Free-Radical Polymerization in Ionic Liquids: The Case for a Protected Radical

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ABSTRACT: The free-radical polymerization of methyl methacrylate (MMA) in ionic liquids at low monomer concentration is reported with emphasis on elucidating the “magic” rate and molecular weight enhancement that are often observed. We show that traditional methods of molecular weight capping using dodecylmercaptan as chain transfer agent significantly reduces the molecular weight of the polymer, but to a much lesser extent than analogous reactions in xylene. Similarly, the adverse effect of elevated temperatures upon reactions of this type is much less significant for polymerizations conducted in ionic liquids than those in organic solvents. Indeed, almost quantitative yield can be obtained for polymerization at temperatures up to 120 °C in ionic liquid, while almost no polymer is observed in an organic solvent case due to rapid initiator burnout. These factors lead to the proposal that a “protected” radical mechanism is in operation; however, elucidation of the exact nature of this protection remains elusive. As an extension of this hypothesis, block copolymers of methyl methacrylate, grown from styrene, have been prepared and characterized by NMR, GPC-MALLS, GPEC, and DSC. The absence of poly(methyl methacrylate) homopolymer in the final product suggests that the monomer is only initiated from “protected” polystyrene macroradicals in the ionic liquid. This process cannot be reproduced in organic solvents, unless additional control agents are present. Furthermore, we report much higher molecular weights of A–B block copolymers than those previously reported in the literature.

Introduction

The recent upsurge of interest in ionic liquids (ILs) as reaction media for organic reactions has led to a wealth of publications in this area.[1] This has been fueled partly by the desire to replace volatile organic solvents, but also by the advantageous properties of the ionic liquids themselves. For the specific case of polymerization reactions, the ionic, noncoordinating properties of the solvent hold particular advantages (for example, when an inorganic catalyst is used), but also, in a more general sense, the negligible vapor pressure is a significant driver in terms of both environment and indeed industrial safety. These properties, along with the increased viscosity of the IL compared to most common organic solvents (OSs), lead to many interesting reaction effects being observed.

The preparation of polymers by free-radical polymerization in ILs has been reported extensively in the literature.[2–4] Indeed, over the past decade numerous publications have extolled the interesting molecular weight and rate-enhancing effects that are observed when polymerizations are conducted in an IL. These observations appear to be independent of the IL employed; consequently, this has opened up considerable academic debate on the mechanism that may lead to these effects. While many authors have presented arguments for either a “protected” radical mechanism or a viscosity-controlled free-radical mechanism, there appears to be little conclusive evidence for either of these theories in the current literature. Furthermore, a number of publications strenuously refute such mechanisms entirely.[5,6]

Recently, Mays and co-workers suggested that block copolymers could be formed by sequential addition of monomers to the IL medium.[5] The success of this process was attributed to the precipitation and consequent protection of the propagating polymer radical. However, there exists some doubt as to whether the copolymer is a result of a block-forming or graft mechanism.[6] In addition, the application of these results to other systems has not been forthcoming in the literature, perhaps due to the difficulty in characterizing or controlling systems of this type.

Block copolymers have been formed via controlled polymerization routes.[7–11] Haddleton et al. showed that atom transfer radical polymerization (ATRP) works effectively in an IL medium[7] and that block copolymers can be formed. More recently, Perrier and co-workers[8] have shown that reversible addition fragmentation chain transfer polymerizations (RAFT) also controls reaction kinetics in ILs. However, while reaction rates are slightly increased, the enhanced kinetics that typifies conventional IL polymerizations are not observed.

In this paper we report a comprehensive and systematic investigation of the molecular weight and rate enhancement that is observed during free radical polymerization in ILs. We provide the first conclusive evidence that protected radicals directly cause these effects. Furthermore, we demonstrate that this has implications for both academic and industrial research, providing the possibility to prepare “catalyst-free”, high molecular weight block copolymers.

Experimental Section

Materials. Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used as received without further purification. 1-Methylimidazole was distilled from solid NaOH prior to use. Diethyl sulfate (>99% purity) was obtained from Fluka and used without further purification.

Ionic Liquid Syntheses. Ionic liquids 1-ethyl-3-methylimidazolium ethylsulfate ($C_2MIM\ EtSO_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ($C_4MIM\ PF_6$), and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($C_8MIM\ NTf_2$) were prepared according to literature procedures.[12–14] IL identity and indeed

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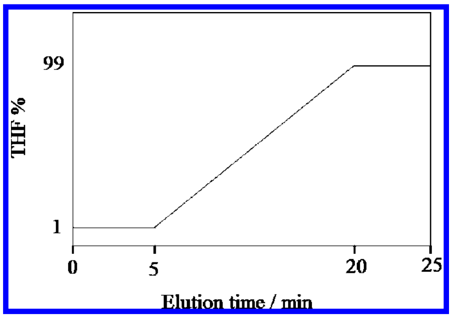

Figure 1. Gradient polymer elution chromatography profile used to separate homopolymers of PSTY and PMMA from the block copolymers. THF and MeOH were used as the good and poor solvent, respectively.

purity were confirmed by ^{1}H and ^{13}C NMR. The water content of the ILs was determined by coulometric Karl Fischer titration using a Mitsubishi CA-100 moisture meter and were shown to be below 200 ppm in all cases.

