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Free Radical Polymerization of *n*-Butyl Methacrylate in Ionic Liquids

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ABSTRACT: Ionic liquids based on imidazolium, pyridinium, and alkylammonium salts were investigated as solvents in free radical polymerization of the model monomer *n*-butyl methacrylate. The properties of the ionic liquids were systematically varied by changing the length of the alkyl substituents on the cations, and by employing different anions such as tetrafluoroborate, hexafluorophosphate, tosylate, triflate, alkyl sulfates and dimethyl phosphate. Results were compared to analogous polymerizations in toluene and in bulk. The solvents have no detectable influence on polymer tacticity. However, the molar masses obtained and the degree of polymerization, respectively, are very sensitive to the choice of the solvent. The degrees of polymerization are significantly higher when polymerizations were carried out in ionic liquids compared to polymerization in toluene, and can even exceed the values obtained by bulk polymerization. Imidazolium salts unsubstituted at C-2 result in an increase in the degree of polymerization of the poly(butyl methacrylate) with increasing viscosity of these ionic liquids. Methyl substitution at C-2 of the imidazolium ion results in an increase in the viscosity of the ionic liquid and in a viscosity independent degree of polymerization of the poly(butyl methacrylate). Ionic liquids based on imidazolium salts seem preferable over pyridinium and alkylammonium salts because of the higher degree of polymerization of the poly(butyl methacrylate)s obtained in the imidazolium salts. The glass transition temperatures and thermal stabilities are higher for poly(butyl methacrylate)s synthesized in the ionic liquids compared to the polymer made in toluene.

Introduction

Conventional polymerizations have usually been carried out in volatile organic solvents or in water. Recent studies investigated ionic liquids[1−4] and supercritical fluids[5] as new solvents in polymerizations. Whereas the latter require special equipment and safety measures due to the high pressures involved, ionic liquids offer the advantage that standard reaction vessels can be used, and the solvent properties can be varied widely by adjusting the structures of the cation and the anion. This structural variability is inherently limited by the stability of the ionic liquids under the reaction conditions. The benefit in using of ionic liquids can be seen in their negligible volatility and nonflammability, their ability to dissolve homogeneously many organic and inorganic compounds, and the possibility to influence the chemical reaction products. Free radical,[6−20] coordination,[21,22] cationic,[23,24] group transfer,[25] enzymatic,[26] electrochemical,[27−29] and step−growth polymerizations[30,31] have been reported in ionic liquids. The few reports on the use of ionic liquids in classical free radical polymerization mentioned occasionally the modified copolymerization behavior,[3,32] and even higher molar masses were obtained in comparison with standard organic solvents.[3,6,8,33−35] The reported effects were sometimes modest,[33] and in other cases they were perhaps overestimated by comparison with organic solvents exhibiting nonnegligible chain transfer constants.[34] It seems that at least in certain cases propagation constants are higher,[8−12] and termination constants are lower[11] than in classical organic solvents. It was proposed that the latter effects are caused by the high viscosity of ionic liquids compared to most standard solvents.[11] However, this explanation remained hypothetical. In fact, the beneficial effect of ionic liquids on the molar masses of the polymers obtained is not a general feature because in other examples small or even negative effects on the molar masses were reported when using ionic liquids as solvents for polymerization.[18,33] Moreover, most free radical polymerization studies have focused on the use of 1-butyl-3-methylimidazolium hexafluorophosphate.[6−9,11−14,32,36−39] In any case, a systematic investigation of the influence of the ionic liquid structure on the molar mass and the properties of polymers synthesized in these solvents is missing.

This paper investigates the effect of the chemical structure and the viscosity of ionic liquids on the molar mass and the degree of polymerization, respectively, and thermal properties of the polymers obtained. We studied *n*-butyl methacrylate (**BMA**) because its polymer is soluble in standard eluents, such as THF, for size exclusion chromatography (SEC) and its tacticity can be readily analyzed by ^{1}H NMR spectroscopy. Furthermore, the thermal stability and the glass transition temperature of poly(butyl methacrylate) are in a convenient range to be studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The polymerization was initiated by 4,4′-azobis(isobutyronitrile) (**AIBN**). Analogous polymerizations in toluene and in bulk served as references. Toluene possesses a low chain transfer constant for methacrylates (0.5×10^{-4} at 70 °C).[40] Various 1-alkyl-3-methylimidazolium salts with different substituents at N-1 and C-2, and with different anions were selected as ionic liquids for this purpose, and were complemented by two 1-butyl-4-methylpyridinium salts, and by one aliphatic ammonium methyl sulfate (Table 1). To facilitate the interpretation of the results, key properties of the ionic liquids employed such as melting behavior

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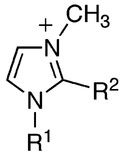
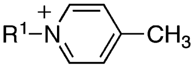
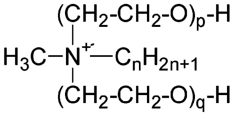
Table 1. Chemical Structure of Ionic Liquids Investigated in Polymerization of BMA at 70 °C Using AIBN as the Initiator

