

Supporting Information

Exploration of a Living Anionic Polymerization Mechanism into Polymerization-Induced Self- Assembly and Site-Specific Stabilization of the Formed Nano-Objects

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Experimental Procedures

Materials

Styrene (S, 99 %, Sinopharm Chemical Reagent Co. (SCR)), *p*-*tert*-butylstyrene (*t*BS, 94 %, Alfa), *p*-methylphenylene (*p*MS, 98 %, Acros), α -methylstyrene (α MS, 98 %, TCI), and 1,1-diphenylethene (DPE, 98 %, Acros) were dried over CaH₂, distilled under reduced pressure, and stored in refrigerator below 0 °C. Isoprene (I, 99 %, SCR) was dried over CaH₂, distilled and stored in refrigerator below 0 °C. Heptane (99 %, SCR) was dried over CaH₂ and distilled just before use. *n*-Butyllithium (*n*Bu⁻Li⁺, 1.6 M in hexane, J&K) was used as received. Divinylbenzene (DVB, 99 %, SCR) was used as received and the impurities were consumed by the addition of *n*Bu⁻Li⁺. Tetrahydrofuran (THF, 99 %, SCR) was refluxed and distilled from potassium naphthalenide solution. All other reagents were purchased from SCR and used as received except for additional declaration.

Typical LAP PISA Process for Diblock Copolymer PI-*b*-PS

Using the LAP PISA system for diblock copolymer PI₆₀-*b*-PS₁₁₈ with weight solid content of 18 % w/w as an example. First, the dry solvent of *n*-heptane (325.9 mL, 221.58 g) and THF (2.0 mL, 1.79 g), monomer of isoprene (18.0 mL, 12.26 g) were sequentially charged into a 1L baked ampoule with a stirrer, and the system was immersed into a water bath maintaining at room temperature. Then, the impurities in the mixture was pre-consumed by the addition of *n*Bu⁻Li⁺, and the metred initiator of *n*Bu⁻Li⁺ (1.5 mL, 2.45 mmol) was rapidly added to initiate the polymerization. After 2.0 h, 5.0 mL of the mixture was withdrawn for characterization and the monomer of styrene (S) (40.5 mL, 36.77 g) was subsequently added. The dispersion was gradually formed and polymerization was continued for another 5.0 h. Before the following operation for cross-linking of the nano-objects, 5.0 mL of the mixture was withdrawn for characterization.

Macro-initiator PI, SEC: $M_{n,SEC} = 4,100$ g/mol, $M_w/M_n = 1.09$. $^1\text{H NMR}$ (CDCl_3 , δ , ppm, TMS): 0.81 (CH_3CH_2-), 1.22-2.25 (m, $-\text{C}(\text{CH}_3)-$, aliphatic main chain $-\text{CH}_2\text{CH}-$), 1.86 (m, $-\text{C}(\text{CH}_3)=\text{CH}-$ of 1,4-addition, $-\text{C}(\text{CH}_3)=\text{CH}_2$ of 3,4-addition), 4.61-4.69 ($-(\text{CH}_3)\text{C}=\text{CH}_2$ of 3,4-addition), 4.95 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 5.06 ($-\text{CH}=\text{C}(\text{CH}_3)-$ of 1,4-addition), 5.70 ($-\text{CH}=\text{CH}_2$ of 1,2-addition). PI-*b*-PS, SEC: $M_{n,SEC} = 14,400$ g/mol, $M_w/M_n = 1.17$. $^1\text{H NMR}$ (CDCl_3 , δ , ppm, TMS): 0.81 (CH_3CH_2-), 1.22-2.25 (m, $-\text{C}(\text{CH}_3)-$ on PI, aliphatic main chain $-\text{CH}_2\text{CH}-$ on PI and PS), 1.86 (m, $-\text{C}(\text{CH}_3)=\text{CH}-$ of 1,4-addition, $-\text{C}(\text{CH}_3)=\text{CH}_2$ of 3,4-addition), 4.61-4.69 ($-(\text{CH}_3)\text{C}=\text{CH}_2$ of 3,4-addition), 4.95 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 5.06 ($-\text{CH}=\text{C}(\text{CH}_3)-$ of 1,4-addition), 5.70 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 6.30-7.30 (m, 5H, aromatic $-\text{C}_6\text{H}_5$ on PS).