Polymerization. In a typical experiment, 1 mL of monomer, initiator (0.5 wt % with respect to monomer unless otherwise specified), and 9 mL of ionic liquid were charged into a round-bottom flask fitted with a three-way tap for sample extraction. The contents were degassed by three consecutive freeze–pump–thaw cycles to 10^{-3} Torr. The reaction was blanketed with argon prior to heating to the desired temperature for 4 h. All yields were determined by NMR by monomer conversion.

Instrumentation. Molecular weights were determined using a PL120 GPC system fitted with 2 × C-packed columns in series (Polymer Laboratories). The polymer was eluted using HPLC grade THF at a flow rate of 1 mL min^{-1}. The polymer was detected using a refractive index detector, and polymer conformation was measured by a Wyatt 8 angle Mini-Dawn system. ^{1}H NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300.14 MHz for ^{1}H. Gradient polymer elution chromatography (GPEC) was performed on a PLRS 300 column (Polymer Laboratories) with a gradient controlled mixture of methanol and tetrahydrofuran (THF) as the mobile phase. An ELS-1000 detector (Polymer Laboratories) was used to determine the elution time of each polymer. In a typical experiment, 5 mg of sample was dissolved in 1 mL of 1:1 mixture of THF and methanol, and 20 μL of the solution was adsorbed onto the column. The column was flushed for 5 min with 99% methanol. The solvent was then gradually changed from 1% THF to 99% THF over 15 min. Finally, the column was washed for 5 min with 99% THF (Figure 1).

Results and Discussion

The free-radical polymerization of MMA in ILs has been extensively reported in the literature.[2] However, a satisfactory explanation for the combined observation of enhanced molecular weight and reaction rate in ILs remains elusive. Therefore, we began our investigation by conducting an in-depth study of the reaction kinetics of MMA polymerization in both ILs and OSs. This was followed by a comprehensive assessment of the effects that occur upon altering (a) monomer concentration, (b) reaction temperature, and (c) chain transfer agent concentration. These key experiments pointed toward the existence of protected radicals in the IL systems that are not present in the OS equivalents. Furthermore, this led us to successfully apply an IL-based approach toward the synthesis of block copolymers, using the protected radicals to successfully synthesize high molecular weight A−B block copolymers in the absence of additional control agents. This is a procedure that cannot be reproduced in equivalent organic solvent systems without additional control agents.

Polymerization Kinetics. The reaction kinetics of MMA was investigated in a model IL, C$_4$MIM PF$_6$. Reaction sampling proved to be an issue since at intermediate conversions (>40%) the reaction mixture became viscous, almost to the point of solidifying. The terms solidify and solidification have been used in preference to gel and gelation in this case because the materials that result from the experiments can be fully redissolved in organic solvent and analyzed by GPC. This contrasts to the standard definition of gel which is the formation of an extended, cross-linked 3-dimensional and hence insoluble network. Thus, meaningful kinetic data were only observed up to ~40% monomer conversion.

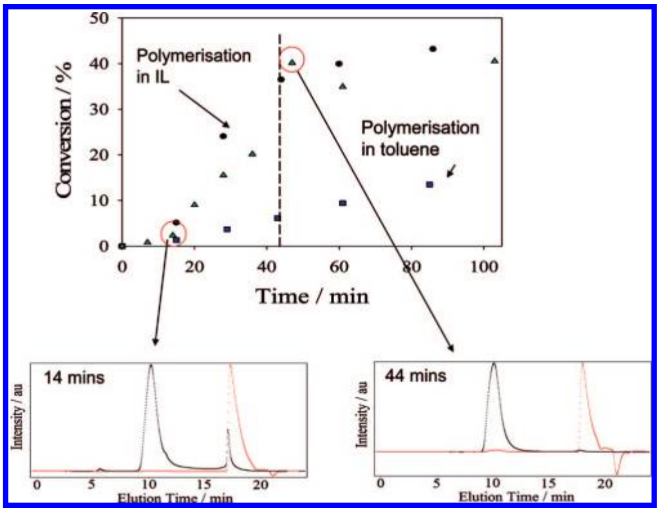

Figure 2. Plot of conversion vs time for polymerization of MMA in IL (circle) and toluene (squares) at 80 °C, monomer concentration 10%. The polymerization in IL was repeated to show reproducibility (triangle). The dashed line signifies the solidification point in the IL experiments. Also shown are the RI and MALLS GPC traces for the sample at 14 and 44 min. MALLS shows that high molecular weight polymer is present even after only 14 min.

Figure 2 shows a comparison of conversion vs time for the free radical polymerization of MMA in C$_4$MIM PF$_6$ and toluene at 70 °C. The reaction in the IL is considerably faster than that in toluene. This effect has been observed previously, and it has been shown that k_p (propagation rate constant) increases with increasing concentration of IL in the reaction,[15] while k_t (termination rate constant) decreases.[16] This increased ratio of k_p/k_t adequately describes the enhanced molecular weight effects that are observed, but an explanation for the increase in rate is not forthcoming in the literature.

