Electronic Supplementary Information for:

Unexpected increase in water solubility by the introduction of hydrophobic units into imidazolium-based polymeric ionic liquids with carboxylate counteranions

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Contents:

Experimental Section

Materials. 2-Chloroethyl vinyl ether (CEVE; TCI, >97%) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight over sodium sulfate, and distilled twice under reduced pressure from calcium hydride. Isobutyl vinyl ether (IBVE; TCI, >99.0%) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight over potassium hydroxide, and distilled twice from calcium hydride. 2-Ethylhexyl vinyl ether (EHVE; TCI, >97%) was distilled twice from calcium hydride under reduced pressure. 1-Isobutoxyethyl acetate (IBEA) was synthesized from IBVE 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 then distilled from lithium aluminum hydride. 2,6-Di-*tert*-butylpyridine (Sigma-Aldrich, 97%) was distilled twice from calcium hydride under reduced pressure. Toluene (Wako; >99.5%) was dried using solvent purification columns (Glass Contour; Solvent Dispensing System). $Et_{1.5}AlCl_{1.5}$ (Nippon Aluminum Alkyls, 1.0 M in toluene), $SnCl_4$ (Sigma-Aldrich, 1.0 M in dichloromethane), *N*,*N*-dimethylformamide (DMF; Nacalai Tesque, 99.5%), methyl isobutyl ketone (MIBK; Nacalai Tesque, 99.5%), 1-methylimidazole (TCI, >99.0%), sodium iodide (Fujifilm-Wako, 99.5+%), sodium octanoate (TCI, >98.0%), sodium nonanoate (TCI, >98.0%), and sodium decanoate (TCI, >99.0%) were used as received. Sodium 2-naphthoate was synthesized from 2-naphthoic acid (TCI, >98.0%) and sodium hydroxide (Nacalai Tesque, >97%) in water (this salt was used in an aqueous solution state without isolation). The synthesized sodium 2-naphthoate was used for the first to third counteranion exchange reactions and a commercial sodium 2-naphthoate (TCI, >98.0%) was used for the final exchange reaction.

Synthesis of the Precursor Statistical Copolymers by Living Cationic Copolymerization. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki, PJ-206A; air temperature of approximately 450 ºC) under a dry nitrogen atmosphere. Toluene, 1,4-dioxane, a solution of DTBP in toluene, and a solution of IBEA in hexane/toluene were added into the tube using dry syringes. The solution was cooled at 0 ºC and then a prechilled solution of $Et_{1.5}AlCl_{1.5}$ in toluene was added into the tube. After 15 min, a prechilled solution of $SnCl_4$ in toluene was added. The mixture solution of CEVE and IBVE 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 dilute hydrochloric acid, aqueous NaOH solution, and deionized water to remove initiator residues. The volatiles were removed under reduced pressure at 50 ºC to yield a polymer product. The polymer was dried under reduced pressure for over six 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 CEVE Units of the Copolymers. The poly(IBVE-*stat*-CEVE) was dissolved in DMF (polymer: 5

wt%, copolymers that contain less IBVE than CEVE units) or DMF/MIBK (2/1 v/v, polymer: 2.5 wt%, copolymers that contain more IBVE than CEVE units). Alkylimidazole and sodium iodide (the molar ratio of the CEVE units in a polymer/alkylimidazole/sodium iodide = 1/10/10) were added into the solution and heated at 80 ºC. 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 methanol three times to remove residual salts. Solvents were removed under reduced pressure at 70 ºC to yield a polymer. The polymer was dried under reduced pressure for over six hours at 60 ºC. The introduction ratio of carboxylate counteranions was determined by ^{1}H NMR analysis of the polymer in DMSO-d_6 at 100 ºC.

Preparation of Polymer Solutions in Water. A suitable amount of a polymer was placed in a glass vial. To the vial, ultrapure water (Milli-Q water, by Merck Direct-Q UV3) was added to adjust at a predetermined polymer concentration. When a polymer solution was partly turbid, the solution was heated.

Characterization. The molecular weight distributions (MWDs) of the polymers were measured by size exclusion chromatography (SEC) in chloroform at 40 ºC with polystyrene gel columns [Tosoh, TSKgel GMH$_{\mathrm{HR}}$-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 JASCO RI-4030 refractive-index detector. The number-average molecular weight (M_{n}) and the polydispersity ratio (weight-average molecular weight/number-average molecular weight [$M_{\mathrm{w}}/M_{\mathrm{n}}$]) were calculated from the chromatographs based on 16 polystyrene standards (Tosoh; $M_{\mathrm{n}} = 5.0 \times 10^2$ to 1.09×10^6, $M_{\mathrm{w}}/M_{\mathrm{n}} < 1.2$). NMR spectra were recorded with a JEOL JNM-ECA 500 spectrometer (500.16 MHz for ^{1}H). 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). The particle size was measured by dynamic light scattering (DLS) with an Otsuka Electronics FPAR-1000HG analyzer ($\lambda = 632.8$ nm, scattering angle = 90°).

Reference

S1. Aoshima, S.; Higashimura, T. *Macromolecules* **1989**, *22*, 1009–1013.

