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Statistical radical copolymerization of styrene and methyl methacrylate in a room temperature ionic liquid

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Received (in Columbia, MO, USA) 7th February 2003, Accepted 22nd April 2003
First published as an Advance Article on the web 9th May 2003

Use of a room temperature ionic liquid as the medium for conventional free radical copolymerization of styrene and methyl methacrylate resulted in reactivity ratios that were significantly different from those obtained in conventional organic solvents or in bulk, demonstrating that polymerization in this alternative medium offers potential to create copolymers having new monomer sequences.

The compositions and microstructures of copolymers produced by statistical free radical copolymerization have been shown to be sensitive to the solvent utilized during polymerization.[1] Ito and Otsu first described the solvent effect on copolymerization of styrene (ST) and methyl methacrylate (MMA) in 1969.[2] Since then many reports detailing solvents effects on copolymerization have been published. In general, the influence of solvents on copolymerization reactivity ratios is strongly dependent on the nature of the monomers and solvents involved. Although numerous explanations of the observed phenomena have been given,[1,3] the most satisfying one is embodied in the so-called "bootstrap" model.[4] The nature of the solvent can also affect free-radical copolymerization reactions through polarity effects, radical–solvent complexes, or monomer–solvent complexes.[1,5–8]

Room temperature ionic liquids (RTILs) have received increasing attention as environmentally preferable alternative solvents because of their extremely low vapor pressures. Based on this promise, RTILs have been explored as reaction media in various organic transformations.[9,10] In addition, the unique properties exhibited by RTILs (ionic, non-coordinating, *etc.*) can lead to significant improvements in the rate, yield and/or selectivity of reactions.[11] The use of RTILs as a polymerization medium has also recently attracted considerable interest.[12–19] Conventional or controlled radical polymerizations of ST,[12] MMA,[12–15] and acrylates,[16] have been carried out in various RTILs. Recent papers describe atom-transfer radical copolymerizations of N-hexylmaleimide with ST[17] and of butyl acrylate with methyl acrylate,[18] as well as block copolymers of ST with MMA using a trapped radicals approach.[19] Here we report the first study of statistical copolymerization in 1-butyl-3-methylimidazolium hexafluorophosphophate ([bmim]PF_6) using conventional free radical polymerization.

Copolymerizations of ST and MMA were carried out in [bmim]PF_6 using azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) as initiator.† The experimental data are summarized in Table 1. Reactivity ratios were calculated from copolymer composition data by using a conventional linear least-square regression method (Kelen–Tüdos)[20] or a non-linear regression approach, the CONTOUR program of van Herk[21] with the assumption that the kinetics model is terminal. The low conversions allowed us to calculate reactivity ratios using the Kelen–Tüdos method that were essentially identical to those obtained *via* the non-linear regression method, as discussed below and summarized in Table 2.

Control measurements on the copolymerization of ST and MMA in benzene were done, and the reactivity ratios were calculated based on the copolymer composition obtained from ^{1}H-NMR (Table 2). If the peaks at δ = 2.5–3.7 ppm (methoxy proton from MMA) were used to calculate the compositions, the resulting reactivity ratios were quite different from the literature values. 2-D DEPT-HMQC and 2-D NOESY experiments revealed that the peaks of MMA methoxy proton signal (δ = 2.1–3.7 ppm) overlapped with the ST methine proton signal (δ = 1.5–2.5 ppm) due to spatial proximity of methoxy to ST phenyl group. However, the MMA α-methyl proton signal (δ = 0.1–1.0 ppm) was completely separated from other backbone proton signals and can thus be used as the integration peak for MMA composition (Fig. 1). The peaks at δ = 6.2–7.2 ppm

Table 1 Copolymerization data for the system styrene–methyl methacrylate in [bmim]PF_6[a]

f_s/ST mol%	F_s/ST mol%	$M_n/\times10^{-3}$	M_w/M_n	Conversion (wt%)
9.94	15.87	500.5	2.93	16.04
20.80	28.37	430.2	1.92	9.20
28.76	34.43	264.7	1.92	5.44
48.86	47.85	166.5	2.03	2.48
61.23	55.83	142.8	1.91	1.39
69.12	61.88	130.6	2.01	1.40
80.20	67.54	105.1	2.49	0.89
89.31	80.44	118.4	2.12	1.09

[a] [Monomers] = 1 mol L^{-1}, [AIBN] = 8 × 10^{-3} mol L^{-1}, 60 °C, $\frac{1}{2}$ hour.

Table 2 Reactivity ratios for styrene–methyl methacrylate at different temperatures in benzene, in bulk, and in [bmim]PF_6

Reaction medium	Temp./°C	r_{ST}	r_{MMA}
	60[a]	0.54 ± 0.04	0.50 ± 0.04
Benzene	60[b]	0.589	0.481
	70[c]	0.585	0.512
Bulk	60[a]	0.56 ± 0.04	0.44 ± 0.04
[bmim]PF_6	60[c]	0.381 ± 0.02	0.464 ± 0.02

[a] Johnson *et al.*[24] [b] Ito and Otsu.[2] [c] This work by the non-linear method.

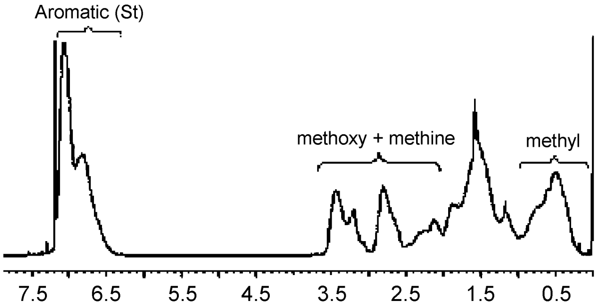

Fig. 1 Typical ^{1}H-NMR spectrum of styrene–methyl methacrylate random copolymer (F_s = 0.509).

