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ORIGINAL PAPER

Methacrylate-based ionic liquid: radical polymerization/copolymerization with methyl methacrylate and evaluation of molecular weight of the obtained homopolymers

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Abstract Azobisisobutyronitlite (AIBN)-induced free radical polymerization of a methacrylate-based ionic liquid monomer, 1-(2-methacryloxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (Met-IL) was carried out in a common organic solvent, *N*,*N*-dimethylformamide (DMF), and an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI). The molecular weight of the obtained poly(Met-IL) was evaluated by transforming it to non-ionic poly(methyl methacrylate) with hydrolysis of the imidazolium-salt-substituted pendant ester groups and methyl esterification. Radical copolymerization with methyl methacrylate (MMA) was also carried out in both DMF and EMImTFSI. Analysis of copolymer composition revealed that the reactivity of Met-IL was lower than that of MMA in both DMF and EMImTFSI solutions.

Keywords Ionic liquid · Radical polymerization · Copolymerization · Imidazolium · Poly(ionic liquid)

Introduction

Poly(ionic liquid)s, which can be prepared by polymerization of ionic liquid monomers, have recently attracted the attention of many researchers from both academic and industrial points of view, as new functional materials. Various poly(ionic liquid)s have been prepared so far by polymerization of acrylic/methacrylic esters derivatives [1–13], styrene derivatives [7, 14, 15],

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N-vinylimidazoliums [16–19], vinyl ethers [20], pyrroles [21], and epoxides [22]. Ohno and coworkers reported that polyacrylates and polymethacrylates having imidazolium salt structures showed relatively high ionic conductivity in a dry condition [1, 2, 8]. Shen et al. reported that imidazolium-substituted polystyrene and polymethacrylate derivatives exhibited high ability in absorbing CO_2 [6, 7, 14] and microwave [15]. Aoshima and coworkers reported a LCST behavior of vinyl-ether-based poly(ionic liquid)s [20]. Gnanou et al. synthesized a block copolymer of methacrylic acid and methacrylate ester having an imidazolium salt structure by reversible addition fragmentation chain transfer (RAFT) polymerization techniques and studied the micelle formations [12]. Endo et al. prepared a thermo-responsible block copolymer composed of poly(*N*-isopropylacrylamide) and poly(*N*-vinylimidazolium) also by RAFT polymerization techniques [19].

Copolymerization of ionic liquid monomers with usual non-ionic monomers is a simple and useful way to improve and tune the specific properties of poly(ionic liquid)s as well as to modify or functionalize the poly(ionic liquid)-based materials. Therefore, copolymerization should be investigated in detail under various conditions. Elabd's research group recently reported the detailed study of random copolymerization of methacrylate ester having an imidazolium salt structure with hexyl methacrylate and the ionic conductivity of the obtained copolymers [13]. However, radical copolymerization of other ionic monomers and usual vinyl monomers has not been investigated in detail. The objective of our research was to elucidate the fundamental copolymerizability of ionic liquid vinyl monomers with usual non-ionic vinyl monomers which may be necessary for further application as functional materials. Here, we report radical homopolymerization of a simple and versatile ionic liquid vinyl monomer, 1-(2-methacryloylethyl)-1-methylimidazolium bis(trifluoromethanesulfonyl)imide (Met-IL) in a common organic solution and ionic liquid solution, evaluation of molecular weight of the obtained poly(Met-IL), copolymerization of Met-IL with methyl methacrylate (MMA), and examination on the thermal properties of Met-IL homopolymers and Met-IL/MMA copolymers.

