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Modification of the Solvent Influence on the Free Radical Polymerization in Ionic Liquids by Microwave Irradiation

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Summary: Microwave irradiation is supposed to disturb the polar interactions between the ionic liquid and the monomer molecules or the polymer radicals which probably leads to a decrease in k_p compared to conventional heating. This work deals with the comparison of the influence of microwave heating and conventional heating on polymerizations in the ionic liquids [EMIM]$EtSO_4$ and [BMIM]BF_4. Different monomers were homo- and copolymerized at 60 and 80 °C in DMF or methanol and [EMIM]$EtSO_4$ or [BMIM]BF_4 as solvent. Lower conversions were observed under microwave irradiation when polymerizing in the ionic liquid (IL), but not when polymerizing in DMF or methanol. Nevertheless there were no systematical differences in the molecular weights and in the copolymer compositions between microwave heating and conventional heating.

Keywords: copolymerization; ionic liquids; microwave irradiation; radical polymerization; rate constants

Introduction

Ionic liquids (ILs) have attracted enormous attention within the last decade. In general they consist of a bulky organic cation and a complex anion and are liquid at temperatures below 100 °C. Ionic liquids possess some characteristic physical and chemical 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 and chemical stability, their wide liquid range and their negligible vapor pressure.[1]

While ILs are already applied in organic syntheses, their use as reaction media for radical polymerizations is rather limited. Studies on the polymerization kinetics show that ILs strongly influence the overall 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.[2–20]

Studies on the propagation rate constant k_p for the homopolymerization of methyl methacrylate (MMA) and glycidyl methacrylate (GMA) in the ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) and 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM]$EtSO_4$) showed that k_p is strongly increased with increasing IL content in the reaction mixture.[2,3] Haddleton et al. [4] and we[2] presume that the increase of the propagation rate coefficient k_p can be ascribed to a lowering of the activation energy of propagation E_A. Haddleton et al. [4] discuss that this lowering of E_A is most likely caused by the increased polarity of the ionic liquid solution which leads to increased contributions from charge-transfer structures in the transition state. In previous

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studies, we[2] were able to show that a lowering of the peak maximum position of the carbonyl stretching of MMA can be observed via infrared spectroscopy when passing from pure MMA to MMA/IL solutions. This can be ascribed to an enhancement of the polar interactions between monomer and IL. Recently we were able to show by quantum mechanical and semi empirical calculations for a number of monomers that these interactions are caused by hydrogen bonding between the carbonyl group of the monomer and both the cation and the anion of the IL.[21]

As reported by Haddleton et al. [4] there is an influence of $[BMIM]PF_6$ on the rate coefficient of termination k_t for the homopolymerization of MMA, too. It was found that k_t decreases with increasing IL content in the reaction mixture which is considered to be due to the relatively high viscosity of the ionic liquids. That means the high polymerization rate is due to both the increase of k_p and the diffusion-controlled termination, reflecting the high viscosity of the used solvent.[3,6]

In the last years a steadily growing interest in the use of microwave irradiation for polymerizations could be observed. Many advantages like better reproducibility,[22] shorter reaction times[23] or higher yields[24] are described for microwave-assisted processes. Microwave heating is therefore used in many fields of polymer chemistry. Reviews concerning microwave-assisted polymer synthesis were published by Schubert et al.[25,26], Bogdal et al.[27] and Ritter et al.[28]. Kappe,[29] even though with focus on organic chemistry supplies a good overview about different types of microwave effects described in literature.

Wasserscheid et al. reported that ionic liquids are excellent microwave absorbers and therefore reaction mixtures containing ILs can be heated very rapidly using microwave irradiation.[30] Thus it seems to be very interesting to combine the accelerative effect of ionic liquids as reaction medium with microwave irradiation as efficient heat source for polar solvents with focus on free-radical polymerization reactions, but so far only few papers can be found for microwave-assisted free-radical polymerizations in ionic liquids. Schubert et al. recently investigated the microwave-assisted free-radical polymerization of MMA in the ILs 1-butyl-3-methylimidazolium trifluoromethanesulfonate and $[BMIM]BF_4$ and found higher heating rates in comparison to the corresponding bulk polymerizations.[31] They did not compare the microwave-assisted polymerization reactions to those performed with conventional heating.

When polar solvents are heated up using a microwave oven the dipole or ion field of the molecules perpetually tries to align in the applied oscillating electric field during microwave irradiation. Therefore it is possible that the microwave irradiation disturbs the polar interactions between the ionic liquid and the monomer molecules or polymer radicals which are mainly responsible for the high overall polymerization rates in these solvents. Consequently, k_p and therefore the overall polymerization rate should decrease under microwave irradiation. To verify this assumption we thoroughly compared the microwave-assisted homopolymerization of MMA in $[EMIM]EtSO_4$ and dimethylformamide (DMF) at 60 and 80 °C using either 2,2′-azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) as initiators with the polymerizations performed under conventional heating (heating block). Furthermore, the homopolymerization of styrene (S) as well as the copolymerizations of S with acrylonitrile (AN) and MMA with *N*-phenyl maleimide (NPI) in $[EMIM]EtSO_4$ or $[BMIM]BF_4$ and in DMF or methanol were investigated using either microwave or conventional heating.

