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Supplementary Material

Cluster–Micelle Transition of a Thermo/Photoresponsive ABC Triblock Copolymer in an Ionic Liquid

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Experimental section

Materials

sec-Butyllithium (*sec*-BuLi) was purchased from Kanto Chemical Co. Phosphazene base (*t*-BuP$_4$)/*n*-hexane solution was purchased from Sigma-Aldrich. Ion exchange zeolite KW-2000® was kindly provided by Kyowa Chemical. Styrene (St) and ethylene oxide (EO) were purchased from Wako Chemical and Nippon Ekitan, respectively, and distilled with calcium hydride before use. *N*-isopropylacrylamide (NIPAm) was generously provided by Kojin Corporation and recrystallised twice using toluene as a good solvent and *n*-hexane as a poor solvent. 2,2′-Azobis(isobutyronitrile) (AIBN) was purchased from Wako Chemical and purified by recrystallisation from methanol. 1-Ethylpiperidine hypophosphite (EPHP) was purchased from Sigma–Aldrich. Nitrosobenzene, 4-aminobenzamide, and acetic acid were purchased from TCI. Super dehydrated solvents and other reagents were purchased from Wako Chemical. All chemical reagents were used as received, unless otherwise noted.

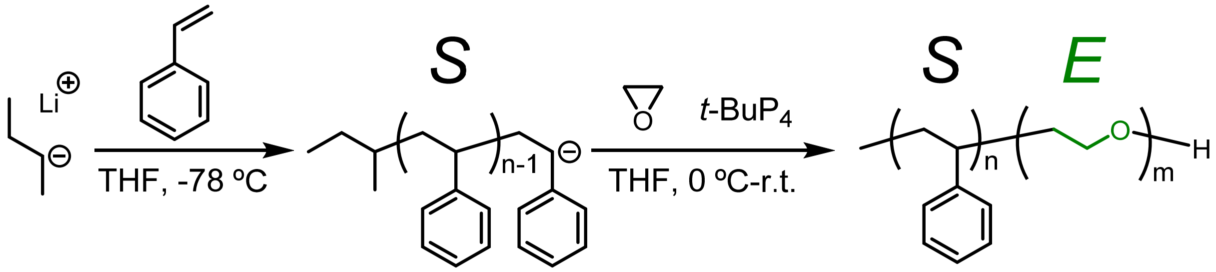
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C$_2$mim][NTf$_2$]),[S1] *S*-1-dodecyl-*S*'-(α,α'-dimethyl-α''-acetic acid)trithiocarbonate (chain transfer agent (CTA)),[S2] *N*-acryloxysuccinimide (NAS)[S3] were synthesized according to previously reported procedures and characterized by ^{1}H-NMR. ^{1}H-NMR spectra (300 MHz, 400 MHz, 500 MHz) were recorded on a Bruker DRX300 spectrometer, a JEOL-ECX400 NMR spectrometer, and a Bruker DRX500 spectrometer, respectively.

Preparation of the ABC Triblock Copolymer (SEAN)

The ABC triblock copolymer, PSt-*b*-PEO-*b*-poly(4-phenylazobenzylacrylamide-*r*-NIPAm) (PSt-*b*-PEO-*b*-P(AzoBnAm-*r*-NIPAm), denoted SEAN) was synthesised using a combination of anionic polymerisation and reversible addition-fragmentation chain transfer (RAFT) polymerisation as described below.

