Supporting Information for the Manuscript Entitled

Laterally Nanostructured Vesicles, Polygonal Bilayer Sheets, and Segmented Wormlike Micelles

Zhibo Li,[†] Marc A. Hillmyer,[,†] and Timothy P. Lodge*[,†,‡]*

University of Minnesota, Minneapolis, Minnesota 55455

[†]Department of Chemistry

[‡]Department of Chemical Engineering and Materials Science

*Authors for correspondence: hillmyer@chem.umn.edu (M.A.H), lodge@chem.umn.edu (T.P.L.)

Experiments

Materials. Three polyethylethylene-*b*-poly(ethylene oxide) (EO) diblock copolymers, with a hydroxyl group at the block junction, were synthesized by two successive anionic polymerizations; the E block was obtained by catalytic hydrogenation of a 1,2-polybutadiene precursor, prior to initiation of the PEO block.[1] The mid-hydroxyl functionality was obtained by use of 2-methoxymethoxymethyl-oxirane as the terminating agent in the butadiene polymerization. The μ-(polyethyleethylene)poly(ethylene oxide)poly(perfluoropropylene oxide) [μ-EOF] miktoarm star terpolymers were obtained through a coupling reaction between the mid-hydroxyl functionalized EO diblock copolymer with an acid-chloride end-functionalized poly(perfluoropropylene oxide) homopolymer (PFPO) according to an established procedure.[2] The detailed synthesis and molecular characterization of the μ-EOF terpolymers can be found elsewhere.[2] The terpolymers are designated as μ-EOF(x-y-z), where x, y, and z denote the molecular weights in kg mol^{-1} of the E, O, and F blocks, respectively. The PEE and PFPO blocks have glass transition temperatures of approximately –20 °C[3] and –63 °C,[4] respectively.

General Methods. Size exclusion chromatography (SEC) was performed on a Hewlett Packard series 1100 liquid chromatography system equipped with a Hewlett Packard 1047A refractive index (RI) detector and three Jordi polydivinylbenzene columns of 10^4, 10^3, and 500 Å pore sizes, calibrated with polystyrene standards. THF was used as the mobile phase (40 °C and 1 mL/min). NMR spectra were acquired using Varian INOVA 300 or 500 spectrometers at room temperature. PFPO was dissolved in Freon-113 and μ-EOF terpolymers were dissolved in a mixture of Freon-113 and $CDCl_3$.

Cryogenic Transmission Electron Microscopy (cryoTEM). CryoTEM samples were prepared in a controlled environment vitrification system, which was saturated with water vapor. All the samples were prepared at room temperature. Typically, a micropipette was used to load a drop of micelle solution (~5 μL) onto a lacey supported grid, held by tweezers. The excess solution was blotted with a piece of filter paper, resulting in the formation of thin films of *ca.* 100 ~ 300 nm thickness in the holes. After allowing about 20 seconds for relaxation, the samples were quickly plunged into a reservoir of liquid ethane near its melting temperature (-183 °C) cooled by liquid nitrogen. The vitrified samples were then stored in liquid nitrogen until they were transferred to, and mounted on, a cryogenic sample holder (Gatan 626) and examined with a JEOL 1210 TEM (120 keV) at –178 °C. The phase contrast was enhanced by underfocus. The images were recorded on a Gatan 724 multiscan CCD and processed with DigitalMicrographs version 3.3.1. The ramp-shaped optical density gradients in the background were digitally corrected. In the cryoTEM images shown in this paper, the F domains appear dark and E domains appear gray due to the electron density difference. The O coronas are well solvated with water and normally invisible.

