Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Polymerization-Induced Self-Assembly Process for All-Styrenic Nano-objects Using the Living Anionic Polymerization Mechanism

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EXPERIMENTAL SECTION

Materials

p-*Tert*-butylstyrene (*t*BS, 94 %, Alfa), styrene (S, 99 %, Sinopharm Chemical Reagent Co. (SCR)), and heptane (99 %, SCR) were dried over CaH_2 and distilled under reduced pressure before use. *n*-Butyllithium (*n*Bu$^-$Li$^+$, 1.6 M in hexane, J&K) was used as received. 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.

LAP PISA Process for Nano-objects from Diblock Copolymer P*t*BS-*b*-PS

The LAP PISA process for nano-objects from diblock copolymer P*t*BS$_{27}$-*b*-PS$_{124}$ with solids content of 20 % w/w was illustrated. Typically, the dry monomer of *p*-*tert*-butylstyrene (17.1 mL, 15.00 g), solvent of *n*-heptane (349 mL, 237.60 g) and THF (2.7 mL, 2.40 g) were sequentially charged into a 500 mL baked ampoule with a stirrer. Then, the remained impurities in the mixture was pre-consumed by the dropwisely addition of *n*Bu$^-$Li$^+$, and the metred initiator of *n*Bu$^-$Li$^+$ (2.10 mL, 3.33 mmol) was rapidly injected to initiate the polymerization. After 2.0 h, 5.0 mL of the mixture was withdrawn for characterization. Subsequently, the monomer of styrene (49.5 mL, 45.00 g) was added, and polymerization was continued for another 5.0 h. Finally, the dispersion was formed and the polymerization was terminated by exposure to the air.

Macro-initiator P*t*BS, SEC: $M_{n,PtBS}$ = 4,300 g/mol, M_w/M_n = 1.07. ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 0.82 (C***H***$_3$CH$_2$-), 1.10-2.20 (m, -C(C***H***$_3$)$_3$, aliphatic main chain -C***H***$_2$C***H***-), 6.10-7.30 (m, 4H, aromatic –C$_6$***H***$_4$). Diblock copolymer P*t*BS-*b*-PS, SEC: $M_{n,PtBS\text{-}b\text{-}PS}$ = 23,500 g/mol, M_w/M_n = 1.06. ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): ^{1}H NMR ($CDCl_3$, δ, ppm, TMS): 0.82 (C***H***$_3$CH$_2$-), 1.10-2.20 (m, -C(C***H***$_3$)$_3$, aliphatic main chain -C***H***$_2$C***H***-), 6.10-7.30 (m, 4H, aromatic –C$_6$***H***$_4$ on P*t*BS; 5H, aromatic –C$_6$***H***$_5$ on PS).

Characterization.

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.

^{1}H Nuclear Magnetic Resonance (NMR) spectra of polymers were recorded on a Bruker (400 MHz) spectrometer in deuterochloroform ($CDCl_3$) with tetramethylsilane (TMS) as the internal reference at 298 K.

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 heptane was used as solvent.

The transmission electron microscopy (TEM) was performed using a JEOL JEM-1230 instrument operated at 80 kV. The crude dispersion was diluted into heptane 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.

