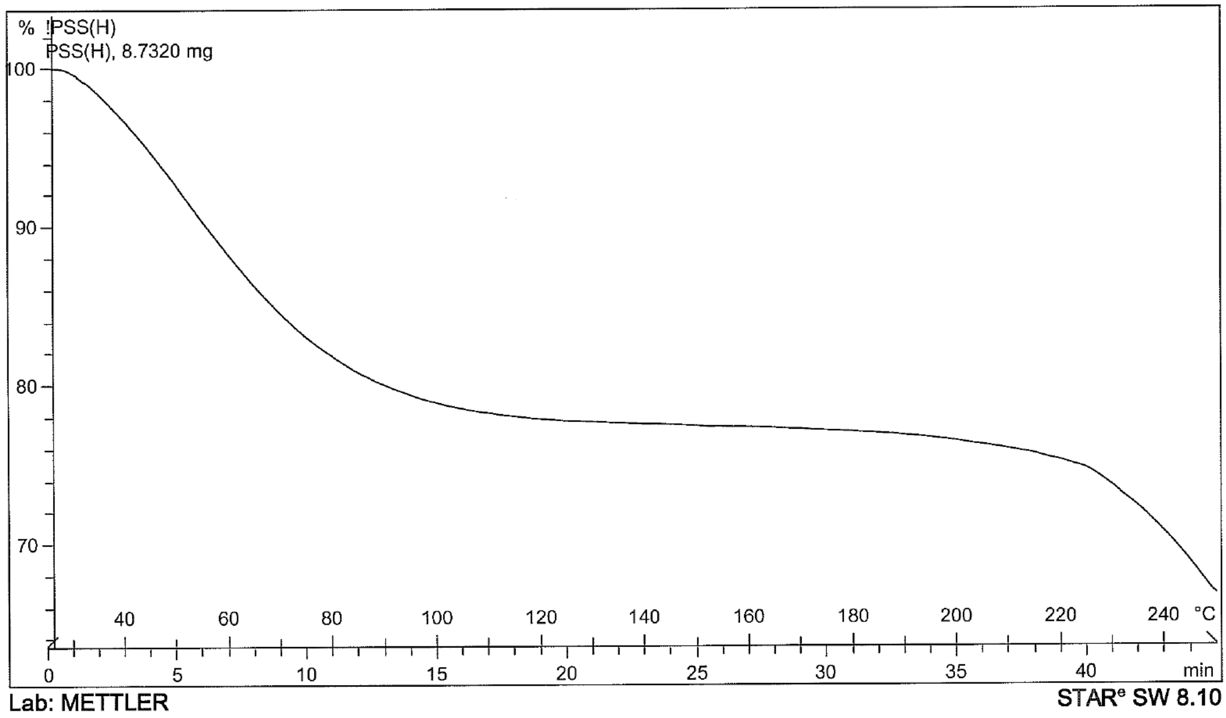


Figure 1. TGA curve of PSSH sample, saturated with water.

### 2.1.2. Preparation of solutions and the upturn problem

A dissolution of PSS samples in all taken solvents happened rather quickly, in few minutes in water and in few hours in the organic solvents, depending on the form of PSS samples and desired concentration. This dissolution was achieved by using stirring. For DMSO as a solvent heating at around $60^oC$ was used as well. After getting a visually homogeneous system the latter was kept during one day to avoid macromolecular association and to achieve dissolution at molecular level. If macromolecules are associated in some extent, this provides an existence of heterogeneities and an appearance of a so-called upturn at small $q$-values at scattering profile. This upturn can complicate the determination of $q^*$, if the electrostatic peak is shifted to small $q$-values. Another source of the upturn appearance can be mica, used as a window in a cell prepared for scattering measurements. A scanning of empty cell, that is mica without solution with its subsequent subtraction is a way to decrease the last kind of upturns. Although a complete elimination of the upturn caused by mica is difficult to reach, because a number of factors including a mica orientation influences this upturn.

## 2.2. Influence of the nature of counterions on the PSS behavior in solution

### 2.2.1. A difference between PSSH and PSSNa behaviors

Aqueous solutions of PSSH and PSSNa were investigated by SAXS in order to see a difference in behavior of PSS with basically different counterions. Solutions of the both forms were taken at $c_{PSS} = 0.22$M. The scattering curves are shown in Figure 2.

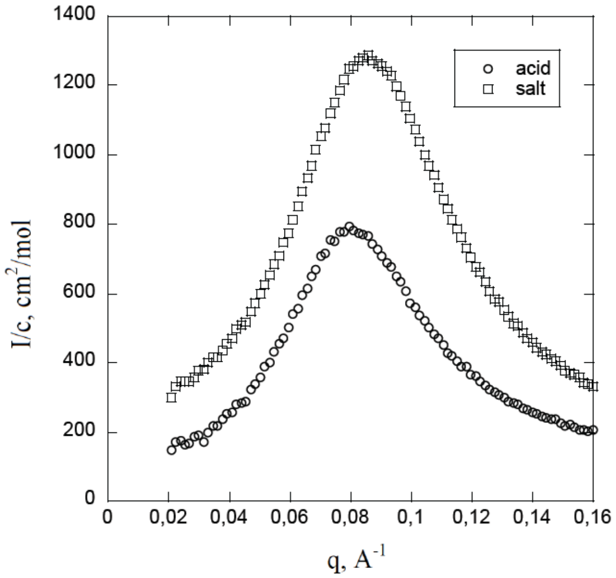


Figure 2. SAXS profiles of the PSS acid and salt forms at $c_{PSS} = 0.22M$.

We see a difference between scattering profiles of PSSH and PSSNa, in particular a difference between corresponding $q^*$-values. In the case of PSSNa the total scattering function includes contributions from macroion and counterions, while for PSSH it is equal in first approximation to the macroion scattering function. That is related to the absence of electrons in $H^+$-counterion and small size of the latter. Thus protons don't scatter X-rays and almost don't change macroion volume and scattering length density when condensed. So using equation (1) and considering $l_B$, $b$ and $c$ as constants for both PSSH and PSSNa solutions we see that if $f_{eff}$ is constant too, we should obtain $q^*_{acid} > q^*_{salt}$. While we have the contrary. As the upturn does not contribute to the scattered intensity in considered region of $q$-values, observed difference in the peak positions should be attributed to a difference in $f_{eff}$-values. That is we have $(f_{eff})_{acid} < (f_{eff})_{salt}$.

### 2.2.2. $f_{eff}$-values of PSS and specificity of $H^+$-counterions

To calculate $f_{eff}$-values one should measure $q^*$-values for different $c$. For salt forms of deuterated PSS ($PSS_D$) with $Na^+$ and $N(CH_3)_4^+$ as counterions this was performed before by SANS in order to neglect the counterion partial scattering function[18]. $f_{eff}$ appeared equal to *0.36*. In order to determine its value for PSSH we prepared aqueous solutions of the acid form at different concentrations in the semidilute regime. Results of SAXS are demonstrated in Figure 3.

A dependence $q^*$ *vs.* $c$ for aqueous solutions of the PSS acid and salt forms is given in Figure 4. A first point to note is that slope of a linear fit of the dependence is equal to *0.5* in both cases. This demonstrates a PSS hydrophilic behavior and invisibility of counterions in both series of scattering experiments.

Calculated $(f_{eff})_{acid}$-value for PSSH appeared equal to *0.27*. Thus it's shown experimentally that protons have a stronger tendency to condensation on PSS macroanion compared to $Na^+$-cations. Extremely small size of protons and the absence of electrons allow to decrease significantly the distance between interacting species: counterions and charged functional groups of the macroions. A character of link between protons and sulfo groups is not purely electrostatic, being partially covalent as well. So increased electrostatic interaction and partial covalent linking lead to higher degree of counterions condensation and lower $f_{eff}$-value for aqueous solutions of PSSH compared to those of PSSNa. This not so large change of $f_{eff}$ is nevertheless significant, being well detected due to the use of basically different counterions.

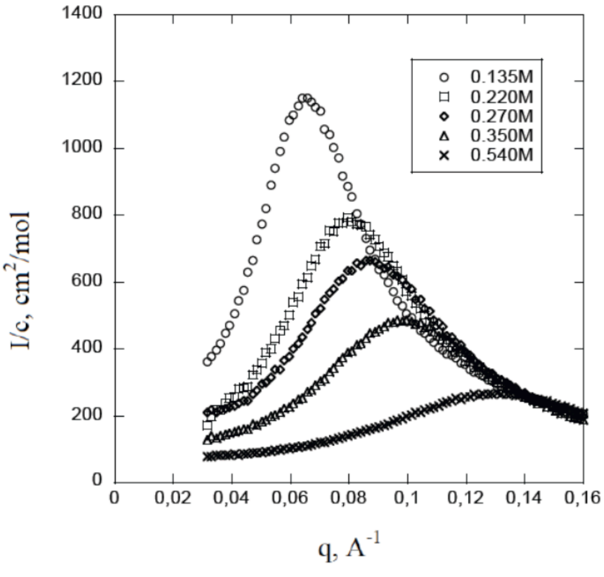


Figure 3. SAXS curves for PSSH aqueous solutions at different concentration.

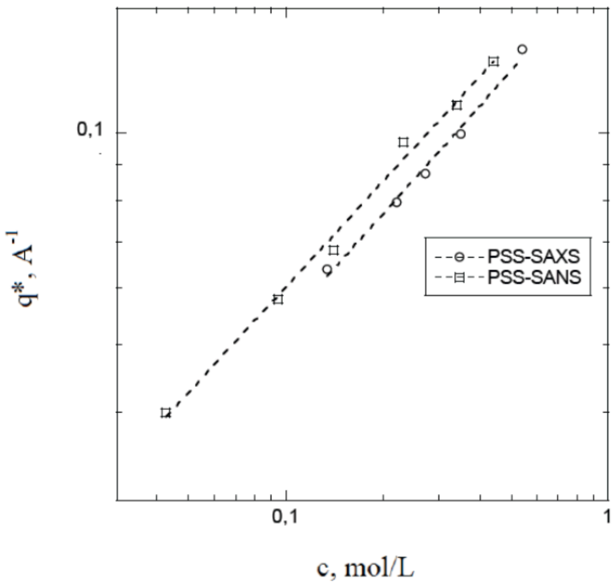


Figure 4. *q* vs. c* dependence obtained by SAXS for the PSS acid form and by SANS for the $PSS_D$ salt forms with $Na^+$ and $N(CH_3)_4^+$ as counterions.

## 2.3. Influence of the solvent nature on the PSS behavior in solution

### 2.3.1. Scaling laws *q* vs. c*

After the study of aqueous solutions of PSSH this PE was investigated in organic solvents ethanol and DMSO to see a role of the solvent nature in type of PSSH behavior. DMSO and ethanol have lower polarity compared to water, moreover their chemical structure contains small nonpolar fragments. So the PE is not only put in a medium with another $\varepsilon$, but locally another types of interaction between solute and solvent can be realized.

Following equation (1) for solvophilic behavior one should observe $q^* \sim c^{1/2}$. If a solvophobic effect appears we have $q^* \sim c^n$ with $n < ½$. To find *n*-values for the cases of PSSH in DMSO and ethanol we prepared and explored by SAXS corresponding solutions at different concentrations in the semidilute regime. Scattering profile and *q* vs. c* dependence for the case of DMSO is shown in Figure 5 and for the case of ethanol in Figure 6.

A couple of important points concerning these SAXS measurements should be briefly discussed. For PSSH solutions in DMSO the solvent molecule has a relatively heavy atom of S in rather high content. Thus DMSO strongly absorbs X-rays and a long counting time is required

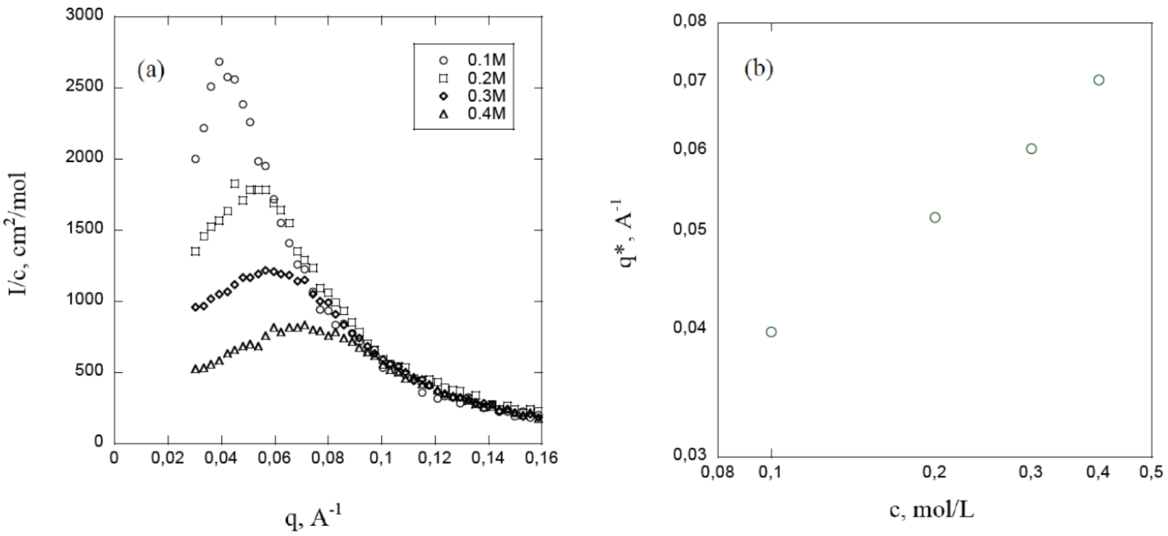


Figure 5. PSSH solutions in DMSO: scattering profile (a) and *q* vs. c* dependence (b).

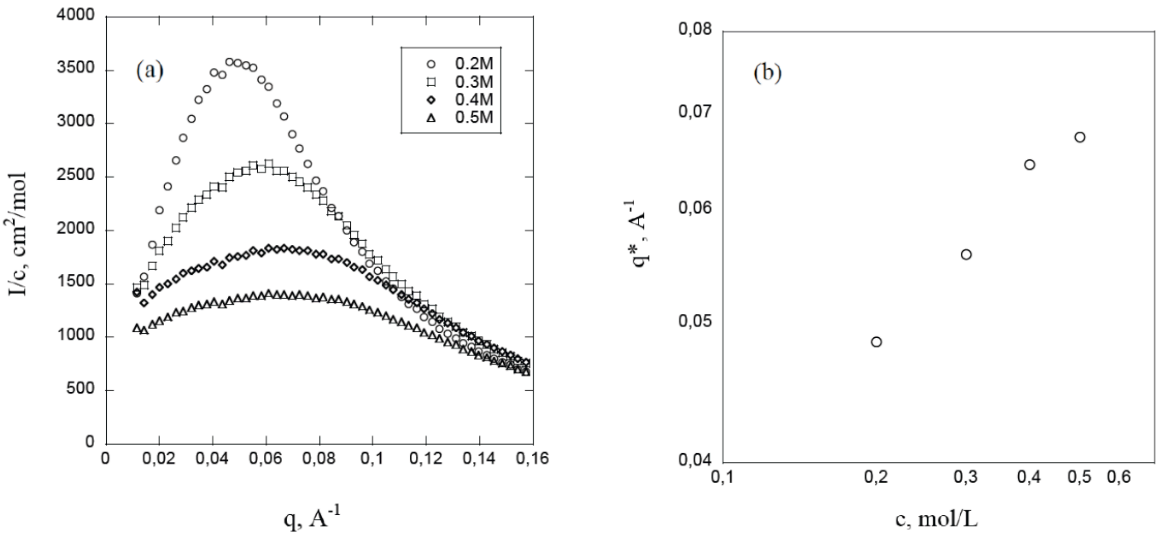


Figure 6. PSSH solutions in ethanol: scattering profile (a) and *q* vs. c* dependence (b).

to obtain scattering profile with a good statistics for corresponding solutions. An interesting observation for PSSH solutions in ethanol is a quick disappearance of heterogeneities after solutions preparation. So there is no need to wait about one day before scattering measurements and the latter can be performed right after preparation of a solution without subsequent upturn appearance at scattering profile. This feature of PSSH solutions in ethanol is probably related to a low viscosity of the solvent.

From the results shown in Figure 5 and Figure 6 *n*-values are calculated and appeared equal to *0.40* for PSSH solutions in DMSO and *0.38* for those in ethanol. As we have in both cases $n < ½$ thus in both taken organic solvents PSS behavior is partially hydrophobic.

2.3.2. Decrease in PSS $q^*$-values for the organic solvents

Another important observation from above-shown results is a large decrease in $q^*$-value for PSSH in the organic solvents compared to that in water. Let's consider an expected change of $q^*$-value induced by change in the solvent polarity with the same type of PSSH behavior. Using equation (1) and taking into account

$$f_{eff} = b/l_b$$

we obtain

$$q^* = (b/l_b)^{2/7}(l_B/b)^{1/7}(bc)^{1/2}$$

and thus

$$q^* = (b/l_b)^{1/7}(bc)^{1/2}$$

Using

$$l_B = e^2/4\pi\varepsilon_0\varepsilon kT$$

we get

$$q^* = (4\pi\varepsilon_0\varepsilon kT/e^2)^{1/7}b^{9/14}c^{1/2} \qquad (2)$$

So we have $q^* \sim \varepsilon^{1/7}$. Let's compare $q^*$ *vs.* $c$ dependences for all studied PSS-solvent systems, introducing two another dependencies corresponding to PSSH in hypothetical solvents S1 and S2. For this solvents we have next conditions: $\varepsilon_{S1} = \varepsilon_{DMSO}$ and $\varepsilon_{S2} = \varepsilon_{ethanol}$ with solvophilic PSSH behavior in both S1 and S2. That is $q^*$-value is changed in this hypothetical solvents compared to water only due to a change in the solvent polarity, maintaining the same type of PSSH behavior. The comparison is given in Figure 7.

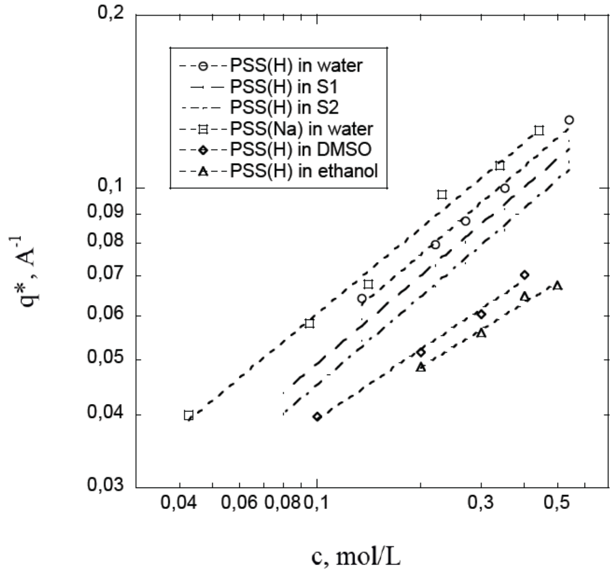


Figure 7. *q* vs. c* dependence for PSS in different forms and solvents.

One can see a significant decrease of *q**-values for PSS in DMSO and ethanol compared to model solvents S1 and S2. So when changing water by the organic solvents *q**-value of PSS in solution decreases not only due to lower *ε*-value of the last ones. Partially solvophobic character of PSS behavior in the organic solvents plays an important role too. So, such a PSS behavior is responsible both for the change of *n*-value in *q* vs. c* dependence and for the strong decreasing of *q**-values as well.

# Conclusions

A new insight is given by the present study on the influence of counterions and solvent on the PSS behavior in solution.

Manning-Oosawa approach is not applicable for all types of counterions. If the latter are highly specific by their nature, an experimental deviation from an approach prediction becomes significant. In particular it's shown that $H^+$-counterions possess stronger tendency to condensation on PSS macroion compared to $Na^+$-counterions. Thus $f_{eff}$-value in aqueous solutions is lower for PSSH compared to PSSNa. This is obviously related to stronger interaction of protons with PSS sulfo groups due to increase of electrostatic attraction and existence of partial covalent linking. In PSSH aqueous solutions $q^*$ determined by SAXS scales like $c^{1/2}$, demonstrating hydrophilic behavior of the PE and an absence of contribution from counterion partial scattering function to the total one.

By using the acid form of PSS we achieved solubility of the latter in organic solvents DMSO and ethanol. The PE behavior in this case appeared not completely solvophilic, as $n < ½$ for the scaling law $q^* \sim c^n$. Moreover $q^*$-values are much lower compared to those in corresponding aqueous solutions. This decrease is larger than expected from decrease of $\varepsilon$-value of the solvent. That is another consequence of the partially solvophobic PSSH behavior in the taken organic solvents.

## References

[1]J.-L. Barrat and J.-F. Joanny, *Adv. Chem. Phys.*, **94** (1996), 1
Theory of polyelectrolyte solutions

[2]A.V. Dobrynin and M. Rubinstein, *Prog. Polym. Sci.*, **30** (2005), 1049
Theory of polyelectrolytes in solutions and at surfaces

[3]J.-P. Cotton and M. Moan, *J. Phys. Lett.*, **37** (1976), 75
Inter-polyionic orientation in polyelectrolyte solution, observed by small angle neutron scattering

[4]P.-G. de Gennes, P. Pincus, R.M. Velasco and F. Brochard, *J. Phys. (Paris)*, **37** (1976), 1461
Remarks on polyelectrolyte conformation

[5]A.V. Dobrynin, R. H. Colby and M. Rubinstein, *Macromolecules*, **28** (1995), 1859
Scaling theory of polyelectrolyte solutions

[6]N. Anik, M. Airiau, M.-P. Labeau, C.-T. Vuong, J. Reboul, P. Lacroix-Desmazes, C. Gérardin and H. Cottet, *Macromolecules*, **42** (2009), 2767
Determination of polymer effective charge by indirect UV detection in capillary electrophoresis: toward the characterization of macromolecular architectures

[7]I. Sabbagh, Thesis, Université Paris VII (1997)
I. Sabbagh, M. Delsanti and P. Lesieur, *Eur. Phys. J. B*, **12** (1999), 253
I. Sabbagh and M. Delsanti, *Eur. Phys. J. E*, **1** (2000), 75

[8]G.S. Manning, *J. Chem. Phys.*, **51** (1969), 924, 934
*Annu. Rev. Phys. Chem.*, **23** (1972), 117
*Ber. Bunsen-Ges. Phys. Chem.*, **100** (1996), 909

[9]F. Oosawa, *Biopolymers*, **6** (1968), 134
A theory on the effect of low molecular salts on the dissociation of linear polyacids

[10]M. Muthukumar, *J. Chem. Phys.*, **120** (2004), 9343
Theory of counter-ion condensation on flexible polyelectrolytes: Adsorption mechanism

[11]F. Hofmeister, *Arch Exp Pathol Pharmakol*, **24** (1888), 247
Zur Lehre von der Wirkung der Salze
Title translation: About the science of the effect of salts

[12]B. Kojic-Prodic and K. Molcanov, *Acta Chim. Slov.*, **55** (2008) 692
The nature of hydrogen bond: new insights into old theories

[13]T. Kortemmea, A. V. Morozova and D. Bakera, *J. Mol. Biol.*, **326** (2003), 1239
An orientation-dependent hydrogen bonding potential improves prediction of specificity and structure for proteins and protein–protein complexes

[14]T. A. Waigh, R. Ober, C. E. Williams and J.-C. Galin, *Macromolecules*, **34** (2001), 1973
Semidilute and concentrated solutions of a solvophobic polyelectrolyte in nonaqueous solvents

[15] P. Aldebert, G. Gebel, B. Loppinet and N. Nakamura, *Polymer*, **36** (1995), 431
Polyelectrolyte effect in perfluorosulfonated ionomer solutions

[16] W. Essafi, M.-N. Spiteri, C. Williams and F. Boue, *Macromolecules*, **42** (2009), 9568
Hydrophobic polyelectrolytes in better polar solvent. Structure and chain conformation as seen by SAXS and SANS

[17] M. Heinrich, Thesis, Université Louis Pasteur de Strasbourg (1998)
Structure de solutions aqueuses de polyelectrolytes en etoile
Title translation: Structure of aqueous solutions of star polyelectrolytes

[18] J. Combet, F. Isel and M. Rawiso, *Macromolecules*, **38** (2005), 7456
Scattering Functions of Flexible Polyelectrolytes in the Presence of Mixed Valence Counterions: Condensation and Scaling

# *CHAPTER 3*

# *PSS solutions in molecular solvents at condition of PE charge screening*

## Introduction

A solution of polyelectrolyte in polar solvent contains both polyions and counterions to satisfy a requirement of electroneutrality. A part of counterions is condensed on PE chains resulting in decrease of its $f_{eff}$-value. In the same time a presence of free counterions leads to a partial screening of Coulombic repulsion between charged units of macroions. Moreover a counterion-induced attraction between like-charged PE units arises[1].

