

Viscometric Behavior of Ternary Concentrated Solutions of Hydroxypropyl Cellulose and Ethyl Cellulose in *m*-Cresol

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SYNOPSIS

The shear viscosity of blend solutions of hydroxypropyl cellulose (HPC) and ethyl cellulose (EC) in *m*-cresol (both HPC/*m*-cresol and EC/*m*-cresol systems form lyotropic liquid crystals) was determined by cone-plate-type and capillary-type viscometers. The textures for the same systems at rest and undergoing shear were also observed with a polarized microscope.

At shear rate of 1 s^{-1} , viscosity exhibited a maximum and a minimum with respect to temperature, and this suggested that the phase of the matrix dominated the viscometric behavior of the ternary systems; the blend composition dependence of the viscosity was not additive, and this suggested that HPC and EC were immiscible. At relatively high shear stress, the blend composition dependence of the viscosity greatly depended on the total polymer concentration of the solutions and was quite different from that at low shear rate; the texture of the anisotropic solutions was also different from that at low shear rate. Our findings suggested that the dependence of viscosity on shear and concentration for pure HPC solution was different from that for pure EC solution.

INTRODUCTION

This article is a sequel of our previous paper on the rheology of hydroxypropyl cellulose (HPC) in *m*-cresol.¹ *m*-Cresol acts as a cosolvent for the blend of HPC and ethyl cellulose (EC). Both HPC/*m*-cresol and EC/*m*-cresol systems formed lyotropic liquid crystals at ca. 20 and ca. 30 wt % at room temperature.¹ *m*-Cresol is a better solvent than acetic acid, which acts as a cosolvent for HPC and EC,² because *m*-cresol has a higher boiling point and because the difference between the critical concentrations (C_a) for HPC/*m*-cresol and EC/*m*-cresol is relatively great. Therefore, our system (HPC/EC/*m*-cresol) is a good model for investigating characteristics of a blend system containing at least a liquid crystal. The phase transformations of the ternary systems containing liquid crystal-forming cellulose derivatives have been investigated by Marsano et al.,³ Seurin et al.,^{4,5} Laivins and Sixou,⁶

Siekmeyer et al.,⁷ and Wang et al.,⁸ but there are few rheological data on the ternary systems.⁹ The viscometric behavior of the ternary system is expected to depend on the polymer concentration and blend composition.¹⁰

In this study, we prepared the blend solutions of HPC and EC in *m*-cresol, which have almost the same weight-average molecular weight, and determined the blend composition dependence of shear viscosity for isotropic, biphasic, and single-phase anisotropic solutions by using two kinds of viscometer: a cone-plate type and a capillary type. The textures of the ternary solutions at rest and undergoing shear were also observed with a polarized microscope.

EXPERIMENTAL

Samples

HPC and EC were of commercial reagent grade (Tokyo Kasei Kogyo Co.). Weight-average and number-average molecular weights (\bar{M}_w and \bar{M}_n) for

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HPC were 19.2×10^4 and 8.9×10^4 and those for EC were 18.7×10^4 and 5.86×10^4 . Molar substitution of HPC was 3.48 and degree of substitution of EC was 2.49. In our previous paper,¹ we used another HPC, of which \bar{M}_w and \bar{M}_n were 11.7×10^4 and 5.2×10^4 and MS was 4.25. In this study, we chose the HPC sample noted above because molecular weights of HPC and EC were almost the same.

HPC and EC powders were used after vacuum-drying at 60°C for 24 h. *m*-Cresol was of commercial reagent grade (Wako Pure Chemical Ind.).

Preparation of Concentrated Blend Solutions of HPC and EC

Given compositions of blends of HPC and EC were prepared and then *m*-cresol was added. The total polymer concentrations (HPC + EC) were 20, 25, 35, and 40 wt %. The compositions for each concentration are shown in Table I. The blend compositions are denoted by the letters HPC/EC followed by numbers indicating the wt % of HPC and EC. The ternary system was vigorously stirred by a glass rod once a week to distribute the components through the system and stored in the dark for 5–6 months at room temperature.

Viscometry

Two types of viscometer were employed. A cone-plate-type viscometer was used for determining the temperature dependence of shear viscosity at a shear rate of 1 s^{-1} . The details of the determinations have been described in our previous papers.^{11,12} A capillary viscometer (constant load type) was used for determining the shear viscosity at given shear stresses at $25 \pm 1^\circ\text{C}$. To eliminate the end effect,¹³ a long die was used. The diameter was 0.5 mm and the length-diameter ratio (L/D) was 100. The difference between true stress estimated using our previous data

of the Bagley coefficient for the HPC/*m*-cresol¹ and EC/*m*-cresol¹⁴ systems and apparent stress calculated in the usual manner was better than 4%. Consequently, our die is reasonably long enough to eliminate the end effect. The capillary rheometry, except for the use of a long die, has been described in detail elsewhere.^{13,14}

Optical Microscopy

An Olympus microscope equipped a camera was used to observe the liquid crystalline texture in the solutions between two glass plates. The glass plates were cleaned with cotton soaked in acetone. Each glass plate containing a 300 μm deep cavity was prepared by two adhesive tapes placed parallel to each other on both sides of the glass plate. The texture of the solutions was observed after storing them in the dark at room temperature for 1 week. The textures at rest and at shear rate of ca. 1 s^{-1} were observed. The texture at the latter conditions was observed by sliding the upper plate at a given rate.

