

Capillary rheometry of lyotropic liquid crystals of hydroxypropyl cellulose

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Rheological properties of hydroxypropyl cellulose solutions which exhibit liquid crystalline behaviour under certain conditions were determined by using a capillary rheometer. The Bagley end correction was taken into consideration by using three kinds of dies. Measurements included the shear and concentration dependence of the shear viscosity and three elastic parameters: the Bagley correction factor (ν), the entrance pressure drop (ΔP_{ent}) and the die swell (B). The shear viscosity exhibits a general behaviour as a lyotropic liquid crystal. The shear dependence of ν greatly depends on concentration, and ν shows a maximum and minimum with respect to concentration. The pressure drop ΔP_{ent} increases with shear rate for all concentration ranges and the concentration dependence of ΔP_{ent} is the same as that of the shear viscosity. The die swell B increases with shear stress only for a single phase (isotropic or anisotropic) and decreases for the biphasic range; B also exhibits a maximum and minimum with respect to concentration.

There seems to be a great similarity between the shear viscosity and the elastic parameters with respect to concentration; however, there is no similarity between them with respect to shear. The Bagley correction factor or entrance pressure drop is simply related to the die swell and the following relations are expressed experimentally:

$$\begin{aligned}\nu &\propto B^n \\ \Delta P_{\text{ent}} &\propto B^{n'}\end{aligned}$$

where n and n' are constants which are dependent on concentration and shear range. More rheological data are required to establish those relations between the elastic parameters.

(Keywords: hydroxypropyl cellulose; lyotropic liquid crystal; shear viscosity; Bagley end correction; entrance pressure drop; die swell)

INTRODUCTION

In previous papers^{1,2}, we have reported the die swell behaviour of lyotropic liquid crystals of hydroxypropyl cellulose (HPC). Our major findings were that the die swell has a maximum and a minimum with respect to concentration and that this concentration dependence of the die swell is similar to that of the shear viscosity. However, only the apparent shear viscosity and shear stress have been determined.

For capillary rheometry, a series of corrections is appropriate to determine the true shear viscosity³. Generally, the most important correction is that due to the 'end effect'. This effect is negligible when the die used has a large ratio of length (L) to diameter (D). However, an exact criterion for this ratio L/D of the die has not been established. The end effect can be eliminated by using two or more dies of the same diameter but different length⁴: if the pressure drop over a finite length (ΔP) is plotted *versus* L/D for the same shear rate in each die, the so-called Bagley plots should be linear and the intercept at $\Delta P = 0$ determines the end correction factor or Bagley correction factor (ν); the true shear stress at the capillary wall (σ_{true}) can be calculated by taking ν into consideration:

$$\sigma_{\text{true}} = \frac{D}{4} \left(\frac{\Delta P}{L + \nu D} \right) \quad (1)$$

Therefore, the true shear viscosity can be determined according to this procedure.

In this paper, we describe the true shear viscosity of lyotropic liquid crystals of HPC for a wide range of concentration, using three capillary dies. We also describe the phenomena that are involved in elasticity of liquid crystals, namely:

- (1) Bagley correction factor (ν),
- (2) pressure drop at the capillary die entrance (ΔP_{ent}),
- (3) die swell at the capillary die exit (B).

The Bagley correction factor can be evaluated experimentally according to the Bagley procedures noted above⁴. The second parameter ΔP_{ent} can also be obtained experimentally in the same procedures: the intercept on the ΔP axis at $L/D = 0$ determines it. With regard to the third parameter, we have already investigated and demonstrated that the die swell reflects the elasticity and is strongly related to the first normal stress difference².

In order to understand the anomalous flow behaviour of liquid crystals, both viscous and elastic properties must be determined⁵⁻⁷. Baird *et al.*⁸ have investigated not only the viscosity but also the elastic parameters and have

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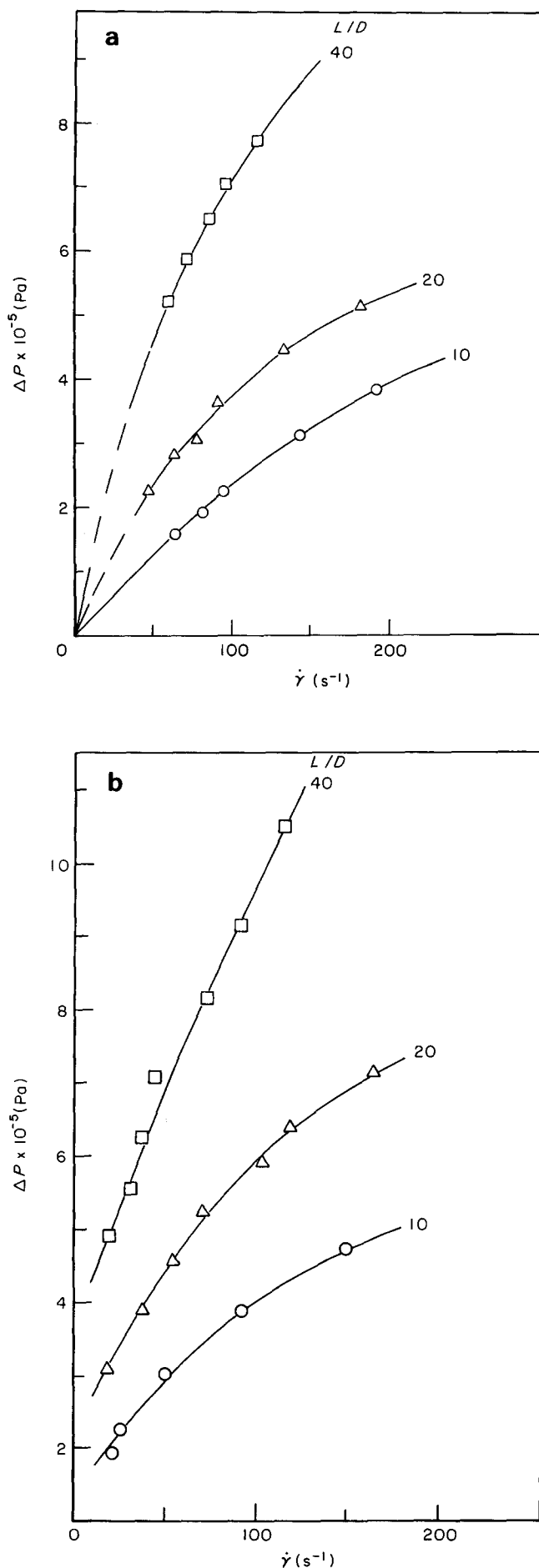


Figure 1 Pressure drop across die vs. shear rate for (a) 35 wt% solution of HPC in DMSO, and (b) 55 wt% solution of HPC in DMSO

showed that there was no correlation between the parameters (2) and (3) noted above for a thermotropic liquid crystal. However, rheological measurements are still insufficient to establish the flow behaviour of liquid crystals.

It is our main objective to determine the concentration and shear dependence of the true shear viscosity and the elastic parameters for the lyotropic liquid crystalline systems by means of a capillary rheometer. Another object is to discuss the correlation between the elastic parameters. The lyotropic liquid crystalline systems used in this study are HPC/dimethylsulphoxide, HPC/dimethylacetamide and HPC/water.

EXPERIMENTAL

Samples

Hydroxypropyl cellulose (HPC) was commercial reagent grade as supplied by Tokyo Kasei Kogyo Co. Ltd. The weight-average molecular weight of the HPC was 9.3×10^4 . Before use, HPC powder was dried *in vacuo* at 60°C for about 24 h.

