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Homopolymerization of a highly polar zwitterionic methacrylate in ionic liquids and its copolymerization with a non-polar methacrylate

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Abstract: Free radical homo- and copolymerization of the highly polar 3-(*N*-[2-methacryloyloxyethyl]-*N,N*-dimethylammonio)propane sulfonate with the nonpolar n-butylmethacrylate was investigated in the ionic liquids 1-butyl-3-methyl imidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluoro phosphate, and compared to analogous polymerizations in standard solvents. Higher molar masses are obtained for the zwitterionic homopolymer when the polymerization is carried out in an ionic liquid compared to the classical reaction in water. Although homopolymerization of the sulfobetain monomer as well as of *n*-butylmethacrylate results in phase separation during the polymerization process, copolymerization of a stoichiometric ratio of the two monomers in the ionic liquids produced transparent gels indicating that no macrophase separation occurs. The use of ionic liquids as reaction medium improved the copolymerization behavior of the two methacrylates significantly. Whereas only minor amounts of n-butyl methacrylate were incorporated in the copolymer when synthesized in acetonitrile, the content of the non-polar monomer units in the zwitterionic copolymer approached increasingly its content in the polymerization mixture when ionic liquids were employed as solvents.

Introduction

Copolymerization enables the preparation of polymers with widely varying properties from a limited number of monomers. Statistical copolymers are the most widely encountered type of copolymers. The preferred method to synthesize statistical copolymers is free radical copolymerization. As many monomers do not show too different relative reactivities for this method, fair amounts of all employed monomers can be incorporated into the copolymer. In fact, statistical copolymerizations occur smoothly if the monomers are well soluble in the solvent used for the reaction as well as the intermediate radicals formed have comparable reactivities. The composition of the copolymers obtained depends typically on the relative reactivity of the monomers and their relative amounts used. Interactions between the solvent and the monomers may also influence the composition of the copolymers, but generally, such effects are small [1, 2]. However, especially in the case where monomers have strongly differing polarities, it is difficult to find a solvent in which both monomers dissolve well. Moreover, statistical copolymerization often becomes difficult even if a common solvent can be found for such systems, as one of the monomers may become extremely favoured over the other. Alternatively, the copolymers obtained may show a marked blocky structure, indicating the inhomogeneity of the macroscopically homogeneous reaction mixtures at the microscopic level, which interferes with a smooth incorporation of both monomers. The propagation step may involve preferential solvation of the growing macroradical site by the corresponding monomer, thus leading to apparent reactivity ratios [3]. For instance, the statistical copolymerization of zwitterionic and non-polar monomers is far from trivial, and the macroscopically observed relative reactivities of identical polymerizable groups become increasingly different with increasing differences in polarity between the monomers [4 -5].

Ionic liquids are new solvents for polymerization reactions [6 – 9]. These solvents excel not only by low vapour pressures and good thermal stabilities [10]. They are also good solvents for many low molar mass compounds of differing polarity. This includes many different monomers. So far, the few polymerization studies in ionic liquids have focused on homopolymerizations. Reports on copolymerization in ionic liquids are surprisingly rare [10-13], although ionic liquids seem to be advantageous solvents for copolymerization of monomers with markedly different polarities. Therefore, we have looked at the copolymerization of such monomer systems in ionic liquids. In this study, we focused on a model system consisting of two differently substituted methacrylates, namely on the highly polar zwitterionic 3-(N-2-[methacryl oyloxyethyl]-N,N-dimethyl-3-ammonio)propane sulfonate (*1*) and the rather non-polar *n*-butylmethacrylate (*2*) (Fig. 1). For comparison, analogous copolymerizations were conducted in a traditional solvent mixture, in which the monomers are apparently well soluble.

