Free Radical Copolymerization of Methyl methacrylate and *N*-Phenyl maleimide in 1-Butyl-3-methylimidazolium tetrafluoroborate

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Summary: We investigated the free radical copolymerization of methyl meth-acrylate (MMA) and *N*-phenyl maleimide (NPI) in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4). Dimethyl formamide (DMF) was used as reference solvent. The influence of the ionic liquid (IL) on the polymerization rate r_p, the molecular weights M_n, the copolymer composition, the glass-transition temperature and the rheological behavior of the copolymers was studied. In [BMIM]BF_4 r_p strongly decreases with increasing initial concentration of NPI and becomes even lower than in DMF for 70 to 90 mol% NPI in the monomer feed. In addition, M_n of the copolymers produced in the IL strongly decreases with increasing NPI content, but is always higher than in DMF.

Keywords: free radical copolymerization; ionic liquids; molecular weight distributions; polymerization rates; reactivity ratios

Introduction

Within the last decade ionic liquids (ILs) attracted enormous attention. In general, ILs consist of a bulky organic cation and a complex anion and are liquid at temperatures below 100 °C. Ionic liquids have some characteristic chemical and physical properties which can be varied in a wide range by appropriate combination of cations and anions. Very interesting characteristics of ILs are their high thermal stability, their wide liquid range, their partly bad miscibility with water and their low vapor pressure.[1]

While there is already a large number of papers dealing with the application of ionic liquids in organic syntheses, their use as reaction media for radical polymerizations is still rather limited[2–27]. Studies on the polymerization kinetics show that ILs strongly influence the polymerization rate r_p and the properties of the obtained polymers. An enhancement of r_p and the molecular weights which can be observed for the few studied polymerizations in ILs, exceeds the previously discussed influence of conventional organic solvents.

For the polymerization of methyl methacrylate and glycidyl methacrylate in three different ionic liquids – [BMIM]BF_4, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6), and 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM]$EtSO_4$) – an increase of the propagation rate constant k_p was observed with increasing IL content in the reaction mixture using pulsed laser polymerization (PLP) technique[2–4]. Haddleton et al.[4] and we[2] presume that the increase of the propagation rate constant k_p is due to the higher polarity of the reaction medium caused by the addition of ionic liquids which leads to a lowering of the activation energy of propagation E_A.

As described by Haddleton et al.[4] there is a strong influence of [BMIM]PF_6 on the

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rate coefficient of termination k_t for the polymerization of MMA, too. It was found that k_t decreases by one order of magnitude with increasing IL content in the reaction mixture. These results seem to verify the assumption made in[3] and[5] that the high polymerization rate is due to both the diffusion-controlled termination, reflecting the high viscosity of the used solvent and the increase of k_p.

Recently the free radical homopolymerization of methacrylates[2–11,13–18,27], styrene (S) [5–7], 2-hydroxyethyl methacrylate[6–8], vinyl acetate[7,8], 1-vinylimidazole[8], acrylonitrile (AN)[7,12,19,27], 1-vinyl-3-ethylimidazolium salts[27], a highly zwitterionic methacrylate and its copolymerization with butyl methacrylate[22,23] as well as the free radical copolymerization of MMA with S[20,21] and AN[14,19] and the free radical copolymerization of AN with S[14,24,25], MMA [19] and methyl acrylate[26] in different 1,3-dialkylimidazolium and tetraalkylphosphonium based ionic liquids were investigated.

This contribution deals with the free radical copolymerization of methyl methacrylate (MMA) with *N*-phenyl maleimide (NPI) in $[BMIM]BF_4$. NPI is known to be a relatively strong electron acceptor monomer ($Q = 3.23$, $e = 1.48$)[28]. The Q- and e-values of MMA are $Q = 0.78 \pm 0.06$ and $e = 0.40 \pm 0.08$[29]. There are different opinions whether MMA in the case of the copolymerization with NPI acts as a donor monomer [30,31] or a neutral monomer[32,36]. Elsabee et al.[30] found that the copolymerization of MMA/NPI is dependent on the type of solvent. The reactivity ratios were reported to vary appreciably with the type of solvent[30].

As the IL is a quite polar solvent it possibly influences the copolymerization behavior of the MMA/NPI system. Thus we investigated the influence of $[BMIM]BF_4$ on the polymerization rate, the molecular weights as well as the molecular weight distributions, the glass-transition temperature, the copolymer composition and the rheological behavior.

Experimental Part

MMA (FLUKA) was distilled to remove inhibitors, NPI (ALFA AESAR) was recrystallized from methanol. 2,2′-azobisisobutyronitrile (AIBN, MERCK) was recrystallized from diethyl ether/ethanol before use. The solvents $[BMIM]BF_4$ (purum ≥98%, Lot-No.: 99/602, SOLVENT INNOVATION GMBH) and DMF were used as received.