The counterion condensation happens below a critical temperature, as translational entropy of counterions is reduced in this process. Thus a decrease in temperature enhances a counterion condensation and a decrease of chain dimension. That is the presence of counterions causes a decreasing of solvent quality below critical temperature.

If PE concentration corresponds to dilute regime, $r_D$-value is rather high. That is a concentration of counterions is not enough to screen completely Coulombic repulsion. So the electrostatic correlation length $\xi$ still characterizes spatial correlations in such kind of solutions.

In order to decrease $r_D$-value below $l_B$-value and to eliminate long-range electrostatic repulsion LME should be added to a solution[2-6]. At enough high LME-concentration $\xi$ decreases and becomes equal to correlation length for uncharged polymer in a solution. An addition of LME leads to a release of a part of condensed counterions, but a total amount of condensed low-molecular ions increases, as ions of LME are partially condensed too.

The counterion-induced attraction between like-charged PE units and a collapse of PE chain are enhanced by LME addition. If taken LME contains multivalent ions this effects becomes more significant[7]. In this case both aggregation of several chains with their subsequent precipitation and a collapse of a single chain were observed. But if concentration of added multivalent ion is further increased, redissolution and restretching respectively take place. The latter is attributed to repulsion between condensed low-molecular ions. In general the counterion-induced attraction can be realized between PE units of the same or different chains, depending on PE concentration regime.

To determine characteristics of a single chain the dilute regime should be provided to neglect intermolecular correlations. Thus solutions at different PE concentration should be studied by scattering technique following by drawing of Zimm plot. The latter gives us values of $N$, $R_g$ and $A_2$, as described in *General Introduction*. A form factor of a single polymer chain $P(q)$ can be determined as well by extrapolation of scattering curves at $c = 0$ following by normalization at $I(0)$. Another way to $P(q)$ determination is zero average contrast method (ZAC), used in SANS[8,9]. For those mixtures of protonated and deuterated solute and solvent are taken in such a composition that contrast between them is equal to zero. Thus only one measurement at certain PE concentration and without added LME is enough to obtain *P(q)*.

*P(q)* being $I(q)/I(0)_{c=0}$ *vs.* $q$ dependence scales in a different way in every $q$-region for a particular case of polymer behavior[10-12]. That is from the knowledge of the scaling law we can conclude about polymer conformation and solvent quality. In particular at intermediate $q$-range for the case of a good solvent one should have $P(q) \sim q^{-1.7}$ (excluded volume statistics). If solvent quality is decreased an absolute value of the exponent should increase and for θ-solvent one has $P(q) \sim q^{-2}$ (ideal chain statistics). A determination of the scaling law should be performed with a lot of care as wrong background subtraction can cause a mistake in exponent calculation.

As LME for PSSH aqueous solutions we took HCl. The latter has the same cation like the PE. As discussed in *Chapter 2* the nature of monovalent cations is usually not taken into account by classical theories. Nevertheless effects of different cations are basically different and this difference is significant in some cases. In order to account easily for a particular cation nature one should create a system with the only cation type.

PE solutions in aqueous medium at condition of charge screening are studied in details. The ones in organic medium are less common, being nevertheless examined too. Let's discuss briefly some demonstrative results for the last kind of solutions.

Classical neutral polymer poly(ethylene oxide) (PEO) can get a PE behavior in methanol and acetonitrile upon addition of small amount of potassium iodide[13]. This happens due to complexation between PEO chains and the LME. This PE behavior and corresponding peak at scattering profile disappear when LME concentration is increased, as ionic strenght is increased in this way. Such a behavior of PEO with added LME is not observable in aqueous solutions.

The counterion-induced attraction between macroions was demonstrated for rodlike ionogenic polymers in organic solvent chloroform[14]. This attraction led to aggregation between chains. Added to the system LME enhanced the aggregation.

A formation of multilayers was studied by changing different factors, in particular solvent quality[15]. It was shown that decrease of the latter results in more compact conformation of PEs with decreasing of excluded volume. Thus higher degree of PEs adsorption was achieved.

Due to insolubility of usual salt forms of fully sulfonated PSS in organic solvents this kind of systems was not studied neither without added LME neither at condition of PE charge screening. A use of the acid form provided PSS solubility in some polar organic solvents, which are able to hydrogen bonding. In particular ethanol was taken to study PSS behavior in organic solvent with added LME. As the latter toluene-4-sulfo acid (TosH) was taken as the one easily available in individual form and soluble in ethanol. In their turn HCl is usually available in the form of aqueous solution and NaCl is not soluble in the taken organic solvent. TosH is a strong acid like HCl and also has an advantage of common with PSSH cation. Moreover anion chemical structures in TosH and PSSH unit are almost identical.

In general if classical organic solvent is applied for studied problem and compared to water, some expectations can be pointed. Considered in particular ethanol like the most of organic solvents has lower polarity and another type of chemical structure in comparison with water. Lower $\varepsilon$-value of ethanol leads to increase of solvent $l_B$-value and to decrease of PSS $f_{eff}$-value as well. Thus lower LME concentration should be necessary to achieve PSS behavior like for a neutral polymer.

An important point should be noted here. Although ethanol is around three times less polar compared to water, these two solvents are bases of approximatively the same force. That is a change of one proton in water molecule by ethyl radical strongly decreases polarity of the substance, but doesn't change significantly donor properties of oxygen atom, which is responsible for basic properties. Thus PSSH as well as TosH should be fully dissociated from chemical point of view in ethanol like they are in water. So the observed and discussed in *Chapter 2* decrease of PSS $f_{eff}$-value in ethanol compared to water corresponds only to higher degree of counterion condensation in the organic solvent.

Thus a comparison between PSSH behavior in water and ethanol at condition of PE charge screening was performed. Form factor of single PSS chain was calculated for both kinds of systems. A process of the PE charge screening in both solvents was followed by gradual addition of LME. These experiments helped us to check the theoretical considerations discussed above and to observe some another effects as well.

## 3.1. PSSH solutions in water with added LME

PSSH aqueous solutions at $c_{PSS}$ corresponding to dilute regime and with added LME are studied by SAXS in order to determine characteristics of a single polymer chain. $N$-value of the taken PSS sample is equal to *790* as determined by SEC. To provide complete PE charge screening HCl as LME is added at $c_{HCl} = 0.22M$. This HCl was bought in Aldrich like *37%* aqueous solution. The most concentrated by PSS solution at $c_{PSS} = 0.11M$ is prepared, being further diluted to obtain another solutions at lower $c_{PSS}$-value. Finally PSS aqueous solutions at four different $c_{PSS}$ with added HCl are explored by SAXS, as well as *0.22M* aqueous solution of HCl without polymer.

In general scattering profiles of aqueous solutions of LME should represent straight lines at small $q$-values, like that of pure water does, because long-range correlations are absent in this type of solutions. Nevertheless a scattered intensity and a height of this straight line depend on a kind and concentration of dissolved LME. That is to obtain a solvent background in each case we should measure an aqueous solution of taken LME at particular $c_{LME}$. This considered difference is provided by different scattering length densities of the substances (water and LMEs), as well as by compressibility of a particular whole system. For example we have demonstrated, that at rather small $c_{HCl}$ in corresponding aqueous solution scattering curve of the latter is below than that of pure water. Although HCl scatters X-ray stronger compared to $H_2O$, but at small $c_{HCl}$ more significant effect is a decreasing of system compressibility due to HCl addition. This happens due to strongly hydrophilic character of HCl and due to formation of ionic species in the system. Thus a rather significant decrease of compressibility is resulted in lower scattered intensity.

Obtained scattering curves of PSSH in the considered solvent system are shown in Figure 1. The first observation is an absence of the scattering peak due to screening of electrostatic repulsion between PSS macroions.

To extract characteristics of a single polymer chain from these results the latter should be transformed into Zimm plot, as discussed in *Introduction*. The plot obtained in this way is demonstrated in Figure 2. By double extrapolation of experimental data to $c = 0$ and to $q = 0$ we have found $N$-value, appeared equal to *870*. This value is rather close to that determined by SEC. Thus SAXS results in this case seem to be correct, in particular a calculation of the contrast factor $K^2$. Indeed this calculation is sometimes difficult to perform. Although we have tabulated values of scattering length densities for components of a solution, these values are not completely correct for a real solution. This is due to a mutual influence of the components, in

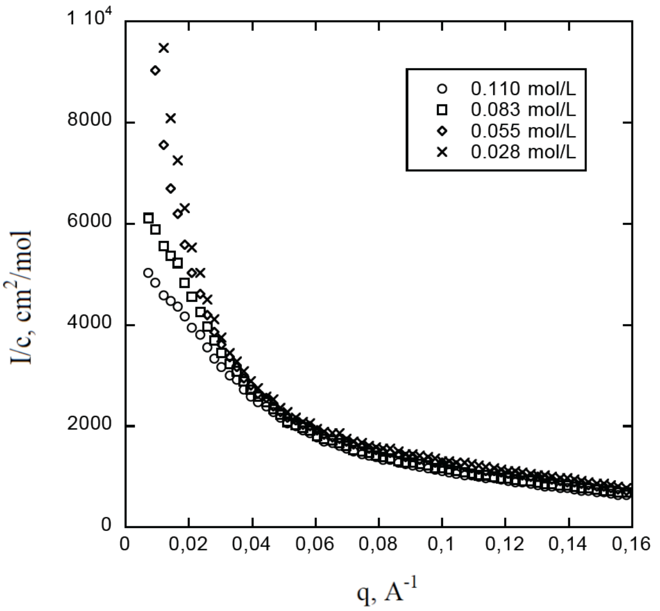


Figure 1. SAXS profiles of PSSH aqueous solutions with added HCl at different $c_{PSS}$ and at fixed $c_{HCl} = 0.22M$.

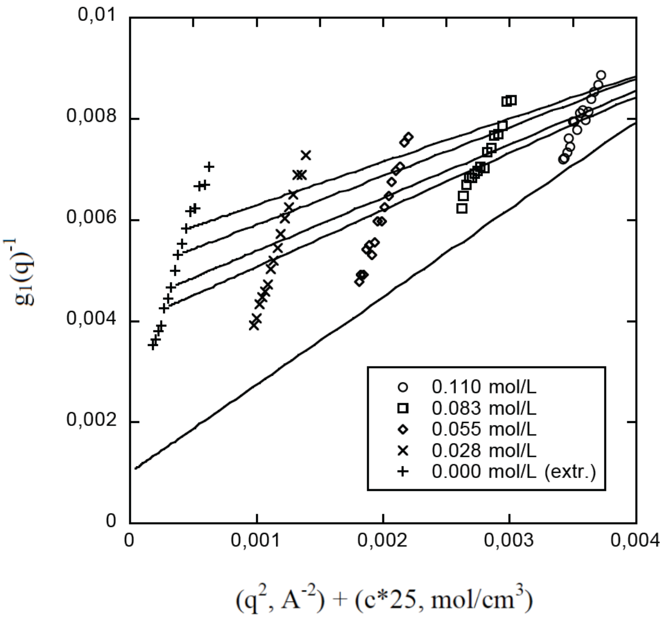


Figure 2. Zimm plot for PSSH aqueous solutions with added HCl.

particular via the process of solvation. Thus a control on SAXS results is important to check a correctness of performed calculations.

Another important characteristic extracted from Figure 2 is $A_2$-value, which appeared equal to $6.49*10^{-4}$ $mol*mL*g^{-2}$. It's well known that water is a good solvent for PSS. This was proven by using mainly salt forms of PSS. Nevertheless water is a good solvent for PSS macroion in particular. Obviously if we introduce hydrophilic protons like counterions, we maintain good solvent quality of water with respect to our particular form of PSS, that is to the acid one. So given $A_2$-value can be considered like the one for the case of a good solvent quality. In such a case we can use this value for comparison with the ones for PSS solutions in other solvents and to conclude about quality of the latter with respect to the PE. Such a comparison is mainly done for PSS in ILs, as discussed in the next chapters, because ILs solvent quality with respect to PSS is unknown.

Explored region of $q$-values doesn't contain enough points at $qR_g < 1$, so a correct determination of $R_g$-value from the drawn Zimm plot is impossible. To calculate this value we performed the fit of $g_1(q)$ with Debye function $g_D(q)$ like described in *Introduction*. This fit is represented in Figure 3.

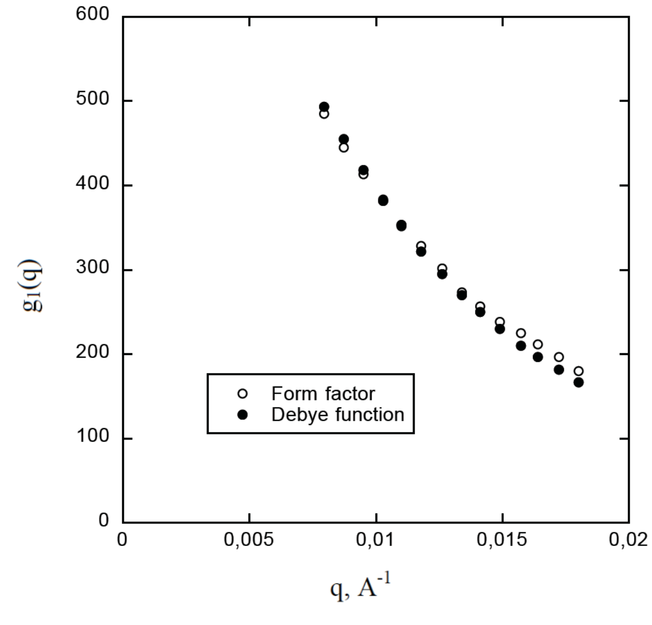


Figure 3. Fit of the form factor $g_1(q)$ with the Debye function $g_D(q)$ for PSSH aqueous solutions with added HCl.

Determined in this way $R_g$-value is equal to *14 nm*. Again this value can be considered like the one for the case of a good solvent.

## 3.2. PSSH solutions in ethanol with added LME

A use of the PSS acid form allows to achieve PSS solubility in ethanol, which is classical polar protic organic solvent. Thus PSSH solutions in ethanol with added LME could be prepared and studied by SAXS. Similar PSS concentration range was taken like for the corresponding aqueous solutions. As LME we applied TosH, which is easily available in individual form and soluble in ethanol. In addition this LME is almost identical by chemical structure to the PSSH unit. TosH was bought in Aldrich in a solid form as monohydrate. $c_{TosH}$ is chosen equal to *0.1M*. This value is enough to screen electrostatic interaction between PSS chains in ethanol medium, as $l_B$-value of this solvent is rather high.

SAXS results for considered solutions are shown in Figure 4.

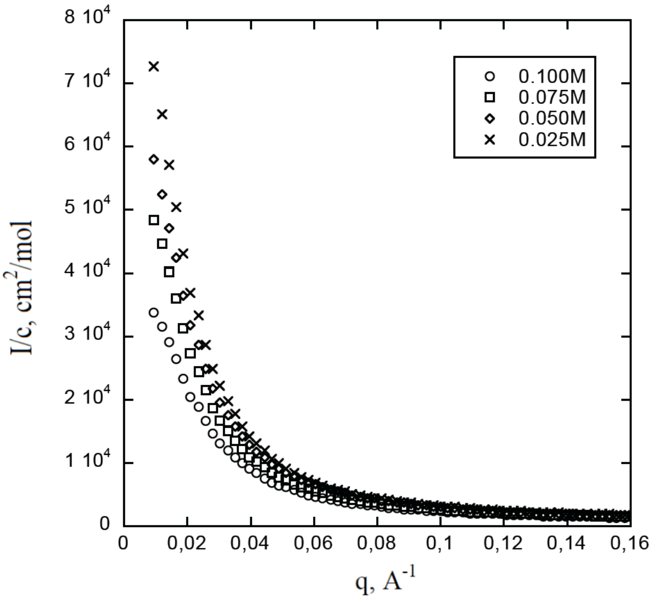


Figure 4. SAXS profiles of PSSH solutions in ethanol with added TosH at different $c_{PSS}$ and at fixed $c_{TosH}$ = *0.1M*.

Like for the case of LME-free PSSH solutions in ethanol we are not disturbed here by upturns at small *q*-values. Also one should pay an attention on high *(I/c)*-values. Good statistics of experimental data, especially well observable at curves of *P(q)* below, is another interesting point. These two features of SAXS profiles of considered systems are attributed to an increased contrast for PSS solutions in ethanol compared to the aqueous ones. Thus a quick disappearance of heterogeneities along with high contrast makes PSS solutions in ethanol convenient for SAXS measurements.

In order to calculate values of *N* and $A_2$ we have built Zimm plot shown in Figure 5.

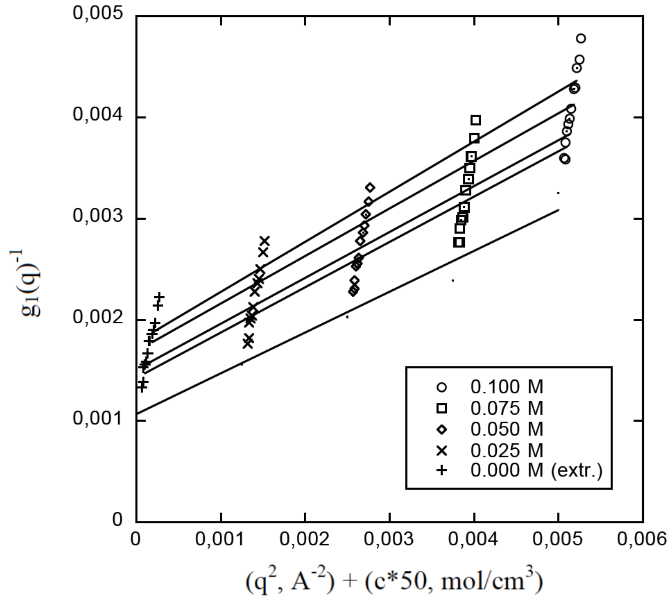


Figure 5. Zimm plot for PSSH solutions in ethanol with added TosH.

From this Zimm diagram we have $N = 855$ and $A_2 = 2.95*10^{-4}\ mol*mL*g^{-2}$. Again $N_{SAXS} \cong N_{SEC}$, thus our calculations seem to be correct. Concerning $A_2$-value, it indicates good solvent quality of ethanol with respect to PSS, although this value is lower compared to the one for aqueous solutions.

For determination of $R_g$-value the fit of $g_1(q)$ with $g_D(q)$ is performed and shown in Figure 6. $R_g$-value appeared equal to *9.0 nm*. The latter is quite low and normally should correspond to θ-solvent.

To conclude about solvent quality and PE conformation for PSS in ethanol, we can perform next considerations. The solvent quality seems to be good, as indicated by $A_2$-value, but there should be some factor, which causes more compact conformation of the PE, leading to low $R_g$-value. Like such a factor we can suppose an existence of intramolecular hydrogen bonds in PSS. Indeed ethanol is less polar medium compared to water, moreover its own ability to hydrogen bonding is lower too. PSSH itself can form intramolecular hydrogen bonds, but the latter are broken in aqueous medium. Obviously in organic media stability of this intramolecular bonding

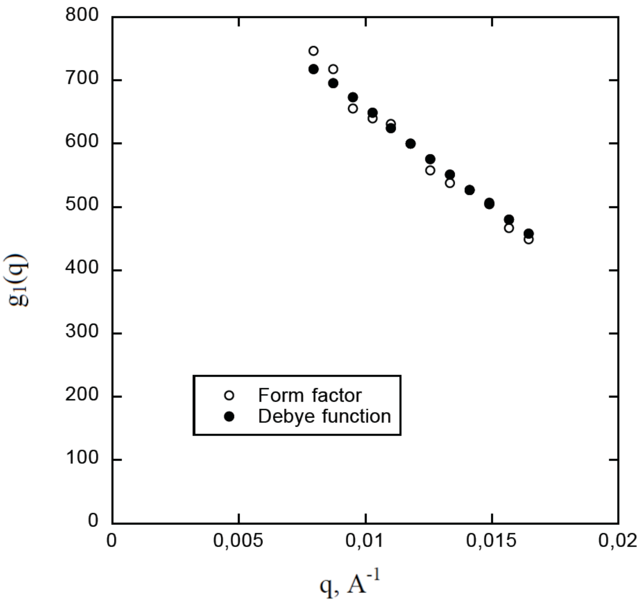


Figure 6. Fit of the form factor $g_1(q)$ with the Debye function $g_D(q)$ for PSSH solutions in ethanol with added TosH.

should be higher. This explanation seems to be reasonable, but it remains only an assumption. Let's note that a possible intramolecular hydrogen bonding is a unique feature of the acid form of PSS, being impossible in the salt forms.

## 3.3. Form factor of PSS in water and ethanol

### 3.3.1. Form factor of PSS in aqueous solutions with added LME by SAXS

To get $P(q)$ for PSSH aqueous solutions with added HCl the scattering curves obtained by SAXS were extrapolated at $c = 0$. In Figure 7 we show $P(q)$ *vs.* $q$ dependence, as well as $P(q)*q^{1.7}$ *vs.* $q$ one, which allows to see better a $P(q)$ scaling behavior in intermediate $q$-range. From the last representation we note that for scaling law $P(q) \sim q^n$ $n$-value is close to $-1.7$ (a little bit lower by modulus if more precisely), which is typical for excluded volume statistics.

Another important characteristic, persistence length $l_p$ can be extracted from Figure 7:

$$l_p = 3.5/q* \qquad (1)$$

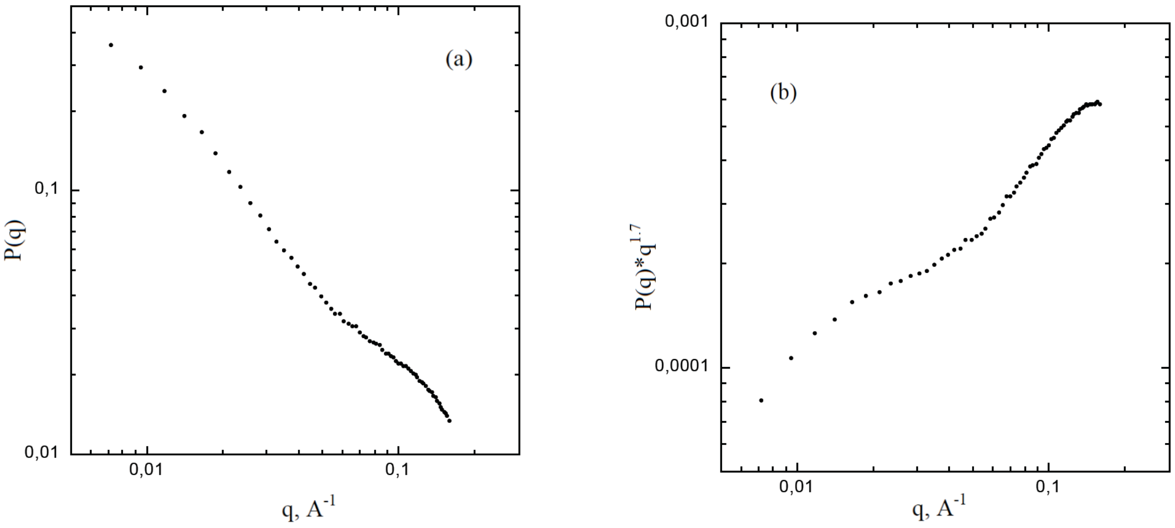


Figure 7. PSSH aqueous solutions with added HCl studied by SAXS: (a) *P(q) vs. q*; (b) *P(q)*$q^{1.7}$ vs. q*.

with $q*$ being a crossover between different $q$-ranges: intermediate and so-called asymptotic one[16-18]. Using equation 1 we find $l_p = 8.5\ nm$. Actually this method of determination of $l_p$-value is not precise, thus the calculated value should be accepted with care, just to follow a tendency of its variation.

A small remark should be pointed concerning all considered *P(q) vs. q* dependences. As one can see on corresponding plots, *P(q)*-curve doesn't reach value of *1* at small $q$-values, like it should do. That is due to the fact, that we don't reach $q = 0$ at our plots. Absolute values of *P(q)* for different systems are calculated by taking into account, that at $q = 0$ we should have $P(q) = 1$.

