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Aspects of Free Radical Polymerization of Styrene and *n*-Butylmethacrylate in Imidazolium Tosylates

Veronika Strehmel,[1]* *Eric Reynaud,*[1] *Hendrik Wetzel,*[2] *Eckhard Görnitz,*[2]
André Laschewsky[1,2]

Summery: A series of 1-alkyl-3-methylimidazolium tosylates was explored as new solvents for the free radical polymerization of *n*-butylmethacrylate and styrene. The use of these ionic liquids results in high yields and high molecular weights of the polymers, often even exceeding the molecular weights achieved in bulk polymerization. The obtained molecular weights and their distributions are sensitive to the structure of the ionic liquids, namely to substituents of the imidazolium ring. The broad and bimodal molecular weight distributions of the polystyrene made in the 1-alkyl-3-methylimidazolium tosylates is caused by a heterophase polymerization.

Keywords: ionic liquids; poly(butylmethacrylate); polystyrene; radical polymerization

Introduction

Solvents are crucial for free radical polymerizations because of the exothermic character of these reactions and the Trommsdorff-Norrish effect occurring in the absence of any solvent.[1–4] Ionic liquids have found an increased interest as new solvents for free radical polymerizations by virtue of their low vapor pressure.[5,6] Furthermore, free radical polymerization in ionic liquids results in polymers with higher molecular weights compared to traditional solvents.[7–16] The molecular weight can even exceed that of polymers obtained by polymerization in bulk.[10] Moreover, ionic liquids favor the copolymerization of monomers exhibiting strong difference regarding their polarity.[9,14–16]

Most ionic liquids that have been used in free radical polymerization of methacrylates contain 1-alkyl-3-methylimidazolium cations. Out of this group, 1-ethyl-3-methylimidazolium tosylate is particularly attractive because it is free of any halogen, and it is not sensitive to hydrolysis as the most common imidazolium tetrafluoroborates and hexafluorophosphates.[17–20] Furthermore, the use of 1-ethyl-3-methylimidazolium tosylate as solvent for polymerization of *n*-butylmethacrylate results in poly (*n*-butylmethacrylate) with an extremely high molecular weight.[10] Moreover, 1-ethyl-3-methylimidazolium tosylate was shown to be an efficient solvent for copolymerizing of *n*-butylmethacrylate with a zwitterionic sulfobetaine methacrylate.[16] Previous studies demonstrated that the variation of the alkyl chain N-bound at the imidazolium ring in tetrafluoroborate and hexafluorophosphate ionic liquids affects the structures of both the homo- and copolymers of *n*-butylmethacrylate and a hydrophilic zwitterionic methacrylate when synthesized in these ionic liquids.[10,11,16] Therefore, we have gained interest to explore the analogous substitution effects of the 1-alkyl-3-methylimidazolium tosylates and their use in free radical polymerization. Because long alkyl substituents tend to result in both high melting points and high viscosities of the imidazolium salts, we have focused on the investigation of free radical polymerization in 1-alkyl-3-methyl-imidazolium

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[1] University of Potsdam, Institute of Chemistry, Applied Polymer Chemistry, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam-Golm, Germany
E-mail: vstrehme@uni-potsdam.de

[2] Fraunhofer Institute for Applied Polymer Research, D-14476 Potsdam-Golm, Geiselbergstr. 69, Germany

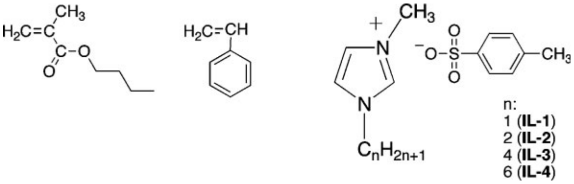

Figure 1.
Chemical structure of the monomers *n*-butylmethacrylate and styrene and the 1-alkyl-3-methylimidazolium tosylates **IL-1**, **IL-2**, **IL-3**, and **IL-4** used as solvents for free radical polymerization.

tosylates with C_1 to C_6 substituents (Figure 1).[9,10,21]

For these investigations, *n*-butylmethacrylate and styrene were selected as model monomers. Whereas styrene is a model for a non-polar monomer substituted with an aromatic ring, *n*-butylmethacrylate is aliphatic and slightly more polar due to the ester structure. These structural differences of the monomers may influence their interactions with the ionic liquid surrounded during the polymerization. In contrast to styrene, the ester moiety of *n*-butylmethacrylate may hydrogen bond with the acidic hydrogen atom at C-2 of the imidazolium ring.

