

유방성 액정고분자계에 있어서 중간상의 분자배열 규칙성의 유변학적 해석

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Rheological Implications of Mesomorphic Order in the Lyotropic Liquid Crystalline Polymer Systems

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요 약

등방상에서는 폴리파라페닐렌테레프탈아미드(PPD-T)와 히드록시 프로필 셀룰로오스(HPC)가 비슷한 유변학적 거동을 보였다. 그러나 이방상에서는 네마틱상을 형성하는 PPD-T와 콜레스테릭상(또는 꼬인 네마틱상)을 형성하는 HPC는 상이한 유변학적 특성을 나타냈다. 이방상을 나타내는 임계농도(C*) 이상의 농도에서 Herschel-Bulkey 모델에 의해 얻어진 항복응력을 보면 HPC의 경우 농도에 관계없이 거의 일정한 값을 나타낸 반면 PPD-T의 경우에는 농도증가와 더불어 항복응력값이 크게 증가하였다. 또한, PPD-T가 일반적으로 HPC보다 큰값의 항복응력을 나타냈다. 진동수 1 rad/s에서는 PPD-T와 HPC 모두 탄성계수 $G'/2G''$ 가 농도의 증가와 더불어 증가하였다. 그러나 100 rad/s에서는 HPC의 경우 임계농도이상의 농도에서 농도증가와 더불어 탄성계수값이 단순 감소한 반면 PPD-T의 경우에는 포화농도(B-point) 이상의 농도에서 농도증가와 더불어 탄성계수값이 계속적으로 증가하였다. HPC의 경우 저장탄성률이 변형정도의 영향을 받지 않았으나 PPD-T의 경우에는 저장탄성률이 변형정도에 매우 민감하였다.

Abstract— At the isotropic phase poly(p-phenylene terephthalamide) (PPD-T) and hydroxy propyl cellulose (HPC) showed similar rheological behavior. At the anisotropic phase, however, the nematic PPD-T and the cholesteric HPC exhibited different rheological responses in dynamic rheological measurements. Evaluation on the Herschel-Bulkey model by the least-square method revealed that at the concentrations higher than the critical concentration (C*) the yield stress of HPC remained almost constant with increasing concentration whereas that of PPD-T was notably increased. Further, PPD-T gave much greater yield stress than HPC. At 1 rad/s, both PPD-T and HPC showed increase of the ratio of storage modulus (G') to twice loss modulus (G''), $G'/2G''$, with increasing concentration. At 100 rad/s, HPC showed monotonical decrease in $G'/2G''$ with concentration at the concentrations higher than the C*, whereas the ratio of PPD-T was increased at the concentrations higher than the saturated concentration (B-point). The G' of the nematic PPD-T was sensitive to the strain level adopted while that of the cholesteric HPC exhibited little dependence on the strain level.

Keywords: Lyotropic liquid crystalline polymer, Poly(p-phenylene terephthalamide), Hydroxy propyl cellulose, Nematic phase, Cholesteric phase, Dynamic rheological properties

1. Introduction

The liquid-crystalline phase possesses the characteristic properties of both ordered crystal and disordered fluid[1-3]. Depending on the molecular order polymeric liquid crystals have been largely classified to three types; nematic, cholesteric (or twisted nematic), and smectic. In the nematic phase the centers of gravity of particles are randomly arranged, giving rise to little positional long-range order. In

the cholesteric phase, however, only orientational order exists and the direction of the long axis of the molecules changes continuously within the specimen. Thus, the nematic and the cholesteric liquid crystalline polymers (LCP's) possess their own peculiar spatial arrangement of molecules.