N,N-Dimethylacetamide (DMAc) and dimethylsulphoxide (DMSO) were commercial reagent grade (Wako Pure Chemical Ind. Ltd) and were predistilled by standard procedures. Distilled and deionized water prepared in our laboratory was also used.

Solutions over the concentration range 35 to 55 wt% for all systems were prepared by magnetically mixing for about a week and were then stored in the dark for about three months at room temperature. The solutions were mixed once a week to prevent sedimentation of the polymer during prolonged storage. The critical concentrations (A point) in volume fraction are 0.394, 0.440 and 0.461 for HPC/water, HPC/DMSO and HPC/DMAc, respectively⁹. Those critical concentrations were determined by means of a cone-plate type rheometer at a shear rate of 1 s^{-1} and 25°C. The experimental conditions are quite different from those in this study, and so those critical concentrations are just a quick guide to the estimation of the solution phase.

Capillary rheometry

The constant-load type capillary rheometer used in this study has been described in detail elsewhere^{1,2}. The main feature in this study was that three different dies are used to take the Bagley correction into consideration. The diameter D was always 0.5 mm and the length-to-diameter ratios L/D were 10, 20 and 40; the entrance angle was 180°. The true shear stress at the die wall was calculated using equation (1). The shear rate was obtained using the following equation³:

$$\dot{\gamma} = 32Q/\pi D^3 \quad (2)$$

where Q is the volumetric flow rate. The true shear viscosity was obtained as the ratio between σ_{true} and $\dot{\gamma}$. All measurements were made at 25°C.

RESULTS AND DISCUSSION

Bagley plots

Figures 1a and 1b show typical plots of the pressure drop ΔP vs. shear rate in each die for the 35 wt% (isotropic) and 55 wt% (biphasic) solutions of HPC in

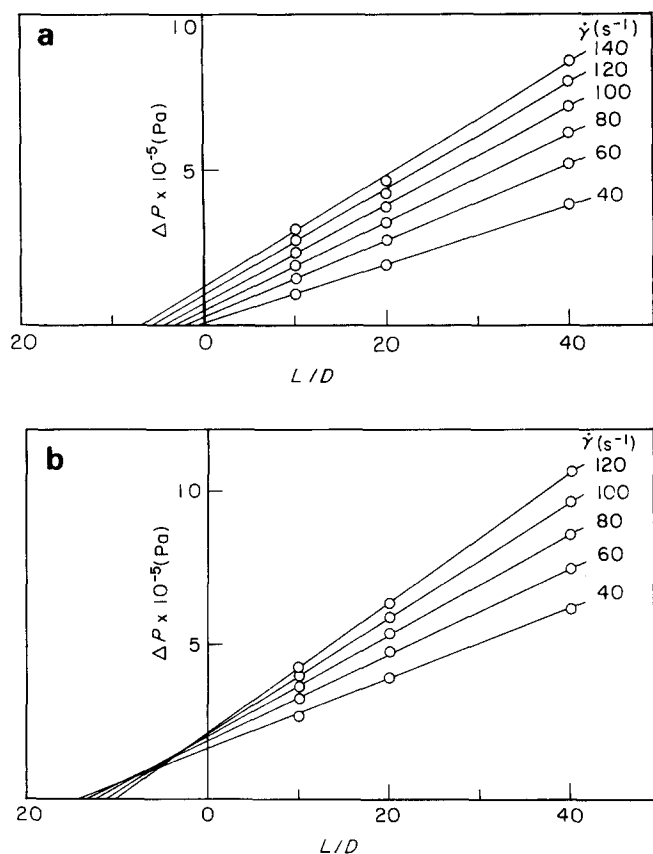


Figure 2 Bagley plots for (a) 35 wt% solution of HPC in DMSO, and (b) 55 wt% solution of HPC in DMSO

DMSO, respectively. ΔP increased with increasing shear rate or increasing length-to-diameter ratio L/D . For other concentrations and systems, the same behaviour as in Figure 1 was observed. Typical Bagley plots in the form of ΔP vs. L/D at given shear rates are shown in Figures 2a and 2b for the same solutions as in Figure 1. Following Bagley analysis⁴, Figure 2 enables us to evaluate both the Bagley correction factor ν and the entrance pressure drop ΔP_{ent} . The values of ν in this study depended greatly on the shear rate, concentration and solvent. Our finding suggests that when we use a capillary die with a given L/D and eliminate the end effect in evaluating the shear stress at the die wall, we need the long die for which L/D should be greater than 80. It was also apparent that L/D required for anisotropic solutions is greater than that for isotropic solutions. This may be attributed to a difference in relaxation times between the anisotropic and isotropic solutions¹⁰. Further details on ν and ΔP_{ent} will be discussed later. Figure 3 shows the true shear stress obtained using equation (1) as a function of shear rate in each die for the HPC/DMSO system. The shear stresses for each die were generalized to a single curve and this generalization was valid for the other concentrations and systems. This means that the Bagley procedures are applicable to not only isotropic systems but anisotropic ones, too.

Shear viscosity

The true shear viscosity is shown as a function of shear rate for each concentration in Figure 4. The viscosity increased drastically with decrease in shear rate and this tendency became distinct as the concentration increased. This means that those solutions have a yield stress. The

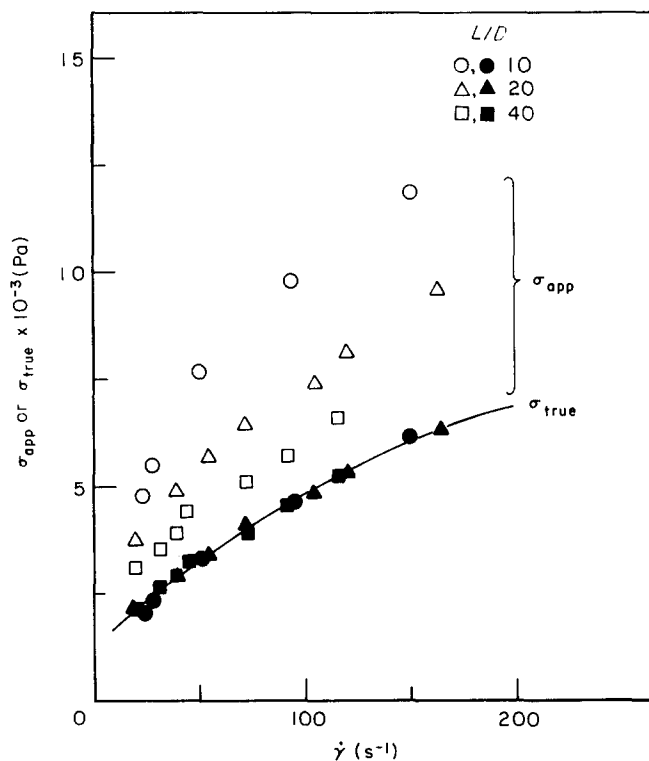


Figure 3 Apparent or true shear stress vs. shear rate for 55 wt% solution of HPC in DMSO