Cross-linking and Stabilization of the Nano-objects Formed in LAP PISA Process

Aiming to stabilize the nano-objects formed in LAP PISA, the DVB agent (5.0 mL, 4.60 g, 35.2 mmol) was added after the polymerization of styrene monomer. After another 2.0 h, the polymerization was terminated by exposure to the air. The obtained dispersions were diluted into heptane or THF for further characterization.

Typical LAP PISA Process for Diblock Copolymer PI-*b*-P(S-*co*-X) (X = *p*MS, *t*BS, *a*MS, or DPE)

Using the LAP PISA system for diblock copolymer $\text{PI}_{62}\text{-}b\text{-P}(\text{S}_{81}\text{-}co\text{-}p\text{MS}_{36})$ with targeted MW ratio $M_{n,P(S-co-X)}/M_{n,PI} = 3/1$, molar ratio $[\text{S}]_0 / [\text{X}]_0 = 2/1$, and weight solid content of 18 % w/w as an example. Similar to the above procedure for PI-*b*-PS, the synthesis of macro-initiator PI was firstly synthesized. Differently, by referring our previous work,^{1,2} the comonomer of styrene (S) and *p*-methylphenylene (*p*MS) were mixed and injected into the polymerization system in 24.0 h with a constant addition rate controlled by a programmed syringe pump (KD Scientific Legato 100)

in the second polymerization stage. After the addition of the comonomers, the polymerization was continued for another 2.0 h, and the polymerization was finally terminated by exposure to the air.

Macro-initiator PI, SEC: $M_{n,SEC} = 4,200$ g/mol, $M_w/M_n = 1.08$. $^1\text{H NMR}$ (CDCl_3 , δ , ppm, TMS): 0.81 (CH_3CH_2 -), 1.22-2.25 (m, $-\text{C}(\text{CH}_3)$ -), aliphatic main chain $-\text{CH}_2\text{CH}-$, 1.86 (m, $-\text{C}(\text{CH}_3)=\text{CH}-$ of 1,4-addition, $-\text{C}(\text{CH}_3)=\text{CH}_2$ of 3,4-addition), 4.61-4.69 ($-(\text{CH}_3)\text{C}=\text{CH}_2$ of 3,4-addition), 4.95 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 5.06 ($-\text{CH}=\text{C}(\text{CH}_3)-$ of 1,4-addition), 5.70 ($-\text{CH}=\text{CH}_2$ of 1,2-addition). PI-*b*-P(*S-co-pMS*), SEC: $M_{n,SEC} = 13,600$ g/mol, $M_w/M_n = 1.33$. $^1\text{H NMR}$ (CDCl_3 , δ , ppm, TMS): 0.81 (CH_3CH_2 -), 1.22-2.25 (m, $-\text{C}(\text{CH}_3)$ - on PI, $\text{CH}_3(\text{C}_6\text{H}_4)$ - on P(*S-co-pMS*)), aliphatic main chain $-\text{CH}_2\text{CH}-$ on PI and P(*S-co-pMS*)), 1.86 (m, $-\text{C}(\text{CH}_3)=\text{CH}-$ of 1,4-addition, $-\text{C}(\text{CH}_3)=\text{CH}_2$ of 3,4-addition), 4.61-4.69 ($-(\text{CH}_3)\text{C}=\text{CH}_2$ of 3,4-addition), 4.95 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 5.06 ($-\text{CH}=\text{C}(\text{CH}_3)-$ of 1,4-addition), 5.70 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 6.30-7.30 (m, 5H, aromatic $-\text{C}_6\text{H}_5$, $\text{CH}_3(\text{C}_6\text{H}_4)$ - on P(*S-co-pMS*)).