Experimental Part

Methyl methacrylate (FLUKA), styrene (FLUKA) and acrylonitrile (ACROS) were distilled to remove inhibitors. 2,2′-azobisisobutyronitrile, benzoyl peroxide and *N*-phenyl

maleimide (ALFA AESAR) were recrystallized before use. Methanol, dimethylformamide, 1-ethyl-3-methylimidazolium ethylsulfate (puriss. 99%, Lot-No. RS/085, SOLVENT INNOVATION GMBH) and 1-butyl-3-methylimidazolium tetrafluoroborate (purum ≥98%, Lot-No.: 99/602, SOLVENT INNOVATION GMBH) were used as received.

The polymerizations were performed in ampoules either in the microwave or in a preheated heating block. For the microwave experiments a multimode microwave reactor (microPREP 1500 with fibre-optic temperature control, MLS GMBH MIKROWELLEN LABORSYSTEME) was used.

1.5 g monomer, 0.05 g initiator (AIBN (MERCK) at 60 °C or BPO (FLUKA) at 80 °C) and 6 mL [EMIM]$EtSO_4$, [BMIM]BF_4, DMF or methanol were weighed into ampoules. Each ampoule was purged with nitrogen and then sealed before polymerization. After polymerization the reaction was stopped immediately by fast cooling down. The conversions were determined gravimetrically after precipitation of the polymer in methanol. For the determination of the polymerization rate r_p the initial slope of conversion versus reaction time was used.

The microwave power was adjusted automatically in order to keep the desired reaction temperature. A typical temperature-power profile for a polymerization performed in the microwave as well as a temperature profile for an ampoule in the heating block is shown in Figure 1. The complete heating up took about two minutes under microwave irradiation and ten minutes under conventional heating. The temperatures were measured directly in the reaction mixture.

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. For PMMA a three columns system (Nucleogel 103-5, Nucleogel 104-40 and Phenogel 5 linear) with a differential refractometer detector (calibration with PMMA standards) and in case of PS, P(S-*co*-AN) and P(MMA-*co*-NPI) a four columns system (mixed A from PL) with a differential refractometer detector (calibration with PS standards) was used.

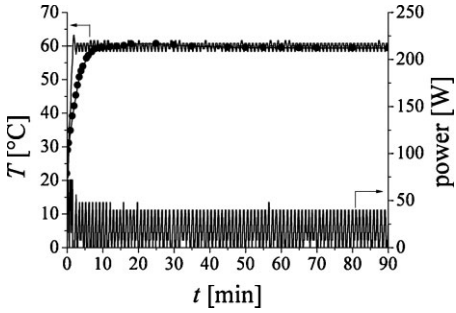

Figure 1.
Exemplary temperature profiles for a polymerization in ionic liquid performed in the microwave (—) and in the heating block (●) as well as power profile for the corresponding microwave process.

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).

Copolymer compositions were determined by elemental analysis (C, H, N in the case of P(S-*co*-AN) and C, H, N, O in the case of P(MMA-*co*-NPI)). Elemental Analysis VarioEL (ELEMENTAR ANALYSENSYSTEME GMBH) was used, calibrated with acetanilide and benzoic acid.

Results and Discussion

When using microwave heating for polymerizations in IL we expect to find a reduction of k_p and thus a reduced rate of conversion in comparison to reactions carried out under conventional heating. We assume that this reduction of k_p is caused by a disturbance of the interactions between IL and monomer molecules[21] or polymer radicals by microwave irradiation. As the viscosity should remain unchanged under microwave irradiation no or only slight influences on the molecular weights are expected. To exclude an influence of

microwave irradiation on the initiator decomposition we worked with two different initiators (AIBN and BPO) at two different reaction temperatures.

The polymerization of MMA was carried out at 60 and 80 °C in DMF and [EMIM]$EtSO_4$ as solvents. At 60 °C AIBN was used as initiator and reactions at 80 °C were performed using BPO as initiator.

Figure 2 shows that no differences between conventional heating and microwave heating were observed in the case of DMF as conventional solvent using different initiators. This is in good agreement with Greiner et al. who investigated the homopolymerization of styrene (S) and its copolymerization with MMA under microwave heating and conventional heating with different initiators in toluene and DMF as conventional solvents.[32,33] In most cases they did not find any differences in the rate of conversion between the two heating methods either. In addition they did not observe any differences in the molecular weights.