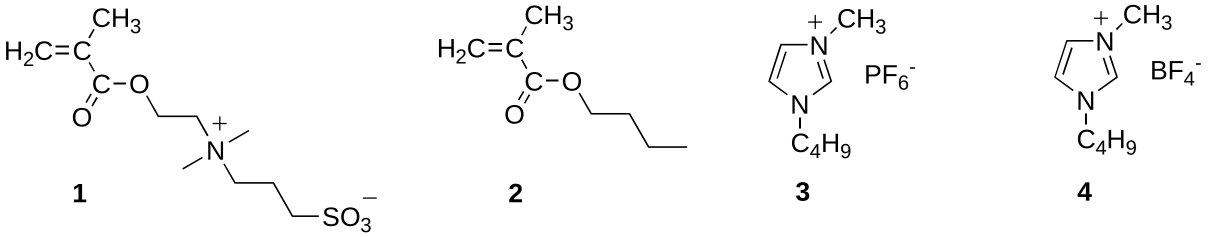

Fig. 1. Structure of 3-(N-[2-methacryloyloxyethyl]-*N,N*-dimethylammonio)propane sulf onate (**1**), *n*-butylmethacrylate (**2**), 1-butyl-3-methylimidazolium hexafluorophosphate (**3**), and 1-butyl-3-methylimidazolium tetrafluoroborat (**4**) used for polymerization experiments.

Results and Discussion

The ionic liquids depicted in Fig. 1 dissolve the highly polar sulfobetain monomer *1* as well as the non-polar butyl methacrylate *2*. The good solvation for both monomers, which considerably differ in their polarity, can be attributed to the particular structure of the imidazolium salts. The ionic character of the ionic liquids provides efficient interaction with the highly polar sulfobetaine group of *1*, while the aromatic core with the alkyl substituents assure favorable interactions with the non-polar monomer *2*. Additionally, favorable interactions between the cationic centers and the methacryloyl moieties may occur [14, 15].

Whereas the homopolymerization of butyl methacrylate *2* in ionic liquids was studied intensively, the zwitterionic methacrylate *1* has been mentioned only briefly in this context [12, 13]. Therefore, *1* was homopolymerized first in *3* and *4* under similar conditions as described for the copolymerization experiments (see below), providing *poly-1* (Tab. 1). Although the monomer was well soluble in the ionic liquids *3* and *4*, phase separation occurs during free radical homopolymerization of *1*. This was not too surprising as polyzwitterions, such as *poly-1*, are notoriously difficult to dissolve in aprotic solvents, they require mostly strongly protic organic solvents, or brine [4, 15, 16]. Nevertheless, the polymer was swollen by both ionic liquids, which proved very difficult to remove quantitatively from *poly-1*. We attribute this to the strong attractive electrostatic interactions between the individual ions of the ionic liquid and the oppositely charged ions of the zwitterionic moieties of the polymer. In fact, the affinity of zwitterionic polymers to inorganic as well as organic salts in solution and in bulk is well established [16-18]. Tetrafluoroborate and hexafluorophosphate are found in the close proximity of iodide and perchlorate within the Hofmeister series [19, 20]. Therefore, the strong binding of tetrafluoroborate and hexafluorophosphate by polymers containing *1* conform to the established selectivities for anion binding to poly(sulfobetaine)s [21- 25]. Considering previous studies on the ion binding of polysulfobetaines, it may be assumed that one molar equivalent of ionic liquid is electrostatically bound to the sulfobetaine structures of the polymer. From a practical point of view, the strong binding of ionic liquids to polymers bearing charged groups may limit their use for the synthesis of such polymers. On the other hand, residual amounts of ionic liquid in the zwitterionic polymers may be even advantageous in certain cases, as they greatly enhance their solubility in classical solvents such as water or trifluoroacetic acid.

Although homopolymerization of *1* proceeds well in water or other protic highly polar solvents to give polymers with high molar masses [21, 26, 27], the use of ionic liquids as polymerization solvents increase the molar masses of *poly-1* even more (Tab. 1). The viscosity average molar mass of poly-1 is about four times higher if the polymerization is carried out in *3* compared to the otherwise identically conducted reaction in water. Interestingly, increasing the monomer concentration from 10 wt % to 20 wt % results in a slight decrease in the molar mass of *poly-1*. The molar mass of *poly-1* is similar when employing *3* or *4* as solvent under otherwise identical conditions. The high yields and the very high molar masses obtained for the polymerizations of *1* in ionic liquids agree well with results of the homopolymerization of *2* [12].