By changing *pMS* as *tBS*, αMS , or DPE, the PI-*b*-P(*S-co-X*) with different core-forming block can be synthesized in LAP PISA system.

Instruments and characterizations

The molecular weight (MW) and molecular weight distribution (M_w/M_n) of polymers were analyzed by size exclusion chromatography (SEC) measurement, which was performed in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent 1100 equipped with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector. One 5 μm LP gel column (molecular range 500 - 2×10^4 g/mol) and two 5 μm LP gel mixed bed columns (molecular range 200 - 3×10^6 g/mol) were calibrated by PS standards. The injection volume was 20 μL , and the concentration was 5-10 mg/mL.

The proton nuclear magnetic resonance (^1H NMR) spectra of polymers were recorded on a Bruker (400 MHz) spectrometer in CDCl_3 with tetramethylsilane (TMS) as the internal reference at 298 K.

The dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS90 was employed to determine the average hydrodynamic diameter and distribution, and the scattered light was detected at an angle of 173° . The used solvent was heptane or THF.

The transmission electron microscopy (TEM) was performed using a JEOL JEM-1230 instrument operated at 80 kV. The as-prepared nano-objects were diluted into heptane or THF to give 0.1 - 0.3 % w/w dispersion. After one drop of the dispersion was deposited onto carbon coated copper grids, the copper grids were dried in air for 24 h and used for TEM measurement.

The Kinexus Pro rheometer (Malvern Instrument Inc., UK) equipped with a steel parallel-plate geometry of 40 mm diameter was used to determine the rheological properties of the nano-objects. Loss modulus and storage modulus were measured as a function of percentage strain. The angular frequency and temperature were fixed at 10 rad/s and 25°C , respectively.

The small-angle X-ray scattering (SAXS) measurements were performed using a Xenocs Xeuss 2.0 instrument (8 KeV Cu $K\alpha$ radiation) equipped with a Pilatus 3R 200K-A area detector and a beam-stop. The SAXS patterns were recorded over a scattering vector q range of $0.045 \text{ \AA}^{-1} < q < 0.24 \text{ \AA}^{-1}$. The instrument is equipped with a liquid sample holder. The liquid sample is sealed in a capillary tube and placed on a liquid sample holder for testing. The SAXS studies of the dispersions (10 % w/w) were conducted at 25°C under vacuum.