1. Synthesis of polystyrene-*b*-poly(ethylene oxide) (PSt-*b*-PEO, SE)

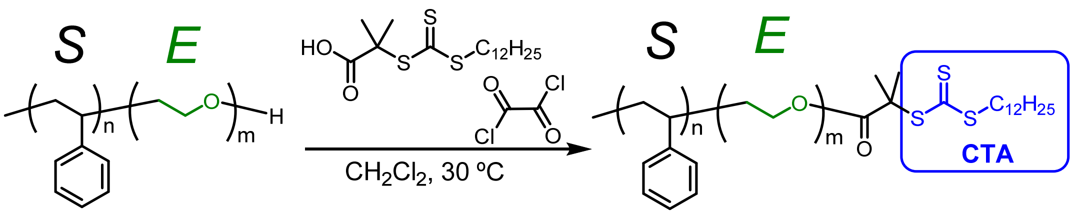
PSt-*b*-PEO was synthesised by anionic polymerisation using *sec*-BuLi as an initiator (**Scheme S1**). Tetrahydrofuran (THF, anhydrous, 100 mL), *sec*-BuLi (2.44 mL, 2.51 mmol), and St (10 mL, 87.0 mmol) were sequentially added to a round-bottom flask filled with Ar at –78 °C and stirred for 1 h. Next, EO (10.28 mL, 529 mmol) and *t*-BuP$_4$ (1 mL, 0.8 mmol) were sequentially added to the flask.[S4,S5] The reaction was carried out in an ice bath. Then, the reaction was allowed to proceed at room temperature for 1 week and quenched with HCl aqueous solution (3 mL, 1 mM). After the evaporation of THF, the resulting solids were dissolved in toluene with KW-2000® to trap the lithium salt, and the solution was stirred for 1 day, followed by filtration to remove of the KW-2000®. The resulting solution was purified by reprecipitation using *n*-hexane as a poor solvent. Reprecipitation was repeatedly carried out with THF as the good solvent and *n*-hexane as the poor solvent. The obtained white powder was dried under vacuum at 35 °C overnight.



Scheme S1 Synthetic procedure for PSt-*b*-PEO (SE) diblock copolymer by anionic polymerisation.

2. Synthesis of polystyrene-*b*-poly(ethylene oxide) macroinitiator (SE-CTA)

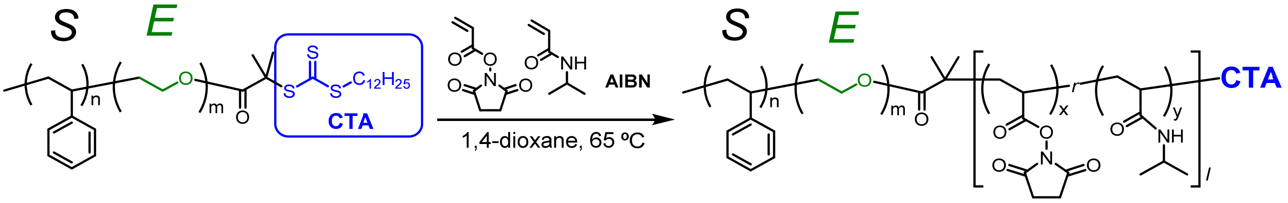
The macroinitiator for RAFT polymerisation was prepared by the modification of the hydroxyl end groups of SE with the CTA (**Scheme S2**). Oxalyl chloride (0.7 mL, 8.91 mmol) and the CTA (0.541 g, 1.48 mmol) were dissolved in dichloromethane (anhydrous, 25 mL) under an Ar atmosphere and stirred for 2 h at 30 °C. By-products, such as CO, CO_2, and HCl, were then removed under vacuum. The residue was dissolved in dichloromethane (anhydrous, 10 mL) again, followed by the addition of SE (5.00 g, 0.291 mmol) dissolved in dichloromethane (anhydrous, 50 mL). The SE was dried by azeotropic distillation with toluene before use. The reaction proceeded for 15 h at 30 °C. The resulting solution was reprecipitated twice using THF/*n*-hexane, and the precipitate was dried in a vacuum at 35 °C overnight.



Scheme S2 Modification of SE with the CTA.

