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Role of Choline Formate Ionic Liquid in the Polymerization of Vinyl and Methacrylic Monomers

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ABSTRACT: Polymerizations of vinyl and methacrylate monomers (2-hydroxyethyl methacrylate, styrene, and methyl methacrylate) were carried out in a choline formate ionic liquid at room temperature without the addition of peroxide-based initiators. Choline formate acted as both an initiator and a solvent and produced high-molecular-weight polymers. Gel permeation chromatography and electron paramagnetic resonance measurements indicated that the polymerizations predominantly occurred by a free-radical mechanism. This method of polymerization provides an alternate route to eliminate the use of toxic initiators and solvents. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3733–3739, 2011

Key words: biocompatibility; ESR/EPR; gel permeation chromatography (GPC); radical polymerization

INTRODUCTION

The polymerization of vinyl and methacrylate monomers has been widely studied with methods such as free-radical, ionic, and charge-transfer initiation.[1–3] Each of these methods is based on a different set of reaction conditions and solvents; nevertheless, in all cases, the addition of an initiator is necessary for polymerization. Free-radical polymerization is one of the most important ways of producing commercial polymers.[4] The major advantages of radical polymerization lie in the relative ease with which the monomer undergoes polymerization in comparison with ionic polymerization, in which impurities and moisture restrict polymerization reactions.[5] Yet another advantage of this process is that it can be applied to a broad range of monomers. The drawback of this process[6] is the use of toxic peroxides (as initiators) and chlorinated solvents and the high energy requirements for initiating the reaction (temperatures $> 60^{\circ}C$). In the case of industrial polymerization processes, the decomposition of peroxide can cause thermal runaway if proper controls are not applied.[7] Hence, there is a need for a relatively safe and nontoxic free-radical initiator. Attempts have been made in the past to use either nontoxic catalysts/initiators such as enzymes[8] or nontoxic solvents such as supercritical fluids[9,10] in free-radical polymerization. To the best of our knowledge, there is no information yet on replacing both toxic solvents and initiators.

In this study, an attempt was made to use a relatively nontoxic solvent based on the choline cation, choline formate (CF), which can act as an initiator and a solvent to initiate action on vinyl and methacrylate monomers.

Ionic liquids are organic salts that are liquid at room temperature; they display no measurable vapor pressure in general and thus eliminate the possibility of gaseous emissions.[11,12] This vapor-pressure advantage renders ionic liquids greener and environmentally more friendly than organic solvents. The availability of halogen-free, metal-free, and organic-solvent-free synthetic routes to ionic liquids further enhances their green status.[13,14] In addition, their nonflammability makes them safer in practice. The major advantage of ionic liquids is their ability to appreciably dissolve a wide range of organic and ionic compounds. Their polarity, lack of volatility, and high thermal stability are important features. The use of ionic liquids as solvents has recently been reported for free-radical polymerization,[15,16] transition-metal-mediated living free-radical polymerization,[17] cationic polymerization,[18] and charge-transfer polymerization.[19,20] In an earlier communication,[21] we demonstrated that ionic gels were obtained with CF. There was no reference to the polymerization of vinyl and methacrylate monomers in CF acting as an initiator and a solvent.

The main objective here was to replace the traditional solvents with a choline-based ionic liquid and investigate the potential of CF as an initiator for the

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polymerization of styrene, methyl methacrylate (MMA), and 2-hydroxyethyl methacrylate (HEMA). The ionic liquid method provides an alternate route for producing polymers and offers an easy method for recycling the ionic liquid employed in the process. Other objectives were the optimization of the reaction parameters and the investigation of the mechanistic aspects of polymerization.

EXPERIMENTAL

Materials

Analytical-grade MMA (Merck, Germany), HEMA (Sigma, Australia), styrene (Sigma), choline hydroxide (20% aqueous solution), and formic acid (Sigma) were used. The synthesis of the CF ionic liquid and the purification of the monomers followed known procedures.[21,22] CF was characterized by electrospray mass spectroscopy, and the expected cation and anion were observed (cone ± 35 V).

m/z [relative intensity (%)]: ES^+, 103.7 ($Me_3NCH_2CH_2OH$, 100); ES^-, 44.8 (formate, 100).

