Electronic Supplementary Information

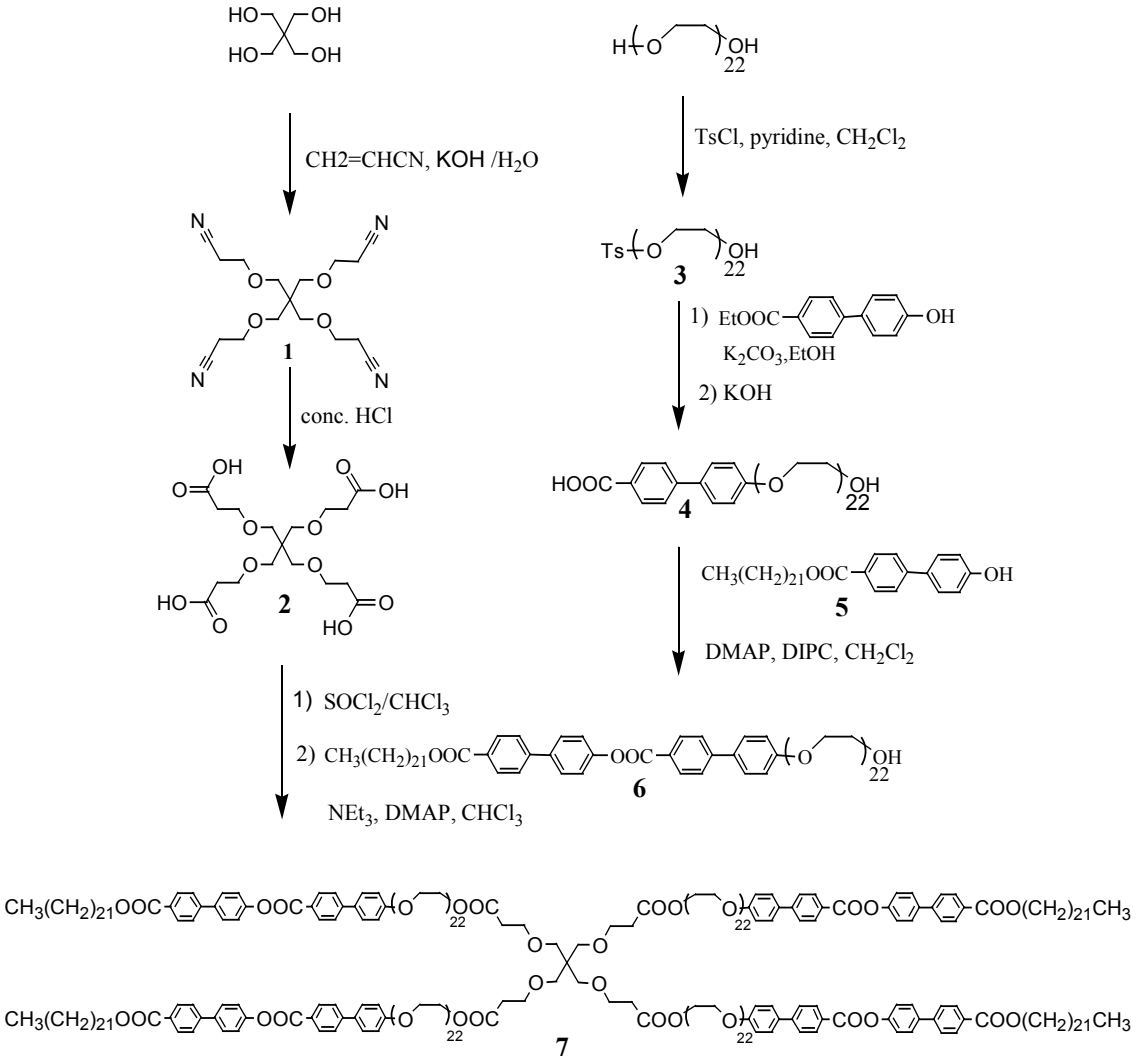
Organization of Branched Rod-Coil Molecule into a 3-D Tetragonally Perforated Lamellar Mesophase

Nam-Keun Oh, et al.

