

Electronic Supplementary Information for:

Imidazolium-based polymeric ionic liquids with diverse carboxylates: precision synthesis and LCST- and UCST-type thermoresponsivity in water

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Experimental Section

Materials. 2-Chloroethyl vinyl ether (CEVE; TCI, >97.0%) was washed with 10 wt% aqueous sodium hydroxide solution for three times and then with water for several times, dried over sodium sulfate overnight, and distilled twice from calcium hydride under reduced pressure. 1-Isobutoxyethyl acetate (IBEA) was synthesized from isobutyl vinyl ether (TCI, >99.0%) and acetic acid according to the reported procedure.^{S1} 1,4-Dioxane (Fujifilm-Wako, 99.5+%) was dried over the mixture of molecular sieves 3A and 4A overnight, distilled from calcium hydride, and distilled from lithium aluminum hydride. 2,6-Di-*tert*-butylpyridine (Sigma-Aldrich, ≥97%) and 4-methylbenzaldehyde (pMeBzA; TCI, >98%) were distilled twice from calcium hydride under reduced pressure. Toluene (Fujifilm-Wako, superdehydrated grade, water content < 0.001%) was dried by passage through solvent purification columns (Glass Contour). Et_{1.5}AlCl_{1.5} (Nippon Aluminum Alkyls, 1.0 M in toluene), SnCl₄ (Sigma-Aldrich, 1.0 M in heptane or dichloromethane), *N,N*-dimethylformamide (DMF; Nacalai Tesque, ≥99.5%), 1-methylimidazole (TCI, >99.0%), 1,2-dimethylimidazole (TCI, >98.0%), 1-butylimidazole (TCI, >98.0%), sodium iodide (Fujifilm-Wako, 99.5+%), sodium hexanoate (TCI, >99.0%), sodium heptanoate (TCI, >97.0%), sodium octanoate (TCI, >98.0%), sodium nonanoate (TCI, >98.0%), sodium laurate (TCI, >97.0%), sodium benzoate (TCI, >98.0%), sodium 2-naphthoate (TCI, >98.0%), hydrochloric acid (Nacalai Tesque, 35~37%), 1,2-dimethoxyethane (Fujifilm-Wako, 99.0+%), acetone (Nacalai Tesque, ≥99.5%), and methyl ethyl ketone (Nacalai Tesque, ≥99.0%) were used as received. Sodium 9-anthracenoate was synthesized from 9-anthracenecarboxylic acid (TCI, >97.0%) and sodium hydroxide (Nacalai Tesque, ≥97.0%) in water according to the reported procedure^{S2} (this salt was used in an aqueous solution state without isolation).

Polymerization Procedure. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki, PJ-206A; air temperature of approximately 450 °C) under a dry nitrogen atmosphere. Toluene, 1,4-dioxane, a solution of DTBP in toluene, CEVE, and a solution of IBEA in hexane/toluene were added into the tube using dry syringes. The solution was cooled at 0 °C and then a prechilled solution of Et_{1.5}AlCl_{1.5} in toluene was added into the tube. After 5 min, a prechilled solution of SnCl₄ in heptane/toluene was added to start the polymerization. After predetermined time, the polymerization was quenched by adding an excess amount of methanol containing a small amount of aqueous ammonia. The quenched reaction mixture was diluted with dichloromethane and subsequently washed with deionized water for several times. The volatiles were removed under reduced pressure at 50 °C to yield a polymer product. The polymer was dried under reduced pressure for over 6 hours at room temperature. The monomer conversion was determined by gas chromatography analysis (column packing material: GL Science, PEG-20M-Uniport HP) of the quenched reaction mixture.

Introduction of Imidazolium Moieties and Carboxylate Counteranions into the Side Groups of Poly(CEVE). The poly(CEVE) obtained above was dissolved in DMF (polymer: 5 wt%). Alkylimidazole and sodium iodide (molar ratio of the monomer units in a polymer/alkylimidazole/sodium iodide = 1/5/5) were added into the solution and heated at 80 °C. After 72 hours, deionized water was added to quench the reaction. The quenched reaction solution was sealed in a cellulose tube (As One, pore size = 1.25 nm, cut-off MW = approximately 3500) and dialyzed in deionized water for three times and then in methanol once to remove residual alkylimidazole and salts. The polymer solution in methanol was transferred into a vial. A sodium carboxylate (molar ratio of the monomer units in a polymer/sodium carboxylate = 1/5) was added into the vial and then magnetically stirred for several hours. The reaction solution was sealed in a cellulose tube and dialyzed in ultrapure water (by Merck Millipore, Direct-Q UV 3) or methanol twice and then in methanol once to remove residual salts. Solvents were removed under reduced pressure at 50 °C to yield a polymer. The polymer was dried under reduced pressure for over 6 hours at 60 °C. The introduction ratio of carboxylate counteranions was determined by ¹H NMR analysis of the polymer in DMSO-*d*₆ at 100 °C. (The ¹H NMR spectra were recorded at 100 °C to observe sharp

peaks. However, ^{13}C and 2D NMR spectra were recorded at 50 °C because measurements at high temperature for a long time may cause degradation of polymers.) Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was conducted with a Shimadzu/Kratos Axima-Performance spectrometer using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile and sodium trifluoroacetate as a matrix and a cationizing agent, respectively.

Characterization. The molecular weight distributions (MWDs) of the polymers were measured by gel permeation chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [Tosoh, TSKgel GMH_{HR}-M × 2 (exclusion limit molecular weight = 4×10^6 ; bead size = 5 μm, column size = 7.8 mm i.d. × 300 mm); flow rate = 1.0 mL/min] connected to a JASCO PU-4580 pump, a Tosoh CO-8020 column oven, a Tosoh UV-8020 ultraviolet detector, and a Tosoh RI-8020 refractive-index detector. The number-average molecular weight (M_n) and the polydispersity ratio (weight-average molecular weight/number-average molecular weight [M_w/M_n]) were calculated from the chromatographs based on 16 polystyrene standards (Tosoh; $M_n = 5.0 \times 10^2$ to 1.09×10^6 , $M_w/M_n < 1.2$). NMR spectra were recorded with a JEOL JNM-ECA 500 spectrometer (500.16 MHz for ^1H) or a JEOL JNM-ECS 400 spectrometer (100.53 MHz for ^{13}C). The transmittance of the polymer solutions was measured with a JASCO V-500 UV-vis spectrometer equipped with a Peltier-type thermostatic cell holder (ETC-505).

References.

- S1. Aoshima, S.; Higashimura, T. *Macromolecules* **1989**, *22*, 1009–1013.
- S2. Ueno, A.; Moriwaki, F.; Osa, T.; Hamada, F.; Murai, K. *J. Am. Chem. Soc.* **1988**, *110*, 4323–4328.

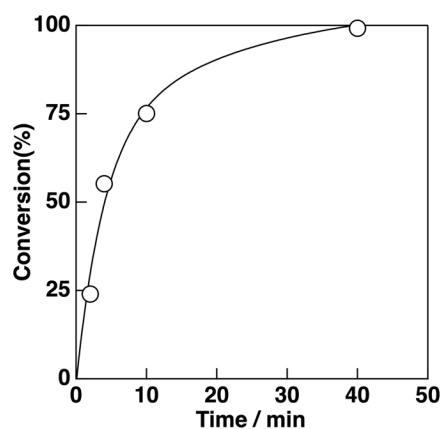


Figure S1. Time–conversion plots of the living cationic polymerization of CEVE. See Figure 1 for the polymerization conditions.

