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Pulsed Laser Polymerization in an Ionic Liquid: Strong Solvent Effects on Propagation and Termination of Methyl Methacrylate

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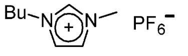
ABSTRACT: The rate constants of propagation and termination of methyl methacrylate (MMA) in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate were measured using the pulsed laser polymerization technique across a range of temperatures, and Arrhenius parameters were calculated for the rate of propagation at ionic liquid concentrations of 0, 20, and 50% v/v. Point estimates for these values are $A = 2.4 \times 10^6$ L mol^{-1} s^{-1} (0% v/v ionic liquid), 2.1×10^6 L mol^{-1} s^{-1} (20% v/v), and 2.5×10^6 L mol^{-1} s^{-1} (50% v/v) and $E_A = 22.1$ kJ mol^{-1} (0% v/v), 21.0 kJ mol^{-1} (20% v/v), and 20.4 kJ mol^{-1} (50% v/v). The decrease in activation energy leads to large increases in the rate of propagation. In addition, the rate of termination decreases by an order of magnitude as the ionic liquid concentration is increased to 60% v/v. The increase in propagation rate was attributed to the increased polarity of the medium, while the decrease in the termination rate is due to its increased viscosity.

Introduction

Ionic liquids have received substantial interest as nonvolatile, recyclable reaction media for a wide range of chemical reactions.[1] Their use leads to significant improvements in rate and yield in many organic reactions.[2] Recently, a number of reports have described the use of ionic liquids as media for radical polymerizations.[3−6] These reports have commented on the large increases in both the rate of polymerization and the molecular weights that are observed in polymerizations of methyl methacrylate when ionic liquids are used in place of conventional organic solvents. In addition, there have been several recent reports on atom transfer radical (co)polymerizations in ionic liquids.[7−11] It has also been reported that the tendency of *N*-hexylmaleimide and styrene to form an alternating copolymer under atom transfer radical polymerization conditions is stronger in ionic liquid than in anisole.[7]

In a recent communication,[12] we described the first application of the pulsed laser polymerization (PLP) technique[13] in ionic liquids with a preliminary report into the polymerization of methyl methacrylate (MMA) in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$], **1**). Pulsed laser polymerization is the IUPAC-recommended method for the measurement of the rate of propagation in radical polymerization and has been used to establish benchmark values for a number of common monomers,[14−16] including MMA.[15]



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Application of PLP to the polymerization of MMA in [bmim][PF$_6$] revealed a very large solvent effect on the rate constant of propagation, k_p. At 25 °C and 50% v/v [bmim][PF$_6$], the k_p of MMA was found to be 680 L mol^{-1} s^{-1}, compared to 323 L mol^{-1} s^{-1} in bulk MMA at the same temperature (IUPAC benchmark value[15]). The only reported solvent-induced accelerations of propagation of greater magnitude are in the polymerization of acrylic and methacrylic acids, which show 2−6-fold increases in k_p in aqueous solution compared to that in bulk or solutions in DMSO or methanol.[17] This was attributed to differing levels of monomer self-association in the different solvents. In the case of MMA, such self-association through hydrogen bonding is impossible and cannot be responsible for the increased rates observed.

Our preliminary results indicated, however, that the increase in k_p cannot be wholly responsible for the overall increase in the rate of polymerization and molecular weight, suggesting that the rate of termination is also affected by the ionic liquid medium. We now report the results of further PLP studies on the MMA−[bmim][PF$_6$] system. These studies were carried out with the aim of determining the magnitude and cause of solvent effects on propagation and termination.

Experimental Section

Materials. Methyl methacrylate (99%) was obtained from Aldrich and passed through a basic alumina column to remove the inhibitor before use. Benzoin (Aldrich, 98%) and AIBN (Acros Organics, 98%) were recrystallized from methanol, and [bmim][PF$_6$] was synthesized according to the method of Huddleston et al.[18]

Pulsed Laser Polymerizations. The principal components of the pulsed laser system are a Quanta-Ray GCR-11 Nd:YAG laser with a KDP-based harmonic generator (Quanta-Ray HG-2) and dichroic mirror harmonic separator (Quanta-Ray PHS-1) producing pulsed laser light at 355 nm with a 6 ns pulse width and a power output of 10 mJ/pulse. Temperature control was maintained using a thermostated cylindrical copper vessel that surrounded the sample, which was oriented such that the laser beam irradiated the entire sample. Samples of MMA, benzoin, and varying proportions of [bmim][PF$_6$] were contained in cylindrical glass vials (dimensions 10 × 50 mm) and degassed by sparging with N$_2$. Prior to polymerization, samples were immersed in a water bath set to the desired temperature and allowed to equilibrate. Care was taken to minimize the exposure of the samples to ambient UV light. Samples were exposed to the pulsed laser for varying amounts of time such that conversion did not exceed 9% (in most cases < 5%) and at pulse rates of 5, 10, or 15 Hz. As monomer concentrations changed slightly during the course of the reaction, an average monomer concentration equal to ([M]$_{\text{initial}}$ + [M]$_{\text{final}}$)/2 was used in all calculations. Immediately on completion of irradiation,

