

Recoverable Shear Strain of Liquid Crystal-Forming Concentrated Hydroxypropyl Cellulose Solutions

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ABSTRACT: The recoverable shear strain (S_R) for the liquid crystal-forming hydroxypropyl cellulose solutions was determined by means of a concentric cylinder rotational apparatus as functions of shear stress prior to recovery and concentration of the solutions at 30°C. S_R greatly depended on shear stress and concentration; the phase of the solution (the single phase or biphasic) governed the dependences of S_R on stress and concentration. S_R increased with increasing stress for the single phase and decreased for the biphasic. S_R seemed to be related to the die swell (B): $S_R \propto B^n$. S_R exhibited a maximum and a minimum with respect to concentration. S_R for the cellulosic cholesteric liquid crystalline solutions was greater than that for the isotropic solutions. A model was proposed for explaining the greater S_R . © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 865–872, 2002

Key words: recoverable shear strain; hydroxypropyl cellulose; cholesteric liquid crystal; shear stress; concentration

INTRODUCTION

We have determined the die swell behavior of cellulosic cholesteric liquid crystalline solutions.^{1–4} Our numerical values of the die swell were relatively greater than others observed by some other researchers.^{5–7} Now, it seems to be that generally the liquid crystals have less die swell than the isotropic solutions or melts, contrary to our data. We need to confirm our finding: the behavior of relatively greater die swell for the cellulosic cholesteric liquid crystalline solutions. Therefore, we try to obtain the behavior of another elastic parameter of the same cellulosic cholesteric liquid crystalline solu-

tions at almost the same shear conditions as those of determining the die swell.

Recoverable shear strain (S_R) is an elastic parameter and is more general than the die swell.⁸ S_R was correlated with the die swell for isotropic solutions and melts,^{9–13} despite less data of S_R for liquid crystals.^{14,15} Consequently, we chose S_R as another elastic parameter in this study.

To determine S_R , much attention was denoted to the following: (1) the range of shear stress is as close as possible to the range of shear stress determining the die swell; (2) S_R is obtained after cessation of a steady-state flow. It seems to be difficult that two conditions noted above can be satisfied at the same time by means of the commercial instruments. We tried to design and construct an apparatus, a concentric cylinder rotational viscometer, because of its mechanical simplicity.

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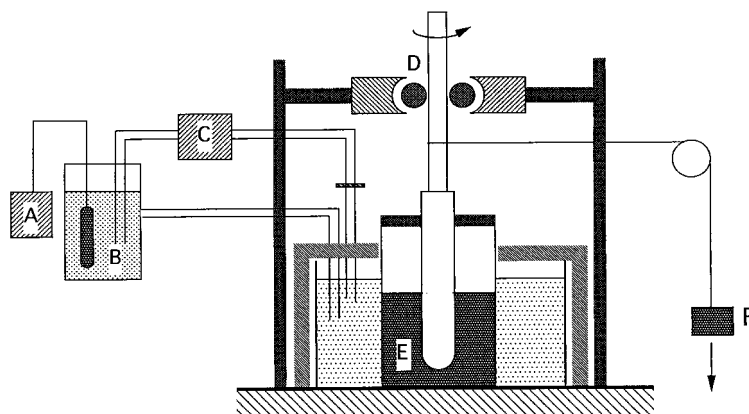


Figure 1 Schematic drawing of apparatus for recovery measurement; A: thermoregulator; B: thermostat; C: pump; D: ball bearing; E: sample solution; F: load.

We, first, show the validity of our apparatus and then determine simultaneously the shear viscosity at steady state and S_R after cessation of the steady-state flow for the hydroxypropyl cellulose (HPC) solutions in dimethylacetamide (DMAc) and in *m*-cresol as functions of shear and concentration. The viscosity is determined to identify the phase transformation of the solutions. The difference in S_R in the isotropic and anisotropic solutions and the reason for our relatively greater die swell data of cellulosic cholesteric liquid crystalline solutions are discussed.

