Birefringence of Amorphous Polymers. 1. Dynamic Measurement on Polystyrene

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ABSTRACT: An apparatus was developed to measure the dynamic complex modulus and the birefringence of polymeric films. Measurements were performed for a polystyrene film over the frequency range of 1–130 Hz and the temperature of 100–176 °C. The complex strain-optical coefficient corresponding to the complex Young's modulus changed sign at the high-frequency end of the glass-to-rubber transition region. The stress-optical law held valid only at relatively low frequencies corresponding to the rubbery plateau zone. In a preliminary analysis with the method of the reduced variables, the Young's modulus and the strain-optical coefficient exhibited different temperature dependences from each other. The relaxation spectrum calculated from the composite master curve presenting the birefringence was composed of a negative box-type section at short times and a positive wedge-type section at long times. The shape of the relaxation spectrum in each region was very similar to that for the mechanical relaxation spectrum except around the time where it changed sign. The data were analyzed with a modified stress-optical rule with regards to the relaxation spectrum: the mechanical relaxation spectrum is assumed to be a sum of two components, and the stress-optical rule holds valid for each component but with different stress-optical coefficients. One component of the spectrum, located at short relaxation times, varied more strongly with temperature than the other at longer times. The shift factor, a_T, for the latter was proportional to the viscosity. This component could be represented by a bead–spring segment model, with each segment composed of about 10 monomer units.

Introduction

When a polymeric material is deformed, the refractive index as well as the stress becomes anisotropic. The relation between the refractive index and the stress has been an important subject in the rheooptical study. In the case of dilute solutions, the birefringence is originated not only by the optical anisotropy of segments (intrinsic birefringence) but also by the anisotropic shape of the molecule (form birefringence).[1] For rubbers[2] and melts (or concentrated solutions),[3,4] the form birefringence is negligible and the birefringence is related with the stress through the stress-optical rule: the anisotropic part of refractive index tensor, $\Delta\mathbf{n}$, is proportional to the anisotropic part of the stress tensor, σ.

$$\Delta\mathbf{n}(t) = C\sigma(t) \qquad (1)$$

The proportionality coefficient, C, is called the stress-optical coefficient and is independent of the time, the magnitude of strain, or the rate of strain. The rule was first realized under the steady shear flow and then time-dependent shear flows.[4] The normal stress difference can be evaluated from the birefringence in steady shear flow as well as in the transient shear flow. The stress-optical rule also holds good in the stress relaxation process at long times. The birefringence measurement was used for examining the theoretical prediction of the shape of the entangled polymer molecules in complicated flow histories.[5] Recently, the method has been applied to mixed systems such as block copolymers[6] or polymer mixtures,[7] which contain segments of different chemical species.

For solid materials, the relation known as photoelasticity has widely been used to study the state of stress in the field of structure analysis. The magnitude of the birefringence produced is proportional to the applied stress, provided that the stress is not too large.

$$\Delta n = C_P\sigma \qquad (2)$$

In spite of the similarity between eqs 1 and 2, there is an important difference between the stress-optical rule and the photoelasticity. The photoelasticity usually is defined for an instantaneous response on the deformation and does not take account of the effect of time. For the case of polymers, both Δn and σ may depend on time even in the glassy state. The coefficient C_P of polymers such as polystyrene[8] varies with time over the time range in which the stress varies. Another difference between eqs 1 and 2 is the difference in the values of the proportionality coefficients. For example, the reported value of C for polystyrene is -5.0×10^{-9} Pa^{-1} and C_P is 8.81×10^{-12} Pa^{-1};[8] for many polymers $|C_P|$ is much smaller than $|C|$. From the difference between C and C_P, one can easily predict that the stress-optical rule does not hold good over the time range including the glass-to-rubber transition region.

