Photopolymerization Kinetics of Ionic Liquid Monomers Derived from the Neutralization Reaction Between Trialkylamines and Acid-Containing (Meth)Acrylates

ZULMA JIMÉNEZ,[1] CHRISTOPHER BOUNDS,[1] CHARLES E. HOYLE,[2] ANDREW B. LOWE,[1] HUI ZHOU,[2]
JOHN A. POJMAN[1]

[1]Department of Chemistry and Biochemistry, The University of Southern Mississippi, Hattiesburg, Mississippi 39406

[2]Department of Polymer Science, The University of Southern Mississippi, Hattiesburg, Mississippi 39406

Received 4 December 2006; accepted 14 February 2007
DOI: 10.1002/pola.22055

ABSTRACT: Polymerizable ionic liquids were synthesized from the neutralization reaction between trialkylamines (tributylamine, trihexylamine, trioctylamine, 2-(dimethylamino)ethyl acrylate, and 2-(dimethylamino)ethyl methacrylate) and acid-containing (meth)acrylates to study the kinetics of their photopolymerization. The ionic liquids formed from acrylic acid and methacrylic acid with trialkylamines showed low or moderate increases in rate compared to their monofunctional analogues. The ionic liquids formed from (meth)acrylic acid and a tertiary amine with a pendant acrylate exhibited rates typical of traditional di(meth)acrylates, although the (meth)acrylates were not covalently attached to the same molecule. All of the phosphate-based ionic liquids exhibited very rapid polymerization rates and strong dependence on the initial viscosity. © 2007 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 45: 3009–3021, 2007
Keywords: acrylates and methacrylates; ionic liquid monomers; ionic polymers; kinetics; photopolymerization; radical polymerization

INTRODUCTION

Ionic liquids are salts with melting temperatures below the boiling point of water. They often possess important and unusual properties such as nonvolatility, nonflammability, high ion density, and high ionic.[1] The most commonly studied systems contain ammonium, phosphonium, pyridinium, or imidazolium cations. Common anions that yield useful ionic liquids include hexafluorophosphate, $[PF_6]^-$, tetrafluoroborate, $[BF_4]^-$, bis(trifyl) imide, $[NTF_2]^-$, and chloride.[2]

Ionic liquids have been used in free-radical, acid-catalyzed cationic, transition-metal catalyzed, Ziegler-Natta, metathesis and living radical polymerizations as solvents, catalysts and plasticizers.[1,3–7] Since 1973 synthesis, characterization and polymerization of ionic liquid monomers have been reported.[8] Ohno and coworkers have developed a series of imidazolium-based monomers and macromonomers with the aim of producing polymer electrolytes of high ionic conductance.[9–12] They used azobisisobutyronitrile (AIBN) to initiate free-radical polymerization. The polymers had rubber-like properties regardless of the anion and were conductive.

In 2002, Ohno and coworkers[13] synthesized ionic liquid monomers by a neutralization reaction of 1-vinylimidazole with vinylsulfonic acid or 3-sulfopropyl acrylate. Those monomers

---

Correspondence to: C. E. Hoyle or J. A. Pojman
(E-mail: Charles.Hoyle@usm.edu or john@pojman.com)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 45, 3009–3021 (2007)

contained polymerizable groups in both the acid and base components; free-radical polymerization was initiated with AIBN. Depending on the polymerization time, the copolymers showed different physical characteristics. Ionic liquid monomers with several acids including acrylic acid, *p*-styrenesulfonic acid, vinylsulfonic acid, and vinylphosphonic acid were also synthesized by neutralization with *N*-ethylimidazole.[14] Many other ionic liquid salts have been polymerized by traditional[15,16] and controlled[17,18] radical polymerizations. However, in no case have the free-radical polymerization kinetics been characterized with respect to the monomer structure and type. Herein, we report for the first time a study of the free-radical polymerization kinetics of several acrylate and methacrylate ionic liquids and relate the kinetics to the monomer structures. Our interest in those compounds is attributable to their possible lack of vapor pressure, which makes them less hazardous and more useful in different polymerization methods as for example frontal polymerization in open systems.

All the compounds we report are liquid at room temperature and are extremely simple to prepare, viz., by a simple neutralization reaction as has been used before to prepare highly conductive compounds.[19–21]

EXPERIMENTAL

Materials

Methanol d_4 (99.8%), acrylic acid (>99%), methacrylic acid (>99%), ethylene glycol methacrylate phosphate (92%), tri(ethylene glycol) dimethacrylate (TEGDMA, 95%), di(ethylene glycol) diacrylate (DEGDA, 75%), 2-(dimethylamino) ethyl acrylate (>99.0%) and 2-(dimethylamino) ethyl methacrylate (>99.0%) were purchased from Aldrich Chemical Company; isobutyric acid (>99.5%), tributylamine (>99.0%), trihexylamine (>99.0%), and trioctylamine (>99.0%) were purchased from Fluka and used as received. The photoinitiators, Darocur 1173 and Irgacure 651 were obtained from Ciba Specialty Chemicals and used without further purification.

Characterization

FTIR spectra were recorded on a Nicolet NEXUS 470 spectrometer, and NMR spectra were recorded on a Spectrospin-Bruker 300 MHz Spectrometer. Methanol-d_4 was used as the solvent for NMR measurements.

Monomer Synthesis

As an example of the synthetic process, 6.55 mL of tributylamine and 1.86 mL of acrylic acid were mixed with constant stirring for 5 h. The reaction was carried out in a room temperature water bath to remove the large heat of neutralization. The same methodology was used with other amines and acids. A 1:1 M relation for acid:base was used in all cases. Characterization of each ionic liquid follows.

Additional peaks that appear in the spectra around 4.7 (1) ppm, 3.1 (5) in ^{1}H NMR and 48–49 (7) ppm in ^{13}C NMR correspond to methanol-d_4 (solvent). Ionic liquids prepared with ethylene glycol methacrylate phosphate showed other peaks around 7.1 (1) ppm in ^{1}H NMR and 125–127 (3) ppm in ^{13}C NMR corresponding to benzene, an impurity from the original chemical.

The following abbreviations are used to show the multiplicity obtained by NMR for the individual compounds synthesized: s = singlet, d = doublet, dd = double doublet, t = triplet and m = multiplet.

Tributylammonium acrylate. ^{1}H NMR (CD_3OD, δ ppm) 5.82 (2H, m, $H_2C{=}C{-}CO$), 5.30 (1H, dd, $C{=}CH{-}CO$), 2.81 (6H, m, $N^+{-}(CH_2{-}C)_3$), 1.37 (6H, m, $N^+{-}(C{-}CH_2{-}C)_3$), 1.11 (6H, m, $N^+{-}(C{-}C{-}CH_2{-}C)_3$), 0.677 (9H, m, $N^+{-}(C{-}C{-}C{-}CH_3)_3$). ^{13}C NMR ($CD_3OD$, δ ppm) 173.7 ($^-O{-}\mathbf{C}O{-}C$), 135.7 ($O{=}C{-}\mathbf{C}H{=}C$), 126.7 ($O{=}C{-}CH{=}\mathbf{C}H_2$), 53.24 ($N^+{-}(\mathbf{C}H_2{-}C{-}C{-}C)_3$), 26.41 ($N^+{-}(C{-}\mathbf{C}H_2{-}C{-}C)_3$), 20.82 ($N^+{-}(C{-}C{-}\mathbf{C}H_2{-}C)_3$), 14.11 ($N^+{-}(C{-}C{-}C{-}\mathbf{C}H_3)_3$).

Trihexylammonium acrylate. ^{1}H NMR (CD_3 OD, δ ppm) 5.89 (1H, m, $H_2C{=}C{-}CO$), 5.77 (1H, m, $H_2C{=}CCO$), 5.24 (1H, dd, $C{=}CH{-}CO$), 2.78 (6H, m, $N^+{-}(CH_2{-}C)_3$), 1.38 (6H, m, $N^+{-}(C{-}CH_2{-}C)_3$), 1.06 (18H, m, $N^+{-}(C{-}C{-}CH_2{-}CH_2{-}CH_2{-}C)_3$), 0.620 (9H, m, $N^+{-}(C{-}C{-}C{-}C{-}C{-}CH_3)_3$). ^{13}C NMR ($CD_3OD$, δ ppm) 174.8 ($^-O{-}\mathbf{C}O{-}C$), 136.8 ($O{=}C{-}\mathbf{C}H{=}C$), 125.6 ($O{=}C{-}CH{=}\mathbf{C}H_2$), 53.19 ($N^+{-}(\mathbf{C}H_2{-}C)_3$), 32.23 ($N^+{-}(C{-}\mathbf{C}H_2{-}C)_3$), 27.47 ($N^+{-}(C{-}C{-}\mathbf{C}H_2{-}C)_3$), 24.67 ($N^+{-}(C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 23.84 ($N^+{-}(C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 14.06 ($N^+{-}(C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_3)_3$)

