

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at http://pubs.acs.org/page/copyright/permissions.html



Copyright © 1998 American Chemical Society

Table 1. Spectroscopic data of the triblock molecules.

The synthesis of the triblock molecules (1-6) was performed by substitution reaction of appropriate 4-oxy-4'-biphenylcarboxylic acid terminated poly(ethylene oxide)s with docosyl 4-hydroxy-4'-biphenyl carboxylate.

1; ¹H-NMR (250 MHz, CDCl₃, δ) 8.26 (d, 2Ar-H, *o* to COOphenyl, J = 7.5 Hz), 8.12 (d, 2Ar-H, *o* to COOCH₂, J = 7.5 Hz), 7.65-7.72 (m, 6Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate and *m* to COOCH₂), 7.56 (d, 2Ar-H, *m* to CH₂O, J = 7.5 Hz), 7.34 (d, 2Ar-H, *o* to biphenylcarboxylate, J = 7.5 Hz), 7.04 (d, 2Ar-H, *o* to CH₂O, J = 7.6Hz), 4.33 (t, 2H, CH₃(CH₂)₂₀CH₂, J = 7.5 Hz), 4.19 (t, 2H, CH₂CH₂O-phenyl, J = 7.5Hz), 3.89 (t, 2H, CH₂CH₂O-phenyl, J = 7.5 Hz), 3.52-3.74 (m, 24H, OCH₂), 3.37 (s, 3H, CH₃O), 1.78 (t, 2H, CH₃(CH₂)₁₉CH₂, J = 10.0 Hz), 1.17-1.45 (m, 38H, CH₃(CH₂)₁₉CH₂), 0.85 (t, 3H, CH₃(CH₂)₂₁ J = 7.5 Hz); ¹³C NMR (62.5 MHz, CDCl₃, δ) 166.9, 165.4, 159.6, 151.4, 146.4, 145.0, 138.1, 132.6, 131.1, 130.5, 129.7, 128.8, 127.7, 127.3, 127.0, 122.6, 115.5, 77.9-67.9, 67.0, 65.6, 59.4, 32.3-23.0, 14.5; Anal. Calcd for C₆₃H₉₂O₁₂: C, 72.76; H, 9.06. Found: C, 72.27; H, 8.98; M_w/M_n = 1.04 (GPC).

2; ¹H NMR (250 MHz, CDCl₃, δ) 8.25 (d, 2Ar-H, *o* to COOphenyl, J = 7.5 Hz), 8.12 (d, 2Ar-H, *o* to COOCH₂, J = 10.0 Hz), 7.65-7.72 (m, 6Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate and *m* to COOCH₂), 7.60 (d, 2Ar-H, *m* to CH₃O, J = 7.5 Hz), 7.33 (d, 2Ar-H, *o* to biphenylcarboxylate, J = 7.5 Hz), 7.03 (d, 2Ar-H, *o* to CH₂O, J = 10 Hz), 4.32 (t, 2H, CH₃(CH₂)₂₀CH₂, J = 7.5 Hz), 4.19 (t, 2H, CH₂CH₂O-phenyl, J = 7.5 Hz), 3.89 (t, 2H, CH₂CH₂O-phenyl, J = 7.5 Hz), 3.52-3.74 (m, 40H, OCH₂), 3.37 (s, 3H,

° 3

CH₃O), 1.77 (t, 2H, CH₃(CH₂)₁₉CH₂, J = 10.0 Hz), 1.18-1.47 (m, 38H, CH₃(CH₂)₁₉CH₂), 0.85 (t, 3H, CH₃(CH₂)₂₁, J = 7.5 Hz); ¹³C NMR (62.5 MHz, CDCl₃, δ) 166.9, 165.4, 159.6, 151.4, 146.4, 145.0, 138.1, 132.6, 131.1, 130.5, 129.7, 128.8, 127.7, 127.3, 127.0, 122.6, 115.5, 77.9-67.9, 67.0, 65.6, 59.4, 32.3-23.0, 14.5; Anal. Calcd for C₇₃H₁₁₂O₁₇: C, 69.48; H, 8.95. Found: C, 69.55; H, 8.42; M_w/M_n = 1.03 (GPC).

