Thermotropic and lyotropic mesophase formation of poly(ethylene oxide) substituted rod-coil oligomer

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Summary

The synthesis and characterization of the rod-coil oligomer consisting of a molecular rod and a poly(ethylene oxide) with degree of polymerization of 12 (**5**) are presented. The rod-coil oligomer **5** shows a crystalline phase with microphase segregation. However, the complexation of the rod-coil oligomer **5** with $LiCF_3SO_3$ induces a thermotropic smectic liquid crystalline phase. In aqueous solution, the rod-coil oligomer **5** shows various lyotropic mesophases such as lamellar, cubic and cylindrical micellar mesophases, depending on the oligomer concentration. These results characterized by differential scanning calorimetry and optical polarized microscopy are described.

Introduction

Rod-coil molecular system consisting of a flexible coil and a rigid rod provides the opportunity to study new aspects of liquid crystalline behavior.[1-4] The degree of immiscibility is expected to be large because of the large chemical differences between stiff rod and flexible coil segments. This allows block segregation to occur at relatively short chain lengths compared to that in typical flexible block copolymers. As a result of microphase segregation, the rod-coil molecules self-assemble into well-defined supramolecular structures such as lamellar and cylindrical structures in melt state as well as in solution as predicted by theoretical works.[1,4]

In this respect, we have investigated liquid crystalline rod-coil molecules containing poly(ethylene oxide). Liquid crystalline molecule containing a poly(ethylene oxide) has several advantages, particularly due to its complexation capability with alkali metal cation, which can induce various liquid crystalline supramolecular structures.[5-7] The goal of this paper is to describe the synthesis and thermal characterization of a rod-coil oligomer (**5**) based on poly(ethylene oxide) with three-phenyl ring system. Then it will be described the thermotropic phase behavior of the complexes with $LiCF_3SO_3$ and the lyotropic phase behavior of the aqueous solution.

Experimental
Techniques

^{1}H-NMR spectra were recorded from $CDCl_3$ solution on a Bruker AM 300 spectrometer operating at 300 MHz proton frequency. TMS was used as internal standard. A Perkin Elmer DSC-7 differential scanning calorimeter, equipped with a 1020 thermal analysis controller, was used to determine the thermal transition temperatures which were taken at the maximum of transition peaks. Heating and cooling rates were 10 °C/min. A Nikon Optiphot 2-pol optical polarized microscope

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(magnification: 100x) 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 the anisotropic textures.[8,9] Molecular weight distribution was determined by size exclusion chromatography (SEC) with a Waters R401 instrument equipped with US HR5E-500-H22 column and a Millenum data station. The measurements were made at 40°C using a UV detector with THF as solvent (1 ml/min) and a calibration plot constructed with polystyrene standards was used to determine the molecular weight distribution. Microanalysis was performed with a Perkin Elmer 240 elemental analyzer.

Materials

All materials were of commercial origin and were used as received or purified as described previously.[5] 4-Dimethylaminopyridinium p-toluene sulfonate (DPTS) was prepared as described in the literature.[10]

Synthesis of rod-coil oligomer (5)

The rod-coil oligomer of poly(ethylene oxide) monomethyl ether ($<M_w>$=550) with three-phenyl ring (5) system was synthesized as outlined in Scheme 1. The compounds 2 and 4 were synthesized according to the procedure described previously.[5]
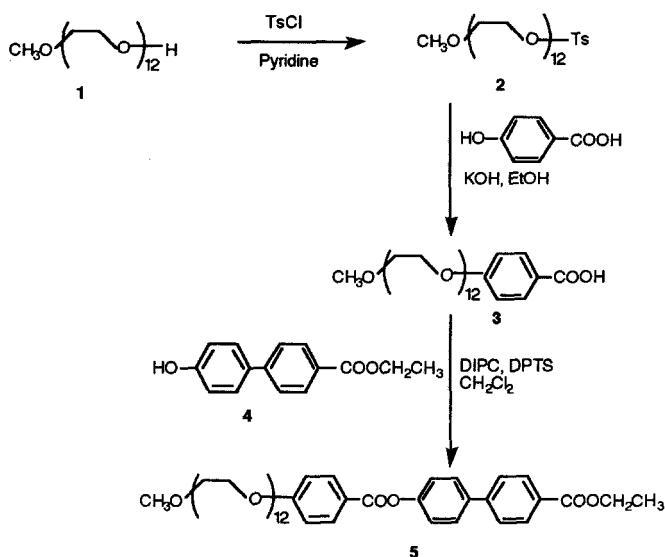
Scheme 1; Synthesis of Rod-Coil Oligomer 5

4-[Methyloxy poly(ethyleneoxy)ethyloxy]benzoic acid (3)

To a solution of 4-hydroxybenzoic acid (1.5 g, 10.9 mmol) and KOH (1.4 g, 25.0 mmol) in methanol was added tosylated poly(ethylene oxide) monomethyl ether (7.68 g, 10.9 mmol). After being refluxed for 24 h, the solution was poured into 1N-HCl aqueous solution and extracted with chloroform. The chloroform solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotavapor, and the crude product was then purified by column chromatography (silica gel, methlyene chloride/methanol=15/1 as eluent) to yield 3.5 g (48%) of colorless liquid.

