

Rapid Communication

DESIGN AND SYNTHESIS OF NOVEL CHIRAL IONIC LIQUIDS AND THEIR
APPLICATION IN FREE RADICAL POLYMERIZATION OF METHYL
METHACRYLATE*

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Abstract Two new chiral ionic liquids, 1-((-)-menthoxycarbonylmethylene)-3-methylimidazolium hexafluorophosphate and 1-((-)-menthoxycarbonylmethylene)-3-hexadecylimidazolium hexafluorophosphate, were designed and prepared. Their chemical structures were characterized by $^1\text{H-NMR}$. Reverse atom transfer radical polymerization of methyl methacrylate (MMA) in these two ionic liquids was carried out using AIBN/ $\text{CuCl}_2/\text{bipy}$ as the initiating system. The resultant well-defined polymethyl methacrylate (PMMA) was employed as a macroinitiator to induce the atom transfer radical polymerization of menthyl methacrylate (MnMA) in chlorobenzene, which yielded a PMMA-*b*-PMnMA diblock copolymer with narrow polydispersity.

Keywords Chiral ionic liquids, Reverse ATRP, Free radical polymerization, Methyl methacrylate, Menthyl methacrylate

INTRODUCTION

It has been common practice to use ambient temperature ionic liquids (ILs) as green solvents of chemical reactions, since they are non-volatile, non-flammable and recyclable^[1, 2]. Chiral ILs, which contain asymmetric atoms in molecules, are thought to be able to play important roles in asymmetric synthesis and chiral separation techniques. Howarth and coworkers first reported the use of ILs containing chiral imidazolium cations in Diels-Alder reactions^[3]. Seddon *et al.* studied the same type reaction in IL with chiral anions^[4]. Wasserscheid described a synthetic route to prepare chiral ILs from a “chiral pool”^[5]. A novel imidazolium-based IL with planar chirality was reported by Saigo and coworkers^[6]. Chiral ionic liquid crystals have also been investigated^[7, 8].

In the past several years, room temperature ILs have been introduced successfully as polymerization solvents. Examples of these include coordination polymerization of olefins via Ziegler-Natta catalyst^[9–11], oxidative dehydropolycondensation of benzene to polyphenylene^[12, 13], enzymatic synthesis of polyesters^[14], free radical polymerizations and copolymerization of vinyl monomers^[15–26]. We have demonstrated, in a recent publication, that the initiating system of AIBN/ $\text{CuCl}_2/\text{bipy}$ can promote the reverse ATRP of MMA in a well-controlled manner if 1-butyl-3-methylimidazolium hexafluorophosphate is used as solvent^[27]. However, until now there has been no report on the application of chiral ILs in polymerization.

The goal of our current work is to design and synthesize novel chiral ionic liquids based on 1,3-disubstituted imidazolium salt, and to investigate the possibility of using them as auxiliary solvents in stereospecific free radical polymerization of vinyl monomers. We report here the preparation and physical properties of 1-((-)-

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menthoxycarbonylmethylene)-3-methylimidazolium and 1-((-)-menthoxycarbonylmethylene)-3-hexadecylimidazolium hexafluorophosphates. In addition, their application in reverse ATRP of MMA with AIBN/CuCl₂/bipy as the initiating system is also presented.

