Well-shaped poly(dimethylsiloxane)-based copolymer nanowires from spherical micelles via kinetic shape evolution

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Experiment section

Synthesis of diclock copolymers PCEMA-*b*-PMMA and PDMS-*b*-PMMA

The diblock copolymer PCEMA-*b*-PMMA was synthesized by three steps. First, the macroinitiator P(HEMA-TMS)-Br was synthesized by ATRP method. CuCl (0.01 g, 0.10 mmol) and a dry magnetic stirrer were placed in a Schlenk flask, sealed with a rubber septum and purged with nitrogen gas for 30 min. A mixture of EBiB initiator (0.02g, 1.00 mmol), HEMA-TMS (40.00 g, 213.00 mmol), PMDETA (0.03 g, 0.17 mmol) and 90 ml CYC was placed into this flask. Then this flask was putted into an oil bath and heated up to 90 °C. The reaction was stopped after 24 h, adding THF to dilute the crude product and stirring under air. The catalyst was removed by passing this solution through a column filled with alumina and the residual solvent was removed under reduced pressure distillation. Eventually, the P(HEMA-TMS)-Br was obtained by isolating following *re*- precipitation in methanol and dried in vacuum oven overnight.

Then, the diblock copolymer P(HEMA-TMS)-*b*-PMMA was synthesized by ATRP method. CuCl (0.01 g, 0.10 mmol) and a dry magnetic stirrer were placed in a Schlenk flask, sealed with a rubber septum and purged with nitrogen gas for 30 min. A mixture of P(HEMA-TMS)-Br initiator (1.20g, 1.00 mmol), MMA (20.00 g, 200.00 mmol), PMDETA (0.03 g, 0.17 mmol) and 90 ml CYC was placed into this flask. Then this flask was putted into an oil bath and heated up to 80 °C. The reaction was stopped after 24 h, adding THF solvent to dilute the crude product and stirring under air. The catalyst was removed by passing this solution through a column filled with alumina and the residual solvent was removed under reduced pressure distillation. Subsequently, the P(HEMA-TMS)-*b*-PMMA was obtained by isolating following *re*- precipitation in methanol and dried in vacuum oven overnight.

Finally, the P(HEMA-TMS) block was converted to PCEMA by selective acidic hydrolysis of the TMS groups and then esterificating with cinnamoyl chloride. The diblock copolymer (7.68g, 0.24 mmol) was dissolved in 30 mL THF，adding 1mL trifluoracetic acid (CF_3COOH) as catalyst. The mixture was stirred for 30 min at room temperature and the solvent was removed by evaporation. The newly formed hydroxyl groups of the PHEMA block were reacted with a 4 fold excess of cinnamoyl chloride in THF with TEA and DMAP at room temperature for 48 h. The resultant PCEMA-*b*-PMMA

was obtained by removing the white solid of the reaction system through centrifugation and volatilizing solvent under vacuum.
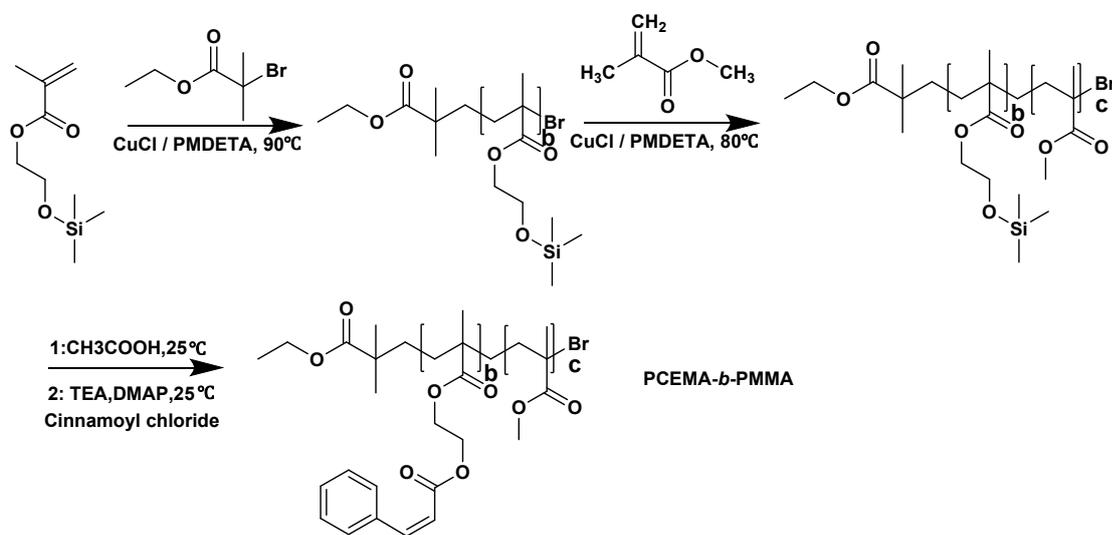
Scheme S1. Synthesis of PCEMA-*b*-PMMA copolymers.