Trioctylammonium acrylate. ^{1}H NMR (CD_3OD, δ ppm) 5.95 (1H, m, $H_2C{=}C{-}CO$), 5.87 (1H, m, $H_2C{=}C{-}CO$), 5.29 (1H, dd, $C{=}CH{-}CO$), 2.82 (6H, m, $N^+{-}(CH_2{-}C)_3$), 1.43 (6H, m, $N^+{-}(C{-}CH_2{-}C)_3$), 1.12 (30H, m, $N^+{-}(C{-}C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}C)_3$), 0.662 (9H, m, $N^+{-}(C{-}C{-}C{-}C{-}C{-}C{-}C{-}CH_3)_3$). ^{13}C NMR ($CD_3OD$, δ ppm) 174.7 ($^-O{-}\mathbf{C}O{-}C$), 136.7 ($O{=}C{-}\mathbf{C}H{=}C$), 125.5 ($O{=}C{-}CH{=}\mathbf{C}H_2$), 53.78 ($N^+{-}(\mathbf{C}H_2{-}C)_3$), 33.14 ($N^+{-}(C{-}\mathbf{C}H_2{-}C)_3$), 30.48 ($N^+{-}(C{-}C{-}\mathbf{C}H_2{-}C)_3$), 30.46 ($N^+{-}(C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 28.05 ($N^+{-}(C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 24.92 ($N^+{-}(C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 23.91 ($N^+{-}(C{-}C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 14.74 ($N^+{-}(C{-}C{-}C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_3)_3$).

Tributylammonium methacrylate. ^{1}H NMR (CD_3OD, δ ppm) 5.38 (1H, m, $H_2C{=}C{-}CO$), 4.87 (1H, m, $H_2C{=}C{-}CO$), 2.69 (6H, m, $N^+{-}(CH_2{-}C)_3$), 1.53 (3H, t, $O{=}C{-}C{-}CH_3$), 1.29 (6H, m, $N^+{-}(C{-}CH_2{-}C)_3$), 1.04 (6H, m, $N^+{-}(C{-}C{-}CH_2{-}C)_3$), 0.615 (9H, m, $N^+{-}(C{-}C{-}C{-}CH_3)_3$). ^{13}C NMR ($CD_3OD$, δ ppm) 176.5 ($^-O{-}\mathbf{C}O{-}C$), 144.6 ($O{=}C{-}\mathbf{C}{=}C$), 120.3 ($O{=}C{-}C{=}\mathbf{C}H_2$), 53.23 ($N^+{-}(\mathbf{C}H_2{-}C{-}C{-}C)_3$), 26.40 ($N^+{-}(C{-}\mathbf{C}H_2{-}C{-}C)_3$), 20.81 ($N^+{-}(C{-}C{-}\mathbf{C}H_2{-}C)_3$), 20.16 ($O{=}C{-}C{-}\mathbf{C}H_3$), 14.38 ($N^+{-}(C{-}C{-}C{-}CH_3)_3$).

Trihexylammonium methacrylate. ^{1}H NMR (CD_3OD, δ ppm) 5.48 (1H, m, $H_2C{=}C{-}CO$), 4.96 (1H, m, $H_2C{=}C{-}CO$), 2.78 (6H, m, $N^+{-}(CH_2{-}C)_3$), 1.62 (3H, t, $O{=}C{-}C{-}CH_3$), 1.39 (6H, m, $N^+{-}(C{-}CH_2{-}C)_3$), 1.08 (18H, m, $N^+{-}(C{-}C{-}CH_2{-}CH_2{-}CH_2{-}C)_3$), 0.635 (9H, m, $N^+{-}(C{-}C{-}C{-}C{-}C{-}CH_3)_3$). ^{13}C NMR ($CD_3OD$, δ ppm) 174.8 ($^-O{-}\mathbf{C}O{-}C$), 142.8 ($O{=}C{-}\mathbf{C}{=}C$), 119.3 ($O{=}C{-}C{=}\mathbf{C}H_2$), 52.36 ($N^+{-}(\mathbf{C}H_2{-}C)_3$), 31.48 ($N^+{-}(C{-}\mathbf{C}H_2{-}C)_3$), 26.55 ($N^+{-}(C{-}C{-}\mathbf{C}H_2{-}C)_3$), 23.64 ($N^+{-}(C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 22.58 ($N^+{-}(C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 19.21 ($O{=}C{-}C{-}\mathbf{C}H_3$), 13.47 ($N^+{-}(C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_3)_3$).

Trioctylammonium methacrylate. ^{1}H NMR (CD_3OD, δ ppm) 5.47 (1H, m, $H_2C{=}C{-}CO$), 4.96 (1H, m, $H_2C{=}C{-}CO$), 2.75 (6H, m, $N^+{-}(CH_2{-}C)_3$), 1.62 (3H, t, $O{=}C{-}C{-}CH_3$), 1.38 (6H, m, $N^+{-}(C{-}CH_2{-}C)_3$), 1.07 (30H, m, $N^+{-}(C{-}C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}C)_3$), 0.612 (9H, m, $N^+{-}(C{-}C{-}C{-}C{-}C{-}C{-}C{-}CH_3)_3$). ^{13}C NMR ($CD_3OD$, δ ppm) 176.0 ($^-O{-}\mathbf{C}O{-}C$), 144.1 ($O{=}C{-}\mathbf{C}{=}C$), 120.6 ($O{=}C{-}C{=}\mathbf{C}H_2$), 53.40 ($N^+{-}(\mathbf{C}H_2{-}C)_3$), 33.06 ($N^+{-}(C{-}\mathbf{C}H_2{-}C)_3$), 30.36 ($N^+{-}(C{-}C{-}\mathbf{C}H_2{-}C)_3$), 30.35 ($N^+{-}(C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 27.97 ($N^+{-}(C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 24.80 ($N^+{-}(C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 23.84 ($N^+{-}(C{-}C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 20.35 ($O{=}C{-}C{-}\mathbf{C}H_3$), 14.74 ($N^+{-}(C{-}C{-}C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_3)_3$).

Tributylammonium (2-methacrylate)ethyl phosphate. ^{1}H NMR (CD_3OD, δ ppm) 5.85 (1H, m, $H_2C{=}C{-}CO$), 5.35 (1H, m, $H_2C{=}C{-}CO$), 4.03 (2H, m, $O{=}C{-}O{-}CH_2{-}C$), 3.81 (2H, m, $O{=}C{-}O{-}C{-}CH_2{-}O$), 2.83 (6H, m, $N^+{-}(CH_2{-}C)_3$), 1.65 (3H, t, $O{=}C{-}C{-}CH_3$), 1.41 (6H, m, $N^+{-}(C{-}CH_2{-}C)_3$), 1.14 (6H, m, $N^+{-}(C{-}C{-}CH_2{-}C)_3$), 0.706 (9H, t, $N^+{-}(C{-}C{-}C{-}CH_3)_3$). ^{13}C NMR ($CD_3OD$, δ ppm) 168.7 ($^-O{-}\mathbf{C}O{-}C$), 137.8 ($O{=}C{-}\mathbf{C}{=}C$), 129.5 ($O{=}C{-}C{=}\mathbf{C}H_2$), 65.78 ($O{=}C{-}O{-}\mathbf{C}H_2{-}C$), 64.63 ($O{=}C{-}O{-}C{-}\mathbf{C}H_2{-}O$), 53.25 ($N^+{-}(\mathbf{C}H_2{-}C{-}C{-}C)_3$), 26.57 ($N^+{-}(C{-}\mathbf{C}H_2{-}C{-}C)_3$), 21.14 ($N^+{-}(C{-}C{-}\mathbf{C}H_2{-}C)_3$), 18.69 ($O{=}C{-}C{-}\mathbf{C}H_3$), 14.20 ($N^+{-}(C{-}C{-}C{-}CH_3)_3$).

Trihexylammonium (2-methacrylate)ethyl phosphate. ^{1}H NMR (CD_3OD, δ ppm) 5.87 (1H, m, $H_2C{=}C{-}CO$), 5.37 (1H, m, $H_2C{=}C{-}CO$), 4.05 (2H, m, $O{=}C{-}O{-}CH_2{-}C$), 3.82 (2H, m, $O{=}{-}O{-}C{-}CH_2{-}O$), 2.83 (6H, m, $N^+{-}(CH_2{-}C)_3$), 1.68 (3H, t, $O{=}C{-}C{-}CH_3$), 1.45 (6H, m, $N^+{-}(C{-}CH_2{-}C)_3$), 1.11 (18H, m, $N^+{-}(C{-}C{-}CH_2{-}CH_2{-}CH_2{-}C)_3$), 0.664 (9H, m, $N^+{-}(C{-}C{-}C{-}C{-}C{-}CH_3)_3$). ^{13}C NMR ($CD_3OD$, δ ppm) 168.8 ($^-O{-}\mathbf{C}O{-}C$), 137.7 ($O{=}C{-}\mathbf{C}{=}C$), 129.5 ($O{=}C{-}C{=}\mathbf{C}H_2$), 65.86 ($O{=}C{-}O{-}\mathbf{C}H_2{-}C$), 64.68 ($O{=}C{-}O{-}C{-}\mathbf{C}H_2{-}O$), 53.62 ($N^+{-}(\mathbf{C}H_2{-}C)_3$), 32.65 ($N^+{-}(C{-}\mathbf{C}H_2{-}C)_3$), 27.63 ($N^+{-}(C{-}C{-}\mathbf{C}H_2{-}C)_3$), 24.61 ($N^+{-}(C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 23.75 ($N^+{-}(C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3$), 18.74 ($O{=}C{-}C{-}\mathbf{C}H_3$), 14.62 ($N^+{-}(C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_3)_3$).

