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Complex Shear Viscosity of Liquid Crystals in the Isotropic Phase of Nematics†

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By use of the torsional quartz crystal method, the real and imaginary parts of the complex shear mechanical impedance of several nematogenic materials were measured as functions of the temperature at frequencies ranging from 50 to 150 kHz. From the impedance, we have determined the real and imaginary parts of the complex shear viscosity, in which a remarkable pretransitional anomaly is observed in the isotropic phase near the isotropic–nematic phase transition temperature, T_c. In the nematic phase and the isotropic phase except for the vicinity of T_c, the Newtonian behaviour is observed.

The behaviour of the complex shear viscosity in the isotropic phase has been analyzed by the theory of de Gennes, and it is shown that the observed behaviour can be well described by the theory.

I INTRODUCTION

In the isotropic phase just above the isotropic–nematic phase transition temperature, T_c, many experimental studies have revealed pretransitional anomalies both in static and dynamic properties of nematics.[1,2] As well known, these anomalies are successfully described on the basis of the phenomenological theory proposed by de Gennes.[1,3] According to his prediction on the shear wave propagation property in the isotropic phase near T_c, the effective complex shear viscosity will show a dispersion anomaly if we measure it in an appropriate frequency range. The existence of the predicted anomaly has been reported by several authors.[4,5,6]

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In this paper, we will report on the complex shear viscosity of two nematogenic materials, MBBA (*p*-methoxybenzylidene *p*-*n*-butylaniline) and EBBA (*p*-ethoxybenzylidene *p*-*n*-butylaniline), at frequencies ranging from 50 to 150 kHz. Putting our main focus on the behaviour in the isotropic phase, we will analyze our results on the basis of the theory of de Gennes. We also report on the temperature dependence of the complex shear viscosity of CBOOA (*p*-cyanobenzylidene *p*-*n*-octyloxyaniline) measured at 70 kHz.

II EXPERIMENTAL

For measuring the complex shear viscosity we used the quartz torsional crystal method.[7] The directly measured quantities in this method are the differences in the resonant frequency, Δf_r, and the equivalent electrical resistance at resonance, ΔR_r, of a torsional crystal when it is in air, *i.e.* without load, and in a sample liquid. From these quantities, the real part, R_M, and the imaginary part, X_M, of the complex shear mechanical impedance, Z^*, are given as follows:

$$\begin{aligned} Z^* &= R_M + iX_M, \\ R_M &= \Delta R_r/K_1, \\ X_M &= \Delta f_r/K_2 - B\rho, \end{aligned} \tag{1}$$

where K_1, K_2 and B are the crystal constants, and ρ is the density of the liquid. The term $-B\rho$ is a correction term made neccessary by the roughness of the surface of crystal. In our measurements we made use of a frequency synthesizer to drive the crystal, and a transformer bridge to measure the resistance at the resonant frequency. The crystal constants were determined experimentally by measurements of ΔR_r and Δf_r on a series of normal Newtonian liquids. Details of the experimental method together with the crystal constants are given in our previous paper.[6]

The impedance is related to the complex shear viscosity, η^*, as,

$$\begin{gathered} \eta^* = \eta' - i\eta'', \\ \eta' = 2R_M X_M/\omega\rho, \quad \eta'' = (R_M^2 - X_M^2)/\omega\rho, \end{gathered} \tag{2}$$

where η' and η'' are the real and imaginary parts of η^*, respectively, and ω is the angular frequency of the motion.

We used four quartz torsional crystals, whose resonant frequencies were 50, 70, 100 and 150 kHz, respectively. On the greater part of the surface of crystal were deposited thin gold films as electrodes. We did not pay any attention to specify the orientation of liquid crystals on the surface.

MBBA and EBBA were obtained from Eastman Organic Chemicals Ltd. and used as received. CBOOA was synthesized in our laboratory and recrystallized twice from methanol.