The diblock copolymers PDMS-*b*-PMMA were synthesized by ATRP method. Typically, CuCl (0.01 g, 0.10 mmol) and a dry magnetic stirrer were placed in a Schlenk flask, sealed with a rubber septum and purged with nitrogen gas for 30 min. A mixture of PDMS-Br macroinitiator (10.00 g, 1.00 mmol), MMA (20.00 g, 200.00 mmol), PMDETA (0.03 g, 0.17 mmol) and 90 ml CYC was placed into this flask. Then this flask was putted into an oil bath and heated up to 90 °C. The reaction was stopped after 24 h, adding THF solvent to dilute the crude product and stirring under air. The catalyst was removed by passing this solution through a column filled with alumina and the residual solvent was removed under reduced pressure distillation. Subsequently, the PDMS-*b*-PMMA was obtained by isolating following *re*-precipitation in methanol and dried in vacuum oven overnight.
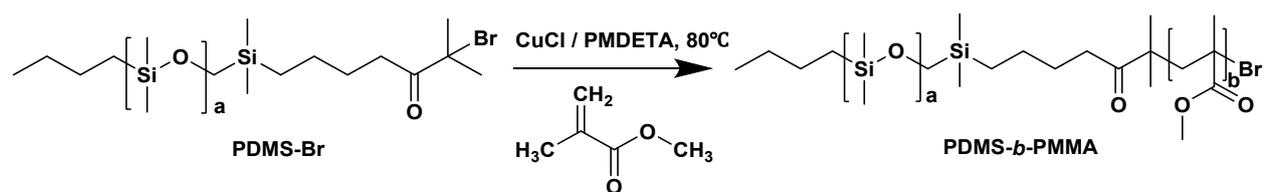
Scheme S2. Synthesis routes of PDMS-*b*-PMMA copolymers.

Table S1 Detailed polymerization condition and recipes for copolymers.

Copolymers	PDMS-Br /mol	CuCl /mol	PMDETA /mol	HEMA-TMS /mol	MMA/ mmol	M_w [g/mol]	PDI
		1	1.5	20	-	4.40×10^4	1.20
PDMS-*b*-PCEMA	1	1	1.5	10		2.45×10^4	1.30
		1	1.5	5		1.44×10^4	1.20
PDMS-*b*-PMMA	1	1	1.5	-	20	3.61×10^4	1.08
PCEMA-*b*-PMMA	0.1[a]	1	1.5	10	20	3.75×10^4	1.45

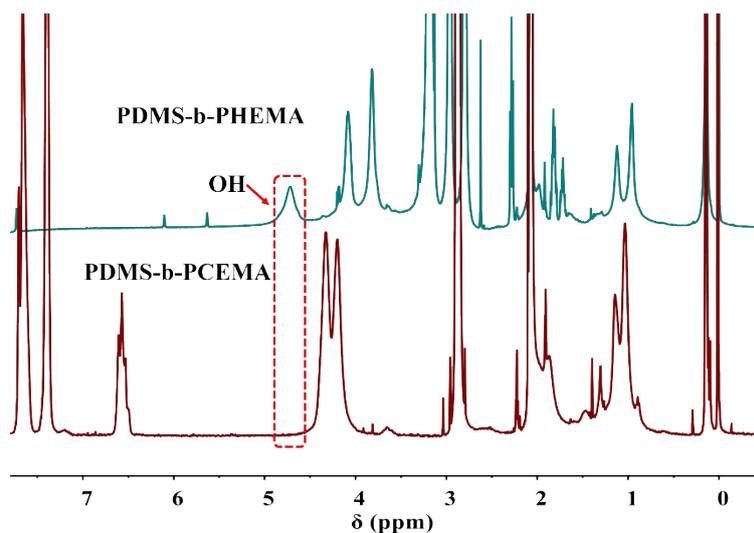[a]The initiator used for PCEMA-*b*-PMMA was EB*i*B.

Figure S1. ¹H-NMR spectra of PDMS-*b*-PHEMA and PDMS-*b*-PCEMA.

