Macromolecules **2006,** *39,* 4615−4618 **4615**

On the Relationship between Viscoelastic Segments and Kuhn Segments; Strain-Induced Chain Orientation in Fast Deformation

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Received February 22, 2006; Revised Manuscript Received April 14, 2006

ABSTRACT: The viscoelastic segment has been estimated from the limiting modulus at high frequencies with the aid of the modified stress−optical rule. For the case of polymer melts, experimental studies show that thus estimated viscoelastic segment size is close to the Kuhn segment size, which is calculated from the chain dimension. Molecular origin of this correspondence is revisited with the theoretical consideration of the initial chain orientation after step strains. By assuming pseudo-affine orientation of repeating units, we show that the correspondence between the viscoelastic and Kuhn segments can be naturally obtained in the frame of the stress−optical rule. Effects of the nonaffine orientation and the nematic interaction on the correspondence are also discussed.

Introduction

When polymeric materials are deformed, they become anisotropic. For rubbery materials, the refractive index tensor can be related with the stress tensor through the stress−optical rule.[1] This empirical rule indicates that the molecular origin of the stress and birefringence for rubbery materials is the orientation of segments. In the following, we will limit our attention to the small tensile deformations for simplicity. For such a case, the stress−optical rule may be formulated for the complex modulus, $E^*(\omega)$, and the complex strain optical coefficient, $O^*(\omega)$, the latter being defined as the ratio of birefringence, Δn to the oscillatory strain, ϵ:

$$O^*(\omega) = C_R E^*(\omega) \tag{1}$$

Here, C_R is the stress−optical coefficient. As described later, C_R can be related to the anisotropy of segments.

Around the glass transition zone, the molecular origin of the stress and birefringence becomes somehow complex. For such a case, the birefringence can be related with the stress through the modified stress−optical rule, MSOR.[2]

$$E^*(\omega) = E_R^*(\omega) + E_G^*(\omega) \tag{2}$$

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

The coefficients, C_R and C_G, can be determined experimentally, and therefore, $E_R^*(\omega)$ and $E_G^*(\omega)$ can be evaluated by solving these simultaneous equations for E_R^* and E_G^*.

Since the R component satisfies the ordinary stress−optical rule, $O_R^*(\omega) = C_R E_R^*(\omega)$, the R component represents the reorientation process of the viscoelastic segments. To characterize the initial orientation of segments in the glassy region, we may use the limiting modulus at high frequencies, $E_R'(\infty)$. The molecular weight of the viscoelastic segment can be estimated from this $E_R'(\infty)$ as

$$M_S = \frac{3\rho RT}{E_R'(\infty)} \tag{4}$$

Here, ρ is the mass density of the polymer, R is the gas constant, and T is the absolute temperature. In a previous study, we found that the viscoelastic segment size is very close to the Kuhn segment size.[3]

$$M_S \approx M_K \tag{5}$$

The Kuhn segment size can be determined from the chain dimension.

$$M_K = \frac{M}{n_S} = \frac{\langle R^2 \rangle M}{R_{max}{}^2} \tag{6}$$

$$\langle R^2 \rangle = b_K{}^2 n_S = K_1 b^2 n_b \tag{7}$$

$$R_{max} = b_K n_S = K_2 b n_b \tag{8}$$

Here, $\langle R^2 \rangle$ is the mean length of square of the end-to-end distance and R_{max} is the end-to-end distance of the fully extended chain. b_K is the end-to-end distance of the Kuhn segment, and n_s is the number of the Kuhn segments per chain. b is the bond length and n_b is the number of bonds per chain. K_1 and K_2 are constants that depend on chain statistics and bond angle. Thus, M_K can be estimated from the $\langle R^2 \rangle$ data. M_K values for some polymers are shown in Table 1 together with M_S values.[3] Data for some other polymers can be found in ref 3. The experimental accuracy is roughly estimated to be 10% from the scattering of reported value of $\langle R^2 \rangle$.

The agreement of M_S and M_K seems to be reasonable. However, these parameters have a different physical meaning, and the molecular origin of equality (eq 5) has not been verified. In addition, in the framework of bead−spring theory, eq 5 is somehow curious because it is not clear and suspicious whether one Kuhn segment can work as an entropic spring.

On the other hand, M_S becomes significantly larger than M_K in dilute solutions. [4−8] For example, M_S of polystyrene becomes about 5 times larger than M_K. Recently, Larson proposed a new molecular model to explain the difference between M_S and M_K.[9] However, the model is only applicable for dilute polymer solutions. Thus, the physical meaning of M_S and $E_R'(\infty)$ in melts has not been clear. In this paper, we revisit the molecular origin of M_S with consideration of the initial orientation of structural units.

