

## Free Radical Polymerization in Ionic Liquids - Explanation of the Solvent Influence

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### Abstract

The analysis of the influence of ionic liquids in polymer synthesis as an alternative for common organic solvents is still an active field of research.<sup>[1]</sup> 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 the influence of the ionic liquid (IL) ([EMIM]EtSO<sub>4</sub>) on polymerization kinetics of methyl methacrylate (MMA) and styrene/acrylonitrile (50/50 mol%) (S/AN) was investigated. 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  $k_t$ <sup>[2-4]</sup>. The rate constant of termination  $k_t$  decreases when the concentration of ionic liquid and also the viscosity is increased, whereas the propagation rate coefficient  $k_p$  increases with increasing IL content. The viscosity of ILs can be varied by either working with mixtures of ILs with conventional organic solvents – here the IL [EMIM]EtSO<sub>4</sub> was mixed with DMF – or by variation of the temperature.

Furthermore we examined the copolymerization behaviour of styrene (S) and methyl (MMA), glycidyl (GMA) and 2-hydroxypropyl (HPMA) methacrylate with acrylonitrile (AN).

Keywords: Free radical polymerization, ionic liquids, copolymerization, viscosity influence, r-value

### 1. Introduction

Ionic liquids are new solvents for polymerization reactions. Very important characteristics of ionic liquids (IL) are a high thermal stability, a wide liquid range in comparison to water and conventional organic solvents and the very low vapour pressure. The application of ILs as solvent 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 synthesis – especially catalysis – has been given in <sup>[5]</sup>.

Recently ionic liquids are also 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 pulsed laser initiated polymerization (PLP) technique in combination with polymer analysis by size-exclusion chromatography (SEC) study 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<sub>6</sub>) in the reaction mixture compared to the polymerization in bulk<sup>[2,3]</sup>.

We measured the propagation rate constant for the MMA and glycidyl methacrylate (GMA) polymerization in [BMIM]PF<sub>6</sub>, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF<sub>4</sub>), 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM]EtSO<sub>4</sub>) and 1-ethyl-3-methylimidazolium hexylsulfate ([EMIM]HexSO<sub>4</sub>)<sup>[4]</sup>. For both MMA and GMA polymerized in ionic liquid solutions an increase of  $k_p$  can be observed in comparison to the bulk polymerization. For [BMIM]PF<sub>6</sub>, [BMIM]BF<sub>4</sub> and [EMIM]EtSO<sub>4</sub> no significant differences between them can be found and therefore it can be considered to have the same influence on the propagation rate coefficient  $k_p$ . In ILs [BMIM]PF<sub>6</sub> to [EMIM]EtSO<sub>4</sub> the propagation rate constant for the MMA polymerization is 4 times higher than in bulk. The results we got from the investigations of the temperature dependence of the polymerizations of MMA and GMA in ionic liquids show in agreement with<sup>[2,3]</sup>, 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  $E_A = 22.4 \text{ kJ}\cdot\text{mol}^{-1}$ <sup>[4]</sup> whereas it is  $18.1 \text{ kJ}\cdot\text{mol}^{-1}$ , when the reaction is carried out in a solution containing 80 vol% of ionic liquid [BMIM]PF<sub>6</sub> or [EMIM]EtSO<sub>4</sub>. The infrared spectra of pure MMA and its solutions in IL [EMIM]EtSO<sub>4</sub> measured at room temperature show a shift in the valence stress of the C=O bond of MMA<sup>[4]</sup>, that indicates interactions between monomer and ionic liquids. These interactions can activate the monomer and therefore it becomes more reactive. In addition Haddleton<sup>[2,3]</sup> and we<sup>[4]</sup> have described a decrease of the propagation rate coefficient with decreasing IL concentration. But this extension cannot explain the significant increase in the brutto 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. Haddleton<sup>[2,3]</sup> showed that  $k_t$  for MMA is influenced by [BMIM]PF<sub>6</sub>, too. It was found that  $k_t$  decreases with increasing IL concentration which can be related to the increasing viscosity of the reaction mixture.

We vary the viscosity of the reaction solution by mixtures of ILs with organic solvents or by variation of the temperature systematically. These studies of the MMA and acrylonitrile (AN) polymerization and the MMA copolymerization with AN and styrene (S) (MMA/comonomer = 90/10 mol%) and the S/AN copolymerization were carried out with the aim of determining the influence of the solvent viscosity on propagation, termination, conversion and MWD.

