

# RAFT-Mediated Polymerization of Styrene in Readily Biodegradable Ionic Liquids

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Received December 16, 2008; Revised Manuscript Received January 8, 2009

**ABSTRACT:** Two novel and readily biodegradable ionic liquids were used as solvents in the successful reversible addition–fragmentation chain transfer (RAFT)-mediated radical polymerization of styrene. The polymerizations reached high conversions with slightly higher rates than that observed in toluene, and the molecular weight distributions were consistent with that of an ideal “living” radical polymerization. This represents a significant advance as previous attempts to conduct RAFT-mediated polymerizations of styrene in ionic liquids had failed. With a detailed kinetic analysis we found that the ratio of termination to propagation rate constants remained relatively constant over the conversion range, suggesting that “trapped” or “protected” radicals were not present in our systems.

## Introduction

Ionic liquids (ILs)<sup>1–5</sup> show great promise as solvents for polymerization of a wide range of monomers. Their low volatility, high thermal and chemical stability, and potential to be recycled make ILs attractive as an environmentally friendly alternative to organic solvents (e.g., toluene, xylene, dichloromethane) used in many industrial polymerization processes.

IL's high chemical and thermal stability also raised questions about their ability to accumulate in the environment. Accordingly, the ionic liquids based on 1-butyl-3-methylimidazolium cation with a wide variation of anions biodegrade poorly.<sup>6</sup> Recently, Scammells and co-workers have directed their focus toward the design and synthesis of imidazolium<sup>6–8</sup> and pyridinium<sup>9,10</sup> ionic liquids with improved biodegradability. A number of ILs have now been identified that have proven to be “readily biodegradable” in the CO<sub>2</sub> headspace test (ISO 14593). In all cases, the incorporation of an ester moiety afforded significantly higher levels of biodegradation. Ester-containing pyridinium ILs based on either pyridine or the nontoxic natural product, nicotinic acid, recorded high levels of biodegradation after relatively short time frames (typically >60% after 14 days). The great potential of these designer ILs as truly environmentally friendly solvents has led us to evaluate them in the reversible addition–fragmentation chain transfer (RAFT)<sup>11,12</sup> mediated polymerization of styrene.

The first “living” radical polymerization (LRP) in ILs was carried out for metal-catalyzed LRP experiments and showed a significant increase in the rate of polymerization but with less control over the MWD.<sup>13–16</sup> The reason for the rate enhancement was found to be an increase in the kinetic rate parameters. Harrison et al.<sup>17,18</sup> found that the rate coefficient for propagation,  $k_p$ , for methyl methacrylate (MMA) increased from 323 L mol<sup>−1</sup> s<sup>−1</sup> in bulk to over 800 L mol<sup>−1</sup> s<sup>−1</sup> in 60 vol % IL at 25 °C, which was proposed to be due to an increased polarity. The authors then determined that the rate coefficient of termination,  $k_t$ , decreased by an order of magnitude from bulk polymerization to 60 vol % IL due to an increase in viscosity. Utilizing this

rate enhancement, Percec and Grigoras<sup>19</sup> found that their imidazolium IL catalyzed the LRP of MMA in the presence of Cu<sub>2</sub>O/2,2'-bipyridine to make PMMA rapidly with polydispersity indexes (PDIs) between 1.1 and 1.2 while maintaining high initiator efficiencies.

The origin of the rate increase in ILs has been proposed to be due to (i) their high polarity, (ii) a bootstrap effect where the local concentration of the monomer swelling the polymer coil is much greater than the global concentration, (iii) protection of the radical attributed to precipitation of the polymer in solution, or (iv) a viscosity-controlled mechanism. An excellent review by Winterton<sup>20</sup> on the dissolution of polymers by ionic liquids suggested that solubilization plays an important role. This is highlighted in the RAFT-mediated polymerizations of MMA, methyl acrylate, and styrene, in which only MMA and methyl acrylate reached high conversions with excellent control of the MWD in the imidazolium IL.<sup>21</sup> Styrene, on the other hand, reached less than 2% conversion due to the insolubility of polystyrene (PSTY) in the IL.

In this publication, we report the RAFT-mediated radical polymerization of styrene in pyridinium ILs (see Scheme 1) at 90 °C and initiated with Vazo88. Two ILs were chosen as they are readily biodegradable.<sup>10</sup> The rates of polymerization were found to be slightly faster than a comparative polymerization carried out in toluene but gave excellent control of the MWDs. In addition, the kinetic parameters such as initiator efficiency ( $f$ ) and the ratio of  $k_t/k_p$  were determined, and a mechanism to explain the data was proposed on the basis of the solubilization (or occlusion) of polystyrene in the ILs.