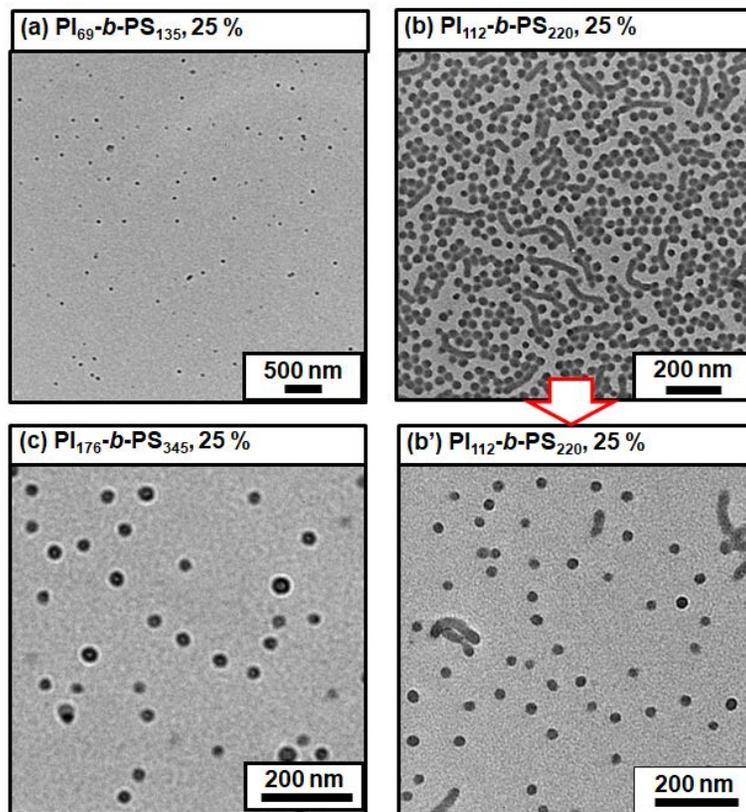


Figure S1. TEM images of nano-objects (diluted into 0.1~0.3 % w/w dispersions, and the sample on copper grid was not stained) formed in LAP PISA process by fixing targeted MW ratio $M_{n,PS}/M_{n,PI}$ as 3/1 and weight solid content as 25 % w/w: (a) spherical micelles prepared from $PI_{69}-b-PS_{135}$, (b, b') spherical and short wormlike micelles prepared from $PI_{112}-b-PS_{220}$, (c) spherical micelles prepared from $PI_{176}-b-PS_{345}$.

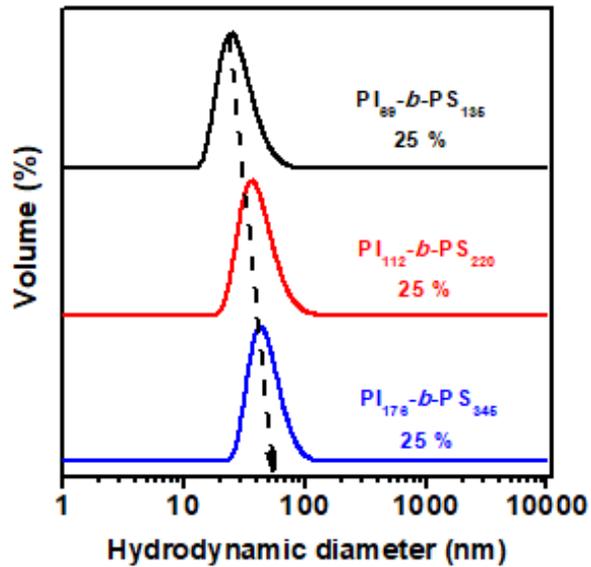


Figure S2. DLS results of nano-objects formed in LAP PISA process by fixing targeted MW ratio $M_{n,PS}/M_{n,PI}$ as 3/1 and weight solid content as 25 % w/w: (a) spherical micelles prepared from PI₆₉-*b*-PS₁₃₅, (b, b') spherical and short wormlike micelles prepared from PI₁₁₂-*b*-PS₂₂₀, (c) spherical micelles prepared from PI₁₇₆-*b*-PS₃₄₅.

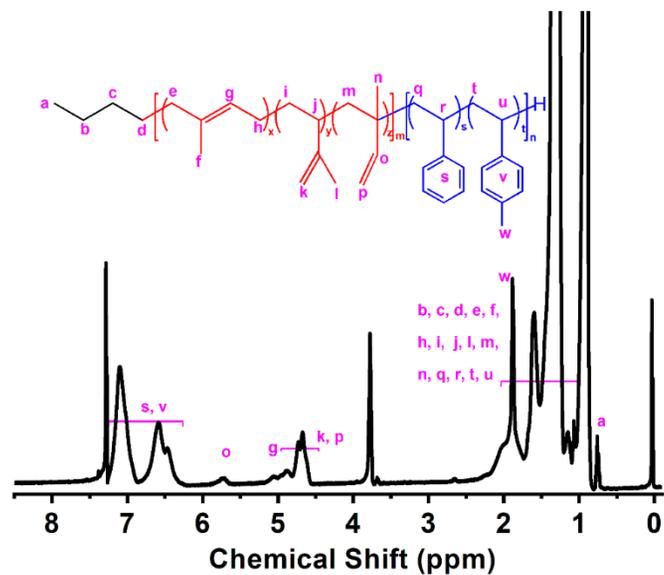


Figure S3. The ^1H NMR spectrum for crude diblock copolymer PI-*b*-P(S-*co*-*p*MS) (in CDCl_3).