EXPERIMENTAL

Samples

Commercial reagent grade HPC (Tokyo Kasei Kogyo Co. Ltd.) was used as received. The weight- and number-averaged molecular weights determined by gel permeation chromatography with tetrahydrofuran as the carrier solvent and polystyrene standards were 11.7×10^4 and 5.2×10^4 , respectively. The molar substitution of HPC was 4.25, determined by means of NMR spectroscopy.¹⁶ Commercial reagent grade DMAc and *m*-cresol (Wako Pure Chemical Industry Co. Ltd., Japan) were used without further purification.

Preparation of Concentrated Solutions

Given amounts of HPC powder and DMAc or *m*-cresol were mixed and the mixtures were vigorously stirred until the powder dissolved. The solutions were allowed to stand in the dark at $\sim 10^\circ\text{C}$ for ~ 2 months. The solution concentra-

tions in this study were 40–60 wt % for the HPC/DMAc system and 20–35 wt % for the HPC/*m*-cresol system.

Rheometry of Concentrated Solutions at 30°C

A schematic drawing of our apparatus for determining the shear viscosity and S_R was shown in Figure 1. The constant load-type apparatus was chosen. The inner cylinder was held by ball bearings and rotated by applying a load directly over pulley. The angular velocity (ω) of the inner cylinder was dependent on the load. The falling velocity of the load for given concentrations of solutions was determined and divided by the radius of the inner cylinder (R_1 : 0.9 cm) for calculating the angular velocity of the inner cylinder. Figure 2 shows the falling velocity of the load against the distance of the falling load. Each measurement was repeated at least three times. Although there were some scatter, the trends were probably true. The reproducibility was better than 5%. The fluctuation of the inner cylinder during rotation was negligible. The longer the distance of the falling load, the slower the falling velocity. Finally, the falling velocity became almost constant; the inner cylinder rotated at a steady state. We needed ~ 2 m of the distance of the falling load to obtain the steady state for the liquid crystalline solutions. The shear rate was calculated by using

$$\dot{\gamma} = \omega_0 R_0 / (R_0 - R_1) \quad (1)$$

where ω_0 is the angular velocity at the steady state and R_0 is the inside radius of outer cylinder (1.35 cm). The shear stress is calculated by using

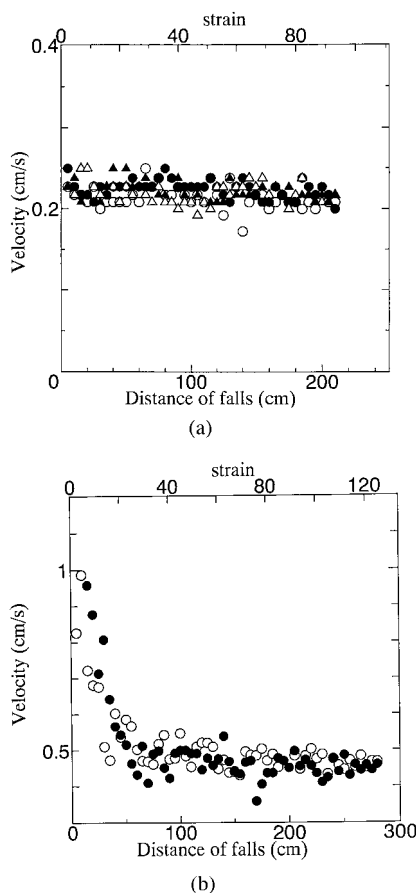


Figure 2 Falling velocity of load versus distance of falling load for solution of HPC/DMAc at 30°C; (a) 40 wt %, stress: 64.8 (Pa). ○: first trial; ●: second trial; △: third trial; ▲: fourth trial; (b) 60 wt %, stress: 216 (Pa). ○: first trial; ●: second trial.

$$\sigma = T/(2\pi LR_1^2) = M/(2\pi LR_1) \quad (2)$$

where T is the torque and is equal to the product of the applied load and R_1 , M is load, and L is the effective length of the inner cylinder, the soaking length in the sample solution (8 cm). The shear viscosity at the steady state (η) is calculated by using eqs. (1) and (2).

