e-Polymers **2007**, no. 100

http://www.e-polymers.org
ISSN 1618-7229

Influence of Ionic Liquids on the Free Radical Copolymerization of Styrene with Acrylonitrile

Inga Woecht, *Gudrun Schmidt-Naake*[*]

Technische Universität Clausthal, Institut für Technische Chemie, Erzstraße 18, 38678 Clausthal-Zellerfeld; Fax: +(49) 5323 723655; Email: gudrun.schmidt@tu-clausthal.de.

(Received: 30 March, 2007; published: 8 September, 2007)

Abstract: Free radical copolymerization of styrene (S) and acrylonitrile (AN) in the ionic liquids (ILs) 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6), 1,3-dimethylimidazolium dimethylphosphate ([MMIM]Me_2PO_4) and 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM]$EtSO_4$) were investigated. 2,2'-azobisiso butyronitrile (AIBN) and dibenzoyl peroxide (BPO) were used as initiators and dimethyl formamide (DMF) and methanol as reference solvents. The influence of the viscosity on the conversion and the molecular weights was studied by variation of the reaction temperature and the IL concentration. At reaction temperatures of 80 - 85 °C already after 30 minutes a conversion of about 80 % and almost a doubling of the molecular weights is reached for the S/AN (50/50 mol%) copolymerization. In addition the copolymerization behavior of S/AN in [EMIM]$EtSO_4$ was investigated. With increasing concentration of AN in the monomer feed the polymerization rate as well as the molecular weights of the copolymers increase. The influence of the ionic liquid on the copolymer composition, glass-transition temperature and rheological behavior was studied.

Introduction

Ionic liquids are new solvents for polymerization reactions. In general, they consist of a voluminous organic cation and a complex anion. The most common types of cations used in ILs are imidazolium, pyridinium, ammonium and phosphonium ions. As anions the hexafluorophosphate (PF_6^-) and the tetrafluoroborate (BF_4^-) ion are mostly used. ILs have some characteristic chemical and physical properties, which can be varied in a wide range by appropriate combination of cations and anions. Very important characteristics of ionic liquids are their high thermal stability, their wide liquid range, their partly bad miscibility with water and their low vapour pressure [1].

Recently ionic liquids are used to replace conventional organic solvents in free radical polymerizations but there are not many publications concerning these reactions so far [2-21, 25, 26].

Studies on the polymerization kinetics show that ILs strongly influences the reaction rate and the properties of the obtained polymers. An enhancement of the rates of polymerization and molecular weights which can be observed for the few studied polymerizations in ILs, exceeds the previously discussed influence of conventional organic solvents.

Haddleton et al. [2] observed an increase of the propagation rate constant k_p with increasing concentration of [BMIM]PF_6 in the reaction mixture using pulsed laser polymerization (PLP) technique. The propagation rate constant for the polymerization of methyl methacrylate (MMA) in bulk, which was measured at a pulse rate of 10 Hz is 330 $L \cdot mol^{-1} \cdot s^{-1}$. For a reaction mixture containing 60 vol% of ionic liquid a k_p of 808 $L \cdot mol^{-1} \cdot s^{-1}$ was found. Haddleton et al. [4] and we [5] presume that the increase of the propagation rate constant is due to the higher polarity of the reaction medium caused by the addition of ionic liquids which leads to a lowering of the activation energy of propagation E_A.

In [4] it was also found that the termination rate constant k_t for the polymerization of MMA decreases with increasing concentration of $[BMIM]PF_6$ in the reaction mixture by one order of magnitude. These results seem to verify the assumption in [2] and [3] that the high rate of polymerization is most of all due to the diffusion-controlled termination, reflecting the high viscosity of the used solvent and only to a minor degree due to the increase of k_p.

The free radical homopolymerization of methacrylates [2-13, 25, 26], styrene (S) [3, 6, 7, 25], 2-hydroxyethyl methacrylate [6-8], vinyl acetate [7, 8], 1-vinylimidazole [8] and acrylonitrile [7, 12, 17] in *N,N*-dialkyl imidazolium salts of $[PF_6]$, $[BF_4]$ and $[N(SO_2CF_3)_2]$ and the free radical copolymerization of MMA with S (in $[BMIM]PF_6$) [14, 15], with acrylonitrile (AN) [17], the copolymerization of a highly zwitterionic methacrylate with butyl methacrylate [18, 19] and the copolymerizations of AN with S [20] and methyl acrylate (MA) [21] were investigated.

The studies in [12, 17, 20] show that the free radical homopolymerization of AN and copolymerizations with MMA [17] and S [20] in ionic liquids based on 1,3-dialkyl-substituted imidazoles lead to high conversions and high molecular weights of the polymers in dependence on the nature of the ILs. Additionally, in [20] the occurrence of bimodal molecular weight distributions (MWDs) is described which is most likely due to low compatibility of the reaction systems caused by immiscibility of the copolymer with the ionic liquids.

In this paper we want to present the copolymerization behavior of S with AN in ionic liquids. The S/AN copolymerization can be classified as a weak donor/acceptor copolymerization because acrylonitrile (Q = 0.6; e = 1.2) is known as a weak acceptor monomer and styrene (Q = 1.0; e = -0.8) is a strong donor monomer.

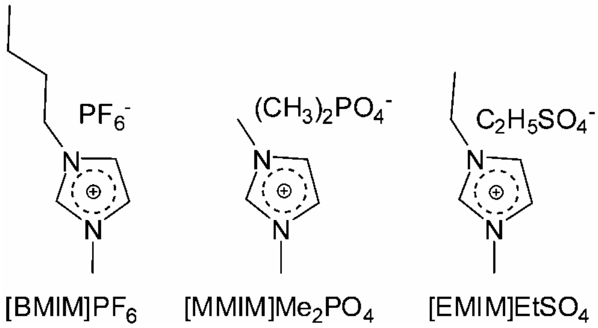
In previous work we have intensely dealt with the influence of different organic solvents on the reaction behavior of donor/acceptor systems [22].

As ionic liquids are quite polar solvents they possibly influence the copolymerization behavior of the S/AN system. Thus investigations concerning polymerization rate, copolymer composition, glass-transition temperature and rheological behavior were done. In addition the dependence of the conversion and the molecular weights on the reaction temperature and the IL concentration was studied.

Results and discussion

Variation of the IL

Preliminary tests on the influence of room-temperature ionic liquids on the free radical copolymerization of styrene with acrylonitrile (comonomer composition of S/AN = 50/50 mol%) were carried out in $[BMIM]PF_6$, $[MMIM]Me_2PO_4$ and $[EMIM]EtSO_4$ as solvents (Scheme 1). The chosen ILs are imidazolium salts which especially differ in the structure of their anions. There is only a slight difference in the substituents of the imidazolium cation. As reference solvents DMF and methanol were used.



Scheme 1. Structures of the ionic liquids used for the polymerizations: 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM]PF_6, 1,3-dimethylimidazolium dimethylphosphate [MMIM]Me_2PO_4 and 1-ethyl-3-methylimidazolium ethylsulfate [EMIM]$EtSO_4$.