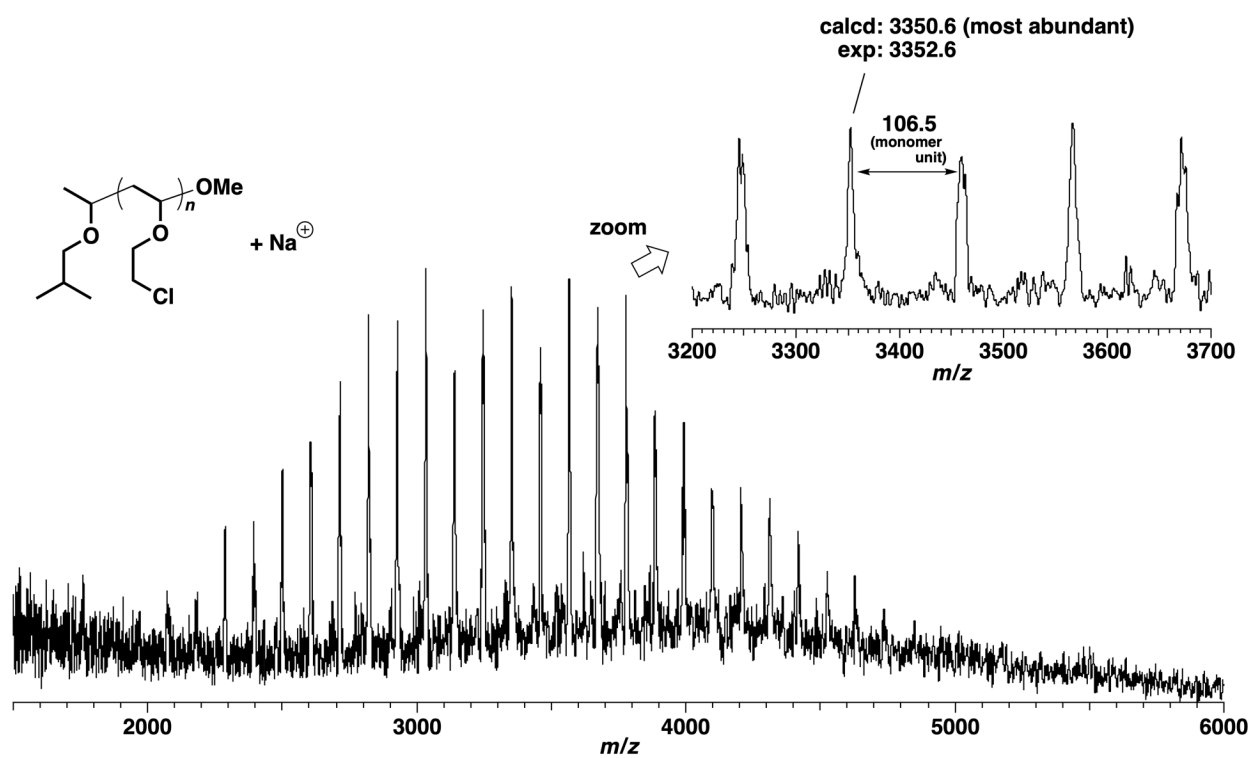


Figure S2. MALDI-TOF-MS spectrum of a poly(CEVE) (a polymer synthesized under the same conditions as those for the polymerization shown in Figure 1; $M_n(\text{GPC}) = 2.8 \times 10^3$).

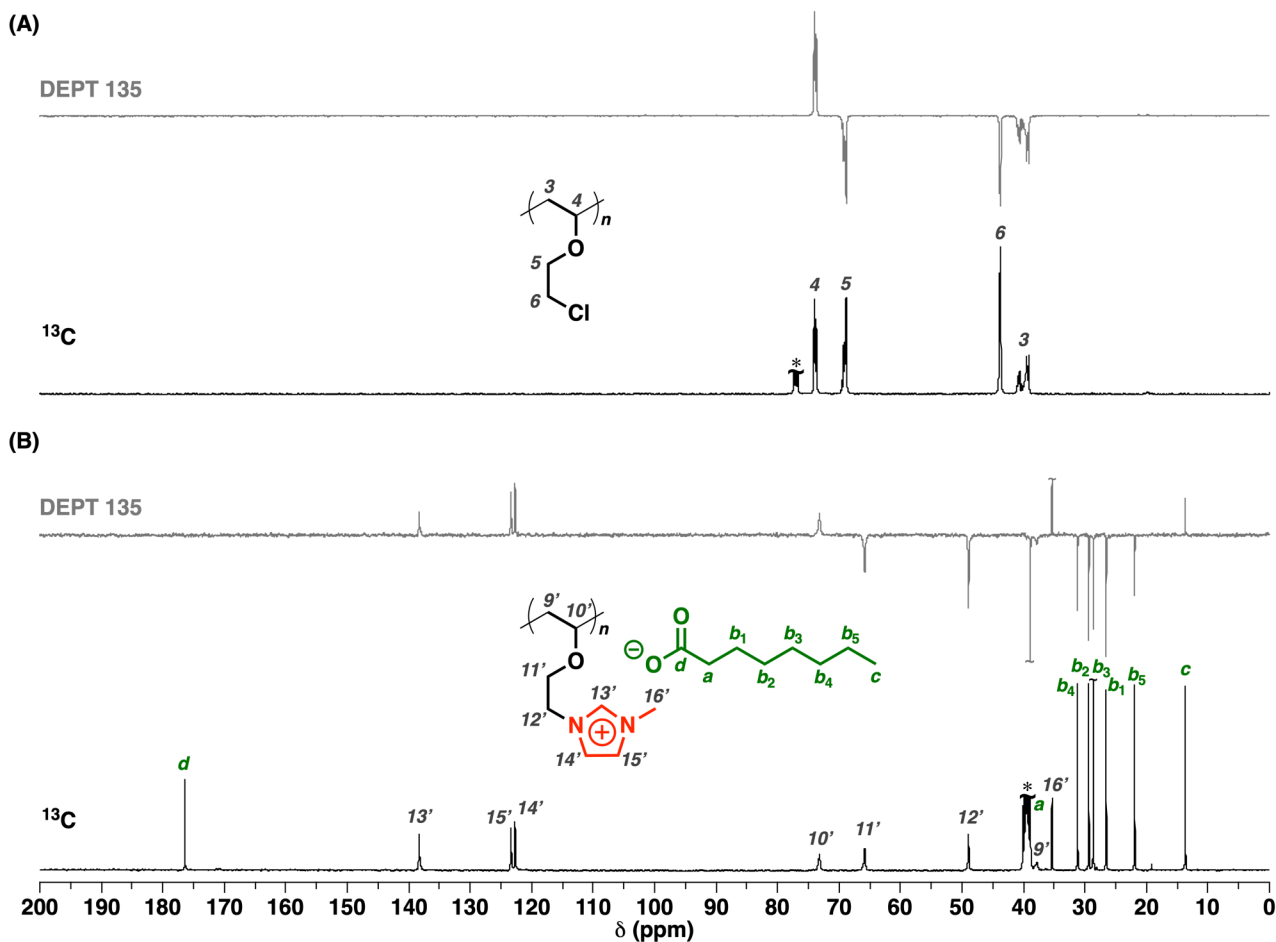


Figure S3. ¹³C and DEPT 135 NMR spectra of (A) poly(CEVE) (a polymer obtained under similar conditions to those for Figure 1; [CEVE]₀ = 1.2 M, [IBEA]₀ = 4.0 mM, [Et_{1.5}AlCl_{1.5}]₀ = 5.0 mM, [SnCl₄]₀ = 10 mM, [DTBP]₀ = 10 mM, [1,4-dioxane] = 1.2 M, in toluene at 0 °C; *M_n*(GPC) = 20.2 × 10³; in CDCl₃ at 30 °C) and (B) poly([MeIm][C8]) (a polymer different from that shown in Figure 2 and entry 4 in Table 1; *M_n*(GPC) of the precursor poly(CEVE) = 4.6 × 10³; in DMSO-*d*₆ at 50 °C). * CDCl₃ or DMSO-*d*₆.

