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Selection of Ionic Liquids for Free Radical Polymerization Processes

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Summary: Ionic liquids are efficient solvents for free radical homo- and copolymerization. Important parameters for selection of ionic liquids are their liquidus range, their viscosity, and their polarity. Viscosity of ionic liquids strongly influences the degree of polymerization of homopolymers. Micropolarity of ionic liquids can be used to explain differences in the composition of copolymers made on the basis of a relatively nonpolar methacrylate and a highly polar zwitterionic methacrylate.

Keywords: copolymerization; degree of polymerization; micropolarity; radical polymerization; viscosity

Introduction

Free radical polymerization has become an important method for manufacturing of polymers until today attributing to their tolerance to many functional groups attached at the monomers and impurities. The exothermic behavior of free radical polymerizations and the Trommsdorff-Norrish effect require a solvent to carry out these polymerizations as safe processes.[1–4] This solvent can be an ionic liquid exhibiting negligible vapor pressure. Dilution of monomer initiator systems by solvents influences the reaction rate. This may have an impetus on the structure of the polymers obtained.[5–7] Traditional solvents such as water or organic solvents are limited in their applicability because of their boiling point and their relative high vapor pressure. This limitation can be overcome by ionic liquids, which exhibit a negligible vapor pressure and a high thermal stability.[8–10] Furthermore, the structure of ionic liquids can be varied in a broad region by selection of different cations and anions, and therefore, the properties of ionic liquids can be tailor made for the specific demands of special applications. In general, ionic liquids differ from molecular solvents by their ionic structure and their higher viscosity that may influence polymerization processes.[8,11,12] Examples for some ionic liquids are given in Figure 1.

Viscosity and polarity are key factors describing the influence of solvents on radicals formed during free radical polymerization.[11] Furthermore, the solvation effect of the solvent on monomers, initiator, radicals formed during polymerization, and polymers obtained may influence the polymerization process and the structure of these polymers. Various approaches exist to describe the influence of molecular solvents on polymerization processes to make selection of solvents more easy.[1,13–15] In contrast to this, a lot of work is necessary to understand the influence of ionic liquids on free radical polymerization processes because of the high complexity of these polymerizing systems. In this work, polymers were investigated that were synthesized on the basis *n*-butylmethacrylate (**1**), benzylmethacrylate (**2**), and 3-(*N*-[2-methacryloyloxyethyl]-*N,N*-dimethylammonio)propane sulfonate (**3**) in ionic liquids.

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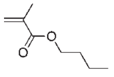

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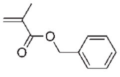

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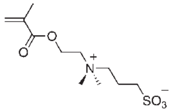

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A systematic variation of the ionic liquid structure, and therefore, of the ionic liquid properties and investigation of their influences on free radical polymerization processes are an approach to understand the effects of ionic liquids on radical polymerization processes to make an efficient selection of ionic liquids for these applications. In this work, the structure of imidazolium and ammonium based ionic liquids is systematically varied. Thermal stability, melting behavior, viscosity, and polarity of ionic liquids are discussed regarding the suitability of ionic liquids in free radical polymerization processes.

Liquidus Range of Ionic Liquids

An advantage of ionic liquids as processing solvent is their extremely low vapor pressure. In contrast to this, the vapour pressure of molecular solvents is significantly higher and strongly temperature dependent. The liquidus range of molecular solvents is determined by the solid liquid phase transition and the liquid vapor phase transition. The lower limit of the liquidus range of ionic liquids is the solid liquid phase transition as in the case of molecular solvents. The solid liquid phase transition can be a melting point (T_m) or a glass transition (T_g) in the case of ionic liquids. Because some ionic liquids can form plastic crystals or liquid crystals the phase transition temperature into the isotropic melt (T_i) is used for determination of the lower limit of their liquidus range. A liquid vapor phase transition does not exist in the case of most ionic liquids. Therefore, the temperature where no decomposition of the ionic liquids was observed is taken as upper limit for the liquidus range of ionic liquids. This is analyzed by thermogravimetric analysis under nitrogen. Examples for the temperature dependence of the mass loss of ionic liquids are shown in Figure 2, demonstrating the stability of these ionic liquids under nitrogen up to 250 °C and higher. The high thermal stability of ionic liquids results in a significantly broader liquidus range of ionic liquids in comparison with traditional solvents. Impurities such as small amounts of

