Macromol. Symp. **2007**, 259, 226–235 DOI: 10.1002/masy.200751327

Ionic Liquids - New Solvents in the Free Radical Polymerization

Gudrun Schmidt-Naake, Inga Woecht, Anne Schmalfuß*

Summary: The analysis of the influence of ionic liquids (ILs) in polymer synthesis as an alternative for common organic solvents is still an active field of research.[1] Using ILs as solvents for free radical polymerizations implies a significant increase in polymerization rates and molecular weights which can be observed. In this work we examined the copolymerization behaviour of styrene (S) and methyl methacrylate (MMA), glycidyl methacrylate (GMA) and 2-hydroxypropyl methacrylate (HPMA) with acrylonitrile (AN) in 1-etyhl-3-methylimidazolium ethylsulfate ([EMIM]EtSO$_4$). ILs are liquids with comparable high polarities and viscosities. These two characteristic properties are strongly correlated with the rate coefficients of propagation k_p and termination k_t.[2–4] The rate constant of termination k_t decreases when the IL concentration and therefore the viscosity of the reaction mixture is increased, whereas the propagation rate coefficient k_p increases with increasing IL content. The viscosity of the IL can be varied by either working with mixtures of IL with conventional organic solvents – here the IL [EMIM]EtSO$_4$ was mixed with DMF – or by variation of the temperature. The influence of the viscosity of the IL ([EMIM]EtSO$_4$) on polymerization kinetics of methyl methacrylate (MMA) and styrene/acrylonitrile (S/AN) was investigated.

Keywords: copolymerization; free radical polymerisation; ionic liquids; r-values; viscosity influence

Introduction

Ionic liquids are new solvents for polymerization reactions. Very important characteristics of ionic liquids (IL) are the high thermal stability, the wide liquid range in comparison to water and conventional organic solvents and the very low vapour pressure. The application of ILs as solvents in organic syntheses has an effect on the reactivity and selectivity of the applied processes as well. An overview on synthesis and characteristic properties of ILs and applications in organic syntheses – especially catalysis – has been given in ref.[5]

Recently ionic liquids are also used as solvents in free radical polymerizations to replace conventional organic solvents. Their use in free-radical polymerizations is still limited. It has been shown that polymer synthesis in solution using ionic liquids as solvents may be associated with remarkable advantages, e.g. with higher polymerization rates and higher molecular weights.

In a first PLP-SEC study (pulsed laser initiated polymerization (PLP) technique in combination with polymer analysis by size-exclusion chromatography (SEC)) it was observed that k_p for methyl methacrylate (MMA) is up to 2.5 times higher with 60 vol.-% 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF$_6$) in the reaction mixture compared to the polymerization in bulk.[2,3]

We measured the propagation rate constant for the MMA and glycidyl methacrylate

---

Institut für Technische Chemie, Technische Universität Clausthal, Erzstr. 18, 38678 Clausthal-Zellerfeld, Germany
Fax: (+49) 05323 723655;
E-mail: gudrun.schmidt@tu-clausthal.de

(GMA) polymerization in [BMIM]PF_6, 1-butyl-3-methylimidazoliumtetrafluoroborate ([BMIM]BF_4), 1-ethyl-3-methylimidazlium ethylsulfate ([EMIM]$EtSO_4$) and 1-ethyl-3-methylimidazolium hexylsulfate ([EMIM]-$HexSO_4$).[4] For both MMA and GMA polymerized in IL solutions an increase of k_p can be observed in comparison to the bulk polymerization. In ILs [BMIM]PF_6, [BMIM]BF_4 and [EMIM]$EtSO_4$ the propagation rate constant for the MMA polymerization is 4 times higher than in bulk when a IL concentration of 80 vol.-% is used. The results we got from the investigations of the temperature dependence of the polymerizations of MMA and GMA in IL show in agreement with Haddleton et al.[2,3] that the main effect which leads to the increase of the propagation rate coefficient k_p is a decrease of the activation energy of propagation E_A. The polymerization of MMA in bulk requires an activation energy of propagation $E_A = 22.4\ \mathrm{kJ \cdot mol^{-1}}$ whereas it is $18.1\ \mathrm{kJ \cdot mol^{-1}}$, when the reaction is carried out in a solution containing 80 vol.-% of IL [BMIM]PF_6, [BMIM]BF_4 or [EMIM]$EtSO_4$.[4] The infrared spectra of pure MMA and its solutions in the IL [EMIM]$EtSO_4$ measured at room temperature show a shift in the valence stress of the C=O bond of MMA[4] which indicates interactions between monomer and ionic liquids. These interactions can activate the monomer and therefore it becomes more reactive. In addition Haddleton et al.[2,3] and we[4] have described a decrease of the propagation rate coefficient with decreasing IL concentration. But this cannot fully explain the significant increase in the overall polymerization rate. All the results indicate that there must be a corresponding decrease in the termination rate coefficient k_t which leads to a higher k_p/k_t ratio and can probably be used to explain the high overall polymerization rate. It was found that k_t decreases with increasing IL concentration which can be related to the increasing viscosity of the reaction mixture.[2–4]