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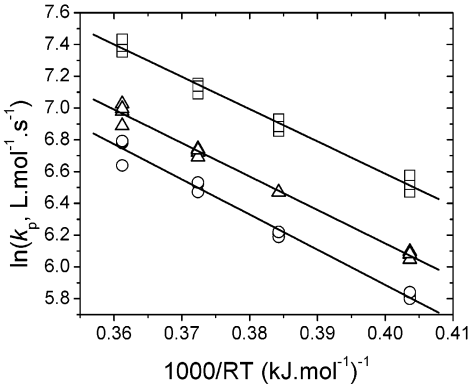

Figure 1. Arrhenius plots for polymerization of MMA at varying concentrations of ionic liquid **1** (○, bulk MMA; △, 20% v/v [bmim][PF$_6$]; □, 50% v/v [bmim][PF$_6$]). Temperature range 25−60 °C. Points at 25 °C are taken from ref 12.

the polymer was precipitated from methanol and subsequently dried under vacuum at 80 °C. Conversions were measured by gravimetry. Full experimental details are given in the Supporting Information.

Analysis. Molecular weight distributions were obtained by size exclusion chromatography using a Polymer Laboratories modular system equipped with a guard column, two 5 μm mixed D columns (Polymer Laboratories), and a differential refractive index detector calibrated with 12 linear poly(methyl methacrylate) standards ranging from 200 to 1.64 × 10^6 g mol^{-1} using a third-order polynomial as the calibration curve. The eluent used was 95:5 THF:TEA at a flow rate of 1.0 mL min^{-1}, and the PL gel columns were thermostated at 25 °C. Results were analyzed using Polymer Laboratories' Cirrus software package (version 1.2). Viscosity measurements were obtained using a Brookfield DV-II+ viscometer with a small sample adapter (SSA 18/13R).

Results

Propagation. In PLP, the monomer solution (containing the photoinitiator) is irradiated with a sequence of evenly spaced laser pulses, producing a periodically changing radical concentration. The majority of polymer chains initiated during one laser pulse are terminated by the subsequent pulse, producing a characteristic molecular weight distribution that contains a peak corresponding to the number of propagation steps that have occurred during the dark time between laser pulses. Overtone peaks are observed at integer multiples of the main peak; these are due to polymer chains that have survived one or more pulses to be terminated by the flux of radicals arising from a subsequent pulse. The most accurate estimator of k_p is given by the degree of polymerization, ν, of the inflection point on the low molecular weight side of the main peak, which is related to k_p by eq 1, in which [M] represents the monomer concentration and t_d the dark time between pulses.[13]

$$\nu = k_p[M]t_d \quad (1)$$

Experiments were carried out at 40, 50, and 60 °C using MMA containing 0, 20, and 50% v/v of the ionic liquid, **1**. The k_p data obtained (Figure 1, Table 1) were combined with data from ref 12 in order to determine the effect of the ionic liquid on the Arrhenius parameters of the propagation reaction. Point estimates for the Arrhenius parameters are given in Table 2; 95% joint confidence intervals for these parameters are shown in Figure 2. Good agreement was obtained with the IUPAC benchmark Arrhenius parameters for bulk MMA, also shown in the figure.

Table 1. Effect of [bmim][PF$_6$] on k_p (in L mol^{-1} s^{-1}) of Methyl Methacrylate at 25, 40, 50, and 60 °C

[bmim][PF$_6$] (% v/v)	T (°C)			
	25^{a,b}	40^b	50^b	60^b
0	333	495	681	880
	339	499	682	885
	330	487	647	764
	344	503	687	892
20	445	646	849	1127
	437	646	830	1075
	423	646	807	981
	439		842	1094
50	647	1004	1281	1651
	686	1022	1254	1561
	679	948	1200	1617
	718	976	1259	1691

^{a} Data from ref 12. ^{b} Units of L mol^{-1} s^{-1}.

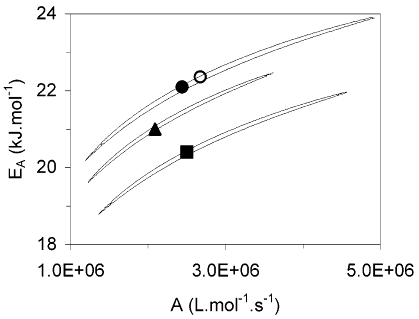

Figure 2. 95% joint confidence intervals and point estimates for Arrhenius parameters of k_p of MMA in bulk (●), 20% v/v [bmim][PF$_6$] (▲), and 50% v/v [bmim][PF$_6$] (■). The IUPAC-recommended values for bulk MMA[15] are shown for comparison (○).