Table 1 summarizes the results received from the S/AN copolymerization carried out in different ILs and conventional organic solvents. Conversions X was determined gravimetrically. The number average molecular weights M_n and the polydispersities Pd were measured via SEC using polystyrene standards. The amount of AN in the copolymers $x_{AN,copolymer}$ was calculated with data received from elemental analysis.

As can be seen from Table 1 [BMIM]PF_6 and [EMIM]$EtSO_4$ have a greater influence on conversion and molecular weights than [MMIM]Me_2PO_4. The copolymerizations carried out in [BMIM]PF_6 and [EMIM]$EtSO_4$ are faster than that performed using [MMIM]Me_2PO_4 as solvent although the viscosity of the latter is relatively high. Thus there has to be another factor which strongly influences the polymerization rate besides the viscosity of the ionic liquids. As can be seen in Table 1 the pH values of [EMIM]$EtSO_4$ and [MMIM]Me_2PO_4 strongly deviate from each other. This may be a possible reason for the different influences of the ILs on conversion and molecular weights of the S/AN (50/50 mol%) copolymerization. Probably the nature of the anions plays an important role, too. To be able to explain the different influences of the ILs on the copolymerization of S/AN, more detailed and more systematic investigations are necessary.

Tab. 1. Vicosity η, $pH_{solvent}$, conversions X, number average molecular weights M_n, polydispersities *Pd* and amounts of AN in the copolymer $x_{AN,copolymer}$ received for the copolymerization of S/AN (50/50 mol%) in ILs [BMIM]PF_6, [MMIM]Me_2PO_4, [EMIM]$EtSO_4$ and reference solvents DMF and methanol. Reaction conditions: 1.5 g monomer feed, 0.1 g AIBN, 4 mL solvent, T = 65 °C, t = 60 min.

solvent	η (20°C) [mPa·s]	$pH_{solvent}$	X [%]	M_n [g·mol^{-1}]	*Pd*	$x_{AN,copolymer}$ [mol%]
[BMIM]PF_6	352.2 [23]	-	63	97 000	2.36	41.8
[EMIM]$EtSO_4$	100.3	7.75	69	95 000	4.56	39.8
[MMIM]Me_2PO_4	391.1 [23]	2.38	45	85 000	5.27	43.4
DMF	-	-	31	22 000	1.57	47.2
methanol	-	-	31	18 000	1.63	41.3

The polydispersities of the polymers produced in ionic liquids are always higher than those of the products received from the reactions in the conventional organic solvents DMF and methanol.

A comparison of the amounts of AN and S contained in the copolymers shows, that the influence on the copolymer composition can be neglected for the S/AN (50/50 mol%) copolymerization.

As the preliminary tests showed the influence of [EMIM]EtSO$_4$ on the polymerization was quite similar to that of [BMIM]PF$_6$, but this IL has some important advantages: [EMIM]EtSO$_4$ is not as expensive as [BMIM]PF$_6$ and is already available in large scales. In addition toxicological investigations of [EMIM]EtSO$_4$ showed that it does not require any labelling [24]. Thus further investigations on the copolymerization behavior and the influence of the viscosity of the solvent on the conversion and molecular weights were carried out in [EMIM]EtSO$_4$ as solvent.

Variation of the IL concentration

Ionic liquids are solvents which have a relatively high viscosity in comparison to conventional organic solvents [1].

To lower the viscosity of the reaction solution the copolymerization of AN with styrene was carried out using solvent mixtures of [EMIM]EtSO$_4$ with DMF varying the IL concentration from 0 to 100 vol%. Investigations were made using a monomer feed containing 80 mol% of AN because we found a relatively intense difference of the conversion for the reaction carried out either in IL or in methanol (Fig. 7a) and the molecular weights of the products were still experimentally measurable.

The experimentally obtained viscosity of the solvent mixtures (Fig. 1a) can be explained by the following equation:

$$\eta_{\text{solvent}} = 0.812 \cdot e^{0.032 \cdot c_{IL}} \qquad (1)$$

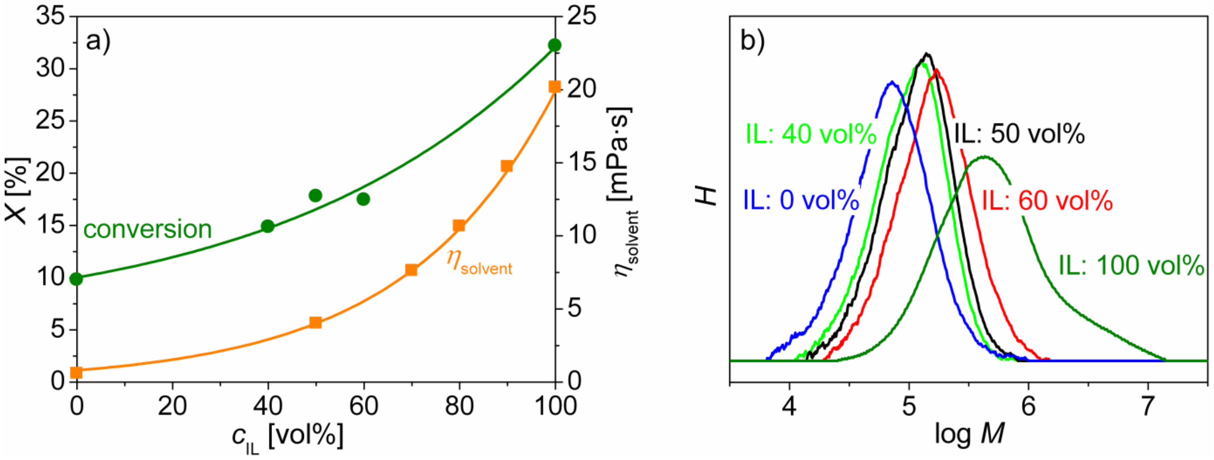


Fig. 1. a) Conversion of the S/AN copolymerization (20/80 mol%) after 30 minutes (●) and viscosity of [EMIM]EtSO$_4$ η_{solvent} at 60 °C in dependence of the IL concentration c_{IL}(■). The solvent viscosity was measured with a cone-plate rheometer; b) molecular weight distributions (MWD) of the products in dependence of c_{IL}. Reaction conditions: 1.5 g monomer feed, 0.05 g AIBN, 6 mL solvent mixture of [EMIM]EtSO$_4$ and DMF with c_{IL} = 0 (—), 40 (—), 50 (—), 60 (—), 100 (—) vol%, T = 60 °C, t = 30 min.

It is obvious that the conversion after a reaction time of 30 minutes decreases with decreasing IL concentration (Fig. 1a). It can also be seen that the conversion and viscosity of the reaction solution show a similar curve progression. This relatively strong dependence of the conversion on the viscosity of the reaction solution gives us a good hint that the rate constant of termination k_t is considerably affected by the ionic liquid.

We found that the molecular weight distributions (MWDs) shift to lower molecular weights when the concentration of [EMIM]EtSO$_4$ in the reaction mixture is decreased (Fig. 1b). Working with solvent mixtures containing between 50 and 60 vol% [EMIM]EtSO$_4$ leads to about 2 times higher values of M_n in comparison to the reaction carried out in pure DMF and furthermore the molecular weights can still be detected by SEC analysis (Table 2). In addition, the polydispersities of the products are relatively low. This is a great advantage towards the copolymerization performed in pure ionic liquid which leads to products with high polydispersities containing parts with extremely high molecular weights that cannot be detected via SEC.