Techniques ^{1}H-NMR spectra were recorded from $CDCl_3$ solutions on a Bruker AM 250 spectrometer. The purity of the products was checked by thin layer chromatography (TLC; Merck, silica gel 60). A Perkin Elmer DSC-7 differential scanning calorimeter equipped with a 1020 thermal analysis controller was used to determine thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks. In all cases, heating and cooling rates were 10℃ min^{-1}. A Nikon Optiphot 2-pol optical polarized microscopy (magnification: 100 X) equipped with a Mettler FP 82 hot-stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyze anisotropic texture. Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at the Organic Chemistry Research Center. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C2 and 4C1 X-ray beam line at the Pohang Accelerator Laboratory, South Korea. In order to investigate structural changes on heating, the sample was held in an aluminum sample holder, which was sealed with a window of 7μm thick Kapton films on both sides. The sample was heated with two cartridge heaters and the sample temperature was monitored by a thermocouple placed close to the sample. Background scattering correction was attained by subtracting the scatterings from the Kapton.

Molecular weight distributions ($\overline{M}_w/\overline{M}_n$) were determined by gel permeation chromatography (GPC) with a Waters R401 instrument equipped with Stragel HR 3, 4 and 4E columns, M7725i manual injector, column heating chamber and 2010 Millennium data station. Measurements were made by using a UV detector, with $CHCl_3$ as solvent (1.0mL min^{-1}). Molecular density (ρ) measurements were performed in an aqueous sodium chloride solution at 25℃. The molecular length was calculated using Material Studio Software.

Synthesis A general outline of the synthetic procedure is shown in Scheme 1.



Scheme 1. Synthesis of tetra-branched triblock molecule (tetramer).

Synthesis of 3-[3-(2-cyanoethoxy)-2,2-bis-(2-cyanoethoxymethyl)propoxy]-propionitrile [**1**]

Pentaerythritol (6.84g, 0.05mole) and KOH solution (1ml, 40% w/v) was dissolved in 20mL of dioxane and 2ml of water. The mixture was stirred in ice bath (0^oC) and then added acrylonitrile (16.2 g, 0.30mmol) to mixture. The reaction mixture was stirred for 48h at room temperature. The resulting solution was removed in a rotary evaporator, and the crude product was extracted with methylene chloride. The methylene chloride solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by flash column chromatography (silica gel, ethyl acetate: methylene chloride (1:4) eluent) to yield 3.1 g (18%) of colorless oil.

1. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) 3.66 (t, 8H, O$\underline{CH_2}CH_2CN$), 3.48 (s, 8H, C$\underline{CH_2}$O), 2.60 (t, 8H, O$\underline{CH_2}CH_2CN$).

Synthesis of 3-[3-(2-carboxyethoxy)-2,2-bis-(2-carboxyethoxymethyl)propoxy]-propionic acid [**2**]

Compound **1** (3.1 g, 8.9 mmol) was dissolved in conc. HCl 15 ml. The resulting mixture was stirred at 70^oC for 5h. The resulting mixture was poured into water and extracted with diethyl ether. The diethyl ether was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator and the crude product was then purified by recrystallization from a mixture of diethyl ether and *n*-hexane to yield 1.2g (31%) of a white solid.

2. ^{1}H-NMR (250 MHz, $CDCl_3$, δ , ppm) 3.49 (t, 8H, O$\underline{CH_2}CH_2CO$), 3.23 (s, 8H, C$\underline{CH_2}$O), 2.36 (t, 8H, O$\underline{CH_2}CH_2CO$).

Synthesis of oxypoly(ethyleneoxy)ethyl Tosylate [**3**]

Poly (ethylene glycol) (31.2g, 32.1mmole) was dissolved in 10mL of dry pyridine under argon. A solution of *p*-toluenesulfonyl chloride (7.8g, 40.6mmol) was dissolved in dry methylene chloride and then added dropwise to the mixture. The reaction mixture was stirred overnight at room temperature under argon. The resulting solution was poured into water and extracted with methylene chloride. The methylene chloride solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by flash column chromatography (silica gel, methylene chloride: methanol (8:1) eluent) to yield 20 g (52%) of colorless oil.