The following reaction setup was used: comonomers (1.5 g) and AIBN (3.3 wt.-%) were weighed into ampoules and 6 mL of solvent ($[BMIM]BF_4$ or DMF) were added separately. The ampoules were purged with nitrogen and then sealed. Polymerizations were carried out in a heating block at 60 °C and stopped by fast cooling of the reaction mixture. Products were received by precipitation in methanol, filtering and drying under vacuum to constant weight. To completely purify the polymers synthesized in $[BMIM]BF_4$, they were washed with water for 24 hours, filtered and dried under vacuum to constant weight.

Molecular weights were determined via size exclusion chromatography (SEC) measurements which were carried out on a KNAUER size exclusion chromatograph in tetrahydrofurane (THF) at 25 °C. A four columns system (mixed A from PL) with a differential refractometer detector was used for all polymer samples except the PNPI samples. The PNPI samples were measured on a WATERS size exclusion chromatograph in THF at 25 °C because of their very low molecular weights. A two columns system (mixed C from PL) with a differential refractometer detector was used. Polystyrene standards were used for calibration.

Copolymer compositions were determined by elemental analysis (C, H, N, O). Elemental Analysis VarioEL (ELEMENTAR ANALYSE-SYSTEME GMBH) was used, calibrated with acetanilide and benzoic acid.

Glass-transition temperatures were measured in a differential scanning calorimeter DSC 25 (METTLER TOLEDO).

Rheological measurements were done with a Dynamic Analyzer RDA II

(RHEOMETRICS SCIENTIFIC). The measurement setup is a rheometer with a plate-plate geometry (plate diameter: 13 mm; plate material: aluminium).

Results and Discussion

Investigations on the copolymerization behavior of MMA/NPI in [BMIM]BF_4 were carried out by varying the composition of the monomer feed. We found that in dependence of the comonomer composition the reaction mixture was either heterogeneous or homogeneous.

Heterogeneous reaction mixtures were observed for the homopolymerization of both MMA and NPI as well as the copolymerization of MMA/NPI with 10 to 20 mol% of NPI in the monomer feed. For these comonomer compositions the polymerization proceeds under precipitation of the polymer. In case of the copolymerization with 20 mol% NPI in the monomer feed the precipitation does not start until a conversion of about 50% is reached. The fact that the MMA homopolymerization in [BMIM]BF_4 proceeds under precipitation is different from what we found earlier.[15] Using [EMIM]$EtSO_4$ as solvent a strong gelation of the reaction mixture can be observed, but no precipitation of the polymer occurs.[15] When the copolymerization of MMA/NPI is carried out with a NPI content of 30 to 90 mol% in the monomer feed, the reaction mixture stays homogeneous independent of the conversion. Therefore in this range of monomer feed compositions the polymerization can be carried out in solution. As most of the comonomer compositions result in a solution polymerization DMF was used as reference solvent.

From the conversion-time curves shown in Figure 1 it can be seen that using [BMIM]BF_4 instead of DMF as solvent for the copolymerization of MMA/NPI mostly results in higher conversion and therefore a higher overall polymerization rate r_p. In case of the MMA/NPI copolymerization in [BMIM]BF_4 r_p strongly decreases with increasing NPI content in the monomer feed.

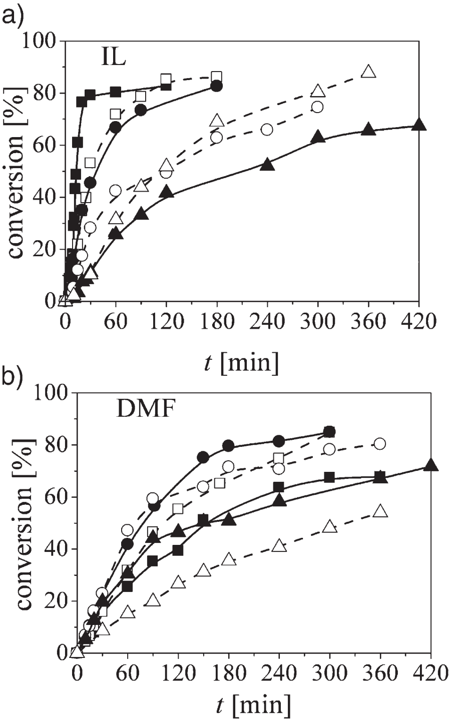


Figure 1.
Conversion-time curves of the MMA/NPI copolymerization in a) [BMIM]BF_4 and b) DMF with 0 mol% (■), 20 mol% (□), 40 mol% (●), 60 mol% (○),80 mol% (▲) and 100 mol% (△) NPI in the monomer feed. Reaction conditions: 1.5 g monomer feed, 3.3 wt.-% AIBN, 6 mL solvent, $T = 60\,^{\circ}C$.

