Electronic Supplementary Information for:

Precise synthesis of UCST-type amphiphilic diblock copolymers with pendant imidazolium ionic liquid segments and their thermosensitive physical gelation at extremely low concentrations in water

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Experimental section

Materials

Isobutyl vinyl ether (IBVE: TCI; >99%) was washed with 10 wt% aqueous sodium hydroxide solution and then with water, dried overnight over potassium hydroxide (pellets), and distilled twice over calcium hydride. 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 over calcium hydride. Toluene (Wako; >99.5%) was dried using solvent purification columns (Glass Contour; Solvent Dispensing System). 2,6-Di-tertbutylpyridine (DTBP: Sigma-Aldrich; 97%) was distilled twice over calcium hydride under reduced pressure. 1,4-Dioxane (Wako; 99.5%) was distilled over calcium hydride and then lithium aluminum hydride. Ethyl acetate (Wako; >99.5%) was dried overnight over molecular sieves 3A and 4A and distilled twice over calcium hydride. The adduct of IBVE with acetic acid [IBEA; CH₃CH(OiBu)OCOCH₃] was prepared from the addition reaction of IBVE with acetic acid according to the literature method.^{S1} Et_{1.5}AlCl_{1.5} (Nippon Aluminum Alkyls; 1.0 M solution in toluene), SnCl₄ (Sigma-Aldrich; 1.0 M solution in heptane), and TiCl₄ (Aldrich; 1.0 M solution in toluene) were used without further purification. 1,2-Dimethylimidazole (Wako; >97%), sodium tetrafluoroborate (Aldrich; 98%), sodium iodide (Wako; >99.5%), and all solvents expect for a polymerization solvent were used without further purification.

Polymerization of the precursor block copolymer

Polymerization was carried out under a dry nitrogen atmosphere in a glass tube equipped with a three-way stopcock. The glass tube was baked using a heat gun (Ishizaki; PJ-206A; blow temperature: approximately 450 °C) under dry nitrogen for 10 min before use. A prechilled $Et_{1.5}AlCl_{1.5}$ solution or a TiCl₄ solution was added to a prechilled mixture containing IBEA, an added base, IBVE, DTBP and toluene at 0 °C using dry syringes. The polymerization was initiated by the addition of a prechilled $SnCl_4$ solution. The polymerization that was conducted without $SnCl_4$ was initiated by the addition of a prechilled $Et_{1.5}AlCl_{1.5}$ solution. After a predetermined period, CEVE was added to the mixture solution to start the second stage polymerization. The polymerization was quenched using methanol containing a small amount of an aqueous ammonia solution. The quenched reaction mixture was diluted with dichloromethane and subsequently washed with water to remove the initiator residues. The product polymer was recovered from the organic layer by evaporation of volatiles under reduced pressure and subsequently vacuum-dried for at least 6 h. The monomer conversion was determined by a gravimetric method and ¹H NMR analysis of the product.

Substitution of the chlorine atoms in the copolymer with imidazole derivatives

IBVE-*b*-CEVE (5 wt%) was dissolved in a DMF solution containing 1,2-dimethylimidazole and NaI (five times the molar amounts of CEVE units). The solution was stirred with a magnetic stir bar at 80 °C for 72 h. The reaction mixture was dialyzed against deionized water at least 24 h to remove DMF, the unreacted imidazole, and residual salts. After purification, the polymer solution was dialyzed against deionized water in the presence of NaBF₄ (five times the amounts of CEVE units) at least 24 h to exchange the counteranions from I⁻ to BF₄⁻, followed by evaporation under reduced pressure. The obtained polymer was vacuum-dried at 60 °C for at least 6 h. The degree of substitution to the imidazolium moieties was determined by ¹H NMR analysis.

Characterization

The molecular weight distribution (MWD) of polymers in chloroform was measured at 40 °C using gel permeation chromatography (GPC) with polystyrene gel columns [Tosoh TSKgel GMH_{HR}-M × 2 (exclusion limit molecular weight = 4×10^6 ; bead size = 5 μ m; column size = 7.8 mm i.d. × 300 nm; flow rate = 1.0 mL min⁻¹)] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average

molecular weight (M_w/M_n)] were calculated from the chromatograph with respect to 16 polystyrene standards (Tosoh; 292–1.09 × 10⁶, $M_w/M_n \leq 1.1$). The absolute molecular weight was determined using a GPC system composed of a pump (Viscotek VE 1122), two polystyrene gel columns [TSKgel GMH_{HR}-M × 2; flow rate = 0.7 mL min⁻¹], and Viscotek TDA 305 triple detector [refractive index detector, laser light scattering detector ($\lambda = 670$ nm, 90° and 7°; RALS and LALS), and differential pressure viscometer]. ¹H NMR spectra were recorded using JEOL ECA500 (500 MHz) spectrometer at 30 °C. The particle size was measured by dynamic light scattering (DLS; Otsuka Electronics FPAR-1000HG, $\lambda = 632.8$ nm, scattering angle = 90°). The dynamic viscoelasticity measurement was performed with the stress-controlled rheometer MCR302 (Anton Paar) using a cone-plate with a diameter of 40 mm and an angle of 4°. For the dynamic viscoelastic measurements, the angular frequency sweep tests were carried out from 0.1 to 100 rad s⁻¹.