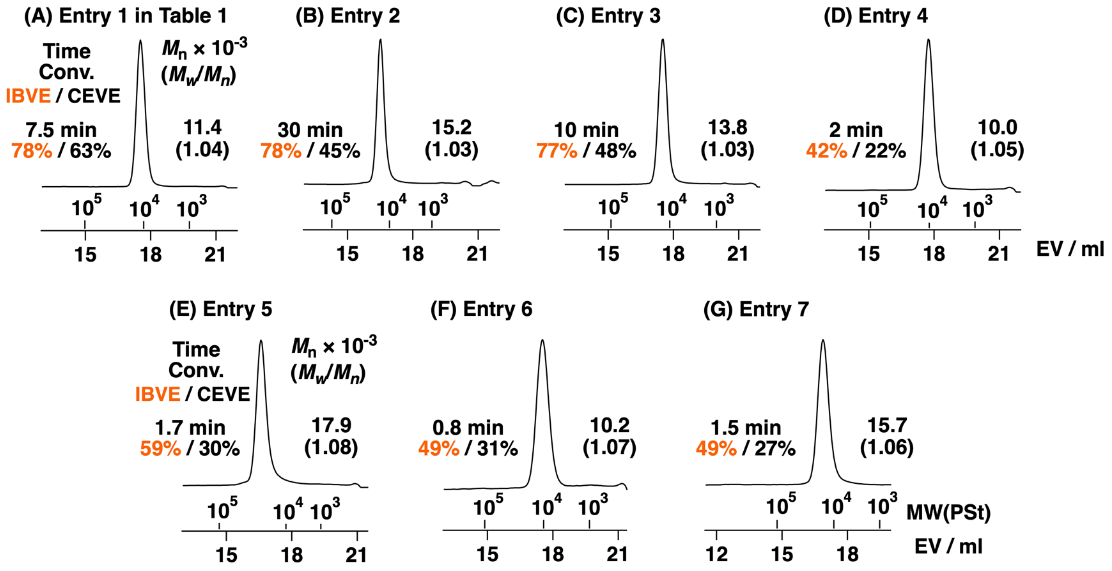


Figure S1. MWD curves of the products obtained by the copolymerization of IBVE and CEVE. See Table 1 for the polymerization conditions.

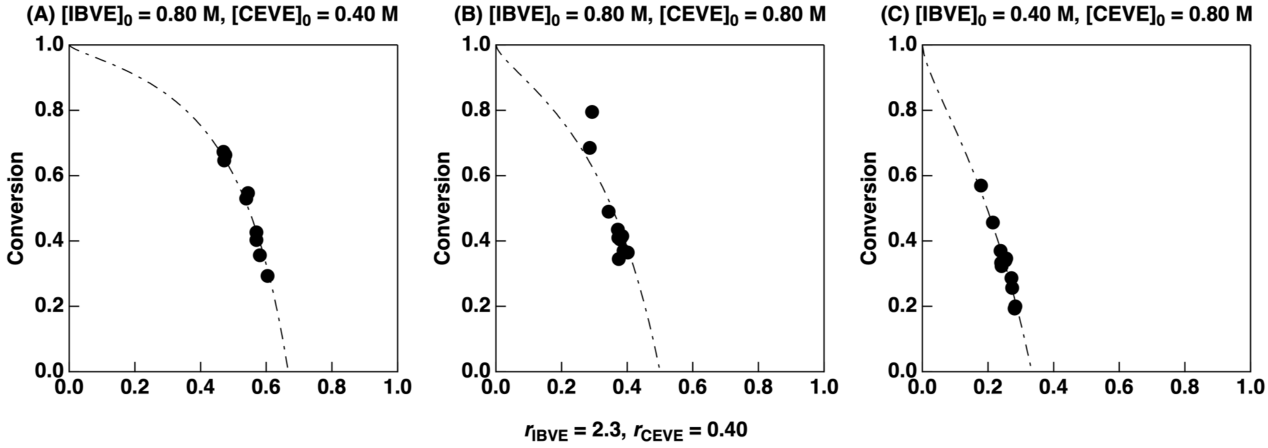


Figure S2. Graphs for the determination of monomer reactivity ratios by the Meyer–Lowry method. The dotted lines were drawn using the r values that most likely fit the data points ($r_{\text{IBVE}} = 2.3$, $r_{\text{CEVE}} = 0.40$ for all the graphs). Polymerization conditions: $[\text{IBVE}]_0 = 0.40$ or 0.80 M, $[\text{CEVE}]_0 = 0.40$ or 0.80 M, $[\text{IBEA}]_0 = 4.0$ mM, $[\text{Et}_{1.5}\text{AlCl}_{1.5}]_0 = 10$ mM, $[\text{DTBP}]_0 = 10$ mM, $[\text{SnCl}_4]_0 = 10$ mM, [1,4-dioxane] = 1.2 M, in toluene at 0 ºC.