Ionic liquid	Cation	R^1	R^2	Anion X^-	CAS number
1a		C_2H_5	H	BF_4^-	143314-16-3
1b		C_4H_9	H	BF_4^-	174501-65-6
1c		C_5H_{11}	H	BF_4^-	244193-49-5
1d		C_6H_{13}	H	BF_4^-	244193-50-8
1e		C_7H_{15}	H	BF_4^-	244193-51-9
1f		C_8H_{17}	H	BF_4^-	244193-52-0
1g		C_9H_{19}	H	BF_4^-	244193-55-3
1h		$C_{10}H_{21}$	H	BF_4^-	244193-56-4
1i		C_4H_9	CH_3	BF_4^-	402846-78-0
1k		C_6H_{13}	CH_3	BF_4^-	384347-21-1
2a		C_2H_5	H	PF_6^-	155371-19-0
2b		C_4H_9	H	PF_6^-	174501-64-5
2c		C_5H_{11}	H	PF_6^-	280779-52-4
2d		C_6H_{13}	H	PF_6^-	304680-35-1
2e		C_7H_{15}	H	PF_6^-	357915-04-9
2f		C_8H_{17}	H	PF_6^-	304680-36-2
2g		C_9H_{19}	H	PF_6^-	343952-29-4
2h		$C_{10}H_{21}$	H	PF_6^-	362043-46-7
2i		C_4H_9	CH_3	PF_6^-	227617-70-1
2k		C_6H_{13}	CH_3	PF_6^-	653601-27-5
3		C_2H_5	H	Tosylate	328090-25-1
4		C_2H_5	H	Ethylsulfate	342573-75-5
5		C_4H_9	H	Octylsulfate	445473-58-5
6a		C_6H_{13}	H	$CF_3SO_3^-$	460345-16-8
6b		C_6H_{13}	CH_3	$CF_3SO_3^-$	797789-01-6
7		CH_3	CH_3	Dimethylphosphate	654058-04-5
8		C_4H_9	-	BF_4^-	343952-33-0
9		C_4H_9	-	PF_6^-	401788-99-6
10	 $H_3C-\overset{(CH_2\text{-}CH_2\text{-}O)_p\text{-}H}{\underset{(CH_2\text{-}CH_2\text{-}O)_q\text{-}H}{N^+}}-C_nH_{2n+1}$ n=12-18 p+q=5	-	-	Methylsulfate	68989-03-7

and viscosity were analyzed (Table 2). Furthermore, the recycling potential of ionic liquids after the polymerization was studied because it is crucial for their economical and ecological use.

Experimental Section

1-Ethyl-3-methylimidazolium tetrafluoroborate (**1a**) (purity ≥98%), 1-ethyl-3-methylimidazolium hexafluorophosphate (**2a**) (purity ≥97%), 1-butyl-3-methylimidazolium octyl sulfate (**5**) (purity

Table 2. Water Content and Physical Properties of the Ionic Liquids Investigated[a]

ionic liquid	water (wt %)	T_g (°C)	$T_{recryst}$ (°C)	T_m (°C)	η_{10} (mPa·s) at 23 °C	η_{10} (mPa·s) at 70 °C
1a	0.6	−97	−67	16 13	33	10
1b	1.6	−87			86	15
1c	0.3	−87			77	22
1d	0.4	−86			177	22
1e	0.9	−86			175	26
1f	0.5	−86			294	28
1g	0.7	−82	−58 −45 −18	−39 −7 2	306	34
1h	0.2			−10 8	578	40
1i	0.2	−73	−18	39	458	39
1k	1.0	−74	−15	2 12	667	55
2a	0.01			62		20
2b	0.1	−78		−12	231	32
2c	0.3	−76			195	31
2d	0.2	−74			499	35
2e	0.1	−72			601	45
2f	0.1	−72	−9	2	488	48
2g	0.2	−71	−32	3 15	859	64
2h	0.3			7 19		96
2i	0.2	−60	1	16	2312	79
2k	0.3	−58	−14	41		123
3	1.9	−46	12	53		21
4	0.4	−92			55	17
5	1.3			−33 34		73
6a	0.3			−8 22	127	15
6b	0.02			76		
7	0.08	−64			276	11
8	0.2	−74			194	22
9	0.03	−55	1	20		39
10	1.4			broad peak from −70 to −25	2029	145

[a] T_g = glass transition temperature, $T_{recryst}$ = temperature of recrystallization, T_m = melting temperature, all values derived from DSC heating scans; η_{10} = viscosity at a shear rate of 10 s^{-1}.