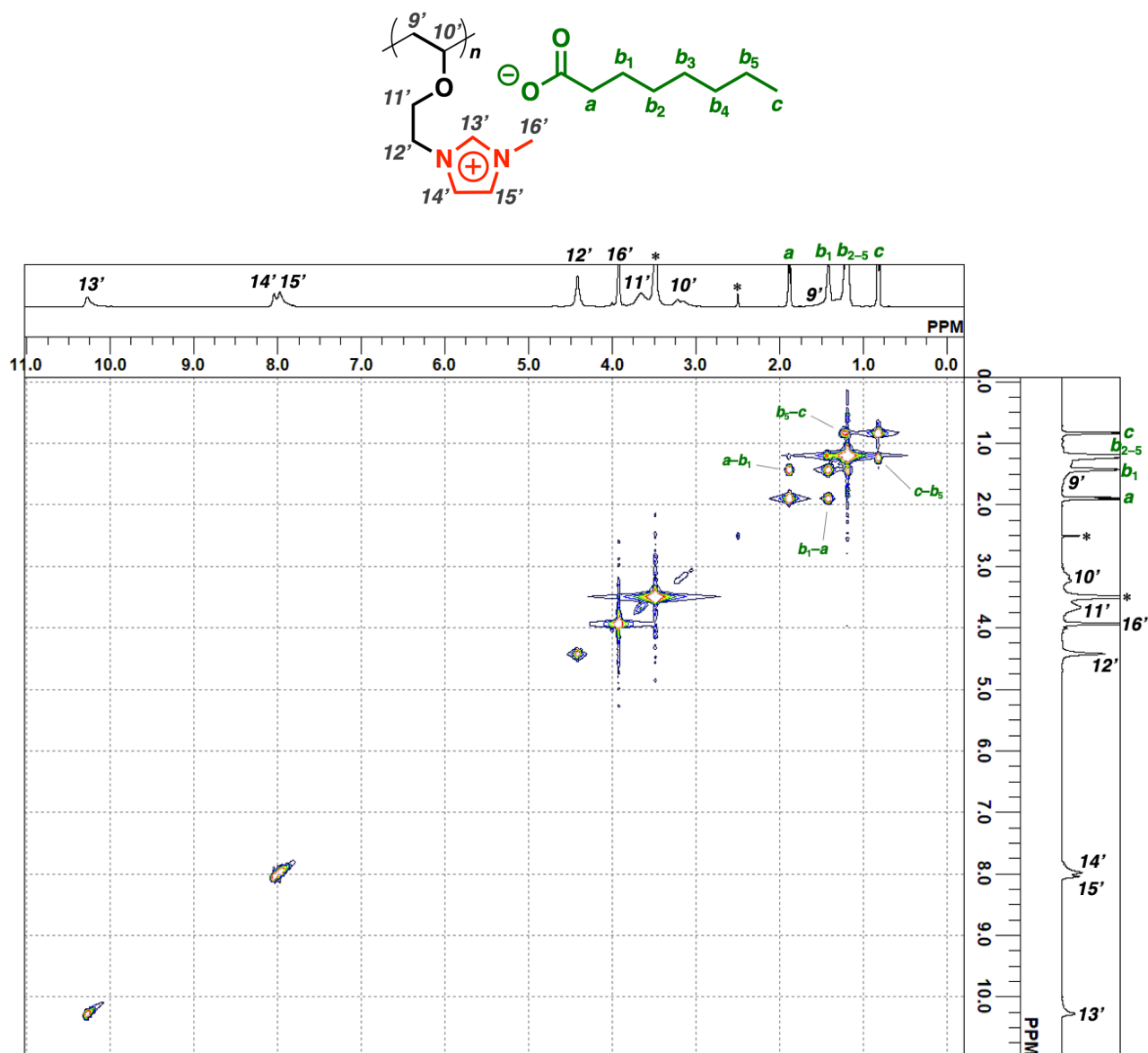


Figure S4. ^1H - ^1H COSY spectrum of poly([MeIm][C8]) (in $\text{DMSO-}d_6$ at $50\text{ }^\circ\text{C}$; the same sample as that shown in Figure S3B).

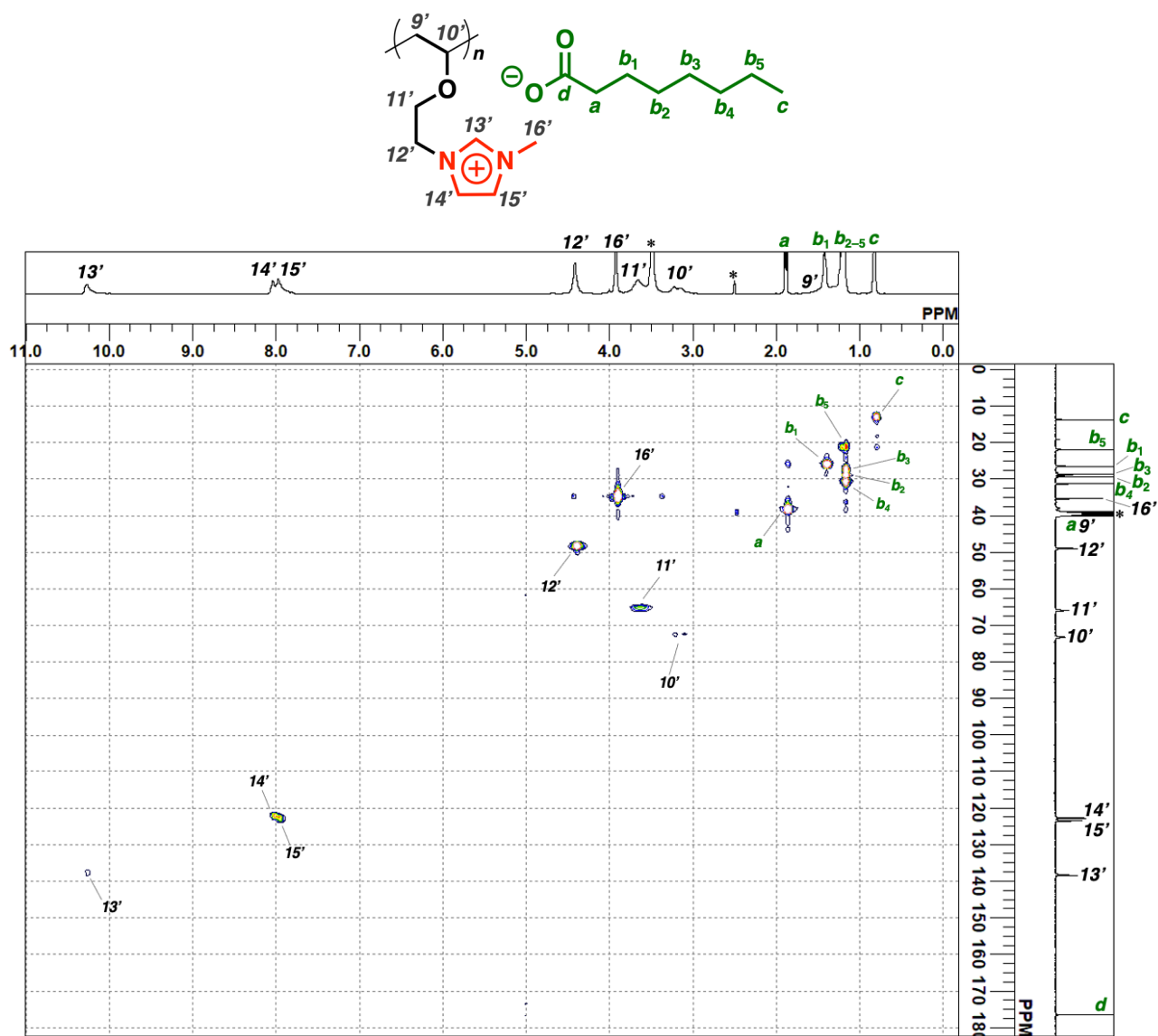


Figure S5. ^1H - ^{13}C HSQC spectrum of poly([MeIm][C8]) (in $\text{DMSO-}d_6$ at $50\text{ }^\circ\text{C}$; the same sample as that shown in Figure S3B).

