

High frequency rheo-optical spectroscopy by means of ultrasonically induced light diffraction

超音波光回折を用いた

高周波レオ・オプティクス スペクトロスコピー

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1. Introduction

In the study of soft materials, for example, polymer melts and solutions, it is very important to combine frequency dependent complex strain-optical coefficient and shear or Young moduli to analyze dynamic properties. In the case of complex shear modulus, shear impedance spectrometer using the AT cut quartz crystal enables measurement from 5 to 205 MHz range [1]. The method has been applied to observe the relaxation of the LiClO₄-propylene carbonate solutions [2] and ionic liquids [3]. Therefore development of methods to obtain complex strain-optical coefficients in the corresponding frequency range of the shear modulus measurement is highly desired.

We had reported from 5 to 25 MHz complex strain-optical coefficients measurement of isotropic phase liquid crystal, 4-cyano-4'-pentylbiphenyl (5CB), using ultrasonically induced light diffraction method [4]. In this study, we improved that system to raise upper frequency limit to 75 MHz. We also measured shear relaxation spectra to analyze viscoelastic behavior in comparison with complex strain-optical coefficient spectra of 5CB.

2. Experiment

2.1. Sample

Sample 4-cyano-4'-pentylbiphenyl (5CB) was supplied from Merck and used without further purification.

2.2. Rheo-optical spectroscopy

The measurement system is similar to those used in our previous study [4] with improvement of light detection unit, optical axis and cell shape to raise the upper frequency limit. Fig.1 schematically shows the measurement system. Measurements were carried out from 5 to 75 MHz at 40, 50 and 60 ±0.1°C.

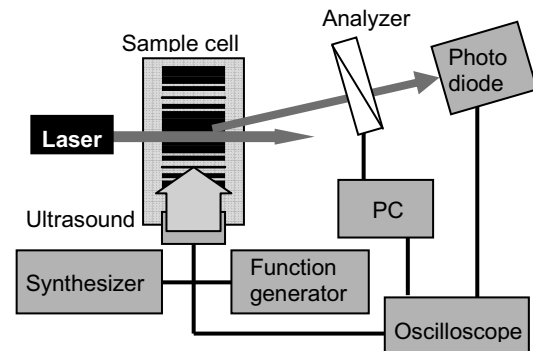


Fig.1 Scheme of ultrasonically induced light diffraction measurement system.

2.3. Shear relaxation spectroscopy

We measured shear relaxation spectra using shear impedance spectrometer, proposed by Kaatz et al. [1] and improved by Yamaguchi et al. [2-3]. Measurements were carried out from 5 to 205 MHz at 40, 50 and 60 ±0.1°C.

3. Results and Discussions

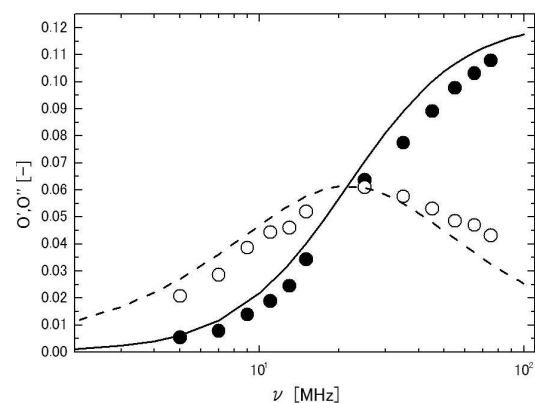


Fig.2 Frequency dependence of complex strain-optical coefficients (5CB at 60°C). The real and imaginary parts are plotted as the filled and open circles, respectively. The solid and dotted curves indicate real and imaginary values, respectively, which are calculated from reorientational relaxation rate and modulus of flow birefringence.

