Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Triazole-based nano-objects by polymerization induced self-assembly and modifications of triazole motifs

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Experimental Section

Materials. 2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97 %) was purified by recrystallization from MeOH. *N*-Vinyl-1,2,4-triazole (NVTri) was prepared by the reaction of 1*H*-1,2,4-triazole with vinyl acetate, as described previously.[1,2] Styrene (St, Kanto Chemical, 99%) was purified by distillation under reduced pressure. *N*-Phenylmaleimide (PMI, TCI, > 99%) was purified by recrystallization from MeOH. Divinylbenzene (DVB, > 50.0 %) was purified by distillation under reduced pressure. 2-Cyano-2-propyl dodecyl trithiocarbonate (CTA, Aldrich, >97%), MeOH (Kanto Chemical, >99.5%), *N*,*N*-dimethylformamide (DMF, Kanto Chemical, 99.5%), Zinc(II) trifluoromethanesulfonate ($Zn(OTf)_2$, Tokyo Kasei, > 98.0%) and other materials were purchased and used without further purification.

Synthesis of PNVTri Macro-Chain Transfer Agent (CTA)

The preparation of PNVTri by RAFT polymerization was conducted using our reported procedure[3,4] as follows: NVTri (1.4 g, 15 mmol), CTA (0.10mg, 0.30 mmol), AIBN (9.6 mg, 0.060 mmol), and DMF (7.5 mL) were placed in a dry ampule, and then the solution was degassed by three freeze–evacuate–thaw cycles. After the ampule was flame-sealed under vacuum, it was stirred at 60 ºC for 12 h. The product was purified by precipitation from diethyl ether and dried under vacuum to yield PNVTri as a pale-yellow solid (1.3 g, yield = 79 %, $M_{n,NMR}$ = 5000, $M_{n,SEC}$ = 4500, M_w/M_n = 1.18), which was employed as a macro-CTA. The molecular weight of PNVTri ($M_{n,NMR}$) was determined using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy by comparison of the peaks at 7.49–8.24 ppm, attributed to the triazole ring (2H), and the peak at 0.78–0.93 ppm, attributed to the methyl protons (3H) of CTA (Figure S1), as rereported previously.[4]

RAFT polymerization of St in the presence of PNVTri macro-CTA

For the synthesis of PNVTri-*b*-PSts, RAFT dispersion polymerizations were performed as follows: the trithiocarbonate-terminated PNVTri (50 mg, 0.01 mmol, M_n = 5000, M_w/M_n = 1.18), St (1.04 g, 10 mmol, target DP = 1000), AIBN (0.16 mg, 0.001 mmol, macro-CTA/initiator molar ratio = 10), and MeOH (1.26 mL, St/MeOH = 1.04, w/w) 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 80 °C for different polymerization times (3,12, and 24 h). The reaction was stopped by rapid cooling with liquid nitrogen. The resulting PNVTri-*b*-PSt dispersion was dialyzed (Spectra Pore; MWCO 1000 Da) in MeOH for 3 d, by which the residual St was removed. After the purification, a small portion of the dispersion was taken for transmission electron microscopy (TEM) and dynamic light scattering (DLS). After the solvent was removed by reduced pressure, the product was dried under vacuum at room temperature to afford the product as a white solid. The yield of the block copolymer was determined gravimetrically (0.20 g, yield = 18 % for 24 h). The copolymer composition was determined using the nitrogen content determined by elemental analysis and ^{1}H NMR spectroscopy by comparison of the peaks by comparison of the peaks at 7.6–8.1 ppm, attributed to the triazole ring (2H), and the peak at 6.4–7.4 ppm, attributed to the aromatic protons (5H) of St in CD_2Cl_2/DMSO-d_6 = 3/1 (Tables S1-S2, and Figure S2). The number-average molecular weight (M_n) and dispersity (M_w/M_n) were verified by size-exclusion chromatography (SEC) measurement.

RAFT polymerization of St and PMI in the presence of PNVTri macro-CTA

Synthesis of PNVTri-*b*-P(St-*alt*-PMI) was conducted using St and PMI using the similar procedure described above. In a typical protocol, the trithiocarbonate-terminated PNVTri (50 mg, 0.01 mmol), St (521 mg, 5.0 mmol), PMI (866 mg, 0.5 mmol), and MeOH/DMF (6.52/0.602 mL, 0.24 w/w) were placed in a dry glass ampule and degassed. The mixture was stirred at 80 °C for different polymerization times (10 min, 30 min, 3 h, 12 h, 24 h). After the purification via dialysis with MeOH for 3 d, TEM, DLS, ^{1}H NMR, SEC, and gravimetry measurements were conducted. The targeted copolymer was obtained as a white solid (1.1 g, yield = 81 % for 24 h). The copolymer composition was determined by ^{1}H NMR spectroscopy by comparison of the peaks by comparison of the peaks at 7.6–8.1 ppm, attributed to the triazole ring (2H), and the peak at 6.4–7.4 ppm, attributed to the aromatic protons (10H) of St and NPM in CD_2Cl_2/DMSO-d_6 = 3/1.

RAFT polymerization of St and DVB in the presence of PNVTri macro-CTA

Synthesis of PNVTri-*b*-P(St-*co*-DVB) was conducted using St and DVB using the similar procedure described above. In a typical protocol, the trithiocarbonate-terminated PNVTri (50 mg, 0.01 mmol), St (1.04 g, 10 mmol, target DP = 1000), AIBN (0.16 mg, 0.001 mmol), DVB (13 mg, 0.1 mmol), and MeOH (1.26 mL, 1.04 w/w) were placed in a dry glass ampule and degassed. The mixture was stirred at 80 °C for different polymerization times (2 h, 3 h, 12 h). After the purification via dialysis with MeOH for 3 d, TEM, DLS, and gravimetry measurements were conducted. The targeted copolymer was obtained as a white solid (0.24 g, yield = 12 % for 3 h). The copolymer composition was determined using the nitrogen content determined by elemental analysis.

Zinc Complexation

A representative example of the formation of PNVTri-*b*-P(St-*co*-DVB)/Zn(OTf)$_2$ complex is as follows: PNVTri$_{50}$-*b*-P(St-*co*-DVB)$_{92}$ (40 mg, NVTri unit = 1.3×10^{-4} mol) and DMF (6.6 mL, 1.0 wt%) were added into a two-necked round-bottom flask under nitrogen. Zinc(II) trifluoromethanesulfonate (Zn(OTf)$_2$, 23 mg, 63 mmol, NVTri:Zn molar ratio = 2:1) dissolved in 0.23 mL of DMF was added and the mixture was stirred at room temperature (25 °C) for 24 h. After removing the solvent by evaporator, the product was dried under vacuum at 60 °C for 48 h to afford pale yellow solid. Structural confirmation was performed by Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) measurement.

Synthesis of PNEVTriBr macro-CTA

The preparation of PNEVTriBr by RAFT polymerization was conducted using our reported procedure[3] as follows: NVETrBr (0.52 g, 2.5 mmol), CTA (17 mg, 0.050 mmol), AIBN (1.6 mg, 0.010 mmol), and dry MeOH (1.25 mL) were placed in a dry ampule, and then the solution was degassed by three freeze–evacuate–thaw cycles. After the ampule was flame-sealed under vacuum, it was stirred at 60 °C for 12 h, and then the reaction was stopped by rapid cooling with liquid nitrogen. After the crude polymer was diluted with a small amount of MeOH, it was purified by reprecipitation into a large excess of acetone/chloroform (7/3 vol%), and the resulting product was dried under vacuum to afford PNVETriBr as a pale yellow solid. The molecular weight of PNVETriBr ($M_{\mathrm{n,NMR}}$) was determined using ^{1}H NMR spectroscopy by comparison of the peaks at 9.2–9.8 ppm, attributed to the triazolium ring (1H), and the peak at 0.7–1.0 ppm, attributed to the methyl protons (3H) of CTA (Figure S26).

RAFT polymerization of St in the presence of PNVETriBr macro-CTA

For the synthesis of PNVETriBr-*b*-PSts, RAFT dispersion polymerizations were performed as follows: the trithiocarbonate-terminated PNVETriBr (98 mg, 0.01 mmol, $M_{\text{n,NMR}}$ = 9800), St (1.04 g, 10 mmol), AIBN (0.16 mg, 0.001 mmol), and MeOH (1.26 mL, St/MeOH = 1.04, w/w) were placed in a dry glass ampule and degassed. The mixture was stirred at 80 °C for different polymerization times (3 h, 24 h). After the purification via dialysis with MeOH for 3 d, TEM, DLS, ^{1}H NMR, and gravimetry measurements were conducted.

For the synthesis of PNVTri/PNVETriBr-*b*-PSts, the trithiocarbonate-terminated PNVTri (25 mg, 0.005 mmol), the trithiocarbonate-terminated PNVETriBr (49 mg, 0.005 mmol), St (1.04 g, 10 mmol), AIBN (0.16 mg, 0.001 mmol), and MeOH (1.26 mL, St/MeOH = 1.04, w/w) were placed in a dry glass ampule and degassed. The polymerization and subsequent purification were conducted using the same procedures for PNVETriBr-*b*-PSts.

Instrumentation.

The ^{1}H NMR (400 MHz) spectra were recorded using a JEOL JNM-ECX400. The SEC analysis was performed on a Tosoh HPLC HLC-8220 system equipped with refractive index and ultraviolet detectors. The column set was as follows: four consecutive hydrophilic vinyl polymer-based gel columns [TSK-GELs: α-M (bead size = 13 μm, exclusion limited molecular weight >1 × 10^7), α-4000 (10 μm, 4 × 10^5), α-3000 (7 μm, 9 × 10^4), α-2500 (7 μm, 5 × 10^3), 30 cm each] and a guard column

[TSK-guardcolumn α]. The system was operated at the flow rate of 1.0 mL/min using DMF containing 10 mM LiBr as the eluent at 40 ^{o}C. The column system was calibrated with polystyrene standards (Tosoh) ranging from 1050 to 1090000. FT-IR spectroscopy was recorded using a JASCO FT-IR 210 spectrometer. Thermal properties of the products were evaluated by TGA using a Seiko TGA6200 and DSC using a Seiko EXSTER DSC 6200 at a heating rate of 10 ^{o}C min^{-1} under a nitrogen atmosphere. For the TGA measurement, the sample was treated at 100 ^{o}C for 20 min under a nitrogen atmosphere before the measurement.

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. The samples were not stained. When the sample was stained, a drop of the OsO_4 solution (2.0 wt %) was placed onto the sample located on the carbon-coated Cu grid, followed by air-drying at room temperature. DLS was performed using a Zetasizer Nano (Sysmex) with a He-Ne laser (633 nm). Scattered light signals were collected at detection angle of 173°. The intensity-averaged hydrodynamic diameters were calculated by the manufacturer's software, utilizing the Stokes–Einstein equation. For the sample preparation of DLS measurement, after the dialysis, a small portion of the dispersion was taken and diluted with MeOH (10 times of the original volume). The diluted dispersion was subject to centrifugal separation (25 °C, 4400 rpm, 1 min) to remove large aggregates and supernatant was used for the measurement in MeOH.

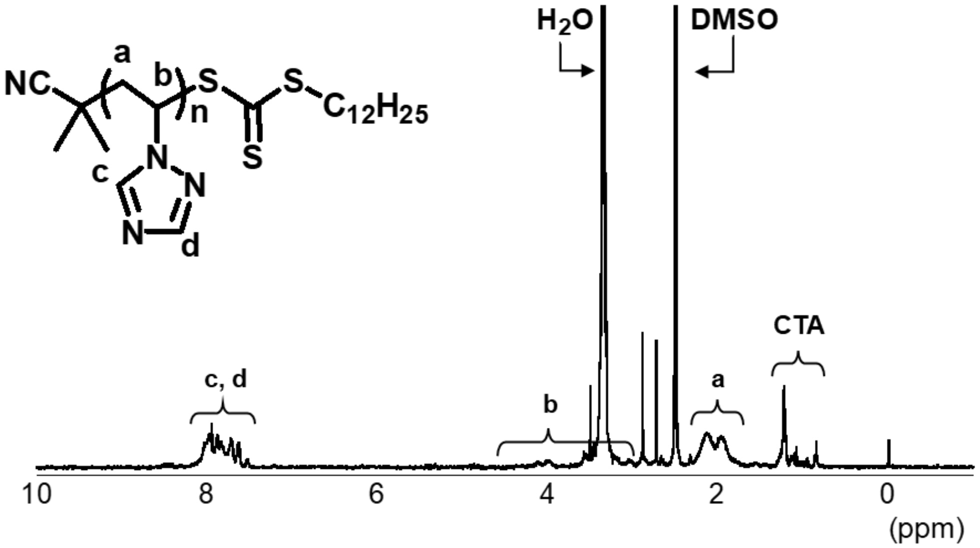
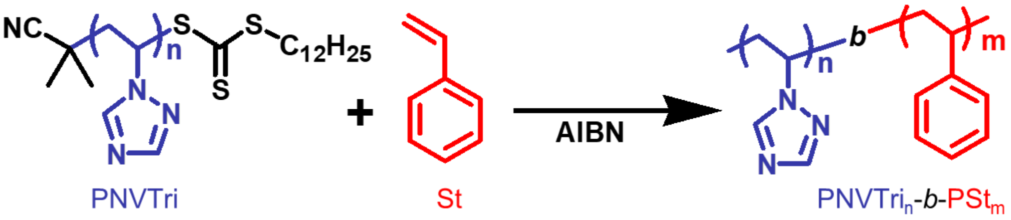


Figure S1. ^{1}H NMR spectrum of PNVTri macro-CTA in DMSO-d_6.