3. Synthesis of polystyrene-*b*-poly(ethylene oxide)-*b*-poly(*N*-acryloyloxysuccinimide-*r*-*N*-isopropylacrylamide) (SE-*b*-P(NAS-*r*-NIPAm), SENN)

RAFT polymerisation of P(NAS-*r*-NIPAm) from the SE-CTA macroinitiator was conducted as follows (**Scheme S3**). SE-CTA (0.966 g, 0.0570 mmol), NAS (86.8 mg, 0.513 mmol), and NIPAm (0.495 g, 4.37 mmol) ([NAS]/[NIPAm] = 10/90 by mol%) were dissolved in 1,4-dioxane (2 mL) in a round-bottom flask filled with Ar. The mixture was degassed by Ar bubbling for 30 min at room temperature. AIBN (0.011 mmol) dissolved in 1,4-dioxane (0.94 mL) was also degassed and added to the mixture. RAFT polymerisation was carried out at 65 °C for 28 h and quenched by contact with air. The product was reprecipitated three times using THF as a good solvent and *n*-hexane as a poor solvent. The precipitate was dried under vacuum at 35 °C overnight, and the ABC triblock copolymer, SENN-CTA was obtained as a light-yellow powder (conversion: NAS 59.8%, NIPAm 54.1%).

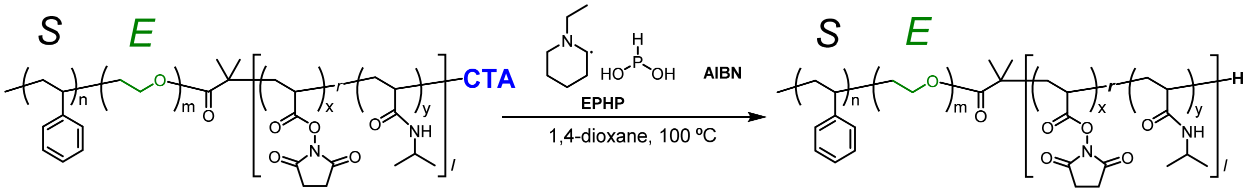


Scheme S3 Synthetic procedure of P(NAS-*r*-NIPAm) via RAFT polymerisation from the SE macroinitiator.

4. Elimination of CTA from SENN-CTA

The dodecyltrithiocarbonate moiety derived from the CTA attached to the polymer terminal was removed as follows (**Scheme S4**). SENN-CTA (0.662 g, 0.0310 mmol) and EPHP (30 mg, 0.124 mmol) were dissolved in 1,4-dioxane (5 mL) and degassed by Ar bubbling. Then, a degassed

AIBN/1,4-dioxane solution (2.2 mL, AIBN:0.0078 mmol) was added to the solution. The cleavage reaction was carried out at 100 °C for 3 h under an Ar atmosphere. The product was purified by repetitive reprecipitation using THF/*n*-hexane. A white powder was obtained after drying under vacuum at 35 °C overnight.

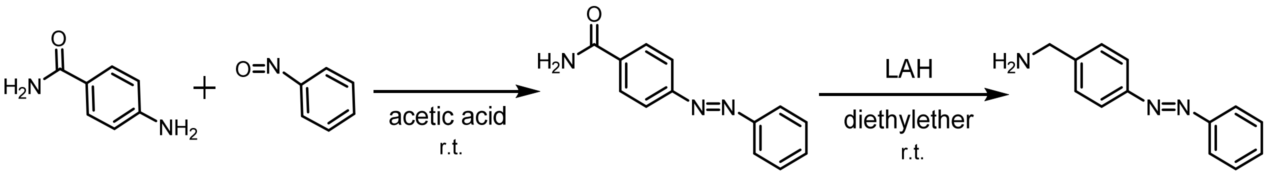


Scheme S4 Elimination of CTA from SENN-CTA after RAFT polymerisation.

5. Synthesis of 4-phenylazobenzyl methanamine (azoamine)

Azoamine was synthesised by the Mills reaction,[S6] followed by reduction using lithium aluminium hydride (LAH)[S7] (**Scheme S5**). Nitrosobenzene (5.24 g, 49.0 mmol) and 4-aminobenzamide (6.05 g, 44.0 mmol) were mixed in acetic acid (50 mL) and stirred at room temperature for 24 h to synthesise azoamide, the precursor of azoamine, by the Mills reaction. The residual solid was collected by filtration and washed with cold ethanol to yield an orange powder. The product, azoamide (3.00 g, 13.3 mmol), was dissolved in diethyl ether (dehydrated, 30 mL), and a suspension of lithium aluminium hydride (3.03 g, 79.7 mmol) in diethyl ether (dehydrated, 25 mL) was added to the solution. The solution was stirred in a round-bottom flask under Ar gas flow for 3 h at room temperature. H_2O (3 mL), 15 wt% NaOH aq. (3 mL), and H_2O (9 mL) were sequentially dropped into the flask slowly to stop the reaction. The solution was filtered and washed with water five times. The solution was dehydrated by sodium sulfate, followed by concentration by evaporation.