### 3.3.2. Form factor of PSS in aqueous solutions by SANS: ZAC method

As discussed in *Introduction* to this chapter, another way to *P(q)* determination is ZAC method by SANS. To carry out this measurement we took equimolar composition of $PSSH_h$ and $PSSH_d$ and dissolved it in a mixture of $H_2O$ and $D_2O$ containing 70% of the last one. Thus a condition of zero average contrast between solute and solvent was realized. The result of this measurement is shown in Figure 8. As one can see a statistics of the curve is not very good, but this is natural as the average contrast is equal to zero. Again in intermediate $q$-range we see a scaling law $P(q) \sim q^n$ which corresponds to the case of a good solvent and this time exponent

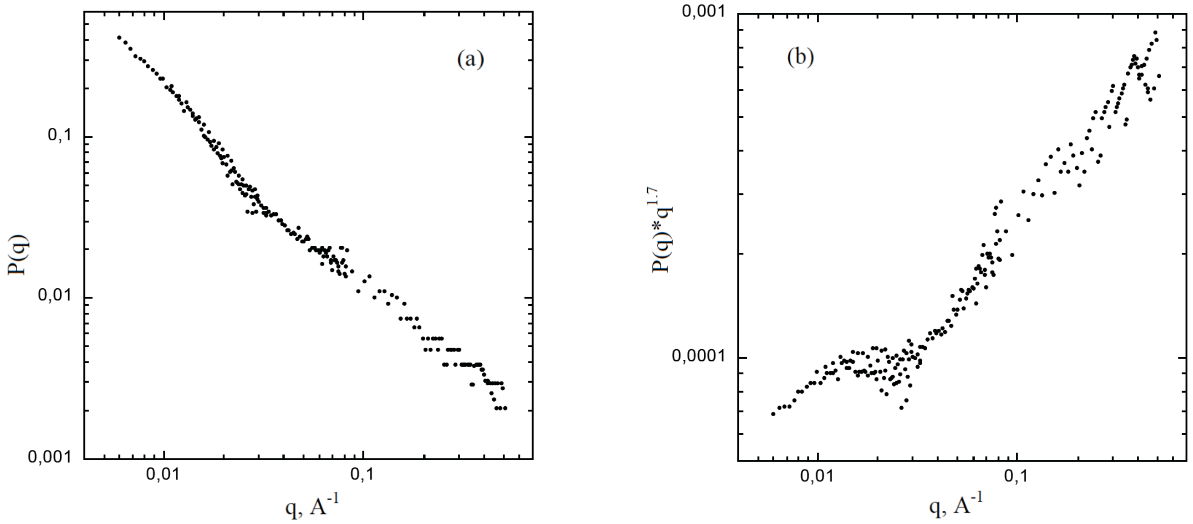


Figure 8. PSSH aqueous solutions studied by SANS at ZAC condition: (a) *P(q) vs. q*; (b) $P(q)*q^{1.7}$ *vs. q*.

value is really very close to *-1.7*. Using equation (1) we find $l_p = 11\ nm$. This value is higher compared to the one at presence of LME. That is expectable, as addition of LME usually leads to a decreasing of $l_p$-value[19].

### 3.3.3. Form factor of PSS in ethanol with added LME by SAXS

*P(q)* for PSSH solutions in ethanol with added TosH is calculated by extrapolation of scattering curves for different $c_{PSS}$ obtained by SAXS at $c_{PSS} = 0$. Distinct representations of *P(q)* are shown in Figure 9. For universal behavior we have $P(q) \sim q^n$ with *n*-value close to *-1.7*. If more precisely, $n < -1.7$, that is solvent quality of ethanol is not completely good for PSS. It's similar to the result, which we have for LME-free PSS solution in ethanol. But in the case of added LME such a solid conclusion cannot be done, as calculated *n*-value is very sensitive to different factors, in particular to correctness of background subtraction. So a small deviation of *n*-value from *-1.7* cannot be surely attributed to a change of solvent quality. Anyway $n \cong -1.7$, thus ethanol can be considered like a rather good solvent for PSS, although some solvophobic effect can take place. Concerning $l_p$-value, it appeared equal to *3.2 nm*. Even taking into account rather low accuracy of $l_p$ determination by this method, a decrease of PSS stiffness in ethanol compared to that in water is clear. Probably the main reason for that is a much lower $f_{eff}$-value of PSS in the organic solvent, as determined and discussed in *Chapter 2*. Finally one should pay an

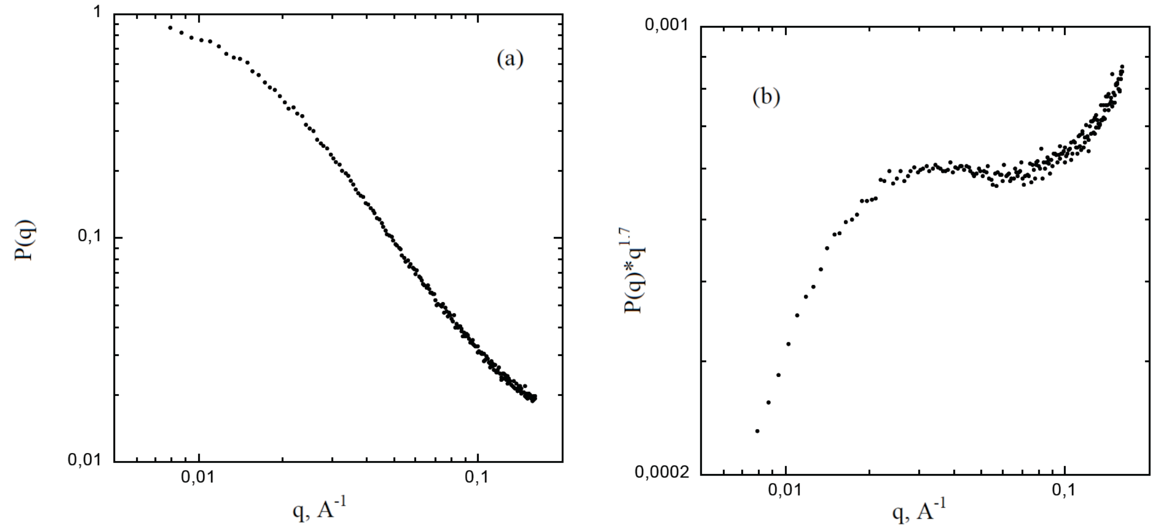


Figure 9. PSSH solutions in ethanol with added TosH studied by SAXS: (a) *P(q) vs. q*; (b) $P(q)*q^{1.7}$ *vs. q*.

attention to a good statistics of *P(q)* curve for PSS in ethanol, provided by a high contrast in this system.

In the end of this subchapter we should mention an article, where authors consider PSSNa aqueous solutions in comparison with a melt of polystyrene[20]. They show that going from the nonpolar polymer to the PE we largely increase stiffness of the polymer chain, even if we maintain the same basic polymer structure. That is an introduction of a polar and especially charged group in polymer side chains leads to a significant increase of polymer stiffness. For PSS aqueous solution $l_p$-values found by us are not far away from those given in the mentioned article. In the same time a strict comparison is impossible, as we use different PSS forms and in addition uncertainty in $l_p$-value determination is rather high. Another studied problem, behavior and stiffness of fully sulfonated PSS in an organic solvent is not yet treated in the literature.

## 3.4. PSS charge screening at LME addition in water and ethanol

A system PSSH-TosH-ROH with R = H or $C_2H_5$ is studied to follow an influence of LME addition on PSS behavior in different solvents: water and ethanol. $c_{PSSH} = 0.22M$ is taken and TosH is gradually added at $c_{TosH} = 0.055M$, $0.110M$ and $0.220M$. The results are represented in

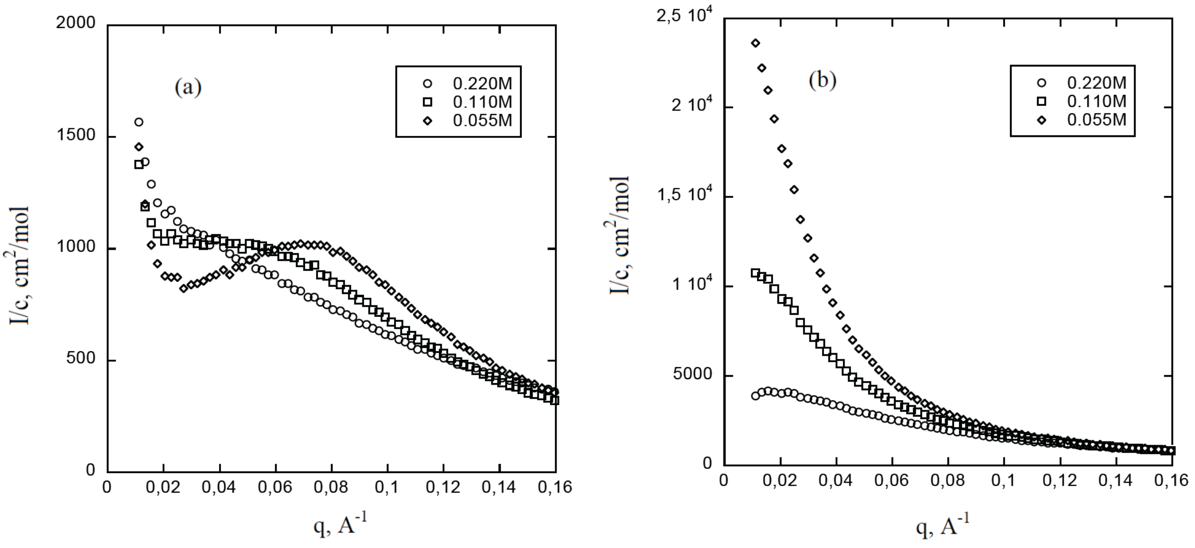


Figure 10. PSSH solutions ($c_{PSSH}$ = *0.22M*) with gradually added TosH ($c_{TosH}$ = *0.055M*, *0.110M* and *0.220M*) in water (a) and ethanol (b).

Figure 10. We see that in ethanol the electrostatic peak disappears at much lower $c_{LME}$. That is lower $c_{LME}$ is required to achieve PSS charge screening. Indeed $\varepsilon$ of ethanol is lower thus its $l_B$ is higher compared to those values for water. This leads to a decreasing of $f_{eff}$ of PSS in ethanol. Moreover, as shown in *Chapter 2*, PSS behavior in ethanol is partially solvophobic and this causes additional decreasing of $f_{eff}$. Thus very small concentration of low-molecular ions is required to screen electrostatic interaction for PSS in corresponding solutions.

In Figure 10 we left upturns thus one can compare aggregation state of PSS chains in two kinds of solutions. In the aqueous ones heterogeneities still exist in one day after solutions preparations. For the ones in ethanol dispersed at molecular level PSS state is achieved more quickly.

## Conclusions

PSS solutions in molecular solvents water and ethanol at condition of the PE charge screening have been studied. In this way an information about single PSS chain behavior could be obtained, in particular values of $N$, $R_g$ and $A_2$ could be calculated. It appeared that organic solvent ethanol is a good one for PSS, although the conformation of the latter is much more compact in this solvent compared to that in water. As a possible explanation of this phenomenon an existence of intramolecular hydrogen bonds for PSSH in ethanol is supposed.

$P(q)$ calculated for PSS in both solvents show their good quality with respect to PSS. A strong decrease of $l_p$ of PSS in ethanol compared to that in water is observed. This decrease of polymer stiffness is probably related to a decrease of $f_{eff}$ in ethanol. In its turn $l_p$ for PSS in aqueous solutions is determined for cases of LME-free ones and for the ones with added LME. In the latter case a decrease of $l_p$ is shown, obviously caused by PSS charge screening.

Finally a process of the PE charge screening at gradual addition of LME is explored and compared in the two solvents. Much lower $c_{LME}$ appeared enough for elimination of electrostatic interaction between PSS macroions in ethanol than in water. This is explained by much lower $f_{eff}$ of PSS in the organic solvent.

So an idea to use the acid form of PSS provided a solubility of this PE in some new solvents. In particular widely used organic solvent ethanol appeared a good one for PSS, nevertheless behavior of the latter in ethanol is particular and distinct from the one in water. In addition ethanol is well adapted as a solvent for SAXS study of PSS solutions, providing high contrast and quick disappearance of heterogeneities. From general considerations about problems of contrast and upturns, these useful features of ethanol as a solvent for SAXS should be conserved for the most of other PEs as well.

# References

[1]H. Schiessel and P. Pincus, *Macromolecules*, **31** (1998), 7953
Counterion-condensation-induced collapse of highly charged polyelectrolytes

[2]M. Drifford, L. Belloni, J. P. Dalbiez and A. K. Chattopadhyay, *Journal of Colloid and Interface Science*, **105**, 2 (1985), 587
Light scattering of micellar and polyelectrolyte solutions: Influence of added salt

[3]T. Hofmann, R. G. Winkler and P. Reineker, *J. Chem. Phys.*, **119**, 4 (2003), 2406
Influence of salt on the structure of polyelectrolyte solutions: An integral equation theory approach

[4]Z. Adamczyk, B. Jachimska, T. Jasinski, P. Warszynski and M. Wasilewska, *Colloids and Surfaces A: Physicochem. Eng.* Aspects, **343** (2009), 96
Structure of poly (sodium 4-styrenesulfonate) (PSS) in electrolyte solutions: Theoretical modeling and measurements

[5]V. M. Prabhu, M. Muthukumar, G. D. Wignall and Y. B. Melnichenko, *J. Chem. Phys.*, **119**, 7 (2003), 4085
Polyelectrolyte chain dimensions and concentration fluctuations near phase boundaries

[6]P. R. Holyk, J. Srymczak and P. Ander, *The Journal of Physical Chemistry*, **80**, 14 (1976), 1626
Electrical conductivity of aqueous solutions of polystyrenesulfonate salts containing simple salts

[7]J.-S. Jan and V. Breedveld, *Macromolecules*, **41** (2008), 6517
Microrheological study of polyelectrolyte collapse and reexpansion in the presence of multivalent counterions

[8]T. Csiba, G. Jannink, D. Durand, R. Papoular, A. Lapp, L. Auvray, F. Boué, J. P. Cotton and R. Borsali, *J. Phys. II France*, **1** (1991), 381
Diffusion in semi-dilute polymer solutions. A complementary experiment

[9]J. P. Cotton, *Advances in Colloid and Interface Science*, **69** (1996), l
Variations on contrast in SANS: Determination of self and distinct correlation functions

[10]J. S. Pedersen, P. Schurtenberger, *Journal of Polymer Science: Part B: Polymer Physics*, **42** (2004), 3081
Scattering functions of semidilute solutions of polymers in a good solvent

[11]J. P. Cotton, *J. Physique – LETTRES*, **41** (1980), L-231
Polymer excluded volume exponent *v*: an experimental verification of the *n* vector model for *n* = 0

[12]R. M. Robertson, S. Laib and D. E. Smith, *PNAS*, **103**, 19 (2006), 7310
Diffusion of isolated DNA molecules: Dependence on length and topology

[13]F. Hakem and J. Lal, *Europhys. Lett.*, **64**, 2 (2003), 204
Polyelectrolyte-like behaviour of poly(ethylene-oxide) solutions with added monovalent salt

[14]M. Susoff, D. Winter, C. D. Eisenbach and W. Oppermann, *J. Phys. Chem.*, 2008
Aggregation behavior of rodlike ionogenic polymers in chloroform

[15]P. Zhang, J.-W. Qian, L.-J. Xuan, Y.-X. Bai and Q.-F. An, *Chinese Journal of Polymer Science*, **27**, 3 (2009), 297
Studies on relation between intrinsic viscosity of polyelectrolytes in solutions used for layer-by-layer selfassembly and their corresponding adsorbtion amount in the resultant multulayer membranes

[16]M. Rawiso, *J. Phys. IV France*, **09** (1999), Pr1-147-Pr1-195
De l'intensité à la structure en physico-chimie des polymères

[17]M. Rawiso, R. Duplessix, C. Picot, *Macromolecules*, **20** (1987), 630-648
Scattering function of polystyrene

[18]M. Rawiso, J.P. Aime, J.L. Fave, M. Schott, M.A. Müller, M. Schmidt, H. Baumgartl, G. Wegner, *J. Phys. France*, **49** (1988), 861-880
Solutions of polydiacetylenes in good and poor solvents : a light and neutron scattering study

[19]T. T. Nguyen and B. I. Shklovskii, *Physical Review E*, **66** (2002), 021801
Persistence length of a polyelectrolyte in salty water: Monte Carlo study

[20]Brulet, F. Boue and J-P- Cotton, *J. Phys. II France*, **6** (1996) 885
About the experimental determination of the persistence length of wormfike chains of polystyrene

# *CHAPTER 4*

# *PSS solutions in ionic liquids*

## Introduction

PEs and ILs represent classes of compounds interesting from both theoretical and industrial points of view. They are discussed in more detail in *General Introduction*. In the same time PEs and ILs are both charged systems, thus their combination can provide some interesting effects. The issue about the mutual influence of PEs and ILs in different kinds of their mixtures is the main one considered in this chapter. In addition ILs became a new type of solvents with a number of known advantages for different classes of compounds, so it's reasonable to test their solvent properties with respect to PEs. At present a number of publications about systems composed of PEs and ILs is quite limited[1-3]. In particular there is a lack of works about the average conformation and dispersion state of PEs in ILs, as well as about solvent quality of the latter with respect to PEs. Nevertheless, one can find some articles, which consider other aspects of PEs and ILs mutual influence. That is an idea to study systems composed of PEs and ILs and sometimes of other components is not completely new, but only a few number of such systems have been explored for the moment. Let's discuss some articles from this field to get general understanding of challenges provided by this new kind of systems.

Certain PEs with $Li^+$-counterions have been successfully used as solid state batteries materials[4]. These $Li^+$-based PEs are fully dissociated from chemical point of view, nevertheless the most part of the cations remains in proximity of strongly charged polyanion. Thus a part of mobile cations which contributes to electrical conductivity is rather small. A problem of dissociation enhancement is the main one related to the increase in the conductivity of a PE gel. This problem can be resolved in different ways. The most common one is the use of copolymers instead of homopolymers. If charged polymer units are separated by noncharged ones (by so-called «spacers»), the ionic dissociation is then increased. As spacers, polar units with high affinity to the selected solvent are usually chosen. Another method to enhance dissociation is the use of a polyanion with poorly coordinating charged species, for example fluorinated ones. But the problem of polyanion repulsion remains in the last case, so this way is not very efficient. To decrease simultaneously a polyanion-counterion coordination and polyanion repulsion new approaches are proposed. The first one is the use of boroxine compounds, which are strongly coordinated to polyanion due to electrodeficiency of Boron atoms. The second approach is the use of ILs. The latter have tendency to coordination with both a polyanion and $Li^+$-counterions. Moreover they provide screening of electrostatic repulsions between macroions. In particular ILs based on dicyanamide anion appeared very efficient enhancers for PE dissociation. Conductivities about $10^{-2}$ *S/cm* could be achieved in this way. This efficiency of dicyanamide anion is explained by its high coordinating ability with respect to $Li^+$-cations. Some highly coordinating organic solvent like ethers are also reported to increase conductivity for $Li^+$-based PEs, as well as highly polar organic solvents like ethylene carbonate. In general an effect of ILs on the PEs ionic dissociation is governed by viscosity and hydrophilicity of these solvents, as well as by acid-base properties of particular cation and anion in taken IL.

In another article authors compare conductivity of homopolymer poly(lithium 2-acrylamido-2-methyl propanesulfonate) and that of its copolymer with N-vinyl formamide[5]. As solvent IL N-hexyl-N,N,N-tributyl ammonium methanesulfonate is taken. This IL has an anion similar to the PE unit, which leads to increased solubility of the PE in the IL. Let's recall that our IL1 is also chosen in a way to have similar anion chemical structure in IL and PE, and solubility also appeared high. The comparison between conductivity of the homopolymer and the copolymer in considered article showed an increase of counterion mobility when noncharged units are introduced in polymer structure.

Similar problem is treated in another article of the same team[6]. Lithium 2-acrylamido-2-methyl-1-propanesulfonic acid in the form of homopolymer and like copolymer with N,N'-dimethylacrylamide is tested in IL 1-ethyl-3-methylimidazolium dicyanamide. The latter has excellent conductivity $2.2*10^{-2}$ *S/cm* at $22^oC$. Every of two homopolymers being dissolved in the IL gives a material with high conductivity, and the latter can be further increased by use of the copolymer. *10* or *15 wt.-%* solution of the latter in the IL gives flexible gel with conductivity higher than $8*10^{-3}$ *S/cm* at $30^oC$ and with good mechanic properties.

An immobilization of ILs on solid substrates is highly desirable according to economical aspects of ILs use and to provide new applications of these substances[7]. Such an immobilization can be achieved by both covalent and noncovalent bonding between a IL and a surface. In the same time PEs are known to be easily deposited on different types of substrates. Thus an idea to create polyelectrolyte-functionalized ILs (PFILs) appeared. In particular a carboxyl terminated IL is grafted covalently to a PE with amine terminal groups, specifically polyethylenimine (PEI). Obtained in this way and further immobilized PFLI has shown electrocatalysis activity towards oxidation of b-nicotinamide adenine dinucleotide (NADH). Moreover via Layer-by-Layer (LbL) self-assembly of the PFLI a surface with electrochemically controlled wettability can be constructed. Several other application areas of this PFIL are considered in different articles of the same group. Let's briefly discuss them.

The PFIL can be used in electrolyte-free systems for electrochemistry, being immobilized on electrode in a form of thin film, in which electrochemical reactions take place[8]. In general electrochemistry in such systems is similar to the one in usual electrolyte-containing systems.

But the absence of added electrolyte makes this process a «green» one. Concerning PFIL, IL component gives to the substance high ionic conductivity and affinity to different other substances. In its turn PE component provides stability in aqueous media and ability to deposition.

A multilayer composed of PFIL and Prussian blue (PB) nanoparticles can be obtained via electrostatic LbL assembly[9]. Specifically polycation of PFIL is self-assembled with negatively charged nanoparticles. PFIL/PB film demonstrated high electrocatalytic activity towards reduction of $H_2O_2$.

The considered PFIL can be applied as stabilizing agent for gold nanoparticles in aqueous media[10]. A size-controlled synthesis of these nanoparticles is realized via reduction of $HAuCl_4$ by $NaBH_4$. The size of the particles is determined by $HAuCl_4$ concentration, and resulting nanoparticles have narrow size distribution. To resolve a problem of metal nanoparticles stabilization in water both polymers and ILs were used. The authors of the discussed article have proven that the use of the PFIL as stabilizing agent leads to gold nanoparticles, which are stable in aqueous media during at least one month. In addition they are rather stable at pH 7-13 and at high NaCl concentration. Moreover the nanoparticles showed electrocatalytical activity with respect to oxidation of $\beta$-nicotinamide adenine dinucleotide (NADH for short, a cofactor in enzymatic reactions of $NAD^+/NADH^-$-dependent dehydrogenases).

From above described four articles about the PFIL we see that a combination of PE and IL in one substance can lead to conservation of properties of both components, as well as to appearance of new important characteristics. The latter include convenience of PFIL practical application and increased electrocatalytical activity compared to that of individual components.

We have considered above the problems of PE solution in IL and chemical combination of PE and IL components. Let's take under consideration in certain sense more complex question, specifically solution of a polymer functionalized by IL in an IL. Cellulose modified with IL and dissolved in another IL is explored to get a rheological behavior of this system[11]. A modification of cellulose is carried out by using three ILs with different cations. As solvent in all cases IL 1-ethyl-3-methylimidazolium acetate (EMIM-Ac) is taken. A Newtonian flow behavior is observed for all cellulose samples at a concentration of *5 wt.%* in EMIM-Ac. The viscosity is reduced by at least one decade compared to unmodified cellulose and can be further controlled by hydrophobicity and steric characteristics of IL cation. The viscosity–temperature dependence can be well described by the Vogel–Fulcher–Tammann equation and the flow activation energies are determined by Arrhenius plots.

