Dynamic Birefringence of Bisphenol-AP Polycarbonate

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The complex strain-optical coefficient and the complex Young's modulus of Bisphenol-AP Polycarbonate were measured around the glass-to-rubber transition zone. The data were analyzed with the modified stress-optical rule, and two component functions (denoted by G and R) were determined. The results were compared with those of Bisphenol A polycarbonate, and the effect of the displacement of methyl side groups by phenyl groups was discussed. The displacement reduced the modified stress-optical coefficient of the R component which is related to the orientation of polymer chains and determines the viscoelastic behavior in the rubbery plateau and flow zones, but did not affect the coefficient of the G component in the glassy zone. The displacement also affected the glass transition temperature and entanglement spacing.

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 rheo-optical study. For rubbers[1] and polymer melts (or concentrated solutions)[2,3], the birefringence is related with the stress through the stress-optical rule: the anisotropic part of refractive index tensor, Δn, is proportional to the anisotropic part of the stress tensor, σ.

$$\Delta n(t) = C_F \sigma(t) \tag{1}$$

The proportionality coefficient, C_F, is called the stress-optical coefficient and independent of the time, the magnitude of strain, or the rate of strain.

For solid materials, the proportional relation between birefringence and stress is known as photoelasticity.

$$\Delta n = C_P \sigma \tag{2}$$

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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 is usually defined for an instantaneous response on the deformation and does not take account of the effect of time. Another difference between eqs 1 and 2 is the difference in the values of the proportionality coefficients. From the difference between C_F and C_P, one can easily deduce that the stress-optical rule does not hold well over the time range including the glass-to-rubber transition zone.

Birefringence measurements may be made during the creep or stress relaxation. Dynamic birefringence, the birefringence in oscillatory deformation, was first measured by Onogi and Stein on a polyethylene in 1961.[4] The measurements of dynamic birefringence on several amorphous polymers were performed by Read in 1960's.[5] Some of the data were analyzed with a modified stress-optical rule to interpret complicated behavior of birefringence in the glass-to-rubber transition zone by Read in 1983.[6] Recently, the measurement was applied on a polystyrene by Inoue et al., and consequently a new version of the modified stress-optical rules was proposed.[7] The rule says that both of the complex Young's modulus, $E^*(\omega)$, and the complex strain-optical coefficient, $O^*(\omega)$, are composed of two component functions (designated by G and R), and that the stress-optical rule separately holds well for each component:

$$E^*(\omega)=E_G{}^*(\omega)+E_R{}^*(\omega) \tag{3}$$
$$O^*(\omega)=C_G E_G{}^*(\omega)+C_R E_R{}^*(\omega) \tag{4}$$

Here, C_G and C_R are the stress-optical coefficients associated with the G and R components, respectively. C_R is equal to the stress-optical coefficient of flow birefringence, C_F, for polymer melt and concentrated solutions, and C_G is a different coefficient defined as the ratio O''/E'' at high frequencies. The rule bases on the finding that O'', the imarginary part of O^* is proportional to E'', the imarginary part of E^*, in the glassy zone.

We can determine the two modified stress-optical coefficients, and therefore can solve eqs 3 and 4 for the G and R component functions. The separation into two components successfully explained the complicated behavior of viscoelasticity and birefringence around the glass transition zone. The modified stress-optical rule makes the dynamic birefringence measurement combined with the stress-measurement as a powerful and unique technique to study the viscoelasticity around the glass-to-rubber transition zone.

Bisphenol-A polycarbonate, PC, is an important material for polymer industries and thought to be most suitable for magneto-optical memory disk substrate because of its excellent thermal, mechanical, and hydroscopic properties. However, PC has low fluidity and a high C_F, and these features cause the difficulty in the injection molding of optical disk. Some derivatives of PC were tested to decrease the molecular anisotropy by the displacement of side-chain methyl groups by other groups.[8] In this work, two different stress-optical coefficients were measured: one is the stress-optical coefficient estimated by melt spinning method, C_m, which can be related to C_F, and the other one is that for photoelasticity in the glassy state, C_P. However, the relaxation behavior of birefringence around the glass transition zone was not discussed, and the modified stress-optical rule says that C_G is a more fundamental material coefficient than C_P. In this study, we investigate the birefring-

ence behavior of a polycarbonate with displaced side chain methyl groups by phenyl groups using the modified stress-optical rule, and discuss viscoelasticity and the origin of birefringence in the rubbery and the glassy zones.

EXPERIMENTAL SECTION

A Bisphenol AP Polycarbonate, PCAP, (poly(oxycarbonyloxy-1,4-phenylene(methyl)-phenylmethylene-1,4-phenylene) was kindly supplied from Unitika Co. Ltd. A film was cast from 5wt% dichloromethane solution and dried in a vacuum dry oven at 180°C for a few days prior to measurements.