Tab. 1. Homopolymerization of *1* using 1 mole % of 4, 4'-azobisisobutyronitrile (*AIBN*) relative to the monomer in the ionic liquids *3* and *4* at 70°C. Polymerization in water served as reference.

Solvent	Content of **1** in the solvent (wt %)	Polymer yield (%)	M_η (kg/mole)
water	10	74	770
3	10	quantitative	3220
3	20	86	2300
4	20	94	2210

Copolymerization of *1* and *2* was first attempted in acetonitrile containing 4 wt% of water in order to dissolve monomer *1* completely. Although this solvent seems to dissolve both monomers well, the copolymers separate from the solution in the course of the reaction. The composition of the resulting copolymers was analyzed by elemental analysis and by integration of the ^{1}H NMR spectra. The latter method is useful to cross-check the results of the first method, though it is not very accurate in particular when only small amounts of *2* are incorporated, because the signals of the characteristic protons of the butyl group between 1 ppm and 2 ppm are broad and slightly superposed by signals of the polymer backbone (cf. Fig. 2). As compiled in Tab. 2, the analysis of the data revealed that only very small amounts of the non-polar monomer *2* were incorporated, even if a large excess of *2* was used.

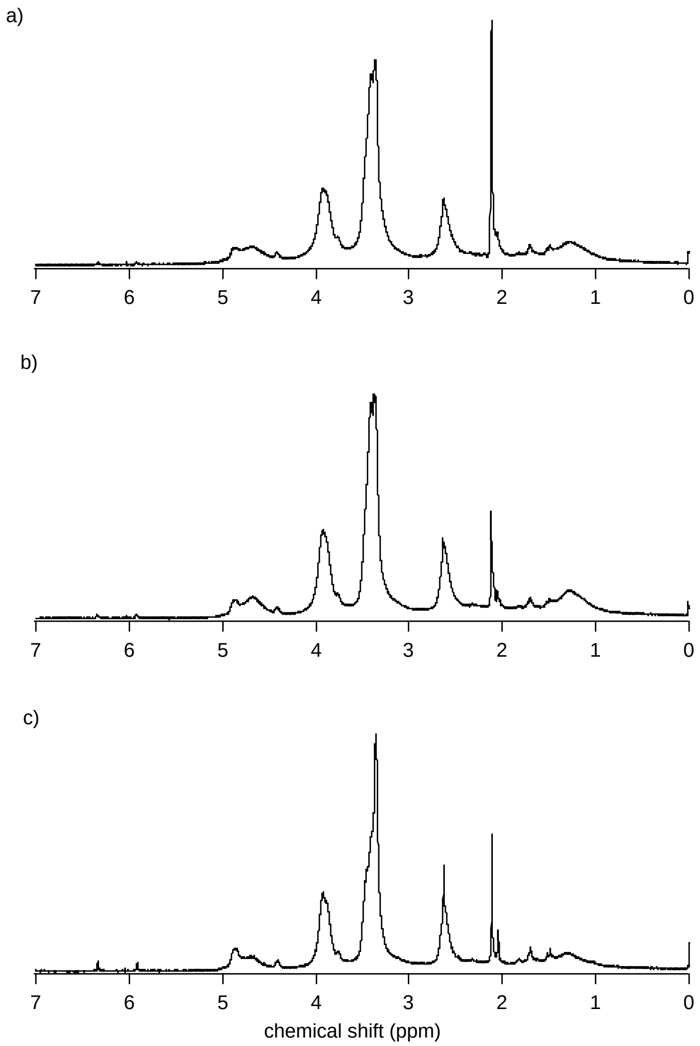

Fig. 2: ^{1}H NMR spectra of copolymers synthesized in acetonitrile containing 4.6 wt% of water using a molar ratio of monomer *1* to monomer *2* of 3 : 1 (a), 1 : 1 (b), 1 : 3 (c), measured in d-trifluoroacetic acid.

In fact, virtually no change of the low content of *n*-butylmethacrylate segments in the copolymers was observed with increasing amounts of *n*-butylmethacrylate employed in copolymer synthesis (Tab. 2). Accordingly, the ^{1}H NMR spectra were visually nearly independent on the molar ratio of the monomers used for copolymer synthesis in 96 wt % aqueous acetonitrile (Fig. 2).