RESULTS AND DISCUSSION

Behavior at a Shear Rate of 1 s^{-1}

Figure 1 shows the dependence of viscosity on the reciprocal of absolute temperature for the 20, 25, 35, and 40 wt % solutions as a function of blend composition. For the 20 wt % solutions, the logarithm of the viscosity increased linearly with increasing $1/T$ regardless of blend composition as in a normal isotropic solution. For the 25 wt % solutions, HPC-rich solutions exhibited a maximum and a minimum of viscosity at intrinsic temperatures (those temperatures designated $1/T_{\text{max}}$ and $1/T_{\text{min}}$).^{11,12} For the 35 and 40 wt % solutions, contrary to the 25 wt % solutions, EC-rich solutions exhibited a maximum and a minimum. For each concentration, the vis-

Table I The Blend Composition for Each Total Polymer Concentration

| Polymer Concentration (wt %) | Blend Composition ^a (HPC/EC in wt %) | | | | | |
|------------------------------|---|-------|-------|-------|-------|-------|
| 20 | 0/100 | 15/85 | 30/70 | 50/50 | 70/30 | 100/0 |
| 25 | 0/100 | 15/85 | 30/70 | 50/50 | 70/30 | 100/0 |
| 35 | 0/100 | 15/85 | 30/70 | 50/50 | 70/30 | 100/0 |
| 40 | 0/100 | 15/85 | 30/70 | 50/50 | 70/30 | 100/0 |

^a For capillary rheometry, there were no data for the blend composition of 15/85.

cosity for pure EC was greater than that for pure HPC.

From the viscometric behavior of binary systems (a liquid crystal-forming polymer and a solvent), we can estimate the phase of solutions.^{11,12} The linear region in the curves shows the single-phase regardless of isotropic or anisotropic phase: At temperatures above T_{\max} , the solutions are isotropic; at temperatures below T_{\min} , the solutions are anisotropic; and between T_{\max} and T_{\min} , the solutions are biphasic. The meanings of isotropic, biphasic, and single-phase anisotropic binary solutions were definite. However, for the ternary systems (two polymers that form liquid crystals and a cosolvent), the phase of those solutions was not so simple as that for the binary systems. The isotropic solution means (a-1) an isotropic single phase and (a-2) isotropic HPC and isotropic EC; the biphasic solution means (b-1) isotropic EC and anisotropic HPC, (b-2) isotropic HPC and anisotropic EC, (b-3) isotropic EC and biphasic HPC, (b-4) biphasic EC and isotropic HPC, and (b-5) biphasic EC and single-phase anisotropic HPC; and the single-phase anisotropic solution means (c-1) single-phase anisotropic EC and single-phase anisotropic HPC and (c-2) anisotropic single-phase (HPC miscible EC).

In a strict sense, (a-2) and (c-1) solutions are biphasic. However, in this study, for comparison with the binary systems, we identify for convenience the meanings of isotropic, biphasic, and single-phase anisotropic solutions as noted above. In our solutions prepared, (a-1) and (c-2) solutions were not observed because HPC and EC seemed to be immiscible and (b-2) and (b-4) solutions could not be prepared because C_a for HPC was not greater than that for EC.

As noted in the Introduction, the critical concentrations C_a at 25°C were ca. 20 wt % for HPC/*m*-cresol and ca. 30 wt % for EC/*m*-cresol.¹ Then, for the 20 wt % solutions, HPC/*m*-cresol and EC/*m*-cresol systems were both isotropic; for the 25 wt % solutions, HPC/*m*-cresol was biphasic and EC/*m*-cresol was still isotropic; for the 35 wt % solutions, HPC/*m*-cresol was single-phase anisotropic and EC/*m*-cresol was biphasic; and for the 40 wt % solutions, HPC/*m*-cresol and EC/*m*-cresol were both single-phase anisotropic.

The phase of the solutions noted above could be confirmed by polarized microscopy. Figure 2 shows the typical polarized microphotographs of the solutions. For the 20 wt % solutions, we could observe no texture. Figure 2(a) shows the texture for 25 wt % solution: HPC/EC: 15/85. The isolated spherical

domains of liquid crystalline HPC were suspended in the matrix of isotropic EC. The typical fingerprints were seen in the HPC domains. Figure 2(b) shows the texture for the 35 wt % solution: HPC/EC: 70/30. Spherical domains of EC were observed in the background of the liquid crystalline HPC phase. It is noteworthy that the texture of liquid crystalline EC domains is quite different from that of HPC domains. This suggests that our system is a suitable model for investigating the blend of liquid crystals because we can easily distinguish the domains of HPC and EC from only a polarized microscopical approach. Figure 2(c) shows the texture for the 40 wt % solution: HPC/EC: 70/30. The texture was almost the same as that for the 35 wt % solution shown in Figure 2(b), and EC domains were observed in the HPC liquid crystalline matrix. Figure 2(d) shows the texture for the 40 wt % solution: HPC/EC: 100/0. This is the typical texture for lyotropic cholesteric liquid crystals and we can see the fingerprints.

The textures shown in Figure 2 were almost the same as those reported by Ambrosino et al.² for the HPC/EC/acetetic acid system. They have described the phase diagram for their ternary system. The cosolvent and critical concentrations for their system were different from those for ours; however, the phase diagrams for their and our systems are expected to be almost the same. Here, in comparison with the phase of our solutions, on the basis of observation with a polarized microscope at room temperature, and the viscometric behavior shown in Figure 1, we can estimate the phase of our solutions in each temperature range. The 20 wt % solutions exhibited simple behavior for each blend composition. They were isotropic and exhibited no maximum and minimum. The 25 wt % solutions with an HPC-rich composition were single-phase anisotropic at temperatures below T_{\min} , were biphasic between T_{\min} and T_{\max} , and were isotropic at temperatures above T_{\max} . For the 35 and 40 wt % solutions, HPC-rich solutions were single-phase anisotropic in our experimental temperature range, whereas the phase of the EC-rich solutions changed in the temperature range.