We systematically varied the viscosity of the reaction solution by diluting the ILs with organic solvents or by variation of the temperature. These studies of the MMA and the S/AN polymerization were carried out with the aim of determining the influence of the solvent viscosity on propagation, termination, conversion and the molecular weight distributions (MWDs).

Futhermore we examined the homo- and copolymerization behavior of AN with S, MMA, GMA and HPMA in [EMIM]-$EtSO_4$ as solvent.

Experimental Part

The monomers S, AN, MMA, GMA and HPMA were distilled to remove inhibitors. The ionic liquid [EMIM]$EtSO_4$ (ECOENG^{TM} 212, Solvent Innovation GmbH) as well as DMF and methanol were used as received. 2,2′-azobisisobutyronitrile (AIBN) and dibenzoyl peroxide (BPO) were recrystallized before use.

Reaction setup: 1.5 g monomer feed 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, then the ampoules were purged with nitrogen for 10 minutes and sealed. Temperature dependent polymerizations were carried out at 60 to 100 °C. The concentration dependence and the copolymerization behavior were investigated at 60 °C. The temperature and the concentration dependent polymerizations were stopped after 30 minutes. For the investigations on the copolymerization behavior of S/AN and methacrylates/AN in [EMIM]$EtSO_4$ 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 515 size exclusion chromatograph in tetrahydrofurane at 25 °C. Polystyrene and polymethylmethacrylate standards were used for calibration.

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).

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

Results

Copolymerization Behaviour

We have investigated the homo- and copolymerization behavior of S and methacrylates (MMA, GMA, HPMA) with AN.[6,7] The IL [EMIM]EtSO$_4$ (Scheme 1) and methanol are used as solvents.

The homopolymerization of AN and the copolymerization HPMA/AN can be carried out in solution independent of the conversion. The other polymerizations proceed under precipitation at conversions higher than ~10%.

Figure 1 displays that the polymerization rate r_p (slope of the conversion time curve) and the M_n values increase with increasing content of AN in the monomer feed for the reaction carried out in the IL.

Molecular weight measurements were carried out using tetrahydrofurane (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 $g \cdot mol^{-1}$).

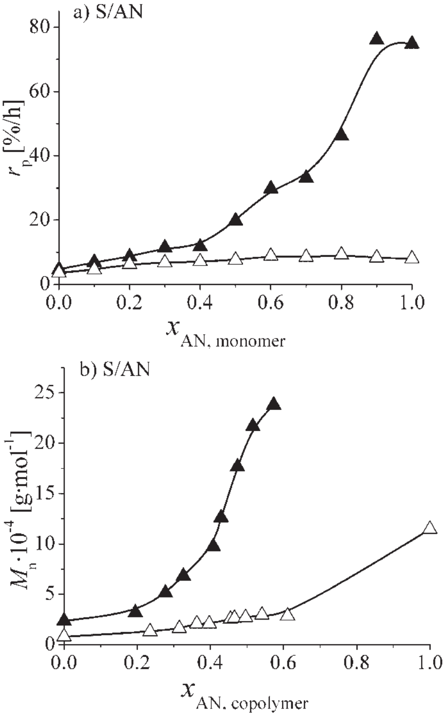
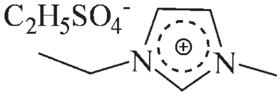


Figure 1.
S/AN copolymerization in [EMIM]EtSO$_4$ (▲) and methanol (△): a) Polymerization rate (r_p) as a function of the molar fraction of AN $x_{AN,monomer}$ in the monomer feed, b) number average molecular weights (M_n) versus $x_{AN,copolymer}$, $T = 60\,°C$.



Scheme 1.
Structure of the IL 1-etyhl-3-methylimidazolium ethylsulfate ([EMIM]EtSO$_4$).

