Electronic Supplementary Material (ESI) for Polymer Chemistry.

Temperature-Controlled Formation of Inverse Mesophases Assembled from a Rod–Coil Block Copolymer

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Table of Contents

Synthesis of PEO-*b*-PMPCS

The monomethyl ether PEO2000 used was bought from Aldrich-Sigma. Its molar mass was confirmed by gel permeation chromatography (GPC) and matrix-assisted laser desorption/ ionization time of flight (MALDI-TOF) mass spectrometry, which was consistent with the label of the monomethyl ether PEO2000. The macroinitiator was prepared through esterification reaction between PEO2000 and 2-bromoisobutyryl bromide, and the purified white product was obtained by recrystallization for five times in diethyl ether.[1] Its chemical structure was confirmed by ^{1}H NMR (Fig. S2a). The synthesis of the monomer 2,5-bis[(4-methoxyphenyl)-oxycarbonyl]styrene (MPCS) can refer to the previous work.[2-3] And poly(ethylene oxide)-*b*-poly{2,5-bis[(4-methoxyphenyl)-oxycarbonyl]styrene} (PEO-*b*-PMPCS) was synthesized by atom-transfer radical polymerization (ATRP).[1] The ^{1}H NMR results of the block copolymers are shown in Fig. S2c.

Table S1. PEO-*b*-PMPCS Samples Characterized by ^{1}H NMR and GPC

	^{1}H NMR [a]			**GPC** [c]			
Sample	**Notation**	**M_n (g/mol)**	**f_{PMPCS} (%)** [b]	**Notation**	**M_n (g/mol)**	**f_{PMPCS} (%)** [b]	**$Đ_M$** [d]
1	$E_{45}M_{59}$	25800	91.3	$E_{45}M_{37}$	16900	86.8	1.16
2	$E_{45}M_{62}$	27000	91.7	$E_{45}M_{40}$	18100	87.7	1.17
3	$E_{45}M_{70}$	30300	92.6	$E_{45}M_{50}$	22300	90.0	1.20
4	$E_{45}M_{76}$	32700	93.1	$E_{45}M_{53}$	23400	90.4	1.25

[a] The DPs of PMPCS and number-averaged MWs were determined by ^{1}H NMR.

[b] The densities of PEO and PMPCS at 1.13 g/cm^3 and 1.28 g/cm^3, respectively, were used to calculate the volume fraction of PMPCS (f_{PMPCS}).

[c] The DPs of PMPCS and number-averaged MWs were determined by GPC.

[d] The molar-mass dispersity ($Đ_M$) values were determined by GPC.

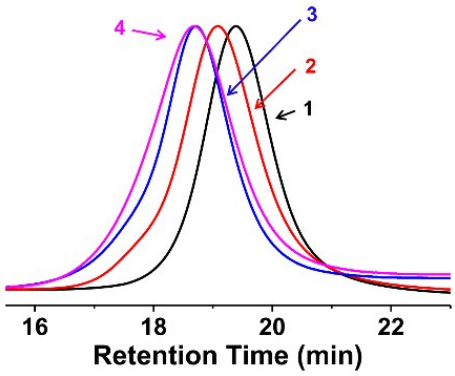

Fig. S1 GPC curves of PEO-*b*-PMPCS with different molecular weights.

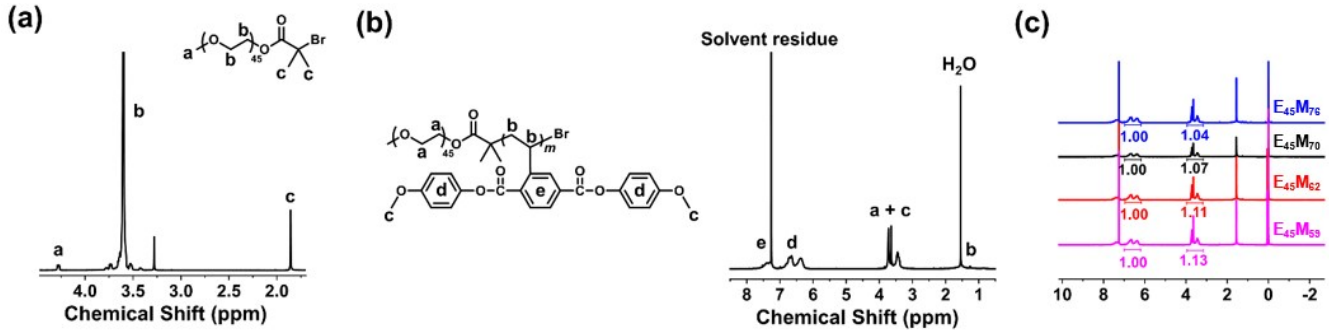

Fig. S2 ^{1}H NMR spectra of PEO with D_2O as the solvent (a), PEO-*b*-PMPCS with $CDCl_3$ as the solvent (b), and the four PEO-*b*-PMPCS used in this work with $CDCl_3$ as the solvent (c). (*m* is calculated with the equation, $m = 22.5 / (I_{a+c}/I_d - 0.75)$, where I_{a+c} and I_d are the integrals of hydrogen peaks shown above.).