Procedure

Polymerization was carried out by the addition of the appropriate quantities of the ionic liquid and the monomer at the desired temperature. Typically, 0.25 g (1.67 mmol) of CF was dissolved in 0.25 g (1.92 mmol) of HEMA, and the reaction mixture was kept at the desired temperature (including room temperature). After the desired reaction time, the polymer was quenched with an excess of methanol. The ionic liquid was soluble in methanol, and the polymer was precipitated. The ionic liquid was recovered separately by the evaporation of methanol under reduced pressure. The polymer was then washed many times with fresh methanol and dried in a vacuum oven at room temperature. The yield was calculated gravimetrically. The polymers were characterized for their thermal properties.

Measurements

Electron paramagnetic resonance (EPR) measurements were carried out at the ambient temperature (25°C) with a Bruker EMX X-band EPR spectrometer: Silberstreifen, Germany. The EPR spectra of various samples containing 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) in an aqueous medium were measured with a quartz flat cell. The operating conditions were as follows: a microwave frequency of 9.683 GHz, a modulation frequency of 100 kHz, a modulation amplitude of 3 G, a microwave power of 3 mW, and a receiver gain of 7.1×10^3. A standard DMPO solution was prepared by the addition of 210 mg to 7 mL of distilled water. This solution was filtered through activated charcoal. The colorless, purified DMPO solution thus obtained was used for further measurements. $FeSO_4$ and hydrogen peroxide (H_2O_2) solutions were prepared with concentrations of 1 and 10 m*M*, respectively. Blank EPR spectra were recorded for pure DMPO, DMPO and $FeSO_4$, and DMPO and H_2O_2. To test for the presence of OH radicals, 350 μL of DMPO (200 m*M*), 30 μL of $FeSO_4$ (1 m*M*), and 20 μL of H_2O_2 (10 m*M*) were mixed in a small vial and transferred to a flat cell. A strong four-line EPR spectrum was obtained and indicated the presence of an adduct of DMPO and the OH radical.

The molecular weights and their distributions were determined with gel permeation chromatography at room temperature. The setup consisted of a Waters, USA pump equipped with a PLgel mixed column (7.5 mm × 600 mm, particle size = 10 μm, porosity = 50–106 Å), which was calibrated with different polystyrene standards, and a differential refractometer detector with tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min.

Thermal stability was determined by thermogravimetric analysis. Polymer samples (4–10 mg) were analyzed at a heating rate of 10°C/min under a nitrogen purge at a flow rate of 50 mL/min.

The glass-transition temperature (T_g) was determined with a TA, USA Instruments differential scanning calorimeter. For this, the sample (5–10 mg) was placed in a differential scanning calorimetry pan. The instrument was calibrated with indium. The carrier gas was helium, and a flow rate of 40 mL/min was maintained during the analysis.

RESULTS AND DISCUSSION

Homopolymerization of HEMA

Effect of temperature

The polymerization of HEMA (with different HEMA/CF weight ratios) was carried out at 40 or 60°C; in the reaction mixtures, the weight of CF was kept constant, and the weight of HEMA was varied. The results are presented in Figures 1 and 2, respectively.

Figure 1 shows that the polymerization depended on the HEMA/CF weight ratio and was comparatively rapid with the 1 : 1 ratio versus the 5 : 1 ratio, with which there was no polymerization after 150 h. Therefore, CF was acting as an initiator in the polymerization of HEMA, and a minimum concentration was necessary. The effect of the complete conversion of the monomer in short intervals of time depended on the concentration of CF used in the reaction. The reaction was carried at 60°C, and the polymerization time decreased with the temperature for the complete conversion of the gels. The results are shown in Figure 2.