$$\eta = \sigma/\dot{\gamma} \quad (3)$$

After reaching steady state, the rotation of the inner cylinder was ceased by taking away the load. The inner cylinder rotated slowly in the reverse direction. The recovered distance was measured by means of a traveling microscope. The recovered distance was determined at 1, 30, and 60 min. Generally, the recovered distance

increases with time as a function of the applied shear stress and the curve can be superimposed by plotting the total strain $\dot{\gamma}_0 t$, where $\dot{\gamma}_0$ is the steady shear rate prior to recovery and t is the time after the cessation of applied load.¹⁴ In our study, the total strain was on order of $\sim 5 \times 10^3$. The recovered distance attained an equilibrium at ~ 30 min. The recovered angular displacement (α) was calculated by dividing the equilibrium recovered distance by the radius of the inner cylinder. The recoverable shear strain (S_R) is calculated by using

$$S_R = 2R_0\alpha/(R_0^2 - R_1^2) \quad (4)$$

where S_R was determined at least three times at the same conditions.

In this study, as the inner cylinder a conicylinder was used to minimize the end effects. The effect of inertia on the recovery of the inner cylinder could be negligible within our experimental precision. The Weissenberg effect (a thrust of the inner cylinder) was ignored.

The shear viscosity was also determined by means of a commercial cone-plate type viscometer (Soliquidmeter MR-3, Rheology Ltd., Kyoto, Japan), in comparison to the viscosity determined by means of our apparatus.

RESULTS AND DISCUSSION

Comparison of Shear Viscosities Determined by Different Viscometers

As shown in Figure 2, the falling velocity of the load was independent of the distance of the falling load for the solutions of relatively lower concentrations and was dependent on the distance for the solutions of relatively higher concentrations. For the solutions of higher concentrations, the falling velocity decreased with the distance and finally became constant. From the constant velocity, the shear rate was calculated. Later on in this work, we will show that the solutions of lower or higher concentrations are isotropic or anisotropic, respectively. This agreed with the general view that the anisotropic solutions needed greater total strain to reach steady state.^{14,17}

Figure 3 shows the shear viscosities at the steady state determined by means of our apparatus and the cone-plate type rheometer. For our two systems (HPC/DMAc and HPC/*m*-cresol), the data of the dependences of viscosity on shear rate

could yield almost a single curve, although the data determined with our apparatus tended to be lower than those with another rheometer by $\sim 4\%$. This suggested that the shear viscosity determined with our apparatus was reasonable; shear rate and shear stress in our study were reasonable. Consequently, our apparatus was appropriate for determining shear properties and the recoverable shear strain as a function of shear stress was reasonable.

Phase Transformation of Our Systems

Our two systems are widely known to form lyotropic liquid crystals at a critical concentration.^{18,19} We need to show the critical concentration for each system, because the rheological behavior greatly depends on the phase (isotropic, biphasic, and fully anisotropic). The critical concentration can be evaluated from the viscosity-concentration curve and from the polarized microscopy. Figure 4 shows the dependence of shear viscosity on the concentration for our systems; a maximum and a minimum were exhibited. Around the maximum, the anisotropic phase first forms, and around the minimum, the isotropic phase finally disappears. The HPC/DMAc system exhibited the maximum around 48 wt % and the minimum around 53 wt %, and the HPC/*m*-cresol system exhibited the maximum around 25 wt % and the minimum around 30 wt %. Although the conditions (shear rate) were slightly different from those in this work, the critical concentrations for both systems were almost the same as those already determined for the same systems by our group.^{18,19} The data in Figure 4 indicated that

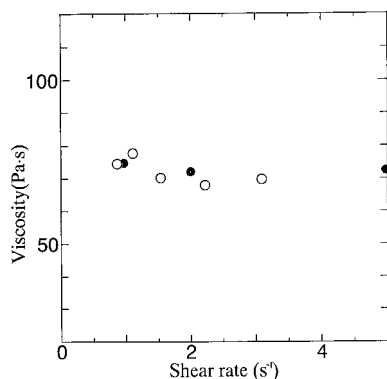


Figure 3 Dependence of viscosity on shear rate for the 40 wt % solution of HPC/DMAc. ○: by means of our apparatus; ●: by means of cone-plate type viscometer.