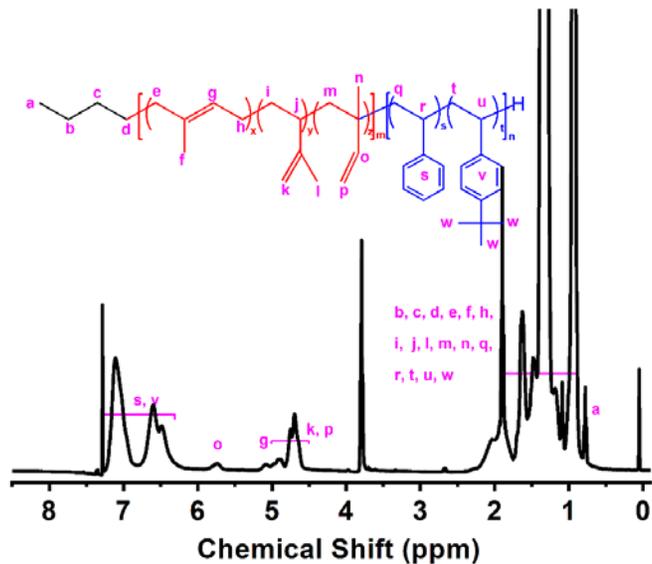


Figure S4. The ^1H NMR spectrum for crude diblock copolymer PI-*b*-P(S-*co*-*t*BS) (in CDCl_3).

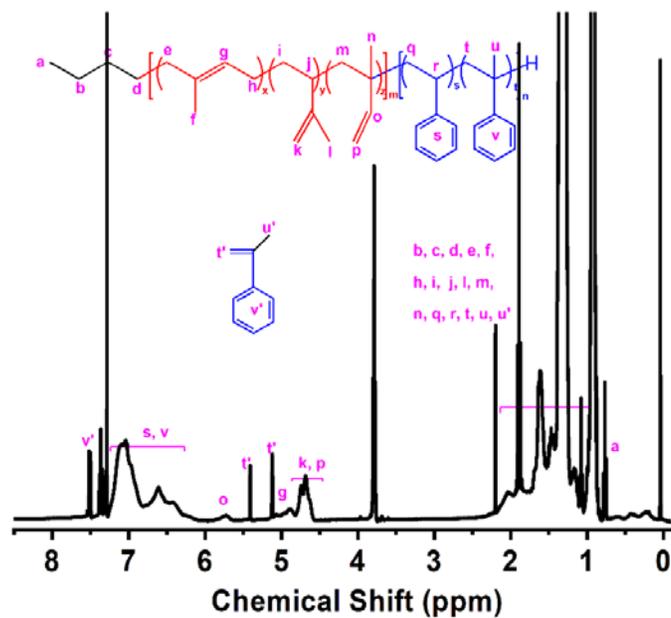


Figure S5. The ^1H NMR spectrum for crude diblock copolymer PI-*b*-P(S-*co*-aMS) (in CDCl_3).