Theoretical Consideration

In the following discussion, we assume that the stress−optical rule, eq 1, holds well for the whole frequency region. This

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10.1021/ma060390v CCC: $33.50

Table 1. Molecular Weight of the Viscoelastic Segment and the Kuhn Segment for Some Polymers[3]

	polystyrene	poly(α-methylstyrene)	Bisphenol A polycarbonate	poly-isoprene	poly-isobutylene
M_S	850	730	490	150	200
M_K	840	960	650	170	260

assumption may be accepted from the validity of the modified stress−optical rule. One important material constant is the stress−optical coefficient, C_R. According to the Kuhn and Grun, C_R for freely jointed chain can be related to the anisotropy of the polarizability tensor of the "optical segments", $\Delta\beta$.[1,10,11]

$$C_R = \frac{2\pi}{45k_BT}\frac{(n^2+2)^2}{n}\Delta\beta \tag{9}$$

Here, n is the mean refractive index and k_B is the Boltmann constant. This equation is originally derived for cross-linked polymer networks. However, C_R is believed to be essentially the same for the stress relaxation process of non-cross-linked polymers. Equation 9 is based on the special molecular model, but we may use eq 9 as an experimental definition of $\Delta\beta$. The experimental values for $\Delta\beta$ were tabulated by Tsvetkov.[12]

Another important quantity related to the orientational birefringence is the intrinsic birefringence, Δn_0. Δn_0 is defined as follows.

$$\Delta n = \Delta n_0 P = \Delta n_0 \frac{3\langle\cos^2\theta\rangle - 1}{2} \tag{10}$$

Here, P is the orientation degree for the structural units and θ is the angle between the stretch direction and main axis of the structural unit. $\langle\cdots\rangle$ represents the statistical average. Δn_0 can be related to the anisotropy of the polarizability tensor of the structural units, $\Delta\alpha$.[11]

$$\Delta n_0 = \frac{2\pi}{9}\frac{(n^2+2)^2}{n}\frac{\rho N_a}{M_0}\Delta\alpha \tag{11}$$

Here, M_0 is the molar mass of the structural units. Δn_0 represents the birefringence of the polymer at the fully extended state, $P = 1$. For the case of freely rotating chains, $\Delta\alpha$ can be related to the anisotropy of polarizabiliy of bonds, $\Delta\alpha_b$ with a geometrical factor, $\Delta\alpha = K_4\Delta\alpha_b$. When bond angle θ_b is $\cos^2(\theta_b/2) = {}^2/_3$, K_4 becomes ${}^1/_2$.

The parameter representing the limiting behavior of orientational birefringence at high frequencies is the strain-optical coefficient for the R component at high frequencies, $O_R'(\infty)$, which is the ratio of birefringence to the tensile strain, ϵ.

$$O_R'(\infty) = C_R E_R'(\infty) = \frac{\Delta n}{\epsilon} = \frac{\Delta n_0 P}{\epsilon} = \Delta n_0\xi \tag{12}$$

Here, we defined as $\xi = P/\epsilon$. Note that P represents the orientation degree of the structural unit, not of the segments.

According to the pseudo-affine model,[13] the parameter ξ can be calculated as

$$\xi = \frac{P_R}{\epsilon} = \frac{3}{5} \quad \text{(pseudo-affine or affine)} \tag{13}$$

From eq 12,

$$M_S = \frac{3\rho RT}{E_R'(\infty)} = \frac{3\rho RT}{\xi}\frac{C_R}{\Delta n_0} = \frac{3}{5}\frac{M_0}{\Delta\alpha}\Delta\beta\frac{1}{\xi} \tag{14}$$

Thus, we obtain

$$\frac{M_S}{M_0} = \frac{\Delta\beta}{\Delta\alpha}\frac{3}{5\xi} \tag{15}$$

Equation 15 indicates that the flexibility parameter defined from the viscoelastic segment, M_S/M_0, agrees with the flexibility parameter defined from the optical segments, $\Delta\beta/\Delta\alpha$, when the structural units are oriented pseudo-affinely to give $\xi = 3/5$.