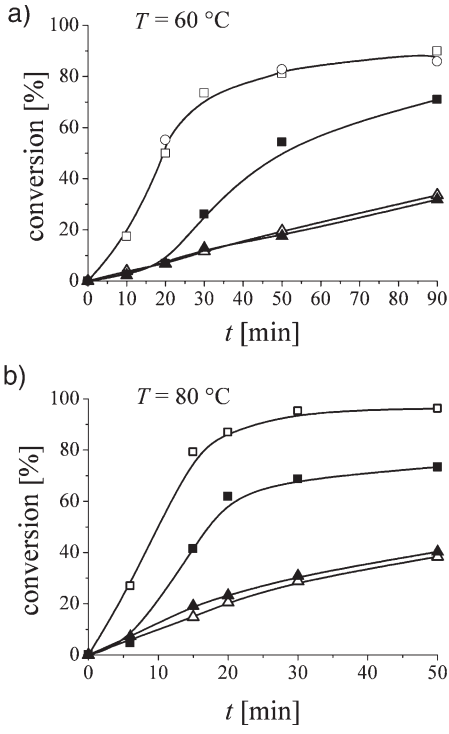

Figure 2.
Conversions of the polymerizations of MMA at a) 60 °C and b) 80 °C in DMF (microwave heating: ▲, heating block: △) and in [EMIM]$EtSO_4$ (microwave heating: ■, heating block: □, water bath: ○).

Thus the microwave irradiation does not seem to affect the initiator efficiency for the polymerization of MMA in DMF.

Looking at Figures 2a and 2b it gets clear that the conversion and therefore the overall polymerization rate r_p (initial slope of conversion versus reaction time) of the MMA polymerization in [EMIM]$EtSO_4$ is in all cases higher than r_p of the corresponding polymerization in DMF. At $T = 60$ °C under conventional heating a 6.3 times higher r_p can be found when using IL instead of DMF as solvent whereas at $T = 80$ °C r_p for the MMA polymerization in [EMIM]$EtSO_4$ is only 5.1 times higher than that of the polymerization in DMF. As expected the increase of r_p in IL compared to DMF decreases with increasing temperature and decreasing viscosity. The overall polymerization rates of all polymerizations and copolymerizations carried out in the microwave and in the heating block can be found in Table 4.

Another possible reason for the strong enhancement of r_p and the molecular weights could be an influence of ILs on the initiation kinetics. But studies of Thurecht et al. showed that both the decomposition rate and the initiator efficiency of AIBN are not significantly affected by ILs[34] and therefore they can be considered to be not responsible for the strong increase in the polymerization rate and the molecular weights.

Comparing the rates of conversion of the polymerizations of MMA in [EMIM]$EtSO_4$ (Figure 2) under microwave irradiation and conventional heating it strikes that the rate of conversion in the case of microwave heating is at both temperatures significantly lower than that under conventional heating. For the MMA polymerization a 2.6 times lower overall polymerization rate r_p can be observed at $T = 60$ °C whereas at $T = 80$ °C r_p is only 1.8 times lower when microwave heating is used instead of conventional heating (Table 4).

In order to exclude that the deviation of the overall polymerization rate r_p of the MMA polymerization in [EMIM]$EtSO_4$ results from different reaction conditions (stirring in the microwave and shaking in the heating block) the polymerization of MMA was additionally carried out in a water bath under stirring at 60 °C. As can be seen in Figure 2a the same results for r_p can be obtained when the homopolymerization of MMA is performed under conventional heating using either a heating block (shaking) or a water bath (stirring). Thus the reaction conditions do not seem to be responsible for the significant differences.

We assume that the lowering of the rate of conversion of the free radical polymerization of MMA in [EMIM]$EtSO_4$ under microwave heating is due to a disturbance of the polar interactions between the IL and the monomer molecules as well as the polymer radicals, because the dipole or ion field perpetually tries to align in the applied oscillating electric field during microwave irradiation. In contrast to convective heat transfer in the heating block in case of microwave heating the heating up occurs from inside outwards of the reaction mixture. When the dipole or ion field tries to realign with the alternating electric field, energy in the form of heat is lost through molecular friction and dielectric loss.

No influence of microwave heating on the polymerization of MMA in DMF was observed because the polar interactions between the solvent molecules and the monomer molecules are first of all lower than in the case of the IL and furthermore, in contrast to DMF, the ionic liquid strongly absorbs microwave irradiation.

As expected there is no systematical effect on the number average molecular weights M_n of PMMA synthesized in DMF and [EMIM]$EtSO_4$ using either microwave heating or conventional heating (Figure 3). But as expected the molecular weights are in all cases higher when polymerizing in IL compared to DMF. At a reaction temperature of 60 °C up to 10 times higher molecular weights (M_n) can be obtained when using [EMIM]$EtSO_4$ as solvent (Figure 3a).