Trioctylammonium (2-methacrylate)ethyl phosphate. ^{1}H NMR (CD_3OD, δ ppm) 5.89 (1H, m, $H_2C{=}C{-}CO$), 5.39 (1H, m, $H_2C{=}C{-}CO$), 4.07 (2H, m, $O{=}C{-}O{-}CH_2{-}C$), 3.86 (2H, m, $O{=}C{-}O{-}C{-}CH_2{-}O$), 2.86 (6H, m, $N^+{-}(CH_2{-}C)_3$), 1.69 (3H, t, $O{=}C{-}C{-}CH_3$), 1.45 (6H, m, $N^+{-}(C{-}CH_2{-}C)_3$), 1.13 (30H, m, $N^+{-}(C{-}C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}C)_3$), 0.676 (9H, m, $N^+{-}(C{-}C{-}C{-}C{-}C{-}C{-}C{-}CH_3)_3$). ^{13}C NMR ($CD_3OD$, δ ppm) 168.6 ($^-O{-}\mathbf{C}O{-}C$), 137.6 ($O{=}C{-}\mathbf{C}{=}C$), 126.5

$(O{=}C{-}C{=}\mathbf{C}H_2)$, 65.82 $(O{=}C{-}O{-}\mathbf{C}H_2{-}C)$, 64.49 $(O{=}C{-}O{-}C{-}\mathbf{C}H_2{-}O)$, 53.42 $(N^+{-}(\mathbf{C}H_2{-}C)_3)$, 33.02 $(N^+{-}(C{-}\mathbf{C}H_2{-}C)_3)$, 30.35 $(N^+{-}(C{-}C{-}\mathbf{C}H_2{-}C)_3)$, 30.29 $(N^+{-}(C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3)$, 27.84 $(N^+{-}(C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3)$, 24.50 $(N^+{-}x(C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3)$, 23.76 $(N^+{-}(C{-}C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_2{-}C)_3)$, 18.66 $(O{=}C{-}C{-}\mathbf{C}H_3)$, 14.61 $(N^+{-}(C{-}C{-}C{-}C{-}C{-}C{-}C{-}\mathbf{C}H_3)_3)$.

(2-Acrylate)ethyl dimethylammonium acrylate. ^{1}H NMR (CD_3OD, δ ppm) 6.47 (1H, dd, $H_2C{=}C{-}CO{-}O{-}C$), 6.24 (1H, dd, $H_2C{=}C{-}CO{-}O^-$), 6.14 (2H, m, $H_2C{=}C{-}CO{-}O{-}C$), 5.95 (1H, dd, $C{=}CH{-}CO{-}O^-$), 5.62 (1H, dd, $C{=}CH{-}CO{-}O^-$), 4.46 (2H, m, $O{-}CH_2{-}C$), 3.27 (2H, m, $N^+{-}CH_2{-}C$), 2.76 (6H, s, $N^+{-}(CH_3)_2$). ^{13}C NMR (CD_3OD, δ ppm) 173.9 $({}^-O{-}\mathbf{C}O{-}C)$, 166.9 $(C{-}O{-}\mathbf{C}O{-}C)$, 134.9 $(C{-}O{-}CO{-}\mathbf{C}H{=}C)$, 132.3 $({}^-O{-}CO{-}\mathbf{C}H{=}C)$, 128.9 $(C{-}O{-}CO{-}C{=}\mathbf{C}H_2)$, 126.8 $({}^-O{-}CO{-}C{=}\mathbf{C}H_2)$, 60.49 $(O{-}\mathbf{C}H_2{-}C)$, 57.23 $(N^+{-}\mathbf{C}H_2{-}C)$, 44.04 $(N^+{-}(\mathbf{C}H_3)_2)$.

(2-Methacrylate)ethyl dimethylammonium methacrylate. ^{1}H NMR (CD_3OD, δ ppm) 5.58 (1H, m, $H_2C{=}C{-}CO{-}O{-}C$), 5.27 (1H, m, $H_2C{=}C{-}CO{-}O^-$), 5.08 (1H, m, $H_2C{=}C{-}CO{-}O{-}C$), 4.77 (1H, m, $H_2C{=}C{-}CO{-}O^-$), 3.87 (2H, m, $O{-}CH_2{-}C$), 2.66 (2H, m, $N^+{-}CH_2{-}C$), 2.15 (6H, s, $N^+{-}(CH_3)_2$), 1.36 (3H, m, ${}^-O{-}CO{-}C{-}CH_3$), 1.32 (3H, m, $C{-}O{-}CO{-}C{-}CH_3$). ^{13}C NMR (CD_3OD, δ ppm) 175.2 $({}^-O{-}\mathbf{C}O{-}C)$, 168.0 $(C{-}O{-}\mathbf{C}O{-}C)$, 141.8 $({}^-O{-}CO{-}\mathbf{C}{=}C)$, 137.2 $(C{-}O{-}CO{-}\mathbf{C}{=}C)$, 127.0 $(C{-}O{-}CO{-}C{=}\mathbf{C}H_2)$, 121.8 $({}^-O{-}CO{-}C{=}\mathbf{C}H_2)$, 61.31 $(O{-}\mathbf{C}H_2{-}C)$, 57.21 $(N^+{-}\mathbf{C}H_2{-}C)$, 44.28 $(N^+{-}\mathbf{C}H_3)$, 43.63 $(N^+{-}\mathbf{C}H_3)$, 19.91 $({}^-O{-}CO{-}C{-}\mathbf{C}H_3)$, 18.61 $(C{-}O{-}CO{-}C{-}\mathbf{C}H_3)$.

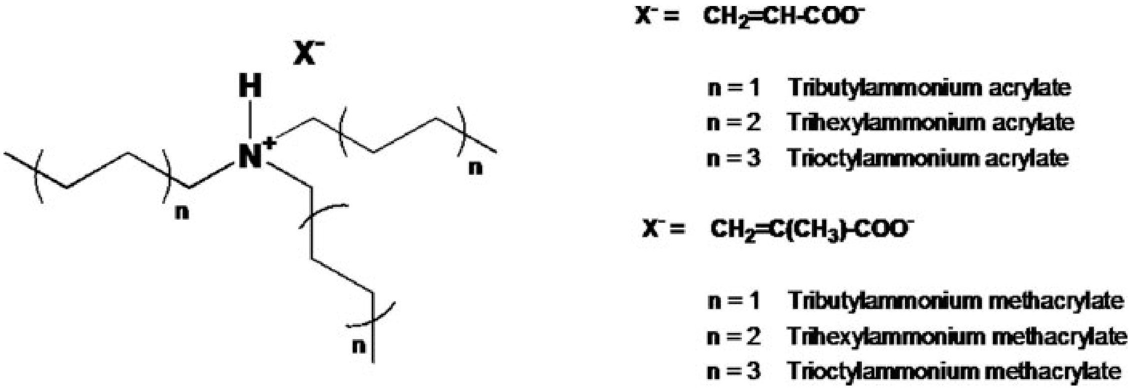
(2-Methacrylate)ethyl dimethylammonium (2-methacrylate)ethyl phosphate. ^{1}H NMR (CD_3OD, δ ppm) 5.86 (1H, m, $H_2C{=}C{-}CO{-}O{-}C{-}C{-}N^+$), 5.79 (1H, m, $H_2C{=}C{-}CO{-}O{-}C{-}C{-}O{-}P$), 5.37 (1H, m, $H_2C{=}C{-}CO{-}O{-}C{-}C{-}N^+$), 5.29 (1H, m, $H_2C{=}C{-}CO{-}O{-}C{-}C{-}O{-}P$), 4.18 (2H, m, $CO{-}O{-}CH_2{-}C{-}N^+$), 3.99 (2H, m, $CO{-}O{-}CH_2{-}C{-}O{-}P$), 3.75 (2H, m, $CO{-}O{-}C{-}CH_2{-}O{-}P$), 3.07 (2H, m, $CO{-}O{-}C{-}CH_2{-}N^+$), 2.53 (6H, s, $N^+{-}(CH_3)_2$), 1.62 (3H, t, $N^+{-}C{-}C{-}CO{-}C{-}CH_3$), 1.59 (3H, t, $P{-}O{-}C{-}C{-}CO{-}C{-}CH_3$). ^{13}C NMR ($CD_3OD$, δ ppm) 168.7 $(P{-}O{-}C{-}C{-}O{-}\mathbf{C}O{-}C)$, 167.9 $(N^+{-}C{-}C{-}O{-}\mathbf{C}O{-}C)$, 137.7 $(P{-}O{-}C{-}C{-}O{-}CO{-}\mathbf{C}{=}C)$, 137.1 $(N^+{-}C{-}C{-}O{-}CO{-}\mathbf{C}{=}C)$, 129.5 $(N^+{-}C{-}C{-}O{-}CO{-}C{=}\mathbf{C}H_2)$, 127.5 $(P{-}O{-}C{-}C{-}O{-}CO{-}C{=}\mathbf{C}H_2)$, 65.93 $(CO{-}O{-}\mathbf{C}H_2{-}C{-}O{-}P)$, 64.73 $(CO{-}O{-}C{-}\mathbf{C}H_2{-}O{-}P)$, 60.89 $(CO{-}O{-}\mathbf{C}H_2{-}C{-}N^+)$, 57.06 $(CO{-}O{-}C{-}\mathbf{C}H_2{-}N^+)$, 44.17 $(N^+{-}\mathbf{C}H_3)$, 18.67 $(P{-}O{-}C{-}C{-}O{-}CO{-}C{-}\mathbf{C}H_3)$, 18.65 $(N^+{-}C{-}C{-}O{-}CO{-}C{-}\mathbf{C}H_3)$.