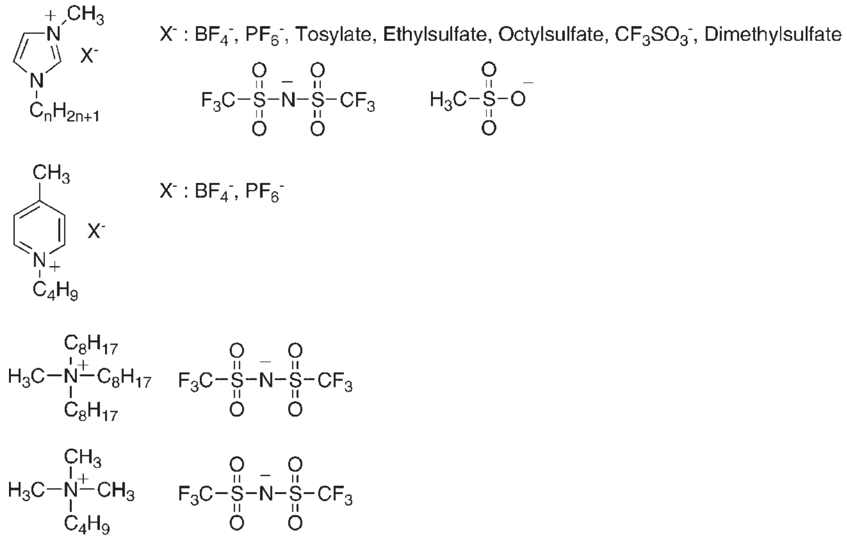


Figure 1.
Structure of some selected ionic liquids.