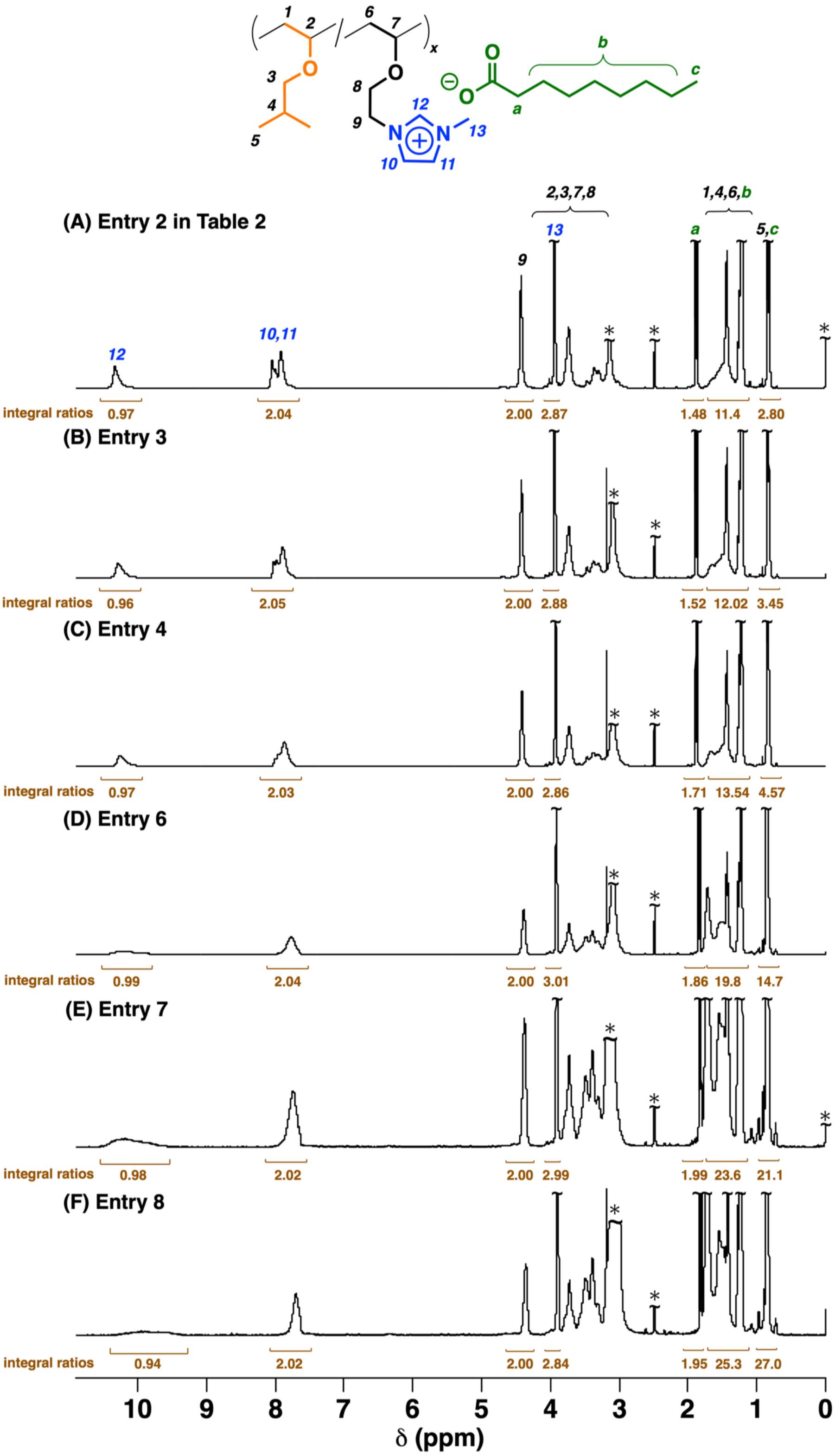


Figure S3. ^{1}H NMR spectra of p[IBVE$_n$-*stat*-([MeIm][C9])$_m$]s (entries 2–4 and 6–8 in Table 2). In DMSO-d_6 at 100 ºC. * Me$_4$Si, water, or solvent. A imidazolium incorporated ratio was determined from the integral ratios of the methylene peak of the CEVE units (peak *6*; the integral ratios of overlapping peaks were subtracted) and the nitrogen-adjacent methylene peak (peak *9*). A carboxylate incorporated ratio was determined from the integral ratios of the nitrogen-adjacent methylene peak (peak *9*) and the methyl group of nonanoate anions (peak *a*).

Table S1. Imidazolium and carboxylate incorporated ratios of the statistical copolymers listed in Table 2.

Entry (in Table 2)	IBVE or EHVE unit (mol%)	Imidazolium incorporated ratio (%)	Carboxylate incorporated ratio (%)
2	10	90	74
3	17	86	76
4	25	88	86
5	51	80	91
6	63	74	93
7	71	77	>99
8	76	>99	98
9	25	>99	78

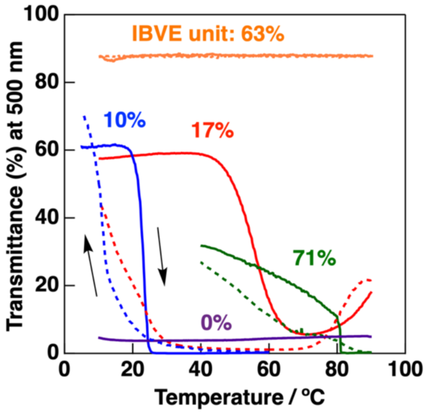


Figure S4. Turbidity measurements of aqueous solutions of p[IBVE$_n$-*stat*-([MeIm][C9])$_m$]s (entries 1, 2, 3, 6, and 7 in Table 2; polymer concentration: 3 wt%). Solid line: the heating scan (the same data as those shown in Figure 3A). Broken line: the cooling scan. Scan rate = 1 °C min^{-1}.