Selected Physical Properties of 1-Alkyl-3-methylimidazolium Tosylates

Physical properties of the imidazolium tosylates such as melting behavior and viscosity were studied as they may be important for their use as solvents for polymerization. The tosylates **IL-1** to **IL-4** are solids at room temperature. Although the imidazolium tosylates substituted with either butyl (**IL-3**) or hexyl substituents (**IL-4**) are well crystallizing compounds, the short chain analogues **IL-1** and **IL-2** are semicrystalline. This means they become glassy upon cooling but recrystallize when reheated. Furthermore, **IL-4** shows an additional mesomorphic phase transition. Interestingly, the melting point of the ionic liquids does not evolve monotonously with the increase of the alkyl chain length. Thus, 1,3-dimethylimidazolium tosylate (**IL-1**) with the smallest substituent has the highest melting point with 95 °C. An increase in the length of one alkyl substituent reduces the melting point notably to 53 °C for **IL-2** caused by the unsymmetric substituents at the imidazolium ring. A further increase of the alkyl chain length results in higher melting points as compared to **IL-2**, e.g. 69 °C for **IL-3**, and 88 °C for **IL-4** (Table 1). The melting point may limit the thermal window for polymerization experiments.

The viscosities of the imidazolium tosylates depend only slightly on the length of the alkyl substituents (Table 1). Viscosity measurements at the polymerization temperature (70 °C) are limited to **IL-2** and **IL-3** because of the high melting points of **IL-1** and **IL-4** and the crystallization tendency during shearing of the melt (Table 1). The viscosities do approximately double during

Table 1.
Water content, glass transition temperature (T_g), temperature for recrystallization ($T_{recryst}$), melting point (T_m) (DSC heating rate 5 K/min), and viscosity at a shear rate of 10 s^{-1} (η_{10}) of 1-alkyl-3-methylimidazolium tosylates at 70 °C and 100 °C (n.d. = not determined).

ionic liquid	water content (wt-%)	T_g (°C)	$T_{recryst}$ (°C)	T_m (°C)	η_{10} (mPa s) at 70 °C	η_{10} (mPa s) at 100 °C
IL-1	n.d.	−38	4	95	n.d.	n.d.
IL-2	1.9	−47	12	53	69	43
IL-3	2.8	–	–	69	77	38
IL-4	0.4	–	–	56 (T_{m1}) 88 (T_{m2})	n.d.	42

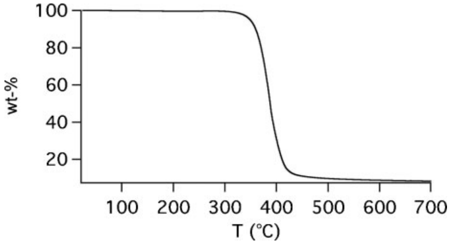

Figure 2.
Thermogravimetric analysis of **IL-2** measured under nitrogen using a heating rate of 20 K/min.

cooling from 100 °C to 70 °C. These values are more than two times higher as compared with the viscosities of analogous imidazolium hexafluorophosphates and more than five times higher than the viscosities of analogous imidazolium tetrafluoroborates.[10] Nevertheless, the viscosity is low enough to enable these ionic liquids as solvents for polymerization processes.

Thermogravimetric analysis of imidazolium tosylates demonstrates the low vapor pressure of the ionic liquids and their high thermal stability under nitrogen (Figure 2). Thermal onset starts only above 300 °C. The TGA curve depicted in Figure 2 is representative for the imidazolium tosylates investigated in this work.

