1854 *Macromolecules* **1996,** *29,* 1854−1856

Thermotropic and Lyotropic Mesophase Behavior of Some Novel Phthalocyanine-Centered Poly(oxyethylene)s

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Received August 31, 1995
Revised Manuscript Received November 6, 1995

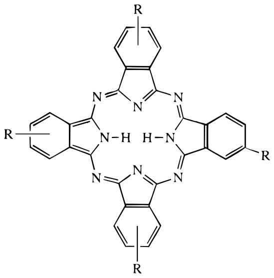
Nonionic amphiphiles which incorporate poly(oxyethylene) are used extensively as detergents, emulsifiers, and encapsulating agents.[1] Association in aqueous solution is crucial to their utility and can also lead to the formation of lyotropic mesophases. In recent years, nonionic amphiphiles with disk-shaped (discotic) hydrophobic cores have been prepared by the substitution of triphenylene[2] and tetrabenzocyclododecatetraene[3] with short oligo(oxyethylene) side chains. These low molecular mass materials form columnar lyotropic mesophases in water due to aggregation of the hydrophobic discotic cores.

The phthalocyanine macrocycle is a discotic system which displays fascinating electronic and optical properties. In recent years, a large number of derivatives of Pc have been prepared to enhance and tailor these properties and to facilitate the exploitation of Pcs in various applications including gas sensors, photoconduction, and solar energy conversion.[4] Pcs show a very strong tendency to self-associate to form stable columnar thermotropic[5] and lyotropic mesophases.[6] Recent work in our laboratory has shown that Pc derivatives substituted by four or eight short oligo(oxyethylene) chains display both thermotropic and lyotropic columnar mesophases.[7,8] This communication describes our preliminary investigation into whether such columnar assemblies are exhibited by phthalocyanines substituted by longer, nonuniform poly(oxyethylene) side chains. We term these materials *phthalocyanine-centered poly(oxyethylene)s.*

Pc-centered poly(oxyethylene)s containing four or eight side chains, with average lengths of 8, 12, and 16 oxyethylene subunits, were prepared from the readily available poly(oxyethylene) monomethyl ethers of average molecular masses 350, 550, and 750 Da, respectively. The Pc-centered poly(oxyethylene)s **1**−**3** with four side chains were prepared by the synthetic route shown in Scheme 1. The appropriate poly(oxyethylene) monomethyl ether precursor reacted with 4-nitrophthalonitrile to give phthalonitrile-terminated derivatives via a base-catalyzed aromatic nucleophilic nitro-displacement reaction.[7] Lithium pentyl oxide catalyzed cyclization of the phthalonitrile-terminated poly(oxyethylene)s produced the dark blue materials **1**−**3** in reasonable yield.

The Pc-centered poly(oxyethylene)s **4**−**6**, containing eight side chains were prepared using the synthesis outlined in Scheme 2. 4,5-Dibromocatechol was alkylated using the tosylate of the appropriate poly(oxyethylene) monomethyl ether. The nitrile displacement of bromine using copper(I) cyanide[8] produced the phthalonitrile precursors, which were readily cyclotetramized to form deep-green macromolecules **4**−**6**.

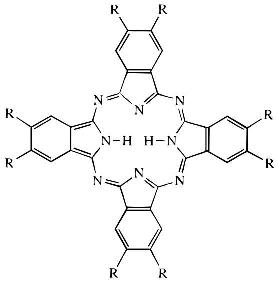
The Pc-centered poly(oxyethylene)s **1**−**6** were purified, in each case, by column chromatography using a mixed solvent system of dichloromethane/ethanol as eluent. The average number of side-chain oxyethylene subunits could be calculated, using high-resolution (500 MHz) ^{1}H NMR, by comparing the intensity of the large peak corresponding to the majority of the poly(oxyethylene) side chains ($\delta = 3.55-3.8$) with that of the well-resolved signals ($\delta = 3.8-4.6$) representing the two oxyethylene subunits adjacent to the Pc core.[9] These protons are relatively deshielded due to the effect of the strong aromatic ring current. The calculated average lengths of the poly(oxyethylene) chains of **1**−**6** (Table 1) correlate well with the obtained elemental analyses[9] and to the lengths of side chain in the corresponding phthalonitrile precursors, which were determined by fast atom bombardment mass spectrometry in addition to ^{1}H NMR and elemental analysis.