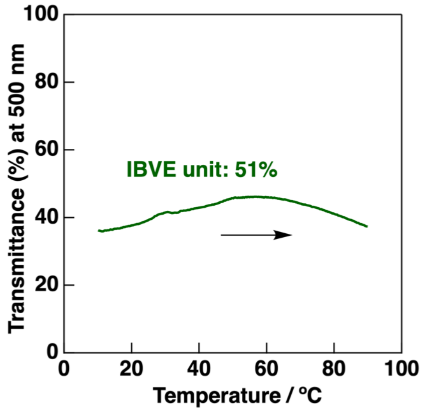


Figure S5. Turbidity measurement of an aqueous solution of p[IBVE$_{44}$-*stat*-([MeIm][C9])$_{42}$] (entry 5 in Table 2; polymer concentration: 3 wt%). Scan rate = 1 °C min^{-1}.

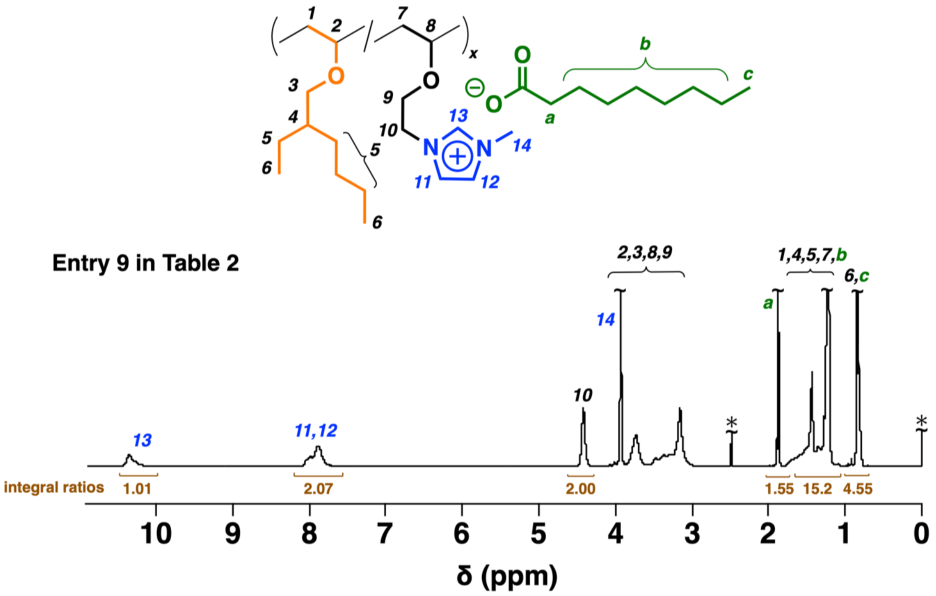


Figure S6. ^{1}H NMR spectrum of p[EHVE$_{47}$-*stat*-([MeIm][C9])$_{139}$] (entry 9 in Table 2). In DMSO-d_6 at 100 ºC. * Me$_4$Si, water, or solvent. A imidazolium incorporated ratio was determined from the integral ratios of the methylene peak of the CEVE units (peak *7*; the integral ratios of overlapping peaks were subtracted) and the nitrogen-adjacent methylene peak (peak *10*). A carboxylate incorporated ratio was determined from the integral ratios of the nitrogen-adjacent methylene peak (peak *10*) and the methyl group of octanoate anions (peak *a*).

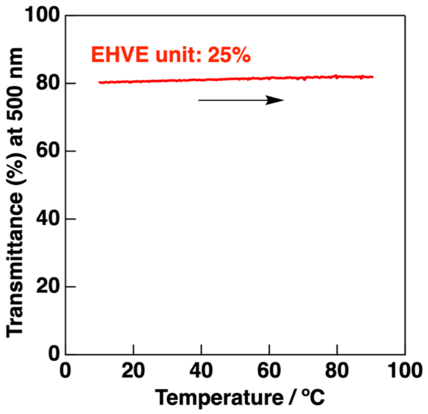


Figure S7. Turbidity measurement of an aqueous solution of p[EHVE$_{47}$-*stat*-([MeIm][C9])$_{139}$] (entry 9 in Table 2; polymer concentration: 3 wt%). Scan rate = 1 ºC min^{-1}.