Table 2. Point Estimates for Arrhenius Parameters of k_p of MMA at Different [bmim][PF$_6$] Concentrations

[bmim][PF$_6$] (% v/v)	A (L mol^{-1} s^{-1})	E_A (kJ mol^{-1})
0	2.4 × 10^6	22.1
20	2.1 × 10^6	21.0
50	2.5 × 10^6	20.4

The presence of ionic liquid causes a decrease in the activation energy of propagation, while the preexponential factor is unaffected. This finding supports the hypothesis that the increase in the rate of propagation in ionic liquids is due to the increased polarity of the medium, which allows an increased contribution of charge-transfer structures (in which an electron is transferred from the monomer to the polymeric radical or vice versa) to the transition state. A recent review[19] has illustrated the importance of such charge-transfer structures in many radical reactions, particularly those where the radical has strongly electron-withdrawing or donating α-substituents, such as −CN or −OH. These effects are strongest in cross-propagation reactions (e.g., addition of CH_2OH radical to acrylonitrile) but are also apparent in homopropagation reactions. For example, in the addition of CH_2CN radical to acrylonitrile, an increase in dielectric constant, ϵ, from 2 to 40 has been predicted to decrease the reaction barrier by 0.8 kJ mol^{-1}.[22] A dielectric constant of approximately 2 is typical of nonpolar solvents such as toluene ($\epsilon = 2.43^{20}$) or bulk MMA ($\epsilon = 2.9^{21}$), while 40 is representative of polar solvents such as DMF ($\epsilon = 37.06^{20}$) or DMSO ($\epsilon = 46.71^{20}$). The magnitude of this effect is similar to the decrease in activation energy observed in the current work.

Several polar aprotic solvents show significant solvent effects on MMA propagation: polymerization of MMA in 80% v/v DMF leads to a 40% increase in k_p relative to bulk MMA,[23] while an 80% increase was observed in DMSO[24] at 70% v/v. Acetonitrile[25] (50% v/v) and methanol[26] (5−20% v/v) have no effect on the rate of propagation of MMA. It should be noted, however, that the acetonitrile data were collected before the introduction of the PLP technique and may be subject to significant errors,[27] while the study on the effect of methanol was limited to relatively low concentrations due to the low solubility of PMMA in methanol.

Alternative explanations for the increase in rate are possible; these include a "bootstrap" effect caused by poor solvation of the polymer, leading to an increase in local monomer concentration around the active site, or the formation of radical−solvent or monomer−solvent complexes with increased reactivity. As the PLP technique measures the product k_p[M], rather than k_p itself, a pronounced increase in the monomer concentration in the vicinity of the active chain end relative to the overall concentration will produce an apparent increase in k_p. The observed increase in k_p in these experiments, however, would require the local monomer concentration to be approximately equal to that of bulk MMA (9.35 M at 25 °C), even at 60% v/v ionic liquid if it is to be explained by a bootstrap effect. Under the conditions of these experiments, [bmim][PF$_6$] formed homogeneous mixtures with MMA, and no polymer was observed to precipitate during the reaction. As methanol, a nonsolvent for poly(methyl methacrylate), has no effect on k_p of MMA,[26] such a large bootstrap effect on the part of [bmim][PF$_6$] seems unlikely.

Many solvent effects have been attributed to the formation of monomer−solvent or radical−solvent complexes.[23,28] In the case of monomer−solvent complex formation, this should produce an increase in the preexponential factor due to the increased mass of the complex.[28] No such effect was observed in this work (Figure 2).

Radical−solvent complexes cannot be ruled out, but since the complex must be more stable than the uncomplexed radical (or else it would not form), it should propagate more slowly, unless there is a compensating effect that lowers the energy of the transition state or increases the preexponential factor. Strong solvent effects on MMA in benzyl alcohol[23,28] and *N*-methylpyrrolidone[23] have been attributed to the formation of solvent−radical complexes. Propagation of MMA in these solvents has significantly increased activation energy, reflecting stabilization of the radical. This in itself should decrease the rate of propagation but is accompanied by an increase in the preexponential factor, causing an overall increase in the propagation rate.[23] In [bmim][PF$_6$], the activation energy is decreased, suggesting that any stabilization of the radical that may occur through complexation is compensated for by stabilization of the transition state, possibly by the participation of charge-transfer structures as discussed above. Thus, the observed acceleration appears to be mainly due to the increased polarity of the medium, which allows a greater contribution from charge-transfer structures, lowering the energy of the transition state.