Experimental section

Materials

Methacryloyl chloride, 2-bromoethanol, triethylamine, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), 0.1 mol/L $AgNO_3$ aqueous solution, and methyl ethyl ketone (MEK) were purchased from Wako Pure Chemical Industry (Osaka, Japan). 2-Bromoethanol was purchased from Tokyo Chemical Industry (Tokyo, Japan). 1-Methylimidazole, 2,6-di-*tert*-butyl-4-methylphenol, tetramethylammonium hydroxide pentahydrate, and 2.0 M trimethyldiazomethane hexane solution were purchased from Aldrich (WI, USA). They were used as delivered. MMA was purchased from Wako Pure Chemical Industry and washed three times with 1 M NaOH aqueous solution, three times with distilled water, dried with anhydrous Na_2SO_4, and then distilled over CaH_2 before use. Dichloromethane, *N*,*N*-dimethylformamide (DMF), toluene, and diethyl ether were purchased from Wako Pure

Chemical Industry and distilled over CaH_2 before use. 2-Bromoethyl methacrylate was prepared by a reaction of methacryloyl chloride with 2-bromoethanol and triethylamine in dichloromethane and purified by vacuum distillation. Azobisisobutyronitorile (AIBN) was purchased from Wako Pure Chemical Industry and purified by recrystallization from methanol. 1-Ethyl-3-methylimidazolium bis(trifluoromethaesulfonyl)imide (EMImTFSI) was prepared according to the reported procedures [23]. Chloroform-d ($CDCl_3$) and Aetone-d_6 (CD_3COCD_3) were purchased from Cambridge Isotope Laboratories, Inc. (MA, USA).

Preparation of Met-IL

After addition of 1.27 g (15.5 mmol) of 1-methylimidazole and 20 mg of 2,6-di-*tert*-butyl-4-methylphenol to 2.96 g (15.4 mmol) of 2-bromoethyl methacrylate, the mixture was stirred for 48 h at 40 °C. The products were washed with diethyl ether and dried in vacuo to give 1-(2-methacryloylethyl)-3-methylimizadolium bromide 3.96 g (14.5 mmol) in 94% yield. The obtained 1-(2-methacryloylethyl)-3-methylimizadolium bromide (3.96 g, 14.5 mmol) was dissolved in 4 mL of distilled water, and a solution of LiTFSI (4.40 g, 15.4 mmol) in distilled water (4 mL) was added, and the mixture was stirred at 45 °C for 24 h. The mixture gradually separated into two layers, and the lower layer was collected and washed with distilled water three times. Vacuum drying of the oil gave a colorless viscous liquid of 1-(2-methacryloylethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (Met-IL) (5.28 g, 11.1 mmol) in 76.6% yield. IR (KBr) 423, 449, 483, 514, 571, 618, 653, 706, 742, 791, 815, 845, 950, 1100, 1141, 1200, 1300, 1500, 1568, 1577, 1637, 1722, 3000, 3123, and 3160 cm^{-1}. ^{1}H-NMR ($CDCl_3$) $\delta = 1.8$ (s, 3H), 4.0 (s, 3H), 4.7–4.8 (t, 2H), 4.5–4.6 (t, 2H), 5.6–6.15 (d, 4H), 7.6–7.9 (d, 2H), 9.1 (s, 1H). ^{13}C-NMR ($CDCl_3$) $\delta = 19.41$, 37.46, 49.62, 64.00, 124.0, 138.0, 148.0, and 163.0. Elemental analysis: Calcd for $C_{12}H_{15}F_6N_3O_6S_2\cdot0.5H_2O$: C, 29.75; H, 3.33; N, 8.67; S, 13.24; F, 23.53. Found: C, 29.43; H, 3.02; N, 8.80; S, 13.03; F, 24.29. The addition of the Met-IL to 0.1 mol/L $AgNO_3$ aqueous solution did not cause any precipitations, which confirmed that the obtained compound was free of bromide ion contamination.

Polymerization of Met-IL in DMF

In a schlenk tube with a three-way stopcock, 250 mg (0.53 mmol) of Met-IL and 1.6 mg of AIBN (0.010 mmol) were dissolved in DMF (0.35 mL). The mixture was degassed by three freeze–thaw cycles and the schlenk tube was filled with nitrogen. The mixture was heated at 70 °C for 2 h. After cooling to room temperature, the resulting mixture was poured into a large amount of methanol to precipitate the polymeric compounds. The precipitate was collected by filtration, washed with methanol, and dried in vacuo to give a solid poly(Met-IL) (210 mg) in 84% yield.