An interesting article describes a use of IL as solvent for multilayer thin films formation[12]. In general construction of multilayer is complex process from physicochemical point of view, being realized due to a number of interactions between components. In particular hydrogen-bonding, metal–ligand interactions, charge-transfer interactions, covalent attachment, sol–gel reaction, molecular recognition and hydrophobic interactions are considered to be important in LbL assembly with different degree of influence depending on chemical nature of the components. Usually aqueous systems are taken for multilayers formation. But some processes like corrosion and hydration take place, thus water is not a suitable solvent for construction of some electronic devices. Other possible solvents are polar organic ones, in which specific interactions like hydrogen-bonding and molecular recognition can be realized too. In the same time, traditional components for LbL assembly often have difficulties with being dissolved in organic solvents. In addition application of organic solvents becomes restricted due to strong environmental concerns related to volatile organic compound (VOC) regulations. Thus a problem of finding of nonaqueous and green system remains. As such a system ILs have been proposed. Specifically, 1-ethyl-3-methylimidazolium sulfate (EMIM-EtSO$_4$) is taken like a solvent for PSSNa and PEI. Diluted solutions of both PEs in the IL are prepared and used for corresponding multilayer formation. One should pay here an attention on the achieved PSSNa dissolution in IL. This happened because EMIM-EtSO$_4$ was chosen by authors as a solvent with relatively high dielectric constant among a wide range of investigated ILs. Moreover a solution of PSSNa at a concentration as low as 5 mg/mL was prepared. To accelerate the dissolution process, a co-solvent evaporation method was applied. Actually, screening of electrostatic interactions in IL media decreases affinity between polycation and polyanion. But the authors showed that enough strong interactions between components are nevertheless provided due to other above-mentioned interaction types. Moreover the process of multilayer formation is mainly based on ion-exchange mechanism and is governed by entropic contribution due to the release of counterions. Another multilayer constructed from the same IL is composed of PSS-modified single-wall carbon nanotubes and poly(vinyl alcohol). So, the use of the IL provided green nonaqueous solvent system for LbL process and allowed to obtain new materials for electronic and optoelectronic applications.

A cationic PE with regioregular polyalkylthiophene backbone and IL-like side groups is synthesized via modification of corresponding neutral polymer by IL[13]. High-regioregular (above 92%) poly[3-(6-bromohexyl)thiophene-2,5-diyl] reacted with 1-methylimidazole forming poly{3-[6-(1-methylimidazolium-3-yl)hexyl]thiophene-2,5-diyl bromide} (PMHT-Br). The latter is characterized by the same regioregularity like initial neutral polymer. This PE appeared soluble in water and water miscible solvents such as methanol and DMSO. In aqueous solutions

PMHT-Br exists in a form of micelles with poly(3-hexylthiophene) core and 1-methylimidazolium bromide shell. High PMHT-Br solubility in water and polar organic solvents gives possibility to prepare composites of this PE with noble-metal nanoparticles, anionic PEs and some other substances.

In the end of this literature overview we should mention a detailed review about polymeric ILs[14], which represent another important type of systems containing both PE and IL structures. Indeed polymeric ILs can be considered like ILs and like PEs as well. In this sense they are similar to PFILs, nevertheless their chemical structure and methods of synthesis are distinct. In general as one can see the systems containing both PE and IL components are quite diverse. In particular PE and IL moieties can belong either to different chemical species either to the same one.

Now let's start a discussion about results of PEs-ILs systems study, beginning with particular aspects of their preparation and manipulations with this special kind of binary systems.

## 4.1. Preparation of PSS solutions in ILs and scattering measurements

### 4.1.1. Preparation of PSS solutions in ILs

PSS taken for preparation of solutions in IL1 and IL2 is always the acid form. So let's call further in this chapter PSSH as simply PSS.

The process of PSS dissolution in both IL1 and IL2 is carried out at $T$ around $70^oC$, accompanied by stirring. This process is rather slow, first of all due to high viscosity of ILs, and takes from several hours to several days. So it's desirable to use a temperature as high as possible avoiding thermal decomposition of solution components. ILs are highly thermostable (decomposition point is around several hundred degrees) and PSS begins to decompose at around $200^oC$. On the other hand, we don't know the influence of ILs on PSS decomposition. Indeed catalytic activity of ILs in different processes is noted, thus it's reasonable not to reach high temperature in order to avoid any chemical process in such a complex system. But certain heating is necessary, because at room temperature even stirring is complicated due to high viscosity of the system. Practically a silicone oil bath was applied to maintain certain temperature.

Like for the case of aqueous solution after getting a homogeneous system one should wait some time, specifically around three days to achieve PSS dissolution at molecular level and to be not disturbed by upturns in the scattering profiles.

### 4.1.2. Preparation of cells for scattering experiments

When PSS is added to ILs, viscosity of the latter is increased. Thus corresponding PSS solutions are very viscous systems, the most concentrated among those used in this study don't flow. So, filling of cell cannot be realized by means of pipette and should be done with some kind of spatula.

Another particular aspect concerning cells preparation is related to air bubbles captured by solution. Again due to high viscosity of the latter it's difficult to remove the air. At the timescale of the scattering measurements small bubbles usually aggregate in a big one. If the latter is situated on the path of the beam, results of measurements will be disturbed. Nevertheless, by following applied method of solutions preparation that assumes heating, air content in final solution is not high and resulting bubbles are not disturbing.

### 4.1.3. Problems of contrast and background

For SAXS, contrast between solute and solvent in our systems is not very high. That is natural, as chemical structures of the components of solutions are rather similar. Thus rather long counting time is required to get scattering profiles with a good statistics.

For SANS, to have a good contrast one should use solute and solvent in different forms: protonated and deuterated ones. To decrease background caused by incoherent scattering a solvent should be taken in deuterated form and consequently a solute in protonated one. But ILs are hardly available in deuterated form. In addition, at small $q$-values where our measurements are performed, incoherent scattering is not so disturbing like at high ones. Thus we applied protonated ILs and deuterated form of PSS. The latter is synthesized in the same way like protonated one is, following Makowski et al. procedure described in detail in annex.

Concerning SANS experiments we have to note the next important remark. Upturns caused by mica and typical for SAXS are absent in the case of SANS. Thus, in the latter, heterogeneities in the solution can be the only source of an upturn in the resulted scattering profile.

### 4.1.4. Scattering measurements

A detailed description of SAXS and SANS diffractometers applied for the present investigations is given in annex.

The SAXS diffractometer is adapted for usual non specialized laboratory. A flux of X-ray is rather low and a time about several hours is required to perform one measurement. In its turn SANS diffractometer belongs to specialized neutron facilities situated at Institut Laue-Langevin (ILL) (Grenoble, France). A beam flux is strong and one measurement usually requires less than one hour to be performed. In general, the experiment duration for a particular sample decreases if contrast, polymer concentration or explored $q$-values increase. An experiment time decreases as well if thickness of spacer containing polymer solution increases. But too big thickness can cause significant multiple scattering, thus being damaging for correctness of results. In the same time solutions with high X-ray absorption should be measured with spacers of small thickness in order to increase the transmission. For X-ray scattering the absorption of radiation is mainly a true absorption, contrarily to neutron scattering.

Along with scanning of the solution those of the solvent and empty cell are required to account for different types of scattering background, which have to be removed to obtain the scattering from polymer. Measurements of different standards are required as well to make a correct instrument adjustment and calibration. A set of these preliminary measurements depends on a type of irradiation and particular instrument.

## 4.2. PSS solutions in IL1

### 4.2.1. PSS with *N = 790* in IL1 by SAXS

The first investigation of PSS behavior in IL1 was done by SAXS for the same PSS sample as in the case of solutions in molecular solvents (see *Chapter 3*), that is for the one with $N = 790$ as determined by SEC. The most concentrated solution with $c_{PSS} = 0.110M$ is prepared and further diluted to obtain four PSS solutions at different $c_{PSS}$. These solutions as well as free IL1 are scanned at SAXS diffractometer. The results of measurements are demonstrated in Figure 1 in standard form of profile related to scattering from polymer.

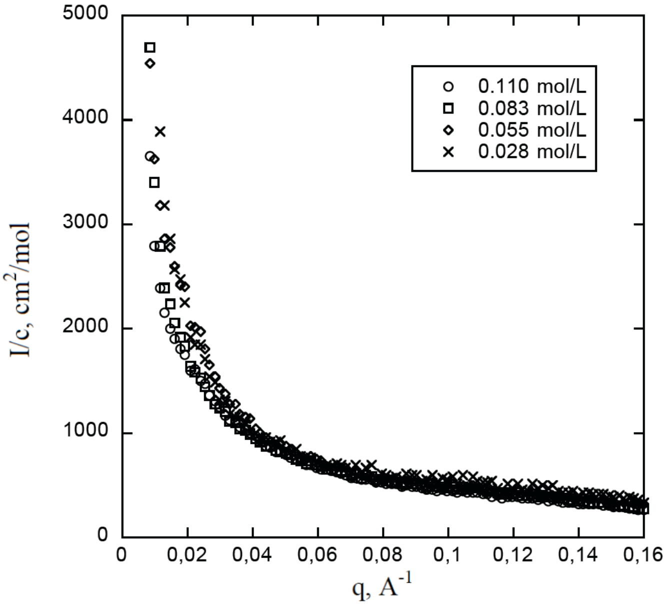


Figure 1. Scattering profile of PSS ($N = 790$) solutions in IL1 obtained by SAXS.

The first important point to note from these curves is an absence of the classical electrostatic peak observed in LME-free aqueous solutions with the same PE. LME is not added to these solutions and the PE charge screening is provided by ions of the IL. If to apply classical considerations for this case, we can conclude the following. $\varepsilon$-value of IL1 is rather low compared to that of water, thus $l_B$-value should be rather high. In the same time concentration of low-molecular ions is very high, because the IL is entirely composed of ions. So $r_D$-value should be very low. Obviously we have $r_D < l_B$ and electrostatic interaction between PSS chains is screened in this system.

These simple considerations are useful to provide some understanding of observations; nevertheless they should be accepted with care. First, $\varepsilon$-value is not very suitable characteristic to describe dielectric properties of ILs as these properties strongly depend on local effects. Specifically positions and orientations of IL ions are important and depend on the presence of a third component, for example the macroion. That is in vicinity of macroion the latter and the IL components influence each other. So such an integral characteristic of pure IL as $\varepsilon$-value doesn't describe precisely the IL effect on PE electrostatic interactions. Second, IL1 is weakly basic compound, because tosylate anion corresponds to strong acid. Basic properties of IL1 (and of IL2 too) are much weaker compared to those of water, ethanol and DMSO, the solvents discussed before. Actually tosilate anion has about the same tendency to accept proton like unit of PSS anion does, according to their similar chemical structure. So, one can suppose that the acid form of PSS is not fully dissociated from a chemical point of view in considered ILs, and protons are distributed between macroanions and low-molecular ones (remember that protons never exist in a solution in a free state due to their huge charge density and very strong field, being linked to some base). That is important consideration, but which is difficult to check in practice, because it's quite hard in a some experiment to distinguish between non dissociated and condensed protons, especially in ionic media. Even a strict boundary between these two kinds of protons cannot be drawn, because there are a lot of intermediate cases provided by hydrogen bonding. If to conclude, such a multicomponent ionic system is quite complex with respect to a question about real state of every component. Thus we continue to regard PSS like a strong PE as it's classically considered, but possibility of only partial dissociation should be kept in mind when analyzing the results.

To finish with the special nature of proton, let's briefly discuss another question, directly related to the most of our systems. As told above, proton is always linked to some base. In particular, when PSS is dissociated in water, the molecule of the latter accepts proton, forming oxonium cation. One can suppose that even in PSS samples which contain some water, protons are linked with the latter, that is we have oxonium poly(styrene sulfonate). Of course, oxonium cation has much bigger size than proton, being comparable by this characteristic with alkali metal cations. But contrary to the latter oxonium is not spherically symmetric ion. Proton is situated on the periphery of oxonium cation and is readily available for interaction with another bases. In general, the complexation of proton with solvent molecule doesn’t eliminate special character of this cation.

To calculate characteristics of the single polymer chain scattering curves represented in Figure 1 have to be transformed in the form of Zimm plot. The latter resulted from such a transformation is shown in Figure 2.

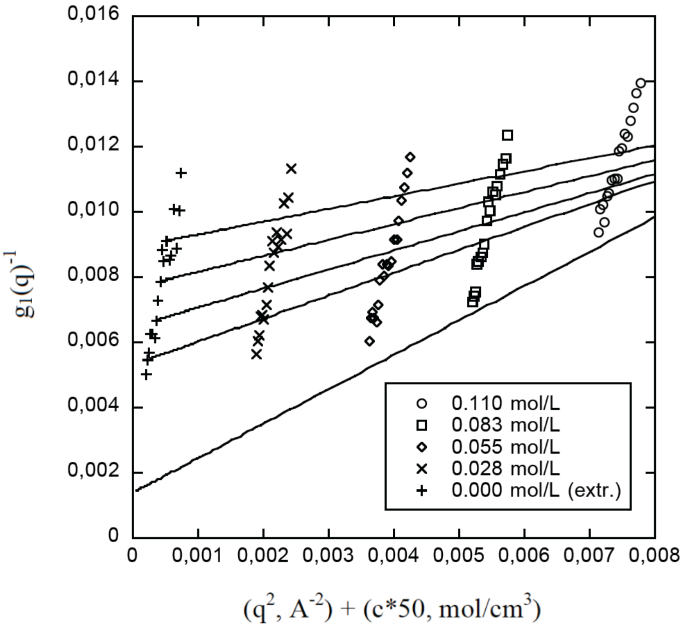


Figure 2. Zimm plot for PSS (*N* = *790*) solutions in IL1 (SAXS).

From Figure 2 *N*-value appeared equal to *760*, being in a good agreement with that determined by SEC. Another important characteristic, $A_2$-value is equal to $7.97*10^{-4}$ *mol*mL** $g^{-2}$. This value is comparable with the one for PSS aqueous solutions in presence of LME, thus IL1 behaves like a good solvent for PSS.

To get value of $R_g$ we have performed the fit of form factor $g_1(q)$ with the Debye function $g_D(q)$, demonstrated in Figure 3. In this way we obtained $R_g = 16$ *nm.* This value is also close to the corresponding one for PSS aqueous solutions with added LME. So both $A_2$ and $R_g$-values demonstrate that PSS behaves in IL1 like neutral polymer in a good solvent.

A good solvent quality and extended polymer conformation in PSS-IL1 system can be surprising. Indeed IL1 belongs to solvents with intermediate polarity. Organic solvents with *ε*-value in this range either don’t dissolve PEs (and PSS in particular) either don’t display good solvent quality. Special behavior of IL1 should be attributed to complex chemical structure of both solute and solvent. A number of interactions can be realized between them, increasing an

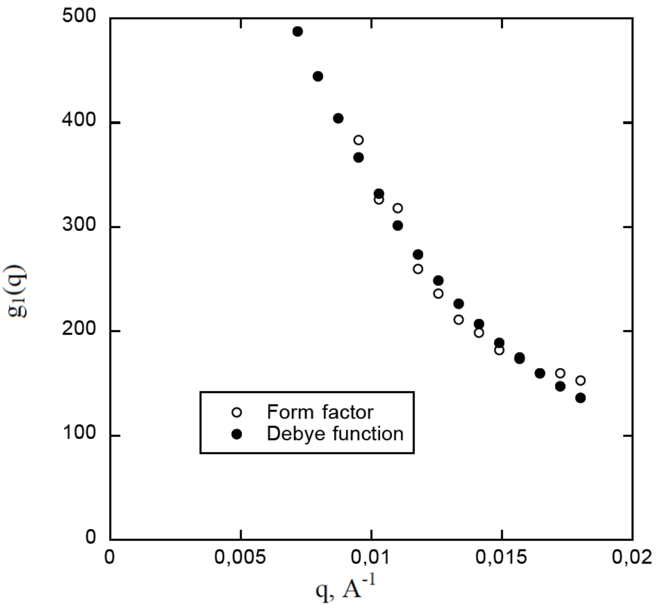


Figure 3. Fit of $g_1(q)$ with $g_D(q)$ for PSS ($N = 790$) solutions in IL1 (SAXS).

affinity between PSS and IL1 and solvent quality of the latter. These interactions discussed above in *Introduction* include not only electrostatic one but some specific ones as well.

Relative role of a certain interaction for IL-containing systems is a point of active discussion and is obviously dependent on chemical structures of particular components. In the most cases electrostatic effects for these systems are not dominant, as ions of ILs are usually large and often have diffuse or even strongly delocalized charges. In the same time presence of different functional groups provides some specific interactions that are often more significant by their total energy compared to the electrostatic one. In general although electrostatic effects in IL-containing systems cannot be neglected, their role is less important compared to the case of molten salts.

### 4.2.2. PSS with $N = 790$ in IL1 by SANS

PSS sample with the same $N = 790$ but in the deuterated form was dissolved in protonated IL1 in order to carry out SANS measurements. An aim of the latter was the same like of those performed by SAXS and discussed above, that is to study single polymer chain. This SANS experiment was done to check a correctness of the previous measurements by using another scattering technique. Resulted SANS curves corresponding to different $c_{PSS}$ in dilute regime are

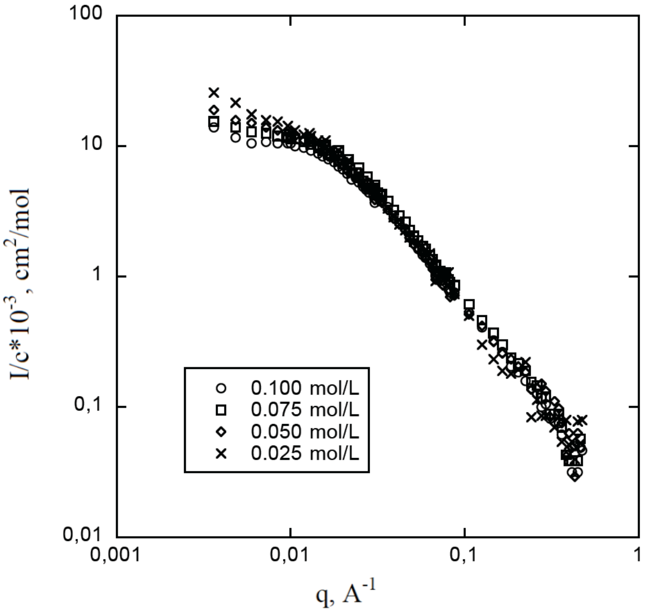


Figure 4. Scattering profile of PSS (*N = 790*) solutions in IL1 obtained by SANS.

shown in Figure 4. Here the profile is represented in logarithmic coordinates, as it's clearly more convenient to analyze SANS results. From Figure 4 one can see again screening of the PE electrostatic interaction in the IL media.

Zimm plot corresponding to the curves shown in Figure 4 is built (Figure 5), and fit of $g_1(q)$ with $g_D(q)$ is performed (Figure 6) to calculate macromolecular characteristics for PSS with *N = 790* in IL1. One has to pay an attention on rather good statistics of the scattering curves obtained by SANS, resulted in proper extrapolations in Zimm plot and good fitting between $g_1(q)$ and $g_D(q)$ as well. This good statistics arises from high contrast between protonated and deuterated substances and from strong neutron flux in applied instrument as well. High values of scattered intensity in the case of SANS compared to SAXS measurements is another consequence of higher contrast in neutron scattering experiments. In addition discussed results demonstrate that for the range of small *q*-values high incoherent scattering of protonated IL1 is not a significant obstacle to obtain scattering curves of appropriate quality for dissolved polymer.

Thus required characteristics of single macromolecule are calculated. We obtained *N = 815*, $A_2 = 7.38*10^{-4}\ mol*mL*g^{-2}$ and $R_g = 15\ nm$. These values are rather close to the ones obtained by SAXS. So our conclusions about PSS extended conformation and IL1 good solvent quality in considered solutions seem to be correct. Nevertheless another measurements are performed and presented further in this chapter to confirm our conclusions in another way and to learn more about PSS behavior in IL1.

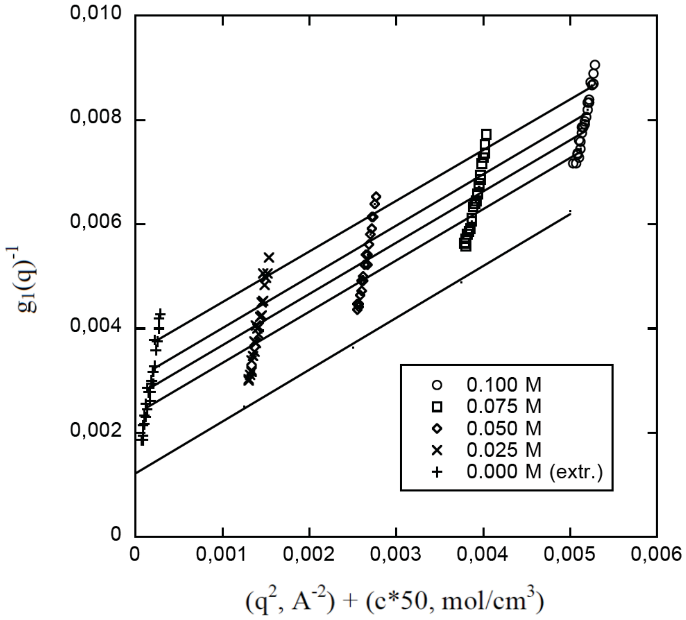


Figure 5. Zimm plot for PSS (*N = 790*) solutions in IL1 (SANS).

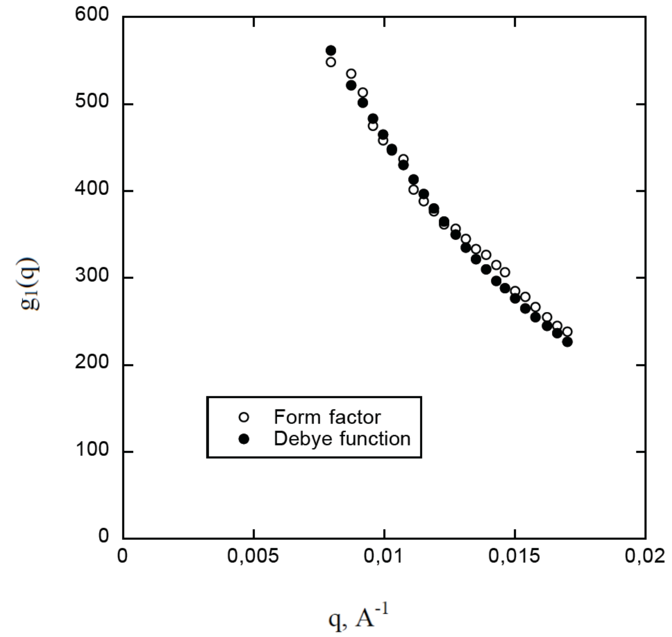


Figure 6. Fit of $g_1(q)$ with $g_D(q)$ for PSS (*N = 790*) solutions in IL1 (SANS).

### 4.2.3. PSS with *N = 300* in IL1 by SANS

Investigation of PSS samples of different degree of polymerization can provide additional information about the structure of PSS in solution. First, *P(q)* for different *N*-values can be obtained and compared to explore type of PSS behavior in studied solutions. Second, we can conclude about PSS behavior by determination of ν-value in $R_g \sim M_w^{\nu}$ dependence as well. Thus PSS samples with another *N*-values are taken to perform similar measurements as done for the $N = 790$ case. Specifically $N = 300$ and $N = 17850$ are chosen, as corresponding deuterated poly(styrene) samples were available. In general any *N*-values can be taken for such a study, if applied diffractometer allows to study Guinier range for corresponding polymer sample. In our case variation of sample-detector distance in applied instrument could be largely realized, thus wide range of *q*-values was available for exploration. That's why PSS samples with so different *N*-values could be taken. Let's discuss the most low-molecular PSS sample with $N = 300$.

PSS solutions with $c_{PSS}$ in dilute regime are prepared. In considered case $c^*$ being the crossover between dilute and semidilute regimes is higher as *N* is lower, and maximum $c_{PSS}$ is equal to *0.2M*. Let's say few words about $c^*$ determination. As indicated in *General Introduction*, $c^* = 1/[\eta]$. In its turn $[\eta] = K^*M^{\alpha}$ with *K* and *α* being characteristic constant for taken polymer, solvent and temperature. Thus changing *M* we can follow how $c^*$ is changed. But values of *K* and *α* are not tabulated for such a rather unusual system as PSS in IL1. So these values were taken for another system, specifically for PSS in water. As IL1 and water are both good solvents for PSS, we can suppose that *K* and *α* values are rather close for PSS in both these solvents. Anyway values of these constants were taken only to evaluate $c^*$, and actual $c_{max}$ was always taken to be below $c^*$ in order to provide dilute regime with high probability. To finish with $c^*$ evaluation we should note, that for higher accuracy *K* and *α* values corresponding to PSS aqueous solutions should be taken, and not those for poly(styrene) in toluene. Although the last system is the classical one for poly(styrene) backbone in a good solvent, polymer in this case is not polar. So its conformation is completely different from that of PSS in water for the same *N*-values of both polymers as discussed in *Chapter 3*.

