Supplementary Information

Crystallization-driven one-dimensional self-assembly of polyethylene-*b*-poly(*tert*-butylacrylate) diblock copolymers in DMF: Effects of crystallization temperature and corona-forming block

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Synthesis of polyethylene-*b*-poly(*tert*-butylacrylate) (PE-*b*-P*t*BA) diblock copolymers

Materials. All manipulations involving air- and/or moisture-sensitive compounds were carried out in a glove box or by using Schlenk technique. Trimethylsulfoxonium iodide (Acros, 98%), benzyltributylammonium chloride (Acros, 98+%), Celite-545 (Acros), borane dimethyl sulfide (Acros, 1 M in CH_2Cl_2), phenolphthalein (Acros, 98.5%), trimethylamine *N*-oxide dehydrate (Acros, 98%), and 2-bromo-2-methylproplonyl bromide (Acros, 98%) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, Alfa, 98%) were used as received without further purification. *tert*-butylacrylate (*t*-BuA, Alfa, 99%) was washed with 5% (w/v) aqueous NaOH solution and then washed with distilled water. After drying over calcium hydride and filtering off the drying agent, the monomer was distilled under vacuum. Copper (I) bromide (Acros, 99.9%) was purified by washing with 3% (v/v) aqueous glacial acetic acid solution, followed by ethanol and diethyl ether, and finally dried under vacuum overnight. Sodium hydride (NaH, Acros, 60%, dispersed in mineral oil) was washed thrice with *n*-hexane to remove mineral oil before use. Toluene and *n*-hexane were refluxed over sodium flakes/benzophenone and distilled under N_2 before use. Pyridine was dried over NaOH for several days before use. Other chemicals were all used as received.

Polymer characterization. All ^{1}H-NMR (300 MHz) spectra were recorded on a Varian Mercury plus spectrometer in 1,2-dichlorobenzene-d_4 at 120 °C. GPC analyses of PE-OH and PE-*b*-P*t*BA were performed on a Polymer Laboratories PL-220 instrument equipped with three PL-gel columns (PL-gel 10 μm MIXED-B, 300×7.5 mm). The instrument was calibrated with polystyrene standards. The samples (3.0

mg/mL in 1,2,4-trichlorobenzene) were run using 1,2,4-trichlorobenzene as eluent with a flow rate of 1.0 mL/min at 150 °C.

Preparation of hydroxyl terminated polyethylene. Hydroxyl terminated polyethylene (PE-OH) was prepared through polyhomologation of dimethylsulfoxonium methylide and the subsequent oxidation of trisorganoborane using trimethylamine-*N*-oxide dihydrate.[1]

Dimethylsulfoxonium chloride: A biphasic mixture of CH_2Cl_2 (400 mL) and H_2O (570 mL) with trimethylsulfoxonium iodide (63.1 g, 287 mmol, 1.0 equiv.) and benzyltributylammonium chloride (98.5 g, 316 mmol, 1.1 equiv.) was vigorously stirred in a flask under darkness for 28 h. The aqueous phase was separated, washed with CH_2Cl_2 (*3* × 60 mL), and evaporated under vacuum. The white solid was recrystallized in methanol/toluene (95/5 v/v) mixed solvent, then ground into fine powder, and dried in a vacuum at 50 °C for 24 h to yield a white powder product (36.6 g, 99.2% yield).

Dimethylsulfoxonium methylide: Sodium hydride (60% dispersion in oil, 7.5 g, 186.6 mmol, 1.5 equiv.) was washed with hexane (3 × 50 mL) under nitrogen. Trace of solvent was removed under vacuum. Trimethylsulfoxonium chloride (16 g, 124.4 mmol, 1.0 equiv.) and toluene (150 mL) were transferred to the flask. The heterogeneous reaction mixture was heated to reflux until no H_2 was released (usually 2-4 h). The contents were cooled to room temperature and filtered under nitrogen through pre-dried Celite 545 to afford a colorless solution of ylide (0.76 M in toluene, 88.0% yield). The solution was stored at -20 °C. An aliquot of the solution (1.0 mL) was added to H_2O (5 mL) and titrated with standardized HCl solution before use.

α-Hydroxypolyethylene: $BH_3·SMe_2$ (1.0 M in CH_2Cl_2, 0.1 mL, 0.1 mmol) was added rapidly via syringe to a solution of ylide (0.68 M in toluene, 103.5 mL, 70.4

mmol) at room temperature under N_2 followed with heating to 90 °C. After 15 min, a drop of the reaction mixture was added to H_2O (3 mL) containing phenolphthalein and if the aqueous solution did not turn into red then it can be confirmed that ylide had been consumed. The solution was cooled to room temperature, and trimethylamine-*N*-oxide dihydrate (70 mg, 70.6 mmol) was added to the flask under N_2, then the solution was heated to 90 °C and held for 2 h. The solution was cooled to room temperature and precipitated with acetonitrile (200 mL). The precipitate was filtered and successively washed with CH_3CN (20 mL), acetone (20 mL), and hexane (20 mL), and then dried to give a white solid (1.00 g, >99% yield).

Preparation of PE-*b*-P*t*BA diblock copolymers. The PE-macroinitiator was first prepared via esterification of end hydroxyl group in PE-OH with 2-bromo-2-methylpropionyl bromide.[2] In a typical procedure, PE-OH (1 g; 0.364 mmol of -OH groups), toluene (100 mL), pyridine (0.35 mL, 4.36 mmol) and 2-bromo-2-methylpropionyl bromide (0.45 mL, 3.64 mmol) were successively added into a nitrogen-purged, round-bottom flask (250 mL) equipped with a stirring bar and a condenser. The mixture was stirred vigorously at 100 °C for 12 h, then cooled to room temperature and poured into 500 mL of acidic methanol (containing 30 mL of 1 M aqueous HCl). The resulting polymer was collected by filtration, and successively washed with methanol (30 mL, ×2), 1 M aqueous HCl solution (10 mL, ×2), methanol (20 mL, ×2), and finally dried at 50 °C overnight in vacuum to yield an off-white solid polymer.