Poly(*n*-butylmethacrylate)

The polymerization of *n*-butylmethacrylate initiated by *N,N′*-azobisisobutyronitrile (AIBN) proceeds smoothly in the imidazolium tosylates. The polymerization was carried out up to high conversion in all examples. For the examples investigated, a reaction time of 8 h was not enough to have an almost completed reaction. Thus, we used a reaction time of 24 h because most of the examples demonstrate a significant higher conversion under such reaction conditions. A further study will be carried out to collect data between 8 h and 24 h to understand the entire reaction in more detail. As expected, the yields and the average molecular weights of poly(*n*-butylmethacrylate) are significantly higher when it is polymerized in the 1-alkyl-3-methylimidazolium tosylates compared to the use of toluene as solvent under otherwise similar conditions (Table 2, Figure 3). In fact, yields and molecular weights compare even favorably with the polymer obtained by bulk polymerization. Characteristically, the polydispersities of the polymers made in bulk or in the ionic liquids are higher than when made in toluene. Remarkably, employing **IL-2** and **IL-3** as reaction medium results in yields and weight average molecular weights that exceed even markedly the values obtained if the polymerization was carried out without any solvent. The highest values are obtained when polymerizing in **IL-2**. In the case of using **IL-3**, the particularly high polydispersity observed is due to a certain content of a relatively low molecular weight fraction (Figure 3).

The lower yield of poly(*n*-butylmethacrylate) obtained by polymerization in **IL-4** may be caused by difficulties during purification of the polymer. This effect was also reported in the case of other ionic liquids substituted with a longer alkyl chain at one nitrogen atom of the imidazolium ring.[10]

Table 2.
Yield, number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity of poly(*n*-butylmethacrylate) synthesized in toluene, in the absence of any solvent or in the imidazolium tosylates **IL-2, IL-3**, **IL-4** using a monomer concentration of 10 wt-% and 1 mole-% AIBN relative to the monomer (polymerization time: 24 h).

Solvent	T (°C)	Yield (%)	M_n (kDalton)	M_w (kDalton)	Polydispersity
Toluene	70	16	32	49	1.5
without	70	81	152	460	3.0
IL-2	70	93	417	1308	3.1
IL-3	70	98	120	829	7.0
IL-4	80	63	69	158	2.3

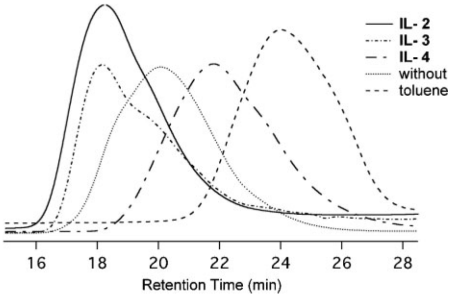

Figure 3.
GPC curves poly(*n*-butylmethacrylate) made in **IL-2**, **IL-3**, and **IL-4**, in toluene, or in the absence of any solvent using a monomer concentration of 10 wt-%, 1 mole-% AIBN relative to the monomer and 70 °C (**IL-2**, **IL-3**, toluene, and without solvent,) or 80 °C (**IL-4**), (polymerization time: 24 h) after purification by Soxhlet extraction with methanol for 4 h.

The gelpermeation chromatograms (GPC) of poly(*n*-butylmethacrylate) in Figure 3 illustrate the different molecular weight distributions obtained. As a general trend, the molecular weight decreases with increasing length of the alkyl substituents at the imidazolium ring. When imidazolium tosylates are used for the synthesis of poly(*n*-butylmethacrylate), the molecular weight distributions are similarly broad or even broader compared to bulk polymerization (Figure 3). The shoulders visible in the chromatograms of poly(*n*-butylmethacrylate) synthesized in **IL-2** and **IL-3** suggest bimodal distributions. A careful analysis of the molecular weight distribution of the polymer made in bulk shows a weak shoulder, too, suggesting also bimodality. In any case, the high yields and the high molecular weights of poly(*n*-butylmethacrylate) made in the ionic liquids demonstrate that imidazolium tosylates are efficient solvents for polymerization.