Complementary cryoTEM results

In order to give a more detailed picture and elucidate the vesicle growth mechanism, we present a series of cryoTEM images obtained from aqueous solutions of these terpolymers. The three specifically selected μ-EOF star terpolymers have comparable chain length between E and F blocks. The volume ratio of hydrocarbon (E) to fluorocarbon (F) (V_E/V_F = 1.2) is less than those μ-EOF terpolymers reported elsewhere.[5] The fully stretched lengths of E and F blocks are estimated to 5.9 and 5.2 nm, respectively, based on a zig-zag chain conformation. Figure S1 shows the cryoTEM images obtained from a 1 wt% aqueous solution of μ-EOF(1.4-5-2.5), which forms predominate segmented worm-like micelles with a broad length distribution. Also, no micelle morphology transition observed after the same micelle solution was annealed at 50 °C for a few days demonstrated by cryoTEM images shown in Figure S2. This result indicates that the segmented wormlike micelle is the thermodynamically preferred morphology by μ-EOF(1.4-5-2.5) in contrast to μ-EOF(1.4-3-2.5).

Figure S3 provides complementary cryoTEM images to Figure 2. After considerable annealing time (~20 days) at room temperature, the hexagonal shaped bilayer sheet is the dominant micelle morphology from a collection of cryoTEM images. It was well known that bilayer sheets are the intermediate structure in the transition from micelle to vesicles.[6-10] Meanwhile, the bilayer sheets were rarely observed as a stable structure for lipid surfactants because the large energy penalty for the edge in terms of line tension.[11,12] The exceptions are in the catianionic surfactant system, i.e., a mixture of cationic and anionic surfactants, where the disk edge can stabilized by electrostatic interactions,[13-15] or in polymeric surfactant with high molecular weight, where the bilayer structures were kinetically frozen.[16,17]

Figure S4 shows the cryoTEM images from a 1 wt% μ-EOF(1.4-3-2.5) micelle solution, which was stirred at room temperature for 17 days and at 50 °C for 3 days. Apparently, a slightly thermal anneals substantially increases the vesicles proportion to bilayer sheets and segmented worms in contrast to the images shown in Figure 2 and Figure S3. This result demonstrates that the nanostructured bilayer sheets are the intermediate transition structures to vesicles, however with laterally distributed nano-compartments composed of different chemical identities.

For the sample μ-EOF(1.4-2-2.5), a terpolymer with shorter O block than μ-EOF(1.4-3-2.5), a vesicle morphology must be thermodynamically preferred due to further increased edge energy. Large proportions of fully formed vesicles or nearly complete closure of vesicles with a protruding segmented worm are observed in Figure S5. A feature here is that no bilayer sheets were observed coexisting with worms and vesicles. Although μ-EOF(1.4-2-2.5) terpolymer thermodynamically prefers vesicle morphology, its dissolution proceeds much slower than that of μ-EOF(1.4-3-2.5) because of its shorter O blocks. Long time thermal annealing is necessary to obtain substantial vesicle formation.