Scheme S1. RAFT dispersion polymerization of St via PISA using PNVTri macro-CTA.

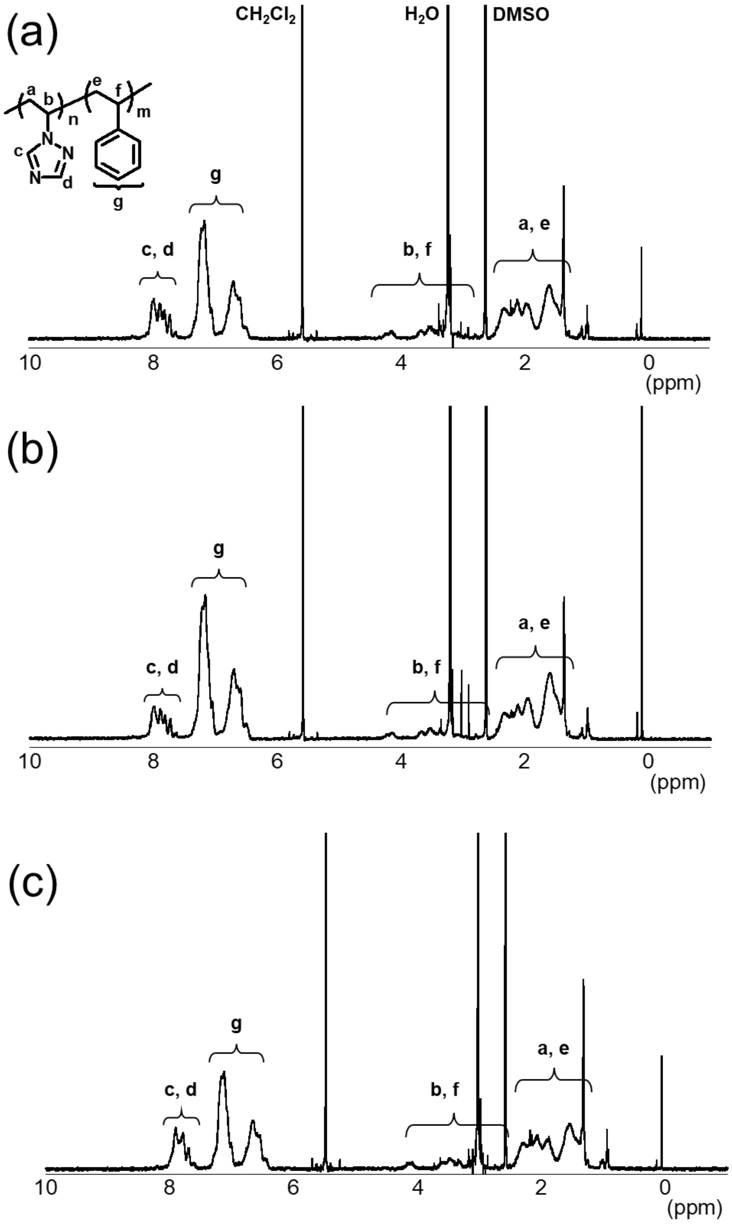


Figure S2. ^{1}H NMR spectra (CD_2Cl_2/DMSO-d_6 = 3/1) of PNVTri-*b*-PSts prepared in (a) MeOH, (b) MeOH/DMF, and (c) MeOH/H_2O for 3 h.

Table S1. Synthesis of PNVTri-*b*-PSts via PISA at 80 °C [a)]

Entry	Solvent	Time (h)	Yield [b)] (%)	M_n [c)] (theory)	M_n [d)] (NMR)	M_n [e)] (SEC)	M_w/M_n [e)] (SEC)	n:m [d)] (NMR)	D_h [f)] (nm)	Morph. [g)]
1-1	MeOH	3	11	17,000	14,000	7,600	1.23	50:83	374 [h)]	M, W
1-2		12	17	23,000	26,000	10,000	1.19	50:197	285	V
1-3		24	18	24,000	35,000	12,000	1.18	50:284	599 [i)]	AV
1-4	MeOH/ DMF = 9/1	3	12	18,000	16,000	9,400	1.17	50:106	255	W
1-5		12	17	23,000	28,000	12,000	1.16	50:226	122	V
1-6		24	18	24,000	37,000	13,000	1.22	50:303	423	N
1-7	MeOH/ H_2O = 9/1	3	11	16,000	16,000	10,000	1.16	50:112	164	W, V
1-8		12	17	22,000	29,000	15,000	1.15	50:226	370	V
1-9		24	18	23,000	40,000	20,000	1.19	50:339	451	AV

[a)] $[I]_0/[\text{macro-CTA}]_0/[M]_0$ = 1/10/10000, St/Solvent = 1.0 w/w, macro-CTA: M_n = 5000, M_w/M_n = 1.18. [b)] Dialysis in MeOH for 3 days. [c)] The theoretical molecular weight ($M_{n,\text{theory}}$) = (MW of St) × $[M]_0/[CTA]_0$ × yield + (M_n of Macro-CTA). [d)] Calculated by ^{1}H NMR in CD_2Cl_2/DMSO-*d₆* = 3/1. [e)] Measured by SEC using PSt standard in DMF (10 mM LiBr). [f)] Measured by DLS in MeOH. [g)] Morphology (Morph.) was judged by TEM, where M = micelle, W = worm, V = vesicle, AV = aggregation of vesicle, and N = nanotube, respectively. Zeta potential = (h) -1.4 mV and (i) -0.77 mV.

Table S2. Elementary analysis of PNVTri-*b*-PSts prepared in MeOH [a)]

Entry	Time (h)	Wt. (μg)	C (%)	H (%)	N (%)	S (%)	M_n [b)] (EA)	n:m [b)] (EA)
1-1	3	1264.0	71.16	6.65	16.34	0.83	16,000	50:98
1-2	12	1204.1	80.36	7.59	8.77	0.14	23,000	50:188
1-3	24	1170.0	80.97	7.28	8.45	0.58	26,000	50:200

[a)] $[I]_0/[\text{macro-CTA}]_0/[M]_0 = 1/10/10000$, St/Solvent = 1.0 w/w, macro-CTA: $M_n = 5000$, $M_w/M_n = 1.18$ (see Table S1). [b)] Calculated by elemental analysis (nitrogen content).

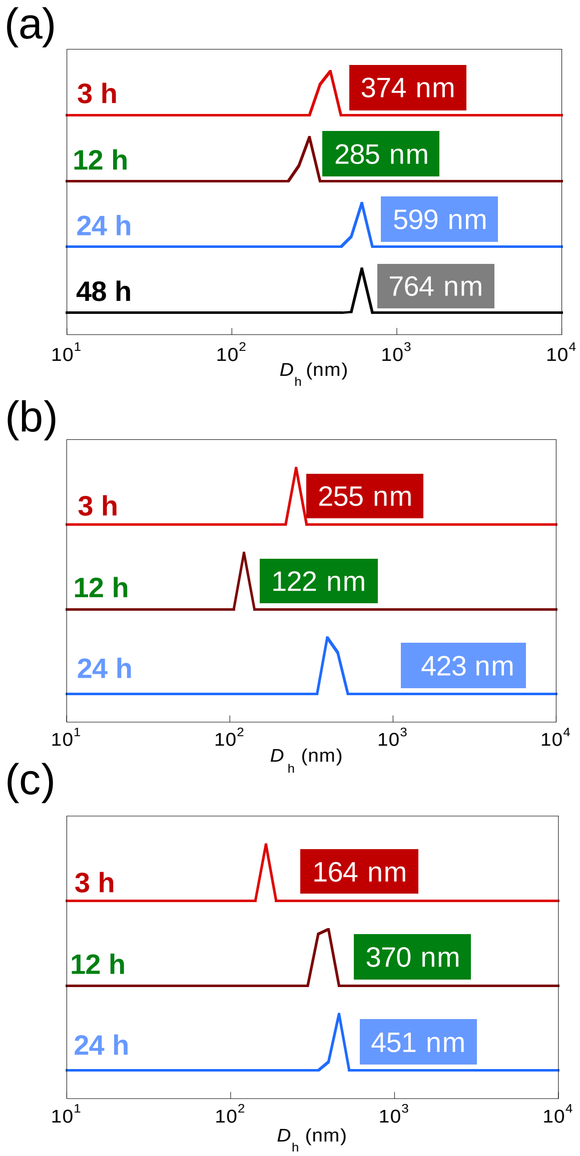


Figure S3. DLS traces (MeOH) of PNVTri-*b*-PSts prepared in (a) MeOH, (b) MeOH/DMF, and (c) MeOH/H_2O.

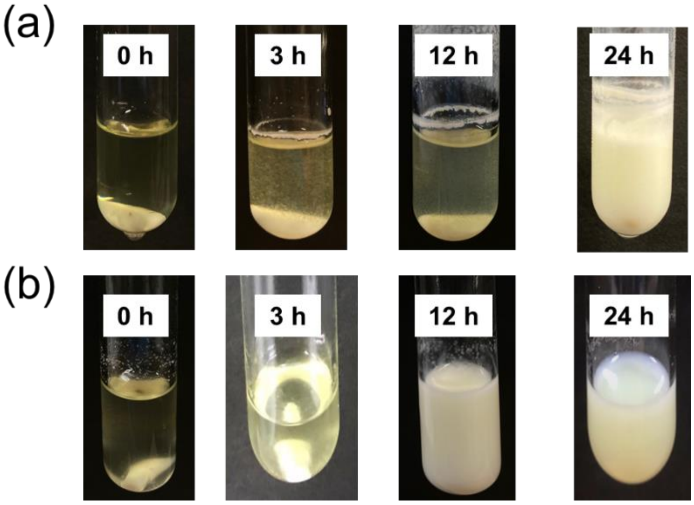


Figure S4. Turbidity change of PNVTri-*b*-PSts prepared in (a) MeOH/DMF and (b) MeOH/H_2O.

Table S3. Synthesis of PNVTri-*b*-PSt via PISA in EtOH/DMF = 8/2 [a]

Entry	Time (h)	Temp (ºC)	Yield [b] (%)	M_n [c] (theory)	M_n [d] (NMR)	M_n [e] (SEC)	M_w/M_n [e] (SEC)	n:m [d] (NMR)	D_h [f] (nm)	Morph. [g]
1	3	70	8.6	14,000	10,000	7,000	1.15	50:50	220	M
2	12		13	19,000	27,000	12,000	1.25	50:210	167	M
3	24		27	34,000	64,000	21,000	1.18	50:568	167	M
4	24	80	21	9,400	39,000	17,000	1.17	50:330	302	-

[a] $[I]_0/[\text{macro-CTA}]_0/[M]_0$ = 1/10/10000, St/Solvent = 1.0 w/w, macro-CTA: M_n = 5000, M_w/M_n = 1.18. [b] Dialysis in MeOH for 3 days. [c] The theoretical molecular weight ($M_{n,\text{theory}}$) = (MW of St) × $[M]_0/[CTA]_0$ × yield + (M_n of Macro-CTA). [d] Calculated by ^{1}H NMR in CD_2Cl_2/DMSO-d_6 = 3/1. [e] Measured by SEC using PSt standard in DMF (10 mM LiBr). [f] Measured by DLS in EtOH. [g] Morphology (Morph.) was judged by TEM, where M = micelle.

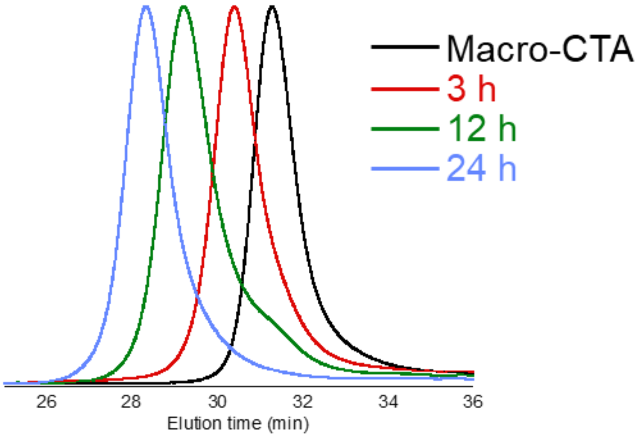


Figure S5. SEC curves of PNVTri-*b*-PSts prepared by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St] = 1/10/10000 using PNVTri macro-CTA (M_n = 5000, M_w/M_n = 1.18) (St/Solvent = 1.0 w/w) in EtOH/DMF = 8/2.

