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Lyotropic mesophase formations of HPC/imogolite mixture

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SUMMARY

The mesophase formation was observed from the system of mixed organic polymer (hydroxypropyl cellulose) and inorganic polymer (imogolite) in acetic acid aqueous solution. The phase diagram of the mesophase formation was drawn as a function of imogolite content. The mesophase structure was found to change from the helicoidall arrangement of nematic sheets to the pile of pleated nematic sheets with increasing imogolite content.

INTRODUCTION

A compatible or miscible polymer pair is rare even in the blend systems of organic polymer pairs of similar chemical composition[1,2)]. No miscible polymer pair has been reported for inorganic and organic polymer pairs, although a considerable number of organic polymers have been blended in practice with inorganic materials.

Imogolite[3)] is a naturally occurring inorganic polymer composed of alumina-silicate (Al_2O_3•SiO_2•$2H_2O$), and has been characterized as a rigid rod molecule of 25Å in cross-sectional diameter and several thousands Å's in length[4,5)] with OH groups on its cylindrical surface (see Fig.1). Imogolite is dispersed molecularly in acetic acid aqueous solution by ultrasonic wave treatment. Since hydroxypropylcellulose (HPC) possesses also OH groups, HPC is expected to be miscible with imogolite in acetic acid aqueous solution.

The liquid crystal structure of imogolite is regarded as nematic or columnar structure[6,7)], while HPC is characterized as cholesteric of helicoidally arranged nematic sheets[8)]. Thus it is an attractive object to investigate the mesophase formation of the mixture of HPC and imogolite in acetic acid aqueous solutions. This report aims to establish the phase diagram for the system of HPC/imogolite mixtures to describe the phase transition from isotropic to anisotropic phase, and to characterize the mesophase structure.

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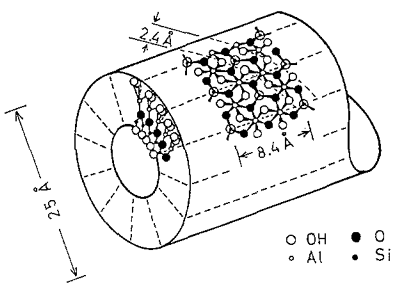

Fig.1 Schematic view of an imogolite cylinder.

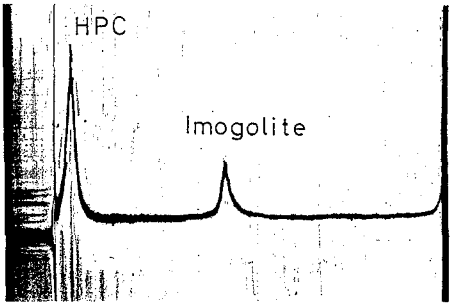

Fig.2 Sedimentation profile of imogolite/HPC mixture.

EXPERIMENTAL

The preparative method of imogolite solution was established in a previous report[4], as summarized briefly as follows: Imogolite gel purified from contamination in the raw material was dispersed in acetic acid aqueous solution (pH 3.0) by applying 20 kHz ultrasonic wave for one hour and the undissolved portion of this solution was separated by one-hour centrifugation at 10,000 rpm. The supernatant solution was concentrated to approximately 0.5 g/dl and used as a stock solution. The weight average molecular weight M_w of the imogolite sample was estimated from it's intrinsic viscosity $[\eta]$ (dl/g) as 1.1×10^6 by using the following equation[4]

$$[\eta]=(9.35\times10^{-12})M_w^2/\ln M_w \qquad (1)$$

This M_w value is equivalent to 1940 Å in terms of rod length of imogolite molecule.

Two HPC samples were purchased from Tokyo Kasei Co. Ltd., and their M_w were estimated from the intrinsic viscosity in ethanol at 25°C by using the following equation[9]

$$[\eta]=(2.6\times10^{-5})M_w^{0.915} \qquad (2)$$

The samples coded HPC-1 and HPC-2 have M_w of 8.47×10^5 and 9.53×10^4, respectively. The degree of substitution (DS) and the molar substitution (MS) in terms of hydroxypropyl groups of HPC were, respectively, 2.4 and 4.9 for both samples according to NMR measurements.