Figure S1. ${}^{1}\text{H}-{}^{1}\text{H}$ COSY NMR spectrum of poly(CEVE): $M_{n}(\text{GPC}) = 1.0 \times 10^{3}$, $M_{w}/M_{n}(\text{GPC}) = 1.23$ ([CEVE]₀ = 0.040 M, [IBEA]₀ = 4.0 mM, [Et_{1.5}AlCl_{1.5}]₀ = 20 mM, [1,4-dioxane] = 1.2 M in toluene at 30 °C); in CDCl₃ at 30 °C

Note for Figure S1

A peak at 5.6–5.7 ppm (†) is correlated to a peak (10) assigned to the acetal structure, which likely indicates that a part of the elimination of 2-chloroalcohol from a main chain occurred near the ω -end.





Figure S2. ¹H–¹³C HSQC of NMR spectrum of poly(CEVE): $M_n(GPC) = 1.0 \times 10^3$, $M_w/M_n(GPC) = 1.23$ ([CEVE]₀ = 0.040 M, [IBEA]₀ = 4.0 mM, [Et_{1.5}AlCl_{1.5}]₀ = 20 mM, [1,4-dioxane] = 1.2 M in toluene at 30 °C); in CDCl₃ at 30 °C; *solvent.



Figure S3. ¹H–¹³C HMBC NMR spectrum of poly(CEVE): $M_n(\text{GPC}) = 1.0 \times 10^3$, $M_w/M_n(\text{GPC}) = 1.23$ ([CEVE]₀ = 0.040 M, [IBEA]₀ = 4.0 mM, [Et_{1.5}AlCl_{1.5}]₀ = 20 mM, [1,4-dioxane] = 1.2 M in toluene at 30 °C); in CDCl₃ at 30 °C; *solvent.



Figure S4. ¹H NMR spectrum of poly(CEVE): $M_n(GPC) = 3.0 \times 10^3$, $M_w/M_n(GPC) = 1.08$ ([CEVE]₀ = 0.12 M, [IBEA]₀ = 4.0 mM, [Et_{1.5}AlCl_{1.5}]₀ = 20 mM, [1,4-dioxane] = 1.2 M in toluene at 0 °C); in CDCl₃ at 30 °C; * toluene, water.



Figure S5. Generation of an IBVE–HCl adduct through an exchange reaction between the acetoxy group of IBEA and a chlorine atom in $Et_{1.5}AlCl_{1.5}$.^{S2}

Table S1. Synthesis of poly(IBVE-*b*-CEVE)s with various lengths of IBVE and CEVE segments by living cationic copolymerization a

| Entry | IBVE | CEVE | $M_{\rm n}({ m GPC}) 	imes 10^{3 b}$ | $M_{\rm w}/M_{\rm n}({ m GPC})^{b}$ |
|-------|------|------|--------------------------------------|-------------------------------------|
| 1 | 50 | 400 | 47.1 | 1.06 |
| 2 | 50 | 600 | 59.4 | 1.03 |
| 3 | 50 | 800 | 68.5 | 1.04 |
| 4 | 100 | 400 | 49.5 | 1.05 |
| 5 | 200 | 50 | 26.2 | 1.05 |
| 6 | 200 | 100 | 30.3 | 1.05 |
| 7 | 200 | 200 | 39.0 | 1.05 |
| 8 | 200 | 400 | 59.3 | 1.05 |

^{*a*} [IBVE]₀ = 0.20-0.80 M, [CEVE]_{add} = 0.20-3.2 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.

^b Determined by GPC in chloroform on the basis of polystyrene calibration.



Figure S6. MWD curves of IBVE-*b*-CEVE (the entries correspond to those listed in Table S1).