PE-*b*-P*t*BA BCPs were prepared by atom transfer radical polymerization (ATRP) of *tert*-butylacrylate in toluene in the presence of PE-macroinitiator, which followed the procedure of Lu et al.[2] In a typical procedure, PE-macroinitiator (0.3 g, 0.103 mmol), toluene (5 mL), PMDETA (52 μL, 0.248 mmol) and *t*BA monomer (1.5 mL,

10.3 mmol) were successively added into a nitrogen-purged, 25 mL Schlenk flask equipped with a stirring bar. After the PE-macroinitiator was completely dissolved at 80 °C, the flask was cooled to room temperature and deoxygenated by degassing and backfilling with nitrogen for thrice. Then, CuBr (18 mg, 0.124 mmol) was added into the flask under N_2. The polymerization was performed at 100 °C for 4 h. The polymerization was stopped via cooling with a liquid nitrogen bath. The reaction mixture was poured into a beaker with cold methanol (500 mL) and water (100 mL) under magnetic stirring. The diblock copolymer PE-*b*-P*t*BA was filtered, washed with methanol and water for several times, and then dried overnight at 40 °C under vacuum. The molecular weight of PE-*b*-P*t*BA was controlled via monomer feed ratio and polymerization time.
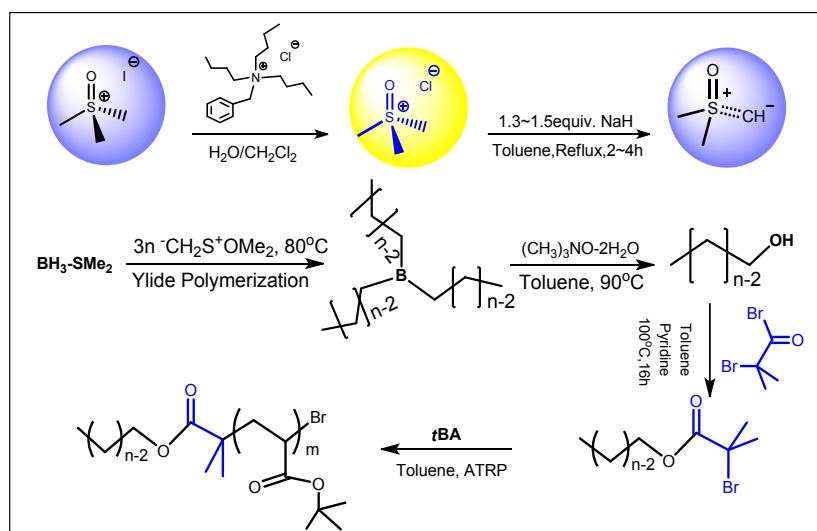
Scheme S1 Synthetic route of PE-*b*-P*t*BA.

The synthesis route of PE-*b*-P*t*BA diblock polymers is illustrated in Scheme S1. Figure S1 shows the ^{1}H-NMR spectra of PE-OH, PE-macroinitiator and PE-*b*-P*t*BA. The integral ratio of peak *d* (-*CH$_2$O*-, $\delta = 3.60$ ppm) to peak *a* (-*CH$_3$*, $\delta = 1.02$ ppm) in PE-OH was 1/3, the ideal ratio should be 2/3 and this can be ascribed to the incorporation of dimethylsulfoxonium ethylide impurity in ylide which has already

been mentioned in the literature.[1] The absolute number-average molecular weight was calculated from the ^{1}H-NMR spectrum (Figure S1(I)) using following equations below:

$$N_{\text{chain}} = A_d/2 \qquad \text{(S1)}$$

$$\text{DP} = A_{b+c}/4N_{\text{chain}} + 1 \qquad \text{(S2)}$$

$$M_n = \text{DP} \times 28 \text{ (g/mol)} \qquad \text{(S3)}$$

Where N_{chain} represents the number of polyethylene blocks, DP is the degree of polymerization, M_n is the number-average molecular weight of PE calculated from ^{1}H-NMR. The smaller values of polydispersity index (PDI) indicated that the living polymerization of sulfoxide ylide was well-controlled, as illustrated in Table S1 and Figure S2.

The ^{1}H-NMR of macroinitiator PE-Br and PE-OH is also shown in Figure S1. One can see that the triplet peak d, which is assigned to methylene protons next to the oxygen atom (-CH_2O-, δ = 3.60 ppm) in the ^{1}H-NMR of PE-OH (I in Figure S1), is vanished in the ^{1}H-NMR of PE-macroinitiator (II in Figure S1). The appearance of three new peaks (d' (-CH_2O-, δ = 4.18 ppm), e (-$C(CH_3)_2Br$, δ = 1.95 ppm) and c' (-CH_2CH_2O-, δ = 1.67 ppm)) in II of Figure S1 indicated that the α-haloester end-capped polyethylene was formed. The integral ratio of peak d' to peak e was 1/3. Besides, the integral ratio of peak d' to peak a in PE-macroinitiator was the same with that of peak d to peak a in PE-OH. All of the information shown above proved that the esterification of PE-OH proceeded quantitatively (~100%).

The ATRP of tBA was conducted in toluene with CuBr/PMDETA as catalyst. Monomer conversion was monitored by ^{1}H-NMR by comparing the integrals of the triplet peak d'' at δ = 4.26 ppm from PE-macroinitiator (-CH_2O-) (III in Figure S1) and the peak g at δ = 2.67 ppm (III in Figure S1), which is attributed to the protons

located at the backbone of P*t*BA. As shown in Table 1, the conversion of monomer is about 30% and this may attributed to the high viscosity of the reaction product in toluene at the late reaction stage; By changing the molar ratio of *t*BA to the macroinitiator, three BCPs, PE_{100}-P*t*BA_{30}, PE_{100}-P*t*BA_{48} and PE_{100}-P*t*BA_{70} (where the subscripts refer to the polymerization degrees of PE and P*t*BA) were synthesized. As shown in Figure S2, the molecular weight of the BCPs increases with the increasing length of the P*t*BA block. The PDIs of the obtained PE-*b*-P*t*BA BCPs were slightly larger than that of PE-macroinitiator, but were still in an acceptable range (Figure S2 and Table S1).
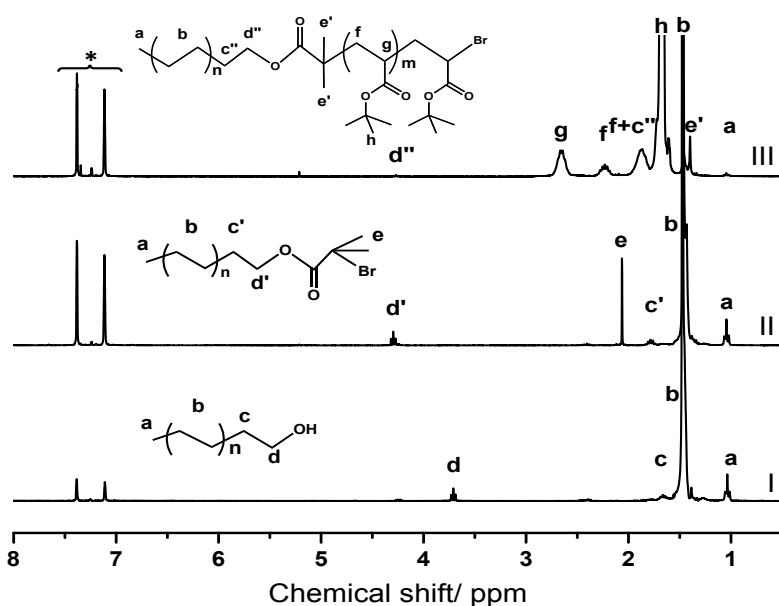
Figure S1. ^{1}H-NMR spectra of PE-OH (I), PE-macroinitiator (II) and PE-*b*-P*t*BA (III) (* solvent).
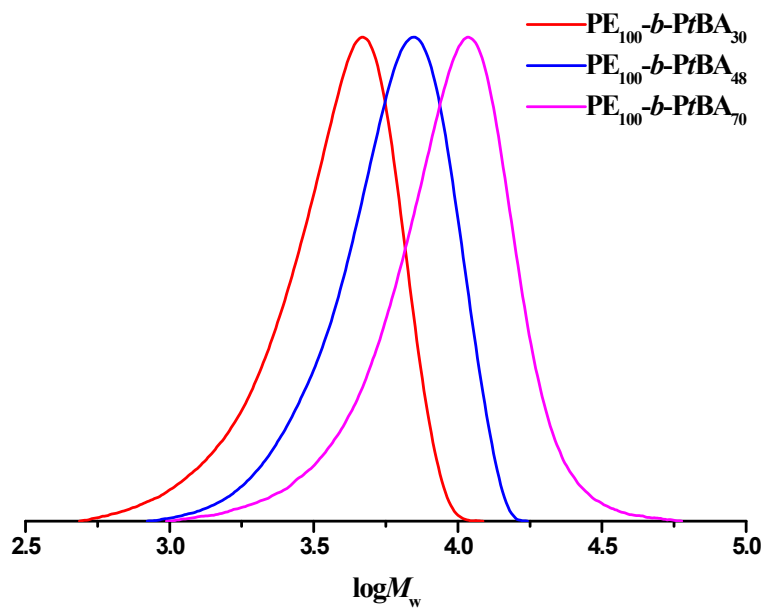
Figure S2. GPC profiles of PE based block copolymers.