Scattering curves for PSS ($N = 300$) solutions in IL1 obtained in SANS experiment are demonstrated in Figure 7. Again statistics is good, allowing proper determination of single polymer chain characteristics. For that Zimm plot is constructed (Figure 8) and fit of $g_1(q)$ with $g_D(q)$ is done (Figure 9).

From Figure 8 we have found $N = 275$. Concerning $A_2$-value it appeared equal to $11.51*10^{-4}$ $mol*mL*g^{-2}$. So we observe slight increase of $A_2$-value with decreasing of *N*-value. By the fit shown in Figure 9 we have found $R_g = 8.5\ nm$. An analysis of $R_g$ *vs.* $M_w$ dependence completed by third $M_w$-value will be done below.

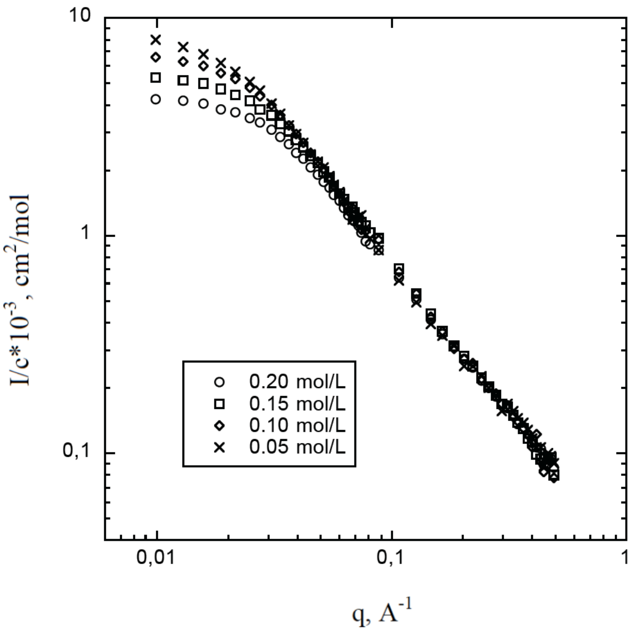


Figure 7. Scattering profile of PSS (*N* = *300*) solutions in IL1 obtained by SANS.

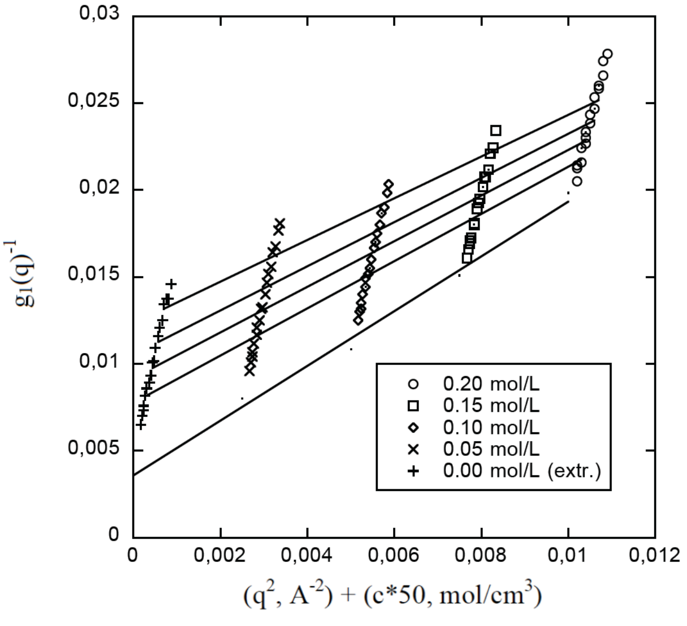


Figure 8. Zimm plot for PSS (*N* = *300*) solutions in IL1 (SANS).

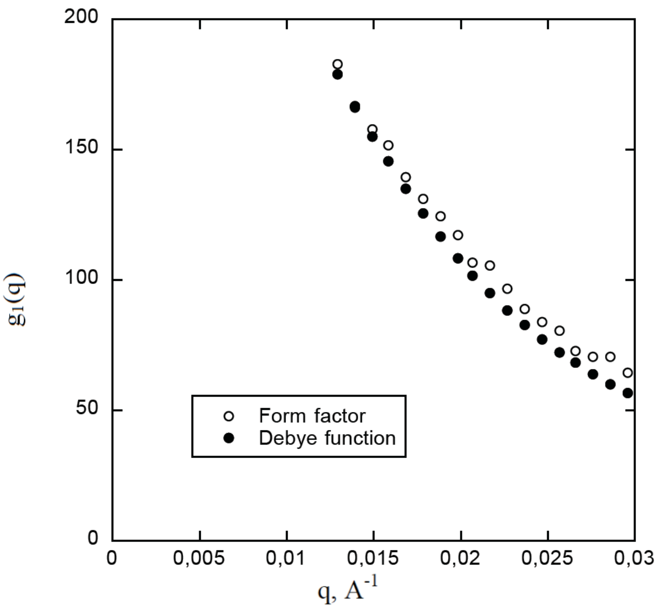


Figure 9. Fit of $g_1(q)$ with $g_D(q)$ for PSS ($N = 300$) solutions in IL1 (SANS).

### 4.2.4. PSS with $N = 17850$ in IL1 by SANS

Solutions of deuterated PSS sample with $N = 17850$ in protonated IL1 were further explored by SANS to get the variation of $R_g$ with $M_w$. For this the most high-molecular PSS sample $c^*$-value is evidently very low. Thus a problem appeared due to a difficulty of preparation of several PSS solutions at $c_{PSS}$ detectable by SANS technique. So only two $c_{PSS}$ are taken for construction of Zimm plot and calculation of $P(q)$. The results for considered solutions are shown in Figure 10 (scattering profile), Figure 11 (Zimm plot) and Figure 12 (fit of the form factor with the Debye function).

For characteristics of single PSS chain we obtained next values: $N = 20350$, $A_2 = 1.27*10^{-4}$ $mol*mL*g^{-2}$ and $R_g = 87\ nm$. As one can conclude from $N$-value these results seem to be rather correct despite the use of only two PSS concentrations. $A_2$-value is reduced for this the most high-molecular PSS sample. For $R_g$ *vs.* $M_w$ variation we have three points now to see the dependence. Let's explore the latter in the next subchapter to make more conclusions about PSS behavior in IL1.

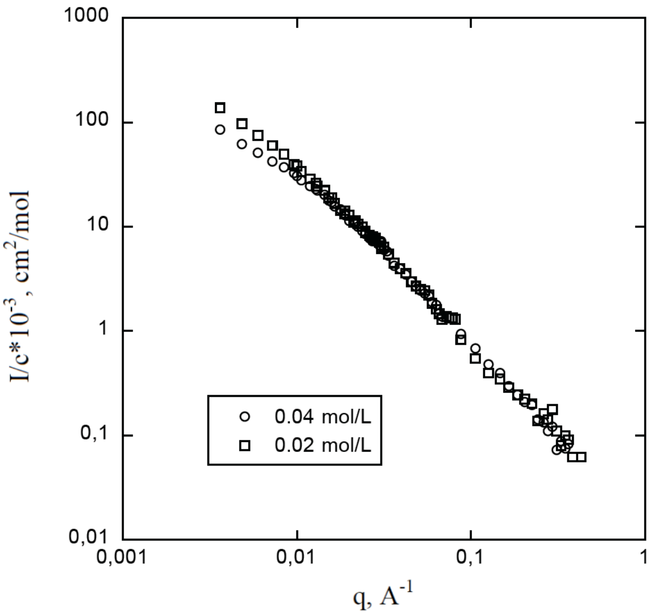


Figure 10. Scatering profile of PSS (*N* = *17850*) solutions in IL1 obtained by SANS.

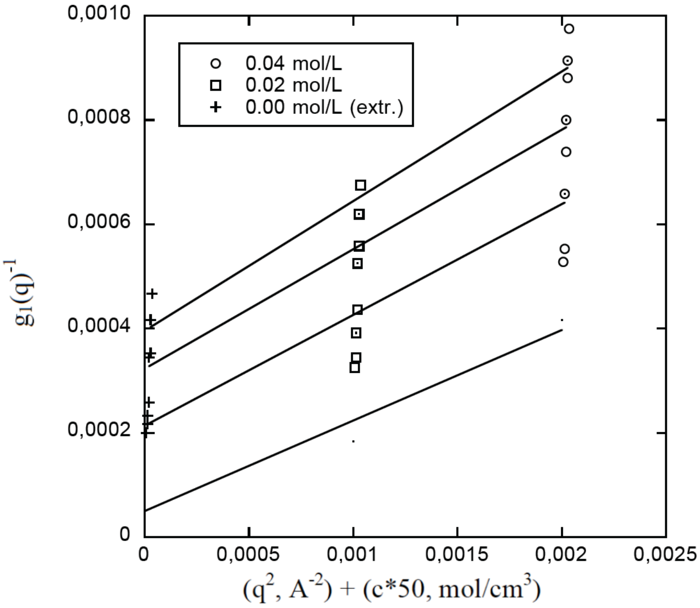


Figure 11. Zimm plot for PSS (*N* = *17850*) solutions in IL1 (SANS).

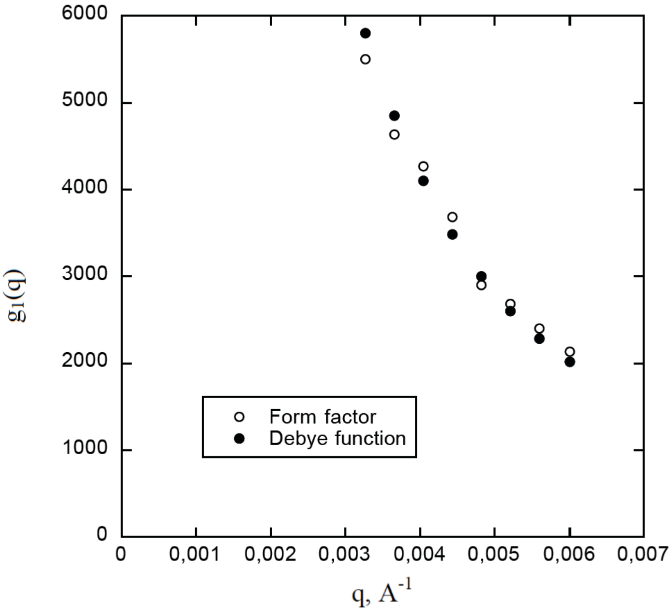


Figure 12. Fit of $g_1(q)$ with $g_D(q)$ for PSS ($N = 17850$) solutions in IL1 (SANS).

4.2.5. $R_g$ *vs.* $M$ dependence for PSS solutions in IL1

In order to learn more about character of PSS behavior in IL1 found values of $R_g$ are plotted against corresponding $M$-values. A slope of this dependence provides information about

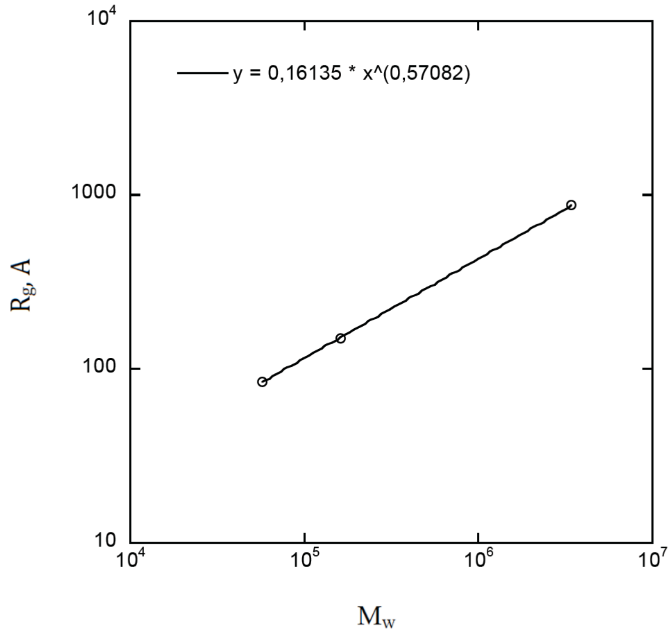


Figure 13. Variation of $R_g$ against $M$.

statistics that should be applied for PSS solutions in IL1. The discussed plot is demonstrated in Figure 13.

For the dependence $R_g \sim M^{\nu}$ we obtained $\nu$-value close to *0.588*. The latter is typical for excluded volume statistics, that is for the case of a good solvent. That is another confirmation of IL1 good solvent quality for PSS.

### 4.2.6. *P(q)* for solutions of PSS with different *N* in IL1

Form factors *P(q)* for PSS with different *N* in IL1 are calculated by extrapolation of scattering curves at $c = 0$. These *P(q)* are represented in Figure 15.

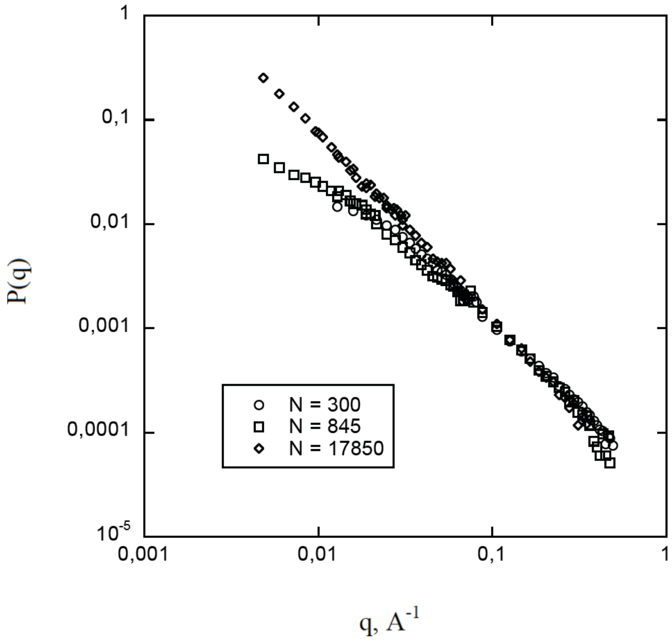


Figure 14. *P(q)* for different PSS samples in IL1 media.

In intermediate $q$-range, that is in the range of universal behavior *P(q)* scales like $q^{-1/\nu}$ with $\nu$ close to *0.588* (a little bit more if to specify). So we have excluded volume statistics for polymer behavior in considered solutions.

### 4.2.7. PSS with $N = 300$ in IL1 at 80°C by SANS

An interesting point is to follow PSS behavior in IL1 at high temperature. Due to limited thermal stability of PSS and to unknown influence of IL1 on PSS thermal decomposition the temperature for considered measurements is fixed at 80°C. Heating is provided in applied SANS instrument. Experiment course was the same like for measurements at room temperature, except additional time required for heating. The scattering curves resulted from this experiment are shown in Figure 15.

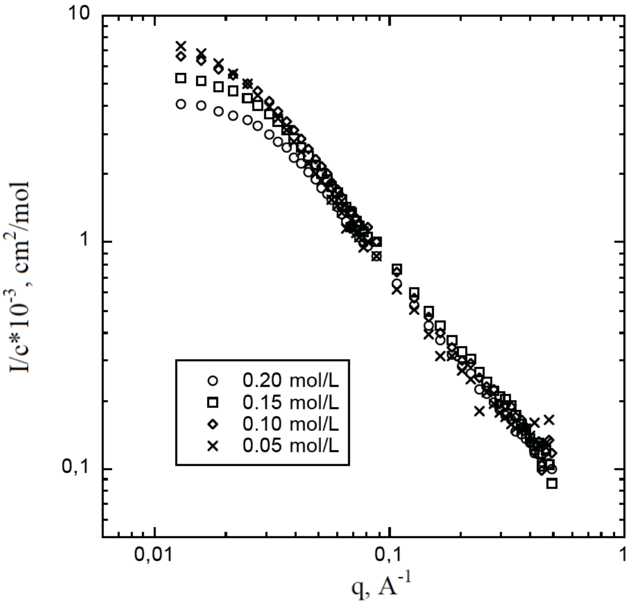


Figure 15. Scatering profile of PSS ($N = 300$) solutions in IL1 at 80°C obtained by SANS.

These curves are completely the same (in limits of experimental uncertainty) like the ones obtained for this system at room temperature. There is no need to build Zimm plot and to do the fit of $g_1(q)$ with $g_D(q)$ as results obviously will be approximatively the same (because volumes variations at heating until 80°C are not significant too). Thus in explored rather narrow temperature range there are no changes in PSS behavior in IL1 media. In particular good solvent quality of IL1 is conserved.

## 4.3. PSS solutions in IL2

Deuterated PSS sample with $N = 300$ is dissolved in IL2 and studied by SANS. Again the IL was taken in protonated form, nevertheless it was not a significant problem for considered study. Solubility of PSS in IL2 is lower compared to that in IL1 and maximum PSS concentration taken for the study, specifically $0.2M$ is close to limit of PSS solubility in IL2. Solutions at lower $c_{PSS}$ were obtained by dilution of the most concentrated one.

As discussed in *Chapter 1* IL2 displays an aggregation at nanoscale length and a peak at $q \cong 0.25A^{-1}$ arises. When PSS is added the peak position moves a little bit to smaller $q$-values. Thus a calculation of $P(q)$ of PSS from obtained scattering profile (Figure 16) is impossible. Indeed scattering from heterogeneities in IL2 interferes with that of PSS and variation of $q^*$-value disturbs the subtraction of solvent scattering. As the peak is partially situated in intermediate $q$-region we can't explore $P(q) \sim q^n$ dependence there. Nevertheless values of $A_2$ and $R_g$ still can be determined as there is no scattering from solvent nanoformations in Guinier range. For that Zimm plot is built (Figure 17) and fit of $g_1(q)$ with $g_D(q)$ is performed (Figure 18).

So for PSS ($N = 300$) solutions in IL2 we have found $N = 315$, $A_2 = 1.33*10^{-4}\ mol*mL*g^{-2}$ and $R_g = 5.3\ nm$. $N$-value shows us that indeed there is no influence of scattering from IL2

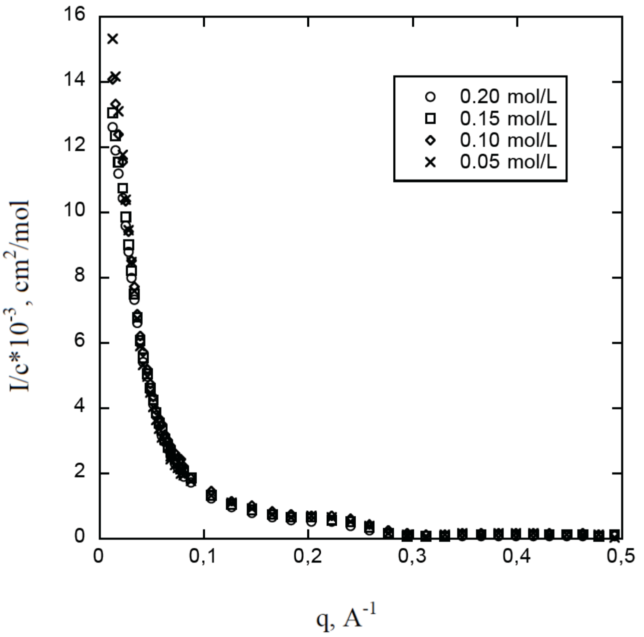


Figure 16. Scattering profile of PSS ($N = 300$) solutions in IL2 obtained by SANS.

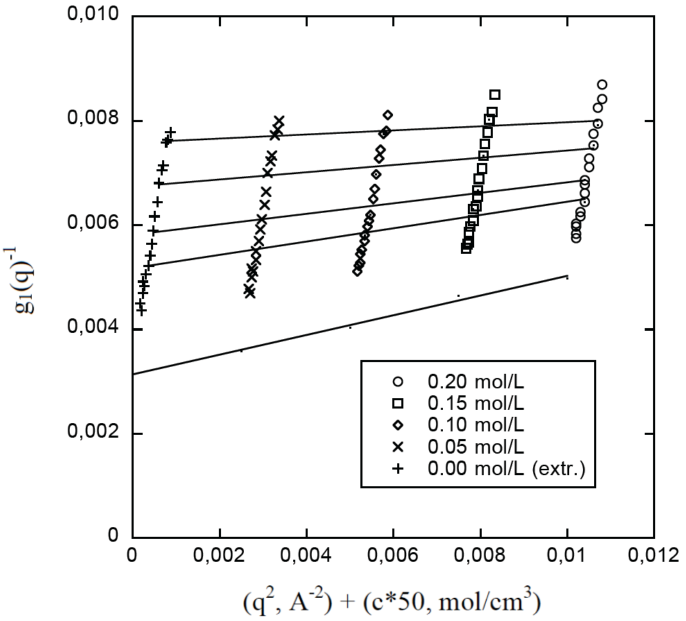


Figure 17. Zimm plot for PSS (*N* = *300*) solutions in IL2 (SANS).

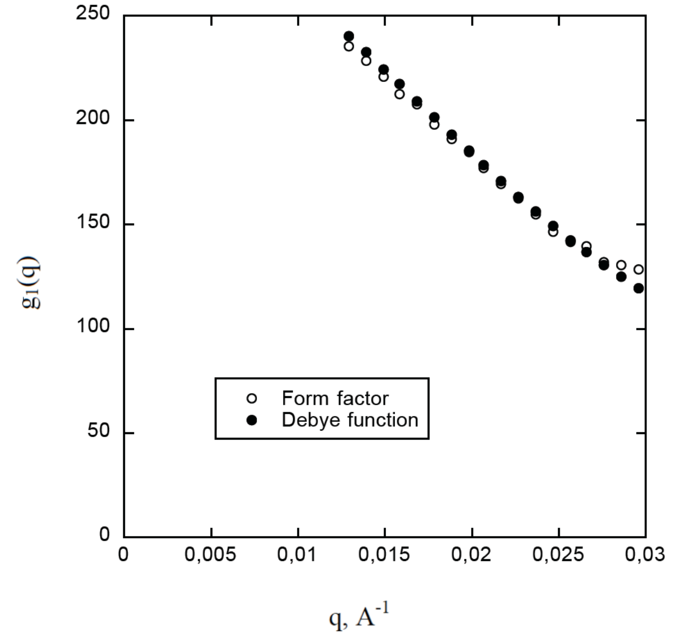


Figure 18. Fit of $g_1(q)$ with $g_D(q)$ for PSS (*N* = *300*) solutions in IL2 (SANS).

heterogeneities on scattering from PSS chains at small *q*-values. $A_2$ and $R_g$ values are quite small and reveal a decrease in the solvent quality and a shrinkage of the polymer conformation.

Thus, we see that the replacement of tosylate anion in IL by octylsulfate one significantly decreases IL solvent quality with respect to PSS. Gross formula of both anions is similar, but their chemical nature is basically different. Tosylate is an aromatic anion and is more active in sense of interaction with PSS solute. In its turn octylsulfate anion is of aliphatic type, being less polar and less active with respect to PSS. In particular aromatic π-π interaction cannot be realized in the latter case. In addition tosylate anion and PSS unit are almost identical by chemical structure. Thus partial replacement of IL anion by units of added polyanion should not significantly change IL structure. This is not only theoretical consideration but is proven by us, when influence of PSS addition on IL1 nanostructure was explored (*Chapter 1*). This conservation of IL1 structure is probably another factor which favors good solvent quality of this IL with respect to PSS. A probable increasing of IL polarity from IL2 to IL1 can be pointed as additional factor that should increase solvent quality of the latter IL. The difference in ILs nanoscale structure probably plays an important role for polymer conformation in a solution as well. More aggregated IL2 can provoke additional shrinkage of polymer chain due to adsorption of the latter on ion aggregates.

Let’s remind that IL3 in which long aliphatic tail is linked to cation does not dissolve PSS at room temperature. This is probably related to the fact that IL cation is the main responsible for interaction with PSS macroanions. That is another indication that problem of solute-solvent interactions is a basic one in PE-IL systems. Slightly increased size of heterogeneities in IL3 compared to that in IL2 should lead to additional shrinkage of polymer conformation as well.

## Conclusions

Solutions of PSS in two different ILs have been studied by scattering techniques to explore the PE conformation and dispersion state, as well as the solvent quality in these new systems.