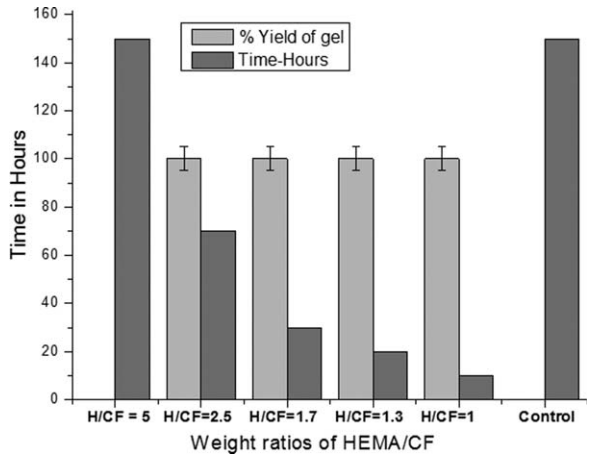


Figure 1 Effect of the HEMA/CF weight ratios on the gel conversion at 40°C

Effect of water on polymerization

The ratio of HEMA to CF was maintained at 1 : 1 (on a weight basis), and the water in the reaction mixture was raised from 9 to 35%. The results revealed that water did not inhibit the polymerization, although the gel yield (%) decreased with an increase in the water content (Table I). The gel yield dropped to 44% when the water concentration in the reaction mixture was 35%.

Effect of pH

Phosphoric acid (0.1*M*), alkali (0.1*M*), and a buffer (pH 7.4) were added in separate experiments with a 1 : 1 weight ratio of HEMA to CF. The results indicated that hydrogels were obtained with a reaction time of approximately 6 h. This showed that the polymerization of HEMA in CF took place regardless of the pH of the medium; also, the porosity of these gels visually differed. This suggested that the gels could be produced under physiological conditions for *in vivo* drug release (work in this direction is in progress).

Effect of CF on the other monomers

CF (as an initiator and solvent) was tried in the polymerization of styrene and MMA. Both monomers did undergo slow polymerization at room temperature, although the effect was greater with the MMA system (Table II). Polymerization was also carried out with sodium acetate (NaAc) as an initiator and CF as a solvent (entries 1a and 2a) and with CF as an initiator mixed with NaAc (entry 1c) in a trihexyl tetradecylphosphonium ionic liquid. The yields were not significant. However, the yields improved with the addition of NaAc and the crosslinker triethylene glycol diacrylate (TEGDA) along with CF (entries 1d and 2c).

Effect of CF on copolymerization

Copolymerization of MMA and HEMA

The effects of CF on the comonomers of HEMA Styrene and MMA and the copolymer systems involving these monomers were studied. For the copolymerization of HEMA and MMA, the individual monomers at different concentrations (10–100%) were mixed with CF, and the polymerization was carried out at 60°C for 20 h. After the desired reaction time, the reaction mixture was quenched in methanol to remove CF, and the respective copolymers were dried for further characterization. The results showed that the copolymer yield remained almost constant with individual monomer concentrations up to 50% in the feed and then increased with an increase in the HEMA concentration in the feed (Table III). This explained the affinity of CF toward HEMA in the reaction mixture.

Copolymerization of styrene and MMA with CF as the initiator

Another set of copolymerization systems involving styrene and MMA was tested with CF (as an initiator and solvent) at 60°C, and the reaction was terminated at 20 h through the quenching of the mixture in methanol. The concentrations of the comonomers in the feed along with the yields are listed in Table III. Here, unlike the case of the HEMA–MMA system, the copolymer yields were very low and decreased with an increase in the styrene concentration. This showed that the polymerization was inhibited with the addition of styrene to the copolymer system. CF was more active in MMA polymerization than styrene polymerization in accordance with the homopolymer systems.

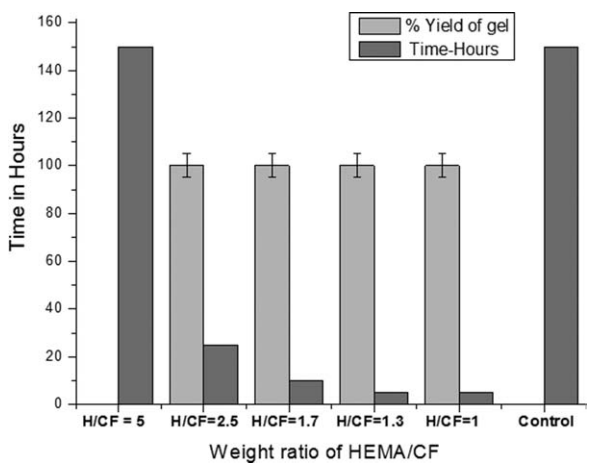


Figure 2 Effect of the HEMA/CF weight ratios on the gel conversion at 60°C.