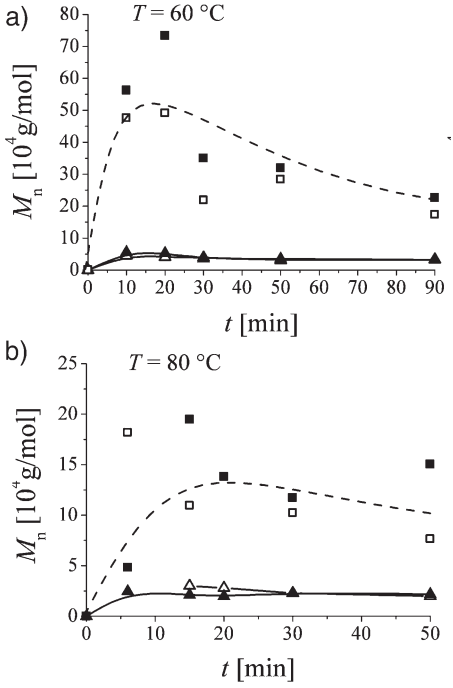

Figure 3.
Number average molecular weights M_n of the polymerizations of MMA at a) 60 °C and b) 80 °C in DMF (microwave heating: ▲, heating block: △) and in [EMIM]$EtSO_4$ (microwave heating: ■, heating block: □).

The fact that there are no significant differences in the number average molecular weights between microwave heating and conventional heating and the fact that there are no differences in the rate of conversion between the two heating methods when polymerizing in DMF both indicate that the observed differences are not due to a changed decomposition rate of the initiator under microwave heating.

Figure 3b shows that M_n strongly decreases when the reaction temperature is changed from 60 to 80 °C independent of the solvent and the heat source. But it can also be observed that at 80 °C M_n of PMMA synthesized in the IL is only up to 5 times higher than M_n of the polymers received from the reaction in DMF. This strong decrease of M_n is due to a strong dependence of the viscosity of the IL on the reaction temperature as we already described in former papers.[11,12]

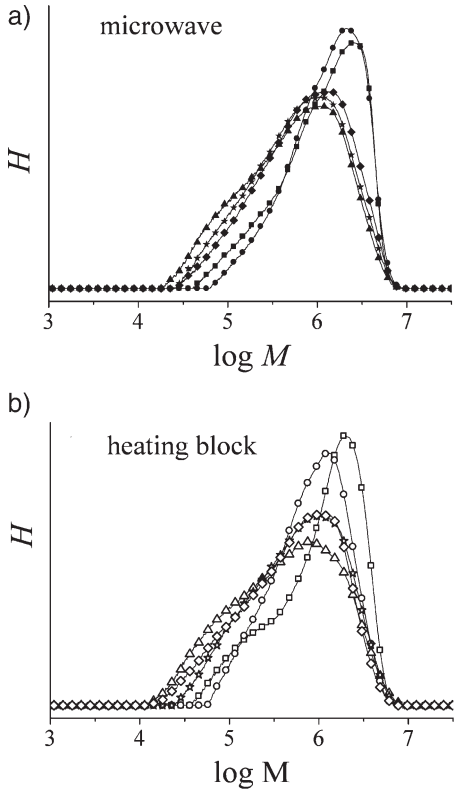

Figure 4.
Molecular weight distributions of PMMA produced in [EMIM]$EtSO_4$ at 60 °C a) in the microwave (filled symbols) and b) in the heating block (open symbols) obtained after 10 (●, ○), 20 (■, □), 30 (◆, ◇), 50 (★, ☆) and 90 (▲, △) minutes of reaction time.

The temperature dependence of the viscosity of conventional organic solvents like DMF is not that pronounced at reaction temperatures between 60 and 80 °C. The decrease of the molecular weights with increasing temperature can be ascribed to an increase of the radical concentration. That explains why a smaller difference between M_n of PMMA synthesized in [EMIM]EtSO4 and M_n of PMMA synthesized in DMF can be found when the polymerization is carried out at higher temperatures (80 °C instead of 60 °C).

The molecular weight distributions (MWDs) which are shown in Figure 4 at the example of the poylmerization of MMA in [EMIM]$EtSO_4$ at 60 °C do not show any remarkable differences between the two heating methods either.

Table 1 compares the polydispersities of the polymerizations of MMA in DMF and [EMIM]$EtSO_4$ at 60 and 80 °C. The polydispersities are higher when polymerizing in IL compared to DMF, but there are no remarkable differences between the polymers synthesized via microwave heating and conventional heating (heating block).

A comparison of the rheological behavior of PMMA synthesized in [EMIM]$EtSO_4$ at 60 °C under microwave heating and in the heating block shows that both the storage modulus G' and the loss modulus G'' remain constant down to a frequency of $\omega = 10^{-2}$ rad s^{-1} (Figure 5). This behavior can be ascribed to the high number of entanglements caused by the high molecular weights of the polymers synthesized in ionic liquids.[12] No differences in the rheological behavior between the two samples synthesized under different heating methods can be observed. This is due to the comparable molecular weights of the polymers.