Over the last two decades, high-modulus/high-strength organic fibers based on the LCP have been developed with significant commercial importance[4-8]. In the LCP fibers, the liquid crystalline domains are believed to play a role of reinforcement. Due to the long relaxation time, LCP maintains the oriented structure developed during the fabrication

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step to the solidification step. In consequence, it is essential to precisely control the liquid crystalline domain morphology to obtain products with desired properties. Unfortunately, however, there has been little definite method to measure the morphology of LC domains under complex shear conditions frequently encountered in the polymer processing. Hence little efforts have been made to relate the mesomorphic ordering to the rheological responses, which may be of great help to the fabrication process.

This study investigates the difference in the dynamic rheological responses of two typical lyotropic systems, PPD-T in H₂SO₄ and HPC in water, which are known to form the nematic and the cholesteric liquid crystals, respectively.

2. Experimental

2.1. Materials

Two LCP's tested were PPD-T and HPC with inherent viscosity of 2.52 dl/g in 100% H₂SO₄ and 0.99 dl/g in water, respectively. PPT-A was prepared by polycondensation of terephthaloyl dichloride and p-phenylene diamine in dimethyl acetamide containing LiCl. HPC was a commercial grade. The polymers were dissolved in an airtight ampoule to prevent evaporization of solvent during the long dissolution period. Particularly with HPC more than 3 months were needed to obtain homogeneous solution.

2.2. Measurement of Rheological Properties

The rheological properties were measured by Rheometrics dynamic spectrometer RDS-7700 (Rheometrics, Inc.,

USA) at 30°C. In the dynamic rheological measurement, a parallel-plate geometry was employed. The plates were made of glass to permit observation of stir-opalescence during measurement and to avoid corrosion by H₂SO₄. Plates with diameters of 25, 50 and 100 mm, were used to properly accommodate the torque exerted by the polymer solutions. The gap between plates was 2 mm. Sometimes the lyotropic polymer systems give very complicated rheological behavior which is dependent on the method of sample loading because they are heterogeneous at the molecular level. To relax all residual stresses during sample loading the solution samples were placed still for 30 min without any turbulence. This enabled us to obtain reproducible rheological data.

3. Results and Discussion

Viscosity curves of the solutions of PPD-T in H₂SO₄ and HPC in water at 30°C are shown in Figs. 1 and 2, respectively. At the concentrations yielding an isotropic phase both polymer solutions give viscosity curves typical of homogeneous solutions of most flexible polymers. They give the lower Newtonian flow region, followed by shear thinning at high frequencies. On the whole, PPD-T gives much smaller power-law index than HPC, reflecting that the rod-like PPD-T molecules are more readily oriented by shear than the helicoidal HPC molecules. Both solutions clearly exhibit the C* and the B-point[9]. The B-point represents the boundary concentration between anisotropic and anisotropic+solid phases, at which the minimum viscos-

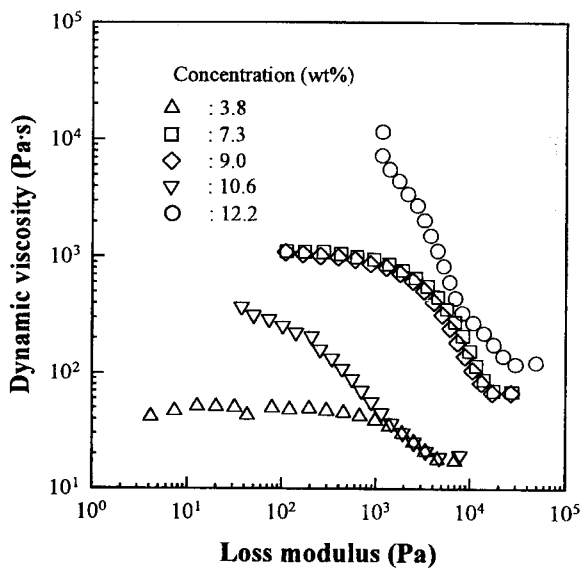


Fig. 1. Viscosity curve of the solutions of PPD-T in H₂SO₄ at 30°C.