Polymerization of Met-IL in EMImTFSI

In a schlenk tube with a three-way stopcock, 250 mg (0.53 mmol) of Met-IL and 1.6 mg of AIBN (0.010 mmol) were dissolved in EMImTFSI (206 mg). The mixture was degassed by three freeze–thaw cycles and the schlenk tube was filled with nitrogen. The mixture was heated at 70 °C for 2 h. After cooling to room temperature, the resulting mixture was poured into a large amount of methanol to precipitate the polymeric compounds. The precipitate was collected by filtration, washed with methanol, and dried in vacuo to give a solid poly(Met-IL) (205 mg) in 82% yield.

Transformation of poly(Met-IL) to poly(MMA)

To a solution of poly(Met-IL) (92 mg, 0.19 mmol/unit) in MEK (1 mL), was added 15% aqueous tetramethylammonium hydroxide (320 mg, 0.50 mmol), and the mixture was stirred for 72 h at 70 °C. The resulting mixture was poured into 1 mol/L aqueous HCl to precipitate the polymeric products. The precipitates were recovered with filtration, and dried in vacuo. Complete hydrolysis of the ester pendant groups were confirmed by FT-IR and ^{1}H-NMR analysis of the polymer in acetone-d_6. The obtained polymer (10 mg, 0.12 mmol/unit) was then dissolved in toluene/diethyl ether (0.5/0.1 mL, v/v) and excess amount of 2.0 M trimethylsilyldiazomethane hexane (0.50 mL, 1.0 mmol) was added at room temperature, and the mixture was stirred for 2 days. The resulting mixture was then poured into water, and the products were extracted with toluene. The organic layer was concentrated, and the organic residues were dried in vacuo to give poly(MMA) (8.5 mg, 0.085 mmol/unit) in 73% yield. The obtained polymer was analyzed by FT-IR and ^{1}H-NMR in acetone-d_6 and was identified as polyMMA. The molecular weight of the polymer was evaluated by GPC using DMF (containing 50 mM LiBr) as an eluent.

Copolymerization of Met-IL and MMA in DMF

Copolymerization at various compositions of Met-IL and MMA (Table 2) was examined in DMF. A typical example of the copolymerization procedure is as follows. In a schlenk tube with a three-way stopcock, 150 mg of Met-IL (0.32 mmol), 32 mg of MMA (0.32 mmol), and 0.6 mg of AIBN (0.032 mmol) were dissolved in DMF (0.21 mL). The mixture was degassed by three freeze–thaw cycles and the schlenk tube was filled with nitrogen. The mixture was heated at 70 °C for 3 h. After cooling to room temperature, the resulting mixture was poured into a large amount of methanol to precipitate the polymeric compounds. The precipitate was collected by filtration and washed with methanol and dried in vacuo to give a solid poly(Met-IL)-*co*-polyMMA (121 mg).

Copolymerization of Met-IL and MMA in EMImTFSI

Copolymerization of various compositions of Met-IL and MMA (Table 3) was examined in EMImTFSI. A typical example of the copolymerization procedure is as follows. In a schlenk tube with a three-way stopcock, 150 mg of Met-IL (0.32 mmol), 32 mg of MMA (0.32 mmol), and 0.6 mg of AIBN (0.032 mmol) were dissolved in EMImTFSI (129 mg). The mixture was degassed by three freeze–thaw cycles and the schlenk tube was filled with nitrogen. The mixture was heated at 70 °C for 3 h. After cooling to room temperature, the resulting mixture was poured into a large amount of methanol to precipitate the polymeric compounds. The precipitate was collected by filtration, washed with methanol, and dried in vacuo to give a solid poly(Met-IL)-*co*-polyMMA (110 mg).