In order to confirm the prementioned results further polymers and copolymers

Table 1.
Polydispersities of PMMA received from the polymerization in [EMIM]$EtSO_4$ and DMF at 60 °C and 80 °C in the heating block (HB) and under microwave heating (MW).

60 °C					80 °C				
t [min]	DMF		[EMIM]$EtSO_4$		t [min]	DMF		[EMIM]$EtSO_4$	
	HB	MW	HB	MW		HB	MW	HB	MW
10	2.0	2.0	3.2	2.9	6	–	1.8	5.1	3.7
20	1.7	2.0	2.3	2.3	15	1.6	1.9	4.9	3.8
30	1.8	1.8	4.1	3.4	20	1.6	2.0	4.3	4.9
50	2.0	1.9	3.6	3.9	30	1.9	1.9	4.3	5.6
90	1.8	1.8	5.1	5.0	50	1.8	2.0	5.1	4.8

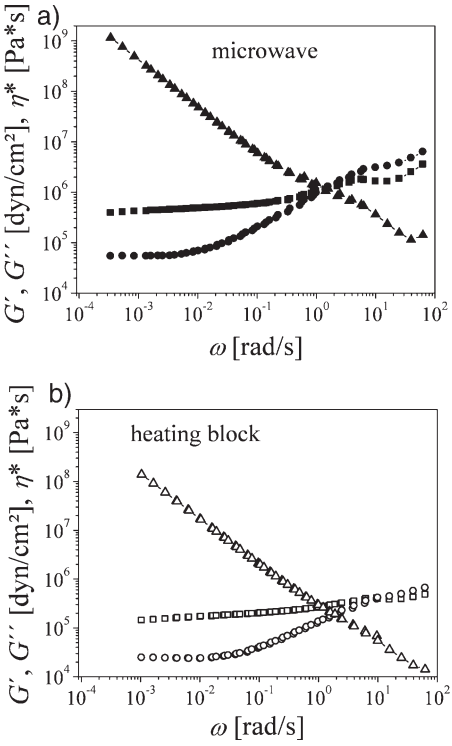

Figure 5.
Storage modulus G' (MW: ■, HB: □), loss modulus G'' (MW: ●, HB: ○) and complex viscosity η^* (MW: ▲, HB: △) of poly(methyl methacrylate) synthesized in [EMIM]$EtSO_4$ at 60 °C for 90 minutes a) under microwave heating (conversion: 70.9%, $M_n = 225900$ g/mol, $T_g = 129$ °C) and b) in the heating block (conversion: 89.9%, $M_n = 173200$ g/mol, $T_g = 130$ °C) in dependence of the frequency ω; temperature range: 145–185 °C; reference temperature: 145 °C.

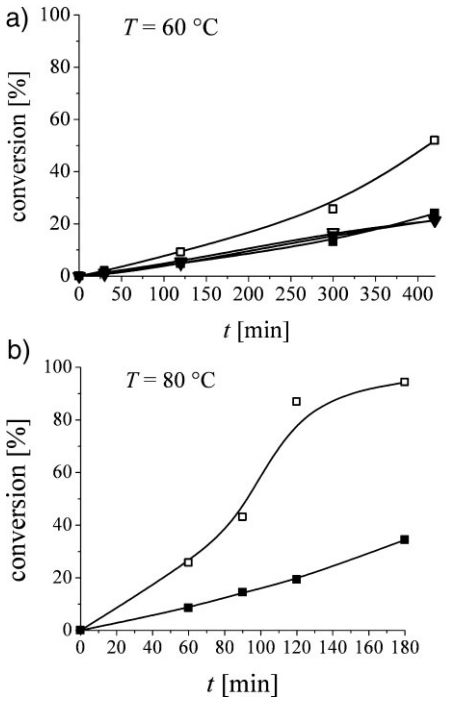

Figure 6.
Conversions of the polymerizations of styrene in methanol (microwave heating: ▼, conventional heating: □) and in [EMIM]$EtSO_4$ (microwave heating: ■, conventional heating: □) at a) 60 °C and b) 80 °C.

were synthesized with microwave and conventional heating. First of all styrene was polymerized in methanol and [EMIM]$EtSO_4$ at 60 °C. The polymerization proceeded under precipitation in both cases. As styrene is a quite unpolar monomer in comparison to MMA only weak interactions (H-bonds) can be found.[21] Therefore we expected to find a less significant influence of the IL on k_p and therefore on r_p.