In Figure 2 it can clearly be seen that the dependence of r_p on $x_{NPI,monomer}$ is strongly influenced by the used solvent. For the MMA/NPI copolymerization carried out in [BMIM]BF_4 r_p strongly decreases with increasing NPI content in the comonomer mixture. A similar effect was found for the copolymerization of the methacrylates with AN where the polymerization rate strongly decreased with increasing AN content in the monomer feed.[14] This finding was explained by the great difference in r_p of the homopolymerizations of the methacrylates and AN. We found that the IL always had a stronger influence on the homopolymerizations of the methacrylates which induced higher polymerization rates.[14]

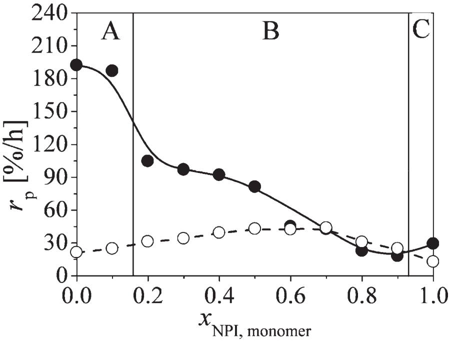
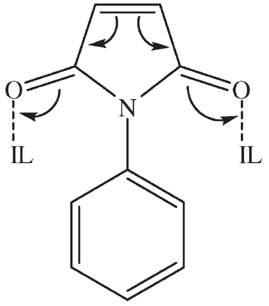


Figure 2.
Polymerization rate r_p in dependence of the NPI content in the monomer feed for the MMA/NPI copolymerization in $[BMIM]BF_4$ (●) and DMF (○). A and C: polymerization in the IL under precipitation of the polymer, B: solution polymerization in the IL. Reaction conditions: see Figure 1.



Scheme 1.
Schematic description of the H-bonds between NPI and $[BMIM]BF_4$ which lead to a decrease of the electron density of the C=C-double bond.

This can also be observed for the MMA/NPI system. The homopolymerization of MMA is more affected by the presence of $[BMIM]BF_4$ than the NPI homopolymerization. Therefore the MMA homopolymerization in $[BMIM]BF_4$ ($r_p = 191\%/h$) is about 6.6 times faster than the homopolymerization of NPI in $[BMIM]BF_4$ ($r_p = 29\%/h$). This would explain the strong decrease of r_p with increasing $x_{NPI,monomer}$.

The influence of the IL on the polymerization rate strongly r_p decreases with increasing NPI concentration in the initial comonomer mixture. In an earlier paper we described that interactions between monomers and ILs occur which are visible in a frequency shift to lower wavenumbers of the carbonyl stretching mode in passing from pure MMA to MMA/IL mixtures.[2] With Monte-Carlo- and dynamical simulations we were recently able to show that these interactions are due to hydrogen bonds formed between monomer molecules and both the anion and the cation of the IL.[33] For monomers bearing a carbonyl group the strongest H-bonds were calculated to occur between the imidazolium-cation of the IL and the carbonyl group of the monomer. For methacrylates the increase of the polymerization rate can be explained with these strong H-bonds. NPI even has two carbonyl groups. The strong H-bonds between the C=O-groups and the protons of the cations lead to a decrease of the electron density of the C=C-double bond (Scheme 1) and therefore NPI is a stronger acceptor monomer when it is dissolved in ILs.

The low electron density of the C=C-double bond in ILs leads to strong interactions between the NPI monomer and the BF_4^- anion of the IL. The partial complexing of the NPI monomer with the BF_4^- anion of the IL can reduce the reactivity at the polymerization. This most likely results is a hindrance of the reaction between NPI and polymer radicals or even initiator radicals and the copolymerization of MMA/NPI is therefore strongly decelerated.

In addition it is noteworthy that in the area with $x_{NPI,monomer} = 0.7–0.9$ the overall polymerization rate r_p of the MMA/NPI copolymerization in the IL runs through a minimum and is even lower than in DMF (Figure 2). This minimum of r_p at $x_{NPI,monomer} = 0.9$ can be explained as follows. The dependency of r_p on $x_{NPI,monomer}$ can be divided into three different stages A, B and C (Figure 2).

In stage A the polymerization proceeds under precipitation which leads to a stronger hindrance of the termination reaction. Additionally the termination reaction is also hindered because of the relatively high viscosity of the ionic liquid. Due to these two facts the radical concentration is supposed to be higher than for an analogue solution polymerization. This increased radical concentration leads to the high r_p values which can be found in stage A.