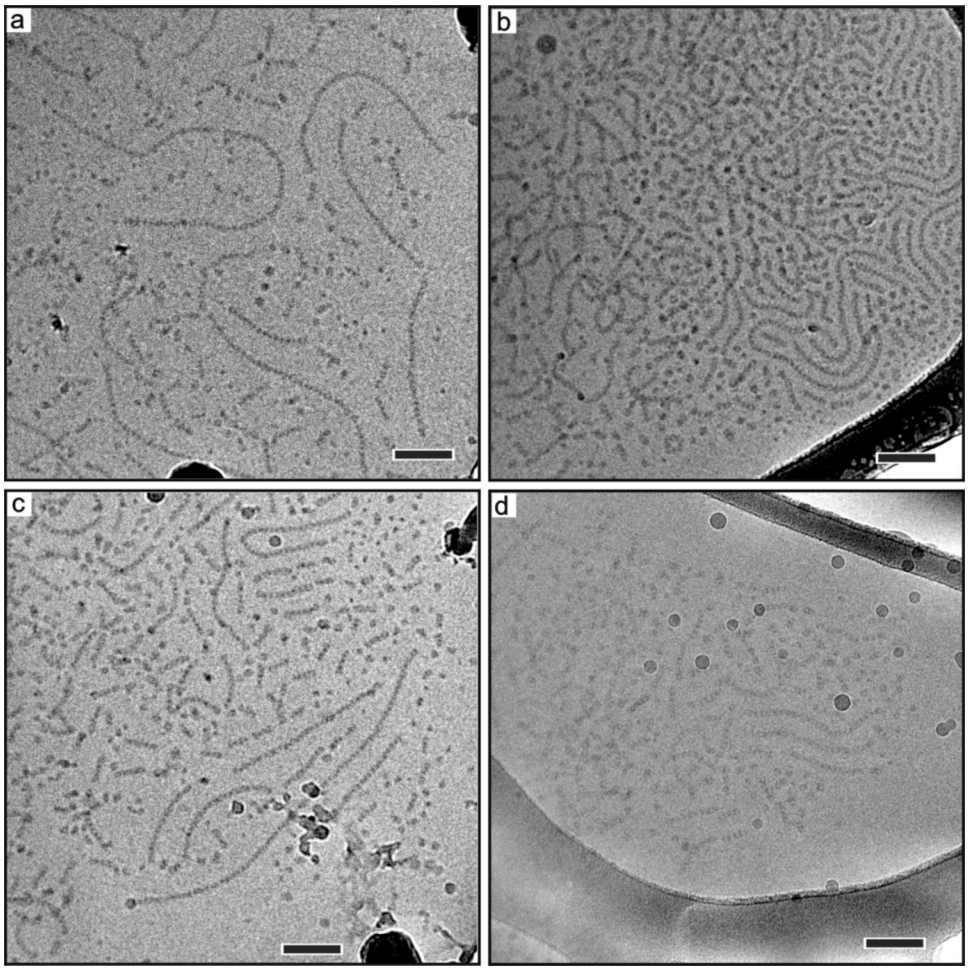


Figure S1. Segmented wormlike micelles formation from μ-EOF(1.4-5-2.5) terpolymer. The cryoTEM images were obtained from a 1 wt% aqueous solution of μ-EOF(1.4-5-2.5) stirred at room temperature for 23 days. Scale bar indicates 100 nm.

