Mz): 3.0, 3.6 (9 H, methyl). UV (CH_2Cl_2, nm): λ_{max} 272.

(13) MNDO calculation indicates that the high-frontier π-electrodensity in the p position of diphenyl sulfide is higher than those in the m position and the o position. This indicates that the 1,4-structure is preferentially formed by the electrophilical attack of the sulfonium cation to the p position of the benzene ring.

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A Novel Self-Organized, Nonbilayer-Type Assembly in a Composite Film Made of Cholesterol, Dimethyldioctadecylammonium, and Poly(styrenesulfonate)

Cholesterol is a common component of mammalian cellular membranes, and among lipids it has an outstanding chemical structure characterized by a relatively small hydrophilic group (3β-OH) and a bulky fused ring that is a stereochemically rigid flat group. For these reasons, the effects of cholesterol on phospholipid in model membrane systems have been widely studied with a variety of techniques.[1-3] The nature of the cholesterol–lipid mixture is not completely understood; however, one functional role of cholesterol has been suggested to be to control the fluidity of the lipid hydrocarbon chain and stabilize the membranes. Cholesterol is also known to affect the morphology of a lipid assembly[4] as well as the physical properties of lipid bilayers.

We studied the effect of cholesterol on the polyion complex films prepared from cationic lipid surfactants and anionic polymers, which are unique materials having physically stable bilayer structure,[5] in order to modify the physical property, e.g., the rigidity of the films. Then we found that, by adding a small amount of cholesterol, the structure of the polyion complex was changed from bilayer to nonbilayer at a limited concentration range accompanying a change in mechanical property. In this paper, we report the novel morphology found in the composite films as studied X-ray diffraction.

According to the procedure reported previously,[5] the polyion complexes, I and II, which have stoichiometric composition of surfactants and ionic polymers, were prepared from dimethyldioctadecylammonium bromide and sodium poly(styrenesulfonate) and from dimethyldihexadecylammonium bromide and sodium poly[2-(acrylamido)-2-methyl-1-propanesulfonate] (kindly supplied by Nittoh Co., Ltd., Tokyo), respectively. About 5% chloroform solutions of the mixture of cholesterol (Nakarai Chemicals Co., Ltd., Tokyo) and the polyion complexes were cast on flat glass plates siliconized with octadecyltrichlorosilane. When the solvent was evaporated and vacuum dried, transparent films with thickness of about 200 μm were obtained. The films were annealed in water at 60 °C for the formation of the novel morphology.

Calorimetric data as shown in Figure 1 were obtained using a Du Pont 9900 differential scanning calorimeter at a heating rate of 10 K/min. Samples were hermetically sealed in aluminum sample pans with the same weight of water as pieces of the films. Addition of 20 wt % cholesterol into the polyion complexes caused a broadening of the phase transition from the gel to liquid-crystalline state and a loss in the transition enthalpy accompanied by a decrease in the transition temperature. The DSC results suggest that cholesterol has a significant effect on the property of the polyion complexes, which was comparable to that on the phospholipid bilayer systems.[1]

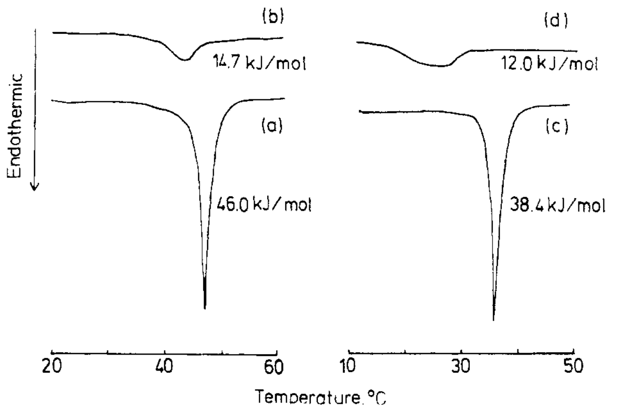

Figure 1. Differential scanning calorimetry of the composite films containing cholesterol. Heating rate: 10 K/min. (a) Dimethyldioctadecylammonium–poly(styrenesulfonate) film (I); (b) I containing 20 wt % cholesterol; (c) dimethyldihexadecylammonium–poly[2-(acrylamido)-2-methyl-1-propanesulfonate] film (II); (d) II containing 20 wt % cholesterol.

