

Dynamic Birefringence of Amorphous Polyolefins I. Measurements on Poly[1-ethyl-5-methyl-octahydro- 4,7-methano-1*H*-indene-1²,3-diyl]

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(Received March 1, 1993)

ABSTRACT: The complex strain-optical coefficient and the complex Young's modulus of an amorphous polyolefin, poly[1-ethyl-5-methyl-octahydro-4,7-methano-1*H*-indene-1²,3-diyl], PEMOMID, were measured around the glass-to-rubber transition zone. The data was analyzed with a modified stress-optical rule, and two components of complex modulus, E_G^* and E_R^* , and two associated stress-optical coefficients, C_G and C_R , were determined. The result was compared with one for a Bisphenol A polycarbonate, PC. C_R , stress-optical coefficient in the rubbery plateau zone, for the polyolefin was $1.7 \times 10^{-9} \text{ Pa}^{-1}$ and about three times smaller than that for PC. C_G for PEMOMID is negative and this was in contrast to a usual positive value for polymers containing phenyl rings in their repeating units.

KEY WORDS Viscoelasticity / Dynamic Birefringence / Stress-Optical Rule / Polyolefin / Glass Transition / Modified Stress-Optical Rule / Polymer Rheology / Strain-Optical Coefficient / Stress-Optical Coefficient /

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 rubbers¹ and polymer melts (or concentrated solutions),^{2,3} the birefringence is related with the stress through the stress-optical rule, SOR: the anisotropic part of refractive index tensor, Δn , is proportional to the anisotropic part of the stress tensor, σ .

$$\Delta n(t) = C_F \sigma(t) \quad (1)$$

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 holds well, and this relation is called photoelasticity.

$$\Delta n = C_p \sigma \quad (2)$$

Equation 2 is believed to hold well in the glassy state of amorphous polymers.

In spite of the similarity between eq 1 and 2, there is an important difference between the stress-optical rule for polymer melts and the photoelasticity for polymer glasses. 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 eq 1 and 2 is the difference in the values of the proportionality coefficients for the same polymer

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species. From the difference between C_F and C_P , one can deduce that SOR fails over the time range of the glass-to-rubber transition zone.

Dynamic birefringence, the birefringence in oscillatory deformation, was first measured by Onogi *et al.* 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, dynamic measurement was performed on a polystyrene by Inoue *et al.*, and consequently a new version of the modified stress-optical rule, MSOR, was proposed.^{7a} The MSOR 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:

$$E^*(\omega) = E_G^*(\omega) + E_R^*(\omega) \quad (3)$$

$$O^*(\omega) = C_G E_G^*(\omega) + C_R E_R^*(\omega) \quad (4)$$

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 $O''(\omega)/E''(\omega)$ at high frequencies. The new version of MSOR is based on the finding that $O''(\omega)$, the imaginary part of $O^*(\omega)$, is proportional to $E''(\omega)$, the imaginary part of $E^*(\omega)$, in the glassy zone. The new version is superior in several aspect to the Read's version, in which C_G is taken equal to C_P .

With thus determined C_G and C_R , we can solve eq 3 and 4 simultaneously for the component functions, E_G^* and E_R^* . The separation to two components successfully explained the complicated behavior of viscoelas-

ticity and birefringence around the glass transition zone of polystyrene: The G component relaxes in the glass transition zone, and then it is not important in the modulus associated with the longer relaxation times corresponding to the rubbery-plateau and the flow zones. In these zones, the R component is dominant and hence the ordinary stress-optical rule holds well between the birefringence and the stress. On the other hand, in the glass transition and glassy zones both of the R and G components contribute to the birefringence. Its behavior in these zones is fairly complicated due to the variety of combinations of the stress-optical coefficients, C_G and C_R , for various polymers. Thus, the analysis with MSOR enables a quantitative separation of the stress into two components of presumably different mechanisms. MSOR has been applied to a number of polymers; The following is a summary of the experimental results obtained in the previous studies.⁷