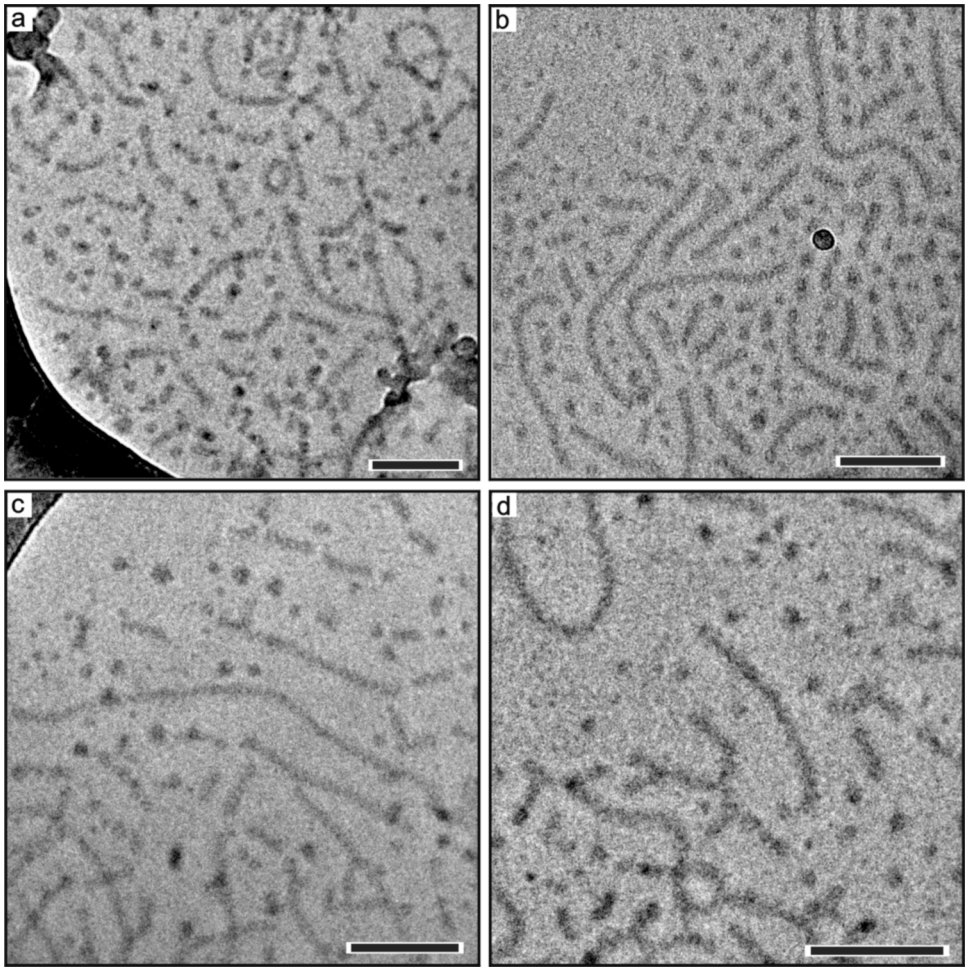
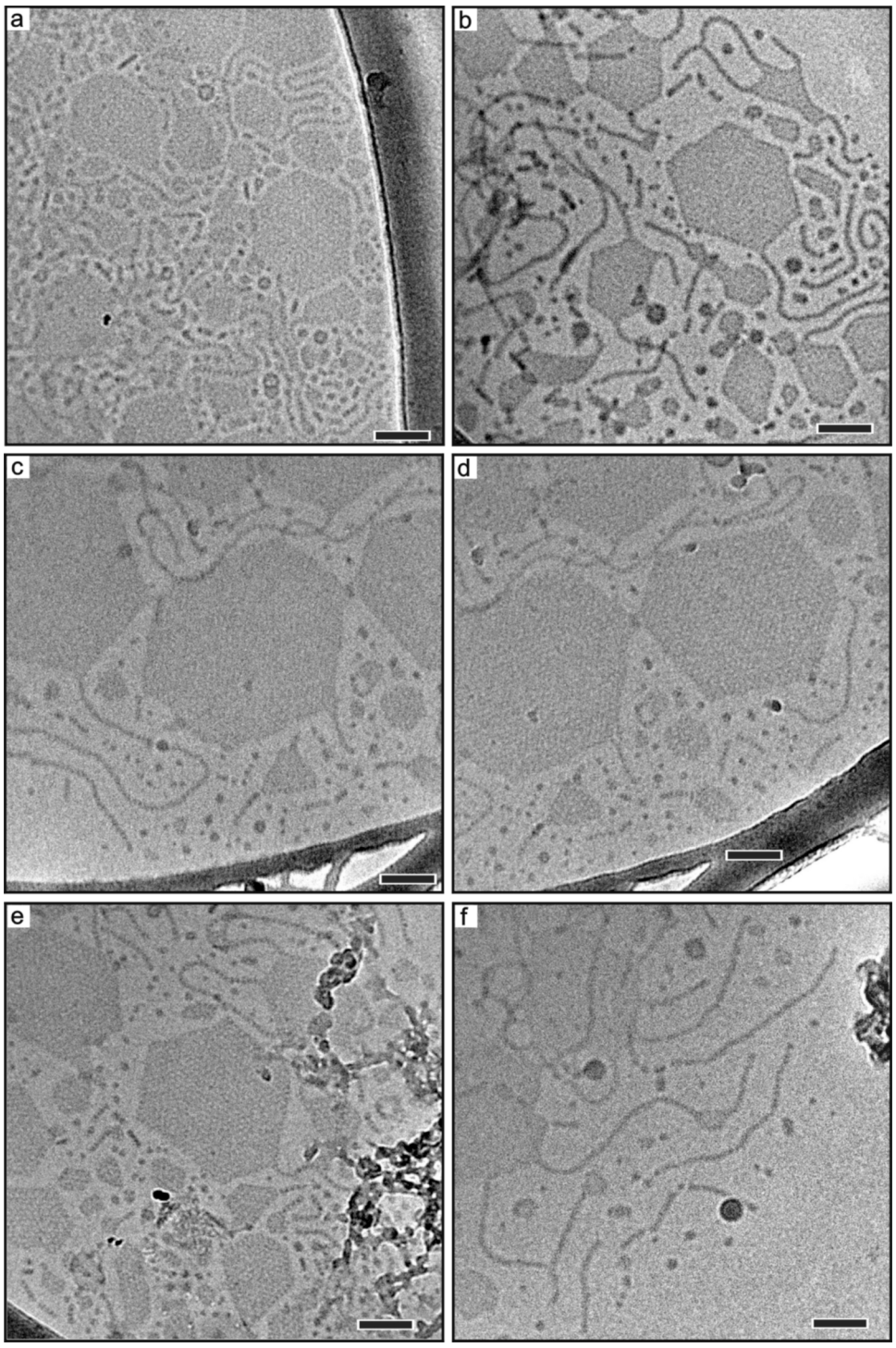


