

Transient Shear Response of Liquid Crystal-Forming Hydroxypropyl Cellulose Solution in Dimethylacetamide.

I. Stress Growth and Relaxation Behavior

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SYNOPSIS

The stress growth and relaxation behavior of liquid crystalline hydroxypropyl cellulose solutions in dimethylacetamide was characterized by using exponential functions. The parameters evaluated for the stress growth and relaxation processes were compared and the shear history effect on the parameters was determined. The exponential functions proposed were valid for our system. The isotropic solutions had one retardation time and one relaxation time, whereas the liquid crystalline solutions had plural retardation and relaxation times. The concentration dependence of the parameters for the stress growth process was similar to that for the stress relaxation process and to that for the steady-state shear viscosity. The stress growth and relaxation behavior for the liquid crystalline solutions was originated from the change (deformation or decrease) in liquid crystalline domains. The deformation of liquid crystalline domains with shear seemed to be slower than the recovering of the domains to original shape. The stress growth process was a progressive event, whereas the relaxation process was a sudden event. Stress relaxation behavior for the liquid crystalline solutions was sensitive to the shear history. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Liquid crystals (LCs) are widely known to exhibit an anomalous stress growth and relaxation behavior.¹⁻¹² The anomalous behavior originates from the change in polydomain structure of LCs.^{2,13} The data, however, are still insufficient to understand fully the anomalous behavior. Furthermore, some mathematical equations are needed to characterize the anomalous behavior.

In our previous paper,¹⁴ we proposed an analytical method for characterizing the stress relaxation behavior of lyotropic ethyl cellulose liquid crystalline solution (LCS) in *m*-cresol, and have described that there are two relaxation mechanisms for the LCS, and one mechanism for the isotropic solutions.

In this study, we try to confirm the analytical method proposed in our previous paper,¹⁴ using another cellulosic LCS: hydroxypropyl cellulose (HPC) solution in *N,N*-dimethylacetamide (DMAc). We also try to extend the analytical method to the stress growth behavior of the HPC LCS, compare both parameters for the stress growth and relaxation behavior, and determine the effect of shear history on the stress relaxation behavior.

EXPERIMENTAL

Samples

HPC (Tokyo Kasei Kogyo Co. Ltd.) was used as received. The weight-average and number-average molecular weights were 11.7×10^4 and 5.2×10^4 , and the molar substitution was 4.25.¹⁵ A commercial

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reagent grade DMAc (Wako Pure Chemical Ind. Ltd.) was used without further purification. The concentrated solutions were prepared as the same procedure described in our previous papers.¹⁵⁻¹⁷ The concentrations of the solutions prepared were 35, 40, 43, 45, 48, 50, 52, 55, 57, and 60 wt %.

Transient Stress Behavior

A cone-plate type viscometer (Tokyo Keiki Co. Ltd.) was used. The precautions (storage and rest of LCS) before starting measurements were the same as those reported in detail elsewhere.¹⁴ All behavior was determined at $25^\circ \pm 0.3^\circ\text{C}$. Our experimental method, that is, shear history and shear stress pattern, is shown schematically in Figure 1. First, the solution was subjected to constant shear rate of 2 s^{-1} until the shear stress reached a steady state, and the state was continued for 20 min. This was a stress growth process. Then, the shear rate was abruptly changed to 1 s^{-1} , and the change in stress was followed as a function of time until another steady state was reached. This was a stress relaxation process. This was the first cycle. After 45 min rest, the second cycle was restarted. The third cycle was tried for some concentrations. In the second and third cycles, only relaxation behavior was analyzed, and the effect of shear history on the relaxation behavior was determined. It is needless to say that the stress pattern, particularly stress growth pattern, greatly depends on the experimental and material conditions. In Figure 1, the general behavior for an isotropic solution was drawn as example.

