Rheology of Liquid Crystalline Solutions of Hydroxypropyl Cellulose in m-Cresol

INTRODUCTION

Much attention has been given to polymer blends and alloys from engineering and industrial viewpoints. Those blend systems have been mainly polymers of flexible chains.[1] However, very recently some articles have appeared on polymer blends in which at least one component exhibits liquid crystalline behavior.[2-4]

Most cellulose derivatives form liquid crystals at suitable conditions.[5] The liquid crystalline cellulosic blends were investigated as to their phase diagram by Sixou et al.[6,7] and Ciferri et al.[8,9] However, very few studies have considered the rheological behavior of the liquid crystalline cellulosic blend systems. It is well-known that the rheological behavior of the liquid crystals (a polymer in a solvent or in a bulk) is strongly related to the phase transformation of the system.[10] However, for the ternary system (liquid crystalline polymer/liquid crystalline polymer/cosolvent) the relation between the rheological behavior and the phase transformation is still unclear.

Hydroxypropyl cellulose (HPC) is a cellulose derivative which forms liquid crystals in the widest range of solvents.[5] The liquid crystalline HPC, however, seems to be of less commercial importance because of its excellent solubilities in water and common organic solvents. One of the modifications of HPC is the polymer blend. We have investigated the viscometric behavior of the blends of HPC/polyvinylpyrrolidone/water[11] and of HPCs with different molecular weight/dimethylacetamide[12] and have reported that interaction between different polymers acts an important role. As a next stage, we choose the blend system of HPC and ethyl cellulose (EC) as a model system, because the rheological properties of HPC and EC have been investigated by us previously,[13,14] and since both HPC (water-soluble) and EC (water-insoluble) form lyotropic liquid crystals.[5]

First we need to find a suitable cosolvent for the blend of HPC and EC. Gray[5] has tabulated the solvents that form lyotropic liquid crystals for HPC and EC; acetic acid is the only common solvent for HPC and EC. The HPC/EC/acetic acid system phase diagram is reported in an article[7] published during our investigation. We think acetic acid is not the best solvent for the investigation of the rheological properties of that blend system, because it evaporates somewhat even at room temperature and the concentration of that system changes during viscometry; furthermore, a viscometer is corroded by the acetic acid vapor at relatively high temperature.[15] Therefore, we tried to find another cosolvent for the blend system and finally settled on *m*-cresol: HPC/*m*-cresol system forms lyotropic liquid crystal at ~ 20 wt% by polarized microscopy at room temperature.[16] *m*-Cresol has higher boiling point than acetic acid; this means the rheological properties can be determined in a wider range of temperature than acetic acid. *m*-Cresol has been known to form lyotropic liquid crystal with EC.[5]

In this note, as a preliminary step, we determine the rheological properties of a binary HPC/*m*-cresol system in a wide range of temperature and concentration before determining those of the ternary HPC/EC/*m*-cresol system.

EXPERIMENTAL

Hydroxypropyl cellulose was purchased from Tokyo Kasei Kogyo Co. Ltd. The weight-average and number-average molecular weights of HPC, which were determined in tetrahydrofuran (THF) at 25°C by gel permeation chromatography (GPC), were 11.7×10^4 and 5.2×10^4, respectively. The molar substitution of HPC was 4.25 which was determined by nuclear magnetic resonance (NMR).[17] Reagent-grade *m*-cresol (Wako Pure Chemical Ind. Ltd.) was purified by distillation at reduced pressure prior to use.

The mixture of HPC and *m*-cresol was allowed to dissolve for 5–6 months at room temperature in the dark. In the case of relatively higher concentrations, the mixtures could not dissolve easily, and in that case were vigorously stirred by use of glass rod once a week.

Journal of Applied Polymer Science, Vol. 37, 1147–1151 (1989)

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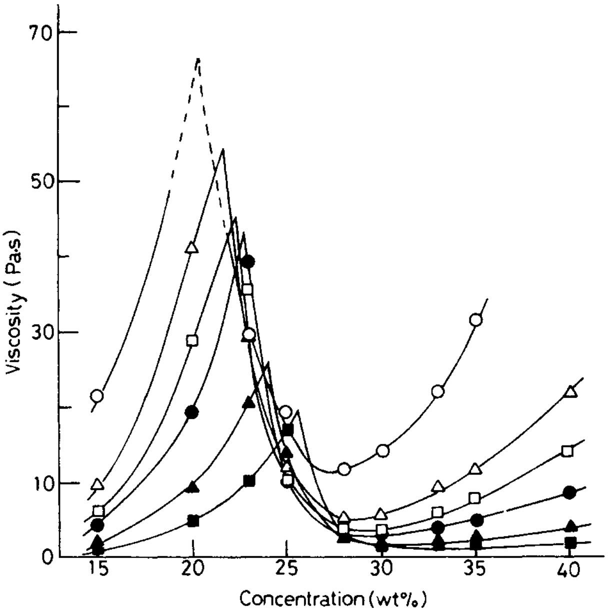

Fig. 1. Concentration dependence of viscosity at shear rate of 1 s^{-1} for HPC/*m*-cresol system; temperature: (○) 10, (△) 20, (□) 25, (●) 30, (▲) 40, (■) 50°C.