The transition temperatures of the samples determined by a polarizing microscope with Mettler FP-52 micro furnace were as follows:

$$\text{MBBA: Crystal} \xrightarrow{21.7^\circ\text{C}} \text{Nematic} \xrightarrow{45.0^\circ\text{C}} \text{Isotropic,}$$

$$\text{EBBA: Crystal} \xrightarrow{35.2^\circ\text{C}} \text{Nematic} \xrightarrow{78.9^\circ\text{C}} \text{Isotropic,}$$

CBOOA:

$$\text{Crystal} \xrightarrow{73.2^\circ\text{C}} \text{Smectic A} \xrightarrow{82.7^\circ\text{C}} \text{Nematic} \xrightarrow{107.7^\circ\text{C}} \text{Isotropic,}$$

where the crystallization temperatures were measured with increasing temperature and the other transition temperatures with decreasing temperature. The rate of temperature sweep in both cases were 0.2°C/min. The transition temperature, T_c, decreased in the course of the successive measurements of the complex shear viscosity, and it may be due to a slight degradation of the sample. As the decrease in T_c was small, 0.7°C for MBBA and 0.5°C for EBBA, we compared the data of the same material with different T_c using a reduced temperature scale $T - T_c$ if necessary.

The sample was contained in a glass cell, which was immersed in an oil bath. The temperature of the oil bath was controlled by electrical heaters to within 0.05°C. In each run of the measurement, temperature was always decreased from the isotropic phase far above T_c, at an average decreasing rate of about 5°C/hr. The densities of MBBA and EBBA were measured by a pycnometer and reported elsewhere.[8] For CBOOA, the density was measured by a dilatometer calibrated by mercury.

III RESULTS AND DISCUSSION

Figure 1 shows the real and imaginary parts of the shear mechanical impedance of EBBA as functions of temperature. At T_c the real part, R_M, and the imaginary part, X_M, show abrupt changes. Except for the isotropic phase close to T_c, R_M and X_M are nearly equal to each other, and at each temperature the ratio of the mechanical impedances of two different frequencies is substantially equal to the square root of the ratio of the two frequencies. In the isotropic phase near T_c, however, R_M and X_M differ with each other. The difference becomes larger as the temperature approaches to T_c and as the frequency of measurements becomes higher in our frequency range used. These observations imply that in the nematic phase and in the isotropic

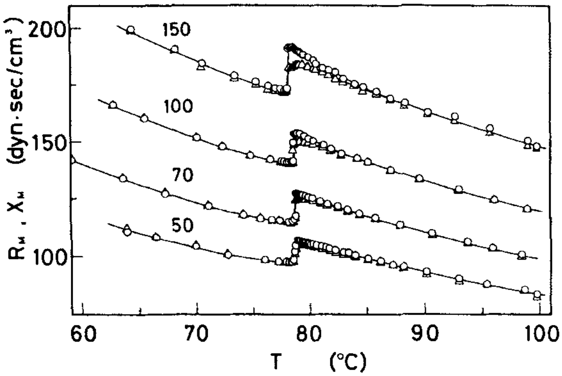

FIGURE 1 The complex shear mechanical impedance of EBBA plotted against temperature. Circles are for the real part, R_M, and triangles are for the imaginary part, X_M. Numbers beside the each pair of curves represent measuring frequencies in kHz.

phase sufficiently far from T_c, EBBA shows the normal Newtonian behaviour, and in the isotropic phase near T_c a dispersion anomaly in the complex shear viscosity associated with the phase transition, as is predicted by de Gennes.[3]

Figure 2 shows R_M and X_M of MBBA at 150 kHz, and those of CBOOA at 70 kHz. The temperature dependences of R_M and X_M are similar to those of