Tab. 2. Number average molecular weights M_n and polydispersities *Pd* of the copolymers synthesized using solvent mixtures of varying IL concentration. Reaction conditions: see Figure 8.

c_{IL} [vol%]	M_n [g·mol^{-1}]	*Pd*
0	51300	1.82
40	78100	1.58
50	91400	1.57
60	123800	1.71
100	306300	3.01
	+ small shoulder above calibration	

In conclusion the strong enhancement of the k_p/k_t ratio with increasing concentration of [EMIM]EtSO$_4$ in the reaction mixture due to the decrease of k_t and the increase of k_p results in a higher concentration of radical chains in the reaction mixture, a higher conversion and higher molecular weights of the polymers. An advantage of the polymerization in ILs is the high conversion after short time.

Variation of the temperature

Another way to decrease the viscosity of the IL and therefore the reaction mixture is to increase the reaction temperature. The viscosity η of a solvent is associated with the temperature via the Arrhenius-Andrade equation:

$$\eta = \eta_0 \cdot e^{\frac{E_A}{R \cdot T}} \qquad (2)$$

η_0 is a material constant, E_A is the activation energy and R is the general gas constant.

Figure 2 shows that the reaction temperature intensely affects the viscosity of [EMIM]EtSO$_4$. Thus we varied the reaction temperature from 60 to 100 °C.

Figure 3a shows that the conversion of the S/AN (50/50 mol%) copolymerization increases when the reaction temperature is increased as was expected independent of the solvent. This is due to an increased radical concentration and a higher rate constant of propagation k_p. The strongest influence of the reaction temperature on the conversion can be found when pure ionic liquid is used as solvent for the copolymerization. The reason for this is the strong decrease of the solvent viscosity with increasing temperature (Fig. 2).

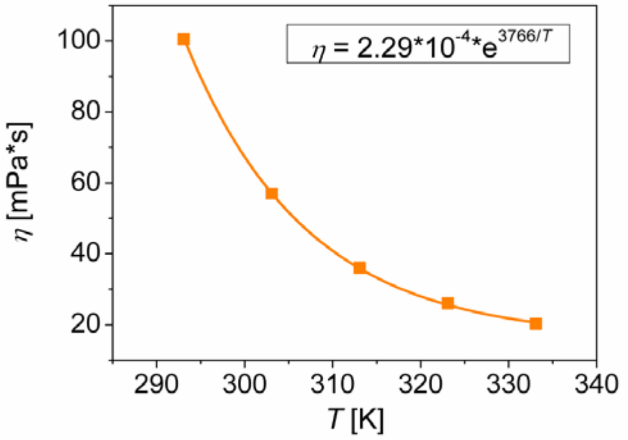


Fig. 2. Arrhenius-Andrade plot for [EMIM]$EtSO_4$.

It is remarkable that a limit conversion of about 90 % is approximately reached already after 30 minutes of reaction time when the S/AN copolymerization is performed in pure IL at temperatures above 85°C.

The conversions for the reactions carried out in the solvent mixture are about 1.3 to 1.7 times higher than those for the reactions performed in DMF and between 1.1 and 2.8 times lower than those found for the copolymerization in pure [EMIM]$EtSO_4$ (Fig. 3a).

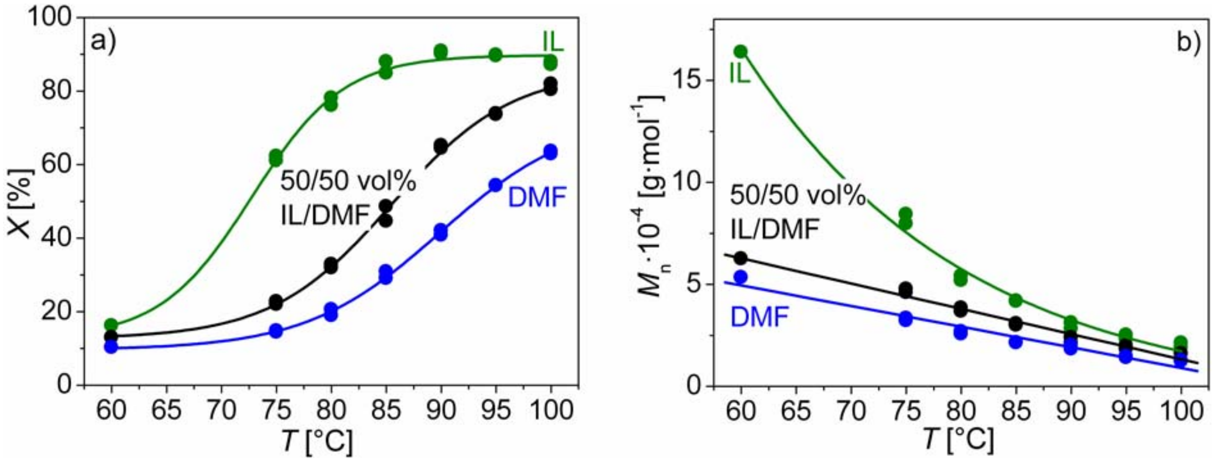


Fig. 3. a) Conversion versus temperature plots of the S/AN copolymerization (50/50 mol%) in [EMIM]$EtSO_4$ (●), in a mixture of [EMIM]$EtSO_4$ with DMF (50/50 vol%, ●) and in DMF (●); b) M_n versus temperature plots of the copolymers synthesized in [EMIM]$EtSO_4$ (●),in a mixture of [EMIM]$EtSO_4$ with DMF (50/50 vol%,●) and in DMF (●). Reaction conditions: 1.5 g monomer feed, 0.05 g AIBN (for T = 60°C) or BPO, 6 mL solvent, t = 30 min, T = 65, 75, 80, 85, 90, 95, 100 °C.

For the copolymerization of S/AN in pure IL as well as in the solvent mixture and in pure DMF a decrease of M_n can be observed with increasing reaction temperature T.

In case of the products synthesized in DMF and the solvent mixture a linear decrease can be noticed whereas M_n of the copolymers obtained from the copolymerization in [EMIM]EtSO$_4$ seems to be exponentially correlated with T. At high temperatures the three curves approach each other. The pronounced decrease of M_n which can be observed when the reaction is carried out in pure ionic liquid indicates that for the polymerization in the IL two opposite effects occur: (1) the polymer radical concentration increases with increasing temperature and (2) the polymer radical concentration decreases due to the decreasing viscosity which leads to an increase of the rate constant of termination k_t. Thus the polymer chains are shortened by the increasing concentration of the polymer radicals (reason: increase of temperature) and by the increased probability of termination reactions (reason: increase of k_t with decreasing viscosity).

Comparing the results obtained for the S/AN copolymerization in the solvent mixture and in pure IL it can clearly be seen that the dilution of [EMIM]EtSO$_4$ with 50 vol% DMF leads to a strongly decreased influence of the solvent on the molecular weights of the copolymers. Due to the dilution the viscosity of the solvent is strongly decreased and the termination rate coefficient is increased. This leads to an earlier termination of the radical chains and therefore to a decrease of the molecular weights of the products. The deviation from the polymerization in DMF is based on the differences in the k_p values (see Fig 3).