ANALYSIS

Stress Relaxation

We have proposed the following equation.¹⁴

$$\begin{aligned} (\sigma^-(t) - \sigma_f) / (\sigma_i - \sigma_f) &= \sigma^* \\ &= A_1 \exp(-t/\tau_1) \quad \text{for } t < t_c \\ &= A_2 \exp(-t/\tau_2) \quad \text{for } t > t_c \end{aligned} \quad (1)$$

where σ_i and σ_f are steady-state shear stresses at shear rate $\dot{\gamma}_i(2\text{ s}^{-1})$ and $\dot{\gamma}_f(1\text{ s}^{-1})$, $\sigma^-(t)$ is time-dependent stress decay function, A_1 and A_2 are constants, and τ_1 and τ_2 are relaxation times, t is time, and t_c is a characteristic time. The parameters A_1 and A_2 are supposed to be correlated to the volume fractions of the components that contribute to each relaxation process. Strictly speaking, this is ambiguous, as discussed in our previous paper.¹⁴ When logarithm of σ^* was plotted against time, one straight line was obtained for isotropic solutions, and two straight lines for LCSs. The correlation coefficients (R^2) were better than 0.998, regardless of polymer concentrations. The parameters τ_1 , τ_2 and A_1 , A_2 could be evaluated from the slopes and intercepts of the straight lines, respectively. For LCSs, the two straight lines were extrapolated to find the characteristic time t_c .

An alternative equation (a double exponential equation) has been proposed by Mercer and Weymann.¹⁸ However, we prefer eq. (1) to the other

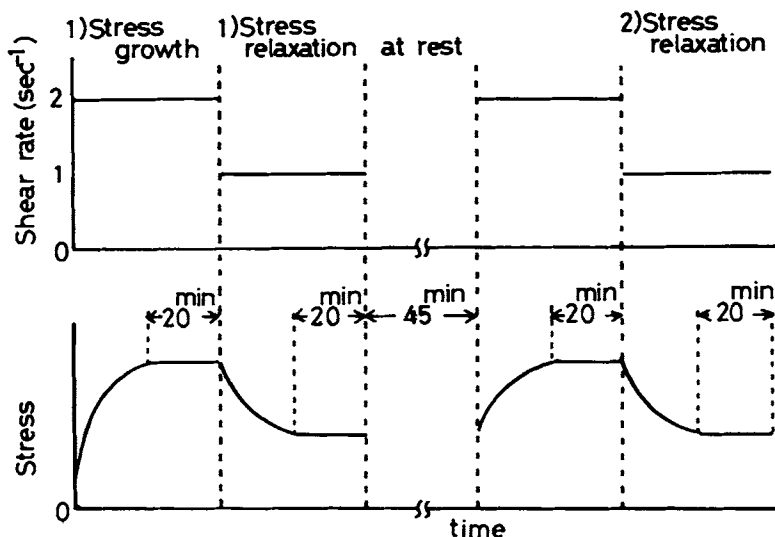


Figure 1 Schematic shear rate and typical shear stress response for interrupted shear.

equation because of former's simplicity. Simple analysis is suitable for the sake of providing some perspective of relaxation mechanisms.

Stress growth

Figure 2 shows the schematic representation of stress growth behavior for LCSs. We now propose a similar equation as the eq. (1) for stress growth behavior of LCSs.

$$\begin{aligned}
 (\sigma_f - \sigma^+(t)) / (\sigma_f - \sigma_i) &= \sigma^* \\
 &= B_1 \exp(-t/S_1) \quad \text{for } 0 < t < t_{c1} \\
 &= B_2 \exp(-t/S_2) \quad \text{for } t_{c1} < t < t_{c2} \\
 &= B_3 \exp(-t/S_3) \quad \text{for } t_{c2} < t \quad (2)
 \end{aligned}$$

where $\sigma^+(t)$ is time-dependent stress growth function, B_1 , B_2 , and B_3 are constants, S_1 , S_2 , and S_3 are retardation times, and t_{c1} and t_{c2} are characteristic times. The physical meanings of pre-exponential factors are ambiguous, but we suppose that they are correlated to the volume fractions of the components that contribute to each stress growth process, as A_1 and A_2 for the stress relaxation. For stress growth behavior, $\sigma_i = 0$. In a similar manner as the relaxation, when σ^* is plotted against time, one straight line is obtained for isotropic solutions and three straight lines for LCSs. The parameters, S_1 , S_2 , S_3 , and B_1 , B_2 , and B_3 can be evaluated from the slopes and intercepts of the straight lines, respectively. The characteristic times t_{c1} and t_{c2} also can be evaluated by extrapolation method.