Characterization

Proton NMR spectra were recorded on Varian UNITY INOVA 400 in chloroform-d or acetone-d_6 with tetramethylsilane as an internal standard. IR spectra were recorded on a Perkin Elmer SPECTRUM ONE spectrometer equipped with a universal ATR Sampling Accessory. Gel permeation chromatography was performed using a Tosoh HPLC-8220 GPC system equipped with three consecutive polystyrene gel columns [TSK-gels (bead size, exclusion limited molecular weight); super-AW4000 (6 μm, 4×10^5), super-AW3000 (4 μm, 6×10^4), and super-AW2500 (4 μm, $>2 \times 10^3$)] using DMF (containing 50 mM LiBr) as an eluent. Number-averaged molecular weight (M_n) and weight-averaged molecular weight (M_w) were determined based on polystyrene standards. Differential scanning calorimetry (DSC) was carried out with a Seiko Instrument Inc. DSC-6200 using an aluminum pan under a 20 mL/min N_2 flow at the heating rate of 10 °C/min. Thermal gravimetric analysis (TGA) was performed with a Seiko Instrument Inc. TG-DTA 6200 using an alumina pan under a 50 mL/min N_2 flow at a heating rate of 10 °C/min.

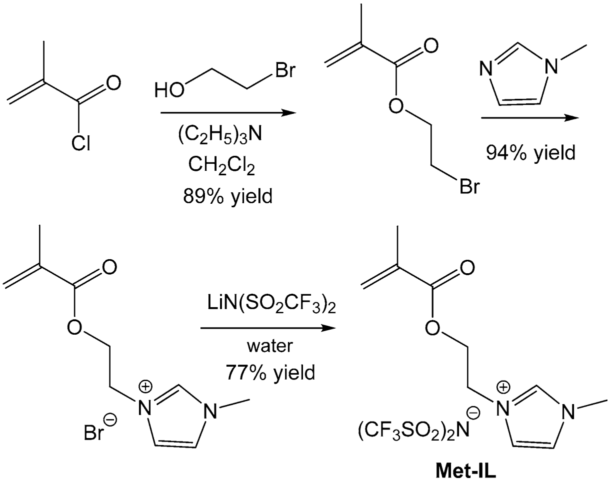
Results and discussions

Synthesis of Met-IL

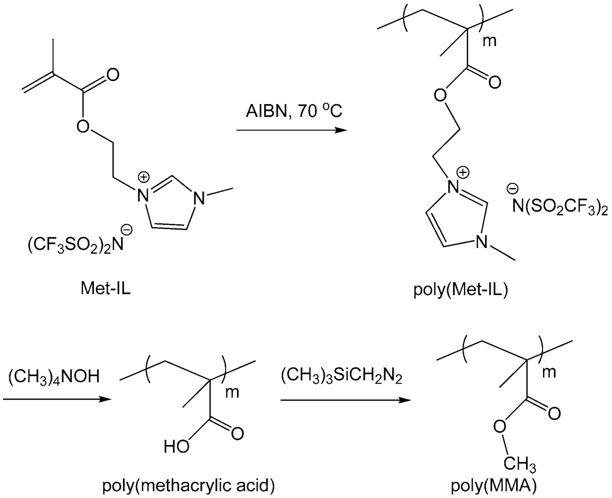
1,3-Dialkyl-substituted imidazolium bis(trifluoromethanesulfonyl)imide salts are the most popular and well-investigated among many ionic liquids. They showed high thermal stability, high ionic conductivity, and high compatibility to various organic compounds with relatively low viscosity. Therefore, we chose a methacrylate ester having a 1,3-dialkyl-substituted imidazolium TFSI salt structure in the pendant group, 1-(2-methacryloxyethyl)-3-methylimidazolium TFSI salt (Met-IL), as an ionic liquid monomer to be studied here. It could be easily synthesized via three steps starting from methacryloyl chloride and 2-bromoethanol, reaction with 1-methylimidazole, and then ion exchange with LiTFSI in good yield as shown in Scheme 1. The detailed synthetic procedures are described in "Experimental section."