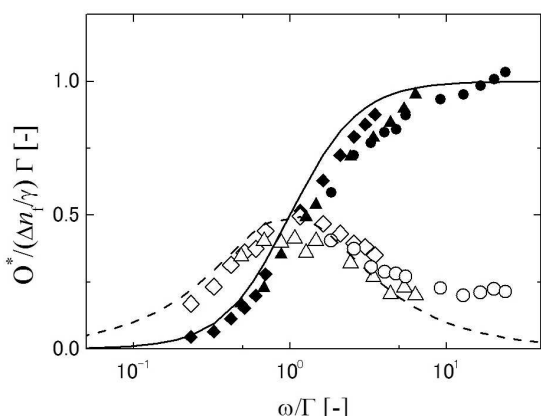


Fig.3 The normalized complex strain-optical coefficients, $O^*/(\Delta n_l/\gamma)\Gamma$, at 40 (circles), 50 (triangles) and 60°C (squares) are plotted against angular frequency, ω , divided by reorientational relaxation rate, Γ . The real and imaginary parts are plotted as the filled and open symbols, respectively. The solid and dotted curves indicate real and imaginary values, respectively, which are calculated from reorientational relaxation rate and modulus of flow birefringence.

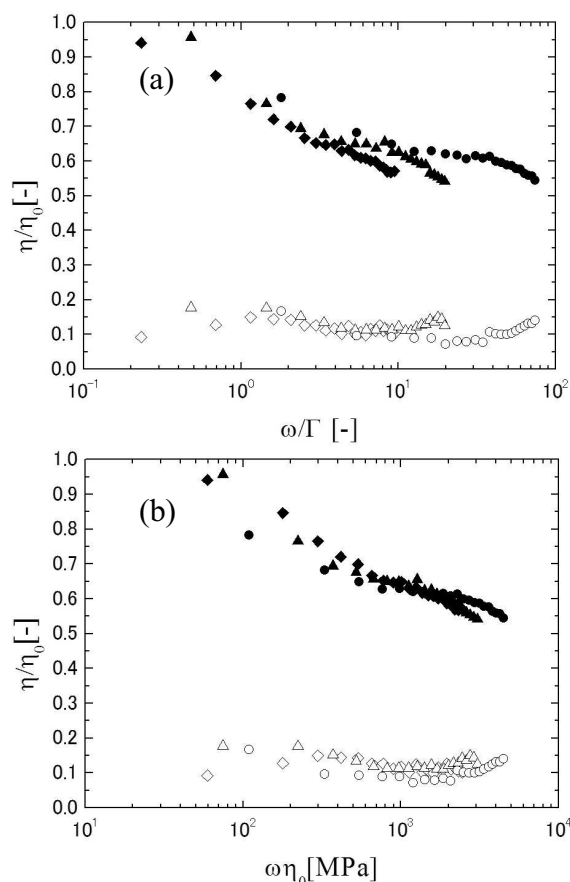


Fig.4 The normalized shear relaxation spectra at 40 (circles), 50 (triangles) and 60°C (squares) are plotted against (a) angular frequency divided by reorientational relaxation rate and (b) the product of the angular frequency and zero-frequency shear viscosity. The real and imaginary parts are plotted as the filled and open symbols, respectively.

Fig.2 exhibits frequency dependence of complex strain-optical coefficient spectra of 5CB at 60°C. Solid and dots curves indicate calculated value. As you can see, measured and calculated values are in good agreement.

Fig.3 exhibits the normalized complex strain optical coefficient spectra of 5CB at 40, 50 and 60 °C plotted against angular frequency divided by reorientational relaxation ratio, Γ , with calculated curves. A vertical axis is normalized by high-frequency limit of the Debye type relaxation. In previous studies, 5CB has only one relaxation due to orientation, which can be observed by heterodyne dynamic light scattering [5], but spectra in Fig.3 show that 5CB has another relaxation in high frequency range.

Fig.4 exhibits the normalized complex shear relaxation spectra of 5CB at 40, 50 and 60 °C plotted against (a) angular frequency divided by reorientational relaxation rate and (b) the product of the frequency and zero-frequency shear viscosity. We can see that spectra at each temperature reduce to a single master curve as the function of frequency in low frequency of (a). In the same way, in high frequency of (b) spectra lie on a single curve. These mean that the first relaxation in low frequency is assigned reorientation and the second relaxation in high frequency is to viscoelastic one.

4. Conclusion

We have improved the apparatus to measure frequency dependent complex strain - optical coefficient using ultrasonically induced light diffraction method. We succeeded in measurement from 5 to 75 MHz. We also measured shear relaxation spectra from 5 to 205MHz and compared them with strain optical coefficients. We have revealed existence of another relaxation in high frequency range, which has not been observed by the heterodyne dynamic light scattering.

Acknowledgment

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