1; **R** = $-O-(CH_2CH_2O)_8-CH_3$

2; **R** = $-O-(CH_2CH_2O)_{12}-CH_3$

3; **R** = $-O-(CH_2CH_2O)_{16}-CH_3$



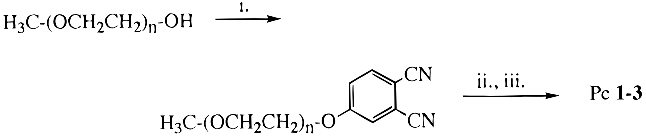
4; **R** = $-O-(CH_2CH_2O)_8-CH_3$

5; **R** = $-O-(CH_2CH_2O)_{12}-CH_3$

6; **R** = $-O-(CH_2CH_2O)_{16}-CH_3$

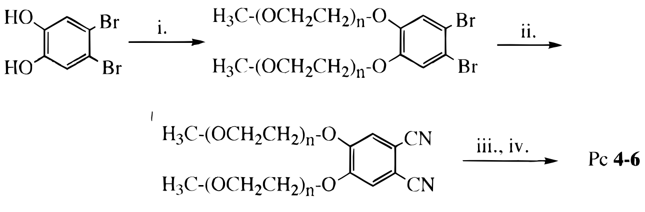
Table 1 gives the thermal behavior of **1**−**6**. Only Pc **4** exhibits a pure (i.e., nonbiphasic) thermotropic mesophase. A structural investigation of this mesophase by powder X-ray diffraction indicates it to be columnar with two-dimensional hexagonal ordering of the Pc stacks (as indicated by two small-angle diffraction rings with *d*-spacings in the ratio 1:$\sqrt{3}$). The intercolumnar distance was calculated to be 38.8 Å. A sharp diffraction ring corresponding to a *d*-spacing of 3.4 Å is consistent with the strong intracolumnar periodicity associated with the D_{ho} mesophase commonly encountered in alkoxy-substituted Pcs.[10] In addition, the mixture of homeotropic regions and fanlike optical texture exhibited by the mesophase **4**, observed by polarizing optical microscopy, is characteristic of a D_{ho} structure.[11] Shearing of the fluid mesophase produced a uniform birefringent mass and confirmed that the

Scheme 1[a]



[a] Reagents and conditions: (i) 4-nitrophthalonitrile, DMF, anhydrous K_2CO_3; (ii) $LiOC_5H_{11}-C_5H_{11}OH$, 135 °C; (iii) AcOH.

Scheme 2[a]



[a] Reagents and conditions: (i) $CH_3(OCH_2CH_2)_nOTs$, acetone, anhydrous K_2CO_3; (ii) CuCN, DMF, 150 °C; (iii) $LiOC_5H_{11}-C_5H_{11}OH$, 135 °C; (iv) AcOH.

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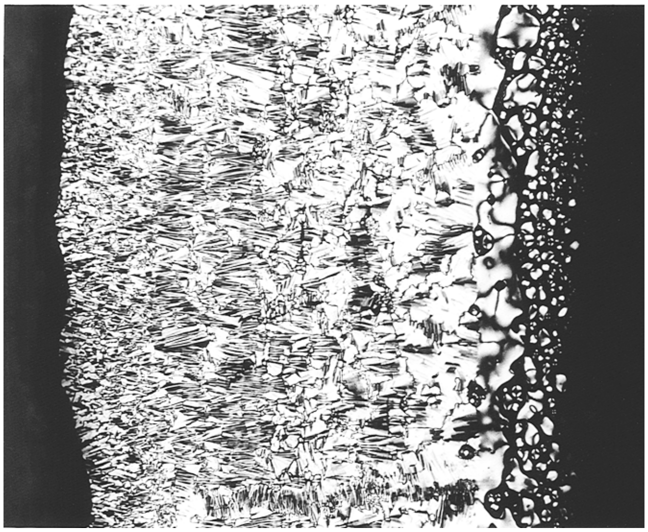

Figure 1. Photomicrograph (×100, crossed polarizers) of the lyotropic mesophases formed from an aqueous solution of **1** at 50 °C. A concentration gradient was established by evaporation of water from the edge of the slide (left). The columnar nematic mesophase (N_c), forming as droplets, lies at the boundary of the isotropic solution (right) and the C_H mesophase. A dark band of isotropic, dry material has formed between the edge of the slide and the C_H mesophase.