3. ^{1}H-NMR (250 MHz, $CDCl_3$, δ , ppm) 7.80 (d, 2Ar-H, *o* to SO_3, J = 7.5 Hz), 7.33 (d, 2Ar-H, *o* to CH_3, J = 7.6 Hz), 3.47-4.15 (m, 88H OCH_2), 2.44 (s, 3H, CH_3 phenyl).

Synthesis of 4'-(hydroxypoly(ethyleneoxide)oxy)-4-biphenyl-4-carboxylic acid [**4**]

Ethyl 4-hydroxy-4-biphenyl carboxylate (3.6g, 14.7mmole) and K_2CO_3 (2.0g, 14.7mmol) were dissolved in absolute ethanol 100mL. The mixture was heated at reflux for 1h, and compound 3 (5.7g, 4.9mmol) was added dropwise. The resulting solution was heated at reflux for 24h, and then cooled to room temperature, and excess KOH was added. The mixture solution was stirred at room temperature for 12h. The resulting solution was poured into water and extracted with methylene chloride. The methylene chloride was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator and the crude product was then purified

by flash column chromatography [silica gel, ethyl acetate: methylene chloride: methanol (4:4:1) eluent] to yield 3.3 g (57%) of a white waxy solid.

4. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm) 8.07 (d, 2Ar-H, *o* to COOH, *J* = 8.3 Hz), 7.60 (d, 2Ar-H, *m* to COOH, *J* = 8.4 Hz), 7.57 (d, 2Ar-H, *m* to CH_2O, *J* = 8.8 Hz), 7.00 (d, 2Ar-H, *o* to CH_2O, *J* = 8.7 Hz), 3.47-4.20 (m, 88H, OCH_2).

Synthesis of dococyl 4'-hydroxy-4-biphenyl carboxylate [**5**]

4'-hydroxy-4-biphenyl carboxylic acid (2 g, 9.33 mmol), 1-bromodocosane (2.8 g, 7.18 mmol), and K_2CO_3 (0.64 g, 4.63 mmol) were dissolved in dry 100mL ethanol. The mixture was heated at reflux for 50h under nitrogen, and then cooled to room temperature. The solvent was removed in a rotary evaporator, the resulting mixture was poured into water and extracted with methylene chloride. The methylene chloride was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator and the crude product was then purified by recrystallization from a mixture of methanol and hexane to yield 3.0g (60%) of a white solid.

5. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm) 8.06 (d, 2Ar-H, o to COO, J = 8.3 Hz), 7.62 (d, 2Ar-H, m to COO, J = 8.3 Hz), 7.53 (d, 2Ar-H, m to OH, J = 8.3 Hz), 6.95 (d, 2Ar-H, o to OH, J = 8.3 Hz), 4.35 (t, 2H, $CH_3(CH_2)_{20}CH_2$, J = 6.6 Hz), 1.77 (m, 2H, $CH_3(CH_2)_{19}CH_2$), 1.24-1.47 (m, 38H, $CH_3(CH_2)_{19}$), 0.87 (t, 3H, $CH_3(CH_2)_{21}$, J = 6.8 Hz); Elemental analysis for $C_{35}H_{54}O_3$, Calc.: C, 80.41; H, 10.41. Found: C, 80.57; H, 10.37.

Synthesis of docosyl 4'-[4'-[methyloxypoly(ethyleneoxy)ethyloxy]-4-

biphenylcarboxyloxy]-4-biphenylcarboxylate [**6**]

Compound **4** (1.5g, 1.24mmol), **5** (0.59g, 1.24mmol), and 4-dimethylaminopyridine (DMAP) (0.18g, 1.50mmol) were dissolved in 50ml of dry methylene chloride under argon. The resulting mixture was stirred for 1h and diisopropylcarbodiimide (DIPC) (0.23ml, 1.5mmole) was stirred overnight at room temperature and then poured into methanol, the resulting precipitate purified by flash column chromatography [silica gel, eluent; ethyl acetate and methylene chloride and methanol (8:1) eluent] to yield 1.30g (64%) of a white solid.