Also shown are the GPC traces for the product at 14 and 44 min after the set reaction temperature has been attained. The MALLS trace is shown because it is not concentration dependent and in fact has a greater response for high molecular weight products. For example, in the 14 min trace at ~3% monomer conversion, very little high molecular weight product is evident in the trace using an RI (concentration dependent) detector (red), but it is clearly visible in the MALLS trace. After 44 min reaction time when monomer conversion approaches 40%, the high molecular weight peak becomes evident in the trace using the RI detector. Significantly, the molecular weight of the product does not change from 3 to 40% conversion, with the product having an M_n = 1.1 MDa and PDI of 1.3 when measured by MALLS. This is surprising for two reasons. First, the formation of much higher molecular weight polymer than would be expected from reaction at a particular temperature seems to occur immediately after starting the reaction. Second, there is no evidence for peak broadening or multimodal peaks as different length chains are propagating when the reaction mixture is still a miscible liquid. This suggests that the radicals are in a protected state, such that only a limited number of chains propagate. However, this still leaves the observation that these few chains propagate at a significantly enhanced rate to form very high molecular weight polymer. This enhanced rate and the broadening of the polydispersity of the polymer molecular weights following solidification will be discussed in more detail later in this report.

One factor that may be contributing to the enhanced rate and high molecular weights is the initiation kinetics of AIBN. The decomposition rate of AIBN has been shown to be dependent on the solvent system that is used and thus may be influenced by the use of ILs as solvent. the decomposition kinetics of AIBN were followed by UV spectroscopy at 65 °C following literature reported methods.[17,18] The UV–vis spectrum of AIBN has a strong absorbance at 347 nm, which decreases as the initiator decomposes. A plot of $\ln(A_0/A_t)$ vs time, where A_0 and A_t are the initial absorbance and absorbance at time t, yielded a value of K_d for AIBN in IL at 80 °C of 1.9×10^{-4} s^{-1}. This value is similar to that found in toluene (1.55×10^{-4} s^{-1}).[19] This difference is clearly not of the magnitude required to produce the differences in rate and molecular weight observed in the reported IL polymerizations.

The initiator efficiency, *f*, describes how well the radical can initiate propagation. This value is affected by physical factors such as viscosity, and hence, the value changes as the reaction proceeds and the medium becomes more viscous.[20] Thus, initiation efficiency can have huge implications on the yield and molecular weight of the final polymer product that is observed. The initiation efficiency for AIBN in ILs in the absence of monomer and polymer was measured by observing the changing absorbance of the radical scavenger, galvinoxyl, as it reacts with the AIBN. Galvinoxyl was chosen for this experiment because it has been shown to be equally reactive toward both oxygen- and carbon-centered radicals. A plot of absorbance (762 nm) vs time gives the initiator efficiency according to the following equation

$$A_t = A_0 - (2fk_d[I]_0\epsilon l)t \tag{1}$$

where A_t and A_0 are the absorbance of galvinoxyl at time t and 0, respectively, $[I]_0$ is the concentration of AIBN, ϵ is the molar absorptivity of galvinoxyl, and l is the path length.[21]

Unfortunately, galvinoxyl was not soluble in C_4MIM PF_6. However, a search of available ILs showed that it was soluble to the required level in C_8MIM NTF_2; this is thought to be due to the increased lipophilicity provided by the larger pendant C8 chain. Consequently, it was chosen as the medium for this study; although this approach is clearly nonideal in terms of providing a direct comparison to the polymerization studies, it did allow comparisons to be drawn between the initiator efficiency in both organic solvents (OSs) and ionic liquid systems (ILs). Hence, we are interested in the order of magnitude of the results from comparative experiments rather than the finite value. The value of *f* was found to be ~0.4 for AIBN in C_8MIM NTF_2 at 80 °C, if the decomposition rate of AIBN in C_4MIM PF_6 was used in the above equation as the nearest readily available IL-based value. Once again, this value was not significantly different than that measured for conventional solvents; *f* is 0.7 for AIBN in toluene at 80 °C. Indeed, a slight decrease in *f* may be expected due to the increase in viscosity of the IL systems compared to OS equivalents. It is also important to note that the initiator efficiency changes considerably with conversion as the reaction medium becomes more viscous. However, for reactions at low conversion, the initiation kinetics appear to play no significant role in the rate and molecular effects that are observed but may be attributed to more detailed effects such as PDI broadening in IL polymerizations as conversions increase and solidification occurs.

The key conclusion from this study of AIBN decomposition in ILs is that initiation appears to be similar to that recorded in OSs such as toluene and xylene. Thus, initiation effects cannot be the sole cause of the rate and molecular weight differences between the IL and OS systems.

Table 1. Comparison of Polymer Products from Two Ionic Liquids Used in This Study[a]

ionic liquid	M_n/kDa[b]	M_w/kDa[b]	PDI	yield/%
C_4MIM PF_6	69	184	2.6	87
C_2MIM $EtSO_4$	63	195	3.0	94

[a] Reaction performed at 80 °C for 4 h in 50% IL. [b] Determined using RI detector and polystyrene calibrants.