TABLE I
Effect of Water on the Polymerization of HEMA

Sample	Water (g)	Water in the mixture (%)	CF in the mixture (%)	Water with respect to HEMA (%)	Gel yield (%)
1	0.05	9.09	45.5	20	100
2	0.10	16.6	41.6	40	96
3	0.15	23.1	38.5	60	80
4	0.20	28.2	35.2	80	73
5	0.28	35.5	32.2	110	44

Characterization of the polymers

Molecular weights of the polymers

The polymer samples of MMA and styrene synthesized in CF were characterized by gel permeation chromatography. The results are presented in Table IV. High-molecular-weight polymers were obtained with CF (entry 3) in the absence of an initiator and a crosslinker, whereas with the addition of NaAc (entry 4), the molecular weight decreased; with the further addition of a crosslinker (entry 2), the molecular weights were reduced. This could be due to a chain termination mechanism (due to transfer of the initiator) in the process, which would lead to low molecular weights. Interestingly, the molecular weight distribution for poly(2-hydroxyethyl methacrylate) could not be determined because of its poor solubility in most solvents and especially tetrahydrofuran. This could be due to the high molecular weight of the polymer. The formation of high molecular weights in this system indicated that the polymerization could be initiated by the free-radical mechanism.

Thermal studies of the copolymers: T_g

The interaction between two monomeric components of a random copolymer affects T_g as though the copolymer is a mixture of individual homopolymers. The T_g values of such copolymers depend on the homopolymers and on the ratio of the two monomeric components:

$$1/T_g(\mathrm{AB}) = W_A/T_g(\mathrm{A}) + W_B/T_g(\mathrm{B})$$

where T_g(A), T_g(B), and T_g(AB) represent the glass-transition temperatures of homopolymers A and B and copolymer AB, respectively, and W_A and W_B are the weight fractions of the respective monomer components in the copolymer.

Copolymers with different HEMA–MMA compositions were characterized for T_g by differential scanning calorimetry to determine the effects of the comonomers. The results are shown in Table III. The T_g values of poly(2-hydroxyethyl methacrylate) and poly(methyl methacrylate) were observed to be 85 and 131°C, respectively, whereas the T_g values of the corresponding copolymers of HEMA and MMA were between those of the respective homopolymers; this points to the formation of copolymers. In a similar manner, the T_g values of copolymers of styrene and MMA were also determined, and they are listed in Table III. The values of the respective copolymers were between those of the corresponding homopolymers and thus emphasized the formation of copolymers.

Thermal stability of the HEMA–MMA copolymers

The thermal stability of copolymers of HEMA and MMA with different feed compositions was determined with thermogravimetric analysis, and the results for copolymers with low, high, and intermediate levels of MMA are shown in Figure 3. The copolymers were generally stable up to 250°C (with a maximum weight loss of ca. 10%), and this was followed by rapid decomposition beyond 325°C.

TABLE II
Polymerization of MMA and Styrene

Sample	Monomer (g)	Initiator (g)	Solvent (g)	Time	Yield (%)
1	MMA (0.2)	CF (0.5)	—	5 days	80
1a	MMA (0.2)	NaAc (0.02)	CF (0.5)	3 days	67
1c	MMA (0.2)	NaAc + CF (0.02 + 0.02)	P66614 TFSA (0.5)	3 days	20
1d	MMA (0.2)	NaAc (0.03) TEGDA (0.01)	CF (0.7)	20 h	99
1e	MMA (0.2)	NaAc (0.03)	$[P_{6,6,6,14}]$ $[NTf_2]$ (0.5)	3 days	—
2	Styrene (0.2)	CF (0.5)	—	3 days	23
2a	Styrene (0.2)	NaAc (0.02)	CF (0.5)	3 days	35
2b	Styrene (0.2)	CF (0.02)	$[P_{6,6,6,14}]$ $[NTf_2]$ (0.5)	3 days	<3
2c	Styrene (0.2)	NaAc (0.03) TEGDA (0.01)	CF (0.5)	3 days	99