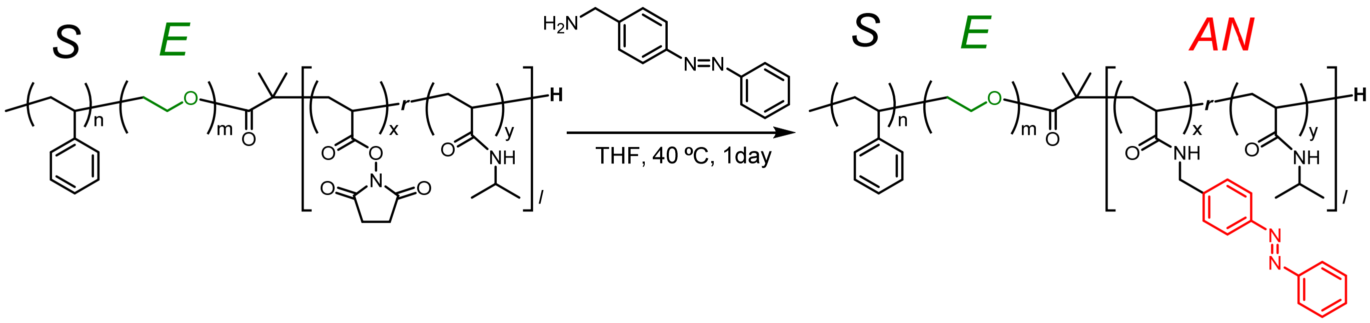
The solid was purified by column chromatography using silica gel 60N (spherical, neutral) as a stationary phase and chloroform as a mobile phase (insoluble substances in chloroform were removed by filtration beforehand). The thin layer chromatography (TLC) showed three spots. Azoamine, corresponding to the second spot, was collected. The solution was concentrated by evaporation and subsequently dried under vacuum at room temperature to obtain orange azoamine.



Scheme S5 Synthetic procedure of azoamine.

6. Synthesis of SE-*b*-P(AzoBnAm-*r*-NIPAm) (SEAN)

The succinimide moiety of SENN was exploited to introduce the azobenzene moiety by reaction with azoamine (**Scheme S6**). SENN (0.20 g, 0.091 mmol) and azoamine (45 mg, 0.19 mmol) were dissolved in THF (3 mL), and the reaction was carried out at 40 °C for 24h under an Ar atmosphere. The product was purified by reprecipitation using THF/*n*-hexane, followed by drying under vacuum at 35 °C to obtain orange SEAN.



Scheme S6 Synthesis of SEAN through the amidation reaction of NAS with azoamine.

Photoirradiation

A 500-W high-pressure mercury lamp (Ushio Optical Modulex USH-500SC, BA-H500) was used as the light source. A bandpass filter was used to adjust the wavelength of irradiated light (366 nm with 8 mW cm^{-2}). A heat-absorbing filter was also used to reduce the heat generated by the mercury lamp.[S8]

Turbidity Measurements

3 wt% SEAN/[C_2mim][NTf_2] solution was obtained by a conventional cosolvent method. An appropriate amount of SEAN and [C_2mim][NTf_2] were dissolved in THF, followed by evaporating the THF. SEAN/[C_2mim][NTf_2] solution was placed on a glass plate (PYREX® 7740 GLASS CELL, Type S15-G-1). The optical path length for the turbidity measurements was 1 mm. The glass plate was placed on a hot stage (Imoto), which enabled temperature control. The transmittance of the solution was monitored at 600 nm, using Ocean Optics LS-1 tungsten halogen light source and an Ocean Optics USB-2000 fiber optic spectrometer at a cooling rate of 0.1 °C/min. The cloud point was defined as the temperature at which the transmission dropped to 50%. During the measurements for P(*cis*-AzoBnAm-*r*-NIPAm), UV light was continuously irradiated on the SEAN solution to minimize the effect of thermal *cis*-to-*trans* relaxation.