The X-ray photographs of the composite films were obtained by using Ni-filtered Cu Kα radiation (1.542 Å) for short spacings and V-filtered Cr Kα radiation (2.291 Å) for long spacings. The distance between the sample and X-ray film was 80 and 110 mm, respectively. The wide-angle X-ray diffraction of the film (I) containing cholesterol showed a broad ring having the interplannar distance of 4.6 Å (see Figure 3). This distance was longer than that of the "pure" polyion complex film (4.1 Å). The pure polyion complex film had also a meridional diffraction at 34 Å (the longest spacing) during X-ray irradiation parallel to the film surface. However, in the case of the polyion complex containing cholesterol, the equatorial diffraction appeared at 53 Å (the longest spacing) and 18 Å during X-ray irradiation parallel to the film surface. This suggests that the film containing cholesterol had a quite different higher order structure. The same features were observed in the case of II, except for the difference in long spacings (48 and 17 Å).

A stretched film was prepared in order to clarify the structure of the composite film. After immersing the film in water at 60 °C, the film was slowly stretched to about 250%. In Figure 4, the arrangement of the stretched sample and X-ray photographic films is shown. Orientation of the film caused a drastic change in the X-ray diffraction pattern but had virtually no effect on the long spacing. The direction of the diffraction pattern during X-ray irradiation along the *X* and *Z* axes was perpendicular to the stretch direction, as shown in parts a and b of Figure 4. On the contrary, the diffraction pattern during X-ray irradiation along the *Y* axis had no directionality (part c).

We propose a simple model of the supramolecular structure of the composite films as shown in Figure 3e. Considering the X-ray photographs in Figure 3 showing that the long spacing pattern had directionality in (a) but not in (c), a basic microstructure may be a rodlike assembly composed of ionic polymer, surfactant, and cholesterol. When the film was stretched mechanically the rods were directed in the same manner as the polymer main chain without changing long spacings. This fact supports the existence of microrods in the film. The original cast film has a macroscopic supramolecular assembly made up of the rodlike microassembly oriented in the direction perpendicular to the film surface.

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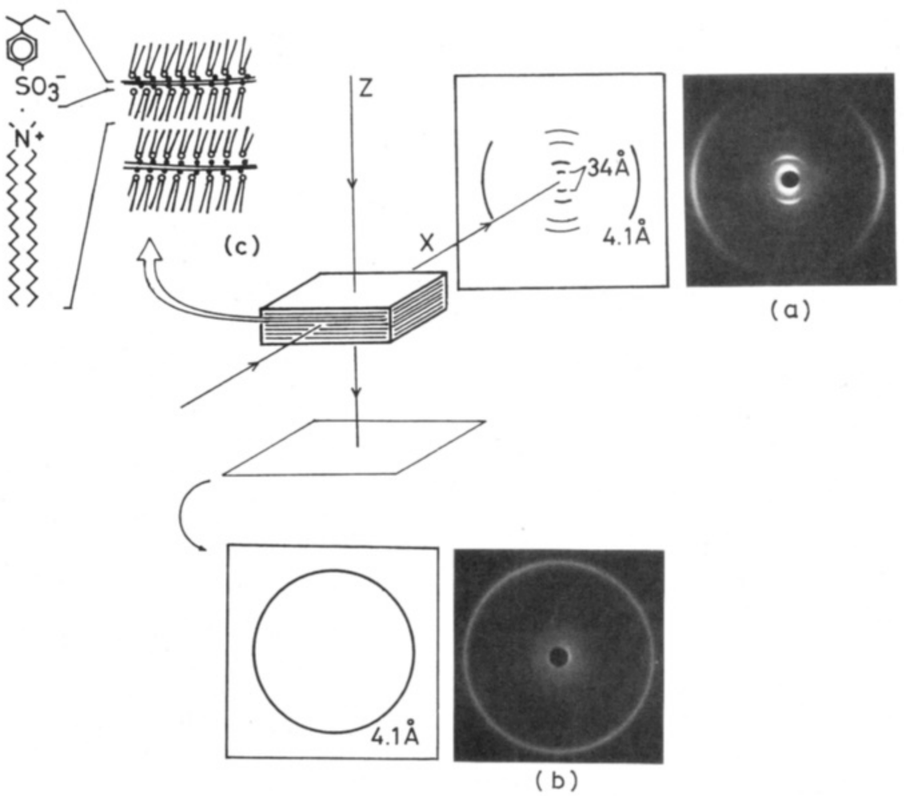

Figure 2. X-ray diffraction pattern of the polyion complex film of I and the schematic drawing of the structure (c). The photographs (a) and (b) were taken by Cu Kα irradiation of 2 h with a sample to film distance of 80 mm.