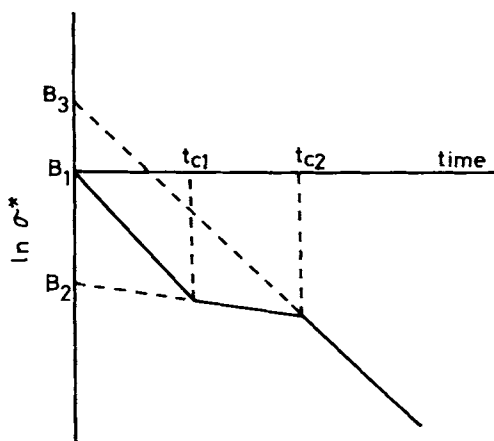


Figure 2 Schematic representation of stress growth behavior for liquid crystalline solutions.

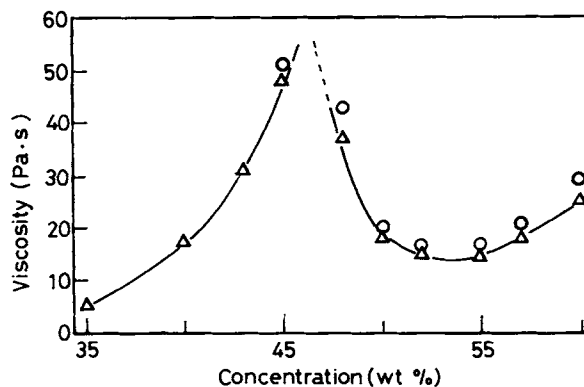


Figure 3 Concentration dependence of steady-state shear viscosity. Shear rate (s^{-1}): \circ 1; Δ 2.

RESULTS AND DISCUSSION

Steady-State Viscosity

Figure 3 shows the dependence of steady-state viscosity on concentration at given shear rates. The viscosity exhibited a typical behavior for liquid crystal-forming solutions: the viscosity exhibited a maximum and a minimum with respect to concentration.¹⁹⁻²³ Around the maximum (Ca), liquid crystalline phase first forms, and the formation of liquid crystalline phase is accomplished around the minimum (Cb).²⁰⁻²² The critical concentrations Ca and Cb of our system at 25°C were 47 and 54 wt %, respectively. The critical concentration Ca was verified using polarized microscopy. Clearly, for the isotropic solutions, the viscosity was independent of shear rate, whereas for the LCSs, the viscosity was dependent on shear rate. This dependence of viscosity on shear rate for the LCSs suggested that the shear rate region in this study is the region I of Onogi and Asada model,¹³ not region III.

Stress relaxation behavior

Plotting the logarithm of σ^* versus time, one straight line was obtained for the isotropic solutions, whereas two straight lines were obtained for the LCSs as shown in Figure 4. Therefore, eq. (1) was valid for our system and four parameters in eq. (1) could be evaluated. Clearly, our LCSs had two relaxation mechanisms and our isotropic solutions had one mechanism. This was the same as that reported in our previous paper.¹⁴ Figure 5 shows the concentration dependence of the parameters in the eq. (1). Relaxation time τ_1 exhibited a maximum and a minimum at Ca and Cb, respectively. Over the 45 wt %

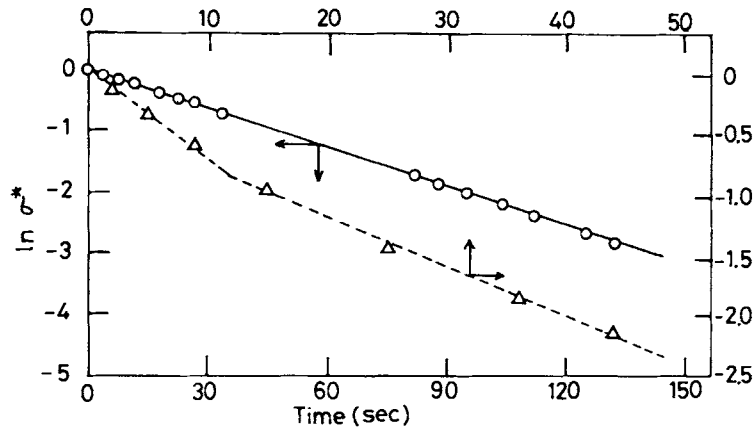


Figure 4 Typical relaxation behavior of reduced stress as a function of time for (O) 45 and (Δ) 55 wt % solutions.

