Supporting Information

Cationic nano-objects produced by polymerization induced self-assembly using sulfonium-macro chain transfer agents with different counter anions

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Experimental Section

1. Materials.

2,2'-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97 %) was purified by recrystallization from MeOH. Styrene (St, Kanto Chemical, 99%) was purified by distillation under reduced pressure. *N*-Phenylmaleimide (PMI, TCI, > 99%) was purified by recrystallization from MeOH. 2-Cyano-2-propyl dodecyl trithiocarbonate (Sigma-Aldrich, 97%), MeOH (Kanto Chemical, >99.5%), 1,4-dioxane (Kanto Chemical, 99.5 %), *N*,*N*-dimethylformamide (DMF, Kanto Chemical, 99.7%), 2-(methylthio)ethanol (TCI, >98.0%), acryloyl chloride (TCI, >99.0%), triethylamine (TCI, >99.0%), iodomethane (TCI, >99.5%), LiTFSI (TCI, >98.0%), LiOTf (TCI, >98%), NaCl (Kanto Chemical, 99.5%) and other materials were purchased and used without further purification. 2-(Methylthio)ethyl acylate (MTEA) were prepared, according to previously reported procedure.^{1, 2}

2. Instrumentation

¹H NMR spectra were collected on a JEOL JNM-ECX400 (resonance frequency of 400 MHz). Diffusion-ordered NMR spectroscopy (DOSY) was recorded on a JEOL ECZ-600 at a resonant frequency of 600 MHz. The iProbe SmartProbe 5-mm BBFO probe was used. DOSY sequences were acquisitioned using 8 scans of 16 increments. Size-exclusion chromatography (SEC) was performed using a Tosoh HPLC HLC-8220 system equipped with four consecutive hydrophilic vinyl polymerbased gel columns [TSK-GELs (bead size, exclusion limited molecular weight): α -M (13 μ m, > 1 x 10^7), α -4000 (10 μ m, 4 x 10⁵), α -3000 (7 μ m, 9 x 10⁴), α -2500 (7 μ m, 5 x 10³)] and a guard column [TSK-guardcolumn a]. The system was operated with refractive index and ultraviolet detectors at 40 °C at the flow rate of 1.0 mL/min using DMF containing 10 mM LiBr as the mobile phase. The molecular weights and dispersities were evaluated using polystyrene standards (Tosoh, molecular range 1050–1090000) as a calibration. Elemental analysis was carried out on a Perkin-Elmer 2400 II CHNS/O analyzer. Dynamic light scattering (DLS) was performed using a Zetasizer Nano (Sysmex) with a He-Ne laser (633 nm) at a detection angle of 173°. The intensity-averaged hydrodynamic diameters were calculated by the manufacturer's software, utilizing the Stokes-Einstein equation. Zeta potential data in MeOH was collected on a Zetasiser Nano-ZS instrument. Transmission electron microscopy (TEM) measurements were performed on a JEOL TEM-2100F field emission electron microscope at an accelerating voltage of 200 kV. The sample for TEM observation was prepared by mounting a drop of the MeOH dispersion obtained after the dialysis on carbon-coated Cu grids and air-dried at room temperature. In all cases, the samples were not stained, unless otherwise noted. When the sample was stained, a drop of the OsO₄ solution (2.0 wt %) was placed onto the sample located on the carbon-coated Cu grid, followed by air-drying at room temperature.

3.1 Synthesis of 2-(methylthio)ethyl acylate (MTEA)

MTEA was prepared by reaction of acryloyl chloride with 2-(methylthio)ethanol according to a previously reported procedure.^{1, 2} Into a two-necked flask, 2-(methylthio)ethanol (12.6 mL, 0.15 mol), triethylamine (27.3 mL, 0.2 mol), and dry CH₂Cl₂ (150 mL) were added under nitrogen. After the mixture was cooled down to 0 °C, acryloyl chloride (10.7 mL, 0.133 mol) dissolved in 25 mL of dry CH₂Cl₂ was added dropwise to the mixture solution, which was stirred at 25 °C for overnight under nitrogen. After the solvent was removed in vacuo, the crude product was diluted with methylene chloride and extracted with saturated NaCl water, and dried with MgSO₄, filtered, and concentrated. Finally, the product was purified by column chromatography with diethyl ether/hexane (v/v, 9/1) as the eluent to afford MTEA as a transparent liquid (15.3 g, 79 %).

3.2. Synthesis of PMTEA macro-CTA

For the synthesis of PMTEA macro-CTA,² AIBN (16 mg, 0.1 mmol), 2-cyano-2-propyl dodecyl trithiocarbonate (35 mg, 0.2 mmol), MTEA (1.46 g, 10 mmol), and dry DMF (5 mL) were placed in a dry glass ampule equipped with a magnetic stirring bar, and the solution was degassed by three freeze-evacuate-thaw cycles. After sealing the ampule by flame under vacuum, the mixture was stirred at 60 °C for 24 h. The reaction mixture was quenched by immersing the tube in liquid nitrogen, and opened. The resulting polymer was diluted by adding a small amount of DMF, and then dropped into a large excess of a MeOH, and collected by decantation. Then the product was finally dried under vacuum to give PMTEA as a pale yellow viscous material (1.21 g, yield = 81 %). The molecular weight of PMTEA ($M_{n,NMR}$) was determined using proton nuclear magnetic resonance (¹H NMR) spectroscopy by comparison of the peaks at 4.1–4.2 ppm corresponding to the methylene protons adjacent to the ester group (broad, 2H, -COO-CH₂-) in the MTEA repeating unit to that of the peak at 0.8–0.9 ppm corresponding to three protons of the end group (Z-group), as shown in Figure 2a.