Figure S2. Thermal stability of segmented wormlike micelles formed from μ-EOF(1.4-5-2.5) terpolymer. The cryoTEM images obtained from a 1 wt% aqueous solution of μ-EOF(1.4-5-2.5) stirred at room temperature for 12 days and at 50 °C for 3 days . Scale bar indicates 100 nm.



Continue on next page

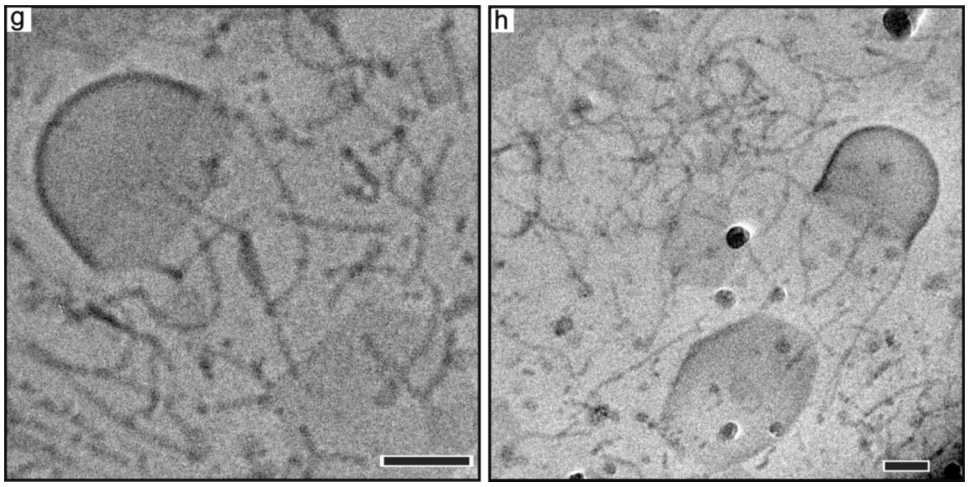


Figure S3. Nanostructured bilayer sheets and semi-vesicles formation from μ-EOF(1.4-3-2.5) terpolymer. CryoTEM images obtained from a 1 wt% aqueous solution of μ-EOF(1.4-3-2.5) stirred at room temperature for 20 days. Scale bar indicates 100 nm.