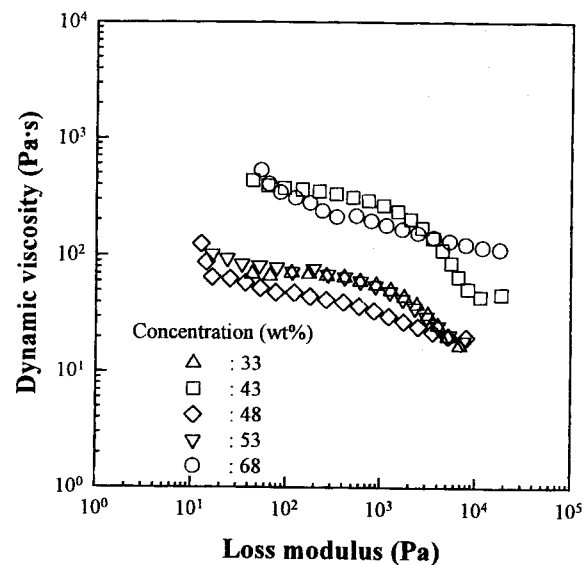


Fig. 2. Viscosity curve of the solutions of HPC in H₂O at 30°C.

ity is observed in the critical concentration curve. The approximate values of the C^* and B-point for PPD-T and HPC estimated from the viscosity curves are 7 and 10 wt%, and 40 and 55 wt%, respectively. At the concentrations higher than the C^* both anisotropic solutions do not show any plateau region at low frequencies in the viscosity curves.

The disappearance of the lower Newtonian flow region indicates that the solutions become heterogeneous with forming liquid crystalline domains. Thus, the yield behavior at the concentrations higher than the C^* originates from formation of the mesomorphic phase. The yield value of a heterogeneous system can be estimated by the Herschel-Bulkley equation [10].

$$\sigma = \sigma_y + k \dot{\gamma}^n \quad (1)$$

in which, σ is the shear stress, σ_y is the yield stress, $\dot{\gamma}$ is the shear rate, and k is the constant. Considering analogy between $\dot{\gamma}$ in the steady shear flow and G'' and frequency (ω) in the oscillatory shear flow Eq. (1) may be rewritten as Eq. (2)

$$G'' = G''_y + k\omega^n \quad (2)$$

in which G''_y may be regarded as a measure of σ_y . Parameters of Herschel-Bulkley model for the two lyotropic systems are evaluated on this background by applying the least-square method and given in Table 1. It is interesting to see that over the range of concentrations higher than the C^* the yield stress of HPC remains almost constant with increasing concentration whereas that of PPD-T is notably increased. Further, the yield stress of the nematic PPD-T is much greater than that of the cholesteric HPC. These facts imply that the rodlike PPD-T molecules can associate more effectively than the helical HPC molecules at the anisotropic phase.

Table 1. Parameters of Herschel-Bulkley Model for Two Lyotropic Systems

| LC System | Phase | Conc. (wt%) | σ_y (Pa) | K (Pa · s) | n |
|----------------------|-------|-------------|-----------------|--------------|------|
| PPD-T (Nematic) | I | 3.80 | 0 | 58.5 | 0.89 |
| | I | 7.33 | 0 | 936 | 0.84 |
| | A | 9.40 | 0 | 444 | 0.81 |
| | A | 10.61 | 186.3 | 55 | 0.82 |
| | AS | 12.17 | 2358 | 419 | 0.78 |
| HPC (Cholesteric) | I | 33 | 0 | 114 | 0.99 |
| | A | 43 | 0 | 335 | 0.87 |
| | A | 48 | 3.0 | 123 | 0.97 |
| | A | 53 | 3.0 | 74 | 0.87 |
| | AS | 68 | 3.3 | 224 | 0.79 |

I : Isotropic, A : Anisotropic, AS : Anisotropic Solid.