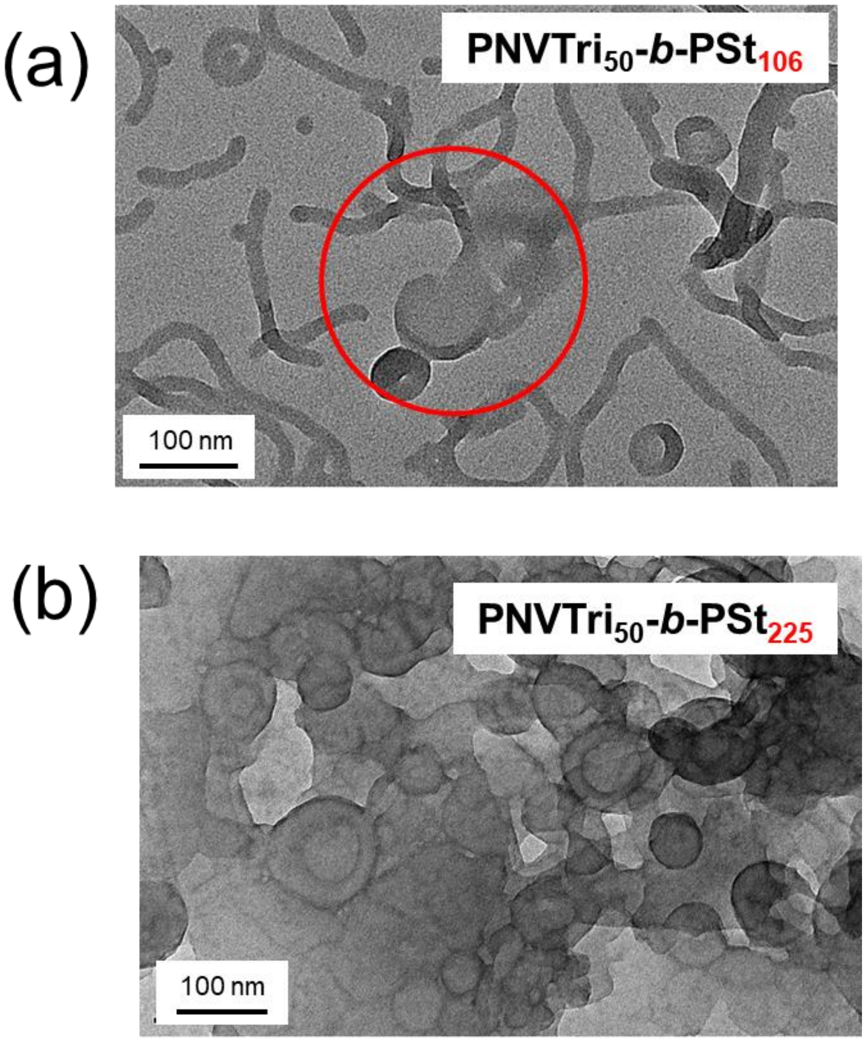


Figure S6. TEM images of PNVTri-*b*-PSts obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St] = 1/10/10000 using PNVTri macro-CTA (M_n = 5000, M_w/M_n = 1.18) in MeOH/DMF = 9/1 (St/Solvent = 1.0 w/w) at 80 °C for (a) 3 h and (b) 12 h. The samples were stained with OsO_4 solution.

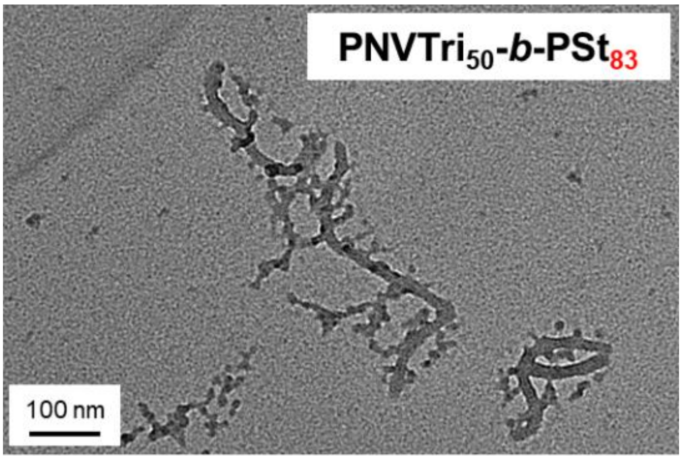


Figure S7. TEM image of PNVTri-*b*-PSt obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St] = 1/10/10000 using PNVTri macro-CTA (M_n = 5000, M_w/M_n = 1.18) in MeOH (St/Solvent = 1.0 w/w) at 80 ℃ for 3 h. The sample was stained with OsO_4 solution.

Table S4. Synthesis of PNVTri-*b*-PSts via PISA in MeOH at 80 °C for 24 h [a]

Entry	$[I]_0$/[Macro-CTA]$_0$/$[M]_0$	Yield [b] (%)	M_n [c] (theory)	M_n [d] (NMR)	M_n [e] (SEC)	M_w/M_n [e] (SEC)	n:m [d] (NMR)	D_h [f] (nm)
1	1/5/10000	16.1	39,000	64,000	24,000	1.35	50:568	564
2	1/2/10000	15.9	88,000	130,000	40,000	1.36	50:1184	848

[a] $[I]_0/[\text{macro-CTA}]_0/[M]_0$ = 1/10/10000, St/Solvent = 1.0 w/w, macro-CTA: M_n = 5000, M_w/M_n = 1.18. [b] Dialysis in MeOH for 3 days. [c] The theoretical molecular weight ($M_{n,\text{theory}}$) = (MW of M) × $[M]_0/[CTA]_0$ × conv.(yield) + (M_n of Macro-CTA). [d] Calculated by ^{1}H NMR in CD_2Cl_2/DMSO-d_6 = 3/1. [e] Measured by SEC using PSt standard in DMF (10 mM LiBr). [f] Measured by DLS in MeOH.

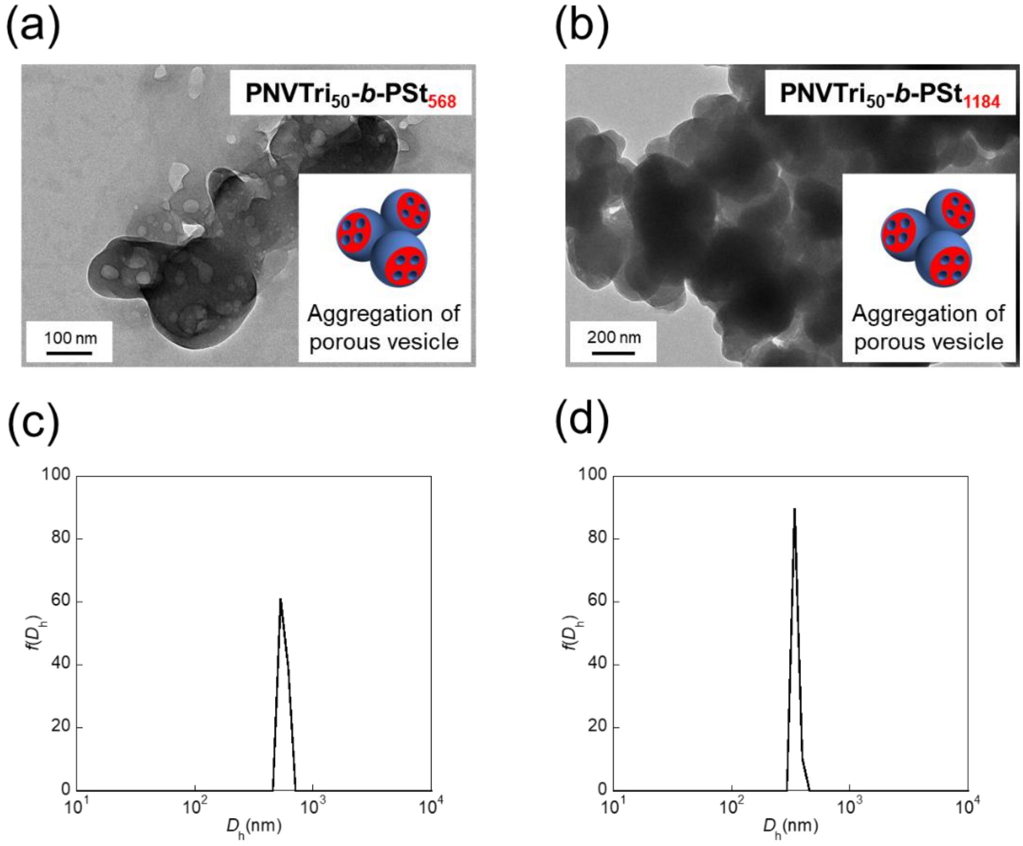


Figure S8. (a,b) TEM images and (c,d) DLS traces (MeOH) of PNVTri-*b*-PSts obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St] = (a,c) 1/5/10000 or (b,d) 1/2/10000 using PNVTri macro-CTA (M_n = 5000, M_w/M_n = 1.18) in MeOH (St/Solvent = 1.0 w/w) for 24 h. TEM images were obtained without staining.

Table S5. Synthesis of PNVTri-*b*-PSts via PISA in MeOH at 60 °C [a]

Solvent	Time (h)	Yield [b] (%)	M_n [c] (theory)	M_n [d] (NMR)	M_n [e] (SEC)	M_w/M_n [e] (SEC)	n:m [d] (NMR)	D_h [f] (nm)
MeOH	3	3.1	8300	-	6000	1.13	-	-
	24	15	20000	21,000	13000	1.19	50:155	705
	48	19	25000	45,000	19000	1.28	50:384	934
MeOH/H_2O = 9/1	3	3.5	8,800	-	4,600	2.33	-	-
	24	4.3	9,600	6,600	4,000	1.39	50:31	-

[a] $[AIBN]_0/[macro\text{-}CTA]_0/[St]_0$ = 1/10/10000, St/Solvent = 1.0 w/w, macro-CTA: M_n = 5000, M_w/M_n = 1.18. [b] Dialysis in MeOH for 3 days. [c] The theoretical molecular weight ($M_{n,\mathrm{theory}}$) = (MW of St) × $[M]_0/[CTA]_0$ × yield + (M_n of Macro-CTA). [d] Calculated by ^{1}H NMR in CD_2Cl_2/DMSO-d_6 = 3/1. [e] Measured by SEC using PSt standard in DMF (10 mM LiBr). [f] Measured by DLS in MeOH.

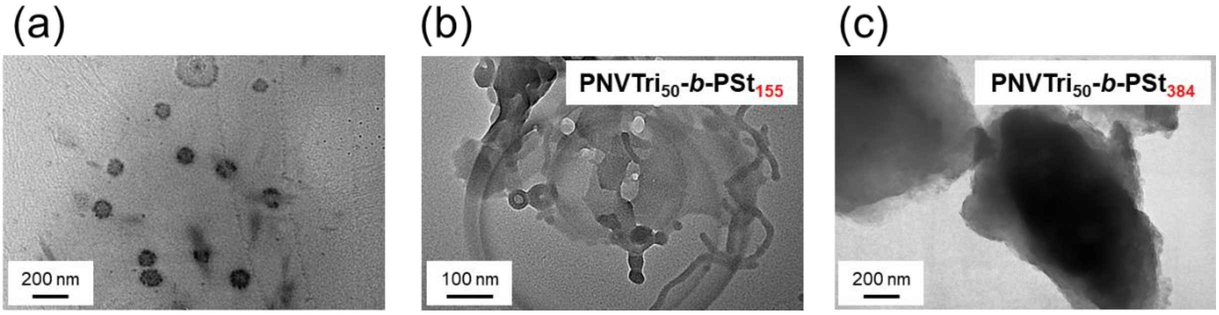


Figure S9. TEM images of PNVTri-*b*-PSts obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St] = 1/10/10000 using PNVTri macro-CTA (M_n = 5000, M_w/M_n = 1.18) in MeOH (St/Solvent = 1.0 w/w) at 60 °C for (a) 3 h, (b) 24 h and (c) 48 h. TEM images were obtained without staining.

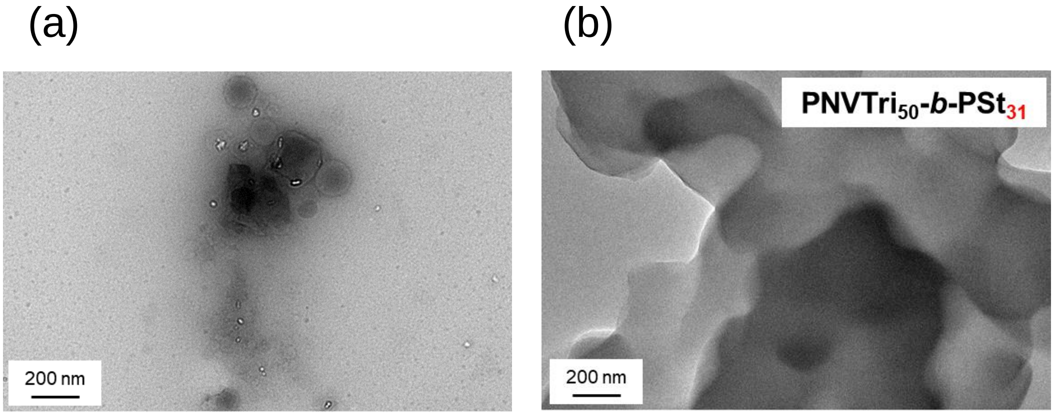
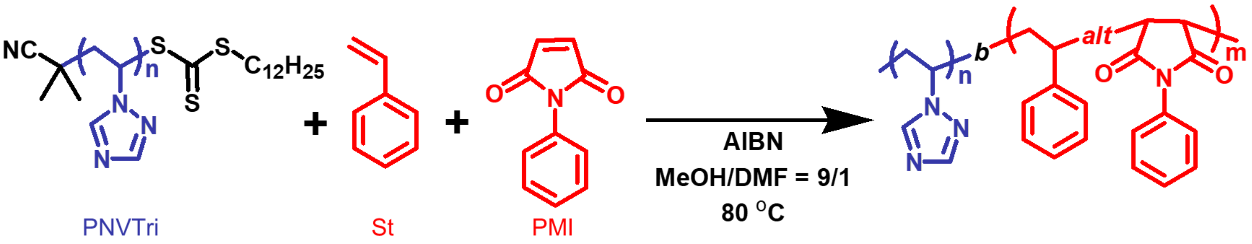


Figure S10. TEM images of PNVTri-*b*-PSts obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St] = 1/10/10000 using PNVTri macro-CTA (M_n = 5000, M_w/M_n = 1.18) in MeOH/H_2O = 9/1 (St/Solvent = 1.0 w/w) at 60 °C for (a) 3 h and (b) 24 h. TEM images were obtained without staining.