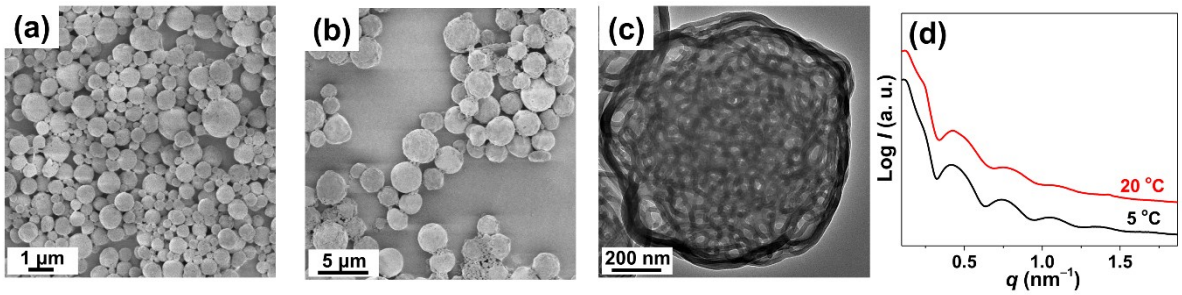

Fig. S3 SEM micrograph of the spongy structure self-assembled by $E_{45}M_{59}$ at 5 °C (a); SEM (b) and TEM (c) micrographs of the spongy structure self-assembled by $E_{45}M_{59}$ at 20 °C; SAXS profiles of spongy structures self-assembled by $E_{45}M_{59}$ at 5 and 20 °C (d).