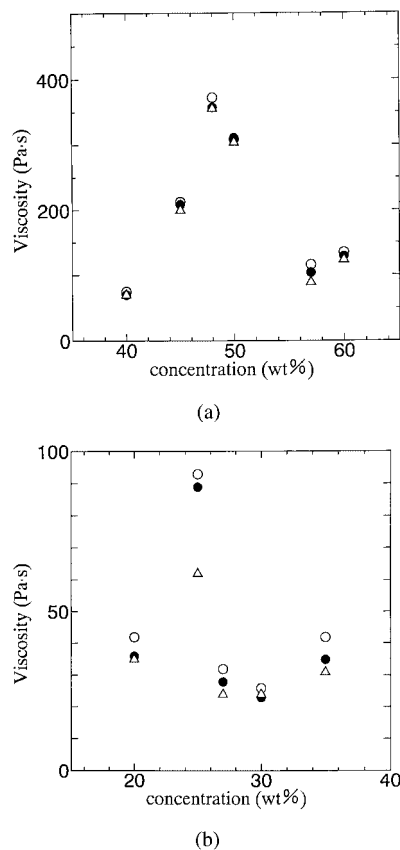


Figure 4 Dependence of viscosity on concentration; (a) HPC/DMAc, stress (Pa): ○: 64.8; ●: 108; △: 216; (b) HPC/*m*-cresol, stress (Pa): ○: 21.6; ●: 32.4; △: 64.8.

the HPC/DMAc system was isotropic below 48 wt %, biphasic between 48 and 53 wt %, and fully anisotropic above 53 wt %. The HPC/*m*-cresol system was isotropic below 25 wt %, biphasic between 25 and 30 wt %, and fully anisotropic above 30 wt %. The phase noted above was confirmed by observation of polarized microscopy. The difference in the plots between the falling velocity and the distance of the falling load shown in Figure 2 also suggested the phase of each solution: the curve was independent of the distance of the falling load for the isotropic solutions and was dependent on the distance of the falling load for the anisotropic ones.

Dependence of S_R on Shear Stress Prior to Recovery

Figure 5 shows the dependence of S_R on shear stress prior to recovery for our systems. Although relatively great scatter for the biphasic solutions was shown in Figure 5, the trends were probably

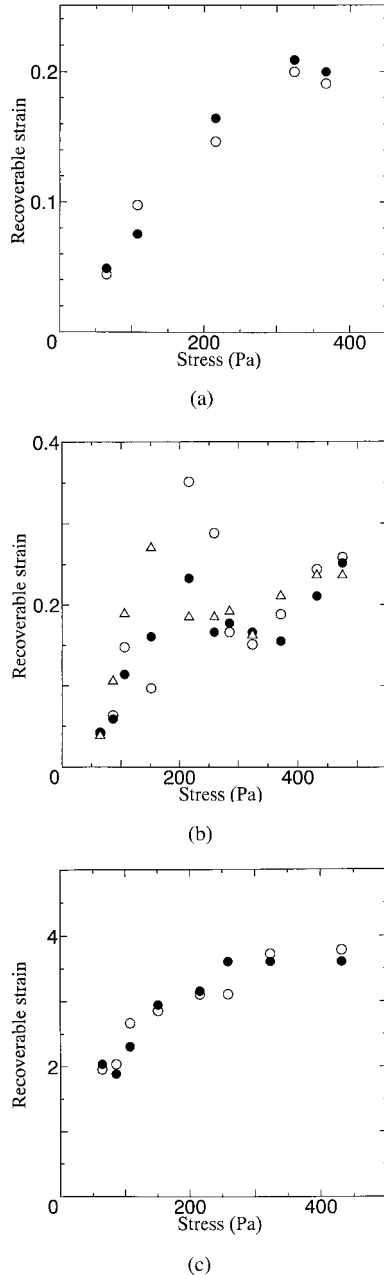


Figure 5 Dependence of recoverable strain on stress for HPC/DMAc, (a) 45 wt %; (b) 48 wt %; (c) 60 wt %. ○: first trial; ●: second trial; △: third trial.