Our findings suggest that it depends mainly on the phase of matrix whether the viscosity increases or decreases with increasing temperature. This means that the temperature dependence of the viscosity for liquid crystalline solutions reflects the phase transformation regardless of the binary or ternary system; the phase is single-phase anisotropic at temperatures below T_{\min} , biphasic between T_{\min}

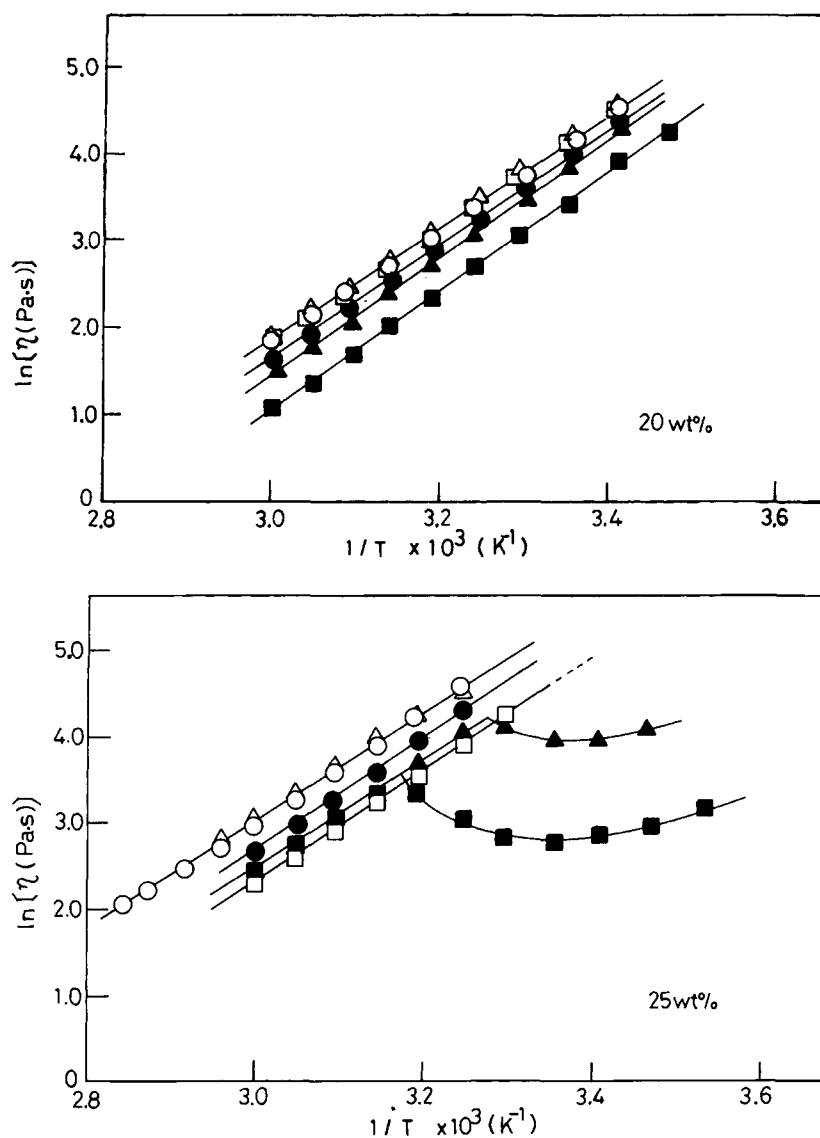


Figure 1 Viscosity (shear rate of 1 s^{-1}) vs. the reciprocal of absolute temperature for solutions of (a) 20 wt %, (b) 25 wt %, (c) 35 wt %, and (d) 40 wt %; blend composition (HPC/EC): (○) 0/100; (△) 15/85; (□) 30/70; (●) 50/50; (▲) 70/30; (■) 100/0.

and T_{\max} , and isotropic at temperatures below T_{\max} . However, the estimation of the phase of solutions from viscometry was interpreted with caution. The textures of solutions at rest (polarized microscopy) and undergoing shear (viscometry) were strictly not the same. Figure 3 shows the texture for the 25 wt % solution: HPC/EC: 15/85 at shear rate of ca. 1 s^{-1} . We can compare the textures at rest [Fig. 2(a)] and undergoing shear. The domains of HPC deformed to the direction of shear. Similar behavior has been reported by Ambrosino et al.² for the HPC/

EC/acetic acid system. After prolonged shearing, the domains disappeared. Therefore, our data on the viscometric behavior at steady state, strictly speaking, did not correspond to the findings with the polarized microscope at rest.

Figure 4 shows the dependence of the viscosity on blend composition for the 20, 25, 35, and 40 wt % solutions at given temperatures. In these figures, we denoted the phase of the solutions estimated. Open marks are isotropic, half-marks are biphasic, and full marks are single-phase anisotropic. Clearly,

