6240 *Macromolecules* **1996,** *29,* 6240−6245

Dynamic Birefringence of Vinyl Polymers

Tadashi Inoue,* Yoshihiro Mizukami, Hirotaka Okamoto, Hiroto Matsui, Hiroshi Watanabe, Toshiji Kanaya, and Kunihiro Osaki

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Received February 6, 1996; Revised Manuscript Received June 11, 1996[⊗]

ABSTRACT: The complex strain-optical ratio, $O^*(\omega)$, and the complex Young's modulus, $E^*(\omega)$, of four vinyl polymers, atactic polypropylene, 1,2-polybutadiene, poly(ethylethylene), and poly(4-vinylbiphenyl), were measured from the rubbery plateau to the glassy zone to investigate the origin of the birefringence and the chain orientation in the glassy zone. The data, including those for polystyrene and poly(vinyl naphthalene), were analyzed through a modified stress-optical rule: The rule states that $O^*(\omega)$ and $E^*(\omega)$ are described as a sum of two component functions (denoted by R and G) and that a proportional rule similar to the ordinary stress-optical rule holds well for each of the R and G components with different stress-optical coefficients. The R and G components have been interpreted to be respectively related to the orientation of the main chain axis toward the stretch direction and tilting of the structural units by a rotational orientation about the main chain axis. According to this interpretation, the stress-optical coefficients for the R and G components are predicted to decrease and increase, respectively, with increasing size of the side chain. The present study shows the validity of this prediction. In addition, it is suggested that the degree of the rotational orientation responsible for the G component becomes larger with increasing size of the side chain.

I. Introduction

Amorphous polymers become anisotropic and birefringent under deformation. Strain-induced birefringence has been an important subject in the field of rheo-optics since it is strongly related to the stress. For melts or concentrated solutions, the birefringence, $\Delta n(t)$, is proportional to the stress, $\sigma(t)$

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

Here the proportionality coefficient, C, is called the stress-optical coefficient (SOC). The relation holds valid even when the birefringence and the stress vary with time, t, as in the stress relaxation process. The rule is known as the stress-optical rule and its validity has been confirmed for many polymeric materials.[1]

A similar rule holds valid between the stress and the glassy birefringence, the birefringence produced in glassy polymers.

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

This relation is different from eq 1 in that it is valid only for instantaneous values of the birefringence and the stress on application of the strain. The coefficient C_P is called the photoelastic coefficient (PEC) and is not equal to the SOC. Thus it is obvious that the birefringence in the glass-transition zone is not proportional to the stress. The origin of the birefringence of glassy materials is not well understood whereas it is well established that the birefringence and the stress in the rubbery and flow zones are attributed to the polymer chain orientation.

In a series of our studies on the birefringence and the viscoelasticity around the glass-transition zone, we have shown that the birefringence can be related to the stress through a modified stress-optical rule (MSOR).[2] The MSOR states that the birefringence and the stress are composed of two component functions designated by the subscripts R and G, respectively. For oscillatory tensile deformation, the rule reads

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

$$O^*(\omega) = O_G^*(\omega) + O_R^*(\omega) \tag{4}$$

where $O^*(\omega) = O'(\omega) + iO''(\omega)$ and $E^*(\omega) = E'(\omega) + iE''(\omega)$ are the complex strain-optical ratio and the complex Young's modulus; $E_i^*(\omega)$ and $O_i^*(\omega)$ (i = G, R) are the complex component functions of the Young's modulus and the strain-optical coefficient for component i; ω is the angular frequency in oscillatory simple elongation. A further feature of MSOR is that a relation similar to the ordinary SOR holds valid for each component,

$$O_i^*(\omega) = C_iE_i^*(\omega) \qquad (\mathrm{i} = \mathrm{R\ and\ G}) \tag{5}$$

where C_i are the associating stress-optical coefficient for the component i. MSOR is based on the experimental results, i.e., validity of the ordinary SOR in the rubbery zone and the proportionality of $O''(\omega)$ to $E''(\omega)$ in the glassy zone.[3] The coefficient C_R is equal to C in the ordinary SOR, and C_G is defined as $O''(\omega)/E''(\omega)$ in the glassy zone. Since eqs 3−5 give a complete set of equations describing $E_G^*(\omega)$ and $E_R^*(\omega)$, the two component functions can be evaluated *quantitatively* from $O^*(\omega)$ and $E^*(\omega)$ data.