Both monomers bear the same polymerizable moiety. Accordingly, they are expected to exhibit very close reactivities in their copolymerization, and the composition of the copolymers should therefore closely reflect the composition of the reaction mixtures [28]. This is obviously not the case. It can be only speculated about the reasons. For instance, the strongly differing polarities of the monomers may result in the preferential solvation of the growing macroradical site by one of the monomers [29]. Alternatively, monomer clusters of the sulfobetain monomer might exist in the organic solvent, favoring the incorporation of monomer **1** over butylmethacrylate **2**. In fact, the difficulties encountered for the monomer pair **1** and **2** are not unusual, as the copolymerization of monomer pairs of strongly differing polarity has been known to be problematic [28].

Tab. 2. Copolymerization of methacrylates *1* and *2* in acetonitrile/water (96/4 w/w), and in the ionic liquids *3* and *4* (monomer content always 10 wt %). Initiator = 1 mol% of *AIBN* relative to the monomers. The ratio of the monomer segments *1 : 2* was determined from ^{1}H NMR spectra in d-trifluoroacetic acid or in d-trifluoroacetic acid containing NaCl and a small amount on $CDCl_3$, and from the ratio of carbon to sulfur in the copolymers measured by elemental analysis

molar ratio of monomer *1* to monomer *2*	solvent	copolymer yield (%)	ratio of monomer segments *1 : 2* in the copolymer	
			^{1}H NMR	elemental analysis
1 : 3	CH_3CN	20	1 : 0.1	1:0.03
1 : 1	CH_3CN	34	1 : 0.1	1:0.02
3 : 1	CH_3CN	42	1 : 0.1	1:0.03
1 : 3	*3*	54	1 : 1.4	1:1.4
1 : 1	*3*	53	1 : 0.6	1:0.4
3 : 1	*3*	89	n.d.	1:0.02
1 : 1	*4*	21	1 : 0.7*	1:0.5

n.d.= not determined.

Subsequently, copolymerization of *1* and *2* was attempted in the ionic liquids *3* and *4* (Tab. 2). Remarkably, although phase separation occurs during the homo polymerization of *1* (see above), or of *2* [12], respectively, in *3* and *4*, clear transparent gels are formed by copolymerization of stoichiometric mixtures of monomers *1* and *2* in these ionic liquids. As for the homopolymer *poly-1*, the ionic liquids proved difficult to remove quantitatively from the copolymers. Analysis of the purified copolymers synthesized in the ionic liquids by elemental analysis and ^{1}H NMR spectroscopy (Tab. 2) revealed that the relative monomer reactivites improved substantially in these solvents. The solubility of the copolymers is low in the solvents tested and different as compared to the homopolymers. This indicates already qualitatively that true copolymers were formed. Furthermore, the solubility of the copolymers strongly depends on the content of the segments of *1* and *2*. Mostly, solubility of the copolymers is just enough for ^{1}H NMR analysis. This effect makes analysis of copolymers based on monomers with strongly different polarity more difficult. Moreover, while zwitterionic polymers are already inherently difficult to analyze due to their strong intra- and intermolecular interactions, the amphiphilic nature of copolymers made from *1* and *2* favoring aggregation adds to the difficulties. The addition of salts can reduce this aggregation only to a limited extent.