Table S1. Sample information of PE-OH and PE-*b*-P*t*BA BCPs.

Sample [a]	*t*BA [b]	t_{ATRP}	M_n (g/mol)	PDI [c]	W_{PE}
PE$_{100}$-OH	0	0 h	2800	1.03	100%
PE$_{100}$-*b*-P*t*BA$_{30}$	100	4 h	6600	1.27	42%
PE$_{100}$-*b*-P*t*BA$_{48}$	200	4 h	8900	1.24	31%
PE$_{100}$-*b*-P*t*BA$_{70}$	300	8 h	11800	1.31	23%

[a] calculated from ^{1}H-NMR. [b] *t*BA equiv. times as mole amount of PE-macroinitiator.
[c] measured by high temperature GPC and calibrated with PS standards.
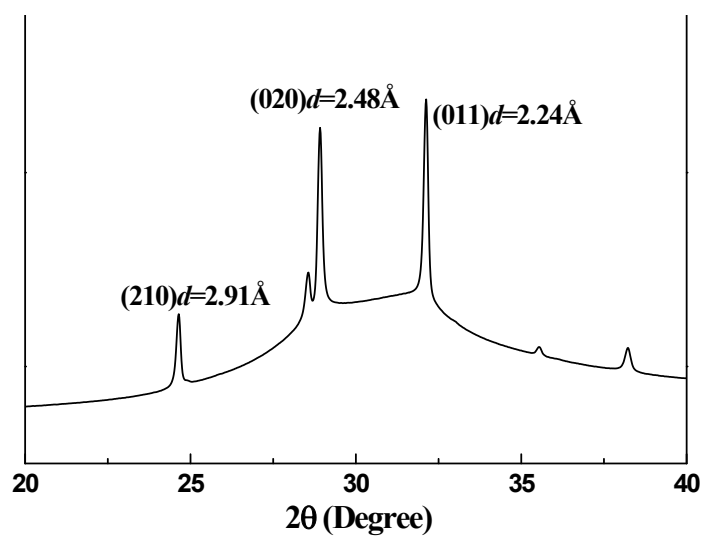
Figure S3. WAXD pattern of dried PE_{100}-b-PtBA$_{30}$ micelles, the micelles were prepared in DMF (5mg/ml) at T_c of 25 °C. Three diffraction peak were obtained in the PE_{100}-b-PtBA$_{30}$ micelles solution and can be indexed into the (210) reflection, (020) reflection and the (011) reflection of the typical polyethylene orthorhombic unit cell. [3]
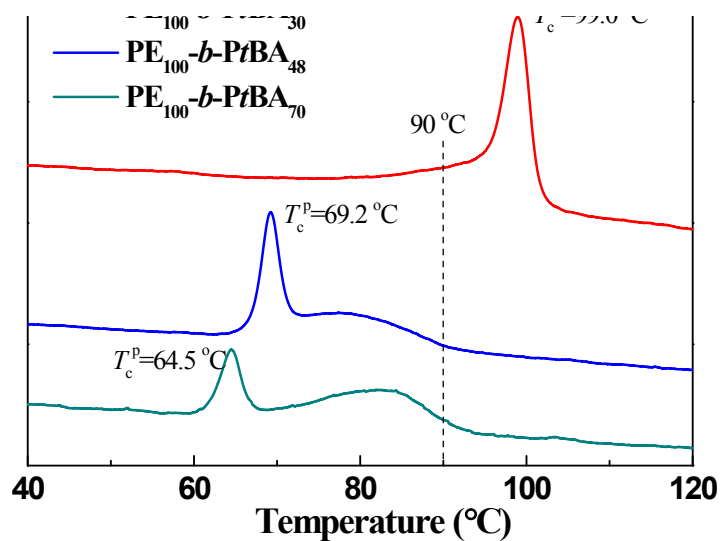
Figure S4. DSC crystallization curves of the PE-*b*-P*t*BA/DMF (1/0.63 w/w) mixtures. The cooling rate is 1 °C/min.

