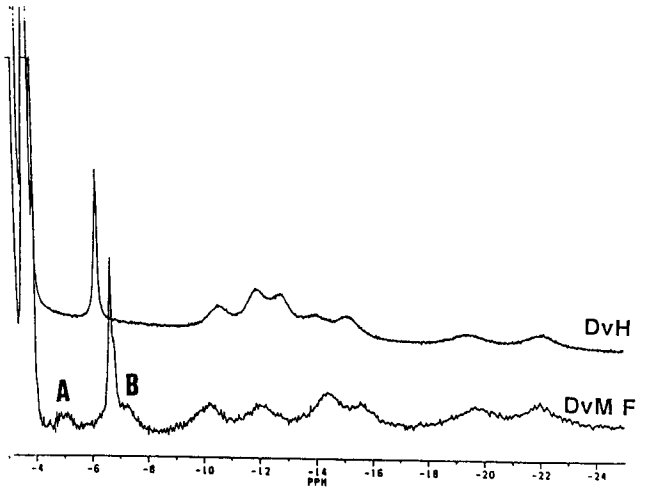

Figure 2. ^{1}H NMR spectra of cytochrome c_3 from *Desulfovibrio vulgaris* Miyazaki (bottom) and Hildenborough (top) in a high field region.

C2 proton signal of a histidyl imidazole group usually appears in the region from 7 to 9 ppm. Such extremely upfield shift can be explained either by the tilting of the axial ligand, or the imidazole nature of the ligand.[8,9] Since no significant tilting was found in crystal structure of both cytochrome c_3 molecules, the major reason of the upfield shift was ascribed to the imidazole nature of the histidine ligand. The imidazole nature of the ligand can explain, at least partly, the extremely low redox potentials of the cytochrome c_3 molecules in comparison with other *c*-type cytochromes. The spectrum of the C2 protons in the high field region was also reported for cytochrome c_3 from *Dv*H as shown in Figure 2(top).[10] It is shown in figure 2 along with that from *Dv*MF. It is clear from the figure that two lower signals (designated as A and B in Figure 2) of the C2 protons in *Dv*MF shift to the high field by several ppm in the spectrum of *Dv*H. Therefore, it is most plausible that two major differences with regard to the heme structure between both proteins could be responsible for the spectral changes of the C2 protons of the ligated imidazole groups. The upfield shift of the C2 proton signals can partly explain the lower redox potentials of the cytochrome c_3 from *Dv*H.

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Lyotropic Aggregation of Rod-Coil Oligomers-containing Poly(Ethylene Oxide)s

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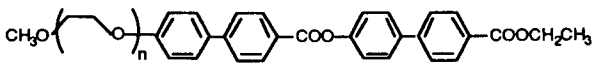
The rod-coil diblock molecule is of considerable interest due to its capability of forming well defined supramolecular structures such as layered smectic phase and cylindrical micellar phase as the relative volume fraction of block varies.[1~5] Another interesting aspect of rod-coil molecules is of course the high immiscibility between rod and coil segments which allows block segregation to occur at relatively smaller molecular weights of each segment than in typical flexible diblock molecules. In previous publications,[6,7] we reported the synthesis of monodisperse rod-coil oligomers containing one rigid and one flexible poly(ethylene oxide) segment joined covalently to share the same molecular backbone and showed that the oligomers form a layered assembly with nanoscale dimensions. Complexation of the rod-coil molecules with $LiCF_3SO_3$, which might increase the relative volume fraction of poly(ethylene oxide) coil segment, gave rise to transformation of the layered assembly into the cylindrical micellar phase, most probably to relieve coil stretching penalty.[7] The supramolecular structure of these rod-coil oligomers may also vary as a function of oligomer concentration in a selective solvent in which the rod blocks are immiscible, while the flexible coil blocks are highly miscible, due to the variation of the relative coil volume fraction. This experimental system has therefore enabled us to study lyotropic aggregation behavior in a selective solvent which causes the relative volume fraction of coil segments to change, particularly in view of theoretical predictions.[1,4]

In this communication, we describe the lyotropic aggregation behavior of the monodisperse rod-coil oligomers containing poly(ethylene oxide)s as coil segments in aquous solution. Scheme 1 outlines the structure of the rod-coil molecules.



rod-coil oligomer 1 ; n=16
rod-coil oligomer 2 ; n=12

Scheme 1. Chemical structure of rod-coil oligomer.