Copolymers manufactured from an excess of the highly polar monomer *1* are soluble in D_2O containing $NaNO_3$ and in d-trifluoroacetic acid containing NaCl. If the content of the nonpolar monomer segments is increased in the copolymer, the solubility in D_2O containing $NaNO_3$ is markedly reduced, and solvents such as d-trifluoroacetic acid containing NaCl are better suited for ^{1}H NMR spectroscopy. As shown in Fig. 3, NMR analysis of the copolymer synthesized from a stoichiometric ratio of the monomers *1* and *2* in *4* shows significant differences in D_2O containing $NaNO_3$ and in d-trifluoroacetic acid containing NaCl. The hydrophobic segments of the copolymer are more visible in d-trifluoroacetic acid containing NaCl than in D_2O containing $NaNO_3$. In contrast to this, the hydrophilic segments of the copolymer show similar signals as *poly-1* if D_2O containing $NaNO_3$ is used as solvent for NMR analysis of this copolymer. This behavior suggests that the hydrophobic butyl groups are associated in D_2O, and that the copolymer behaves as an amphiphile of a polysoap type forming micelle-like aggregates in aqueous solvents [30]. In any case, the ^1H NMR spectra depicted in Fig. 3 demonstrate that the copolymer manufactured from a stoichiometric ratio of the monomers *1* and *2* in *4* contains important quantities of both monomers. The same was found for the copolymers prepared in the ionic liquid *3* using various stoichiometric ratios of the monomers *1* and *2* (Fig. 4).

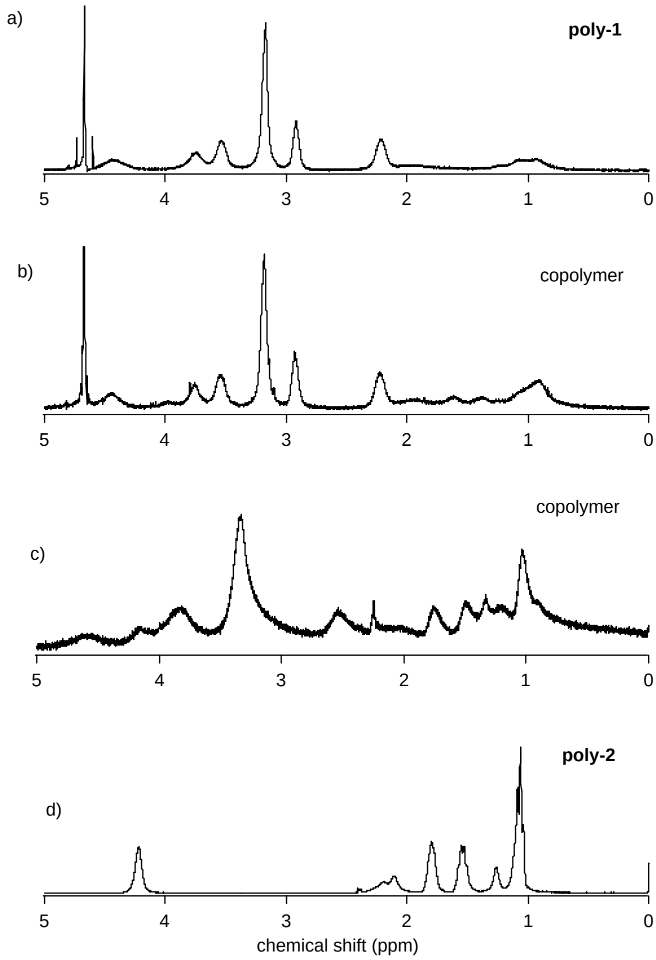

Fig. 3. ^1H NMR spectra of *poly-1* in D_2O (a), of the copolymer of *1* and *2* (equimolar amounts of monomers reacted) in *4* and measured in D_2O ($NaNO_3$ was added to increase the solubility of the copolymer) (b) and in d-trifluoroacetic acid (NaCl and a small amount of $CDCl_3$ were added to improve the solubility of the copolymer) (c), and of *poly-2* in d-trifluoroacetic acid (d).

Elemental analysis data (Tab. 2) and ^1H NMR spectra of the copolymers (Figs. 2 and 4) show considerable differences concerning the content of the nonpolar monomer segments between the copolymers synthesized in the ionic liquid *3* and the copolymers manufactured in acetonitrile. Although the molar ratio of the monomers used for these copolymerization experiments was varied identically, the content of butylmethacrylate segments relative to sulfobetaine substituted segments in the copolymers is significantly higher for the copolymers made in the ionic liquid. However, the incorporation of the highly polar monomer *1* is still preferred if the ionic liquid is used as solvent (Tab. 2). Nevertheless, the content of the nonpolar monomer in the copolymer is increased if higher amounts on *n*-butylmethacrylate relative to the polar monomer are used in the copolymer synthesis. Furthermore, the composition of the copolymers was similar when using *3* or *4* as solvent in polymer synthesis.