The G' of the isotropic and anisotropic solutions of PPD-T and HPC is plotted against frequency in Figs. 3 and 4, respectively. The isotropic solutions (Fig. 3) give a master curve independent of the shear strain level. The slope over the frequency range 0.1 to 1 rad/s is 1.3, which is comparable with 2 for common flexible chain polymers [9]. On the other hand, the anisotropic solutions (Fig. 4) give slopes ranging 0.4 to 0.5. Further, the slope noticeably varies with the shear strain level. Particularly with the anisotropic PPD-T solution at the strain level of 50%, there is a range of frequencies over which the G' does not vary with frequency. The frequency range exhibiting a constant modulus corresponds to "the secondary rubbery plateau" region, suggested by Onogi *et al.* [11,12]. This results from the relaxation of pseudonetwork structure formed by liquid crystalline domains. That is, the physical crosslinking between liquid crystalline domains would keep the liquid crystalline systems in an equilibrium state without flowing over a range of shear rates just like the interparticle interactions in the suspension systems. Hence the secondary plateau region is observed at relatively high shear rates.

Unlike the nematic PPD-T phase, the cholesteric HPC phase does not exhibit a notable dependence on the strain level. However, the anisotropic HPC solution clearly shows a secondary rubbery plateau region as well. Of the two

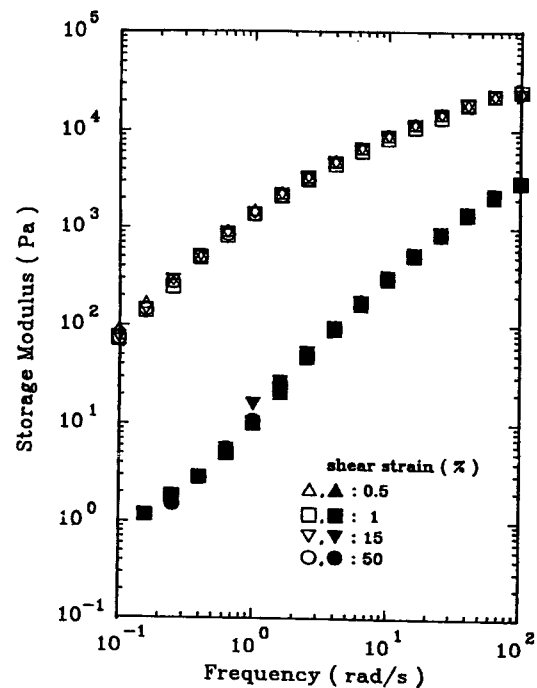


Fig. 3. Plot of G' vs. for the isotropic solutions of PPD-T in H_2SO_4 (8.0 wt.%; open symbols) and HPC in H_2O (33.0 wt.%; fill symbols) at 30°C.

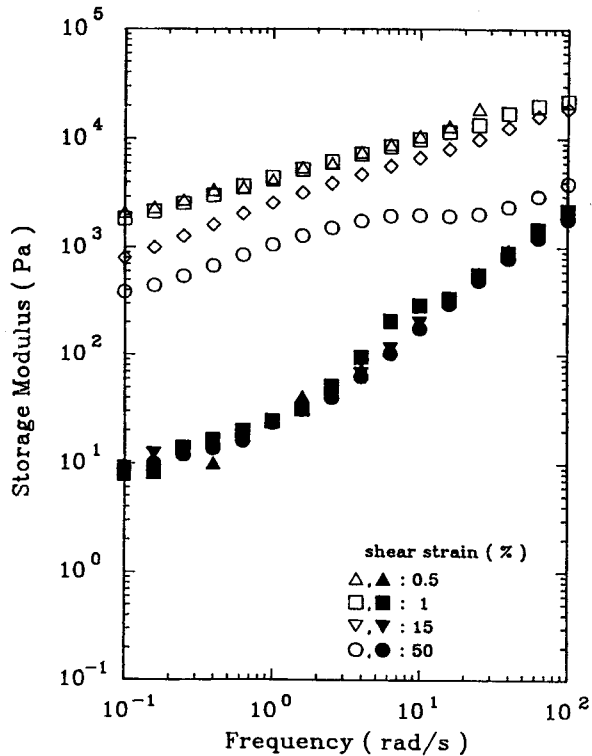


Fig. 4. Plot of G' vs. for the anisotropic solutions of PPD-T in H_2SO_4 (10.6 wt.%; open symbols) and HPC in H_2O (48.0 wt.% filled symbols) at $30^\circ C$.