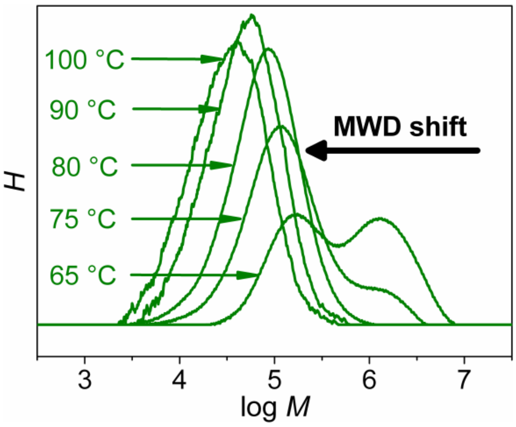


Fig. 4. Molecular weight distributions (MWDs) of the products received from the S/AN (50/50 mol%) copolymerization in [EMIM]EtSO$_4$ after t = 30 min in dependence of the reaction temperature. Reaction conditions: see Fig. 3.

Figure 4 clearly shows that at a temperature of about 80 °C or higher the MWDs become monomodal which is most likely due to the high conversions that are reached.

If the polymerization is carried out at 80 °C in [EMIM]EtSO$_4$, already after 30 minutes a conversion of about 80 % and almost a doubling of M_n is obtained. This results in the possibility to control the reaction time and the molecular weights of the products by variation of the reaction temperature.

The time dependent copolymerization of S/AN (50/50 mol%) at 80 °C in [EMIM]EtSO$_4$ as solvent leads to the following results:

In Figure 5a) the conversion-time dependence of the polymerization in DMF and in [EMIM]EtSO$_4$ are compared. After 45 min a limit conversion of 90 % is reached in the

IL because the growing and the dead polymers reduce the mobility of the polymer chains and the monomers when even the propagation step is slowed down by the high viscosity.

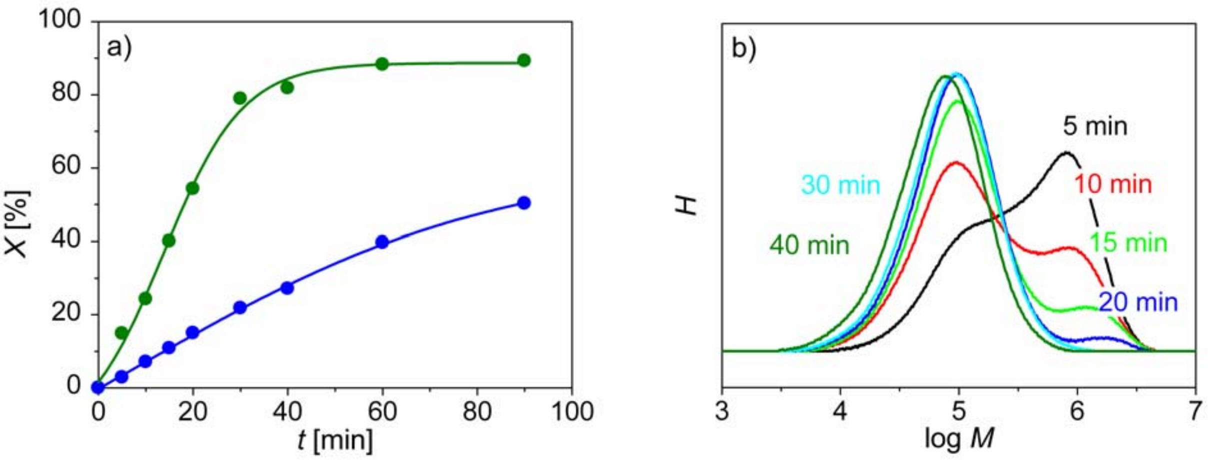


Fig. 5. a) Conversion versus time plot of the S/AN (50/50 mol%) copolymerization in [EMIM]EtSO$_4$ (●) and DMF (●) at T = 80 °C; b) MWDs of obtained copolymers in dependence of the reaction time. Reaction conditions: 1.5 g monomer feed, 0.05 g BPO, 6 mL solvent, t = 5 (—), 10 (—), 15 (—), 20 (—), 30 (—), 40 min (—), T = 80 °C.

The MWDs of the products of the S/AN copolymerization performed at 80 °C in [EMIM]EtSO$_4$ become monomodal when a conversion of about 80 % is reached (Fig. 5b). Thus the polydispersities of the copolymers synthesized in the IL decrease with increasing reaction time and increasing conversion, respectively (Table 3).

In [25, 26] a certain inhomogenity of the monomer/IL mixture is discussed as a reason for the bimodality of the MWDs. From our point of view a possible reason for the bimodality of the MWD at low conversions (< 80%) and low temperatures (< 80°C) is most likely the insolubility of the obtained polymers in [EMIM]EtSO$_4$. The bimodality, i.e. the high molecular weights, can additionally be explained by the gel effect, the diffusion control of the termination. With an increasing conversion (from ~80 % to the limit conversion of ~90%) the growing and the dead polymers strongly reduce the mobility of the polymer chains and the monomers.

Tab. 3. Number average molecular weights M_n and polydispersities Pd of the products received from the S/AN (50/50 mol%) copolymerization. Reaction conditions: see Figure 6.

t [min]	$M_{n,IL}$ [g·mol^{-1}]	Pd_{IL}	$M_{n,DMF}$ [g·mol^{-1}]	Pd_{DMF}
5	168600	3.47	33100	1.68
10	86900	4.5	29500	1.65
15	73000	3.64	29400	1.63
20	63500	2.6	27500	1.66
30	58300	2.04	26700	1.67
40	45800	2.07	26100	1.66
60	43100	2.05	25400	1.67
90	45200	2.11	24200	1.67

Diffusion controlled termination and propagation reactions control the kinetics of the polymerization and therefore the part of the polymers with low molecular weight increases.

In Figure 6 the influence of both the reaction temperature and the IL concentration on the MWDs of the copolymers received from the S/AN (50/50 mol%) copolymerization after 30 minutes of reaction time are compared. An increased reaction temperature of 80 °C of the IL as well as a solvent mixture IL/DMF (50/50 vol%) leads to comparable viscosities of the reaction solution. It is obvious that both methods lead to a shift of the MWDs to lower molecular weights (IL: T = 65 °C $\Rightarrow$ M_n = 240800 g·mol^{-1}; T = 80 °C $\Rightarrow$ M_n = 58300 g·mol^{-1}; IL/DMF(50/50 vol%): T = 65 °C $\Rightarrow$ M_n = 48900 g·mol^{-1}; DMF: T = 65 °C $\Rightarrow$ Mn = 26700 g·mol^{-1}) and to a loss of the bimodality of the MWDs. Figure 6 clearly shows that when the viscosity of the solvent is reduced either by dilution of the IL with 50 vol% DMF or by increasing the reaction temperature of 15 °C the diffusion control on the termination reaction gets lost and k_t increases. The increase of k_t seems to be quite similar for both methods.