## Experimental Section

**Chemicals.** Styrene (STY, 99%, Aldrich) was purified by filtration through basic alumina (70–230 mesh) to remove inhibitors prior to use. 1,1-Azobis(cyclohexanecarbonitrile) (VAZO88, 99%, Du Pont) was recrystallized twice from methanol. The ionic liquids, IL1 and IL2, were synthesized according to the procedure described in the literature.<sup>10</sup> All other reagents used in the synthesis of RAFT agents (described below) were obtained from Aldrich (99% purity or greater) and used as received. Structures of the RAFT agent and ionic liquids are given in Scheme 1.

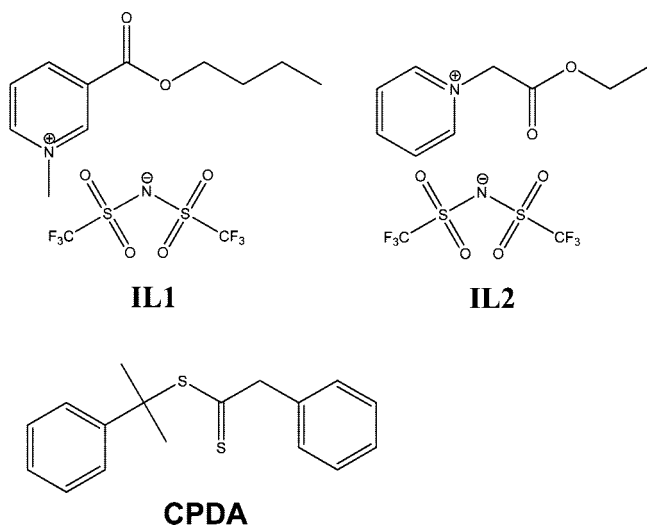
**Synthesis of Cumyl Phenylldithioacetate (CPDA).**<sup>22</sup> Benzyl chloride (40 g) was added dropwise to a mixture of magnesium

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**Scheme 1. RAFT Agent Cumyl Phenylthioacetate (CPDA) and Ionic Liquids 3-(Butoxycarbonyl)-1-methylpyridinium Triflimide (IL1) and 1-(2-Ethoxycarbonyl)methylpyridinium Triflimide (IL2)**



turnings (7.5 g) in dry diethyl ether (150 mL), and the mixture was refluxed for 3 h. The reaction mixture was then placed in an ice water bath, and carbon disulfide (24.0 g) was added dropwise over 30 min. The mixture was then stirred for an additional 3 h at 0 °C and poured into water (300 mL), with the aqueous portion collected following four washes with diethyl ether. A final layer of diethyl ether was added, and the mixture was acidified using 30% aqueous HCl. Phenylthioacetic acid (~14 g) was collected after rotary evaporation of the ether as a thick orange oil. Following collection, the acid was combined with  $\alpha$ -methylstyrene (20% excess, ~18 g) and a small amount of acid catalyst (0.2 g of *p*-toluenesulfonic acid) in chloroform (30 mL) and refluxed at 80 °C for 18 h. The crude product was dissolved in a diethyl ether/hexane (1:4) mixture and crystallized at 0 °C to yield orange crystals. These were filtered, washed, and recrystallized a second time using the procedure described above to yield cumyl phenylthioacetate (CPDA) as large orange crystals (27.9 g, 30.8%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.9 (s, 6H, 2  $\times$  CH<sub>3</sub>),  $\delta$  = 4.3 (s, 2H, CH<sub>2</sub>),  $\delta$  = 7.2–7.4 (m, 8H), 7.5 (d, 2H).

**A Typical Procedure for the RAFT-Mediated Polymerization of STY.** A reaction mixture containing styrene (2 mL, 8.73 M), VAZO88 (0.024 g, 49.65 M), and CPDA (0.057 g, 100 mM) was degassed by four successive freeze–pump–thaw cycles, sealed under vacuum, and polymerized at 90 °C. Conversion was measured gravimetrically by drying the samples in a vacuum oven at ambient temperature to constant weight, and the molecular weight distribution was determined by size exclusion chromatography (SEC).