Scheme S2. RAFT dispersion copolymerization of St and PMI via PISA using PNVTri macro-CTA.

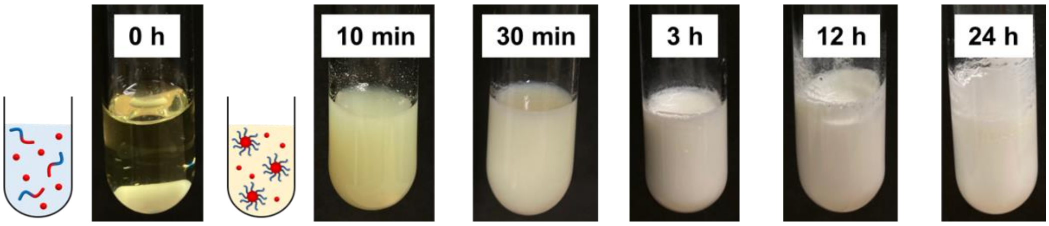


Figure S11. Turbidity change of PNVTri-*b*-P(St-*alt*-PMI)s prepared by RAFT dispersion copolymerization in MeOH/DMF (9/1 vol-%) at 80 °C.

Table S6. Synthesis of PNVTri-*b*-P(St-*alt*-PMI)s via PISA in MeOH/DMF (9/1 vol-%) at 80 °C [a)]

Entry	Time	Yield [b)] (%)	M_n [c)] (theory)	M_n [d)] (NMR)	M_n [e)] (SEC)	M_w/M_n [e)] (SEC)	n:m [d)] (NMR)	D_h [f)] (nm)	Morph. [g)]
2-1	10 min	8.2	16,000	14,000	9,500	2.11	50:31	1120	W, S
2-2	30 min	17	29,000	42,000	19,000	2.25	50:134	869	S
2-3	3 h	66	94,000	120,000	71,000	1.75	50:423	255	N
2-4	12 h	75	110,000	250,000	95,000	1.36	50:894	377	PN
2-5	24 h	81	120,000	310,000	140,000	1.52	50:1130	459	PN

[a)] $[AIBN]_0/[macro\text{-}CTA]_0/[St]_0/[PMI]_0 = 1/10/5000/5000$, (St+PMI)/Solvent = 0.24 w/w, macro-CTA: $M_n = 5000$, $M_w/M_n = 1.18$. [b)] Dialysis in MeOH for 3 days. [c)] The theoretical molecular weight ($M_{n,\text{theory}}$) = (MW of M) × $[M]_0/[CTA]_0$ × yield + (M_n of Macro-CTA). [d)] Calculated by ^1H NMR in CD_2Cl_2/DMSO-d_6 = 3/1. [e)] Measured by SEC using PSt standard in DMF (10 mM LiBr). [f)] Measured by DLS in MeOH. [g)] Morphology (Morph.) was judged by TEM, where W = worm, S = sheet, N = nanotube, and PN = porous nanotube, respectively.

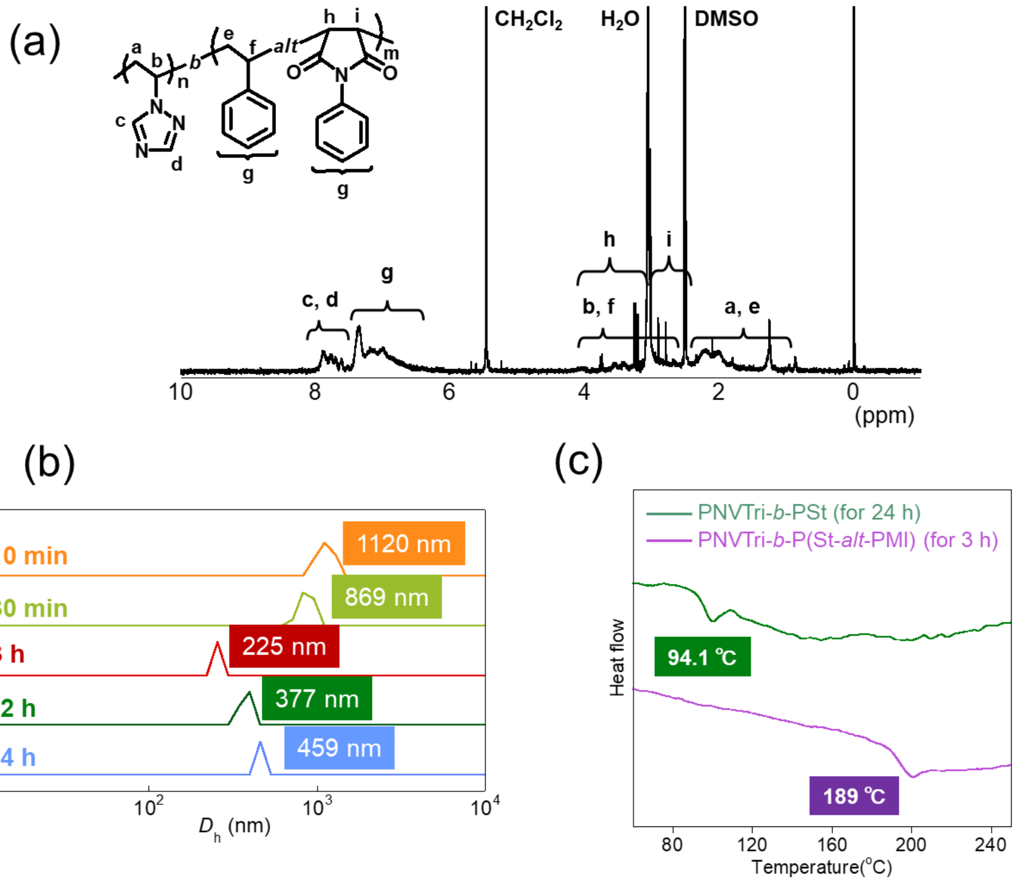


Figure S12. (a) ^{1}H NMR spectrum (CD_2Cl_2/DMSO-d_6 = 3/1) and (b) DLS traces (MeOH) of PNVTri-*b*-P(St-*alt*-PMI)s prepared by RAFT dispersion polymerization (see Table S6 for detailed polymerization conditions). (c) DSC traces of representative PNVTri-*b*-P(St-*alt*-PMI) and PNVTri-*b*-PSt.

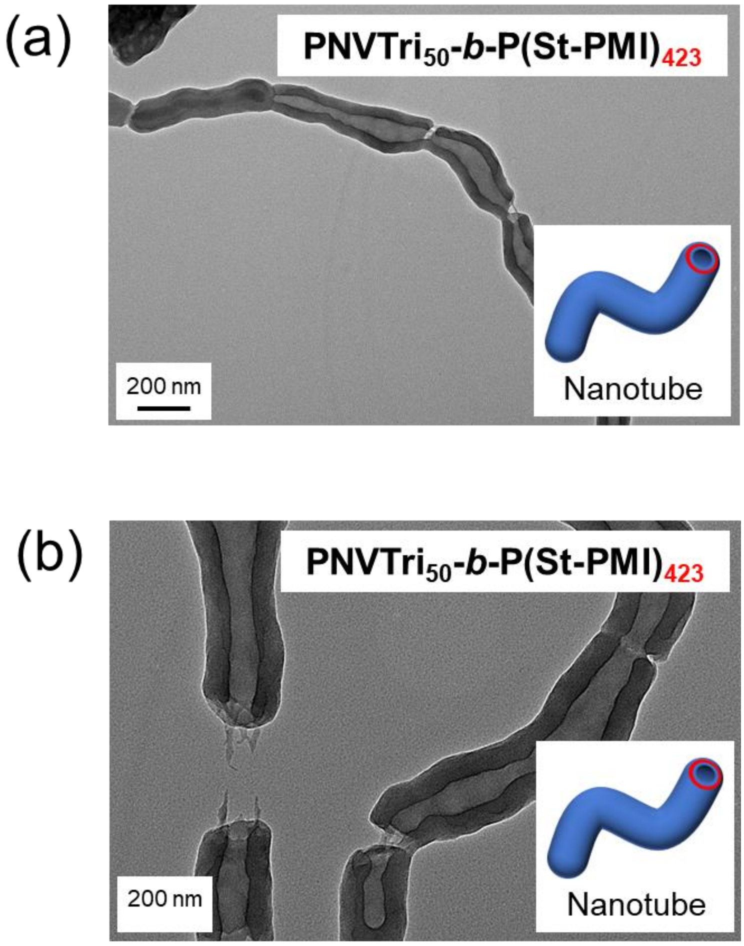


Figure S13. TEM images of PNVTri$_{50}$-*b*-P(St-*alt*-PMI)$_{423}$ prepared by RAFT dispersion polymerization in MeOH/DMF (9/1 vol-%) at 80°C for 3h (see Figure 5g for detailed polymerization conditions).

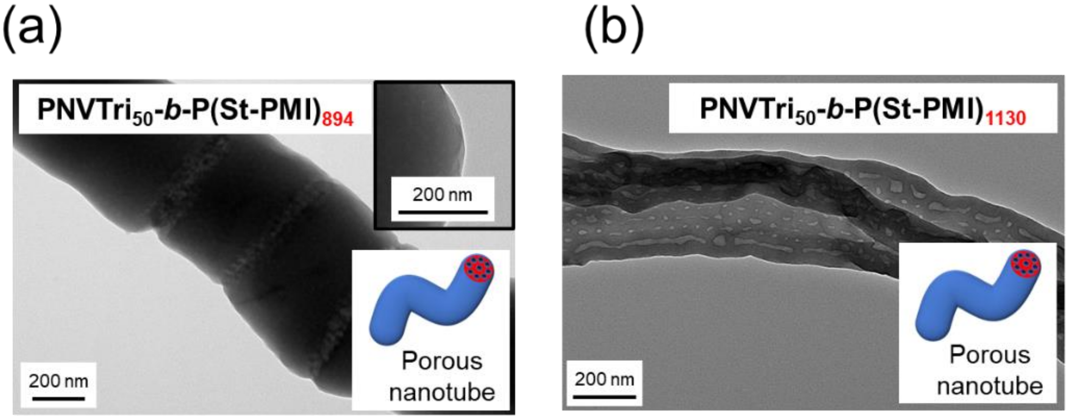


Figure S14. TEM images of PNVTri-*b*-P(St-*alt*-PMI)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/10/5000/5000 using PNVTri macro-CTA (M_n = 5000, M_w/M_n = 1.18) in MeOH/DMF (9/1 vol-%) ((St+PMI)/Solvent = 0.24 w/w) at 80°C for (a) 12 h and (b) 24 h.