3.3. Synthesis of P(MTEA(S⁺)[TFSI⁻]) macro-CTA

P(MTEA(S⁺)[TFSI⁻]) macro-CTA was prepared by quaternization of PMTEA with iodomethane according to a reported procedure³ with some modifications. PMTEMA (430 mg, 3.0 mmol monomer unit, $M_{n,NMR} = 7300$, $M_{n,SEC} = 7000$, $M_w/M_n = 1.18$) dissolved in DMF (10 mL) was placed into a two-necked flask under nitrogen, and then methyl iodide (1.8 mL, 30 mmol, 10 equivalent to the sulfide unit) was added dropwise to the solution. The mixture was stirred at room temperature for 24 h. Afterward, the resulting mixture was dialyzed against 0.03 M LiTFSI (Spectra Pore; MWCO 1000) for 1 day to exchange the counterion to TFSI⁻ and then dialyzed against MeOH for 1 day. The polymer solution was finally dried overnight under vacuum to obtain a pale yellow viscous material (1.06 g, 80 %).

The degree of the substitution was determined using ¹H NMR spectroscopy by comparison of the peaks at 4.5–4.3 ppm, attributed to the methylene protons (2H) of MTEA(S^+)[TFSI⁻] unit, and the peak at 4.2–4.1 ppm, attributed to the methylene protons (2H) of MTEA unit using the following equation (1).

$$\frac{2x}{2(1-x)} = \frac{Integral \ at \ 4.5 - 4.3 \ ppm}{Integral \ at \ 4.2 - 4.1 \ ppm} \ (1)$$

3.4. Synthesis of P(MTEA(S⁺)[OTf⁻]) macro-CTA

For the synthesis of P(MTEA(S⁺)[OTf]) macro-CTA, PMTEMA (430 mg, 3.0 mmol monomer unit, $M_{n,NMR} = 7300$, $M_{n,SEC} = 7000$, $M_w/M_n = 1.18$) dissolved in DMF (10 mL) was placed into a two-necked flask under nitrogen, and then methyl iodide (1.8 mL, 30 mmol, 10 equivalent to the sulfide unit) was added dropwise to the solution. The mixture was stirred at room temperature for 24 h. Afterward, the resulting mixture was dialyzed against 0.03 M LiOTf for 1 day to exchange the counterion to OTf⁻

and then dialyzed against MeOH for 1 day. The polymer solution was finally dried overnight under vacuum to obtain a pale yellow viscous material (612 mg, 66 %).

The degree of the substitution was determined using ¹H NMR spectroscopy by comparison of the peaks at 4.7–4.5 ppm, attributed to the methylene protons (2H) of MTEA(S⁺)[OTf] unit, and the peak at 4.2–4.1 ppm, attributed to the methylene protons (2H) of MTEA unit.

3.5. Synthesis of P(MTEA(S⁺)[Cl⁻]) macro-CTA

For the synthesis of P(MTEA(S⁺)[Cl⁻]) macro-CTA,³ PMTEA (430 mg, 3.0 mmol monomer unit, $M_{n,NMR} = 7300$, $M_{n,SEC} = 7000$, $M_w/M_n = 1.18$) dissolved in DMF (10 mL) was placed into a two-necked flask under nitrogen, and then methyl iodide (1.8 mL, 30 mmol, 10 equivalent to the sulfide unit) was added dropwise to the solution. The mixture was stirred at room temperature for 24 h. Afterward, the resulting mixture was dialyzed against 0.1 M NaCl for 1 day to exchange the counterion to Cl⁻ and then dialyzed against MeOH for 1 day. The polymer solution was finally dried overnight under vacuum to obtain a pale yellow viscous material (299 mg, 51%).

The degree of the substitution was determined using ¹H NMR spectroscopy by comparison of the peaks at 4.6–4.5 ppm, attributed to the methylene protons (2H) of MTEA(S^+)[Cl⁻] unit, and the peak at 4.2–4.1 ppm, attributed to the methylene protons (2H) of MTEA unit.

4.1. Synthesis of P(MTEA(S⁺)[TFSI⁻])-b-P(St-alt-PMI)

For the synthesis of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI)s, RAFT dispersion polymerizations were was conducted using St and PMI. In a typical protocol, the trithiocarbonate-terminated P(MTEA(S⁺)[TFSI⁻] ($M_{n.calcd} = 21500, 105 \text{ mg}, 0.005 \text{ mmol}$), St (104 mg, 1.0 mmol), PMI (173 mg, 1.0 mmol), AIBN (0.16 mg, 0.001 mmol), and MeOH/1,4-dioxane (1.35 mL/0.44 mL, corresponding to 1.07 g/0.45 g, solid content = 20 wt%) were placed in a dry glass ampule and degassed. The mixture was stirred at 80 °C for 3 h. Conversion was determined by the integration of the monomer C=C-H resonance (1H) at around 5.8 ppm compared with the sum of aromatic peak intensities (5H from St and 5H from PMI) of the copolymer and the monomers at around 6.4–7.4 ppm, using the following equation (2).

x (%) = (Integral at 7.4-6.4 ppm–10×Integral at 5.8 ppm)/(Integral at 7.4-6.4 ppm)×100 (2)

After the purification via dialysis (Spectra Pore; MWCO 1000) with MeOH for 3 d, ¹H NMR and gravimetry measurements were conducted. The targeted P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI) was obtained as a white solid (0.294 g, yield = 77 %). The copolymer composition was determined by ¹H NMR spectroscopy by comparison of the peaks at 4.1–4.5 ppm, attributed to the methylene protons (2H) of MTEA(S⁺), and the peak at 6.4–7.4 ppm, attributed to the aromatic protons (10H) of St and PMI in CDCl₃/DMSO-*d*₆ = 1/1, using the following equation (3).

$$\frac{10x}{2(1-x)} = \frac{Integral \ at \ 7.4 - 6.4 \ ppm}{Integral \ at \ 4.5 - 4.1 \ ppm} \quad (3)$$

Where x is the fraction of St and PMI and 1 - x is the fraction of MTEA(S⁺)[TFSI⁻] in the copolymer.