**A Typical Differential Scanning Calorimetry (DSC) RAFT Polymerization of STY.** The DSC polymerizations were all performed in duplicate. A reaction mixture containing styrene (2 mL, 8.73 M), VAZO88 (0.024 g, 49.65 mM), and CPDA (0.057 g, 100 mM) was degassed by four successive freeze–pump–thaw cycles and transferred into gastight DSC pans using a glovebag under nitrogen. The sample weights in the DSC pans ranged between 30 and 65 mg and were measured by mass difference between empty and full pans. The polymerizations were carried out isothermally at 90 °C, and the heat of polymerization measured by comparing the heat flow from the polymerization pan and an empty pan on a Perkin-Elmer DSC 7 with a TAC 7/DX thermal analysis instrument controller. The DSC instrument was calibrated with a standard indium sample of known mass, melting point temperature, and associated enthalpy change. The rate of polymerization ( $R_p$ ) and monomer conversions ( $x$ ) were calculated using literature values for the heat of polymerization of STY ( $\Delta H_p$  = –73 kJ mol<sup>–1</sup>).<sup>23</sup>

**Size Exclusion Chromatography.** Size exclusion chromatography (SEC) measurements were performed using a Waters Alliance 2690 separations module equipped with an autosampler, column heater, differential refractive index detector, and a photodiode array (PDA) connected in series. Tetrahydrofuran (HPLC grade) was used as eluent at a flow rate of 1 mL min<sup>–1</sup>. The columns consisted of three 7.8  $\times$  300 mm Waters Styragel GPC columns connected in series, comprising two linear Ultrastaygel and one Styragel HR3 column. Polystyrene standards ranging from 517 to 2 000 000 g mol<sup>–1</sup> were used for calibration. SEC of the gravimetric and DSC polymerizations were compared and found to be identical, and as such we are confident that our SEC data are accurate.

## Calculations

**Determination of the Initiator Decomposition Rate Coefficient,  $k_d$ .** For polymerizations involving long reaction times and where initiator concentrations decrease to very low levels, the dead-end polymerization technique can be used to determine the rate coefficient of initiator decomposition.<sup>24–26</sup> At long reaction times, the reaction conversion,  $x$ , approaches a limiting value  $x_f$ . Under these conditions, it can be shown that  $k_d$  is related to the time,  $t$ , and conversion,  $x$ , via the following equation:

$$-\ln\left[1 - \frac{\ln(1-x)}{\ln(1-x_f)}\right] = \frac{k_d t}{2} \quad (1)$$

Thus,  $k_d$  can be easily determined by taking the initial slope from a plot of the left side of eq 1 vs  $t$ .

**Determination of the Initiator Efficiency,  $f$ , with  $x$  from Conventional Free-Radical Polymerization Molecular Weight Data.** The rate coefficient for initiator decomposition,  $k_d$ , has been found to be relatively constant in either organic solvents or ionic liquids (see above). Conversely,  $f$  has been found to vary significantly in ionic liquids.<sup>27</sup> Thus, the evolution of  $f$  with conversion,  $x$ , was determined using experimental data from the evolution of the degree of polymerization,  $DP_n$ , with  $x$ .

During a conventional free-radical polymerization, the number-average degree of polymerization,  $DP_n$ , is determined by the number of monomer units per chain as follows:<sup>26</sup>

$$DP_n = \frac{x[M]_0}{fa([I]_0 - [I]_t)} \quad (2)$$

Here,  $[M]_0$  is the initial monomer concentration,  $f$  is the initiator efficiency,  $a$  refers to the mode of termination (i.e., equal to 1 for termination by disproportionation and 2 for termination by combination),  $[I]_0$  is the initial initiator concentration, and  $[I]_t$  is the initiator concentration at time  $t$ . The time evolution of  $[I]_t$  is given by eq 3.

$$[I]_t = [I]_0 e^{-k_d t} \quad (3)$$

From eqs 2 and 3, the evolution of  $f$  with  $x$  was determined for the conventional free-radical polymerization of styrene in solution using known values of  $[M]_0$  and  $[I]_0$  via eq 4.

$$f = \frac{x[M]_0}{a[I]_0(1 - e^{-k_d t})DP_n} \quad (4)$$

Equation 2 was based on the assumption that chain transfer reactions to solvent or monomer are not a great contributor to the number of polymer chains formed throughout the polymerization compared to those from initiator-derived radicals. This assumption seems valid under our experimental conditions as  $f$  determined from eq 4 for the polymerizations carried out in

**Table 1. Experimental Conditions for Conventional and RAFT-Mediated Radical Polymerizations of Styrene at 90 °C in Toluene, 3-(Butoxycarbonyl)-1-methylpyridinium Triflimide (IL1), and 1-(2-Ethoxycarbonyl)methylpyridinium Triflimide (IL2)**

	M:S % v/v	solvent	[S] <sub>0</sub> , mol L <sup>-1</sup>	[I] <sub>0</sub> , mol L <sup>-1</sup>	[CPDA] <sub>0</sub> , mol L <sup>-1</sup>	<i>k<sub>d</sub></i> , <sup>a</sup> s <sup>-1</sup>	density, <sup>b</sup> g mL <sup>-1</sup>
1	50	toluene	4.69	0.025		4.0 × 10 <sup>-5</sup>	0.865
2	50	IL1	1.51	0.025		4.0 × 10 <sup>-5</sup>	1.43
3	50	IL2	1.86	0.025		4.8 × 10 <sup>-5</sup>	1.66
4	50	toluene	4.69	0.025	0.05	5.2 × 10 <sup>-5</sup>	
5	50	IL1	1.51	0.025	0.05	6.0 × 10 <sup>-5</sup>	
6	50	IL2	1.86	0.025	0.05	7.0 × 10 <sup>-5</sup>	