6. ^{1}H NMR (250 MHz, $CDCl_3$, δ , ppm) 8.26 (d, 4Ar-H, *o* to COOphenyl, J = 7.5 Hz), 8.12 (d, 4Ar-H, *o* to $COOCH_2$, J = 7.5 Hz), 7.65-7.72 (m, 12Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate and *m* to $COOCH_2$), 7.56 (d, 4Ar-H, *m* to CH_2O, J = 7.5 Hz), 7.34 (d, 4Ar-H, *o* to biphenylcarboxylate, J = 7.5 Hz), 7.04 (d, 4Ar-H, *o* to CH_2O, J = 7.6 Hz), 4.33 (t, 4H, $CH_3(CH_2)_{20}\underline{CH_2}$, J = 7.5 Hz) 4.19 (t, 4H, $CH_2\underline{CH_2}O$-phenyl, J = 7.5 Hz), 3.89 (t, 4H, $\underline{CH_2}CH_2O$-phenyl, J = 7.5 Hz), 3.52-3.74 (m, 80H, $O\underline{CH_2}$), 1.78 (t, 4H, $CH_3(CH_2)_{19}\underline{CH_2}$, J = 10 Hz), 1.25-1.45 (m, 48H, $CH_3(\underline{CH_2})_{19}CH_2$), 0.85 (t, 6H, $\underline{CH_3}(CH_2)_{21}$ J = 7.5 Hz).

Synthesis of tetramer [**7**]

Compound **2** (0.066g, 0.156mmol) dissolved in $SOCl_2$ (0.068ml, 0.933mmol) were refluxed for 3h, and then excess $SOCl_2$ solution was removed under reduced pressure. The residue was dissolved in dry chloroform (10ml), and the flask was cooled to 0^{o}C by an ice bath. Compound **6** (1.3g, 0.78mmole), DMAP (0.01g), and triethylamine (0.2ml) were added dropwise to the mixture at 0^{o}c. The resulting mixture was stirred overnight at room temperature. The solvent was removed in a rotary evaporator, the resulting

mixture was poured into water and extracted with methylene chloride. The methylene chloride was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator and the crude product was then purified by flash column chromatography [silica gel, tetrahydrofuran: methanol (8:1) and methylene chloride: methanol (8:1)] to yield 0.15g (21%) of a white solid.

7. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm); 8.26 (d, 4Ar-H, *o* to COOphenyl, *J* = 7.5 Hz), 8.12 (d, 4Ar-H, *o* to $COOCH_2$, *J* = 7.5 Hz), 7.65-7.72 (m, 12Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate and *m* to $COOCH_2$), 7.56 (d, 4Ar-H, *m* to CH_2O, *J* = 7.5 Hz), 7.34 (d, 4Ar-H, *o* to biphenylcarboxylate, *J* = 7.5 Hz), 7.04 (d, 4Ar-H, *o* to CH_2O, *J* = 7.6 Hz), 4.33 (t, 4H, $CH_3(CH_2)_{20}\underline{CH_2}$, *J* = 7.5 Hz) 4.19 (t, 4H, $CH_2\underline{CH_2}O$-phenyl, *J* = 7.5 Hz), 3.89 (t, 4H, $\underline{CH_2}CH_2O$-phenyl, *J* = 7.5 Hz), 3.52-3.74 (m, 80H, $O\underline{CH_2}$), 3.49 (t, 8H, $O\underline{CH_2}CH_2CO$), 3.23 (s, 8H, $C\underline{CH_2}O$), 2.36 (t, 8H, $O\underline{CH_2}CH_2CO$), 1.78 (t, 4H, $CH_3(CH_2)_{19}\underline{CH_2}$, *J* = 10 Hz), 1.25-1.45 (m, 48H, $CH_3(\underline{CH_2})_{19}CH_2$), 0.85 (t, 6H, $\underline{CH_3}(CH_2)_{21}$ *J* = 7.5 Hz), Elemental analysis for $C_{385}H_{620}O_{116,}$ Calc.: C, 65.08; H, 8.80. Found: C, 65.02; H, 8.81, M_n/M_w= 1.04.