≥98%), 1-butyl-4-methylpyridinium tetrafluoroborate (**8**) (purity ≥97%), and 1-butyl-4-methylpyridinium hexafluorophosphate (**9**) (purity ≥97%) were purchased from Fluka. 1-Hexyl-3-methylimidazolium trifluoromethansulfonate (**6a**) (purity 99%) and 1-hexyl-2,3-dimethylimidazolium trifluoromethansulfonate (**6b**) were purchased from Acros. 1-Ethyl-3-methylimidazolium tosylate (**3**) (purity ≥98%), 1-ethyl-3-methylimidazolium ethyl sulfate (**4**) (purity ≥98%), 1,3-dimethylimidazolium dimethyl phosphate (**7**) (purity ≥98%) and *N*-alkyl-*N*-methyl-*N*,*N*-bis(oligo(oxyethyl))-ammonium methyl sulfate (**10**) (ECOENG 500, purity ≥98%, alkyl length mixture $C_{12}-C_{18}$, average content of oxyethyl units = 5, average composition $C_{24}H_{53}NO_9S$) were provided by Solvent Innovation. 1-Alkyl-3-methylimidazolium tetrafluoroborates (**1b**−**1h**) and 1-alkyl-3-methylimidazolium hexafluorophosphates (**2b**−**2h**) were synthesized from 1-methylimidazole and the respective alkyl bromide followed by anion metathesis using hexafluorophosphoric acid or tetrafluoroboric acid.[41] 1-Alkyl-2,3-dimethylimidazolium tetrafluoroborates (**1i**−**1k**) and 1-alkyl-2,3-dimethylimidazolium hexafluorophosphates (**2i**−**2k**) were prepared analogously from 1,2-dimethylimidazole and butyl chloride. *n*-Butyl methacrylate (**BMA**) (Aldrich, 99%, stabilized with 10 ppm of 4-hydroquinonemonomethyl ether), 4,4′-azobis(isobutyronitrile) (**AIBN**) (Acros, purity ≥ 98%), and all commerical ionic liquids were used as received.

For solution polymerization in toluene, 3.00 g of **BMA** (0.02 mol) was dissolved in 27 g of toluene, and heated to 70 °C while stirring and purging with nitrogen. After 1 h, the polymerization was initiated by addition of **AIBN** (34.6 mg, 2.1×10^{-4} mol). The polymerization was continued for 24 h at 70 °C while stirring and purging with nitrogen. The polymer was precipitated using 200 mL of methanol. Drying the polymer for 24 h at room temperature and for another 48 h at 55 °C under vacuum (9 mbar) provided 0.48 g of polymer.

For polymerization of **BMA** in bulk 3.00 g of monomer (0.02 mol) was purged with nitrogen for 1 h. After heating to 70 °C **AIBN** (34.6 mg, 2.1×10^{-4} mol) was added and the polymerization was continued for 24 h at 70 °C while purging with nitrogen and stirring as long as possible. The glassy polymer was dissolved in 30 mL acetone, and the polymer was precipitated from this solution using 100 mL of methanol. After the polymer was dried as described above, 2.43 g of polymer was obtained.

For polymerization in ionic liquids monomer solutions (10 wt %) in the ionic liquid were used containing 1 mol % of the initiator (**AIBN**) relative to the monomer. In a typical procedure, **BMA** (3.00 g, 0.02 mol) was dissolved in 27 g of **1a** and heated to 70 °C with stirring and purging with nitrogen. After 1 h, the polymerization was initiated by addition of **AIBN** (34.6 mg, 2.1×10^{-4} mol). A few minutes later, the liquid homogeneous reaction mixture becomes cloudy. The polymerization was continued for 24 h at 70 °C while stirring and purging with nitrogen. Precipitation of the white polymer swollen with the ionic liquid starts about 1 h after addition of the initiator. The colorless polymer separates at the surface of the reaction mixture. The ionic liquid was decanted from the polymer while the polymer was continuously squeezed to separate as much as possible of the ionic liquid. In this way 26.38 g of the ionic liquid was recovered. The swollen polymer was washed 8 times with 25 mL portions of methanol, and dried as described above to yield 1.93 g of crude polymer. Residual traces of the ionic liquid in the polymer were removed by Soxhlett extraction, e.g. 1.04 g of clean polymer was obtained from 1.07 g of the crude polymer by Soxhlett extraction with 65 mL of methanol for 4 h followed by drying the extracted polymer as described above. Polymerizations using the other ionic liquids followed the same procedure. In the case of ionic liquids that were solid at room temperature or when the polymer did not phase separate from the ionic liquid, methanol (25 mL) was added to the reaction mixture in order to precipitate the polymer. Purification of all polymers synthesized in the ionic liquids was carried out as described above. The purified poly(*n*-butyl methacrylate) samples were analyzed by ^{1}H NMR spectroscopy, GPC, DSC, and TGA.

Water contents of ionic liquids were coulometrically determined by the Karl Fischer method.[42,43] Shear rate dependent viscosities of ionic liquids were determined in duplicates at 23 °C and at 70 °C by a rheometer with cone plate geometry (Rheometrics DSR 200) in the steady stress modus. Thermal stability of the polymers was investigated under nitrogen with a Mettler-Toledo TGA/SDTA 851^e using a heating rate of 20 K/min. Temperature accuracy was checked with the onset of the melting peaks of indium (onset of the melting peak = 156.6 °C) and of aluminum (onset of the melting peak = 660.3 °C). Thermal transitions were determined by differential scanning calorimetry (DSC 822^e, Mettler-Toledo) using heating and cooling rates of 5 K/min in the case of the ionic liquids and of 10 K/min in the case of the polymer. The glass transition temperature (T_g) was determined from the point of intersection of the tangents on the DSC curve. The melting temperature (T_m) corresponds to the endothermic maximum, and the temperature of recrystallization was taken from the exothermic maximum. Indium (T_m = 156.6 °C; ΔH_m = 28.45 J·g^{-1}) and zinc (T_m = 419.6 °C; ΔH_m = 107.5 J·g^{-1}) were used for calibration of the DSC. Molar mass distributions of the polymers were measured by size exclusion chromatography (SEC) from Waters: column bank, 7.8 mm × 300 mm Waters Styragel HR5 (50000−1000000 g/mol), HR4 (5000−600000 g/mol), and HR3 (500−30000 g/mol); mobile phase, THF, 1 mL/min; RI detector; calibration by poly(methyl methacrylate) standards from Polymer Laboratories. The particle size of the column materials was 5 μm, and the temperature of the column oven was 20 °C. NMR measurements were carried out with a 300 MHz AVANCE 300 spectrometer of Bruker.

