Electronic Supplementary Material (ESI) for Soft Matter

Self-assembled Aggregates of Dendritic-linear Copolymers: Vesicles and Microspheres

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Experimental:

Materials

The monomer 2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene (MPCS) was synthesized according to the procedure reported previously.[1] Copper (I) chloride (CuCl) (Aladdin Reagent Co.) was dissolved in concentrated hydrochloric acid, precipitated by DI water, washed by ethanol and ethyl ether and dried in vacuum. N, N, N′, N″, N″-pentamethyldiethylenetriamine (PMDETA, TCI, 99.5%), *p*-xylene (Aladdin Reagent Co.) were used as purchased. Chlorobenzene, acetone and dichloromethane (Sinopharm Chemical Reagent Co.) was distilled from calcium hydroxide (Sinopharm Chemical Reagent Co.) prior to be used as the polymerization solvent. Unless otherwise specified, all other solvents and reagents were purchased from Sinopharm Chemical Reagent Co. and used as received.

Chemical Charaterizations

^{1}H NMR spectra were recorded on a Varian Mercury plus 400M spectrometer with $CDCl_3$ as the solvent and TMS as the internal reference. The number-average molecular weights (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI, M_w/M_n) were determined by gel permeation chromatography (GPC) instrument with a G1362A refractive index detector. Tetrahydrofuran (THF) was employed as the eluant at a flow rate of 1.0 mL/min at 35 ^{o}C and the calibration curve was obtained with monodispersed polystyrenes as standards.

Synthesis

Dendron molecules were synthesized according to the process reported by Percec et.al.[2] Dendritic-linear copolymers dendron-*b*-PMPCS were prepared by solution polymerization in chlorobenzene via ATRP of MPCS with dendron molecule as the macroinitiator. Typical polymerization procedure is: MPCS (0.4 g, 1 mmol), dendron macroinitiator (26.3 mg, 0.0125 mmol), CuCl (1.24 mg, 0.0125 mmol), PMDETA (2.1 mg, 0.0125 mmol) and chlorobenzene (0.6 g) were successively taken in a 25mL reaction tube. The reaction tube was degassed by three freeze-pump-thaw cycles, and then placed in an oil bath at 90 ^{o}C. After 2 hours, the polymerization was stopped and the solution was diluted by 5 mL THF, passed through a neutral alumina (Al_2O_3) column to remove the catalyst and precipitated in 300 mL methanol. For purification, crude product was completely dissolved in THF followed by adding the methanol gradually. The precipitation was then dried in vacuum for 24 h (0.33g, yield 82.5%). ^{1}H NMR (δ, ppm, 400MHz, $CDCl_3$): 0.88 (t, CH_3- protons of dendron), 1.2-2.0 (b, -CH_2-protons of dendron and -CH_2CH- protons in PMPCS backbone), 3.1-4.2 (b, -CH_2O-Ar protons of dendron and -OCH_3 protons of MPCS), 6.2-7.0 (b, phenyl ring protons ortho to CH_2 of dendron and outer phenyl ring protons of MPCS), 7.2-8.0 (b, phenyl ring protons ortho to CH_2Cl of dendron and inter phenyl ring protons of MPCS).

Table S1 Properties of dendron-*b*-PMPCS block copolymers

Sample	M_n (10^4)	PDI
S-1	3.3	1.25
S-2	4.9	1.37
S-3	5.6	1.15

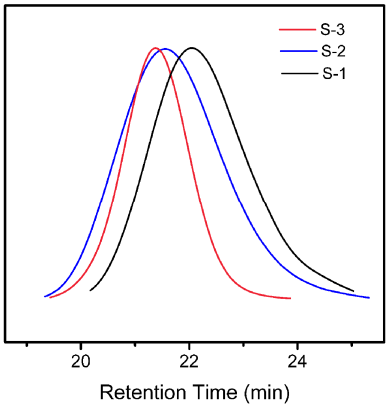

Figure S1. The GPC trace of three dendron-b-PMPCS copolymers.

Vesicles and micro-sphere Characterizations

Transmission electron microscopy (TEM) observations were performed on a Hitachi H-600 electron microscope. The samples were prepared by dip-casting of the polymer solutions onto the plasma treated carbon coated copper grids and allowing it to dry freely in air.

Scanning Electron Microscopy (SEM) was carried out on TESCAN 5136MM scanning electron microscopy after coated with gold. And Field Emission Transmission Electron Microscopy (FETEM) was performed on a Hitachi S-4800 field emission transmission electron microscopy. Samples were prepared by dip-casting of solutions onto mica sheet.

Dynamic light scattering (DLS) study was performed by using a Malvern Zetasizer-Nano Instruments. The DLS measurements were taken at angle of 90° at 25 ±0.1 °C.

^{1}H NMR spectra of polymer in deuterated acetone and DCM were also recorded on a Varian Mercury plus 400M spectrometer. The concentration of solution was *ca.* 2mg/mL.