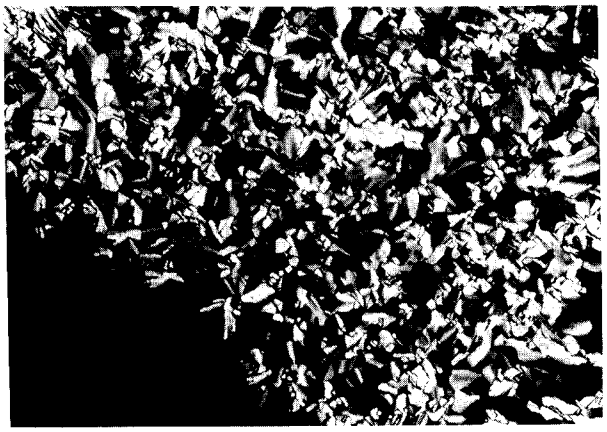


Figure 1. Representative polarized optical micrograph (100 X) of the texture exhibited by the lyotropic mesophase of rod-coil oligomer 1 at room temperature. A concentration gradient was established by evaporation of an aquous solution of the rod-coil material from the edge of the microscope slide. A cylindrical micellar phase has formed from the isotropic solution with digitate star shaped texture.

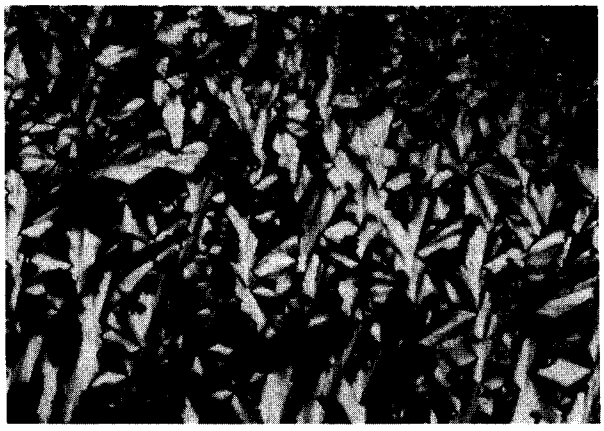


Figure 2. Representative optical polarized micrograph (100 X) of the texture exhibited by the lamellar mesophase of the 50 wt.% solution of rod-coil oligomer 1 at 40 ℃ on the cooling scan.

The rod-coil oligomers and the complex of rod-coil oligomer 2 with 0.3 mol of $LiCF_3SO_3$ per ethylene oxide unit were synthesized and purified as described in previous publications.[6]

All the rod-coil materials are water soluble. Therefore, preliminary investigation of possible lyotropic mesophases of the rod-coil oligomers 1, 2 and the complex of rod-coil oligomer 2 with 0.3 mol of $LiCF_3SO_3$ per ethylene oxide unit was performed by placing a drop of dilute isotropic rod-coil polymer solution between a microscopic slide glass and a

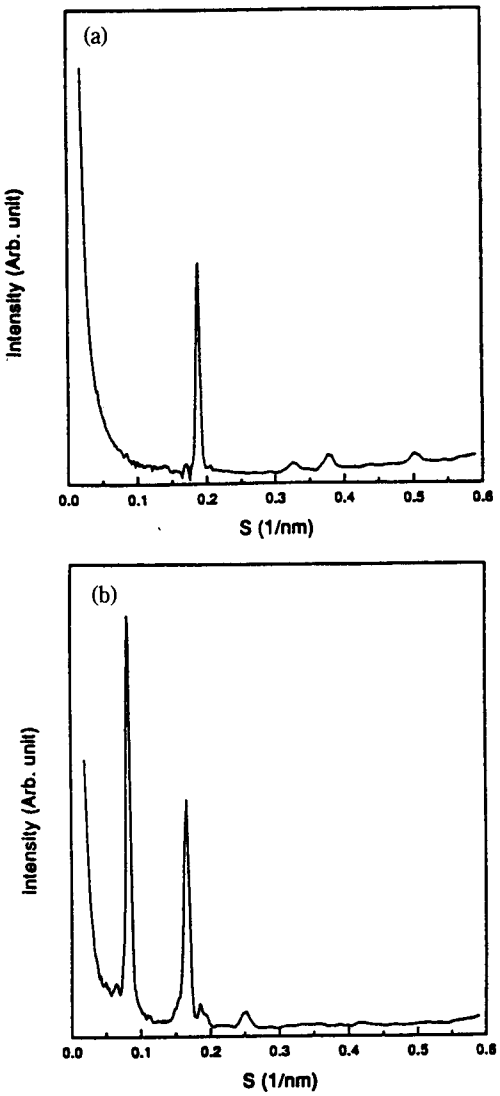


Figure 3. Desmeared SAXS intensities for the complex of rod-coil oligomer 2 with 0.3 mol of $LiCF_3SO_3$ plotted against s ($=2\sin\theta/\lambda$); (a) the complex solution at 88 wt.% in water. (b) the complex without water. The curves show the data obtained at room temperature.