Stock solutions of low solute concentrations were prepared individually from HPC-1 and HPC-2. Then the solutions of HPC-1/imogolite and HPC-2/imogolite mixtures were prepared by mixing respective stock solutions with an appropriate ratio varying the imogolite composition. The solutions were concentrated by gradual evaporation of solvent until the partial anisotropic phase in the isotropic phase was first observed under a polarized optical microscope (referred to as the A point), and further until the transition was completed from the biphase to the entire anisotropic phase (referred to as the B point). Here a particular care was taken to maintain the pH value of solutions to 3.0 by occasional dialysis in order to prevent imogolite molecules from flocculating at higher pH's.

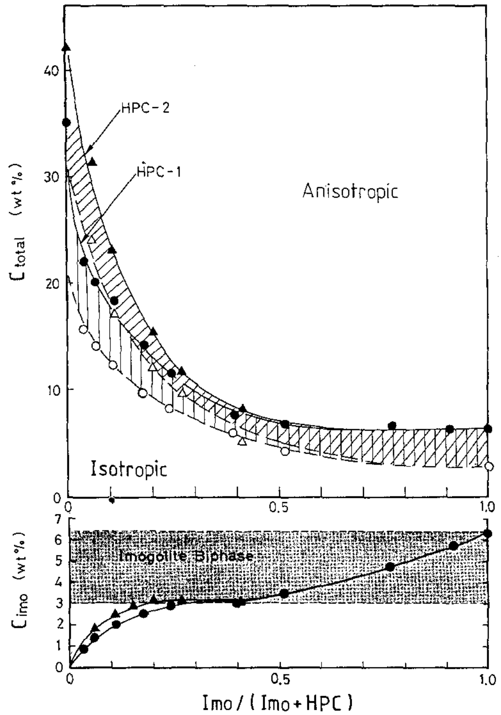

Fig.3 Phase diagram for acetic acid aqueous solution of imogolite/HPC-1 (○, ●) and imogolite/HPC-2 (△, ▲) mixture. White and black symbols denote A- and B-points, respectively.

RESULTS AND DISCUSSION

Both solutions of HPC/imogolite mixtures were optically clear, and no precipitation was observed when respective stock solutions were mixed with various imogolite compositions. The cast films of the mixture solutions were also transparent, and the scanning electron microscopy and X-ray scattering results showed no indication of the micro-domain structure due to phase separation into respective phases of component polymers. The results will be discussed in detail in a succeeding report[10]. Those observations suggest that imogolite molecules are miscible with HPC molecules.

Sedimentation transport analysis.

There is a possibility to form some complexes of imogolite and HPC through hydrogen bonds in dilute solutions. The dilute solution of 47/53 mixture of HPC-1/imogolite was examined by ultracentrifugal transport method, where the sedimentation boundary yielded two separate peaks assigned to imogolite and HPC-1, respectively , as shown in Fig.2.

Since each component peak is smeared by the Johnston-Ongston effect[11] in the mixture, the apparent sedimentation coefficients should be corrected for the values of single-component runs. Here an apparent sedimentation coefficient S_{app} is evaluated by

$$S_{app}=\ln(r_p/r_m)/\omega^2 t \qquad (4)$$

where r_p and r_m are the peak and meniscus position from a center of rotation, respectively, and ω and t are an angular velocity and rotational time, respectively. Both apparent sedimentation coefficients corresponding to respective component peaks were extrapolated to an infinite dilute concentration. The linearly extrapolated values are 29.0 S (Svedberg unit) for imogolite and 3.33 S for HPC-1, which are identical to those measured individually for respective components. Thus no specific complex is formed in the dilute solution of the system of HPC/imogolite mixture.

Phase diagram for mesophase formation of HPC/imogolite system.

A single-component solution of imogolite (M_w=1.1×10^6) separates first into the isotropic and anisotropic phase at the concentration of 3.0 wt.% (A point), and the entire solution becomes anisotropic above the concentration of 6.4 wt.% (B point). The anisotropic phase exhibited a typical fingerprint texture under a polarized optical microscope (POM), as shown in Fig.4(H) for an example. The liquid crystal structure is assigned to a nematic-like or columnar structure, as the fingerprint texture is caused by pleating nematic-like sheets[6,7)].

The liquid crystal structure of HPC in aqueous solution was characterized as cholesteric of helicoidally arranged nematic sheets, and the texture observed in the HPC-1 aqueous solution is shown in Fig.4(A). The B points of HPC-1 and HPC-2 samples were determined to be approximately 35 and 42 wt.%, respectively. Since imogolite and HPC are considered as a compatible pair, the co-mesophase formation of these polymers is expected.