Because of the low sensitivity of DSC, the PE-*b*-P*t*BA/DMF mixtures with a high BCP concentration, instead of the micellar solutions with a low BCP concentration, were used for DSC experiments. Moreover, since growth of the crystalline micelles was isothermally performed at a T_c, a slow cooling rate (1 °C/min) was applied to the non-isothermal DSC experiments for selection of suitable T_cs.
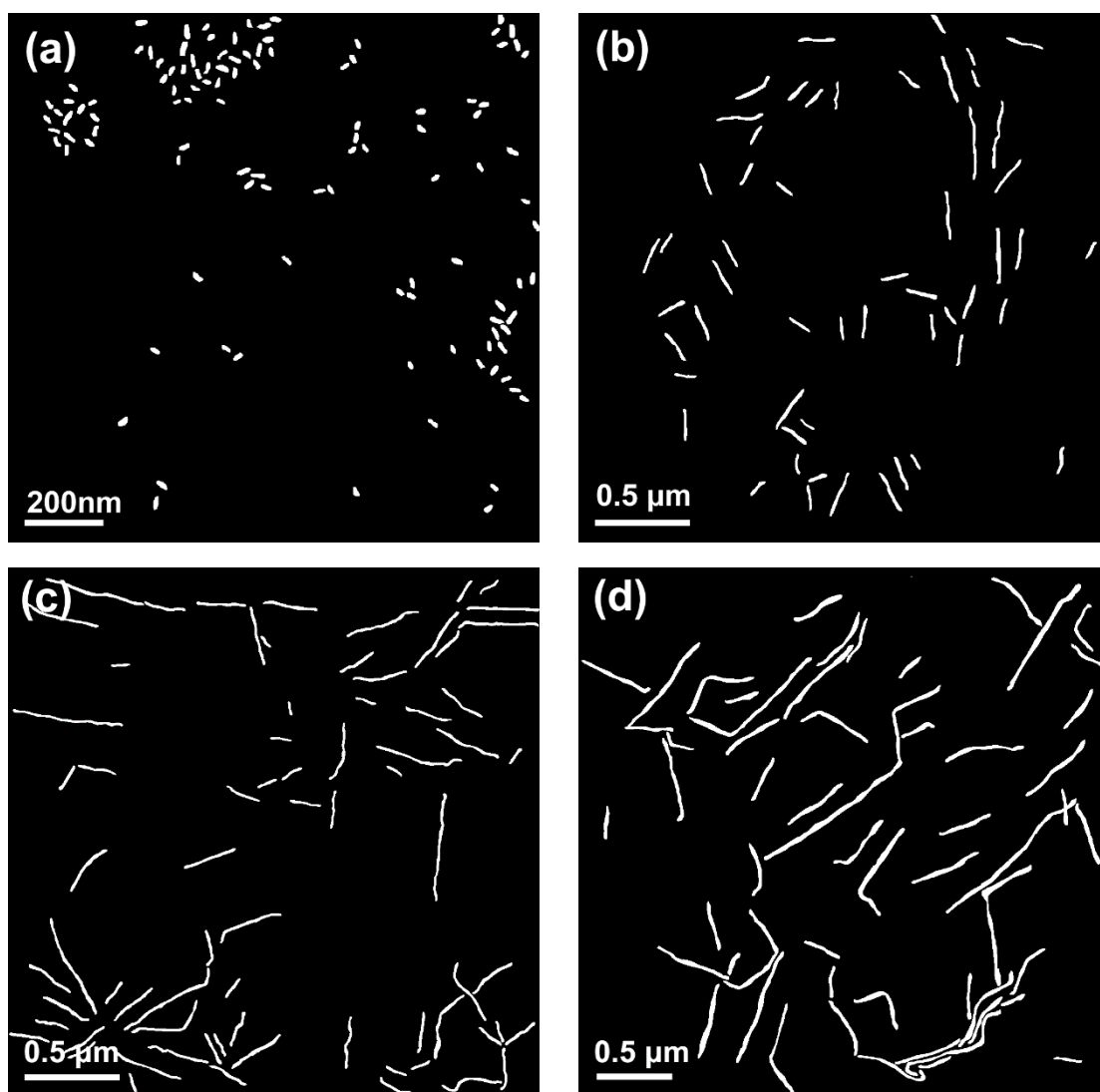
Figure S5. Outlines of the long PE_{100}-*b*-P*t*BA$_{70}$ micelles after growth at selected T_cs for 12 h. (a) T_c=25 °C, (b) T_c=50 °C, (c) T_c=70 °C, (d) T_c=90 °C.
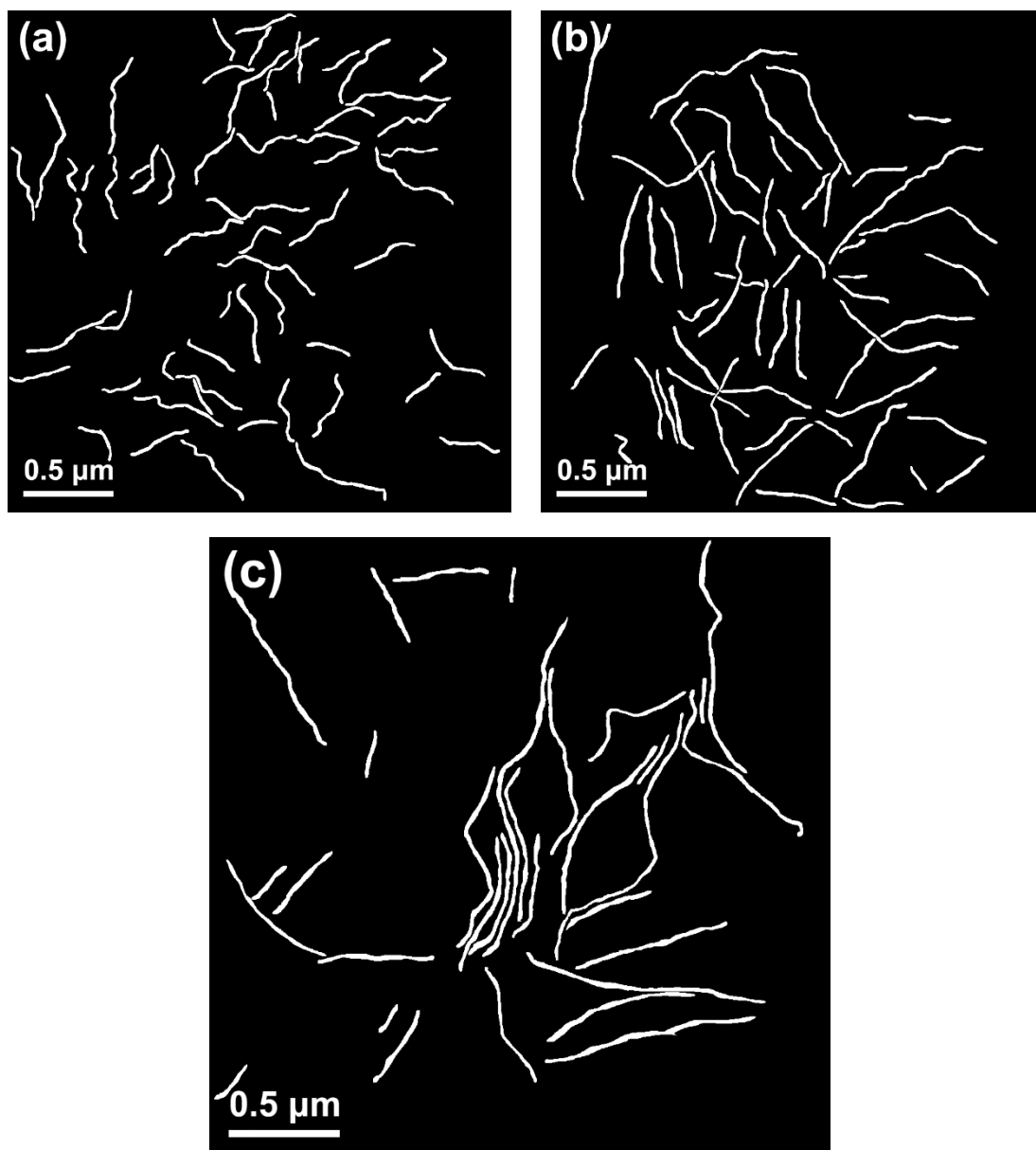
Figure S6. Outlines of the long PE-*b*-P*t*BA micelles after growth at T_c=90 °C for 60 h. (a) PE$_{100}$-*b*-P*t*BA$_{30}$, (b) PE$_{100}$-*b*-P*t*BA$_{48}$, (c) PE$_{100}$-*b*-P*t*BA$_{70}$.
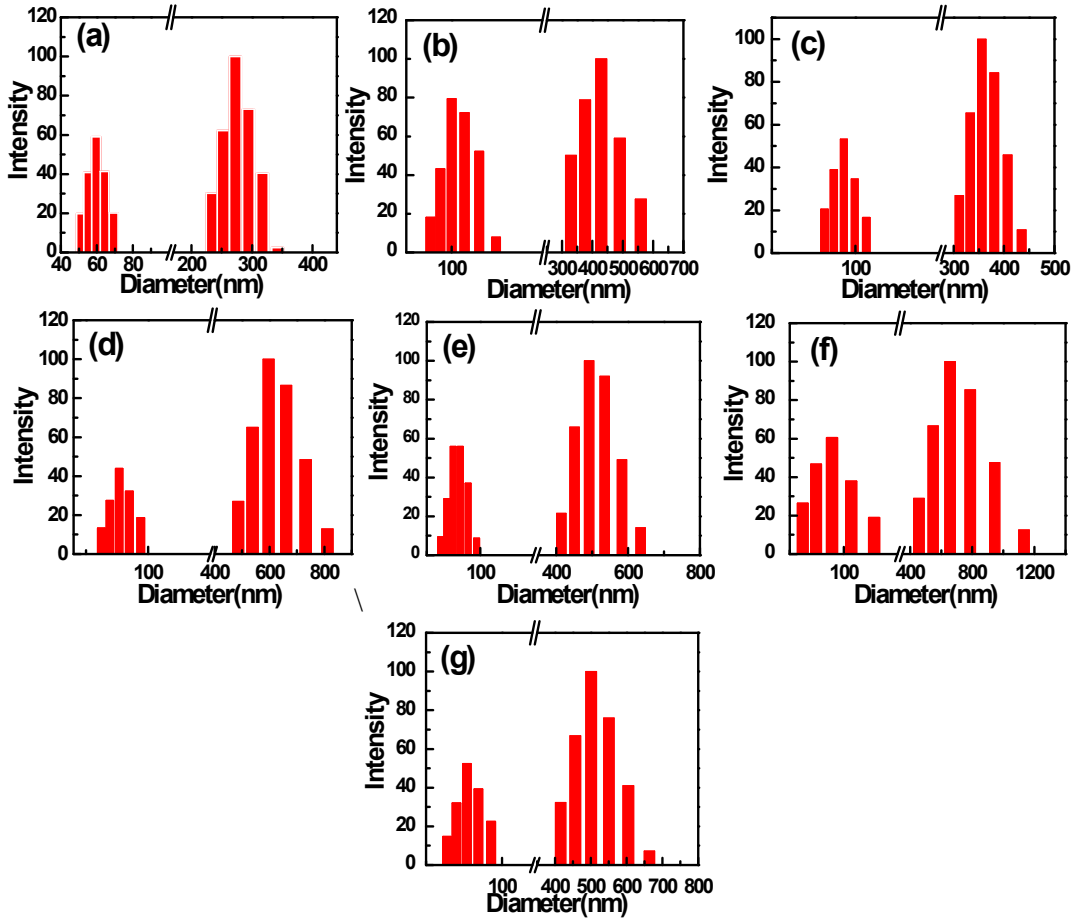
Figure S7. CONTIN size distributions of PE-*b*-P*t*BA micelles in DMF after growth at selected T_cs for t hours and then cooling to 25 °C. The scattering angle is 90°. (a) PE$_{100}$-*b*-P*t*BA$_{70}$, T_c=25 °C, t=12 h; (b) PE$_{100}$-*b*-P*t*BA$_{70}$, T_c=50 °C, t=12 h; (c) PE$_{100}$-*b*-P*t*BA$_{70}$, T_c=70 °C, t=12 h; (d) PE$_{100}$-*b*-P*t*BA$_{70}$, T_c=90 °C, t=12 h; (e) PE$_{100}$-*b*-P*t*BA$_{70}$, T_c=90 °C, t=60 h; (f) PE$_{100}$-*b*-P*t*BA$_{48}$, T_c=90 °C, t=60 h; (g) PE$_{100}$-*b*-P*t*BA$_{30}$ T_c=90 °C t=60 h.