As shown by Volkenstein, $\Delta\beta/\Delta\alpha$ does not perfectly agree with the flexibility parameter defined from the Kuhn segments, M_K/M_0. [14] For the case of rotational isomer model, $\Delta\beta$ can be related with $\Delta\alpha$ as follows.

$$\left(\frac{\Delta\beta}{\Delta\alpha}\right) = \frac{K_3K_1}{K_4} \tag{16}$$

The parameter K_3 depends on details of the chain statistics. Thus,

$$\left(\frac{\Delta\beta}{\Delta\alpha}\right)\Big/\left(\frac{M_K}{M_0}\right) = \frac{K_3K_2^{\,2}}{K_4} \tag{17}$$

For the case of the freely rotating chain having tetrahedral bond angle, $(\Delta\beta/\Delta\alpha)/(M_K/M_0) = {}^5/_6 \sim 0.8$. This ratio is insensitive to statistical weight of the rotational isomeric states.[14] Thus, in the first approximation, the following relationship can be accepted.

$$\frac{\Delta\beta}{\Delta\alpha} \approx \frac{M_K}{M_0} \tag{18}$$

Under this assumption, eq 15 becomes

$$\frac{M_S}{M_0} = \frac{\Delta\beta}{\Delta\alpha}\frac{3}{5\xi} \approx \frac{M_K}{M_0}\frac{3}{5\xi} \tag{19}$$

Thus, for the case of pseudo-affine deformation, we obtain

$$M_S \approx M_K \tag{20}$$

Experimentally, most polymers satisfy eq 20 reasonably well.[3] This result means that the instantaneous orientation of the structural units induced by the strain is close to the pseudo-affine orientation.[15]

As described before, M_S becomes larger than M_K in dilute solutions.

$$M_S \approx 5M_K \tag{21}$$

In contrast, $\Delta\beta$ remains almost constant over the whole concentration regime. [8] Considering these results and eq 19, we speculate that deviation from the eq 20 for dilute polymer solutions may be attributed to nonaffine orientation of the structural units.

$$\xi \sim \frac{3}{25} \tag{22}$$

This nonaffine behavior may be related to a difference in the rigidities of the solvent and polymer chains against an instantaneous strain.[8] For the case of polymers in melt, a chain is surrounded by the same species of chain. They should be deformed equally and therefore affine-like deformations would be favorable. Actual deformation of each structure unit may be quite different from the affine orientation, but the average orientation would be similar to the affine orientation because every structure units have equal rigidity or probability to orient. In other words, nonaffine deformations mean the localization of strain. This would not happen for the relatively homogeneous system of melts. On the other hand, in solution, the surrounding solvent molecules can change their position much more freely than the chain because the solvent molecules are not connected by chemical bonds. In this context, the solvent molecules can be regarded as a soft matrix, where the localized strain can be stored. In such a soft matrix, the chain does not need to follow the affine orientation in the scales of structure units.

Larson proposed a model for the molecular origin of nonaffine orientation of segment in dilute solutions.[9] Considering the rate of conformational change of segments surrounded by fast moving solvents, he showed that the conformational change of segments are restricted under shear flow due to the rotational barrier of bonds. This restriction results in the reduction of the limiting modulus or, equivalently, the reduction of the bead−spring mode number at high frequencies. According to his result, M_S depends on the activation energy of the rotational motion of bonds, ΔE_a.

$$M_S = \exp\left[\frac{\Delta E_a}{(3\nu + 1)k_B T}\right] M_K \tag{23}$$

Here, ν is the Flory exponent. Typical ΔE_a value leads us to the reasonable difference in M_S and M_K. In his calculation, the rate of conformation change plays an essential role. However, as shown in this paper, M_S is a measure of the initial orientation against the strain as long as the stress−optical rule holds well. In the limit of small strains, it is not clear whether the conformational transition, which is relatively large motion, is necessary for causing the small initial orientation. For the consistent explanation, a further study is desired.

Ideal Polymers

We may define the ideal polymers as those satisfying the following relationship.

$$\frac{M_S}{M_0} = \frac{\Delta\beta}{\Delta\alpha} \tag{24}$$

This equation equivalently holds for the pseudo-affine orientation of the structural units. Then, for the ideal polymers, the intrinsic birefringence can be related to $C_R E_R'(\infty)$

$$\Delta n_0 = \frac{5}{3} C_R E_R'(\infty) \tag{25}$$

Thus, Δn_0 can be estimated from the MSOR analysis.

From the following relationship

$$\frac{\Delta\beta}{\Delta\alpha} = \frac{M_K}{M_0} \tag{26}$$

the viscoelastic segment size of the ideal polymers agrees with the Kuhn segment size.