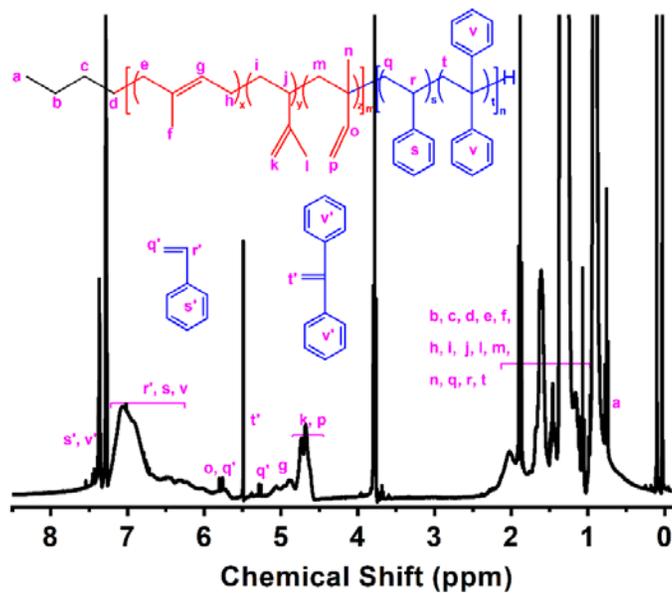


Figure S6. The ^1H NMR spectrum for crude diblock copolymer PI-*b*-P(S-*co*-DPE) (in CDCl_3).

Table S1. The formulation and characterization data for diblock copolymer PI-*b*-PS with different macro-initiator PI, targeted MW ratio $M_{n,PS}/M_{n,PI}$, and weight solid content.

Samples	Weight solid content (wt %)	Targeted MW ratio $M_{n,PS}/M_{n,PI}$	The first polymerization stage			The second polymerization stage			Morphology ^[d]
			$M_{n,PI}$ ^[a]	M_w/M_n ^[a]	DP_{PI} ^[b]	$M_{n,PI-b-PS}$ ^[a]	M_w/M_n ^[a]	DP_{PS} ^[c]	
PI ₈₇ - <i>b</i> -PS ₁₁₄	10	2/1	5,900	1.10	87	21,000	1.12	114	Spherical and short wormlike micelles
PI ₈₂ - <i>b</i> -PS ₁₆₁	10	3/1	5,600	1.09	82	26,300	1.14	161	Spherical and short wormlike micelles
PI ₈₂ - <i>b</i> -PS ₂₁₄	10	4/1	5,600	1.08	82	28,500	1.07	214	Wormlike micelles
PI ₇₀ - <i>b</i> -PS ₄₆	18	1/1	4,800	1.06	70	8,600	1.11	46	Irregular morphology
PI ₁₁₀ - <i>b</i> -PS ₇₂	18	1/1	7,500	1.10	110	16,600	1.11	72	Irregular morphology
PI ₁₀₁ - <i>b</i> -PS ₁₁₉	18	1.8/1	6,900	1.03	101	22,400	1.09	119	Spherical micelles
PI ₈₄ - <i>b</i> -PS ₁₁₁	18	2/1	5,700	1.09	84	16,400	1.16	110	Spherical micelles
PI ₁₃ - <i>b</i> -PS ₂₆	18	3/1	900	1.17	13	3,600	1.21	26	Irregular morphology
PI ₄₉ - <i>b</i> -PS ₉₆	18	3/1	3,300	1.06	49	14,300	1.10	96	Wormlike micelles
PI ₆₀ - <i>b</i> -PS ₁₁₈	18	3/1	4,100	1.09	60	14,400	1.17	118	Wormlike micelles
PI ₈₈ - <i>b</i> -PS ₁₇₃	18	3/1	6,000	1.08	88	19,700	1.05	173	Spherical and short wormlike micelles
PI ₁₀₉ - <i>b</i> -PS ₂₁₄	18	3/1	7,400	1.11	109	26,300	1.13	214	Spherical and short wormlike micelles
PI ₈₇ - <i>b</i> -PS ₂₂₈	18	4/1	5,900	1.07	87	29,700	1.07	228	Wormlike micelles
PI ₂₉ - <i>b</i> -PS ₁₁₄	18	6/1	2,000	1.09	29	14,800	1.17	114	Wormlike micelles
PI ₁₀₀ - <i>b</i> -PS ₃₉₂	18	6/1	6,800	1.05	100	47,600	1.09	392	Wormlike micelle
PI ₁₃ - <i>b</i> -PS ₁₀₄	18	8/1	3,100	1.09	46	25,600	1.18	238	Wormlike micelle
PI ₁₃ - <i>b</i> -PS ₁₀₄	18	12/1	900	1.15	13	13,700	1.11	104	Precipitate
PI ₂₂ - <i>b</i> -PS ₁₇₃	18	12/1	1,500	1.12	22	20,800	1.12	173	Precipitate
PI ₄₃ - <i>b</i> -PS ₃₃₅	18	12/1	2,900	1.07	100	34,700	1.18	335	Wormlike micelles
PI ₈₄ - <i>b</i> -PS ₆₅₉	18	12/1	5,700	1.08	84	86,400	1.16	659	Spherical micelles
PI ₂₈ - <i>b</i> -PS ₃₂₉	18	18/1	1,900	1.08	28	33,100	1.16	329	Precipitate
PI ₆₉ - <i>b</i> -PS ₁₃₅	25	3/1	4,700	1.08	69	15,600	1.15	135	Spherical micelles
PI ₁₁₂ - <i>b</i> -PS ₂₂₀	25	3/1	7,600	1.11	112	23,100	1.11	220	Spherical and short wormlike micelles
PI ₁₇₆ - <i>b</i> -PS ₃₄₅	25	3/1	12,000	1.11	176	33,100	1.19	345	Spherical micelles

