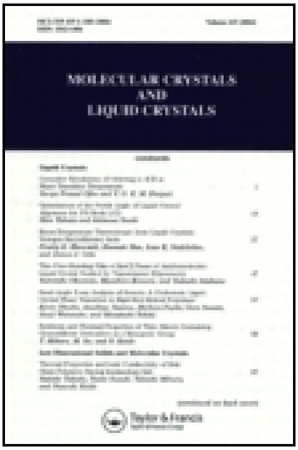

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Self-Assembly of Rod-Coil Molecules into Cylindrical Supramolecular Architectures Through Ionic Interaction

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SELF-ASSEMBLY OF ROD-COIL MOLECULES INTO CYLINDRICAL SUPRAMOLECULAR ARCHITECTURES THROUGH IONIC INTERACTION

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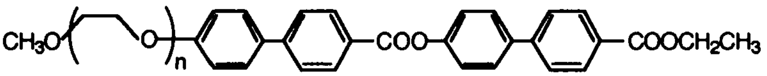
Abstract The mesomorphic behaviors of two rod-coil molecules containing poly(ethylene oxide)s with degree of polymerization of 12 (**12-4**) and 16 (**16-4**) and their complexes with $LiCF_3SO_3$ are discussed. Both rod-coil molecules discussed in this paper exhibits a microphase separated lamellar crystalline phase as well as a layered smectic mesophase. The complexation with $LiCF_3SO_3$ induced a cylindrical micellar mesophase from a smectic phase of uncomplexed molecule. These results characterized by a combination of techniques by DSC, optical polarized microscopy and X-ray scattering experiments are discussed in terms of the change of the relative volume fraction of coil to rod segments through complexation with $LiCF_3SO_3$.

INTRODUCTION

Rod-coil diblock system consisting of a flexible coil and a rigid rod offers 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 micro-phase segregation, the rod-coil diblock molecules self-assemble into well defined microstructures such as lamellar and cylindrical structures in the melt state depending on the block composition.[1]

We have investigated the liquid crystalline rod-coil molecules containing poly(ethylene oxide), particularly due to ocurring microphase separation between each block and their complexation capability with alkali metal cation, which can induce various liquid crystalline supramolecular structures.[5,6] The goal of this paper is to discuss the thermal and morphological properties of rod-coil polymers **12-4** and **16-4**, and their complexes with $LiCF_3SO_3$.



12-4; n=12

16-4; n=16

The chemical structure of **12-4** and **16-4**

EXPERIMENTAL

The details of the synthesis and characterization of the rod-coil molecules and the complexes were reported in the previous publications.[5,6]

A Perkin Elmer DSC-7 differential scanning calorimeter, equipped with a 1020 thermal analysis controller was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks, respectively. A Nikon Optiphot 2-pol optical polarized microscope (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. X-ray scattering measurements were performed in transmission mode with Nickel-filtered Cu Kα radiation supplied by a Rigaku Denki generator operating at 40 kV and 40 mA. The small angle X-ray scattering measurements was performed with a Kratky camera fitted with an M. Broun linear position sensitive detector.

RESULTS

Phase Transitions of the Complexes

As shown in Figure 1 which is plotted from the data collected the second DSC heating scan,[5] **12-4** exhibits a crystalline melting which corresponds to the poly(ethylene oxide) coil block followed by a crystalline phase of the rod block which, in turn, undergoes melting into a smectic A mesophase, regardless of the thermal history of the sample. The complex with 0.05 mol of $LiCF_3SO_3$ per ethylene oxide unit of **12-4** exhibits two crystalline melting transitions followed by a smectic A phase on heating. Complexes of **12-4** with 0.1-0.2 mol of $LiCF_3SO_3$ displays only a crystalline melting which corresponds to the rod block and an enantiotropic smectic A mesophase. The transition temperature associated with the mesomorphic-isotropic increases up to the complex with 0.10 mol of $LiCF_3SO_3$ per ethylene oxide

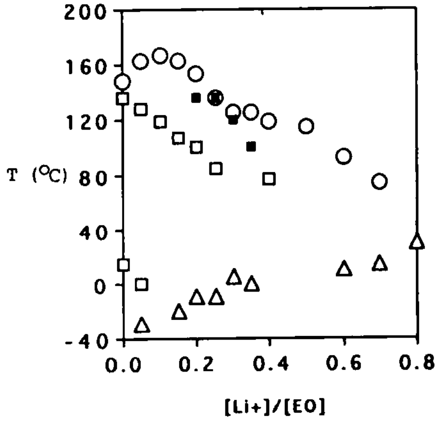


Figure 1; The dependence of phase transition temperatures of the complexes of **12-4** with lithium triflate on the [$LiCF_3SO_3$]/[EO], data from second heating scan; Δ-Tg; □-$T_{k\text{-}k}$; □-T_m; ■-$T_{OI\text{-}sA}$, $T_{OI\text{-}i}$ or $T_{OI\text{-}M}$; O-Ti.