Results and Discussion

General Properties of the Ionic Liquids Used. To fulfill the requirements as a polymerization solvent, ionic liquids should preferentially exhibit good thermal and chemical stability, a broad temperature window for the liquid state, and low melt viscosity. These properties depend sensitively on the nature and the substitution pattern of the organic cation, and the nature of the anion. They are also markedly influenced by the water content.[44] The ionic liquids summarized in Table 1 are distinguished by the substitution pattern of the cation and by the nature of the anion. The anions comprise either classical examples, such as tetrafluoroborate (**1**) and hexafluorophosphate (**2**), or oxyanions with low nucleophilicity, such as tosylate (**3**), ethyl sulfate (**4**), octyl sulfate (**5**), trifluoromethanesulfonate (**6**), and dimethyl phosphate (**7**). The latter anions should be chemically more inert and less toxic.[45] For comparison, the series of imidazolium based ionic liquids were complemented by singular examples of *N*-alkyl-4-methylpyridinium tetrafluoroborate (**8**) and hexafluorophosphate (**9**), and of the alkylammonium methyl sulfate (**10**) bearing long alkyl chains. The physical properties of the ionic liquids vary broadly as a function of their molecular structure (Table 2).

DSC studies (Table 2) show that ionic liquids can be glass forming materials (**1b**−**1f**, **2c**−**2e**, **4**, **7**, and **8**), semicrystalline materials (**1a**, **1g**, **1i**, **1k**, **2b**, **2f**, **2g**, **2i**, **2k**, **3**, and **9**) or crystallizing substances (**1h**, **2a**, and **2h**, **5**, **6a**, and **6b**). The alkylammonium salt **10** bears a very broad melting region that can be explained by the chemically inhomogeneous substituents on the nitrogen atom.

The ionic liquids discussed above form melts at 70 °C, the temperature chosen for the free radical polymerization of **BMA**. An exception is **6b** (mp 76 °C). Nevertheless, supercooling of the melt of **6b** and the addition of monomer prevent crystallization, and enables the use of this ionic liquid as solvent at 70 °C.

The viscosity of ionic liquids is important for the polymerization process and for the handling of these solvents at room temperature. Therefore, viscosity data of the melts are compared for 70 °C and for room temperature using shear rates of 10 s^{-1} (Table 2) because viscosities are rate independent for all ionic liquids at this rate. A discussion of the shear rate dependence of the viscosity of selected ionic liquids is given in the Supporting Information. As expected, the viscosities of all ionic liquids are much lower at 70 °C compared to room temperature. Furthermore, the viscosity is strongly affected by the structure of the ionic liquid. Viscosity of imidazolium salts increases with the length of the alkyl substituent at the nitrogen atom and by methyl substitution at C-2 of the imidazolium ring. Comparing the influence of different anions on the viscosity of imidazolium based ionic liquids with identical cations increases in the order $CF_3SO_3^- < BF_4^- <$ ethyl sulfate $< PF_6 <$ tosylate, octyl sulfate.

We also notice that the melts of 1-butyl-4-methylpyridinium salts **8** and **9** are more viscous compared to the analogous 1-butyl-3-methylimidazolium salts **1b** and **2b**. The alkylammonium salt **10** shows the highest melt viscosity (145 mPa·s at 70 °C), which is about 15 times higher than that of the lowest viscous ionic liquid **1a**. We attribute this high value to the long alkyl substituents at the cation.

Polymerization in Ionic Liquids. The polymerization of **BMA** in the various ionic liquids initiated by **AIBN** was carried out under classical conditions. Polymerization experiments in toluene or of the bulk monomer were performed under identical conditions as reference reactions. The ^{1}H NMR spectra of the poly(butyl methacrylate)s depicted in Figure 1 demonstrate that the polymers are free of residual monomer and solvent, and they give information about their tacticity. Analyzing the signals, which are indicative for the stereochemistry of the methylene protons in the polymer backbone as well as for the methyl group fixed to the backbone, suggests the formation of atactic poly(methacrylate)s with a preference for syndiotactic triades.[46,47] A precise quantitative analysis is difficult due to the partial superposition of these signals and the signals of the butyl side chains. Importantly, the ^{1}H NMR spectra of all samples look identical, if synthesized either in ionic liquids, toluene, or in bulk. This indicates that the choice of the solvent does not influence the stereochemistry of the polymer formed measurably. This finding agrees well with other studies reporting only small effects on polymer tacticity even if chiral ionic liquids were employed in polymer synthesis.[6,15,20]