Table 2. Comparison of Polymer Product Formed by Different Ratios of Monomer to Solvent in Xylene and C_2MIM $EtSO_4$[a]

solvent	monomer:solvent	M_n/kDa[b]	M_w/kDa[b]	PDI	yield/%
xylene	10:90	23	40	1.8	2.5
xylene	50:50	31	63	2.0	92
xylene	90:10	35	87	2.5	97
C_2MIM $EtSO_4$	10:90	116	304	2.6	95
C_2MIM $EtSO_4$	50:50	70	184	2.6	87
C_2MIM $EtSO_4$	90:10	60	194	3.2	92

[a] Reaction performed at 80 °C for 4 h. [b] Determined using RI detector and polystyrene calibrants.

Solvent Effects. C_4MIM PF_6 has been one of the most popular IL solvents for polymerization reactions.[2] This is probably due to its widespread use in the literature for organic reactions. While C_4MIM PF_6 yielded fast reaction rates and high molecular weight products, the synthesis of this IL is multistepped, and extraction of polymer from the IL is not straightforward. For this reason, C_2MIM $EtSO_4$ was chosen as a model IL for comparison. The synthesis of C_2MIM $EtSO_4$ is achieved in a single step, with no unwanted side products. Furthermore, it is immiscible with many common solvents including THF, enabling the isolation of polymer products in a single step. This is highly advantageous for scale-up and industrial processes. A comparison between C_2MIM $EtSO_4$ and C_4MIM PF_6 as IL for the polymerization of MMA is given in Table 1.

In both cases, solidification is observed after ~15 min at 80 °C. In the case of C_2MIM $EtSO_4$, precipitation of the PMMA is also observed. The solidification is presumably due to the synthesis of very high molecular weight polymer chains and their contribution toward increasing the viscosity of the system. Additionally, there is also evidence that C_4MIM PF_6 may participate in hydrogen bonding with PMMA.[22] Of particular interest is the similar yields and molecular weights observed for each IL. PMMA is less soluble in C_2MIM $EtSO_4$, and this would generally be expected to affect the molecular weight that is produced. Thus, high molecular weight polymer is achieved in both ILs, and the reaction rate is also much higher than in conventional organic solvents. Therefore, when possible, all further reactions were undertaken using C_2MIM $EtSO_4$ rather than C_4MIM PF_6.

A comparison between xylene and C_2MIM $EtSO_4$ as solvent is shown in Table 2. Notable differences exist between both the yields and molecular weights observed for different ratios of monomer:solvent. The largest difference between the two solvents is observed when a very low concentration of monomer is used. For the case of OS (Table 2, row 1), the yield is predictably low due to the very low reaction kinetics expected. In contrast, the analogous reaction in C_2MIM $EtSO_4$ (Table 2, row 4) led to the formation of relatively high molecular weight polymer with high monomer conversion, suggesting that a much higher reaction rate is present in the IL. Furthermore, it suggests that the radicals produced in the IL case are protected from termination to a greater extent than in the OS system leading to a high yield.

There is clearly a step change in the polymerization performance between the OS and IL system in the region between

Table 3. Comparison of Polymer Produced in C_2MIM $EtSO_4$ and Xylene as a Function of Temperature[a]

temp/°C	solvent	M_n/kDa[b]	M_w/kDa[b]	PDI	yield (NMR)/%
60	C_2MIM $EtSO_4$	350	820	2.34	83
	xylene	NA	NA	NA	0
70	C_2MIM $EtSO_4$	591	795	1.34	100
	xylene	35	71	2.00	32
80	C_2MIM $EtSO_4$	201	535	2.66	93
	xylene	24	36	1.48	46
90	C_2MIM $EtSO_4$	113	437	3.87	100
	xylene	17	26	1.52	47
100	C_2MIM $EtSO_4$	94	279	2.97	94
	xylene	18	27	1.54	51
110	C_2MIM $EtSO_4$	46	191	4.14	89
	xylene	21	31	1.47	41
120	C_2MIM $EtSO_4$	77	224	2.91	93
	xylene	20	26	1.28	26

[a] Reaction performed for 4 h. [b] Determined using RI detector and polystyrene calibrants.

50% down to 10% monomer concentrations. In our view there are three possible explanations for this observation: (1) increased reactivity of the monomer due to adduct formation between the IL and the monomer increasing the capacity for low monomer systems to polymerize, (2) a marked decrease in initiator efficiency and termination due to the increased viscosity (and eventual solidification) of the system, or (3) decreased termination due to the protection of the radical by the formation of radical—IL adducts. The fact that the initiation efficiency in IL is similar to that in OS at low monomer conversion, coupled with the observation that very high molecular weight polymer is formed very early in the reaction, suggests that viscosity is not the predominant or sole factor involved in the enhanced kinetics and molecular weights that are observed. The presence of IL coupling to a radical or monomer would lead to both a decrease in the termination rate in the polymerization, consequently enhancing rates (if coupled to the monomer), and molecular weight (if coupled to the radical).