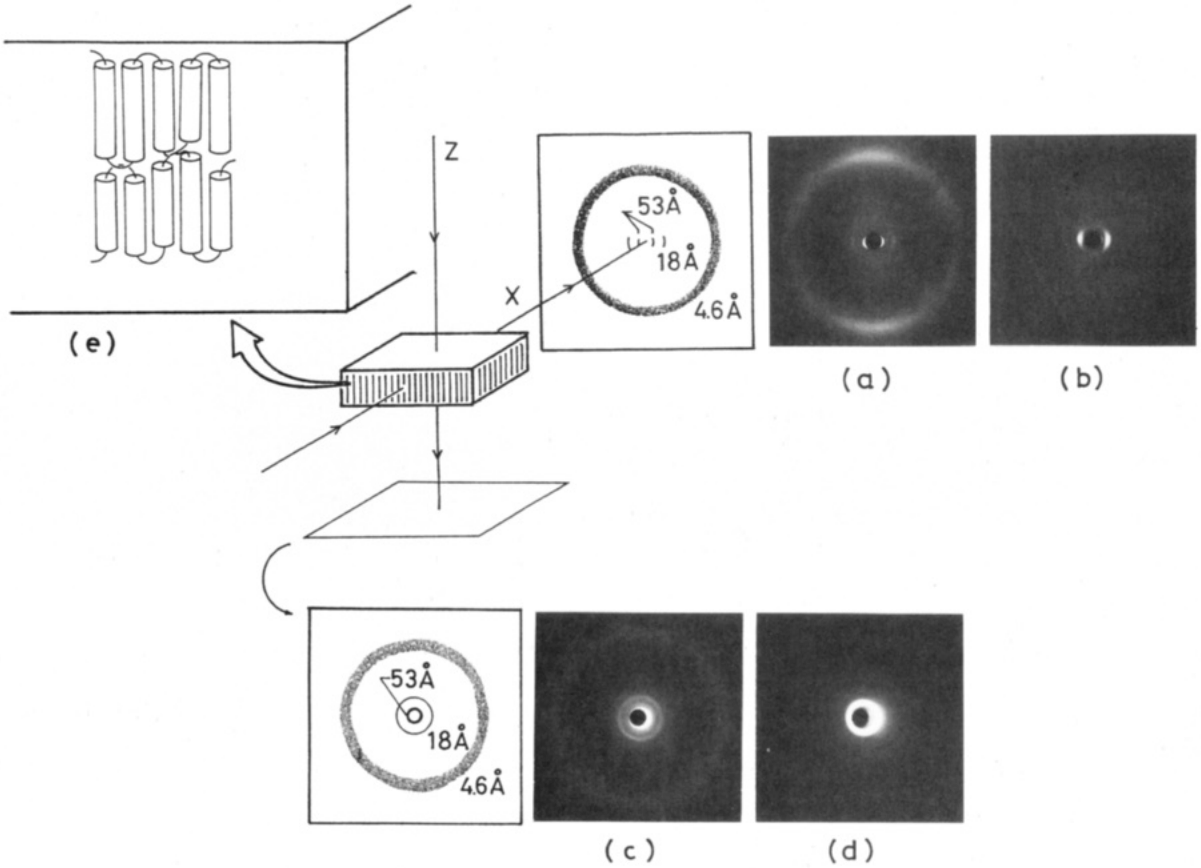

Figure 3. X-ray diffraction photographs of the composite films (I) containing 20 wt % cholesterol and proposed structure of the film (e). Each rod is connected with polymer chains. The microrods are oriented in the direction perpendicular to the film surface. The photographs (a) and (c) were taken by Cu Kα irradiation of 2 h with a sample to film distance of 80 mm. (b) and (d) were taken by Cr Kα irradiation of 3 h with a sample to film distance of 110 mm.