(2-Acrylate)ethyl dimethylammonium isobutyrate. ^{1}H NMR (CD_3OD, δ ppm) 5.84 (1H, dd, $H_2C{=}C{-}CO{-}O{-}C$), 5.61 (1H, dd, $H_2C{=}C{-}CO{-}O{-}$), 5.32 (1H, dd, $C{=}CH{-}CO{-}O{-}$), 3.79 (2H, m, $O{-}CH_2{-}C$), 2.52 (2H, m, $N^+{-}CH_2{-}C$), 2.04 (6H, s, $N^+{-}(CH_3)_2$), 1.78 $({-}O{-}CO{-}CH)$, 0.496 (6H, d, ${-}O{-}CO{-}C{-}(CH_3)_2$). ^{13}C NMR (CD_3OD, δ ppm) 184.4 $({-}O{-}CO{-}C)$, 167.1 $(C{-}O{-}CO{-}C)$, 132.3 $(C{-}O{-}CO{-}CH{=}C)$, 129.2 $(C{-}O{-}CO{-}C{=}CH_2)$, 61.10 $(O{-}CH_2{-}C)$, 57.38 $(N^+{-}CH_2{-}C)$, 44.36 $(N^+{-}(CH_3)_2)$, 36.44 $({-}O{-}CO{-}CH{-}C)$, 20.23 $({-}O{-}CO{-}C{-}(CH_3)_2)$.

(2-Methacrylate)ethyl dimethylammonium isobutyrate. ^{1}H NMR (CD_3OD, δ ppm) 5.57 (1H, m, $H_2C{=}C{-}CO{-}O{-}C$), 5.08 (1H, m, $H_2C{=}C{-}CO{-}C$), 3.83 (2H, m, $O{-}CH_2{-}C$), 2.57 (2H, m, $N^+{-}CH_2{-}C$), 2.07 (6H, s, $N^+{-}(CH_3)_2$), 1.83 $({-}O{-}CO{-}CH)$, 1.36 (3H, m, $C{-}O{-}CO{-}C(CH_3)\ {=}C$), 0.537 (6H, d, ${-}O{-}CO{-}C{-}(CH_3)_2$). ^{13}C NMR (CD_3OD, δ ppm) 184.7 $({-}O{-}CO{-}C)$, 168.2 $(C{-}O{-}CO{-}C)$, 137.3 $(C{-}O{-}CO{-}C(CH_3)\ {=}C)$, 127.0 $(C{-}O{-}CO{-}C{=}CH_2)$, 61.63 $(O{-}CH_2{-}C)$, 57.45 $(N^+{-}CH_2{-}C)$, 44.52 $(N^+{-}(CH_3)_2)$, 36.86 $({-}O{-}CO{-}CH{-}C)$, 20.29 $({-}O{-}CO{-}C{-}(CH_3)_2)$, 18.58 $(C{-}O{-}CO{-}C(CH_3)\ {=}C)$.

Photopolymerization

The kinetics of UV-induced polymerization was measured by real-time FTIR (RT-FTIR). The infrared spectra were recorded as a function of irradiation time on a modified Bruker spectrometer as described by Lee et al.[22] The change in absorption intensity for the acrylate or methacrylate double bond C=C (~1638, 990, and 812 cm^{-1}) with time was deduced. A 187-W high-pressure mercury-xenon lamp (Oriel Co)



Scheme 1. Ionic liquids from acrylic or methacrylic acid and trialkylamines.

served as the light source for inducing free-radical polymerization. A neutral density filter was used to reduce the light intensity from 187 to 18.7 mW/cm^2. Each sample was run three times. The sample contained the ionic liquid monomer and 2% of Darocur 1173.

The percentage conversion was calculated with the change in the intensity of the appropriate bands and plotted versus the irradiation time. From this plot the maximum polymerization rate was calculated from the maximum slope of the curve.

Viscosity

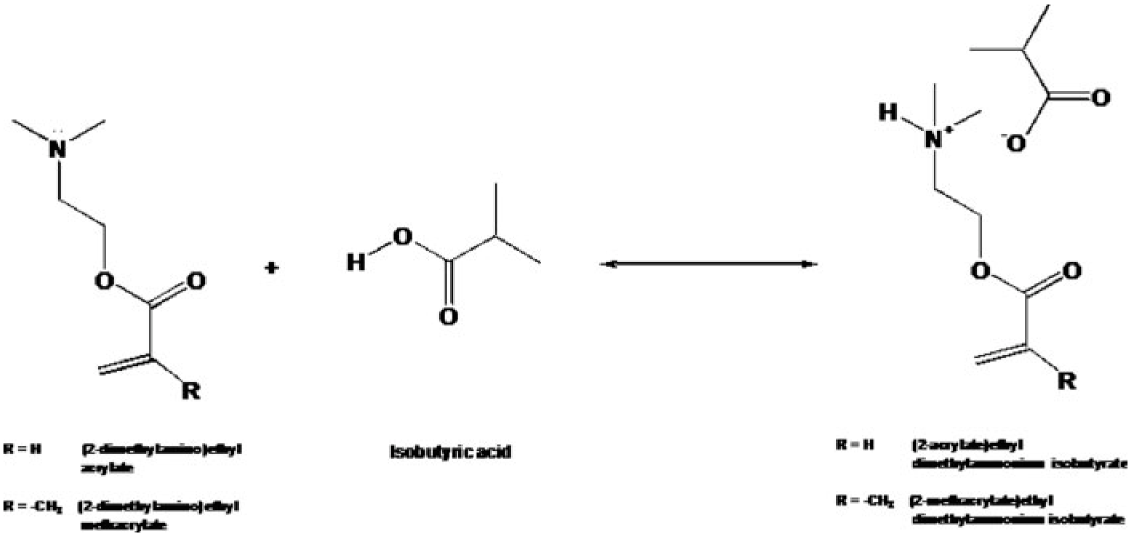
Viscosity measurements of the neat compounds were performed with a Brookfield Digital Viscometer Model DV-II at room temperature; for acrylates a No 18 spindle and speed of 12 rpm, for methacrylates a No 18 spindle and speed of 30 rpm and for ethyl phosphate methacrylate a No 31 spindle and speed of 6 rpm were used.

Film Preparation

A sample of the ionic liquid with 1% of Irgacure 651 was placed on a stainless steel plate that was placed into a chamber under nitrogen atmosphere and then cured with a UV fusion line EPIQ 6000 (D bulb, 3.15 W/cm^2, UVA-UVC) at a line speed of 3 m/min; the plate was passed through the line 20 times. The thickness of the film was 6 μm.

Hardness

Properties of the film were obtained by using a PTC Instruments Type A Durometer (model



Scheme 2. Synthesis of monofunctional ionic liquids from 2-(dimethylamino)ethyl acrylate or 2-(dimethylamino)ethyl methacrylate and isobutyric acid.