In stage B (Figure 2) the MMA/NPI copolymerization in [BMIM]BF_4 can be carried out in solution. Thus only the hindrance of the termination reaction due to the increased viscosity of the system and the increasing interaction of the NPI with the BF_4^- anion have an influence on r_p which leads to the strong decrease of r_p that can be observed when going from stage A to stage B. Within stage B a nearly linear decrease of r_p with increasing NPI content in the reaction mixture can be observed which is due to the fact that the homopolymerization of NPI is so much slower than the MMA homopolymerization. The homopolymerization of NPI (stage C, Figure 2) is accelerated again because it proceeds under precipitation of the polymer.

In case of the MMA/NPI copolymerization in DMF which is a solution polymerization in the whole range a maximum of r_p was found at $x_{\mathrm{NPI,monomer}} = 0.7$ which is in good agreement with our previous work.[34]

The number average molecular weights M_n are influenced by the presence of [BMIM]BF_4 in the reaction mixture, too (Figure 3). It is obvious that M_n is higher when the IL is used for the MMA/NPI copolymerization instead of DMF. But the molecular weights strongly decrease with increasing NPI content in the copolymer. This finding is in good agreement with the results concerning the overall polymerization rate r_p of the copolymerization of MMA/NPI in [BMIM]BF_4. In Figure 3 M_n for PNPI produced in the ionic liquid is missing because the polymer was found to be insoluble in THF.

Taking together the results depicted in Figures 2 and 3 the most significant influence of the ionic liquid on r_p and M_n can be found when the copolymerization is carried out with low amounts of NPI in the monomer feed. The more the NPI content in the reaction mixture is increased the more the influence of [BMIM]BF_4 on r_p and M_n seems to decrease.

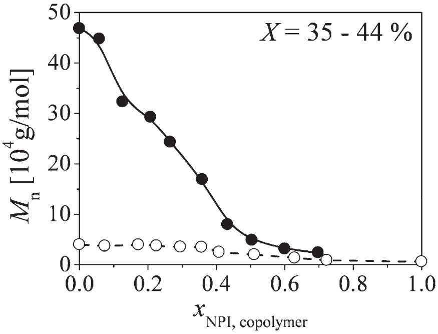


Figure 3.
Number average molecular weights M_n of P(MMA-*co*-NPI) synthesized in [BMIM]BF_4 (●) and in DMF (○) in dependence of the NPI content $x_{\mathrm{NPI,copolymer}}$ in the copolymer. M_n was determined via SEC using THF as solvent. Polystyrene standards were used for calibration; conversion: 35–44%. Reaction conditions: see Figure 1.

One reason that the number average molecular weights M_n of the products polymerized in the IL are generally higher than those of the copolymers received in DMF is the relatively high viscosity of [BMIM]BF_4. As already described in literature [3-5] due to the high viscosity the diffusion control of the termination reaction is strongly increased and therefore the rate constant of termination k_t is strongly decreased. This diffusion-controlled termination reaction can be considered to be the main factor of the increased M_n.

The results summarized in Table 1 clearly show that the polydispersities of P(MMA-*co*-NPI) received from the MMA/NPI (70/30 mol%) copolymerization in DMF do not strongly change with increasing conversion. In contrary the products received from the analogue reaction carried out in [BMIM]BF_4 have increased polydispersities when higher conversions are reached.

To better visualize this increase of the polydispersities and therefore the broadening of the molecular weight distributions (MWDs) with increasing reaction time and conversion, respectively, we standardized the MWDs by multiplying $w(\log M)$ with the degree of conversion (d.o.c.). The resulting standardized MWDs are depicted

Table 1.
Conversions and polydispersities of P(MMA-*co*-NPI) received from the MMA/NPI (70/30 mol%) copolymerization in $[BMIM]BF_4$ and DMF.

$[BMIM]BF_4$			DMF		
t [min]	conversion [%]	*Pd*	*t* [min]	conversion [%]	*Pd*
5	4	2.1	10	6	2.2
10	15	2.1	20	12	2.1
20	37	2.1	30	22	2.0
30	49	2.1	60	37	2.1
60	71	2.5	94	50	2.0
90	76	2.8	180	71	2.1
180	85	4.8	300	86	2.5

in Figures 4a and 4b. It can clearly be seen that a broadening to lower log *M* values with increasing conversion occurs when the copolymers are synthesized in [BMIM]BF4 (Figure 4a).