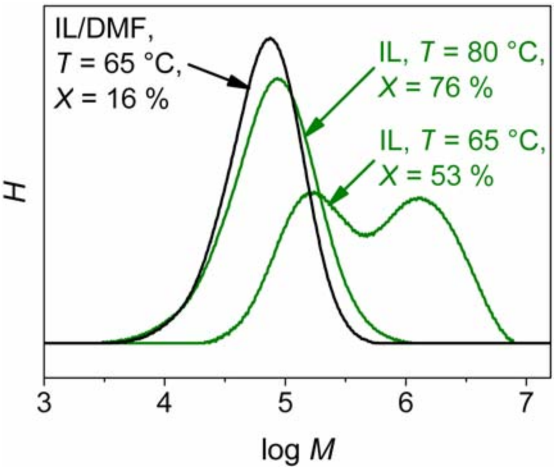


Fig. 6. Molecular weight distributions (MWDs) of the products received from the S/AN (50/50 mol%) copolymerization in [EMIM]EtSO$_4$ (—) or [EMIM]EtSO$_4$/DMF (50/50 vol%; —) after *t* = 30 min in dependence of the reaction temperature. Reaction conditions: see Fig. 3.

Although both methods for decreasing the solvent viscosity lead to similar results concerning the MWDs they strongly differ in their influence on the rate of polymerization (see Fig. 6). The dilution of the IL leads to a strong decrease of the polymerization rate which is expressed by the relatively low conversion (16 %) after 30 minutes of reaction time whereas the increase of the reaction temperature results in a rise of the conversion (76 % after *t* = 30 min). These two opposite effects can be explained by the differing influence of the solvent or the solvent mixture on k_p. As is described in [4] and [5] k_p is increased for reactions carried out in ILs due to the high polarity of these solvents which leads to a decrease of the activation energy of propagation. Thus a higher polymerization rate can be observed (Fig. 6). When the IL is diluted by addition of DMF the influence on k_p decreases due to a loss of polarity. This results in a lower rate of polymerization.

That is to say by enhancement of the reaction temperature the polymerization rate of the S/AN (50/50 mol%) copolymerization with [EMIM]EtSO$_4$ as solvent can be increased fundamentally, the MWDs become monomodal and the M_n values are doubled at most in comparison with the polymerization in DMF.

Variation of the AN content in the monomer feed

The copolymerization behavior of S/AN in [EMIM]EtSO$_4$ was examined by varying the monomer feed composition.

It was found that the homopolymerization of AN can be carried out in solution independent of the conversion. The reaction with 80 to 90 mol% AN in the monomer feed is a solution polymerization for small conversions up to 15 %, too. With increasing amount of S the copolymerization proceeds under precipitation independent of the monomer conversion. Thus methanol was used as reference solvent.

It can be noticed that the influence of the ionic liquid on the conversion decreases with increasing concentration of S in the monomer feed. This can be explained with the different solubilities of PAN and PS in [EMIM]EtSO$_4$. PAN shows a good solubility in this IL whereas PS is nearly insoluble. The bad solubility of PS in the ionic liquid leads to an early precipitation of the growing polymer chains. The precipitation most likely leads to a loss of the influence of the IL on the further polymerization.

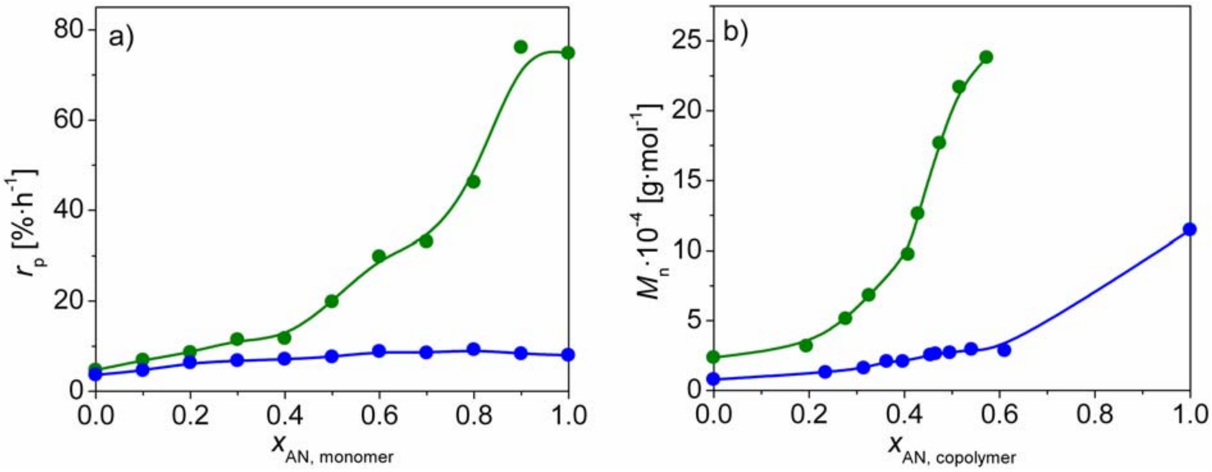


Fig. 7. a) Dependence of the overall polymerization rate r_p on the mole ratio of acrylonitrile in the monomer feed for the S/AN copolymerization in [EMIM]EtSO$_4$ (●) and methanol (●). b) Number average molecular weights M_n of the S/AN copolymers synthesized in [EMIM]EtSO$_4$ (●) and in methanol (●) in dependence on the content of AN in the copolymer. M_n was determined via SEC using THF as solvent. M_n of the PAN sample synthesized in methanol was determined via SEC using DMF as solvent. Polystyrene standards were used for calibration; conversion: 2-6%. Reaction conditions: 1.5 g monomer feed, 0.05 g AIBN, 6 mL solvent, T = 60 °C.

Fig. 7a) displays that the polymerization rate r_p (slope of the conversion time curve) increases with increasing content of AN in the monomer feed for the reaction carried out in the ionic liquid. This enhancement of r_p is more pronounced than that observed for the copolymerization of S/AN performed in methanol. The strong increase of the polymerization rate r_p for polymerizations carried out in ILs is explained by an increase of k_p and a coexistent decrease of k_t and therefore a higher k_p/k_t ratio in comparison to the reaction in conventional solvents [2-5]. With increasing the AN amount in the monomer feed the polymer solubility increases. The longer the growing polymer chains stay in solution the greater is the influence of the ionic liquid on the polymerization.

Molecular weight measurements were carried out using tetrahydrofuran (THF) as solvent via SEC measurements. The poly(acrylonitrile) samples and the copolymers synthesized in [EMIM]EtSO$_4$ using 90 mol% of AN in the monomer feed are insoluble in this solvent. Although these samples could be measured via SEC using a DMF solution, we were not able to measure their molecular weights because they were above our calibration (molecular weights up to 7.5 million g·mol^{-1}).