As increasing the total concentration of HPC/imogolite mixture in acetic acid aqueous solution (pH 3.0), an anisotropic phase is observed by POM. The A and B points were determined as the lowest concentration to observe a partial anisotropic phase and as the highest concentration prior that the dark isotropic phase disappears under a POM, respectively. Based on the POM observation, the phase diagram was drawn for the isotropic-anisotropic phase transition of the mixture by varying the imogolite composition, as given in Fig.3. The sole imogolite concentrations C_{imo} in the mixture solutions at the B point were also plotted in the lower part of Fig.3. The total polymer concentration C_{tot} at the A and B points decreases sharply with increasing the relative imogolite content, and then remains almost constant till the relative imogolite concentration reaches 100%. That is, the A and B points in the intermediate range of the relative imogolite content are equal to those for a single imogolite solution in terms of the total polymer concentration in wt.%. The molecular weight dependence of the A and B points on the HPC component was observed only in the phase diagram at the region of imogolite content lower than about 40 wt.%. Here the higher B point was observed for the lower molecular weight HPC-2 sample. When the imogolite content exceeds 50 wt.%, no difference was observed in the mesophase formation behavior between both mixture systems of HPC-1/imogolite and HPC-2/imogolite, although there is about a 10-fold difference in terms of the molecular weight between HPC-1 and HPC-2 sample. The C_{imo} value was found always lower than 6.4 wt.%, which corresponds to the B point for the single-component solution of imogolite. The C_{imo} value increases at first till the imogolite content exceeds 20 wt.%, remains rather constant between 20-50 wt.%, and then increases again to the B point of the imogolite solution.

Both A and B points of HPC or imogolite solutions are suppressed by mixing another component in terms of the concentration of a single conponent. An example will be seen at a right hand side of Fig.4 where C_{imo} at the B point decreases sharply by mixing HPC. Thus the mesophase formation of the HPC/imogolite system is not only due to hard core repulsion, but also due to attractive interaction between imogolite and HPC molecules. The mixture may form a co-mesophase which will be discussed with X-ray diffraction results in a succeeding report[10)].

