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Unprecedented solvent-induced acceleration of free-radical propagation of methyl methacrylate in ionic liquids†

Simon Harrisson, Stuart R. Mackenzie and David M. Haddleton*
Department of Chemistry, University of Warwick, Coventry, UK. E-mail: d.m.haddleton@warwick.ac.uk; Fax: 44 2476 528267; Tel: 44 2476 523256

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The rate of propagation in the free-radical polymerization of methyl methacrylate in an ionic liquid has been determined and shows unprecedented solvent-induced acceleration, partially explaining the surprising increase in overall rates of polymerization and molecular weights in these solvents.

Ionic liquids are salts that are liquid at low temperatures (< 100 °C). The use of these liquids in place of conventional organic solvents can lead to significant improvements in the rate and yield of reactions. In addition, they have valuable properties such as low vapour pressure and ease of recycling that facilitate product recovery and may reduce environmental emissions. The chemistry of ionic liquids is comprehensively covered in a number of recent review articles.[1] Recently there have been several investigations into radical polymerization in ionic liquids;[2–4] in general these comment on the substantial increases in both the rate of polymerization and the molecular weight of the final polymer compared to polymerizations in conventional solvents.[3,4] A series of pulse radiolysis studies on radical oxidation, addition and H· abstraction reactions (of $^{\cdot}CF_3$ and $CCl_3O_2^{\cdot}$) in ionic liquids have shown similar rates to those observed in acetonitrile or methanol, and generally lower than in water.[5]

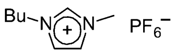
Radical polymerization is a complex process, and the observed polymerization rate is a composite of several different rate coefficients, most importantly the rate constant of propagation (k_p) and the average rate coefficient of termination ($\langle k_t \rangle$). The overall rate of polymerization is proportional to $k_p/k_t^{½}$. The pulsed laser polymerization (PLP) technique[6] allows the direct measurement of k_p, permitting analysis of the effect of the ionic liquid on individual processes within the polymerization reaction.

In PLP, the monomer solution (containing a photoinitiator) is irradiated with a sequence of evenly spaced laser pulses, producing a regular flux of radicals. 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 pulses. Additional overtone peaks are observed at integer multiples of the main peak due to polymer chains that have survived one or more pulses to be terminated by the second or subsequent pulses. 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 eqn. 1, in which [M] represents the monomer concentration and t_d the dark time between pulses.[6]

$$\nu = k_p.[\mathrm{M}].t_d \qquad (1)$$

This method is the IUPAC-recommended procedure for k_p determination, and has been used to determine accurate k_p values for a wide range of monomers.[7,8]

In this work the PLP technique was used to determine the k_p of methyl methacrylate in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6], Scheme 1) at 25 °C over a range of concentrations.‡



Scheme 1 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]).

In all cases, molecular weight distributions with clear PLP characteristics were observed. The calculated k_p's were independent of initiator type and pulse rates used (10–15 Hz), and there was good agreement between k_p measured at 0% of [bmim][PF_6] and the IUPAC benchmark of 323 $L.mol^{-1}.s^{-}$ for k_p of MMA at 25 °C.[7]

The k_p of MMA increased steadily as the concentration of ionic liquid was increased (Fig. 1, Table 1). At 50 vol% [bmim][PF_6], k_p was approximately twice that of bulk MMA. The only reported solvent-induced acceleration of similar magnitude in a radical propagation reaction is in the polymerization of methacrylic and acrylic acids in water in which 2- to 6-fold increases in k_p were observed compared to polymerizations in bulk, DMSO or methanol.[9] This was attributed to different levels of self-association of the acidic monomers in the different solvents. Such an explanation is not possible in the case of MMA, which cannot self-associate to form oligomeric species through hydrogen-bonding.

The underlying cause of these effects on k_p remains unclear. It is unlikely to be due wholly to poor solvation of the monomer causing an increased monomer concentration in the vicinity of the radical chain end, as the local monomer concentration would need to be equal to that of pure MMA in order to produce the observed rates. While this mechanism may be partially responsible for the increase in k_p, such a high degree of partitioning seems unlikely given that both MMA monomer and polymer form homogeneous solutions in [bmim][PF_6] at the concentrations used in these experiments. Methanol, a non-solvent for PMMA, has no effect on the k_p of MMA, suggesting that this mechanism is not usually significant,[10] although a similar phenomenon (reduced local monomer concentration at the chain end) has been implicated in the chain-length dependence of k_p.[11]