solution, τ_2 could be obtained and exhibited a minimum at Cb. Furthermore, τ_2 was greater than τ_1 . The order of the relaxation times was 10^1 s (less than 50 s). A_1 was unity and was independent of concentration. A_2 was 0.7–0.9 and tended to exhibit

a minimum at Cb. Another system (HPC/water) prepared by us also exhibited the same behavior as that described above. Very recently, Moldenaers et al.¹¹ and Odell et al.¹² also reported that the stress for the LCS relaxes in two regions. The order of the relaxation time for initial region¹² was almost the same as that for τ_1 , but the order for another region was greater than that for τ_2 . Figure 6 shows the dependence of characteristic time t_c on concentration. The t_c exhibited a minimum at Cb. The values of t_c were almost the same as those of the time (t_b) after cessation of shear one needs for the band formation.²⁴ The relation between t_c and t_b will be discussed in our following paper.²⁵

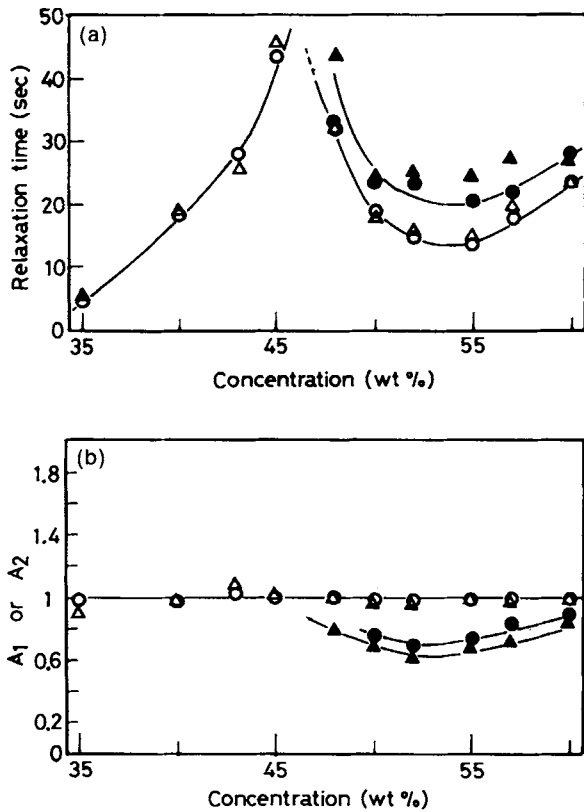


Figure 5 Concentration dependence of parameters in eq. (1) in the first (open marks) and second (closed marks) cycles. (a) relaxation times: O, ● τ_1 , Δ, ▲ τ_2 ; (b) constants A: O, ●, A_1 , Δ, ▲ A_2 .

Stress Growth Behavior

The stress exhibited a monotonous increase with time as shown in Figure 1 for the isotropic solutions (less than 45 wt %), but exhibited a shoulder for

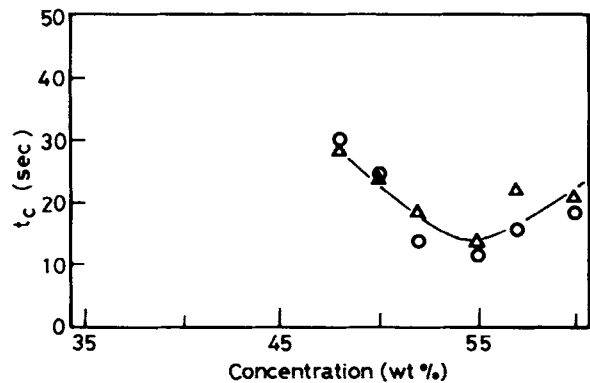


Figure 6 Concentration dependence of a characteristic time t_c in the first (O) and second (Δ) cycles.