The stress-optical rule may be derived from various polymer models composed of Gaussian segments.[1-4,9] The failure of the stress-optical rule in the glass transition region may mean that the concept of the segment breaks down. In the transition region of amorphous polymers, the most widely accepted theory is the one based on the Rouse model, or the bead–spring segment model.[10] According to this theory, the relaxation spectrum, $H(\tau)$, is inversely proportional to the square root of the relaxation time, τ.

$$H(\tau) \propto \tau^{-1/2} \qquad (3)$$

Experimental results for many amorphous polymers show that such a power law holds good only in the long-time part of the transition region.[11] At the shorter relaxation times, the function H decreases more rapidly with τ. Moreover, the value of the glass modulus is about 2 decades larger than that predicted by the Rouse model with reasonable segment sizes. The features of the glass-to-rubber transition region may be described by considering an additional relaxation spectrum. Stockmayer has theorized the possibility of two distinct modes in the dielectric relaxation of polymers.[12] Actually the existence of two modes can be inferred by comparison of dielectric and viscoelastic data.[13] However, the experimental method for separate evaluation of the viscoelastic relaxation spectrum for each mode has not been established.

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Birefringence measurements may be made during the creep or stress relaxation. The measurement on oscillatory deformation, or the dynamic birefringence method, is more suitable for the study of the short-time relaxation. The dynamic birefringence was first measured by Onogi et al. on polyethylene in 1961.[14] Pioneering studies on amorphous polymers were performed by Read.[15] Here we propose a new method of analyzing dynamic birefringence data for amorphous polymers and show that the birefringence measurement is a good tool in investigating the details of the relaxation mechanism in the glass-to-rubber transition region. A similar method was reported by Priss et al.[16] and Read.[17] They derived the method with an assumption of the stress-optical rule for glass and got a conceptually different result from ours. Detailed differences will be described in the Discussion section.

Experimental Section

Principle of Dynamic Birefringence Measurements. We take a polymer film of length l_0 and change its length according to the relation

$$l = l_0(1 + \epsilon \sin \omega t) \tag{4}$$

where ϵ ($\ll 1$) is the amplitude of the tensile strain, ω is the angular frequency, and t is the time. The tensile stress leads the strain by a phase angle δ and varies as

$$f = f_0 \sin (\omega t + \delta) \tag{5}$$

The complex Young's modulus is obtained by

$$E' = (f_0/\epsilon) \cos \delta \tag{6}$$

$$E'' = (f_0/\epsilon) \sin \delta \tag{7}$$

In the same oscillatory deformation, the birefringence of the film will vary as

$$\Delta n_f = \Delta n_0 \sin (\omega t + \delta_B) \tag{8}$$

where the phase angle δ_B may be different from δ. A complex strain-optical coefficient corresponding to Young's modulus may be defined as

$$O' = (\Delta n_0/\epsilon) \cos \delta_B \tag{9}$$

$$O'' = (\Delta n_0/\epsilon) \sin \delta_B \tag{10}$$

The stress-optical rule with respect to these quantities reads

$$O'(\omega) = CE'(\omega)$$

$$O''(\omega) = CE''(\omega) \tag{11}$$

where C, the stress-optical coefficient, should be independent of the frequency. One can deduce from the results of earlier studies that the relation holds valid for amorphous polymers at relatively low frequencies, i.e., in the rubbery plateau and terminal flow zones of viscoelasticity.[2-4]

Suppose a material with birefringence is placed in between a crossed pair of polarizing films and a light beam of strength I_0 is passed. The strength of the passing light is related to the retardation, R, through

$$I = I_0 \sin^2 (R/2) \tag{12}$$

The effect of the absorption of light by the material and the polarizing films was neglected in deriving the equation. The birefringence is easily calculated from the light intensity.

Apparatus. The details of the apparatus and the data acquisition system were reported previously.[18] A schematic diagram of the apparatus is shown in Figure 1. An optical system was attached to the oscillatory rheometer (Rheospectoler DVE 3, Rheology Co., Ltd., Kyoto, Japan). This apparatus is capable of applying the oscillation of the amplitude ranging from 0.1 to 100 μm to a film of a few centimeters long over the frequency range of 1–1000 Hz. The measurement of Young's modulus is limited to the range of 1–130 Hz due to an undesirable vibration of the apparatus. The optical system was simply composed of a helium–neon gas laser, two polarizing films, a compensator, and an optical detector. The signal from the optical detector was analyzed with a lock-in amplifier.