Since some T_cs are above the limit temperature of the instrument, the micellar solutions are first held at T_c for 12 h or 60 h and then cooled to 25 °C for DLS measurement. As a result, the solutions contain both grown long cylindrical micelles and short cylindrical ones formed by the unimers cooling to 25 °C. A stretched exponential function is used to describe the electric field autocorrelation function:[4]

$$g'(t) = A_{\text{fast}} \exp(-t/\tau_{\text{fast}}) + A_{\text{slow}} \exp[-(t/\tau_{\text{slow}})^\gamma] \qquad \text{(S4)}$$

where τ_{fast} and τ_{slow} are the relaxation times of the fast and slow motions, respectively. The stretched exponent γ is inversely proportional to the distribution width of the decay time. The pre-factors A_{fast} and A_{slow} are the amplitudes of the fast and slow relaxation modes, respectively, and the sum of A_{fast} and A_{slow} is close to 1.

At T_c=25 °C, no stepwise crystallization occurs and the short cylindrical micelles are directly formed via simultaneous micellization/crystallization of the unimers. However, a bimodal size distribution is still observed for the micelles at T_c=25 °C. As the number of the short cylindrical micelles generated via micellization/crystallization of the unimers is much larger than the micelles generated through crystallization of the amorphous spherical micelles, the scattering signal from these two kinds of micelles can be separated easily. The fast relaxation mode is assigned to micelles formed by crystallization of the amorphous spherical micelles, and the slow relaxation mode is attributed to the cylindrical micelles formed by the unimers. On the other hand, at T_cs above 25 °C, both short and long cylindrical micelles co-exist in the BCPs solution. These short cylindrical micelles are formed through crystallization of the amorphous spherical micelles and micellization of the unimers when being cooled from various T_cs to 25 °C. As most of the unimers are consumed at T_c, fewer micelles are formed through micellization/crystallization of the unimers when being cooled from various T_cs, so the scattering intensity from the micelles formed by crystallization of the amorphous spherical micelles and short cylindrical micelles cannot be separated. The fast relaxation mode is assigned to the motion of the micelles formed via micellization of un-consumed unimers and the micelles formed by crystallization of the amorphous spherical micelles, while the slow relaxation mode corresponds to the motion of the long cylindrical micelles formed at T_c. When

the micelles have the same shape, the relaxation time can be correlated to the micellar size. The larger the micellar size, the larger the relaxation time.