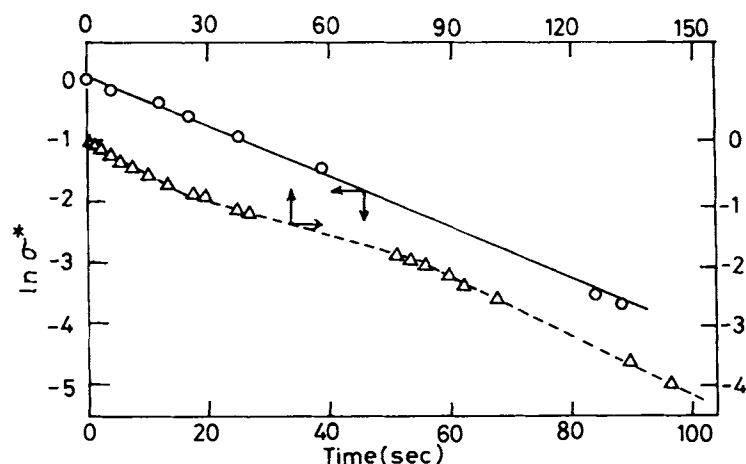


Figure 7 Typical growth behavior of reduced stress as a function of time for (O) 40 and (Δ) 55 wt % solutions.

the LCSs (greater than 45 wt %). After vigorous mechanical stirring of the LCSs, the shoulder was disappeared.²⁶ In our experimental range, no marked stress-overshoot was observed. The stress growth data suggested the existence of liquid crystalline domains.

When logarithm of σ^* was plotted against time, the isotropic solutions exhibited a single line and the LCSs exhibited three lines as shown in Figure 7. This clearly showed that the eq. (2) is valid for our system. Consequently, our data showed that our LCSs had three growth mechanisms and our isotropic solutions had one growth mechanism. Strictly speaking, the data for the region of shouldering were not so significant; between t_{c1} and t_{c2} the line was not so linear as the other regions ($t_{c2} < t$ and $t < t_{c1}$). Figure 8 shows the concentration dependence of the parameters in the eq. (2). The order of retardation times was 10^1 s (less than 100 s). S_1 exhibited a maximum and a minimum at the same concentrations as the ones shown in Figure 3, that is, Ca and Cb. S_2 was the greatest in the retardation times and S_3 tended to be greater than S_1 . B_1 was almost unity and was independent of concentration. B_2 was 0.7–0.85 and tended to exhibit a minimum at Cb. B_3 was the greatest in the B -constants and decreased with concentration. As noted above, we supposed that the constants B are correlated to the volume fractions of each component. However, the physical meaning of B_3 was not true, because the values of B should be less than unity. Therefore, we need to correct the method for estimating B_3 constant. The B_2 process corresponds to the shouldering region and the transition region from the first process to the final process, as will be discussed below. Here, we

neglect the B_2 process in order to evaluate the B_3 process. Therefore, as shown in Figure 9, the third line was shifted from t_{c2} to t_{c1} parallel. The values of corrected B_3 were less than unity. The corrected

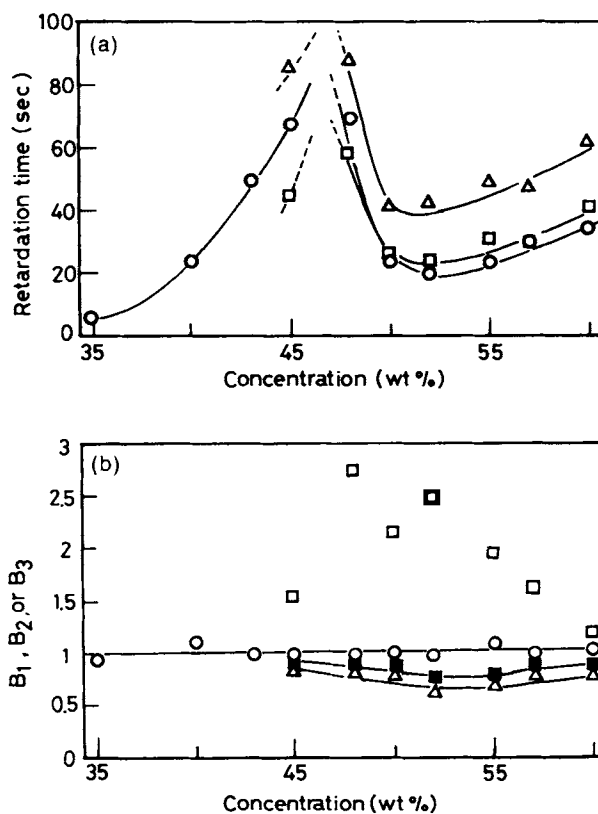


Figure 8 Concentration dependence of parameters in eq. (2). (a) retardation times: O S_1 , Δ S_2 , □ S_3 ; (b) constants B : O B_1 , Δ B_2 , □ B_3 , ■ B'_3 (corrected value of B_3 , see in Figure 9).