Polystyrene

The dissolution of styrene in the ionic liquids **IL-1** to **IL-4** provides slightly cloudy solutions at the polymerization temperature. Therefore, polymerization of styrene in these ionic liquids apparently occurs as heterophase reaction. As for the polymerization mixtures of *n*-butylmethacrylate in imidazolium tosylates, the polymerization of styrene results in high molecular weight polymers in high yields (Table 3).

Again, the yields and the average molecular weights of polystyrene made in the ionic liquids exceed significantly the values obtained when using toluene as solvent under otherwise similar conditions for the polymerization experiments. Also, the molecular weight of polystyrene made in the ionic liquids **IL-1** - **IL-4** exceeds the molecular weight of the polymer obtained by bulk polymerization. However, different from poly(*n*-butylmethacrylate), the yields of polystyrene obtained in the ionic liquids are somewhat lower than in bulk. This may be caused by the influence of the ionic liquid on the polymerization process.

Noteworthy, the polydispersities of the polymers made in the ionic liquids are very

Table 3.
Temperature used for the polymerization experiments (T), yield, number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity of polystyrene synthesized in toluene, imidazolium tosylates **IL-1** - **IL-4**, which are depicted in Figure 1, or in the absence of any solvent using a monomer concentration of 10 wt-% and 1 mole-% AIBN relative to the monomer (polymerization time: 24 h).

Solvent	T (°C)	Yield	M_n (kDalton)	M_w (kDalton)	Polydispersity
Toluene	70	37	3.4	9.6	2.8
without	70	91	35	118	3.4
IL-1	70	60	61	597	9.8
IL-2	70	53	50	654	13.2
IL-2	80	72	68	571	8.4
IL-2	90	71	49	444	9.1
IL-2	120	72	15	114	7.8
IL-3	70	59	48	363	7.5
IL-4	80	76	45	235	5.2

high (Table 3). In fact, bimodal molecular weight distributions are clearly seen for polystyrene in several cases (Figure 4), namely when employing **IL-1** and **IL-2**. Moreover, when employing **IL-3** and **IL-4**, the GPC chromatograms show shoulders, which suggest even more complex molecular weight distributions for these systems. This is attributed to the heterogeneous character of the styrene polymerization in the imidazolium tosylates. In fact, the lower molecular weight fraction of polystyrene seems to compare well to the polymer made in bulk. Beside the relatively low molecular weight fraction, a significant amount of a high molecular weight fraction is seen in the GPC chromatograms, in particular when the polymer is made in **IL-1** and **IL-2**. These results strongly point to a heterogeneous polymerization process for styrene in these ionic liquids. The two phases may be small droplets of a bulk styrene phase dispersed in the ionic liquid phase saturated with styrene. The bulk phase of the styrene results in the molecular weight fraction, which is comparable with the polymer obtained by classical bulk polymerization. The other styrene fraction, which is presumably dissolved in the ionic liquid, gives the higher molecular weight fraction. Accordingly, styrene behaves very different from *n*-butylmethacrylate that is readily soluble in the imidazolium tosylates in the concentration range of interest. The better compatibility of the *n*-butylmethacrylate can be attributed to its ester moiety, which may interact more strongly with the ionic liquid moieties due to its high dipole moment or due to the formation of hydrogen bonds with the slightly acidic hydrogen at C-2 of the imidazolium ring. Such interactions do not exist in the case of styrene. This exemplifies the complexity of the polymerization in ionic liquids.

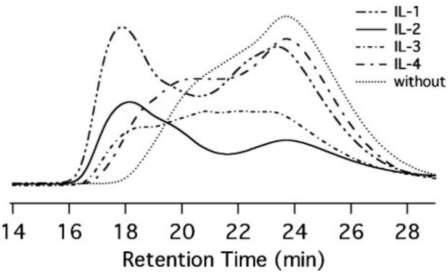

Figure 4.
GPC chromatograms of polystyrene made in **IL-1**, **IL-2**, **IL-3**, **IL-4**, or in the absence of any solvent using a monomer concentration of 10 wt-%, 1 mole-% AIBN relative to the monomer and 70 °C (**IL-1** - **IL-3**, without solvent) or 80 °C (**IL-4**) (polymerization time: 24 h) after purification by Soxhlet extraction with methanol for 4 h.