<sup>a</sup> Rate coefficient of initiator decomposition, *k<sub>d</sub>*, determined using the dead-end polymerization technique. <sup>b</sup> Density determined by weight of solvent per volume.

the three solvents (see Figure 3) were close to that found in the literature. Additional support also comes from the observation that the polydispersity index (PDI) values were less than 1.5, which suggests chain transfer was not dominant in our systems. It should be noted that the value of *f* has a very small influence on the important value of *k<sub>t</sub>/k<sub>p</sub><sup>2</sup>* determined by eq 5.

**Determination of log(*k<sub>t</sub>/k<sub>p</sub><sup>2</sup>*) values with *x*.** The log *k<sub>t</sub>/k<sub>p</sub><sup>2</sup>* vs conversion profiles were determined for the conventional and RAFT-mediated polymerizations of styrene in bulk and in solution, using accurate reaction rate data and eq 5.

$$\frac{k_t}{k_p^2} = \frac{[M]^2(R_{th} + 2fk_d[I]_0e^{-k_d t})}{R_p^2} \quad (5)$$

Equation 5 is derived from the steady-state approximation (*R<sub>i</sub>* = *R<sub>t</sub>*), where the rates of initiation and termination are given by eqs 6 and 7, respectively.

$$R_i = R_{th} + 2fk_d[I], \quad (6)$$

$$R_t = k_t[P^*]^2 \quad (7)$$

Because of the relatively high reaction temperature (90 °C), self-initiation of styrene could not be excluded, and the rate of autoinitiation, *R<sub>th</sub>*, was included in eq 6.<sup>22</sup> Equation 5 is then derived by combining eqs 6 and 7 and substituting eq 8 for the radical concentration, [*P*\*].

$$\frac{-d[M]}{dt} = R_p = k_p[M][P^*] \quad (8)$$

Thus, according to eq 5, *k<sub>t</sub>/k<sub>p</sub><sup>2</sup>* can be determined using accurate *R<sub>p</sub>* data and known reaction rate coefficients. Reliable reaction rate coefficients used in conjunction with eq 5 were taken from the literature and are given in Table 1. The initiator efficiency, *f*, determined experimentally above was substituted into eq 5. However, it is worthwhile noting that although an experimentally determined conversion-dependent *f* was implemented into eq 5, log *k<sub>t</sub>/k<sub>p</sub><sup>2</sup>* values were unaffected by the change in *f* with *x* (i.e., whether *f* was constant or decreased with *x*).

## Results and Discussion

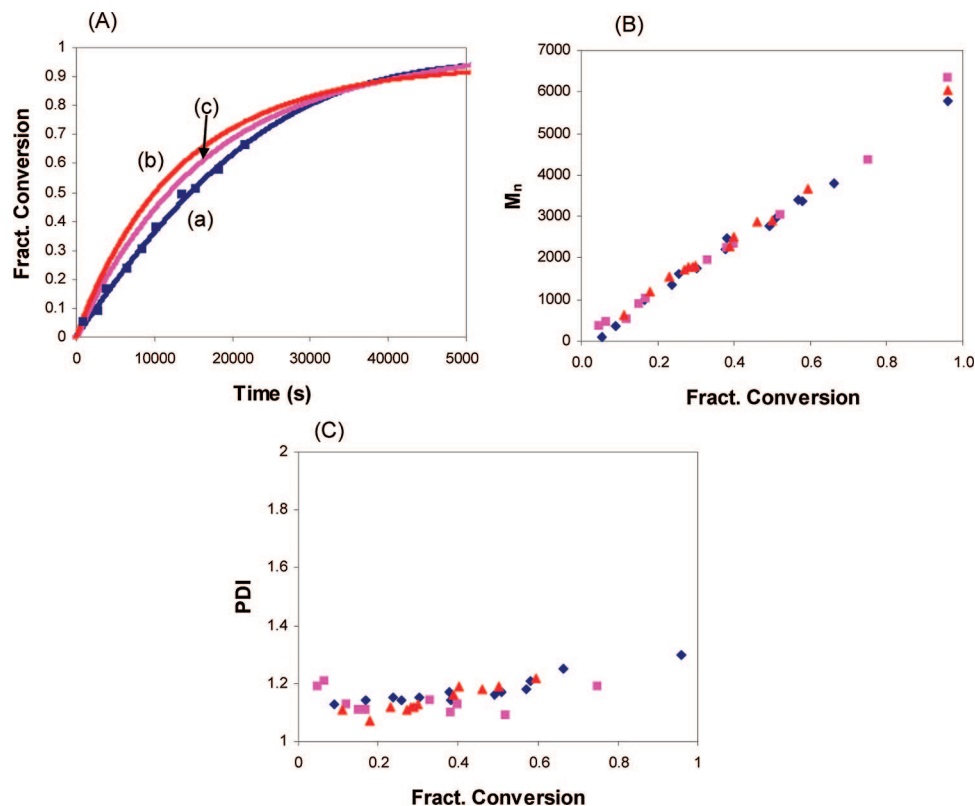
**RAFT-Mediated Polymerization of Styrene in Ionic Liquids.** Previous work<sup>21</sup> on the polymerization of styrene in the presence of RAFT agent 2-(2-cyanopropyl)dithiobenzoate in an imidazolium IL, 1-alkyl-3-methylimidazolium hexafluorophosphate, showed that little or no polymer was formed, with less than 2% conversion after 24 h. In this work, we demonstrate the successful RAFT-mediated polymerization of styrene in readily biodegradable ionic liquids (Scheme 1) initiated with VAZO88 at 90 °C (see Table 1 for experimental details). It was observed that the reaction mixtures of these RAFT-mediated polymerizations were clear and homogeneous in the ILs. The viscosity of IL1 was lower than IL2, in good correlation with their respective densities of 1.43 and 1.66 g mL<sup>-1</sup>. Based only on viscosity change, the rate of polymerization should be faster