Temperature Effects. In order to gain an understanding of the kinetic mechanism, the polymerization was conducted at various temperatures, and a comparison was made between IL- and OS-based polymerizations (Table 3). In order to minimize the effects of solidification, thereby highlighting any fundamental differences between these two solvent systems, this study was limited to reactions in low monomer concentration (10:90 ratio of monomer to IL).

Here, the interesting properties of IL for polymerization are clearly demonstrated. When the temperature increases from 60 to 120 °C, the yields of polymer in the xylene reactions followed the expected pathway: At low temperature the radical flux is very low, and hence yield is negligible; at approximately 80–90 °C, the yield reaches a maximum (~50%) due to the relatively "ideal" initiator decomposition rate; at 120 °C, the yield and molecular weight are very low due to rapid initiator consumption or "burnout", leading to poor initiation and propagation kinetics. Yields at 80–90 °C were not at levels >90% in the OS case due to the low concentration of monomer. Indeed, when the concentration of OS is decreased to 50%, monomer conversions of greater than 90% are observed. On the other hand, the IL results seem so show little effect of temperature on the yield, even at low monomer concentration; in all cases near-quantitative yields are observed. The molecular weight tends to decrease with increasing temperature. This is expected for an increase in radical flux leading to more propagating polymer chains. However, even at reaction temperatures of 120 °C, the M_n is approaching 80 kDa in the IL case. This is considerably larger than that observed in xylene at the same temperature (20 kDa) and in fact is still double the M_n obtained at 70 °C in xylene.

Table 4. Effect of DDM on Polymer Product Formed in C_2MIM $EtSO_4$ and Toluene[a]

solvent	DDM/vol % wrt monomer	M_n/kDa[b]	M_w/kDa[b]	PDI	yield/%
toluene	0	31	63	2.0	93
toluene	9	5.0	7.7	1.5	80
toluene	17	5.3	8.5	1.6	59
C_2MIM $EtSO_4$	0	69	184	2.6	87
C_2MIM $EtSO_4$	9	18	30	1.7	69
C_2MIM $EtSO_4$	17	10	14	1.4	34

[a] Reaction performed at 80 °C for 4 h. [b] Determined using RI detector and polystyrene calibrants.

The combination of both quantitative yield and the exceptionally high molecular weights for the reactions in ILs provides further evidence for a "protected" radical. At high temperatures, radical–radical recombination is enhanced compared to lower temperatures due to the much higher radical flux (the half-life of AIBN at 120 °C in xylene is about 100 s). Hence, to achieve the very high yields evident in the IL experiments but not in the OS system, radical protection must be occurring to reduce/prevent this radical coupling.

Furthermore, this radical protection may in fact explain the slight time lag observed at the start of the reaction before polymerization. In this case, after 14 min the conversion is observed to be 3% while after 44 min it has reached in excess of 40%. This can be explained by the fact that at these high IL concentrations the initial radicals formed from the AIBN decomposition are protected by the presence of the IL. It is only once a significant radical flux is produced can it "swamp" the protective effect, and the polymerization is observed to begin in earnest.

Molecular Weight Control. The reactions performed in IL show uncharacteristically large molecular weights; such weights are often only attainable under conditions of extremely low initiator loading. One method of decreasing the molecular weight is to use chain transfer agents—one of the most common classes in industrial use being mercaptans. The mechanism is very well studied and involves a thiol unit reacting with the propagating radical whereby chain termination occurs via hydrogen atom transfer to form a sulfur-centered radical and saturated chain end.[23] This is a common industrial method of decreasing chain length and controlling runaway radical reactions. Dodecylmercaptan (DDM) was used as a chain-transfer agent to investigate the ability to form low molecular weight polymer in ILs. A comparison between the effect of DDM on reactions performed in IL and toluene is presented in Table 4.

The effect of DDM is clearly evident in both OS and IL, where a marked decrease in the polymer molecular weight is observed as well as the accompanied reduction in PDI. However, in the case of toluene the polymer chain is easily capped, and very low molecular weight chains ($M_n \sim 5$ kDa) can be achieved. On the other hand, much more DDM is required to effectively suppress the molecular weight in the IL. Indeed, even when the DDM concentration is as high as 17 wt %, M_n is still 10 kDa—double that which is observed for the tolulene case. Furthermore, the observation from the experiments that increase the level of DDM from 9% to 17% in OS showed that no further molecular weight drop occurred. However, in the IL, the molecular weight of the material is still being reduced with a 17% level of DDM present. This suggests that at 9% DDM the minimum possible reduction of molecular weight in OS has been achieved, while in IL at 17% DDM further reduction in the molecular weight is still possible.[24] This suggests that the DDM must work exceptionally hard to react with the propagating radical in the IL and achieve the chain transfer effect. However, it is also observed in these experiments that there is a greater reduction in polydispersity in the IL case (PDI = 2.6 to 1.4) compared to the OS systems (PDI = 2.0 to 1.6). This suggests that the radical loss during the chain transfer event is less in IL compared to OS- and/or the DDM-based termination which occurs as part of the chain transfer event actually constitutes a greater "percentage" of the total overall chain termination that occurs in the IL system than in the analogous OS system, hence leading to a greater PDI reduction. Both of these observations lead to the conclusion either that diffusion of the DDM through the medium is restricted (i.e., a viscosity effect) or that a radical protecting mechanism is active which prevents DDM interaction with the growing radical at low levels of chain transfer agent (CTA). However, as the levels of CTA increase, it begins to become the dominant termination process in the reaction due to the much reduced termination in the IL system. The fact that the initiator efficiency of AIBN in IL is similar to that in toluene suggests that the latter explanation is more likely. This is because the initiator efficiency provides information on, among other things, the diffusion characteristics of small molecules in a medium. Since f is similar in the ILs used in this study and OSs for AIBN, we would expect (a) the MWts to be similar and (b) the DDM should readily diffuse through the IL medium. Thus, as a result, we believe the differences in rates, molecular weights, and yields that are observed for the "DDM-controlled" polymerizations in ILs compared to OS is due to a radical protection mechanism.