For the sample preparation of DLS and TEM measurements, after the dialysis, a small portion of the dispersion was taken and diluted with MeOH (typically 10 times of the original volume). Same protocols were employed for RAFT dispersion polymerization using different macro-CTAs.

4.2. Synthesis of P(MTEA(S⁺)[OTf])-b-P(St-alt-PMI)

In a typical protocol, the trithiocarbonate-terminated P(MTEA(S⁺)[OTf]) ($M_{n.calcd} = 15200, 76.2 \text{ mg}, 0.005 \text{ mmol}$), St (104 mg, 1.0 mmol), PMI (173 mg, 1.0 mmol), AIBN (0.16 mg, 0.001 mmol), and MeOH/1,4-dioxane (1.15mL/0.39 mL, corresponding to 0.91 g/0.40 g, solid content = 20 wt%) were placed in a dry glass ampule and degassed. The mixture was stirred at 80 °C for 3 h. After the purification via dialysis with MeOH for 3 d, the targeted P(MTEA(S⁺)[OTf])-*b*-P(St-*alt*-PMI) was obtained as a white solid (0.113 g, yield = 32 %). The copolymer composition was calculated by the nitrogen content determined by elemental analysis (equation 4).

Wt of nitrogen (%)

$$= \frac{DP \text{ of second monomer} \times MW \text{ of nitrogen}}{DP \text{ of second monomer} \times MW \text{ of } (St \text{ and } PMI) + M_n \text{ of } P(MTEA(S^+)[OTf^-])} \times 100 \text{ (4)}$$

4.3. Synthesis of P(MTEA(S⁺)[Cl⁻])-*b*-P(St-*alt*-PMI)

In a typical protocol, the trithiocarbonate-terminated P(MTEA(S⁺)[Cl⁻]) ($M_{n,calcd} = 9800, 49 \text{ mg}, 0.005 \text{ mmol}$), St (104 mg, 1.0 mmol), PMI (173 mg, 1.0 mmol), AIBN (0.16 mg, 0.001 mmol), and MeOH/1,4-dioxane (1.15mL/0.38 mL, corresponding to 0.91 g/0.39 g, solid content = 20 wt%) were placed in a dry glass ampule and degassed. The mixture was stirred at 80 °C for 3 h. After the purification via dialysis with MeOH for 3 d, the targeted P(MTEA(S⁺)[Cl⁻])-*b*-P(St-*alt*-PMI) was obtained as a white solid (0.111 g, yield = 34 %). The copolymer composition was determined by ¹H NMR spectroscopy by comparison of the peaks at 4.1–4.6 ppm, attributed to the methylene protons (2H) of MTEA(S⁺), and the peak at 6.4–7.4 ppm, attributed to the aromatic protons (10H) of St and PMI in CD₂Cl₂, using the following equation (5).

$$\frac{10x}{2(1-x)} = \frac{Integral at 7.4 - 6.4 \, ppm}{Integral at 4.6 - 4.1 \, ppm} \tag{5}$$

Where x is the fraction of St and PMI and 1 - x is the fraction of MTEA(S⁺)[Cl⁻] in the copolymer.

4.4. Synthesis of P(MTEA(S⁺)[TFSI⁻])-b-PSt

In a typical protocol, the trithiocarbonate-terminated P(MTEA(S⁺)[TFSI⁻] ($M_{n.calcd}$ = 21500, 105 mg, 0.005 mmol), St (208 mg, 2.0 mmol), AIBN (0.16 mg, 0.001 mmol), and MeOH (1.58 mL, corresponding to 1.25 g, solid content = 20 wt%) were placed in a dry glass ampule and degassed. The mixture was stirred at 80 °C for 24 h. After the purification via dialysis with MeOH for 3 d, the targeted P(MTEA(S⁺)[TFSI⁻])-*b*-PSt was obtained as a white solid (0.066 g, yield = 21 %). The copolymer composition was determined by ¹H NMR spectroscopy by comparison of the peaks at 4.1–4.5 ppm, attributed to the methylene protons (2H) of MTEA(S⁺), and the peak at 6.4–7.4 ppm, attributed to the aromatic protons (5H) of St in CDCl₃/DMSO-*d*₆ = 1/1, using the following equation (6).

$$\frac{5x}{2(1-x)} = \frac{Integral \ at \ 7.4 - 6.4 \ ppm}{Integral \ at \ 4.5 - 4.1 \ ppm} \tag{6}$$

Where x is the fraction of St and 1 - x is the fraction of MTEA(S⁺)[TFSI⁻] in the copolymer.