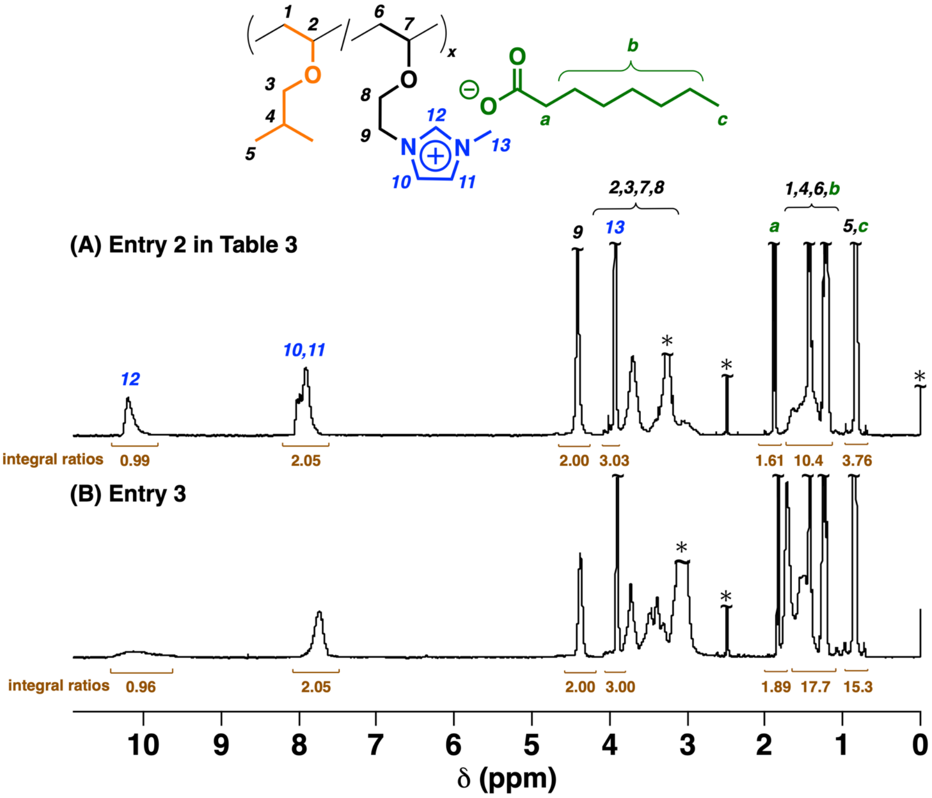


Figure S8. ^{1}H NMR spectra of p[IBVE$_n$-*stat*-([MeIm][C8])$_m$]s (entries 2 and 3 in Table 3). In DMSO-*d*$_6$ at 100 ºC. * Me$_4$Si, water, or solvent. A imidazolium incorporated ratio was determined from the integral ratios of the methylene peak of the CEVE units (peak *6*; the integral ratios of overlapping peaks were subtracted) and the nitrogen-adjacent methylene peak (peak *9*). A carboxylate incorporated ratio was determined from the integral ratios of the nitrogen-adjacent methylene peak (peak *9*) and the methyl group of octanoate anions (peak *a*).