Dynamic light scattering (DLS) measurements

The mixture of SEAN and $[C_2mim][NTf_2]$ dissolved in THF was passed through 0.20-μm filters to remove dust, followed by drying under vacuum at 60 °C for 12 h to evaporate the THF. About 2 mL SEAN solution was added into sample tube (depth: 120 mm, calibre: 12 mm, ASAHI GLASS, Japan). DLS measurements were performed on an Otsuka Electronic DLS-8000 equipped with an ALV digital correlator. A He–Ne laser (632.8 nm) was used as the light source because the wavelength of the He–Ne laser does not overlap with the absorption wavelength of azobenzene. Experiments were performed at various temperatures (5–60 °C). When observing the micelle-cluster transition under UV, UV light was constantly irradiated from above the sample tube during temperature change. The optical path length for the DLS was approximately 2 cm. The second-order autocorrelation functions ($g^{(2)}(t)$) were recorded for 100 s at a scattering angle of 90°. The electric field correlation function ($g^{(1)}(t)$) was obtained by converting $g^{(2)}(t)$ using the Siegert relationship.[S9]

When a solution contains polydisperse particles, $g^{(1)}(t)$ can be described using the decay rate distribution function $G(\Gamma)$, as shown in Eq. (1).

$$g^{(1)}(t) = \int_0^\infty G(\Gamma)e^{-\Gamma t}\,d\Gamma \tag{1}$$

$G(\Gamma)$ was first obtained by CONTIN analysis [S10] based on the fact that $g^{(1)}(t)$ corresponds to the Laplace transform of $G(\Gamma)$.

When the CONTIN analysis indicated that the solution contained only unimodally dispersed particles, the decay rate Γ was analysed by the cumulant method, as shown in Eq. (2).[S11]

$$g^{(1)}(t) = A\exp(-\Gamma t)[1 + (1/2!)\mu_2 t^2 + (1/3!)\mu_3 t^3] \tag{2}$$

Here, μ_2/Γ^2 represents the width of the distribution. In contrast, when a bimodal distribution was determined by CONTIN analysis, Γ was obtained by double exponential analysis.

$$g^{(1)}(t) = A_1\exp(-\Gamma_1 t) + A_2\exp(-\Gamma_2 t) \tag{3}$$

R_h can be estimated using the Stokes–Einstein equation (Eq. (4)).

$$R_h = k_B T/6\pi\eta D_0 \tag{4}$$

Here, k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the solvent, and $D_0 = \Gamma/q^2$ (the scattering vector, q, is given by ($4\pi n/\lambda$ sin(θ/2)) is the translational diffusion coefficient.

Cryo-Transmission Electron Microscope (TEM)

1 wt % SEAN in [C_2mim][NTf_2] was diluted with THF and dropped on a TEM copper grid, followed by evaporating THF at room temperature to form thin sample. Then the sample was immersed into liquid ethane (−183 °C) and subsequently plunged to liquid nitrogen (−196 °C) to obtain freeze-dried sample. The measurement was performed on a JEM-2100F transmission electron microscope (JEOL, Japan) at an accelerating voltage of 120 kV. The sample was measured in the dark because of impossible to irradiate by UV light during the TEM measurements.