real. The dependence greatly depended on the phase of the solutions; for the single phase (isotropic and fully anisotropic), S_R increased monotonically with increasing shear stress, whereas S_R exhibited a maximum and a minimum at given critical shear stresses for the biphasic solutions. The critical shear stress at the maximum seemed to be independent of the solution concentrations

and was ~ 200 Pa for the HPC/DMAc system and was ~ 40 Pa for the HPC/*m*-cresol system. When the data in Figure 5 were plotted on a logarithmic scale, they were positioned almost on a straight line with some scatter. The slope of the line calculated by the least-squares method was shown as a function of concentration in Figure 6. The slope was ~ 1.1 for the isotropic solutions and ~ 0.5 for the fully anisotropic solutions. For the biphasic solution (48 wt %), the slope had two values; one value was for the isotropic domain over the range of relatively lower stress, and another value was for the fully anisotropic value over the range of relatively higher stress.

We have already determined the die swell (B) through a long capillary die for the same HPC/DMAc system.⁴ Here, we compare the dependences of S_R and B on shear stress. Figure 7 shows the logarithmic plots of both parameters versus shear stress for the HPC/DMAc system. Both parameters versus stress were linear over our range of stress. For the isotropic solution (40 wt %), the slopes of S_R and B were 1.58 and 0.57, respectively; for the fully anisotropic solution (60 wt %), the respective slopes were 0.44 and 0.23.

As shown in Figure 7, S_R and B versus stress were linear. Then, the following relations can be obtained,

$$S_R \propto \sigma^n \quad (5)$$

$$B \propto \sigma^{n'} \quad (6)$$

where n and n' were constants. It is noteworthy that the ranges of stress for S_R and B were different in one order. Therefore, we assume that

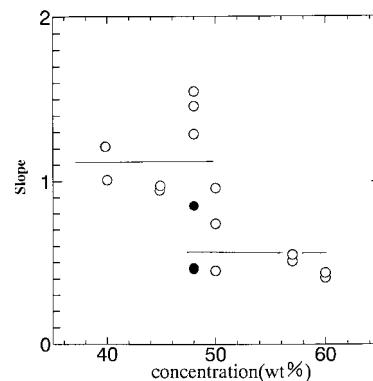


Figure 6 Dependence of slope of $\log S_R$ versus $\log \sigma$ on concentration for HPC/DMAc. For the slope (●), refer to the text.

eqs. (5) and (6) are valid over the range in stress from 102 to 103.5 Pa. Consequently, S_R can be related to B as

$$S_R \propto B^{n/n'} \quad (7)$$

Our results, shown in Figure 7, indicated that the value of n/n' was ~ 2.8 for the isotropic solutions and was ~ 1.9 for the fully anisotropic solutions. Tanner derived the following relation¹⁰ for isotropic solutions,

$$S_R \propto B^3 \quad (8)$$

Our value of n/n' for the isotropic solution was close to 3. This suggested that eq. (7) was valid for