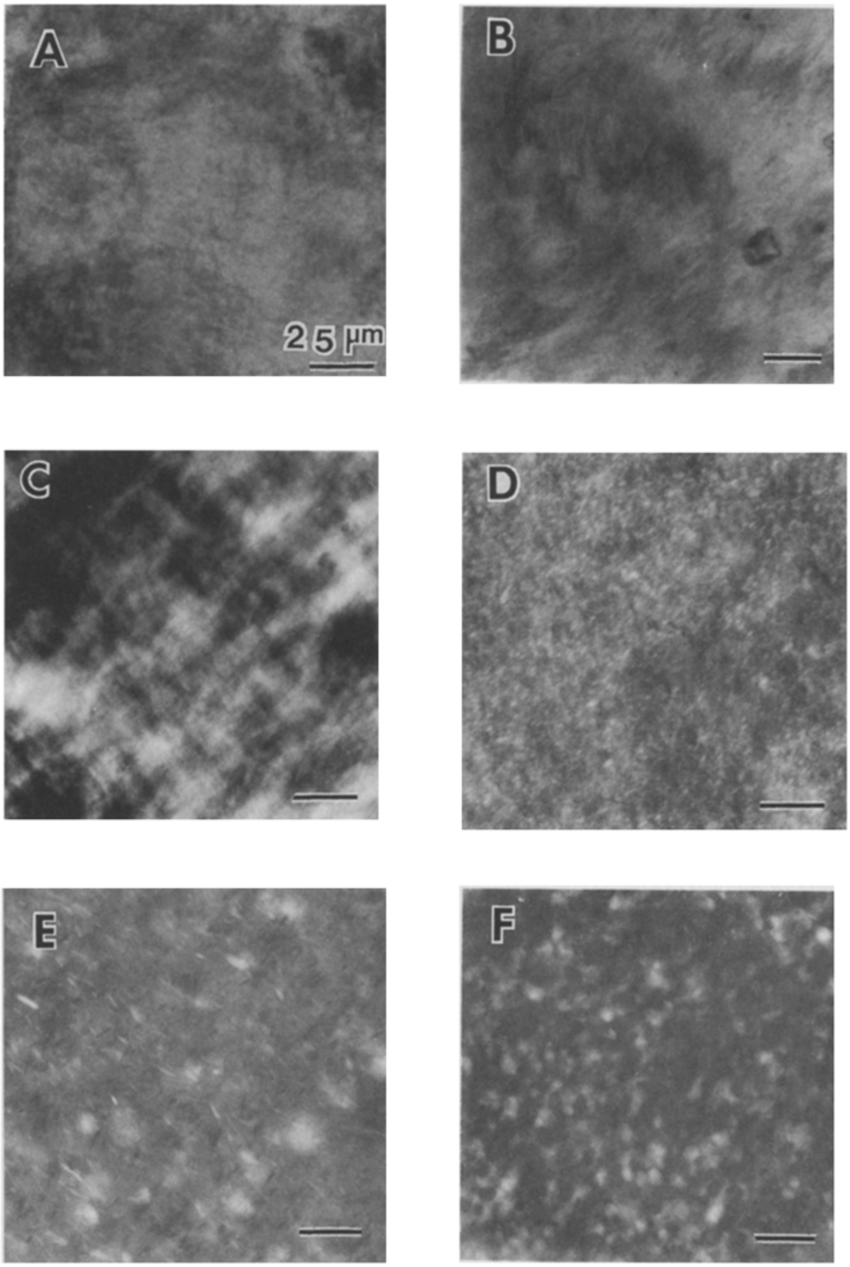

Fig.4 POM observation of the mesophase from the imogolite/HPC-1. The imogolite contents are varried 0% (single HPC) (A), 3% (B), 18% (C), 35% (D), 50% (E), 75% (F), 90% (G), and 100% (single imogolite) (H). A scale bar in each photograph represents 25 μm.

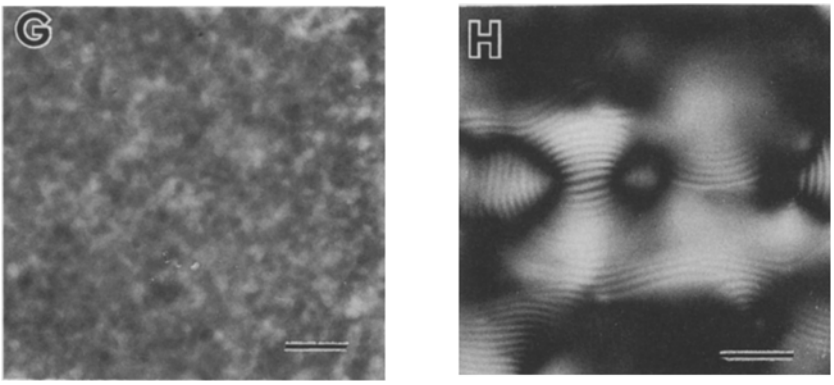

Fig.4 (continued.)

Fig.4 summarizes the POM photographs taken at respective B points of the mixture of HPC-1 and imogolite with various imogolite compositions. Here the observed textures shown in (B) and (C) are similar to the texture in (A) of the HPC-1 mesophase solution, while the other textures shown from (D) to (G) are different from either texture of a single-component mesophase of HPC or imogolite. The mesophase of the mixture containing 3 wt.% imogolite exhibited iridecent color, suggesting that a liquid crystal structure is cholesteric of helicoidally arranged nematic sheets in the mesophase with a lower imogolite content.

Characterization of HPC/imogolite mixture mesophase at lower imogolite content

The mesophase of HPC-2 in acetic acid aqueous solution is susceptive to a circular dicroism (CD) and UV absorption spectroscope. According to Shindo and Ohmi[12)], nonideal optics and electronics of CD spectrometers may result the artifacts which prevent a quantitative analysis of cholesteric liquid crystal. Thus, we used here a CD spectrometer only for the determination of a cholesteric helicoidal sign, and the helix pitch was monitored by the selective UV absorption position in terms of wave length.