for IL2 as compared with IL1 due to a decrease in the *⟨k<sub>t</sub>⟩*.<sup>22,28–30</sup> Figure 1 shows the kinetic profiles for the RAFT-mediated polymerization of styrene in toluene, used as the control, and two pyridinium ILs. It was found from the conversion–time profiles (Figure 1A) that the rate of polymerization was slightly faster for IL2 (curve c) than in IL1 (curve b). Viscosity differences between the two solvents could be used to provide a satisfactory explanation for the rate differences in line with other work for the conventional free-radical polymerization of *n*-butyl methacrylate,<sup>31</sup> but as will be shown below, there is a little, if any, difference when styrene is polymerized in the absence of RAFT agent due to the heterogeneous nature of the system. Conversions for both polymerizations were greater than 80% after only 10 h, a significant improvement on the previous styrene polymerization attempts.<sup>21</sup>

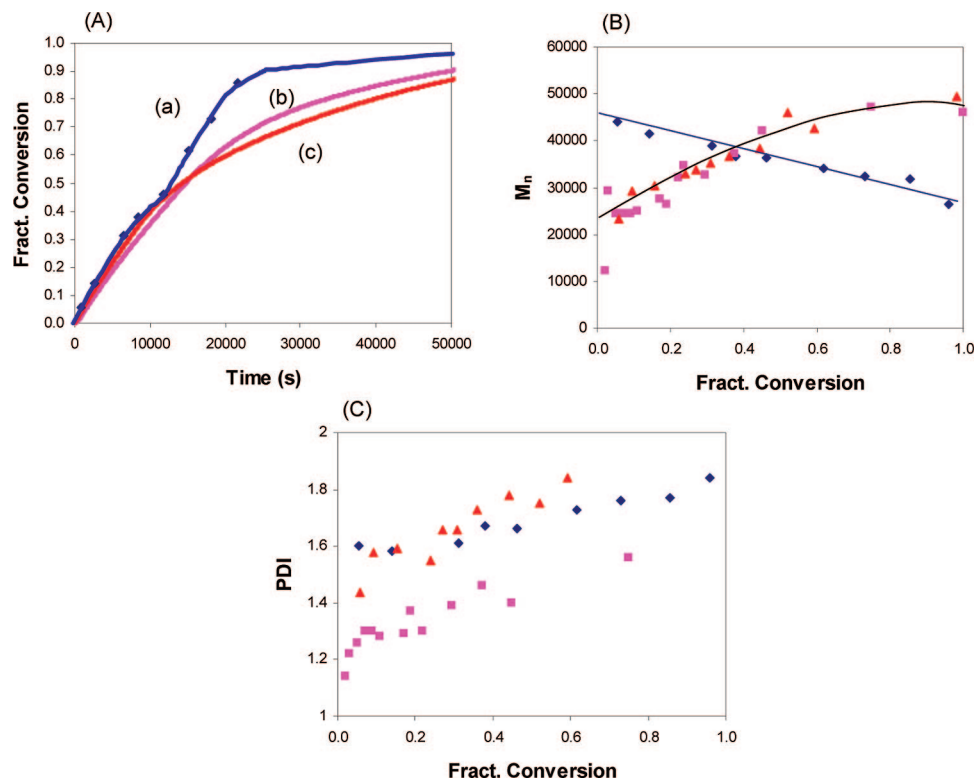
The molecular weight distributions as a function of conversion were all found to be narrow. In accord with ideal “living” radical behavior,<sup>32</sup> a linear increase in the number-average molecular weight (*M<sub>n</sub>*) was observed in all three solvents (Figure 1B), reaching close to 6000 at high conversions. The polydispersity indexes (PDIs, Figure 1C) were found to be low and below 1.2, further supporting ideal “living” radical behavior. A concentration ratio of 2:1 for CPDA to VAZO88 was used in these experiments in order to reach high conversions while maintaining good control of the MWD. This high rate allowed accurate rate data to be obtained using DSC.