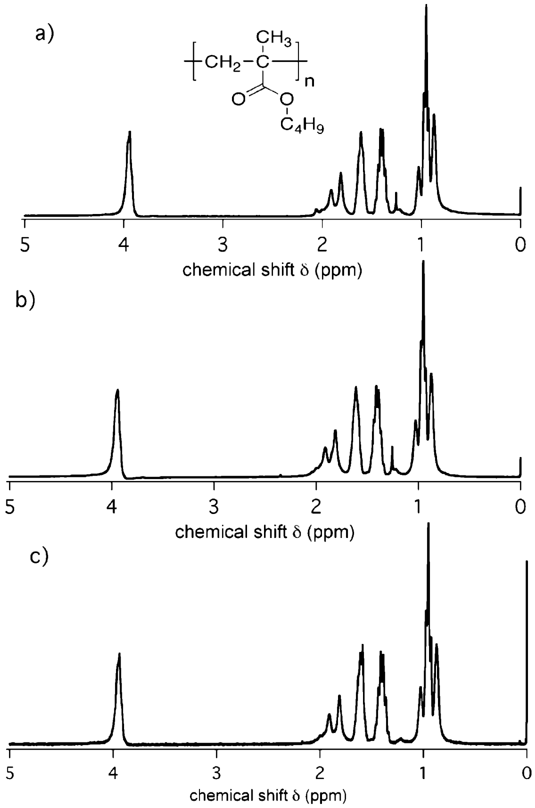


Figure 1. ^{1}H NMR spectra of poly(butyl methacrylate) in $CDCl_3$ obtained by polymerization (a) in toluene, (b) in **3**, and (c) in bulk after purification.

The polymer yields varied markedly with the specific solvent used for polymer synthesis although the conditions were the same in all cases (Table 3). Mostly, yields are higher for the polymers prepared in ionic liquids than for the polymer made in toluene. The yield on polymer synthesized in **1c**, **1d**, **2f**, **2k**, **5**, **9**, and **10** is similar to the yield of bulk polymerization, and even exceeds this value when **1e** or **3** are used as solvents for polymerization. Interestingly for certain examples of ionic liquids, the polymer yield was very low (**1h**) or zero (**2g**, **2h**) under the conditions of the experiments. Careful analysis of the ionic liquids gave no indication for contamination of these solvents by inhibitors. Therefore, these results may be attributed to a change in the interactions between the imidazolium ions substituted with long alkyl chains at the nitrogen and the corresponding anions on one hand and the monomer on the other hand.[48]

Table 3. Gravimetric Yield, Number Average Molar Mass (M_n), Weight Average Molar Mass (M_w), and Polydispersity (PD) of Poly(*n*-butyl methacrylate)s Synthesized in Ionic Liquids, in Toluene, or in Bulk, the Amounts of Recovered Ionic Liquid Obtained by Simple Decanting ($IL_{decanted}$), by Subsequent Extraction of the Polymerization Mixture with Methanol ($IL_{methanol}$) at Room Temperature and Evaporation of Methanol under Vacuum, and the Total Amount of Recovered Ionic Liquid (IL_{total})[a]

solvent	polymer yield (%)	M_n (kg/mol)	M_w (kg/mol)	PD	$IL_{decanted}$ (%)	$IL_{methanol}$ (%)	IL_{total} (%)
toluene	16	32	49	1.5			
bulk	81	152	460	3.0			
1a	64	54	147	2.7	95	4	99
1b	71	127	560	4.4	88	9	97
1c	80	67	428	6.4	53	43	96
1d	83	118	637	5.4	0	92	92
1e	92	83	378	4.6	0	92	92
1f	72	204	909	4.5	0	89	89
1h	2	120	771	6.4	0	92	92
1i	70	298	853	2.9	66	30	96
1k	30	227	925	4.1	0	81	81
2a	68	400	1215	3.0	61	35	96
2b	64	134	475	3.5	74	17	91
2c	63	148	835	5.6	0	78	78
2d	63	198	724	3.7	0	56	56
2f	87	406	1377	3.4	0	n. d.	n.d.
2g	0						
2h	0						
2i	74	278	936	3.4	50	46	96
2k	78	217	857	3.9	0	n.d.	n.d.
3	93	417	1308	3.1	0	93	93
4	74	127	546	4.3	n.d.	21	21
5	86	191	1068	5.6	0	89	89
6a	14	62	515	8.3	86	13	99
6b	47	243	796	3.3	0	n.d.	n.d.
7	75	233	885	3.8	84	16	100
8	41	43	474	11.0	0	98	98
9	88	55	347	6.3	0	67	67
10	88	59	290	4.9	0	64	64

[a] n.d. = not determined

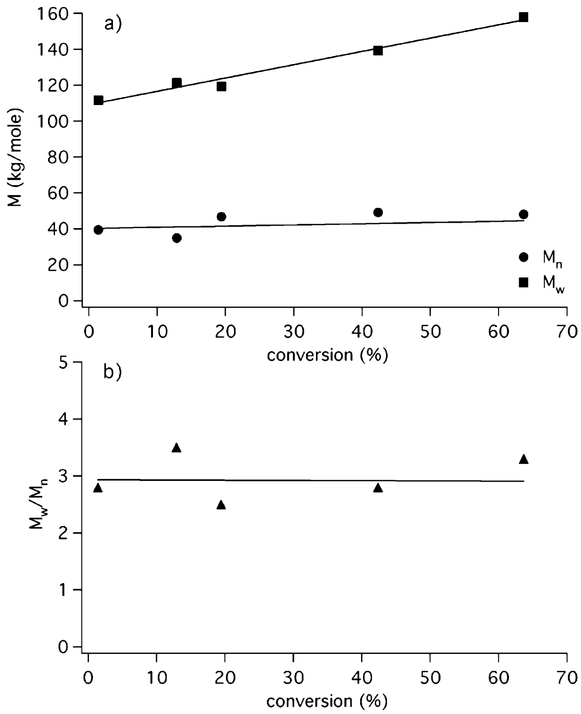


Figure 2. Molar mass (number-average molar mass (M_n) and weight-average molar mass (M_w)) (a) and polydispersity (b) of poly(butyl methacrylate) obtained by free radical polymerization of **BMA** (10 wt %) in **1a** initiated by **AIBN** (1 mol % relative to **BMA**) at 70 °C as a function of the conversion on monomer.