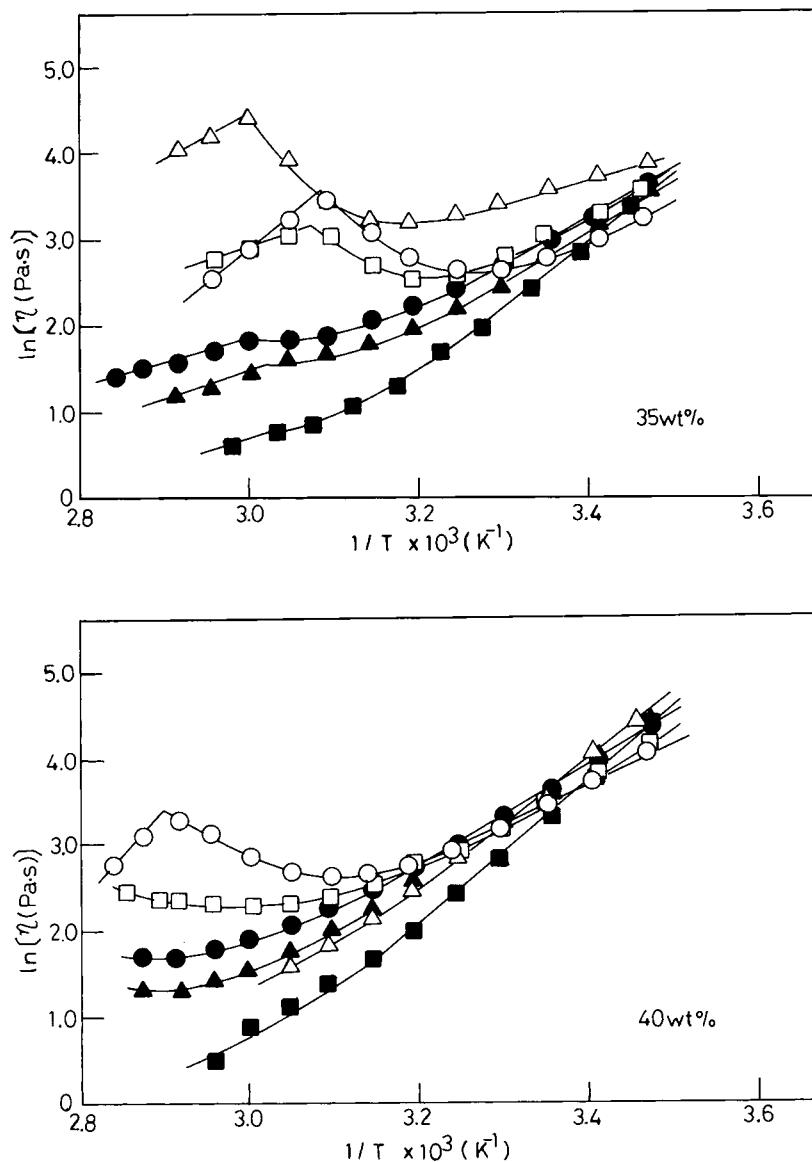


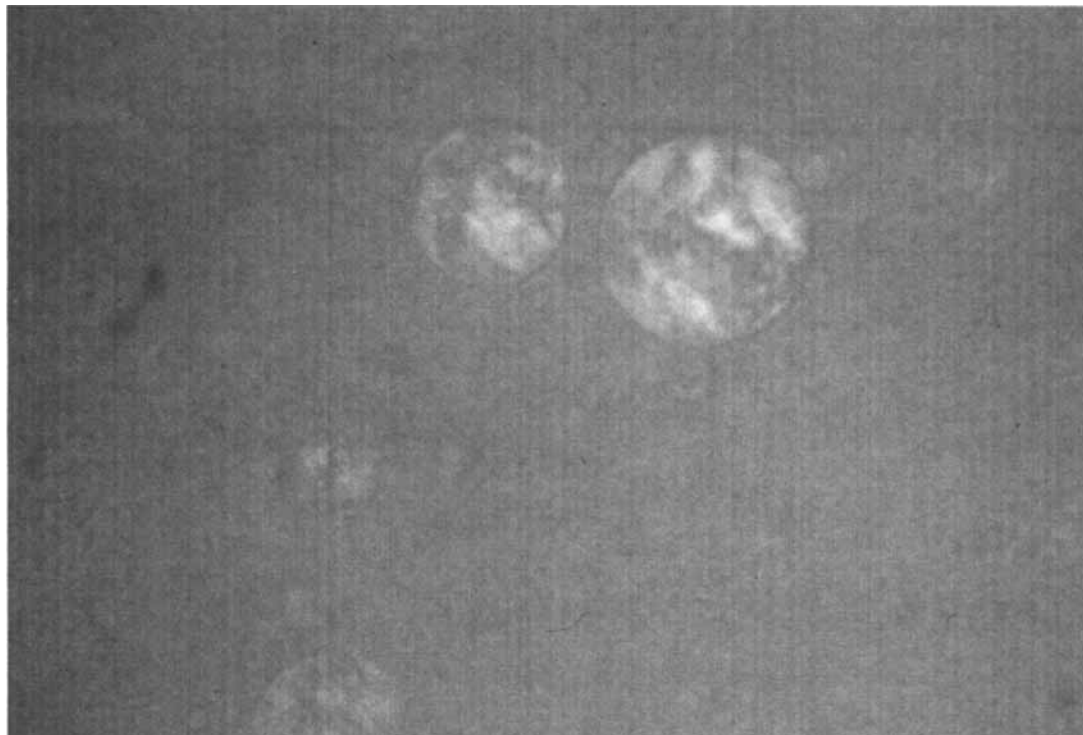
Figure 1 (Continued from the previous page)

the viscosity at given temperatures was not an additive property with respect to blend composition, even for the isotropic 20 wt % solution. The phases of the 20 and 40 wt % solutions with each composition were the same in our experimental conditions (temperature and blend composition) and the curves at given temperatures did not cross. On the other hand, the curves for the 25 and 35 wt % solutions crossed due to the difference in phase with blend composition. For the relatively simple 20 wt % solution, curves were upward. Except for the 25 wt % solution, the viscosity exhibited a maximum at the composition of HPC/EC: 15/85. Those results sug-