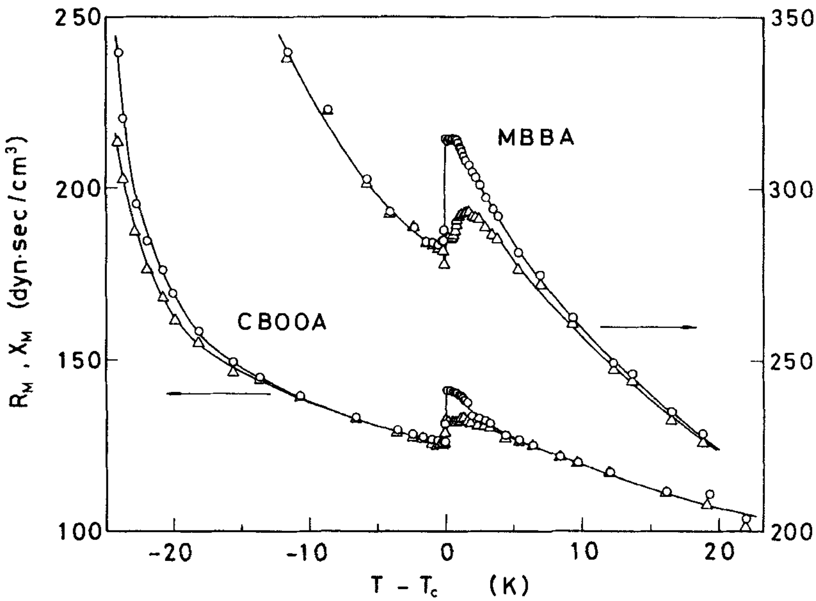

FIGURE 2 The complex shear mechanical impedance of MBBA at 150 kHz and that of CBOOA at 70 kHz plotted against $T - T_c$. Symbols are the same as in Figure 1.

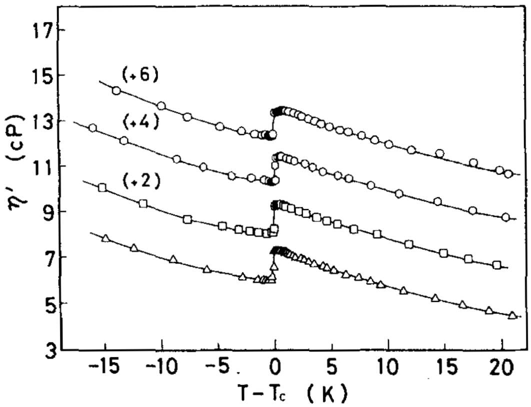

FIGURE 3 The real part of the complex shear viscosity, η', of EBBA plotted against $T - T_c$. Triangles are for 50 kHz, squares for 70 kHz, hexagons for 100 kHz, and circles for 150 kHz. Numbers in parentheses represent the magnitude of upward shift of each curve along the vertical axis.

EBBA. The frequency dependence of the impedance of MBBA is also similar to that of EBBA and the pretransitional effect manifests itself more clearly as can be seen from the data at 150 kHz in Figures 1 and 2. Detailed results of MBBA have been reported elsewhere.[6]

From the complex shear mechanical impedance, we can calculate the complex shear viscosity as shown in Eq. (2). In Figures 3 and 4, the real part, η', and the imaginary part, η'', of the complex shear viscosity of EBBA are plotted against $T - T_c$, respectively. In Figures 5 and 6, η' and η'' of MBBA and those of CBOOA are plotted against temperature, respectively. As is clear from Figures 3 and 5, η' of the isotropic phase in the vicinity of T_c

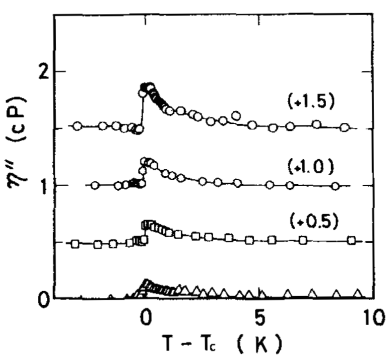

FIGURE 4 The imaginary part of the complex shear viscosity, η'', of EBBA plotted against $T - T_c$. Symbols are the same as in Figure 3.