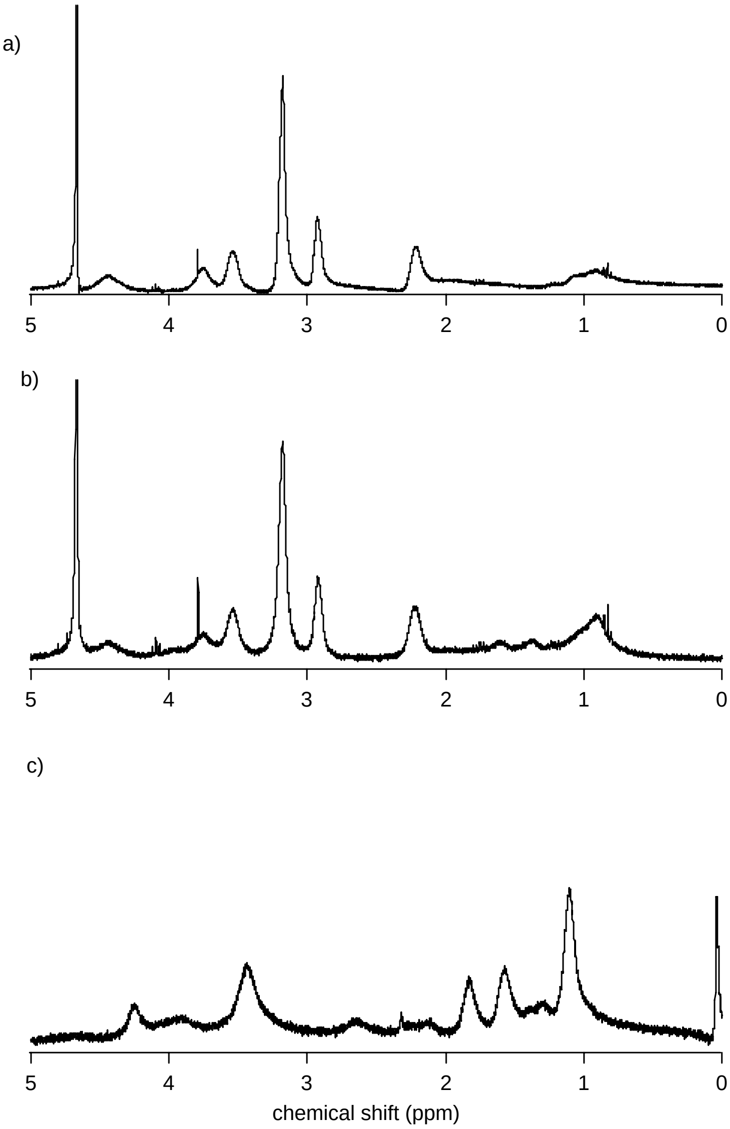

Fig. 4. ^{1}H NMR spectra of copolymers from sulfobetaine *1* and butylmethacrylate *2* synthesized in the ionic liquid *3*, employing a ratio of monomer *1* to monomer *2* of (a) 3 : 1, (b) 1 : 1, and (c) 1 : 3. Spectra were taken in D_2O containing $NaNO_3$ ((a) and (b)) or d-trifluoroacetic acid containing NaCl (c).

Conclusions

Ionic liquids open new possibilities for copolymerization of monomers with strongly differing polarities. These new solvents are able to dissolve both non-polar and highly polar monomers. As exemplified for copolymerization of a highly polar methacrylate bearing a zwitterionic sulfobetain moiety, and *n*-butylmethacrylate as rather non-polar monomer, the use of ionic liquids as solvents produces copolymers, which incorporate substantial amounts of both monomers in high yields. This is in marked contrast to the copolymerization conducted in an organic solvent, which visually fails. Using an ionic liquid, the content of the highly polar segments and of the nonpolar segments in the statistical copolymer can be varied, as for a conventional copolymerization, by the molar ratio of the monomers used in the copolymerization. The higher conversion of the monomers and the enhanced incorporation of the nonpolar monomer in the copolymers exemplify the usefulness of ionic liquids as solvents for copolymerization of monomers with strongly different polarities.