In case of the MWDs of P(MMA-*co*-NPI) received from the copolymerization in DMF a broadening to lower log *M* values with increasing conversion can also be observed (Figure 4b), but it is not so

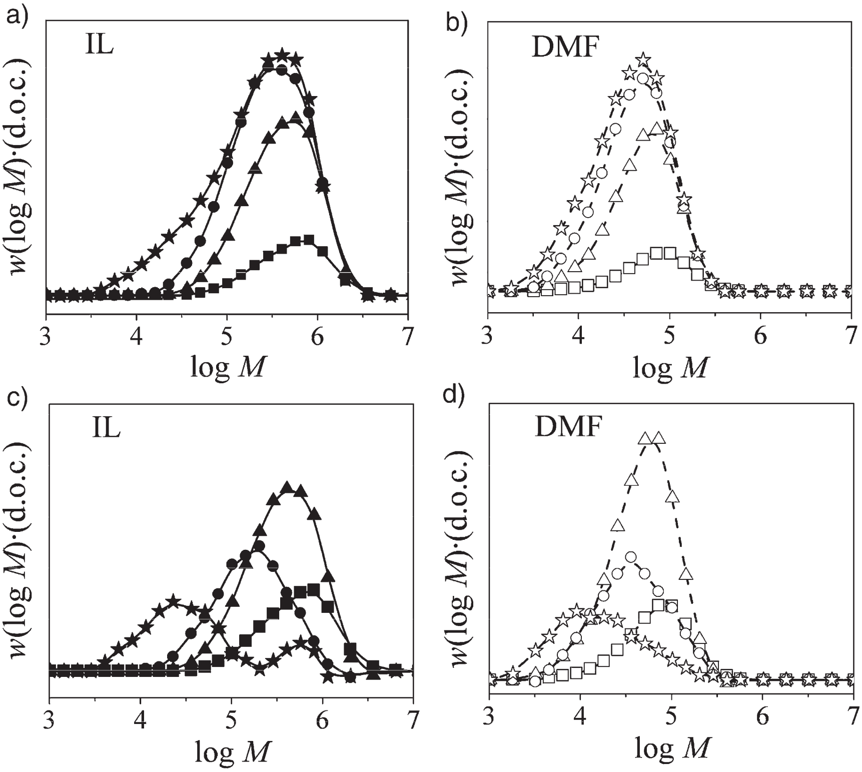


Figure 4.
Molecular weight distributions (MWDs) of the products of the MMA/NPI (70/30 mol%) copolymerization in a) $[BMIM]BF_4$ after 10 (■, $X = 15\%$), 30 (▲, $X = 49\%$), 60 (●, $X = 71\%$) and 180 (★, $X = 85\%$) minutes of reaction time and in b) DMF after a reaction time of 20 (□, $X = 12\%$), 94 (△, $X = 50\%$), 180 (○, $X = 71\%$) and 300 (∗, $X = 86\%$) minutes standardized on the conversion; subtracted standardized MWDs of the copolymers produced in different time intervals c) $[BMIM]BF_4$ for 10-0 (■), 30-10 (▲), 60-30 (●) and 180-60 (★) minutes and in d) DMF for 20-0 (□), 94-20 (△) and 180-94 (○) and 300-180 (☆) minutes. Reaction conditions: see Figure 1.

pronounced as in the case of the copolymerization in IL.

Using the standardized MWDs shown in Figures 4a and 4b we were able to calculate the fraction of molecular weights which is generated in a certain period of the polymerization. For this purpose we subtracted the MWDs of the copolymers received at t_n from those obtained at t_{n+1}. The resulting MWDs are shown in Figures 4c and 4d.

For the copolymerization of MMA/NPI (70/30 mol%) carried out either in [BMIM]BF_4 or in DMF it can be observed that high molecular weight material is formed in the first step at relatively low conversion ($X < 15\%$). When the conversion increases during the following time periods lower molecular weights can be observed which lead to the above mentioned broadening of the MWDs.

Figures 4c and 4d clearly show that with increasing reaction time and conversion, respectively, the molecular weights of the copolymer which is formed decrease. This behavior can be observed for both the polymerization carried out in DMF and [BMIM]BF_4, but regarding the polydispersities (Table 1) the shift to lower log M values seems to be more pronounced when [BMIM]BF_4 is used as solvent although in both cases comparable conversions are reached. This shift to lower log M values is an effect which is typical for free radical polymerizations. At the beginning of the reaction the conversion of the monomer is really low. Thus enough monomer molecules are present in the reaction mixture which can react with the radicals that are formed in the starting reaction to form long polymer chains. When the polymerization proceeds and the monomer consumption increases the radicals that are formed during the starting reaction at a later state of the polymerization have less monomer molecules to react with and therefore can only form shorter polymer chains.