^{1}H-NMR (CDCl$_3$, TMS, δ, ppm) 3.34 (s, 3H, C$\underline{H}_3$O), 3.50-4.20 (m, 48 H, OCH$_2$), 6.97 (d, 2Ar-H, o to CH$_2$O, J=8.7 Hz), 8.11 (d, 2Ar-H, o to COOH, J=8.3 Hz).

Ethyl 4'-[4-[methyloxy poly(ethyleneoxy)ethyloxy]benzoyloxy]-4-biphenylcarboxylate (5)

Compound 3 (2.3 g, 3.43 mmol), compound 4 (0.83 g, 3.43 mmol) and DPTS (1.0 g, 3.43 mmol) were dissolved in 50 ml dried CH$_2$Cl$_2$ under argon. The resulting mixture was stirred for 1 h and 1,3-diisopropylcarbodiimide (DIPC, 1.24 ml) was then added. The reaction mixture was stirred at room temperature for 12 h and was then poured into methanol, and the precipitate was filtered off and dried under vacuum. The obtained product was purified by column chromatography using silica gel (methylene chloride/methanol=15/1 eluent) to yield 1.1 g (35%) of white solid and was then further purified by recrystallization from a mixture of methylene chloride and n-hexane.

^{1}H-NMR (CDCl$_3$, TMS, δ, ppm); 1.39 (t, 3H, CH$_2$C$\underline{H}_3$, J=7.2 Hz), 3.35 (s, 3H, C$\underline{H}_3$O), 3.50-3.75 (m, 44 H, OC$\underline{H}_2$), 3.88 (t, 2H, C$\underline{H}_2$CH$_2$O-phenyl, J=5.1 Hz), 4.20 (t, 2H, CH$_2$C$\underline{H}_2$Ophenyl, J=5.1 Hz), 4.39 (q, 2H, OC$\underline{H}_2$CH$_3$, J=7.1 Hz), 7.00 (d, 2Ar-H, o to CH$_2$O, J=8.7 Hz), 7.30 (d, 2Ar-H, o to benzoate, J=8.8 Hz), 7.60-7.70 (m, 4 Ar-H, m to benzoate and m to COOEt), 8.10 (d, 2 Ar-H, o to COOCH$_2$, J=8.5 Hz), 8.15 (d, 2 Ar-H, o to COO-phenyl, J=8.4 Hz): Elemental analysis for C$_{47}$H$_{68}$O$_{17}$; Calc. C; 62.37%, H; 7.57 %, Found; C; 62.65 %, H; 7.46 %.

Preparation of complexes of 5 with LiCF$_3$SO$_3$

Complexes of 5 with lithium triflate were prepared by mixing solutions of 5 (10 mg/ml) in dry methylene chloride with an appropriate volume of 0.724 mmol/ml salt in dry acetonitrile solution, followed by slow evaporation of the solvent under reduced pressure at room temperature, and subsequent drying in a vacuum oven at 60 ^{o}C to maintain constant weight. Addition of a solution of the salt in acetonitrile to methylene chloride gives a precipitate free of 5.

Preparation of aqueous solutions of 5 and measurements of lyotropic properties

The aqueous solutions of 5 were prepared by mixing the desired amount of 5 and water, shaking for 7 days for equilibrium condition. The phase transition temperatures for lyotropic solutions were determined by optical polarized microscopy for samples sealed in a cell as the onset or disappearance of birefringence on heating.

Results and Discussion

The synthesis of rod-coil oligomer is outlined in Scheme 1. Commercially available poly(ethylene oxide) monomethyl ether (average molecular weight <M$_w$>=550) was used as starting material for 5. The rod-coil oligomer 5 could be isolated by column chromatography (silica gel) from the resulting mixture of each esterification reaction using a mixture of CH$_2$Cl$_2$ and methanol (15:1 v/v) as eluent. The rod-coil oligomer was then recrystallized from methylene chloride and n-hexane to obtain a highly monodisperse polymer with 1.02 of polydispersity determined from SEC as shown in Table 1. Figure 1 presents the ^{1}H-NMR spectrum of 5 with its protonic assignments. The resonances of the expected methoxy chain end in the coil and ethyl chain end in the rod can be easily observed at 3.35 ppm and 4.39 ppm, respectively. No other signals indicative of impurities are observed.