Homopolymerization of Met-IL

Homopolymerization of Met-IL were examined in both common organic solvent (DMF) and ionic liquid (EMImTFSI), using AIBN as a radical initiator (Scheme 2). The time–conversion curves for the polymerizations are shown in Figs. 1 and 2. The



Scheme 1 Synthesis of Met-IL



Scheme 2 Homopolymerization of Met-IL and transformation to poly(MMA)

polymerization proceeded smoothly at 70 °C and completed within 3 h in both conditions, and no practical difference was observed between DMF and EMImTFSI as solvents. These results indicate that the imidazolium pendant group is not harmful for a radical polymerization of methacryaltes as Ohno et al. [2] or Chen et al. [13] previously reported. In addition, the results suggest that ionic liquid EMImTFSI can be used as a polar solvent for radical polymerizations. The obtained poly(Met-IL) was soluble in moderately polar organic solvent such as DMF, DMSO, acetonitrile, THF, and acetone, but insoluble in water, methanol, and diethyl ether. Figure 3 shows the ^{1}H-NMR spectrum of poly(Met-IL) obtained in the polymerization in

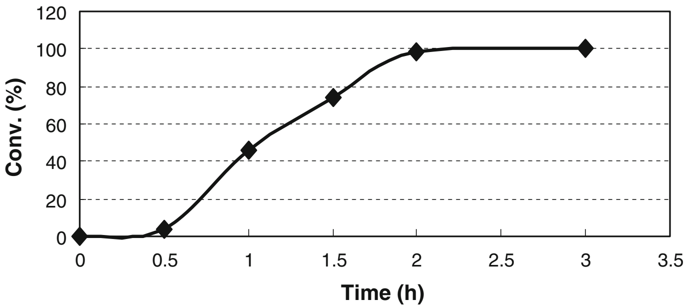


Fig. 1 The time–conversion curve for polymerization of Met-IL in DMF

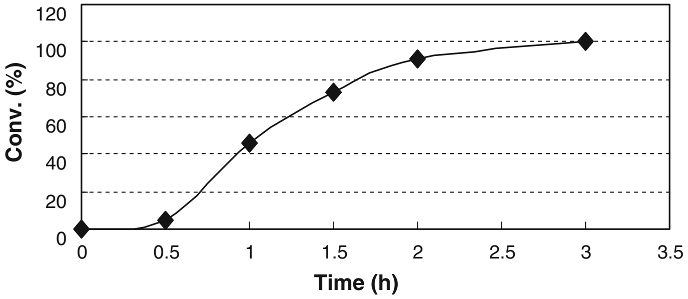


Fig. 2 The time–conversion curve for polymerization of Met-IL in EMImTFSI

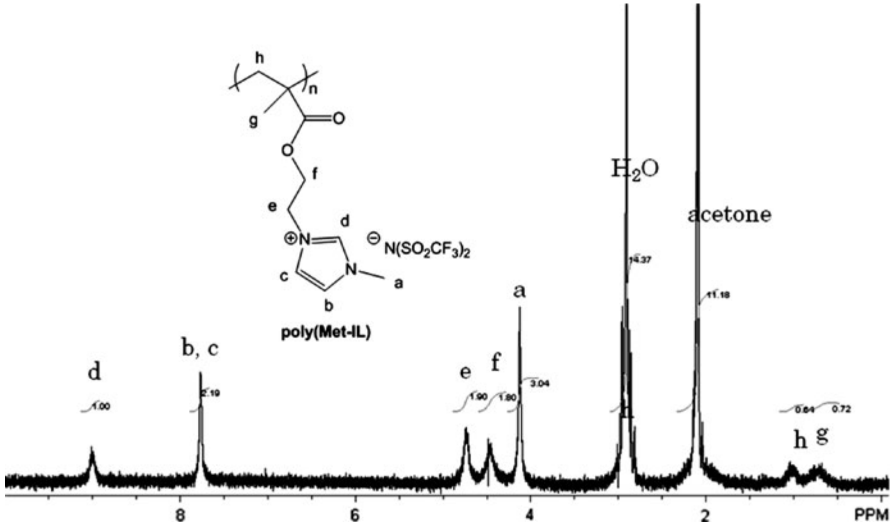


Fig. 3 ^{1}H-NMR spectrum in acetone-d6 of poly(Met-IL) prepared in DMF

DMF, from which the chemical structure of the polymer could be confirmed. The molecular weights of the poly(Met-IL) were not directly determined by GPC analysis using THF or DMF as an eluent, because the poly(Met-IL) was absorbed on the

Table 1 Thermal properties of Met-IL homopolymers prepared in different solvents

Polymerization solvent	T_{d5} (°C)	T_g (°C)
DMF	372	178
EMImTFSI	375	177

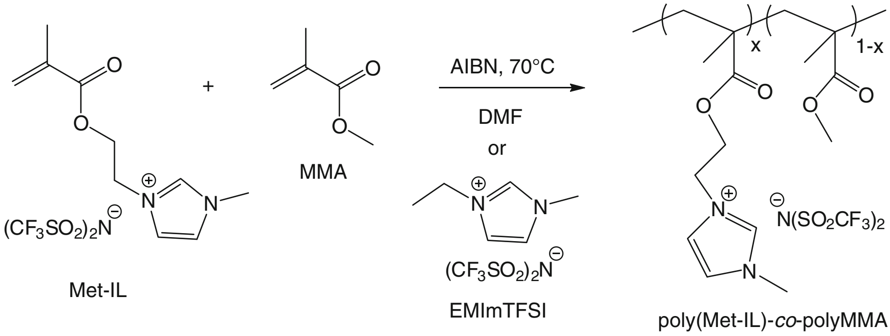