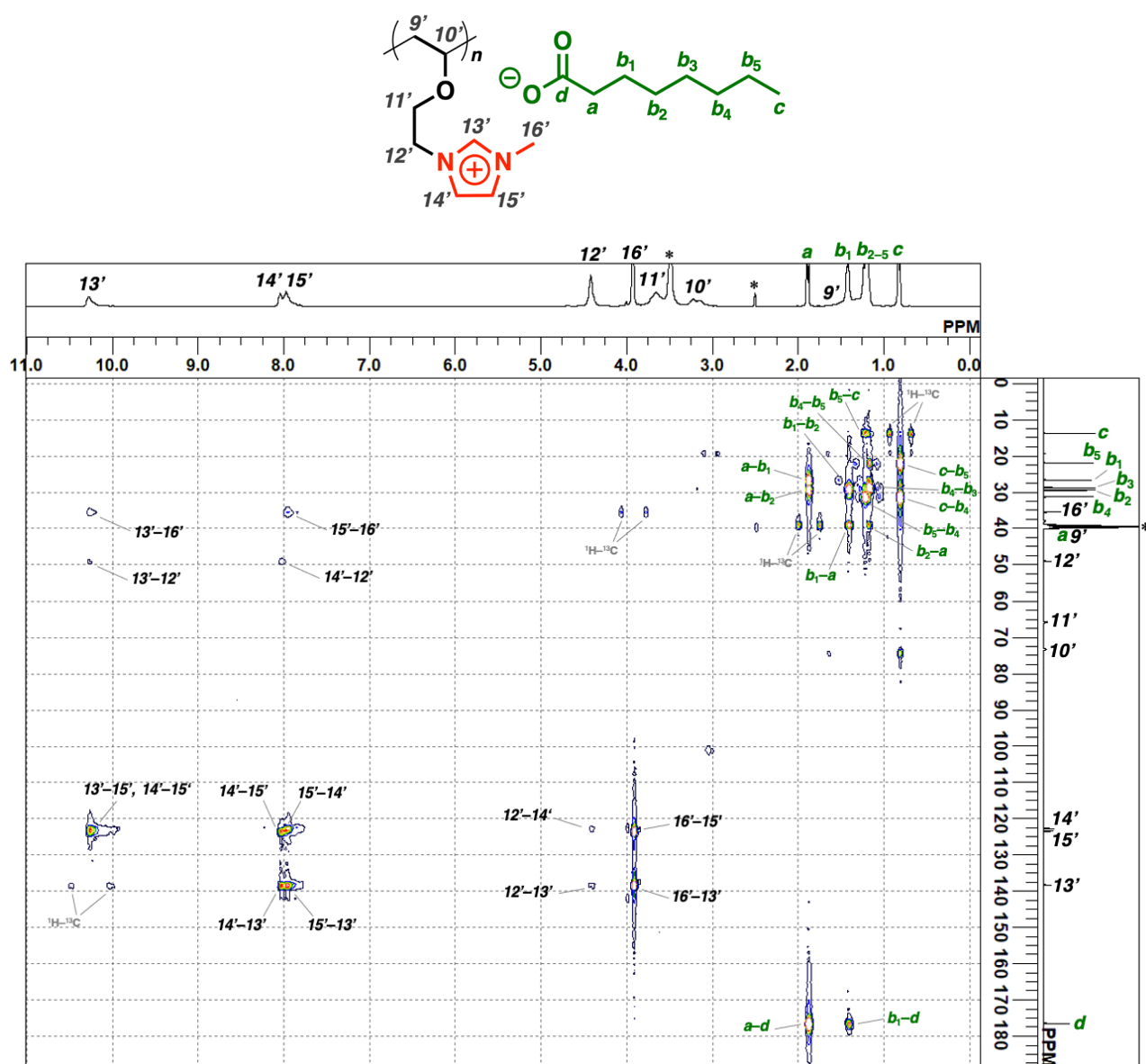


Figure S6. ¹H-¹³C HMBC spectrum of poly([MeIm][C8]) (in DMSO-*d*₆ at 50 °C; the same sample as that shown in Figure S3B).