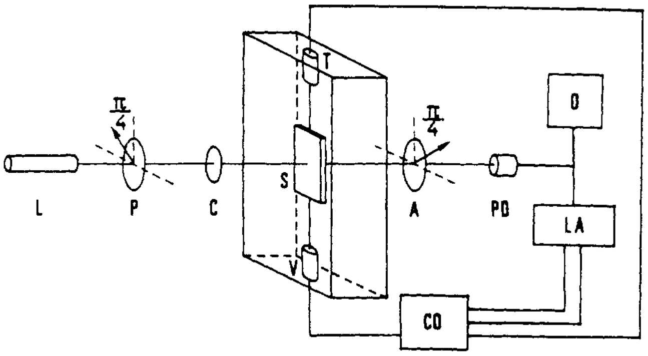

Figure 1. Block diagram of the apparatus for measurement of the complex Young's modulus and the complex strain-optical coefficient: L, laser; P, polarizer; C, compensator; S, sample film; A, analyzer; PD, photodetector; V, vibrator; T, force transducer; O, oscilloscope; LA, lock-in-amplifier; CO, computer.

The retardation of the system, R, is composed of one from oscillatory load, R_f, one from the load added to maintain the sample, R_l, and one from the compensator, R_c.

$$R = R_f + R_l + R_c \tag{13}$$

$$R_f = (2\pi \Delta n_0 d/\lambda) \sin (\omega t + \delta_B) \tag{14}$$

Here, d is the thickness of the film, and λ is the wavelength of light in the vacuum. R_c is constant; we assumed that R_l is constant during the measurement. Two methods were pursued for measurements of Δn_0 and δ_B.

(i) We put $R_l + R_c = 0$ and assume that Δn_0 is small. The eq 12 reduces to

$$I = I_0(\pi d/\lambda)^2 \Delta n_0^{\,2}[1 - \cos 2(\omega t + \delta_B)]/2 \tag{15}$$

The film birefringence is derived from the amplitude and the phase angle of the oscillation with angular frequency 2ω. The sign of Δn_0 cannot be determined with this method.

(ii) We put $R_l + R_c = \pi/4$ and assume that Δn_0 is small. Then we obtain from eq 12

$$I = I_0\{1/2 - (\pi d/\lambda)\Delta n_0 \sin (\omega t + \delta_B)\} \tag{16}$$

The amplitude and the phase of the oscillation with angular frequency ω are measured.

Either of the conditions can be attained by adjusting the compensator. The results of the two methods were in good agreement with each other.[18] One can also use the Senarmont optical system where a polarizer and a quaterwave plate are each orientated at 45° to the strain axis.[19]

Sample. The polymer used in this study is a polystyrene supplied by Tosoh Co., Ltd. (Tokyo). The weight-average molecular weight was $M = 3 \times 10^6$. The specimens were made with a hot press at 150 °C and cooled down to 80 °C in 3 h. A typical dimension of the film for measurement was 1 mm × 5 mm × 10 mm. Measurements were performed at several temperatures in the range of 100–176 °C. The hysteresis of the test specimen was removed by keeping it for 1 h at each temperature prior to measurements.

Results and Discussion

Young's Modulus and the Strain-Optical Coefficient. The complex Young's moduli, E' and E'', of the polystyrene at various temperatures are plotted against the frequency in Figure 2. At the highest temperature, 176 °C, the real part of the complex Young's modulus, E'

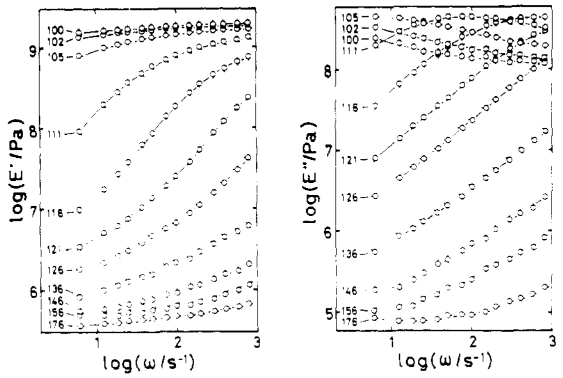

Figure 2. Frequency dependence of the complex Young's modulus. Temperatures in degrees centigrade are indicated in the figure.