lyotropic liquid crystalline systems the nematic PPD-T phase gives larger G' than the cholesteric HPC phase in the second rubbery plateau region at the strain level of 50%, indicating that the rodlike PPD-T forms stronger LC domains than the helicoidal HPC.

The G'' is plotted against frequency for the PPD-T and HPC solutions in Figs. 5 and 6, respectively. In the isotropic phase, over the range of frequencies 0.1 to 20 rad/s, PPD-T (3.8 and 7.3 wt.%) and HPC (33.0 wt.%) give similar values of slope, 0.93 and 0.92, respectively. The slope of HPC solutions remains almost constant over the concentrations examined irrespective of phase change. On the other hand, the slope of PPD-T varies with concentration. The slope is abruptly reduced to 0.4 at the concentration of 9.0 wt.%. The slope increases to 0.93 at the B-point, and decreases to 0.63 at the concentration 12.2 wt.%.

In addition, both PPD-T and HPC give maximum of G'' in the biphasic and exhibit a plateau region over a short range of frequencies at the concentrations higher than the biphasic concentration. With HPC the anisotropic+solid phase and the 33 wt.% solution (isotropic)/48 wt.% solution (anisotropic) follow the biphasic, and minimum of G'' is observed in the vicinity of the B-point. With PPD-T, however, the B-point/

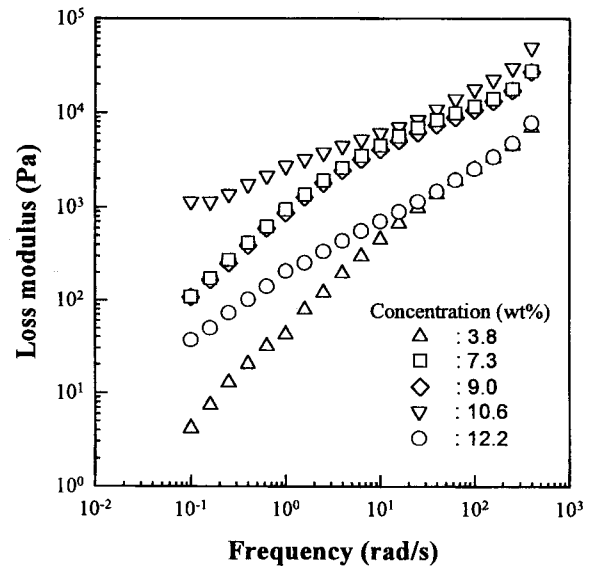


Fig. 5. Plot of G'' vs. for the solutions of PPD-T in H_2SO_4 at $30^\circ C$ (Symbols are the same as in Fig. 1).