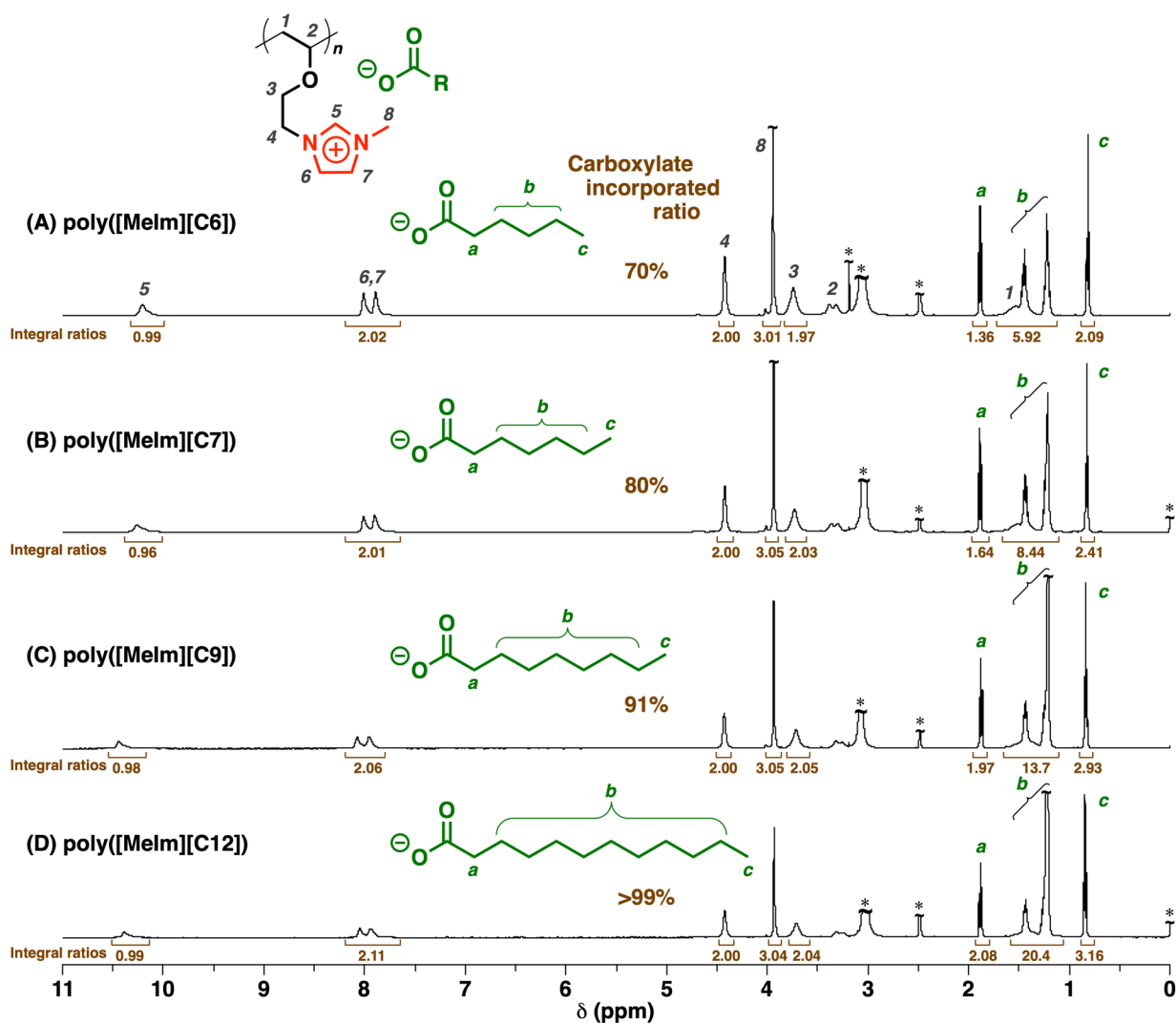


Figure S7. ^1H NMR spectra of (A) poly([MeIm][C6]) (entry 2 in Table 1), (B) poly([MeIm][C7]) (entry 3), (C), poly([MeIm][C9]) (entry 6), and (D) poly([MeIm][C12]) (entry 8). In $\text{DMSO-}d_6$ at $100\text{ }^\circ\text{C}$. * TMS, water, solvent, etc. Carboxylate incorporated ratios were determined from the integral ratios of peaks *c* and *4*.

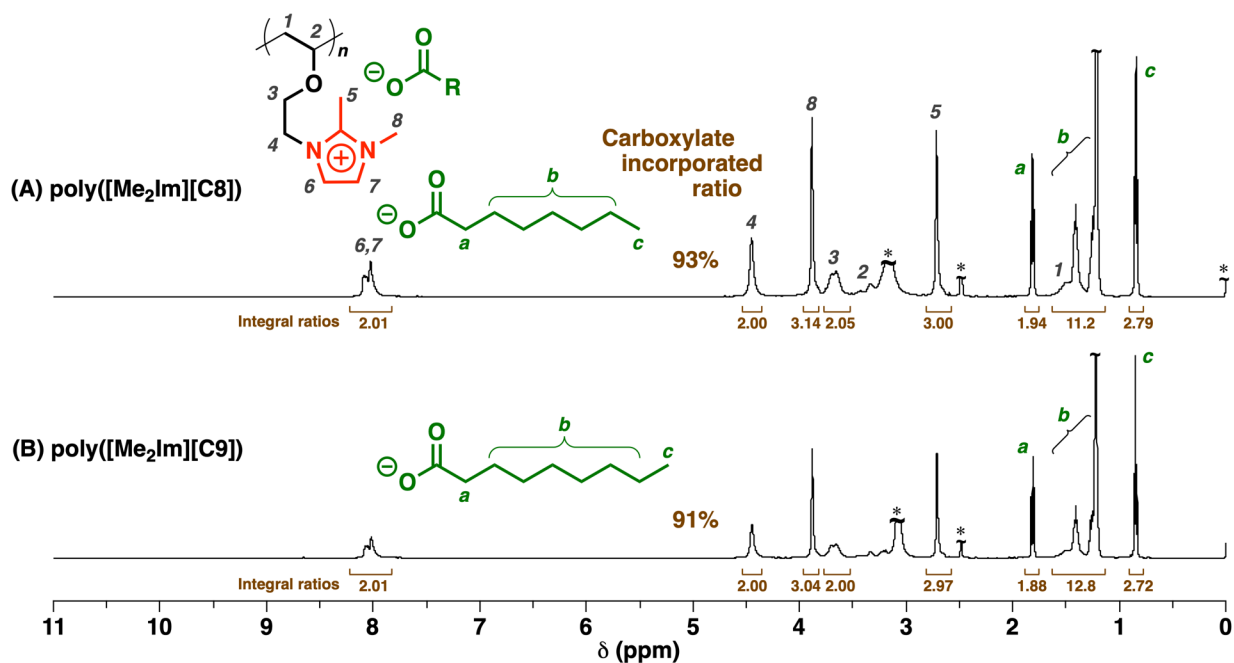


Figure S8. ^1H NMR spectra of (A) poly([Me₂Im][C8]) (entry 5 in Table 1) and (B) poly([Me₂Im][C9]) (entry 7). In DMSO-*d*₆ at 100 °C. * TMS, water, or solvent. Carboxylate incorporated ratios were determined from the integral ratios of peaks *c* and 4.

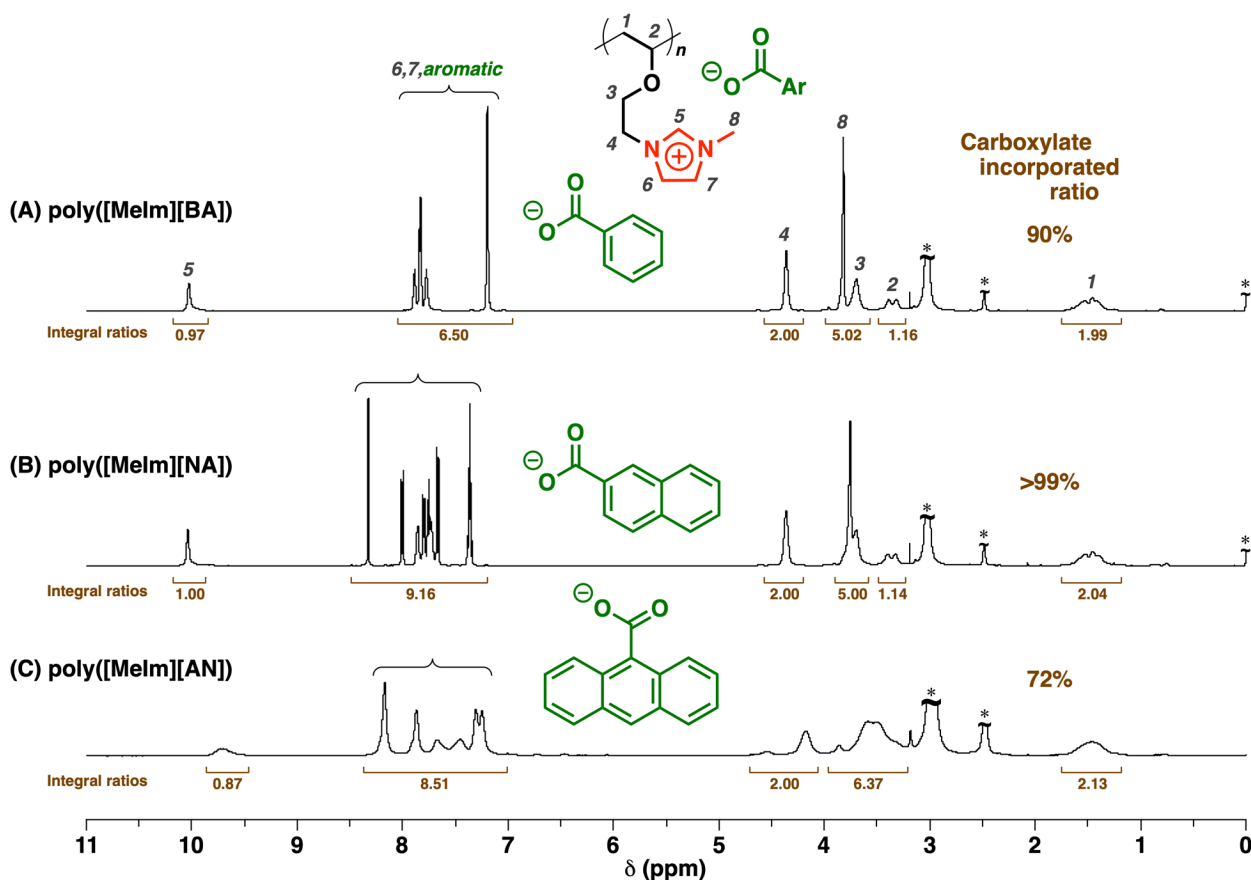


Figure S9. ^1H NMR spectra of (A) poly([MeIm][BA]) (entry 9 in Table 1), (B) poly([MeIm][NA]) (entry 10), and (C) poly([MeIm][AN]) (entry 11). In DMSO-*d*₆ at 100 °C. * TMS, water, or solvent. Carboxylate incorporated ratios were determined from the integral ratios of the aromatic peaks and peak 4.