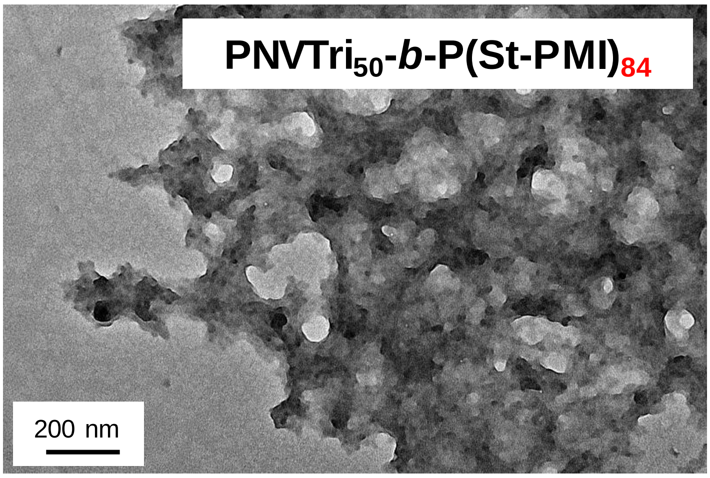
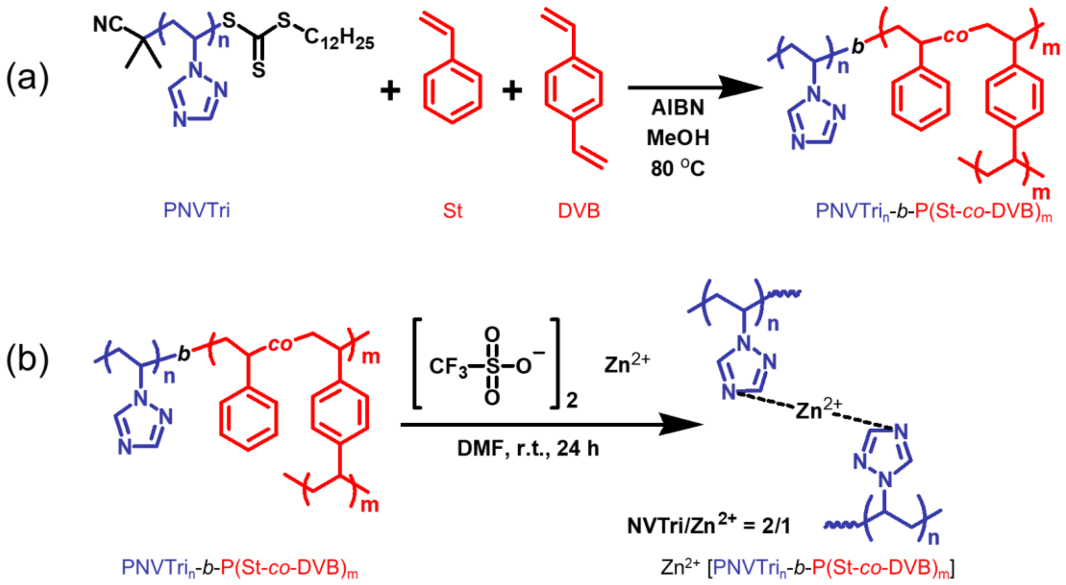


Figure S15. TEM images of PNVTri-*b*-P(St-*alt*-PMI) obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[PMI] = 1/10/5000/5000 using PNVTri macro-CTA (M_n = 5000, M_w/M_n = 1.18) in MeOH/DMF (9/1 vol-%) ((St+PMI)/Solvent = 0.12 w/w) at 80°C for 1 h.



Scheme 3. (a) RAFT dispersion copolymerization of St and DVB via PISA using PNVTri macro-CTA and (b) formation of zinc complexes.

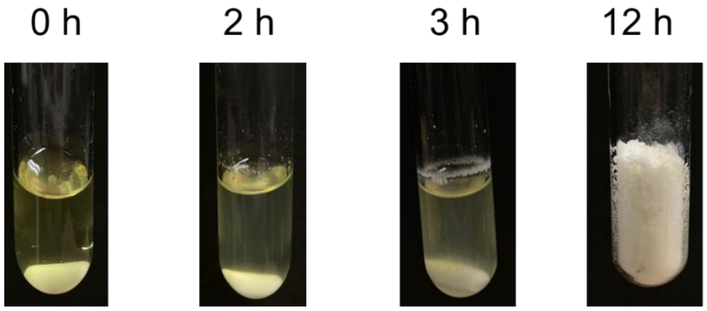


Figure S16. (a) Turbidity change of PNVTri-*b*-P(St-*co*-DVB)s obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[DVB] = 1/10/10000/100 using PNVTri macro-CTA (M_n = 5000, M_w/M_n = 1.18) in MeOH ((St+DVB)/solvent = 1.0 w/w).

Table S7. Synthesis of PNVTri-*b*-P(St-*co*-DVB) via PISA in MeOH at 80 °C [a)]

Entry	Time (h)	Yield [b)] (%)	M_n [c)] (theory)	M_n [d)] (EA)	n:m [d)] (EA)
3-1	2	11	16,000	13,000	50:80
3-2	3	12	17,000	16,000	50:92
3-3	12	85	94,000	160,000	50:1523

[a)] $[I]_0/[\text{macro-CTA}]_0/[St]_0/[DVB]_0$ = 1/10/10000/100, conc. = (St+DVB)/solvent = 1.0 w/w, macro-CTA: M_n = 5000, M_w/M_n = 1.18. [b)] Dialysis in MeOH for 3 days. [c)] The theoretical molecular weight ($M_{n,\text{theory}}$) = (MW of M) × $[M]_0/[CTA]_0$ × yield + (M_n of Macro-CTA). [d)] Calculated by elemental analysis.

Table S8. Elementary analysis of PNVTri-*b*-P(St-*co*-DVB)s prepared via PISA in MeOH at 80 °C[a)]

Entry	Time (h)	Wt. (μg)	C (%)	H (%)	N (%)	S (%)	M_n [b)] (EA)	n:m [b)] (EA)
3-1	2	1187.0	72.83	7.01	15.36	0.22	13,000	50:80
3-2	3	1225.8	75.20	7.02	13.62	-	15,000	50:92
3-3	12	1190.5	90.37	7.98	1.25	-	160,000	50:1523

[a)] $[I]_0/[\text{macro-CTA}]_0/[St]_0/[DVB]_0$ = 1/10/10000/100, conc. = (St+DVB)/solvent = 1.0 w/w, macro-CTA: M_n = 5000, M_w/M_n = 1.18. [b)] Calculated by elemental analysis (nitrogen content).

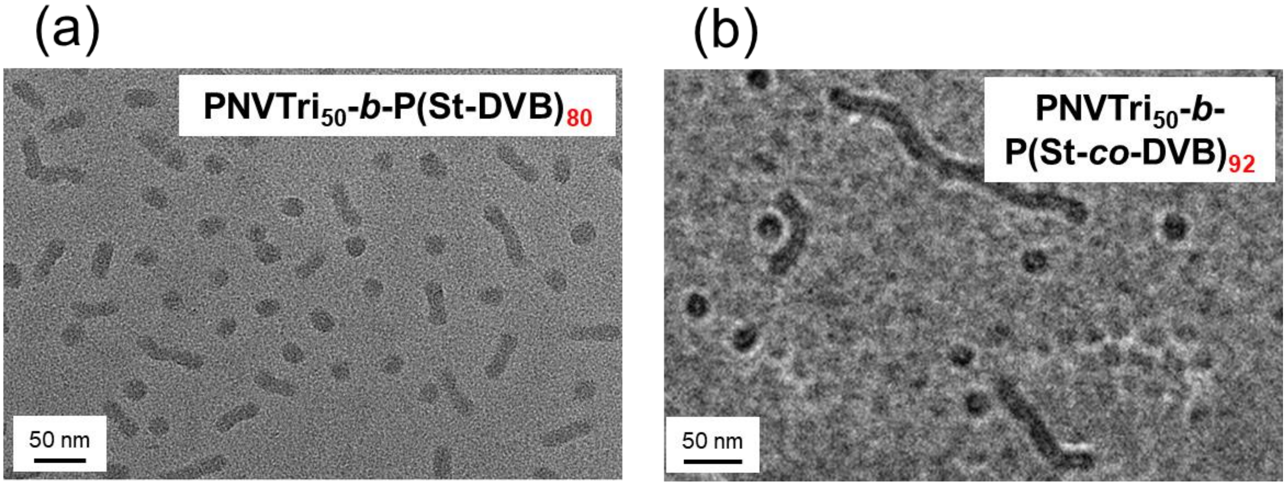


Figure S17. TEM images of (a) PNVTri$_{50}$-*b*-P(St-*co*-DVB)$_{80}$ and (b) PNVTri$_{50}$-*b*-P(St-*co*-DVB)$_{92}$ obtained by RAFT dispersion polymerization and dialysis (see Table S7, Figures 7a and 7b for detailed preparation conditions of pristine assemblies). TEM samples were prepared from DMF solutions.

Table S9. Synthesis of PNVTri-*b*-P(St-*co*-DVB) via PISA in MeOH at 80 °C for 3 h [a)]

Entry	$[St]_0/[DVB]_0$	Yield [b)] (%)	M_n [c)] (theory)	M_n [d)] (EA)	n:m [d)] (EA)
3-4	6000/4000	11	16,000	16,000	50:105
3-5	7000/3000	10	15,000	15,000	50:100
3-6	8000/2000	9	14,000	19,000	50:134
3-7	9000/1000	13	18,000	18,000	50:127

a) $[I]_0/[\text{macro-CTA}]_0/[St]_0/[DVB]_0$ = 1/10/6000/4000–1/10/9000/1000, conc. = (St+DVB)/solvent = 1.0 w/w, macro-CTA: M_n = 5000, M_w/M_n = 1.18. b) Dialysis in MeOH for 3 days. c) The theoretical molecular weight ($M_{n,\text{theory}}$) = (MW of M) × $[M]_0/[CTA]_0$ × yield + (M_n of Macro-CTA). d) Calculated by elemental analysis.

Table S10. Elementary analysis of PNVTri-*b*-P(St-*co*-DVB)s prepared via PISA in MeOH at 80 °C[a)]

Entry	Wt. (µg)	C (%)	H (%)	N (%)	S (%)	M_n [b)] (EA)	n:m [b)] (EA)
3-4	1179.7	76.59	7.54	12.68	0.34	16,000	50:105
3-5	1131.6	76.06	7.28	13.4	0.71	15,000	50:100
3-6	1214.7	78.88	7.04	10.68	0.62	19,000	50:134
3-7	1125.8	78.09	6.31	10.99	-	18,000	50:127

a) $[I]_0/[\text{macro-CTA}]_0/[St]_0/[DVB]_0$ = 1/10/6000/4000–1/10/9000/1000, conc. = (St+DVB)/solvent = 1.0 w/w, macro-CTA: M_n = 5000, M_w/M_n = 1.18. b) Calculated by elemental analysis (nitrogen content).

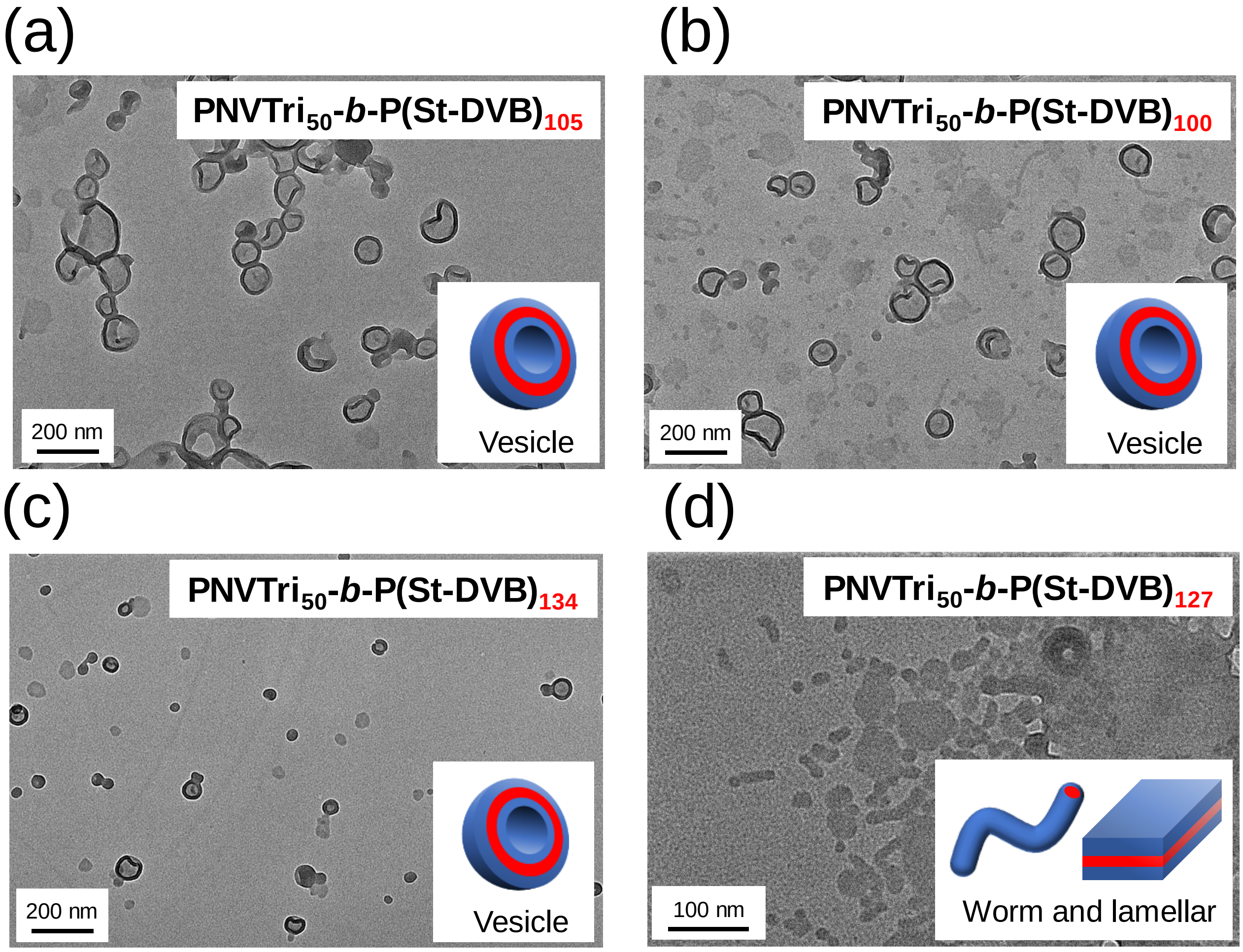


Figure S18. TEM images of (a) PNVTri$_{50}$-*b*-P(St-*co*-DVB)$_{105}$, (b) PNVTri$_{50}$-*b*-P(St-*co*-DVB)$_{100}$, (c) PNVTri$_{50}$-*b*-P(St-*co*-DVB)$_{134}$, and (d) PNVTri$_{50}$-*b*-P(St-*co*-DVB)$_{127}$ obtained by RAFT dispersion polymerization and dialysis.