Table 1. Thermal Transitions of monomer and tetramer molecules. (Data are from second heating and first cooling scans.)

molecule	phase transitions (°C) and corresponding enthalpy changes (kJ/mol)	
	heating	cooling
monomer	$k_1$65.7 (104.9)$k_2$88.0(25.5)$k_3$90.0(34.0)col95.4(0.56)M105.3(0.3)i	i104.1(0.2)M93.9(0.3)co185.8(39.4)$k_3$60.2(7.3)$k_2$32.9(85.7) k_1
tetramer	$k_1$39.1 (97.4)$k_2$88.7(10.6)$k_3$92.7(211.9)TPL101.1(1.0)col120.1(3.4)M128.7(4.0)i	i 126.4 (5.6)M117.4(4.1)col98.9(1.5)TPL84.4(206.2)$k_3$64.0(9.9)$k_2$19.4(226.5)k_1

k_1 = first crystalline, k_2 = second crystalline, k_3 = third crystalline, TPL = tetragonally perforated lamellar, col = hexagonal columnar, M = spherical micellar, i = isotropic.

Table 2. Characterization of monomer and tetramer by small-angle XRD.

molecule	crystalline phase			liquid crystalline phase											
	lamellar			tetragonally perforated lamellar						hexagonal columnar			spherical micellar		
	first(k_1)	second(k_2)	third(k_3)	d_{110} (Å)	d_{002} (Å)	lattice constant a (Å)	lattice constant c (Å)	perforation diameter d (Å)	wall thickness W(Å)	d_{100} (Å)	lattice constant a (Å)	diameter of rod core d (Å)	primary peak (Å)	diameter d (Å)	diameter of rod bundle d_{rod} (Å)
	d_{001} d (Å)														
monomer	174.2	167.8	165.4							105.4	121.7	30.0	100.0	123.0	75.4
tetramer	158.3	153.3	147.2	210.8	113.0	298.1	226.0	232.0	66.0	104.7	120.9	29.0	97.1	119.4	72.4