Linking the Observed Effects to Rate Enhancement. The key relationship that must be considered is the *simultaneous* increase in polymerization rate and molecular weight in ILs compared to OSs. If the increase in polymer molecular weight is due to a "protected" radical system alone, then a *decreased* rate would probably be expected since radical interaction would be inhibited through the protection. This is clearly not the case. Thus, we explain the combination of these effects by the formation of monomer domains within the IL together with protection of the radical. In this way, the reaction is essentially carried out under "bulklike" conditions; the rate is much greater than in solution polymerization. In addition, the protection of the AIBN radical implies that it is partitioned into the IL–MMA interface and perhaps into the IL itself. Thus, although the radical decomposition and primary initiation efficiency of AIBN are essentially the same in IL as in conventional solvents, this positioning of the radicals in the IL limits their availability to the monomer to begin polymerization. Therefore, the resultant "true" radical flux in the monomer phase is much lower than would be expected from the measured decomposition kinetics. This low level of radicals leads to the exceptionally high molecular weight polymers that are observed—even at very short time. Furthermore, we postulate that the monomer domains within the IL are extremely small, leading to a large interface between monomer and IL. This gives the growing chains high exposure to the IL, and as a result, significant radical protection of the growing polymer chains is also achieved by interaction with the IL.

This theory can also explain the apparent reduced chain transfer effect that is observed in IL compared to OS. The partitioning of the thiol at the IL–monomer interface is likely because the R group is not sufficiently large to drag it fully into the monomer phase. Hence, the chain-transfer event is inhibited by this partitioning effect and combines with radical protection to decrease the efficiency of chain transfer in two ways. First, the partitioning of the thiol enhances the competition of the monomer over the thiol for reaction with the radical compared to polymerizations in OSs. Second, the new radical formed upon reaction with the thiol, which will be close to the IL interface and can then in turn be protected by the IL to decrease the rate growth away from the chain transfer produced radical. This effect can be overcome by swamping the system with thiol such that the "bulklike" reaction medium has an exceptionally high degree of chain transfer; this leads to the lowered PDI and molecular weights observed in Table 4 at high CTA loading. A similar argument of catalyst/CTA partitioning in the IL can also be put forward for the results previously reported for ATRP and RAFT in IL.[7,8]

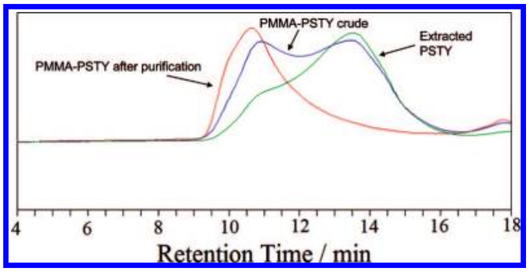

Figure 3. GPC traces showing the crude product that is formed that is a blend of both copolymer and homo-PSTY, the extracted homo-PSTY, and the subsequent block copolymer after extraction of polystyrene. The loss of the homo-PSTY peak following purification shows successful extraction of the PSTY homopolymer from the mixture.

One important question that arises is, what is the driving force behind our perceived domain separation? It has been reported that ILs will within themselves form domains that are organic-rich and Coulombic/ionic-rich.[25] It is our belief that at low monomer concentration the monomer swells these domains into monomer-rich regions throughout the medium. This explains why yields of up to 100% can be achieved in IL when the system solidifies at ~40% conversion; monomer diffusion throughout a solidified bulk is not necessary since all the reactant is already present in the monomer-rich phase. This is similar in many respects to standard emulsion polymerization, the kinetics of which exhibit similar characteristics to these IL systems. We are currently investigating this hypothesis to provide further evidence for the domain-type reactions in ILs.

Block Copolymers. One of the ultimate applications for a "protected" radical system is the formation of block copolymers without the need for living radical catalysts. Mays and co-workers recently presented a short communication reporting the synthesis of polystyrene–poly(methyl methacrylate) copolymers in IL without any catalyst present.[5] However, because of the lack of sufficient polymer characterization and the synthetic method by which they were produced, doubt exists as to the structure of these polymers—the possibility for graft polymer rather than linear block copolymer.