data of B_3 were shown in Figure 8. The characteristic times (t_{c1} and t_{c2}) exhibited a maximum at Ca as shown in Figure 10.

Comparison with Stress Growth and Relaxation

Comparison between Figures 5 and 8 showed that the retardation time S_1 and relaxation time τ_1 exhibit similarly with respect to concentration; the concentrations at a maximum and a minimum for both retardation and relaxation times are almost the same and are the same as those for the steady-state viscosity (Fig. 3). This clearly showed that both stress growth and relaxation behavior depends on the solution phase: the isotropic solutions have one retardation time and one relaxation time and the LCSs have plural retardation and relaxation times except for the 45 wt % solution which exhibits plural retardation times and one relaxation time. The 45 wt % solution was in the close vicinity of the Ca (47 wt %) which was estimated from the steady-state viscosity data (Fig. 3). We suppose the existence of a precursor of domain or a pseudo-domain in the 45 wt % solution.¹⁴ The pseudo-domains in the solution disappeared with shear during the stress growth process and then the steady-state viscosity and stress relaxation behaved isotropically. For the relaxation behavior of the LCSs, one mechanism transforms suddenly into the subsequent mechanism at a critical point (characteristic time t_c). However, for the stress growth behavior of the LCSs, one mechanism transforms into the subsequent mechanism through another mechanism which is corresponded to the shouldering behavior. Comparison between values of retardation and relaxation times for the same concentrations showed that S_1 and S_3

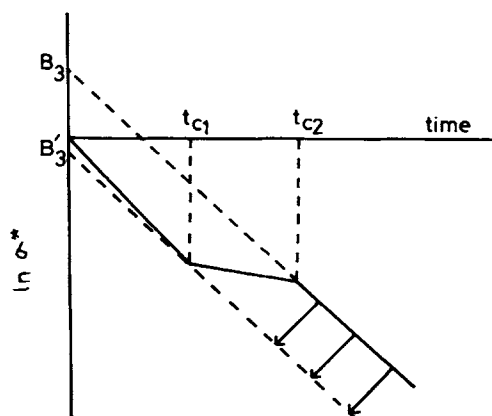


Figure 9 Schematic representation for correcting the constant B_3 .

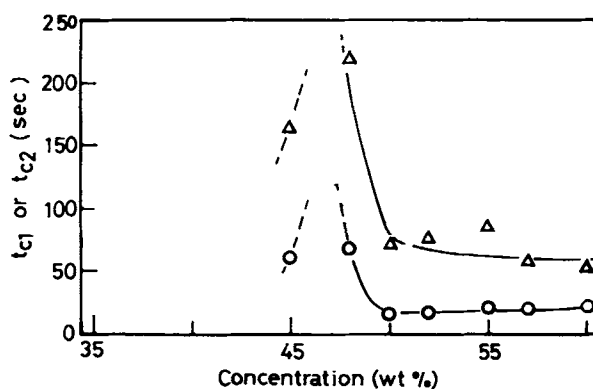


Figure 10 Concentration dependence of characteristic times. O: T_{c1} , Δ : T_{c2} .

are greater than τ_1 and τ_2 , respectively. This strongly suggested that the recovering of domains to original shape is faster than the deformation of domains with shear, and that the relaxation process is a sudden event, whereas the stress growth process is a progressive event. The dependence of constants A on concentration was similar to that of constants B : A_1 and B_1 were independent of concentration, and A_2 and B_3 (corrected value) exhibited a minimum. The values of A_2 were smaller than those of B_3 (corrected value). The difference in values of A_2 and B_3 suggested that the volume of liquid crystalline domains decreases more or less during stress growth process. The characteristic time t_c for relaxation behavior exhibited similarly as the characteristic times for growth behavior did, with respect to concentration.