The apparatus for dynamic birefringence measurements were reported previously.[9] An optical system was attached to an oscillatory rheometer (Rheology, DVE 3, Kyoto, Japan). A Senarmont optical system was used to compensate the static birefringence induced by load to maintain the sample; He-Ne laser, polarizer, quarter-wave plate, analyzer, and photodetector were placed on an optical bench. The sample was placed between the polarizer and the quarter-wave plate with their axes at 45° to the strain axe in the specimen. The measurements were performed at isothermal condition over the frequency range 1-130 Hz.

RESULTS AND DISCUSSION

Master Curve.

The method of reduced variables[10] is widely used to obtain the composite curve. The data of viscoelastic function at different temperatures, plotted in double-logarithmic scales, are shifted along abscissa (time or frequency) so that data at each temperature lay on one composite curve as closely as possible. With the help of the method, we can investigate a wide time (frequency) scale of the relaxation. However, some authors reported the breakdown of the method of reduced variables for viscoelastic functions in the glass-to-rubber transition zone with very careful experiments.[11] This may come from the complex nature in the transition zones as will be discussed. In spite of these difficulties, we believe that the application of this method makes it easy to see the characteristic behavior of Young's modulus and strain-optical coefficient.

The composite curves of Young's modulus and the strain-optical coefficient using the method of reduced variables are presented in Fig. 1. Here, the reference temperature is chosen as 188°C. The superposition for both mechanical and optical quantities are fairly well. From the sight, however, one can easily realize that the frequency ranges of the viscoelastic and optical curves are different from each other. This comes from the different temperature dependence of the mechanical and optical properties, i.e. $E^*(\omega)$ varies more drastically with temperature than $O^*(\omega)$. Different temperature dependence suggests that these quantities are not thermo-rheologically simple and the success of superposition is fortuitous. The breakdown of the method of reduced variables will be discussed later.

The (apparent) composite curve of the Young's modulus shows that the measurements are performed over the range from the rubbery plateau zone to the glassy zone. In the lowest three decade of frequency region, E' scarcely varies with increasing of frequency.
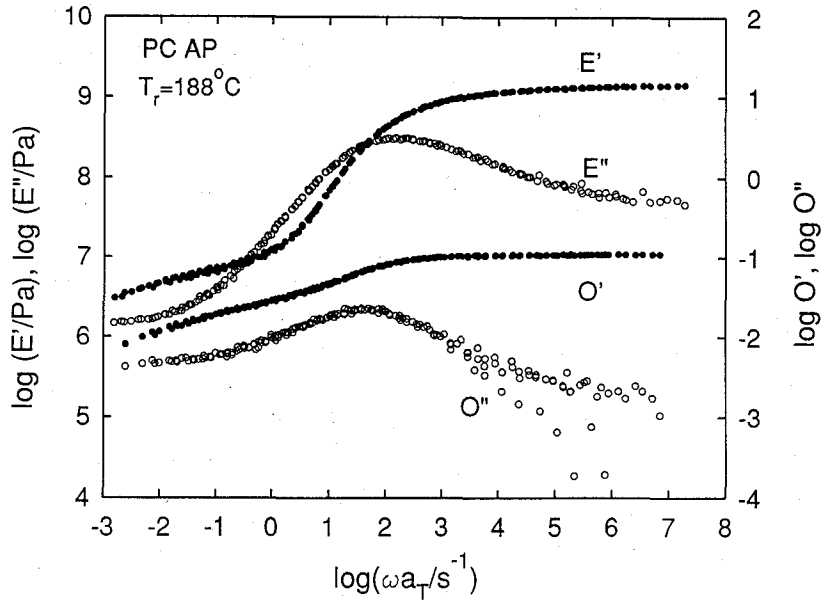
Fig. 1. Composite curves of the complex Young's modulus and the strain-optical coefficient for Bisphenol AP polycarbonate. Reference temperature is 188°C.

This region may correspond to the rubbery plateau zone. The plateau modulus at low frequencies is slightly lower than 10^7 Pa. The limiting value of E' at high frequencies is just over 10^9 Pa, and this is a typical value of the glassy modulus for PC.

The complex strain-optical coefficient is positive over the whole frequency range, and shows very weak frequency dependence in comparison with the complex Young's modulus: O' varies only less than one decade in the glass-to-rubber transition zone. These characteristic behaviors are almost the same as PC. However, values of O^* are smaller than those for PC in all tested frequency range.