polysytrene gel in the column. Therefore, the molecular weight was evaluated after transforming the polymer to non-ionic polymer by polymer reactions (Scheme 2) and conducted to GPC measurements, as described in the next section. Glass transition temperature (T_g) and 5% weight loss temperatures (T_{d5}) of the Met-IL homopolymers prepared in DMF and EMImTFSI were summarized in Table 1. Both polymers showed high T_{d5} and T_g, indicating their high thermal stability. In addition, the thermal properties of the homopolymers were almost unchanged regardless of the solvents used for the polymerization. The ionic conductivity of the obtained poly(Met-IL) was very low ($<1.0 \times 10^{-4}$ S/m), and the homopolymer was almost insulating. This is probably because the poly(Met-IL) has high T_g and it is in a glassy state at room temperature.

Evaluation of the molecular weight of poly(Met-IL)

Hydrolysis of the imidazolium-salt-substituted pendant ester groups of the poly(Met-IL) was examined under various conditions, and we found that a quaternary ammonium hydroxide such as tetramethylammonium hydroxide was highly effective as a base for hydrolysis of the pendant groups. Heating the poly(Met-IL) with 2.6 equivalent of the aqueous tetramethylammonium hydroxide in MEK at 70 °C for 72 h gave the corresponding poly(methacrylic acid) quantitatively. Then, the polymer was esterified using trimethylsilyldiazomethane as a methylating agent to afford non-ionic poly(MMA). The whole transformation process including the polymerization of Met-IL was depicted in Scheme 2. The number-averaged molecular weight (M_n) and weight-averaged molecular weight (M_w) of the converted polyMMA determined by GPC were 14,000 and 39,000, respectively. From these values, M_n and M_w of the original poly(Met-IL) were evaluated as 67,000 and 190,000, respectively, which were sufficiently high as a poly(ionic liquid). By these experiments, we could demonstrate an efficient and practical way to evaluate the molecular weight of poly(ionic liquid)s, which are difficult to be analyzed directly.