In theories of birefringence, the Lorentz−Lorenz relation is usually used to connect the refractive index to the polarizability. The relation between the birefringence and the anisotropy of the polarizability, $\Delta\beta$, of units with molecular weight M may be described as follows:

$$\Delta n = \frac{2\pi}{9}\frac{(n^2+2)^2}{n}\frac{\rho N_a}{M}\Delta\beta \tag{6}$$

where n denotes the refractive index and ρ is the density. $\Delta\beta$ includes the intrinsic anisotropy of polarizability and the orientation degree of the structural unit (cf. eq 7). The factor $\rho N_a/M$ represents the number of repeating units per volume, with N_a being Avogadro's number. A molecular interpretation of MSOR was proposed by Osaki et al.[4] They used a model in which

---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

S0024-9297(96)00190-8 CCC: $12.00

a polymer is supposed to be composed of identical units that do not change shape over the time scale investigated. The polymer chain can change its shape by the rotational motion about the connecting bonds. The polarizability tensor of the unit is assumed to be diagonal with respect to the local frame fixed to the unit (molecular frame) for simplicity, and the components are α_1, α_2, and α_3, where the subscript represents the coordinate of the molecular frame; 1 represents the direction of the chain axis, and the 2 axis is taken in the plane of the unit if the unit can be regarded as flat to any extent. The birefringence can be related to the polarizability and orientation function of the structural unit.

$$\Delta n \propto \Delta\beta = \{\alpha_1 - (\alpha_2 + \alpha_3)/2\}P_R + (\alpha_2 - \alpha_3)P_G/4 \quad (7)$$

The orientation functions, P_R and P_G, are defined as follows.

$$P_R = (3\langle\cos^2\theta\rangle - 1)/2 \quad (8)$$

$$P_G = 3\langle\sin^2\theta\cos 2\phi\rangle \quad (9)$$

Here, θ and ϕ are the Euler angles: θ is the angle between the chain axis and the stretch direction, and ϕ is the rotation angle of the structural unit about the chain direction. According to the affine deformation or the quasi-affine deformation model, P_R becomes $(3/5)\epsilon$ in infinitesimal elongational strain, ϵ.

For the case of the stress, one can define a local stress tensor acting on each unit, $\sigma_j(t)$, in the same local reference frame. Contrasting to the polarizability tensor, the local stress tensor depends on the packing state of the surrounding units and so varies with time and from unit to unit. However, Gao and Weiner performed molecular dynamics simulation studies of a polyethylene-like polymer model and observed that $\sigma_j(t)$ for each unit was well approximated by a constant during the process of stress relaxation.[5] Using the average value of the components of the local stress tensor, $\langle\sigma_i\rangle$, the tensile stress may be written as

$$\sigma \propto \{\langle\sigma_1\rangle - (\langle\sigma_2\rangle + \langle\sigma_3\rangle)/2\}P_R + (\langle\sigma_2\rangle - \langle\sigma_3\rangle)P_G/4 + \sigma_T \quad (10)$$

Here, the last term represents the contribution of a fluctuation effect and is believed to disappear in very short time region for type I polymers for which MSOR holds valid. The explicit form of this term is given in a previous study.[4]

Since the R component is related to the chain orientation, the first terms in eqs 7 and 10 correspond to the R component and the second terms to the G component. Therefore the stress-optical coefficients of the components are respectively related to the components of the polarizability tensor as follows.

$$C_R \propto \Delta\alpha_R = \alpha_1 - (\alpha_2 + \alpha_3)/2 \quad (11)$$

$$C_G \propto \Delta\alpha_G = (\alpha_2 - \alpha_3)/4 \quad (12)$$

Equation 11 is identical to the relation of the stress-optical coefficient of polymer networks. On the other hand, eq 12 indicates that C_G is determined by the local anisotropy of polarizability in the plane perpendicular to the main chain axis.

In the present study, the validity of the above interpretation, in particular the molecular mechanism of the birefringence responsible to the G component, is experimentally tested. For this purpose, we examine the dynamic birefringence of a series of vinyl polymers with various side groups. According to eqs 11 and 12, an increase in α_2 (for larger side group) should lead to a decrease in C_R and an increase in C_G. The vinyl polymers studied here are atactic polypropylene (aPP), 1,2-polybutadiene (vPB), hydrogenated vPB (hvPB), polystyrene (PS), and poly(vinylbiphenyl) (PVBPh).