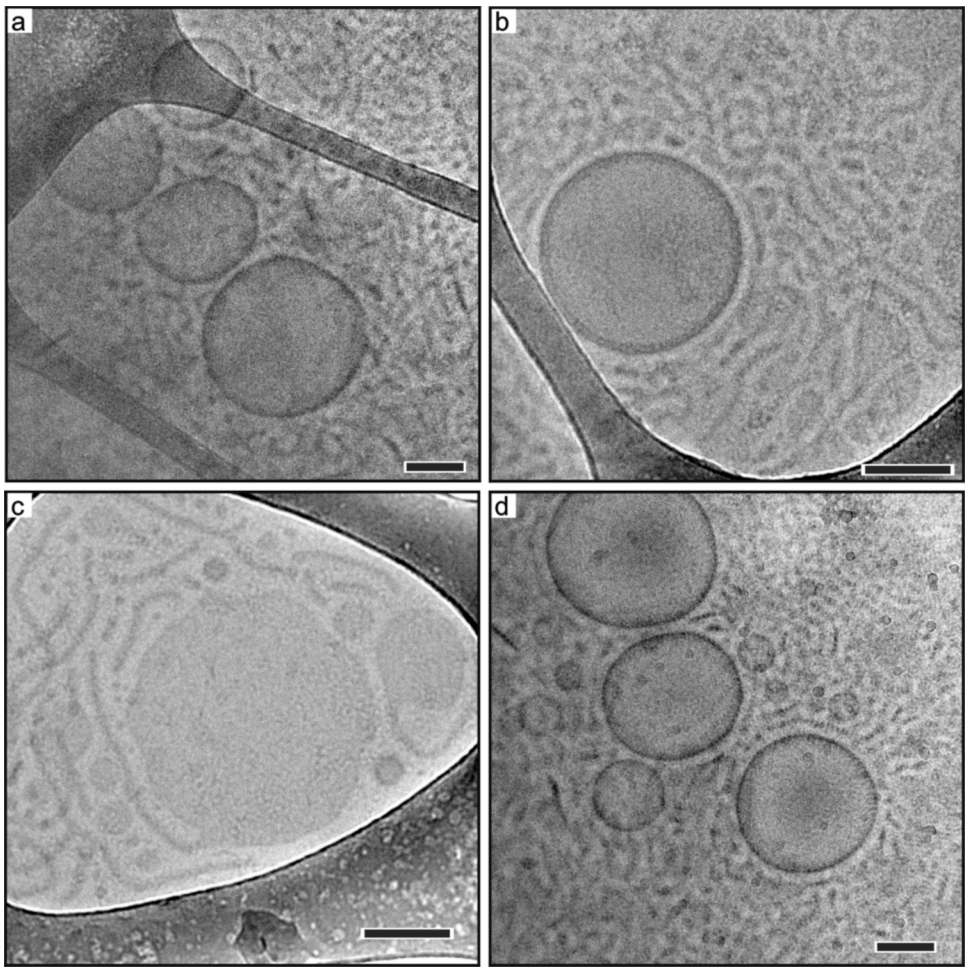


Figure S4. Thermal induced transition from bilayer sheets to vesicles in μ-EOF(1.4-3-2.5) micelle solution. The cryoTEM were images obtained from a 1 wt% aqueous solution of μ-EOF(1.4-3-2.5) stirred at room temperature for 17 days and at 50 °C for 3 days. Scale bar indicates 100 nm.

