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<th>Molecular Rheology of Glassy Polymers (FUNDAMENTAL MATERIAL PROPERTIES-Molecular Rheology)</th>
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Viscoelasticity of amorphous polymers is brought about by molecular motions of polymer chain. The aim of our study is to find molecular origins 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, \( \Delta n \), 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].

\[
E^*(\omega) = E^G(\omega) + E^R(\omega) \quad (1) \\
O^*(\omega) = C_R E^R(\omega) + C_G E^G(\omega) \quad (2)
\]

where \( O^*(\omega) = \Delta n^*(\omega)\) is the complex strain-optical coefficient and \( E^*(\omega) \) is the complex Young’s modulus. \( E^G(\omega) \) 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 \( O^*(\omega) = C_G E^G(\omega) \) in the glassy zone. \( E^*(\omega) \) 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].

\[
\Delta n = \frac{1}{4} (\alpha_2 - \alpha_3) P_R + \frac{1}{4} (\alpha_2 + \alpha_3) P_G \quad (3)
\]

Here, \( \alpha_i \) 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
ext. Here, the tensor was assumed to be diagonal with respect to the molecular frame for simplicity. The orientational functions $P_R$ and $P_G$ are given as follows.

$$P_R = (1/2)(3<\cos^2\theta>-1)$$  \hspace{1cm} (4)

$$P_G = 3<\sin\theta \cos\phi>$$  \hspace{1cm} (5)

Here, $\theta$ and $\phi$ are the polar and azimuthal angles of the stretch direction in each repeating unit, respectively. $P_R$ reflects the tilting of the structure unit about main chain axis. $P_G$ is a reduced strain-optical ratio at high frequencies. Thus the stress can be related to the same orientation functions as the birefringence.

Fig. 1. Relation between the two reduced strain-optical coefficients for vinyl polymers; (-CH₂CHR-)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 rotates about main chain axis keeping orthogonality between the two axis by an angle which is obtained by quasi-affine orientation. This model gives $P_G=(6/5)e$. The data points for aPP, hvPB, vPB and PS are close to this line. On the other hand, the results for PN and PVBPh suggest that $P_G$ values increases with increasing the size of side chain. Thus our molecular interpretation 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.

References
5. T. Inoue, et al., Polymer, in press.