Taking together this fact and the results depicted in Fig. 7b) the most significant influence of the IL on the molecular weights of the copolymers can be found for the reactions carried out with 90 and 100 mol% of AN in the reaction mixture. The molecular weights of the polymer samples synthesized in [EMIM]EtSO$_4$ are at least 1 to 2 orders of magnitude higher (> 7.5 million g/mol) than those of the products of the reaction in methanol (30 000 g·mol^{-1} (90 mol% AN) and 110 000 g·mol^{-1} (PAN)). The number of growing chains and therefore the radical concentration from initiator decomposition has to be the same for the copolymerization carried out in both IL and methanol. Thus the enhancement of the overall polymerization rate r_p and the number average molecular weights M_n with increasing AN content in the monomer feed can be explained looking at the $k_{p,S}/k_{p,AN}$ ratio.

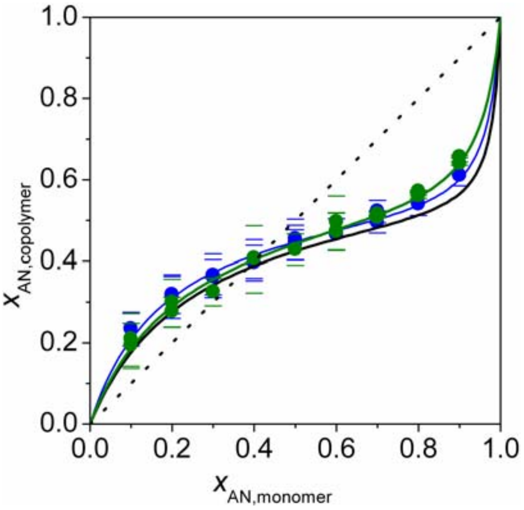


Fig. 8. Copolymerization diagram for the S/AN copolymerization in the ionic liquid [EMIM]EtSO$_4$ (●) and methanol (●). Literature data [28] are depicted by the black line (—). Reaction conditions: see Fig. 7; conversion: 2-10%; reactivity ratios calculated via Kelen-Tüdös [27]; the error intervals are shown as horizontal lines.

The propagation rate coefficient for the homopolymerization of styrene $k_{p,S}$ does not seem to be very much affected by the presence of [EMIM]EtSO$_4$ whereas the rate constant of propagation for the homopolymerization of the polar AN $k_{p,AN}$ in the solution polymerization has to be strongly influenced. The interactions between IL and AN are intensified due to the homogeneous reaction conditions at high amounts of AN in the monomer feed. In addition we have to keep in mind that r_p is increased due to the decrease of the termination rate coefficient k_t and that the reaction becomes homogeneous when the monomer feed contains 80 to 100 mol% of AN (at low conversions). We assume that an even more pronounced influence on k_t can be found for these homogeneous reactions due to the gel effect. The arising long polymer chains form entanglements in solution, too. This formation of entanglements increases the viscosity dramatically and leads to diffusion controlled termination reactions and thus would explain the strong increase of the molecular weights and the conversion when the amount of AN in the monomer feed exceeds 80 mol%.

The copolymerization diagram is depicted in Figure 8. The reactivity ratios r_{AN} and r_S are calculated using the method of Kelen-Tüdös [27] (Table 4). There is no significant difference in the copolymerization behavior to be found using either IL or methanol as solvents for the reaction. The reactivity ratios determined for the copolymerization of S with AN in both [EMIM]EtSO$_4$ and methanol show a good agreement with the values previously calculated for the reaction carried out in 1,4-dioxane [28] (valid to 70 mol% of AN in the monomer feed). Thus we can conclude, that the use of the IL [EMIM]EtSO$_4$ as solvent for the copolymerization of S with AN does not affect the copolymerization behavior. As $r_{AN} = k_{AN,AN} / k_{AN,S}$ is almost unchanged both the rate constant of the homo propagation $k_{AN,AN}$ and the cross propagation rate coefficient $k_{AN,S}$ are affected due to interactions between [EMIM]EtSO$_4$ and AN. $k_{AN,AN}$ as well as $k_{AN,S}$ have to be increased in the same order of magnitude with the increase of the solubility at high AN amount.

Tab. 4. Reactivity ratios for the copolymerization of S/AN in IL [EMIM]EtSO$_4$ and methanol. Reaction conditions: see Figure 7.

solvent	r_{AN}	r_S
[EMIM]EtSO$_4$	0.10 ± 0.02	0.38 ± 0.04
methanol	0.06 ± 0.02	0.31 ± 0.03
1,4-dioxane [28] *	0.04 ± 0.01	0.41 ± 0.05

* valid to 70 mol% of AN in the monomer feed.

As the glass-transition temperatures are influenced by the copolymer composition we expected to find no great differences for the copolymers synthesized either in the ionic liquid or in methanol. The slightly higher glass-transition temperatures of the polymers synthesized in the ionic liquid are due to higher molecular weights of these polymers (Fig. 9). Theoretical glass-transition temperatures were calculated using the equation by Fox:

$$\frac{1}{T_g} = \frac{m_{S,copolymer}}{T_{g,PS}} + \frac{m_{AN,copolymer}}{T_{g,PAN}} \tag{3}$$

In this equation T_g is the glass-transition temperature of the copolymer that is to be calculated (in °C). $m_{S,copolymer}$ and $m_{AN,copolymer}$ describe the mass fraction of S or AN in the copolymer. $T_{g,PS}$ and $T_{g,PAN}$ are the glass-transition temperatures of the homopolymers PS and PAN ($T_{g,PS}$ = 105 °C (IL); $T_{g,PS}$ = 101 °C (methanol); $T_{g,PAN}$ = 135 °C (IL); $T_{g,PAN}$ = 133 °C (methanol)). The experimental data received for the S/AN copolymerization in [EMIM]EtSO$_4$ and in methanol show a relatively good correlation with the calculated T_g (Fig. 9).

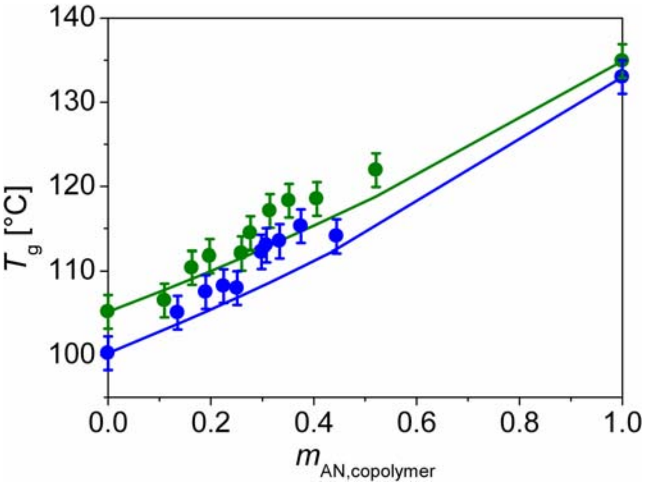


Fig. 9. Measured (dots with error interval) and calculated (lines) glass-transition temperatures T_g of the copolymers produced in IL (●, —) and methanol (●, —) in dependence on the mass fraction $m_{AN,copolymer}$ of AN in the copolymer. Reaction conditions: see Fig. 7.