**Investigation of Polymerization Mechanism of Styrene in Ionic Liquids.** To shed light into the mechanism of polymerization in ILs, conventional free-radical polymerizations of styrene were carried out under conditions identical to the above but in the absence of RAFT agent. In addition, kinetic parameters were determined to elucidate the dominant processes and thus build a mechanistic understanding of the polymerization of styrene in our IL systems. Figure 2A shows the conversion profiles in the three different solvents. The rate of polymerization in toluene was slightly higher than the other two ILs up to ~45% conversion, after which a distinct rate acceleration due to the gel effect<sup>33,34</sup> was observed. In the case of the two ILs, the rates were similar to each other within experimental error, and there was no clear effect of solvent viscosity on the rates as observed in the RAFT-mediated polymerizations. High conversions were reached after only 10 h. Interestingly, there was no rate acceleration (i.e., gel effect) as found in the toluene polymerization.

The gel effect occurs when the polymer overlap concentration (i.e., *c*<sup>\*</sup>)<sup>22,28,29,35</sup> is reached with a significant change in the viscosity of the polymerization mixture. Diffusion of the polymer chains becomes slow<sup>22,28</sup> and consequently increases the rate by lowering *⟨k<sub>t</sub>⟩* relative to *k<sub>p</sub>*. The absence of a gel effect in the ILs points to a different polymerization mechanism. It was observed that in contrast to the RAFT-mediated polymerizations the reaction mixture turned cloudy after a few minutes into the polymerization, strongly suggesting that the polymerizations carried out in these particular ILs resembles a precipitation or heterogeneous polymerization. In such heterogeneous polymerizations, the growing polymeric chain can



**Figure 1.** Kinetic plots for the RAFT-mediated radical polymerization of styrene with cumyl phenyldithioacetate (CPDA) at 90 °C initiated with 1,1-azobis(cyclohexanecarbonitrile) (VAZO88) in 50% v/v (a) toluene (◆), (b) IL1 (■), and (c) IL2 (▲).  $[\text{Styrene}]_0 = 4.35 \text{ M}$ ,  $[\text{VAZO88}]_0 = 0.025 \text{ M}$ , and  $[\text{CPDA}]_0 = 0.05 \text{ M}$ .

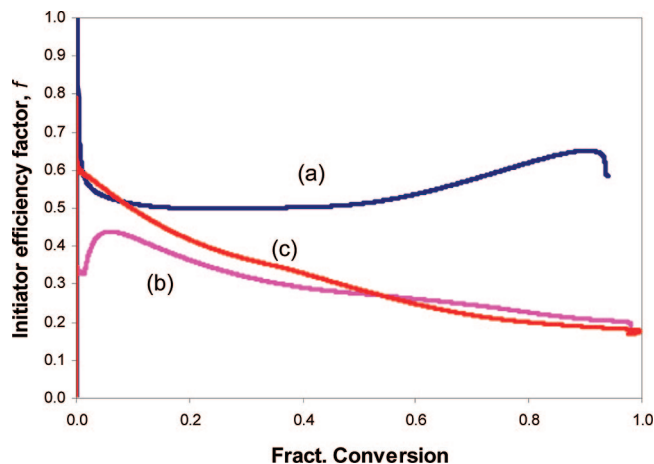


**Figure 2.** Kinetic plots for the conventional free-radical polymerization of styrene at 90 °C initiated with 1,1-azobis(cyclohexanecarbonitrile) (VAZO88) in 50% v/v (a) toluene (◆), (b) IL1 (■), and (c) IL2 (▲).  $[\text{Styrene}]_0 = 4.35 \text{ M}$  and  $[\text{VAZO88}]_0 = 0.025 \text{ M}$ .