Taking together this fact and the results depicted in Figure 1(b) 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 $g \cdot mol^{-1}$ (90 mol% AN) and 110 000 $g \cdot mol^{-1}$ (PAN)).

The strong enhancement of r_p and M_n 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.[2–4] With increasing 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 IL on the polymerization. Thus the enhancement of r_p and M_n with increasing AN content in the monomer feed can be also explained looking at the $k_{p,S}/k_{p,AN}$ ratio. 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.

On the contrary it can be noticed, in the case of the methacrylate/AN copolymers, that the influence of the IL on the conversion decreases with increasing AN content in the monomer feed $x_{AN,monomer}$ (Figure 2(a), (c), (d)). A comparison of the homopolymerizations of the methacrylates and AN in [EMIM]EtSO$_4$ shows that a stronger influence of the IL can be observed for the methacrylate polymerizations.

The products received from the methacrylate/AN copolymerizations were insoluble in THF and the molecular weights could therefore not be determined via SEC analysis. The insolubility of the copolymers is most likely due to crosslinking side reactions in case of GMA/AN and HPMA/AN and extremely high molecular weights of the products in case of all performed methacrylate/AN copolymerizations. Therefore the rheological behavior of these copolymers was studied.

The polymers synthesized in the IL (Figure 2(b)) show a different rheological behavior than the product received from the reaction in methanol. Both the storage

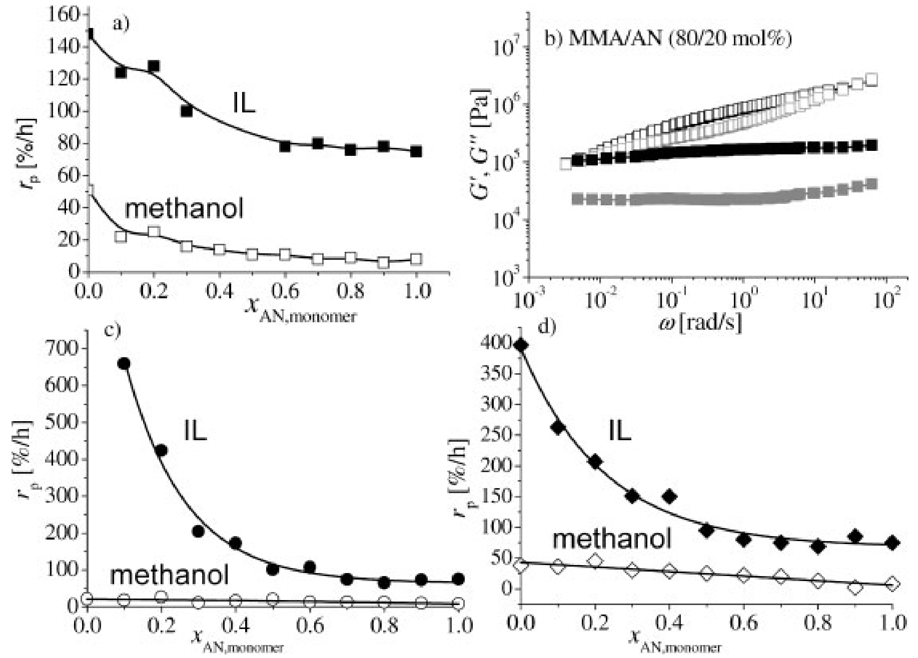


Figure 2.

a), c), d) Polymerization rate (r_p) as a function of the molar ratio of AN in the monomer feed for [EMIM]EtSO$_4$ and methanol, a) MMA/AN, c) HPMA/AN, d) GMA/AN; b) Storage modulus (G') and loss modulus (G'') as a function of angular frequency (ω) of P(MMA/AN) (20 mol% AN in monomer feed) synthesized in [EMIM]EtSO$_4$ (G': ■, G'': ▨) and methanol (G': □, G'': □), T = 60 °C.

Table 1.
r-values of the MMA/S, S/AN and methacrylate/AN copolymerizations.