4.5. Synthesis of PMTEA-b-P(St-alt-PMI)

In a typical protocol, the trithiocarbonate-terminated PMTEA ($M_{n.calcd} = 6600, 66 \text{ mg}, 0.01 \text{ mmol}$), St (208 mg, 2.0 mmol), PMI (346 mg, 2.0 mmol), AIBN (0.32 mg, 0.002 mmol), and MeOH/1,4-dioxane (2.14 mL/0.72 mL, corresponding to 1.69 g/0.76 g, solid content = 20 wt%) were placed in a dry glass ampule and degassed. The mixture was stirred at 80 °C for 3 h. After the purification via dialysis with MeOH for 3 d, the targeted PMTEA-*b*-P(St-*alt*-PMI) was obtained as a white solid (0.167 g, yield = 27 %). The copolymer composition was determined by ¹H NMR spectroscopy by comparison of the peaks at 4.2–4.1 ppm, attributed to the methylene protons (2H) of MTEA, and the peak at 6.4–7.4 ppm, attributed to the aromatic protons (10H) of St and PMI in CD₂Cl₂, using the following equation (7).

$$\frac{10x}{2(1-x)} = \frac{Integral at 7.4 - 6.4 ppm}{Integral at 4.2 - 4.1 ppm}$$
(7)

Where x is the fraction of St and PMI and 1 - x is the fraction of MTEA in the copolymer.



Figure S1. ¹H NMR spectrum of MTEA in CD₂Cl₂.

Dum [Conv. ^{b)}	Yield ^{c)}	$M_{\rm n}{}^{\rm b)}$	$M_{ m n}{}^{ m d)}$	$M_{ m w}/M_{ m n}{}^{ m d)}$
Kuii		(%)	(%)	(¹ H NMR) (SEC)	(SEC)	(SEC)
1	1/4/100	98	60	5,400	5,300	1.11
2	1/2/100	>99	58	7,300	6,600	1.12
3	1/1/100	>99	71	26,000	14,000	1.23

Table S1. Synthesis of PMTEAs by RAFT polymerization of MTEA in DMF at 60 °C for 24 h ^{a)}

^{a)} Polymerization with AIBN and 2-cyano-2-propyl dodecyl trithiocarbonate in DMF (conc. = 20 wt%). ^{b)} Calculated by ¹H NMR in CDCl₃. ^{c)} Methanol insoluble part. ^{d)} Measured by SEC using polystyrene standard in DMF (10 mM LiBr).



Figure S2. SEC curves of PMTEAs prepared by RAFT polymerization in DMF at 60 °C for 24 h.

Due	Time	Conv. ^{b)}	Yield ^{c)}	$M_n^{b)}$	$M_{\rm n}{}^{\rm d)}$	$M_{\rm w}/M_{\rm n}$ ^{d)}
Kull	(h)	(%)	(%)	(¹ H NMR)	(SEC)	(SEC)
1	6	87	57	7,300	7,000	1.18
2	12	96	57	7,000	8,200	1.15
3	24	>99	58	7,300	6,600	1.12

Table S2. Synthesis of PMTEAs by RAFT polymerization of MTEA in DMF at 60 °C ^{a)}

^{a)} $[I]_0/[CTA]_0/[M]_0 = 1/2/100$, CTA: 2-cyano-2-propyl dodecyl trithiocarbonate, solvent = DMF (conc. = 20 wt%). ^{b)} Calculated by ¹H NMR in CDCl₃. ^{c)} Methanol insoluble part. ^{d)} Measured by SEC using polystyrene standard in DMF (10 mM LiBr).



Figure S3. SEC curves of PMTEAs prepared by RAFT polymerization in DMF at 60 °C for 6–24 h.

 Table S3. Solubility of PMTEA at room temperature ^{a)}

Hexane	Toluene	CHCl ₃	CH ₂ Cl ₂	Acetone	THF	AcOEt
-	+	+	+	+	+	+
МеОН	EtOH	1,4-dioxane	DMSO	DMF	H ₂ O	
-	-	+	+	+	-	

^{a)} +: Soluble, -: Insoluble

Table S4. Solubility of PMTEA in MeOH:1,4-dioxane and MeOH:DMF mixed solvents at room temperature ^{a)}

	9:1	8:2	7:3	6:4	5:5
MeOH : 1,4-dioxane	-	-	-	-	+
MeOH : DMF	-	-	-	-	+

^{a)} +: Soluble, -: Insoluble

Run	Metal salt	Yield ^{b)} (%)	Degree of substitution ^{c)} (%)
1	LiTFSI	80	>99
2	LiOTf	66	>99
3	NaCl	51	>99

Table S5. Preparation of $P(MTEA(S^+)[R^-])$ by tertiaryisation of PMTEA^{a)}

^{a)} Reaction of PMTEA ($M_n = 7300$, $M_w/M_n = 1.18$) with iodomethane (CH₃I/thioether = 10 equivalent to the sulfide unit) at room temperature for 24 h. ^{b)} Dialyzed against metal salt (conc. = 0.03–0.1 M) containing water for 1 day and MeOH for 1 day. ^{c)} Calculated by ¹H NMR in DMSO- d_6 and D₂O.

Table S6. Solubility of $P(MTEA(S^+)[R^-])$ at room temperature ^{a)}

	MeOH	1,4-dioxane ^{b)}	H ₂ O	DMSO	CHCl ₃
P(MTEA(S ⁺)[TFSI ⁻])	+	-	-	+	+
P(MTEA(S ⁺)[OTf])	+	-	+	-	-
P(MTEA(S ⁺)[Cl ⁻])	+	-	+	-	-

^{a)} +: Soluble, -: Insoluble. ^{b)} Soluble under diluted condition (20 wt%) by ultrasonication.