The question is, can we control in the case of radical polymerization with IL as solvent the polymerization rate and molecular weight of the polymers by the viscosity of the used IL.

Furthermore we examined the homo- and copolymerization behaviour of AN with S, MMA, GMA and 2-hydroxypropyl methacrylate (HPMA).

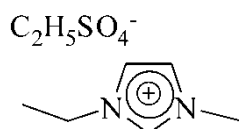
## 2. Results

The rate constant of termination  $k_t$  decreases when the concentration of the ionic liquid and also the viscosity is increased whereas the propagation rate coefficient  $k_p$  increases with increasing IL content.

The viscosity of ILs can be varied by either working with mixtures of ILs with conventional organic solvents or by variation of the temperature.

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 which is expressed by the relatively low conversion whereas the increase of the reaction temperature results in a rise of the conversion. These two opposite effects can be explained by the differing influence of the solvent or the solvent mixture on  $k_p$ .

Here shall be reported about the polymerization of MMA and S/AN (50/50 mol%) in [EMIM]EtSO<sub>4</sub> (see scheme 1) and DMF, focusing on the temperature dependence of the polymerization reaction.



Scheme 1: Structure of the IL 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM]EtSO<sub>4</sub>)

The viscosity of [EMIM]EtSO<sub>4</sub> varies 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 equation experimentally determined  $\ln \eta_{[\text{EMIM}]\text{EtSO}_4} = -8.38 + 3766/T$  the viscosity of the ionic liquid at 75 °C to 100 °C can be calculated (see Fig. 1a).

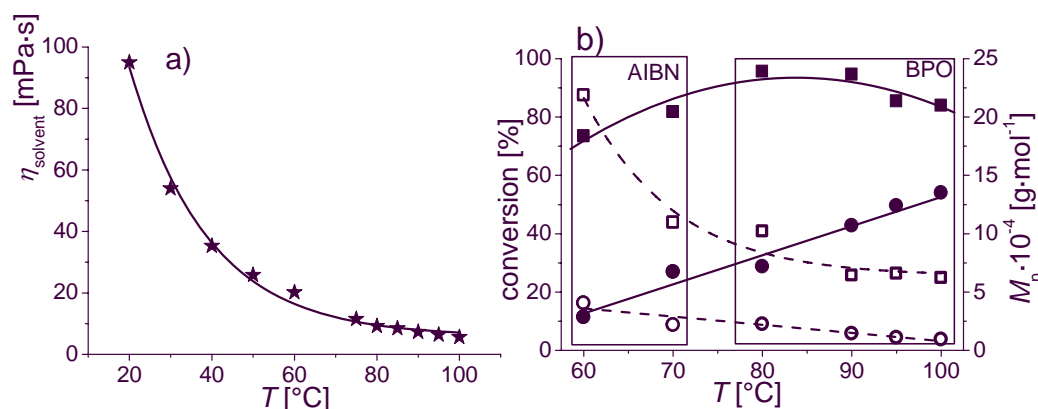


Figure 1: a)  $\eta_{[\text{EMIM}]\text{EtSO}_4}$  as a function of the temperature; b) MMA polymerization in dependence of the temperature in [EMIM]EtSO<sub>4</sub> conversion (■) and  $M_n$  (□) and in DMF conversion (●) and  $M_n$  (○), reaction time = 30 min.

The reaction temperature was varied from 60 °C to 100 °C. The reactions were carried out with 1.5 g monomer feed, either 0.05 g AIBN or 0.05 g BPO as initiator and 6 mL solvent at  $T = 60 - 100$  °C. With increasing reaction temperature the initiator was changed from AIBN (60 °C, 70 °C) to BPO (80 °C – 100 °C). The reaction time was  $t = 30$  min. The conversions  $X$  as well as the number average molecular weights  $M_n$  and the MWDs of the products were determined.