Table 1

Pc-centered poly(oxyethylene)	no. of oxyethylenes in side chain (n)[a]	mp[b] (°C) (ΔH(J/g))	thermotropic mesophase	lyotropic mesophase (H_2O)
1	8.0	*c*	biphasic[d] (D_{ho})	$C_H + N_c$
2	11.8	8 (5.5)		C_H
3	16.4	28 (7.6)		C_H
4	8.1	−6 (102.0)	D_{ho} (−6 to +60 °C)	
5	12.4	20 (46.1)		
6	16.2	27 (75.6)		

[a] Average determined by high-resolution ^{1}H NMR. [b] Determined by DSC, heating cycle, at a rate of 10 °C/min. [c] No melting transition observed down to −100 °C. [d] Clears completely at 40 °C.

initially observed dark regions were of homeotropic alignment rather than isotropic material.

Macromolecules **4**−**6** all possess a distinct melting point (Table 1), as determined by differential scanning calorimetry (DSC), which is dependent on the length of poly(oxyethylene) side chains. In contrast, the four-branched Pc-centered poly(oxyethylene)s **1**−**3** do not show clearly defined thermal behavior, probably due to the effects of the four different substitution patterns of the Pc−core. For example, **1** and **3** are clearly biphasic at room temperature when examined by polarizing optical microscopy; **1** displays islands of D_{ho} mesophase texture in a predominantly isotropic sample, whereas **3** is a mixture of spherulite crystals and isotropic liquid. At room temperature, **2** is a nonbirefringent liquid.

The Pc-centered poly(oxyethylene)s **1**−**6** are readily soluble in cold water and all exhibit cloud points (between 75 and 85 °C) in common with conventional nonionic surfactants. Their visible absorption spectra in aqueous solution show a broad band ($\lambda_{max} = 630$ nm), blue shifted from spectra obtained in toluene[9] and characteristic of Pc cofacial aggregation.[6] Possible lyotropic mesophase behavior due to the formation of these columnar aggregates was investigated, using polarized optical microscopy, by placing a drop of dilute aqueous solution of each of the Pc-centered poly(oxyethylene)s between a microscope slide and cover slip. Evaporation of the water, at room temperture, from the edge of the slide to create a concentration gradient showed that only the Pc-centered poly(oxyethylene)s **1**−**3**, bearing four side chains, possess the ability to form aqueous lyotropic mesophases. The optical texture of the mesophase formed at room temperature is identical to that of the columnar hexagonal lyotropic mesophase, designated C_H by Boden,[3] formed by discotic amphiphiles substituted by short oligo(oxyethylene) side chains.[2,3] The material at the edge of the slide becomes an isotropic fluid on drying. On heating to 50 °C, an edge-evaporated aqueous solution of **1** forms, in addition, a mesophase of schlieren optical texture (Figure 1) at the interface between the originally formed C_H mesophase and the isotropic solution. This texture is characteristic of a columnar nematic mesophase (N_c) in which the columnar aggregates possess only orientational but no long-range positional order.[2,3,7] Only **1** shows this phase transition.

An interesting comparison can be made with a Pc material containing four uniform side chains comprised of eight oxyethylene subunits that we have described previously.[7] This compound, in contrast to **1**, has a well-defined thermotropic mesophase stable up to 170 °C, suggesting that the thermotropic columnar mesophase is severely destabilized by the presence of side chains of nonuniform length. However, the lyotropic behavior of these two materials is directly analogous and the phase boundaries, especially between C_H and N_c, are equally sharp.