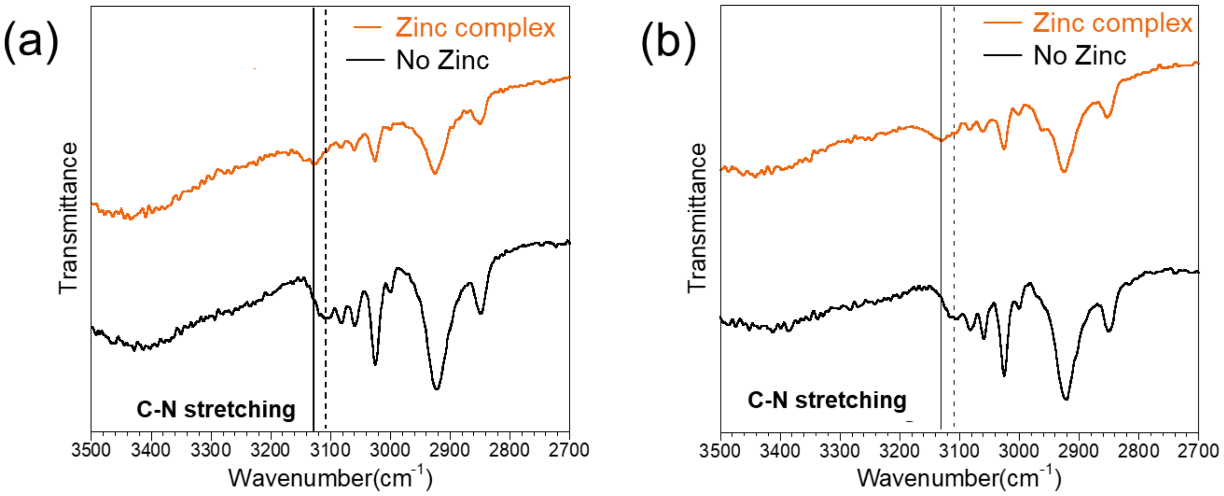


Figure S19. FT-IR spectra of (a) PNVTri$_{50}$-*b*-P(St-*co*-DVB)$_{80}$ and (b) PNVTri$_{50}$-*b*-P(St-*co*-DVB)$_{92}$ obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[DVB] = 1/10/10000/100 using PNVTri macro-CTA (M_n = 5000, M_w/M_n = 1.18) in MeOH ((St + DVB)/solvent = 1.0 w/w) for (a) 2h and (b) 3 h, and their zinc complexes.

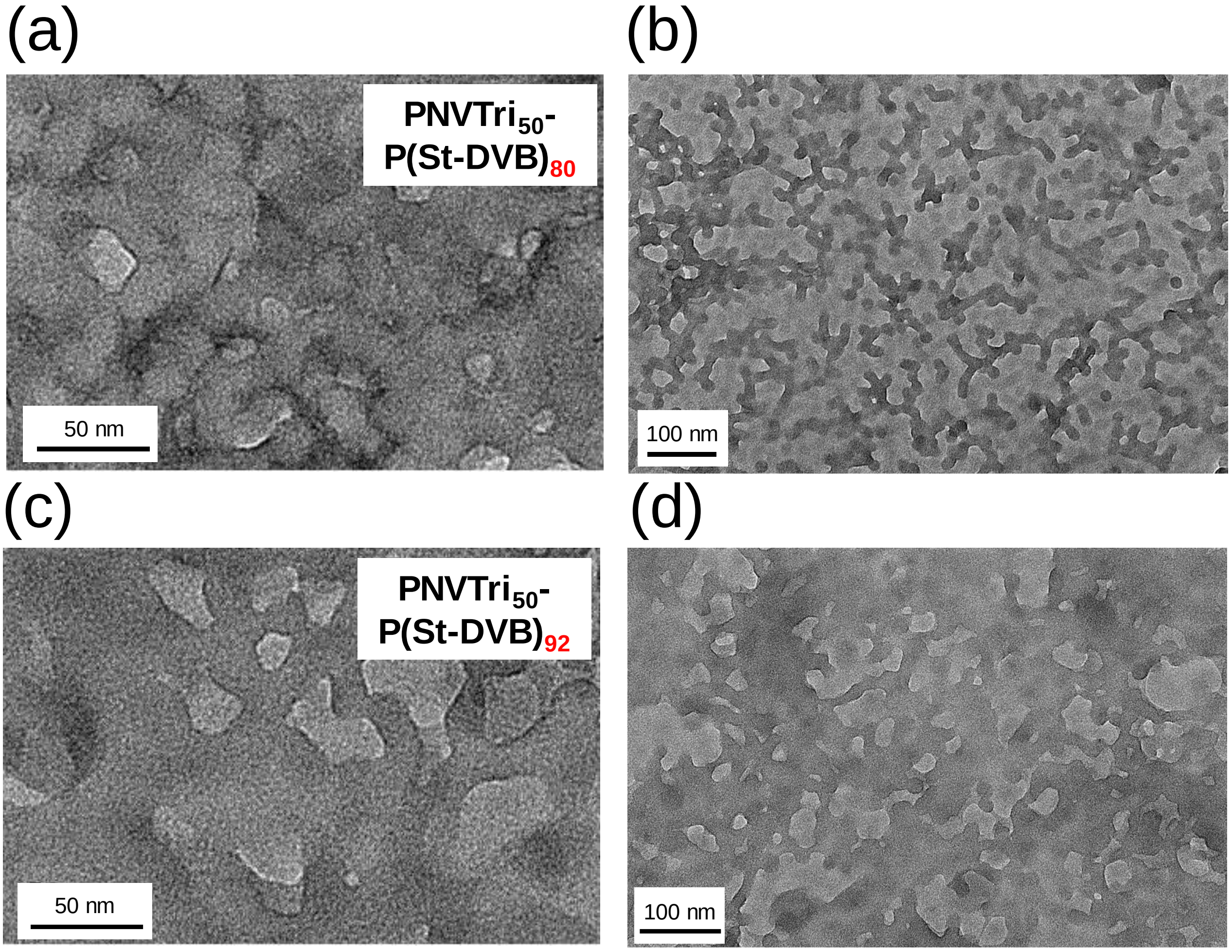


Figure S20. TEM images of zinc complexes (NVTri : Zn^{2+} = 2 : 1) prepared from (a,b) PNVTri$_{50}$-*b*-P(St-*co*-DVB)$_{80}$ and (c,d) PNVTri$_{50}$-*b*-P(St-*co*-DVB)$_{92}$. The PNVTri$_{50}$-*b*-P(St-*co*-DVB)s were prepared by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St]/[DVB] = 1/10/10000/100 using PNVTri macro-CTA (M_n = 5000, M_w/M_n = 1.18) in MeOH ((St + DVB)/solvent = 1.0 w/w) at 80°C after (a,b) 2h and (c,d) 3 h (see Figure 7).

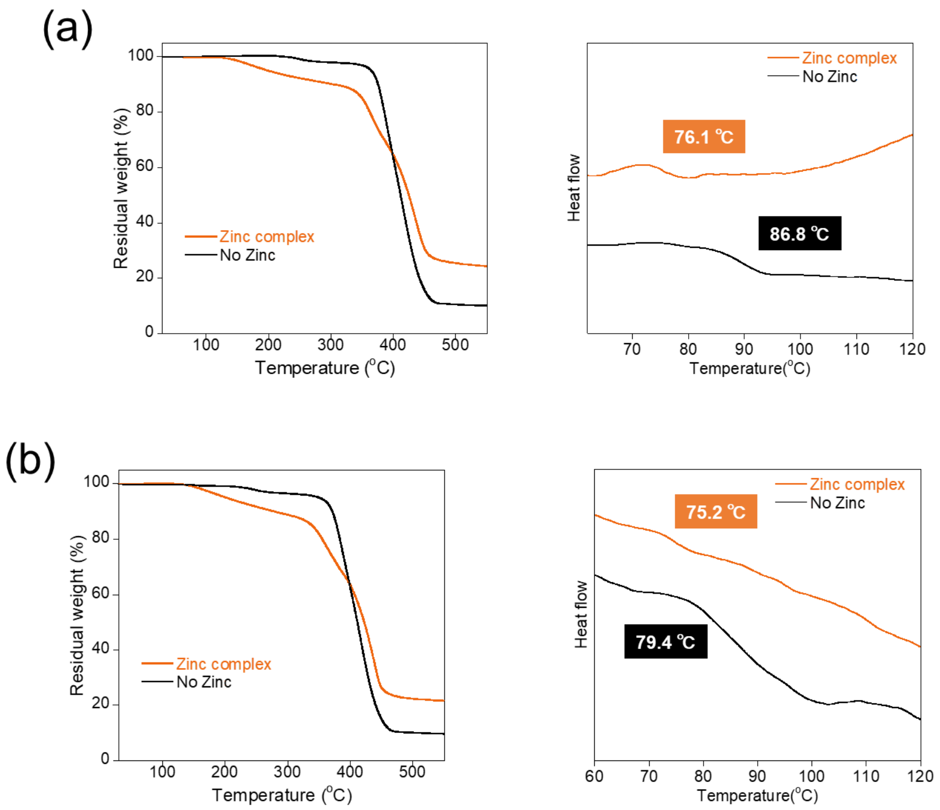
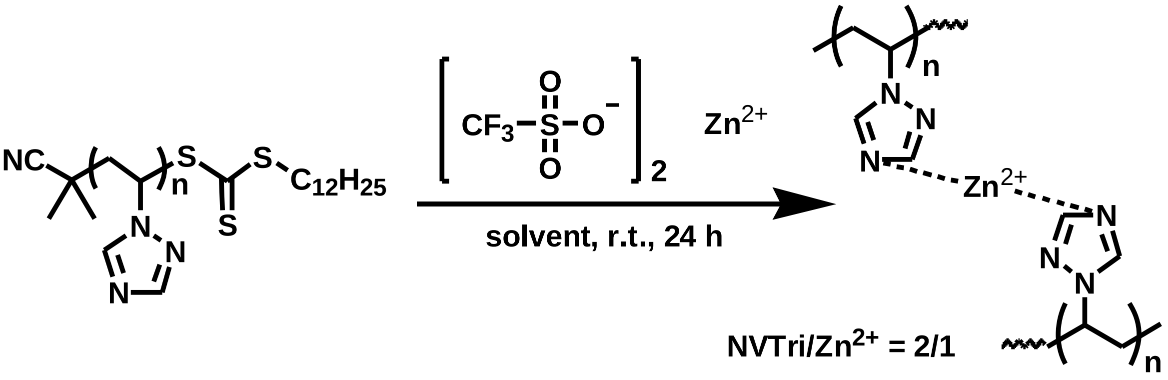


Figure S21. TGA and DSC curves of PNVTri-*b*-(St-*co*-DVB)s prepared by the copolymerization for (a) 2 h (micelles and rods) and (b) 3 h (worms), and their zinc complexes.

Table S11. Summary of thermal properties of PNVTri-*b*-P(St-*co*-DVB)s and zinc complexes [a)]

		T_{d5} [b)] (°C)	Residual weight [c)] (%)	T_g [d)] (°C)
PNVTri$_{50}$-*b*-P(St-DVB)$_{80}$	Pristine sample	364.9	9.9	86.8
	Zinc complex	200.0	23.5	76.1
PNVTri$_{50}$-*b*-P(St-DVB)$_{92}$	Pristine sample	350.6	9.5	79.4
	Zinc complex	202.5	20.9	75.2

a) Zinc complexes were prepared by the reaction of PNVTri-*b*-P(St-*co*-DVB) with Zn(OTf)$_2$ in DMF. b) Temperature for 5wt% weight loss under nitrogen. c) Residual weight of the sample heated at 10 °C/min until 550 °C in TGA under nitrogen. d) Measured by DSC.



Scheme S4. Formation of zinc complex from PNVTri homopolymer.

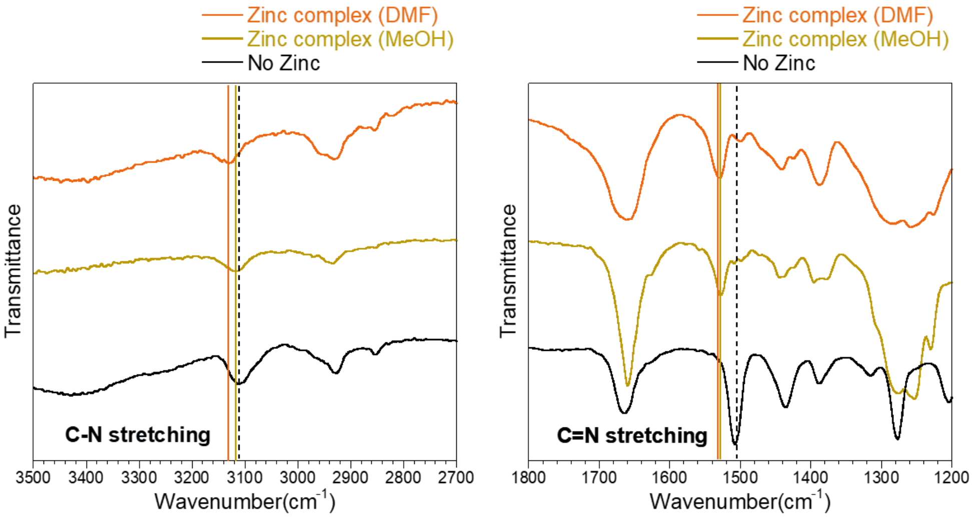


Figure S22. FT-IR spectra of PNVTri homopolymer and zinc complexes.