Run	[I] ₀ /[macro- CTA] ₀ /[M] ₀	Time (h)	Conv. ^{b)} (%)	Yield (%)	n: m ^{b)} (¹ H NMR)	$M_{\rm n}^{\rm b)}$ (¹ H NMR)	$D_{\rm h}^{\rm c)}$ (nm)	Zeta potential (mV)
1	1/5/2000	24	59	21	48: 320	54,000	91, 546	+21.0
2	1/5/1000		40	18	48: 123	34,000	38	+35.2
3	1/5/2000		62	41	48: 319	54,000	89, 495	+26.9
4	1/5/6000	48	83	31	48: 829	107,000	195	+37.2
5	1/5/8000		77	30	48: 1782	207,000	161	+26.4
6	1/5/10000		80	26	48: 2464	277,000	101	+41.8

Table S7. Synthesis of P(MTEA(S⁺)[TFSI⁻])-*b*-PSts in MeOH at 80 °C^{a)}

^{a)} [I]₀/[macro-CTA]₀/[St]₀ = 1/5/1000-10000, solvent = MeOH, conc.= 20 wt%, macro-CTA: $M_n = 21500$. ^{b)} Calculated by ¹H NMR in CDCl₃: DMSO- $d_6 = 1:1$. ^{c)} Measured by DLS in MeOH.



Figure S4. TEM images of P(MTEA(S⁺)[TFSI⁻])-*b*-PSts obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[M] = (a) 1/5/1000 and (b) 1/5/8000 (conc. = 20 wt%) using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$) for 48 h.



Figure S5. DLS traces of P(MTEA(S⁺)[TFSI⁻])-*b*-PSts obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St] = 1/5/1000-10000 (conc. = 20 wt%) using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$) for 24 h and 48 h (see Table S7).



Figure S6. Turbidity changes of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI)s at (a) 10 wt% and (b) 20 wt%.



Figure S7. ¹H NMR spectra of P(MTEA(S⁺)[TFSI⁻]) in DMSO- d_6 and P(MTEA(S⁺)[TFSI⁻])-b-P(Stalt-PMI) in CDCl₃:DMSO- $d_6 = 1:1$.



Figure S8. DOSY NMR spectrum of $P(MTEA(S^+)[TFSI^-])$ in CDCl₃:DMSO- $d_6 = 1:1$.



Figure S9. DOSY NMR spectrum of $P(MTEA(S^+)[TFSI^-])-b-P(St-alt-PMI)$ in CDCl₃:DMSO- $d_6 = 1:1$.



Figure S10. (a) Time-conversion and (b) First-order kinetic plots for RAFT dispersion polymerization of St/PMI using $P(MTEA(S^+)[TFSI^-])$ macro-CTA at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000, solvent = methanol:1,4-dioxane = 7:3 (w/w, solid content = 5–20 wt%).



Figure S11. DLS traces of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 at (a) 10 wt% and (b) 20 wt% for 0.5–3 h using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$).

Run	Time (h)	Conv. ^{b)} (%)	Yield (%)	n: m ^{b)} (¹ H NMR)	$M_{\rm n}^{ m b)}$ (¹ H NMR)	$D_{\rm h}^{\rm c)}$ (nm)	Zeta potential (mV)
1	6	97	43	48/197	75,000	247, 3665	+36.8
2	24	98	43	48/206	77,000	718	+26.8

Table S8. Synthesis of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI) at 80 °C^{a)}

^{a)} [I]₀/[macro-CTA]₀/[St]₀/[PMI]₀ = 1/5/1000/1000, solvent = MeOH:1,4-dioxane = 7:3, conc.= 20 wt%, macro-CTA: M_n = 21500. ^{b)} Calculated by ¹H NMR in CDCl₃:DMSO- d_6 = 1:1. ^{c)} Measured by DLS in MeOH.



Figure S12. TEM image of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI) obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (conc. = 20 wt%) for (a, b) 6 h and (c, d) 24 h using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$).



Figure S13. DLS traces of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/ [St]/[PMI] = 1/5/1000/1000 (conc. = 20 wt%) for 6 h and 24 h using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$).

Time (h)	Conv. ^{b)} (%)	Yield (%)	n: m ^{b)} (¹ H NMR)	$M_{\rm n}^{ m b)}$ (¹ H NMR)	$D_{\rm h}^{ m c)}$ (nm)	Zeta potential (mV)
3	>99	57	48: 217	80,000	1214	+32.3

Table S9. Synthesis of P(MTEA(S⁺)[TFSI⁻])-b-P(St-alt-PMI) at higher concentration (30 wt%)^{a)}

^{a)} [I]₀/[macro-CTA]₀/[St]₀/[PMI]₀ = 1/5/1000/1000, solvent = MeOH:1,4-dioxane = 7:3, temp. = 80 °C, macro-CTA: M_n = 21500. ^{b)} Calculated by ¹H NMR in CDCl₃:DMSO- d_6 = 1:1. ^{c)} Measured by DLS in MeOH.



Figure S14. TEM images of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI) obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (conc. = 30 wt%) using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$).



Figure S15. DLS trace of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI) obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (conc. = 30 wt%) using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$).

Run	MeOH :1,4-dioxane	Conv. ^{b)} (%)	Yield (%)
1	9:1	93	53
2	10:0	96	66

Table S10. Synthesis of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI) at 80 °C^{a)}

^{a)} [I]₀/[macro-CTA]₀/[St]₀/[PMI]₀ = 1/5/1000/1000, conc.= 20 wt%, macro-CTA: $M_n = 21500$. ^{b)} Calculated by ¹H NMR in CDCl₃:DMSO- $d_6 = 1:1$.