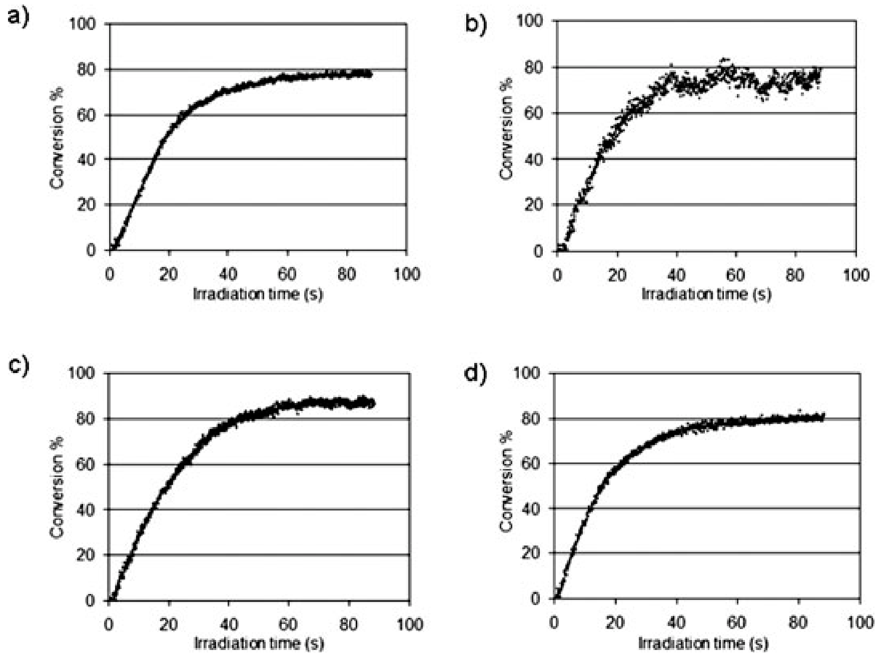


Figure 1. Conversion-Irradiation time plots from RT-FTIR of the photopolymerization of (a) tributylammonium acrylate, (b) trihexylammonium acrylate, (c) trioctylammonium acrylate, and (d) (2-acrylate)ethyl dimethylammonium isobutyrate. The samples contained 2.0 wt % Darocur 1173 (photoinitiator). The light intensity was 18.7 mW/cm^2.

306L) and a Pendulum Hardness Tester (BYK Gardner) in the Persoz mode to measure the time taken for the amplitude of oscillation to decrease from 12° to 4°.

RESULTS AND DISCUSSION

To determine the effect of the ionic liquid state on polymerization rates, two types of systems were evaluated. The first system involved monomethacrylates or monoacrylates where the ionic group was an ionic carboxylate salt attached to the reactive (meth)acrylate vinyl group. There was only one reactive meth(acrylate) group per ionic complex. In the second system, both the acid and basic components forming the ionic complex had reactive (meth)acrylate functionalities. This presented the possibility that the rate might be enhanced via the linking of the two functionalities through the salt complex. Real-time infrared (RT-FTIR) spectroscopy was used to monitor the reactive (meth)acrylate group in each case to obtain a complete conversion profile as a function of time. Using the dual-tethered acrylate and methacrylate ionic liquids, films were prepared and characterized with respect to their solubility in aqueous media and hardness using Persoz and Shore A measurements.

Synthesis and Polymerization of Monomeric Ionic Liquids Based on (Meth)acrylic Acid and 2-(Dimethylamino)ethyl (meth)acrylate

Trialkylammonium salts (Scheme 1) with different alkyl lengths (C_4–C_8) were synthesized by the neutralization reaction between the requisite tertiary amine and either acrylic or methacrylic acid. In addition, (2-methacrylate)ethyl dimethylammonium isobutyrate and (2-acrylate) ethyl dimethylammonium isobutyrate were synthesized (Scheme 2). NMR verified all structures. The ammonium salt monomers were liquids at room temperature and hence suitable for conducting polymerization rate measurements using RT-FTIR.

The conversion versus irradiation time plots for the acrylate and methacrylate groups of the ionic liquid monomers in Schemes 1 and 2, with 2 weight percent of Darocur 1173 photoinitiator, are shown in Figures 1 and 2. To compare the

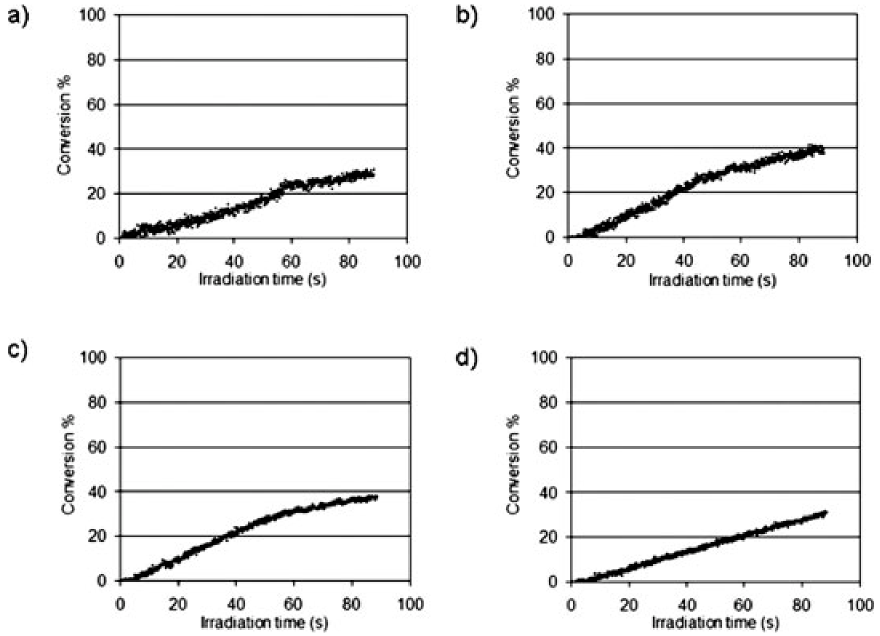


Figure 2. Conversion-Irradiation time plots from RT-FTIR of the photopolymerization of (a) tributylammonium methacrylate, (b) trihexylammonium methacrylate, (c) trioctylammonium methacrylate, and (d) (2-methacrylate)ethyl dimethylammonium isobutyrate. The samples contained 2.0 wt % Darocur 1173 (photoinitiator). The light intensity was 18.7 mW/cm^2.

kinetics of the ionic liquid acrylates, acrylic acid, butyl acrylate, and 2-(dimethylamino)ethyl acrylate were studied; the conversion versus time plots for them are shown in Figure 3. For comparison with ionic liquid methacrylates, the conversion versus time plots for methacrylic acid, butyl methacrylate, and 2-(dimethylamino)ethyl methacrylate are shown in Figure 4.

As is readily seen from examining the rates in Table 1 taken from the initial slopes of the plots in Figure 1, the maximum photopolymerization rates for the four trialkylammonium acrylate ionic liquids are about the same. Ionic liquid acrylates showed much lower rates of photopolymerization than acrylic acid. This is because of the presence of hydrogen bonding between acrylic acid molecules, which is thought to increase the polymerization rate.[23–25]

Polymerization rates for the three trialkylammonium acrylates are only about 33% greater than the one for 2-(dimethylamino)ethyl acrylate (Table 1), due to the presence of the amino group. We next discuss these in light of molecular structure considerations. The amine, 2-(di-

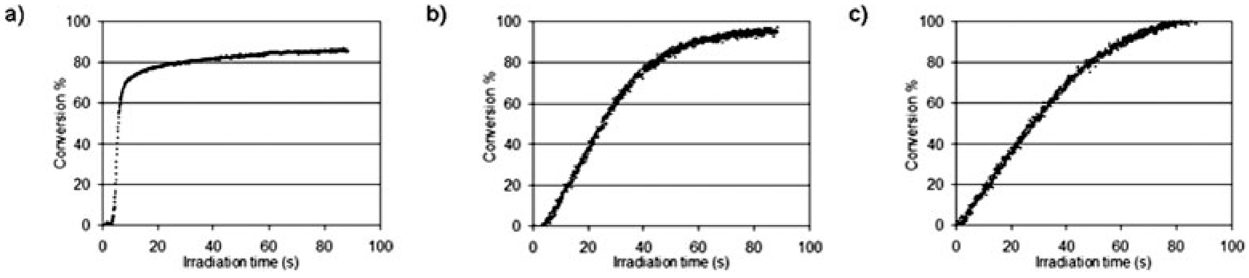


Figure 3. Conversion-Irradiation time plots from RT-FTIR of the photopolymerization of (a) acrylic acid, (b) butyl acrylate and (c) 2-(dimethylamino)ethyl acrylate. Samples contained 2.0 wt % Darocur 1173 (photoinitiator). The light intensity was 18.7 mW/cm^2.