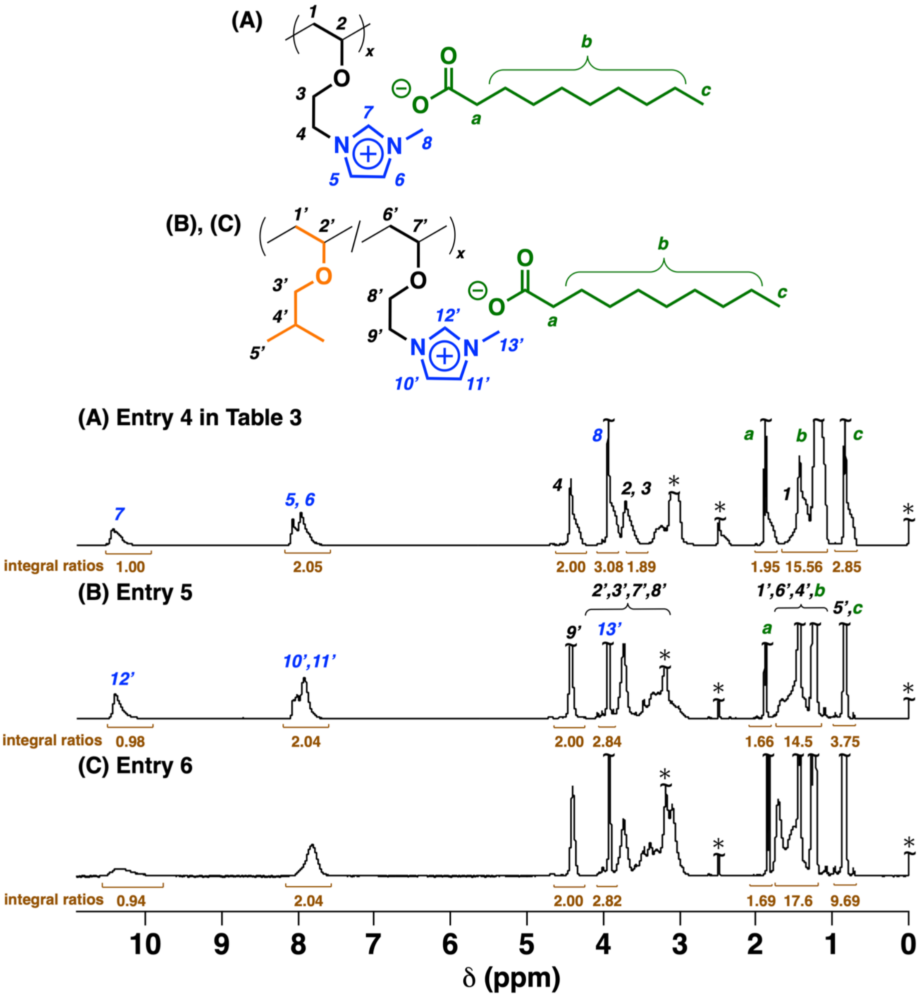
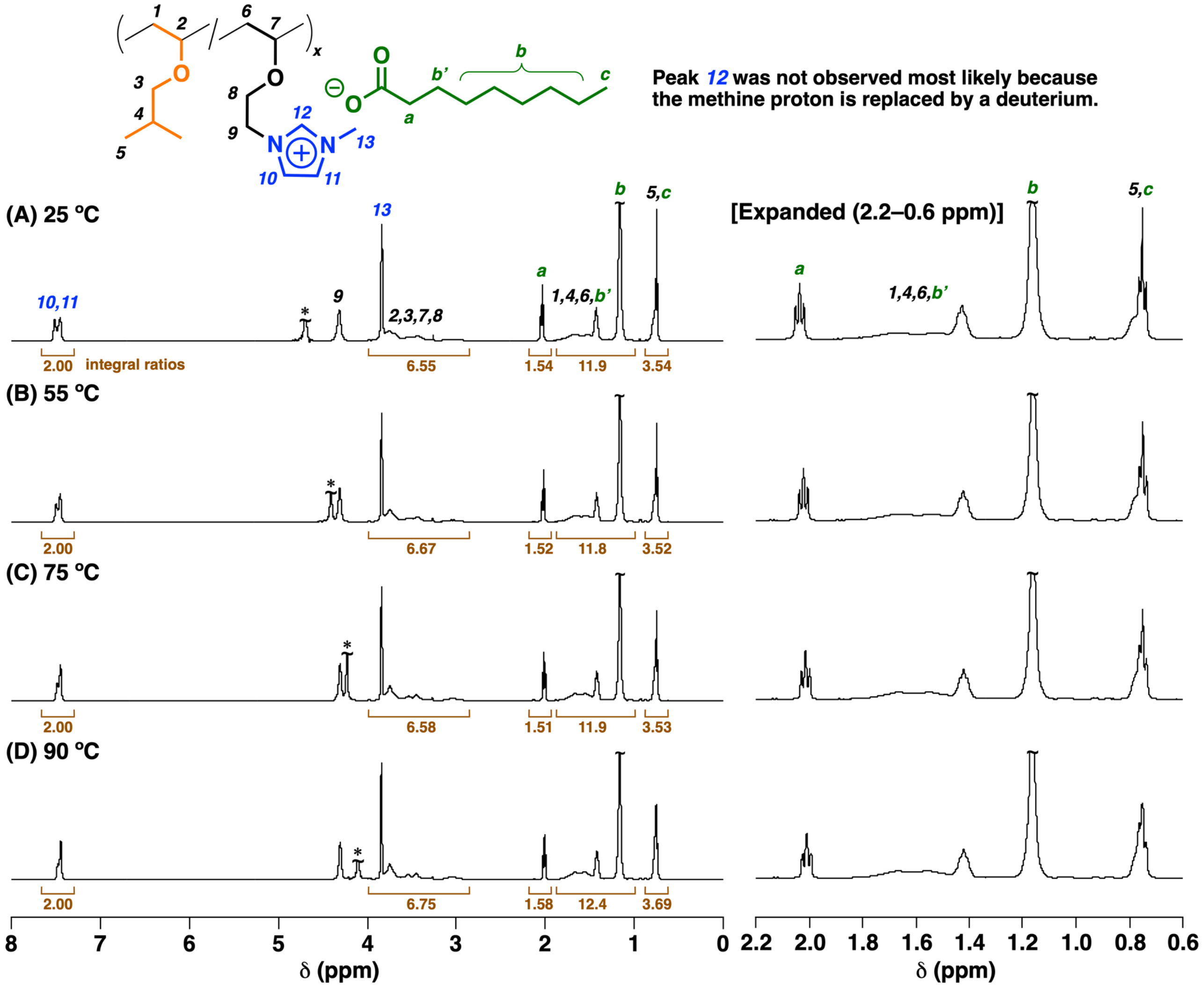


Figure S9. ^{1}H NMR spectra of (A) p([MeIm][C10]) (entry 4 in Table 3) and (B), (C) p[IBVE$_n$-*stat*-([MeIm][C10])$_m$]s (entries 5 and 6 in Table 3). In DMSO-d_6 at 100 ºC. * Me$_4$Si, water, or solvent. A imidazolium incorporated ratio was determined from the integral ratios of the methylene peak of the CEVE units (peak *1* or *6'*; the integral ratios of overlapping peaks were subtracted) and the nitrogen-adjacent methylene peak (peak *4* or *9'*). A carboxylate incorporated ratio was determined from the integral ratios of the nitrogen-adjacent methylene peak (peak *4* or *9*) and the methyl group of decanoate anions (peak *a*).

Table S2. Imidazolium and carboxylate incorporated ratios of the statistical copolymers listed in Table 3.

Entry (in Table 3)	IBVE unit (mol%)	Imidazolium incorporated ratio (%)	Carboxylate incorporated ratio (%)
2	17	>99	81
3	66	99	95
4	0	>99	98
5	17	88	83
6	54	91	85



Peak 12 was not observed most likely because the methine proton is replaced by a deuterium.

Figure S10. ^{1}H NMR spectra of p[IBVE$_{14}$-*stat*-([MeIm][C9])$_{70}$] (entry 3 in Table 2) in D_2O at (A) 25, (B) 55, (C) 75, and (D) 90 °C (polymer: 2 wt%; * water).

Note for Figure S10: ^{1}H NMR spectra of p[IBVE$_{14}$-*stat*-([MeIm][C9])$_{70}$] in D_2O was recorded at a polymer concentration of 2 wt% because the polymer did not dissolve in D_2O at 3 wt% even when cooled in an ice bath. The property difference of H_2O and D_2O likely affected the solubility. The methyl peak (peak *c*) of the nonanoate anion likely broadened at 90 °C (Figure S10D).