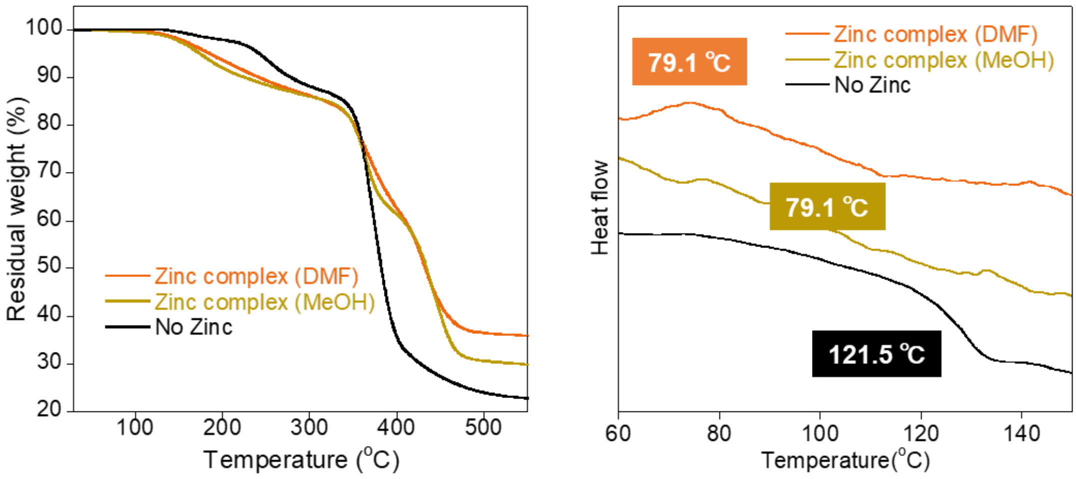
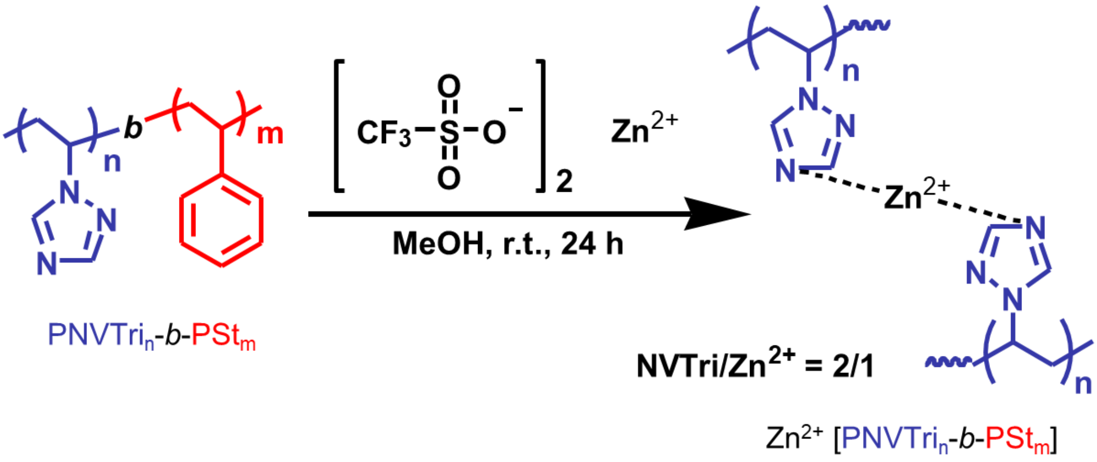


Figure S23. TGA and DSC curves of PNVTri homopolymer and zinc complexes.

Table S12. Summary of thermal properties of PNVTri homopolymer and zinc complexes [a)]

	solvent	T_{d5} [b)] (°C)	Residual weight [c)] (%)	T_g [d)] (°C)
PNVTri		242.6	22.2	121.5
PNVTri:Zn(OTf)$_2$ = 2:1	DMF	185.8	35.3	79.1
	MeOH	174.3	29.1	79.1

[a)] Zinc complexes were prepared by the reaction of PNVTri with Zn(OTf)$_2$ in DMF or MeOH. [b)] Temperature for 5wt% weight loss under nitrogen. [c)] Residual weight of the sample heated at 10 °C/min until 550 °C in TGA under nitrogen. [d)] Measured by DSC.



Scheme S5. Formation of zinc complexes from PNVTri-*b*-PSt.

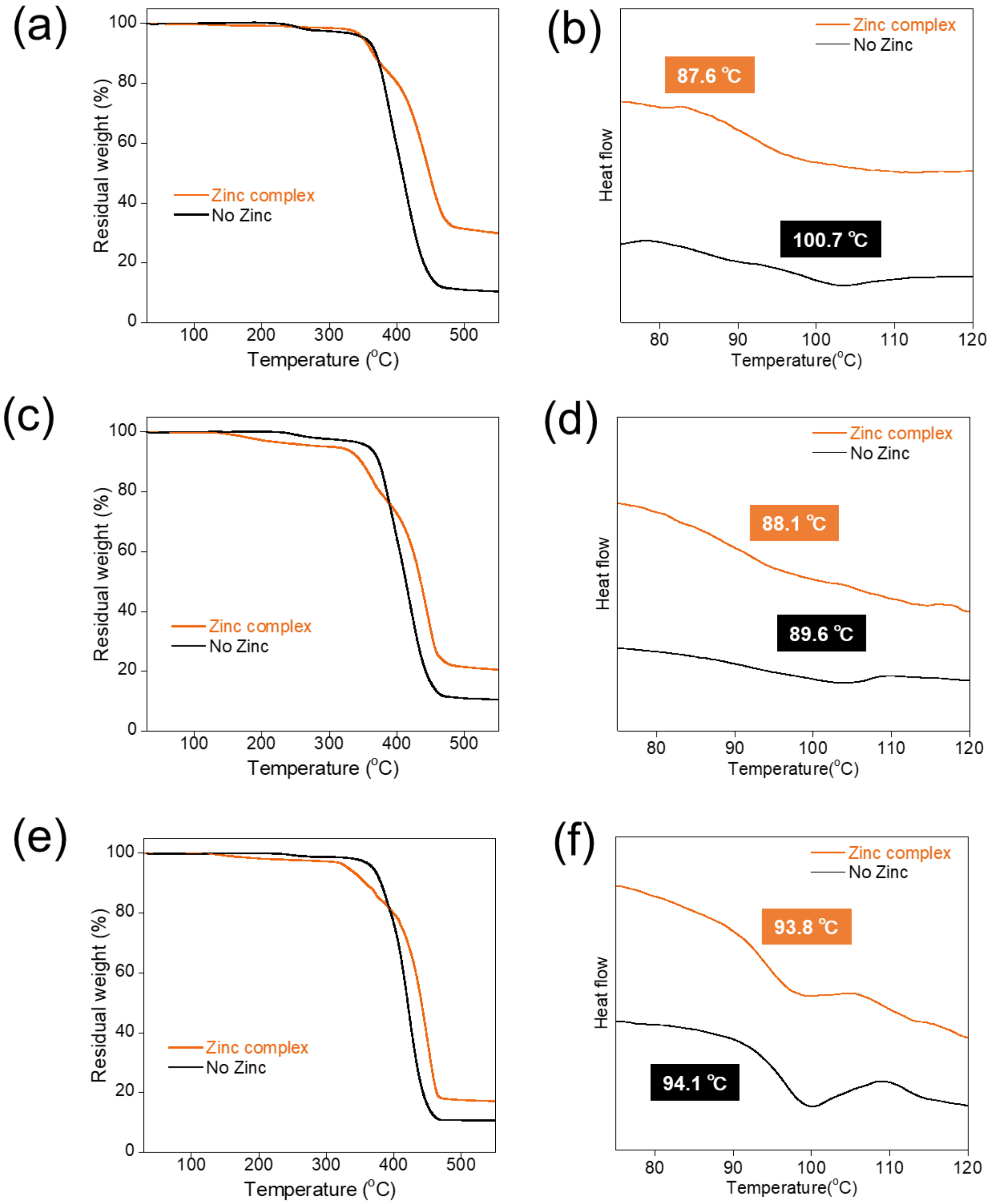


Figure S24. (a,c,e) TGA and (b,d,f) DSC curves of zinc complexes (NVTri : Zn^{2+} = 2 : 1) obtained from (a,b) PNVTri$_{50}$-*b*-PSt$_{83}$, (c,d) PNVTri$_{50}$-*b*-PSt$_{112}$, and (e,f) PNVTri$_{50}$-*b*-PSt$_{303}$ (see Table S1 and Figure 3 for detailed information of the pristine PNVTri-*b*-PSts).

Table S13. Summary of thermal properties of PNVTri-*b*-PSts and their zinc complexes a)

		T_{d5} b) (℃)	Residual weight c) (%)	T_g d) (℃)
PNVTri$_{50}$-*b*-PSt$_{83}$	Pristine sample	352.9	10.1	100.7
	Zinc complex	350.8	28.8	87.6
PNVTri$_{50}$-*b*-PSt$_{112}$	Pristine sample	358.7	10.4	89.6
	Zinc complex	309.2	19.6	88.1
PNVTri$_{50}$-*b*-PSt$_{303}$	Pristine sample	369.5	10.7	94.1
	Zinc complex	333.0	16.7	93.8

a) Zinc complexes were prepared by the reaction of PNVTri-*b*-PSts with Zn(OTf)$_2$ in MeOH. b) Temperature for 5wt% weight loss under nitrogen. c) Residual weight of the sample heated at 10 °C/min until 550 °C in TGA under nitrogen. d) Measured by DSC.

Table S14. Size of PNVTri-*b*-PSt/zinc complexes by DLS

Entry	Morphology a)	D_h b) (nm)	
		Pristine sample	Zinc complex
PNVTri$_{50}$-*b*-PSt$_{83}$	M, W	374	290
PNVTri$_{50}$-*b*-PSt$_{112}$	W, V	164	165
PNVTri$_{50}$-*b*-PSt$_{303}$	N	423	1120

a) Morphology was judged by TEM, where M = micelle, W = worm, V = vesicle, and nano tube = N b) Measured by DLS in MeOH.

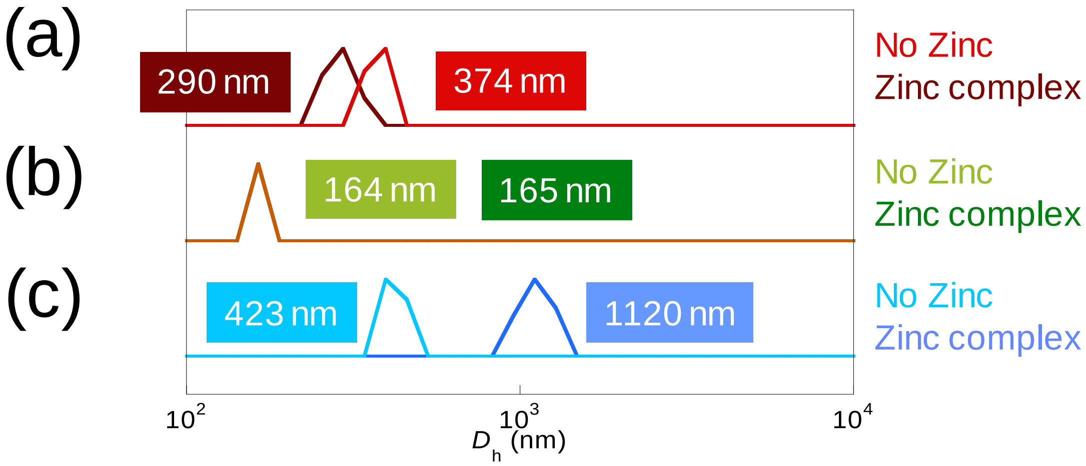
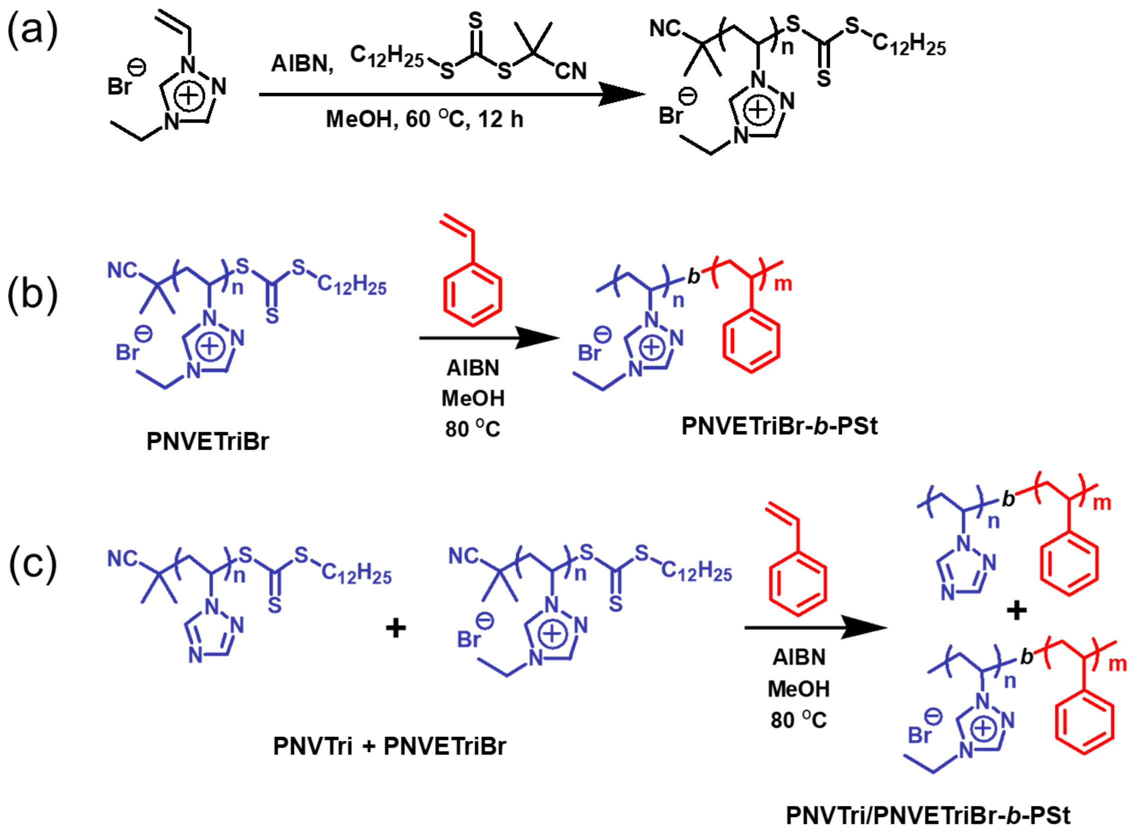