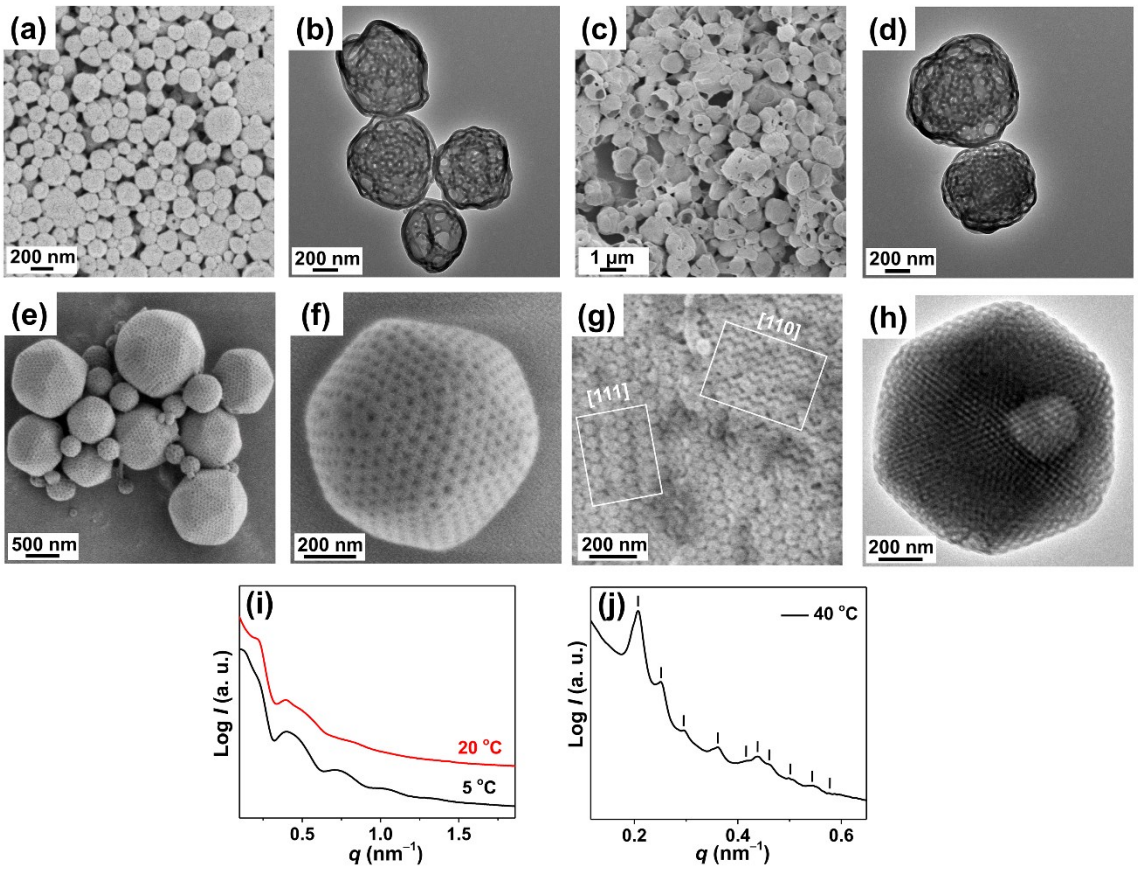

Fig. S4 SEM and TEM micrographs of spongy structures self-assembled by $E_{45}M_{62}$ at 5 °C (a, b) and 20 °C (c, d); low-magnification (e) and high-magnification (f) SEM micrographs, SEM micrograph viewed along the [110] and [111] directions (g), and TEM micrograph (h) of the $Pn\bar{3}m$ polymer cubosome self-assembled by $E_{45}M_{62}$ at 40 °C; SAXS profiles of $E_{45}M_{62}$ self-assembling at 5 °C, 20 °C (i), and 40 °C (j). (The scattering vector ratio of the peaks in Fig. S4j is $2^{1/2}:3^{1/2}:4^{1/2}:6^{1/2}:8^{1/2}:9^{1/2}:10^{1/2}:12^{1/2}:14^{1/2}:16^{1/2}$, corresponding to the (110), (111), (200), (211), (220), (221), (310), (222), (321), and (400) reflections of a $Pn\bar{3}m$ cubic cell with a = 43.1 nm)

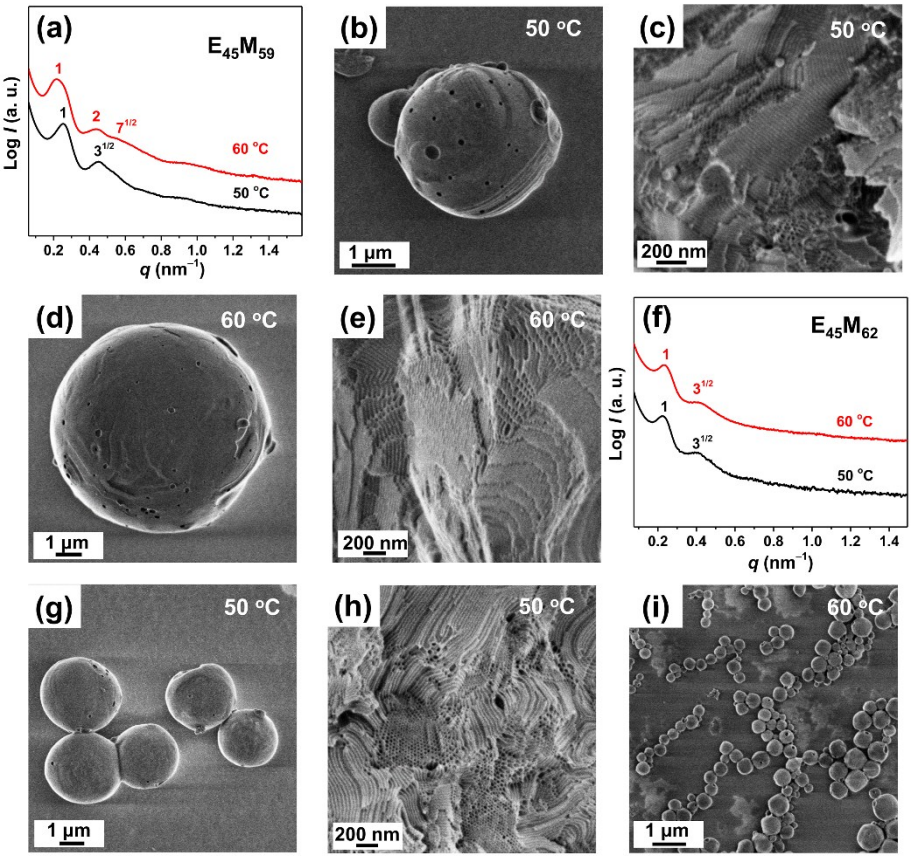

Fig. S5 SAXS profile of *p6mm* polymer hexasomes self-assembled by $E_{45}M_{59}$ at 50 °C and 60 °C (a); SEM micrographs of polymer hexasomes self-assembled by $E_{45}M_{59}$ at 50 °C (b, c) and 60 °C (d, e); SAXS profile of *p6mm* polymer hexasomes self-assembled by $E_{45}M_{62}$ at 50 °C and 60 °C (f); SEM micrographs of polymer hexasomes self-assembled by $E_{45}M_{62}$ at 50 °C (g, h) and 60 °C (i).

