Electronic supplementary information for

# Janus Particles with Tunable Shapes Prepared by Asymmetric Bottlebrush Block Copolymers

Qian Wang,[†] Anqi Xiao,[†] Zhihao Shen,[*,†] and Xing-He Fan[*,†]

[†] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China

* To whom the correspondence should be addressed. E-mail: fanxh@pku.edu.cn (X.-H.F.); zshen@pku.edu.cn (Z.S.).

**Table of Contents**

**Materials**

Nb-PS, Nb-PDMS and BBCPs were prepared according to our previous report.[1] Tetrahydrofuran (THF) was treated by the Braun solvent purification system. All other reagents were obtained from commercial sources and used as received unless otherwise noted.

**Characterization Methods**

NMR spectra were recorded on a Bruker-500 MHz NMR. Gel permeation chromatographic (GPC) experiments were carried out on a Waters equipment, and THF was used as the eluent at a flow rate of 1.0 mL/min. GPC coupled with multi-angle laser light scattering (GPC-MALLS) examination was carried out in THF at 1.0 mL/min at 40 $^{o}$C on two styragel columns (7.8×30 mm) connected in series with a Wyatt Heleo-11 light scattering detector and a Wyatt optilab T-rEX refractive index detector. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker Autoflex III MALDI-TOF spectrometer. Dynamic light scattering (DLS) were performed on NanoBrook Omni (DLS90). Synchrotron-radiation small-angle X-ray scattering (SAXS) measurements were performed at Synchrotron X-ray Beamline BL16B1 in the Shanghai Synchrotron Radiation Facility (SSRF) and Synchrotron X-ray Beamline 1W2A in the Beijing

Synchrotron Radiation Facility (BSRF)[2]. The wavelength of the X-ray beam in SSRF was 0.124 Å and sample-to-detector distance was 4,997 mm. The wavelength of the X-ray beam in BSRF was 0.154 Å and sample-to-detector distance was 4, 955 mm. Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800 field emission SEM at an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) images were taken on a JEM 2100 TEM with an accelerating voltage of 200 kV. STEM-energy dispersive X-ray spectroscopy (EDS) line scan measurement was conducted on a JEM-2100F TEM operated at 200 kV.

**Synthesis of BBCPs**

($g$PDMS)$_{148}$-*b*-($g$PS)$_{131}$ and ($g$PDMS)$_{215}$-*b*-($g$PS)$_{215}$ were synthesized as described in our previous report[1]. And ($g$PDMS)$_{122}$-*b*-($g$PS)$_{93}$ and ($g$PDMS)$_{97}$-*b*-($g$PS)$_{82}$ were prepared in a similar way. Here, ($g$PDMS)$_{122}$-*b*-($g$PS)$_{93}$ is taken as an example to show the detailed information about the preparation and chemical structure characterization.

Grubbs III catalyst (1 equiv, 1.01 mg, 1.14 μmol) was charged into a flask with a stir bar, and then the flask was degassed with three pump−purge cycles with high purity nitrogen. 0.75 mL of $CH_2Cl_2$ solution containing Nb-PDMS (50 equiv, 154 mg, 78.3 μmol) was injected into the flask. After stirring at ambient temperature for 15 min, a solution of Nb-PS (33 equiv, 153 mg, 51.0 μmol) in 1 mL of $CH_2Cl_2$ was added into the mixture, and the mixture was stirred for an additional 2–3 hours. Then, polymerization was quenched with butyl vinyl ether, and the system was stirred for an

additional hour. The resultant mixture was diluted with $CH_2Cl_2$ and passed through a short alumina column to remove the catalyst. Finally, the BBCP was precipitated into 200 mL of menthol to obtain a white solid.

The molecular weight (MW) and polydispersity of the BBCPs were characterized by GPC, as shown in Fig. S1. Even though the peak shape is not quite symmetric for $(g\text{PDMS})_{215}$-*b*-$(g\text{PS})_{215}$, the BBCP is pure because the unreacted macromonomers are then removed by precipitation in menthol following the procedure reported in literature.[3] The chemical structure of $(g\text{PDMS})_{122}$-*b*-$(g\text{PS})_{93}$ is characterized by $^1$H NMR, as shown in Fig. S2.