A second difference which can be observed when the MMA/NPI (70/30 mol%) copolymerization is carried out in [BMIM]BF_4 instead of DMF is that between 90 and 180 minutes of reaction time and a conversion between 71 and 85%, respectively, not only copolymers with lower molecular weights but also copolymers with again higher molecular weights are obtained. As already shown in Figure 3 the molecular weights of the polymers formed in IL are always higher than those of P(MMA-*co*-NPI) synthesized in DMF. This is due to the fact that the viscosity of the initial reaction mixture is relatively high when [BMIM]BF_4 is used as solvent. When the reaction proceeds the reaction mixture gets more and more viscous (conversion is between 71 and 85%) and entanglement networks are formed which leads to a strongly increased diffusion control of the termination. This strong increase of the diffusion control of the termination step leads to longer lifetimes of the long chain radicals. Although the termination is strongly hindered the addition of monomer molecules still can take place and thus high molecular weight polymers can be formed. These observations were only made for the IL system because the viscosity of the reaction mixture is relatively high already at the beginning of the polymerization. Therefore viscosity effects on the termination step can be observed at lower conversions than for the DMF system.

Rheological measurements of polymers with high molecular weights often show an independency of the storage modulus G' and the loss modulus G'' on the frequency ω. This typical rheological behavior can be explained by an increased number of entanglements and therefore a physical network. As P(MMA-*co*-NPI) synthesized in [BMIM]BF_4 with $x_{\text{NPI,copolymer}} = 0.08$ has a very high molecular weight ($M_{n,\text{IL}} =$ 190 700 g/mol, $X = 88\%$) in comparison to the comparable polymer sample produced in DMF ($M_{n,\text{DMF}} = 33\,300$ g/mol, $X = 47\%$) we assumed to find plateaus in G' and G''. In Figure 5a and 5b the storage modulus G', the loss modulus G'' and the complex viscosity η^* are depicted for P(MMA-*co*-NPI) synthesized either in IL (Figure 5a) or in DMF (Figure 5b). It is obvious that both G' and G'' of the P(MMA-*co*-NPI) synthesized in [BMIM]BF_4 are indepen-

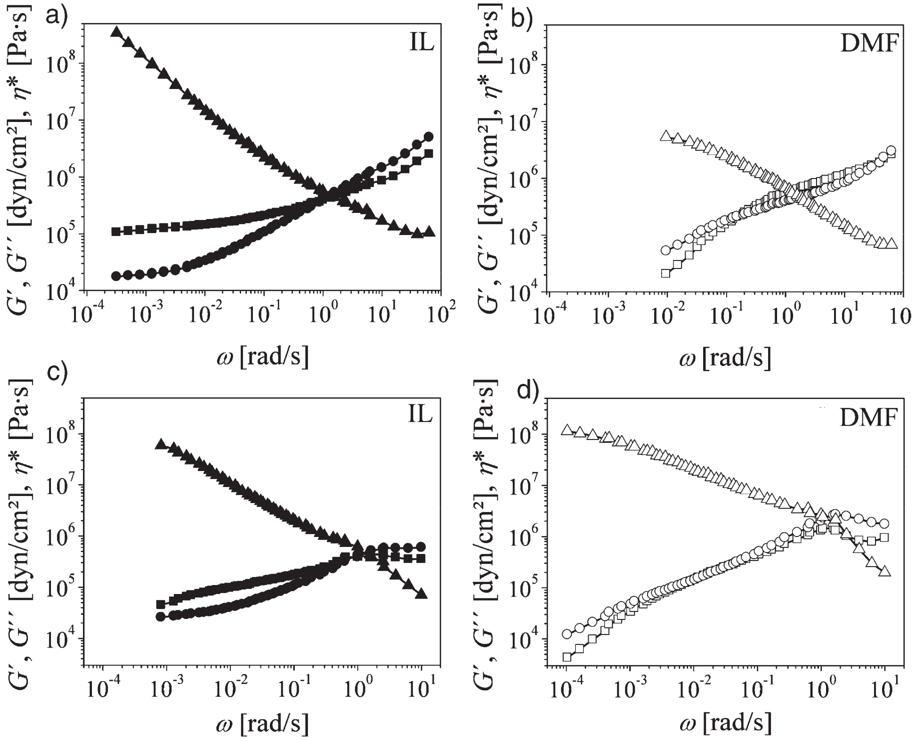


Figure 5.
Storage modulus G′ (■,□), loss modulus G″ (●,○) and complex viscosity $\square^*$ (▲,△) for P(MMA-*co*-NPI) containing 8 mol% NPI synthesized in a) [BMIM]BF_4 (filled symbols) and b) DMF (open symbols) and for P(MMA-*co*-NPI) containing 30 mol% NPI synthesized in c) [BMIM]BF_4 (filled symbols) and d) DMF (open symbols). Temperature range 155–195 °C (a, b), 190–230 °C (c, d), reference temperature: 155 °C (a, b), 190 °C (c, d).Reaction conditions: see Figure 1.

dent of the frequency for $\omega < 4 \cdot 10^{-2}$ $\mathrm{rad} \cdot \mathrm{s}^{-1}$.