In contrast to the homopolymerizations of *1* and of *2* for which phase separation occurred during the polymerization process, a transparent gel was obtained in the copolymerization process in the ionic liquids, if a stoichiometric ratio of the monomers is used. This may be attributed to the strong interactions between the different polar segments of the copolymer and the individual ions of the ionic liquids. Such a bonding of ionic liquid to the segments of the copolymer forming gel structures seems attractive for electrochemical devices.

Experimental part

The monomers 3-(*N*-2-[methacryloyloxyethyl]-*N,N*-dimethyl-3-ammonio)propane sulfonate (*1*) (Raschig, Germany), and *n*-butylmethacrylate (*2*) (stabilized with 10 ppm of 4-hydroquinonemonomethylether, Aldrich), 4,4'-azobisisobutyronitrile (*AIBN*) (Acros), and acetonitrile (p.a., Fluka) were used as received. The ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate (*3*) and 1-butyl-3-methylimidazolium tetrafluoroborate (*4*) were synthesized by alkylation of 1-methylimidazole with *n*-butylbromide followed by anion metathesis using tetrafluoroboric acid or hexafluoro phosphoric acid [31]. Information about the properties and the purity of ionic liquids are given elsewhere [12].

Solutions of the monomer *1* (Tab. 1), or of known mixtures of the monomers *1* and *2* (Tab. 2), respectively, in the ionic liquids were polymerized at 70°C using *AIBN* as initiator. In a typical procedure, *1* (2.00 g = 0.007 mol) and *2* (1.03 g = 0.007 mol) were dissolved in 27 ml of *3* by stirring and heating to 70°C while purging with nitrogen for 1 h. Then, the polymerization was initiated by addition of *AIBN* (24.2 mg = 0.00014 mol). After a few minutes, the viscosity increased dramatically and a transparent gel was formed. The polymerization mixture was kept under nitrogen at 70°C for 24 h. The soft gel obtained was washed 6 times with 40 ml portions of acetonitrile each to remove as much of the ionic liquid from the copolymer as possible. The copolymer was dried at room temperature for 24 h and then at 55°C under vacuum (9 mbar) for 48 h. 1 g of the crude copolymer was further purified by Soxhlett extraction for 9 h using 65 ml of acetonitrile. The extracted copolymer was dried at first at room temperature and than at 55°C under vacuum as described before. The ionic liquid separated by the various washing and extraction processes was recovered by evaporation of the acetonitrile under vacuum. The copolymers obtained from other molar ratios than a stoichiometric one are opaque, and the homopolymers precipitate from the ionic liquids. Nevertheless, the purification procedure is the same as described above. Reference homopolymerization of *1* was conducted in water, and reference copolymerization experiments were carried out under similar conditions in acetonitrile containing 4.6 wt% of water. The conditions for the reference polymerization experiments are the same as described for those in ionic liquids. The homopolymer was isolated by evaporation of water, and the co

polymers, which precipitated from the acetonitrile in the course of the reaction, were separated by filtration. All polymers were dried at 55°C for 48 h under vacuum.
The purified polymers were analysed by ^{1}H NMR spectroscopy on a Bruker AVANCE 300 (300 MHz) and by elemental analysis. D-trifluoroacetic acid was used as solvent for NMR analysis of the copolymers, and D_2O containing 0.1 M $NaNO_3$ was selected as solvent for the homopolymer of *1*. NaCl was added to the copolymers synthesized in the ionic liquids to improve their solubility in d-trifluoroacetic acid.
The molar mass of the homopolymer of **1** (**poly-1**) was determined from the intrinsic viscosity of *poly-1* measured in aqueous 1.0 M NaCl solution applying the Kuhn-Mark-Houwink-Sakurada equation (1) [32].

$$[\eta] = 2.29 \cdot 10^{-3} \cdot \overline{M_{\eta}^{0.776}} \qquad (1)$$

The polymer concentration was varied between 0.4 g/l and 2 g/l for measurement of the solution viscosity.

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