The signal at 4.73ppm is corresponded to the -OH groups in PHEMA (PDMS-*b*-PHEMA), which

is the hydrolysis product of PHEMA-TMS (PDMS-*b*-P(HEMA-TMS)). After the esterification with

cinnamoyl chloride (PHEMA and cinnamoyl chloride), the -OH signal disappears completely in

PCEMA (PDMS-*b*-PCEMA), indicating that all the -OH groups are substituted by cinnamoyl chloride.
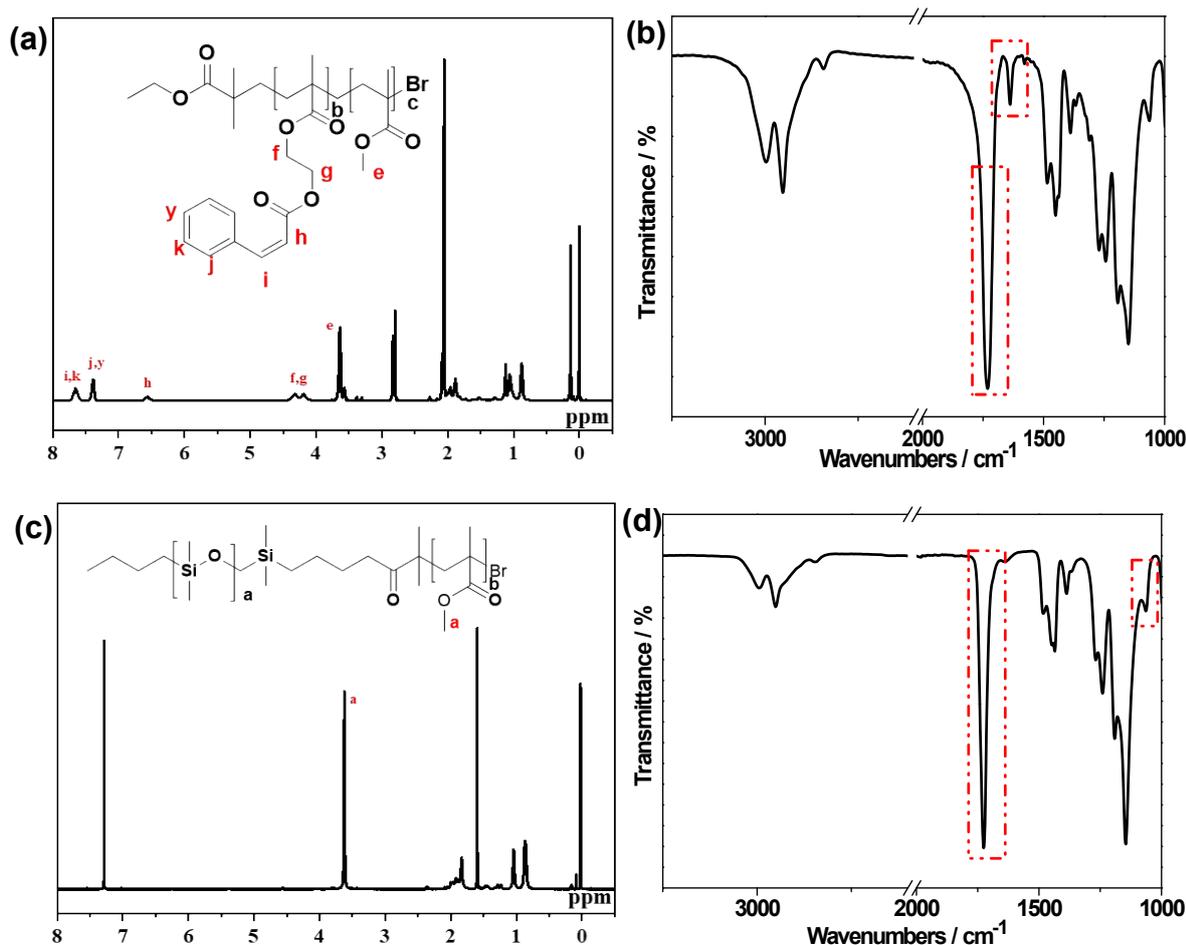
Figure S2. ^{1}H-NMR (a) and FTIR spectra (b) of PDMS-*b*-PMMA and PCEMA-*b*-PMMA copolymers.