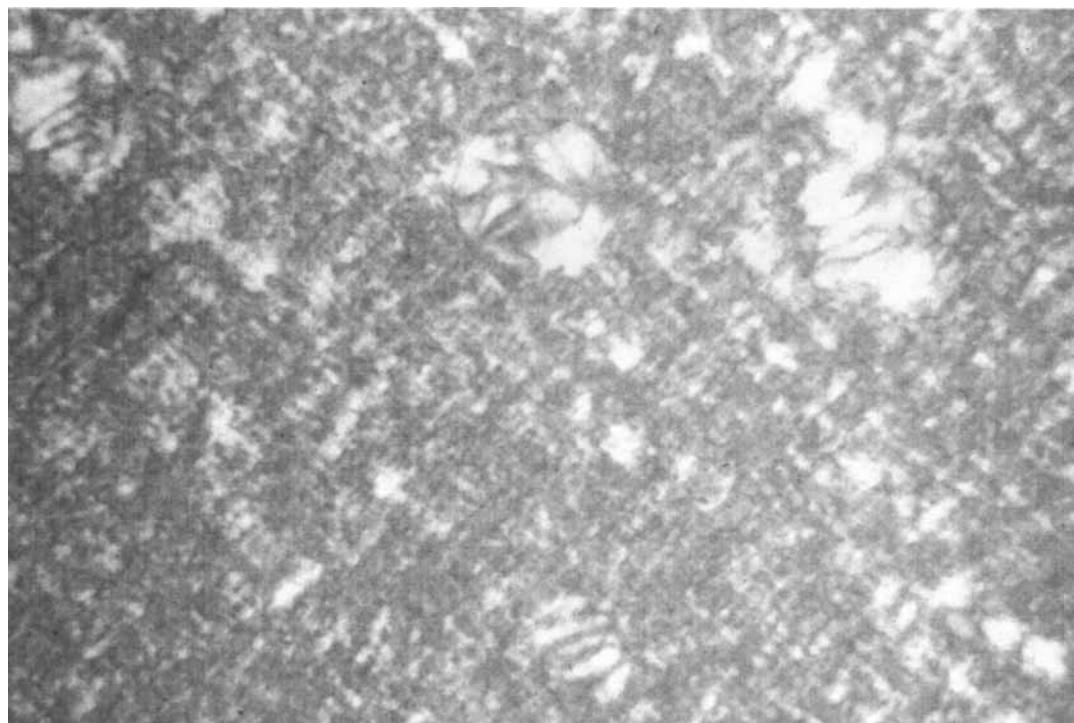
gested that HPC and EC were immiscible in our experimental range of temperature and blend composition.

Behavior at Relatively High Shear Stresses

Figure 5 illustrates the dependence of viscosity on blend composition for the 20, 25, 35, and 40 wt % solutions at given shear stresses. Two striking characteristics were seen in those figures. The first is that the dependence of the behavior on the blend composition greatly depends on polymer concentra-

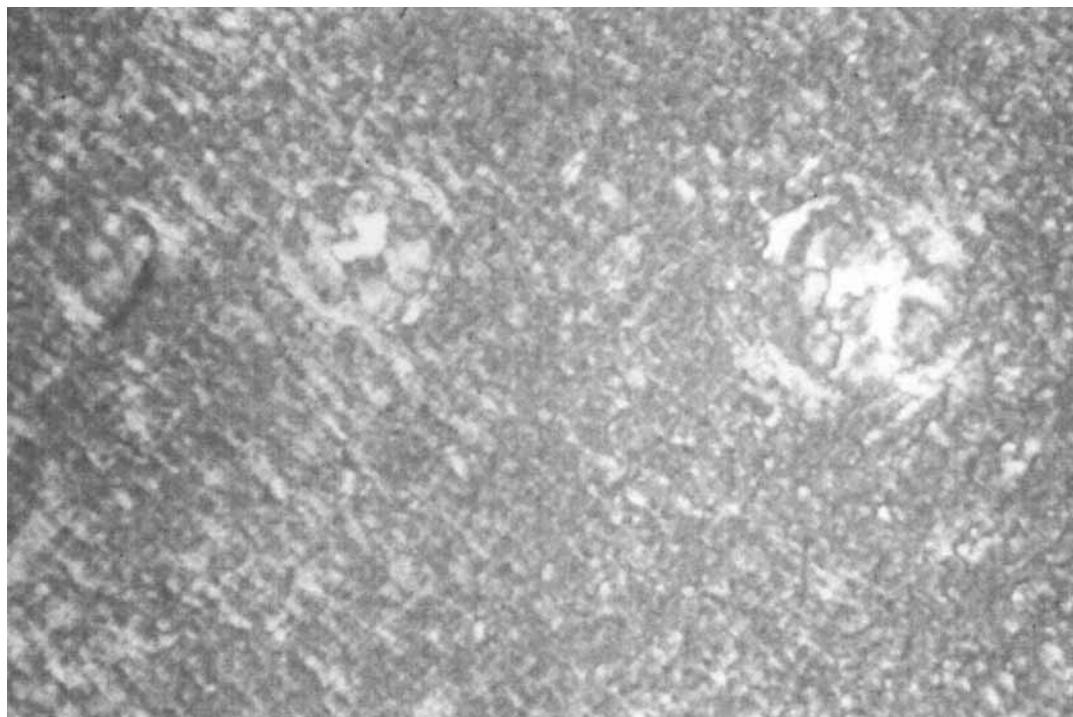


(a)