Figure S16. TEM images of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (conc. = 20 wt%) using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$) in (a, b) MeOH:1,4-dioxane = 9:1 and (c) MeOH.

Dura	Yield ^{b)}	$M_{\rm n}$ ^{c)}	n: m ^{c)}	$M_{ m n}$ $^{ m d)}$	$M_{ m w}/M_{ m n}{}^{ m d)}$	$D_{ m h}$ $^{ m e)}$
Kull	(%)	(¹ H NMR)	(¹ H NMR)	(SEC)	(SEC)	(nm)
1	27	37,000	43: 111	24,000	1.41	185

Table S11. Synthesis of PMTEA-*b*-P(St-*alt*-PMI) at 80 °C for 3 h ^{a)}

^{a)} [I]₀/[macro-CTA]₀/[St]₀/[PMI]₀ = 1/5/1000/1000, solvent = MeOH:1,4-dioxane = 7:3 (conc.= 20 wt%), PMTEA macro-CTA: $M_n = 6600$, $M_w/M_n = 1.18$. ^{b)} Dialysis in MeOH for 3 days. ^{c)} Calculated by ¹H NMR in CD₂Cl₂. ^{d)} Measurement by SEC using polystyrene standard in DMF (10 mM LiBr). ^{e)} Measured by DLS in MeOH.



Figure S17. ¹H NMR spectra of PMTEA and PMTEA-*b*-P(St-*alt*-PMI) in CD₂Cl₂.



Figure S18. SEC curves of PMTEA and PMTEA-*b*-P(St-*alt*-PMI).



Figure S19. TEM images of PMTEA-b-P(St-alt-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (con. = 20 wt%) using PMTEA macro-CTA (M_n = 6600) in MeOH:1,4-Dioxane = 7:3.



Figure S20. DLS trace of PMTEA-*b*-P(St-*alt*-PMI) obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (conc. = 20 wt%) using PMTEA macro-CTA (M_n = 6600) in MeOH:1,4-Dioxane = 7:3.

Run	Time (h)	Solid (wt %)	Conv. ^{b)} (%)	Yield (%)	n: m ^{c)} (EA)	<i>M</i> _n ^{c)} (EA)	$D_{ m h}^{ m d)}$ (nm)	Zeta potential (mV)
1	0.5		85	54	48: 220	76,000	811	+14.1
2	1	10	86	48	48: 226	78,000	492	+6.03
3	3		93	49	48: 210	74,000	170	+33.5
4	0.5		86	54	48: 210	74,000	713	+35.4
5	1	20	93	60	48: 212	74,000	125, 780	+39.6
6	3		99	32	48: 223	75,000	243, 1079	+36.7

Table S12. Synthesis of P(MTEA(S⁺)[OTf])-*b*-P(St-*alt*-PMI)s at 80 °C ^{a)}

^{a)} [I]₀/[macro-CTA]₀/[St]₀/[PMI]₀ = 1/5/1000/1000, solvent = MeOH:1,4-dioxane = 7:3, conc. = 10-20 wt%, P(MTEA(S⁺)[OTf⁻]) macro-CTA: M_n = 15200. ^{b)} Calculated by ¹H NMR in CD₂Cl₂. ^{c)} Calculated by elemental analysis. ^{d)} Measured by DLS in MeOH.



Figure S21. (a) Turbidity changes and (b) DLS traces of P(MTEA(S⁺)[OTf])-*b*-P(St-*alt*-PMI)s at (a) 10-20 wt% and (b) 10 wt%.

Dup	Wt.	С	Н	Ν	S	n:m ^{b)}	$M_{ m n}{}^{ m b)}$
Kull	(µg)	(%)	(%)	(%)	(%)	(EA)	(EA)
1	1160.9	68.52	5.58	4.03	3.79	48: 220	76,000
2	1148.1	69.00	5.47	4.05	3.41	48: 226	78,000
3	1166.9	69.10	5.41	3.99	3.87	48: 210	74,000
4	1189.1	68.77	5.51	3.99	3.87	48: 210	74,000
5	1163.7	68.67	5.42	4.00	4.07	48: 212	74,000
6	1128.0	69.44	5.43	4.04	3.84	48: 223	75,000

Table S13. Elementary analysis of P(MTEA(S⁺)[OTf])-*b*-P(St-*alt*-PMI)s. ^{a)}

^{a)} [I]₀/[macro-CTA]₀//[St]₀/[PMI]₀ = 1/5/1000/1000, solvent = MeOH:1,4-dioxane = 7:3, conc. = 10-20 wt%. P(MTEA(S⁺)[OTf]) macro-CTA: M_n = 15200. ^{b)} Calculated by elemental analysis.

Run	Time (h)	Solid (wt %)	Conv. ^{b)} (%)	Yield (%)	n: m ^{c)} (EA)	$M_{\rm n}^{\rm c)}$ (EA)	$D_{ m h}^{ m d)}$ (nm)	Zeta potential (mV)
1	6	20	94	47	48: 264	88,000	1230	+28.4
2	24	20	95	21	48: 260	87,000	1359	+25.4
3	3	30	99	48	48: 271	90,000	660	+22.7

Table S14. Synthesis of P(MTEA(S⁺)[OTf])-b-P(St-alt-PMI) at 80 °C^{a)}

^{a)} [I]₀/[macro-CTA]₀//[St]₀/[PMI]₀ = 1/5/1000/1000, solvent = MeOH:1,4-dioxane = 7:3, conc. = 20-30 wt%. P(MTEA(S⁺)[OTf]) macro-CTA: M_n = 15200. ^{b)} Calculated by ¹H NMR in CD₂Cl₂. ^{c)} Calculated by elemental analysis. ^{d)} Measured by DLS in MeOH.