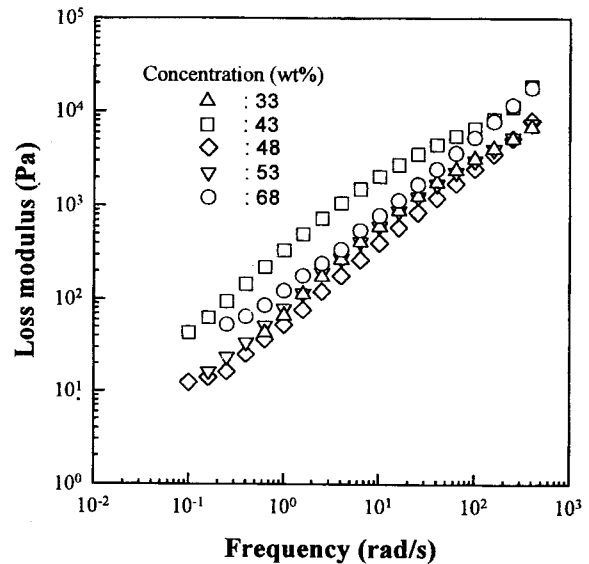


Fig. 6. Plot of G'' vs. for the solutions of HPC in H_2O at $30^\circ C$ (Symbols are the same as in Fig. 2).

7.3 wt.% solution (isotropic) and the anisotropic+solid phase follow the biphasic and minimum of G'' is observed at the polymer concentration of 3.8 wt.% (isotropic).

Figs. 7 and 8 present variation of $G'/2G''$ with concentration at $30^\circ C$ for the solutions of PPD-T and HPC, respectively. The elastic parameter, $G'/2G''$, may be regarded as a measure of recoverable shear strain if one assume similarity between G' and first normal stress difference and G'' and shear stress. At the frequency of 1 rad/s, the elastic parameter of PPD-T and HPC shows similar variation with concentration; they are increased with increasing concentration.

At the frequency of 100 rad/s, however, PPD-T and HPC show different variation with concentration each other although the elastic parameter of both systems shows a maximum value in the vicinity of C^* . The elastic parameter of HPC is monotonically decreased with increasing concentration when the concentration is higher than the C^* . On the other hand, the elastic parameter of PPD-T increases again when the concentration is higher than the B-point. Difference in rheological responses with concentration at high frequencies reflects difference in molecular ordering

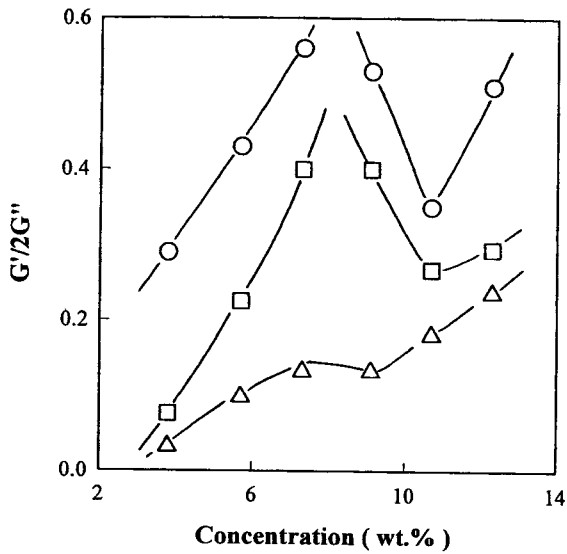


Fig. 7. Variation of $G'/2G''$ with concentration for the solutions of PPD-T in H_2SO_4 at $30^\circ C$ (O: 1 rad/s, □: 10 rad/s, and △: 100 rad/s).

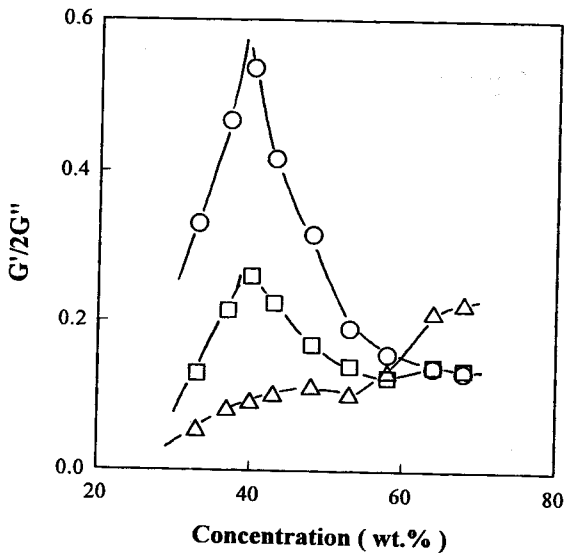


Fig. 8. Variation of $G'/2G''$ with concentration for the solutions of HPC in H_2O at $30^\circ C$ (O: 1 rad/s, □: 10 rad/s, and △: 100 rad/s).