Fig.5 shows the concentration dependence of the maximum absorption position of the UV spectroscopy from HPC-2 in acetic acid solutions (pH 3.0). A similar concentration dependence was observed in the HPC-water system[8)], where the shift of maximum absorption position was shifted to a lower wave length (equivalent to a smaller cholesteric pitch) by increasing the concentration. Based on this result, we prepared the mixed mesophase solutions with a fixed concentration of HPC-2 (64 wt.%) by increasing the imogolite content up to 2.0 wt.%. All of the mixture mesophases showed a negative CD spectra, suggesting right-hand helix, and exhibited sharp selective UV absorption spectra. The result is characteristic of a cholesteric structure, and Fig.6 summarizes the relationship between the maximum peak position of the selective UV absorption and imogolite content. The increase of the amount of imogolite content causes the cholesteric helicoidal pitch to broaden at first below the imogolite content of 0.5 wt.% and then narrow as far as the imogolite content dose not exceed 2.0 wt.%.

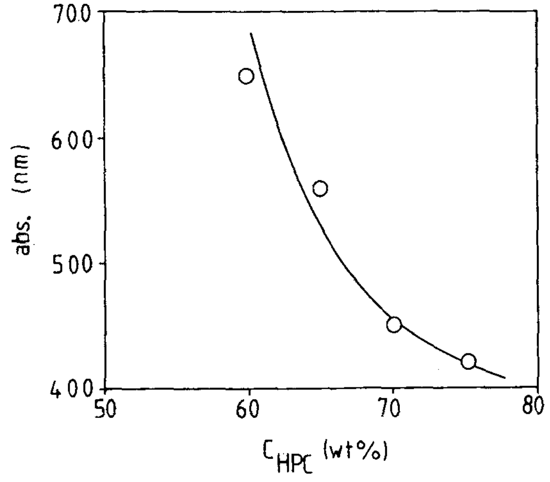

Fig.5 Cncentration dependence of the max. absorption position of the UV spectroscopy in the HPC-2 in acetic acid solution.

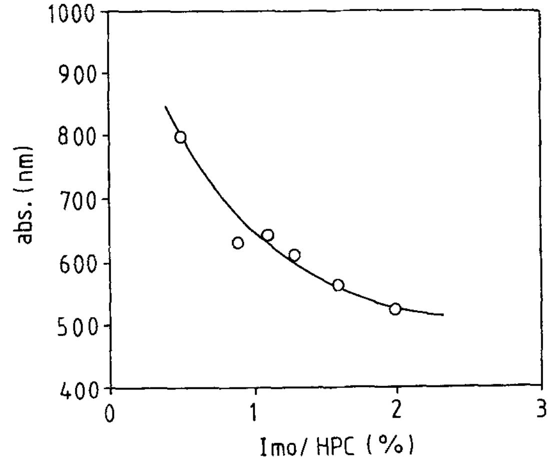

Fig.6 Imogolite-concentration dependence of the max. peak position of the UV absorption in the imogolite/HPC-2 system in acetic acid solution, where the HPC-2 concentration is fixed to 64 wt.%.

The mesophase of the mixture containing a small amount imogolite was confirmed to be cholesteric, and the helical pitch to change with imogolite content. As increasing the imogolite content further, the mesophase becomes less sensitive to CD or UV spectroscope, and no characteristic of the cholesteric structure was observed from the mesophase solution containing 30 wt.% imogolite. The POM textures given in (C) and (D) of Fig.4 may represent the above situation, where the mixture mesophase with 18 wt.% imogolite content exhibits a similar POM texture (C) as HPC-1 but not the mosophase (D) with 38 wt.%. Accordingly, it may be concluded that the mesophase structure of HPC/imogolite mixture is cholesteric of helicoidal arrangement of nematic sheets at lower imogolite content and the helicoidal ordering becomes less distinctive by increasing the imogolite content. The pleated sheet structure characteristic of pure imogolite mesophase[6,7] eventually takes over the helicoidal ordering when the imogolite content exceeds around 90 wt.%. The helicoidal arrangement of nematic sheets seems to be gradually destroyed by the pleating of the nematic sheets, and the mesophase of the mixture with imogolite content between 30 and 90 wt.% assumes a structure characterized by neither single-component mesophase of HPC nor imogolite.

CONCLUDING REMARKS

Inorganic polymer, imogolite, is compatible with HPC, and HPC/imogolite mixture solution forms mesophase as increasing the total polymer concentration. The mesophase structure of the HPC/imogolite system was found to be cholesteric of helicoidally arranged nematic sheets at lower imogolite content and the helicoidal pitch to decrease by increasing with a small amount of imogolite content.

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