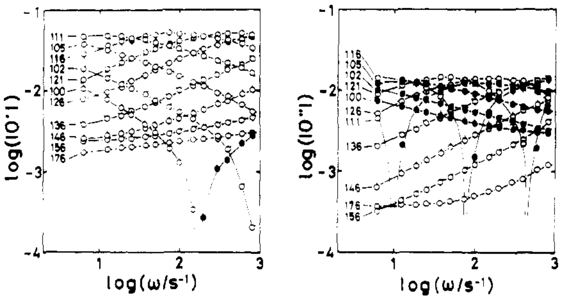

Figure 3. Frequency dependence of the complex strain-optical coefficient. Unfilled circles represent negative values and filled circles positive values. Temperatures in degrees centigrade are indicated.

varies little with frequency and the value is about 5×10^5 Pa. At this temperature, the imaginary part, E'', is about 6 times smaller than E'. These features correspond to the rubbery plateau region. At intermediate temperatures, around 120 °C, E' increases rapidly with increasing frequency, and E'' is larger than E'. At low temperatures, E' reaches to approximately a constant of about 2×10^9 Pa, and E'' weakly decreases with increasing frequency.

Figure 3 shows the complex strain-optical coefficient. Here, absolute values of O' and O'' are plotted. At 176 °C, both O' and O'' are negative, and the frequency dependence of O' and O'' resembles that of E' and E'', respectively. Actually the stress-optical rule of eq 11 holds well at this temperature. With decreasing temperature, the absolute value of O', $|O'|$, increases with increasing frequency, and then $|O'|$ shows a maximum at 111–116 °C. At lower temperatures, $|O'|$ decrease with increasing frequency. At 100 °C O' changes the sign at $\omega = 160$ s^{-1}. The behavior of O'' is similar to that of O': with decreasing temperature, $|O''|$ increases and shows the maximum, and then O'' changes the sign. O'' changes the sign at higher temperatures than O' does.

On comparing Figures 2 and 3, one sees that the stress-optical rule of eq 11 holds well at temperatures higher than 140 °C; the stress-optical coefficient, C, is -5.0×10^{-9} Pa^{-1}. The stress-optical rule did not hold well at any lower temperatures.

Master Curves. We constructed master curves from these data with the method of reduced variables.[20] In the glass-to-rubber transition region, the method of reduced variables sometimes fails because of the complex temperature dependence of the viscoelastic functions. Plazek studied the temperature dependence of the creep compliance of a polystyrene and reported that viscosity and recoverable compliance show different temperature dependences.[21] For birefringence data, the validity of the method has not been confirmed. It is reported that near the glass transition temperature, birefringence behavior becomes very complex and the birefringence in the stress relaxation process can not be analyzed with the method of reduced variables.[8] In spite of all these difficulties, we constructed master curves to get a better prospective and to prepare for the method of analysis proposed later.

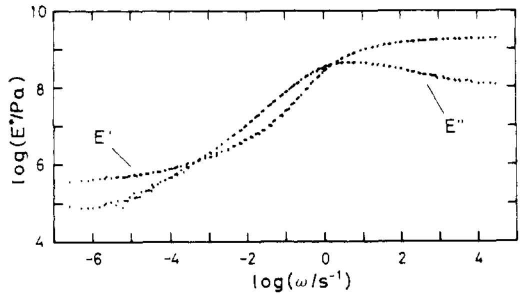

Figure 4. Reduced complex Young's modulus. The reference temperature is 105 °C.