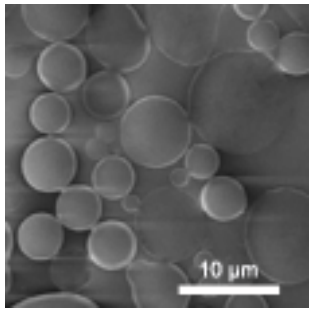

Figure S2. TEM image of giant vesicles made from neat-PMPCS in dichloromethane (4mg/mL).

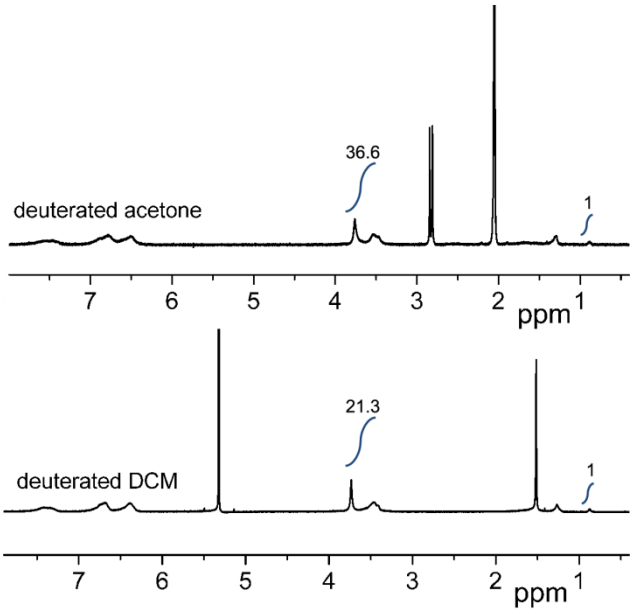

Figure S3. Integrated Area of ^{1}H NMR spectra in deuterated acetone (2 mg/mL) and deuterated DCM (2 mg/mL). δ=0.88 (t, CH_3- protons of dendron), 3.1-4.2 (b, -CH_2O-Ar protons of dendron and -OCH_3 protons of MPCS).

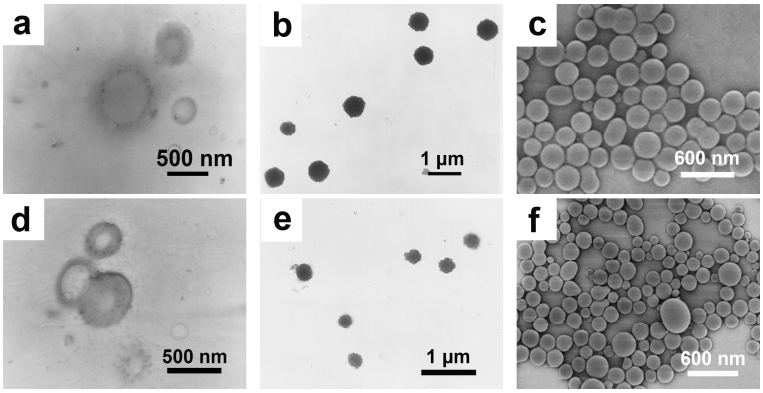

Figure S4. The aggregates morphologies of copolymer S-1(a, b and c) and S-3 (d, e and f): a) and d) vesicles in DCM solution (4 mg/ml), the fuzzy boundaries of vesicles may be due to the deformation of aggregates during solvent evaporation; b) and e) micro spherical micelles in *p*-xylene solution (0.5 mg/ml); c) and f) vesicular structures in acetone solution (2 mg/ml).

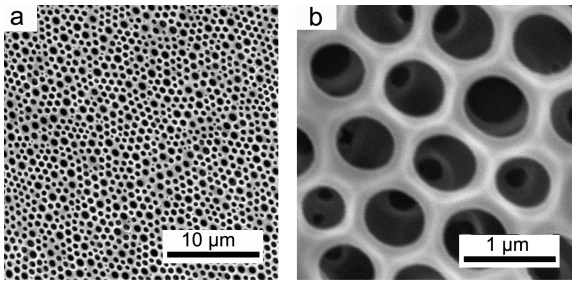

Figure S5. a) and b) honey-comb structure of solvent-casting film from chloroform (4 mg/ml) the scale bar was 10 μm and 1μm respectively.

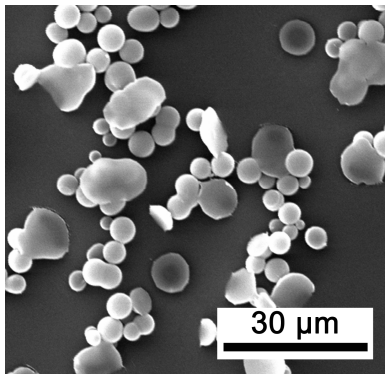

Figure S6. The lammellae aggregates made from copolymer S-2 in the solution of acetone (2 mg/ml).

Reference

1. D. Zhang, Y. X. Liu, X. H. Wan and Q. F. Zhou, Macromolecules, 1999, **32**, 5183-5185.
2. V. S. K. Balagurusamy, G. Ungar, V. Percec and G. Johansson, J. Am. Chem. Soc., 1997, 119, 1539-1555.