3; ¹H NMR (250 MHz, CDCl₃, δ) 8.25 (d, 2Ar-H, *o* to COOphenyl, J = 7.5 Hz), 8.12 (d, 2Ar-H, *o* to COOCH₂, J = 10.0 Hz), 7.65-7.72 (m, 6Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate and *m* to COOCH₂), 7.60 (d, 2Ar-H, *m* to CH₂O, J = 7.5 Hz), 7.33 (d, 2Ar-H, *o* to biphenylcarboxylate, J = 7.5 Hz), 7.03 (d, 2Ar-H, *o* to CH₂O, J = 10 Hz), 4.34 (t, 2H, CH₃(CH₂)₂₀CH₂, J = 7.5 Hz), 4.18 (t, 2H, CH₂CH₂O-phenyl, J = 7.5 Hz), 3.84 (t, 2H, CH₂CH₂O-phenyl, J = 7.5 Hz), 3.52-3.74 (m, 40H, OCH₂), 3.37 (s, 3H, CH₃O), 1.76 (t, 2H, CH₃(CH₂)₁₉CH₂, J = 10.0 Hz), 1.17-1.47 (m, 38H, CH₃(CH₂)₁₉CH₂), 0.86 (t, 3H, CH₃(CH₂)₂₁, J = 7.5 Hz); ¹³C NMR (62.5 MHz, CDCl₃, δ) 166.9, 165.4, 159.6, 151.4, 146.4, 145.0, 138.1, 132.6, 131.1, 130.5, 129.7, 128.8, 127.7, 127.3, 127.0, 122.6, 115.5, 77.9-67.9, 67.0, 65.6, 59.4, 32.3-23.0, 14.5; Anal. Calcd for C₈₁H₁₂₈O₂₁: C, 67.65; H, 8.98. Found: C, 67.56; H, 8.94; M_a/M_a = 1.03 (GPC).

4; ¹H NMR (250 MHz, CDCl₃, δ) 8.25 (d, 2Ar-H, *o* to COOphenyl, J = 7.5 Hz), 8.11 (d, 2Ar-H, *o* to COOCH₂, J = 7.5 Hz), 7.67-7.72 (m, 6Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate and *m* to COOCH₂), 7.61 (d, 2Ar-H, *m* to CH₂O, J = 10 Hz), 7.33 (d, 2Ar-H, *o* to biphenylcarboxylate, J = 7.5 Hz), 7.03 (d, 2Ar-H, *o* to CH₂O, J = 10 Hz), 4.33 (t, 2H, CH₃(CH₂)₂₀CH_{2*} J = 7.5 Hz), 4.19 (t, 2H, CH₂CH₂O-phenyl, J = 7.5 Hz), 3.89 (t, 2H, CH₂CH₂O-phenyl, J = 7.5 Hz), 3.52-3.74 (m, 88H, OCH₂), 3.37 (s, 3H,

٠ .

CH₃O), 1.78 (t, 2H, CH₃(CH₂)₁₉CH₂, J = 10.0 Hz), 1.17-1.44 (m, 38H, CH₃(CH₂)₁₉CH₂), 0.85 (t, 3H, CH₃(CH₂)₂₁, J = 7.5 Hz); ¹³C NMR (62.5 MHz, CDCl₃, δ) 166.9, 165.4, 159.6, 151.4, 146.4, 145.0, 138.1, 132.6, 131.1, 130.5, 129.7, 128.8, 127.7, 127.3, 127.0, 122.6, 115.5, 77.9-67.9, 67.0, 65.6, 59.4, 32.3-23.0, 14.5; Anal. Calcd for C₉₅H₁₅₆O₂₈: C, 69.27; H, 6.18. Found: C, 69.48; H, 6.03; M_w/M_n = 1.04 (GPC).

5; ¹H-NMR (250 MHz, CDCl₃, δ) 8.25 (d, 2Ar-H, *o* to COOphenyl, J = 7.5 Hz), 8.11 (d, 2Ar-H, *o* to COOCH₂, J = 7.5 Hz), 7.65-7.72 (m, 6Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate and *m* to COOCH₂), 7.61 (d, 2Ar-H, *m* to CH₂O, J = 10.0 Hz), 7.33 (d, 2Ar-H, *o* to biphenylcarboxylate, J = 10.0 Hz), 7.03 (d, 2Ar-H, *o* to CH₂O, J = 10.0 Hz), 4.35 (t, 2H, CH₃(CH₂)₂₀CH₂, J = 7.5 Hz), 4.19 (t, 2H, CH₂CH₂O-phenyl, J = 7.5 Hz), 3.89 (t, 2H, CH₂CH₂O-phenyl, J = 7.5 Hz), 3.46-3.73 (m, 104H, OCH₂), 3.37 (s, 3H, CH₃O), 1.78 (t, 2H, CH₃(CH₂)₁₉CH₂, J = 10.0 Hz); 1.17-1.44 (m, 38H, CH₃(CH₂)₁₉CH₂), 0.85 (t, 3H, CH₃(CH₂)₂₁ J = 7.5 Hz); ¹³C NMR (62.5 MHz, CDCl₃, δ) 166.9, 165.4, 159.6, 151.4, 146.4, 145.0, 138.1, 132.6, 131.1, 130.5, 129.7, 128.8, 127.7, 127.3, 127.0, 122.6, 115.5, 77.9-67.9, 67.0, 65.6, 59.4, 32.3-23.0, 14.5; Anal. Calcd for C₁₀₃H₁₁₇₂O₃₂: C, 64.35; H, 9.00. Found: C, 64.48; H, 9.03; M_w/M_n = 1.13 (GPC).