Figure S25. DLS traces (MeOH) of PNVTri-*b*-PSt/zinc complexes and pristine PNVTri-*b*-PSts, (a) PNVTri$_{50}$-*b*-PSt$_{83}$, (b) PNVTri$_{50}$-*b*-PSt$_{112}$, and (c) PNVTri$_{50}$-*b*-PSt$_{303}$.



Scheme S6. (a) Synthesis of PNVETriBr macro-CTA by RAFT polymerization of *N*-vinyl-4-ethyl-1,2,4-triazolium bromide (NVETriBr), (b,c) RAFT dispersion polymerization of St in MeOH, mediated by (b) PNVETriBr macro-CTA and (c) PNVTri/PNVETriBr macro-CTA.

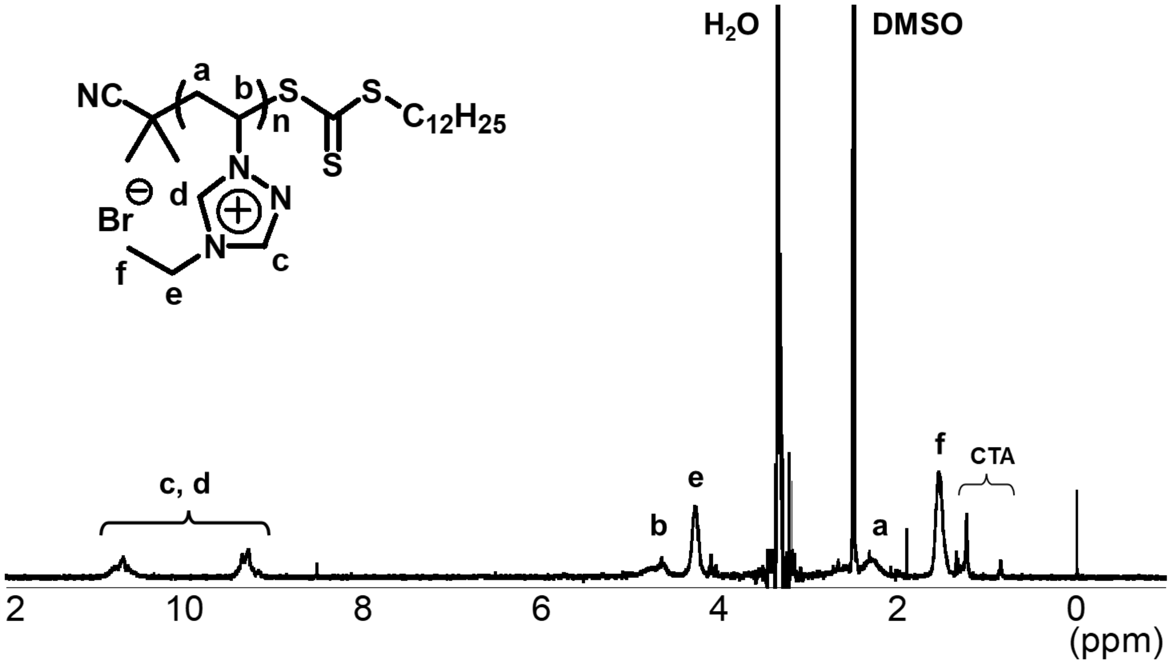


Figure S26. ^{1}H NMR spectrum of PNVETriBr macro-CTA in DMSO-d_6.

Table S15. Synthesis of cationic nano-objects via PISA in MeOH at 80 °C[a)]

Entry	Macro-CTA	Time (h)	Yield [b)] (%)	M_n [c)] (theory)	M_n [d)] (NMR)	n:m [d)] (NMR)	D_h [e)] (nm)	Zeta potential [e)] (mV)
4-3	PNVETriBr	3	14	25,000	35,000	16:84	36, 587	35
4-4		24	20	30,000	45,000	12:88	122	36
4-1	PNVTri + PNVETriBr	3	13	19,000 24,000	26,000 31,000	19:81	73	28
4-2		24	16	21,000 26,000	55,000 60,000	9:91	53, 237	32

[a)] $[I]_0/[\text{macro-CTA}]_0/[M]_0$ = 1/10/10000, St/Solvent = 1.0 w/w, macro-CTA is PNVTri : M_n = 5000, M_w/M_n = 1.18 and PNVETri : M_n = 9800. [b)] Dialysis in MeOH for 3 days. [c)] The theoretical molecular weight ($M_{n,\text{theory}}$) = (MW of St) × $[M]_0/[CTA]_0$ × yield + (M_n of Macro-CTA). [d)] Calculated by ^{1}H NMR in CD_2Cl_2/DMSO-d_6 = 3/1. [e)] Measured by DLS in MeOH.

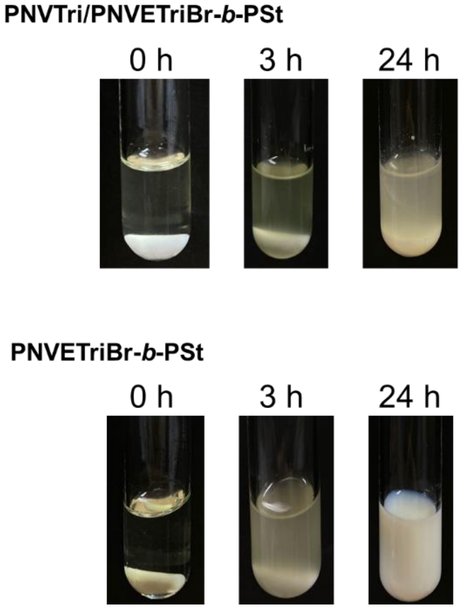


Figure S27. Turbidity change of PNVTri/PNVETriBr-*b*-PSts and PNVETriBr-*b*-PSts.

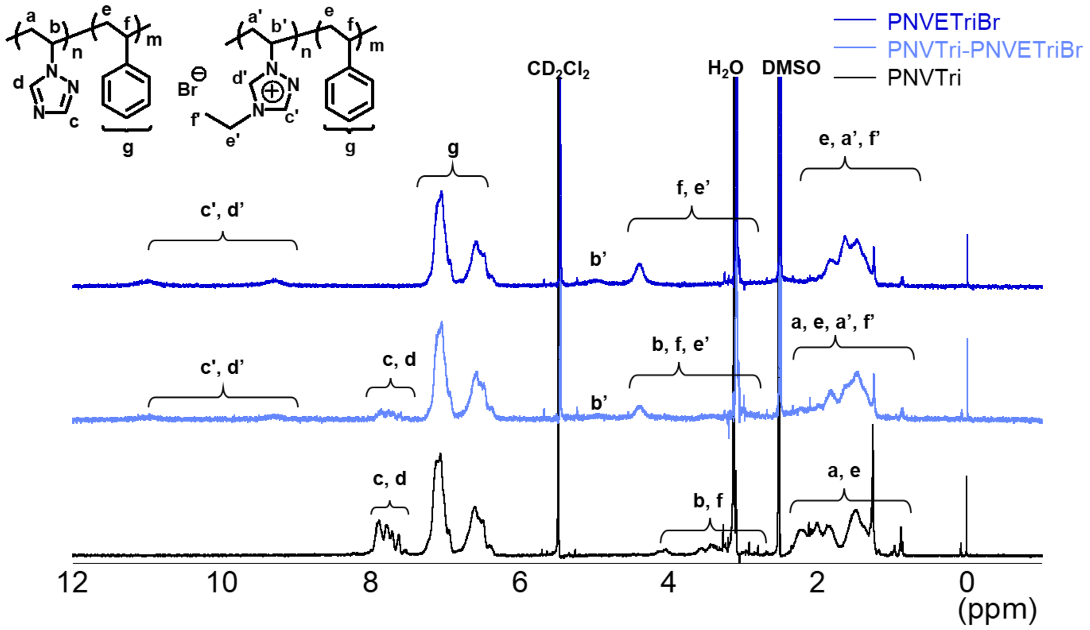


Figure S28. ${}^{1}H$ NMR spectra (CD_2Cl_2/DMSO-d_6 = 3/1) of block copolymers obtained by RAFT dispersion polymerization of St from PNVETriBr, PNVTri/PNVETriBr, and PNVTri in MeOH for 3h.

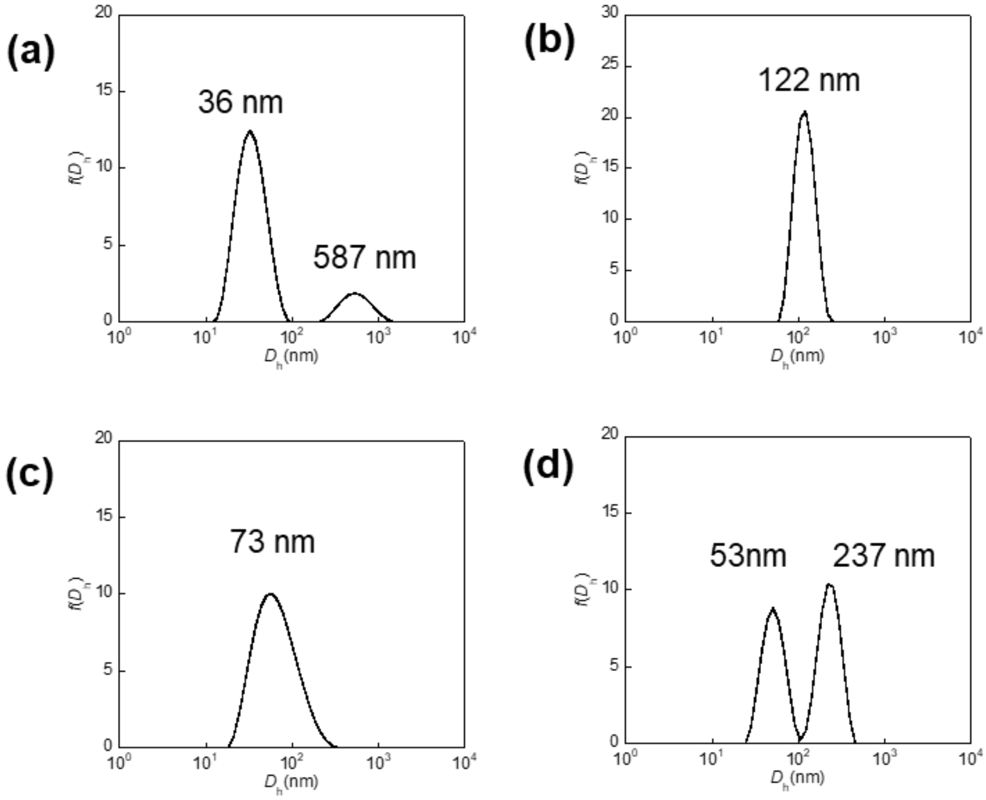


Figure S29. DLS traces of (a,b) PNVETriBr-*b*-PSts and (c,d) PNVTri/PNVETriBr-*b*-PSts obtained by RAFT dispersion polymerization at [AIBN]/[macro-CTA]/[St] = 1/10/10000 using (a,b) PNVTriBr macro-CTA and (c,d) PNVTri/PNVETriBr mixture in MeOH (St/solvent = 1.0 w/w) for (a,c) 3 h and (b,d) 24 h.

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