in the mesomorphic phase. At the concentrations higher than the B-point, the nematic phase formed by rodlike PPD-T molecules possesses a solid character. Hence the elastic parameter is abruptly increased. On the hand, the helicoidal HPC molecules leave room for shear deformation at high frequencies at the concentrations higher than the B-point. Consequently the elastic parameter is monotonically decreased due to increase of energy dissipation resulting from shear deformation.

Plots of dynamic viscosity (η') and G' against strain for the isotropic solutions of PPD-T and HPC are shown in Figs. 9 and 10, respectively. In the case of isotropic solutions of both polymers, η' and G' remain constant over the range of strain levels observed.

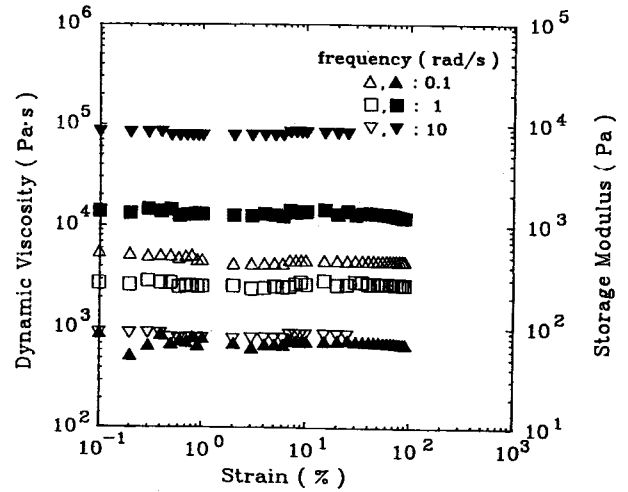


Fig. 9. Variation of η' (open symbols) and G' (filled symbols) of the isotropic solution of PPD-T in H_2SO_4 (8.0 wt.%) with strain level at $30^\circ C$.

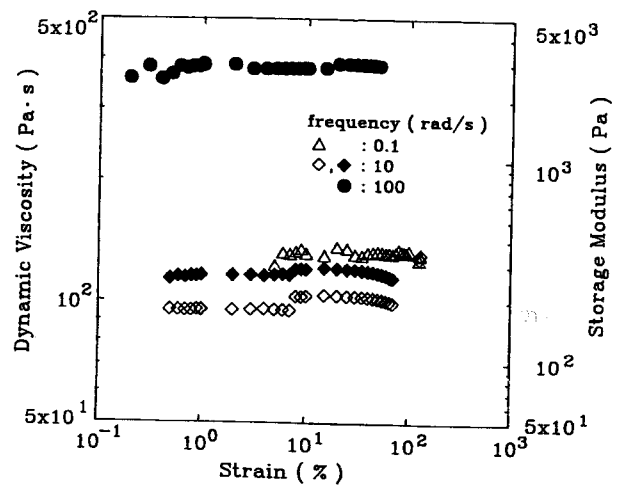


Fig. 10. Variation of η' (open symbols) and G' (filled symbols) of the isotropic solution of HPC (33.0 wt.%) with strain level at $30^\circ C$.