Table S15. Elementary analysis of P(MTEA(S⁺)[OTf])-b-P(St-alt-PMI)s. ^{a)}

Run	Wt.	С	Н	Ν	S	n:m ^{b)}	$M_{\rm n}{}^{\rm b)}$
	(µg)	(%)	(%)	(%)	(%)	(EA)	(EA)
1	1182.0	70.80	5.44	4.17	2.86	48:264	88,000
2	1102.5	69.82	5.47	4.12	3.33	48: 260	87,000
3	1150.8	69.91	5.37	4.19	2.78	48: 271	90,000

^{a)} [I]₀/[macro-CTA]₀//[St]₀/[PMI]₀ = 1/5/1000/1000, solvent = MeOH:1,4-dioxane = 7:3, conc. = 20-30 wt%. P(MTEA(S⁺)[OTf]) macro-CTA: M_n = 15200. ^{b)} Calculated by elemental analysis.



Figure S22. TEM images of P(MTEA(S⁺)[OTf])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (conc. = 20 wt%) for 3 h using P(MTEA(S⁺)[OTf]) macro-CTA ($M_n = 15200$). The sample was stained with OsO₄ solution.



Figure S23. TEM images of P(MTEA(S⁺)[OTf])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (conc. = 20 wt%) for (a, b) 6 h and (c, d) 24 h using P(MTEA(S⁺)[OTf]) macro-CTA ($M_n = 15200$).



Figure S24. DLS traces of P(MTEA(S⁺)[OTf⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (conc. = 20 wt%) for 6 h and 24 h using P(MTEA(S⁺)[OTf⁻]) macro-CTA ($M_n = 15200$).



Figure S25. TEM images of P(MTEA(S⁺)[OTf])-*b*-P(St-*alt*-PMI) obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (conc. = 30 wt%) using P(MTEA(S⁺)[OTf]) macro-CTA ($M_n = 15200$).



Figure S26. DLS trace of P(MTEA(S⁺)[OTf])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (conc. = 30 wt%) for 3 h using P(MTEA(S⁺)[OTf]) macro-CTA ($M_n = 15200$).

Run	Solid (wt%)	Time (h)	Conv. ^{b)} (%)	Yield ^{c)} (%)	n: m ^{b)}	$M_{\rm n}^{\rm b)}$ (¹ H NMR)	$D_{ m h}{}^{ m d)}$ (nm)	Zeta potential (mV)
1		0.5	77	44	48: 144	49,000	1288, 5230	+21.2
2	10	1	88	46	48: 152	53,000	1560, 4750	+23.4
3		3	93	60	48: 192	62,000	912, 3245	+22.4
4		0.5	31	17	48: 59	26,000	125	+29.7
5	20	1	85	61	48: 161	54,000	565	+37.4
6		3	80	34	48: 192	63,000	576	+35.6

Table S16. Synthesis of P(MTEA(S⁺)[Cl⁻])-*b*-P(St-*alt*-PMI)s at 80 °C^{a)}

^{a)} $[I]_0/[macro-CTA]_0/[St]_0/[PMI]_0 = 1/5/1000/1000$, solvent = MeOH:1,4-dioxane = 7:3, conc.= 10-20 wt%. P(MTEA(S⁺)[Cl⁻]) macro-CTA: $M_n = 9800$. ^{b)} Calculated by ¹H NMR in CD₂Cl₂. ^{c)} Dialysis in MeOH for 3 days. ^{d)} Measured by DLS in MeOH.



Figure S27. Turbidity changes of P(MTEA(S⁺)[Cl⁻])-*b*-P(St-*alt*-PMI)s.



Figure S28. ¹H NMR spectra of P(MTEA(S⁺)[Cl⁻]) in D₂O and P(MTEA(S⁺)[Cl⁻])-*b*-P(St-*alt*-PMI) in CD₂Cl₂.



Figure S29. TEM image of P(MTEA(S⁺)[Cl⁻])-*b*-P(St-*alt*-PMI) obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1000/1000 (solid content = 10 wt%) for 1 h using P(MTEA(S⁺)[Cl⁻]) macro-CTA ($M_n = 9800$).



Figure S30. DLS traces of P(MTEA(S⁺)[Cl⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at (a) 10 wt% and (b) 20 wt% for 0.5–3 h using P(MTEA(S⁺)[Cl⁻]) macro-CTA ($M_n = 9800$).

Run	[I] ₀ /[macro-	Time	Conv. ^{b)}	Yield	n: m ^{b)}	$M_{ m n}^{ m b)}$	$D_{ m h}^{ m c)}$	Zeta potential
	CTA]/[St]/[PMI]	(h)	(%)	(%)	(¹ H NMR)	(¹ H NMR)	(nm)	(mV)
1		0.5	62	24	48: 192	73,000	1723	+32.7
2	1/5/1500/1500	1	86	45	48: 245	88,000	3099	+30.8
3		3	93	67	48: 298	102,000	1598, 4974	+35.0
4		0.5	83	43	48: 288	100,000	652, 5183	+25.4
5	1/5/2000/2000	1	94	64	48: 376	124,000	842, 4885	+27.3
6		3	95	62	48: 384	126,000	814, 1884	+30.7

Table S17. Synthesis of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI) at higher monomer-to-macro-CTA ratios ^{a)}

^{a)} $[I]_0/[macro-CTA]_0/[St]_0/[PMI]_0 = 1/5/1500/1500 and 1/5/2000/2000, solvent = MeOH:1,4-dioxane$

= 7:3, conc.= 20 wt%, macro-CTA: M_n = 21500. ^{b)} Calculated by ¹H NMR in CDCl₃:DMSO- d_6 = 1:1. ^{c)} Measured by DLS in MeOH.