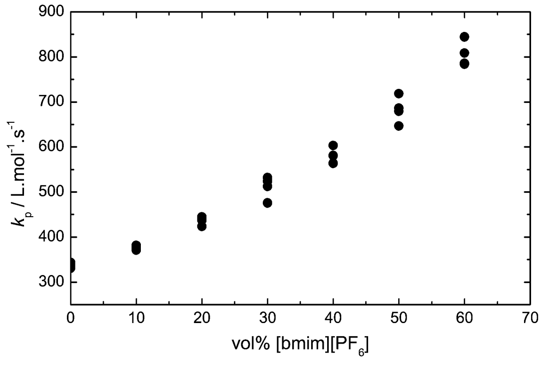


Fig. 1 Effect of ionic liquid concentration on k_p of MMA at 25 °C.

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† Electronic supplementary information (ESI) available: Sample PLP-GPC traces and full experimental data. See http://www.rsc.org/suppdata/cc/b2/b209479g/

Table 1 k_p data for the polymerization of MMA in [bmim][PF$_6$] at 25 °C

Vol% [bmim][PF$_6$]	Pulse rate (Hz)	k_p (L.mol^{-1}.s^{-1})	Vol% [bmim][PF$_6$]	Pulse rate (Hz)	k_p (L.mol^{-1}.s^{-1})	Vol% [bmim][PF$_6$]	Pulse rate (Hz)	k_p (L.mol^{-1}.s^{-1})
0	10	333	20	15	423	50	10	647
0	10	339	20	15	439	50	10	686
0	15	330	30	10	476	50	15	679
0	15	344	30	10	512	50	15	718
10	10	371	30	15	531	60	10	786
10	10	381	30	15	524	60	10	784
10	15	375	40	10	564	60	15	844
10	15	374	40	10	581	60	15	808
20	10	445	40	15	580			
20	10	437	40	15	603			

The increased polarity of the medium may favour transition states involving charge transfer. Several polar solvents have been shown to affect the k_p of MMA, with a 40% increase in k_p in solution in DMF[12] being the largest reported solvent-induced increase to our knowledge. Acetonitrile[13] and methanol,[10] however, have no significant effect on the rate of MMA propagation. Finally, the ionic liquid may be actively involved in the polymerization through complex formation with either the monomer or the radical. This is the mechanism that has been proposed for most reported solvent effects on propagation reactions.[14] In the case of ionic liquids, radical–solvent complexes would be charged, which might also reduce termination by introducing electrostatic repulsion (assuming that the radical preferentially forms complexes with only one of the ions).

None of these explanations are entirely satisfactory, although each may play some role in the total mechanism. Experiments are currently in progress to determine the true cause of the observed acceleration. Furthermore, the acceleration in k_p in the presence of ionic liquids is still not large enough to explain the acceleration of the overall rate of polymerization and increase in molecular weight that is commonly observed—Hong *et al.*[3] report a 10-fold increase in polymerization rate when [bmim][PF$_6$] is used as a solvent in place of benzene, while the largest acceleration in k_p observed in this study is less than 3-fold. This implies that there must be a corresponding decrease in the rate of termination to produce the remainder of the acceleration.

In conclusion, it has been shown that the use of ionic liquid solvents produces a significant increase in the rate of propagation of methyl methacrylate, and that this effect is partially responsible for the observed increases in rate and molecular weight in these polymerizations. With this information it may be possible to design controlled polymerization systems to take advantage of the unique properties of ionic liquids. It has also been shown that the rates of radical reactions may be significantly affected by the use of ionic liquids as a reaction medium, in the case of MMA to a far greater extent than is possible with conventional solvents.

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Notes and references

‡ *Materials.* Methyl methacrylate was obtained from Aldrich and passed through a basic alumina column to remove inhibitor before use. Benzoin (Aldrich, 98%) and AIBN (Acros Organics, 98%) were recrystallized from methanol. [bmim][PF$_6$] was synthesized according to the method of Huddleston *et al.*[15] *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. Temperature control was maintained using a thermostated cylindrical copper vessel that surrounded the sample. 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 of MMA, benzoin or AIBN and varying proportions of [bmim][PF$_6$] were contained in cylindrical glass vials (dimensions 10 × 50 mm) and degassed by sparging with N_2. After the irradiation was complete, the polymer was precipitated from methanol, and subsequently dried under vacuum at 80 °C. Conversions were measured by gravimetry. *Analysis.* Molecular weight distributions were obtained by size exclusion chromatography with a Polymer Laboratories system equipped with a refractive-index detector calibrated with linear poly(methyl methacrylate) standards. 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.

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