Systems	[EMIM]EtSO$_4$	Literature
MMA/S	$r_S = 0{,}35 \pm 0{,}06$	$r_S = 0{,}517$[8]
	$r_{MMA} = 0{,}42 \pm 0{,}06$	$r_{MMA} = 0{,}42$[8]
S/AN	$r_{AN} = 0{,}10 \pm 0{,}02$	$r_{AN} = 0{,}04 \pm 0{,}01$[9]
	$r_S = 0{,}38 \pm 0{,}04$	$r_S = 0{,}41 \pm 0{,}05$[9]
MMA/AN	$r_{AN} = 0{,}20 \pm 0{,}12$	$r_{AN} = 0{,}16 \pm 0{,}06$[10]
	$r_{MMA} = 1{,}68 \pm 0{,}34$	$r_{MMA} = 1{,}24 \pm 0{,}11$[10]
GMA/AN	$r_{AN} = 0{,}12 \pm 0{,}12$	$r_{AN} = 0{,}14$[11]
	$r_{GMA} = 0{,}90 \pm 0{,}20$	$r_{GMA} = 1{,}32$[11]
HPMA/AN	$r_{AN} = 0{,}15 \pm 0{,}03$	–
	$r_{HPMA} = 1{,}06 \pm 0{,}32$	

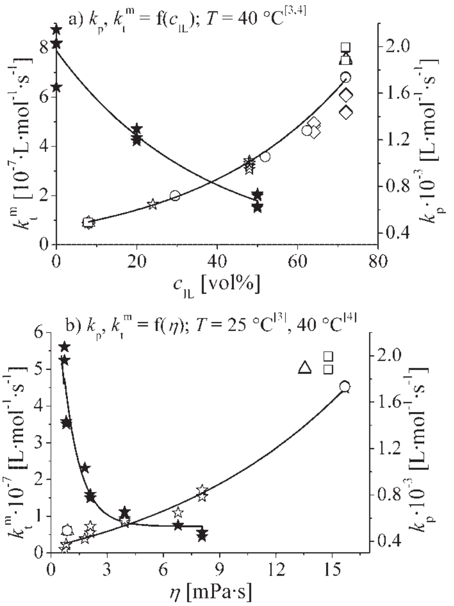


Figure 3.
a) Concentration dependence (c_{IL}) and b) viscosity dependence (η) of the propagation (k_p in [BMIM]PF$_6$ (☆)[3], (○)[4], [BMIM]BF$_4^2$ (△)[4], [EMIM]HexSO$_4$ (◇)[4] and [EMIM]EtSO$_4$ (□)[4]) and the termination rate (k_t^m in [BMIM]PF$_6$ (★)[3]) coefficients of the MMA polymerization carried out at 25 °C and 40 °C.

modulus G' and the loss modulus G'' of the copolymer produced in the IL are independent of the frequency for $\omega < 10^1$ rad · s^{-1}.

The plateau which can be found for the storage modulus G' and loss modulus G'' broadens with increasing molecular weight. Presumably this is due to the increased number of entanglements, reflecting the higher molecular weight of the samples, which can be obtained from the ionic liquid.

The reactivity ratios r_1 and r_2 are calculated using the method of Kelen-Tüdös[12] (Table 1). The reactivity ratios calculated for the copolymerizations in [EMIM]EtSO$_4$ show agreement with the values from literature.[8–11] No significant influence of the IL as solvent can be recognized. The high error in the copolymer composition (for example smallest impurity with the IL) is reason for the large variability of the estimated values.

Influence of the IL Concentration

The PLP technique has recently been extended to allow the determination of average termination rate coefficients, k_t^m from the weight-average degree of polymerization, r_p the rate of polymerization, and the contribution of disproportionation to overall termination.[3] This k_t^m coefficient is a semiquantitative measure of the effect of Ils on the termination process.

In ref.[3] the average termination coefficient k_t^m was calculated. The experimental data[3,4] are represented in Figure 3 for k_p und k_t^m as function of the IL concentration (Figure 3(a)) and the viscosity of the reaction solution (Figure 3(b)). The k_t^m values are measured in [BMIM]PF$_6$[3] and the k_p rate coefficients in [BMIM]PF$_6$[3,4], [BMIM]BF$_4$[4], [EMIM]HexSO$_4$[4] and [EMIM]EtSO$_4$[4] in the temperature range of 25 °C and 40 °C.

The question is if a control of the polymerization rate and molecular weight of the polymers by the viscosity of the used IL in the case of the free radical polymerization with IL as solvent is possible.

The viscosity of ILs can be varied by dilution of the ILs with conventional organic solvents. The free radical polymerization of MMA and S/AN (20/80 mol-%) were carried out using a solvent mixtures of [EMIM]EtSO$_4$/DMF varying the IL concentration from 0 to 100 vol.-% (Figure 4). So the viscosity ($\eta_{solvent}$) of the solvent can be varied in a wide range of ~5 to 20 mPa · s at a temperature of 60 °C.