EXPERIMENTAL

Solvents and Reagents

1-Methylimidazole (99%, Acros), 1-hexadecyl bromide (99%, Beijing Chemical Co., AR), hexafluorophosphoric acid (60 wt% solution in water, Acros), L-(-)-Menthol (99%, Acros) and 2,2'-bipyridine (bipy, Beijing Chemical Co., AR) were used as purchased. Chloroacetyl chloride (Beijing Chemical Co., AR) and pyridine (Beijing Chemical Co., AR) were distilled under reduced pressure. Methyl methacrylate (Beijing Chemical Co., AR) was purified first by silica gel column to remove inhibitor, followed by vacuum distillation from CaH₂. Menthyl methacrylate (MnMA) was prepared from methacryloyl chloride (97%, Acros) and L-(-)-menthol in dry THF with pyridine as catalyst and purified by silica gel column with petroleum ether as an eluent^[28]. Boiling point: 98–99°C/2 mmHg; Optical rotation: $[\alpha]_{589}^{20} = -100.2^\circ$ (THF, $c = 2.0$ g/dL); ¹H-NMR (chloroform-*d*, δ): 6.1 and 5.5 (2 s, 2H, CH₂=); 4.7 (m, 1H, CH–O); 2.1–0.7 (m, 21H, α -methyl and residual protons of menthyl moiety). 2,2'-Azobisisobutyronitrile (AIBN, Wuhan Chemical Co., AR) was recrystallized from ethanol and dried over vacuum. Tetrahydrofuran (THF) and chlorobenzene (all from Beijing Chemical Co., AR) were distilled over CaH₂. CuCl (Beijing Chemical Co., AR) was purified by drying in vacuum after washing with acetic acid and methanol. CuCl₂ (99%, Beijing Chemical Co.) was dried in an oven at 80°C before use. Other solvents and reagents were used without further purification except as noted.

Characterization

The number-averaged molecular weights and molecular weight distributions of PMMA and PMMA-*b*-PMnMA were measured on a Waters 2410 GPC instrument with a set of HT2+HT3+HT4 μ -Styragel columns using THF as eluent (1.0 mL/min) at 35°C. Calibration was made with a series of standard polystyrenes. The ¹H-NMR spectrum was taken at 25°C on a Varian Mercury Plus 200 NMR spectrometer using dimethyl sulfoxide-*d*₆ or chloroform-*d* as solvent and tetramethylsilane (TMS) as an internal reference. Optical rotation was measured at 589 nm wavelength at 20°C using a 1 dm quartz cell with PE polarimeter MODEL-341. The melting point was observed on a Leitz Laborlux 12 polarized microscope with a Leitz 350 hot stage.

Synthesis

1-Hexadecylimidazole

To a solution of imidazole (6.8 g, 0.1 mol) in ethyl acetate (150 mL) maintained at 60°C, 1-hexadecyl bromide (15.2 g, 0.05 mol) was added slowly with rapidly stirring. The reaction was allowed to continued at 60°C for three days. The reaction mixture was cooled to room temperature and separated by filtration. The filtrate was washed with water to remove unreacted imidazole and was dried in vacuum at 60°C after evaporation of ethyl acetate for 24 h. The product was a pale-yellow solid. Yield: 8.45 g, 57.9%; Melting point: 46–47°C.

L-(-)-Menthyl chloroacetate

In a dry flask, 31.2 g (0.20 mol) of L-(-)-menthol and 31.0 mL of Et₃N were resolved in 250 mL of THF and cooled in an ice-water bath. Then, 17.5 mL (0.22 mol) of chloroacetyl chloride was added dropwise. The reaction mixture was stirred overnight at room temperature. After filtration, the filtrate was evaporated at 60°C and yellow oil was obtained. The crude product was further purified on a silica gel column with petroleum as the eluent and 37.2 g of white crystals was obtained. Yield: 80.0%; Melting point: 38–39°C; Optical rotation: $[\alpha]_{589}^{20} = -42.5^\circ$ (THF, $c = 2.0$ g/dL).

1-((-)-Menthoxycarbonylmethylene)-3-methylimidazolium hexafluorophosphate (I-1)

1-Methylimidazole (16.4 mL, 0.2 mol) and menthyl chloroacetate (46.5 g, 0.2 mol) were dissolved in 250 mL acetonitrile and the reaction vessel was placed a preheated oil bath at 70°C for 48 h. After evaporation of the solvent, a pale-yellow solid was obtained. The solid was dissolved in de-ionized (DI) water cooled in an ice-

water bath, the hexafluorophosphoric acid (40 mL, 0.22 mol) was added dropwise and white solids were formed. Saturated aqueous sodium carbonate solution was added to neutralize the acid produced in the reaction. The product (83.6 g) was obtained after filtration and drying in vacuum at 70 °C. Yield: 91.1%; melting point: 99–101 °C; Optical rotation: $[\alpha]_{589}^{20} = -44.3^\circ$ (THF, $c = 2.0$ g/dL).