PSS in IL1 behaves like a neutral polymer in a good solvent. The IL being an ionic media provides screening of the PE electrostatic interaction. Thus there is no characteristic peak at scattering profiles of PSS solutions in IL1. In the same time complex chemical structure of IL1 containing different functional groups causes strong interaction with PSS macrochains. This interaction includes several contribution and leads to extended PSS conformation and good IL1 solvent quality in considered solutions. Thus ILs being not strongly polar solvents nevertheless can display good solvent quality with respect to PSS like water does.

These conclusions are initially obtained by analyzing $A_2$ and $R_g$ values calculated from SAXS data. For that scattering profiles are transformed in a form of Zimm plots and fits of $g_1(q)$ with $g_D(q)$ are performed as well. $A_2$ and $R_g$ values appeared rather high and comparable with those for corresponding PSS aqueous solutions with added LME. *N*-values have been always used to control correctness of scattering measurements by comparison with *N*-values from SEC characterization. Further SANS results have proven in the same way discussed findings. In the next step $R_g$ *vs.* $M_w$ dependence is built using results for PSS samples with different *N*-values. We have found that $R_g$ scales like $M_w^{\nu}$ with $\nu$-value close to *0.588*, which is typical for excluded volume statistics. Finally scattering profiles for different PSS samples are calculated. It appeared that in intermediate $q$-range $P(q)$ scales like $q^{-1/\nu}$ with $\nu$ close again to *0.588*. A use of heating has shown that until 80°C there are no changes in PSS behavior in considered solutions.

PSS solutions in IL2 are explored by SANS to get scattering profiles and to calculate $N$, $A_2$ and $R_g$ values. As IL2 displays nanoscale aggregation we could not see how $P(q)$ scales in intermediate $q$-range. Nevertheless Guinier range was available for correct determination of single chain characteristics. Obtained $A_2$ and $R_g$ values appeared rather low displaying decreased solvent quality and shrunk PSS conformation compared to the IL1 case. Gross formula of this IL is similar to that of IL1, but the chemical structure is basically changed. Anion of aromatic type in IL1 is changed by the one of aliphatic type in IL2. This aliphatic anion is more inert in sense of interactions with PSS solute thus IL solvent quality is reduced in this way and the PE conformation becomes more compact. More pronounced ion aggregation in IL2 should cause shrinkage of polymer chains too.

IL3 can dissolve PSS only at heating. So by putting long nonpolar tail from IL anion to its cation we decrease IL solvent quality with respect to PSS. Probably this is related to the fact that

IL cation is the main responsible for interaction with PSS macroanions. Increased ion segregation in IL3 compared to that in IL2 probably contributes to observed polymer insolubility as well.

Thus ILs solvent properties with respect to PSS are very sensitive to chemical structure of these new solvents. Certain functional groups should be present in ions of taken IL to provide efficient interaction with particular PE. Dependence of ILs solvent properties on their chemical structure is realized via modification of their nanostructure as well. These properties are related to known advantage of ILs consisting in their structural flexibility and making them designer solvents.

In this chapter we mainly considered ILs solvent properties and their relation to chemical structure of these substances. Another interesting point is to explore electrostatic effects in PE-IL systems and local influence of IL on PE behavior. For that we had to choose a PE that would be a priori fully dissociated from chemical point of view in an IL. That is not the case for the acid form of PSS. Such a PE was applied and will be discussed in the next chapter. Some spectacular results about behavior of classical neutral polymer in an IL will be represented in the next chapter as well.

## References

[1]N. Ogata, K. Sanui, M. Rikukawa, S. Yamada and M. Watanabe, *Synthetic Metals*, **69** (1995), 521
Super ion conducting polymers for solid polymer electrolytes

[2]C. Tiyapiboonchaiya, D. R. MacFarlane, J. Sun and M. Forsyth, *Macromol. Chem. Phys.*, **203** (2002), 1906
Polymer-in-ionic-liquid electrolytes

[3]D. Batra, S. Seifert, L. M. Varela, A. C. Y. Liu and M. A. Firestone, *Adv. Funct. Mater.*, **17** (2007), 1279
Solvent-mediated plasmon tuning in a gold-nanoparticle–poly(ionic liquid) composite

[4]M. Forsyth, J. Sun, F. Zhou and D. R. MacFarlane, *Electrochimica Acta*, **48** (2003), 2129
Enhancement of ion dissociation in polyelectrolyte gels

[5]J. Sun, D. R. MacFarlane and M. Forsyth, *Solid State Ionics*, **147** (2002), 333
Lithium polyelectrolyte–ionic liquid systems

[6]C. Tiyapiboonchaiya, J. M. Pringle, D. R. MacFarlane, M. Forsyth and J. Sun, *Macromol. Chem. Phys.*, **204** (2003), 2147
Polyelectrolyte-in-ionic-liquid electrolytes

[7]Y. Shen, Y. Zhang, Q. Zhang, L. Niu, T. You and A. Ivaska, *Chem. Commun.*, (2005), 4193
Immobilization of ionic liquid with polyelectrolyte as carrier

[8]Y. Shen, Y. Zhang, X. Qiu, H. Guo, L. Niu and A. Ivaska, *Green Chem.*, **9** (2007), 746
Polyelectrolyte-functionalized ionic liquid for electrochemistry in supporting electrolyte-free aqueous solutions and application in amperometric flow injection analysis

[9]F. Li, C. Shan, X. Bu, Y. Shen, G. Yang and L. Niu, *Journal of Electroanalytical Chemistry*, **616** (2008), 1
Fabrication and electrochemical characterization of electrostatic assembly of polyelectrolyte-functionalized ionic liquid and Prussian blue ultrathin films

[10]C. Shan, F. Li, F. Yuan, G. Yang, L. Niu and Q. Zhang, *Nanotechnology*, **19** (2008) 285601
Size-controlled synthesis of monodispersed gold nanoparticles stabilized by polyelectrolyte-functionalized ionic liquid

[11]N. Gonsior and H. Ritter, *Macromol. Chem. Phys.*, **212** (2011), 2633
Rheological behavior of polyelectrolytes based on cellulose and ionic liquids dissolved in 1-ethyl-3-methyl imidazolium acetate

[12]T. Nakashima, J. Zhu, M. Qin, S. Hoa and N. A. Kotov, *Nanoscale*, **2** (2010), 2084
Polyelectrolyte and carbon nanotube multilayers made from ionic liquid solutions

[13]D. Bondarev, J. Zednik, I. Sloufova, A. Sharf, M. Prochazka, J. Pfleger, J. Vohlidal, *Journal of Polymer Science: Part A: Polymer Chemistry*, **48** (2010), 3073
Synthesis and properties of cationic polyelectrolyte with regioregular polyalkylthiophene

backbone and ionic-liquid like side groups

[14]D. Mecerreyesa, *Progress in Polymer Science*, **36** (2011) 1629
Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes

# CHAPTER 5

# Polymers behavior in IL1: Extreme cases of chemical charge fractions equal to 1 and to 0

## Introduction

Strong PEs are considered to be fully dissociated from chemical point of view in aqueous solutions. Process of counterion condensation leads to a decrease in the effective charge fraction, nevertheless chemical charge fraction is equal to *1*. In the same time an application of a nonaqueous media can cause a decrease in the chemical charge, in particular if some solvent less polar and less basic compared to water is taken. In previous chapters we have discussed in details special nature of proton counterions and behavior of the PSS acid form. Specifically the latter can exist in non dissociated form with a covalent bond between macroion unit and counterion. In the case of our IL1 and IL2, which are rather low-polar and contain poorly basic anions, one can suppose that PSS is only partially dissociated in these ILs.

It would be interesting to apply another PE that is a priori fully dissociated in any kind of media where it is soluble. That is to take a PE where covalent linking between the macroion and the counterions is basically impossible. Of course the process of counterion condensation can take place, but chemical charge fraction will be a priori equal to *1*. In such a case both solute and solvent would be entirely composed of ions and interesting electrostatic effects could be expected in this system.

To achieve full PE dissociation in IL media we have synthesized and applied for scattering study poly(4-vinylpyridinium tosilate) (P4VP-Tos) which consist of polycation and low-molecular anions. Although nitrogen atom in pyridine ring has rather low basicity, the latter is much higher compared to that of sulfo group in tosylate anion. That is protons are completely linked with nitrogens of macrochains, forming ionic structure of the compound. Obviously covalent linking is possible only via decomposition of this salt and transfer of acidic proton from pyridine nitrogen to tosylate sulfo group. At room temperature this does not take place, so ionic form is the only one possible for this compound, both in free state and in a solution.

This P4VP-Tos was dissolved and studied in IL1, as well as in water with added LME. By comparison of the PE behavior in both solvents we explored IL1 influence on P4VP-Tos chain stiffness. For the moment there is a lack of such studies in literature, thus considered investigation is pioneer in this direction. In addition the used method of P4VP-Tos synthesis is created by us and appeared simple and efficient, providing P4VP-Tos formation and purification in one step. This synthesis is discussed below in this chapter, while in annex we give a detailed description of the synthesis procedure.

One another problem is treated during considered work, specifically behavior of neutral polymers in ILs. Systems containing polymers and ILs are very diverse and a lot of studies in this field have been performed for the moment[1-6]. Thus we didn't aim to explore this problem in details, but to get an insight in this question was important following the next consideration. PEs in ILs behave like neutral polymers due to the charge screening. So it's interesting to compare behavior of PEs at these conditions with that of true neutral polymers.

A number of known advantages of ILs are discussed in previous chapters. The flexibility of IL chemical structure provides a lot of challenges for application of these new substances. The most important application area for the moment is the use of ILs like solvents. In particular a number of substances having absolutely different chemical nature appeared soluble in ILs. Thus, one can imagine that ILs possess excellent solvent properties and the problem to achieve solubility of a particular substance in a IL can be solved rather easily. But this is not the case. As discussed above, solubility in ILs depends on a lot of factors, specifically solute and solvent chemical structures should be chosen in such a way to provide efficient interaction between them. In particular interactions between IL cation and anion, as well as that between functional group of solute should be overcome. The problem of entropy is another one important, usually related to different types of structuration in free IL and in desired solution. Thus the question about solubility in ILs is very complex and only some general trends are established at present[7-10]. To focus more on this significant problem let's discuss one article that considers general rules for solubility of different polymers (neutral and charged ones) in ILs.

Usually highly polar polymers are better soluble in ILs than low-polar ones[11]. That is common rule «like dissolves like» doesn't work in considered case, because ILs themselves don't belong to highly polar solvents. This tendency is explained as follows. Most of ILs have amphiphilic character in some extent and display microphasic segregation. Polar polymers interact with polar fragments of ILs and promote such segregation. Let's remind that studied PSS in IL2 also causes density fluctuation at larger length scale compared to those in free IL2. If taken polar polymer is charged, an additional electrostatic interaction between solute and solvent arises, although the latter is usually non dominant. Even dissolution of neutral polymers in ILs is often supported by PE formation. In particular for cellulose in chloride-containing ILs $Cl^-$-anions are linked via hydrogen bonding with hydroxyl groups of cellulose, giving to the latter a character of polyanion. Except strong interaction with IL this hydrogen bonding provides repulsion between polymer chains and facilitates cellulose dissolution. So in general PEs have enhanced solubility in ILs compared to that of neutral polymers. The latter even being dissolved often display aggregation between macrochains. Thus, it's a complicated problem to achieve dissolution of neutral polymer in IL at molecular level. If to return to PEs and to compare behavior of polycations and polyanions, the latter usually appear better soluble in ILs. It's related to the fact that polyanions interact with IL cation. The latter in the most used ILs belongs to imidazolium type, having rather complex chemical structure with both polar and nonpolar groups. That’s why an interaction of polyion with IL cation is usually more efficient compared to that with anion. Indeed a large part of polymers (both natural and synthetical) well studied in ILs contain polyanion. In general polymers solutions in ILs should be treated like ternary systems, containing polymer, IL cation and IL anion. Mutual interactions between these components determine polymer solubility and conformation.

A number of polar polymers were treated to achieve solubility in IL1. These polymers include poly(ethylene oxide), poly(vinylpyridine), chitosan etc. Only poly(vinylpyrrolidone) (PVP) among tested polymers appeared soluble in IL1. As PVP represents water-soluble polymer we could perform comparative study of its behavior in IL1 and in water. Aqueous solutions of PVP have been explored in numerous works with a focus on different properties[12-15]. In our case we were interested in a particular question about single chain characteristics of PVP in water. Thus we have obtained scattering profile for PVP aqueous solutions and extracted values of $N$, $A_2$ and $R_g$. Than we tried to perform similar investigation for PVP solutions in IL1. Below we represent and analyze results of this study.

## 5.1. P4VP-Tos behavior in water and IL1

### 5.1.1. Synthesis of P4VP-Tos

A choice of P4VP-Tos as a priori fully dissociated PE was done following certain considerations. Anion of this PE is the same like in IL1. In its turn unit of polycation is similar by chemical nature to IL1 cation, as they both have nitrogen-containing aromatic ring with delocalized charge. It's interesting to note that P4VP-Tos in cross-linked form is rather known immobilized catalysis for hydrolysis[16]. In particular it's available in Aldrich. But soluble form of P4VP-Tos is not produced for commercial purposes, thus we had to synthesize it by ourselves. Moreover there is no available synthesis procedure for this substance in literature. That is by knowing properties of reagents and by assuming properties of the product we should create a suitable procedure to synthesize P4VP-Tos. This was done in the next way. Obviously it's reasonable to obtain P4VP-Tos from poly(4-vinylpyridine) (P4VP) and 4-toluenesulfonic acid (TosH). Both these substances are soluble in some polar organic solvents, in particular in ethanol. In the same time P4VP-Tos, which has ionic structure, probably should have lower solubility in ethanol, or even be practically insoluble. Indeed when we mixed ethanol solutions of P4VP and TosH, a precipitate was formed. After removing liquid phase we washed this precipitate several times with free ethanol to remove traces of reagents. Than we left the precipitate at around 60°C for one day to evaporate ethanol. Obtained product as well as initial reagent were analysed by NMR. Indeed the spectra showed that the product corresponds to P4VP-Tos. Moreover poly(4-vinylpyridine) bought in Aldrich was not very pure, containing some low-molecular impurities. But obtained P4VP-Tos doesn't contain them. So impurities from initial polymer rested in ethanol liquid phase, as well as non reacted P4VP and TosH. Thus we created very simple method for synthesis of highly pure P4VP-Tos. This procedure is based on two points. First, P4VP-Tos is the only substance involved in the process, which is not soluble in ethanol. Second, this solvent is very easy to remove by evaporation. In Figure 1 we give a reaction scheme and in annex we provide precise description of synthesis procedure. To control the PE behavior of P4VP-Tos in aqueous solution, we obtained SAXS profile for the case of LME-free solution. Indeed electrostatic peak was observed.

Let's note here another important point. P4VP-Tos is not soluble in ethanol, but appeared soluble in IL1, although polarity of both considered solvents is similar. IL1 should be even less polar than ethanol following general rules for IL polarity. This is another confirmation of unique solvent properties of ILs, which don't correlate with polarity of these substances.

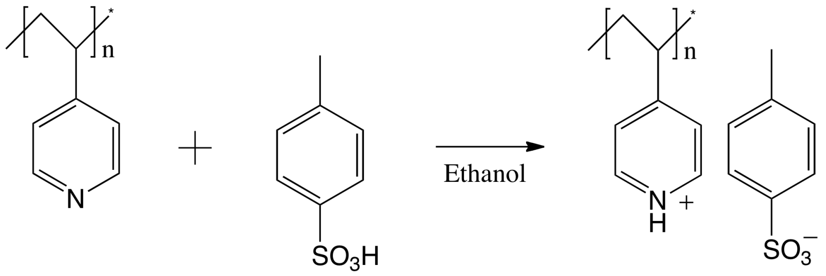


Figure 1. Synthesis of P4VP-Tos.

The similarity of the chemical structures of P4VP-Tos and IL1 probably also contributes to good solubility of this PE in taken IL.

### 5.1.2. P4VP-Tos aqueous solutions with added LME

P4VP-Tos (*N = 790*) solutions are prepared in water in presence of TosH as LME ($c_{TosH} = 0.2M$). To deal with solid results we will discuss only the most concentrated by P4VP-Tos solutions among prepared, specifically the ones with $c_{P4VP\text{-}Tos} = 0.100M$ and $c_{P4VP\text{-}Tos} = 0.075M$. This is related to the fact, that at lower $c_{P4VP\text{-}Tos}$ in IL1 signal becomes rather poor, as contrast in this system is rather low. So results for P4VP-Tos solutions in IL1 at $c_{P4VP\text{-}Tos} < 0.075M$ are not

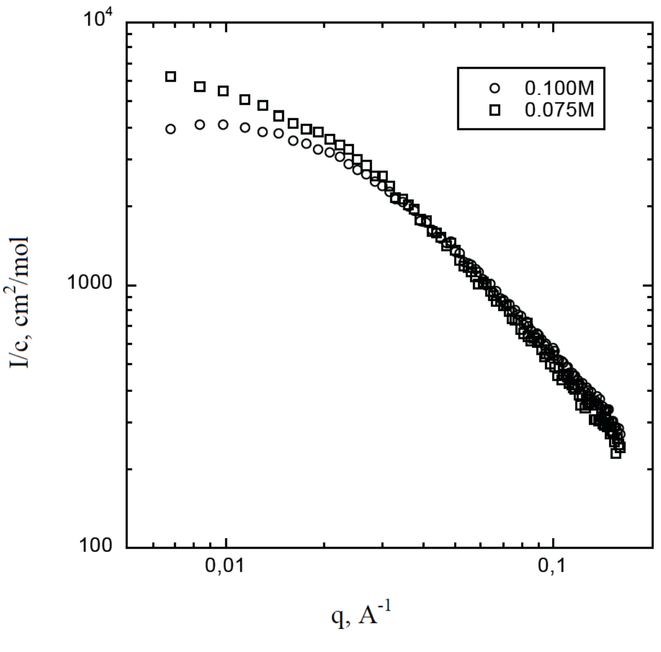


Figure 2. SAXS profile for P4VP-Tos aqueous solutions with added TosH ($c_{TosH} = 0.2M$).

solid. Moreover as will be discussed below, single macrochain characteristics for P4PV-Tos in IL1 cannot be calculated from obtained results, thus we can get only *P(q)* and estimate stiffness of the chains. For this purpose two $c_{P4VP\text{-}Tos}$ are enough. Thus for aqueous solutions there is no reason to explore larger number of $c_{P4VP\text{-}Tos}$ as well. To summarize, for P4VP-Tos solutions in both water (with added LME) and IL1 we need to calculate *P(q)*. For that we take two $c_{P4VP\text{-}Tos}$ well detectable by SAXS in both kinds of solutions: $c_{P4VP\text{-}Tos} = 0.100M$ and $c_{P4VP\text{-}Tos} = 0.075M$.

In Figure 2 we show scattering curves for P4VP-Tos aqueous solutions with added TosH at two different $c_{P4VP\text{-}Tos}$. One can clearly observe the Guinier range and the range of universal behavior. In the latter *P(q)* scales like $q^{-1/\nu}$ with $\nu$ close to $0.588$ (a little bit higher if to specify). So, we observe polymer behavior in a good solvent. Local *q*-range is not reached at discussed profile, as $l_p$ is too low.

### 5.1.3. P4VP-Tos solutions in IL1

P4VP-Tos solutions at two different $c_{P4VP\text{-}Tos}$ are prepared in IL1. Their SAXS study is performed and the results are shown in Figure 3.

A rather unexpected observation should be pointed from the figure. For both $c_{P4VP\text{-}Tos} = 0.100M$ and $c_{P4VP\text{-}Tos} = 0.075M$ a small peak at scattering curves can be seen. This peak is easier detectable at smaller $c_{P4VP\text{-}Tos}$. For both P4VP-Tos concentrations the measurements are

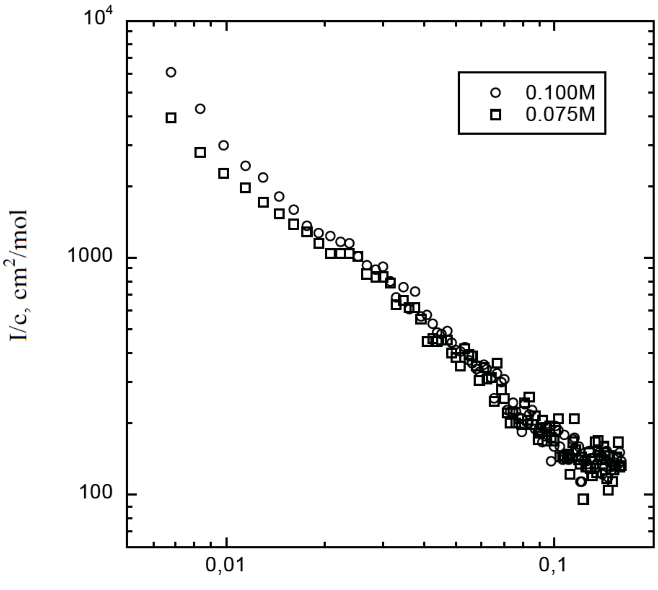


Figure 3. SAXS profile for P4VP-Tos solutions in IL1.

performed two times and in both cases this peak is observable.

To investigate in detail the peak, obviously we should carry out measurements at $c_{P4VP\text{-}Tos} < 0.075M$, but as discussed above it's a complicated task due to low contrast in the system. Very long counting time should be applied to obtain scattering curve with rather good statistics at these conditions. This can be a challenge for further investigations.

Anyway a problem, which is under consideration in this chapter, still can be solved. Indeed we are interested in local *q*-range to investigate macrochain stiffness, and for that the peak is not disturbing. At relatively high *q*-values in Figure 3 both curves are superimposed, thus we can analyze scaling behavior of *P(q)* in this region. Moreover we can analyze whole *P(q)* curve by using scattering curve for $c_{P4VP\text{-}Tos} = 0.100M$ and making two assumptions. First, we can consider P4VP-Tos charge for this $c_{P4VP\text{-}Tos}$ as screened. Even if the peak has electrostatic origin, it's almost absent for $c_{P4VP\text{-}Tos} = 0.100M$. Second, since discussed $c_{P4VP\text{-}Tos}$ is low, we can equate corresponding scattering curve to *P(q)* one. Thus we can treat considered experimental curve like *P(q)* for neutral macrochain in the system. This approach is satisfactory for us, as we need just to estimate *P(q)* scaling behavior in different *q*-regions. Also we can make no difference in this discussion between values of *(I/c)* and *P(q)*, as normalization by $I_0$ is not required to follow scaling character.

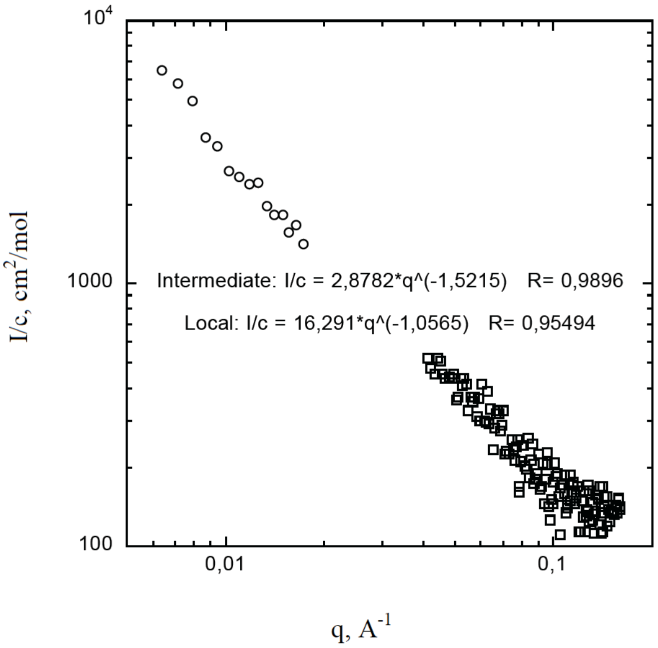


Figure 4. Scattering curve for P4VP-Tos solution ($c_{P4VP\text{-}Tos} = 0.100M$) in IL1: different regions of $P(q) \sim q^{-1/\nu}$ scaling behavior.

As shown in Figure 4, two distinct scaling laws are observable in whole explored $q$-region. At lower $q$-values for $P(q) \sim q^{-1/v}$ dependence we have $v$-value close to $0.588$. At higher $q$-values corresponding $v$-value is close to $1$. So we clearly observe two $q$-ranges: intermediate one and local one. In the same time the Guinier range is not reached.