become occluded with a monomer-rich and solvent-poor environment.<sup>36,37</sup> In general, occlusion polymerization usually results in dramatic rate increases due to protection of the radicals from terminating with other propagating radicals. Termination be-

tween radicals becomes more difficult due to the formation of tighter bound polymer coils in the precipitated state in which segmental diffusion<sup>38,39</sup> is more greatly affected than translational diffusion. This significant slowdown in termination does





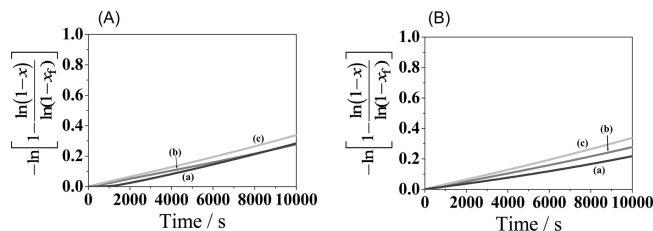
**Figure 3.** Initiator efficiency,  $f$ , vs conversion determined for the free-radical polymerization of styrene (STY, 4.35 M) at 90 °C using 1,1-azobis(cyclohexanecarbonitrile) (VAZO88, 0.025 M) as initiator in 50% v/v (a) toluene (4.69 M), (b) IL1 (1.51 M), and (c) IL2 (1.86 M).

not appear to be occurring in our polymerizations conducted in ILs as no gel effect was observed. It does suggest that the entry of ionic liquid soluble polymeric radicals into these occluded polymer particles occurs with high efficiency, leading to termination with the growing radicals.

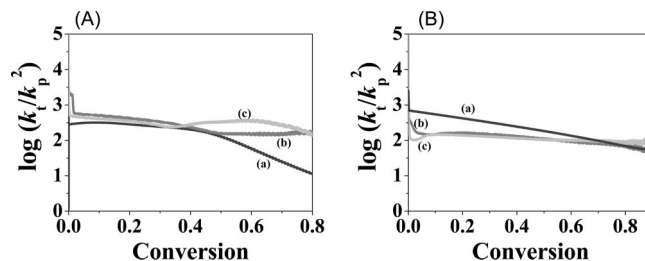
The outcome of a precipitation polymerization can be clearly seen in the  $M_n$  profiles (Figure 2B). In toluene, the  $M_n$  at low conversion was close to 40 000 and decreased to 30 000 at high conversion, in agreement with observations in conventional free-radical polymerization. However, the  $M_n$  profiles for the ILs increased from  $\sim 20$  000 to a value greater than 40 000. Similar trends have been observed in the precipitation polymerization of styrene in diethyl ether (a nonsolvent for polystyrene).<sup>40</sup> The increase in  $M_n$  profiles represents a faster rate of polymerization over the rate of termination with conversion, or the rate of formation of polymer chains is less than conversion of monomer to polymer. In other words, there were more chains formed during the polymerization when toluene was used as solvent compared to the two ILs. The increase in  $M_n$  with conversion for the ILs suggests that another process is at play. We believe that the increase in  $M_n$  with conversion could be due to a decrease in the initiator efficiency factor,  $f$ , due to the occluded nature of the polymeric radical chains and the low IL concentration within the polymer particles significantly reducing the probability of chain transfer to solvent.

The initiator efficiency factor,  $f$ , was determined for all three polymerizations using eq 4. Figure 3 shows the change in  $f$  with conversion remained relatively constant at close to 0.6 for the polymerization carried out in toluene, but for IL1 and IL2 decreased down to 0.2 at high conversions. This was similar to that found in conventional emulsion or dispersion polymerizations and other ILs. The reason postulated for this low  $f$  is based on entry efficiency in emulsion polymerization.<sup>41</sup> The particles will be initially small and under zero-one kinetic control (where one or no radicals can exist in a particle), and any decomposition of initiator to two small radicals inside one of these particles will result in immediate bimolecular coupling and loss of initiator species. Therefore, initiation should only occur in the IL phase, where  $f$  will be now controlled by the efficiency of radicals produced in the IL phase that enter monomer swollen particles.

In ionic liquids, the initiator decomposition rate coefficient,  $k_d$ , was found to remain relatively constant using UV-vis spectroscopy to monitor the loss of initiator with time.<sup>27</sup> Since our polymerizations reached only 80% conversion after 14 h, we utilized the dead-end polymerization technique<sup>24,25</sup> (see



**Figure 4.** Dead-end polymerization technique to determine initiator decomposition rate coefficient,  $k_d$  (see eq 1), for the (A) free-radical and (B) RAFT-mediated polymerizations of styrene (STY, 4.35 M) at 90 °C using 1,1-azobis(cyclohexanecarbonitrile) (VAZO88, 0.025 M) as initiator in 50% v/v (a) toluene (4.69 M), (b) IL1 (1.51 M), and (c) IL2 (1.86 M).