We found that the plateau which can be found for the storage and the loss modulus broadens with increasing molecular weight of the polymer. This is due to the increased number of entanglements, reflecting the higher molecular weight of the samples produced in the IL (compare Figure 2).

The rheological data shown in Figures 5c and 5d were obtained from P(MMA-*co*-NPI) samples produced either in [BMIM]BF_4 or in DMF containing 30 mol% of NPI. For these samples the difference which can be found for M_n is not so pronounced ($M_{n,IL} = 113\,000$ g/mol, $X = 73\%$; $M_{n,DMF} = 33\,000$ g/mol, $X = 57\%$) than for the samples with $x_{NPI,copolymer} = 0.08$. The P(MMA-*co*-NPI) sample synthesized in [BMIM]BF_4 still shows a slight plateau for G'' for frequencies lower than $3 \cdot 10^{-3}$ $\mathrm{rad} \cdot \mathrm{s}^{-1}$, but no plateau can be found for G'. This indicates that there still is an increased number of entanglements within the copolymer due to the relatively high molecular weight, but these entanglements are not so strong than those that can be found for the P(MMA-*co*-NPI) sample with an almost doubled M_n (Figure 5a). The corresponding copolymer synthesized in DMF is completely dependent of the frequency (Figure 5d). Comparing Figures 5a and 5c leads to the conclusion that increasing the NPI content in the copolymer leads to a smaller number of entanglements and the influence on the rheological behavior therefore is diminished.

The copolymerization diagram is depicted in Figure 6. The reactivity ratios

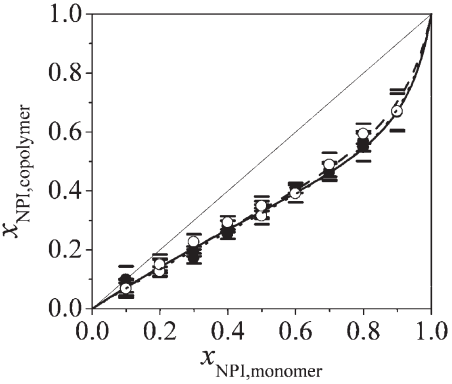


Figure 6.
Copolymerization diagram of the MMA/NPI copolymerization in $[BMIM]BF_4$ (exp. data: ●, calc. data: —), DMF (exp. data: ○, calc. data: ---) and 1,4-dioxane (· · ·).[36] Reaction conditions: see Figure 1.

r_{NPI} and r_{MMA} were calculated using the method of Kelen-Tüdös [35] (Table 2). Looking at Figure 6 there is no significant difference in the copolymerization behavior to be found using either IL or DMF for the copolymerization of MMA/NPI. The reactivity ratios in $[BMIM]BF_4$ as well as in DMF are in good agreement with the values we previously reported for the copolymerization of MMA/NPI in 1,4-dioxane.[36]

Thus we can conclude that the use of the IL as solvent does not significantly affect the copolymerization behavior.

This result is remarkable as we must take into account that the propagation rate coefficient k_p of the homopolymerization of MMA is increased when using $[BMIM]BF_4$ as solvent. In an earlier paper we reported a k_p of 2759 $\mathrm{L \cdot mol^{-1} \cdot s^{-1}}$ at 60 °C [2] in this IL which is about 3 times higher than k_p measured for the solution polymerization of MMA at 60 °C.[37] This increase of k_p was discussed to be due to interactions between monomer and IL which increase the reactivity of the monomer.

Table 2.
Reactivity ratios r_{NPI} and r_{MMA} of the copolymerization of MMA/NPI in $[BMIM]BF_4$, DMF and 1,4-dioxane[36] calculated with the method of Kelen and Tüdös.[35]

solvent	r_{NPI}	r_{MMA}	R^2
$[BMIM]BF_4$	0.15 ± 0.09	1.33 ± 0.18	0.9505
DMF	0.19 ± 0.07	1.35 ± 0.11	0.9777
1,4-dioxane	0.16 ± 0.05	1.42 ± 0.09	—

Our Monte-Carlo- and dynamical model calculation show for a number of monomers, MMA and NPI amongst others, that these interactions between monomer and IL are caused by hydrogen bonding between the carbonyl group of the monomer and both the cation and the anion of the IL [33]. ESR studies of stable free radicals like 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) [38–40], 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPOL) [39,40], 4-trimethyl-ammonio-2,2,6,6-tetramethylpiperidine-1-yloxyl derivatives [41] and 4-sulfonatooxy-2,2,6,6-tetramethyl-piperidine-1-yloxyl derivatives [42] in ionic liquids showed that there are interactions between these radicals and different imidazolium, pyrrolidinium, ammonium and phosphonium based ionic liquids. Based on these investigations we assume that – concerning the MMA/NPI copolymerization – there are not only interactions between the monomer and the ionic liquid but also between the polymer radicals and the IL. The H-bonds that are formed between the carbonyl group on the radical chain end and the IL reduce the conjugative delocalization of the radical and thus the reactivity of the polymer radicals towards the monomers is increased and vice versa. We assume that this increase of the polymer radical reactivity leads to a loss in selectivity and that therefore both the homo propagation rate coefficients $k_{\mathrm{MMA,MMA}}$ and $k_{\mathrm{NPI,NPI}}$ and the cross propagation rate coefficients $k_{\mathrm{MMA,NPI}}$ and $k_{\mathrm{NPI,MMA}}$ are increased nearly in the same magnitude. Therefore no significant change in the reactivity ratios can be observed.