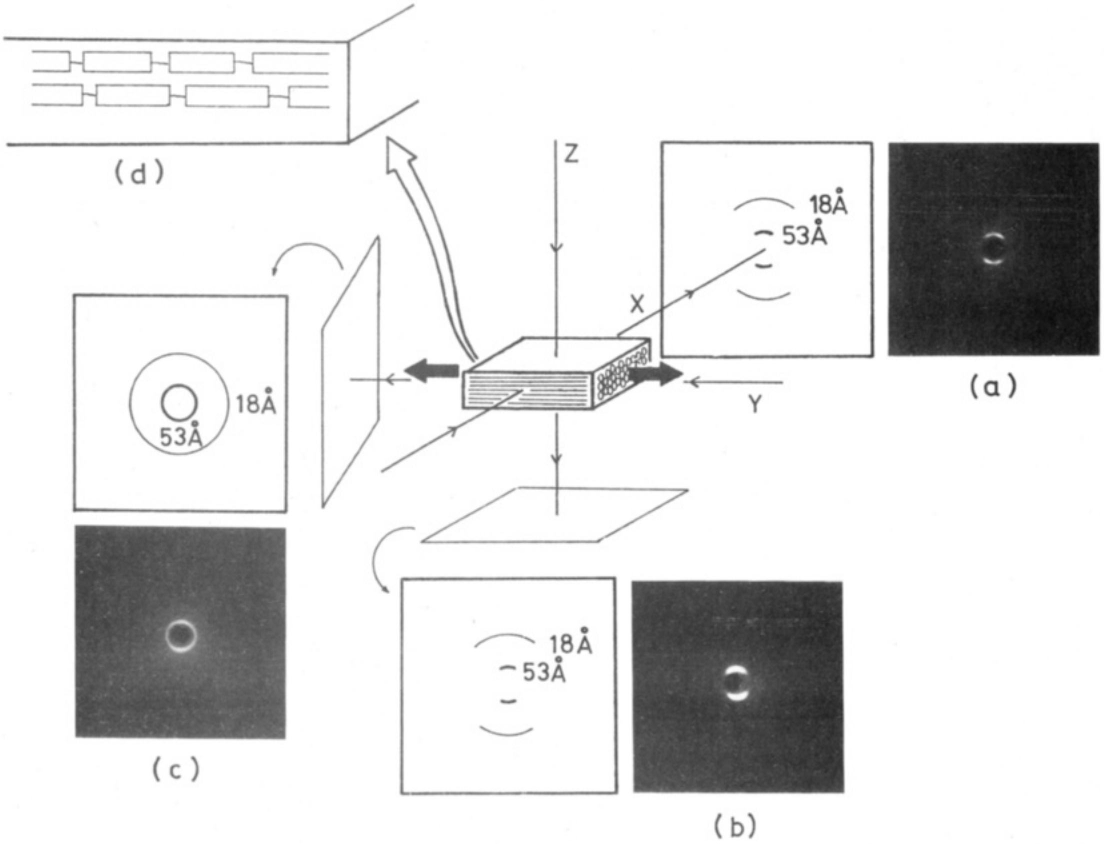

Figure 4. X-ray diffraction photographs of the uniaxially stretched film of I containing 20 wt % cholesterol. Bold arrows indicate the direction of the applied force on the film. The photographs were taken by Cr Kα irradiation of 3 h with a sample to film distance of 110 mm.

It may be difficult to explain such a complicated structure composed of multicomponents completely and precisely. Furthermore, even if the proposed model is correct, other questions concern why such a supramolecular assembly forms by self-organization, what are the molecular structures of the lipid surfactants, additives, and polymers, and what kind of their combination is required. In order to understand these phenomena, further investigation is required. However, this system may be important not only for a novel functional material having higher order structure that is not obtained by other techniques, e.g., Langmuir–Blodgett films, but also for a system to understand a nonbilayer-type assembly such as Hexagonal II.[6]

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Registry No. Cholesterol, 57-88-5; (dimethyldioctadecylammonium bromide)(sodium poly(styrenesulfonate)) (complex), 122846-15-5.

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