1) The high glass modulus and characteristic features of the glass-to-rubber transition are mainly determined by the G component of the complex modulus, $E_G^*(\omega)$, located in the glassy and glass-to-rubber transition zones. This component is similar in shape for polystyrene (PS), poly(α -methyl styrene) (PMS), Bisphenol A polycarbonate (PC), and some other polymers, when plotted against ω in double logarithmic scales.^{7g}

2) The stress and the birefringence in the rubbery and flow zones are represented by the R component, $E_R^*(\omega)$. The R component begins to relax in the low frequency region of the glass transition zone, and its frequency dependence in this region is described by the beads-spring model.^{7a}

3) In contrast with the similarity of $E^*(\omega)$ for various polymers, the frequency dependence of $O^*(\omega)$ shows large variation. This is attributed to the variety of the two stress-optical coefficients, C_G and C_R . C_R is the ordinary stress-optical coefficient in eq 1, C_F , as mentioned before, and its sign and value

vary largely with details of the molecular structure such as the orientation of the phenyl ring with respect to the main chain. On the other hand, C_G values of PS, PMS, and PC are almost equal and are not sensitive to such details of the molecular structure.^{7g}

4) The experiments with large deformations show that the nonlinear viscoelasticity is more marked for the G component than for the R component. Moreover, this nonlinear tendency of the G component varies with the polymer species. For example, the strain dependence of the G component of the relaxation modulus for PC at large elongation is extremely different from that for PS. This contrasts with the similarity of $E_G^*(\omega)$ for these polymers in the linear viscoelastic region.^{7f}

From above results, we may conclude that the origin of the R component is the orientation of the statistical segments (Rouse segments) associated with an optical anisotropy of the segment. The G component is related to the solid nature of the material in deformation. It is presumably in common among various amorphous glassy materials containing common structure unit, and its relaxation may be related to their local molecular motions. However, the molecular dynamics of the G component is not understood quantitatively on the basis of the polymer structures. Comparison among various amorphous polymers, particularly polymers containing no phenyl groups, will clarify the origin of respective components.

Recently, amorphous polyolefin polymers, APO, have been developed as a new optical disc substrate. These polyolefin polymers have high transmittance, low stress-optical coefficient, and the fairly high glass transition temperature ($> 100^\circ\text{C}$). In the first issue of this series, we report the dynamic birefringence of poly[1-ethyl-5-methyl-octahydro-4,7-methano-1*H*-indene-1²,3-diyl], coded PEMOMID. We will show the characteristic behaviors of viscoelasticity and birefringence of amorphous polyolefin polymer. The results will be com-

pared with polycarbonate, a conventional optical substrate, and the difference in viscoelasticity and birefringence will be discussed.

The comparison of C_G is also of interest. C_G for many of polymers containing phenyl groups has a common value, about $3 \times 10^{-11} \text{ Pa}^{-1}$. We have suggested that this common value is related to the large anisotropy of phenyl rings. PEMOMID has no phenyl rings. The relation between C_G values and the polymer structure should be investigated to clarify the origin of the G component.

EXPERIMENTAL

The structure of the amorphous polyolefin polymer, poly[1-ethyl-5-methyl-octahydro-4,7-methano-1*H*-indene-1²,3-diyl] (code PEMOMID), is shown in Figure 1. PEMOMID is made by ring-opening polymerization of methyl-tetracyclododecene, followed by hydrogenation. M_w and M_n were determined as 5.6×10^4 and 2.8×10^4 by GPC. The glass transition temperature measured with DSC was 150°C . A film with about 0.5 mm thickness was made by melt press method. The test film was dried in a vacuum dry oven at 150°C for a few days prior to measurements.

The apparatus for dynamic birefringence measurements was reported previously.⁸ 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

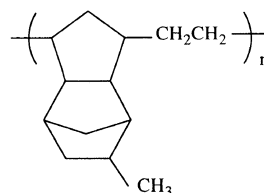


Figure 1. Molecular structure of PEMOMID.

and the quarter-wave plate with their axes at 45° to the strain axis in the specimen. The measurements were performed at isothermal conditions over the frequency range 1–130 Hz.

RESULTS AND DISCUSSION.