A very broad molecular weight distribution without clearly resolved fractions in the GPC chromatograms is obtained when **IL-3** is used as solvent for polymerization of styrene. The polystyrene contains a higher amount on a lower molecular weight fraction if the polymerization is carried out in **IL-4**.

The complex molecular weight distributions seem to result from the superposition of two opposite effects. On the one hand, the increasing length of the alkyl substitutent increases the compatibility of the monomer with the ionic liquid. Consequently, if the fraction of styrene present in the ionic liquid increases also an increase is found in the fraction of the high molecular weight polymer. On the other hand, an increasing length of the alkyl substituents of the ionic liquid tends to decrease the molecular weight obtained, as exemplified above for the polymerization of *n*-butylmethacrylate in the ionic liquids **IL-2** - **IL-4**. It seems that the second effect prevails so that overall the average molecular weight decreases with increasing substituent length in the series **IL-1** - **IL-4**.

Noteworthy, the polymerization temperature also influences the molecular weight and the molecular weight distribution of the polystyrene obtained by polymerization in **IL-2** (Figure 5). An increase in the polymerization temperature from 70 °C to 90 °C results in an increase in the polymer fraction that has a molecular weight comparable with that of bulk polymerization. This finding would go along with a heterogeneous character of the polymerization, implying that the compatibility of the monomer or of the

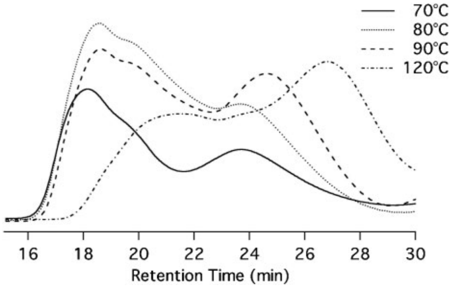

Figure 5.
GPC chromatograms of polystyrene samples made in **IL-2** at 70 °C, 80 °C, 90 °C, and 120 °C using a monomer concentration of 10 wt-% and 1 mole-% AIBN relative to the monomer (polymerization time: 24 h) after purification by Soxhlet extraction with methanol for 4 h.

growing polymer chains with the ionic liquid decreases at higher temperature. Such a phase behaviour of polymers in ionic liquids with a miscibility gap at temperatures above the lower critical solution temperature was reported before.[22] However, when the polymerization temperature is increased to 120 °C termination reaction seems to be significantly increased resulting in a polymer fraction, which has a lower molecular weight than obtained by bulk polymerization. Again, these observations illustrate that the use of ionic liquids as polymerization media shows high complexity.

Degree of Polymerization of Poly(*n*-butylmethacrylate) and Polystyrene

The degree of polymerization is the preferred parameter to compare the different polymers, such as poly(*n*-butylmethacrylate) and polystyrene because of the different molecular weight of the monomer segments of these polymers. Dividing the average molecular weight (M_n and M_w) by the molecular weight of the monomer segment results in the degree of polymerization (X_n and X_w), which gives information about the average number of monomer segments containing in the polymer chain. As expected from the high polydispersity of the polymer samples, the degrees of polymerization related to the weight average molecular weights (X_w) are significantly higher compared to the degrees of polymerization based on the number average molecular weights (X_n) (Figure 6). These values are generally higher for poly (*n*-butylmethacrylate) in comparison with