Table S2. Parameters Obtained by Fitting the DLS Electric-Field Autocorrelation Functions of PE-*b*-P*t*BA Micellar Solutions in DMF.

t (h)	60 h			12 h			
Sample	PE$_{100}$-*b*-P*t*BA$_{30}$	PE$_{100}$-*b*-P*t*BA$_{48}$	PE$_{100}$-*b*-P*t*BA$_{70}$	PE$_{100}$-*b*-P*t*BA$_{70}$			
T_c (°C)	90	90	90	25	50	70	90
$\tau_{\text{slow (ms)}}$	10.7	19.8	25.3	2.65	3.08	3.15	8.18
A_{slow}	0.76	0.62	0.49	0.50	0.45	0.42	0.39
$\tau_{\text{fast (ms)}}$	0.79	0.91	0.80	0.46	0.67	0.79	0.76
A_{fast}	0.25	0.46	0.57	0.51	0.56	0.59	0.60
γ	0.66	0.28	0.26	0.63	0.65	0.68	1

The fitting results of the electric-field autocorrelation functions at the scattering angle of 90° are shown in Figure S8 and the obtained parameters are summarized in Table S2. It is found that, the τ_{slow} of PE$_{100}$-*b*-P*t*BA$_{70}$, which corresponds to the relaxation time of the long cylindrical micelles, increases with raising T_c. Moreover, at T_c=90 °C, the τ_{slow} increase rapidly as the P*t*BA block becomes longer. This indicates that the long cylindrical micelles have a larger dimension in length at a higher T_c and for the PE-*b*-P*t*BA with a longer corona-forming block, which is in accordance with the TEM result. By contrast, the value of τ_{fast}, which is the relaxation time of the micelles formed by unimers and amorphous spherical micelles at 25 °C, does not change greatly with T_c and the length of P*t*BA block. This implies that there is no big difference in the length of the formed short cylinders when the unimers of different PE-*b*-P*t*BA BCPs are cooled from various T_cs. On the other hand, the parameter A_{slow}, which represents the fraction of the long cylindrical micelles formed

through growth of the unimers on the seed micelles at T_c, decreases with increasing

the length of PtBA block at T_c=90 °C and T_c for PE$_{100}$-b-PtBA$_{70}$. This shows that

fewer long micelles are formed when the PtBA block is longer and T_c is higher. This

is understandable, since the solubility of the PE-b-PtBA is better at a higher T_c or for a

BCP with a longer corona-forming block, a smaller amount of seed crystalline

micelles are formed through the stepwise micellization/crystallization process of the

unimers at T_c. By contrast, as the length of PtBA block is changed, A_{fast} exhibits a

tendency opposed to A_{slow}. This means that more short micelles are formed when a

longer PtBA-containing BCP is cooled to 25 °C after growth at T_c=90 °C for 60 h.

This is probably because more unimers are left in the solution of PE$_{100}$-b-PtBA$_{70}$ after

growth at T_c=90 °C for 60 h due to its better solubility in DMF and slower growth rate,

as the growth rate of BCP micelle with longer coronal-forming block is slower.

Moreover, for PE$_{100}$-b-PtBA$_{70}$ after growth for 12 h, T_c has no significant effect on

