

# Hexagonal columnar liquid-crystalline phase from a rod-coil molecule

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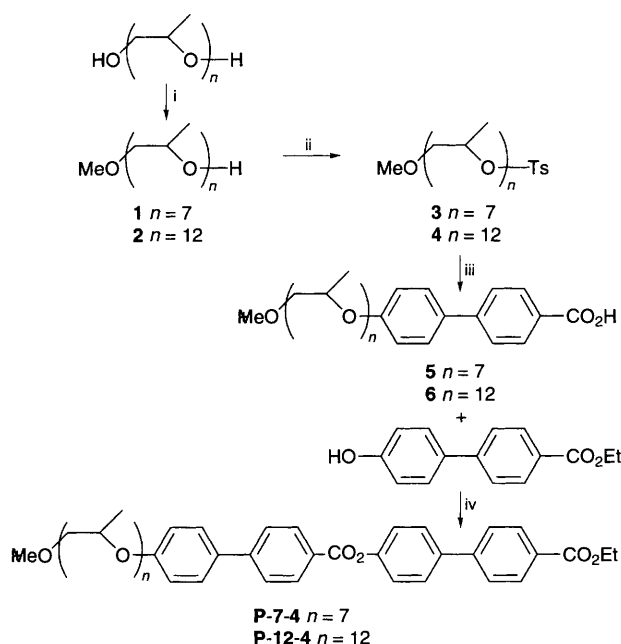
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Liquid-crystalline behaviour of rod-coil molecules is normally associated with the formation of calamitic mesophases; by increasing the volume fraction of coil segments *via* substitution of poly(propylene oxide) with degree of polymerization of 12 to an elongated rod, the rod-like mesogen can be assembled into cylindrical micelles, showing a hexagonal columnar mesophase.

Thermotropic liquid-crystalline phases may be formed by rod-like (calamitic) as well as by disk-shaped molecules. Rod-like molecules with one or two flexible tails give rise to nematic and/or smectic liquid-crystalline phases, whereas discotic molecules self-organize to give discotic nematic and/or columnar phases.<sup>1</sup> Phasmidic,<sup>2,3</sup> biforked<sup>4,5</sup> and board-like molecules<sup>6</sup> have been designed to connect the gap between these two different types of mesophases. While the guiding principle of shape is extensively used in the design of liquid crystals, some efforts in liquid-crystal materials have been made to generate the desired mesophases with rod-coil molecules which are macromolecular analogues of low molar mass smectogens. The covalent linkage between a conventional rod and an elongated flexible coil may be an attractive way of creating new supramolecular structures due to their ability to segregate incompatible segments (*e.g.* rigid rod and flexible coil) of individual molecules.

In this paper, we describe new rod-coil molecules consisting of a conventional calamitic unit (four-phenyl ring system) covalently linked by poly(propylene oxide)s with average lengths of 7 and 12 propylene oxide subunits which were prepared from the readily available poly(propylene glycol) of average molecular masses 425 and 725. The rod-coil molecules were synthesized as shown in Scheme 1.



**Scheme 1** Reagents and conditions: i,  $\text{CH}_3\text{I}/\text{NaH}$ ; ii,  $\text{TsCl}$ ; iii, 4-hydroxy-4'-biphenyl carboxylic acid/ $\text{KOH}$ ; iv,  $\text{DIPC}/\text{DMAP}$

The appropriate poly(propylene oxide) monomethyl ether precursor reacted with toluene-*p*-sulfonyl chloride to give tosyl terminated derivatives. Substitution reaction of tosyl terminated poly(propylene oxide) with 4-hydroxy-4'-biphenyl carboxylic acid produced compounds **5** and **6** in reasonable yield. The rod-coil molecules, **P-7-4** and **P-12-4** were obtained by treating (25 °C, 12 h) **5** and **6** with ethyl 4-hydroxy-4'-biphenyl carboxylate in  $\text{CH}_2\text{Cl}_2$  in the presence of diisopropylcarbodiimide (DIPC) and *p*-dimethylaminopyridine (DMAP). The final rod-coil molecules were purified by column chromatography (silica gel) using methylene chloride-ethanol (8:1 v/v) as eluent, and were obtained in 24–45% yield. Satisfactory analytical data were obtained for both new rod-coil molecules.

The mesomorphic properties of the rod-coil molecules were studied using polarized optical microscopy and differential scanning calorimetry (DSC). The thermal properties of these rod-coil molecules are summarized and compared with those of corresponding rod-coil molecules (**E-7-4** and **E-12-4**) with poly(ethylene oxide)s<sup>7</sup> in Table 1.