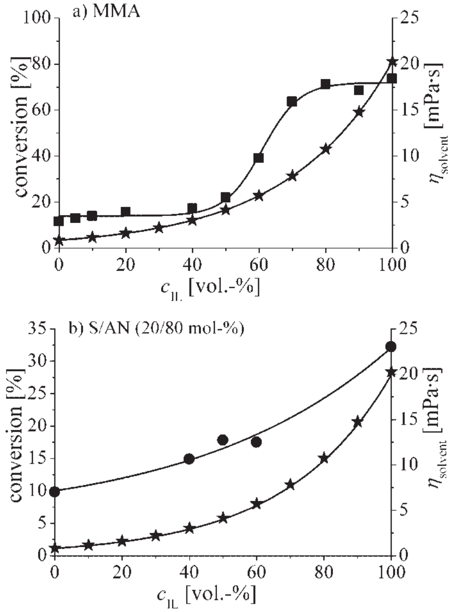


Figure 4.
Conversion of the MMA (■) and S/AN (20/80 mol-%) polymerization (●) after 30 minutes and the viscosity of [EMIM]EtSO$_4$ $\eta_{solvent}$ (★) at 60 °C in dependence of the IL concentration c_{IL}. The solvent viscosity was measured with a cone-plate rheometer.

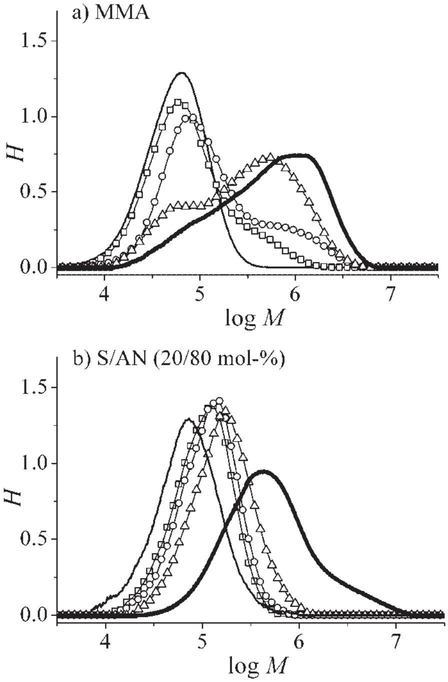


Figure 5.
MWDs of the PMMA and P(S-*co*-AN) products of the S/AN (20/80 mol-%) copolymerization in dependence of the IL concentration c_{IL} in the IL/DMF mixture with $c_{IL} = 0$ vol.-%(—), 40 vol.-%(□), 50 vol.-%(○), 60 vol.-%(△), 100 vol.-%(▬), $T = 60$ °C, $t = 30$ min.

The conversion after 30 min of the MMA and S/AN (20/80 mol-%) polymerization, the molecular weight distributions (MWDs) as well as the viscosity of the solvent mixtures of [EMIM]EtSO$_4$ with DMF ($\eta_{solvent}$) are depicted in Figure 4 and 5 as a function of the IL concentration (c_{IL}) in the solvent mixture.

It is obvious that the conversion after a reaction time of 30 minutes decreases with decreasing IL concentration (Figure 4). It can also be seen that the conversion and the viscosity of the reaction solution show a similar curve progression for S/AN (50/50 mol-%) and for MMA (up to an IL concentration of 70 vol.-%). In case of the MMA polymerization the influence of [EMIM]EtSO$_4$ on the conversion stagnates when the ionic liquid concentration is higher than 70 vol.-%. 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 IL.

Wu et al.[13,14] explain the multimodal MWDs of the products of the radiation induced in situ polymerization of methacrylates with the possibility of monomer present in micro-regions of the IL/organic solvent solution and the immiscibility of resulting polymer.

We have found the following explanation for the MWDs in dependence of the IL concentration. In the pure IL high molecular weights can be found due to high rate coefficients of propagation k_p and very low rate coefficients of termination k_t. The diffusion control of the termination reaction leads to a broad MWD with a high content of long polymer chains. With decreasing IL concentration the viscosity decreases and thus the diffusion control of the termination reaction is lessened. This is not in contrast to [13,14], the monomer and polymer partitioning between IL and polymer phase discussed there gets unimportant with decreasing the IL concentration.