By comparison of P4VP-Tos behavior in water with added LME and in IL1, we see a large increase in the chain stiffness in the second case. Thus IL media provides local effect on PE behavior, leading to increasing of $l_p$-value. If to apply the relationship $l_p = 3.5/q^*$, for $l_p$ we obtain value around $14$ *nm*. But calculation of $l_p$-value in this way is very approximative, as discussed in *Chapter 3*. $R_g$-value is increased as well and for its determination lower $q$-values should be explored to reach the Guinier range.

Now let's make an important assumption. As $l_p$-value of P4VP-Tos in IL1 is very high, one can suppose that there is a residual repulsion between macroion units. In addition observed peak, which decreases in intensity when $c_{P4VP\text{-}Tos}$ is increased, can have electrostatic origin, as it was mentioned above. Thus PE charge screening in IL media can be not complete. Although ILs are entirely composed of ions, the latter have strong tendency to association. So components of ILs can be not enough efficient to provide PE charge screening. Obviously further investigations in this direction should be performed. Our system composed of P4VP-Tos and IL1 seems to be perspective for this aim.

## 5.2. PVP behavior in water and IL1

### 5.2.1. PVP aqueous solutions

PVP is dissolved in water and studied by SAXS to calculate single macrochain characteristics in the solutions. For that a dilute regime is provided, like in the case of PSS discussed in previous chapters. But for PVP aqueous solutions there is no need to add LME for PE charge screening, as PVP belongs to neutral polymers. A polymer sample for this study is bought in Aldrich. Its $N_w$ is determined by SEC and appeared equal to $495$. Thus taken sample is convenient for study at our SAXS diffractometer.

The solutions are prepared in a common way by adding PVP powder to demineralized water. Dissolution passed quickly and resulting solutions have been left for one day to achieve PVP dispersion at molecular level.

Results of scattering study of PVP aqueous solutions at different $c_{PVP}$ are represented in Figure 5.

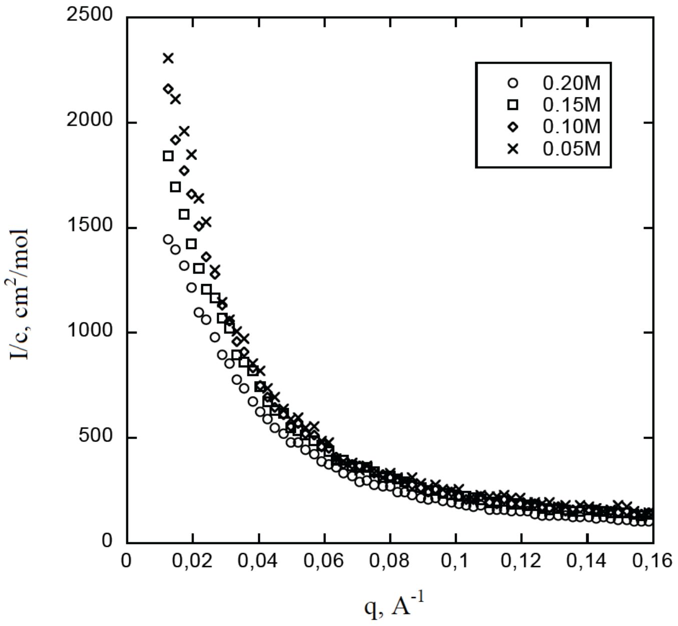


Figure 5. Scattering curves for PVP aqueous solutions.

Guinier range at considered scattering curves is available and non polluted by upturns. Thus calculation of single chain characteristics could be carried out. Specifically values of *N* and $A_2$ are determined by drawing Zimm plot (Figure 6) and value of $R_g$ is extracted by fitting $g_1(q)$ with $g_D(q)$ (Figure 7).

Calculated in this way *N*-value is equal to *420*. So we have appropriate agreement with the SEC result. In its turn $A_2$-value is equal to $3.64*10^{-4}\ mol*mL*g^{-2}$. The latter is rather high, displaying good solvent quality of water with respect to PVP. Determined $R_g$-value appeared equal to *14 nm*. That is PVP conformation is extended in aqueous solutions, showing again PVP behavior in a good solvent. These results are not surprising, but it’s important to determine the exact values in order to compare PVP behavior in aqueous and IL1 media.

Before to start the consideration of PVP solutions in IL1, let’s point again and in more detail an absence of upturns in discussed PVP aqueous solutions. This observation means that a dissolution of PVP at molecular level could be achieved. Obviously this takes place due to strong hydration of PVP units. The latter are polar and specifically contain amide group, which can interact with water molecules via dipole-dipole and hydrogen bonding attraction. The latter type of interaction is extremely important and cannot be realized between PVP units. This makes PVP hydration favorable. Discussed question about PVP aggregation state in a solution is basic one for present study, as will be displayed in the next subchapter.

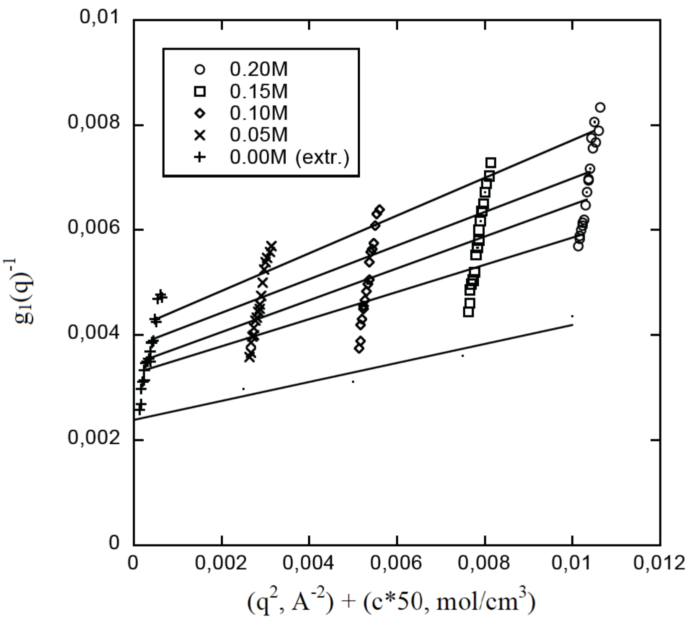


Figure 6. Zimm plot for PVP aqueous solutions.

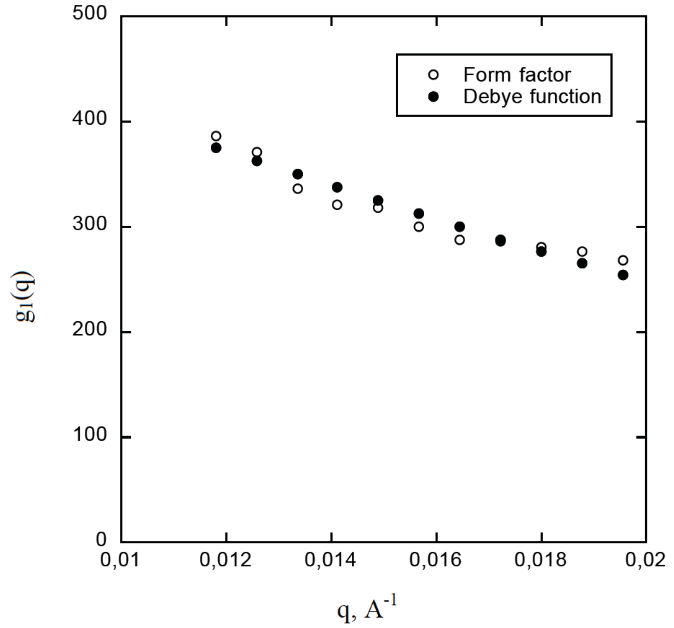


Figure 7. Fit of $g_1(q)$ with $g_D(q)$ for PVP aqueous solutions.

### 5.2.2. PVP solutions in IL1

Solutions of PVP in IL1 are prepared at the same $c_{PVP}$ like for corresponding aqueous ones. Dissolution process was rather slow, and after getting visually homogeneous system the latter has been left for several days. That is more time was given to the solution to reach dispersion state at molecular level, taking into account high viscosity of the system and low mobility of its components. Obtained in this way the most concentrated by PVP solution was diluted to get another ones at lower $c_{PVP}$. Resulting solutions as well as free IL1 are analyzed by SAXS to obtain a scattering profile. The latter is shown in Figure 8, being related to scattering from whole systems.

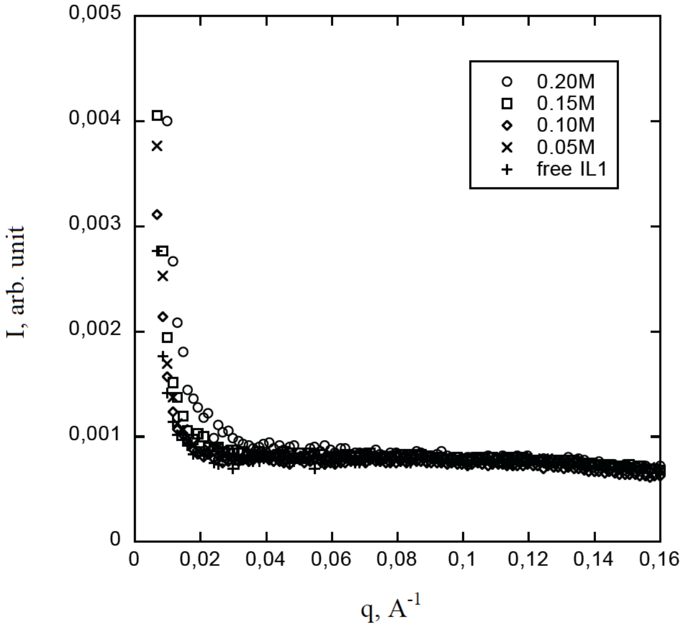


Figure 8. SAXS curves related to scattering from whole PVP solutions in IL1 and from free IL1.

The curves in Figure 8 are rather well superimposed at relatively high *q*-values, because PVP concentration is low. That is an addition of PVP at low content to IL1 doesn't influence essentially the total scattering. But more important is the behavior of scattering curves at relatively low *q*-values. There is no significant signal from polymer. Instead there are big upturns, displaying an existence of aggregates. The same observation can be made from Figure 9, which demonstrates scattering from polymer. The signal in the whole *q*-range is very low,

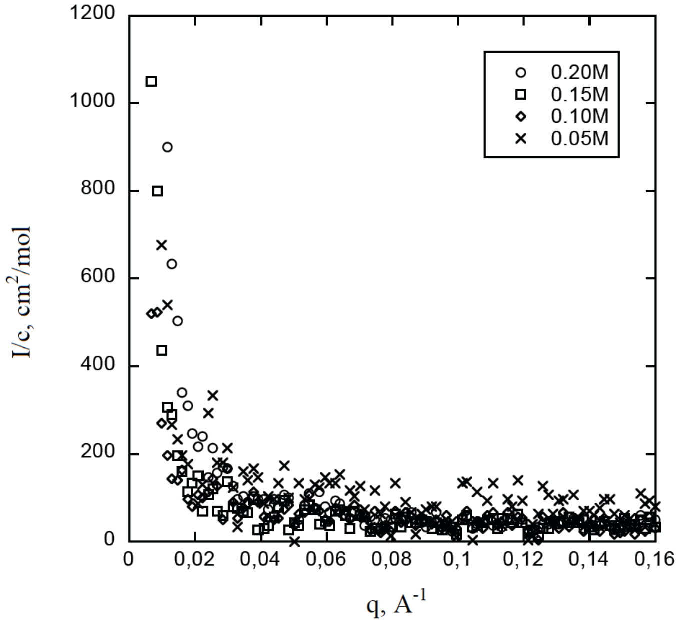


Figure 9. SAXS curves related to scattering from polymer in PVP solutions in IL1.

except upturns at the smallest *q*-values. This means that almost all PVP macrochains are in aggregated state in considered solutions. In such a case, study of single chain characteristics is impossible. Obviously this polymer aggregation is stable in time. Indeed, a tendency of neutral polymers to aggregate in IL media was observed before and discussed in *Introduction* to this chapter. Present study is another example of difficulties in achieving complete polymer dissolution in IL.

So in general PEs and natural neutral polymers are relatively well soluble in ILs, while synthetic neutral polymers have poor tendency to dissolution in ILs. Nevertheless one should remember that problem of polymer solubility in IL should be treated for a particular couple of these substances.

Two main questions considered in this chapter give us a new insight into polymer behavior in ILs, as well as better understanding of challenges provided by PSS acid form application.

Study of P4VP-Tos in IL1 has displayed an electrostatic effect of the IL on stiffness and average conformation of fully charged from chemical point of view PE. P4PV-Tos charge is probably not completely screened in IL media, so the PE behavior can not be considered as the one of neutral polymer. Single macrochain characteristics are dramatically different for this PE in IL1 and in water with added LME.

From another side application of synthetic neutral polymer usually does not provide solubility at molecular level in IL media. This is confirmed by our study and by particular system PVP-IL1. That is we again cannot achieve polymer behavior in IL like it is in aqueous media.

Finally the use of PSS acid form provides rather high polymer solubility in IL without significant electrostatic effect of solvent. Probably this is due to special nature of protonated sulfo groups (or protonated anions in general, as we can suppose). Such a group can exist in non dissociated state in low-polar and low-basic media, in particular in ILs. Thus electrostatic effects are eliminated. Specifically, polyanion repulsion doesn’t arise, even if ILs ability to screen PE charge is rather low. In the same time, protonated sulfo groups are very polar and able to a number of strong intermolecular interactions, in particular to hydrogen bonding. So high polymer solubility, as well as polymer dispersion state at molecular level are realized, supported by good solvent quality of IL.

Thus PSS acid form occupies intermediate position between true PEs and neutral polymers by its properties. The same from a theoretical point of view should be related to acid forms of other polyacids. The use of PSS allows to get polymer behavior in IL similar to that in water with added LME. This is quite important. We can use ILs with a number of their advantages and maintain the same character of polymer behavior like in common molecular solvents in presence of LME.

## Conclusions

Two basic questions have been considered in the present chapter. These questions are not directly linked each to other. However their common analysis has given not only additional information about polymer behavior in ILs, but a new insight into main results of the present work as well.

We have created a method of synthesis of P4VP-Tos, which is a PE fully charged from chemical point of view in any type of media. Study of this PE in IL1 helped to display solvent electrostatic effect on polymer behavior. Specifically, macrochain stiffness is significantly increased and average conformation becomes more extended in IL1 compared to aqueous media. The PE charge is probably not completely screened in the IL and residual repulsion between macroion units takes place.

An application of neutral polymer PVP provided its solubility in IL1, but polymer chains in such a solution are aggregated. Thus study of single macrochain characteristics could not be realized for this system.

In both discussed cases we cannot get polymer behavior like it is in molecular solvents (with or without added LME). While the use of PSS acid form leads to high polymer solubility with dispersion state at molecular level, as well as to elimination of solvent electrostatic effect on polymer behavior, as discussed in *Chapter 4*. That is PSS behavior in ILs is similar to that in molecular media with added LME. This is supported by special character of protonated PSS anion, which is intermediate between character of true PE and that of neutral polymer. As a result, ILs maintaining the same type of PSS behavior can replace common molecular solvents.

## References

[1] J. C. Jansen, K. Friess, G. Clarizia, J. Schauer and P. Izak, *Macromolecules*, **44** (2011), 39
High ionic liquid content polymeric gel membranes: Preparation and performance

[2] Y.-I. Parka, B.-S. Kima, Y.-H. Byuna, S.-H. Leeb, E.-W. Leea and J.-M. Lee, Desalination, **236** (2009), 342
Preparation of supported ionic liquid membranes (SILMs) for the removal of acidic gases from crude natural gas

[3] S. W. Kang, K. Char, J. H. Kim, C. K. Kim and Y. S. Kang, *Chem. Mater.*, **18** (2006), 1789
Control of ionic interactions in silver salt-polymer complexes with ionic liquids: Implications for facilitated olefin transport

[4] C. Guerrero-Sanchez, T. Erdmenger, P. Sereda, D. Wouters and U. S. Schubert, *Chem. Eur. J.*, **12** (2006), 9036
Water-soluble ionic liquids as novel stabilizers in suspension polymerization reactions: Engineering polymer beads

[5] J. Nie, D. E. Tallman and G. P. Bierwagen, *J. Coat. Technol. Res.*, **5**, 3 (2008), 327
The electrodeposition of polypyrrole on Al alloy from room temperature ionic liquids

[6] Y. Jianga, H. Xiaa, J. Yub, C. Guoa and H. Liua, *Chemical Engineering Journal*, **147** (2009), 22
Hydrophobic ionic liquids-assisted polymer recovery during penicillin extraction in aqueous two-phase system

[7] N. Winterton, *J. Mater. Chem.*, **16** (2006), 4281
Solubilization of polymers by ionic liquids

[8] B. G. Kim, E.-H. Sohn, J.-S. Chung, S.-Y. Kwak and J.-C. Lee, *Journal of Applied Polymer Science*, **114** (2009), 132
Solubilization and polymer analogous reactions of polyepichlorohydrin in ionic liquids

[9] E. S. Sashina and N. P. Novoselov, *Russian Journal of General Chemistry*, **79**, 6 (2009), 1057
Effect of structure of ionic liquids on their dissolving power toward natural polymers

[10] C.-A. Teaca, R. Bodirlau and I. Spiridon, *Rev. Roum. Chim.*, **56**, 1 (2011), 33
Dissolution of natural polymers in ionic liquid

[11] Y. Chen, Y. Zhang, F. Ke, J. Zhou, H. Wang and D. Liang, *Polymer*, **52** (2011), 481
Solubility of neutral and charged polymers in ionic liquids studied by laser light scattering

[12] M. Foroutan, *Acta Chim. Slov.*, **53** (2006), 219
Density dependence of the viscosity and excess volume of aqueous solutions of polyvinylpyrrolidone

[13] A. Z. Dakroury, M. B. S. Osman and A. W. A. El-Sharkawy, *International Journal of Thermophysics*, **11**, 3 (1990), 515
Thermal properties of aqueous solutions of polyvinylpyrrolidone in the temperature range 20-80°C

[14] S. Chiyokawa, K. Suyama and K. Takaizumi, *Journal of Solution Chemistry*, **32**, 8 (2003), 743
Volumetric study of the interaction between chloride salts and polyvinylpyrrolidone in aqueous solution

[15] P. Mura, M. T. Faucci and G. P. Bettinetti, *European Journal of Pharmaceutical Sciences*, **13** (2001), 187
The influence of polyvinylpyrrolidone on naproxen complexation with hydroxypropyl-β-cyclodextrin

[16] Z. Li and A. Ganesan, *Synthetic Communications*, **28**, 17 (1998), 3209
Poly(4-vinylpyridinium p-toluenesulfonate) as a polymer-supported catalyst for hydrolisys of tetrahydropyranyl ethers

# *Conclusions and challenges*

A number of problems are investigated in the present work. All of them concern the question about PEs behavior in ILs, either directly or not. Interpretation of results and following conclusions were changing in the process of the work, when some new results were obtained. Let's discuss now final conclusions of the whole work, as well as some challenges for further investigations. Interesting points about practical application of PE-IL systems will be concerned too, although the main importance of the work relates to fundamental research. Indeed considered systems are promising due to important properties of the components and their mutual influence, but study of these systems just begins for the moment.

The first question investigated within the present work relates to nanoscale structure of free ILs and an influence of different factors on this structure. IL1, IL2 and IL3 are investigated and all displayed an existence of nanoscale heterogeneities. The nature of the latter is explored by addition of solvents with different polarity to the ILs. In the case of IL1 an addition of water leads to disappearance of characteristic peak in intermediate $q$-range at scattering profile. Thus water destroys aggregates in IL1. For IL2 water addition causes an increase of both fluctuations intensity and length scale. While an addition of low-polar organic solvent chloroform has an opposite effect, destroying aggregates. Obviously the tendency to aggregation in IL1 is caused by interaction between polar functional groups, while in IL2 it's related to segregation between nonpolar aliphatic tails. Thus in IL1 water hydrates polar groups, leading to disappearance of fluctuations at nanoscale length. For IL2 we have opposite situation: polar media promotes hydrophobic interaction between alkyl radicals, while chloroform interacts with aliphatic chains by itself, thus destroying nonpolar nanodomains in IL2. In the latter IL aggregation is stronger, as characteristic peak is much higher and shifted to smaller $q$-values compared to that for IL1. A tendency to heterogeneities formation grows further from IL2 to IL3, probably due to increasing of length of the longest aliphatic radical, which is responsible for aggregation. Obviously in IL3 heterogeneities are formed due to hydrophobic interaction too, like they are in IL2, as the nature of both ILs is similar, being amphiphilic one.

Another tested factor, which can influence IL nanostructure, is heating. Corresponding measurement are carried out for IL1, but increasing of temperature until $80^{o}C$ doesn't cause changes of IL1 aggregation state. So heterogeneities formed due to polar interactions in IL1 are rather thermostable.

An influence of polymer addition on IL1 and IL2 nanostructure is explored as well. For the first IL added PSS (in concentration until *0.2M*) does not introduce changes in IL1 scattering profile. Probably PSS units partially replace tosylate ions in IL1 structure without its modification. Such a modification theoretically could be caused by covalent linking between PSS units. But as IL1 viscosity is high, interaction between its ions is strong and their mobility is low, partially introduced covalent linking does not provide significant effect. In the same time PSS addition in IL2 (until $c_{PSS} = 0.2M$ as well) causes a shift of characteristic peak to smaller $q$-values. This happens due to interaction of PSS with polar groups of IL2, which leads to increasing of size of nonpolar domains.

Second main problem studied within the present work is related to PSS behavior in different solvent media: aqueous and organic ones. Aqueous solutions of PSS salt forms were studied in details in previous works and polymer behavior didn't depend significantly on applied monovalent counterion. While we have shown that an application of protons like counterions leads to decrease of $f_{eff}$ of PSS, as electrostatic peak at scattering profiles is shifted at smaller $q$-values. That is protons are more condensed counterions compared to other classical monovalent ones. The latter include cations of alkali metals and ammonium ones substituted with alkyl chains. Indeed protons are dramatically distinct by their characteristics from these common counterions, having much smaller size and much higher charge density. This leads to stronger electrostatic interaction of protons with PSS, as well as to provided hydrogen bonding. Increased overall interaction between macroanion unit and cation provides higher degree of counterion condensation and lower PE effective charge fraction. For $q^* \sim c^n$ dependence we obtained $n = 0.5$, thus behavior of PSS acid form in aqueous solutions is hydrophilic, like it is for the common salt forms.

Application of protons like counterions for PSS does not only change PE behavior in water. The solubility of PSS in some organic solvents is provided too. These solvents should be polar and able to hydrogen bonding interaction. In particular ethanol and DMSO are able to solubilize PSS acid form. This solubility is supported by stronger interaction of protons with oxygen atom of Lewis bases compared to that of other monovalent cations, leading to better solvation of protons. In addition hydrogen bonds are provided in the case of PSS acid form, further increasing its solubility.

LME-free solutions of PSS in ethanol and DMSO are studied. Characteristic electrostatic peak is observed and appeared largely shifted to smaller $q$-values compared to its position for corresponding aqueous solutions. This shift is stronger than expected from decrease of solvent polarity. In addition $n$-values in $q^* \sim c^n$ dependence for both ethanol and DMSO are lower than $0.5$. So, PE behavior in these solvents is partially solvophobic.

The convenience of ethanol as a solvent for SAXS study of PSS should be pointed. In corresponding solutions one has high contrast and quick disappearance of upturns at small $q$-values. The latter feature is probably related to low viscosity of this solvent, thus dispersion of PSS macrochains at molecular level is achieved quickly. These properties of ethanol should be maintained for the most of PEs, which are soluble in this organic solvent.

The next problem considered in the present work concerns PSS charge screening in water and ethanol. This screening is achieved by adding LME: HCl in the first case and TosH in the second one. At these conditions characteristics of single macrochains could be studied. In particular values of $N$, $A_2$ and $R_g$ are calculated for PSS in both considered solvents in presence of added LME. These values showed good solvent quality of water with respect to the acid form of PSS and extended average conformation of the latter in aqueous media. In its turn ethanol displayed good solvent quality with respect to PSS as well, but conformation of the PE in the organic solvent appeared much more compact. As a reasonable explanation for that an existence of intramolecular hydrogen bonding for PSS in organic media can be proposed.

