

THE MORPHOLOGY AND STRUCTURE OF ETHYLCYANOETHYL CELLULOSE IN STYRENE AND POLYSTYRENE*

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ABSTRACT

Ethyl-cyanoethyl cellulose ((E-CE)C)/styrene solution could form anisotropic system when the concentration was high enough. The (E-CE)C/polystyrene(PS) multiphase polymer could be obtained by radical polymerization of the styrene in the solution. The (E-CE)C/PS multiphase polymer maintained both the crystalline structure of the (E-CE)C and the amorphous structure of the PS. In the multiphase polymer produced from the isotropic solution, however, the (E-CE)C formed spherulites and spread in the PS amorphous phase. While, in the multiphase polymer produced from the anisotropic solution, the (E-CE)C formed cylinderic crystalline aggregates. Moreover, the ordered lamellar texture was also observed in the multiphase polymer produced from the anisotropic solution.

INTRODUCTION

The investigation of polymer liquid crystals has been quickly developed in the past decade. In 1976, Werbowyj and Gray found^[1] that there was a cholesteric mesophase in the concentrated hydroxypropyl cellulose (HPC)/water solution. Since then, it has been found that cellulose and many of its derivatives can form liquid crystals^[2-4]. Ethylcyanoethyl cellulose((E-CE)C), which is a cellulose derivative with two different ether groups, can form cholesteric mesophase in many organic solvents^[5].

It has been found that lyotropic mesophase can be fixed by polymerization of solvent in the polypeptide/olefinic monomer and the HPC/olefinic monomer solutions^[6-8]. By this method, the electron microscopy can be used to study the structures of cholesteric mesophase. At the same time, this method also provides a possibility to produce the materials which have some specific properties.

The (E-CE)C can be dissolved in the styrene very well and forms mesophase when the concentration is over the critical concentration. The (E-CE)C/PS multiphase polymer can be prepared by radical polymerization of the styrene in the solution. In this report we study the phase transition and the texture of the (E-CE)C/styrene mesomorphic solutions and the morphological and structural characteristics of the (E-CE)C/PS multiphase polymers by using refractometer, polarizing microscopy, X-ray diffraction and electron microscopy.

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EXPERIMENTAL

The (E-CE)C was obtained by reaction of ethyl cellulose and acrylonitrile. The degree of substitution for ethyl was about 2.09 and for cyanoethyl was about 0.56 and the $\overline{M}_n$ was about 38,000. The styrene (The First Reagent Factory in Shanghai) and the azobisisobutyronitrile (AIBN) (The Fourth Reagent Factory in Shanghai), which were not refined before they were used, were chemically pure reagents. The (E-CE)C was mixed with the styrene at room temperature and the solution was sealed up in the test-tube. The sample was held at 5 °C for over 48 hours before it was used. The concentration of the solution was 0.2 — 1.0 wt. /wt.

The (E-CE)C was mixed with the styrene which contained the 0.0025 g/ml AIBN at room temperature and the solution was held for 48 hours at 5 °C. Then, the solution was sealed up in the glass cell (25 × 15 × 1.8 mm) by solid wax and kept at 50 °C for 48 hours and the styrene in the solution was polymerized. The white and opaque (E-CE)C/PS multiphase polymer was obtained.

The mean refractive index of the (E-CE)C/styrene solution was measured by an Abbe refractometer (2WA, Shanghai Optic Instrument Factory, Shanghai, China) at room temperature. The texture of the mesomorphic solution was observed by a polarizing microscope (Leitz, ORTHOPLAN-POL). The sample was heated on a hot stage (Leitz, Microscope Heating stage 350) at about 1 K/min. and observed by the polarizing microscope to determine the critical temperature T_c .

The crystalline structure of the multiphase polymer was studied by an X-ray spectrometer (TUR-M62, East Germany). The scanning electron microscope (S-430, Hitachi Ltd., Tokyo, Japan) and the transmission electron microscope (TEM-100CX/II, JEOL Ltd., Tokyo, Japan) were used to observe the biphasic structure of the multiphase polymers.