Characteristic Behaviors of $E^(\omega)$ and $O^*(\omega)$*

The raw data of the complex Young's modulus, $E^*(\omega)$, and the complex strain-optical coefficient, $O^*(\omega)$, at each temperature are not shown here, but the master curves are shown in Figure 6. The characteristic behaviors of $E^*(\omega)$ and $O^*(\omega)$ are as follows. At the highest temperature, 200°C , $E^*(\omega)$ data corresponded to the onset of the rubbery plateau zone. The ordinary stress-optical rule, eq 1, was found to hold well at low frequencies at this temperature. The estimated C_F was $1.7 \times 10^{-9} \text{ Pa}^{-1}$. At lower temperatures, SOR did not hold well. $O''(\omega)$ was found to be proportional to $E''(\omega)$ in the glassy zone, at the temperatures 155 and 160°C . C_G was determined as $-1.3 \times 10^{-11} \text{ Pa}^{-1}$ from the proportional coefficient.

The obtained C_G and C_F are summarized in Table I. The values for PC^{7e} are also listed. $C_F (= C_R)$ for PEMOMID is about three times smaller than those for PC. The C_G value of PEMOMID is negative and in contrast with positive values of polymers containing phenyl groups.^{7g}

Analysis with Modified Stress-Optical Rule

With use of $C_R (= C_F)$ and C_G , we solved the eq 3 and 4 for the G and R component functions at each temperature. The method of reduced variables⁹ is used for the component

functions, $E_G^*(\omega)$ and $E_R^*(\omega)$, to obtain the respective composite curves. The composite curves of the R and G components are shown in Figure 2. The results of the R component at the two lowest temperatures are eliminated, because $E_R'(\omega)$ is constant, $1.3 \times 10^7 \text{ Pa}$, independent of frequency and temperature and $E_R''(\omega)$ becomes close to 0 and has large scattering of data at these temperatures. The data of $E_G^*(\omega)$ at the highest two temperature is also eliminated because both parts of $E_G^*(\omega)$ is very small with large scattering. The superposition 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 is attributed to the relaxation of the G component. Since the slopes of $E_G'(\omega)$ and $E_G''(\omega)$ at low ω are close to 2 and 1, respectively, the distribution of the relaxation time for the G component in the long time region seems to be sharply cut off around $\omega = 100 \text{ s}^{-1}$. On the other hand, the R component supports just a

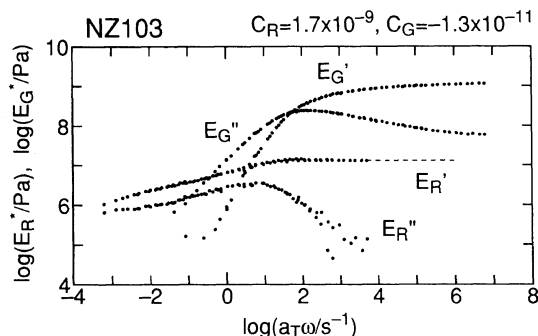


Figure 2. The composite curve of the G and R components of PEMO-MID. The reference temperature is 165°C . The broken line indicates the constant value of $E_R'(\omega)$ at lowest two temperatures.

Table I. Summary of the limiting values of Young's modulus (MPa) and the various stress-optical coefficients (in Brewsters = 10^{-12} Pa^{-1})^a

Polymer	$E_R'(\infty)$	$E_G'(\infty)$	$E_{R,\max}''$	γ^+	C_R	C_G
PEMOMID	13.4	1130	3.7	22.9	1720	-13
PC	25.7	1500	5.0	10.6	5000	35

^a See the text for definition.

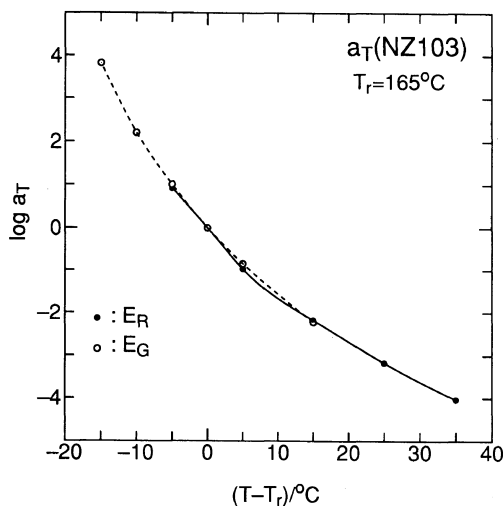


Figure 3. The temperature dependence of the shift factors used for the G and R components.

small percentage of the stress and does not relax in the glassy zone. In the rubbery zones, the G component has relaxed and the mechanical properties and birefringence are determined by the R component.