1-((-)-Menthoxycarbonylmethylene)-3-hexadecylimidazolium hexafluorophosphate (I-2)

The compound I-2 was obtained by the same method as I-1. Yield: 86.3%; melting point: 69–71 °C; Optical rotation: $[\alpha]_{589}^{20} = -31.0^\circ$ (THF, $c = 2.0$ g/dL).

Polymerization

A dry glass tube was charged with 0.500 g (5.0 mmol) of MMA, 0.016 g (0.11 mmol) of CuCl_2 , 0.035 g (0.23 mmol) of bipyridine, 0.008 g (0.049 mmol) of AIBN and 0.170 g of chiral ionic liquids. The mixture was degassed by three freeze-pump-thaw cycles and sealed in vacuum. The tube was placed in a water bath at the desired temperature maintained by a thermostat. After an predetermined time, the tube was placed in an ice-water bath to stop the reaction. The reaction mixture was diluted with THF and added dropwise to a large amount of methanol. After filtration and washing three times by methanol, followed by drying under infrared light for 24 h, PMMA was obtained. The conversion of monomer was determined gravimetrically.

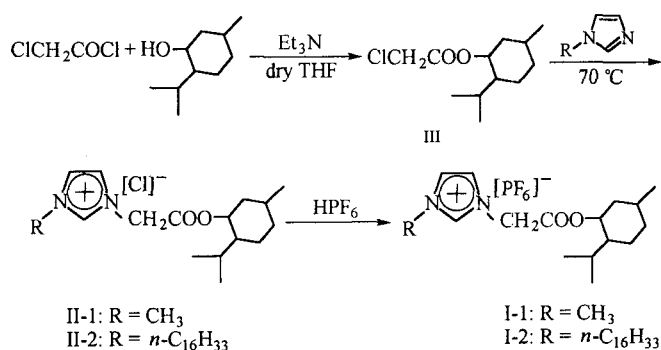
Block Copolymerization

The block copolymerization was performed with a conventional ATRP technique at 80 °C. To a polymerization tube, 0.056 g (9.66×10^{-3} mmol) of PMMA macroinitiator, 0.526 g (2.35 mmol) of MnMA, 0.006 g (6.06×10^{-2} mmol) of CuCl , 0.032 g (0.20 mmol) of bipyridine, 1.052 g of chlorobenzene was added. After three freeze-pump-thaw cycles, the tube was sealed in vacuum and placed in a water bath at 80 °C for 8 h. The block PMMA-*b*-PMnMA was obtained after precipitation in methanol, filtration, washing, and drying under infrared light for 24 h.

RESULTS AND DISCUSSION

Synthesis and Characterization

The two ILs were prepared by the synthetic route as shown in Scheme 1. Esterification of chloroacetyl chloride with *L*-(-)-menthol produced optically active menthyl chloroacetate (III). 1-Methylimidazole was used as received. 1-Hexadecylimidazole was prepared according to the literature method^[29]. Compound (III) reacted with 1-alkylimidazole to yield the salts II-1 and II-2, respectively. The target ILs were prepared by reaction of the appropriate chloride salt with HPF_6 in aqueous solution.



Scheme 1 Synthetic route of chiral ILs

Figure 1 showed the ^1H -NMR spectra of 1-hexadecylimidazole and the compounds I-1, I-2 and III. Each resonance peak was identified accordingly as indicated in Fig. 1. The proton NMR spectra were consistent with the structures of all compounds.