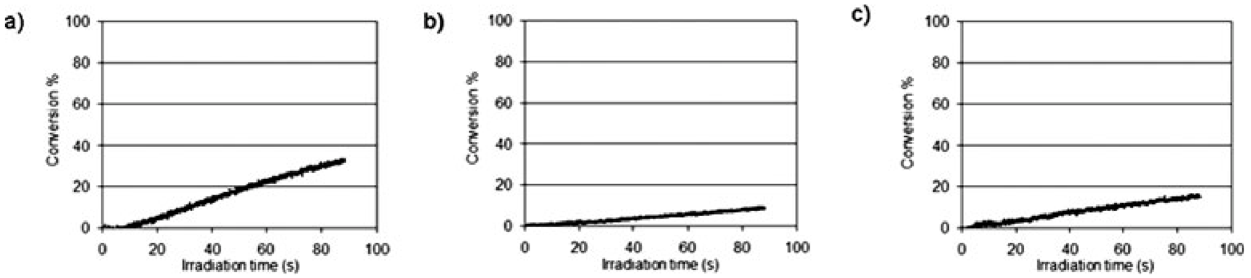


Figure 4. Conversion-Irradiation time plots from RT-FTIR of the photopolymerization of (a) methacrylic acid, (b) butyl methacrylate and (c) 2-(dimethylamino)ethyl methacrylate. Samples contained 2.0 wt % Darocur 1173 (photoinitiator). The light intensity was 18.7 mW/cm^2.

methylamino)ethyl acrylate, showed a lower photopolymerization rate (1.9 s^{-1}) than its ammonium salt (3.6 s^{-1}), (2-acrylate)ethyl dimethylammonium isobutyrate. This decrease in the rate of around a half indicates that the trialkylamine has a greater activity as a chain transfer agent than its ammonium salt during the polymerization process. This result is in agreement with published work showing that electron-rich transfer agents such as trialkylamines have enhanced reactivity with electron-poor monomers, as for example acrylonitrile, methyl acrylate and methyl methacrylate.[26] Also it is known that chain transfer from amines, is more effective for acrylates than for methacrylates.[26,27] We propose that this is why the relationships between the rates of acrylate ester—acrylate ionic liquid and methacrylate ester—methacrylate ionic liquid are not the same. On the other hand the rate of photopolymerization for the ester (Table 1), butyl acrylate, is approximately the same as for the ionic liquid acrylates, which is around 3 s^{-1}.

The initial rates (Table 1) for all ammonium ionic liquid methacrylates in Figure 2 are about the same as for methacrylic acid, but two times greater than for 2-(dimethylamino)ethyl methacrylate (Fig. 4) and about three times greater than the esters. As in the case of acrylates, the trialkylamine 2-(dimethylamino)ethyl methacrylate showed a lower photopolymerization rate than its isobutyrate salt, corroborating the dif-

Table 1. Maximum Photopolymerization Rates of Trialkylammonium (Meth)Acrylates (Scheme 1)

Compound[a]	Maximum Photopolymerization Rate[b,c] (% conversion/s)
Trioctylammonium acrylate	3.0 ± 0.1
Trihexylammonium acrylate	3.0 ± 0.1
Tributylammonium acrylate	3.0 ± 0.1
(2-acrylate)ethyl dimethylammonium isobutyrate	3.6 ± 0.1
Acrylic acid	28 ± 1
Butyl acrylate	2.4 ± 0.1
2-(dimethylamino)ethyl acrylate	1.9 ± 0.1
Trioctylammonium methacrylate	0.58 ± 0.02
Trihexylammonium methacrylate	0.61 ± 0.02
Tributylammonium methacrylate	0.35 ± 0.01
(2-acrylate)ethyl dimethylammonium isobutyrate	0.37 ± 0.01
Methacrylic acid	0.45 ± 0.02
Butyl methacrylate	0.10 ± 0.01
2-(dimethylamino)ethyl methacrylate	0.18 ± 0.01

[a] The samples contained 2.0 wt % Darocur 1173 (photoinitiator).
[b] The light intensity used was 18.7 mW/cm^2.
[c] Standard deviation for the rates was calculated with $n = 4$.

Table 2. Viscosities of Trialkylammonium (Meth) Acrylates (Scheme 1)

Compound	Viscosity (mPa s)
Trioctylammonium acrylate	37
Trihexylammonium acrylate	32
Tributylammonium acrylate	46
Trioctylammonium methacrylate	35
Trihexylammonium methacrylate	30
Tributylammonium methacrylate	13

ference in chain transfer activity of the amines compared with their salts.

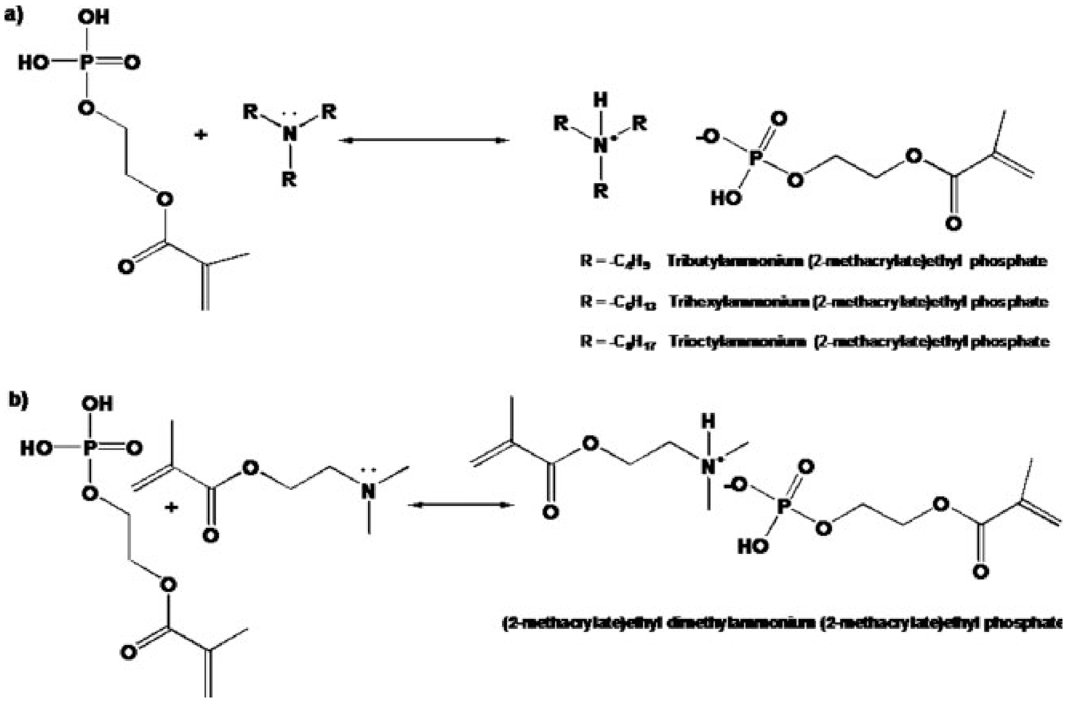
The length of the chain on the ammonium moiety for trialkylammonium acrylates or trialkylammonium methacrylates did not significantly affect the photopolymerization rates (Table 1). Viscosities (Table 2) obtained for those salts are not significantly higher than for acrylate esters and thus viscosity does not affect the maximum polymerization rate, in agreement with the work of Leclercq et al.[28]

In general the fact that monomers are ionic liquids did not show enhancement in the polymerization rates in the case of acrylates, but it did in the case of methacrylates compared with their respective traditional esters.

Synthesis and Polymerization of Ionic Liquids Based on 2-Methacrylate Ethyl Phosphate

Ionic liquid methacrylates were synthesized by reacting ethylene glycol methacrylate phosphate with different tertiary amines, as shown in Scheme 3. The polymerization rates derived from RT-FTIR (Fig. 5) of each of the phosphate monomers are given in Table 3. The rates for the ionic methacrylate phosphate ionic liquids were all comparable to the rates for tri(ethylene glycol) dimethacrylate or (2-methacrylate) ethyl dimethylammonium methacrylate (see next section), and much higher than for butyl methacrylate or any of the monomethacrylate ionic liquids in Table 1.

There are two factors that make these phosphate ionic liquids different from the ionic liquids derived from (meth)acrylic acid. The first factor is the high viscosity, and the second is the bulky group on the β-carbon. Trialkylammonium (2-methacrylate)ethyl phosphate salts exhibited an apparent dependence of the photopolymerization rate (Table 3) on the length of the alkyl chain. The viscosity of the monomer is directly related to the alkyl chain length on the amine; the latter is higher for shorter alkyl chains, and so is the photopoly-



Scheme 3. Synthesis of ionic liquids from ethylene glycol methacrylate phosphate and (a) trialkylamines and (b) 2-(dimethylamino)ethyl methacrylate.