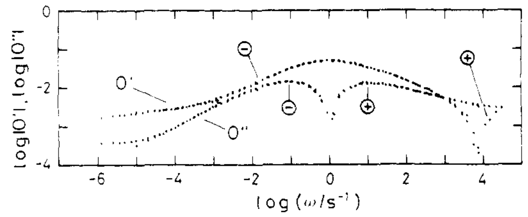

Figure 5. Reduced complex strain-optical coefficient. The reference temperature is 105 °C.

All the data of E', E'', O', and O'' were plotted against ω in double-logarithmic scales and shifted along the abscissa so that each quantity lies on one composite curve as closely as possible. The vertical shift was not used; its effect was small over the limited temperature range studied; the form of the shift factor is still controversial,[22] and the temperature range was too narrow to determine appropriate form.

The complex Young's modulus and the strain-optical coefficient reduced to 105 °C are shown in Figures 4 and 5, respectively. The superposition was fairly good for each quantity except at $\omega = 10^{-2}$–10^{-1} s^{-1}. The scattering at low frequencies is due to the lower accuracy of the raw data. The frequency range of the master curves of the Young's modulus is wider than that of the strain-optical coefficient. Actually the relative location along abscissa of curves varies with varying the choice of the reference temperature. The relatively low reference temperature, 105 °C, was chosen to make it easier to see the difference between the ranges of reduced frequency in Figures 4 and 5. This comes from the different temperature dependences between the Young's modulus and the strain-optical coefficient. Therefore, the fair superposition may be fortuitous. The failure of thermorheological simplicity will be discussed later. For quantitative comparison of Figures 4 and 5, one must note the difference of the corresponding frequency range at a temperature different from the reference temperature, 105 °C.

From Figure 4, one can see that the frequency range studied corresponds to the glass-to-rubber transition zone and the glassy zone. The lowest frequency end may possibly be a part of the rubbery plateau zone.

The real part, O', as well as the imaginary part, O'', of the strain-optical coefficient is negative at low frequencies, and it increases with increasing frequency, passes a maximum, and changes the sign at a certain frequency. The frequency at which O' changes the sign is higher than that where O'' changes sign.

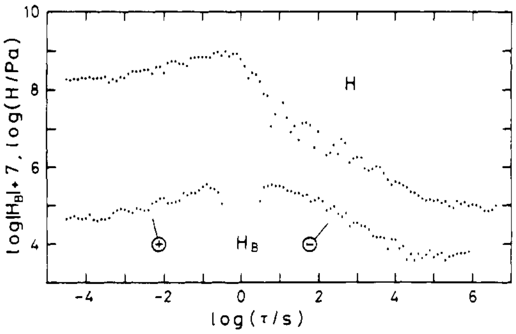

Figure 6. Relaxation spectra, H and H_B. The reference temperature is 105 °C.

It should be noted that all data including those in glassy and glass-to-rubber transition zones were obtained above the glass-to-rubber transition temperature, which is typically 100 °C for polystyrene. This was possible because of the high-frequency range used in this study. Therefore, the glass transition in this study should be understood as the transition of mechanical property and not as the thermodynamic transition. The measurement at high temperatures is advantageous for avoiding the possible effect of thermal hysteresis in the sample.

Viscoelastic and Optical Relaxation Spectra. For the following discussion, we employ the viscoelastic relaxation spectrum, $H(\tau)$, defined as follows:[23]

$$E' + iE''(\omega) = \int_{-\infty}^{\infty} H(\tau) \frac{i\omega\tau}{1 + i\omega\tau} \mathrm{d} \ln \tau \qquad (17)$$

In the same way, we employ the optical relaxation spectrum, $H_B(\tau)$ as follows:[15]

$$O' + iO''(\omega) = \int_{-\infty}^{\infty} H_B(\tau) \frac{i\omega\tau}{1 + i\omega\tau} \mathrm{d} \ln \tau \qquad (18)$$

The calculation method of the spectra from the complex dynamic Young's modulus and strain-optical coefficient is described in the Appendix. The estimated spectra can reproduce the complex Young's modulus and the strain-optical coefficient to within ±10% over the whole range of measurements.