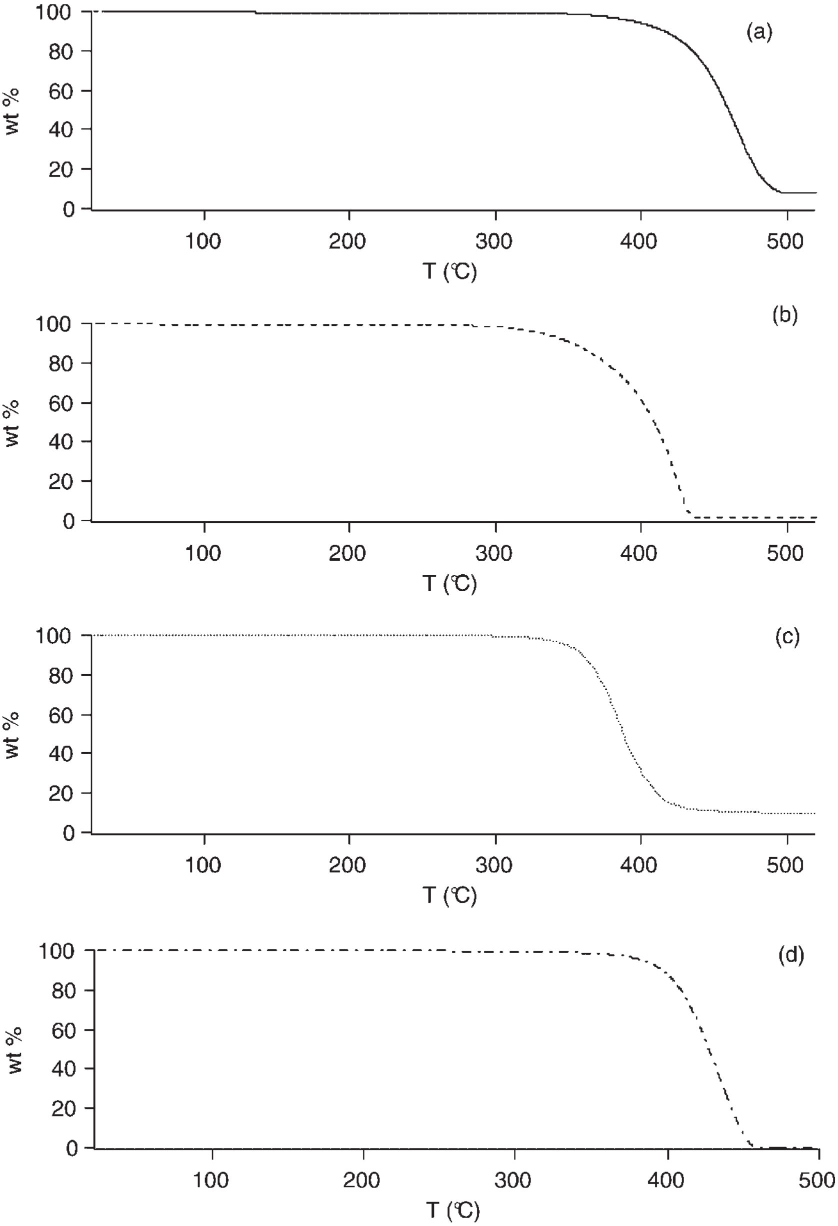


Figure 2.
Temperature dependent mass losses of 1-butyl-3-methylimidazolium tetrafluoroborate (a), 1-butyl-4-methylpyridinium hexafluorophosphate (b), 1-ethyl-3-methylimidazolium tosylate (c), and *N*,*N*,*N*-trioctyl-*N*-methylammonium bistrifluoromethylsulfonylimide (d) determined by thermogravimetric analysis under nitrogen (25 ml/min) using a heating rate of 20 K/min.

water or solvents remaining from manufacturing of ionic liquids may result in a significant decrease of the liquidus range defined in this way. These impurities mainly attribute to the higher vapor pressure of residual solvent in the ionic liquid. Thus, a consequent view of the upper limit of the liquidus range is necessary to get a draw-

Table 1.
Liquidus range of imidazolium and ammonium based ionic liquids.

Ionic liquid	$PT^{a)}$	$T_{<0.5\%}$	$T_{<1\%}$	$T_{<2\%}$	Liquidus range
	°C	°C$^{b)}$	°C$^{b)}$	°C$^{b)}$	K
1-butyl-3-methylimidazolium BF_4	−87 (T_g)	170	333	362	257
1-ethyl-3-methylimidazolium tosylate	53 (T_m)	303	319	332	250
1-decyl-2,3-dimethylimidazolium BF_4	47 (T_i)	238	265	285	191
1-decyl-2,3-dimethylimidazolium PF_6	52 (T_i)	330	358	375	278
1-butyl-4-methylpyridinium PF_6	20 (T_m)	77	273	305	57
1,3-dimethylimidazolium dimethylphosphate	−67 (T_g)	145	175	237	212
N-butyl-*N,N,N*-trimethylammonium bis(trifluoromethylsulfonyl)imide	18 (T_i)	349	366	383	331
N,N,N-trioctyl-*N*-methylammonium bis(trifluoromethylsulfonyl)imide	−81 (T_g)	267	327	359	348
1-Octyl-3-methylimidazolium BF_4	−86 (T_g)	137	145	159	223
1-butyl-3-methylimidazolium octylsulfate	−33 (T_m)	103	249	305	136

a) PT: Phase transition temperature into the isotropic melt (T_m melting point, T_g glass transition temperature, T_i phase transition into the isotropic melt in the case of liquid crystals or plastic crystals);

b) Temperature where <0.5 wt-%, <1 wt-%, and <2 wt-% mass loss was observed in the thermogravimetric measurements under nitrogen using a heating rate of 20 K/min.