II. Experimental Section

Materials. Atactic polypropylene (aPP) was kindly provided by Dr. Bartos and Professor Spiess. The sample was prepared by metallocene-catalyzed polymerization of propylene. Details of the sample characterization were described elsewhere.[6] 1,2-Polybutadiene (vPB) was polymerized with (1,1-diphenylhexyl)lithium in a benzene/diethyl ether mixture at −78 °C, and terminated with methanol. The fraction of 1,2-linkage (87%) was determined by NMR using a JEOL JNM-GSX400 spectrometer. Its molecular weight and polydispersity index were determined to be $M_w = 190\,000$ and $M_w/M_n = 1.1$, respectively, by gel permeation chromatography with small-angle light scattering using PS as a standard. Poly(1-butene) (hvPB) was obtained from hydrogenation of vPB. Hydrogenation was kindly performed by Prof. N. P. Balsara at Polytechnic University. Its M_w and M_w/M_n were 190 000 and 1.1, respectively. Poly(4-vinylbiphenyl) (PVBPh) was purchased from Aldrich. The supplier's data sheet said that $M_W = 115\,000$. The polymer was used without further purification.

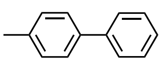
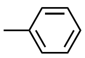
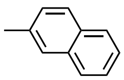
The glass transition temperature (T_g) was determined by DSC (TA Instruments, thermal analysis system 2000 with DSC 2910). All samples were first held for 2 min at $T_g + 30$ K and then cooled to $T_g - 60$ K with a cooling rate of 10 K min^{-1}. After being held at this temperature for 2 min, the samples were reheated at 10 K min^{-1}. T_g was determined from this heating run using the middle point convention. The samples' T_g's are summarized in Table 1.

Sheets of aPP, vPB, and hvPB of 1 mm thickness for dynamic birefringence and dynamic viscoelasticity measurements were obtained by pressing lump samples with two Teflon films and a 1 mm spacer over 1 month at room temperature. The PVBPh sample sheet was prepared by molding at 220 °C.

Dynamic Birefringence Measurement. The apparatus for dynamic birefringence measurements was reported previously. An optical system was attached to an oscillatory rheometer (Rheology DVE 3, Kyoto, Japan). A Sénarmont optical system was used to compensate the static birefringence induced by the load to maintain the sample: the 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 axis at $\pi/4$ to the strain axes in the specimen.

The measurements were performed under isothermal conditions at several temperatures over the frequency range 1−130 Hz. In order to avoid the effect of physical aging, the sample was preheated at $T_g + 15$ °C and kept at this temperature for about 30 min before the measurements. All measurements were performed at least 15 min after the temperature reached the required value. The lowest temperature for each polymer was close to T_g determined by DSC. Thus, the obtained results correspond to those for equilibrium melts. The

Table 1. Summary of Results for Vinyl Polymers ($-CH_2CHR-$)$_n$

polymer	R	T_g (°C)	T_r (°C)	C_R (Br[b])	C_G (Br)	C_d (Br)	$E_R'(\infty)$ (MPa)	$E_G'(\infty)$ (GPa)	M_S	κ	fwhm
aPP	CH_3	−9	2	1230	−14.4	−2.8	19	2.0	310	15	2.8
hvPB	CH_2CH_3	−37	−27	790	−9.5	1.0	20	1.5	290	10	2.9
vPB[a]	$CH{=}CH_2$	−17	−10	200	13.5	17.2	30	1.5	200	7.3	3.0
PVBPh		155	180	−6900	130	8.0	7.9	1.1	850	16	2.8
PS		102	116	−4700	32	81	12	2.5	850	16	2.8
PVN		143	160	−8300	160	110	10	1.7	1400	16	[c]

[a] Vinyl content is 87%. [b] Br = 10^{-12} Pa^{-1}. [c] Type II polymer.

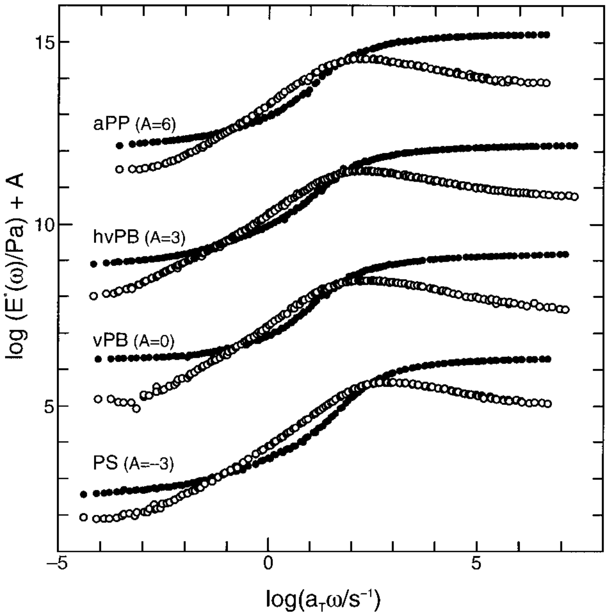


Figure 1. Composite curves of the complex Young's modulus for four vinyl polymers. The reference temperatures, T_rs, are 2 °C for aPP, −27 °C for hvPB, −10 °C for vPB, and 116 °C for PS. Filled and unfilled marks represent respectively the real and imaginary parts of the modulus. The moduli are shifted vertically to avoid overlap of data.