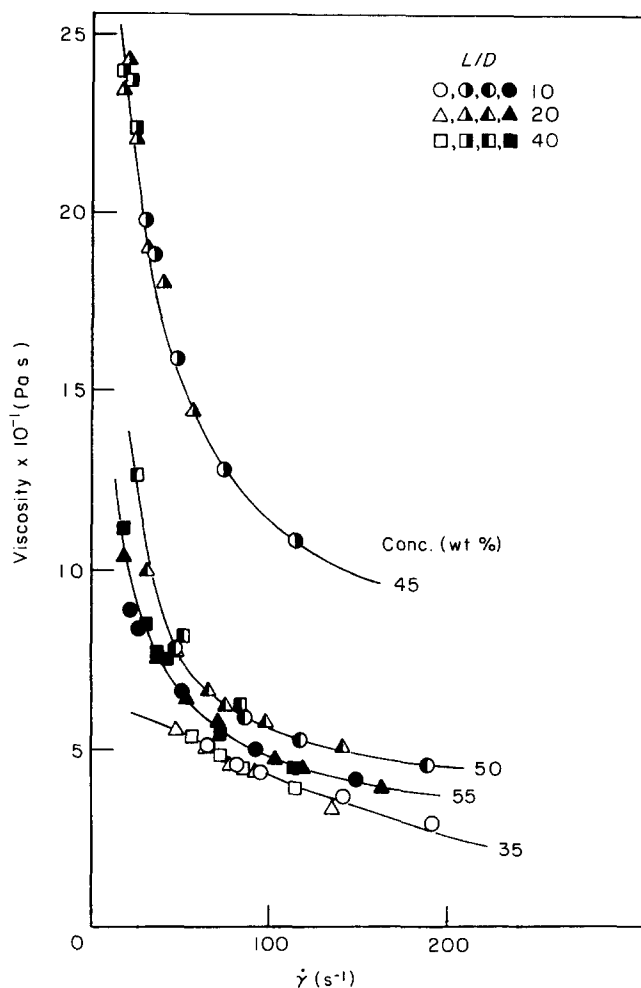


Figure 4 Flow curves for solutions of HPC in DMSO

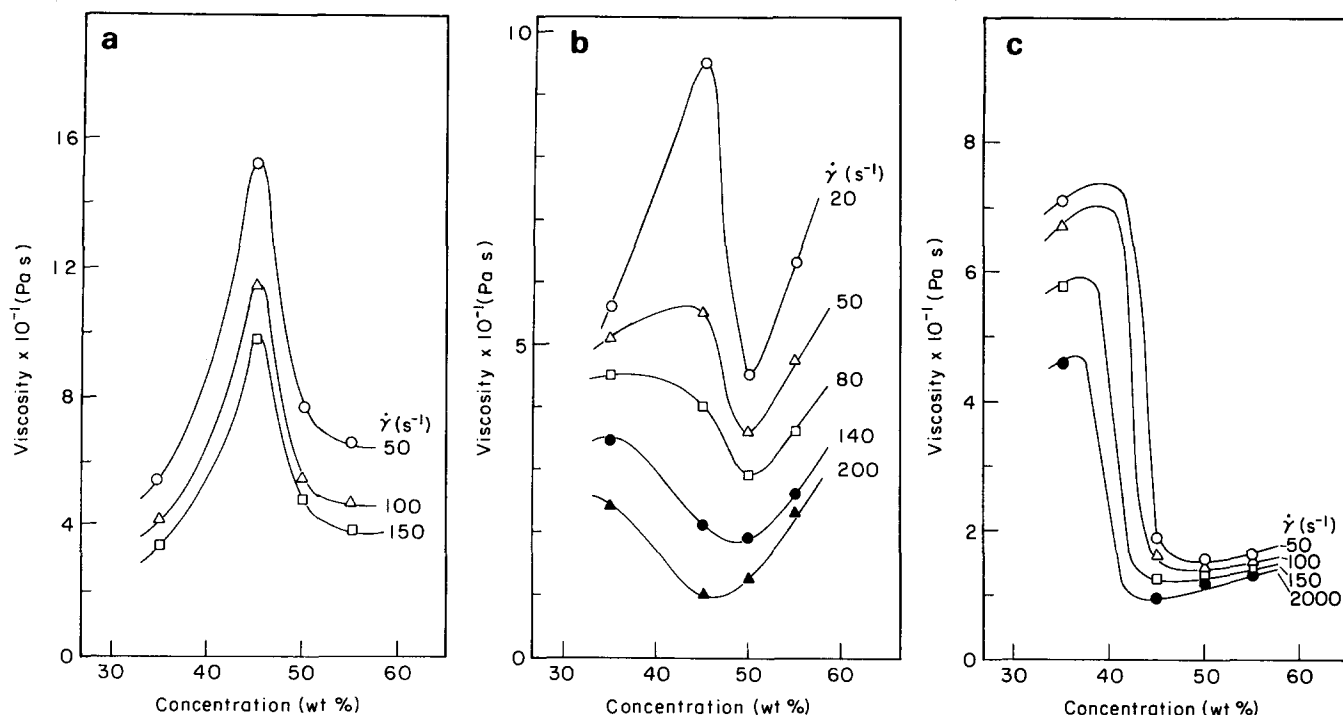


Figure 5 Concentration dependence of shear viscosity for solutions of (a) HPC in DMSO, (b) HPC in DMAc, and (c) HPC in water

data in Figure 4 were replotted in Figure 5a with viscosity as the ordinate and concentration as the abscissa at given shear rates. Figures 5b and 5c are for HPC/DMAc and HPC/water systems, respectively. This concentration dependence of the viscosity is similar to that reported by other investigators¹¹: the shear viscosity first increased with concentration to a maximum, followed by a decrease to a minimum, and then increased again with further increase in concentration. In our concentration region covered, transformations from isotropic to biphasic state and from biphasic to fully anisotropic state were displayed for both HPC/DMAc and HPC/water systems and only the former transformation was shown for HPC/DMSO system. This concentration dependence greatly depended on the shear; at relatively low shear, the viscosity exhibited a distinct maximum and minimum with respect to concentration, whereas at relatively high shear, the maximum became less pronounced. This behaviour is the same as that reported by Porter *et al.*⁶ It is noteworthy that the maximum and minimum tend to shift to lower concentration. Therefore, when we discuss the concentration dependence of the shear viscosity, particular care must be taken over the shear at which the viscosity for each concentration is determined. Asada *et al.*^{12,13} have performed rheo-optical studies on the HPC lyotropic system and noted that the size or orientation of the domain depends on the shear rate. Although the shear rate region they investigated and the type of rheometer they used are different from ours, it can be supposed from their findings that the domain size at higher shear is smaller than that at lower shear and the domains or the individual molecules which constitute the domain are highly oriented at higher shear.

Elastic parameters

Figures 6a, 6b and 6c show the shear rate dependence of the Bagley correction factor ν for HPC/DMSO, HPC/DMAc and HPC/water, respectively. The factor ν

increased with increasing shear rate at some concentrations, and decreased at others. When we compare the data in Figure 5 with Figure 6, the shear rate dependence of ν in the biphasic region seems to be opposite to that in the other single-phase regions (isotropic and anisotropic ones). To clarify this description, examples are given: for HPC/DMSO, 45, 50 and 55 wt% solutions; for HPC/DMAc, 45 wt% solution; and for HPC/water, 45 wt% solution.