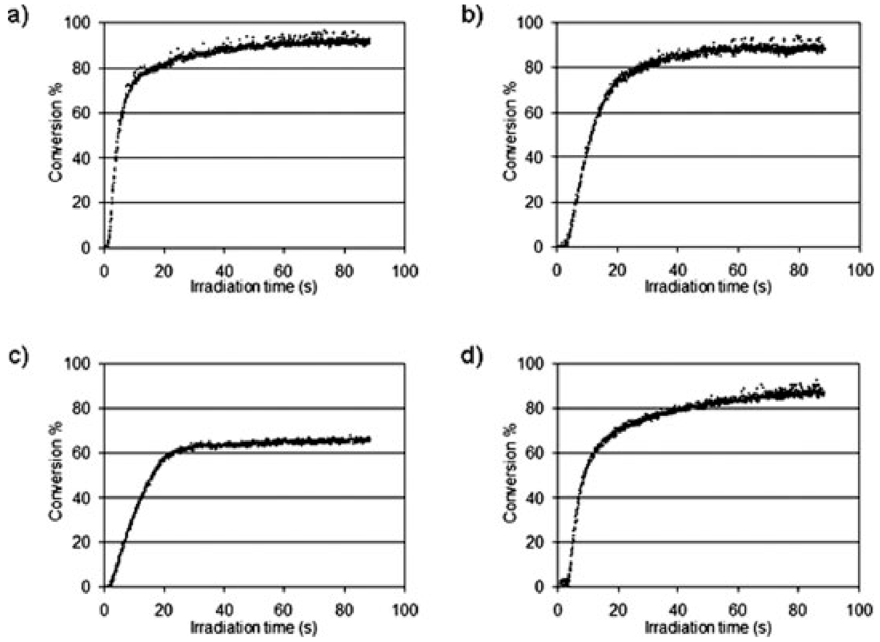


Figure 5. Conversion-Irradiation time plots from RT-FTIR of the photopolymerization of (a) tributylammonium (2-methacrylate)ethyl phosphate, (b) trihexylammonium (2-methacrylate)ethyl phosphate, (c) trioctylammonium (2-methacrylate)ethyl phosphate, and (d) ethylene glycol methacrylate phosphate. The samples contained 2.0 wt % Darocur 1173 (photoinitiator). The light intensity was 18.7 mW/cm^2.

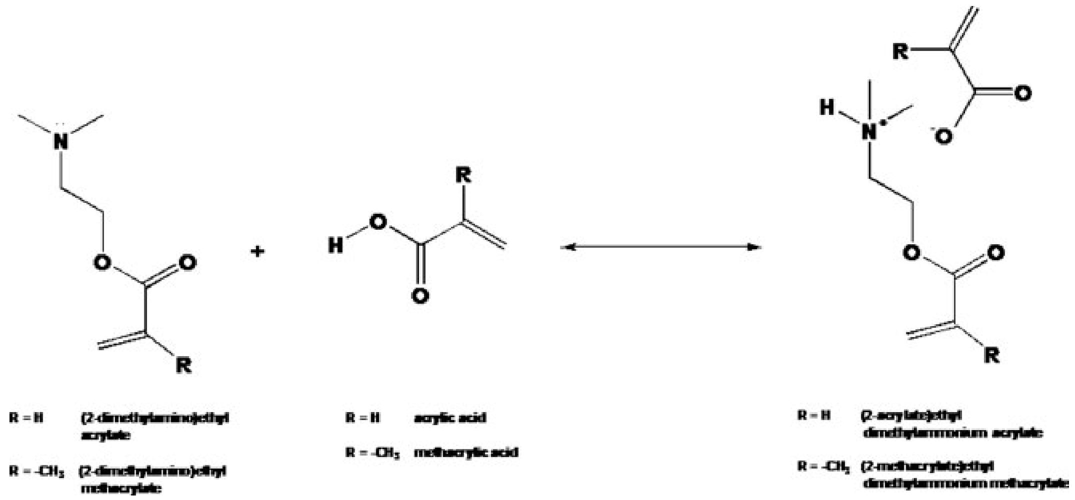
merization rate (Table 3). This is consistent with the well-known Norris-Trommsdorff (gel) effect[29,30] in which the rate of termination diminishes at high viscosity, resulting in an increase in the rate of polymerization. We propose that the differences in the rates are not due to the length of the alkyl chains but due to the viscosity. The viscosities of these monomers are 100 times greater than the viscosities of the trialkylammonium (meth)acrylates, which explains why the other monomers do not exhibit an rate dependence on alkyl chain length.

More research must be done to test our hypothesis that the polymerization rates for the ionic liquid methacrylate phosphates (Scheme 3) polymerize faster than regular monofunctional methacrylates because the phosphate group is on the β-carbon and, therefore, prone to rate acceleration.

Table 3. Viscosities and Initial Photopolymerization Rates of Trialkylammonium (2-Methacrylate)Ethyl Phosphates and (2-Methacrylate)Ethyl Dimethylammonium (2-Methacrylate) Ethyl Phosphate

Compound[a]	Viscosity (Pa s)	Maximum Photopolymerization Rate[b,c] (% conversion/s)
Trioctylammonium (2-methacrylate)ethyl phosphate	1.9	4.0 ± 0.1
Trihexylammonium (2-methacrylate)ethyl phosphate	2.3	6.1 ± 0.2
Tributylammonium (2-methacrylate)ethyl phosphate	3.5	14 ± 1
(2-methacrylate)ethyl dimethylammonium (2-methacrylate)ethyl phosphate	3.1	15 ± 1

[a] The samples contained 2.0 wt % Darocur 1173 (photoinitiator).
[b] The light intensity used was 18.7 mW/cm^2.
[c] Standard deviation for the rates was calculated with $n = 4$.



Scheme 4. Synthesis of difunctional ionic liquids from acrylic acid and 2-(dimethylamino)ethyl acrylate or methacrylic acid and 2-(dimethylamino)ethyl methacrylate.

Synthesis and Polymerization of Di(meth)acrylate Ionic Liquids

Pseudo difunctional (ammonium salt) ionic liquids were prepared by neutralization reactions between acrylic acid or methacrylic acid and am N,*N*-dimethyl tertiary amine attached via an ethylene spacer to a (meth)acrylate functional group (Scheme 4).

The monomers in Scheme 4 are particularly interesting since they represent the potential for polymerizing via kinetics inherent to covalent diacrylates or dimethacrylates, which are well known to polymerize with much faster rates than their monofunctional acrylate or methacrylate counterparts.[32–33]

As can been seen from the conversion versus time plots in Figures 6(a) and 7(a), the difunctional acrylate and methacrylate ionic liquids both polymerize much faster than their mono (meth)acrylate counterparts, (2-methacrylate) ethyl dimethylammonium isobutyrate [Fig. 2(d)] and (2-acrylate)ethyl dimethylammonium isobutyrate [Fig. 1(d)]. The connection of the two acrylate or methacrylate groups via the ionic ammonium salt is essential to the rate enhancement. In fact, as seen from the polymerization rates in Table 4 obtained from the maximum slopes in Figures 6 and 7, there is a 5–10 fold increase in the initial polymerization rates when two methacrylate or two acrylate groups are connected via the ammonium salt linkage. The rates for these ionic liquids are comparable to conventional diacrylates and dimethacrylates whose conversion rates are shown in Figures 6(b and 7(b), respectively. It is known that ionic liquids diffuse as an ion pair,[1] which may explain why those ionic liquids with one polymerizable group in both cation and anion, polymerize with

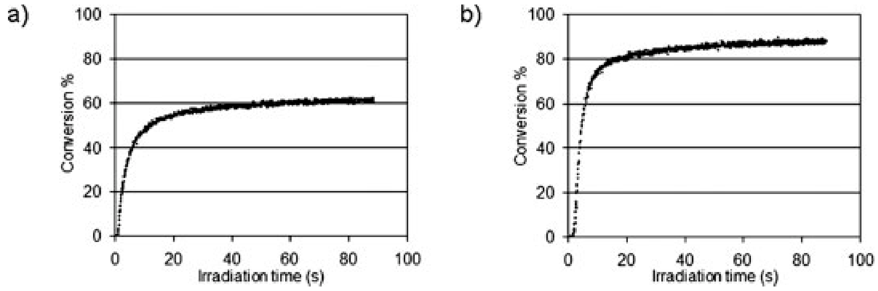


Figure 6. Conversion-Irradiation time plots from RT-FTIR of the photopolymerization of (a) (2-acrylate)ethyl dimethylammonium acrylate, and (b) di(ethylene glycol) diacrylate. Samples contained 2.0 wt % Darocur 1173 (photoinitiator). The light intensity was 18.7 mW/cm^2.