raw data for PS and PVN were previously reported elsewhere.[3,7]

III. Results

Strain-Optical Coefficient. Figures 1 and 2 show composite curves for $E^*(\omega)$ and $O^*(\omega)$ for the four vinyl polymers, respectively. Here the method of reduced variables[8] were applied to build the composite curves. Although the applicability of this method is fortuitous around the glass-to-rubber transition zone,[3,9,10] it is a convenient method to see global behavior. The reference temperature is chosen so that $E''(\omega)$ becomes 10^9 Pa according to the series of MSOR studies. The master curves and the raw data in the present study are available on request.

Comparison of the composite curves in Figure 1 indicates that the complex Young's modulus does not vary particularly with changing side chains. This is especially true around the frequency region where $E''(\omega)$ show a maximum. On the other hand, $O^*(\omega)$ is influenced remarkably by the side groups. The data for PVBPh and PVN, which are not shown here, shows almost the same behavior as PS, including the sign of $O'(\omega)$ and $O''(\omega)$. The shapes of $O^*(\omega)$ for aPP and PS are very similar to each other, but the signs of the real and imaginary parts are exactly opposite. The sign of the parts in the rubbery zone is positive for aPP, vPB, and hvPB while it is negative for PS, PVBPh, and PVN. The sign of $O''(\omega)$ in the glassy zone is negative for polymers with small side chains and positive for those with large side chains. Thus $O^*(\omega)$ is very sensitive to the chemical structure of the polymers.

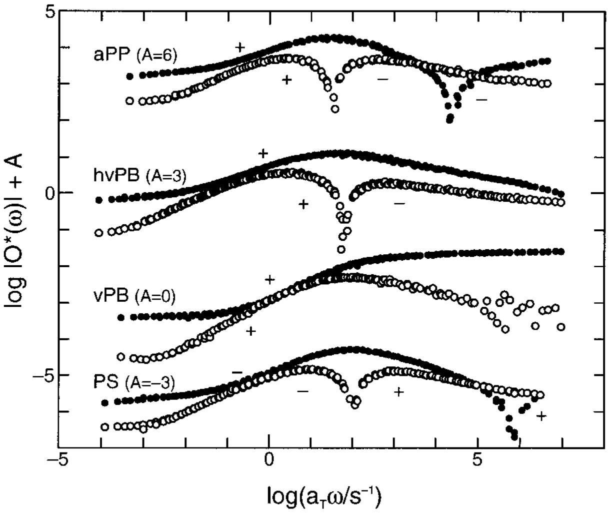


Figure 2. Complex strain-optical ratio for four vinyl polymers at the reference temperature. T_rs are the same as in Figure 1. Filled and unfilled marks represent respectively the real and imaginary parts of the ratio. The coefficients are shifted vertically to avoid overlap of data.

Component Function. The basic requirement to apply MSOR to polymers is a proportionality between $O''(\omega)$ and $E''(\omega)$ in the glassy zone. For all polymers studied here, the ratio $O''(\omega)/E''(\omega)$ became constant in the glassy zone. The obtained stress-optical coefficients are summarized in Table 1. As pointed out by a reviewer, the reported C_R valeus for vPB is *negative* and a relatively small number ($\approx -0.4 \times 10^{-9}$ Pa^{-1}). Therefore, a comment may be needed for our *positive* C_R value for vPB. We believe that this difference is due to the slightly lower vinyl content (87%) of our sample. Since the reported C_R values for *cis*- and *trans*-polybutadienes are positive and of similar magnitude ($\approx 3.5 \times 10^{-9}$ Pa^{-1}),[11,12] it is very natural that C_R changes its sign somewhere at the high vinyl content.