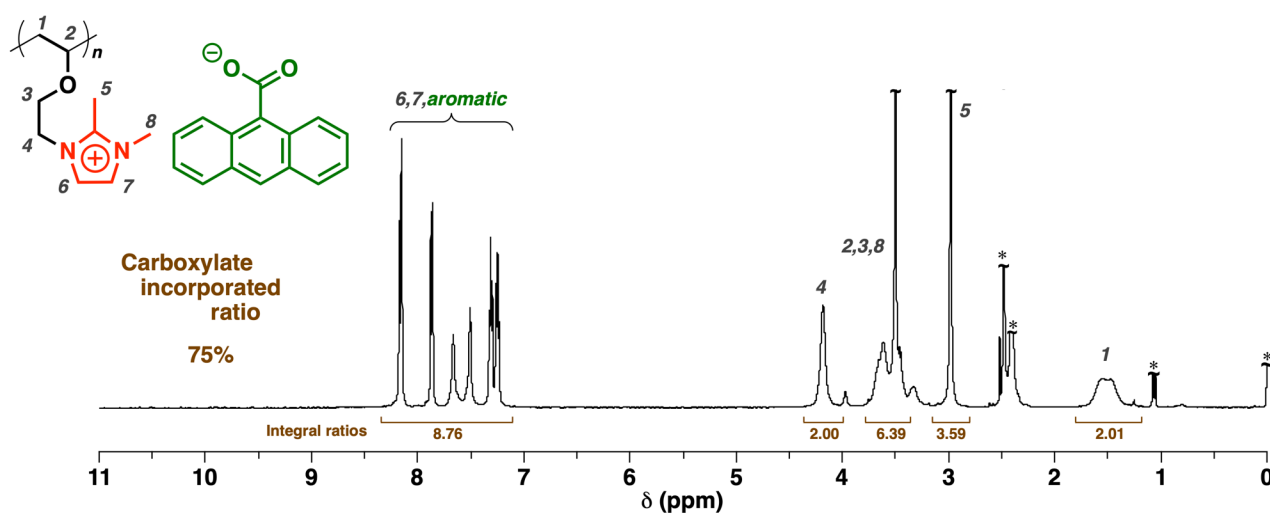


Figure S10. ^1H NMR spectrum of poly([Me₂Im][AN]) (entry 12 in Table 1). In DMSO-*d*₆ at 100 °C. * TMS, water, solvent, etc. A carboxylate incorporated ratio was determined from the integral ratios of the aromatic peaks and peak 4.

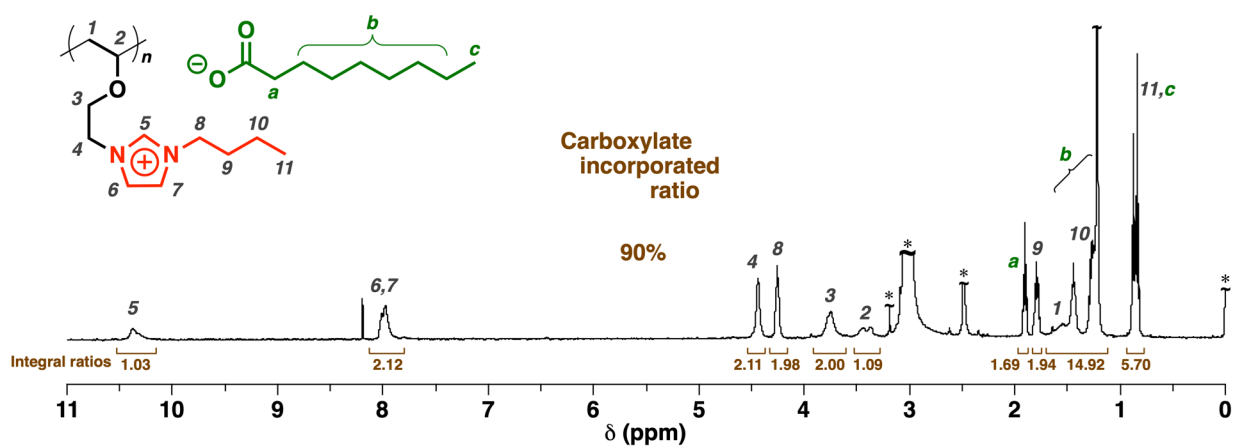


Figure S11. ^1H NMR spectrum of poly([BuIm][C9]) (entry 13 in Table 1). In DMSO-*d*₆ at 100 °C. * TMS, water, solvent, etc. A carboxylate incorporated ratio was determined from the integral ratios of peaks *c*, 11, and 4.

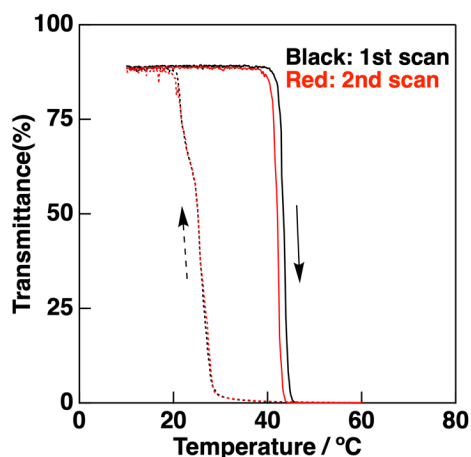


Figure S12. Turbidity measurement of an aqueous solution of poly([MeIm][C8]) (entry 4 in Table 1; polymer concentration: 5 wt%; after filtration with a disc filter (pore size = 0.45 μ m)). Black: the first heating and cooling scan (the same data as that shown in Figure 3A). Red: the second heating and cooling scan. Temperature was changed as follows: 10 $^{\circ}$ C \rightarrow 60 $^{\circ}$ C \rightarrow 10 $^{\circ}$ C \rightarrow 60 $^{\circ}$ C \rightarrow 10 $^{\circ}$ C.