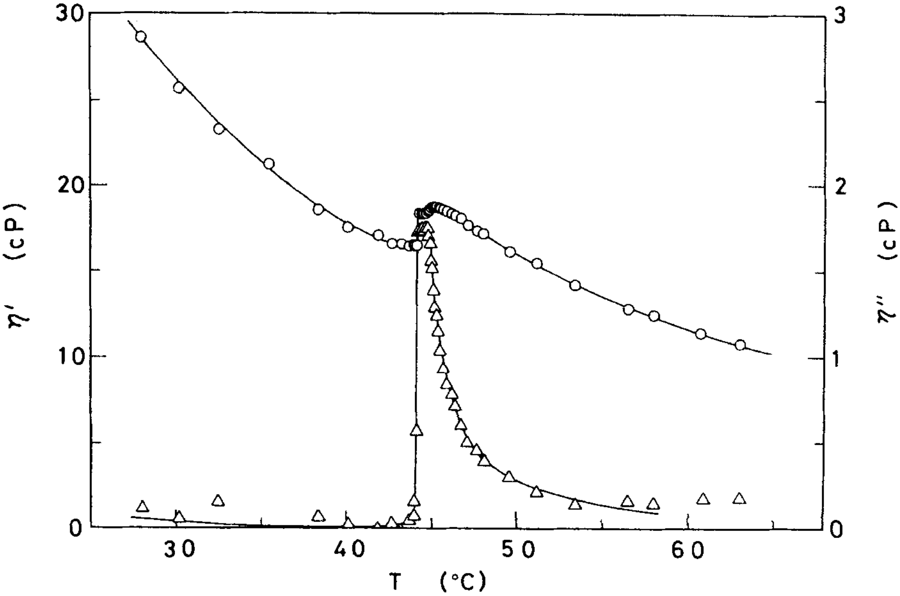

FIGURE 5 The complex shear viscosity of MBBA at 150 kHz plotted against temperature. Circles are for the real part, η', and triangles for the imaginary part, η''.

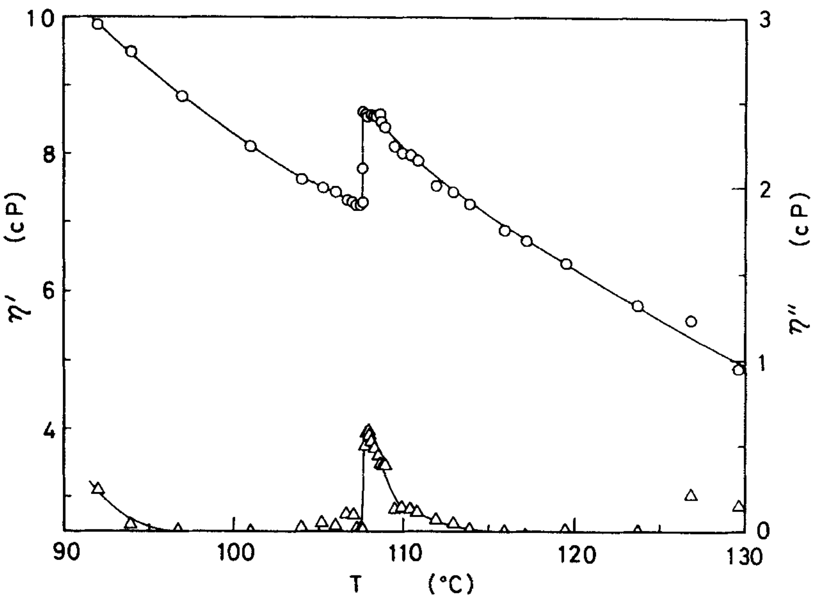

FIGURE 6 The complex shear viscosity of CBOOA at 70 kHz plotted against temperature. Symbols are the same as in Figure 5.

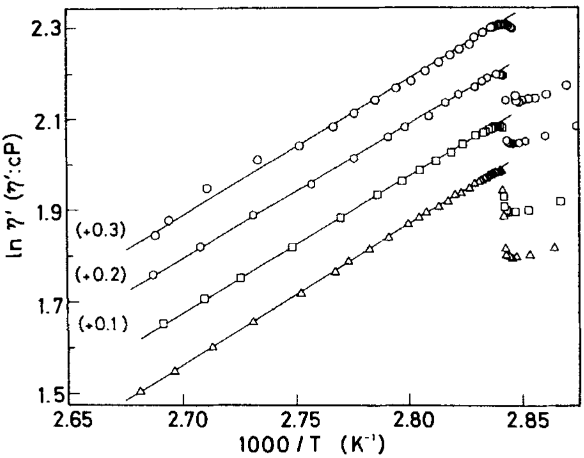

FIGURE 7 The logarithm of the real part of the complex shear viscosity of EBBA plotted against $10^3/T$. Symbols are the same as in Figure 3.