The thermotropic phase behavior of the rod-coil polymer and its complexes with lithium triflate was characterized by differential scanning calorimetry (DSC) and thermal optical polarized microscopy. The experimental data collected from both heating and cooling scans of DSC are summarized in Table 1. Figure 2 shows DSC traces of the second heating scans and the first cooling scans of the rod-coil oligomer

5 and its complexes with 0.10-0.35 mol of lithium triflate per ethylene oxide unit of **5**.

As shown in Figure 2, **5** exhibits a crystalline melting which corresponds to the poly(ethylene oxide) coil segment followed by a crystalline phase of the rod segment which, in turn, undergoes melting into isotropic liquid, regardless of the thermal history of the sample. We believe that the hydrophilic coil and hydrophobic rod segments are highly incompatible, and therefore, become microphase-separated, although the molecular weight of each segment is very low. This gives rise to the two crystalline melting transitions which correspond to each segment. This trend agrees well with previous results available in the literature.[5]

Table 1. Characterization of the Rod-Coil Oligomer **5** and Its Complexes with LiCF3SO3 (s=smectic phase, k=crystalline phases, i=isotropic phase). Data on first line are from first heating and cooling scans. Data on second line are from second heating scan.

Complex [Li+]/[EO]	M_w/M_n (SEC)	phase transitions (°C) and corresponding enthalpy changes (kJ/mol)	
		heating	cooling
0.00	1.02	k 11.5 (38.4) k 59.6 (25.3) i	i 48.2 (24.3) k -7.7 (44.9) k
		k 13.5 (47.8) k 59.7 (23.0) i	
0.10		k 40.1 (11.5) i	i 33.0 (12.6) k
		k 39.0 (12.2) i	
0.20		k 23.0 (7.6) s 57.7 (-)ᵃ i	i 53.2 (-)ᵃ s 12.5 (7.3) k
		k 22.3 (7.4) s 54.1 (-)ᵃ i	
0.25		k 16.1 (4.9) s 72.8 (-)ᵃ i	i 68.7 (-)ᵃ s 9.4 (0.8) k
		k 15.2 (3.9) s 70.7 (-)a i	
0.30		k 11.2 (2.8) s 79.3 (-)ᵃ i	i 74.5 (-)ᵃ s 1.9 (0.03) k
		k 8.2 (0.54) s 78.3 (-)ᵃ i	
0.35		k 3.0 (2.9) s 80.3 (-)ᵃ i	i 75.2a (-)ᵃ s -13.5 (0.02) k
		k 0.2 (0.03) s 80.2 (-)ᵃ i	

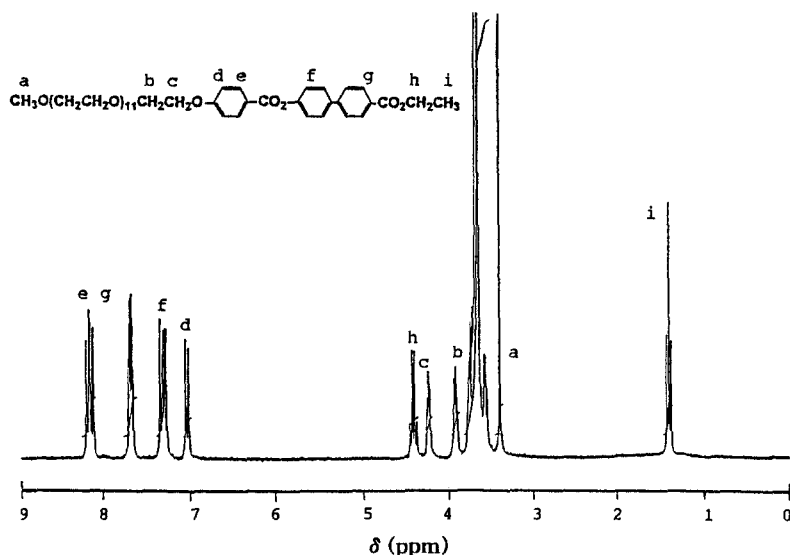ᵃ data obtained from optical polarized microscopy

Figure 1: 300 MHz ^{1}H-NMR spectrum of rod-coil oligomer **5**.