**Determination of the Compositions of the BBCPs**

The compositions of the BBCPs were determined by the following equations as described in our previous report.[1] In the equations, $M_{\text{w, total}}$, $M_{\text{w, Nb-PS}}$, and $M_{\text{w, Nb-PDMS}}$ represent the absolute MW of the BBCP, Nb-PS, and Nb-PDMS, respectively; $DP_{\text{Nb-PS}}$ and $DP_{\text{Nb-PDMS}}$ represent the degrees of polymerization (DPs) of Nb-PS and Nb-PDMS, respectively; *a* and *b* represent the integration of characteristic peaks of Nb-PS and Nb-PDMS macromonomers from $^1$H NMR spectra; *m* and *n* represent the integration of characteristic peaks of PS and PDMS in the BBCP from $^1$H NMR spectra; $w_{\text{PS}}$ and $f_{\text{PS}}$ represent the weight fraction of PS and the volume fraction of PS, respectively.

$$M_{\text{w, total}} = DP_{\text{Nb-PS}} \times M_{\text{w, Nb-PS}} + DP_{\text{Nb-PDMS}} \times M_{\text{w, Nb-PDMS}} \quad (1)$$

$$\frac{m}{n} = \frac{a \times \text{DP}_{\text{Nb - PS}}}{b \times \text{DP}_{\text{Nb - PDMS}}} \quad (2)$$

$$w_{PS} = \frac{DP_{Nb\text{-}PS} \times 3000}{DP_{Nb\text{-}PS} \times 3000 + DP_{Nb\text{-}PDMS} \times 1972} \quad (3)$$

$$f_{PS} = \frac{w_{PS}/\rho_{PS}}{\frac{w_{PS}}{\rho_{PS}} + (1 - w_{PS})/\rho_{PDMS}} \quad (4)$$

**Phase Behaviors of BBCPs in Bulk**

The phase behaviors of the $(g\text{PDMS})_x$-*b*-$(g\text{PS})_y$ BBCPs in bulk were investigated. As shown in Fig. S4, for $(g\text{PDMS})_{122}$-*b*-$(g\text{PS})_{93}$, the diffraction peaks have a scattering vector ratio of 1:2:3, indicating a lamellar structure, which is consistent with the SEM result (Fig. S5a). For $(g\text{PDMS})_{97}$-*b*-$(g\text{PS})_{82}$ (Fig. S4), the scattering peaks are a little broader so that it is difficult to determine the structure from the SAXS profile. With the combination of the SEM result (Fig. S5b), it is found that a mixed structure with lamellae and cylinders is formed for this sample. For $(g\text{PDMS})_{148}$-*b*-$(g\text{PS})_{131}$ and $(g\text{PDMS})_{215}$-*b*-$(g\text{PS})_{215}$, it was found to form cylindrical and spherical morphologies, respectively, in our previous report.[1] The molecular characteristics and morphologies of the BBCPs in bulk are summarized in Table S1. These BBCPs form lamellae, cylinders, and spheres in bulk. The *d*-spacing values calculated from SAXS results are in the range of 87–138 nm.

**Results**

**Table S1.** Molecular Characteristics and Bulk Morphologies of BBCPs.

| BBCP | $M_w$ (kg/mol) [a] | $Đ_M$ [a] | $f_{PS}$ (%) | Morphology [b] | *d*-spacing (nm) [b] |
|---|---|---|---|---|---|
| $(gPDMS)_{122}$-*b*-$(gPS)_{93}$ | 520.3 | 1.38 | 52 | lamella | 87 |
| $(gPDMS)_{97}$-*b*-$(gPS)_{82}$ | 436.8 | 1.33 | 54 | Lamella/cylinder | 88 |
| $(gPDMS)_{148}$-*b*-$(gPS)_{131}$ | 690.2 | 1.44 | 55 | cylinder | 125 |
| $(gPDMS)_{215}$-*b*-$(gPS)_{215}$ | 1075.0 | 1.57 | 58 | sphere | 138 |

[a] Determined by GPC-MALLS in THF. [b] Determined by SAXS results.