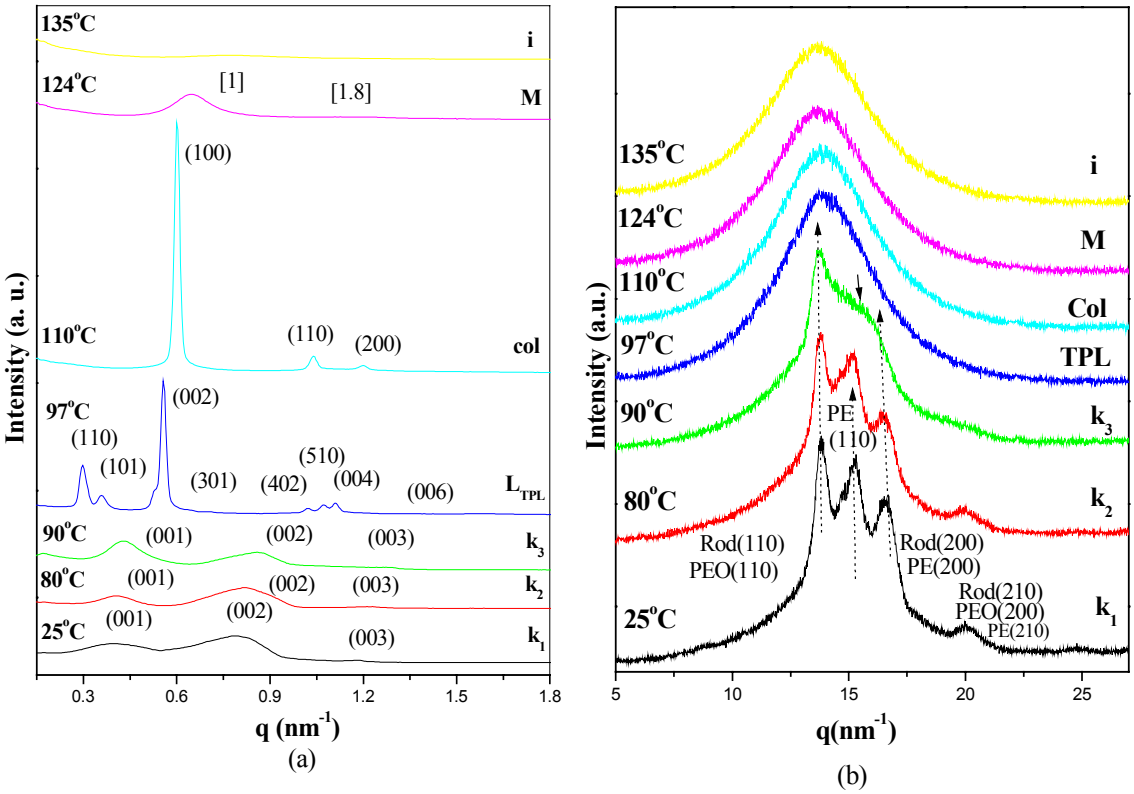


Figure 1. (a) Small and (b) wide-angle XRD patterns of tetramer measured at various temperatures.

Table 3. Characterization of monomer and tetramer by wide angle XRD.

molecule	block	lamellar crystlline phase											
		first(k_1)				second(k_2)				third(k_3)			
		density	unit cell lattice			density	unit cell lattice			density	unit cell lattice		
		[a] ρ (g/cm^3)	[b] a°(Å)	[b] b°(Å)	[c] c (Å)	[a] ρ (g/cm^3)	[b] a°(Å)	[b] b°(Å)	[c] c (Å)	[a] ρ (g/cm^3)	[b] a°(Å)	[b] b°(Å)	[c] c (Å)
monomer	PE	1.00	7.5	5.0	27.4	0.98	7.7	5.0	27.4				
	Rod	1.41	7.5	5.7	21.6	1.38	7.7	5.7	21.6	1.34	7.9	5.7	21.6
	PEO		6.4	6.6									
tetramer	PE	1.00	7.5	5.0	27.4	0.98	7.7	5.0	27.4				
	Rod	1.41	7.5	5.7	21.6	1.38	7.7	5.7	21.6	1.34	7.9	5.7	21.6
	PEO		6.4	6.6									

[a] Determined from molecular weight and unit cell volume [b] Determined from WAXS patterns
[c] Determined using Material Studio Software