In the low frequency (high temperature) regions, the shape of O^* is similar to that of E^*. In fact, at the highest temperature, 215°C, both O' and O'' are proportional to E' and E'', respectively: the ordinal stress-optical rule holds well in the rubbery plateau zone. The stress-optical rule for dynamic tensile measurements can be written from eq. 1 as follows.

$$O' = C_F E' \tag{5}$$
$$O'' = C_F E'' \tag{6}$$

The estimated value of C_F is $2.7 \times 10^{-9} Pa^{-1}$. This value is about half of that for PC. The proportional relation of eq. 5 was found to hold well with the same C_F at lower three temperature ranges over 210-205°C.

On the other hand, in the high frequency (low temperature) region, the stress-optical rule does not hold. However, one may see that O'' is proportional to E'' from Fig. 1 at high frequencies. From the direct comparison of raw data at each temperature, we found

that the following relation holds well in the rage of temperature 175-177°C.

$$O" = C_G E" \text{ (in the glassy region)} \tag{7}$$

This proportionality holds well for polystyrene (PS), PC and so on[12]. As described before, the modified stress-optical rule bases on this finding. The evaluated coefficient, C_G, is $3.3 \times 10^{-11} Pa^{-1}$, and close to that of other polymers including phenyl groups[13].

Analysis with Modified Stress-optical Rule.
   Now, if we have C_R equal to C_F, we can solve the eqs 5 and 6 for the G and R components. The method of reduced variables is used for estimated component functions, E^*_G and E^*_R, at each temperature to obtain the respective composite curves. The obtained composite curves are indicated in Fig. 2. The results of the R component at three lowest temperatures are eliminated, because E'_R is a constant independent of temperature and $E"_R$ becomes very small and has large scattering of data at these temperatures. The superposition shown in Fig. 2 is well for each curve.
   The high glassy modulus is due to the G component, and large decay of the Young's modulus in the glass-to-rubber transition zone can be attributed to the relaxation of the G component. The slope of E'_G and $E"_G$ at low ω are almost 2 and 1, respectively, and this means the distribution of relaxation time for the G component in the long time region is cut off at about $\omega = 100 \ s^{-1}$. On the other hand, the R component is located in long time region of transition zone, and determines the properties in the rubbery plateau zone. The R
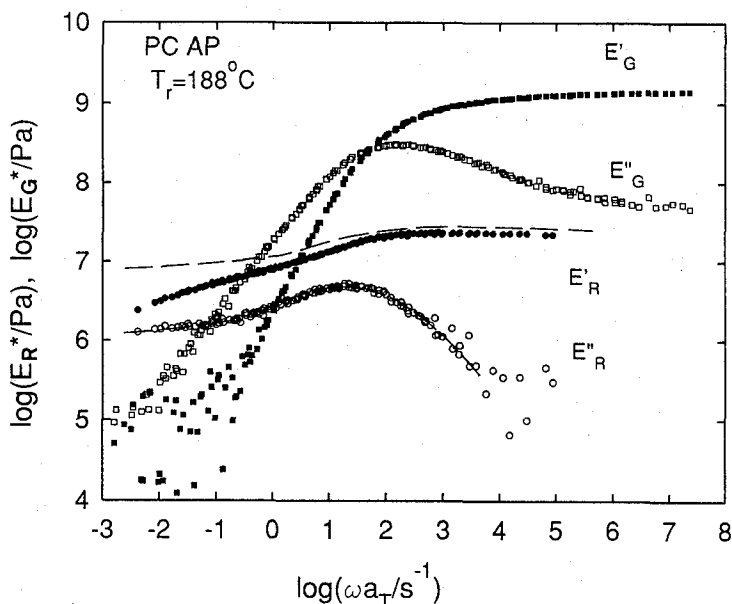

Fig. 2. G and R component functions for Bisphenol AP polycarbonate. Reference temperature is 188°C. Broken lines indicate the results for PC.

component is thought to be related to the statistical segmental motions. E'_R increases only about one decade from rubbery plateau value with increasing of frequency. The limiting value of $E'_R (\infty)$ at high frequencies is 1.2×10^7 Pa.

Comparison with PC.

In Fig. 2, the results for PC[8] are shown for the comparison of two component functions between PCAP and PC. Here, T_r for PCAP is 188°C, and T_r for the R and G component of PC are chosen as about 164 and 162°C, respectively, so that the imerginary part of each component fuction of PC overlaps well that of PCAP around its maximum. This choice of different reference temperatures is needed because of the difference of γ, ratio of the frequencies where the E'_G and E'_R show maximum. γ of PCAP is smaller than that of PC. The characteristic values of modulus and the stress-optical coefficients for PCAP, PC and some other polymers are given in Table 1.

Table 1. Summary of the Limiting Values of the Young's Modulus (MPa) and the Stress-Optical Coefficients (in Brewsters $= 10^{-12} Pa^{-1}$).