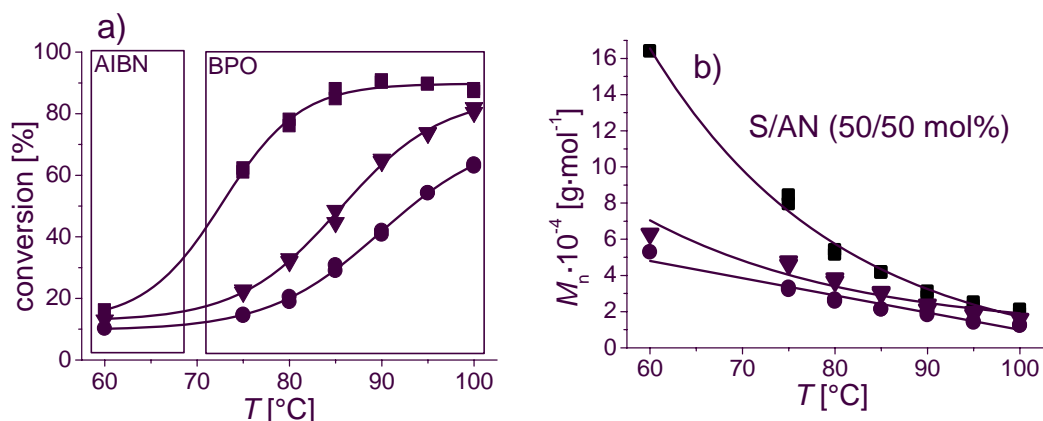


Figure 2: a) conversion versus temperature plots of the S/AN (50/50 mol%) copolymerization with BPO in [EMIM]EtSO<sub>4</sub> (■), in a mixture of [EMIM]EtSO<sub>4</sub>/DMF (50/50 vol%) (▼) and in DMF (●); b)  $M_n$  versus temperature plot of the S/AN copolymers synthesized in [EMIM]EtSO<sub>4</sub> (■), in a mixture of [EMIM]EtSO<sub>4</sub> and DMF (▼) and in DMF (●), reaction time = 30 min.

Figures 1b and 2 show the conversions and number average molecular weights  $M_n$  of the MMA and S/AN (50/50 mol%) polymerizations in [EMIM]EtSO<sub>4</sub> and DMF as a function of temperature after 30 min reaction time. At 80 °C and 30 min reaction time in the case of MMA a conversion of ~ 80 % and at the S/AN copolymerization ~90 % are obtained, using [EMIM]EtSO<sub>4</sub>.

In the temperature range of 60 to 85 °C the  $M_n$ -values of PMMA and S/AN are more reduced than in the polymerization in DMF. This can be explained by decreasing of the activation energy of  $k_p$  (a decrease in  $E_A(k_p)$  by 4.3 kJ·mol<sup>-1</sup> for MMA at a monomer concentration of 20 vol%<sup>[4]</sup>). The pronounced decrease of  $M_n$  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). In the temperature range from 85 to 100 °C the low decreasing viscosity has less influence on  $k_t$ .

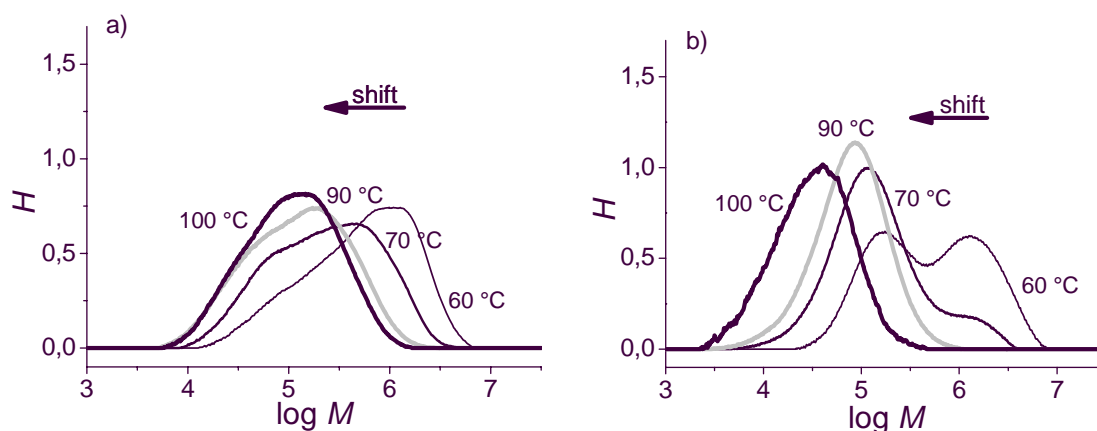


Figure 3: Molecular weight distribution after 30 min as a function of the reaction temperature  
 a) MMA polymerization in [EMIM]EtSO<sub>4</sub> (60, 70, 90 and 100 °C);  
 b) S/AN (50/50 mol%) copolymerization in [EMIM]EtSO<sub>4</sub> (60, 70, 90 and 100 °C).