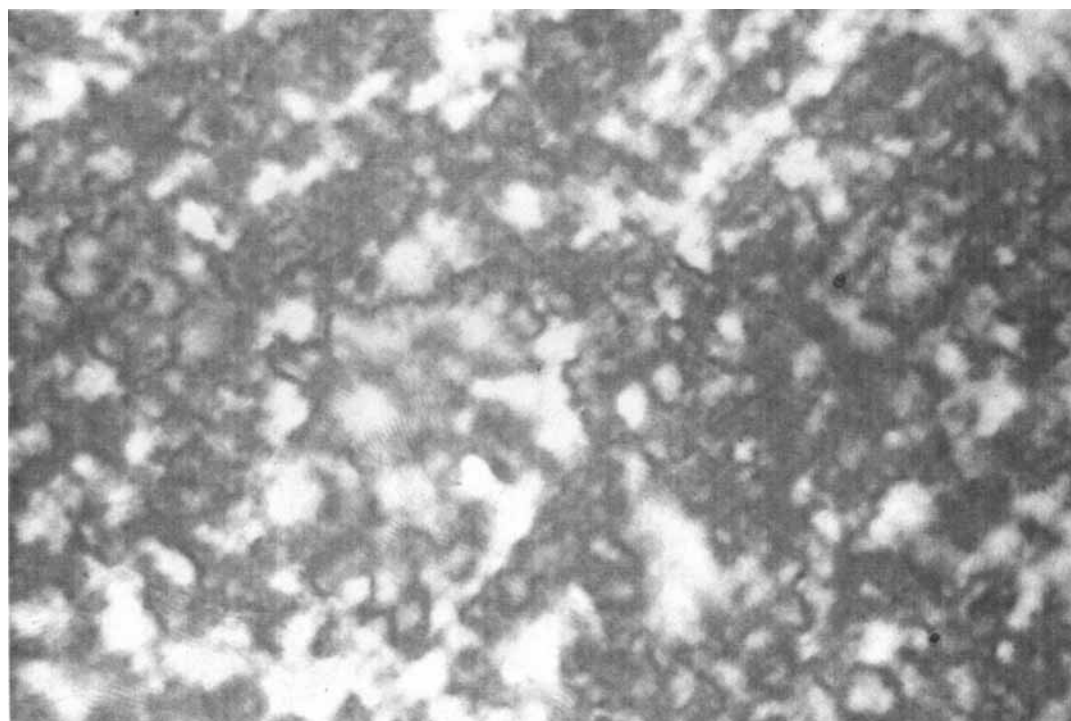


(b)

Figure 2 Polarized microphotographs at rest for solutions of (a) 25 wt %, HPC/EC: 15/85, (b) 35 wt %, HPC/EC: 70/30, (c) 40 wt %, HPC/EC: 70/30, and (d) 40 wt %, HPC/EC: 100/0.



(c)



(d)

Figure 2 (Continued from the previous page)

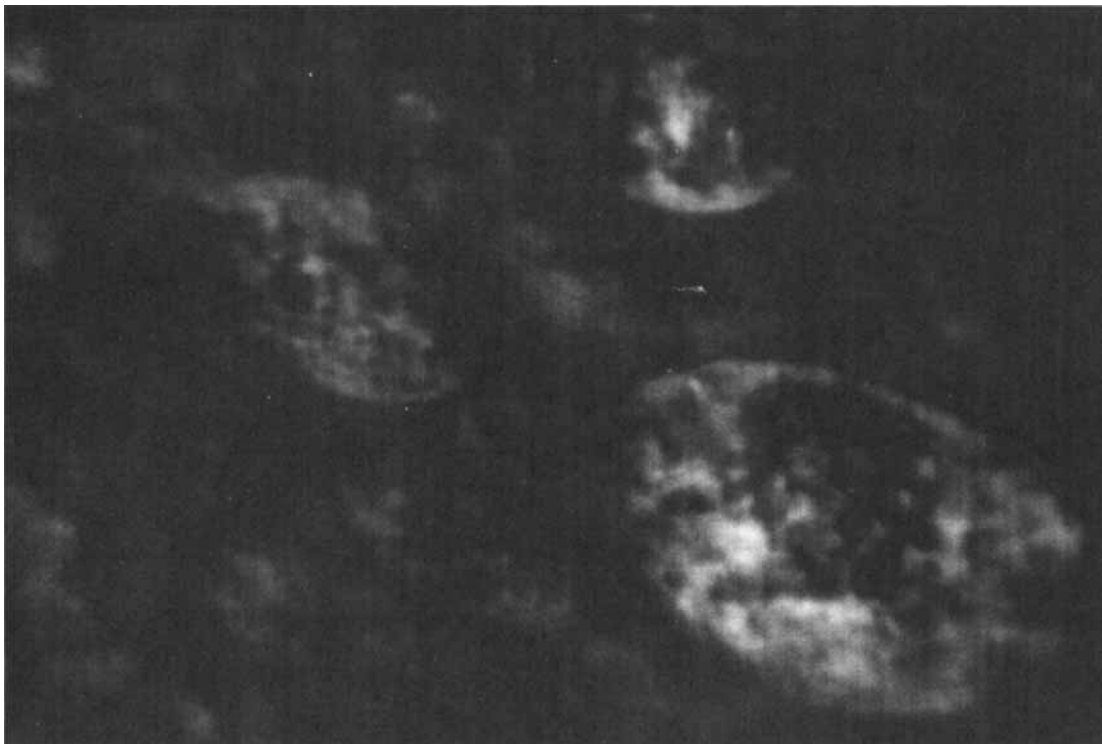


Figure 3 Polarized microphotograph at shear rate of ca. 1 s^{-1} for 25 wt % solution: HPC/EC: 15/85.

tion (phase of solution). The viscosity of the blend for the 20 wt % solution goes through a maximum at a blend composition of HPC/EC: 30/70 at each stress (note, for the capillary rheometry, there were no data on the solutions of HPC/EC: 15/85); the viscosity for the 25 wt % solution exhibited a flatter region of ca. 70–30 wt % of HPC; the viscosity for the 35 wt % solution goes through two minima at ca. 70 and 30 wt % of HPC (W-shaped curves); the viscosity for the 40 wt % solution exhibits a minimum at ca. 30 wt % of HPC.