In addition, the molecular weight distributions (MWDs) shift to lower molecular weights when the concentration of [EMIM]-$EtSO_4$ in the reaction mixture is decreased (Figure 5).

To summarize the results it can be said that using solvent mixture containing 70 vol.-% to 100 vol.-% IL leads to a very high polymerization rate and the molecular weights still are increased, too.

Influence of the Reaction Temperature

The viscosity of [EMIM]$EtSO_4$ can be varied with the temperature. With increasing temperature the viscosity decreases. The viscosity of the IL was experimentally determined.

For this a rheometer with a cone-plate geometry was used applying temperatures from 20 °C to 60 °C. With the help of the experimentally determined Equation (1) the viscosity of the ionic liquid at 75 to 100 °C can be calculated (see Figure 6(a)).

$$\eta_{[\mathrm{EMIM}]\mathrm{EtSO}_4} = 2.29 \cdot 10^{-4} \cdot e^{3766/T} \qquad (1)$$

The reaction temperature was varied from 60 to 100 °C. With increasing reaction temperature the initiator was changed from AIBN (60 °C, 70 °C) to BPO (75 °C–100 °C). The reaction time was 30 minutes. The conversions as well as the number average molecular weights M_n and the MWDs of the products were determined.

Figure 6(b) and 7 show the conversions and number average molecular weights M_n of the MMA and S/AN (50/50 mol-%)

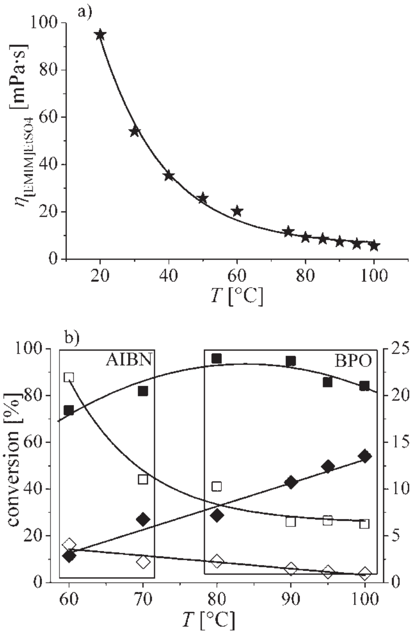


Figure 6.

a) $\eta_{[\mathrm{EMIM}]\mathrm{EtSO}_4}$ (★) as a function of the temperature; b) MMA polymerization in dependence of the temperature in [EMIM]$EtSO_4$ conversion(■) and M_n (□) and in DMF conversion (◆) and M_n (◇), $t = 30$ min.

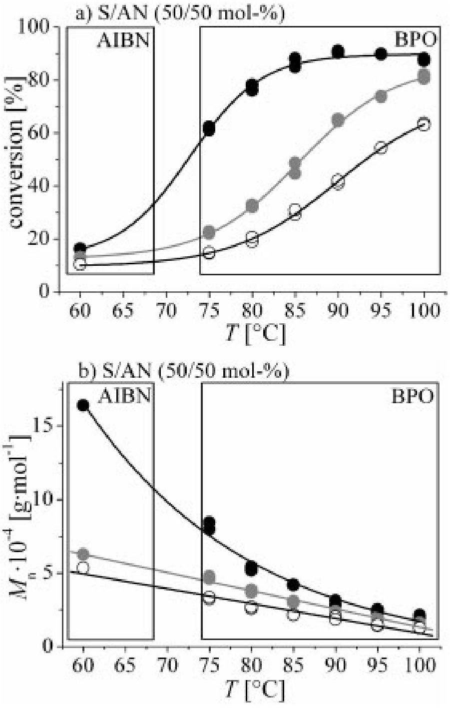


Figure 7.

a) Conversion versus temperature plots of the S/AN (50/50 mol-%) copolymerization with BPO in [EMIM]-$EtSO_4$ (●), in a [EMIM]$EtSO_4$/DMF (50/50 vol.-%) mixture (●) and in DMF (○); b) M_n versus temperature plot of the S/AN copolymers synthesized in [EMIM]$EtSO_4$ (●), in a [EMIM]$EtSO_4$/DMF (50/50 vol.-%) mixture (●) and in DMF (○), $t = 30$ min.