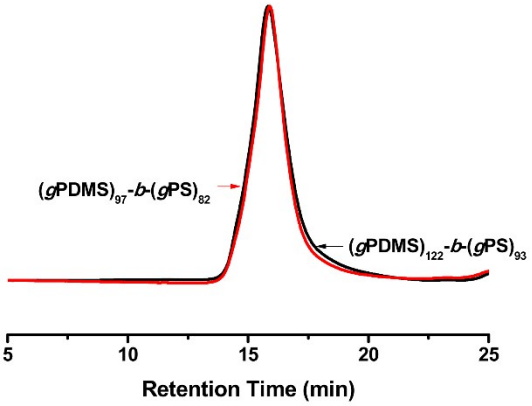


Fig. S1 GPC curves of the BBCPs.

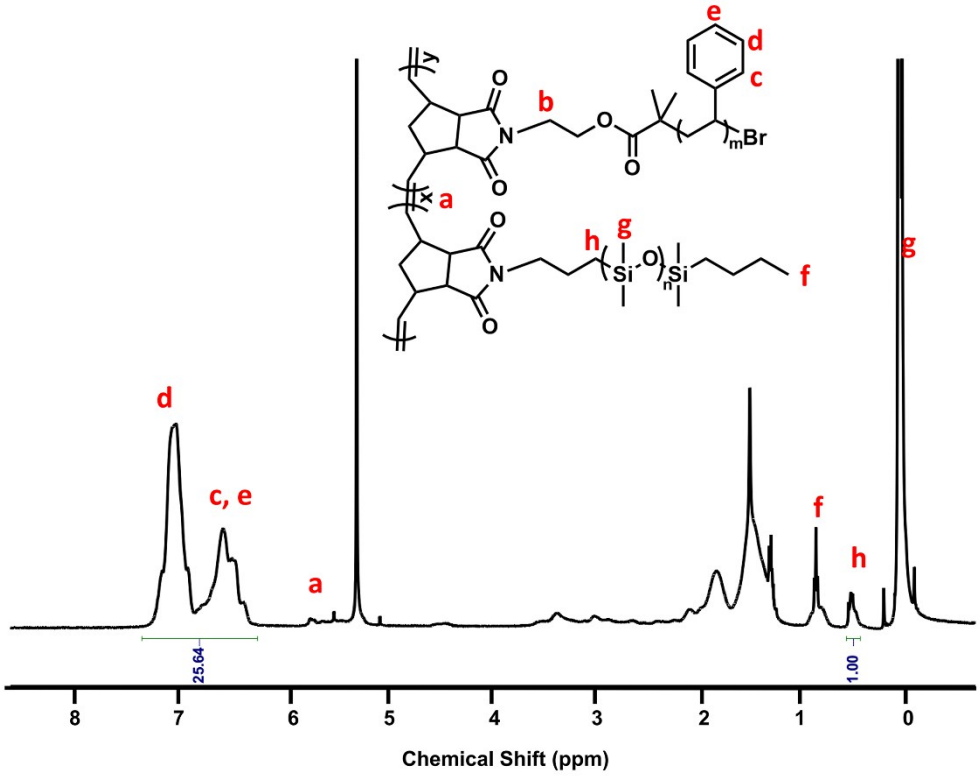

Fig. S2 $^1$H NMR spectrum of $(g\text{PDMS})_{122}$-*b*-$(g\text{PS})_{93}$ in $CD_2Cl_2$.