A_{fast}.
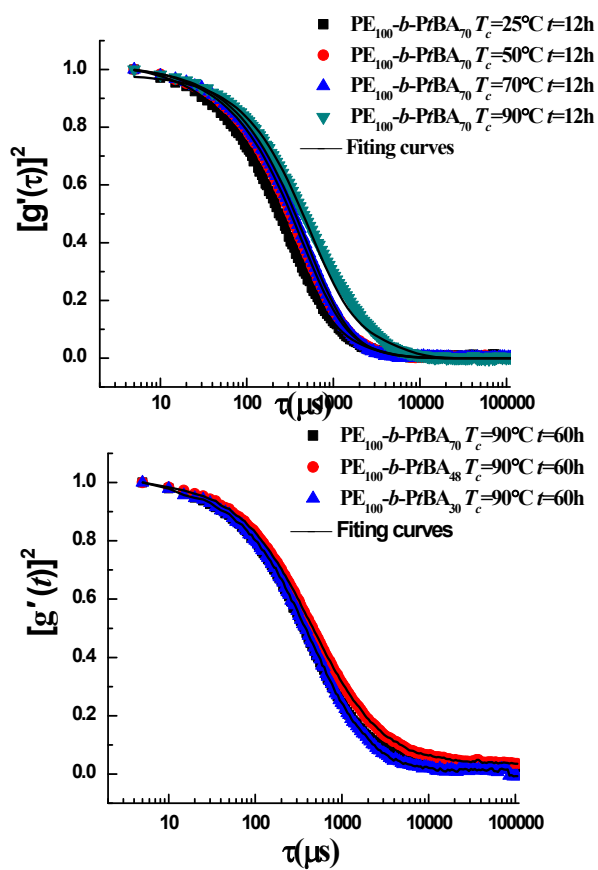
Figure S8. The normalized intensity correlation functions, $g'(t)$, of PE-*b*-P*t*BA micelle solutions in DMF at various T_cs for t hour. The symbols represent the experimental data and the lines are the fitting curves.
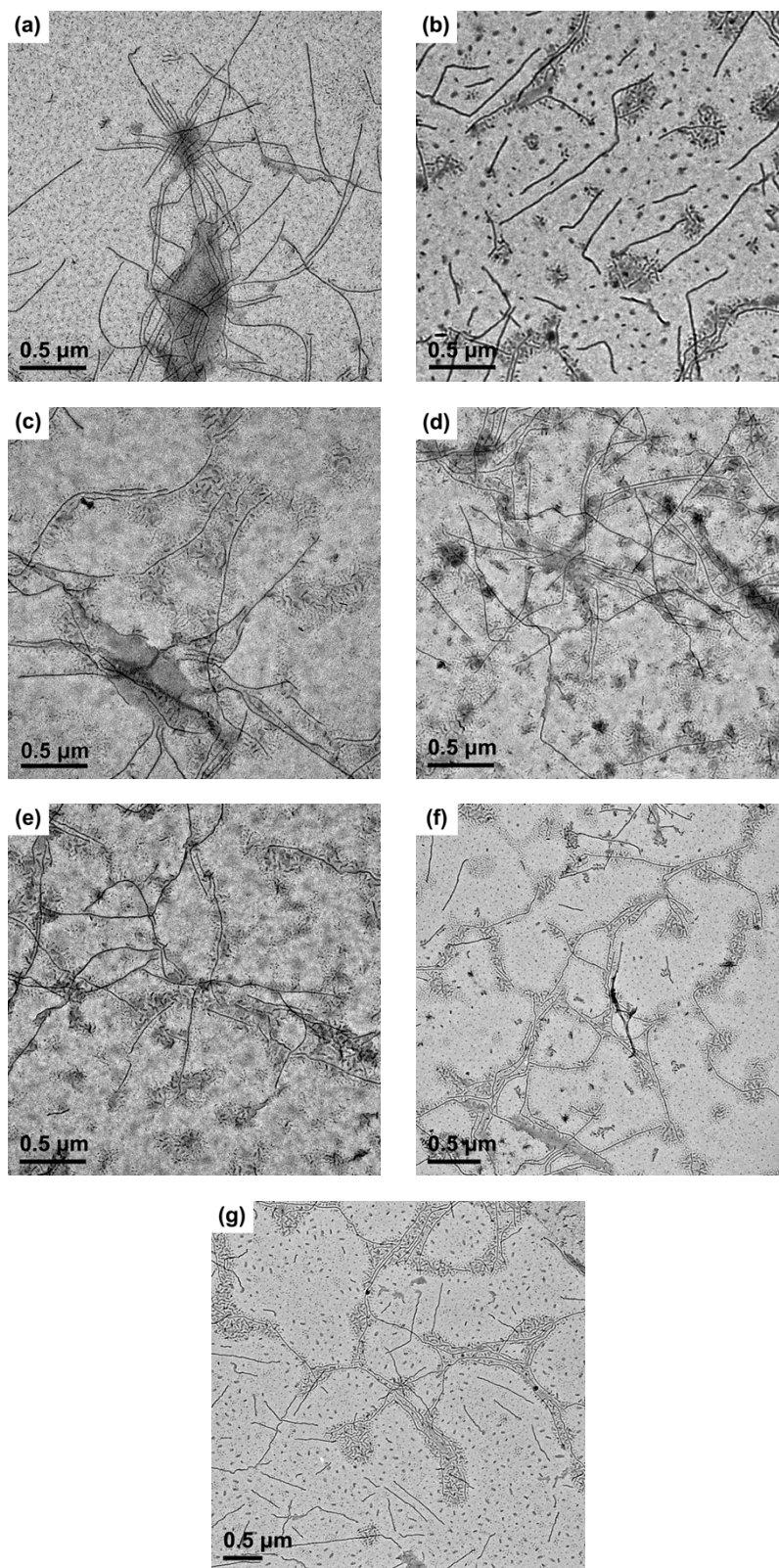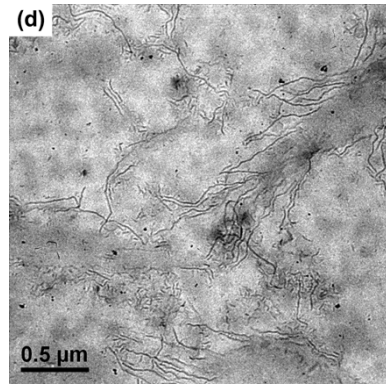
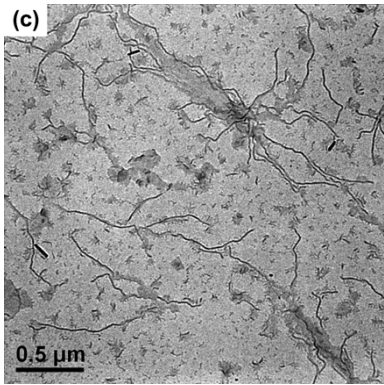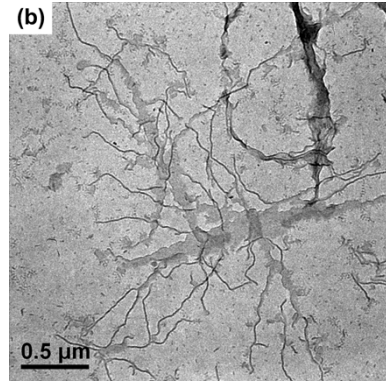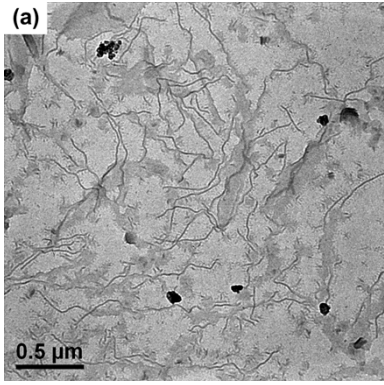**Figure S9.** TEM micrographs for the PE_{100}-*b*-$PtBA_{70}$ micelles in DMF solution after annealing at 130 °C for an hour and then growth at 90 °C for different times. (a) 0.83 h, (b) 12 h, (c) 14 h, (d) 23.5 h, (e) 40.5 h, (f) 60 h, (g) 120 h. These short cylinders formed at sample preparation are neglected in statistics.
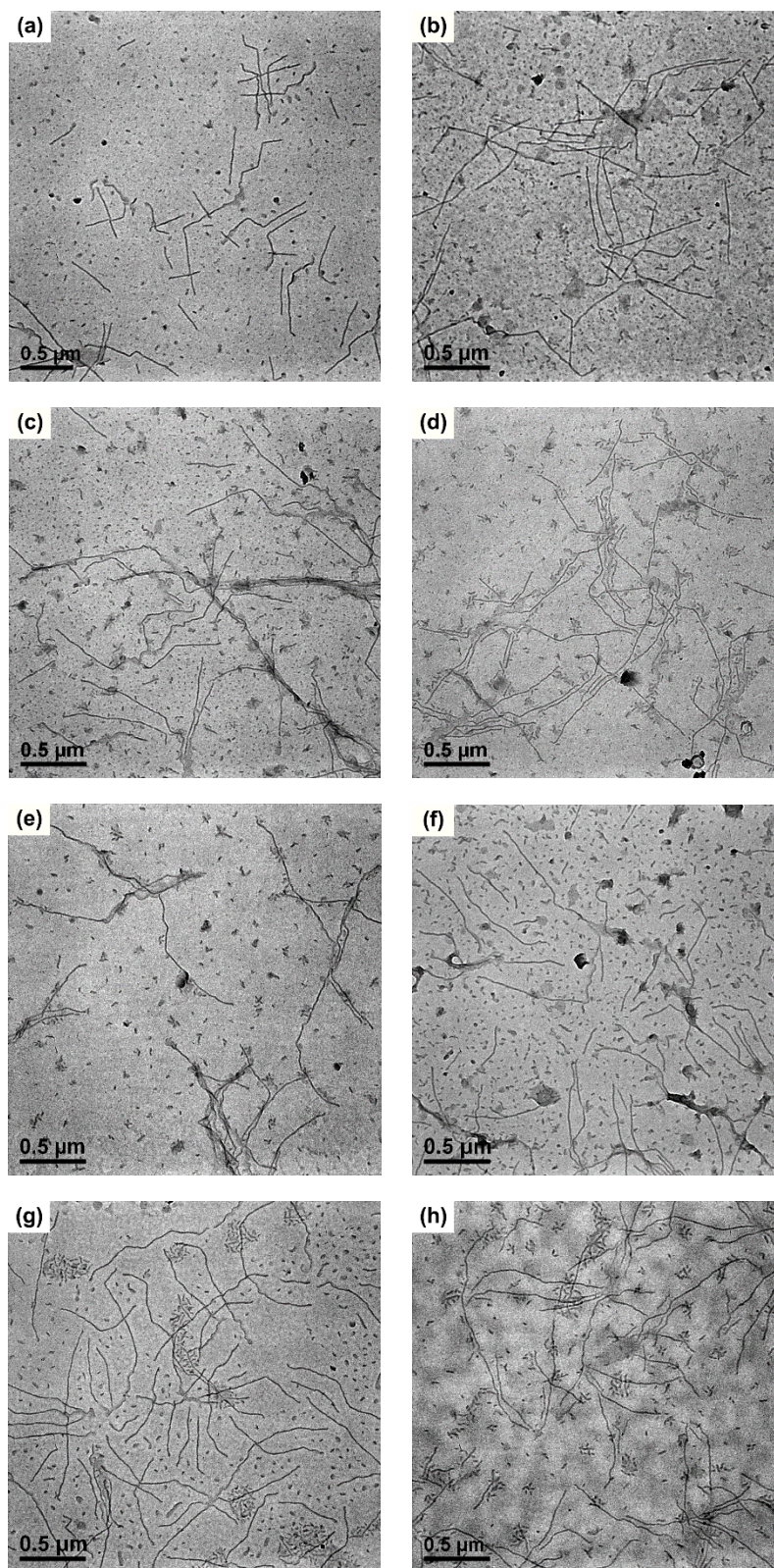
Figure S10. TEM micrographs for the PE$_{100}$-*b*-P*t*BA$_{48}$ micelles in DMF solution after annealing at 130 °C for an hour and then growth at 90 °C for different times. (a) 0.5 h, (b) 1 h, (c) 3 h, (d) 6 h, (e) 14 h, (f) 24 h, (g) 60 h, (h)120 h. These short cylinders formed at sample preparation are neglected in statistics.
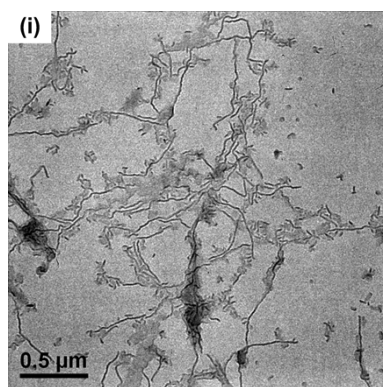
(i)