polymerizations in [EMIM]EtSO$_4$ and DMF as a function of temperature after 30 min reaction time. At 80 °C and 30 minutes reaction time a conversion of ~90% for the MMA homopolymerization and a conversion of ~80% for the S/AN (50/50 mol-%) copolymerization is obtained, using the IL as solvent. For the polymerizations of MMA and S/AN (20/80 mol-%) in [EMIM]EtSO$_4$ carried out at temperatures from 60 to 85 °C a more pronounced reduction of the M_n values of PMMA and P(S-*co*-AN) can be observed in comparison to the polymerizations carried out in DMF. This can be explained by the decreased activation energy of propagation (decrease in $E_A(k_p)$ by 4.3 $kJ \cdot mol^{-1}$ for MMA at a monomer concentration of 20 vol.-%[4]).

The pronounced decrease of M_n indicates that for the polymerization in [EMIM]-EtSO$_4$ two opposite effects occur: i) the polymer radical concentration increases with increasing temperature and ii) 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). If the solubility of the polymer with the reaction temperature possibly increases,the described influence on the constants k_p and k_t is then increased in addition. In the temperature range from 85 to 100 °C the slightly decreasing viscosity has less influence on k_t.

The MWDs of the MMA and the S/AN (50/50 mol-%) polymerization in [EMIM]EtSO$_4$ after 30 minutes reaction time as a function of temperature are shown in Figure 8. The influence of the reduction of the IL viscosity by increasing the reaction temperature on the rate coefficients of termination k_t, can be shown. The influence of the IL on the polymerization is directly correlated to the applied reaction temperature. Figure 8(b) 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.

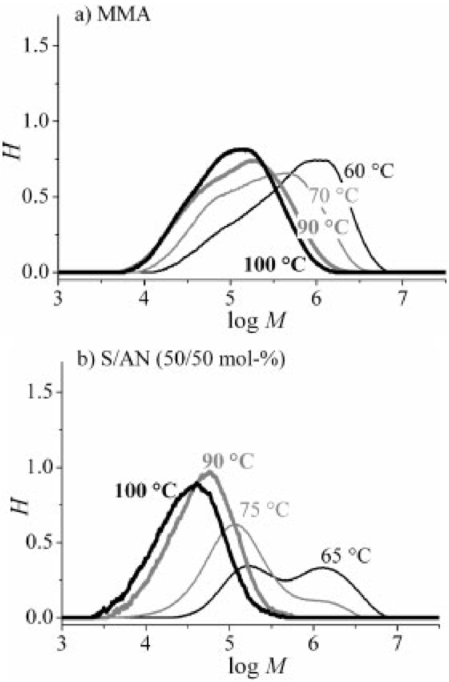


Figure 8.
MWDs as a function of the reaction temperature; a) MMA polymerization in [EMIM]EtSO$_4$ (60, 70, 90 and 100 °C); b) S/AN (50/50 mol-%) copolymerization in [EMIM]EtSO$_4$ (60, 70, 90 and 100 °C), $t = 30$ min.

Comparison: Reduction of the Viscosity by Dilution or by Increasing the Temperature

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 (dilution of the IL or increasing temperature) lead to a shift of the MWDs to lower molecular weights.

The comparison of the MWDs of the MMA polymerization (Figure 9(a)) in the pure IL carried out at 60 and 80 °C with the MWDs from the polymerization in the IL/DMF (50/50 vol.-%) solvent mixture (60 °C) shows that the MWD becomes increasingly bimodal with increasing conversion. The influence of the gel effect diminishes at increasing temperatures and