DOI: 10.1039/b301562a

(aromatic proton from ST) were used to calculate the compositions of the copolymers.

When $\mathrm{[bmim]PF_6}$ was used as the polymerization medium, the molecular weights and conversions of copolymers decreased as the feed ratio of ST (f_s) increased. This agrees with our previous finding that the molecular weight and conversion of homopolymerization of MMA in $\mathrm{[bmim]PF_6}$ were higher than those of ST.[12] The terminal model was also fitted to the composition data and the following reactivity ratios were obatined: $r_{\mathrm{ST}} = 0.390$ and $r_{\mathrm{MMA}} = 0.470$ by the Kelen–Tüdos method (linear regression) and $r_{\mathrm{ST}} = 0.381 \pm 0.02$ and $r_{\mathrm{MMA}} = 0.464 \pm 0.02$ by employing the CONTOUR program (non-linear regression). These results are different from those typically obtained from copolymerizations in ordinary organic solvents or in bulk, in that $r_{\mathrm{MMA}} > r_{\mathrm{ST}}$. For comparisons sake, of the forty entries for the ST–MMA pair in the *Polymer Handbook*,[22] only five show r_{MMA} values appreciably larger than r_{ST}. Many factors could contribute to these differences in reactivity ratios.

The ST–MMA system has been intensively explored and the reactivity ratios for their copolymerization in various solvents and in bulk are available.[22,23] Monomer reactivity ratios are generally but not always independent of the reaction medium. The dipole moment of the solvent, interactions between solvent and monomers (*e.g.* solvent–monomer complexes), viscosity and system heterogeneity are all found to have some effect on reactivity ratios. Johnson *et al.*[24] stated that copolymers made in bulk are richer in MMA than those generated in benzene because of system viscosity. Fernandez-Garcia *et al.*[7] compared reactivity ratios of ST–MMA (and ST–butyl acrylate) in different solvents, and concluded that the relative reactivity of styrene decreases whereas the reactivity of MMA increases with increasing polarity of the solvent. $\mathrm{[Bmim]PF_6}$ is an ionic solvent of polarity similar to methanol, while the permanent dipole moment for benzene is zero. The "bootstrap" effect may arise from these polarity differences. In addition, the viscosity of $\mathrm{[bmim]PF_6}$ is much higher than for conventional organic solvents. Both of these effects could contribute to the observed relative increase in r_{MMA} relative to r_{ST}. Though $\mathrm{PF_6}^-$ is a poor hydrogen-bond acceptor,[25] it has been proposed that $\mathrm{[bmim]PF_6}$ or its components could form complexes with the monomers and/or radical centers.[26] Polystyrene is not soluble in $\mathrm{[bmim]PF_6}$ and this RTIL appears to be a marginal solvent for PMMA (a single glass transition is observed for PMMA prepared in $\mathrm{[bmim]PF_6}$ and retaining this RTIL as a plasticizer; however preformed high molecular weight PMMA does not dissolve readily in $\mathrm{[bmim]PF_6}$). These additional factors also possibly contribute to differences in the reactivity ratios as compared to those in organic solvents. Regardless of their physical origin, however, the differences in reactivity ratios observed in RTILs offer polymer chemists the opportunity to create materials having monomer sequences not readily accessible in conventional organic solvents.

In summary, copolymerizations of ST and MMA were carried out in $\mathrm{[bmim]PF_6}$, and reactivity ratios were calculated by linear and non-linear regression methods. Differences were observed between monomer reactivity ratios in a conventional organic solvent and in $\mathrm{[bmim]PF_6}$, specifically $r_{\mathrm{MMA}} > r_{\mathrm{ST}}$, offering potential to produce copolymers with novel monomer sequences, while retaining other advantages inherent to polymerization in ionic liquids.[12]

This research was supported in part by the National Science Foundation (Grant CTS0086874) and in part by the Division of Material Sciences and Engineering, Office of Basic Energy Sciences, U. S. Department of Energy, under contract No. DE-AC05–00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. We thank Dr. A. M. van Herk for generously sharing his CONTOUR program with us.

Notes and references

† Polymerizations were performed as follows: monomer pairs (1.0 g, 20% v/v) at the different feed ratios (10 ~ 90%) were weighed into ampoules. Initiator (20.0 mg, 2% w/v monomer): BPO or AIBN, and 4 mL (80%) of reaction medium: benzene or $\mathrm{[bmim]PF_6}$ were added into ampoules separately. After five cycles of freeze–vacuum–thaw, the ampoules were flame-sealed and kept in a water bath at 70 °C for BPO or at 60 °C for AIBN initiated polymerizations. Reaction times were limited to $\frac{1}{2}$ hour for $\mathrm{[bmim]PF_6}$ and 2 hours for benzene solution polymerization respectively in order to keep conversions as low as possible, minimizing composition drift. Polymerizations were stopped by precipitation into methanol, washing with large amounts of methanol, filtering, and drying under high vacuum to constant weight. Conversion was determined gravimetrically. The SEC (size exclusion chromatography) experiments were carried out in THF at 30 °C using a Waters 510 pump and Waters 410 differential reflector detector and Linear UV-vis 205 Absorbance detector (flow rate: 1mL min^{-1}, columns: Waters 100 Å, 500 Å, 10^3 Å, 10^4 Å, 10^5 Å) with toluene as internal standard. ^{1}H-NMR spectra were obtained on a Bruker ARX-300 spectrometer at room temperature. 2-D NMR spectra were recorded on a Bruker ARX 400 spectrometer at room temperature at concentrations 10 ~ 25% (w/v) in $\mathrm{CDCl_3}$; TMS was the internal reference.

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