RESULTS AND DISCUSSION

The variation of the mean refractive index of the solution with the concentration can reflect the phase transitions of the mesomorphic solution^[9]. Fig. 1 shows the relationship between the mean refractive index and the concentration of the (E-CE)C/styrene solution. It indicates that with increasing concentration the solution changes from isotropic state to anisotropic one through a biphasic state. The critical concentration C_1^+ , at which the mesophase begins to appear, is about 0.68 wt. /wt and C_2^+ , at which the isotropic phase completely disappears, is about 0.85 wt. /wt.

With the observation by the polarizing microscope, it is also found that at room temperature, the (E-CE)C/styrene solution is isotropic when the concentration is under 0.70 wt. /wt. But when the concentration is over that, the anisotropic phase begins to appear in the solution. Fig. 2 is a simple polygonal texture, which indicates that the liquid crystal in the (E-CE)C/styrene solution is cholesteric^[10].

When the mesomorphic solution is heated and observed by the microscope with a hot stage, it changes from anisotropic state to isotropic one at the critical temperature

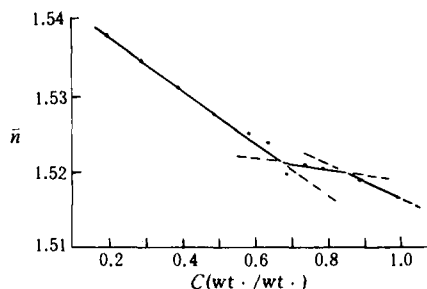


Fig. 1 The mean refractive index vs. the concentration of the (E-CE)C/styrene solution, 22 °C.

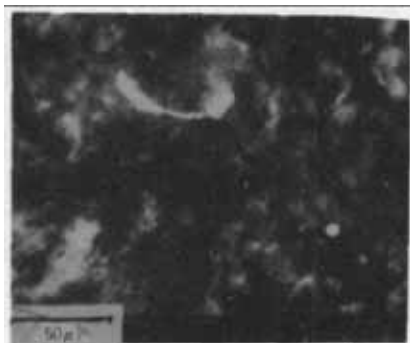


Fig. 2 Polarized micrograph of the 1.00 wt./wt. (E-CE)C/styrene solution, 25 °C.

T_c . The T_c of the 0.90 wt./wt. and 1.00 wt./wt. (E-CE)C/styrene solutions is 91 °C and 107 °C respectively. Generally speaking, the higher the concentration of the mesomorphic solution, the higher the critical temperature.

For the (E-CE)C/styrene solution, the structures of the solution can be fixed by polymerization of the solvent because the solvent, styrene, is an olefinic monomer. The existence of mesophase in the solution is concerned with both the temperature and the concentration. Therefore, the (E-CE)C/PS multiphase polymer can be obtained from both isotropic and anisotropic solution by changing the temperature and the concentration.

Fig. 3 is the X-ray diffraction spectra of the (E-CE)C, PS and the multiphase polymers which are produced in different conditions. It can be seen that the (E-CE)C is semicrystalline polymer, which has two crystalline peaks at the diffraction angle $\theta = 4.5^\circ$ and 5.5° and an amorphous peak at $\theta = 10.5^\circ$ in its X-ray spectrum. The PS is amorphous and in its X-ray spectrum, there are two amorphous peaks when the diffraction angle is about 5.0° and 9.6° . The spectra of the multiphase polymers in Fig. 3 show that the (E-CE)C/PS multiphase polymers keep both the semicrystalline characteristics of the (E-CE)C and the amorphous characteristics of the PS. In the spectra of the multiphase polymers, there are two crystalline peaks when the diffraction angle is about 4.5° and 5.5° and an amorphous peak when the diffraction angle is about 9.6° . Furthermore,

the multiphase polymers produced from both isotropic and anisotropic solutions have the same X-ray diffraction spectrum. This means that the (E-CE)C/PS