0.5 µm
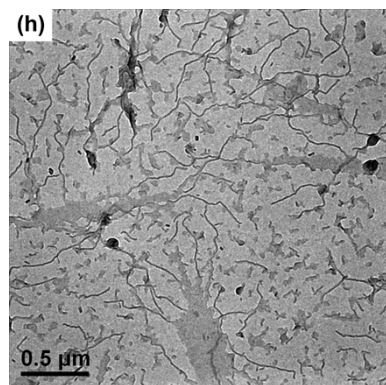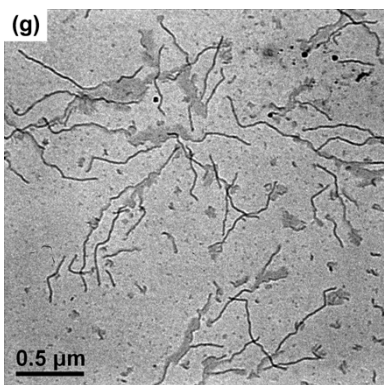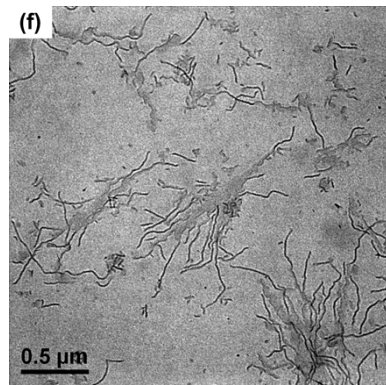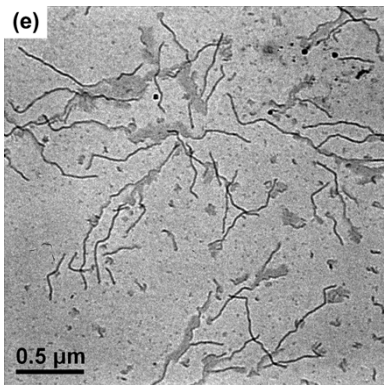
Figure S11. TEM micrographs (left column) and length distributions of the cylindrical PE_{100}-b-$PtBA_{30}$ micelles analyzed from TEM images (right column) after growth at 90°C for different times. (a) 0.5 h, (b) 1 h, (c) 3 h, (d) 5 h, (e) 7 h, (f) 11 h, (g) 25 h, (h) 60 h, (i) 118 h. These short cylinders formed at sample preparation are neglected in statistics.
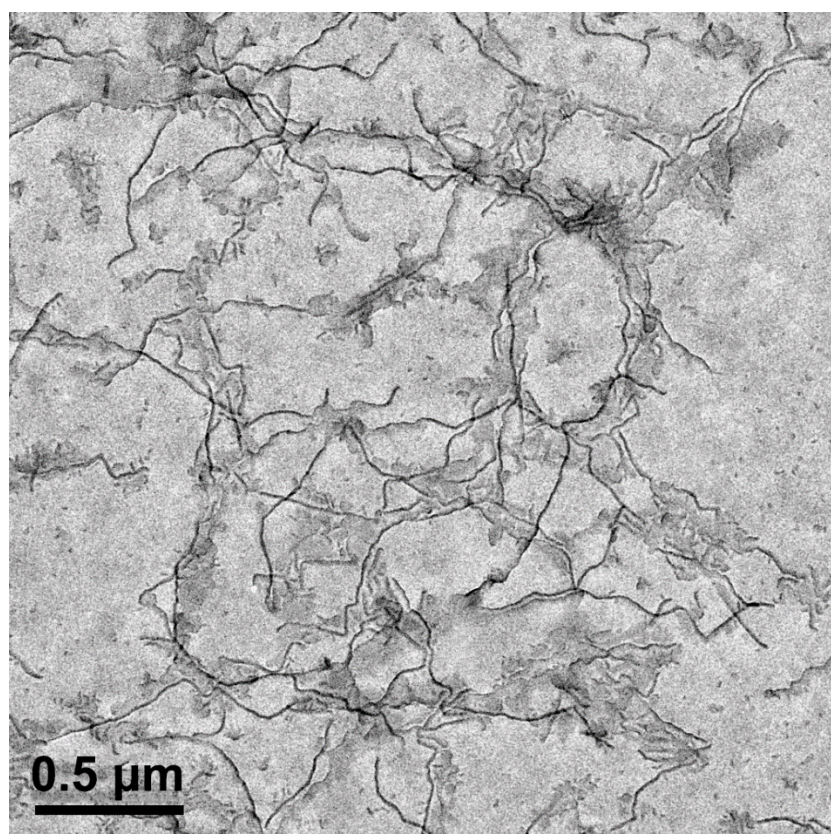

0.5 µm

Figure S12. TEM micrographs for PE_{100}-b-$PtBA_{30}$ micelles solution after annealing at 130 °C for an hour and then growth at 90 °C for 71 h.

References

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