back of the advantages of ionic liquids for the use as solvent for safe polymerization processes. Therefore, traces of evaporable impurities remaining in ionic liquids limit the applications of ionic liquids. Table 1 gives an overview about the content of evaporable impurities in ionic liquids and shows their thermal stability. The temperatures are summarized where <0.5 wt-%, <1 wt-%, and <2 wt-% mass losses were measured during heating under nitrogen (Table 1). The temperature where weight loss is lower than 0.5 wt-% is used as upper limit of the liquidus range of ionic liquids (Table 1). As can be seen from this Table some ionic liquids are temperature stable up to about 300 °C. Therefore, a liquidus range of more than 300 K can be discussed for these ionic liquids. This shows one main advantage of ionic liquids as solvents for polymerization. However, the liquidus range dramatically decreases if evaporable impurities are present in the ionic liquids. Therefore, the temperatures where a slight mass loss was observed (<1 wt-% and <2 wt-%) are additionally included in Table 1. A high difference in the values of <0.5 wt-% and <1 wt-% or <2 wt-% may indicate small amounts of evaporable impurities in the ionic liquids.

Furthermore, suitability of ionic liquids for polymerization processes is limited not only by their liquidus range, also viscosity of ionic liquids is important for the fluidity of the polymerizing mixture especially for the transfer of polymerization heat.

Viscosity of Ionic Liquids and its Influence on Polymerization

Radical polymerization processes are strongly influenced by solvent viscosity and polarity.[11] The viscosity of ionic liquids strongly depends on their structure and on temperature.[8,11,12,16,17] In some cases viscosity of ionic liquids is also shear rate dependent.[17] Because thermal induced polymerization processes occur under stirring and heating, shear rate dependence of viscosity should not significantly influence the polymerization process. Nevertheless, the viscosity of ionic liquids is compared at 10 s^{-1} sheering rates to eliminate the shear rate dependence of the viscosity. Figure 3 gives an overview about the structural dependence of the viscosity of selected imidazolium salts.

As can be seen in Figure 3, the viscosity of ionic liquids increases with an increase in the length of the alkyl chain bound at the nitrogen atom of the imidazolium ring. Furthermore, the viscosity of imidazolium hexafluorophosphates is higher than of comparable imidazolium tetrafluoroborates. Introduction of a methyl substitutent

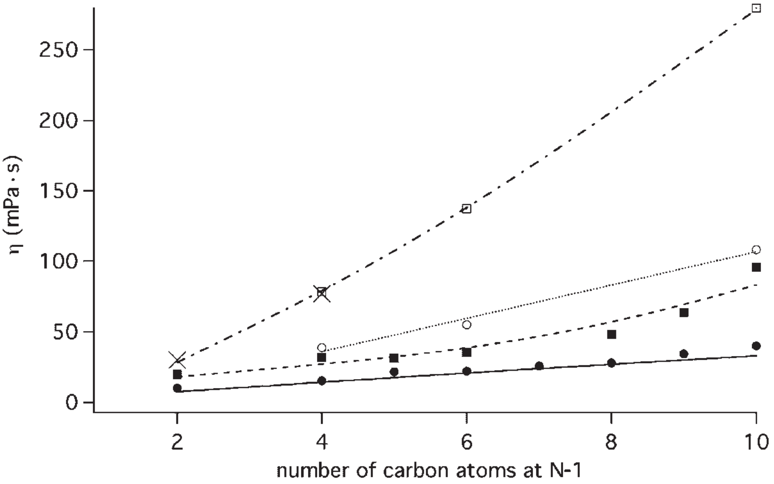


Figure 3.
Viscosity of 1-alkyl-3-methylimidazolium tetrafluoroborates (●), 1-alkyl-2,3-dimethylimidazolium tetrafluoroborates (○), 1-alkyl-3-methylimidazolium hexafluorophosphates (■), 1-alkyl-2,3- dimethylimidazolium hexafluorophosphates (□), and 1-alkyl-3-methylimidazolium tosylates (╳) as function of the alkyl chain length bound at one nitrogen atom of the imidazolium ring. Measurement was carried out at 70 °C and analyzed at a shearing rate of 10 s^{-1}.