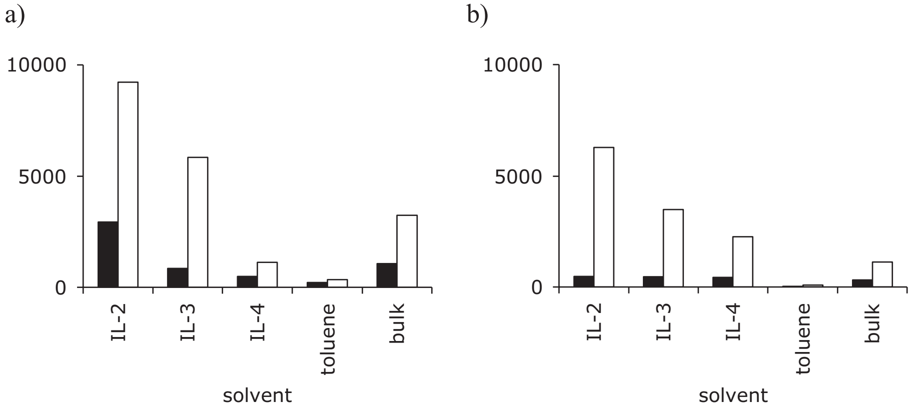

Figure 6.
Degree of polymerization related to the number average molecular weight (X_n) (black column) and weight average molecular weight (X_w) (white column) for poly(*n*-butylmethacrylate) (a) and polystyrene (b) synthesized in the ionic liquids **IL-2**, **IL-3**, and **IL-4**, in toluene, and in the absence of any solvent using a monomer concentration of 10 wt-%, 1 mole-% AIBN relative to the monomer and 70 °C (**IL-2**, **IL-3**, toluene, bulk) or 80 °C (**IL-4**) (polymerization time: 24 h) after purification by Soxhlet extraction with methanol for 4 h.

polystyrene if the same solvent was used for polymerization. This may be caused by the different ratio of the rate constants for propagation and termination. These rate constants are known for traditional solvents used for polymerization. According to the literature, the ratio of the rate constants for the propagation reaction in respect to the termination reaction is higher for *n*-butylmethacrylate than for styrene.[23–29] The degree of polymerization is further influenced by the substituents bound at the imidazolium ring of the ionic liquid. Whereas X_w decreases by substitution at the imidazolium ring with a longer alkyl chain in the case of both polymers, differences exist between poly(*n*-butylmethacrylate) (Figure 6a) and polystyrene (Figure 6b) regarding the X_n-values. The X_n-values exhibit a similar tendency as the X_w-data particular for poly(*n*-butylmethacrylate). In contrast to this, the X_n-values tend to become independent on the imidazolium tosylate structure in the case of polystyrene although the X_w-values exhibit a significant influence of the substituents at the imidazolium ring of the ionic liquid.

Glass Transition Temperature of the Polymers

Differences in the chemical structure of the polymers typically are reflected in differences in their glass transition temperature. This can be seen in Table 4 for poly(*n*-butylmethacrylate) and polystyrene. The particularly high molecular weights of these polymers made in the ionic liquids result in higher glass transition temperatures as compared to the polymers synthesized in toluene. The glass transition temperatures of the polymers synthesized in the ionic liquids are comparable with those of the polymers made by bulk polymerization or these values are even higher in some examples. Interestingly, the notable content on the lower molecular weight fraction in polystyrene does not decrease the glass transition temperature of this polymer. The lower glass transition temperature of poly(*n*-butylmethacrylate) made in **IL-4** is attributed to the lower molecular weight of this polymer.

Table 4.
Glass transition temperature (T_g) of poly(*n*-butylmethacrylate) and polystyrene synthesized in various solvents.

solvent	poly(*n*-butylmethacrylate) T_g (°C)	polystyrene T_g (°C)
toluene	11	85
without	31	92
IL-2	35	102
IL-3	34	103
IL-4	26	103

Conclusion

Although 1-alkyl-3-methylimidazolium tosylates are solid at room temperature, these ionic liquids are highly efficient solvents for free radical polymerization of both *n*-butylmethacrylate and styrene at moderate reaction temperatures, e.g. at 70 °C. The ester group of the methacrylate monomer interacts more strongly with these ionic liquids than the aromatic styrene does. The weaker interaction of the latter monomer seems to result in a heterophase polymerization with small styrene domains on the one hand, and styrene dissolved in the ionic liquid phase on the other hand. This model is supported by pronounced bimodal molecular weight distributions in several cases. Furthermore, the molecular weight and the molecular weight distribution are strongly influenced by the length of the *N*-alkyl substituent at the imidazolium ring. A careful selection of the ionic liquid structure will therefore allow to influence the structure of the polymers obtained by free radical polymerization in ionic liquids.

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