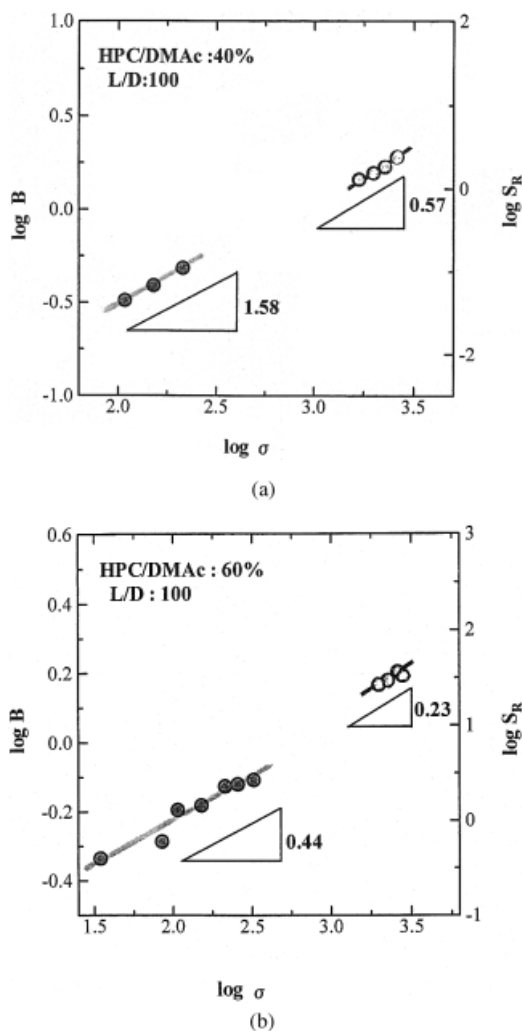


Figure 7 Dependences of S_R (●) and die swell (B , ○) determined through long die of L/D of 100 on stress for HPC/DMAc, (a) 40 wt %; (b) 60 wt %.

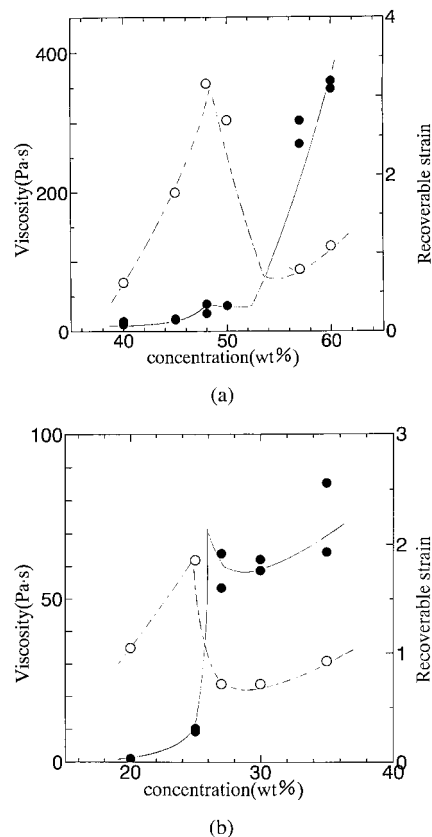


Figure 8 Dependences of viscosity (○) and S_R (●) on concentration; (a) HPC/DMAc, stress: 216 (Pa); (b) HPC/*m*-cresol, stress: 64.8 (Pa).

our isotropic solutions. Therefore, it can be presumed that the value of n/n' for the fully anisotropic solutions is 2; that is, $S_R \propto B^2$ for the fully anisotropic solutions.

Evidently, the data in Figure 7 were not necessarily satisfactory. Further investigation is needed to obtain the general relation between S_R and B for the liquid crystals.

It should be noted that the relation we proposed above was obtained for only the single-phase solutions (isotropic and fully liquid crystalline) and not for the biphasic solutions. At the present stage, it is quite unexpected to obtain the relation between S_R and B for the biphasic solutions.

Dependence of S_R on Concentration

Figure 8 shows the dependence of S_R on the concentration. In this figure, the values of S_R were determined at the stress of 216 Pa, which was over the critical shear stress in Figure 5. In Fig-

ure 8, the shear viscosity determined at the same shear stress was also plotted. S_R exhibited a maximum and a minimum. This showed that the critical concentrations that exhibited the maximum and minimum were the almost the same for both parameters. Our finding clearly indicated that S_R depended on the phase of the solution as the shear viscosity did. This trend of S_R behavior was similar to the first normal stress difference behavior^{20,21} and the die swell behavior.¹⁻⁴ Consequently, the elastic properties for the liquid crystal-forming system depended on the phase of the system as the viscometric properties did.

In Figure 8, there were less data around minimum. The minimum point seemed groundless. We, however, have already obtained the phase diagrams for the same systems (using the same samples) and could easily estimate the critical concentration at 30°C: the critical concentration was 54 wt % for the HPC/DMAc system and 28 wt % for the HPC/*m*-cresol system.^{18,19}

Another important feature in Figure 8 was that S_R for the fully anisotropic phase was greater than that for the isotropic phase. The values of S_R were over 2 for the fully liquid crystalline phase. S_R for the 60 wt % solution increased with increasing stress and was ~ 3.7 at a higher stress, as shown in Figure 5. The value of ~ 3.7 was almost the same as that predicted by Larson and Doi.²² Some groups have reported that the liquid crystals exhibited little or no die swell.⁵⁻⁷ Only our data indicated relatively greater die swell behavior.¹⁻⁴ Our finding in Figure 8 was in harmony with our die swell behavior and was not with other groups' die swell behavior.