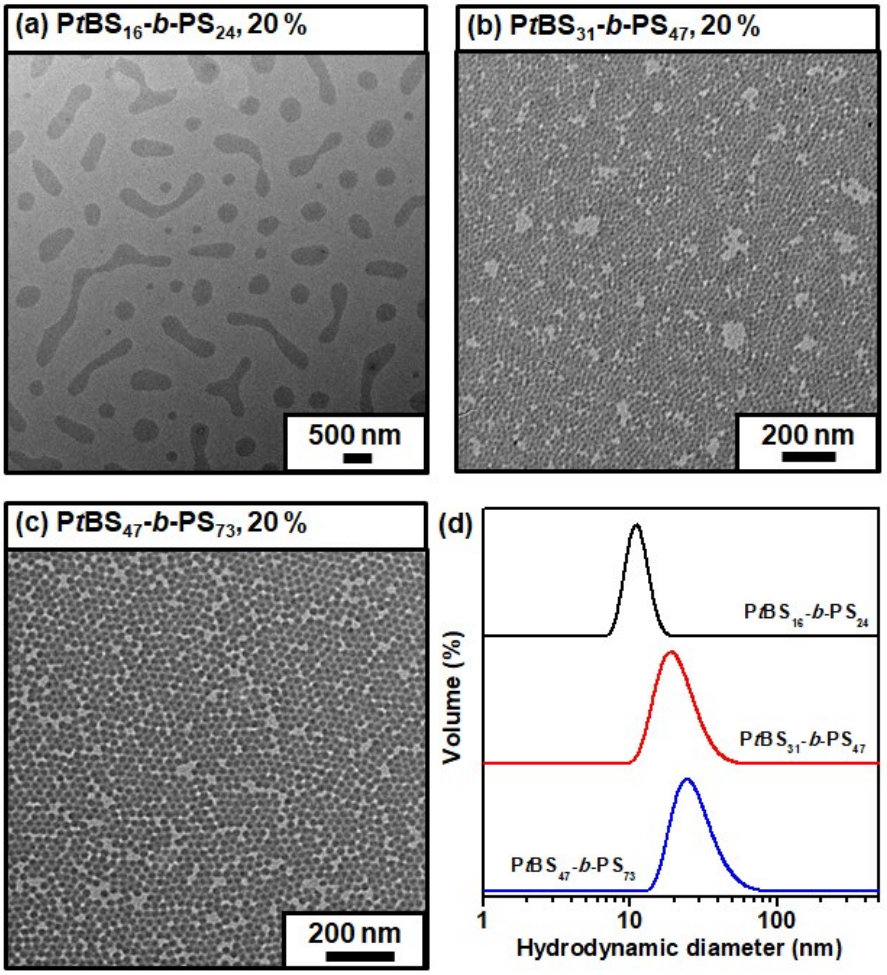

Fig. S1 TEM images of nano-objects formed in LAP PISA process using weight solids content as 20 % w/w, targeted MW ratio $M_{n,PS}/M_{n,PtBS}$ as 1/1, and the macro-initiator P*t*BS with different MWs: (a) irregular morphologies prepared from P*p*TBS$_{16}$-*b*-PS$_{24}$, (b) spherical micelles prepared from P*t*BS$_{31}$-*b*-PS$_{47}$, (c) spherical micelles prepared from P*t*BS$_{47}$-*b*-PS$_{73}$, (d) DLS results of the corresponding nano-objects.