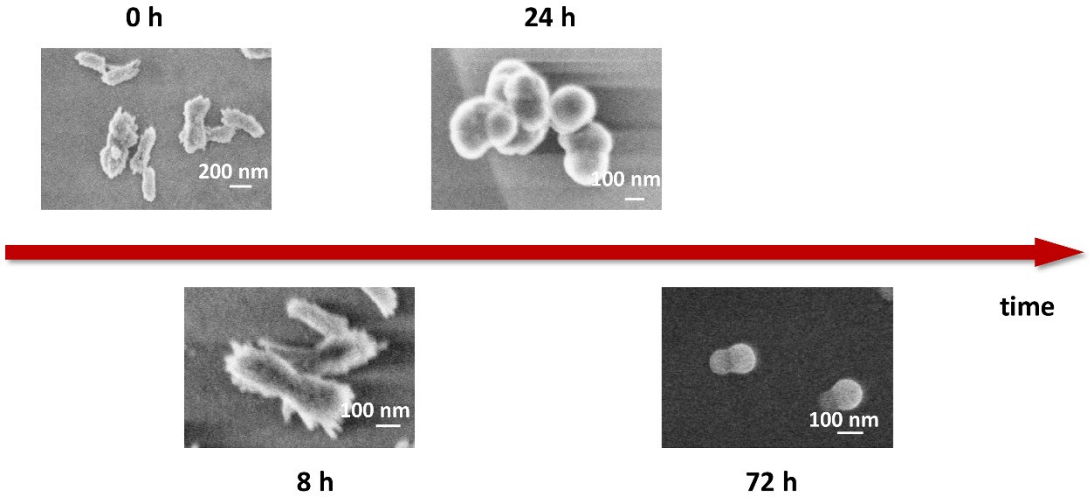


Fig. S3 Morphologies of the aggregates with increasing evaporation time.

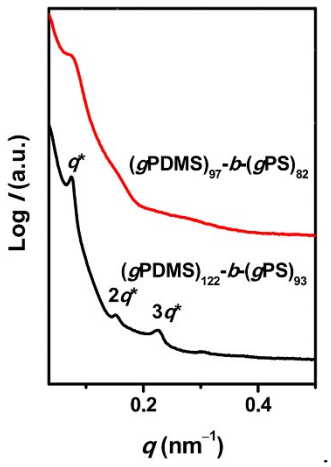


Fig. S4 SAXS profiles of the BBCPs.

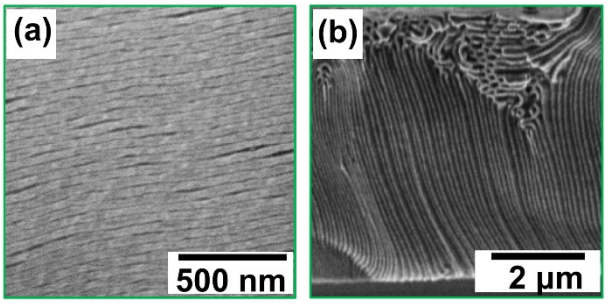


Fig. S5 SEM micrographs of BBCPs self-assembled in bulk (a: $(g\text{PDMS})_{122}$-*b*-$(g\text{PS})_{93}$; b: $(g\text{PDMS})_{97}$-*b*-$(g\text{PS})_{82}$)

## References:

(1). Wang, Q.; Gu, K.-H.; Zhang, Z.; Hou, P.; Shen, Z.; Fan, X.-H., Morphologies and photonic properties of an asymmetric brush block copolymer with polystyrene and polydimethylsiloxane side chains. *Polymer* **2018,** *156*, 169-178.

(2). Li, Z.; Wu, Z.; Mo, G.; Xing, X.; Liu, P., A Small-Angle X-ray Scattering Station at Beijing Synchrotron Radiation Facility. *Instrum. Sci. Technol.* **2014,** *42*, 128-141.

(3). Pesek, S. L.; Lin, Y.-H.; Mah, H. Z.; Kasper, W.; Chen, B.; Rohde, B. J.; Robertson, M. L.; Stein, G. E.; Verduzco, R., Synthesis of bottlebrush copolymers based on poly(dimethylsiloxane) for surface active additives. *Polymer* **2016,** *98*, 495-504.