The pressure drop at the die entrance, ΔP_{ent} , as a function of shear rate is shown in Figures 7a, 7b and 7c for HPC/DMSO, HPC/DMAc and HPC/water. This dependence of ΔP_{ent} on shear rate was little different from that of ν ; ΔP_{ent} increased with increasing shear rate for many concentration ranges except for 35 wt% solution of HPC in water. This response of ΔP_{ent} to the shear rate was similar to that reported by Baird *et al.*⁸ Generally, ΔP_{ent} has been related to entrance vortices observed at the die entrance for isotropic polymer solutions and melts and the increase in ΔP_{ent} results in the increase in the vortices size³. This suggests that the increase in ΔP_{ent} also increases the Bagley correction factor. However, this suggestion seemed to be unfavourable to the feature observed in this study: the suggestion was valid only for the isotropic systems (the larger ΔP_{ent} , the larger ν) and was not valid for the anisotropic solutions. Thus, we require more experimental determinations of the precise flow patterns at the die entrance to understand the origins of ΔP_{ent} and the relation between ΔP_{ent} and ν for the anisotropic systems.

Figures 8a, 8b and 8c show the shear stress dependence of the die swell for three systems. This dependence of the die swell on the stress was quite different from the shear rate dependence of both ν and ΔP_{ent} : the die swell exhibits a maximum for every 45 wt% solution. The 45 wt% solution is very near to the critical concentration at which the liquid crystalline phase first appears, and is very sensitive to the shear. We reported in the previous paper¹

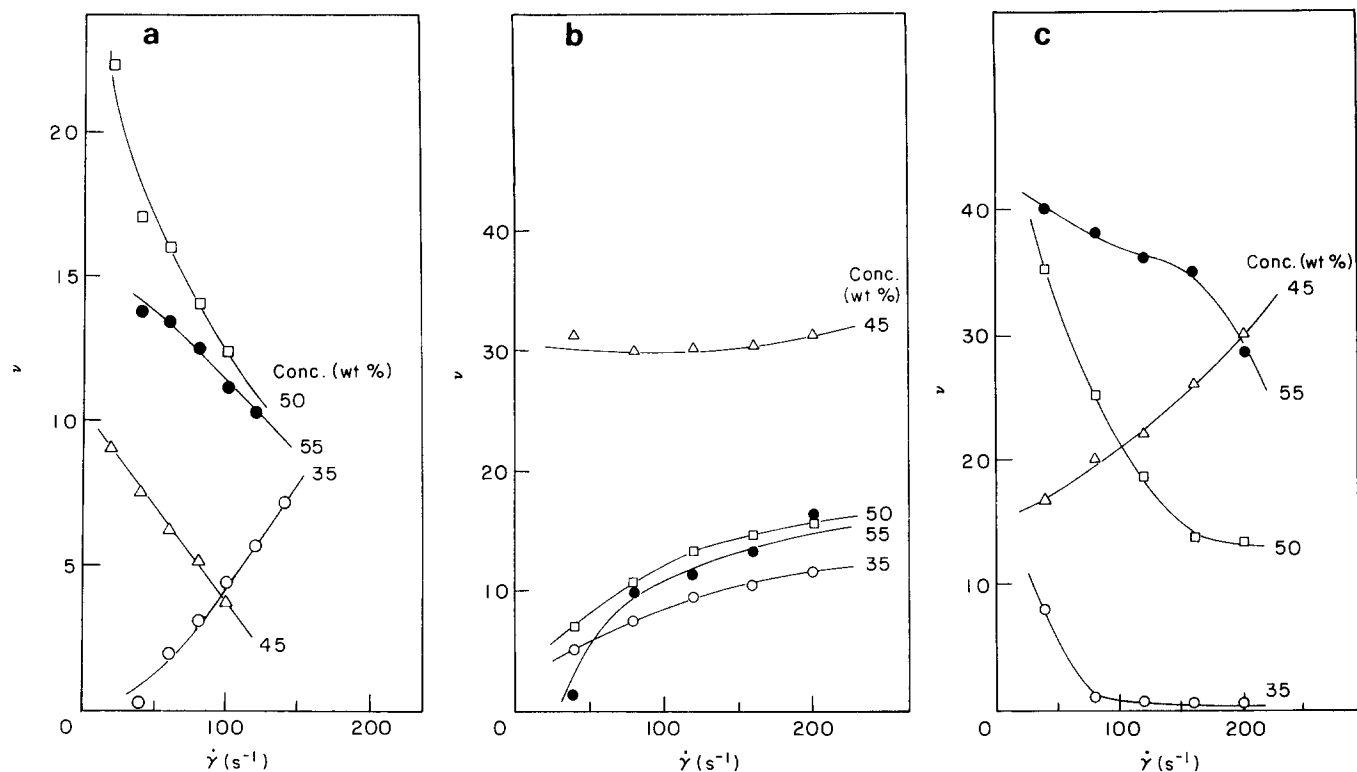


Figure 6 Bagley correction factor vs. shear rate for solutions of (a) HPC in DMSO, (b) HPC in DMAc, and (c) HPC in water

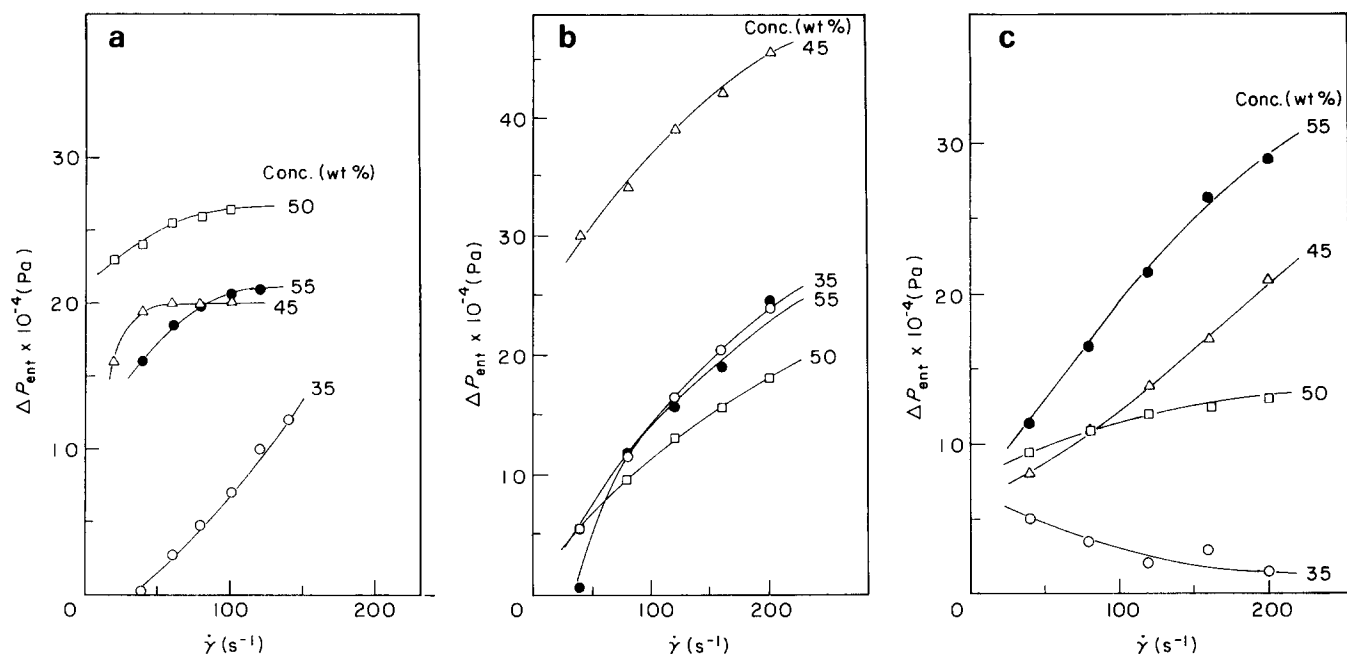


Figure 7 Entrance pressure drop vs. shear rate for solutions of (a) HPC in DMSO, (b) HPC in DMAc, and (c) HPC in water

that the die swell increases with shear stress in the single phase (isotropic and anisotropic ones) and decreases in the biphasic range. Then, we suppose there is a critical shear stress, below which the solution is isotropic, but above which the solution abruptly transfers from isotropic phase to the biphasic region. Consequently, the die swell for 45 wt% solution shows a maximum. The 55 wt% solution of HPC/DMSO and the 50 wt% solution of HPC/water are still in the biphasic region, whereas the 50 wt% solution of HPC/DMAc is fully anisotropic.