Copolymerization of Met-IL with MMA

Copolymerization of Met-IL with MMA was examined in both DMF and EMImTFSI solutions (Scheme 3). Tables 2 and 3 summarizes the copolymer composition calculate from the monomer conversion at the initial stage of polymerization in both conditions. Figures 4 and 5 show the copolymer composition curves for them. In DMF, Met-IL contents in the copolymer composition were slightly lower than the Met-IL content in the initial monomer feed, indicating that



Scheme 3 Copolymerization of Met-IL and MMA

Table 2 Results of copolymerization of Met-IL and MMA in DMF

Entry	Feed ration of Met-IL/MMA	Conversion (%) of Met-IL	Conversion (%) of MMA	Composition (%) of Met-IL	Composition (%) of MMA
1	30/70	7	11	22	78
2	50/50	22	29	40	60
3	70/30	10	15	64	36

Table 3 Results of copolymerization of Met-IL and MMA in EMImTFSI

Entry	Feed ration of Met-IL/MMA	Conversion (%) of Met-IL	Conversion (%) of MMA	Composition (%) of Met-IL	Composition (%) of MMA
1	20/80	9	29	7.2	93
2	50/50	17	31	30	70
3	60/40	12	34	35	65

the reactivity of Met-IL is slightly lower than that of MMA in DMF. In EMImTFSI, the Met-IL content in the copolymer composition was again lower than that in the monomer feed, and it was far lower in this case. This result means that the reactivity of Met-IL was much lower than that of MMA in ionic liquid EMImTFSI. The reason for this low reactivity of the Met-IL in copolymerization has not been understood well, but we assume that the ionic repulsion between the imidazolium groups in the polymer and monomer may reduce the reactivity. Nevertheless, signals of Met-IL segment were clearly detected in addition to signals of MMA segment by ^{1}H-NMR analysis. Figure 6 shows a typical ^{1}H-NMR spectrum of the obtained Met-IL MMA copolymers. These results indicate that copolymers of Met-IL and MMA were obtained in both polymerization conditions.

Thermal properties of poly(Met-IL)$_{0.6}$-*co*-polyMMA$_{0.4}$ obtained in DMF were analyzed by TGA and DSC. T_{d5} of the copolymer was found to be 345 °C. This value was between the decomposition temperature of the Met-IL homopolymer

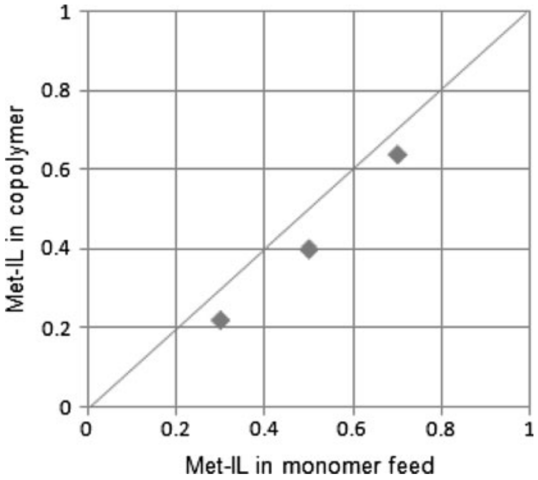


Fig. 4 Copolymer composition curve for polymerization of Met-IL and MMA in DMF

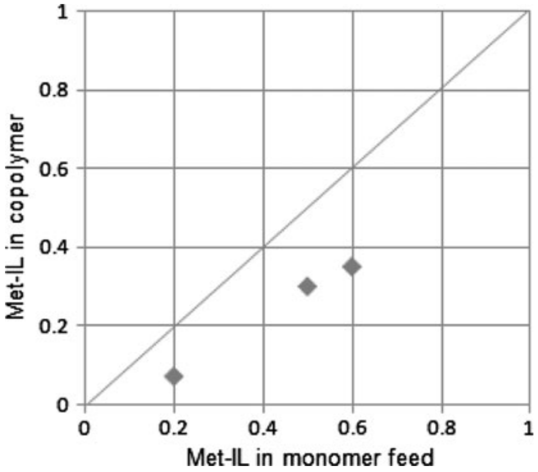


Fig. 5 Copolymer composition curve for polymerization of Met-IL and MMA in EMImTFSI