To summarize, the Pc-centered poly(oxyethylene)s have interesting properties due to the strong tendency of the Pc cores to self-associate. In particular, the macromolecules containing four polymer side chains **1**−**3** display columnar lyotropic behavior despite the absence of a stable thermotropic mesophase. Work is in progress to characterize the phase diagram of these nonionic discotic amphiphiles.

References and Notes

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(9) **1**: Found: C, 58.86; H, 7.57; N, 5.64; $C_{100}H_{154}N_8O_{36}$ ($n = 8$) requires: C, 58.75; H, 7.59; N, 5.48. UV−vis (toluene, λ_{max} (nm)) 702, 666, 641, 606, 394, 340. δ_H (500 MHz, solvent C_6D_6, 60 °C) −2.8 (2H, br s), 3.25 (12H, s), 3.4−4.0 (96H, m), 3.8 (8H, m), 3.95 (8H, m), 4.10 (8H, m), 4.45 (8H, m), 7.70 (4H, m), 8.65 (4H, m), 9.10 (4H, m).

2: Found: C, 57.8; H, 7.8; N, 4.3; $C_{132}H_{218}N_8O_{52}$ ($n = 12$) requires: C, 57.65; H, 7.99; N, 4.07. UV−vis (toluene, λ_{max} (nm)) 702, 666, 641, 606, 394, 340. δ_H (500 MHz, solvent C_6D_6, 60 °C) −3.0 (2H, br s), 3.25 (12H, s), 3.4−4.0 (160H, m), 3.8 (8H, m), 3.95 (8H, m), 4.10 (8H, m), 4.45 (8H, m), 7.70 (4H, m), 8.65 (4H, m), 9.10 (4H, m).

3: Found: C, 57.01; H, 8.14; N, 3.74; $C_{164}H_{282}N_8O_{68}$ ($n = 16$) requires: C, 57.02; H, 8.23; N, 3.25. UV−vis (toluene, λ_{max} (nm)) 702, 666, 641, 606, 394, 340. δ_H (500 MHz, solvent C_6D_6, 60 °C) −2.6 (2H, br s), 3.25 (12H, s), 3.4−4.0 (224H, m), 3.8 (8H, m), 3.95 (8H, m), 4.10 (8H, m), 4.45 (8H,

m), 7.70 (4H, m), 8.65 (4H, m), 9.10 (4H, m).

4: Found: C, 55.8; H, 8.0; N, 2.9. $C_{168}H_{290}N_8O_{72}$ ($n = 8$) requires C, 56.45; H, 8.17; N, 3.13. UV−vis (toluene, λ_{max} (nm)) 698, 664, 642, 600, 422, 348. δ_H (500 MHz, solvent C_6D_6, 60 °C): −3.20 (2H, br s), 3.37 (24H, s), 3.5 (160H, s), 3.64 (16H, t), 3.82 (16H, t), 3.93 (16H, t), 4.08 (16H, t), 4.25 (16H, t), 4.61 (16H, br t), 8.73 (8H, s).

5: Found: C, 55.60; H, 8.25; N, 2.20. $C_{232}H_{418}N_8O_{104}$ ($n = 12$) requires: C, 55.91; H, 8.45; N, 2.25. UV−vis (toluene, λ_{max} (nm)) 698, 664, 642, 600, 422, 348. δ_H (500 MHz, solvent C_6D_6, 60 °C): −3.20 (2H, br s), 3.37 (24H, s), 3.5 (288H, s), 3.64 (16H, t), 3.82 (16H, t), 3.93 (16H, t), 4.08 (16H, t), 4.25 (16H, t), 4.61 (16H, br t), 8.73 (8H, br s).

6: Found: C, 54.36; H, 8.41; N, 1.9. $C_{296}H_{546}N_8O_{136}$ ($n = 16$) requires: C, 55.60; H, 8.61; N, 1.75. UV−vis (toluene, λ_{max} (nm)) 698, 664, 642, 600, 422, 348. δ_H (500 MHz, solvent C_6D_6, 60 °C): −3.20 (2H, br s), 3.37 (24H, s), 3.5 (416H, s), 3.64 (16H, t), 3.82 (16H, t), 3.93 (16H, t), 4.08 (16H, t), 4.25 (16H, t), 4.61 (16H, br t), 8.73 (8H, br s).

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