6; ¹H-NMR (250 MHz, CDCl₃, δ) 8.26 (d, 2Ar-H, *o* to COOphenyl, J = 7.5 Hz), 8.12 (d, 2Ar-H, *o* to COOCH₂, J = 7.5 Hz), 7.65-7.72 (m, 6Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate and *m* to COOCH₂), 7.61 (d, 2Ar-H, *m* to CH₂O, J = 7.5 Hz), 7.34 (d, 2Ar-H, *o* to biphenylcarboxylate, J = 7.5 Hz), 7.03 (d, 2Ar-H, *o* to CH₂O, J = 7.5 Hz), 7.34 Hz), 4.34 (t, 2H, CH₃(CH₂)₂₀CH₂, J = 7.5 Hz), 4.19 (t, 2H, CH₂CH₂O-phenyl, J = 7.5 Hz), 3.89 (t, 2H, CH₂CH₂O-phenyl, J = 7.5 Hz), 3.37-3.73 (m, 132H, OCH₂), 3.37 (s,

° .,

3H, CH₃O), 1.76 (t, 2H, CH₃(CH₂)₁₉CH₂, J = 10.0 Hz), 1.12-1.44 (m, 38H, CH₃(CH₂)₁₉CH₂), 0.85 (t, 3H, CH₃(CH₂)₂₁ J = 7.5 Hz); ¹³C NMR (62.5 MHz, CDCl₃, δ) 166.9, 165.4, 159.6, 151.4, 146.4, 145.0, 138.1, 132.6, 131.1, 130.5, 129.7, 128.8, 127.7, 127.3, 127.0, 122.6, 115.5, 77.9-67.9, 67.0, 65.6, 59.4, 32.3-23.0, 14.5; M_w/M_n = 1.14 (GPC).

coil-rod-coil molecules	phase transitions (°C) and corresponding enthalpy changes (kJ/mol) ^a					
1	k 45.6 (12.3) k 92.2 (11.2) k 102.3 (38.4) s _C 122.9 (3.4) s _A 130.1 (1.1) i					
2	k 64.2 (11.8) k 94.6 (7.7) k 99.7 (61.5) s _C 118.2 (5.2) i					
3	k 65.4 (17.2) k 90.4 (3.6) k 94.6 (56.4) s _C 106.7 (0.4) col 109.2 (3.9) i					
4	k 65.7 (104.9) k 88.0 (25.5) k 90.0 (34.0) col 95.4 (0.6) M 105.3 (0.3) i					
5	k 65.5 (120.0) k 86.6 (26.3) k 88.1 (25.5) col 93.3 (0.3) M 104.3 (0.4) i					
6	k 62.3 (82.3) k 86.5 (0.4) k 90.0 (5.4) col 94.4 (-) ^b M 103.7 (0.8) i					

Table 2. Thermal transitions of coil-rod-coil triblock molecules.

^ak, crystalline; s_A, smectic A; s_C, smectic C; col, hexagonal columnar; M, spherical micellar; i; isotropic. ^bData obtained from optical polarized microscopy.

Rod-coil molecule	DP of coil	Density ρ (g/ml)	Crystalline phase with amorphous coils		Smectic phase		Columnar phase		Micellar phase	
		at 25 °C	Calc. length ^a (Å)	d ₀₀₁ (Å)	d ₀₀₁ (s _C) (Å)	d ₀₀₁ (s _A) (Å)	d ₁₀₀ (Å)	Lattice constant (a) (Å)	Primary peak (Å)	Diameter (d
1	7	1.15	68	134	93	114				
2	12	1.15	82	144	102					
3	16	1.14	93	152	109					
4	22	1.13	110	167			105	122	100	123
5	27	1.13	124	173			107	124	106	130
6	34		144	181					112	138

Table 3. Characterization of the coil-rod-coil triblock molecules by small angle X-ray scattering.

^aCalculated lengths of the rod-coil molecules were based on density measurements.





rod-coil ABC triblock molecules.











Figure 4; Wide angle X-ray diffraction patterns of 5 measured at various temperature.

2-D X-ray patterns of 5







© 1998 American Chemical Society

Am.

chem.

Soc.

èe

a9823619 Supporting Info Page

exagonal columnar(90 C)

These patterns were obtained with 2-D CCD camera

Primary beam size was approximately 0.5mm x 2mm

spherical micellar (102C)

isotropic (110C)

Figure 5.



Figure 6; 1-D small angle X-ray scattering of **5** obtained by sector averaging of 2-D X-ray diffraction patterns.

© 1998 American Chemical Society, J. Am. Chem. Soc., Lee ja9823619 Supporting Info Page 13



(a)



(b)

Figure J. Representative optical polarized micrograph (100×) of; (a) the texture exhibited by the smectic A mesophase of 1 at 125 °C on cooling scan; (b) the texture exhibited by the hexagonal columnar mesophase of 3 at 108 °C on cooling scan.





Figure \$; Representative optical polarized microgrph (100 x) of the texture of the dark area with straight edges exhibited by the optical isotropic micellar phase growing from the hexagonal columnar phase of 5 at 93 °C on the heating scan.



Q.,

5. *9*



V_m (cm³/mol)

Figure 9; The dependence of d^3 of spherical micelle on the molar volume (V_m) of 4, 5 and 6.