Polymer	$E'_R(\infty)$	$E'_G(\infty)$	$E''_{R,MAX}$	γ^+	C_R	C_G
PCAP	21	1350	5.1	5.5	3300	27
PC	26	1500	5.0	10.6	5000	35
PS	12	2500	3.3	44.	−5000	32

+) See the text for definition.

The G components of two polymers show the same frequency dependence. Both E'_R and E'_G of PCAP are almost the same as those of PC. The frequency dependence of E'_R in the low frequency region is slightly different. This may be caused by the difference of the rubbery plateau modulus; the displacement of methyl groups by phenyl groups may change entanglement spacing.

The displacement by phenyl groups gives lower C_R. This is easily understood because the phenyl groups attached to the main chain will decrease the anisotropy of the segments. On the other hand, the significant difference of two C_G values between PCAP and PC is very small as shown in Table 1. The nealy constant C_G values among polymers listed in Table 1 lead to the idea that C_G does not strongly depend on details of molecular structure for polymers including phenyl groups. The photoelastic coefficient, C_P, can be related to C_R and C_G through following equation:[7]

$$C_P = C_G + C_R E'_R(\infty)/E'_G(\infty) \quad \text{(at high frequencies)} \tag{8}$$

The factor $E'_R(\infty)/E'_G(\infty)$ and C_G may be constant, and the reduction of C_R gives lower C_P.

Temperature Dependence.

The temperature dependence of shift factors used for constructing the master curves of
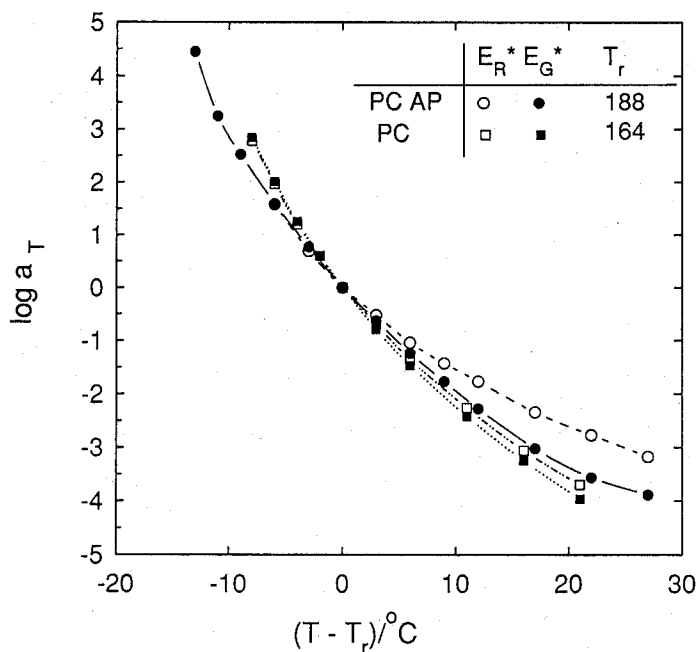
Fig. 3. Temperature dependence of shift factors for the G and R components.

two component functions are presented in Fig. 3. The data for PC is also shown. Here T_r for PC is 164°C. One can see that the shift factors for the G components of PCAP and PC show stronger temperature dependence than those for the R components, respectively. This result is obtained for all previously investigated polymers.[13] The different temperature dependence between two components is the reason why the viscoelastic functions and birefringence are not thermo-rheologically simple as seen in Fig. 1. Since the contribution of the G component is larger to the Young's modulus than to the strain-optical coefficient, E^* indicates stronger temperature dependence.

The temperature dependence of each component for PCAP seems to be weeker than that for PC. In this work T_r is chosen as the temperature where E''_G becomes 10^8 Pa. Different choice of T_r may give a different impression. The smaller γ values of PCAP in Table 1 may be also related to the different temperature dependence. The displacement of side groups may change the local distribution of free volume along the chain. Detailed comparison of temperature dependence among polymers will be performed in further works.

<div align="center">CONCLUSION</div>

We can draw the conclusion for the effect of displacement of methyl groups by phenyl groups as follows. For viscoelasticity, the frequency dependence of G component functions does not change. On the other hand, the rubbery plateau modulus of the R component seems to be affected. PCAP perhaps has higher fluidity than PC. The test with the high-

er molecular weight would be needed. The glass transition temperature increases by the displacement.

The effects for optical properties are fairly simple. The displacement is effective to reduce C_R values, but C_G is insensitive to such a modification. The reduction of C_P is due to that of C_R. Thus, the displacement improves the birefringence behavior. However, in practical use, the fracture properties are also important. Viscoelasticity of PCAP under large deformations will be given in a forthcoming paper.

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