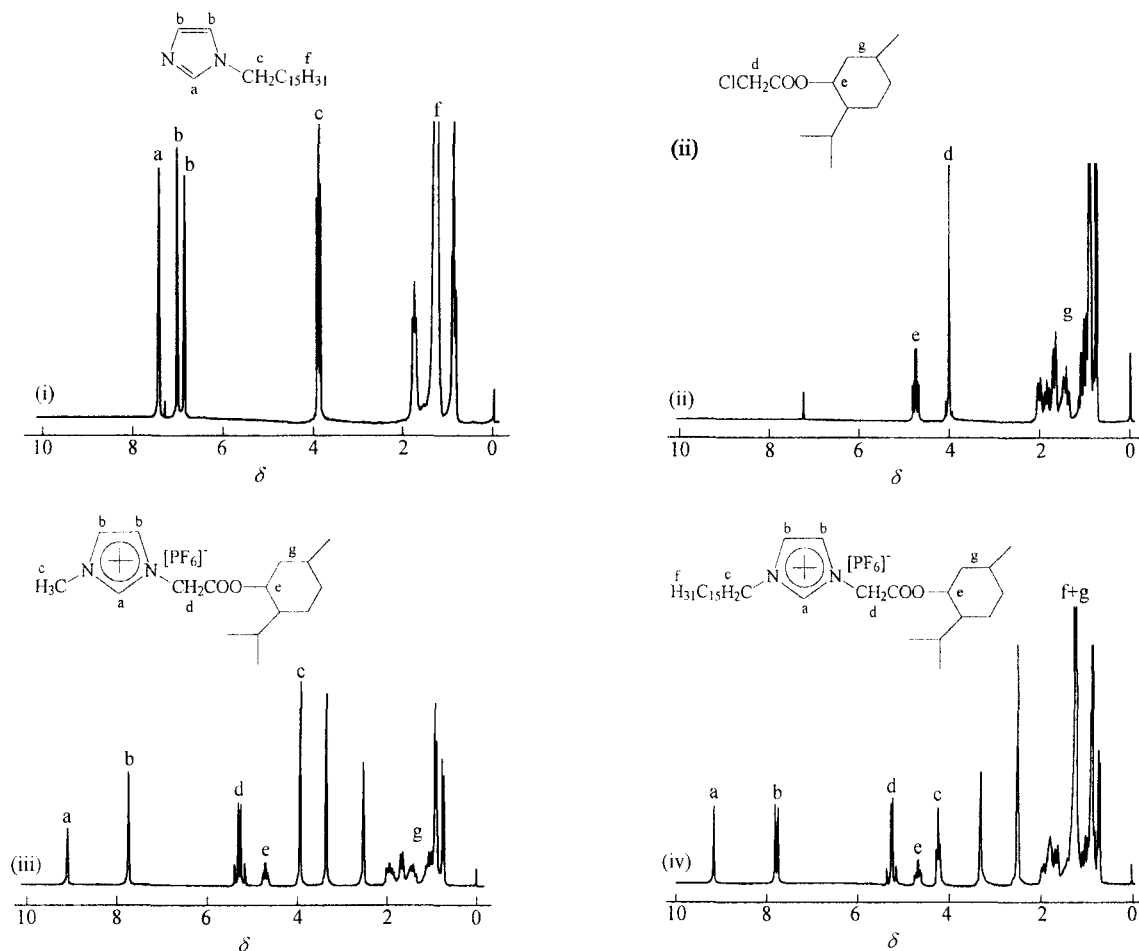


Fig. 1 The ¹H-NMR spectra of 1-hexadecylimidazole (i), menthyl chloroacetate (ii), chiral ILs I-1 (iii) and I-2 (iv). Solvents for (i) and (ii) were chloroform-*d* and for (iii) and (iv) were DMSO-*d*₆, respectively.