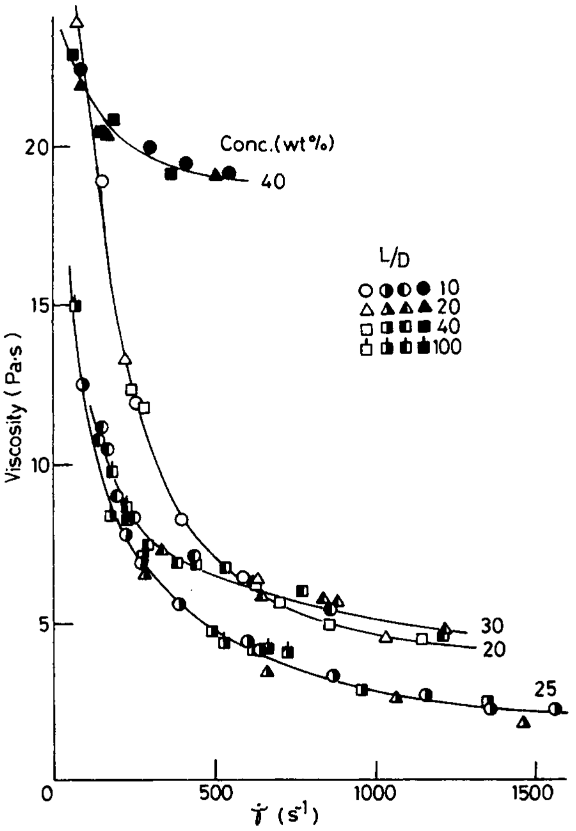

Fig. 2. Shear rate dependence of viscosity at 25°C in each die for each concentration of HPC/*m*-cresol system.

Two types of rheometer were used. A cone-plate-type rheometer was used for determining the temperature dependence of shear viscosity at a shear rate of 1 s^{-1}. A capillary-type rheometer (constant-load type) was used for determining the shear-rate dependence of shear viscosity at 25°C. To take into consideration the Bagley correction, four different dies were used: the diameter was 0.5 mm and the length-to-diameter ratios L/D were 10, 20, 40, and 100. The elastic parameter determined here was entrance pressure drop (ΔP_{ent}). The details of the determinations have been described elsewhere.[13,14]

RESULTS AND DISCUSSION

Figure 1 shows the concentration dependence of shear viscosity at a shear rate of 1 s^{-1} for HPC solutions in *m*-cresol at given temperatures. This concentration dependence of the viscosity shows the typical behavior for the lyotropic liquid crystalline solutions: the viscosity exhibits a maximum and a minimum with respect to increasing concentration.[18] The concentration at the maximum or minimum was dependent on temperature; those critical concentrations increased with temperature. Generally, those critical concentrations are defined as C_a and C_b, respectively.

As reported previously by Doraiswamy and Metzner[19] and by us,[13,14] the so-called Bagley correction was applicable to our liquid crystalline system. The pressure drop at die entrance ΔP_{ent} could be obtained experimentally using Bagley plots in the form of pressure drop through die (ΔP) versus L/D at given shear rates: the intercept on the ΔP axis at $L/D = 0$ indicates ΔP_{ent}.

The true viscosity as a function of shear rate is shown in Figure 2 for each concentration in each die. In this figure, data for the 12, 23, 28, 33, and 35 wt% solutions were omitted for the sake of clarity. This behavior was the same as that for the other cellulosic liquid crystalline solutions.[13,14] The data in Figure 2 are replotted in Figure 3 with viscosity as ordinate and

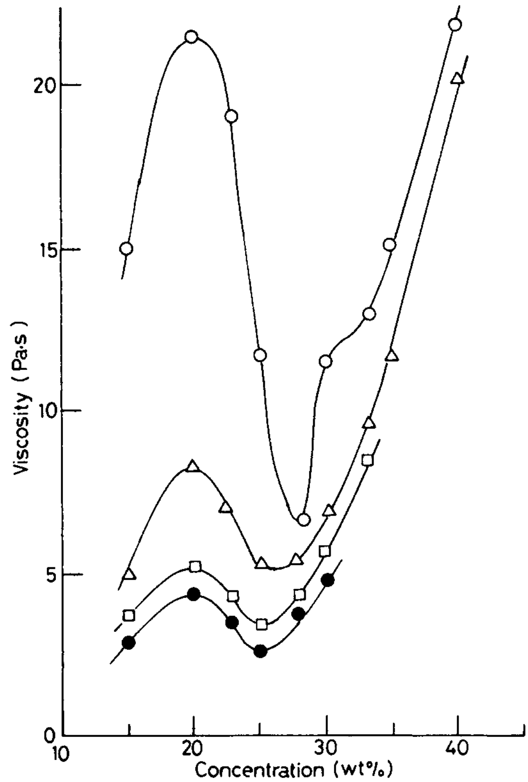

Fig. 3. Concentration dependence of viscosity at 25°C for HPC/*m*-cresol system; shear rate: (○) 100, (△) 400, (□) 800, (●) 1200 s^{-1}.