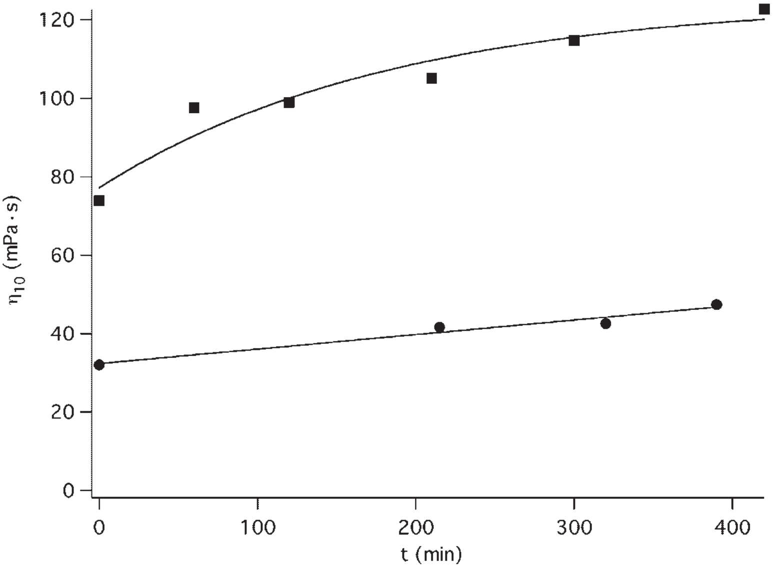


Figure 4.
Viscosity of polymerizing mixtures consisting of **1** and azobisisobutyronitrile as initiator dissolved in 1-butyl-3-methylimidazolium tetrafluoroborate (●) or hexafluorophosphate (■) as function of reaction time after cooling to room temperature (polymerization was carried out at 70 °C).

at C-2 of the imidazolium ring results in a significant increase in the viscosity of 1-alkyl-2,3-dimethylimidazolium salts in comparison with analogous imidazolium salts unsubstituted at C-2. Furthermore, the viscosity of 1-butyl-3-methylimidazolium tosylate is similar to that of 1-butyl-2, 3-dimethylimidazolium hexafluorophosphate. The viscosity of 1-ethyl-3-methylimidazolium tosylate fits also in the same line. Furthermore, the 1-alkyl-3-methylimidazolium tosylates are higher viscous than 1-alkyl-3- methylimidazolium tetrafluoroborates or hexafluorophosphates. Moreover, the 1-butyl-4- methylpyridinium salts are higher viscous than 1-butyl-3-methylimidazolium salts.[17] This demonstrates that viscosity of ionic liquids is influenced by the structure of both the cation and the anion.

Moreover, the viscosity of a mixture consisting of an imidazolium salt and **1** is lower than the viscosity of the pure ionic liquid attributing to the low viscosity of the monomer. The viscosity increases in the course of the polymerization as depicted in Figure 4. Precipitation of the polymer results in a lower viscosity again because nonreacted monomer is still present in the reaction mixture indicating that the polymerization reaction has not been finished yet. The increase in the viscosity of the ionic liquid - monomer - polymer - mixture is attributed to the solubility of small amounts of polymer in the ionic liquid - monomer - mixture, although the polymer is insoluble in the ionic liquids investigated in this work. Conversion of monomer dissolved in the ionic liquid forming polymer in the course of the polymerization process, and therefore, decrease of monomer concentration in the ionic liquid results in precipitation of the polymer formed during polymerization from the reaction mixture. Viscosity increase and precipitation of the polymer show the complexity of polymerizations in ionic liquids.