In the case of anisotropic solutions of PPD-T (9.4 wt.%) and HPC (48.0 wt.%), however, they are decreased with increasing strain level as respectively shown in Figs. 11 and 12. The extent of decreasing η' with increasing strain level is increased with increasing frequency whereas the extent of decreasing G' with strain level is decreased with frequency. The destruction of pseudonetwork structure, probably breaking the polydomain into the smaller monodomains, seems to be the cause of reduction of η' . Of two lyotropic systems, PPD-T is more sensitive to the strain level than HPC. In the case of PPD-T, the extent of reduction in η' and G' at the frequencies higher than 1 rad/s is slightly decreased as frequency is increased. At the fre-

quency of 0.1 rad/s, however, little reduction in η' with strain is noticed. In the case of HPC, there is a discontinuity on the plot of η' against strain at around the strain level of 10% at 0.1 rad/s as shown in Fig. 12. This is attributable to destruction of the initial piled polydomain structure. Further, the critical strain level seems to be decreased as frequency is increased. It should be also noted in Fig. 12 that the G' of cholesteric HPC phase exhibits little dependence on the strain level, reflecting weaker polydomain strength due to bulkier mesogen units.

4. Concluding Remarks

It is easily imagined for the liquid crystalline polymers that the type of molecular ordering might have a significant effect on the rheological properties because the rheological properties stand for collective behavior of respective microstructures. At the anisotropic concentrations, PPD-T forms a nematic phase and HPC develops a cholesteric (or, twisted nematic) phase. The former has one-dimensional order only while the latter possesses 1.5 dimensional order. The difference in molecular ordering seems to offer some analytical results. However, we feel that it still need more special experiments to clarify the rheological difference of the two lyotropic systems because of breakdown of liquid crystalline order, shear-induced phase separation, or reversible transition between nematic and cholesteric phases. In the near future we will carry out two-stage rheological measurements of steady shear and oscillatory flows, and elucidate the phenomena in more detailed way.

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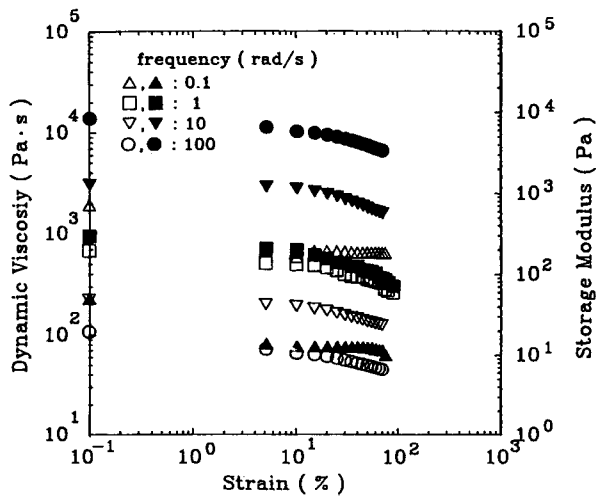


Fig. 11. Variation of η' (open symbols) and G' (filled symbols) of the anisotropic solution of PPD-T in H_2SO_4 (9.4 wt.%) with strain level at 30°C.

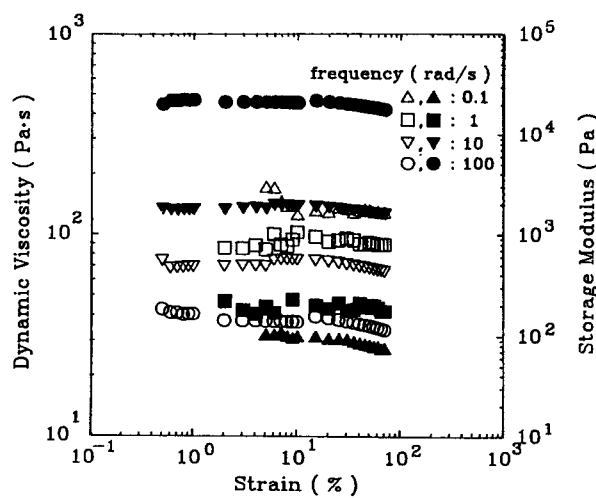


Fig. 12. Variation of η' (open symbols) and G' (filled symbols) of the anisotropic solution of HPC in H_2O (48.0 wt.%) with strain level at 30°C.