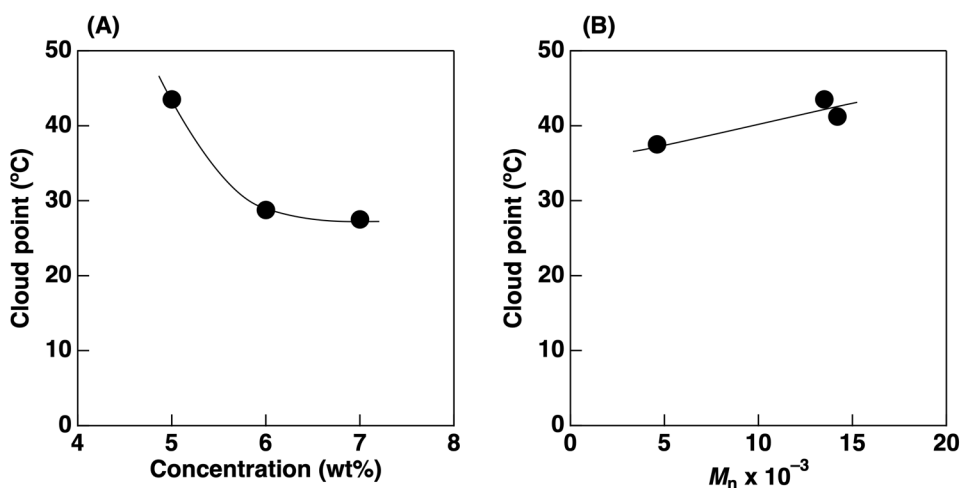


Figure S13. LCST-type thermoresponsive behavior of poly([MeIm][C8]) in water. (A) The dependence of the polymer concentration on cloud points (entry 4 in Table 1; after filtration with a disc filter (pore size = 0.45 μ m)) and (B) the dependence of the M_n values of the precursor poly(CEVE)s on cloud points (polymer concentration: 5 wt%).

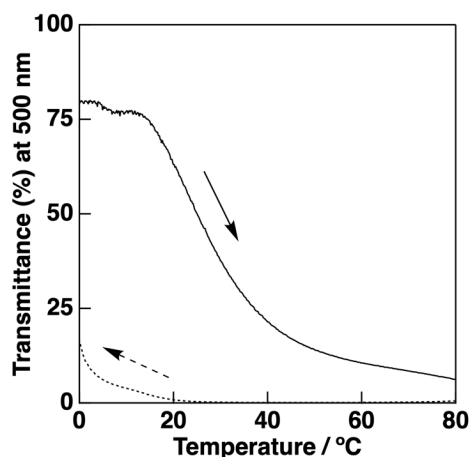


Figure S14. Turbidity measurement of poly([Me₂Im][C9]) (entry 7 in Table 1) in water (polymer concentration: 3 wt%; scan rate = 1 °C /min, solid: heating, dotted: cooling).

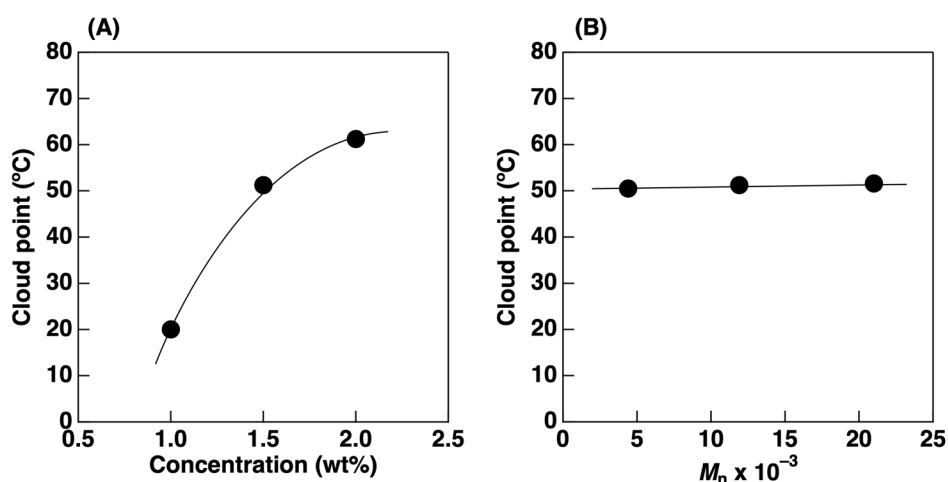


Figure S15. UCST-type thermoresponsive behavior of poly([MeIm][NA]) in water. (A) The dependence of the polymer concentration on cloud points (entry 10 in Table 1) and (B) the dependence of the M_n values of the precursor poly(CEVE)s on cloud points (polymer concentration: 1.5 wt%).

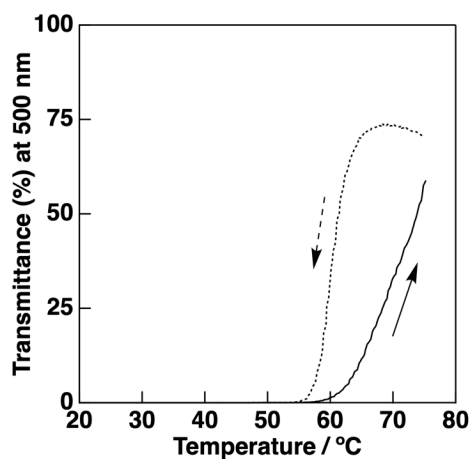


Figure S16. Turbidity measurement of poly([Me₂Im][AN]) (entry 12 in Table 1) in water (polymer concentration: 1 wt%; scan rate = 1 °C /min, solid: heating, dotted: cooling).

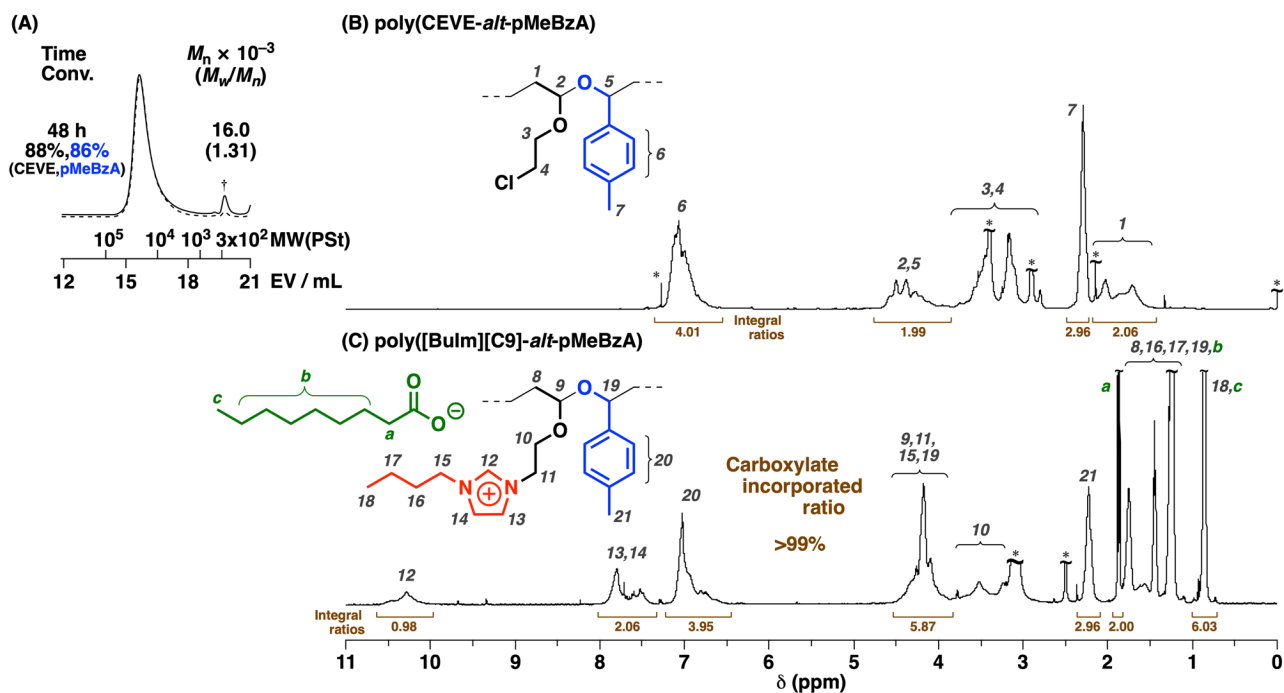


Figure S17. (A) MWD curve of poly(CEVE-*alt*-pMeBzA) obtained by the cationic copolymerization of CEVE and pMeBzA ($[\text{CEVE}]_0 = 0.60$ M, $[\text{pMeBzA}]_0 = 0.60$ M, $[\text{EtSO}_3\text{H}]_0 = 4.0$ mM, $[\text{GaCl}_3]_0 = 4.0$ mM, $[\text{1,4-dioxane}] = 1.0$ M, in toluene at -78 °C; solid line: the original product, dotted line: after reprecipitation in methanol; † cyclic trimer byproduct). ^1H NMR spectra of (B) the poly(CEVE-*alt*-pMeBzA) (in CDCl_3 at 30 °C) and (C) poly([BuIm][C9]-*alt*-pMeBzA) (in $\text{DMSO-}d_6$ at 100 °C).