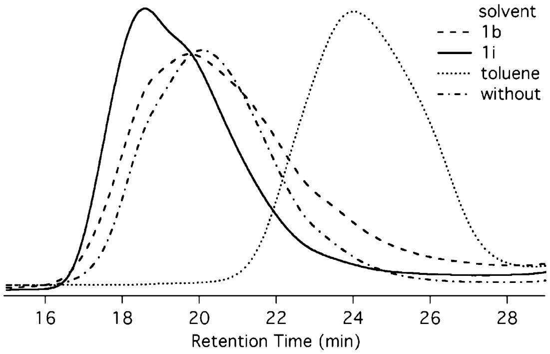


Figure 3. SEC chromatograms of poly(*n*-butyl methacrylate) polymerized in **1b**, **1i**, toluene, and bulk.

Although we did not strive for a kinetic study of the polymerization, the evolution of the molar masses with conversion was followed exemplarily for the reaction conducted in the ionic liquid **1a** (Figure 2). As shown in Figure 2a, the number-average molar mass (M_n) is nearly independent of the conversion of the monomer, while the weight-average molar mass (M_w) increases slightly with monomer conversion. However, the polydispersity does not show a clear tendency (Figure 2b). Accordingly, a marked Trommsdorff effect as typically observed in bulk polymerization[49−53] is absent for the polymerization in this ionic liquid, despite the high viscosity. As M_n proved to be nearly independent of the monomer conversion, we decided to conduct all polymerizations to high conversion, as this is desirable for practical purposes. Therefore, we will use M_n and the degree of polymerization (X_n), respectively for comparative discussions in the following. X_n is preferred for picturing because it is independent of the molar mass of the monomer segments. Moreover, the ionic liquid may influence the mobility of the radicals formed already at the beginning of the polymerization because of the viscosity effect of the ionic liquid. Therefore, the mobility of the radicals may influence the polymerizations in ionic liquids with an onset at the beginning of the polymerization process. This hypothesis is further supported by the high molar mass of the polymers synthesized in ionic liquids (Table 3).

The poly(butyl methacrylate) samples obtained by polymerization in the various ionic liquids were analyzed by SEC. In comparison with the polymer made in toluene, the samples synthesized in ionic liquids show higher molar masses on one hand, and a higher polydispersity on the other hand (Table 3). This general finding is in line with several previous reports in the literature.[6,8,33−35] However, a considerable variation in molar masses was observed when using different ionic liquids. As depicted for example in Figure 3, the molar mass of the polymer synthesized in **1i** is significantly higher than using **1b** as solvent for polymerization. Furthermore, the molar masses of the polymers exceed even the value of the polymer obtained by polymerization in bulk when using the tetrafluoroborates **1f**, **1i** (Figure 3), and **1k**, the hexafluorophosphates **2a**, **2d**, **2f**, **2i**, and **2k**, the tosylate **3**, the octyl sulfate **5**, the trifluormethansulfonate **6b**, and the dimethyl phosphate **7** (Table 3).

The molar mass of polymers synthesized in ionic liquids is strongly influenced by the detailed structure of the latter. Increased molar masses imply that either the propagation rate of the polymerization is increased, or the termination rate is decreased when using ionic liquids instead of traditional solvents. In fact, a short communication reported at least for one case that both effects occur simultaneously when using **2b** in the polymerization of methyl methacrylate.[11] This is reasonable to assume in our case too, as the marked increase of the molar mass seems difficult to be caused by one effect only.

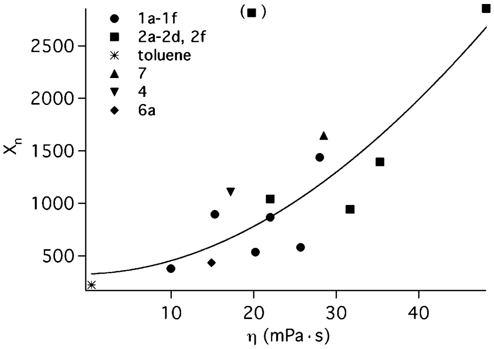


Figure 4. Degree of polymerization (X_n) of poly(*n*-butyl methacrylate)s as a function of viscosity of the solvent (**toluene**, **1a**−**1f**, **2a**−**2d**, **2f**, **4**, **6a**, and **7**) used for polymerization initiated with **AIBN** at 70 °C for 24 h.