TABLE III
HEMA–MMA and Styrene–MMA Copolymerization in CF

Sample	HEMA (g)	MMA (g)	Yield (%)	T_g (°C)	Styrene (g)	MMA (g)	Yield (%)	T_g (°C)
1	—	0.25	46	131	—	0.25	17	131
2	0.025	0.225	51	132	0.025	0.225	20	122
3	0.05	0.20	62	114	0.05	0.20	14	117
4	0.10	0.15	53	121	0.10	0.15	12	107
5	0.125	0.125	61	124	0.125	0.125	10	112
6	0.15	0.10	98	80	0.15	0.10	7	108
7	0.225	0.025	99	85	0.225	0.025	4	109
8	0.25	—	90	87	0.25	—	5	110

However, the thermal stability increased with an increase in the MMA content in the copolymer.

EPR studies of CF-initiated polymerization

The CF-initiated polymerization of HEMA, styrene, and MMA produced high-molecular-weight polymers characteristic of a free-radical-initiated process. To understand the mechanism of CF-initiated polymerization, we used the EPR technique to determine whether free radicals were produced in the process. Experiments were designed, and EPR measurements were carried out for the pure ionic liquid, pure HEMA, and an equal-volume mixture (25 μL) of the ionic liquid (CF) and HEMA. In all these experiments, a 350-μL DMPO solution (200 m*M*) was added, and the components were mixed in a vial and transferred to a flat cell. EPR spectra were recorded at room temperature after 0, 8, 12, 16, 20, and 24 h of mixing. No EPR signal was observed for pure CF, HEMA, and their mixture at 0 h. EPR signals were observed with an increase in the intensity after 8 and 12 h of mixing and remained stable thereafter. Results showing the control and reaction after 8 h are shown in Figure 4(a,b).

The EPR spectrum of a standard 1 m*M* solution of 4-hydroxyl-2,2,6,6-tetramethylpiperidine-*N*-oxyl was recorded under conditions identical to those for the DMPO solutions. The concentration of hydroxyl-trapped DMPO was found to be of the order of 10^{-6} *M* by comparison with that of the standard.

Mechanistic studies

The dissociation of the formate anion is a complex process, and there have been a number of studies involving aqueous formate. For instance, flash photolysis in aqueous formate at 200 nm resulted in the breaking of the C—H bond and photodetachment.[23] Photodissociation of aqueous formate resulted in the formation of the formyl radical, HCO (aqueous), and O^- (aqueous).[24] Recently, the primary photodynamics of aqueous formate anions, studied with femtosecond transient absorption spectroscopy, revealed the formation of O^- (aqueous),[25] and this formation implied the production of geminate radical HCO, which is quite unstable in aqueous media. However, gas-phase HCO has been reported to absorb below 250 nm. From these literature studies, we believe that in CF, the formate anion undergoes photodissociation to produce a transient formyl radical along with O^-. These low-intensity formyl radicals were trapped and detected by EPR spectroscopy. The signals from EPR [Fig. 4(b)] confirmed the presence of radicals, and with increases in the time and temperature, the intensity of the radicals increased (the initiation and the proposed mechanism for CF-initiated polymerization are presented in Scheme 1). Therefore, CF-initiated polymerization involves a free-radical mechanism.

TABLE IV
Characterization of the Polymers: Molecular Weights

Sample	Monomer (g)	Initiator (g)	Weight-average molecular weight × 10^{-5}	Number-average molecular weight × 10^{-5}	Polydispersity index
1	MMA (0.2)	NaAc (0.02)	12.4	7.9	1.57
2	MMA (0.2)	NaAc (0.02) + TEGDA (0.01)	8.6	5.4	1.58
3	Styrene (0.2)	—	14.9	9.8	1.52
4	Styrene (0.2)	NaAc (0.02)	10.8	5.5	1.95