The relaxation spectra, H and H_B, are shown in Figure 6. The viscoelastic relaxation spectrum, H, could not be evaluated accurately over a certain range in the glass-to-rubber transition zone: $1.0 < \log(\tau/s) < 2.5$. This comes from the fact that the slope of E'' in Figure 4 was close to 1 in this region. The difficulty is the same if one employs the approximation formula to derive H.[23] Such a gap was also found for polyisoprene[13] and poly(vinyl acetate).[24] Except for this gap, the overall shape of the mechanical relaxation spectrum is similar to that reported for amorphous polymers in the glassy and glass-to-rubber transition zones.[23] The slope of $-1/2$ of eq 3 is found only in a limited region of long times of the transition zone. The optical relaxation spectrum, H_B, is composed of two sections; one of positive values at short times and another of negative values at long times. A similar optical relaxation spectrum was also reported by Read for several polymers.[15]

As pointed out on Figures 2 and 3, the stress-optical rule, eq 11, held well in the rubbery plateau region. This rule can be rewritten in spectrum form as

$$H_B = CH \qquad (19)$$

One can examine this relation in Figure 6; one must be careful of the difference of the abscissas for H and H_B at temperatures different from 105 °C. The relation holds well at long times with the same value of the stress-optical coefficient given earlier.

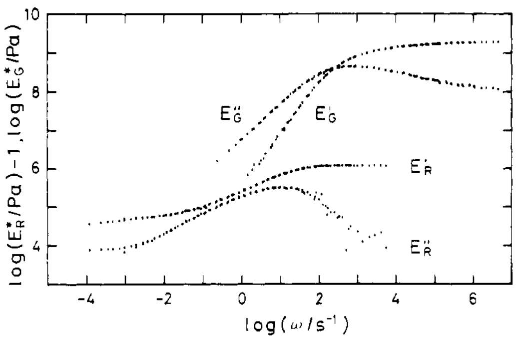

Figure 7. Frequency dependence of E'_R, E''_R, E'_G, and E''_G. The reference temperature is 116 °C.

The same type of relation seems to hold well at short times of Figure 6; it may be remarked that the stress-optical rule, eq 11, was not valid at high frequencies. The proportionality at short times holds over 4 decades up to approximately the peak of H_B. The value of C is 3.2×10^{-11} Pa^{-1}. This is different from the reported value of C_p in the glassy state.[8]

Modification of the Stress-Optical Rule. As seen above, the stress-optical rule of the spectrum form holds valid in the glassy zone and the rubbery plateau zone. We may assume that the viscoelastic spectrum is composed of two distinguishable parts, H_R and H_G, and that the stress-optical rule holds for the respective spectrum with different coefficients. The suffixes R and G stand for rubber and glass, respectively.

$$H = H_R + H_G \qquad (20)$$

$$H_B = C_R H_R + C_G H_G \qquad (21)$$

One can easily derive therefrom the relation for the complex modulus and birefringence

$$E' = E'_R + E'_G \qquad (22)$$

$$O' = C_R E'_R + C_G E'_G \qquad (23)$$

$$E'' = E''_R + E''_G \qquad (24)$$

$$O'' = C_R E''_R + C_G E''_G \qquad (25)$$

where, E'_i and E''_i (i = R, G) are defined according to eq 17 with H_i. Similar equations were employed by Read,[17] but the basic idea is different as seen later. The difference of frequency scales of Figures 4 and 5 for the master curves of Young's modulus and the strain-optical coefficient may be due to the different temperature dependence between H_R and H_G. If one knows the value of the coefficients C_R and C_G, one can solve eqs 22–25 and estimate E'_i and E''_i. In order to allow the different temperature dependences of H_R and H_G, the equations were not solved with the reduced data but with the raw data at each temperature. Here, $C_R = -5.0 \times 10^{-9}$ Pa^{-1} and $C_G = 3.2 \times 10^{-11}$ Pa^{-1} were used.