The second is that the viscosity of the pure HPC solution was lower than that of the pure EC solution for the 20 and 25 wt % solutions, whereas the viscosity of the pure HPC solution was greater for the 35 and 40 wt % solutions.

With respect to the former characteristic, it is impossible to specify the phase of the solutions of each blend composition. In Figure 4, the phase of the solutions was estimated from the data shown in Figure 2; however, in Figure 5, we have no way to estimate the phase of the solutions undergoing shear. As easily supposed from the findings shown in Figure 3, the texture of the solutions at relatively high shear

must be different from that at rest and low shear rate, and the phase of the solutions even with the same compositions is also different possibly at low and relatively high shears. Although there were no data of the texture and phase of the solutions at high shear stresses, comparison with the data in Figures 4 and 5 can be made as an estimate. The comparison showed that the blend composition dependence of viscosity for the 20 wt % solution at lower shear was almost the same as that at relatively higher shear, but the dependence of viscosity for the other solutions was not. This finding strongly suggests that the texture of anisotropic solutions at relatively high shear is greatly different from that at low shear, as expected, and that the decrease in viscosity for HPC with shear is smaller than that for EC.

The latter characteristic suggests that the concentration dependence of viscosity is different for each and viscosity vs. concentration curves for HPC and EC solutions should cross at a certain concentration. This is partially due to the difference of substitution group: The hydroxypropyl group is longer than the ethyl group.

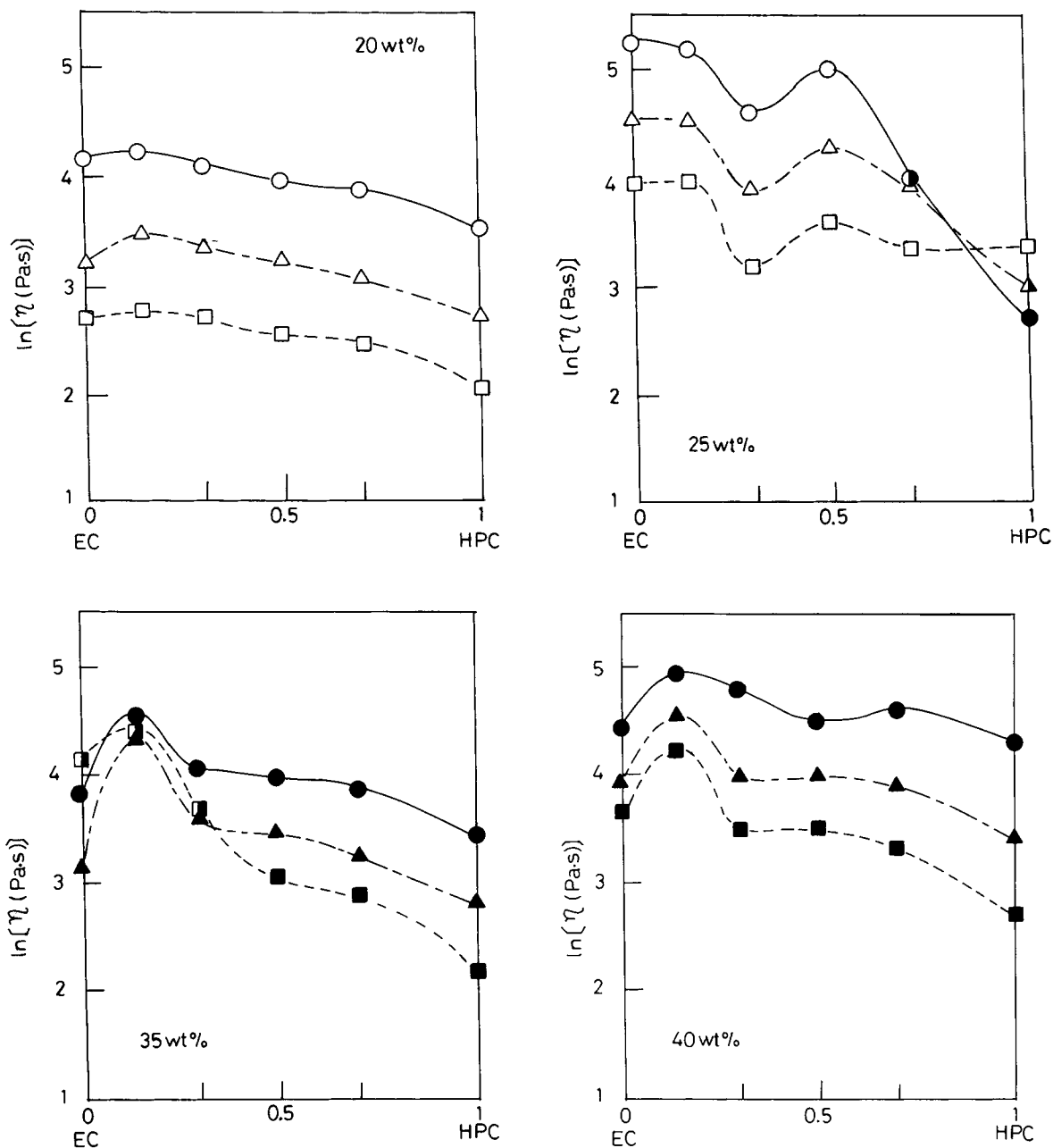


Figure 4 Viscosity (shear rate of 1 s^{-1}) vs. blend composition for solutions of (a) 20, (b) 25, (c) 35, and (d) 40 wt %; temperature ($^{\circ}\text{C}$): (O) 25; (Δ) 35; and (\square) 45; open mark means isotropic; half-mark dose, biphasic; and full-mark dose, single-phase anisotropic.