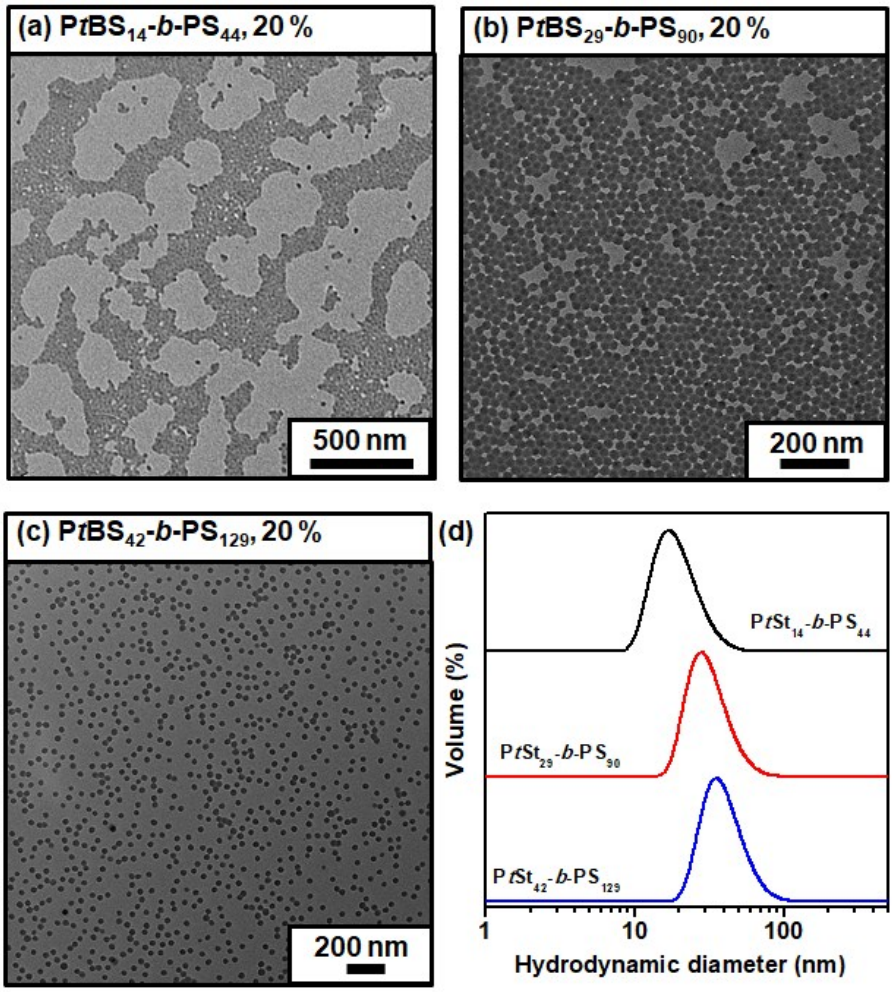

Fig. S2 TEM images of nano-objects formed in LAP PISA process using weight solids content as 20 % w/w, targeted MW ratio $M_{n,PS}/M_{n,PtBS}$ as 2/1, and the macro-initiator P*t*BS with different MWs: (a) irregular morphologies prepared from P*t*BS_{14}-*b*-PS_{44}, (b) spherical micelles prepared from P*t*BS_{29}-*b*-PS_{90}, (c) spherical micelles prepared from P*t*BS_{42}-*b*-PS_{129}, (d) DLS results of the corresponding nano-objects.

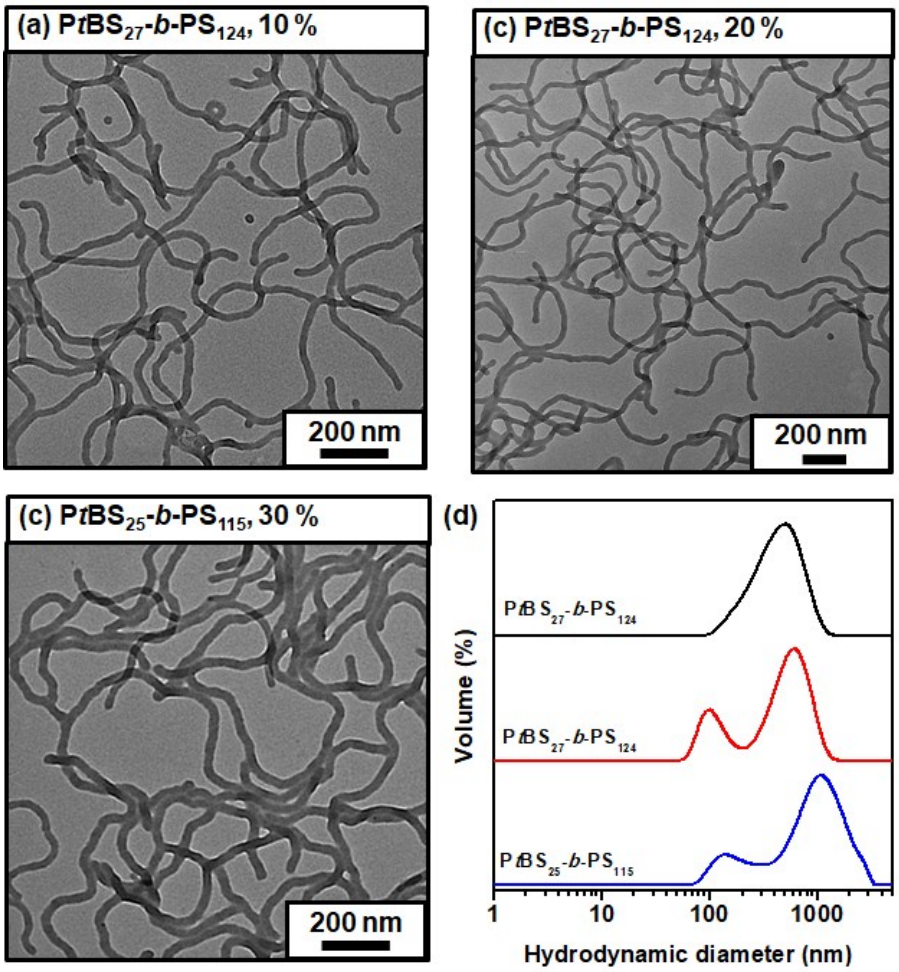

Fig. S3 TEM images of nano-objects formed in LAP PISA process using targeted MW ratio $M_{n,\mathrm{PS}}/M_{n,\mathrm{P}t\mathrm{BS}}$ as 3/1, macro-initiator P*t*BS with MWs between 4,000~4,500 g/mol, and different weight solids content: (a) wormlike micelles prepared from P*t*BS$_{27}$-*b*-PS$_{124}$ (weight solids content was 10 % w/w), (b) wormlike micelles prepared from P*t*BS$_{27}$-*b*-PS$_{124}$ (weight solids content was 20 % w/w), (c) wormlike micelles prepared from P*t*BS$_{25}$-*b*-PS$_{115}$ (weight solids content was 30 % w/w), (d) DLS results of the corresponding nano-objects.