increases more slowly with decreasing temperature than in the higher temperature region of the isotropic phase, and at higher frequencies it decreases with decreasing temperature just above T_c. This trend can be seen more clearly in Figure 7, where the logarithm of η' of EBBA is plotted against $1/T$ in the isotropic phase. Except for a temperature range very close to T_c, the measured values of η' for each frequency can be expressed by a single equation of Arrhenius type, $\eta'_0 = (1.29 \pm 0.10) \times 10^{-3} \exp\{(3060 \pm 20)/T\}$ centi poise. The similar behaviour has been observed for MBBA,[6] and except for a temperature range very close to T_c, η' in the isotropic phase at all the measuring frequencies can also be expressed by an Arrhenius type equation: $\eta'_0 = (2.08 \pm 0.07) \times 10^{-4} \exp\{(3640 \pm 5)/T\}$ centi poise, which is in good agreement with the reported result of the steady flow viscosity measured by a capillary flow method.[4] At T_c, the magnitude of the departure of η' from the simple exponential behaviour, η'_0, is about 0.3 centi poise at 150 kHz for EBBA, whereas it is about 0.3 centi poise at 50 kHz and increases to about 1.3 centi poise at 150 kHz for MBBA.[6] As to η'', it shows a finite value in the isotropic phase near T_c, and it is substantially zero in the isotropic phase far from T_c and in the nematic phase. The value of η'' of MBBA at T_c is about 1.1 centi poise at 50 kHz and it comes up to 1.8 centi poise at 150 kHz,[6] whereas that of EBBA at T_c is very small and it is only 0.5 centi poise even at 150 kHz. The preliminary data on η' and η'' of CBOOA at 70 kHz (Figure 6) also show the similar behaviours as MBBA and EBBA.

Thus the dispersion anomaly associated with the isotropic–nematic phase transition is clearly observed both in η' and η'' in the isotropic phase near T_c and in the frequency range between 50 to 150 kHz. According to de Gennes, the effective, frequency dependent, complex shear viscosity in the isotropic phase near T_c is given as,[3]

$$\eta^*(\omega) = \eta - \frac{2\mu^2}{\nu}\frac{i\omega}{\Gamma + i\omega} \equiv \eta'(\omega) - i\eta''(\omega),$$

$$\eta'(\omega) = \eta - \frac{\mu^2}{\nu}\frac{2}{1 + (\Gamma/\omega)^2},$$

$$\eta''(\omega) = \frac{\mu^2}{\nu}\frac{2(\Gamma/\omega)}{1 + (\Gamma/\omega)^2},$$

$$\Gamma = \frac{a}{\nu}(T - T^*)^\gamma, \tag{3}$$

where η, ν and μ are the viscosities of the isotropic phase, Γ is the relaxation frequency of the order parameter, a and T^* are the constants, and γ is an unknown exponent. Equation (3) suggests that we can expect a dispersion anomaly in the complex shear viscosity associated with the phase transition. In fact the results of MBBA and EBBA imply that we have observed the low frequency side of the anomaly.

For a comparison between the experimental and the theoretical results, we evaluated μ of MBBA using the data on η'' and the theoretical expression of η'' (Eq. (3)). We also used the values, $a = 6 \times 10^5$ erg cm^{-3} K^{-1}, $T_c - T^* = 1$ K, $\gamma = 1$ and $\nu = 3.54 \times 10^{-4} \exp(3570/T)$ centi poise, reported by Stinson *et al.*[9] Though the values of μ thus obtained from η'' were somewhat scattered in the lower frequency regions, those from the data of η'' taken at 100 and 150 kHz can be described by an exponential law except for the vicinity of T_c. In Figure 8, the logarithm of μ from η'' of 150 kHz are plotted