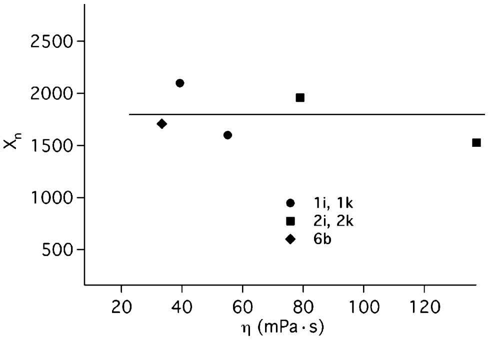


Figure 5. Degree of polymerization (X_n) of poly(*n*-butyl methacrylate) as a function of viscosity of the imidazolium salt bearing a methyl substituent at C-2 (**1i**, **1k**, **2i**, **2k**, and **6b**) used for polymerization initiated with **AIBN** at 70 °C for 24 h. (The viscosity of **6b** is given at 80 °C because of shear induced crystallization during viscosity measurement of **6b** at 70 °C.).

Although we did not undertake a kinetic study, the much higher conversions obtained in our experiments when using ionic liquids suggest that the polymerization rate is higher. The reported decrease of termination rate attributed the effect putatively to the high viscosity of the ionic liquid.[11] However, when analyzing our data, a general increase of the molar mass with the viscosity cannot be found for all ionic liquids investigated in polymerization of **BMA**. Nevertheless, the viscosity of the ionic liquids seems to exert a beneficial influence on polymerization.

Whereas the degrees of polymerization (X_n) obtained when polymerizing in 1-alkyl-3-methylimidazolium tetrafluoroborates (series **1a**−**h**), in 1-alkyl-3-methylimidazolium hexafluorophosphates (series **2a**−**f**), and in the 1-alkyl-3-methylimidazolium salts **4**, **6a**, and **7** tend to increase roughly with the increase in viscosity (Figure 4), all X_n obtained when using ionic liquids with 1-alkyl-2,3-dimethylimidazolium cations (**1i**, **1k**, **2i**, **2k**, and **6b**) are similar although the solvent viscosities differ significantly (Figure 5). Specific interactions between the cations and the anions in 1-alkyl-3-methyl imidazolium salts may be responsible for the observed viscosity dependence of X_n, while the additional methyl substituent at C-2 weakens these interactions between the ions. Nevertheless, the higher viscosity of 1-alkyl-2,3-dimethylimidazolium salts is reflected by higher X_n values of the polymers obtained in comparison with using their 1-alkyl-3-methylimidazolium analogues.

Moreover, the hexafluorophosphate **2a** (Figure 4), the tosylate **3** (X_n is about 2950), and the octyl sulfate **5** (X_n is about 1350) do not fit into the trend of an increase of X_n of the polymer with increasing viscosity of the ionic liquid used for polymerization. The polymers synthesized in **2a** and **3** show a high degree of polymerization although the viscosity of these ionic liquids is not as high. The high melting points of **2a** and **3** and locally ordered structures may favor the polymerization in these solvents. Different from the other imidazolium salts containing only small substituents at the anion, the relatively high viscosity of the octyl sulfate **5** is caused by the long alkyl chain at the anion, which may have a different effect on the polymerization.

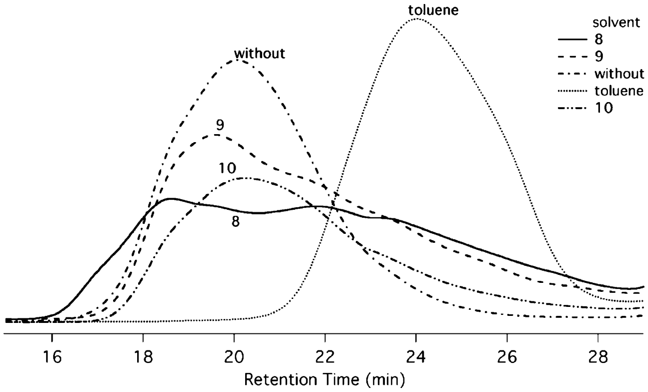


Figure 6. SEC chromatograms of poly(*n*-butyl methacrylate)s synthesized in **8**, **9**, **10**, toluene, and in bulk initiated with **AIBN** at 70 °C for 24 h.

The ionic liquids **8**, **9**, and **10** were used as reference in order to have a general impression on the role of the chemical nature of the cation on the polymerization. Again, much higher degrees of polymerization of poly(*n*-butyl methacrylate)s synthesized in the pyridinium salts **8** ($X_n \approx 300$) and **9** ($X_n \approx 390$) were found compared to the polymerization in toluene ($X_n \approx 220$) under otherwise identical conditions (Figure 6). The use of the *N*-alkyl-4-methylpyridinium salts tends to result in relatively low degrees of polymerization and very high polydispersities compared to the use of the analogously substituted 1-alkyl-3-methyl imidazolium tetrafluoroborate and hexafluorophosphate, although the viscosities of **8** and **9** are higher. Possibly, the benzylic methyl group gives rise to chain transfer side reactions, however, this should be verified in an independent study. In addition, X_n is lower when the polymer was synthesized in the pyridinium salts in comparison with the polymer made in bulk ($X_n \approx 1070$).