Figure S7. M_n and M_w/M_n values of the products obtained with TiCl₄: [IBVE]₀ = 0.40 M, [CEVE]_{add} = 1.6 M, [IBEA]₀ = 4.0 mM, [TiCl₄]₀/[SnCl₄]₀/[DTBP]₀ = 5.0 mM/10 mM/10 mM and [ethyl acetate] = 1.0 M in toluene at 0 °C.

| Entry | $IBVE_{50}$ - <i>b</i> - $[Me_2Im][BF_4]_m$ | Introduction |
|-------|---|------------------------------------|
| | m = | rate ^{a} (%) |
| 1 | 200 | ~100 |
| 2 | 400 | 97 |
| 3 | 600 | 99 |
| 4 | 800 | ~100 |

Table S2. Introduction rates of the 1,2-dimethylimidazolium moieties into the side chains of IBVE*b*-CEVE copolymers.

^a Determined by ¹H NMR spectra of copolymers before and after chemical modifications.



Figure S8. ¹H NMR spectra of (A) $IBVE_{50}$ -b- $CEVE_{400}$ in $CDCl_3$ at 30 °C, (B) $IBVE_{50}$ -b- $[Me_2Im][Cl]_{400}$ in DMSO- d_6 at 100 °C and (C) $IBVE_{50}$ -b- $[Me_2Im][BF_4]_{400}$ in DMSO- d_6 at 100 °C; * solvent, toluene, H₂O, DMSO, acetone.

Note for Figure S8

Anion exchange was confirmed by the peak shift of the protons on the 4 and 5-positions of an imidazolium ring from 8.0 ppm (Figure S8B) to 7.5 ppm (Figure S8C).



Figure S9. Turbidity measurement (scan rate: 1 °C/min) of (A) 1 wt% (black) or 2 wt% (red) aqueous solution of IBVE₅₀-*b*-[Me₂Im][BF₄]₄₀₀ (wavelength: 500 nm), (B) 1 wt% aqueous solution of IBVE₅₀-*b*-[Me₂Im][BF₄]₄₀₀ at different wavelengths [500 (black), 600 (red), 700 (blue), and 800 (green) nm], and (C) 2 wt% aqueous solution of [Me₂Im][BF₄]₂₀₀ [M_n (GPC) = 18.2 × 10³, M_w/M_n (GPC) = 1.08 (for precursor polymer)] (wavelength: 500 nm).

Note for Figure S9

The 1 wt% solution was slightly turbid at low temperature and became considerably transparent at approximately 25 °C. In addition, the transmittance of the 2 wt% solution changed more clearly than that of the 1 wt% solution (Figure S9A). The solutions of the IBVE-*b*-[Me₂Im][BF₄] copolymers were considerably transparent at high temperature probably because the micelles were hydrated and did not form large aggregates in the gel. In contrast, the micelles were dehydrated and likely formed large aggregates at low temperature due to the UCST-type thermosensitive property of [Me₂Im][BF₄] segments (see Figure S9C for the thermosensitive property of the poly([Me₂Im][BF₄]₂₀₀). In addition, the wavelength influenced the maximum transmittance of the aqueous solutions of the block copolymer. The transmittance at 800 nm was approximately 80% at high temperature, while the maximum transmittance at 500 nm was approximately 60% (Figure S9B). The formation of not large aggregates but the aggregates with sizes of a few hundreds nanometer, which correspond to sizes of polymer micelles, is likely responsible for the change in transmittance at this wavelength range. The scan rate did not influence the maximum transmittance (data are not shown).



Figure S10. ¹H NMR spectra of 1 wt% solution of $IBVE_{50}$ -*b*- $[Me_2Im][BF_4]_{400}$ (A) in DMSO-*d*₆ at 100 °C and (B) in D₂O at 10 °C.



Figure S11. DLS measurement for 0.01 wt% aqueous solutions of $IBVE-b-[Me_2Im][BF_4]$ with various lengths of $[Me_2Im][BF_4]$ segments.

Note for Figure S11

The micelle diameter of $IBVE_{50}$ -*b*- $[Me_2Im][BF_4]_{800}$ has not be measured appropriately yet. A peak detected in the 0.01 wt% solution corresponded to the size of unimers (approximately 20 nm). In contrast, the 0.03 wt% solution showed a peak of approximately 370 nm, which indicated that $IBVE_{50}$ -*b*- $[Me_2Im][BF_4]_{800}$ most likely formed larger micelles than those derived from the block copolymers with shorter $[Me_2Im][BF_4]$ segments. However, a peak assigned to unimers (approximately 30 nm) was also sometimes detected in addition to the peak assigned to the micelles

in a few dozen times of measurements. Solutions at larger concentrations, such as 0.05 wt%, had too high scattering intensity to be measured. We are currently examining the appropriate measurement conditions.

References and Notes

- S1. S. Aoshima and T. Higashimura, *Macromolecules*, 1989, 22, 1009.
- S2. T. Yoshida, A. Kanazawa, S. Kanaoka and S. Aoshima, J. Polym. Sci., Part A: Polym. Chem., 2005, 43, 4288-4291.