[a] The M_n and M_w/M_n were obtained by SEC measurement using THF as elution and PS as standard. [b] DP of macro-initiator PI (DP_{PI}) was calculated according to the $M_{n,PI}$ from SEC measurement. [c] DP of PS (DP_{PS}) was calculated according to the DP_{PI} and 1H NMR spectrum. [d] The morphology was monitored by TEM measurement.

Table S2. The formulation and characterization data for diblock copolymer PI-*b*-P(S-co-X) with different comonomers.^[a]

Samples	Weight solid content (wt %)	Targeted MW ratio $M_{n,P(S-co-X)}/M_{n,PI}$	The first polymerization stage			The second polymerization stage						Morphology ^[e]
			$M_{n,PI}$ ^[b]	M_w/M_n ^[b]	DP_{PI} ^[c]	$M_{n,PI-b-P(S-co-X)}$ ^[b]	M_w/M_n ^[b]	Conv. _S ^[d]	Conv. _X ^[d]	DP_{PS} ^[d]	DP_{PX} ^[d]	
PI ₆₂ - <i>b</i> -P(S ₈₁ - <i>co-p</i> MS ₃₆)	20	2/1	4,200	1.08	62	13,600	1.33	100	100	81	36	Spherical micelles
PI ₆₆ - <i>b</i> -P(S ₈₆ - <i>co-t</i> BS ₂₈)	20	2/1	4,500	1.08	66	15,500	1.24	100	100	86	28	Irregular morphology
PI ₇₂ - <i>b</i> -P(S ₉₄ - <i>co-α</i> MS ₃₄)	20	2/1	4,900	1.09	72	14,700	1.32	100	81	94	34	Spherical micelles
PI ₆₃ - <i>b</i> -P(S ₈₃ - <i>co-DPE</i> ₁₆)	20	2/1	43,00	1.10	63	14,500	1.28	94	68	83	16	Wormlike micelles

[a] Targeted MW ratio $M_{n,P(S-co-X)}/M_{n,PI}$ was 3/1, molar ratio $[S]_0 / [X]_0$ was 2/1, and MW of macro-initiator PI was between 4000~5000 g/mol, and weight solid content was 18 % w/w ($X = pMS, tBS, \alpha MS, \text{ or } DPE$). [b] The M_n and M_w/M_n were obtained by SEC measurement using THF as elution and PS as standard. [c] DP of macro-initiator PI (DP_{PI}) was calculated according to the $M_{n,PI}$ from SEC measurement. [d] DP of monomers (DP_{PS}, DP_{PX}), conversion of monomers (Conv._S and Conv._X) were calculated according to the DP_{PI} and ¹H NMR spectrum. [e] The morphology was monitored by TEM measurement.

References

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(2) Shen, H. Y.; Wang, G. W. A versatile flash cyclization technique assisted by microreactor. *Polym. Chem.* **2017**, 8 (36), 5554-5560.