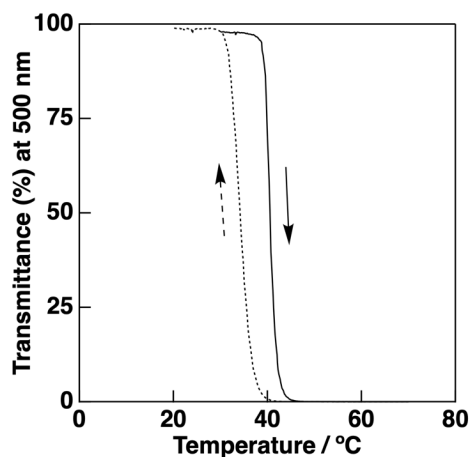


Figure S18. Turbidity measurement of poly([BuIm][C9]-*alt*-pMeBzA) (the sample shown in Figure S17C) in water (polymer concentration: 1 wt%, scan rate = 1.0 °C/min, solid: heating, dotted: cooling).

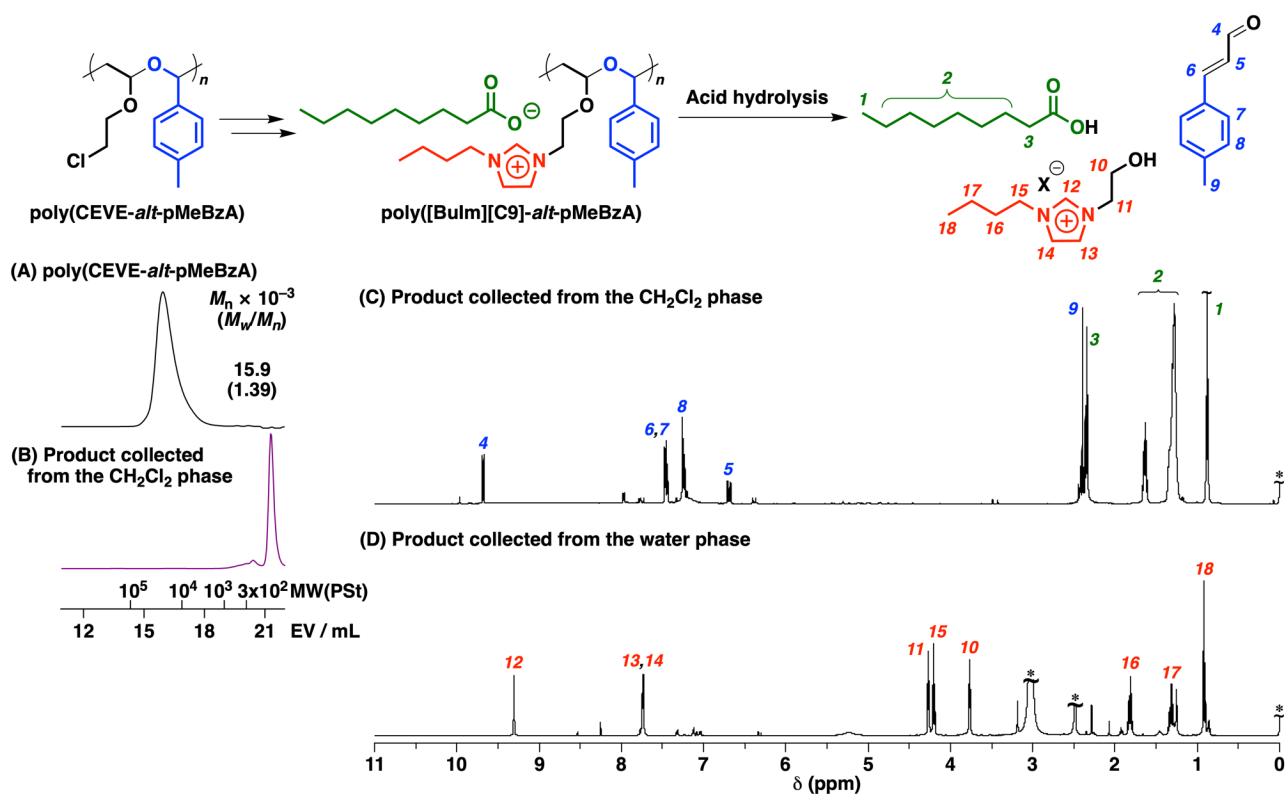


Figure S19. Acid hydrolysis of poly([BuIm][C9]-alt-pMeBzA) (hydrolysis conditions: 0.5 M HCl (aqueous) in 1,2-dimethoxyethane at room temperature for 3 h). MWD curves of (A) poly(CEVE-alt-pMeBzA) (a sample obtained under the same conditions as those for Figure S17A; after reprecipitation in methanol) and (B) a product collected from the dichloromethane phase after acid hydrolysis. ¹H NMR spectra of products collected from (C) the dichloromethane phase (in CDCl₃ at 30 °C) and (D) the water phase (in D₂O at 60 °C) after acid hydrolysis.

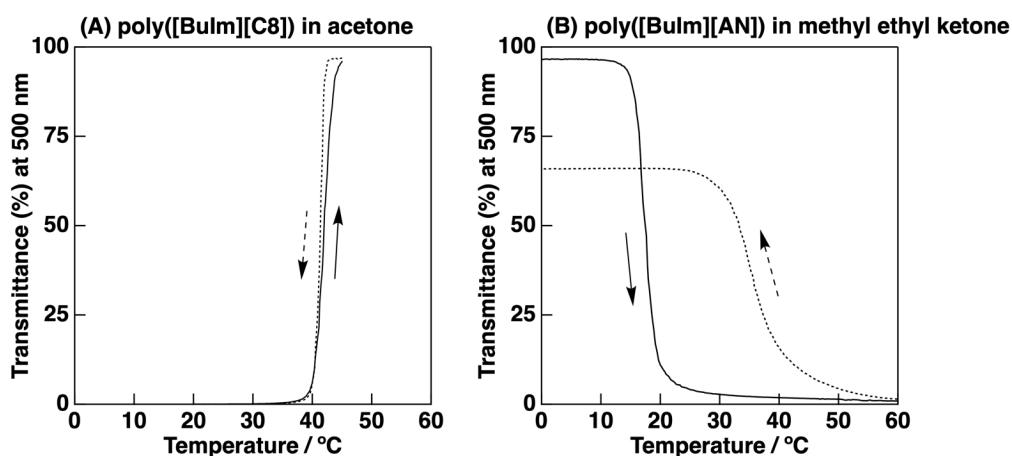


Figure S20. Turbidity measurements of (A) poly([BuIm][C8]) in acetone (polymer concentration: 1.4 wt%) and (B) poly([BuIm][AN]) in methyl ethyl ketone (polymer concentration: 0.5 wt%) (scan rate = 1 °C /min, solid: heating, dotted: cooling).