It has been reported that alkali metal salts are selectively soluble in the poly(ethylene oxide) segments of a block copolymer exhibiting a microphase separated morphology.[11] Therefore, alkali metal ion will be selectively dissolved in the microphase separated poly(ethylene oxide) coil segments of **5** through ion-dipolar interaction, which can give rise to the formation of thermotropic mesophase. In this respect, we have investigated the phase change of **5** on complexation with LiCF$_3$SO$_3$.[12]

The complex with 0.10 mol of LiCF$_3$SO$_3$ per ethylene oxide unit of **5** displays only a crystalline melting which corresponds to the rod block and the crystalline melting corresponding to the coil segments is suppressed. The complexes of **5** with 0.20-0.35 mol of LiCF$_3$SO$_3$ are crystalline and exhibit an enantiotropic smectic mesophase. The dependence of the phase transitions of **5** and its complexes with LiCF$_3$SO$_3$ on the [LiCF$_3$SO$_3$]/[ethylene oxide] determined from the second heating and the first DSC cooling scans are plotted in Figures 3a and 3b, respectively. The temperature associated with the mesomorphic-isotropic transition increases up to the complex with 0.35 mol of LiCF$_3$SO$_3$ per ethylene oxide unit. At the same time, both the crystal melting transitions show a decrease. As a result, the thermal stability of the smectic phase increases with increasing salt concentration up to 0.35 mol of LiCF$_3$SO$_3$. Figure 4a presents a representative texture displayed by the smectic phase exhibited by the complex with 0.25 mol of LiCF$_3$SO$_3$.

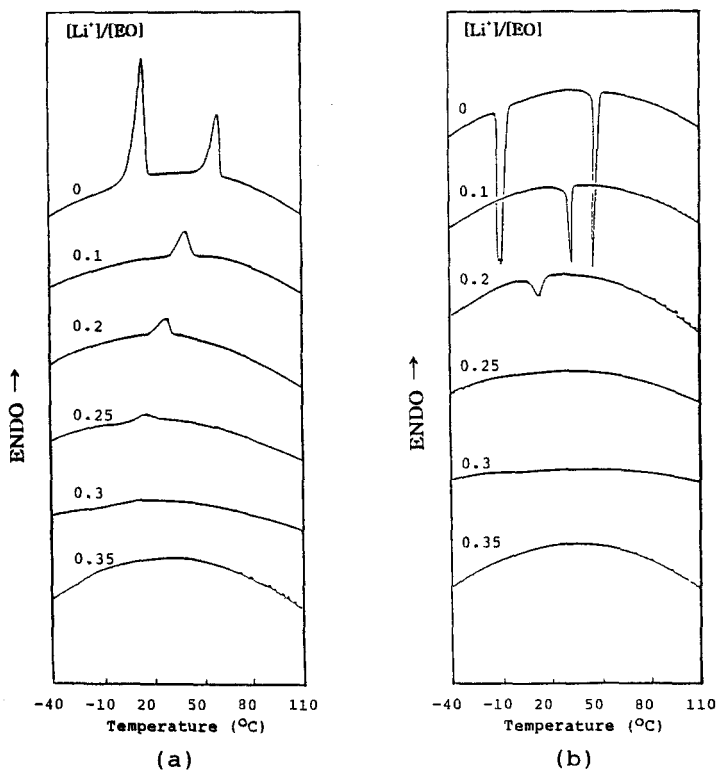Figure 2: DSC traces (10 °C/min) recorded during the second heating scan (a), and first cooling scan (b) of the complexes of **5** with lithium triflate.
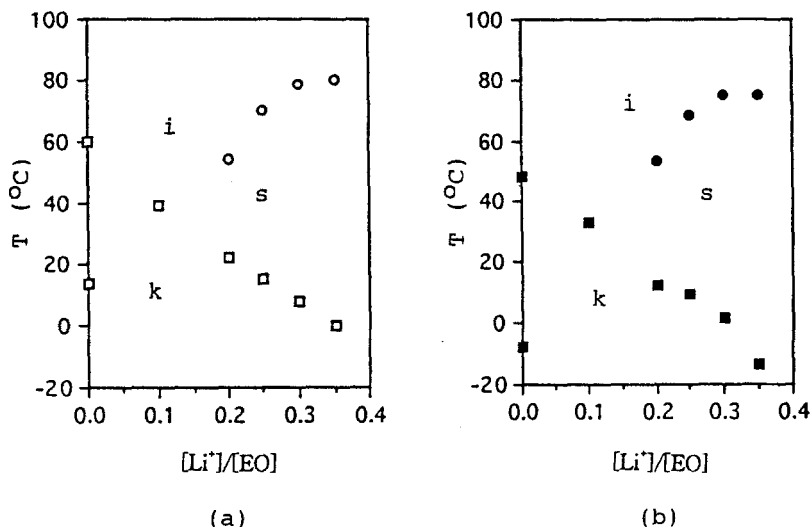
Figure 3: The dependence of phase transition temperatures of the complexes of rod-coil oligomer **5** with lithium triflate on the [LiCF₃SO₃]/[EO]. a) data from second heating scan; □-T_{k-k}, T_{k-s}, T_{k-i}; O-T_{s-i}; b) data from first cooling scan; ■-T_{k-k}, T_{i-k}, T_{s-k}; ●-T_{i-s}.