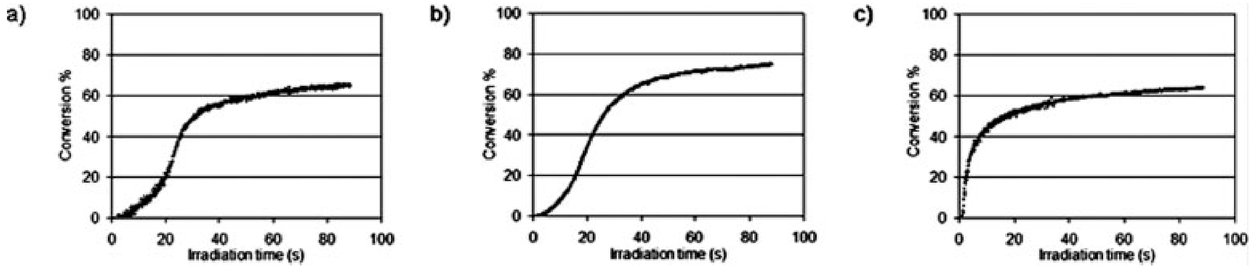


Figure 7. Conversion-Irradiation time plots from RT-FTIR of the photopolymerization of (a) (2-methacrylate)ethyl dimethylammonium methacrylate, (b) tri(ethylene glycol) dimethacrylate, and (c) (2-methacrylate)ethyl dimethylammonium (2-methacrylate)ethyl phosphate. Samples contained 2.0 wt % Darocur 1173 (photoinitiator). The light intensity was 18.7 mW/cm^2.

rates as difunctional monomers and not as a mixture of monofunctional monomers.

The ionic liquid (2-methacrylate)ethyl dimethylammonium (2-methacrylate)ethyl phosphate [Fig. 7(c)] was expected to have a higher rate of photopolymerization than the trialkylammonium phosphate monomers (Table 3); however its rate (Table 3) was very close to that for tributylammonium (2-methacrylate)ethyl phosphate. As it can be seen in Table 3, the viscosities for tributylammonium (2-methacrylate)ethyl phosphate and (2-methacrylate)ethyl dimethylammonium (2-methacrylate)ethyl phosphate are very close, as are also their maximum photopolymerization rates. This indicates that the rate of polymerization is essentially determined by the viscosity and not by the number of functional groups present in the compound. Nevertheless additional investigation needs to be performed.

Having shown that the "diacrylate" and "dimethacrylate" ionic liquid monomers in Scheme 4 polymerize with rates comparable to their di(meth)acrylate counterparts, a film was prepared by polymerization of (2-acrylate)ethyl dimethylammonium acrylate liquid with 1% of Irgacure 651 on a glass plate upon exposure to a total dose of 13.8 J/cm^2 (medium pressure mercury D-bulb). The film readily dissolved in water. Nonetheless the film exhibited properties inherent to moderately hard crosslinked films typically formed by polymerization of acrylate monomers (Perdoz damping of 198 s, Shore A hardness value of 92). The film formed from polymerization of (2-acrylate)ethyl dimethylammonium acrylate shows two major decomposition processes in TGA analysis, one occurring at around 200 °C and the other at around 350 °C. This shows that these films are less stable compare with films formed from regular diacrylates which have one decomposition temperature at 350 °C.

CONCLUSIONS

A series of compounds was synthesized by the neutralization reaction between trialkylamines (tributylamine, trihexylamine, trioctylamine) and (meth)acrylic acid and 2-(dimethylamino)ethyl methacrylate). The photopolymerization kinetics

Table 4. Maximum Photopolymerization Rates for "di(meth)acrylate" Monomers

Compound[a]	Maximum Photo-polymerization Rate[b,c] (% conversion/s)
(2-methacrylate) ethyl dimethylammonium methacrylate	3.7 ± 0.1
Tri(ethylene glycol) dimethacrylate	3.1 ± 0.1
(2-acrylate) ethyl dimethylammonium acrylate	13 ± 1
Di(ethylene glycol) diacrylate	18 ± 1

[a] The samples contained 2.0 wt % Darocur 1173 (photoinitiator).
[b] The light intensity used was 18.7 mW/cm^2.
[c] Standard deviation for the rates was calculated with $n = 4$.

indicated that the monoacrylate or methacrylate ionic liquids showed only small or moderate increases respectively in rate compared to their monofunctional analogues, and no dependence of the alkyl length on the amine was observed. The ionic liquids with the ammonium salt linking two reactive acrylate or methacrylate groups exhibited rates typical of traditional di(meth) acrylates. All of the phosphate-based ionic liquids exhibited very rapid polymerization rates.

Support for this project was provided by NASA (NAG8-1466).

REFERENCES AND NOTES

1. Wasserscheid, P.; Welton, T. Ionic Liquids in Synthesis; Wiley-VCH: Weinheim, 2003.
2. Rogers, R.; Seddon, K. Ionic Liquids as Green Solvents; American Chemical Society: Washington, DC, 2003.
3. Rogers, R.; Seddon, K. Ionic Liquids Industrial Application to Green Chemistry; American Chemical Society: Washington, DC, 2002.
4. Guerrero-Sanchez, C.; Wiesbrock, F.; Shubert, U. In Ionic Liquids in Polymer Systems; Brazel, C. S.; Roges, R. D., Eds.; American Chemical Society: Washington, DC, 2005; pp 37–50.
5. Rahman, M.; Shoff, H.; Brazel, C. In Ionic Liquids in Polymer Systems; Brazel, C. S.; Roges, R. D., Eds.; American Chemical Society: Washington, DC, 2005; pp 103–118.
6. Strehmel, V.; Laschewsky, A.; Wetzel, H.; Gornitz, E. Macromolecules 2006, 39, 923–930.
7. Strehmel, V.; Laschewsky, A.; Kraudelt, H.; Wetzel, H.; Gornitz, E. In Ionic Liquids in Polymer Systems; Brazel, C. S.; Roges, R. D., Eds.; American Chemical Society: Washington, DC, 2005; pp 17–36.
8. Salamone, J.; Israel, S.; Taylor, P.; Snider, B. Polymer 1973, 14, 639–644.
9. Yoshizawa, M.; Ohno, H. Chem Lett 1999, 28, 889–890.
10. Ohno, H. Electrochim Acta 2001, 46, 1407–1411.
11. Yoshizawa, M.; Ohno, H. Electrochim Acta 2001, 46, 1723–1728.
12. Washiro, S.; Yoshizawa, M.; Nakajima, H.; Ohno, H. Polymer 2004, 45, 1577–1582.
13. Yoshizawa, M.; Ogihara, W.; Ohno, H. Polym Adv Technol 2002, 13, 589–594.
14. Ohno, H.; Yoshizawa, M.; Ogihara, W. Electrochim Acta 2004, 50, 255–261.
15. Wang, J. T. S. Polym Prepr 2004, 45, 290–291.
16. Buruiana, E.; Buruiana, T. Macromol Rapid Commun 2002, 23, 130–134.
17. Ding, S.; Tang, H.; Radosz, M.; Shen, Y. J.; Polym Sci Part A: Polym Chem 2004, 42, 5794–5801.
18. Nakajima, H.; Ohno, H. Polymer 2005, 46, 11499–11504.
19. Hirao, M.; Sugimoto, H.; Ohno, H. J Electrochem Soc 2000, 147, 4168–4172.
20. Yoshizawa, M.; Ogihara, W.; Ohno, H. Electrochem Solid-State Lett 2001, 4, E25–E27.
21. Ohno, H.; Yoshizawa, M. Solid State Ionics 2002, 154/155, 303–309.
22. Lee, T.; Kaung, W.; Jonsson, S.; Lowery, K.; Guymon, C.; Hoyle, C. J. Polym Sci Part A: Polym Chem 2004, 42, 4424–4436.
23. Jansen, J.; Dias, A.; Dorschu, M.; Coussens, B. Macromolecules 2003, 36, 3861–3873.
24. Lee, T.; Roper, T.; Jonsson, S.; Guymon, C.; Hoyle, C. Macromolecules 2004, 37, 3659–3665.
25. Zhou, H.; Li, Q.; Lee, T. Y.; Guymon, C. A.; Jönsson, E. S.; Hoyle, C. E. Macromolecules 2006, 39, 8269–8273.
26. Odian, G. Principles of Polymerization, 4th ed.; Wiley: New York, 2004.
27. Moad, G.; Solomon, D. H. The Chemistry of Radical Polymerization; Pergamon: Oxford, 1995.
28. Leclercq, P.; Buisine, J.; Coqueret, X. Macromol Chem Phys 1997, 198, 2977–2984.
29. Norrish, R. G. W.; Smith, R. R. Nature 1942, 150, 336–337.
30. Trommsdorff, E.; Köhle, H.; Lagally, P. Makromol Chem 1948, 1, 169–198.
31. Berchtold, K. A.; Nie, J.; Stansbury, J. W.; Hacioğlu, B.; Beckel, E. R.; Bowman, C. N. Macromolecules 2004, 37, 3165–3179.
32. Kloosterboer, J. G. In Advances in Polymer Science; Springer-Verlag: Berlin, 1988; pp 8–68.
33. Anseth, K.; Kline, L. M.; Walker, T. A.; Anderson, K. J.; Bowman, C. N. Macromolecules 1995, 28, 2491–2499.