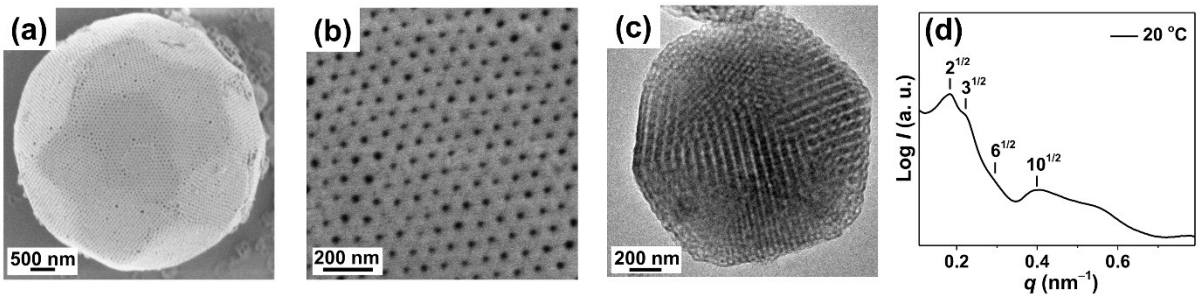

Fig. S6 Low-magnification (a) and high-magnification (b) SEM micrographs, TEM micrograph (c), and SAXS profile (d) of the $Pn\bar{3}m$ polymer cubosome self-assembled by $E_{45}M_{70}$ at 20 °C.

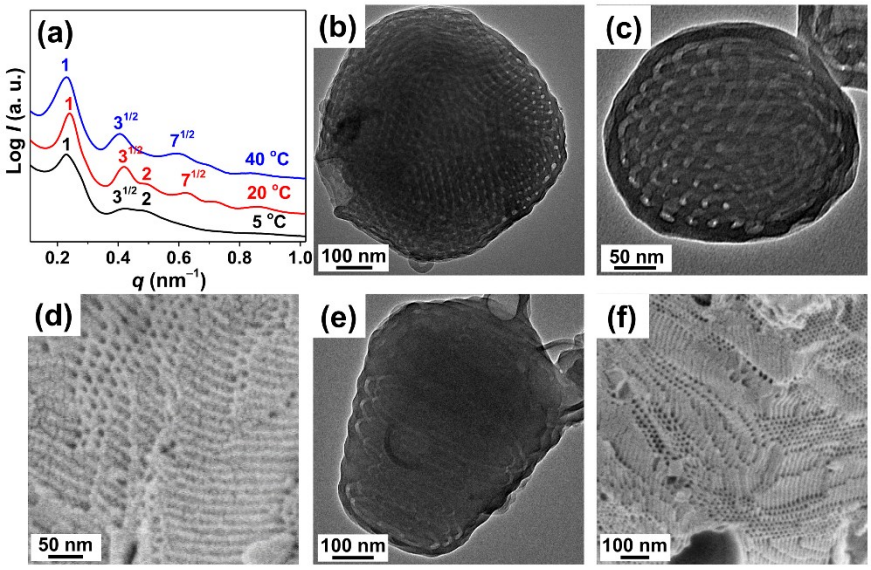

Fig. S7 SAXS profiles of $E_{45}M_{76}$ self-assembling at different temperatures (a); TEM micrograph of the *p6mm* polymer hexasome self-assembled by $E_{45}M_{76}$ at 5 °C (b); TEM and SEM micrographs of *p6mm* polymer hexasomes self-assembled by $E_{45}M_{76}$ at 20 °C (c, d) and 40 °C (e, f).