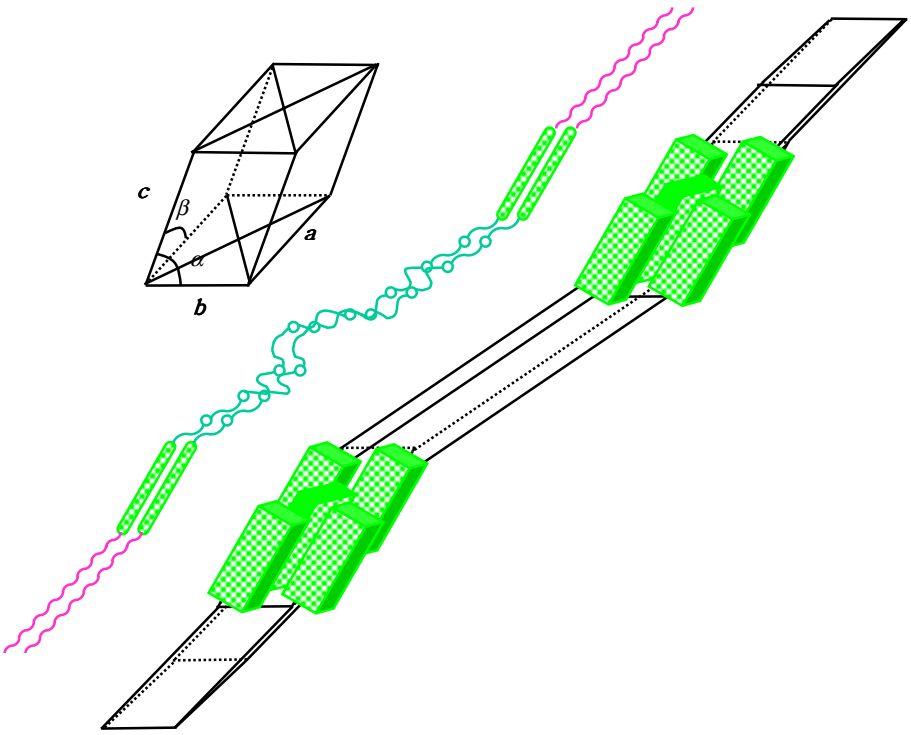


Figure 2. Schematic representation of monoclinic structure of tetramer in the crystalline phase.

Table 4. Characterization of monomer and tetramer by small and wide angle XRD.

molecule	block	lamellar crystlline phase																				
		first(k_1)							second(k_2)							third(k_3)						
		density	unit cell lattice			angle		layer length	density	unit cell lattice			angle		layer length	density	unit cell lattice			angle		layer length
		ρ (g/cm^3)	a (Å)	b (Å)	c (Å)^b	α(^{o})	β(^{o})	l (Å)	ρ (g/cm^3)	a (Å)	b (Å)	c (Å)^b	α(^{o})	β(^{o})	l (Å)	ρ (g/cm^3)	a (Å)	b (Å)	c (Å)^b	α(^{o})	β(^{o})	l (Å)
monomer	PE	1.00	7.5	7.3	27.4	43	90	18.7	0.98	7.7	7.8	27.4	40	90	17.6	0.82						19.6
	Rod	1.41	7.5	7.3	21.6	51	90	16.8	1.38	7.7	7.8	21.6	47	90	15.8	1.34	7.9	8.1	21.6	45	90	15.3
	PEO	1.17	7.5	7.3		65	59	51.6	1.09						50.5	1.09						47.8
	total	[a]1.18						87.1	1.12						83.9	1.07						82.7
tetramer	PE	1.00	7.5	8.1	27.4	37	90	16.5	0.98	7.7	8.5	27.4	36	90	16.1	0.82						17.4
	Rod	1.41	7.5	8.1	21.6	45	90	15.3	1.38	7.7	8.5	21.6	42	90	14.5	1.34	7.9	9.1	21.6	39	90	13.6
	PEO	1.16	7.5	8.1		55	59	47.4	1.09						46.1	1.09						42.6
	total	[a]1.17						79.2	1.12						76.7	1.07						73.6

[a] Experimental density at 25^{o}C. [b] calculated using Materials Studio Software.

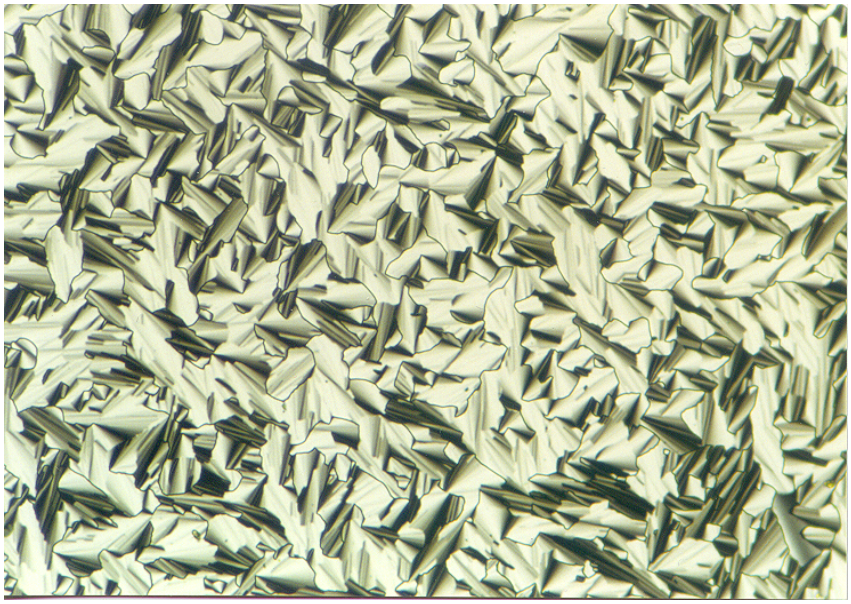


Figure 3. Representative polarized optical micrographs (100×) of the texture of tetramer exhibited by hexagonal columnar mesophase of tetramer at 110 ^{o}C on the cooling scan.