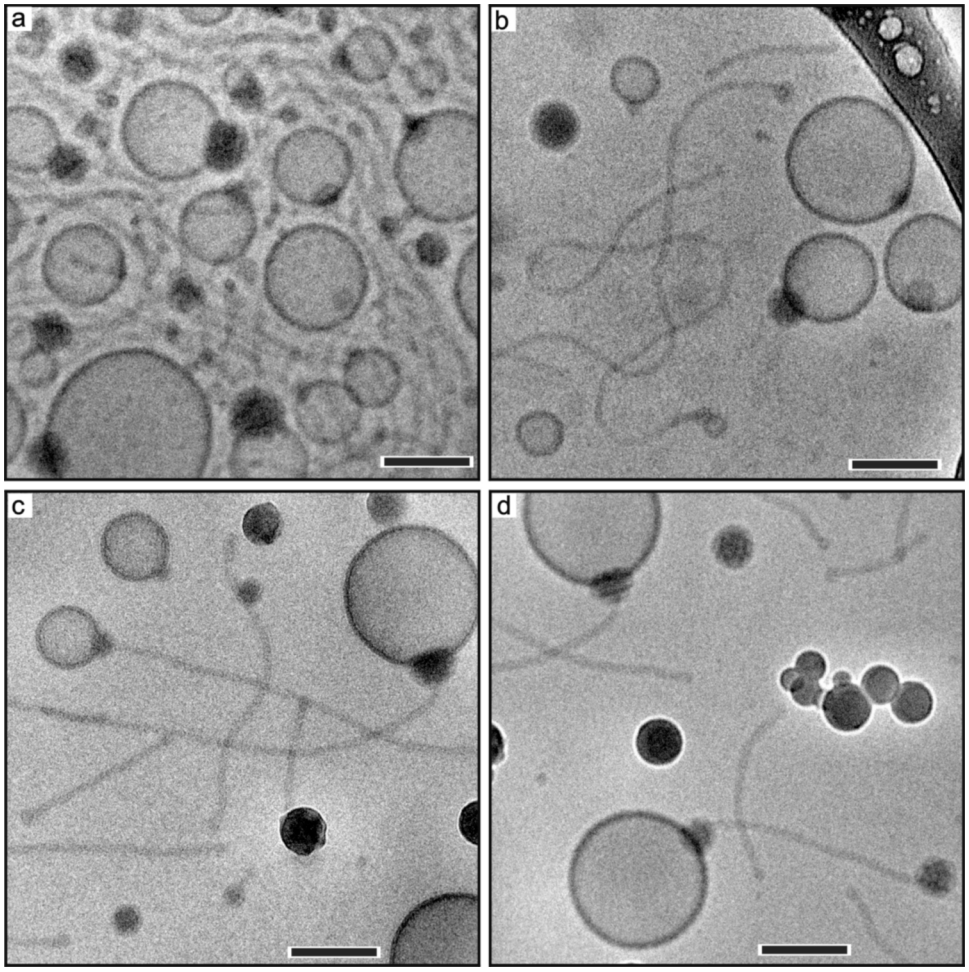


Figure S5. Nanostructured vesicle formation from μ-EOF(1.4-2-2.5) terpolymer. The cryoTEM images were obtained from a 1 wt% aqueous solution of μ-EOF(1.4-2-2.5) stirred at 50 °C for more than 3 weeks. Scale bar indicates 100 nm.

Molecular characterization

The synthesis and characterization of heterobifunctional polyethylethylene (PEE) has be reported elsewhere.[2] The PEE block used here has 22 repeating units determined by both ^{1}H NMR and MALDI-TOF MS, and its polydispersity (PDI) is 1.06 determined by SEC. The obtained mid-functional polyethylethylene-b-polyethylene oxide (PEE-PEO) diblock copolymers after deprotection reaction have relatively narrow molecular weight distribution, i.e., PDI = 1.41, 1.28, and 1.09 for EO(1.4-5), EO(1.4-3), and EO(1.4-2), respectively, as the corresponding SEC traces shown in Figure S13. The conversion of the deprotection is above 95% as confirmed by ^{1}H NMR. The poly(perfluoropropylene oxide) (PFPO) has average 14 repeating units as determined by ^{19}F NMR spectrometry. The desired coupling reaction was confirmed by both ^{1}H NMR and ^{19}F NMR spectrometry. The efficiency of coupling between mid-hydroxyl functionalized EO diblock and acid chloride functionalized PFPO homopolymer is more than 90% as also estimated from ^{1}H NMR. Generally, we followed the identical procedures that we used before.[2] The molecular parameters for these three μ-EOF terpolymers are summarized in Table S1.

Table S1. Molecular parameters of μ-EOF star terpolymers

Sample	$^{a}N_{PEE}$	$^{a}N_{PEO}$	$^{a}N_{PFPO}$	$^{b}f_{PEO}$	$^{b}f_{PFPO}$
μ-EOF(1.4-5-2.5)	22	115	14	0.61	0.18
μ-EOF(1.4-3-2.5)	22	74	14	0.50	0.22
μ-EOF(1.4-2-2.5)	22	46	14	0.38	0.28

[a]Degree of polymerization determined by H or F NMR for E, O, and F blocks, respectively. The volume fractions were calculated using the molecular weight and RT densities of $\rho_{(PEE)}$ = 0.815 g/cm^3,[4] $\rho_{(PEO)}$ = 1.12 g/cm^3 (amorphous),[18] and $\rho_{(PFPO)}$ = 1.9 g/cm^3.[19]