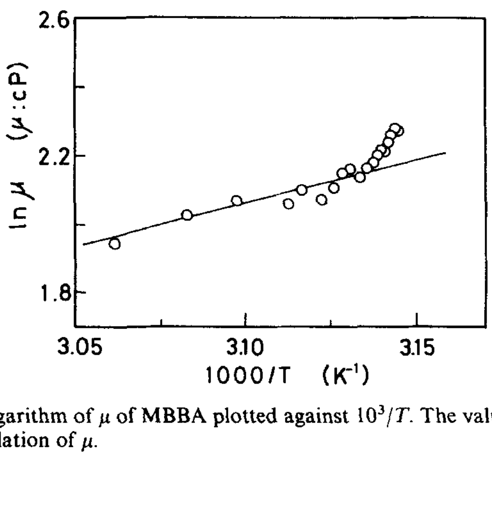

FIGURE 8 The logarithm of μ of MBBA plotted against $10^3/T$. The values of η'' at 150 kHz are used in the calculation of μ.

against $1/T$, and the solid line in the Figure is expressed as $\mu = 4.04 \times 10^{-3} \exp(2440/T)$ centi poise. Our results on μ are in good agreement with the measurement by Martinoty *et al.*,[4] and also show an upward deviation from the simple exponential behaviour near T_c. This departure of μ from the exponential behaviour may be caused by the departure of Γ from the $(T - T^*)^{-1}$ dependence, as was pointed out by Martinoty *et al.*[4] If we take a smaller $T_c - T^*$ value, alternatively, we can also get an exponential law describing μ in a temperature range closer to T_c than above.[6] We, however, have no decisive evidence whether the temperature dependence of Γ should be altered near T_c or μ really shows an anomaly near T_c. Moreover, it seems that the exact value of $T_c - T^*$ is still open to further experiments.[6] We, therefore, will use the exponential expression of μ given above in further discussions. The anomaly in η', $\Delta\eta'$, may be evaluated taking η in Eq. (3) as $\eta = \eta'_0$, and putting $\Delta\eta' = \eta'_0 - \eta'$. As was mentioned just before, η'_0 is not dependent on the measuring frequency, and is in good agreement with the data measured by a capillary flow method, we may safely put as $\eta = \eta'_0$. The magnitude of $\Delta\eta'$ is, however, rather small compared to η'', we have evaluated μ from η'' as shown before. In Figure 9, η'' and $\Delta\eta'$ of MBBA at 150 kHz are shown as functions of $T - T_c$. Here the solid curves show the calculated results by the use of Eq. (3). In the calculation, the values of parameters of Stinson *et al.*[9] quoted above, and the values of μ expressed by the exponential law were used. The departure of experimental points of both η'' and $\Delta\eta'$ from the theoretical curves near T_c are due to the departure of μ from the exponential law. The behaviour of the complex shear viscosity, however, is well described by de Gennes theory.

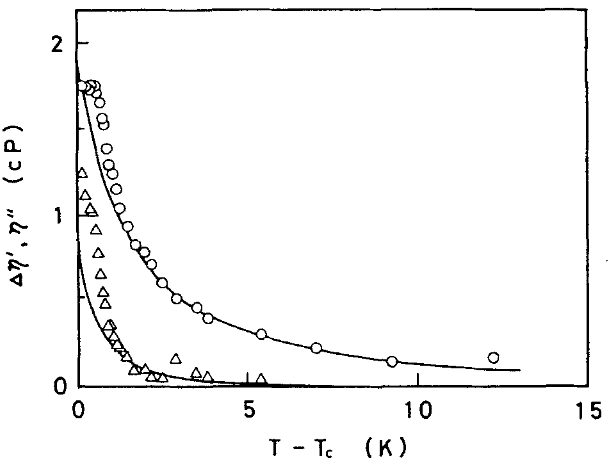

FIGURE 9 The plots of $\Delta\eta'$ and η'' of MBBA at 150 kHz against $T - T_c$. The solid curves represent the de Gennes theory calculated from the values of parameters given in the text.