Effect of Nematic Interaction

For polymers like polyethylene, the stress−optical coefficient becomes larger than the prediction from the molecular calculations. For the case of polyethylenes, experimental value of C_R is about 2 times larger than the calculated value.[16] This deviation is attributed to local ordering (nematic effect). Doi and Watanabe considered the effect of nematic interaction on viscoelasticity and reorientation of segments.[17] According to their results, the nematic interaction increases the stress−optical coefficient.

$$C_R^{\,NI} = \frac{1}{1 - (1/3)\delta}\frac{1}{1 - \delta} C_R^{\,0} = \frac{1}{1 - (4/3)\delta + \delta^2} C_R^{\,0} \approx \frac{1}{1 - (4/3)\delta} C_R^{\,0} \tag{27}$$

Here, δ (<1) is the parameter representing the strength of the nematic interaction. Superscripts NI and 0, respectively, represent the coefficients with and without the nematic interaction. Thus, the nematic interaction apparently increases the optical segment size.

According to their theory, the limiting modulus at high frequencies is modified by the nematic interaction.

$$E_R'^{NI}(\infty) = (1 - \delta) E_R'^{0}(\infty) \tag{28}$$

The birefringence at high frequencies is given as

$$C_R^{\,NI} E_R'^{NI}(\infty) = \frac{1}{1 - (1/3)\delta} C_R^{\,0} E_R'^{0}(\infty) \tag{29}$$

Thus, birefringence, i.e., orientation of structural units is approximately insensitive to the nematic interaction. However, the stress originated by the orientation is modified.

Equation 28 indicates that the viscoelastic segment size increases with the nematic interaction. [18]

$$M_S^{\,NI} = \frac{1}{1 - \delta} M_S^{\,0} \tag{30}$$

Thus, the nematic interaction increases C_R and M_S by the almost same factor. On the other hand, relationship with the Kuhn segments can be derived as follows.

$$\frac{M_S^{\,NI}}{M_0} = \frac{1}{1 - \delta}\frac{M_S^{\,0}}{M_0} = \frac{1}{1 - \delta}\frac{\Delta\beta^0}{\Delta\alpha}\frac{3}{5\xi} \approx \frac{1}{1 - \delta}\frac{M_K}{M_0}\frac{3}{5\xi} \tag{31}$$

$$M_S^{\,NI} \approx \frac{1}{1 - \delta} M_K \tag{32}$$

According to the rheo-optical studies on optically labeled polymer blends, the interaction parameter, δ is estimated to be around 0.3 for polystyrene/poly(phenylene oxide)[19] and hydrogenated/deuterated polyisoprene.[20,21] Equation 32 predicts that the nematic interaction gives slightly larger M_S (+30%), but this miner modification would be canceled out by the nonequality between the optical and geometrical segments for the real systems (see eq 17). Thus, the nematic effect affects the viscoelastic segment size, but it would be negligible for ordinary polymeric systems.

Conclusion

The chain flexibility may be defined experimentally as M_S/M_0, $\Delta\beta/\Delta\alpha$, and M_K/M_0. For the ideal polymers, in which the structural units orient pseudo-affinely, M_S/M_0 agrees with $\Delta\beta/\Delta\alpha$. As already shown long time ago, $\Delta\beta/\Delta\alpha$ approximately agrees with M_K/M_0. Thus, for the ideal polymers, M_S approximately agrees with M_K.

Nonaffine orientation of the structural units violates the equality, $M_S/M_0 = \Delta\beta/\Delta\alpha$. For such a case, M_S possibly becomes larger than M_K as the case in dilute solutions. However, even for such a case, $\Delta\beta/\Delta\alpha$ remains constant because $\Delta\beta/\Delta\alpha$ is essentially determined by the chain statistics.

The nematic interaction increases M_S/M_0 and $\Delta\beta/\Delta\alpha$ by almost the same factor. By checking $\Delta\beta/\Delta\alpha$ value, we can distinguish nonaffine deformation and the nematic interaction. For the case of PS in dilute solution, where C_R is insensitive to concentration over a wide concentration range, we speculate the increase of the M_S is nonaffine deformation of segments.[8]

In the frame of the stress−optical rule, M_S is simply related to the initial chain orientation induced by the instantaneous strain. This initial orientation can be transformed to M_S through C_R. Since C_R is determined by the chain statistic like M_K, M_S has a strong correlation with M_K.

Acknowledgment. This study is partially supported by Grand-in-Aid for Scientific Research (17540381) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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MA060390V