(372 °C) and that of polyMMA (around 300 °C). In addition, T_g of the copolymer was observed at 75 °C, which was far lower than the T_g of poly(Met-IL) (178 °C) and was close to T_g of MMA homopolymer (ca. 70–100 °C). These results indicate that the incorporation of thermally unstable MMA component decreased the thermal stability of Met-IL-based polymers.

At room temperature, the Met-IL/MMA copolymer showed low ionic conductivity ($<1.0 \times 10^{-4}$ S/m) as the Met-IL homopolymer, because the copolymer still has T_g higher than room temperature. This low ionic conductivity is analogous to the low values reported in copolymers composed of hexyl methacryalte and imidazolium-substitute methacrylate at temperatures lower than their T_gs [13].

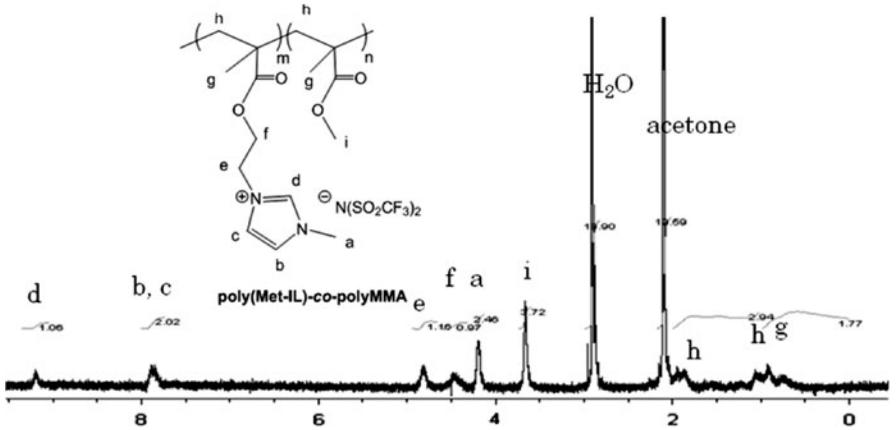


Fig. 6 ^{1}H-NMR spectrum in acetone-d_6 of poly(Met-IL)-*co*-polyMMA prepared in DMF

Conclusions

Poly(ionic liquid)s were prepared by radical polymerization of ionic liquid methacrylate (Met-IL) in both common organic solvent (DMF) and ionic liquid solvent (EMImTFSI). The obtained polymers showed high thermal stability due to the incorporation of the imidazolium salt structure. Transformation of the ionic pendant groups in the poly(Met-IL) to non-ionic groups was an effective way to get the information about the molecular weight of the methacrylate-based poly(ionic liquid)s. Radical copolymerization of the ionic liquid methacrylate (Met-IL) with MMA was also investigated in both DMF and EMImTFSI. Copolymers of Met-IL and MMA were prepared, and the reactivity of Met-IL was found to be lower than that of MMA in both DMF and EMImTFSI solutions. At this stage, we expect that the Met-IL copolymers may be applicable in hybrid material of polymer and ionic liquid, because the incorporation of imidazolium moiety may increase the affinity between polymer chain and imidazolium-based ionic liquid. Furthermore, these fundamental data are useful in the preparation of ionic networked polymers by copolymerization of the ionic liquid methacrylate with various multi-functional methacrylates as cross-linkers, which is reported separately [24, 25].

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