Figures

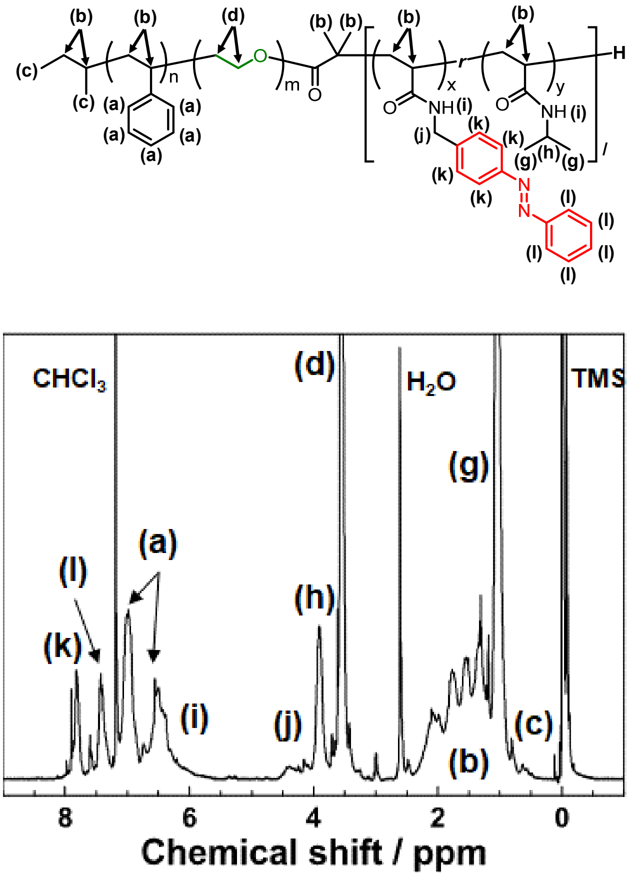


Fig. S1 ^{1}H-NMR spectrum of SEAN in CDCl$_3$.

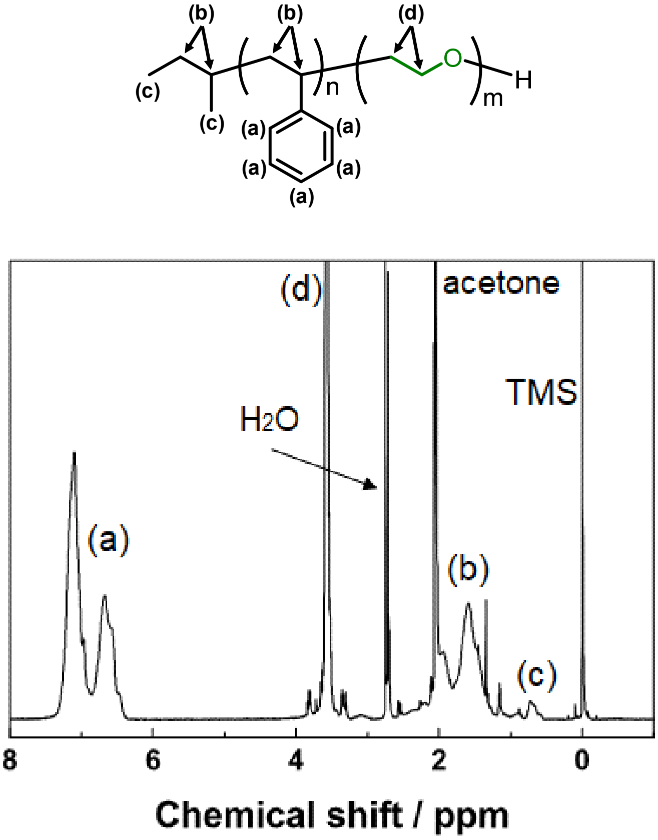


Fig. S2 ^{1}H-NMR spectrum of PSt-*b*-PEO (SE) in acetone-*d*6.