In this study, styrene was first polymerized in the IL (C_2MIM $EtSO_4$) for 8 h at 80 °C and was observed to precipitate from the mixture after about 15 min. This reaction time is equivalent to 8 half-lives of the AIBN and should result in there being essentially no remaining initiator in the reaction system; this is well-known for conventional solvents. The PSTY that was formed acts as the first block in the copolymer. MMA monomer was then injected into the system, and reaction was allowed to proceed for a further 12 h to yield copolymer (PSTY–PMMA). The GPC trace for the copolymer is shown in Figure 3 where a broad bimodal peak is observed. The PSTY homopolymer was extracted from the mixture with cyclohexane using a Soxhlet extractor and was found to be ~30 wt % of the reaction product. The presence of PSTY homopolymer in the reaction product is expected to result from block A homopolymer, which has been subjected to termination in the first stage of the reaction. This level of termination is much less than the amount present in the analogous reaction in OS. The bimodality of the crude PSTY–PMMA product also suggests that a mixture of products was present in the system. The GPC trace for the extracted PSTY is also shown (Figure 3) and is predominantly lower mass product. Indeed, this trace overlays directly the lower

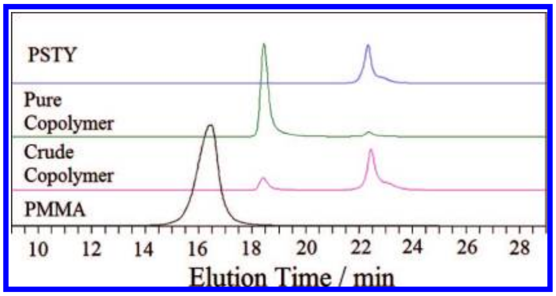

Figure 4. GPEC trace for pure PSTY and PMMA (top and bottom traces, respectively). The middle traces are for the copolymer and show the presence of residual PSTY homopolymer as well as copolymer.

mass peak of the crude copolymer scan. Finally, the copolymer after extraction of the PSTY is also shown (Figure 3). This trace suggests that the copolymer is of very high mass. However, even though there is an obvious shift in molar mass to higher weights from the original PSTY ($M_w = 266$ kDa for PSTY up to $M_w = 415$ kDa for the copolymer), the extremely broad and complicated distribution that results from polymerization of the second block, MMA, in an IL (PDI = 2.5 for crude copolymer) casts some doubt upon whether copolymer is formed or if there is just a mixture of homopolymers.

Therefore, gradient polymer elution chromatography (GPEC) was conducted as it built further on the GPC results and could definitively prove the existence of copolymer. Tetrahydrofuran and methanol were used as good and poor solvents, respectively. The resultant GPEC trace for the copolymer sample is shown in Figure 4 and clearly shows the presence of copolymer and homopolymer PSTY in the crude copolymer product. For comparison, homopolymer PMMA and PSTY have also been included in Figure 4. In this analysis, the PMMA clearly elutes much earlier than the PSTY due to the greater affinity for methanol (16 min PMMA; cf. 22 min PSTY). The copolymer elution trace shows two main peaks: one at an elution time similar to that of PSTY homopolymer and one between that of both PSTY and PMMA. This suggests that copolymer is formed along with some PSTY homopolymer. Interestingly, no PMMA homopolymer is observed in the GPEC trace. This is further evidence for the existence of a "protected" radical effect since this demonstrates that in the second stage block B polymerization can only grow away from the PSTY chain and not homopropagate. This suggests that there is effectively no residual AIBN to partition into the reaction mixture upon addition of the second monomer, and the only initiation source for the MMA is the "protected" radical on the PSTY block. Hence, initiation of the MMA thermally, or otherwise, is negligible under these conditions.

The elution trace for the polymer after extraction with cyclohexane is also shown in Figure 4 and falls midway between that of PSTY and PMMA (pure copolymer). This peak represents pure copolymer with little residual homopolystyrene, indicating the success of the extraction procedure.

Differential scanning calorimetry showed the presence of two distinct endotherms at ~100 °C (Figure 5). These are indicative of the glass transition for both PSTY and PMMA. The presence of two transitions is due to heterophase separation of the respective polymers in the block and is consistent with microphase separation that is intrinsic to block copolymers containing "repulsive" comonomers and very large block components. Indeed, the presence of these two distinct T_gs, and the apparent absence of an intermediate T_g, implies that only block copolymer is formed and that negligible, if any, random copolymer is formed by the presence of residual STY (monomer A) upon addition of MMA (monomer B). The ratio of PSTY: PMMA in the copolymer was determined by ^{1}H NMR and was found to be 30:70 with a large excess of PMMA. This is not surprising since the PSTY that formed homopolymer was removed, while all of the MMA reacted to form copolymer. This lack of 100% regrowth has skewed the relative monomer composition of the copolymers. However, we believe that with further optimization of the system block copolymers of specific composition could be formed.