The comparison of Figures 10 a) and b) displays that the copolymer sample synthesized in the ionic liquid (Fig. 10a) shows a different rheological behavior than the product received from the reaction in methanol (Fig. 10b). Both the storage modulus *G*' and the loss modulus *G*'' of the copolymer produced in [EMIM]EtSO$_4$ are independent of the frequency for $\omega < 10^{-1}$ rad·s^{-1}. The plateau which can be found for the storage and loss modulus broadens with increasing molecular weight. Presumably this is due to the increased number of entanglements, reflecting the higher molecular weight of the samples with 80 mol% AN in the monomer feed, which can be obtained from the influence of the IL as solvent (compare Figure 7b).

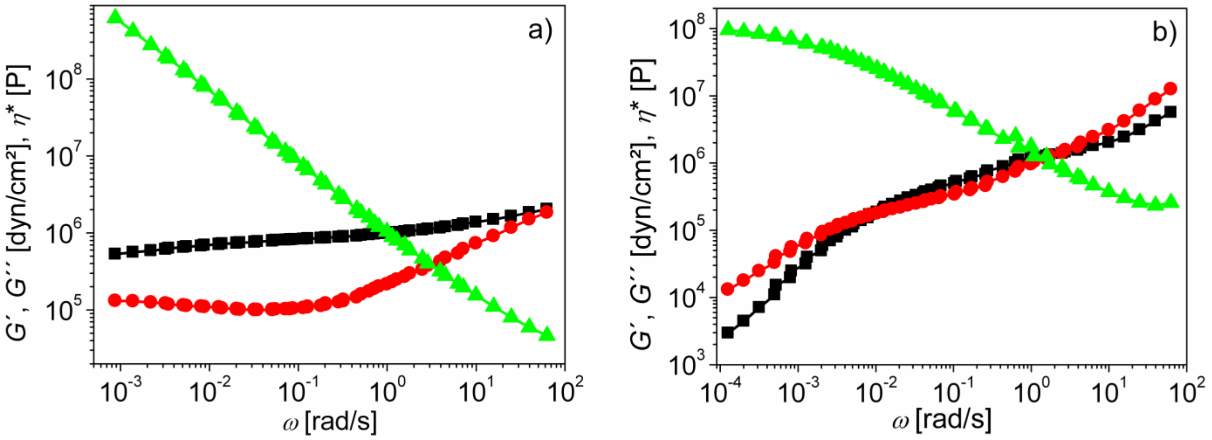


Fig. 10. Storage modulus *G*' (■), loss modulus *G*'' (●) and complex viscosity η^* (▲) a) of the copolymer synthesized in [EMIM]EtSO$_4$ with 80 mol% AN in the monomer feed and b) of the copolymer synthesized in methanol with 80 mol% AN in the monomer feed in dependence of the frequency ω; temperature range: 125-165°C; reference temperature: 125°C.

On the other hand Figure 11 shows the rheological behavior of polystyrene polymerized in [EMIM]EtSO$_4$. This polymer has a relatively low molecular weight (M_n

= 48800 g/mol) and does not show a plateau for the storage and loss modulus. This supports that the appearance of a plateau has to be due to higher molecular weights. The influence of the IL on the very unpolar styrene is very low.

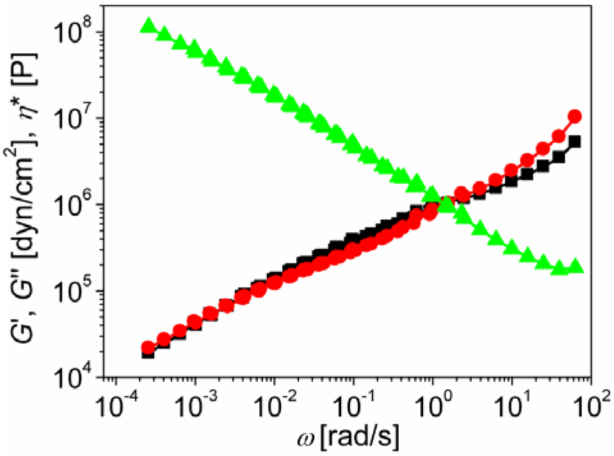


Fig. 11. Storage modulus *G*' (■), loss modulus *G*'' (●) and complex viscosity η^* (▲) of polystyrene produced in [EMIM]EtSO$_4$ in dependence of the frequency ω; temperature range: 125-165 °C; reference temperature: 125 °C.

We found that the influence of [EMIM]EtSO$_4$ on the S/AN copolymerization is strongly dependent on the amount of AN in the monomer feed. The enhancement of the overall polymerization rate as well as the increase of the molecular weights are controlled by the interaction of the IL with AN .

Conclusions

This work confirms the results published in [20] that using ILs as solvents for the copolymerization of S/AN leads to higher molecular weights and higher polymerization rates compared to reactions carried out in DMF and methanol. It can be shown that the three different ILs [BMIM]PF$_6$, [MMIM]Me$_2$PO$_4$ and [EMIM]EtSO$_4$ have varying influences on this copolymerization.

The increased k_p/k_t ratio due to the high viscosities and relatively high polarity of the ILs in comparison to conventional organic solvents is considered to be primarily responsible for the increased molecular weights and polymerization rates. Therefore we investigated the influence of the viscosity of the solvent on the S/AN copolymerization. The viscosity of the reaction solution was varied by mixtures of ILs with organic solvents (shown for S/AN = 20/80 mol%) or by variation of the temperature (shown for S/AN = 50/50 mol%).

The temperature dependent S/AN copolymerization with 50 mol% of AN contained in the monomer feed leads to the result that the influence of the ionic liquid [EMIM]EtSO$_4$ on k_t decreases with increasing temperature and decreasing viscosity, respectively, whereas the influence on k_p is increased. If the copolymerization is carried out at a temperature of 80 °C a conversion of about 80 % is already reached after 30 min for S/AN (50/50 mol%) and still almost a doubling of the molecular weights can be observed. Under this reaction conditions the molecular weight distributions become monomodal.

Comparing the S/AN copolymerization with varied concentrations of AN in the monomer feed done in [EMIM]EtSO$_4$ and methanol at 60 °C impressive differences in the polymerization rates and the number average molecular weights can be found for reaction mixtures containing more than 50 mol% of AN. The higher the concentration of AN in the monomer feed the higher is the influence of the ionic liquid on the copolymerization. Although there is a significant influence on both the polymerization rates and the molecular weights of the products only low differences in the copolymer composition and T_g can be found using the two different solvents. The rheological measurements show that the ionic liquid has a significant influence on the rheological behavior of the polymer samples. For frequencies lower than 10^{-1} rad·s^{-1} the storage and the loss modulus are independent of ω, because the polymer chains with high molecular weights received from the reaction in ionic liquid produce an increased number of entanglements.

This work leads to the conclusion that ILs as solvents for polymer synthesis have a great application potential and should be further investigated. The influence of the ILs on polymerizations can easily be controlled by varying the reaction temperature.

Experimental part

The monomers styrene (BASF) and acrylonitrile (ACROS) were distilled to remove inhibitors. The ionic liquids [BMIM]PF$_6$, [MMIM]Me$_2$PO$_4$ (ECOENG^{TM} 1111P) and [EMIM]EtSO$_4$ (ECOENG^{TM} 212) (Solvent Innovation GmbH) and the reference solvents DMF and methanol were used as received. 2,2'-azobisisobutyronitrile (Merck) and dibenzoyl peroxide were recrystallized before use.