Figures 9a, 9b and 9c show the concentration dependence of ν at given shear rates for three systems. The factor ν exhibits a maximum and minimum with respect to concentration. The dependence of another elastic parameter at the die entrance, ΔP_{ent} , on concentration is shown in Figures 10a, 10b and 10c. The concentration dependence of the die swell is shown in Figure 11. The results shown in Figures 9, 10 and 11 clearly indicate that there is a great similarity between the three elastic parameters. This means that the elastic parameters at the

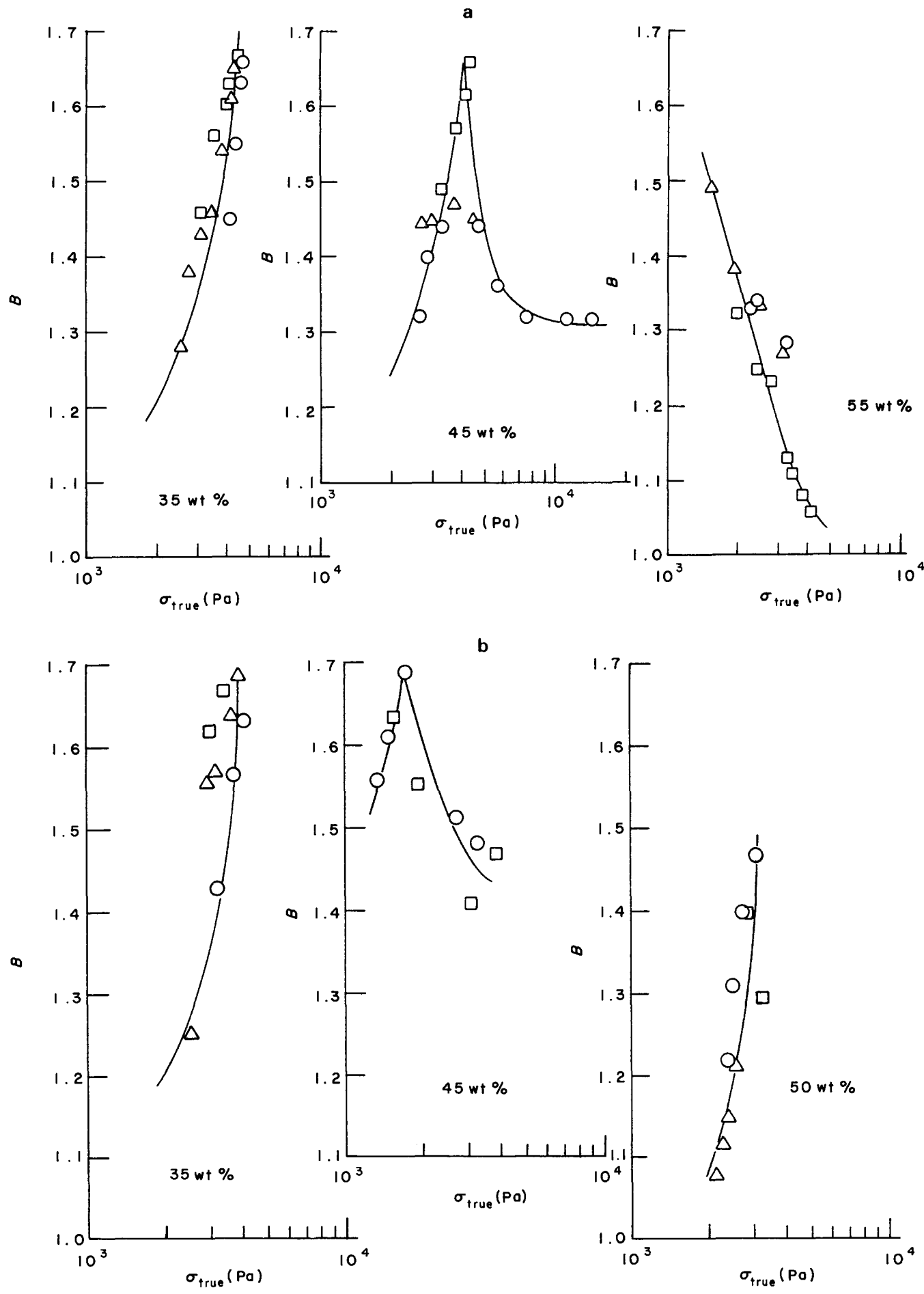


Figure 8 Die swell vs. shear stress for solutions of (a) HPC in DMSO, (b) HPC in DMAc