The chemical structure of PDMS-*b*-PMMA and PCEMA-*b*-PMMA was confirmed by ^{1}H-NMR and FTIR in Figure 1. The typical δ_H (ppm) were detected at 4.23-4.28, 6.57 and 7.39-7.61 which were corresponding to -O-$(CH_2)_2$-O-, -CH= and =CH-C_6H_5 in PCEMA segments in Figure 1a, and the typical δ_H (ppm) at 3.6 in Figure 1a and Figure 1c were corresponding to -O-CH_3 in PMMA segments. Furthermore, the chemical structure of PCEMA-*b*-PMMA and PDMS-*b*-PMMA were further proved by the FTIR spectrum (Figure 1b, 1d). Obviously, for PCEMA-*b*-PMMA, the absorption peaks at 1576 cm^{-1}, 1718 cm^{-1}, and 1450-1492-1625 cm^{-1} were assigned to the absorption peaks of C=C, C=O and C_6H_5 from PCEMA segments and the absorption peaks of C=O from PMMA was overlapped with

PCEMA segments; for PDMS-*b*-PMMA, the absorption peaks at 1011 cm^{-1} and 1718 cm^{-1} were attributed to the Si-O-Si group of PDMS and the C=O group of PMMA. All the results proved the structure of the obtained copolymer PCEMA-*b*-PMMA and PDMS-*b*-PMMA.

Furthermore, the molecular weight of the resulting copolymers was charactered by GPC in Table 1. For these diblock copolymers PCEMA-b-PMMA and PDMS-*b*-PCEMA, the Mw was 3.61×10^4 and 3.75×10^4 g/mol, and the polydispersity index (PDI) of 1.08, 1.45 reveals a narrow distribution of molecular weight, which illustrates that the polymerization was typical living and controllable.
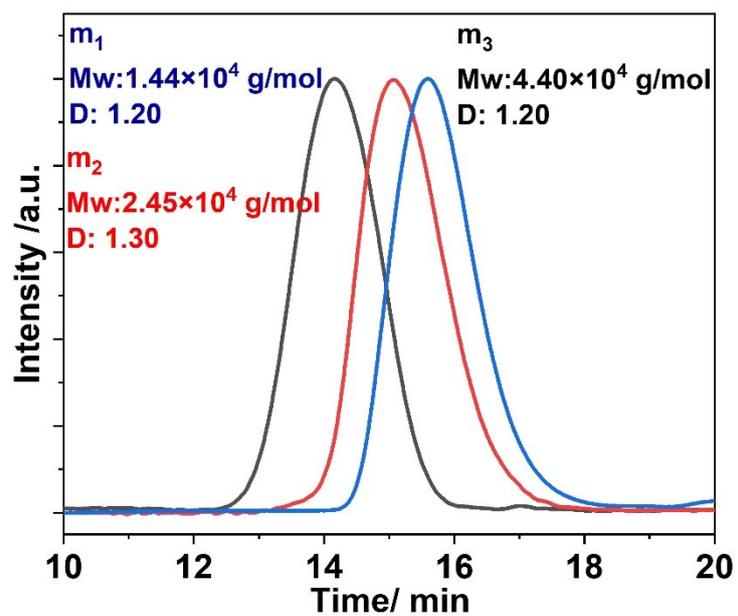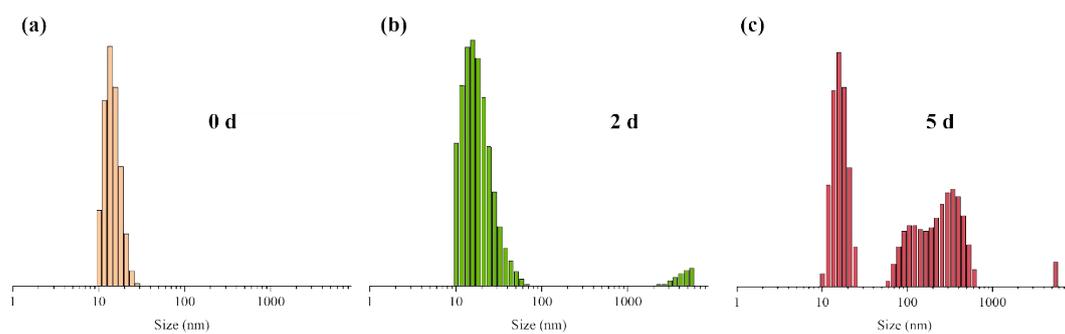
Figure S3. GPC analysis of PDMS-*b*-PCEMA$_m$

Figure S4. The DLS of the assembled micelles formed with PDMS$_{135}$-*b*-PCEMA$_{130}$ in THF at 0 days (a), 2 days (b), and 5 days (c).

Table S2. Permittivity of Different Solvents and The Micellar Morphologies and Sizes in Different Solvents.

Name	Molecular formula	Permittivity	Boiling point / °C	structure	Average diameter /nm
1,4-dioxane	$C_4H_8O_2$	2.21	101.3	Spherical micelles	~25
Tetrahydrofuran	C_4H_8O	7.58	66	Nanowires	~25-35
Dichloromethane	CH_2Cl_2	8.9	39.75	Nanowires	~25-35
Acetone	CH_3COCH_3	20.7	56.53	Spherical micelles	~550