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

Samples	Weight Solids Content (wt %)	Targeted MW ratio $M_{n,PS}/M_{n,PtBS}$	The first polymerization stage			The second polymerization stage				Morphology[e]
			$M_{n,PtBS}$[a]	M_w/M_n[a]	DP_{PtBS}[b]	$M_{n,PtBS\text{-}b\text{-}PS}$[a]	M_w/M_n[a]	DP_{PS}[c]	Conv.$_{St}$[d] (%)	
P*t*BS$_{16}$-*b*-PS$_{24}$	20	1/1	2,500	1.15	16	4,600	1.08	24	100	Irregular morphologies
P*t*BS$_{31}$-*b*-PS$_{47}$	20	1/1	4,900	1.06	31	12,000	1.07	47	100	Spherical micelles
P*t*BS$_{47}$-*b*-PS$_{73}$	20	1/1	7,600	1.07	47	17,000	1.09	73	> 99	Spherical micelles
P*t*BS$_{14}$-*b*-PS$_{44}$	20	2/1	2,300	1.14	14	8,000	1.06	44	100	Irregular morphologies
P*t*BS$_{29}$-*b*-PS$_{90}$	20	2/1	4,700	1.07	29	19,000	1.04	90	100	Spherical micelles
P*t*BS$_{42}$-*b*-PS$_{129}$	20	2/1	6,700	1.06	42	28,000	1.05	129	> 99	Spherical micelles
P*t*BS$_{11}$-*b*-PS$_{49}$	20	3/1	1,700	1.15	11	9,100	1.09	49	100	Precipitate
P*t*BS$_{16}$-*b*-PS$_{72}$	20	3/1	2,500	1.09	16	14,500	1.04	72	100	Precipitate
P*t*BS$_{27}$-*b*-PS$_{124}$	20	3/1	4,300	1.07	27	23,500	1.06	124	100	Wormlike micelles
P*t*BS$_{48}$-*b*-PS$_{222}$	20	3/1	7,700	1.06	48	44,000	1.04	222	> 99	Spherical micelles
P*t*BS$_{80}$-*b*-PS$_{369}$	20	3/1	12,800	1.06	80	80,000	1.04	369	> 99	Spherical micelles
P*t*BS$_{26}$-*b*-PS$_{162}$	20	4/1	4,200	1.07	26	32,500	1.11	162	100	Mixture of spherical, wormlike and vesicular micelles
P*t*BS$_{21}$-*b*-PS$_{163}$	20	5/1	3,400	1.09	21	31,100	1.04	163	100	Precipitate
P*t*BS$_{31}$-*b*-PS$_{236}$	20	5/1	4,900	1.06	31	43,500	1.05	236	100	Mixture of spherical, wormlike and vesicular micelles
P*t*BS$_{45}$-*b*-PS$_{346}$	20	5/1	7,200	1.06	45	73,300	1.04	346	> 99	Spherical micelles
P*t*BS$_{31}$-*b*-PS$_{377}$	20	8/1	4,900	1.06	31	68,700	1.07	377	100	Mixture of spherical and vesicular micelles
P*t*BS$_{28}$-*b*-PS$_{519}$	20	12/1	4,500	1.07	28	124,400	1.07	519	100	Vesicular micelles
P*t*BS$_{27}$-*b*-PS$_{124}$	10	3/1	4,300	1.08	27	24,400	1.05	124	100	Wormlike micelles
P*t*BS$_{25}$-*b*-PS$_{115}$	30	3/1	4,000	1.08	25	21,800	1.05	115	100	Wormlike 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 P*t*BS segment (DP_{PtBS}) was calculated according to the $M_{n,PtBS}$ from SEC measurement. [c] DP of PS segment (DP_{PS}) was calculated according to the DP_{PtBS} and ^1H NMR spectrum. [d] The monomer conversion of styrene ($Conv._{St}$) in the second polymerization stage was calculated according to the ^1H NMR spectrum. [e.] The morphology was monitored by TEM measurement.a