Figure 6a clearly shows that no differences in r_p can be found between microwave heating and conventional heating when polymerizing in methanol. Comparing the polymerization carried out under conventional heating in either [EMIM]$EtSO_4$ or methanol a 1.7 times higher r_p can be observed when using the IL as solvent (Figure 6a). As expected the increase of r_p for the homopolymerization of styrene is not comparable to the increase of r_p for the MMA homopolymerization in [EMIM]$EtSO_4$ (Figure 2, Table 4).

In contrast, under microwave heating no differences in the rate of conversion can be found when either the IL or methanol is used as solvent. In both cases the overall polymerization rate r_p is about 3%/h compared to 5%/h for the homopolymerization of S in [EMIM]$EtSO_4$ in the heating block (Table 4).

That means that microwave heating completely seems to suppress the stronger interactions compared to DMF between the ionic liquid and the monomer molecules or the growing polymer chains which would

Table 2.
Number average molecular weights (M_n in g/mol) of the polymerization of styrene in methanol and [EMIM]$EtSO_4$.

60 °C					80 °C		
t [min]	MeOH		[EMIM]$EtSO_4$		t [min]	[EMIM]$EtSO_4$	
	HB	MW	HB	MW		HB	MW
30	3800	–	25700	28100	60	14100	13900
120	3600	5200	29800	34800	90	16400	14100
300	4200	4900	40600	38900	120	20800	14400
420	4800	4500	50800	–	180	17200	15400

lead to higher conversions when polymerizing in IL. When the polymerization of S in [EMIM]$EtSO_4$ is carried out at 80 °C a r_p of 28%/h can be observed in the heating block and a r_p of only 9%/h and therefore a 3.1 times lower r_p when using microwave heating (Figure 6b, Table 4). As the viscosity of the reaction mixture should be nearly the same for both the homopolymerization of MMA and the homopolymerization of S in [EMIM]$EtSO_4$ we expected to find no strong differences in the influence of the IL on the molecular weights. It can be seen from Table 2 that the M_n values of PS are higher when polymerizing in IL compared to methanol. At 60 °C polymers with up to 10 times higher molecular weights (M_n) can be received when the polymerization is carried out in [EMIM]$EtSO_4$ instead of methanol. This is in good agreement with the results obtained for the MMA polymerization.

Table 2 also shows that again nearly no differences in M_n between the polymers synthesized under microwave heating and in the heating block can be observed. These results are applicable for a reaction temperature of 60 °C as well as 80 °C.

In addition to the homopolymerizations of MMA and S copolymerizations of these monomers with different comonomers were carried out (S/AN (50/50 mol%) and MMA/NPI (50/50 mol%))at 60 and 80 °C. The copolymerizations of S/AN[12] and MMA/NPI[35] in ILs were investigated in detail by us. The MMA/NPI (50/50 mol%) copolymerization was performed using the IL [BMIM]BF_4 instead of [EMIM]$EtSO_4$ as solvent in order to see if the results found for [EMIM]$EtSO_4$ are reproducible in other ILs.

The copolymerization of S/AN (50/50 mol%) was performed at 60 and 80 °C in DMF and [EMIM]$EtSO_4$. Figure 7a and 7b show the same observations as in the case of MMA and styrene homopolymerizations. Using conventional heating a higher overall polymerization rate r_p can be observed at 60 and 80 °C when the

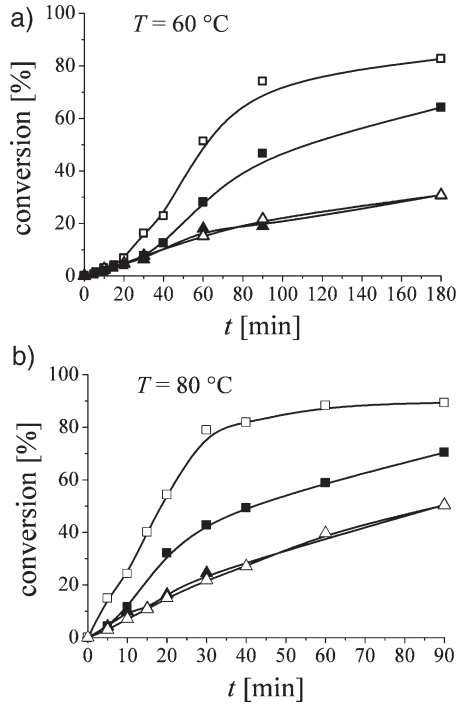

Figure 7.
Conversions of the polymerizations of S/AN (50/50 mol%) in DMF (microwave heating: ▲, conventional heating: △) and in [EMIM]$EtSO_4$ (microwave heating: ■, conventional heating: □) at a) 60 °C and b) 80 °C.

copolymerization is carried out in [EMIM]$EtSO_4$ instead of DMF (Table 4).