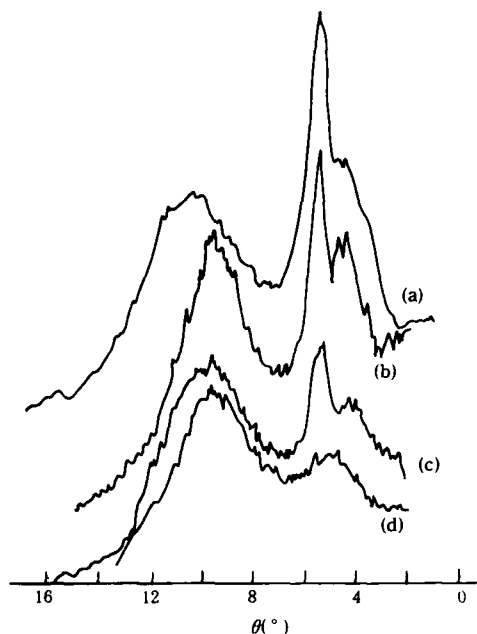


Fig. 3 X-ray diffraction spectra of (a) (E-CE)C (b) multiphase polymer produced from isotropic solution, (c) multiphase polymer produced from anisotropic solution and (d) PS.

This means that the (E-CE)C/PS

multiphase polymer produced from isotropic solution is the same as that produced from anisotropic solution in the crystalline structure and the amorphous structure.

In the biphasic structure, however, the multiphase polymer produced from isotropic solution is much different from that produced from anisotropic solution. From Fig. 4 it can be seen that the broken section of the PS is smooth and homogeneous. But in the multiphase polymer produced from isotropic solution, the (E - CE)C forms spherulites and spread randomly in the PS amorphous phase. The diameter of the spherulites is about $0.1 - 2.0 \mu\text{m}$. In the multiphase polymer produced from anisotropic solution, however, there is a partly oriented lamellar structure in the broken section (Fig. 4c). The oriented range is about $50 - 100 \mu\text{m}$ and the orientation directions are different in different zones. The lamellar structure can be seen more clearly in Fig. 5. The thickness of the lamellae is about $0.1 - 1.0 \mu\text{m}$. At the same time, the picture shows that in the lamellar structure, there is no clear phase separation between the (E - CE)C and the PS.

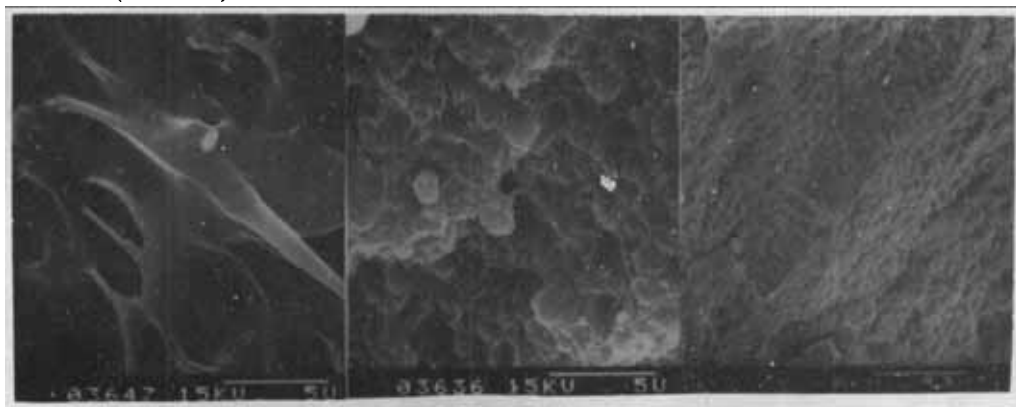


Fig. 4 Scanning electron micrographs of (a) PS. (b) multiphase polymer produced from isotropic solution and (c) multiphase polymer produced from anisotropic solution.

The finer structure of the multiphase polymers can be observed by the transmission electron microscope. Fig. 6 is the transmission electron micrographs of the two slices cut from the across sections, of which one is parallel to the glass plane and the another is perpendicular to it, for the (E - CE)C/PS multiphase polymer produced from isotropic solution. It can be seen that the (E - CE)C crystalline phase is not homogeneous in both size and distribution. The difference in size can be as large as 20 times. But in both cross sections, the shape of the (E - CE)C crystalline phase is nearly circular. Therefore, the result suggests that the (E - CE)C crystalline phase in the multiphase polymer produced from isotropic solution is spheroidal in space.