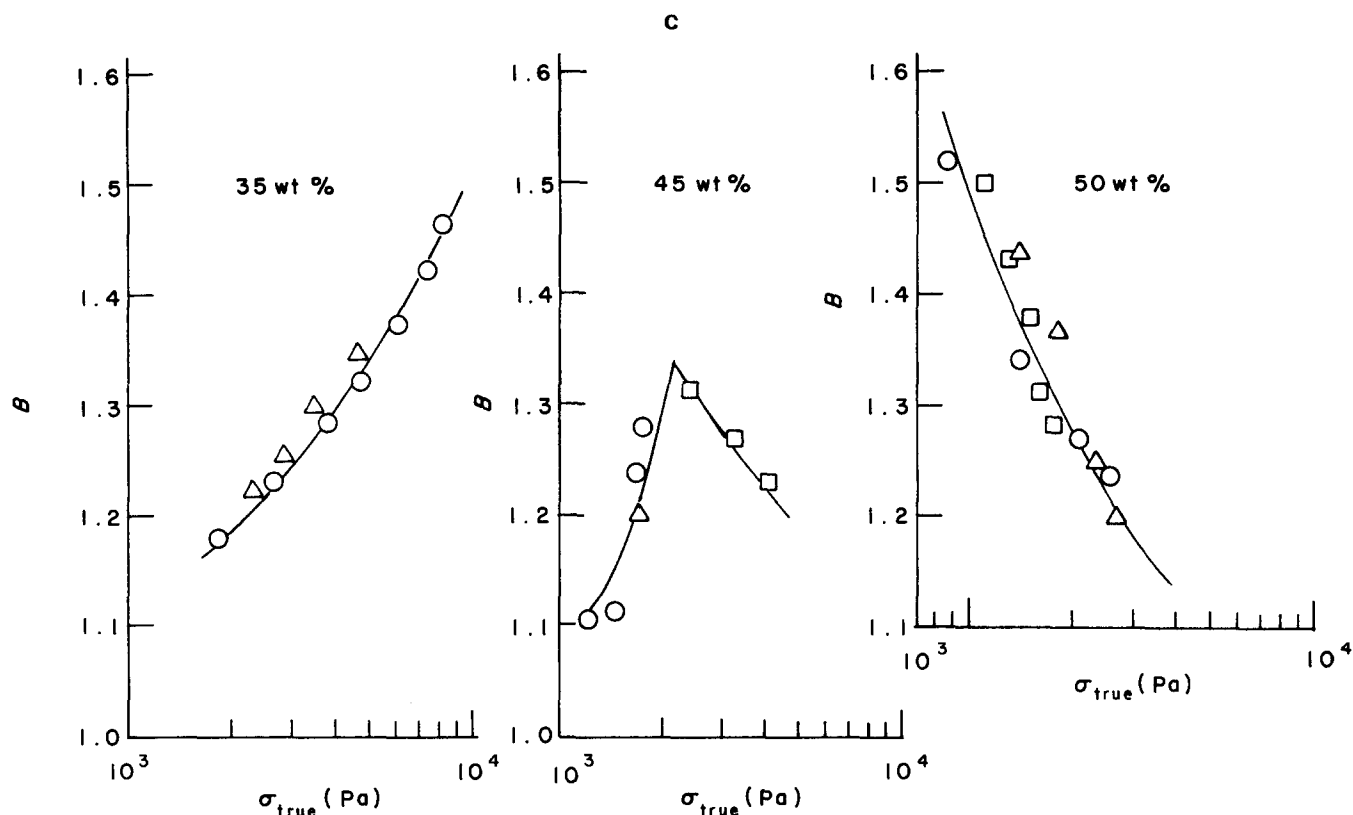


Figure 8 (continued) (c) Die swell vs. shear stress for solutions of HPC in water: $L/D=10$ (○), 20 (△), 40 (□)

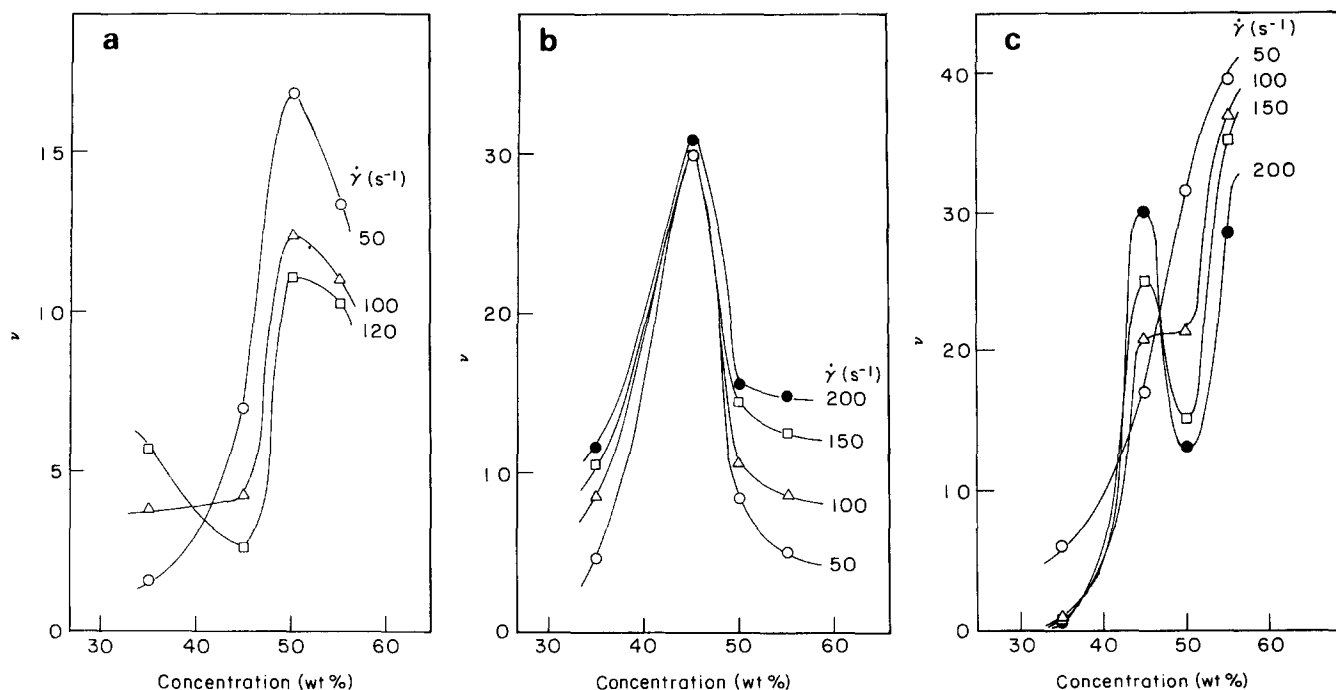


Figure 9 Concentration dependence of Bagley correction factor for solutions of (a) HPC in DMSO, (b) HPC in DMAc, and (c) HPC in water

die entrance and die exit are similar with respect to concentration. Baird *et al.*⁸ have noted that there is no correlation between an elastic parameter at the die entrance, $\Delta P_{\text{ent}}/\sigma$, and that at the die exit, B . Their finding is different from ours. They have employed a different form from ΔP_{ent} in characterizing the elasticity of melts⁸: $\Delta P_{\text{ent}}/\sigma$. However, it is not clear whether these different findings are only due to the different form of the elastic parameter or not.

The elastic parameter maximum becomes more pronounced as shear rate increases, whereas the viscosity maximum becomes less pronounced and finally disappears as shear rate increases. This behaviour is similar to that reported by Porter *et al.*⁶

It is noteworthy that (1) the concentration dependence of the viscosity is very similar to that of the elastic parameters and this is attributed to the transformations both from isotropic to biphasic state and