The rod-coil molecule **E-7-4** which consists of a rod and a poly(ethylene oxide) with a degree of polymerization (DP) of 7 melts into a smectic A phase which is transformed into an isotropic phase on heating, while rod-coil molecule **P-7-4** consisting of a rod and a poly(propylene oxide) with a DP of 7 exhibits both smectic A and C phases. Comparing poly(ethylene oxide) and poly(propylene oxide) shows that the thermal stability of the mesophase decreases if a poly(propylene oxide) coil is incorporated in the rod. This can be attributed to a steric effect caused by side methyl groups of the coil which hinder molecular packing. **E-12-4** containing a poly(ethylene oxide) with a DP of 12 also exhibits a smectic A phase displayed by conventional rod-like mesogens.

In contrast to the phase behaviour of the rod-coil molecules described above, the rod-coil molecule **P-12-4** containing

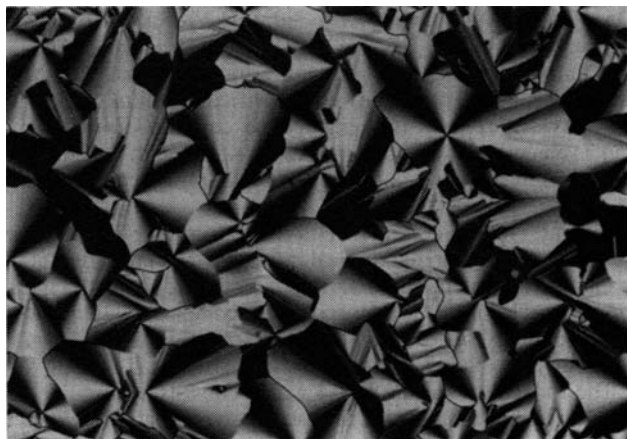
**Table 1** Transition temperatures of the rod-coil molecules; values in parentheses refer to the enthalpy changes ( $\Delta H/\text{kJ mol}^{-1}$ )

Compound	R	$T^a / ^\circ\text{C}$
<b>E-7-4</b>		K 150.6 (11.7) S <sub>A</sub> 232.2 (1.18) I
<b>P-7-4</b>		K 61.5 (20.0) S <sub>C</sub> 119.9 (0.03) S <sub>A</sub> 139.0 (1.45) I
<b>E-12-4</b>		K 134.4 (14.9) S <sub>A</sub> 147.9 (1.95) I
<b>P-12-4</b>		K 21.5 (5.55) Col 33.5 (0.35) I

<sup>a</sup> Abbreviations: K = crystalline, S<sub>A</sub> = smectic A phase, S<sub>C</sub> = smectic C phase, Col = hexagonal columnar phase, I = isotropic phase.

poly(propylene oxide) with a DP of 12, the bulkiest coil in the rod-coil molecules, does not exhibit lamellar smectic phases, but a hexagonal columnar mesophase. On cooling from the isotropic liquid, first a platelet-like growing of texture can be observed with a final development of pseudo-focal conic domains which are characteristic of a hexagonal columnar mesophase exhibited by conventional discotic mesogens as shown in Fig. 1.<sup>8</sup> Preliminary small-angle X-ray diffraction measurements have been performed on the mesophase of **P-12-4**. The X-ray pattern of **P-12-4** exhibits three Bragg reflections at 1.215 (strong), 2.105 and 2.443 nm<sup>-1</sup> of  $q$  value (scattering vector), respectively. The ratio of their positions of 1:  $\sqrt{3}$ :  $\sqrt{4}$  supports the existence of a hexagonal columnar mesophase.<sup>9</sup>

The existence of a hexagonal columnar mesophase is in contrast with the normal behaviour of rigid rod calamitic mesogens which show a lamellar smectic and/or nematic phase.



**Fig. 1** Representative optical polarized micrograph (100  $\times$ ) of the texture exhibited by the rod-coil molecule **P-12-4** at 33  $^{\circ}$ C on the cooling scan

The lamellar smectic structure observed in **E-7-4**, **P-7-4** and **E-12-4** is still the most efficient packing of melt chains, which is similar to that of low molar mass smectogens. In **P-12-4** containing the bulkier coils, however, the volume fraction of coil segments is very large. Smectic ordering of rods would confine rod-coil junctions to a flat interface with a relatively high density of grafting sites, which forces a strong stretching of the coils away from the interface and the system becomes unstable.<sup>10</sup> Consequently, the lamellar smectic structure of the rod-coil molecule will break apart into cylindrical micelles in which the coils grafted onto their top and bottom interfaces fan out into a larger region of space in order to reduce the coil stretching penalty. This might explain qualitatively the phase behaviour of this rod-coil system.

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