The shift factors, $a_{T,i}$ ($i=R, G$), used for constructing the composite curve of the component functions are compared in Figure 3. The stronger temperature dependence of the G component is widely observed in the previous studies.⁷ The different temperature dependence of the R and G component functions means that $E^*(\omega)$ and $O^*(\omega)$ are not thermorheologically simple in the transition zone where two components contribute to $E^*(\omega)$ and $O^*(\omega)$. However, for the case of PEMOMID, the difference between two component functions is not so remarkable, and hence $E^*(\omega)$ and $O^*(\omega)$ may be regarded as thermo-rheologically simple.

The G component functions for PEMOMID and PC^{7e} are compared in Figure 4, and the R components in Figure 5. Here, reference temperatures, T_r are chosen 165°C for PEMOMID and 164°C for PC, so that the imaginary part of the G component function of each polymer at $\omega = 10 \text{ s}^{-1}$ equals 10^8 Pa .

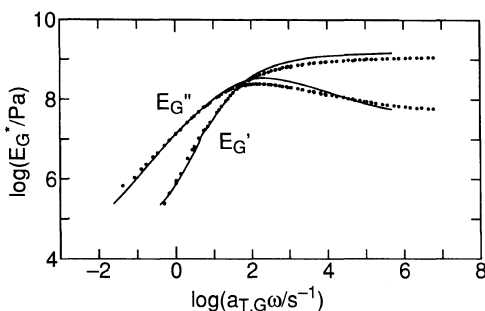


Figure 4. The comparison of the G component between PEMOMID and PC. Solid lines indicate the G component for PC.

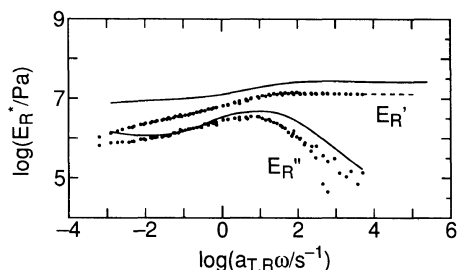


Figure 5. The comparison of the R component between PEMOMID and PC. Solid lines indicate the R component for PC.

The G components of two polymers show nearly the same frequency dependence. $E_G''(\omega)$ of PEMOMID has slightly broader frequency dependence. This may be due to sub-relaxation mechanism at high frequencies like a β -relaxation because PEMOMID has large side groups. The value of $E_G'(\omega)$ at high frequencies, $E_G'(\infty)$, for PEMOMID is about 30% smaller than that for PC as shown in Table I.

In contrast with the similarity of $E_G^*(\omega)$, $E_R^*(\omega)$ of two polymers give different impression in some points. One difference is in $E_R'(\infty)$, which may be related to the size of statistical Rouse segments. PEMOMID has lower $E_R'(\infty)$, and this means that the segment size of PEMOMID is larger than PC. In other words, the main chain of PEMOMID is less flexible than PC. This is perhaps attributed to the steric hindrance of the large side groups of PEMOMID. Another difference is seen in the rubbery plateau modulus, E_N' .

That for PEMOMID is difficult to determine, but it seems about two or three times smaller than PC in sight. This difference corresponds to the larger molecular weight between entanglement points for PEMOMID. High rubbery plateau modulus of PC may give a disadvantage in polymer processing.