In this context, the temperature dependence of C_R should be noted. Zawada et al. reported that the temperature dependence of C_R for vPB (vinyl content $\approx$ 100%) agrees well with the theoretical prediction of $C_R \approx 1/T$ [13] while Arendt et al. reported that C_R for vPB (vinyl content = 96%) strongly depends on temperature.[14] An unusual temperature dependence of C_R is observed for poly(methyl methacrylate) although it is not clear at present that these two findings are related to each other. In our case, although the temperature range where C_R could be determined was limited, we observed that C_R of vPB showed a tendency to slightly decrease with decreasing temperature (≈1%/K). This behavior is not in accord with the theoretical prediction and may be related to the observation by Arendt et al. However, in the following MSOR analysis, C_R was treated as a temperature-independent constant according to the series of MSOR studies because the observed variation is small. In the series of MSOR analysis, temperature dependence of C_R and C_G has not usually been considered because of two reasons: the narrowness of the temperature region where MSOR is applied and the limitation of the temperature range where the two coefficients can be measured. The effect of these simplification was estimated as less than 10%. On the other hand, C_R for hvPB was constant with temperature and that for aPP slightly increased with temperature but less than the factor $1/T$.

With the determined stress-optical coefficient, MSOR was applied to data at each temperature and the composite curves of the two component functions were constructed using the method of reduced variables. Since the component functions are very similar among the polymers and our main goal of the present study is to investigate the relation between the optical properties and the molecular structure, the composite curves are not shown here. Characteristic features of the two component functions are briefly summarized in the following. Examples of the component functions are found in a previous paper.[3]

The characteristic parameters for the R component are the limiting modulus at high frequencies, ($E_R'(\infty)$), and the molecular weight of the segment size (M_S), derived from $E_R'(\infty)$.[2] In order to compare chain flexibility we have calculated the number of main chain carbons per segment, κ. This values is given in Table 1. The κ values are close to each other except for the case of vPB. The reason for the smaller κ value for vPB is not clear at present, but this may come from the fact that vPB includes 13% 1,4-linkage, which is expected to give more flexibility to the chain. This conjecture is in accord with the fact that the κ value increases with hydration.

We have used the full width at half-maximum in logarithmic frequency scale (fwhm), to characterize the shape of the G component in the series of MSOR study.[2] In a previous study, we found a good correlation between the κ value and the fwhm.[2] The fwhm of the G component can be regarded to be approximately constant for the studied polymers although the value for vPB is slightly large. The larger fwhm for vPB might come from the existence of the 1,4-linkage. The almost constant fwhm values are consistent with mostly constant κ values except for vPB. Thus the difference in the component functions among the tested polymers is small. For vPB showing some minor uncommon features, a systematic study varying the content of 1,4-linkage may be needed.

In summary, the functional form of the component functions of the studied vinyl polymers was fairly common in spite of the difference of the side groups. This result suggests that molecular motion during the stress relaxation process in the transition zone originates from the main chain.

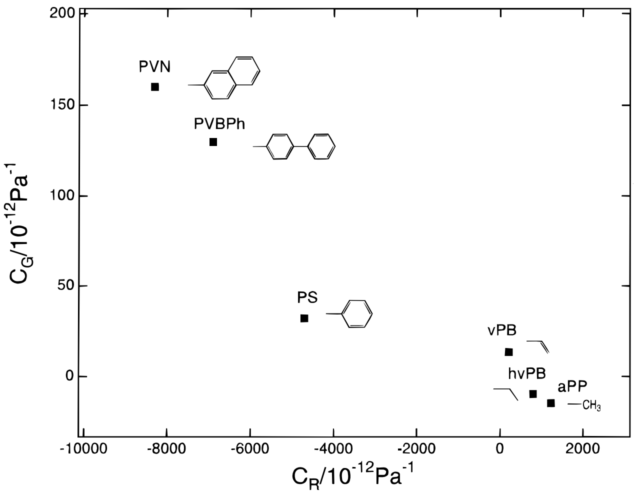


Figure 3. Correlation of the stress-optical coefficient between the G and the R component.

IV. Discussion

Molecular Origin of the Glassy Birefringence. Figure 3 shows a test of a correlation between the two MSOR stress-optical coefficients, C_G and C_R. Here, the data of PVN, which is a type II polymer analyzed by the third-term version of the MSOR, are also included.[4] C_R of the vinyl polymers decreases with increasing size of the side chain. This is due to increasing polarizability of the side chain. On the other hand, C_G of the vinyl polymers increases with increasing size of the side chains.