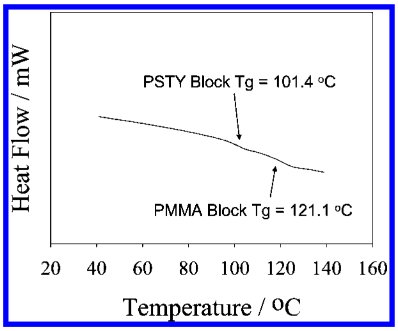

Figure 5. DSC trace showing the presence of two glass transition temperatures for the PMMA block and the PSTY block in the block copolymer.

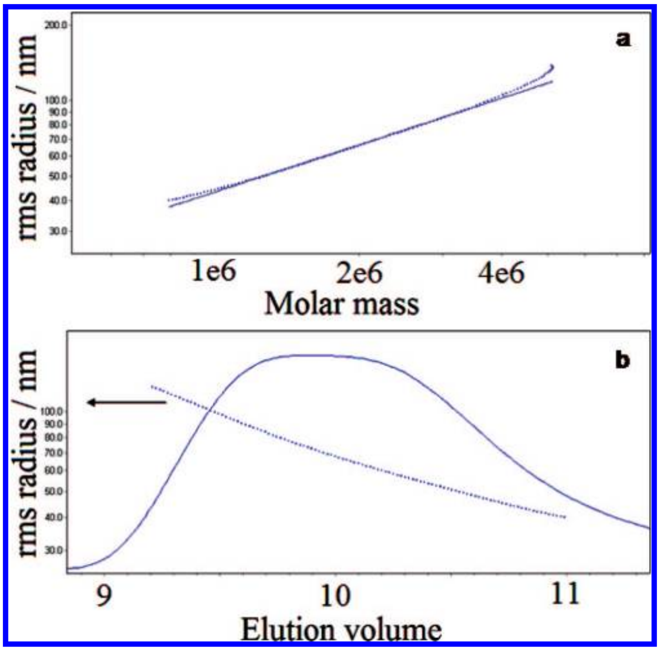

Figure 6. MALLS experiments showing conformational information on the block copolymer. The slope of the conformation plot is 0.62 (a), indicating that the copolymer is in fact a block copolymer, not a branched or graft species. As expected for a linear, non-cross-linked species, the size of the copolymer increases with molecular weight—the rms radius of the polymer chain is overlaid with the RI trace for the copolymer (b).

In previous work it has been suggested that the "protected" radical mechanism does not occur, and hence block copolymers are not formed. Instead, it has been put forward that the copolymers could in fact be formed via a grafting mechanism.[5] It is well-known that grafted or branched polymers tend to arrange into a more spherical structure in solution compared to the random coil structure of a linear polymer. Thus, multiangle laser light scattering (MALLS) was used to determine the molecular structure of the copolymers that were formed.[26] Figure 6 shows the conformation plot (a) and absolute molecular weight profile (b) for the copolymer.

The conformation curve (a) compares the rms radius to the molar mass of the polymer. For a completely linear, randomly coiled polymer, the rms radius will increase linearly as a function of molar mass. For the copolymer formed here, the slope is 0.62, which is indicative of a randomly coiled structure. A branched or grafted polymer would be expected to have a slope of ~0.3 since the conformation approaches that of a sphere. The molecular weight profile (b) is also presented and shows the GPC trace measured by light scattering as observed for the copolymer. A plot of rms radius of the polymer as a function of retention time is also plotted. Thus, MALLS data suggest that block copolymer is indeed formed in this reaction and not the suggested grafted polymer.

The combination of these characterization techniques provides very powerful evidence for the existence of block copolymer. Indeed, while the GPEC shows conclusively that block copolymer is actually formed, we have utilized MALLS to show that linear, block copolymer is most likely formed and that the suggested grafted product is unlikely. This lends significant weight to the existence of a "protected" radical mechanism in ionic liquids—whether this protection is due to precipitation of polymer chains (as suggested by Mays[5]) or by interactions within the ionic liquid.

Conclusion

We have detailed an in-depth study of the free-radical polymerization of MMA in ionic liquids and utilized numerous methods in an attempt to elucidate the mechanism that results in the combined observations of enhanced rate of polymerization, high molecular weight product, and high yields that result from polymerizations that solidify early. The addition of chain transfer agent showed that the extent of molecular weight reduction for a set CTA concentration was much less than the analogous reaction in an organic medium while the observed tightening of PDI as CTA concentration was increased is more pronounced in ILs. Furthermore, while initiator "burnout" was observed for polymerization at high temperatures in OSs, no such effect was seen in C_2MIM $EtSO_4$. The study of these factors suggests that the radical is being protected in the IL as part of the process of monomer separating into extremely small domains in the IL, leading to significant partitioning of the AIBN radical into the IL domain. Additionally, the formation of PSTY−PMMA block copolymer from a "protected" macroradical which had been formed in an IL medium was then investigated, and it was shown that linear copolymer was indeed formed. Furthermore, the only homopolymer observed was the block A polymer, PSTY. The absence of homopolymer PMMA (block B) adds further weight to the "protected" radical mechanism as it has only initiated from the "protected" radical source. Similar regrowth is well-known to be impossible in OS using the same mechanism.

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