The MWDs of the MMA and the S/AN (50/50 mol%) polymerization in [EMIM]EtSO<sub>4</sub> after 30 minutes reaction time as a function of temperature are shown in Figure 3. The influence of the reduction of the IL viscosity by increasing the reaction temperature on the rate coefficients of termination  $k_t$  could be shown. The solvent influence at the polymerization in IL is directly correlated to the applied reaction temperature. Figure 3b) 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.

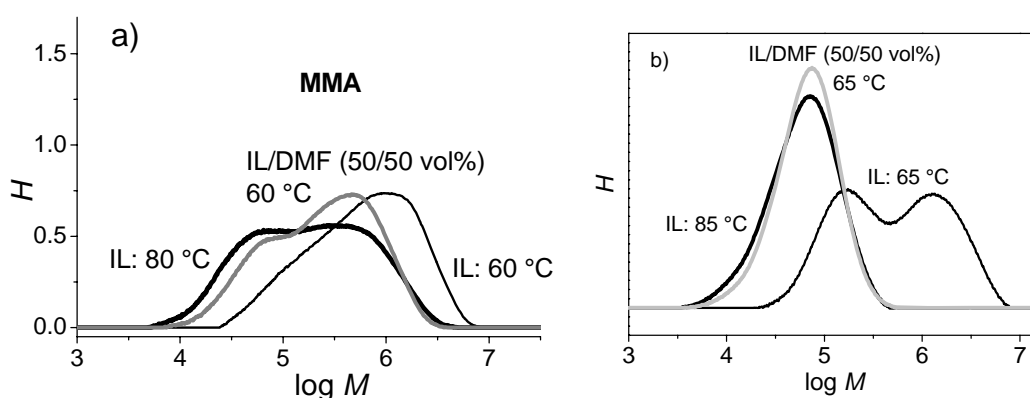


Figure 4: Comparison of the molecular weight distribution at reduction of the IL-viscosity by IL/DMF or temperature rise received from the  
 a) MMA and b) S/AN (50/50 mol%) polymerization in [EMIM]EtSO<sub>4</sub> or [EMIM]EtSO<sub>4</sub>/DMF (50/50 vol%)

In Figure 4 the influence of both the reaction temperature and the IL concentration on the MWDs of the MMA and S/AN (50/50 mol%) polymers is 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 (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 (Fig. 4a) in the IL carried out at 60 °C and 80 °C with the MWDs from the polymerization in the IL/DMF (50/50 vol%) solvent mix (60 °C) show with increasing conversion an increasingly bimodal distribution. The influence of the gel effect diminishes at increasing temperatures, with that the content of high molecular chains is smaller. In the range of high conversion (at 80 °C: ~70 %) the glass effect starts and leads to the production of short chains.

The MWDs of the S/AN (50/50 mol%) copolymerization (Fig. 4b) with [EMIM]EtSO<sub>4</sub> (80 °C) or with IL/DMF (50/50 vol%) solvent mix (60 °C) become monomodal and the  $M_n$  values are doubled at most in comparison with the polymerization in DMF.

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.

That is to say by enhancement of the reaction temperature the polymerization rate of MMA or S/AN (50/50 mol%) polymerization with [EMIM]EtSO<sub>4</sub> as solvent can be increased fundamentally in comparison with the polymerization in DMF<sup>[6,7]</sup>. If the polymerization is carried out at a temperature of ~80 °C a conversion of about 80 % is already reached after 30 min for MMA or S/AN (50/50 mol%) and still almost a doubling of the molecular weights can be observed.

Furthermore, we have investigated the homo- and copolymerization behaviour of styrene (S) and methacrylates (MMA, glycidyl methacrylate (GMA), hydroxyl propyl methacrylate (HPMA)) with AN<sup>[7,8]</sup>. The ionic liquid ECOENG<sup>TM</sup>212 and MeOH are used as solvents.