According to the molecular interpretation of MSOR, the birefringence due to the G component is related to the anisotropy of the unit around the main chain axis, $\alpha_2 - \alpha_3$ (cf eq 12). For the case of vinyl polymers, it can be predicted that larger side groups with relatively larger α_2 would increase C_G and decrease C_R. Figure 3 clearly shows that this prediction is correct. Thus our interpretation that C_G is related to the anisotropy of the local polarizability in the plane perpendicular to the main chain axis is strongly supported by the negative correlation between C_G and C_R for vinyl polymers.

Rotational Orientation Function. The strain-optical coefficient of each component of MSOR reflects the deformation state of the structural unit as well as the molecular anisotropy. We define a reduced strain-optical ratio at high frequencies.

$$\frac{9nM_0}{2\pi(n^2+2)^2\rho N_a} O_i'(\infty) = \frac{\Delta\alpha_i P_i}{\epsilon} \qquad (i = \mathrm{R\ and\ G}) \quad (13)$$

where M_0 is the molecular weight of the repeating unit.Thus the reduced strain-optical ratio is a product of the intrinsic anisotropy of the polarizability ($\Delta\alpha_i$) and the orientation functions (P_i) of the repeating units. If we can estimate $\Delta\alpha_i$, we can discuss P_i/ϵ. For this purpose, we derive the relation between $\Delta\alpha_R$ and $\Delta\alpha_G$ for vinyl polymers.

The polarizability of the repeating unit of vinyl polymers can be divided into main chain and side chain parts, assuming additivity of the polarizability tensor for constituent groups.

$$\alpha = \alpha^{\mathrm{main}} + \alpha^{\mathrm{side}} \qquad (14)$$

In the present study, the local frame of the repeating unit is defined as follows: Axis 1 is the so-called chain

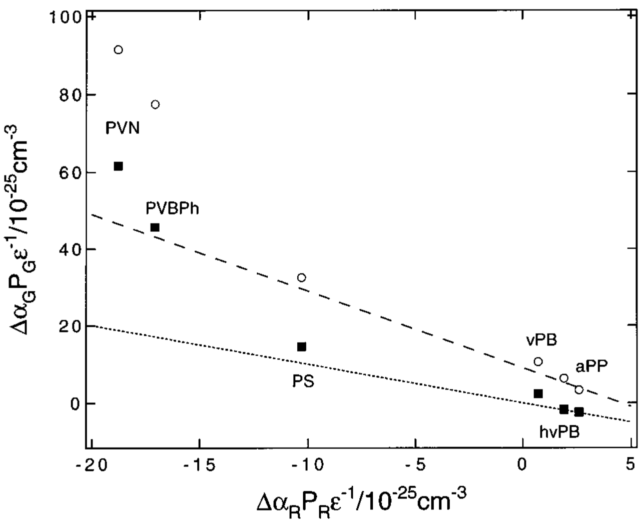


Figure 4. Test of a relation between the birefringence originated by the R and G components. Unfilled and filled marks represent respectively data with and without the lattice effect correction.

direction, the direction of a vector connecting two methylene carbons in two successive repeating units. Axis 2 is set in the direction of the C−C bond connecting the main chain and the side chain. Axis 3 is perpendicular to axes 1 and 2. If we suppose that α^{main} and α^{side} are diagonal and the side chain can freely rotate about axis 2 in the time scale under consideration, then α^{side} can be written as ($\alpha_1$side,$\alpha_2$side,$\alpha_1$side). The assumption of free rotation about the connecting bond to the chain is valid at least for aPP since the methyl group is axially symmetric. The characteristic anisotropies of the two components, $\Delta\alpha_i$, are

$$\Delta\alpha_R = \Delta\alpha_R^{\mathrm{main}} + (\alpha_1^{\mathrm{side}} - \alpha_2^{\mathrm{side}})/2 \tag{15}$$

$$\Delta\alpha_G = \Delta\alpha_G^{\mathrm{main}} + (\alpha_2^{\mathrm{side}} - \alpha_1^{\mathrm{side}})/4 \tag{16}$$

For the case of vinyl polymers, $\Delta\alpha_R^{\mathrm{main}}$ and $\Delta\alpha_G^{\mathrm{main}}$ may be regarded to be constant. We obtain

$$\Delta\alpha_G = \mathrm{A} - \Delta\alpha_R/2 \tag{17}$$

where $A = \Delta\alpha_G^{\mathrm{main}} + \Delta\alpha_R^{\mathrm{main}}/2$ is a constant independent of the side groups. If we assume that P_G/ϵ and P_R/ϵ do not depend on the polymer species,

$$\Delta\alpha_G P_G/\epsilon = \mathrm{A}' - \mathrm{B}'\Delta\alpha_R P_R/\epsilon \tag{18}$$

Here A' and B' are constants. Thus we expect a linear relation between $\Delta\alpha_G P_G/\epsilon$ and $\Delta\alpha_R P_R/\epsilon$.