As the glass-transition temperatures T_g are influenced by the copolymer composition we expected to find no great differences for the copolymers synthesized either in $[BMIM]BF_4$ or in DMF. The slightly higher glass-transition temperatures that can be found for the polymers produced in the ionic liquid are due to the higher molecular weights of these products (Figure 7). Theoretical T_g values were

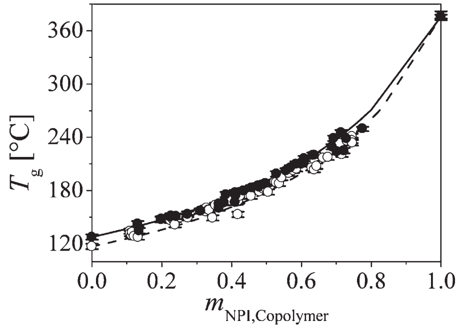


Figure 7.
Measured (dots with error interval) and calculated (lines) glass-transition temperatures of the P(MMA-*co*-NPI) synthesized either in [BMIM]BF$_4$ (●,—) or in DMF (○, ---) in dependence of the mass fraction $m_{NPI,copolymer}$ of NPI in the copolymer. Reaction conditions: see Figure 1.

calculated using the equation by FOX

$$\frac{1}{T_{g,copolymer}} = \frac{m_{NPI,copolymer}}{T_{g,NPI}} + \frac{m_{MMA,copolymer}}{T_{g,MMA}} \qquad (1)$$

where $T_{g,copolymer}$ is the glass-transition temperature of the copolymer which is to be calculated (in °C), $m_{NPI,copolymer}$ and $m_{MMA,copolymer}$ are the mass ratios of NPI and MMA in the copolymer and $T_{g,PNPI}$ and $T_{g,PMMA}$ are the glass-transition temperatures of the homopolymers ($T_{g,PNPI,I} = T_{g,PNPI,DMF} = 376\,°C$, $T_{g,PMMA,IL} = 128\,°C$ and $T_{g,PMMA,DMF} = 117\,°C$).

The curves depicted in Figure 7 show that with increasing NPI content in the copolymer the glass-transition temperature increases significantly. This can be observed for the polymers produced in the ionic liquid as well as in DMF. As expected no great difference of the T_g can be observed because the composition of the copolymers does not differ very much. The experimental and the calculated data show a very good correlation (Figure 7).

Conclusion

We copolymerized MMA/NPI at 60 °C with AIBN as initiator in the ionic liquid [BMIM]BF$_4$ and in the conventional organic solvent DMF. Impressive differences in the overall polymerization rates r_p and the number average molecular weights M_n can be found for reaction mixtures containing less than 50 mol% of NPI. The lower the NPI content in the monomer feed the higher is the influence of the ionic liquid on the copolymerization. It was found that r_p for the MMA/NPI copolymerization in the IL has a minimum at $x_{NPI,monomer} = 0.9$ and that in this region ($x_{NPI,monomer} = 0.7–0.9$) the copolymerization rate is even lower than that observed for the reaction carried out in DMF. This minimum of r_p is most likely due to the fact that the MMA/NPI copolymerization in [BMIM]BF$_4$ can be carried out in solution when the monomer feed contains 30 to 90 mol% NPI, but proceeds under precipitation when NPI is homopolymerized.

Although a significant influence on both the overall polymerization rate and the molecular weights was observed only small differences in the copolymer composition and the glass-transition temperatures can be found using the two different solvents. This observation can be explained by the fact that the rate coefficients for both the homo propagation and the cross propagation are most likely increased in nearly the same order of magnitude. This is due to hydrogen bonding between the carbonyl group of either the monomer or the polymer radicals with the cation and the anion of the IL.

Rheological measurements show that [BMIM]BF$_4$ has a significant influence on the rheological behavior of the polymer samples. A plateau of G' and G'' can be observed for $\omega < 3 \cdot 10^{-2}$ rad · s^{-1} for P(MMA-*co*-NPI) with high molecular weights produced in the IL which is due to an increased number of entanglements between the polymer chains.

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