The evaluated complex Young's moduli E'_i and E''_i were reduced to a reference temperature, 116 °C, with the method of reduced variables and shown in Figure 7. From Figure 7, one can see that E'_R increases with increasing frequency and does not depend on frequency above $\omega > 100$ s^{-1}. The value of the high-frequency limit of E'_R is about 1×10^7 Pa. The E''_R increases with increasing frequency and passes a maximum. E'_G and E''_G are

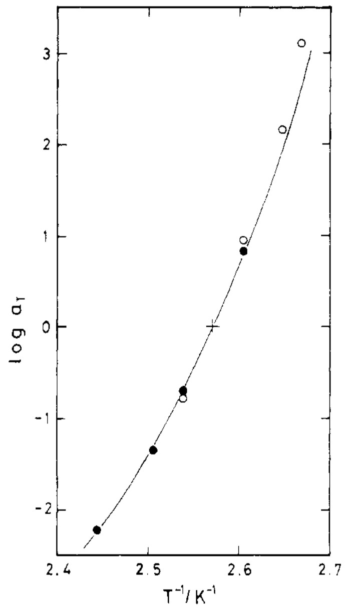

Figure 8. Shift factors a_{TR} (filled circles) and a_{TG} (unfilled circles), respectively, representing the temperature dependence of H_R and H_G. The reference temperature is 116 °C. The solid line represents the temperature dependence of viscosity of polystyrene.[19]

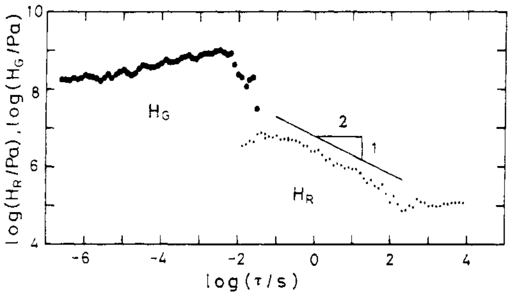

Figure 9. Time dependence of H_R and H_G. The reduced temperature is 116 °C.

approximately the same as E' and E'' at high frequencies; the properties in the glassy zone are determined by E'_G and E''_G.

Figure 8 gives the comparison of shift factors, a_{TR} and a_{TG}, for H_R and H_G, respectively. Irrelevant points for relatively high or low temperatures were not shown. The H_G exhibits a stronger temperature dependence than the H_R. The difference implies the failure of thermorheological simplicity for viscoelastic functions; the success of superposition in Figures 4 and 5 is fortuitous. The temperature dependence of H_R is in accord with that for the viscosity (solid line) reported by Plazek.[21]

Relaxation Spectra, H_R and H_G. The relaxation spectra H_R and H_G calculated from Figure 7 with the method described in the Appendix are shown in Figure 9. Figure 9 shows that H_R decreases with increasing time, and the slope is $-^1/_2$ over approximately 3 decades. This result is consistent with eq 3. The value of the high-frequency limit of E'_R gives the segment molecular weight, M_s, as calculated from $M_s = \rho RT/3E$, as 900. This means that the segment is composed of about 18 main-chain carbon atoms.

The H_G increases with increasing time and shows a maximum. Obviously the properties of the glassy region are mainly determined by the properties of H_G. Opposite signs of C_R and C_G may be the clue to interpret the molecular origin of the relaxation in the glass-to-rubber transition region.

Comparison with an Earlier Method. A similar method of separating the modulus and the strain-optical coefficient into two components was proposed by Priss et al.[16] and Read.[17] Their method is based on the assumption of the stress-optical rule in the glassy zone as well as in the rubbery zone. Thus they separate the stress, σ, into two components, σ_0 and σ_d, according to the following relations.

$$\sigma = \sigma_o + \sigma_d \tag{26}$$

$$\begin{aligned}\Delta n &= \Delta n_o + \Delta n_d \\ &= C_o\sigma_o + C_d\sigma_d\end{aligned} \tag{27}$$

Here C_0 is the stress-optical coefficient in the rubbery zone, and C_d, that in the glassy zone. These equations are formally the same as eqs 22–25, and there is no a priori reason to prefer one to the other. The difference may be summarized as follows.