Also, poly(*n*-butyl methacrylate) synthesized in **10** (Figure 6) has only a rather moderate degree of polymerization ($X_n \approx 420$) although **10** exhibits by far the highest viscosity in our study (Table 2). This X_n value is higher as compared to solution polymerization in toluene ($X_n \approx 220$) and lower than that of the polymer made in bulk ($X_n \approx 1070$). Particular effects may play a role in this case, such as the low solubility of the monomer in **10** at the polymerization temperature or the well-known nonnegligible chain transfer constant of the ethylene glycol fragments present in the cation.[40] A significantly higher solubility of the monomer is observed in imidazolium and pyridinium salts. From these preliminary experiments, it seems that a broad range of ionic liquids is suited as solvents for free radical polymerization, however, imidazolium based ionic liquids are more appropriate.

As shown in Figure 7, the glass transition temperatures of the polymers increase significantly with increasing degree of polymerization for values of X_n below 400. Above this value, the glass transition temperature levels off. The lowest glass transition temperature is observed for the polymer made in toluene that is in agreement with the lowest value of X_n. The majority of the polymers synthesized in ionic liquids show a glass transition temperature similar to the one of the polymer obtained by bulk polymerization.

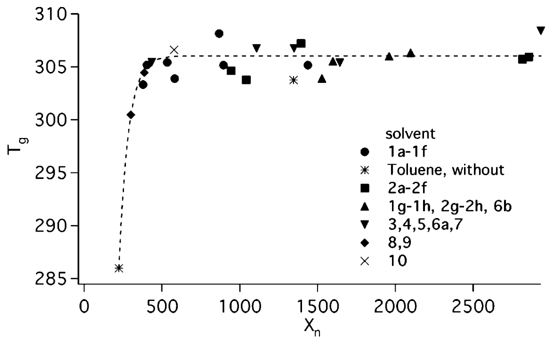


Figure 7. Glass transition temperature (T_g) as a function of the degree of polymerization (X_n) for poly(*n*-butyl methacrylate)s manufactured in toluene, ionic liquids, or in bulk.

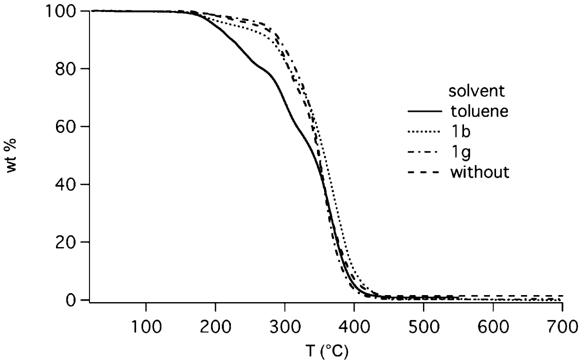


Figure 8. Weight loss of poly(*n*-butyl methacrylate)s manufactured in selected solvents when heated under nitrogen.

Thermogravimetric analysis indicates that in the temperature region between 200 °C and 350 °C thermal stability is lower for the polymer made in toluene compared to the samples made in ionic liquids or in bulk (Figure 8). No significant differences were found between the latter samples. The higher thermal stability of the polymers synthesized in ionic liquids might be explained by the higher degree of polymerization for these polymers leading to less volatile thermolysis fragments. Alternatively, a different ratio of termination by recombination and by disproportionation might be discussed.[54,55]

The use of ionic liquids as solvents in polymerization instead of classical solvents such as toluene offer attractive advantages, e.g., markedly higher degrees of polymerization, higher glass transition temperatures, and higher thermal stabilities. However, additional efforts are necessary for purification of the polymers and recovery of the precious ionic liquids after polymerization. In the case of low viscous ionic liquids, the majority can be conveniently recovered by simple decanting (see Table 3). More viscous ionic liquids and such that are solid at room temperature require extraction with a traditional solvent, e.g., methanol, to separate the polymer from the ionic liquid. The ionic liquid is easily recovered by subsequent evaporation of the methanol (see Table 3). This straightforward procedure allows to recover efficiently the ionic liquids even on the laboratory scale (Table 3), so that their recycling necesssary for practical applications, seems feasible.

Conclusions

Ionic liquids do not only offer some general advantages as new solvents, such as low volatility and nonflammability, they have also a beneficial effect on the polymerization. The use of ionic liquids results in higher molar masses of the polymers, which can exceed even the molar masses obtained by bulk polymerization notably. Consequently, the glass transition temperature of the polymers is increased and their thermal degradation is reduced in comparison with the polymer made by solution polymerization in toluene. The effects are a widespread phenomenon for ionic liquids of different cation and anion structure and are not limited to a few representatives. Nevertheless, significant differences in the molar mass and the polydispersity were found between the polymers synthesized in various ionic liquids, so that optimization of the polymerization requires a careful selection of the ionic liquid to be used. Imidazolium based ionic liquids are preferable over *n*-alkyl-4-methylpyridinium and aliphatic ammonium salts, as they exert a more advantageous effect on polymerization. High molar masses of polymers are favored by high viscosities of the imidazolium salts or by conducting polymerizations close to the melting temperature of the ionic liquids. One may speculate that this behavior is due to locally ordered structures, which favor the polymerization reaction under these conditions. Importantly, efficient recycling of the ionic liquids after polymerization, as needed for practical applications, is feasible by simple decantation and extraction procedures.

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Supporting Information Available: Text giving a discussion of the shear rate dependence of the viscosity of selected ionic liquids including a figure showing viscosity measured as function of shear rate at 23 °C for **2b**, **2d**, and **2i** and at 70 °C for **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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