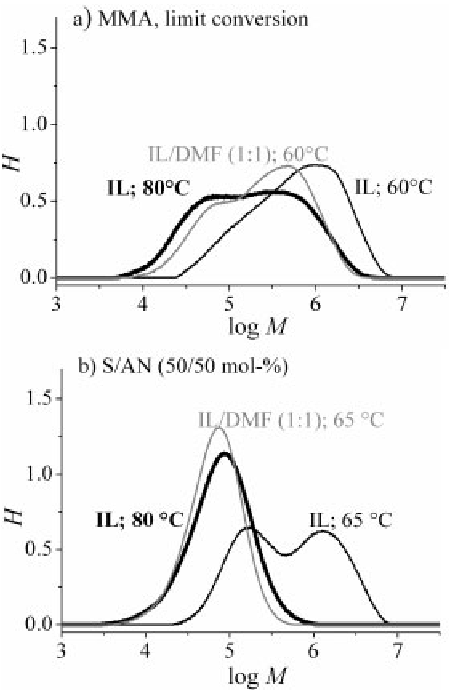


Figure 9.
Comparison of MWDs received for polymers synthesized under reduction of the IL viscosity by dilution with DMF or by temperature enhancement of the a) MMA polymerization in [EMIM]EtSO$_4$ ($T = 60\,^\circ$C: $X = 81\%$, $T = 80\,^\circ$C: $X = 96\%$) or [EMIM]EtSO$_4$/DMF (50/50 vol.-%; $T = 60\,^\circ$C: $X = 78\%$); b) S/AN (50/50 mol-%) copolymerization in [EMIM]EtSO$_4$ ($T = 65\,^\circ$C: $X = 53\%$, $T = 80\,^\circ$C: $X = 76\%$) or [EMIM]EtSO$_4$/DMF (50/50 vol.-%; $T = 65\,^\circ$C: $X = 16\%$).

therefore the content of high molecular chains becomes smaller. In the range of high conversion X (at 60 °C: ~70%) the glass effect starts and leads to the production of short chains and a limit conversion is reached.

The MWDs of the S/AN (50/50 mol-%) copolymerization (Figure 9(b)) in [EMIM]-EtSO$_4$ (65 °C and 85 °C) or in a IL/DMF (50/50 vol.-%) solvent mixture (65 °C) become monomodal with increasing dilution or reaction temperature and still almost a doubling of the M_n values in comparison with the polymerization in DMF can be reached.

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. The dilution of the IL leads to a strong decrease of the polymerization rate whereas the increase of the reaction temperature results in a rise of the conversion. Thus by enhancement of the reaction temperature the polymerization rate of the MMA or S/AN (50/50 mol-%) polymerization in [EMIM]EtSO$_4$ as solvent can be increased fundamentally in comparison to the polymerization in DMF.[6,7] If the polymerization is carried out at a temperature of ~80 °C a conversion of about 80% is already reached after 30 minutes for MMA or S/AN (50/50 mol-%) and still almost a doubling of the molecular weights can be observed.

Conclusion

The ionic liquids 1-ethyl-3-methylimidazolium diethylsulfate ([EMIM]EtSO$_4$), DMF and methanol are used as solvents for the homo- and copolymerization of S and methacrylates (MMA, GMA, HPMA) with AN. The influence of the IL is depending on the monomers and the monomer feed.

Our examinations show the strong influence of the temperature and of the IL concentration on the polymerization rate and the molecular weight distributions. The strong solvent influence of the ILs can better be explained on the basis of the solvent viscosity.

Acknowledgements: The authors acknowledge the Deutsche Forschungsgemeinschaft for financial support within the European Graduate School ''Microstructural Control in Free-Radical Polymerization''.

[1] P. Kubisa, *Prog. Polymer Sci.* **2004**, *29*, 3; *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4675.
[2] S. Harrison, S. R. MacKenzie, D. M. Haddleton, *Chem. Commun.* **2002**, 2850.
[3] S. Harrison, S. R. MacKenzie, D. M. Haddleton, *Macromolecules* **2003**, *36*, 5072.

[4] I. Woecht, G. Schmidt-Naake, S. Beuermann, M. Buback, N. García, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, submitted.

[5] P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926.

[6] G. Schmidt-Naake, I. Woecht, A. Schmalfuß, *Chem. Ing. Techn.* **2007**, submitted.

[7] I. Woecht, G. Schmidt-Naake, *e-Polymers* **2007**, submitted.

[8] A. M. van Herk, R. X. E. Willemse, *J. Am. Chem. Soc.* **2005**, *128*, 4471.

[9] G. Schmidt-Naake, H. Schmidt, B. Litauszki, W. Bieger, *Macromol. Chem.* **1990**, *191*, 2963.

[10] G. Schmidt-Naake, H. Schmidt, B. Litauszki, H. Schmidt, *Wiss. Z. Techn. Univers. Dresden* **1989**, *38*, 131.

[11] J. Brandrup, E. H. Immergut, "*Polymer Handbook*", 3rd Edition, John Wiley & Sons, **1989**.

[12] T. Kelen, F. Tüdös, *J. Macromol. Sci. Chem.* **1975**, *A9*, 1.

[13] Y. Liu, G. Wu, D. Long, G. Zhang, *Polymer* **2005**, *46*, 8403.

[14] G. Wu, Y. Liu, D. Long, *Macromol. Rapid Commun.* **2005**, *26*, 57.