CONCLUSIONS

At low shear rate, (1) the temperature dependence of viscometric behavior for the liquid crystal-forming ternary system was similar to that for the liquid crystal-forming binary system and viscosity exhibited a maximum and a minimum. This suggested

that the phase of the matrix dominates the viscometric behavior for the liquid crystalline ternary system, and (2) the dependence of viscometric behavior on blend composition was dependent on the phase of solution and was not additive. This strongly suggested that EC and HPC are immiscible in our experimental conditions.

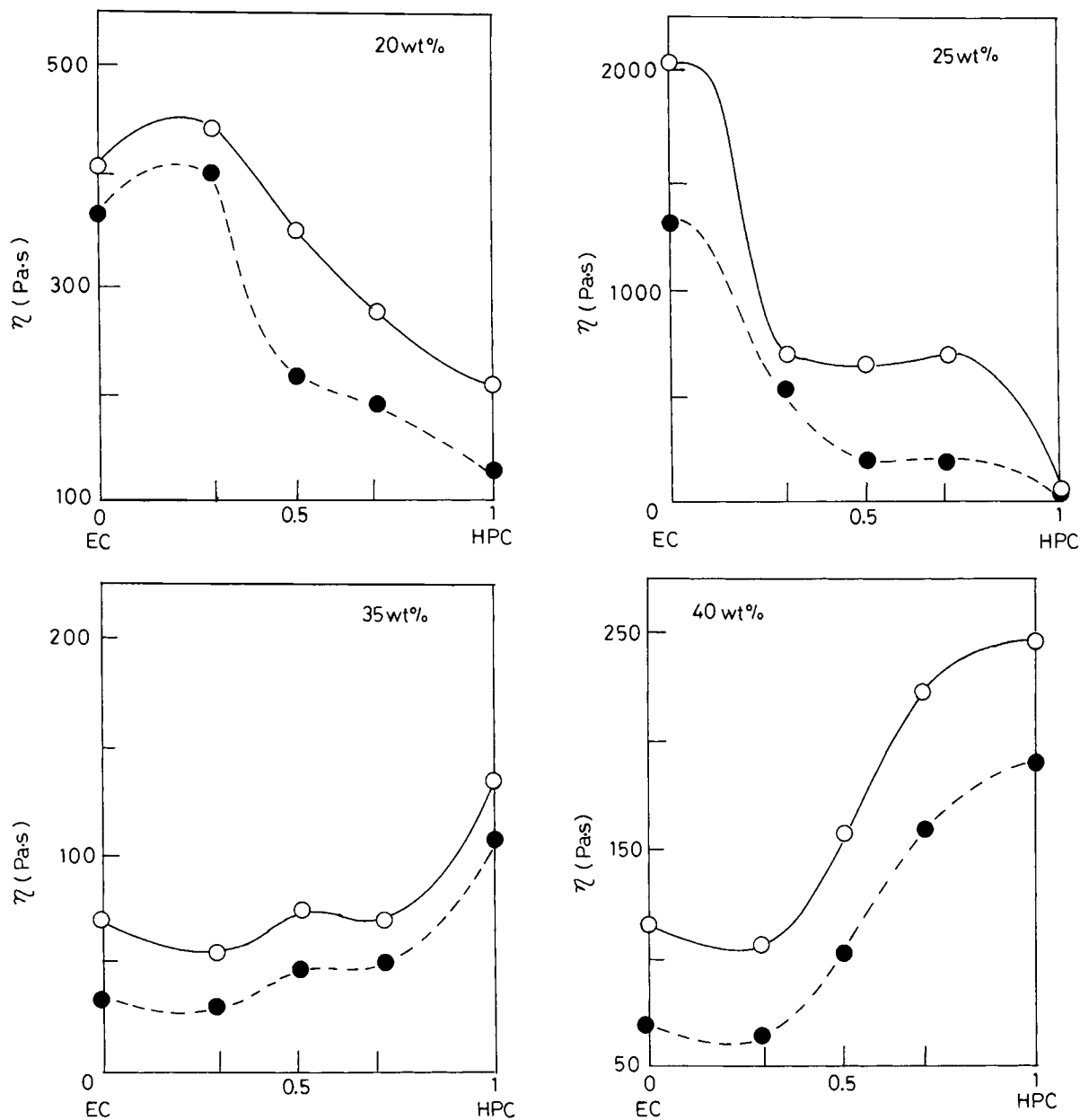


Figure 5 Viscosity (25°C) vs. blend composition for solutions of (a) 20, (b) 25, (c) 35, and (d) 40 wt %; shear stress (Pa): (○) 1.39×10^3 ; (●) 2.55×10^3 .

At relatively high shear stresses, (1) the dependence of viscometric behavior on blend composition greatly depended on the total polymer concentration of solutions, and (2) the dependence for the 20 wt % solution was similar to that at low shear rate, but the dependence for the 25, 35, and 40 wt % solutions was not. This suggested that the texture of anisotropic solutions at relatively high shear is different from that at low shear. Furthermore, our findings

suggested that the dependence of viscosity on shear and concentration for pure EC is quite different from that for pure HPC.

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Received May 22, 1991

Accepted October 10, 1991