The rod-coil oligomer **5** is readily water-soluble. Therefore, preliminary investigation of possible lyotropic mesophases of rod-coil oligomer was performed by placing a drop of dilute isotropic rod-coil oligomer solution between a microscope slide and a cover slip and allowing time for partial evaporation of the solvent from the edge of the solution. In this way, a concentration gradient was created with a higher concentration of material at the edge of the slide. Edge evaporation of a dilute aqueous solution of **5** gave rise to lyotropic mesophase from isotropic solution with an optical texture identical to that exhibited by the conventional hexagonal columnar mesophase, and an optical isotropic texture was also formed at the boundary between those of cylindrical micellar and the crystalline phases as shown in Figure 4b.[13] Examination of a range of aqueous solutions shows that concentrations of **5** of between 5-20% by weight, form a cylindrical micellar mesophase as shown in the binary phase diagram of Figure 5. Solutions of **5** in a range from 25 to 60 weight-% of **5** exhibit the cubic and lamellar mesophases, and the solutions with 70-80 wt.% exhibit only a lamellar mesophase. The phase boundary line to the isotropic solution shows a maximum at 35±1°C for the cylindrical micellar phase and at above 80 °C for the lamellar phase.

In conclusion, the rod-coil oligomer **5** was observed to display a crystalline phase with microphase segregation. The complexation of **5** with lithium cation induced the thermotropic smectic phase in a range of 0.20 and 0.35 mol of lithium salt. In aqueous solution, **5** showed various lyotropic liquid crystalline phases such as lamellar, cubic and cylindrical micellar mesophases depending on the polymer concentration.

(a)
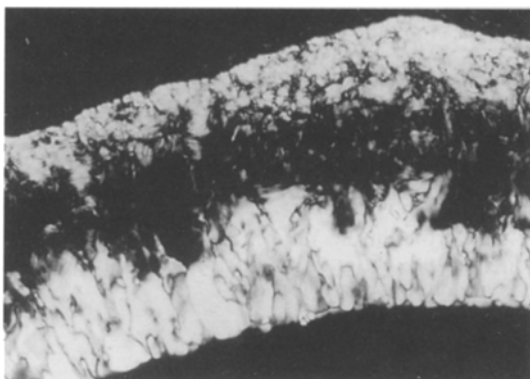
(b)

Figure 4: Representative optical polarized micrographs (100 X) of the textures exhibited by; (a) the thermotropic smectic mesophase of the complex of **5** with 0.25 mol of LiCF$_3$SO$_3$ at 67 °C on the cooling scan; (b) the lyotropic mesophase of **5** at room temperature. A concentration gradient was established by evaporation of an aquous solution of the rod-coil material from the edge of the microscope slide.
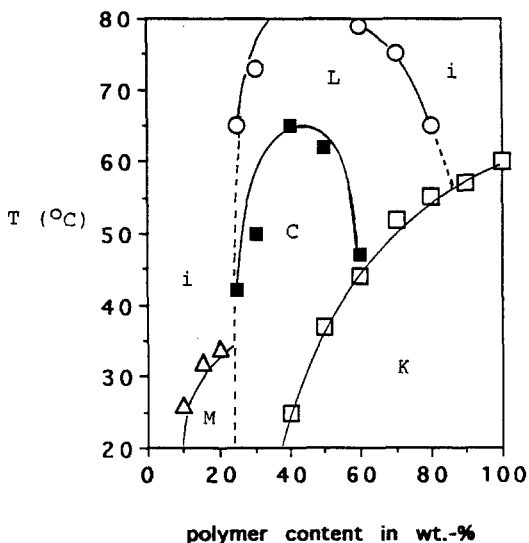
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polymer content in wt.-%

Figure 5: Binary phase diagram of rod-coil oligomer 5-H_2O system based on examination of aqueous solutions with defined oligomer contents over a temperature range of 20 °C to 80 °C. The phase transition temperatures were determined by optical polarized microscopy; K: crystalline; L: lamellar; C: cubic; M: cylindrical micellar; and i: isotropic phases.

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