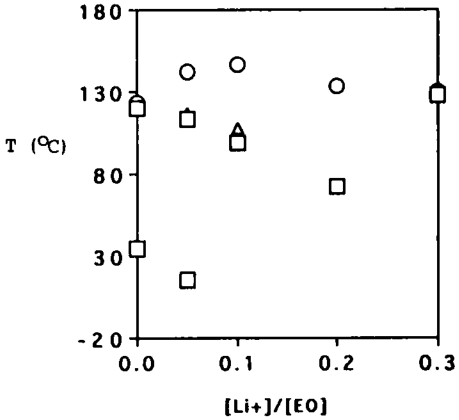


Figure 2; The dependence of phase transition temperatures of the complexes of **16-4** with lithium triflate on the [$LiCF_3SO_3$]/[EO], data from second heating scan; □-Tm; Δ-$T_{sB\text{-}sA}$; O-Ti;

unit and then decreases, consequently it disappears at the complex with 0.8 mol of $LiCF_3SO_3$. In contrast to the phase behavior of the complexes with up to 0.2 mol of $LiCF_3SO_3$, the complexes with 0.3 mol to 0.6 mol of $LiCF_3SO_3$ do not exhibit s_A phase but they display an enantiotropic cylindrical micellar mesophase. On cooling from the isotropic liquid, first a platelet like growing of the texture can be observed with a final development of pseudo-focal conic domains which are characteristic of a conventional disordered columnar mesophase exhibited by discotic liquid crystals.[7]

As shown in Figure 2 which is plotted from the data collected the second DSC heating scan,[6] **16-4** exhibits an enatiotropic smectic B phase in addition to crystalline melting transitions. The complexes of **16-4** with 0.05 mol and 0.1 mol of $LiCF_3SO_3$ per ethylene oxide unit exhibit an enantiotropic smectic A mesophase in addition to the s_B and crystalline phases. However, contrary to the thermal behavior of the complexes with upto 0.1 mol $LiCF_3SO_3$, the complexes with 0.2 mol and 0.3 mol do not exhibit smectic layered mesophase but they display an enantiotropic cylindrical micellar mesophase as their highest temperature mesophase. On cooling from the isotropic phase, first a plateletic growing of the texture can be observed with a final development of pseudo-focal conic domains which is characteristic of a conventional disordered columnar mesophase. The complex with 0.3 mol of $LiCF_3SO_3$ undergoes salt induced crystallization through endothermic and exothermic peaks on the second heating scan followed by the transition from micellar to isotropic. This result indicates that complexation of **16-4** with $LiCF_3SO_3$ also induces a cylindrical micellar mesophase from its layered smectic phase depending on the salt concentration.

X-ray diffraction pattern

In order to investigate the microphase separated morphology, X-ray experiments have been performed with **12-4** before and after melting transition temperature of the rod segments.[5] Small angle X-ray diffraction pattern of **12-4** in the crystalline phase displays three bragg reflections of 6.6 (very strong), 3.3 and 2.2 nm, while a series of sharp strong reflections is observed in wide angle diffraction pattern. Comparison with the calculated length of a fully extend rod-coil unit of ca 6.9 nm suggests that the 6.6 nm periodicity arises from monolayers resulting from the phase segregation of rod and coil segments. In the liquid crystalline phase, a sharp strong reflection and two small peaks are observed in the small angle region suggesting a lamellar phase with 5.8 nm periodicity, while the sharp reflections observed in the wide angle region disappear and only a diffuse halo is observed indicating the melting of the aromatic rods. This supports that **12-4** displays a layered smectic A mesophase with interlayer spacing of 5.8 nm.