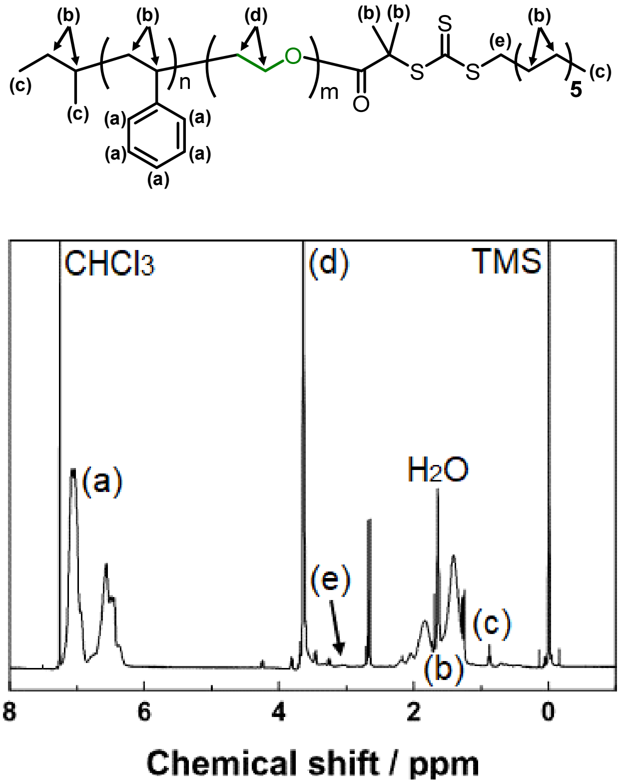


Fig. S3 ^{1}H-NMR spectrum of PSt-*b*-PEO with CTA in $CDCl_3$.

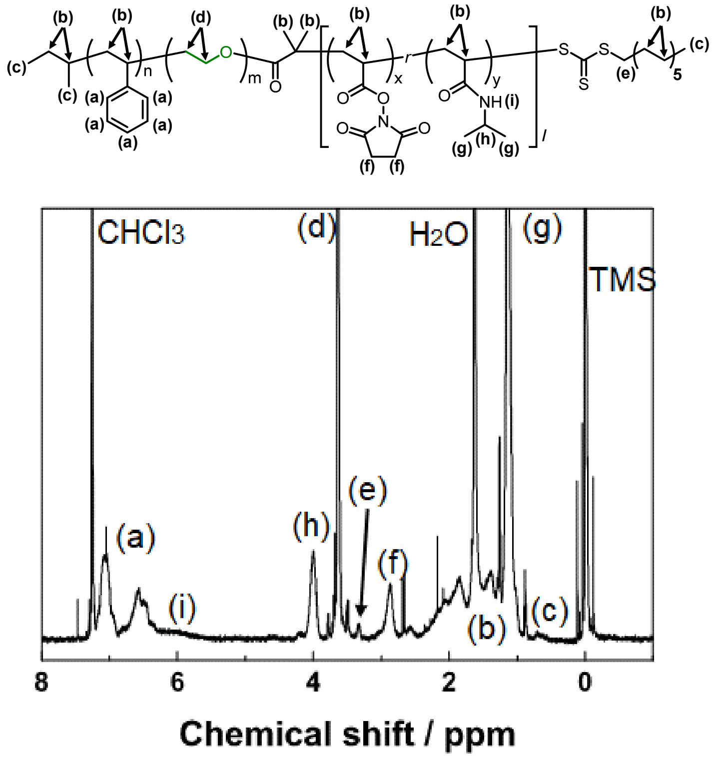


Fig. S4 ^{1}H-NMR spectrum of PSt-*b*-PEO-*b*-P(NAS-*r*-NIPAm) with CTA in $CDCl_3$.