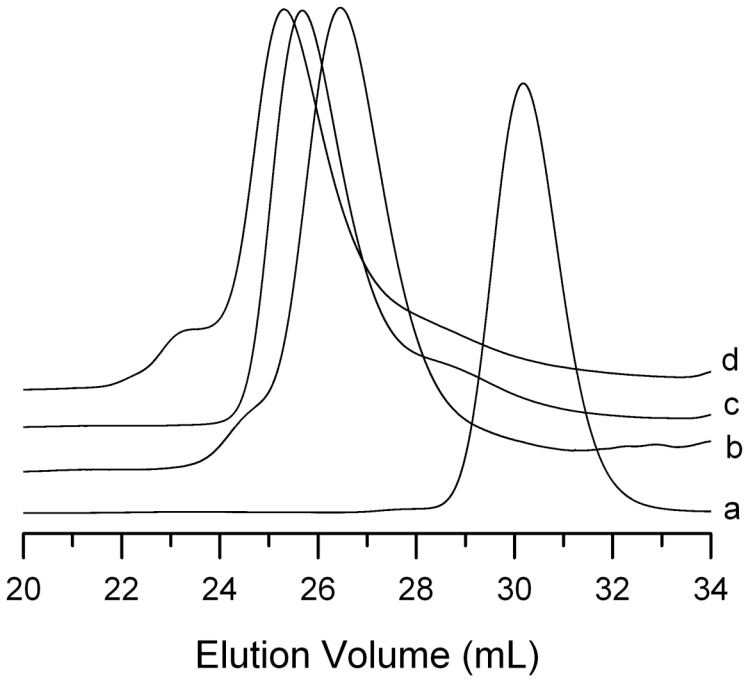


Figure S6. SEC traces of PEE homopolymer and EO diblock copolymers: (a) PEE homopolymer, (b) EO(1.4-2), (c) EO(1.4-3), and (d) EO(1.4-5) diblock copolymers.

References:

(1) Hillmyer, M. A.; Bates, F. S. *Macromolecules* **1996**, *29*, 6994.

(2) Li, Z.; Hillmyer, M. A.; Lodge, T. P. *Macromolecules* **2004**, *37*, 8933.

(3) Zhu, S.; Edmonds, W. F.; Hillmyer, M. A.; Lodge, T. P. *J. Polym. Sci.: Part B: Polym. Phys.* **2005**, *43*, 3685.

(4) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.

(5) Li, Z.; Kesselman, E.; Talmon, Y.; Hillmyer, M. A.; Lodge, T. P. *Science* **2004**, *306*, 98.

(6) Fromherz, P. *Chem. Phys. Lett.* **1983**, *94*, 259.

(7) Egelhaaf, S. U.; Schurtenberger, P. *Phys. Rev. Lett.* **1999**, *82*, 2804.

(8) Shioi, A.; Hatton, T. A. *Langmuir* **2002**, *18*, 7341.

(9) Weiss, T. M.; Narayanan, T.; Wolf, C.; Gradzielski, M.; Panine, P.; Finet, S.; Helsby, W. I. *Phys. Rev. Lett.* **2005**, *94*, 038303.

(10) Sevink, G. J. A.; Zvelindovsky, A. V. *Macromolecules* **2005**, *38*, 7502.

(11) Antonietti, M.; Förster, S. *Adv. Mater.* **2003**, *15*, 1323.

(12) Förster, S. Polymer Vesicles, *In Encyclopedia of Polymer Science and Technology*; John Wiley & Sons: New York, 2005.

(13) Zemb, T.; Dubois, M.; Demé, B.; Gulik-Krzywicki, T. *Science* **1999**, *283*, 816.

(14) Jung, H.-T.; Lee, S. Y.; Kaler, E. W.; Coldren, B.; Zasadzinski, J. A. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 15318.

(15) Jung, H. T.; Coldren, B.; Zasadzinski, J. A.; Iampietro, D. J.; Kaler, E. W. *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 1353.

(16) Jain, S.; Bates, F. S. *Macromolecules* **2004**, *37*, 1511.

(17) Jain, S.; Bates, F. S. *Science* **2003**, *300*, 460.

(18) Smith, G. D.; Yoon, D. Y.; Jaffe, R. L.; Colby, R. H.; Krishnamoorti, R.; Fetters, L. J. *Macromolecules* **1996**, *29*, 3462.

(19) Provided by Dupont.