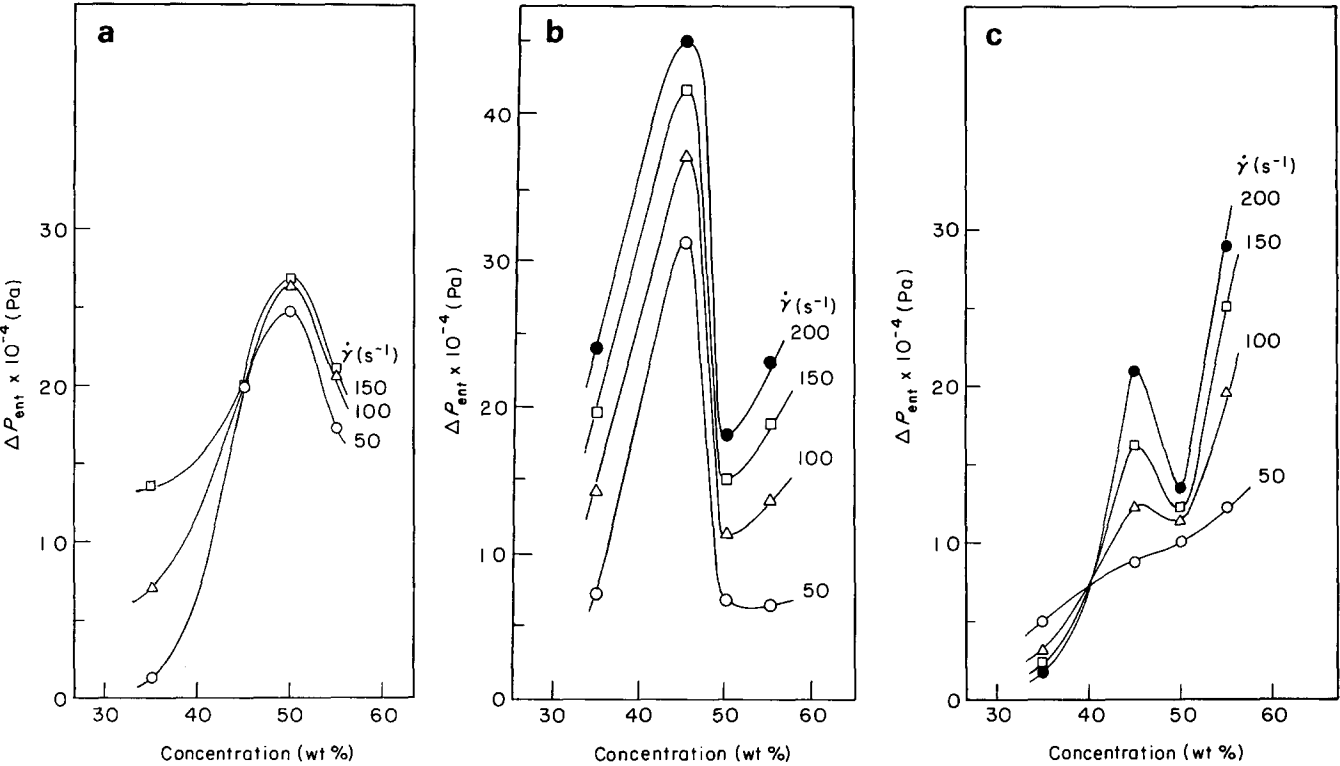


Figure 10 Concentration dependence of entrance pressure drop for solutions of (a) HPC in DMSO, (b) HPC in DMAc, and (c) HPC in water

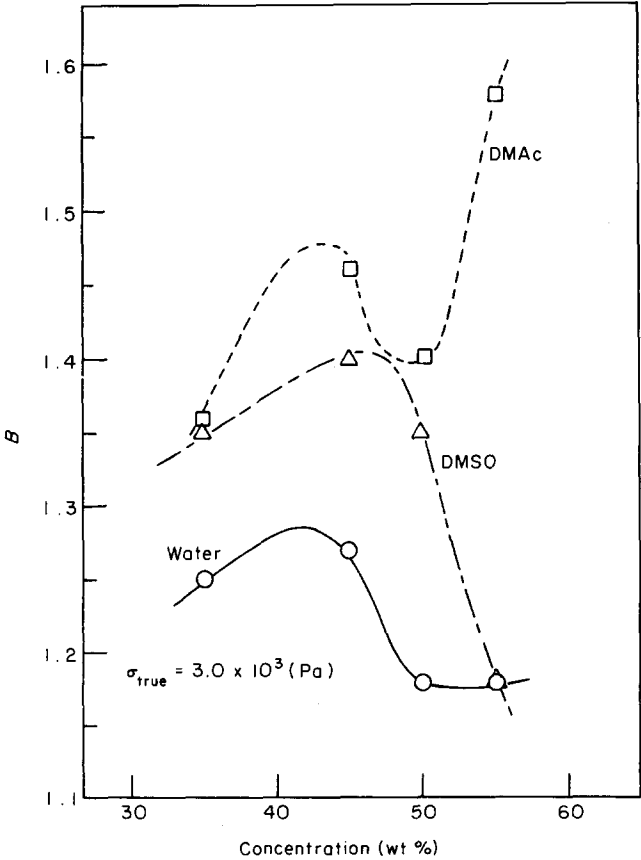


Figure 11 Concentration dependence of die swell for three systems

from biphasic to fully anisotropic state; (2) the viscometric behaviour is different from the elastic behaviour with respect to shear.

Next, we discuss the correlation between the elastic parameters. Philippoff and Gaskins¹⁴ have suggested the following relationship:

$$v \propto S_r \tag{3}$$

where S_r is recoverable shear strain and is a measure of the recoverable deformation that has been imposed on the solution prior to entry into the die. The energy stored by this deformation at the die entrance will be relaxed at the die exit and consequently the relaxation of the energy results in die swell¹⁵. Therefore, it is reasonable that the v behaviour is simply related to the die swell behaviour. In fact, the die swell was related theoretically to S_r by some investigators for isotropic solutions and melts^{16,18}:

$$B^3 \propto S_r \tag{4}$$

$$B^2 \propto S_r \tag{4'}$$

Equation (4)¹⁶ was derived based on Lodge's view¹⁷ of elastic recovery, whereas equation (4') was based on the theory of rubber elasticity¹⁸. Then, equations (3), (4) and equations (3), (4') yield equation (5) and equation (5'), respectively:

$$v \propto B^3 \tag{5}$$

$$v \propto B^2 \tag{5'}$$

According to equation (5) and (5'), when the logarithm of v is plotted against $\log B$, the slope obtained should be 3

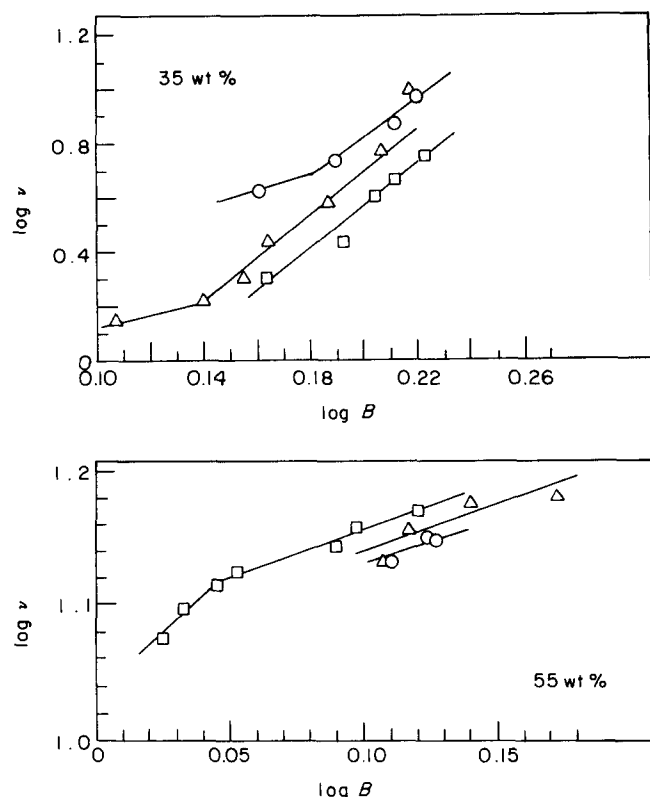


Figure 12 Correlation between logarithm of Bagley correction factor and logarithm of die swell for solutions of HPC in DMSO