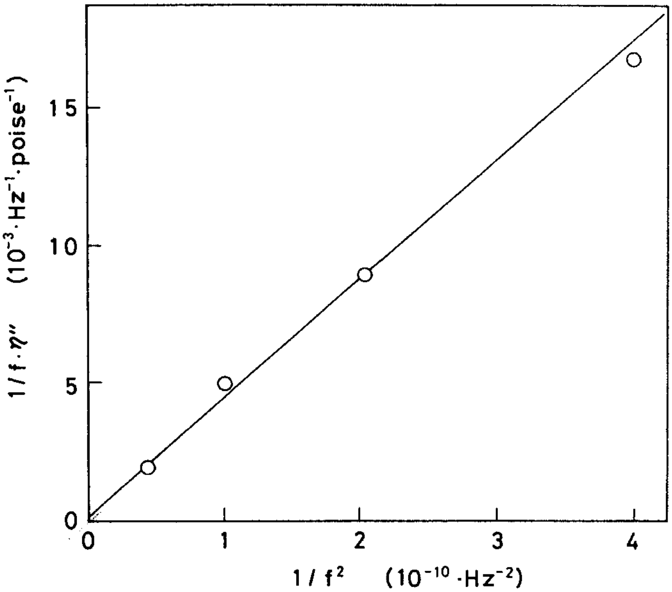

FIGURE 10 The plot of $1/f\eta''$ of EBBA against $1/f^2$.

As the effect of the dispersion anomaly in η' and η'' of EBBA is rather small, we only tried to evaluate ν and μ at T_c from the measured values of η''. From Eq. (3), it is clear that if we plot $1/f\eta''$ against $1/f^2$ at T_c we can expect a straight line, and from the slope and the intercept on the $1/f\eta''$-axis we can calculate Γ and $2\mu^2/\nu$, where f is the frequency of measurement. Figure 10 represents the plot of $1/f\eta''$ versus $1/f^2$ for EBBA at T_c. The values of $\Gamma/2\pi$ and $2\mu^2/\nu$ at T_c are 5.9×10^5 Hz (i.e. $1/\Gamma = 270$ nsec) and 1.34 centi poise, respectively. The magnitude of the relaxation frequency is nearly the same as that reported by Wong and Shen from the measurements of the optical Kerr effect.[10] Using these values of Γ and $2\mu^2/\nu$, and $a = 1 \times 10^6$ erg cm^{-3} K^{-1} by Wong and Shen,[10] $T_c - T^* = 0.8$ K by Filippini and Poggi,[11] and again putting $\gamma = 1$, we evaluated ν and μ at T_c as, 21.5 centi poise and 3.8 centi poise, respectively. They are of the reasonable order of magnitude, and the value of ν agrees well with that evaluated by Wong and Shen.[10]

To discuss the preliminary results of CBOOA, data are not sufficient at present. The behaviour of the complex shear viscosity in the isotropic phase, however, is similar to those of MBBA and EBBA, and the results of CBOOA may be explained on the same basis as these materials.

It is difficult to discuss our results in liquid crystalline phases quantitatively, because we did not specify the orientation of molecules on the crystal surface. In the nematic phase, however, the Newtonian behaviour has been observed.

In the nematic phase of CBOOA near the nematic–smectic A phase transition temperature, η' increases rapidly and η'' shows a finite value (See Figure 2). The full result of CBOOA will be reported in the near future.

References

1. P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford Univ. Press, London, 1974).
2. M. J. Stephen and J. D. Straley, *Rev. Mod. Phys.*, **46**, 617 (1974).
3. P. G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12**, 193 (1971).
4. P. Martinoty, S. Candau, and F. Debeauvais, *Phys. Rev. Letters*, **27**, 1123 (1971); P. Martinoty and S. Candau, *Mol. Cryst. Liq. Cryst.*, **14**, 243 (1971).
5. S. Nagai and K. Iizuka, *Japan. J. Appl. Phys.*, **14**, 567 (1975).
6. Y. Kawamura and S. Iwayanagi, *Sci. Papers I. P. C. R.*, **70**, 38 (1976).
7. R. E. Rouse and K. Sittel, *J. Chem. Phys.*, **24**, 690 (1953).
8. Y. Kawamura, Y. Maeda, K. Okano, and S. Iwayanagi, *Japan. J. Appl. Phys.*, **12**, 1510 (1973).
9. T. W. Stinson, J. D. Litster, and N. A. Clark, *J. Physique*, **33**, Cl-69 (1972).
10. G. K. L. Wong and Y. R. Shen, *Phys. Rev.*, **A10**, 1227 (1974).
11. J. C. Filippini and Y. Poggi, *J. Physique*, **36**, Cl-137 (1975).