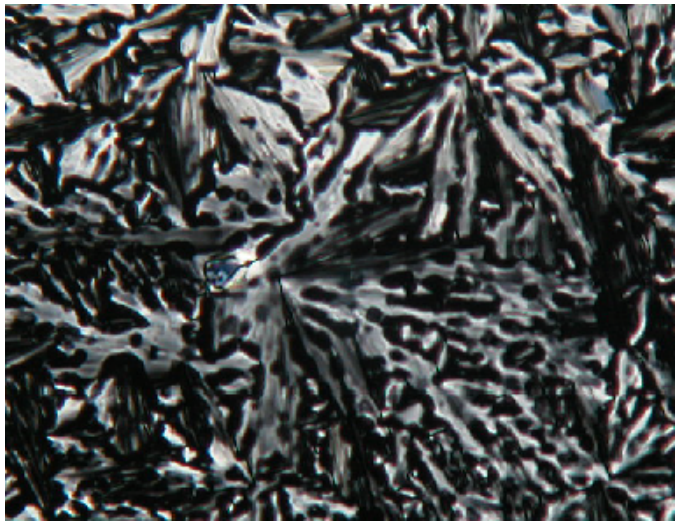


Figure 4. Polarized optical micrographs (100×) of the texture of tetramer exhibited at the transition from the hexagonal columnar phase (pseudo-focal conic domains) to the tetragonally perforated lamellar (dark area) phase of tetramer at 97 ^{o}C on the cooling scan. Isotropic areas appear on pseudo-focal-conic domains and these regions then grow until the entire field of view darkens such as homeotropic texture.

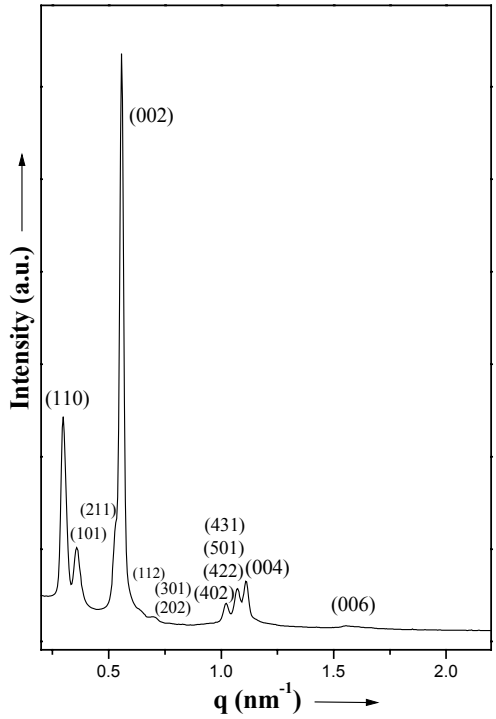


Table 5. Smal-angle XRD data for tetragonally perforated lamellar structure of tetramer.[a]

h	*k*	*l*	q_{obsd} nm^{-1}	q_{calcd} nm^{-1}
1	1	0	0.298	0.298
1	0	1	0.358	0.349
2	1	1	0.535	0.347
0	0	2	0.556	0.556
1	1	2	0.638	0.634
2	0	2	0.694	0.691
3	0	1	0.694	0.691
4	0	2	1.022	1.011
4	2	2	1.074	1.089
5	0	1	1.074	1.089
4	3	1	1.074	1.089
0	0	4	1.112	1.112
0	0	6	1.561	1.668

[a] q_{obsd} and q_{calcd} are the scattering vectors of the observed reflections and calculated for the tetragonally perforated lamellar structure with lattice parameters a =29.8nm and c = 22.6nm.

Figure 5. Small-angle XRD pattern of tetramer measured at 97^{o}C.