Figure 4 shows the comparison of the reduced strain-optical ratios at high frequencies. Again, good correlation is seen between the two components for the vinyl polymers. The slope of the dotted line drawn in the figure is −1. If the free rotation assumption for side group is valid, this line corresponds to $P_G = 2P_R = (6/5)\epsilon$. The data points for aPP, hvPB, vPB, and PS are close to this line. On the other hand, the data points for PVBPh and PVN deviate upward remarkably. It should be noted that the breakdown of the free rotation assumption of side groups cannot account for these deviations for PVBPh and PVN. For the case of PS it is known that the preferred conformation of the phenyl groups is that in which its plane is perpendicular to the chain axis.[15,16] Since such a conformation decreases α_1^{side} and increases α_3^{side}, the actual $\Delta\alpha_R$ and $\Delta\alpha_G$ should have a negative larger and a smaller value, respectively, than those for the free rotation assumption. Then the data point shifts to the lower left from the free rotation assumption. Thus this effect apparently results in decreasing $\Delta\alpha_G P_G/\epsilon$. The agreement of PS with the free rotational side chain scheme may be fortuitous due to cancellation of a lower $\Delta\alpha_G$ and a larger P_G/ϵ. The same effect is expected for the data points for PVBPh and PVN. The correction of this effect results in decreasing $\Delta\alpha_G$, and therefore PVBPh and PVN would have the larger P_G/ϵ values. Thus, we conclude that P_G/ϵ values increase with increasing size of the side chain. For vinyl polymers with short side chains, the strain dependence of P_G is approximately $(6/5)\epsilon$.

In previous studies, we have shown that the nonlinear viscoelasticity of amorphous polymers in the glassy zone is mainly due to nonlinearity of the G component.[17,18] The difference of P_G/ϵ among polymers may be clarified from experiments using large strains.

Effect of Local Field. According to the molecular interpretation of MSOR, C_G should always be positive. On the other hand, some polymers like aPP and hvPB have negative C_G values. In the present study, we tentatively attribute the negative C_G to a lattice effect, which is known for the strain birefringence of inorganic materials.[19] This effect is due to elastic deformation on the local electric field originated by anisotropic distribution of the structural unit. In anisotropic crystals, the local field has been evaluated by summing over all the lattice points using special methods to achieve convergence.[20] For an anisotropic noncrystalline solid, a modification of the Lorentz approach was proposed by Havelock in 1908 for inorganic glasses.[21] This models the local anisotropy of the strained solid by allowing the imaginary spherical cavity of the Lorentz model to deform into an ellipsoid. This effectively compensates for the local anisotropy and allows the continued use of the assumption that the molecules inside the cavity make no net contribution to the field. Havelock assumed that the cavity is deformed by the same amount as the solid. The amount of the birefringence is estimated as

$$\frac{\Delta n}{\epsilon} = \frac{(n^2 - 1)^2}{5n} \tag{19}$$

Note that the birefringence depends only on the refractive index. However, this estimation may be too large because the deformation ratio of the cavity might be smaller than the macroscopic value. Pick and Lovell modified the model, using the measured changes in interchain spacing to give the axial ratio of the ellipsoid.[22] Their result showed that the axial ratio of the ellipsoid is approximately $^1/_3$ the macroscopic value and that the amount of the lattice effect is −0.07 for $n = 1.5$. The value is in accord with $O_G'(\infty)$ of PIB, which is the lowest among studied polymers and can be explained by considering the high symmetry of the repeating unit, that is, $\alpha_2 - \alpha_3 \approx 0$. If the interchain spacing does not vary among polymers under the deformation, the lattice effect is expected to be identical for the polymers. Therefore, the lattice effect may be corrected by the following equation.

$$\left(\frac{\Delta\alpha_{\mathrm{G}} P_{\mathrm{G}}}{\epsilon}\right)_0 = \frac{9nM_0}{2\pi(n^2+2)^2\rho N_{\mathrm{a}}}\left(O_{\mathrm{G}}'(\infty) + \frac{K(n^2 - I)^2}{5n}\right) \tag{20}$$

where K is a factor representing the effective deformation of the cavity. In the present study, K was assumed to be $^1/_3$ for all the polymers. The reduced strain-optical factor corrected with the lattice effect is shown in Figure 4 with open circles. All the data points shifted upward and seem to lie on a smooth curve. The correction is larger for the polymer with larger side groups. This mainly comes from the difference of M_0. Thus even if the lattice effect is taken into account, P_{G}/ϵ increases with increasing size of the side chain and this feature becomes more remarkable.