Figure S31. TEM images of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1500/1500 (conc. = 20 wt%) for (a, d) 0.5 h, (b, e) 1 h and (c, f) 3 h using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$).



Figure S32. TEM images of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1500/1500 (conc. = 20 wt%) for 1 h using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$). The sample was stained with OsO4 solution.



Figure S33. TEM images of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/2000/2000 (conc. = 20 wt%) for (a, d) 0.5 h, (b, e) 1 h and (c, f) 3 h using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$).



Figure S34. DLS traces of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1500/1500 (conc. = 20 wt%) for 0.5–3 h using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$).



Figure S35. DLS traces of P(MTEA(S⁺)[TFSI⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/2000/2000 (conc. = 20 wt%) for 0.5–3 h using P(MTEA(S⁺)[TFSI⁻]) macro-CTA ($M_n = 21500$).

Run	Time (h)	Conv. ^{b)} (%)	Yield (%)	n: m ^{c)} (EA)	$M_{\rm n}^{\rm c)}$ (EA)	$D_{\rm h}^{\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	Zeta potential (mV)
1	0.5	76	38	48: 330	106,000	2067	+30.1
2	1	95	61	48: 346	110,000	2065	+30.6
3	3	96	61	48: 377	119,000	976	+32.6

Table S18. Synthesis of P(MTEA(S⁺)[OTf])-b-P(St-alt-PMI) at 80 °C^{a)}

^{a)} [I]₀/[macro-CTA]₀//[St]₀/[PMI]₀ = 1/5/1500/1500, solvent = MeOH:1,4-dioxane = 7:3, conc.= 20 wt%. P(MTEA(S⁺)[OTf]) macro-CTA: $M_n = 15200$. ^{b)} Calculated by ¹H NMR. ^{c)} Calculated by elemental analysis. ^{d)} Measured by DLS in MeOH.

Table S19. Elementary analysis of P(MTEA(S⁺)[OTf])-b-P(St-alt-PMI)s^{a)}

Run	Wt.	С	Н	Ν	S	n:m ^{b)}	$M_{\rm n}^{\rm b)}$
	(µg)	(%)	(%)	(%)	(%)	(EA)	(EA)
1	1131.4	70.23	5.19	4.32	2.99	48: 330	102,000
2	1108.5	70.70	5.25	4.35	2.76	48: 346	110,000
3	1118.1	70.91	5.45	4.40	2.75	48: 377	119,000

^{a)} [I]₀/[macro-CTA]₀/[St]₀/[PMI]₀ = 1/5/1500/1500, solvent = MeOH:1,4-dioxane = 7:3, conc.= 20 wt%. P(MTEA(S⁺)[OTf⁻]) macro-CTA: $M_n = 15200$. ^{b)} Calculated by elemental analysis.



Figure S36. TEM images of P(MTEA(S⁺)[OTf])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1500/1500 (conc. = 20 wt%) for (a, d) 0.5 h, (b, e) 1 h and (c, f) 3 h using P(MTEA(S⁺)[OTf]) macro-CTA ($M_n = 15200$).



Figure S37. DLS traces of P(MTEA(S⁺)[OTf⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1500/1500 (conc. = 20 wt%) for 0.5–3 h using P(MTEA(S⁺)[OTf⁻]) macro-CTA ($M_n = 15200$).

Run	Solid (wt%)	Time (h)	Conv. ^{b)} (%)	Yield (%)	n: m ^{b)}	$M_{\rm n}{}^{\rm b)}$ (¹ H NMR)	$D_{\rm h}{}^{\rm c)}$ (nm)	Zeta potential (mV)
1		0.5	88	46	202	65,000	2821	+21.3
2	20	1	90	52	273	84,000	1528, 4926	+21.3
3		3	93	34	312	95,000	1610	+30.0

Table S20. Synthesis of P(MTEA(S⁺)[Cl⁻])-*b*-P(St-*alt*-PMI)s at 80 °C^{a)}

^{a)} [I]₀/[macro-CTA]₀//[St]₀/[PMI]₀ = 1/5/1500/1500, solvent = MeOH:1,4-dioxane = 7:3, conc.= 20 wt%. P(MTEA(S⁺)[Cl⁻]) macro-CTA: M_n = 9800. ^{b)} Calculated by ¹H NMR in CD₂Cl₂. ^{c)} Measured by DLS in MeOH.



Figure S38. TEM images of P(MTEA(S⁺)[Cl⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1500/1500 (solid content = 20 wt%) for (a, d) 0.5 h, (b, e) 1 h and (c, f) 3 h using P(MTEA(S⁺)[Cl⁻]) macro-CTA ($M_n = 9800$).



Figure S39. TEM images of P(MTEA(S⁺)[Cl⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1500/1500 (solid content = 20 wt%) for 3 h using P(MTEA(S⁺)[Cl⁻]) macro-CTA ($M_n = 9800$). The sample was stained with OsO4 solution.



Figure S40. DLS traces of P(MTEA(S⁺)[Cl⁻])-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/5/1500/1500 (solid content = 20 wt%) for 0.5–3 h using P(MTEA(S⁺)[Cl⁻]) macro-CTA ($M_n = 9800$).

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