A comparison between r_p of the polymerization in [EMIM]$EtSO_4$ under microwave heating and r_p of the corresponding reaction in the heating block leads to the conclusion that again the polymerization is slowed down by microwave irradiation. At 60 °C the S/AN copolymerization in the heating block is twice as fast as the reaction under microwave heating and at 80 °C a 1.8 times faster reaction can be observed in [EMIM]$EtSO_4$ when it is carried out in the heating block instead of in the microwave (Table 4).

As already described for the homopolymerizations of MMA and S in case of the molecular weights M_n (Figure 8) a good correlation between microwave heating and conventional heating for the polymerization of S/AN in DMF as well as in [EMIM]$EtSO_4$ can be observed. Comparing the M_n values of the copolymers received either from the IL system or the DMF system shows that up to 10 times higher M_n can be obtained at a reaction temperature of 60 °C and up to 4 times higher M_n at 80 °C (Figure 8).

A comparison of the copolymer compositions dependent on the conversion X of S/AN polymerized in DMF and [EMIM]$EtSO_4$ at 80 °C with 50 mol% AN in the reaction mixture shows no significant differences in the molar ratio of AN in the copolymer between microwave heating and conventional heating in DMF and [EMIM]$EtSO_4$ (Table 3).

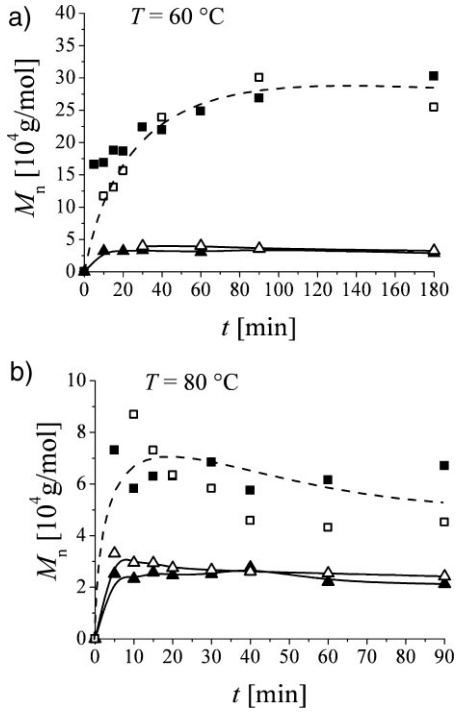

Figure 8.
Average molecular weights of the polymerizations of styrene-*co*-acrylonitrile (50/50 mol%) in DMF (microwave heating: ▲, heating block: △) and in [EMIM]$EtSO_4$ (microwave heating: ■, heating block: □) at a) 60 °C and b) 80 °C.

Furthermore, the copolymer composition does not seem to be strongly affected by the presence of [EMIM]$EtSO_4$ in the reaction mixture as no significant differences in the copolymer composition between DMF and [EMIM]$EtSO_4$ can be found. The reason why the copolymerization

Table 3.
Copolymer compositions of S/AN (50/50 mol%) synthesized in DMF and [EMIM]$EtSO_4$ in the heating block (HB) and under microwave heating (MW) at 80 °C.

DMF				[EMIM]$EtSO_4$			
HB		MW		HB		MW	
X [%]	$AN_{copolymer}$ [mol%]	X [%]	$AN_{copolymer}$ [mol%]	X [%]	$AN_{copolymer}$ [mol%]	X [%]	$AN_{copolymer}$ [mol%]
2.9	46.3	4.3	50.4	14.9	46.4	4.2	43.7
7.1	51.6	9.9	48.4	24.3	44.6	11.5	43.4
15.0	49.8	16.4	46.6	40.1	45.2	32.1	42.7
27.1	46.6	24.6	49.5	54.3	45.0	42.8	43.0
39.7	50.5	30.5	46.4	78.9	46.4	49.3	45.3
50.3	48.5	32.5	44.6	81.8	43.2	58.8	45.3
		50.5	49.6	88.3	44.7	70.4	45.3

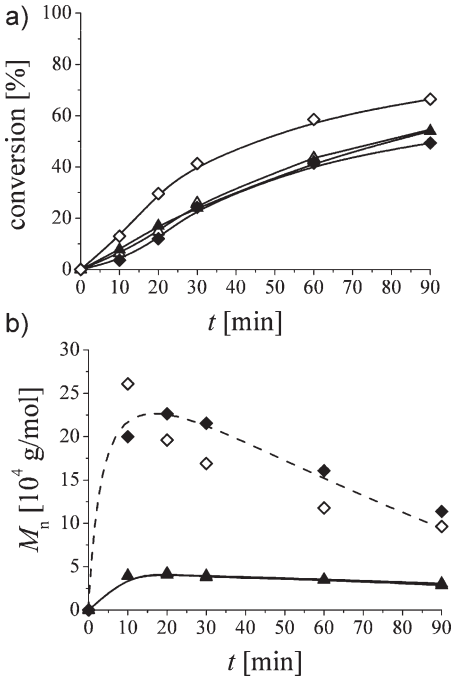

Figure 9.
a) Conversions of the polymerizations of MMA/NPI (50/50 mol%) in DMF (microwave heating: ▲, conventional heating: △) and in [BMIM]BF_4 (microwave heating: ■, conventional heating: □) at 60 °C and b) number average molecular weights M_n of the resulting P(MMA-*co*-NPI) copolymers in dependence of the reaction time.

behavior is not significantly affected by the IL was already recently discussed by us.[12,35] Another reason could be that the composition of the studied system is near the azeotropic composition (61.5/38.5 mol%).