Preliminary tests for the S/AN copolymerization (50/50 mol%) were performed as follows: monomer pairs (1.5 g) and AIBN (0.1 g) were weighed into ampoules. 4 mL of solvent were added into the ampoules separately before they were purged with nitrogen for 10 minutes and sealed. Reactions were carried out in a heating block at 65 °C. Reaction times were limited to 3 hours. Polymerizations were stopped by fast cooling of the reaction mixture and products were received by precipitation in methanol, washing with large amounts of methanol and water, filtering and drying under vacuum to constant weight.

For the investigations of the temperature and concentration dependence as well as for the investigations on the copolymerization behavior the following reaction setup was used: monomer pairs (1.5 g) and initiator (0.05 g AIBN or BPO) were weighed into ampoules and 6 mL of solvent ([EMIM]EtSO$_4$, methanol, DMF or IL/DMF mixture) were added afterwards (sample preparation as described above). For the temperature dependent polymerizations with constant monomer composition (S/AN = 50/50 mol%) the reaction temperature was varied from 75 to 100 °C in steps of 5 °C. The concentration dependence was investigated at 60 °C. Both the temperature and the concentration dependent polymerizations were stopped after 30 minutes. The investigations on the copolymerization behavior of S/AN in [EMIM]EtSO$_4$ were carried out at 60 °C for 40 minutes in order to achieve low conversions. The comonomer composition was varied from 0 to 100 mol% of AN in steps of 10 mol%.

The temperature dependence of the viscosity of [EMIM]EtSO$_4$ was measured with a Bohlin Gemini cone-plate rheometer (MALVERN) at 20 to 60 °C with a constant shear stress of 5 Pa.

Molecular weight measurements were carried out on a Waters 510 size exclusion chromatograph in tetrahydrofuran at 25 °C. A Styragel two columns system (Styragel HR3 with an upper exclusion border of 30000 g/mol and Styragel HR4 with an upper exclusion border of 600 000 g/mol) with a differential refractometer detector was used. Molecular weights measurements of the PAN samples were performed in DMF at 25 °C, a two columns system (PL-Gel with µm mixed B) with a differential refractometer detector was used. Polystyrene standards were used for calibration.

Copolymer compositions were determined by elemental analysis (C, H, N). Elemental Analysis VarioEL (ELEMENTAR ANALYSE-SYSTEME GmbH) was used, calibrated with acetanilide and benzoic acid.

Glass-transition temperatures were measured in a differential scanning calorimeter DSC 25 (METTLER TOLEDO).

Rheological measurements were done with a Dynamic Analyzer RDA II (RHEOMETRICS SCIENTIFIC). The measurement setup is a rheometer with a plate-plate geometry (plate diameter: 13 mm; plate material: aluminium).

References

[1] Wasserscheid, P.; Keim, W. *Angew. Chem.* **2000**, *112*, 3926.
[2] Harrison, S.; MacKenzie, S.R.; Haddleton, D.M. *Chem. Commun.* **2002**, 2850.
[3] Hong, H.L.; Zhang, H.W.; Mays, J.W.; Visser, A.E.; Brazel, C.S.; Holbrey, J.D.; Reichert, W.M.; Rogers, R.D. *Chem. Commun*. **2002**, 1368.
[4] Harrison, S.; MacKenzie, S.R.; Haddleton, D.M. *Macromolecules* **2003**, *36*, 5072.
[5] Woecht, I.; Schmidt-Naake, G.; Beuermann, S.; Buback, B.; Garcia, N. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, submitted.
[6] Benton, M.G.; Brazel, C.S. *Ionic Liquids: Industrial Applications for Green Chemistry*; ACS Symposium Series Vol. 819, R.D. Rogers, K.R. Seddon, Eds.; American Chemical Society; Washington DC, **2002**.
[7] Noda, A.; Watanabe, M. *Electrochim. Acta* **2000**, *45*, 1265.
[8] Tsuda, T.; Nohira, T.; Nakamori, Y.; Matsumoto, K.; Hagowara, R.; Ito, Y. *Solid State Ionics* **2002**, *149*, 295.
[9] Scott, M.P.; Brazel, C.S.; Benton, M.G.; Mays, J.W.; Holbrey, J.D.; Rogers, R.D. *Chem. Commun.* **2002**, 1370.
[10] Benton, M.G.; Brazel, C.S. *Polym. Int.* **2004**, *53*, 1113.
[11] Zhang, H.; Bu, L.; Li, M.; Hong, K.; Visser, A.E.; Rogers, R.D.; Mays, J.W. *Ionic Liquids: Industrial Applications for Green Chemistry*; ACS Symposium Series Vol. 819, Rogers, R.D.; Seddon, K.R. Eds.; American Chemical Society; Washington DC, **2002**.
[12] Cheng, L.; Zhang, Y.; Zhao, T.; Wang, H. *Macromol. Symp.* **2004**, *216*, 9.
[13] Strehmel, V.; Laschewsky, A.; Kraudelt, H.; Wetzel, H.; Görnitz, E. *ACS Symp.*
[14] Zhang, H.; Hong, K.; Mays, J.W. *Macromolecules* **2002**, *35*, 5738.
[15] Zhang, H.; Hong, K.; Jablonsky, M.; Mays, J.W. *Chem. Commun.* **2003**, 1356.
[16] Kubisa, P. *Prog. Polym. Sci.* **2004**, *29*, 3; *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4675.
[17] Vygodskii, Y.S. ; Mel’nik, O.A. ; Lozinskaya, E.I. ; Shaplov, A.S. *Polym. Sci., Part B* **2005**, *47*, 122.
[18] Strehmel, V. ; Laschewsky, A. ; Wetzel, H.; Görnitz, E. *Macromolecules* **2006**, *39*, 923.
[19] Strehmel, V. ; Laschewsky, A. ; Wetzel, H. *e-Polymers* **2006**, no. 011.

[20] Li, J.; Zhang, J.; Liu, Z. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4420.
[21] Li, D.; Zhang, Y.; Wang, H.; Tang, J.; Wang, B. *J. Appl. Polym. Sci.* **2006**, *102*, 4254.
[22] Schmidt-Naake, G.; Schmidt, H.; Berger, W. *Makromol. Chem.* **1990**, *191*, 2957; *Acta Polymerica* **1985**, *36*, 536; *Acta Polymerica* **1985**, *36*, 671; *Acta Polymerica* **1986**, *37*, 16; *Acta Polymerica* **1986**, *37*, 172.
[23] www.solvent-innovation.com
[24] Wagner, M. *Chemistry Today* **2005**, *3*, 32.
[25] Liu, Y. ; Wu, G. ; Long, D. ; Zhang, G. *Polymer* **2005**, *46*, 8403.
[26] Wu, G.; Liu, Y.; Long; D. *Macromol Rapid Commun* **2005**, *26*, 57
[27] Kelen, T.; Tüdös, F. *J. Macromol. Sci. Chem.* **1975**, *A9*, 1.
[28] Schmidt-Naake, G.; Schmidt, H.; Litauszki, B.; Schmutzler, H. *Wissenschaftliche Zeitschrift der TU Dresden* **1989**, *38*, 131.