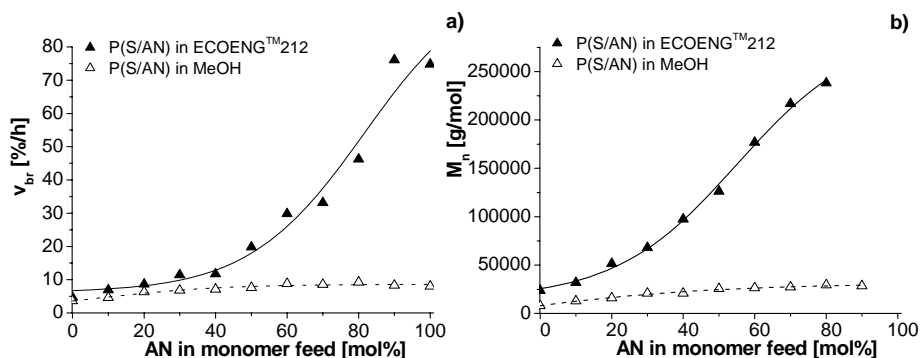


Figure 5: a) Polymerization rate ( $v_{br}$ ) as a function of the molar ratio of AN in the monomer feed b) Molecular weights ( $M_n$ ) versus AN content in monomer feed

The homopolymerization of AN and its copolymerization with HPMA can be carried out in solution independent of the conversion. The other polymerizations proceed under precipitation at conversions higher than  $\sim 10\%$ . It also can be noticed, that the influence of the IL on the conversion increases with increasing styrene concentration in the monomer feed (Fig. 6a).

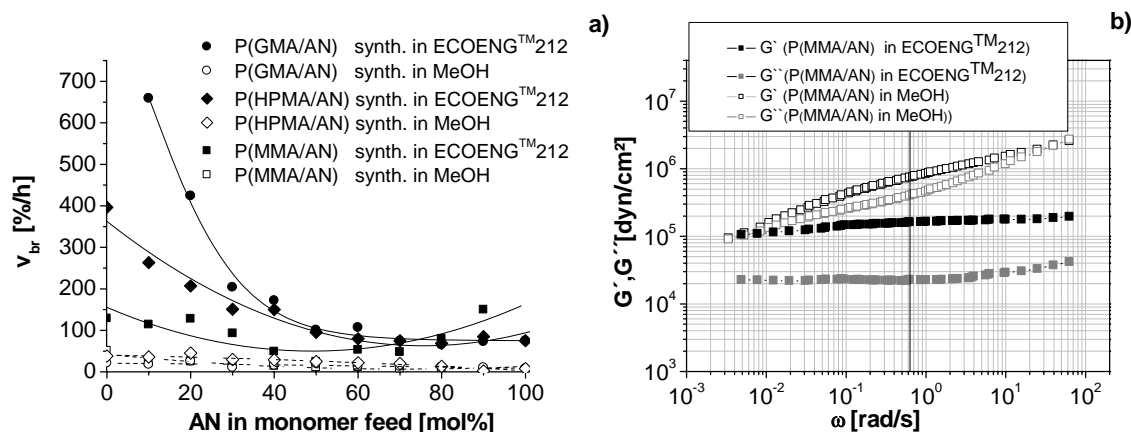


Figure 6: a) Polymerization rate ( $v_{br}$ ) as a function of the molar ratio of AN in the monomer feed  
b) Storage modulus ( $G'$ ); loss modulus ( $G''$ ) as a function of angular frequency ( $\omega$ ) of P(MMA/AN) (80 mol% AN in monomer feed)

The polymers synthesized in the IL (Fig. 6b) shows a different rheological behaviour than the product received from the reaction in methanol. Both the storage modulus  $G'$  and the loss modulus  $G''$  of the copolymer produced in ECOENG™212 are independent of the frequency for  $\omega < 10^1 \text{ rad}\cdot\text{s}^{-1}$ .

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, which can be obtained from the ionic liquid.

### 3. Conclusion

The ionic liquids 1-ethyl-3-methylimidazolium diethylsulfate (ECOENG™212), DMF and methanol (MeOH) are used as solvents of the homo- and copolymerization of styrene (S) and methacrylates (MMA, GMA, HPMA) with AN. Our examinations show the strong influence of the temperature and of the IL content of the solvent on the polymerization reaction rate and the molecular weight. The extreme solvent influence of the ILs can be explained better on this basis.

## References

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