First, the coefficient C_G can be determined by direct comparison of data; see Figure 6. On the other hand, it is usually not possible to obtain a C_d value except with some extrapolation procedure.

The C_d is related to the present quantities through

$$C_d = \lim_{\omega\to\infty} \frac{C_R E'_R + C_G E'_G}{E'_R + E'_G} \tag{28}$$

This equation indicates that C_d can be estimated provided that Young's modulus is obtained at the limit of high frequency. On the other hand, the limiting value may be contaminated by the contribution from other relaxation mechanisms such as the β-relaxation mechanism.[25] Thus the definition of C_d may be ambiguous and possibly depend on the material.

Second, the relaxation spectra H_0 and H_d, corresponding to σ_0 and σ_d, respectively, have complicated shapes including negative portions.[17] The present authors prefer the simple shapes of H_R and H_G. However, the preference is due to no more than the simplicity at this moment.

Third, the present method was good in describing the temperature dependence of Young's modulus and the strain-optical coefficient. The Priss–Read scheme has not been examined to the extent to analyze the temperature dependence of these quantities. Comparison of these two methods is now in progress on a plasticized polystyrene for which the difference of the temperature dependences of H_R and H_G is very large.

Conclusions

We proposed a modified stress-optical rule to explain the behavior of the complex Young's modulus and the complex strain-optical coefficient from the rubbery plateau zone to the glassy zone. With this rule, the relaxation spectrum could be separated into two components: One determines the properties in the rubbery plateau region and the long-time end of the glass-to-rubber transition region and could be described by the bead-spring model. Another determines the properties of the glassy zone. In the glass-to-rubber transition zone, both of the components contribute to the Young's modulus and the birefringence, and the different temperature dependences of the two components give rise to the complex behavior of the Young's modulus and the strain-optical coefficient.

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Appendix

Calculation of the Spectrum. In order to calculate the relaxation spectrum, we start from a formula[20]

$$H_1(\tau) = \frac{2}{\pi}E''(1/\tau) \qquad \text{(A-1)}$$

to calculate the first approximation, H_1, from the data of the loss modulus, E''. Then we calculate the loss modulus from its definition

$$E''_1(\omega) = \int_{-\infty}^{\infty} H_1(\tau)\,\frac{\omega\tau}{1+\omega^2\tau^2}\,\mathrm{d}\ln\tau \qquad \text{(A-2)}$$

where the suffix 1 means that E''_1 is the first-order approximation. For this integration, we need the values of E'' outside the frequency range of measurements. For this purpose E'' curves are smoothly extended (rather arbitrarily) over 2 decades of frequencies at both sides of the low and high frequencies. The difference between the experimental value and the calculated value, $\Delta E''_1$, is used to modify the first-order approximation, and we get the second-order approximation, H_2.

$$\Delta E''_1 = E'' - E''_1 \qquad \text{(A-3)}$$

$$\Delta H_1 = \frac{2}{\pi}\Delta E''_1 \qquad \text{(A-4)}$$

$$H_2(\tau) = H_1(\tau) + \Delta H_1 \qquad \text{(A-5)}$$

The procedure of eqs A-2–A-5 was repeated with an increment in the suffix. After repeating the procedure 20 times and with suitable extension of E'' at both sides, the resulting spectrum could reproduce the experimental data of both E' and E'' at an accuracy of ±10%. The choice of E'' outside the range of measurement may be changed if the final result is no good.

References and Notes

(1) See, for example: Tsvetkov, V. N. In *Newer Methods of Polymer Characterization*; Ke, B., Ed.; Interscience: New York, 1964; Chapter 14.

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