The broken line in Figure 4 has a slope of −2. This corresponds to $P_{\mathrm{G}}/\epsilon \approx 4P_{\mathrm{R}}/\epsilon = (12/5)\epsilon$. The correction of the lattice effect gives a different relation between P_{G}/ϵ and P_{R}/ϵ. The validity of the lattice effect correction can be tested by the direct estimation of P_{G}/ϵ and P_{R}/ϵ in the elastic tensile deformation in the glassy state. This attempt is now in progress by using a computer simulation method.

V. Conclusion

Dynamic birefringence and dynamic viscoelasticity measurements have been carried out on a series of vinyl polymers. It has been found that the functional form of the complex Young's modulus around the glass-to-rubber transition is fairly insensitive to the details of the side groups. In contrast, the dynamic birefringence of the polymers is remarkably affected by the type of side groups. The data were analyzed through the MSOR scheme, and two component functions were obtained. These component functions were essentially insensitive to the molecular structure. The systematic variation of the two stress-optical coefficients with the molecular structure revealed that the G component was related to the rotational movement of the structural unit about the main chain, supporting our previous theoretical interpretation.

Acknowledgment. The authors thank Dr. J. Bartos and Professor H. Spiess for offering atactic polypropylene and Professor N. P. Balsara for hydrogenation of the polybutadiene sample. This work was supported by a Grant-in-Aid for Scientific Research (07455382) of the Ministry of Culture, Science, and Education of Japan.

References and Notes

(1) See, for example: Janeschitz-Kriegl, H. *Polymer Melt Rheology and Flow Birefringence*; Springer-Verlag: Berlin, 1983.
(2) Inoue, T.; Osaki, K. *Macromolecules* **1996**, *29*, 1595.
(3) Inoue, T.; Okamoto, H.; Osaki, K. *Macromolecules* **1991**, *24*, 5670.
(4) Osaki, K.; Okamoto, H.; Inoue, T.; Hwang, E.-J. *Macromolecules* **1995**, *28*, 3625.
(5) Gao, J.; Weiner, J. H. *Macromolecules* **1994**, *27*, 1201.
(6) Zemke, K.; Schmidt-Rohr, K.; Spiess, H. W. *Acta Polym.* **1994**, *45*, 148.
(7) Hwang, E.-J.; Inoue, T.; Osaki, K. *Nihon Reoroji Gakkaishi* **1994**, *22*, 129.
(8) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
(9) Inoue, T.; Hayashihara, H.; Okamoto, H.; Osaki, K. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *30*, 409.
(10) Okamoto, H.; Inoue, T.; Osaki, K. *J. Polym. Sci., Polym. Phys. Ed.* **1995**, *33*, 417.
(11) Ishikawa, T.; Nagai, K. *J. Polym. Sci., Part A-2* **1969**, *7*, 1123.
(12) Ishikawa, T.; Nagai, K. *Polym. J.* **1970**, *1*, 116.
(13) Zawada, J. A.; Fuller, G. G.; Colby, R. H.; Fetters, L. J.; Roovers, J. *Macromolecules* **1994**, *27*, 6851.
(14) Arendt, B. H.; Kannan, R. M.; Zewail, M.; Kornfield, J. A.; Smith, S. M. *Rheol. Acta* **1994**, *33*, 322.
(15) Stinger, R. *Trans. Faraday Soc.* **1936**, *32*, 296.
(16) Abe, Y.; Tonelli, A. E.; Flory, P. J. *Macromolecules* **1970**, *3*, 294.
(17) Okamoto, H.; Inoue, T.; Osaki, K. *Macromolecules* **1992**, *25*, 3413.
(18) Inoue, T.; Okamoto, H.; Osaki, K. *Macromolecules* **1992**, *25*, 7069.
(19) Inoue, T.; Takiguchi, O.; Osaki, K.; Kohara, T.; Natsuume, T. *Polym. J.* **1994**, *26*, 133.
(20) Dunmur, D. A. *Mol. Phys.* **1972**, *23*, 109.
(21) Havelock, T. H. *Proc. R. Soc. London* **1908**, *A80*, 28.
(22) Pick, M.; Lovell, R. *Polymer* **1979**, *20*, 1448.

MA960190R