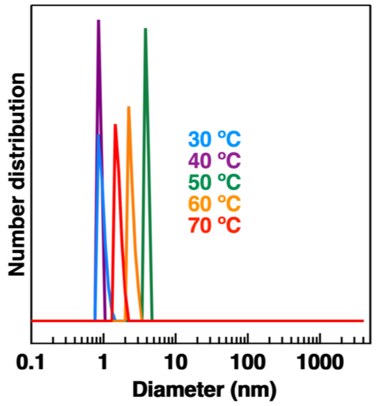


Figure S11. DLS measurement for 0.1 wt% aqueous solution of p[IBVE$_{14}$-*stat*-([MeIm][C9])$_{70}$] (entry 3 in Table 2) at 30–70 ºC.

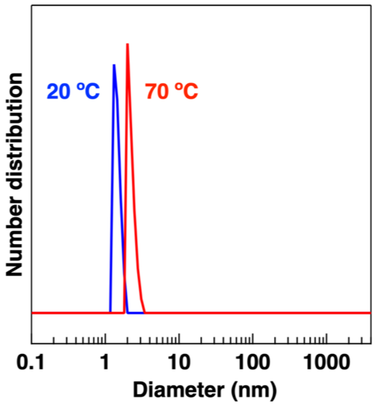


Figure S12. DLS measurement for 0.1 wt% aqueous solution of p[IBVE$_{67}$-*stat*-([MeIm][C9])$_{39}$] (entry 6 in Table 2) at 20 or 70 ºC.

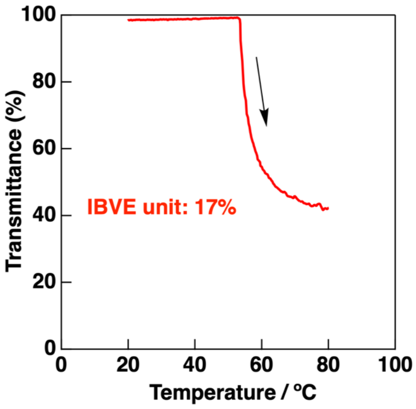


Figure S13. Turbidity measurement of an aqueous solution of p[IBVE$_{14}$-*stat*-([MeIm][C9])$_{70}$] at a low polymer concentration (entry 3 in Table 2; polymer concentration: 0.1 wt%). Scan rate = 1 ºC min^{-1}.