Reverse ATRP of MMA

Following our research into free radical polymerization of vinyl monomers in ILs, reverse ATRP of MMA was carried out in these two chiral ILs at 80°C using AIBN as an initiator and CuCl₂ complexed with bipyridine as a catalyst. The molar ratio of [MMA]:[AIBN]:[CuCl₂]:[bipy] was 100:1:2.4:10. Typically, the weight ratio of monomer to solvent was 3. The reaction time was 8 h. The results of polymerization are shown in Table 1.

Table 1. Reverse ATRP of MMA in chiral ILs

Entry	Solvent	$M_n (\times 10^{-4})$	PDI	Yield (%)
1	None	2.43	2.07	78.6
2	(a)	2.24	1.16	73.3
3	(b)	1.67	1.18	72.0

The monomer conversion was comparable for the reverse ATRP of MMA in bulk to those in ILs. However, the polydispersity of the polymer obtained in the absence of ionic liquids was 2.07, much higher than the values of M_w/M_n of PMMA obtained in ILs. This was consistent with the results in the aforementioned reverse ATRP systems carried out in 1-butyl-3-methylimidazolium hexafluorophosphate^[27] and might reflect the good solubility of catalyst complex in reaction media, which therefore promoted a well-controlled free radical polymerization of

MMA.

Block Copolymerization with MnMA

In order to prove the reverse ATRP mechanism of MMA in the above polymerization system (presence of ω -Cl atom), block copolymerization employing PMMA obtained by reverse ATRP in I-2 as the macroinitiator and MnMA as the second monomer was carried out in chlorobenzene. Figure 2 depicts both GPC curves of the macroinitiator and the PMMA-*b*-PMnMA copolymer. The monomodal nature of GPC traces of macroinitiator and copolymer suggested PMMA obtained in reverse ATRP was terminated with chlorine atom, which could induce the ATRP of MnMA under these conditions.

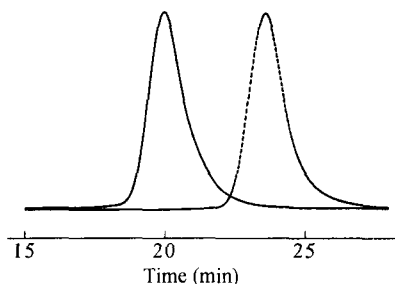


Fig. 2 Copolymerization of PMMA-*b*-PMnMA in chlorobenzene
 Reaction condition: PMMA macroinitiator, MMA = 0.500 g, CuCl₂ = 0.016 g, bipy = 0.037 g, AIBN = 0.008 g, I-2 = 1.500 g, *t* = 2 h, *T* = 80 °C;
 PMMA-*b*-PMnMA, PMMA macroinitiator = 0.056 g, MnMA = 0.526 g, CuCl = 0.006 g, bipyridine = 0.032 g, chlorobenzene = 1.052 g, *t* = 8 h, *T* = 80 °C
 ----- Macroinitiator, *M_n* = 5839; PDI = 1.14
 — PMMA-*b*-PMnMA; *M_n* = 33649; PDI = 1.22

The diblock copolymer was optically active and had an optical rotation of $[\alpha]_{589}^{20} = -89.8^\circ$, while the optical rotation of pure PMnMA (AIBN, 60 °C; *M_n* = 1.73×10^5 , PDI = 1.59) was -104.6° , again suggesting the incorporation of MnMA into the copolymer main chain.

CONCLUSIONS

We have demonstrated the preparation and characterization of two new chiral ILs, which can be employed as solvents of reverse ATRP of MMA. The resultant PMMA had narrow polydispersity ($M_w/M_n < 1.20$) and was able to initiate ATRP of MnMA under conventional conditions to yield PMMA-*b*-PMnMA diblock copolymer, indicating well-defined end group of PMMA. The asymmetric environment of chiral ionic liquids is believed to have some effects on the stereostructure of polymer. Detailed work is currently ongoing in our laboratory and will be published in the near future.

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