The biphasic structures can also be observed by the transmission electron microscope in the multiphase polymer produced from anisotropic solution (Fig. 7). In one section which is parallel to the glass plane, the shape of the (E - CE)C crystalline phase is circular (Fig. 7a),

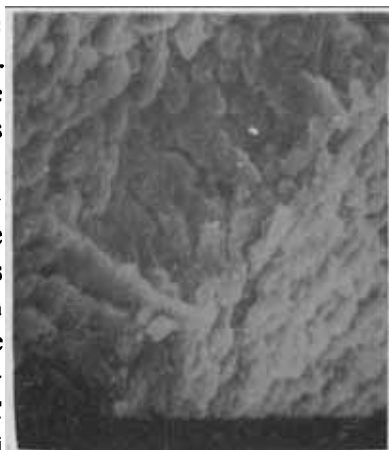


Fig. 5 Scanning electron micrograph of the multiphase polymer produced from anisotropic solution.

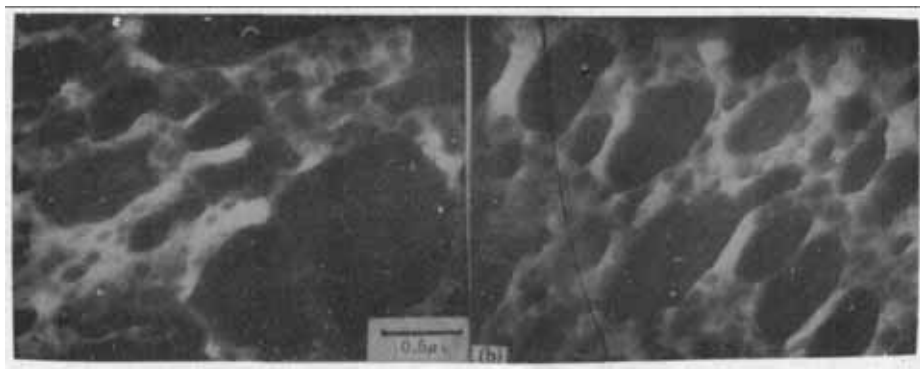


Fig. 6 Transmission electron micrographs of the multiphase polymer produced from isotropic solution, the section is (a) parallel and (b) perpendicular to the glass plane.

but in another section which is perpendicular to the glass plane, it is tripped (Fig. 7b). Therefore, the result suggests that the $(E-CE)C$ forms cylindric crystalline aggregates in the multiphase polymer produced from anisotropic solution. The diameter of the cylindric aggregates is about $0.1 - 0.2 \mu\text{m}$ and the length of them, which can be varied from about $0.1 \mu\text{m}$ to $0.5 - 1.0 \mu\text{m}$, is much different.



Fig. 7 Transmission electron micrographs of the multiphase polymer produced from anisotropic solution, the section is (a) parallel and (b) perpendicular to the glass plane.

The morphology and structure of the multiphase polymer is related to the structures of the $(E-CE)C$ /styrene solution. In the isotropic solution, the $(E-CE)C$ is a random coil structure. In the $(E-CE)C/PS$ multiphase polymer produced from isotropic solution, therefore, the $(E-CE)C$ forms spherulites. In the anisotropic solution, however, the $(E-CE)C$ chains order and orient to form the layers of ordered polymer chains, which further arrange to form the helical structure in cholesteric phase. From the texture of the $(E-CE)C$ /styrene mesomorphic solution (Fig. 2), it can be known that the layers of ordered polymer chains are nearly parallel to the glass plane and the axis direction of the helicoids, which are composed of the layers of ordered $(E-CE)C$ chains, is nearly perpendicular to the glass plane. Because the circumference of round is the smallest, the layers of ordered polymer chains are circular in order to have the smallest interface between the ordered domains. This means that in space the helicoid actually is cylindric. In the $(E-CE)C/PS$ multiphase polymer produced from anisotropic solution, therefore, the $(E-CE)C$ forms cylindric crystalline aggregates.

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