For morphological investigation of the complexes, both small angle and wide angle X-ray scattering experiments have been performed with the complex with 0.4 mol of $LiCF_3SO_3$ at various temperatures.[5] In the crystalline phase, the complex displays several strong wide angle reflections. In the small angle X-ray region, this crystalline phase exhibits the intense fundamental and its second and third harmonic reflections, respectively, at Bragg spacings of 6.8 (very strong), 3.4 and 2.3 nm. Therefore, the crystalline phase of the complex with 0.4 mol of $LiCF_3SO_3$ is generated by layers of 6.8 nm periodicity. Interestingly, this interlamellar distance is very close to 6.6 nm periodicity shown in the crystalline phase of the uncomplexed polymer. In the liquid crystalline phase, the single reflection is observed at scattering vector of 0.2 and the lattice constant is 5.0 nm. While wide angle X-ray experiment shows only a broad halo in the range at about 4.5 Å. The periodicity of the complex is significantly reduced to 5.0 nm in comparison to that (5.7 nm) in the smectic A phase of **12-4**. This large reduction of periodicity together with optical polarized microscopic observations suggests that the mesophase exhibited by the complex is a cylindrical micellar mesophase.

DISCUSSION

It is well known that associated ionic species or ion pairs increase with increasing temperature or increasing salt concentration in polymer-salt complex systems.[8] Therefore, the enhanced thermal motion of the molecules including the increased associated ionic species on melting of the complex causes the flexible coils grafted onto their top and bottom surfaces in the monolayer structure to fan out into a larger region of space. Consequently, this spatial requirement of the coil segments leads to the transformation of the lamellar structure in the crystalline phase changes into a cylindrical micellar mesophase as predicted by theoretical work (Figure 3)[1].

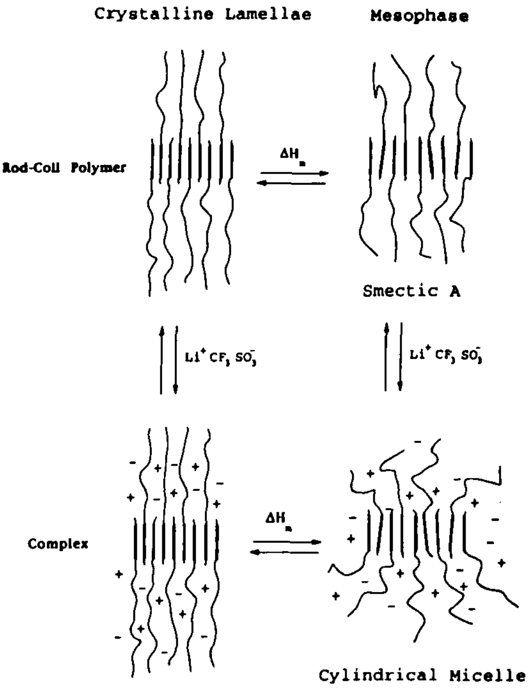


Figure 3; Schematic representation of the possible structures of rod-coil molecule

This micellar structure allows more volume and less coil stretching. This spreading out of the poly(ethylene oxide) chains is reflected in the large reduction observed for the complex with 0.4 mol of $LiCF_3SO_3$ from the layer periodicity in the solid (6.8 nm) to the intermicellar distance in the micellar mesophase (5.0 nm). Comparison the complex of **12-4** with that of **16-4** shows that complexation of **12-4** require more salt concentration than **16-4** for a cylindrical micellar mesophase. This is also explained by the larger relative coil volume fraction in **16-4** and therefore it requires less salt concentration to induce a cylindrical micellar mesophase.

CONCLUSION

The rod-coil molecule with shorter poly(ethylene oxide) coil (**12-4**) exhibits a cylindrical phase at higher than 0.3 mol of $LiCF_3SO_3$, however that with longer coil length (**16-4**) displays a cylindrical phase at higher than 0.2 mol of $LiCF_3SO_3$. This result indicates that the relative volume fraction of coil segments plays an important role for inducing a cylindrical micellar mesophase in the rod-coil diblock system as suggested by theoretical works.[1]

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REFERENCES

1. D. R. M. Williams and G. H. Fredrickson, Macromolecules, 25, 3561 (1992)
2. A. N. Semenov and S. V. Vasilenko, Sov. Phys. JETP, 63, 70 (1986)
3. A. N. Semenov, Mol. Cryst. Liq. Cryst., 209, 191 (1991)
4. A. Halperin, Macromolecules, 23, 2724 (1990)
5. M. Lee, N.-K Oh, H.-K. Lee and W.-C. Zin, Macromolecules, submitted
6. M. Lee and N.-K. Oh, J. Mater. Chem., submitted.
7. C. Destrade, P. Foucher, H. Gasparoux and N. H. Tinh, Mol. Cryst. Liq. Cryst., 106, 121 (1984)
8. L. M. Torell and S. Santz, in Polymer Electrolyte Reviews: J. R. MacCullum and C. A. Vincent Eds. (Elsevior, London, 1989), Vol. 2