MMA/NPI (50/50 mol%) was copolymerized in another IL ([BMIM]BF_4) and DMF at 60 °C using either microwave heating or conventional heating. AIBN was used as initiator. Looking at Figure 9a it can be seen that when working with conventional heating the influence of the IL on the overall polymerization rate r_p is not so strong as for the MMA homopolymerization. r_p of the MMA/NPI (50/50 mol%) copolymerization in [BMIM]BF_4 is only 1.9 times higher than r_p of the corresponding reaction in DMF (Table 4).

Using the microwave as heat source the influence of the IL seems to be totally suppressed like it was already found for the S homopolymerization. The overall polymerization rate r_p in [BMIM]BF_4 is about 43%/h and therefore in the same range than r_p in DMF (Table 4).

No influence of the microwave irradiation can be found for the MMA/NPI (50/50 mol%) copolymerization in DMF as r_p is in the same range using either microwave or conventional heating.

The molecular weights of P(MMA-*co*-NPI) synthesized either in [BMIM]BF_4 or in DMF are not significantly affected by the different heating conditions (Figure 9b).

Table 4 summarizes the overall polymerization rates of the polymerizations of S and MMA as well as the copolymerizations of S/AN and MMA/NPI performed under microwave heating and conventional heating.

Taking together the results obtained for the different homo- and copolymerizations in [EMIM]$EtSO_4$ and the MMA/NPI copolymerization in [BMIM]BF_4 we can conclude that the influence of the microwave irradiation on r_p is not dependent on the IL used as solvent.

Table 4.
Overall polymerization rates r_p [%/h] of the polymerizations and copolymerizations performed under microwave heating (MW) and in the heating block (HB) at 60 and 80 °C in DMF (MMA, S/AN, MMA/NPI) or methanol (S) and IL ([EMIM]$EtSO_4$ (S, MMA, S/AN) and [BMIM]BF_4 (MMA/NPI)).

monomers	60 °C				80 °C			
	HB		MW		HB		MW	
	DMF/MeOH	IL	DMF/MeOH	IL	DMF/MeOH	IL	DMF/MeOH	IL
styrene	3	5	3	3	–	28	–	9
MMA	23	145	22	56	61	310	65	171
S/AN (50/50 mol%)	15	46	13	23	44	159	49	87
MMA/NPI (50/50 mol%)	43	81	44	43	–	–	–	–

Conclusion

The homopolymerizations of MMA and S as well as the copolymerization of S/AN (50/50 mol%) were carried out at 60 and 80 °C and the copolymerization of MMA/NPI (50/50 mol%) was carried out at 60 °C under microwave heating and conventional heating with AIBN and BPO as initiators in conventional solvents (DMF or methanol) and the ionic liquids [EMIM]$EtSO_4$ (for MMA, S, S/AN) and [BMIM]BF_4 (for MMA/NPI). There were no differences in the rate of conversion between microwave heating and conventional heating when polymerizing in DMF or methanol. The rate of conversion in [EMIM]$EtSO_4$ and [BMIM]BF_4 was in all cases higher than that in conventional solvents (methanol and DMF) when the reactions were carried out in the heating block. The overall polymerization rate r_p in the microwave was in all cases found to be lower than that in the heating block when polymerizing in IL. For the homopolymerization of MMA and the copolymerization of S/AN (50/50 mol%) r_p of the reactions performed in the microwave was found to be higher when [EMIM]$EtSO_4$ was used instead of a conventional solvent. r_p of the homopolymerization of S and the MMA/NPI (50/50 mol%) copolymerization performed in the microwave was found to be nearly the same using either IL or conventional organic solvents. These findings can be ascribed to a disturbance of the polar interactions between the ionic liquid and the monomer molecules or polymer radicals. Consequently, the rate constant of propagation k_p in IL seems to be lower when using microwave heating compared to conventional heating which leads to lower overall polymerization rates. The molecular weights are mainly influenced by the termination rate k_t and hence by the viscosity of the reaction mixture. As microwave heating should have no influence on the viscosity of the reaction mixture there are no remarkable differences in the molecular weights between both heating methods, neither in the case of using the conventional organic solvents DMF and methanol nor in the case when the ionic liquids [EMIM]$EtSO_4$ or [BMIM]BF4 are applied as solvent.

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