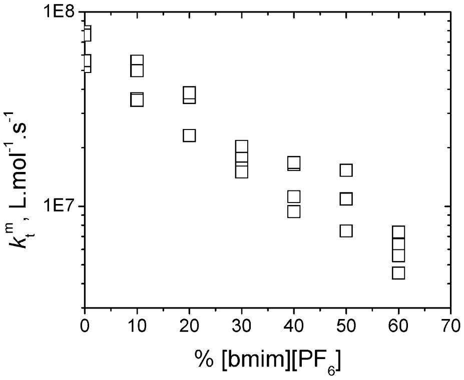

Figure 3. Dependence of k_t^m of MMA on concentration of [bmim][PF$_6$] at 25 °C.

Termination. The PLP technique has recently been extended to allow the determination of termination rate coefficients, k_t, by analysis of the resulting chain length distribution. A simple method of estimating the average termination coefficient in an experiment is given by eq 2.[30]

$$P_w \nu_p = k_p^{\,2}/k_t^{\,m}[M]^2(3 - \delta) \qquad (2)$$

In this equation, P_w represents the weight-average degree of polymerization, ν_p the rate of polymerization, and δ the contribution of disproportionation to overall termination. The quantity k_t^m calculated from this formula underestimates the theoretical rate coefficient of termination by about 20% but still provides a semiquantitative measure of the effect of ionic liquids on the termination process.

The molecular weight distributions from ref 12 were reanalyzed using eq 2, with the rate of polymerization estimated from the total amount of polymer formed divided by the reaction time and δ assumed to be equal to 0.7, following the procedure used by Olaj and Vana.[31] No attempt was made to take into account dependence of k_t on chain length. Because of uncertainties in the true value of δ and variations in chain length from one sample to another, as well as the systematic inaccuracy of the equation, the termination rate coefficients obtained are only expected to indicate the trend followed as the concentration of ionic liquid is increased. Results are shown in Figure 3. There is a relatively large amount of scatter in the data, with polymerizations initiated by benzoin giving consistently higher values for k_t^m than those initiated by AIBN. This may be due to higher levels of chain transfer to initiator in the benzoin polymerizations, which would reduce the molecular weight and cause overestimation of k_t^m.

The rate of termination decreases as the concentration of ionic liquid is increased, spanning an order of magnitude between 0 and 60% v/v ionic liquid. This is in broad agreement with the conclusions of Hong et al.,[3] who speculate that the increased rates and molecular weights observed in polymerizations of styrene and MMA in [bmim][PF$_6$] are due to low termination rates caused by the high viscosity of the ionic liquid and low solubility of the polymer radicals. To verify this conclusion, the viscosities of the [bmim][PF$_6$]/MMA mixtures used were measured. These viscosities were strongly correlated with k_t^m (Figure 4). To a good approximation, the rate of termination is inversely proportional to the solution viscosity, suggesting that translational diffusion of the radicals is the rate-limiting factor in termi-

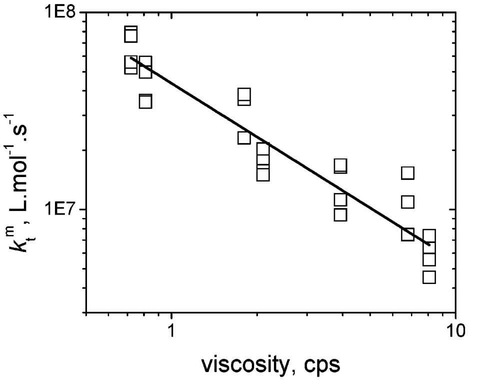

Figure 4. Double-logarithmic plot of k_t^m vs viscosity. Solid line is a least-squares line of best fit showing the relationship $k_t^m = 4.4 \times 10^7(\text{viscosity})^{-0.9}$.

nation, at least for the low conversions explored in these experiments.

Conclusions

The fundamental rate constants of propagation and termination have been investigated for the polymerization of MMA in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate. Both are significantly affected by the ionic liquid. In the case of propagation, the major effect is a lowering of the activation energy of propagation, causing a significant increase in the rate of propagation. We hypothesize that this is due to the increased polarity of the ionic liquid solution, which leads to increased contributions from charge-transfer structures in the transition state. The rate of termination, by contrast, decreases by an order of magnitude as the ionic liquid concentration is raised to 60% v/v. This appears to be due simply to the increased viscosity of the reaction medium. Taken together, these effects explain the fast overall rates and high molecular weights that have been observed for polymerizations of MMA in ionic liquids.

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Supporting Information Available: Sample PLP molecular weight distributions, full experimental data for PLP experiments, and viscosity data for MMA–[bmim][PF$_6$] mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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