Model for Greater S_R

We have employed only cellulosic samples (HPC and ethyl cellulose) for studying rheological behavior of liquid crystals.^{3,4,23} Cellulosic liquid crystals form the cholesteric order, although some derivatives exhibit left-handedness and some exhibit right-handedness. We suggest that the cholesteric order is the key factor for the cellulosic liquid crystal to exhibit the greater S_R and die swell. Figure 9 represents our simple model for explaining greater S_R . During the steady flow, the molecules orient toward the flow direction (monodomain), regardless of the phase of the solutions. After the sudden cessation of stress, the molecules in the isotropic and liquid crystalline solutions return to the original order (i.e., isotropic, or cholesteric liquid crystalline order). The

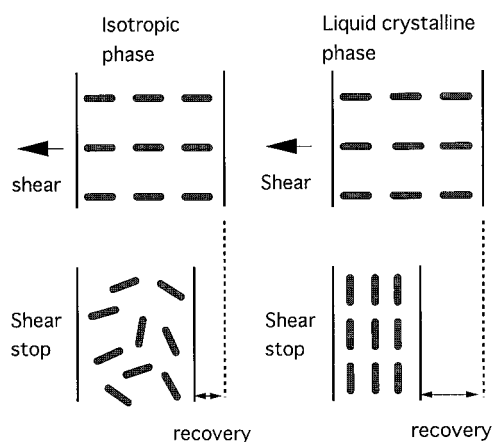


Figure 9 Our model for explaining greater S_R . In the upper half of the figure are given the molecular orientations for both phases; in the lower half is given the recovery after cessation of stress.

oriented direction for the cholesteric liquid crystalline solutions, especially, changes mainly at a right angle to the direction during flow.

Apparently, our model is too simple. Liquid crystalline solutions originally form the polydomain at rest, which is made up of many small domains. The molecules in each small domain are oriented with respect to a director, and the small domains are then oriented with respect to a global director. The molecules after shear stop shown in Figure 9 are not oriented with respect to the director, but the global director; the distance between the oriented molecules shown in Figure 9 for the liquid crystalline phase is regarded as a half-pitch of the cholesteric order.

S_R for the cholesteric liquid crystalline order was greater than that for the isotropic order. The cholesteric order is similar to the imposition of a twist distortion on a nematics. The twist distortion was supposed to govern the elastic behavior for our cellulosic liquid crystalline solutions, having a greater effect on the elastic behavior than a spray or a bend distortion.

When this model is applied to the nematics, it will be suggested that S_R for the liquid crystalline order is smaller than that for the isotropic order or is nearly equal to that for the isotropic order.

Based on our model, polypeptide liquid crystalline solutions will be predictable to exhibit a great die swell.

CONCLUSION

S_R depended on shear stress and concentration. S_R increased monotonically with stress for the

single phase (isotropic and fully anisotropic) and exhibited a maximum and a minimum with regard to stress for the biphasic. The stress dependence of S_R for the isotropic phase was greater than that for the fully anisotropic phase. The biphasic exhibited both dependences of the isotropic and fully anisotropic phases. S_R seemed to be related to the die swell (B); $S_R \propto B^n$, the exponential n depended on the phase of the solutions. S_R exhibited a maximum and a minimum with increasing concentration and the concentrations at the maximum and minimum were almost the same as those for the shear viscosity determined at the same conditions. This strongly suggested that S_R increases with concentration for the single phase (isotropic and fully anisotropic) and decreases with concentration for the biphasic. S_R for our cholesteric liquid crystals was greater than that for the isotropic solutions. This is due to the change in liquid crystalline order: changes from the stress-induced nematic order to the original cholesteric order. The twist distortion was the key factor for our great S_R and B .

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