Our findings on the behavior of the LCSs implied that the stress growth behavior is similar to the stress relaxation behavior and both behavior is governed by the deformation of liquid crystalline structure, that is, polydomain structure. Onogi and Asada¹³ have proposed a model which shows the change in polydomain with shear. Viola et al.² have also described a model in which the polydomain is deformed, oriented, or disrupted with shear. On the base of their models, we¹⁴ have proposed a hypothesis for the relaxation process: the A_1 mechanism is contributed by the individual molecules and the A_2 mechanism is done by the anisotropic domains. When our hypothesis for the relaxation process was valid for our HPC/DMAc system, the contributions of individual molecules and domains could be applied to the stress growth process. The different point in the stress relaxation and growth behavior was that the relaxation process has the reconstruction of domains, whereas the stress growth process has the deformation and disruption of domains with shear.

The concentration dependence of parameters for the relaxation process of our HPC/DMAc system was the same as that for the ethyl cellulose system.¹⁴ Therefore, the contributions proposed by us¹⁴ appeared to be valid for our HPC/DMAc system: the individual molecules both in isotropic and anisotropic phases contribute to A_1 process and the anisotropic domains contribute to A_2 process. For the stress growth process, the individual molecules and domains contribute B_1 and B_3 , respectively and B_2 process was the transition process from B_1 to B_3 processes. Very recently, Odell et al.¹² proposed another mechanism for the first stage of relaxation (A_1 process in our study). They reported that the first stage corresponded to solvent disorientation. If their propose is true, then the relaxation for thermotropic LCs should exhibit only one mechanism.

Effect of Shear History

As shown in Figure 1, after the first cycle, the experiment was restarted as the same shear rate as before. For the stress growth process, σ_f in the first cycle was almost the same as that in the second cycle and the reproducibility of σ_f s was better than 5%; around Ca (45 and 48 wt % solutions), the reproducibility was ca. 5%, and the reproducibility for other solutions was better than 3%. For the relaxation process, the reproducibility of σ_f s in the first and second cycles was better than 3%, including 45 and 48 wt % solutions. Interestingly, σ_f in the third cycle was greater than that in the second cycle by a factor of 2, regardless of the solution concentration. The reason was not clear. Therefore, in this study, the data in the third cycle were not shown.

The parameters for the relaxation process in the first and subsequent cycles were evaluated and were shown in Figure 5. For the isotropic solutions (below Ca), τ_1 in the first cycle was almost the same as that in the second cycle; however, for the LCSs (above Ca), τ_1 in the first cycle was little smaller than that in the second one. τ_2 also exhibited a similar behavior as τ_1 ; the difference in τ_2 between the first and second cycles tended to become more remarkable than that in τ_1 . A_1 was almost independent of shear history, but A_2 in the second cycle was smaller than that in the first one. The decrease in A_2 suggested the decrease in the volume of liquid crystalline domains, due to the shear. The characteristic time t_c in the first cycle was smaller than that in the second one. Those suggested that the steady-state behavior in the first and second cycles is insensitive to the shear history within our experimental conditions, but the transient behavior is sensitive to the shear

history which resulted in the change in volume or shape of liquid crystalline domains.

As discussed in our previous paper,¹⁴ the physical meanings of A and B constants were still not well defined. We need to investigate further.

CONCLUSIONS

The analytical equation (exponential type) proposed in our previous paper was valid for the HPC/DMAc liquid crystalline system. The similar exponential function could be applied to the stress growth behavior for the same LCSs. The isotropic solutions had one retardation time and one relaxation time, but the LCSs had plural retardation and relaxation times except for the 45 wt % solution which was very near the Ca. The concentration dependence of the parameters for the stress growth process was similar to that for the relaxation process and to that for the steady-state shear viscosity. The stress growth and relaxation processes for the LCSs were originated from the deformation of liquid crystalline domains. The retardation times at given concentrations were greater than the relaxation times. This suggested that the recovering of liquid crystalline domains to original shape is faster than the deformation of domains with shear. The stress growth process was a progressive event, whereas the relaxation process was a sudden event. Both stress growth and relaxation behavior for the LCSs was sensitive to the shear history adopted in this study.

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