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 the material at the edge of the slide. Edge evaporation of a dilute aquous solution of the rod-coil oligomer 1 gives rise to lyotropic mesophase from isotropic solution with an optical texture identical to that exhibited by the conventional thermotropic hexagonal columnar mesophase as shown in Figure 1.[8,9] Examination of a range of aquous solutions shows that concentrations of the rod-coil compound 1 of between 10-30% by weight, form a cylindrical micellar mesophase. Solutions of the rod-coil oligomer 1 in a concentration range from 40 to 60 weight-% exhibit the oily-streak or focal conic fan-like texture which is characteristics of a lamellar mesophase as shown in Figure 2.[9,10] Similarly, the rod-coil oligomer 2 exhibits a cylindrical micellar mesophase in water solution at the concentrations of 5-10 weight-%, while it displays a lame-

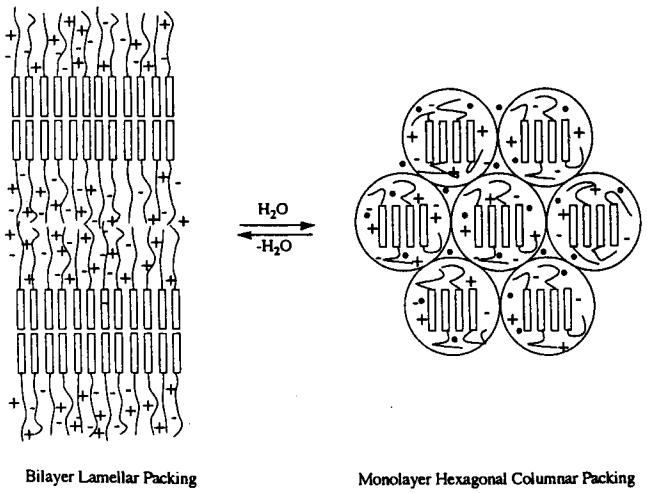


Figure 4. Schematic representation of the possible models of the structural transformation of the bilayer lamellar phase in the pure complex into the monolayer hexagonal columnar phase on addition of water; +, Li^+; −, $CF_3SO_3^-$; ●, H_2O.

llar mesophase in a concentration range from 15 to 50 weight-%. While the aquous solutions of the complex show only cylindrical micellar mesophase in a concentration range from 40 to 95 weight-%.

For morphological investigation of the lyotropic aggregation, both small angle and wide angle X-ray scattering experiments have been performed with the complex solution of 88 wt.% concentration and with the pure complex without water. As shown in Figure 3(a), the complex solution exhibits four Bragg reflections of 0.188 (strong), 0.325, 0.376 and 0.50 nm^{-1}, respectively. Bragg spacings in the ratio with 1: $\sqrt{3}$: $\sqrt{4}$: $\sqrt{7}$ indicate that the molecules organizes into cylindrical hexagonal structure with intercylinder distance of 6.14 nm.[11] While wide angle X-ray experiment gives only a broad halo. The X-ray scattering patterns and polarized optical microscopic observations indicate that the lyotropic mesophase exhibited by the complex solution is a monolayer hexagonal columnar structure. The pure complex without water displays the intense fundamental and its second and third harmonic reflections at Bragg spacings of 0.08 (strong), 0.267 and 0.250 nm^{-1}, respectively, as shown in Figure 3(b). The peak angles in the ratio with 1 : 2 : 3 indicate that the pure complex has a bilayer lamellar structure at room temperature.[11] Figure 4 shows the schematic representation of the structural transformation of the bilayer lamellar phase into the monolayer columnar hexagonal phase on addition of water.

The lamellar structure observed at lower water content in the rod-coil aquous systems and at the pure complex is still the most efficient packing of coils because the volume fraction of coil parts is not large enough. At higher water content or on addition of water in the case of the complex, however, the volume fraction of coil segments is increased by selective penetration of the water molecules into the hydrophilic coil domains and the system becomes unstable due to space crowding of the coil segments. Consequently, the lamellar structure of the rod-coil oligomer will break apart into cylindrical micelles as shown in Figure 4 and predicted by theoretical work.[1,4] This might explain qualitatively the lyotropic phase behavior of this rod-coil system. Work is in progress to examine in more detail the lyotropic aggregation behavior of rod-coil oligomers containing poly(ethylene oxide).

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New Cationic Ammine Complexes of Palladium (II) Having Phenyl and Substituted Phenyl Ligands

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Ammine complexes of late transition metals having organic ligands are rare.[1] Recently there has been a growing interest in the amido complexes of organotransition metals because of their potential applications for catalysis.[2] One class in this category is such complexes of late transition metals having unsubstituted amide ligand NH_2.[1d~e,3] One of the synthetic methods for preparations of such complexes is deprotonation from coordinated ammonia. Ammonia is a very weak acid (pK_a=33) and the N-H bond dissociation energy in ammonia is very high (107 kcal/mol).[4] Ammonia upon coordination to