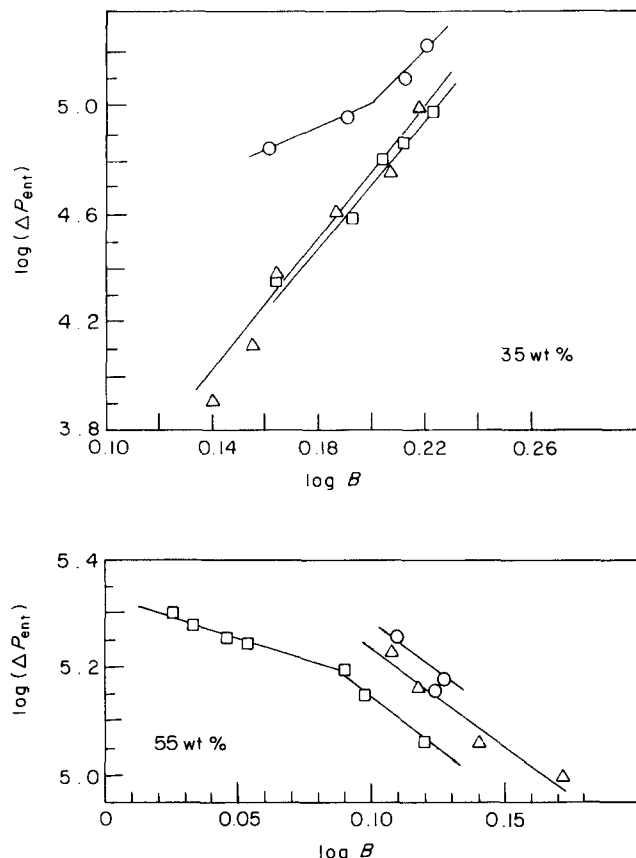


Figure 14 Correlation between logarithm of entrance pressure drop and logarithm of die swell for solutions of HPC in DMSO

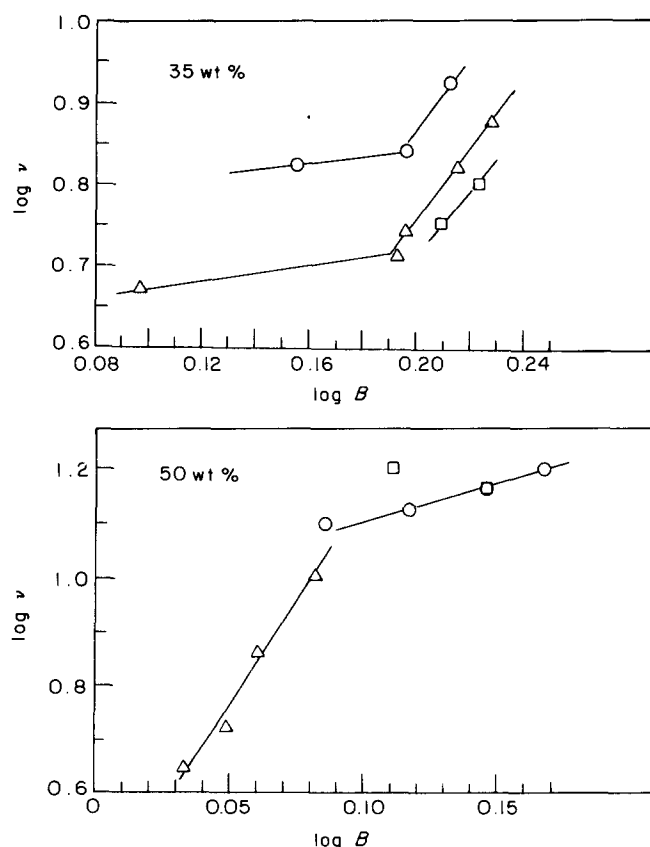


Figure 13 Correlation between logarithm of Bagley correction factor and logarithm of die swell for solutions of HPC in DMAc

or 2. Figure 12 shows this plot for the 35 wt % (isotropic) and 55 wt % (biphasic) solutions of the HPC/DMSO system, and Figure 13 shows it for the 35 wt % (isotropic) and 50 wt % (fully anisotropic) solutions of the HPC/DMAc system. Over a limited region the plots were linear and the slopes for the 35 and 55 wt % solutions of HPC/DMSO were ~ 8 and 0.7 , respectively; and those for the 35 and 50 wt % solutions of HPC/DMAc were 4.3 and 1.4 , respectively. The experimental values of the exponent for isotropic phases were larger than those for anisotropic ones. The exponents for the isotropic solutions were larger than 3 , whereas those for the anisotropic solutions were smaller than 2 . There is a great difference between the exponent predicted by equation (5) and experimental values and the physical meanings of this difference should be discussed in the future. It should be noted that there is a critical shear rate at which the slopes in Figures 12 and 13 change, and that there seems to be no correlation between $\log v$ and $\log B$ for the 45 wt % solutions: v increases monotonically and B exhibits a maximum with increasing shear.

The correlation between ΔP_{ent} and B is shown in Figures 14 and 15. This correlation is almost identical with that between v and B ; however, the slope was negative for biphasic solution (HPC/DMSO, 55 wt %).

Now, we express experimentally the following correlations between the elastic parameter at the die entrance and that at the die exit:

$$v \propto B^n \quad (6)$$

$$\Delta P_{\text{ent}} \propto B^{n'} \quad (7)$$

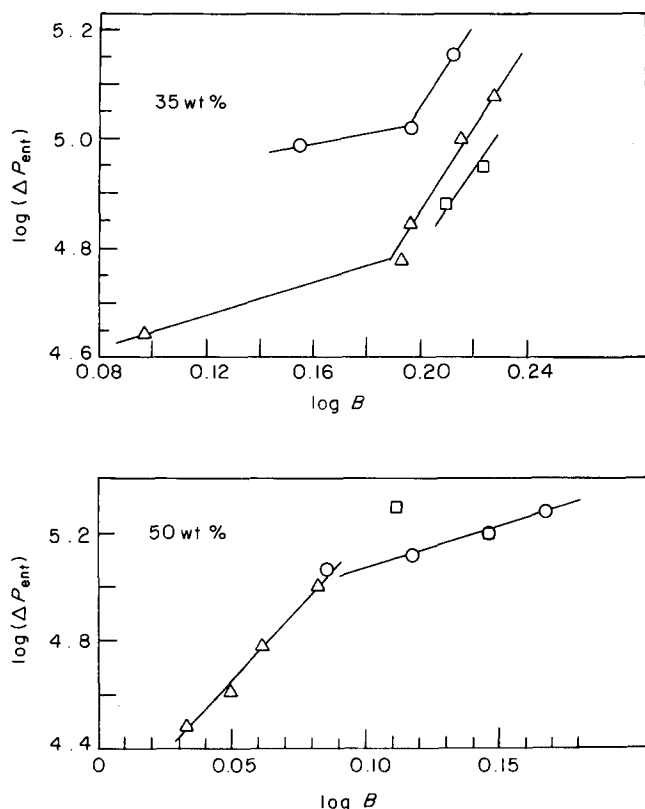


Figure 15 Correlation between logarithm of entrance pressure drop and logarithm of die swell for solutions of HPC in DMAc

where n and n' are constants which are dependent on concentration or shear rate range.

At any rate, v and ΔP_{ent} are simply related with B even for the fully anisotropic systems. If this relationship is established quantitatively, we may derive the correlation between B and the first normal stress difference N_1 for the anisotropic systems. For polymers, the following relation has generally been accepted as a reasonable approximation³:

$$N_1/2\sigma = S_r \quad (8)$$

From our findings on the relation between v and B , the following relations will be supposed:

$$B \propto N_1^m \quad (9)$$

Our approach needs further investigation.

CONCLUSIONS

There seems to be a great similarity between the true shear viscosity and the elastic parameters for our three systems with respect to concentration; however, there is no similarity between them with respect to shear rate. The Bagley correction factor v or the entrance pressure loss ΔP_{ent} is simply related to another elastic parameter B over a limited range; the relations are the following:

$$v \propto B^n$$

$$\Delta P_{\text{ent}} \propto B^{n'}$$

where n and n' are constants which are dependent on concentration and shear rate range. More rheological data are required to establish those relations between the elastic parameters.

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