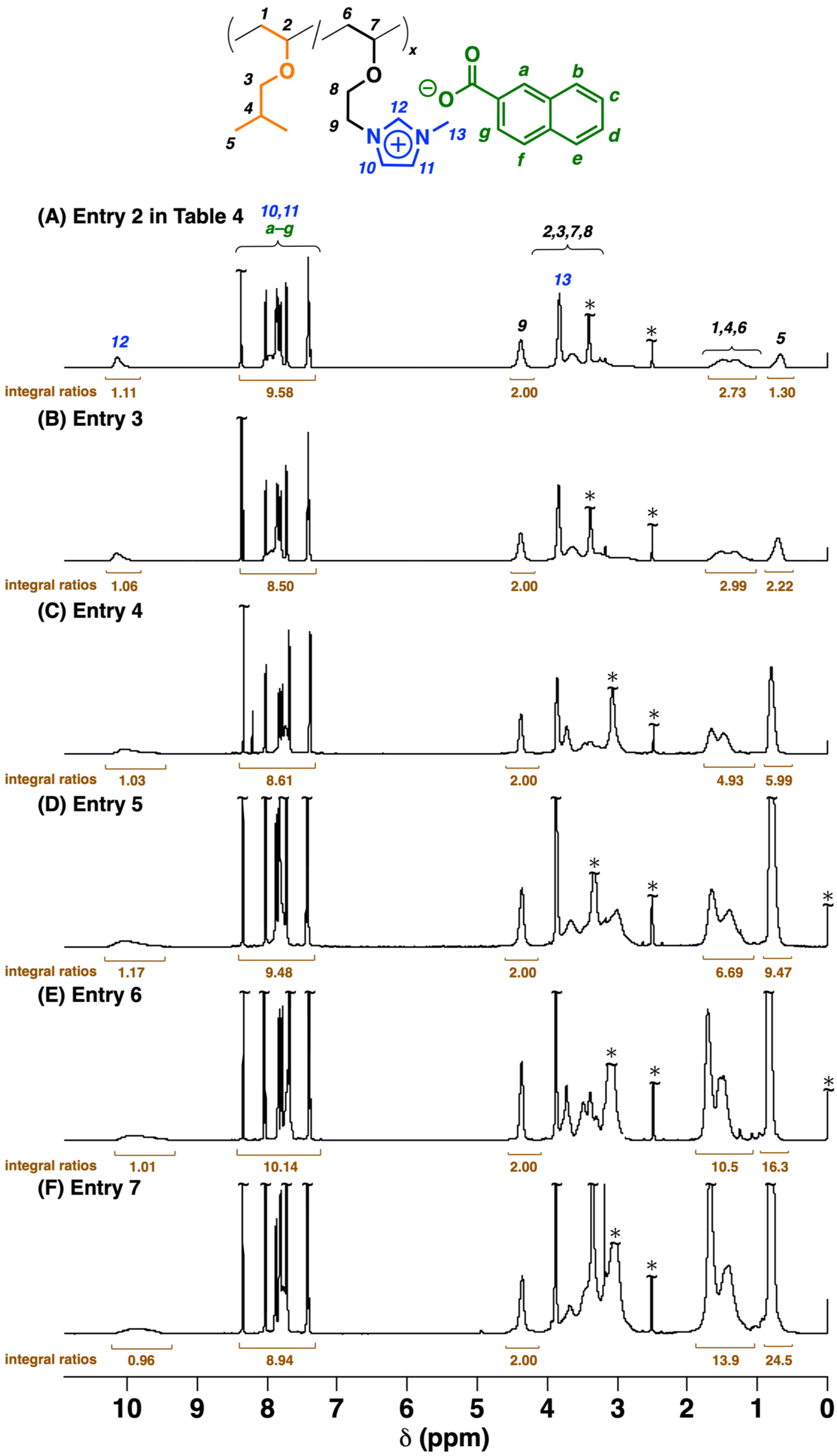


Figure S14. ^{1}H NMR spectra of p[IBVE$_n$-*stat*-([MeIm][NA])$_m$]s (entries 2–7 in Table 4). In DMSO-d_6 at 100 ºC. * Me$_4$Si, water, or solvent. A imidazolium incorporated ratio was determined from the integral ratios of the methylene peak of the CEVE units (peak *6*; the integral ratios of overlapping peaks were subtracted) and the nitrogen-adjacent methylene peak (peak *9*). A carboxylate incorporated ratio was determined from the integral ratios of the nitrogen-adjacent methylene peak (peak *9*) and aromatic peaks.

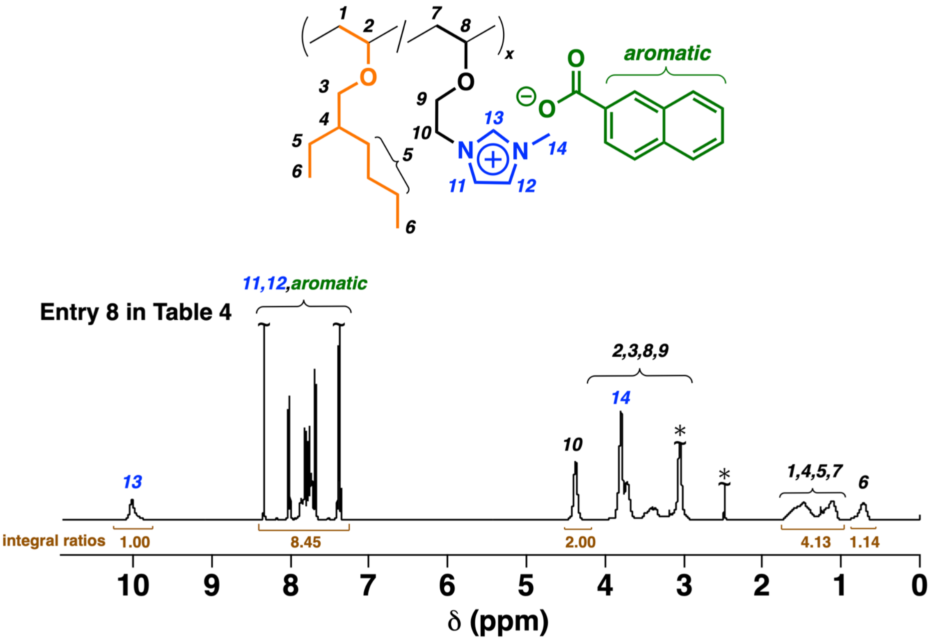


Figure S15. ^{1}H NMR spectrum of p[EHVE$_{18}$-*stat*-([MeIm][NA])$_{103}$] (entry 8 in Table 4). In DMSO-*d*$_6$ at 100 ºC. * Water or solvent. A imidazolium incorporated ratio was determined from the integral ratios of the methylene peak of the CEVE units (peak *7*; the integral ratios of overlapping peaks were subtracted) and the nitrogen-adjacent methylene peak (peak *10*). A carboxylate incorporated ratio was determined from the integral ratios of the nitrogen-adjacent methylene peak (peak *10*) and aromatic peaks.

Table S3. Imidazolium and carboxylate incorporated ratios of the statistical copolymers listed in Table 4.

Entry (in Table 4)	IBVE or EHVE unit (mol%)	Imidazolium incorporated ratio (%)	Carboxylate incorporated ratio (%)
2	16	96	>99
3	27	>99	93
4	48	>99	94
5	58	>99	>99
6	72	85	>99
7	78	>99	99
8	15	98	92

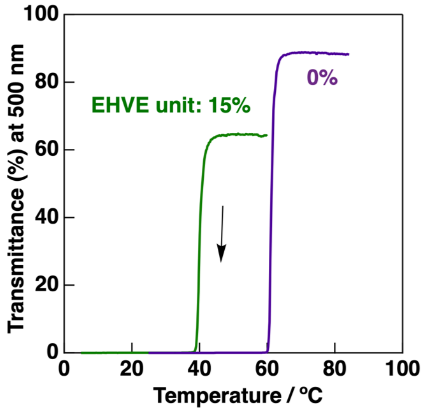


Figure S16. Turbidity measurement of an aqueous solution of p[EHVE$_{18}$-*stat*-([MeIm][NA])$_{103}$] (entry 8 in Table 4; polymer concentration: 2 wt%).