Degree of polymerization (X_n) of **poly-1** and **poly-2** obtained after 24 h polymerization time is significantly higher if ionic liquids are used as solvents for polymerization relative to polymers made in toluene (Figure 5). Interestingly, the degrees of polymerization are similar for **poly-1** and **poly-2** if the same solvents were used for polymerization. However, polydispersity is

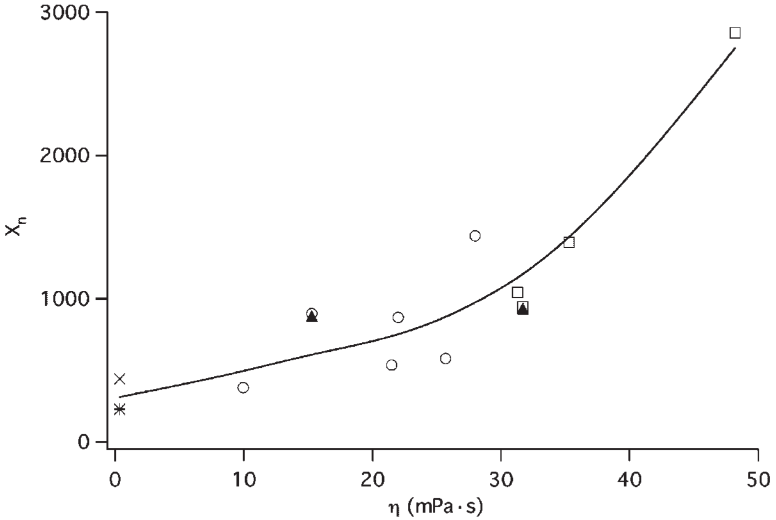


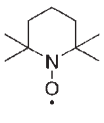
Figure 5.
Degree of Polymerization of **poly-1** synthesized in toluene (✳), 1-alkyl-3-methylimidazolium tetrafluoroborates (●) or 1-alkyl-3-methylimidazolium hexafluorophosphates (■), and of **poly-2** made in toluene (╳), 1-butyl-3-methylimidazolium tetrafluoroborate or hexafluorophosphate (▲).

higher for polymers made in ionic liquids compared to the use of toluene as solvent for polymerization.[17]

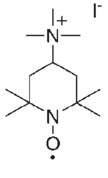
Moreover, the degree of polymerization for **poly-2** is about 690 if *N,N,N*-trioctyl-*N*-methylammonium bis(trifluoromethylsulfonyl)imide was used as solvent for polymerization and about 720 using *N*-butyl- *N,N,N*-trimethylammonium bis(trifluoromethylsulfonyl)imide. These values are slightly lower in comparison with the use of 1-butyl-3-methylimidazolium tetrafluoroborate or hexafluorophosphate as solvent for polymerization.

Polarity of Ionic Liquids and its Function for Copolymerization

Structural variation of ionic liquids results not only in changes in their viscosity. Polarity changes were also observed in the ionic liquids. Several solvatochromic probes [18–20] and spin probes[21–28] give an information about polarity of ionic liquids. Comparing the polarity of ionic liquids with that of molecular solvents results in different behavior depending on the nature of the probes used for investigation and in some examples also on the structure of the ionic liquid.[21–28] Nonpolar spin probes (TEMPO) show a polarity of ionic liquids that is similar to methylenechloride, and spin probes bearing an amino group exhibit a polarity similar to ethanol or ethylen glycol.[22,23,26,27] Spin probes forming hydrogen bondings express a polarity similar to dimethylsulphoxide.[26,27] Furthermore, spin probes bearing an ionic substituent (CAT-1) describe a micropolarity similar to dimethylsulphoxide if the alkyl chain bound at one nitrogren atom of imidazolium tetrafluoroborates is not to long.