**Figure 5.** Ratio of termination to propagation rate coefficients determined from the rate of polymerization (see eq 5) for (A) free-radical and (B) RAFT-mediated polymerizations of styrene (STY, 4.35 M) at 90 °C using 1,1-azobis(cyclohexanecarbonitrile) (VAZO88, 0.025 M) as initiator in 50% v/v (a) toluene (4.69 M), (b) IL1 (1.51 M), and (c) IL2 (1.86 M).

Figure 4), which allows the instantaneous determination of  $k_d$  using eq 1 to calculate it independently of all other kinetic parameters (e.g.,  $f$ ,  $k_p$ ,  $k_t$ ). This technique was used to calculate  $k_d$  in a conventional free-radical polymerization (Figure 4A) and for a RAFT-mediated polymerization (Figure 4B). The  $k_d$ 's determined from the early time slopes of the curves are given in Table 1 were close to the  $k_d$  value found in homogeneous systems, in agreement with previous  $k_d$  determination in ionic liquids.<sup>27</sup>

The conversion data suggest that the rate is not greatly enhanced in either ionic liquid. A rate method, using the efficiency factor from Figure 4,  $k_d$ , and the rate of thermal initiation,  $R_{th}$ , from the literature, was then used to determine the ratio of  $k_t$  to  $k_p$  as a function of conversion for the conventional free-radical and RAFT-mediated polymerizations (Figure 5A,B). The efficiency factor from Figure 4 was used for completeness, but a constant  $f$  could be used to give the same plots as in Figure 5. These two sets of polymerizations will allow us to compare the ratio in a heterogeneous and a homogeneous system. In the heterogeneous free-radical polymerizations (Figure 5A), the ratio ( $\log k_t/k_p^2$ ) for the ILs was higher than the corresponding toluene polymerization and remained relatively constant over the conversion range. The noticeable decrease in the ratio for the toluene polymerization after 40% conversion leading to a gel effect was not observed for the ILs. Thus, we can postulate that diffusion of polymeric radicals is not greatly affected as compared to homogeneous systems in which the viscosity of the polymerization mixture can increase significantly during the course of the polymerization especially after the onset of the gel effect. The RAFT-mediated homogeneous polymerizations (Figure 5B) showed that the ratio for the toluene polymerization was higher than the ILs, in contrast to that found for the heterogeneous systems. This suggests that the ionic liquids either promote propagation or decrease termination. Since the ratio was the same for both ILs, the viscosity difference between the ILs cannot support a decreased termination rate coefficient. Instead, we believe that

ionic liquids increase the  $k_p$  as found in other ionic liquids<sup>17,18</sup> and other polar solvents.<sup>42</sup>

Zhang et al.,<sup>43</sup> Hong et al.,<sup>44</sup> and Thurecht et al.<sup>27</sup> postulated that the polymerization of styrene in imidazolium ionic liquids produced trapped radicals.<sup>45</sup> The use of our ILs suggests that “trapped” radicals are highly unlikely due to the high rate of termination. Our conclusion is in agreement with findings by Gilbert and co-workers<sup>46</sup> on the gamma irradiation polymerizations of styrene, in which no polymerization was observed when the reaction mixture was removed from the gamma source. Our data show that termination in a precipitated polymerization can remain high.

## Conclusion

We have utilized novel biodegradable ionic liquids in the RAFT-mediated polymerization of styrene. This represents a significant advance on the failure of other ionic liquids that gave little or no polymerization in the presence of a RAFT agent. The rates of polymerization for our ILs were similar to that found when the polymerization was carried out in toluene, and the reaction mixture was observed to be clear and homogeneous throughout the polymerization. Ideal “living” radical behavior was found by the linear increase in  $M_n$  with conversion and polydispersity indexes below 1.2. When conventional free-radical polymerizations were carried out in our ILs and in the absence of RAFT agent, the rates were slightly lower than that in toluene. It was observed after a few minutes into the polymerization the cloudy solution appeared, indicating the start of a precipitation polymerization or an occlusion polymerization. A detailed kinetic analysis of the ILs showed a significant drop in the initiator efficiency factor from 0.6 to 0.2. Importantly, the ratio of  $k_t$  to  $k_p$  remained relatively constant over conversion, further supporting a heterogeneous polymerization. There has been some debate in the literature about the case of a trapped radical in conventional free-radical polymerization of styrene in ILs. On the basis of our kinetic analysis, we conclude for the two ILs used “trapped” radicals are not present in our system or have very little or no influence on the kinetics.

**Acknowledgment.** M.J.M. acknowledges financial support from the ARC Discovery grant and receipt of a QEII Fellowship (ARC fellowship).

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MA802795J