We defined a parameter γ as the frequency ratio where E''_G and E''_R have maximum at the reference temperature to characterize the relative position of the two components.^{7e} For many polymers species, $E''_G(\omega)$ and $E''_R(\omega)$ have different temperature dependences, and hence the values of γ depends on the choice of reference temperature. At the reference temperature determined as described in making Figures 4 and 5, γ of PEMOMID is about 2 times larger than that for PC. γ may have as meaning of the relative size of the basic units between the R and G components, because the frequencies where $E''_R(\omega)$ and E''_G have maxima respectively correspond to the relaxation time for the smallest size of the Rouse segment and the most probable relaxation time for the unit that controls the relaxation of the G component. In previous studies, we find empirical relation that γ increases as the ratio $E''_R(\infty)/E''_G(\infty)$ decreases^{7g}. The result for PEMOMID is also in accord with the relation.

The master curves for $E^*(\omega)$ and $O^*(\omega)$ of

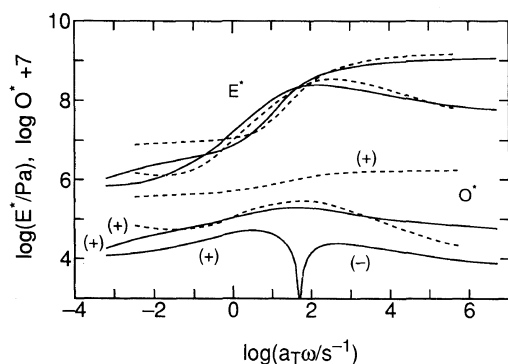


Figure 6. The comparison of the complex Young's modulus and the complex strain-optical coefficient between PEMOMID and PC. Solid lines are for PEMOMID, and broken lines for PC. The reference temperatures are 165°C and 164°C for PEMOMID and PC, respectively.

two polymers are shown in Figure 6. These quantities are calculated by using the composite curves for the two component functions. In general, the temperature dependences of two component functions are different and the Young's modulus and the strain-optical coefficient are not thermo-rheologically simple. For such cases, we can not apply the method of reduced variables to investigate the those quantities over wide frequency region, and we should therefore recalculate those quantities from the master curves of component's functions that are thermo-rheologically simple. For the case of PEMOMID, as described before, the temperature dependence of the R and G components is not found to be so different, and the superposition principle may consequently be available for the Young's modulus and the strain-optical coefficient. However, in following discussion, we use the composite curves calculated from the component functions and their temperature dependence.

Characteristic behavior of $E^*(\omega)$ for two polymers in Figure 6 is similar and typical of amorphous polymers around the glass-rubber transition zone. One minor difference between two polymers is the difference of E_N as we have seen before. The real and imaginary parts of $O^*(\omega)$ for PC are positive over the whole measured frequency range in Figure 6. On the other hand, $O''(\omega)$ for PEMOMID changes its sign in the glass transition zone. The negative value of $O''(\omega)$ in the glassy zone is very contrasted with other polymers studied so far.^{7e,7g} $O'(\omega)$ of PEMOMID has a maximum in the transition zone and decreases with increasing the frequency in the glassy zone. This behavior is expected for polymers with positive C_R and negative C_G with a small absolute value. In the whole frequency regions the difference of $O'(\omega)$ between the two polymers is about ten times. This comes from mainly two points; lower C_R and lower E'_R of the polyolefin. The smaller $O'(\omega)$ means that PEMOMID is a good candidate for an optical disc substrate.

Finally, it may be worthwhile to mention about the negative value of C_G for PEMOMID. In the glassy zone, the Poisson ratio of polymers is usually less than 1/2. This means that the density distribution in deformation is not uniform. For the case of tensile deformation, the linear density along the tensile axis is lower than that perpendicular to the axis. This anisotropic density distribution causes negative birefringence. This birefringence is known as "lattice effect" in the studies of photoelasticity for inorganic glasses.¹⁰ The positive C_G of polymers containing phenyl groups is rather curious. The absolute value of C_G for aromatic polymers is nearly constant, $3 \times 10^{-11} \text{ Pa}^{-1}$, and larger than that for PEMOMID. This result suggests that the orientation of phenyl rings by the deformation may cause the positive birefringence, which overcomes the negative value due to lattice effect. On the other hand, the relaxation spectrum of the G component for the two kinds of polymers is similar. The relaxation mechanism of the G component is perhaps in common in polymeric materials.

Acknowledgment. This study was supported by a Grant-in-Aid for Scientific Research (04750737) from the Ministry of Education, Science, and Culture of Japan.

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