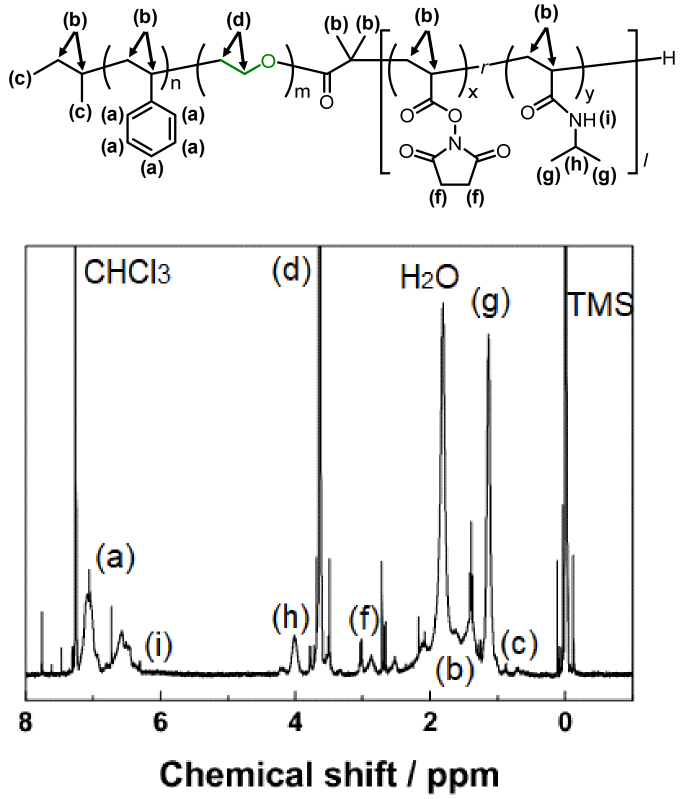


Fig. S5 ^{1}H-NMR spectrum of PSt-*b*-PEO-*b*-P(NAS-*r*-NIPAm) (SENN) in $CDCl_3$.

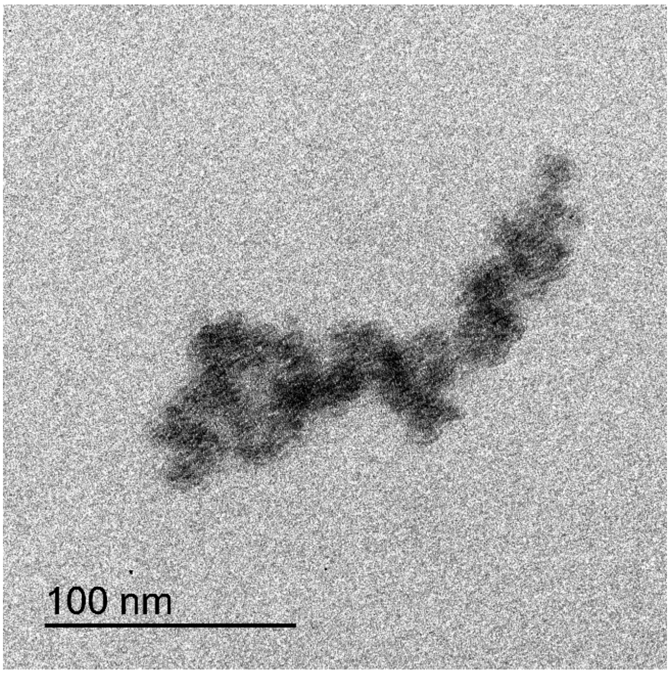


Fig. S6 Cryo-TEM image of 1 wt % SEAN in [C_2mim][NTf_2] quenched by liquid nitrogen.

Reference

[S1] A. Noda, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B* **2001**, *105*, 4603.

[S2] J.T. Lai, D. Filla, R. Shea, *Macromolecules* **2002**, *35*, 6754.

[S3] Z. Wu, *J. Appl. Polym. Sci.* **2008**, *110*, 777.

[S4] H. Dugas, D. Rohe, R. Austin, R.F. Hartman, S.D. Rose, R.F. Hart, F. Heelis, A.G. Cochran, F. Hartman, S.D. Rose, A. Smith, S. Taylor, A. Sancar, S. Jones, et al., **1996**, 3.

[S5] A.A. Toy, S. Reinicke, A.H.E. Müller, H. Schmalz, *Macromolecules* **2007**, *40*, 5241.

[S6] E. Merino, *Chem. Soc. Rev.* **2011**, *40*, 3835.

[S7] T. Shimogaki, S. Oshita, A. Matsumoto, *Macromol. Chem. Phys.* **2011**, *212*, 1767.

[S8] T. Ueki, R. Usui, Y. Kitazawa, T.P. Lodge, M. Watanabe, *Macromolecules* **2015**, *48*, 5928.

[S9] A.J.F. Siegert, *MIT Rad. Lab. Rep.* **1943**, *465*, 1−14.

[S10] S.W. Provencher, *Comput. Phys. Commun.* **1982**, *27*, 229.

[S11] D.E. Koppel, *J. Chem. Phys.* **1972**, *57*, 4814.