$P(q)$ for PSS macrochains in water and ethanol at condition of PE charge screening is calculated. In both solvents in intermediate $q$-range $P(q)$ scales like $q^{-1/v}$ with $v$ close to $0.588$, that is we observe polymer behavior in a good solvent in both cases. For PSS in aqueous solutions $P(q)$ is specifically determined for the ones with added LME (by SAXS) and for LME-free ones (by SANS using ZAC method). From $P(q)$ curves $l_p$-values for PSS in different conditions are estimated. In this way we have observed decrease of polymer stiffness in ethanol compared to that in water. This is probably related to lower $f_{eff}$-value for PSS in the organic media. For PSS in water we obtained higher $l_p$-value for LME-free solutions than for the ones with added LME. Obviously it's related to screening of electrostatic repulsion when low-molecular ions are added to the solutions.

Screening of PSS electrostatic interaction in both considered solvent media is followed by gradual addition of LME as well. In ethanol electrostatic peak at scattering profiles disappears at much lower $c_{LME}$ than in water. This observation is explained by lower $f_{eff}$-value of PSS macrochains in ethanol.

After study of PSS behavior in molecular solvents at condition of charge screening one could explore this PE in ILs. Results for PSS solutions in water and ethanol can be used for comparison with those for IL solvents. Indeed water is a classical solvent media for PSS and for the most of PEs in general. In its turn ethanol is organic molecular solvent, while ILs are organic but ionic systems. PSS solutions in ILs is a basic question of the whole work, and other considered problems are linked to it in a some way.

Specifically PSS solutions in IL1 and IL2 are explored to determine single macrochain characteristics in IL media. A similar study is performed like for PSS solutions in water and ethanol. But in the case of ILs we don't need to add LME for PE charge screening. As ILs are entirely composed of ions, one can suppose that PE charge screening is provided in this media. Indeed scattering profiles of PSS solutions in both IL1 and IL2 don't contain electrostatic peak. Thus electrostatic interaction is eliminated in IL media and one can take under consideration a single macrochain, if diluted regime is provided. In this way values of $N$, $A_2$ and $R_g$ are determined. For the case of IL1, polymer behavior is the one in a good solvent. $A_2$ and $R_g$ values appeared rather high, comparable with those for PSS aqueous solutions.

Good solvent quality of IL1 with respect to PSS can be surprising as polarity of this IL is rather low. Usually organic solvents with a similar polarity don't dissolve PSS at all. Obviously this property of IL1, as well as rather high solubility of PSS in this IL and non aggregated dispersion state of the PE in this system is due to complex chemical structure of IL1. This structure provides several types of interaction with PSS solute, increasing polymer solubility and IL solvent quality. Mentioned interactions include not only electrostatic ones, but also hydrogen bonding, dipole-dipole, aromatic π-π and London dispersion ones. Listed intermolecular non electrostatic interactions are probably dominant in considered system. Role of electrostatic interaction is less important, since interacting particles are rather large and have either delocalized or diffuse charge. In addition, a similarity of chemical structures of PSS unit and Tos anion contributes to discussed polymer behavior too.

Excluded volume statistics for PSS solutions in IL1 is observed at calculated $P(q)$ curves as well. The latter are obtained for PSS samples with different $N$-values and all this curves display scaling law $P(q) \sim q^{-1/v}$ with $v \cong 0.588$ in intermediate $q$-range. In addition $R_g$-values extracted for different PSS samples are plotted against $M_w$. We obtained a power law $R_g \sim M_w^v$ with $v$ again close to $0.588$. All these observations prove that PSS behaves in IL1 like neutral polymer in a good solvent.

An investigation of PSS solutions in IL1 at elevated temperature is performed too. A heating until 80°C appeared to have no importance on polymer behavior in considered system. In particular, a good solvent quality of IL1 is maintained at applied high temperature.

An exploration of PSS solutions in IL2 showed decreased solvent quality and shrunk polymer conformation compared to the IL1 case. This is supported by determined values of $A_2$ and $R_g$ for a particular PSS sample. In the same time $P(q)$ determination for PSS in IL2 is impossible since this IL displays heterogeneities at nanoscale length and corresponding characteristic peak interferes with intermediate *q*-range for taken PSS sample in IL2. As position of this peak is changed upon PSS addition, its correct subtraction for *P(q)* determination is impossible.

In its turn IL3 does not dissolve PSS at room temperature.

Thus one can see how solvent properties of ILs with respect to PSS can be changed via chemical structure modification. All three applied ILs have similar gross formula, while their chemical nature is basically distinct. Aromatic anion of IL1 is substituted by aliphatic one in IL2. This leads not only to modification of IL nanostructure as discussed above, but to significant modification of solvent properties as well. IL2 contains anion which is less active in sense of interaction with solute. In addition a similarity of solute and solvent chemical structures is broken. In IL3 long alkyl tail is linked to cation, which is obviously the main responsible for interaction with PSS. This results in further decrease of IL solvent quality with respect to the PE and in a loss of solubility of the latter. Variation of ILs nanoscale structure is an indirect way, in which their solvent characteristics are modified too. From present investigations we see a flexibility of IL properties, provided by a flexibility of their chemical structure.

PSS solubility in IL1 and IL2 is provided by the use of acid form, like it took place for solutions in organic solvents. Higher solubility of the acid form compared to that of the salt one in considered ILs can be also attributed to hydrogen bonds formation and to the fact that proton is strong Lewis acid. Thus stronger interaction between solute and solvent is provided. In the same time applied ILs are low-polar and low-basic media. This is not the case for used organic solvents, which are rather polar (first of all DMSO) and rather basic (first of all ethanol). So in the organic solvents PSS is completely dissociated from chemical point of view, although degree of counterions condensation is very high in these media. For the case of IL solvents one can suppose that PSS is only partially dissociated from chemical point of view. Indeed for the PSS acid form covalent linking between macroion and counterions is basically possible and can be realized in some kinds of media, as well as it's realized in free state of this PE. In general the state of protons in considered PSS-ILs systems is a complex question, as discussed in details in *Chapter 4*. This question can be an interesting point for further investigations.

Explored PSS belongs to classical strong PEs. In the same time its acid form possesses some specific properties. In particular it can behave like weak PE in some solvents, including ILs. To achieve PE complete dissociation from chemical point of view in ILs we had to apply a PE in which covalent linking between macroion and counterions is basically impossible. Such a PE will display chemical charge fraction equal to *1* a priori. The main problem in this case is to achieve a solubility of fully dissociated PE in IL. ILs don't possess high ability to solvate small inorganic ions, like water does. Thus chosen PE should be composed of large organic ions. As such a PE we have applied P4VP-Tos which has similar chemical structure to that of IL1. This structural similarity is an additional contribution to high solubility, as discussed before. An application of fully charged from a chemical point of view macroion can display interesting electrostatic effects between PE and IL in corresponding system entirely composed of ions.

P4VP-Tos is not commercially available, moreover a method for its synthesis is not given in literature. Hence we had to create an appropriate synthesis method and carry out the latter by ourselves. Indeed we have designed a simple and efficient method, which allowed to synthesize and purify P4VP-Tos in one step. High quality of resulted product is proved by NMR.

In LME-free aqueous solutions P4VP-Tos displays an electrostatic peak. To screen electrostatic interactions TosH is added to these solutions. P4VP-Tos behavior in IL1 is followed as well and compared to that in aqueous solutions with added LME. We have observed a large increasing of $l_p$ for P4VP-Tos in IL1 media. Moreover scattering curves for the last system contain small peak, which probably has electrostatic origin. So we can suppose that charge screening for P4VP-Tos in IL1 media is not complete. Although ILs are entirely composed of ions, aggregation processes of the latter decrease efficiency of these ions to screen electrostatic interaction. To explore better this important problem further investigations are required. In particular it's interesting to study considered solutions at lower $c_{P4VP\text{-}Tos}$, as well as at presence of added LME. As the latter some new one should be introduced to this study, because used by us for nonaqueous systems TosH is probably not fully dissociated in IL1. For example, pyridinium tosylate (or 4-methylpyridinium tosylate), which is similar to P4VP-Tos unit, should be suitable as LME for discussed study.

Considered P4VP-Tos solutions in IL1 represent case of chemical charge fraction equal to 1. An opposite case is the behavior of true neutral polymer in IL1. To find a convenient object for this study, a number of polymers are tested, mentioned in *Chapter 5*, but the only one soluble in IL1 among them is PVP. Solutions of the latter in water and IL1 are investigated. While in water we have available for analysis Guinier range, in IL1 the latter is polluted by big upturns, which are stable in time. That is PVP in IL1 exists in aggregated state and the study of single chain characteristics is impossible. Such a behavior of synthetic neutral polymers in ILs is rather common and achievement of polymer solubility at molecular level is very complicated task for these systems. The problem of solubility of neutral and charged polymers in ILs is significant one and should be treated for every particular couple of polymer and IL.

The study of P4VP-Tos and PVP behavior in IL1 supplemented and gave new insight in the main results of the work related to PSS solutions. For both fully charged from chemical point of view PEs and non charged ones their behavior in ILs and common molecular solvents (with or without added LME) is distinct. In the same time for PSS acid form we can get the same behavior in both considered types of solvents. This PSS acid form occupies intermediate position between strong PE and true neutral polymers by its nature. It can behave as both fully charged PE and non charged one, depending on conditions and solvent nature in particular. In our case an application of protons as counterions provided PSS solubility in ILs, while electrostatic effects in such a system are eliminated due to relatively low PSS chemical charge in these solutions. So we get an opportunity to change molecular solvents by ILs, providing advantages of the latter and maintaining the same type of polymer behavior. However PE-like behavior of ionogenic polymers in ILs is also available as shown by P4VP-Tos example, when high chain stiffness and extended polymer conformation were achieved.

While solutions of synthetic neutral polymers in ILs are hardly available, for PEs and for neutral polymers as well ILs represent promising solvents with modifiable polymer behavior.

# *Annex*

## Diffractometers applied for the structural investigations

### *X-ray scattering diffractometers at the home laboratory (ICS)*

X-ray scattering experiments were carried out by using two diffractometers at ICS. The first one, developed by Molecular Metrology, INC (Elexience in France), and the second one, «Nanostar», produced by Bruker AXS. These diffractometers operate with a pinhole collimation of the beam and two-dimensional gas-filled multiwire detectors. A monochromatic ($\lambda = 1.54$ Å with $\Delta\lambda/\lambda < 4\%$) and focused X-ray beam is obtained through a multilayer optic designed and fabricated by Osmic, Inc. The size of the incident beam on the sample was *200 µm* for the first diffractometer and *300 µm* for the second one. The sample detector distance was set at *1 m* and *0.22 m* respectively. These configurations allow to perform measurements in the $q$-range $0.01 < q < 0.16$ Å$^{-1}$ in the first case and $0.1 < q < 1$ Å$^{-1}$ in the second one. The solutions were held in calibrated mica cells of *1 mm* thickness, avoiding multiple scattering. For scattering data treatment radial averaging was performed with subsequent spectra corrections to take into account electronic noise of the detector, empty cell, absorption and sample thickness. The corrections of the geometrical factors and the detector cell efficiency were done by using $^{55}$Fe source. Normalization to the unit incident flux was performed by applying Lupolen (for the first instrument) and water (for the second one) as standard samples.

*Neutron scattering diffractometers at the specialized neutron facilities (ILL)*

Neutron scattering experiments were performed by using two diffractometers at ILL: D11 and D16. For both them neutrons are produced by nuclear reactor. The latter gives continuous neutron flux with $1.5*10^{15}$ neutrons per second per cm$^2$, with a thermal power of *58.3 MW*.

D11 allows to carry out neutron scattering measurements in small $q$-values range covering $q = 0.003 \div 0.3$ Å$^{-1}$. At this instrument one has $\lambda = 6$ Å with $\Delta\lambda/\lambda < 9\%$. Data were collected at detector with *64x64* pixels resolution and treated by using ILL standard software package. Corrections were made for instrumental background, electronic noise, transmission and empty cell.

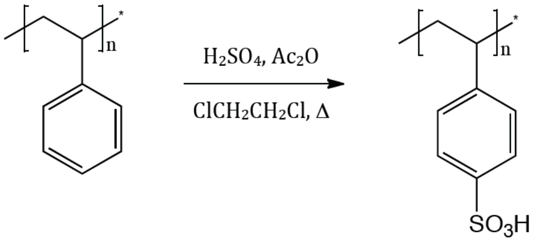
D16 provides wide-angle range with $q = 0.2 \div 2.2$ Å$^{-1}$ available for investigation. $\lambda$-value is equal to *4.7 Å*. Detector with *320x320* pixels resolution is used for data collection. A set of corrections for data treatment is similar to that used for D11.

## Synthesis of PEs applied for the study

### *PSS synthesis*

Poly(4-styrenesulfonic acid) is obtained by sulfonation of PS following Makowski et al. procedure. *4.8 g* of PS is dissolved in *67 ml* of 1,2-dichloroethane. *13.25* ml of acetic anhydride (in excess of *200%* with respect to PS) is added to the solution, with subsequent drop wise addition of *7.68 ml* of sulfuric acid (in excess of 200% with respect to PS). After this the mixture is heated at *50°C* during *30 min* and further at *70°C* during *4 h*. Finally two phases are formed. The bottom one, rich with PSS, is put in *12M* HCl. By decantation a viscous mass is separated and purified by dialysis. After freeze-drying PSS in white solid form is obtained. The product is conserved under argon in darkness.

A synthesis scheme is shown below.

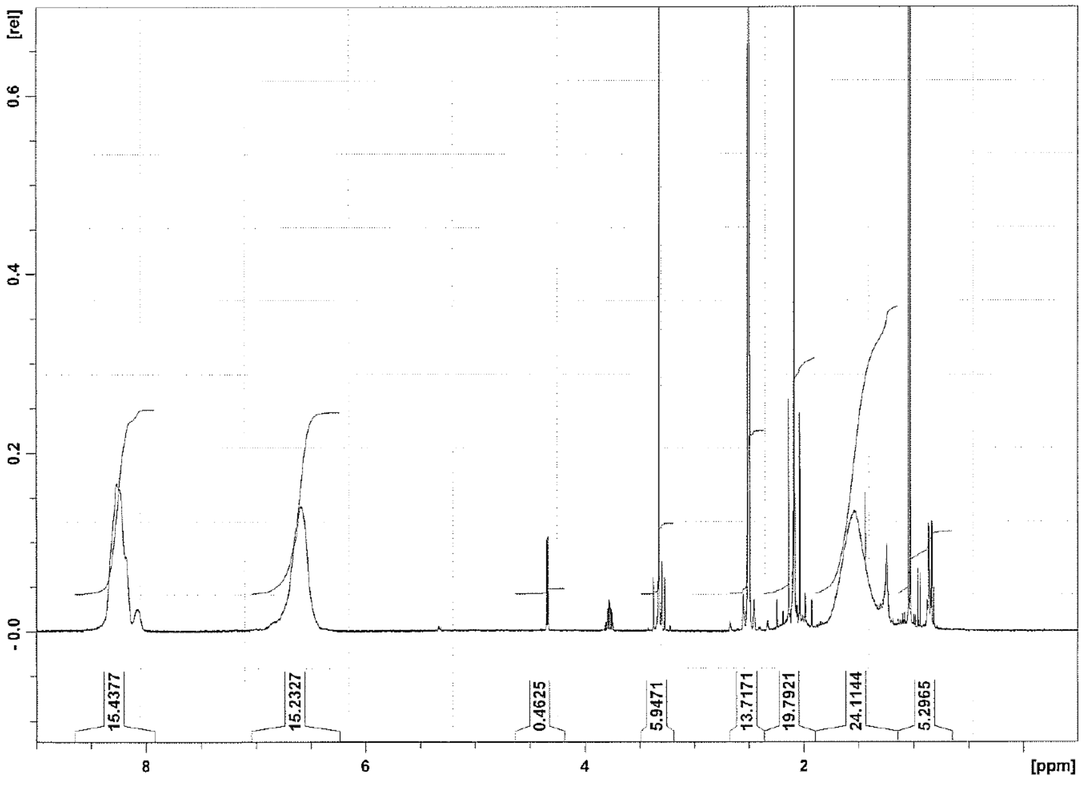


*P4VP-Tos synthesis*

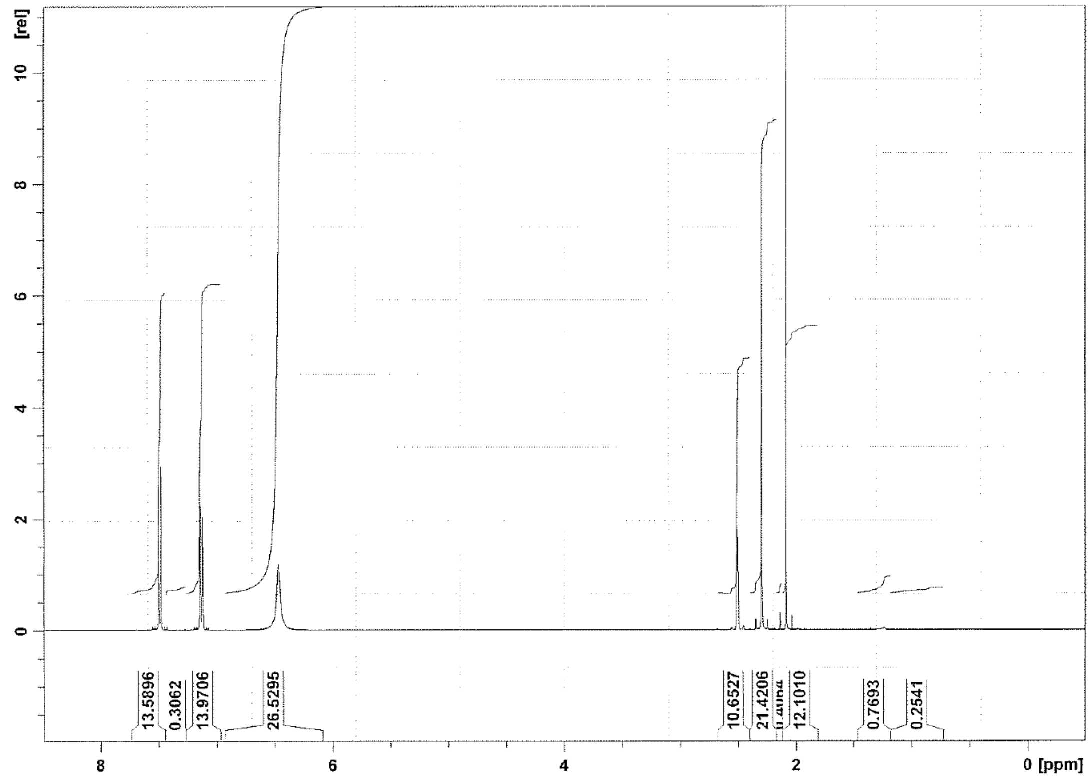
P4VP-Tos is obtained by acid-base reaction between P4VP and TosH in ethanol media following synthesis procedure created by us. Specifically *2 g* of P4VP is dissolved in *48 ml* of ethanol and *3.28 g* of TosH (equimolar quantity with respect to P4VP) is dissolved in *31 ml* of the same solvent. The solution of P4VP is added to that of TosH at stirring with magnetic stir bar. A white precipitate is immediately formed. A system is stirred for *15 min* more to achieve complete protonation of P4VP units. After liquid phase elimination the precipitate is washed two times with free ethanol and left for one day at *60°C* to evaporate the solvent. Resulted product, as well as both reagents are analyzed by NMR to check chemical structure and purity of obtained substance.

Corresponding NMR spectra are represented below.

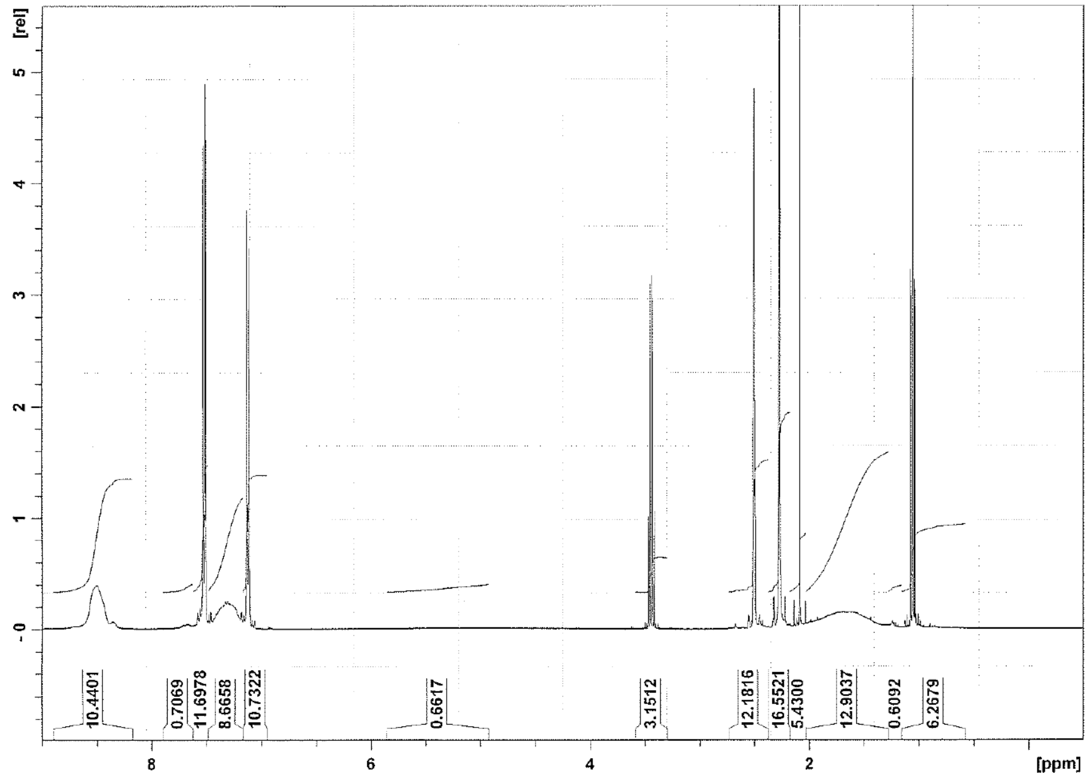
P4VP:



TosH:



P4VP-Tos:



Note: peak corresponding to ethanol at P4VP-Tos spectra takes place because this demonstrated spectra is made in two hours after synthesis before complete solvent evaporation. The aim of this NMR analysis was to control identity of the obtained product to P4VP-Tos. Ethanol content can be easily further decreased by its longer evaporation.

By comparing three represented spectra one can clearly see the formation of P4VP-Tos as a product of performed synthesis. Moreover low-molecular impurities from initial polymer are absent in the final PE.

UNIVERSITÉ DE STRASBOURG

**Georgiy SMOLYAKOV**

# POLYELECTROLYTES ET LIQUIDES IONIQUES

## Résumé

Cette thèse présente une étude de la structure de solutions de polyélectrolytes (PEs) dans les liquides ioniques (LIs) et de la structure locale des LIs en présence de PEs. Les techniques de diffusion de rayons X et de neutrons ont été principalement utilisées pour cette étude. Dans une première partie, la capacité des LIs à former des « clusters » à l'échelle nanoscopique est démontrée. Dans une seconde partie, l'influence de la nature des contreions et du solvant sur le comportement du polystyrène sulfonate (PSS) en solution est abordée. La conformation moyenne du PSS et son état de dispersion dans les milieux aqueux et organiques sont alors explorés dans une troisième partie. Une étude similaire pour le cas spécifique des milieux LIs est présentée dans une quatrième partie. Finalement, d'autres polymères, chargés ou neutres, en solution dans les LIs, sont considérés dans une cinquième et dernière partie.

Mots-clés: polyélectrolytes, liquides ioniques, diffusion de rayonnement aux petits angles, conformation moyenne, état de dispersion, qualité de solvant, structure *à l'échelle nanoscopique*.

## Résumé en anglais

In this thesis the structure of polyelectrolyte (PE) solutions in ionic liquids (ILs) and mutual influence of bothcomponentsthe local structure of the latter in the presence of PEs are studied. X-ray and neutron scatteringtechniques have been mainly used for the present investigation. In a first part, the ability of considered ILs toform clusters at nanoscale is demonstrated. In a second part, the influence of the nature of counterions andthe solvent on the polystyrene sulfonate (PSS) behavior in solution is tackled. PSS average conformation anddispersion state in aqueous and organic media are then explored in a third part. A similar investigation, carriedout on the specific case of PSS in IL media, is described in a fourth part. Finally, other polymers, both chargedand neutral, in IL solutions are considered in a fifth and last part.

Keywords: polyelectrolytes, ionic liquids, small-angle scattering methods, average conformation, dispersionstate, solvent quality, nanoscale structure.