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Molecular Rheology of Glassy Polymers

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Molecular origin of the viscoelasticity around the glass transition zone is investigated by means of dynamic birefringence and dynamic viscoelasticity measurements. The present study show that the viscoelasticity around the glass transition zone has two molecular origins: One is the orientation relaxation of main chain axis and the other one is the rotational motion of structure units about the main chain axis.

Keywords: Viscoelasticity / Birefringence / Stress-optical rule / Orientation / Vinyl polymers

Viscoelasticity of amorphous polymers is brought about by molecular motions of polymer chain. The aim of our study is to find molecular origin which are responsible for viscoelasticity around the glass-to-rubber transition zone. We will discuss how a polymer chain is deformed in the glassy zone in this study.

For polymer melts or concentrated solutions, the strain-induced birefringence, Δn, is proportional to the stress. This rule is called the stress-optical rule (SOR). SOR indicates that molecular origin of the stress and birefringence of rubbery materials is the orientation of chain. However, SOR does not hold valid in the glass transition and glassy zones. We have found that the birefringence can be related to the stress through a modified stress-optical rule (MSOR) in these zones[1-3].

$$E*(\omega) = E_G*(\omega) + E_R*(\omega) \qquad (1)$$
$$O*(\omega) = C_G E_G*(\omega) + C_R E_R*(\omega) \qquad (2)$$

where $O*(\omega) \equiv \Delta n*(\omega)/\varepsilon$ is the complex strain-optical coefficient and $E*(\omega)$ is the complex Young's modulus. $E_i*(\omega)$ and C_i (i=R, G) are the component function and the stress-optical coefficient. MSOR is based on two experimental results; validity of the SOR, $O*(\omega)=C_R E*(\omega)$, in the rubbery zone and $O"(\omega)=C_G E"(\omega)$ in the glassy zone. $E_i*(\omega)$ can be separated quantitatively by reducing eqs. 1 and 2. It has been found that MSOR holds valid for more than ten polymers with a few exceptions[3].

The birefringence and the stress can be related with two characteristic orientation functions of structure units by using a polymer model. In this model the polymer chain is supposed to be composed of identical *flat* units that do not change the shape over the studied time scale. The chain can change its shape by the rotation motion about the connecting bonds. The birefringence of this model can be written as follows[2].

$$\Delta n \propto \{\alpha_1 - (\alpha_2+\alpha_3)/2\}P_R + (1/4)(\alpha_2-\alpha_3)P_G \qquad (3)$$

Here, aα_i and represents the principal values of the polarizability tensor of the structure unit. The subscript represents the coordinate of the molecular frame; "1" represents the direction of the chain axis and "2" is taken in the plane of the unit if the unit can be regarded as flat to any

FUNDAMENTAL MATERIAL PROPERTIES —Molecular Rheology—

Scope of research
The molecular origin of various rheological properties of materials is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluids while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of autocorrelation of the orientation with dynamic dielectric spectroscopy.

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extent. Here, the tensor was assumed to be diagonal with respect to the molecular frame for simplicity. The orientational functions P_G and P_R are given as follows.

$$P_R = (1/2)(3<\cos^2\theta>-1) \quad (4)$$
$$P_G = 3<\sin^2\theta\cos^2\phi> \quad (5)$$

Here, θ and ϕ are the polar and azimuthal angles of the stretch direction in the local coordinates of each structure unit. P_R represents the orientation of the main chain axis and P_G reflects the tilting of the structure unit about main chain axis. Thus, the two components can be related to longitudinal and transverse anisotropies of the structure unit.

On the other hand, the local stress, σ_{ij}^m, acting on each structure unit, may vary from place to place and from time to time. However, it was shown that σ_{ij}^m is well constant in the stress relaxation process[2]. As a result the macroscopic stress, σ, can be written as follows.

$$\sigma = \{<\sigma_1^m> - (<\sigma_2^m> + <\sigma_3^m>)/2\}P_R$$
$$+(1/4)(<\sigma_2^m> - <\sigma_3^m>)P_G \quad (6)$$

Here, $<\sigma_i^m>$ represent the principal values of the statistical average of the local stress tensor. Thus the stress can be related to the same orientation functions as the birefringence. The first terms in eqs. 3 and 6 correspond to the R component and the second to the G component.

Eq. 3 provides molecular origin of the birefringence and the relation between the birefringence and molecular structure. The validity of this molecular interpretation can be examined by a study on a series of vinyl polymers[2].

The characteristic birefringence of each component, $O_i'(\infty)=C_iE_i'(\infty)$ (I = R or G) reflects the orientation of the structure unit as well as the molecular anisotropy. We define a reduced strain-optical ratio at high frequencies.

$$O_i'(\infty)\equiv\{9nM_0/2\pi(n^2+2)^2\rho N_a\}O_i'(\infty)=\Delta\alpha_iP_i/\varepsilon \quad (7)$$

where ρ and M_0 are the density and molecular weight of the repeating unit and $\Delta\alpha_R=\alpha_1-(\alpha_2+\alpha_3)/2$ and $\Delta\alpha_G=(\alpha_2-\alpha_3)/4$. Assuming the additivity of bond polarizability and free rotation of the side group, it can be shown that $2\Delta\alpha_G=A -\Delta\alpha_R$ for vinyl polymers. Here, A is a constant independent of the side groups. With this relation, the relation between $O_R'(\infty)$ and $O_G'(\infty)$ can be reduced to the relation between P_R and P_G.

In Figure 1 $O_G'(\infty)$ is plotted against $O_R'(\infty)$. Two lines in the figure are due to two orientation models with the assumption of free rotation of the side chains[5]. In the first model, we assumed that the main chain axis(axis 1) and the side chain direction (axis 2) orient independently according to the quasi-affine deformation. This model gives $P_G=6P_R$.
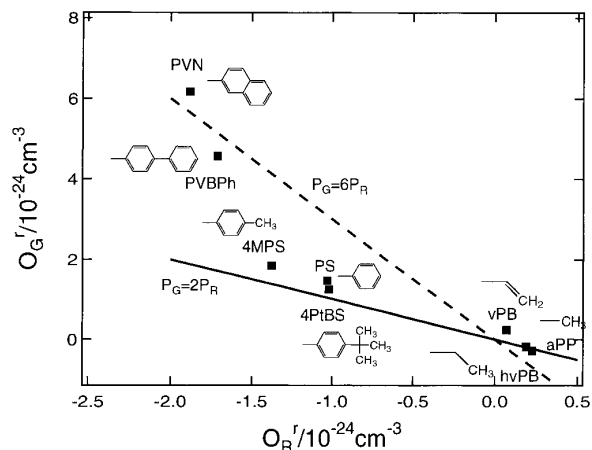

Fig. 1. Relation between the two reduced strain-optical coefficients for vinyl polymers; (-CH$_2$CHR-)n.

However, this model prediction is not correct because this model includes deformation of the structure units which is assumed to be rigid. In the second model, we assumed that the main chain axis orients quasi-affinely and the side chain axis rotates about main chain axis keeping orthogonality between the two axis by an angle which is obtained by quasi-affine orientation. This model gives $P_G=2P_R=(6/5)\varepsilon$. The data points for aPP, hvPB, vPB and PS are close to this line. On the other hand, the results for PVN and PVBPh suggest that P_G/ε values increases with increasing the size of side chain. Thus our molecular interpretation is in accord with experimental results

In conclusion, we have shown that the viscoelasticity and the birefringence of glassy polymers have the two molecular origin around the glass transition zone. One is the orientation relaxation of the structure units along the main chain axis and the other one is the rotational motion of the structure units about the main chain axis.

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