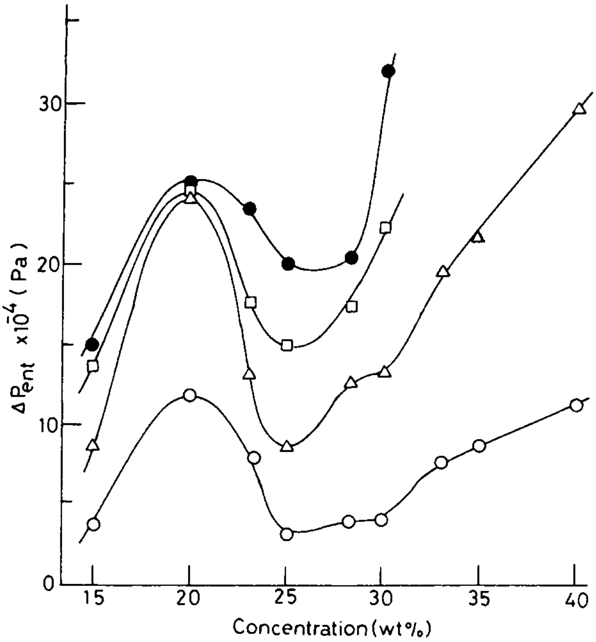

Fig. 4. Concentration dependence of entrance pressure drop at 25°C for HPC/*m*-cresol system; shear rate: (○) 100, (△) 400, (□) 800, (●) 1200 s^{-1}.

concentration as abscissa at given shear rates. The viscosity exhibited a maximum and a minimum with respect to concentration. This behavior was the same as that shown in Figure 1.

Figure 4 shows the concentration dependence of ΔP_{ent} at each shear rate. ΔP_{ent} also exhibited the maximum and minimum, and those critical concentrations were almost identical with those for the viscosity data shown in Figure 3.

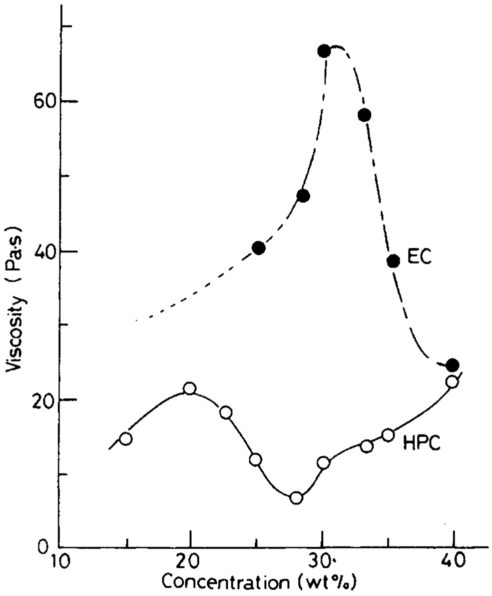

Fig. 5. Concentration dependence of viscosities at 25°C and at shear rate of 100 s^{-1} for HPC/*m*-cresol system (○) and EC/*m*-cresol system (●) (data from Ref. 14).

Our results on the rheological properties clearly show that HPC solutions in *m*-cresol form liquid crystal; the critical concentration C_a and C_b at 25°C are 22.5 and 29 wt%, respectively. Those values were quite small and seem to be the smallest ever reported in scientific literature for the cellulosic liquid crystal.[5] As noted above, our final objective is to investigate the rheological and optical properties of the HPC/EC/*m*-cresol system. The viscoelastic behavior of EC/*m*-cresol system has been reported by us;[14] our findings are shown in Figure 5, compared with the result for EC/*m*-cresol system. It is noteworthy that the critical concentrations for two systems are quite different. Therefore, the viscoelastic behavior for the blend system is supposed to be greatly dependent on the composition of the blend; 15 wt% solution of the blend (HPC/EC) is isotropic/isotropic, 25 wt% solution is biphasic/isotropic, 35 wt% solution is single anisotropic/biphasic, and 40 wt% solution is single anisotropic/single anisotropic. This strongly suggests that HPC/EC/*m*-cresol system is a good model for determining the rheological and optical properties of cellulosic liquid crystalline blend solutions. The investigation on the viscometric behavior for the HPC/EC/*m*-cresol system is in progress.

CONCLUSIONS

m-Cresol is a solvent which forms lyotropic liquid crystal with HPC. The critical concentrations C_a and C_b at 25°C for HPC/*m*-cresol system are 22.5 and 29 wt%, respectively; those values seem to be the smallest of those for cellulosic liquid crystalline systems. *m*-Cresol is a common solvent for HPC and EC. The critical concentrations for HPC/*m*-cresol liquid crystalline system are quite different from those for EC/*m*-cresol liquid crystalline one.

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SHINICHI SUTO
HIROMASA GOTOH
WATARU NISHIBORI
MIKIO KARASAWA

Department of Polymer Chemistry
Faculty of Engineering
Yamagata University
Jonan 4-3-16, Yonezawa
Yamagata 992 Japan