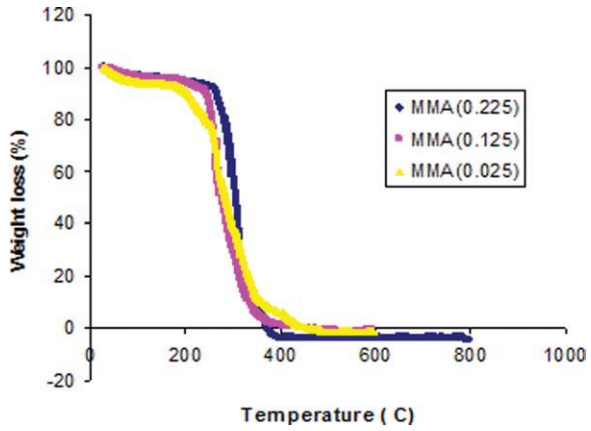


Figure 3 Thermogravimetric analysis curves of the HEMA–MMA copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

CF ionic liquids can initiate homopolymerizations and copolymerizations of HEMA, MMA, and styrene monomers. EPR studies have revealed the formation of free radicals initiating polymerization at room temperature and leading to high-molecular-weight polymers. This process eliminates the need for toxic solvents and peroxide initiators; this is important for manufacturing polymers for bio-implant applications.

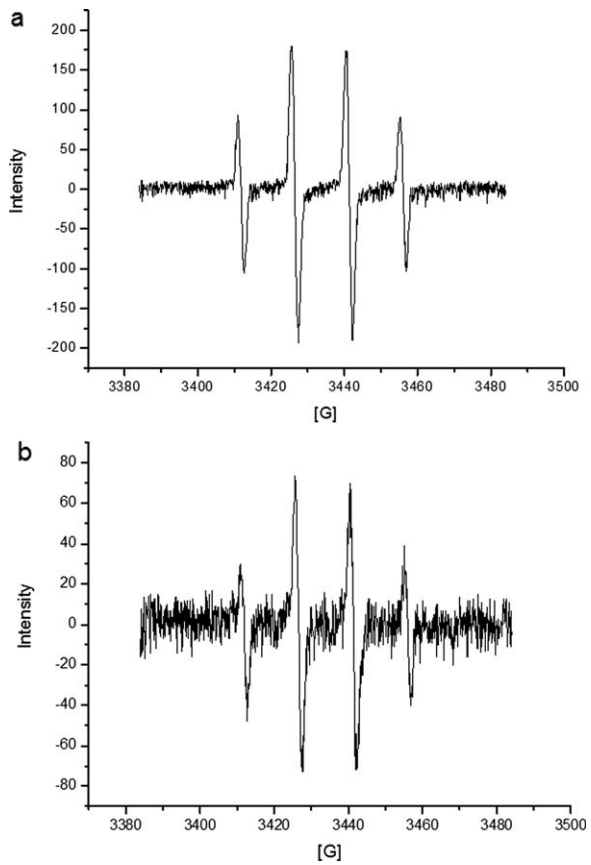
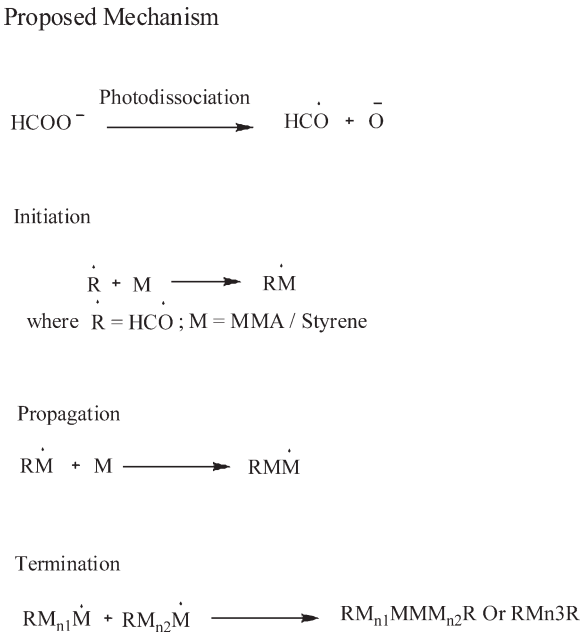


Figure 4 EPR spectra of (a) the control (DMPO, H_2O_2, and $FeSO_4$) and (b) HEMA and CF after 8 h at room temperature.



Scheme 1

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