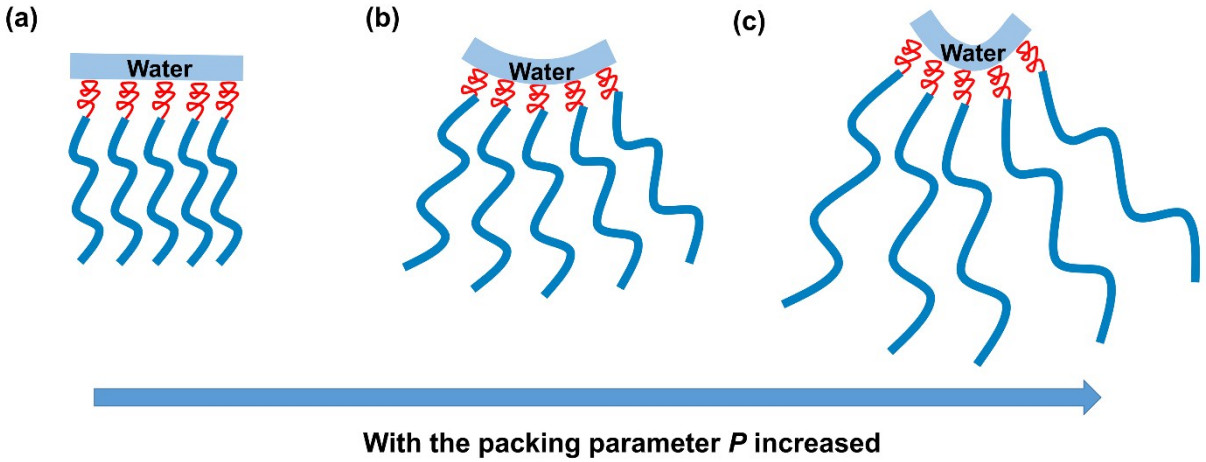

Fig. S8 The variations of the curvature towards the water side and packing parameter with increasing volume and chain length of the hydrophobic part in solutions.

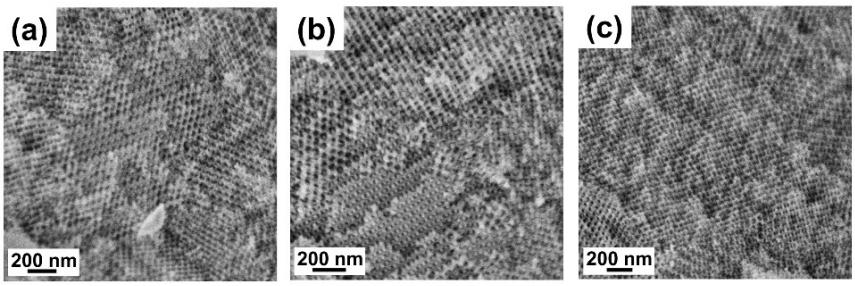

Fig. S9 SEM micrographs of the $Pn\bar{3}m$ silica cubosome observed from different orientations.

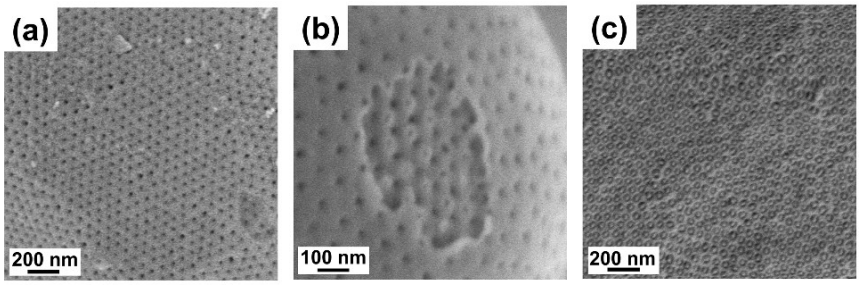

Fig. S10 SEM micrographs of the surface (a) and fractured surface (b) of the $Pn\bar{3}m$ polymer cubosome and that of the surface of the silica cubosome (c).

(1) Lyu, X.; Xiao, A.; Zhang, W.; Hou, P.; Gu, K.; Tang, Z.; Pan, H.; Wu, F.; Shen, Z.; Fan, X.-H. Head-Tail Asymmetry Determines the Formation of Polymer Cubosomes or Hexasomes in A Rod-Coil Amphiphilic Block Copolymer. *Angewandte Chemie International Edition* **2018**, *57*, 10132-10136.

(2) Zhang, D.; Liu, Y.-X.; Wan, X.-H.; Zhou, Q.-F. Synthesis and Characterization of A New Series of "Mesogen-Jacketed Liquid Crystal Polymers" Based on the Newly Synthesized Vinylterephthalic Acid. **1999**, *32*, 5183-5185.

(3) Ye, C.; Zhang, H.-L.; Huang, Y.; Chen, E.-Q.; Lu, Y.; Shen, D.; Wan, X.-H.; Shen, Z.; Cheng, S. Z. D.; Zhou, Q.-F. Molecular Weight Dependence of Phase Structures and Transitions of Mesogen-Jacketed Liquid Crystalline Polymers Based on 2-Vinylterephthalic Acids. **2004**, *37*, 7188-7196.