TEMPO



CAT-1

An alkyl chain containing 8 or more carbon atoms at the imidazolium ring

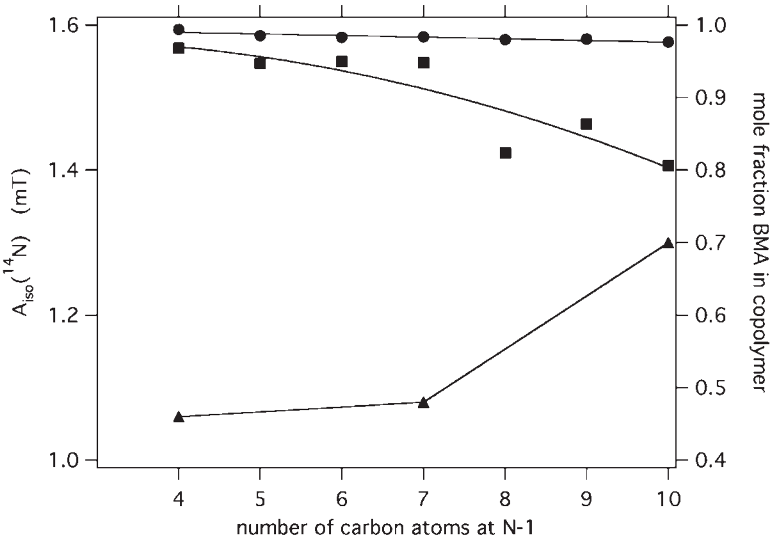


Figure 6.
Mole fraction of *n*-butylmethacrylate segments (▲) in the copolymer of **1** and **3** analyzed by elemental analysis and nitrogen isotropic hyperfine coupling constants ($A_{iso}(^{14}N)$) of the nonpolar spin probe TEMPO (●) and the polar spin probe CAT-1 (■) analyzed from ESR spectra[26] as function of the alkyl chain length bound at one nitrogen atom of 1-alkyl-3-methylimidazolium tetrafluoroborates used as solvents for copolymerization.

results in a significant decrease in micropolarity of the imidazolium tetrafluoroborates.[26] Electrostatic interactions and hydrogen bonding may cause differences in micropolarity of the ionic liquids investigated. The structural effect of ionic liquids on their polarity is important for the use of ionic liquids as solvents for copolymerization of different polar monomers. Copolymerizations of the relatively nonpolar **1** and the highly polar **3** in 1-alkyl-3-methylimidazolium tetrafluoroborates result in copolymers that show a composition, which depends on the polarity of the ionic liquids. A decrease in polarity of imidazolium tetrafluoroborates results in an increase in the content on the lower polar *n*-butylmethacrylate segments in the copolymer (Figure 6).

Although ionic liquids dissolve both **1** and **3**, the higher polar monomer seems to be preferred in copolymerization over the less polar monomer.[16,29] Detection of the polymer radical based on the polar monomer during thermal induced free radical polymerization demonstrates the strong interactions between this polymer radical and the ionic liquid.[27] An increase in the length of the alkyl chain results in a reduction of micropolarity of the ionic liquids as detected by the ionic spin probe (CAT-1) although the nonpolar spin probe (TEMPO) does not detect this effect (Figure 6).[26] From this one can draw the conclusion that a lower polarity of the ionic liquid may cause a reduction of preference of polymerization of the higher polar monomer relative to the less polar monomer. The influence of the imidazolium salts shows the possibility to tailor ionic liquids for manufacture of copolymers by free radical polymerization.

Conclusions

The broad liquidus range of ionic liquids is one main advantage for their use as processing solvents. The higher viscosity of ionic liquids in comparison with traditional solvents and the ionic structure of these solvents may cause a higher degree of polymerization of the polymers synthesized in ionic liquids. This result may be important for other monomers too where polymerization usually results only in oligomeric products. Furthermore, copolymers based on different polar monomers were obtained by free radical polymerization in ionic liquids. Polarity effects of ionic liquids influence the composition of the copolymers.

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