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Communications to the Editor

Comment on “Birefringence in the Softening Zone”

T. Inoue* and K. Osaki

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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A new version of the stress (strain)-optical rule which was recently proposed by Mott and Roland (MR, *Macromolecules* **1998**, *31,* 7095) is examined and compared with an earlier version by Inoue and Osaki (IO, *Macromolecules* **1991**, *24,* 5670). It is shown that the MR version gives unexpected results, and it may not even be consistent with the criticism MR made concerning the IO hypothesis.

The research group of Inoue and Osaki (IO) has studied birefringence and stress in oscillatory elongation of amorphous polymers and have proposed a modified stress−optical rule to correlate the birefringence to the stress in the glass-to-rubber transition zone. Recently, Mott and Roland (MR) criticized the IO hypothesis and proposed a new version of the stress (strain)-optical rule.[1] We here examine the MR hypothesis.

IO Hypothesis. Since details of the IO hypothesis were summarized in the MR note,[1] we here describe it briefly. The strain-induced birefringence of a polymer is related to the stress through the stress-optical rule in the rubbery and flow zones of viscoelastic spectrum: the deviatoric component of the refractive index tensor is proportional to the deviatoric component of stress tensor.[2] In the case of oscillatory elongation of a film, the relation may be written as follows.

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

Here O^* is the strain−optical ratio defined as the complex ratio of birefringence to strain just as the complex Young’s modulus, E^*, is defined as the ratio of stress to strain. The coefficient C is real and independent of angular frequency, ω. In the glass-to-rubber transition and the glassy zones, the simple relation eq 1 is not valid and the constant C becomes a complex function of ω, $C^*(\omega)$.

IO proposed as a simple hypothesis that stress and birefringence could be described in terms of two complex functions, $E_R^*(\omega)$ and $E_G^*(\omega)$, and two real constants, C_R and C_G.[3]

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

$$C^*(\omega) = C_R E_R^*(\omega) + C_G E_G^*(\omega) \tag{2b}$$

The coefficient C_R was identified with the coefficient C of eq 1 so that

$$C_R = O'(\omega)/E'(\omega) = O''(\omega)/E''(\omega)(\text{at low } \omega) \tag{3a}$$

The coefficient C_G was defined as the ratio of the imaginary parts of O^* and E^* in the glassy zone.

$$C_G = O''(\omega)/E''(\omega)(\text{at high } \omega) \tag{3b}$$

The constancy of the ratios in eq 3a is well-established for almost all amorphous polymers.[2] The ratio in eq 3b was found to be constant over a wide frequency range at high frequencies for most amorphous polymers.[4]

Equations 2 and 3 comprise a set of simultaneous equations which may be solved for the two unknown quantities, E_R^* and E_G^*, for given set of data for O^* and E^*, at each frequency. IO investigated the functions, E_R^* and E_G^*, and the coefficients, C_R and C_G, for more than 20 polymers and found some interesting features.[5] The magnitude and the functional form of E_G^* are approximately the same for many polymers and are similar for nonpolymeric glass-forming liquids.[5] The relaxation behavior of E_R^* can be described with the bead−spring model or the Rouse-Mooney theory, if the size of the Rouse segment is equated to the Kuhn statistical segment size.[5] The coefficients C_R and C_G can be related to the monomeric polarizability tensor by assuming that the former represents the monomer orientation along the chain axis and the latter the rotational orientation around the chain axis.[6−8]

Criticism by Mott and Roland. The first criticism of MR is related to a general expression for the creep compliance, $D(t)$, of viscoelastic liquids.

$$D(t) = D_{\text{rec}}(t) + t/\eta \tag{4}$$

Here D_{rec} is the recoverable compliance and η is the elongational viscosity. MR assert from this expression that the strain has an additive nature and that an expression of “stress additivity” such as eq 2a is not reasonable. However, this statement is not correct. Equation 4 is a general phenomenological equation for any viscoelastic liquid, irrespective of the form of the relaxation spectrum.[9] The functional form of eq 2a does not violate the criterion of a liquid, and it is a simple exercise to derive expressions for D_{rec} and η from eq 2a. For simplicity, one may consider a parallel combination of two Maxwell elements. It can easily be shown that this model satisfies both eqs 2a and 4 without any conflict. How could one assess the expression of eq 2a on the basis of the almost purely mathematical statement of eq 4?

The second point raised by MR is that the contribution of E_G^* found by IO is too large at the low-frequency end of the glass-to-rubber transition. They come to this conclusion mostly from the data for dielectric segmental

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* Telephone: +81 774 38-3136. Fax: +81 774 38-3139. E-mail: tinoue@scl.kyoto-u.ac.jp.

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dispersion and the interpretation of creep data by Plazek. This is a quite misleading statement because compliance (strain) and dielectric dispersion are different physical quantities from modulus (stress) even if they reflect the same kind of molecular motion. We will not examine each experimental result here, but how can MR "quantitatively" compare these different quantities? Should all modes assigned to "the segmental mode" in various experimental methods show the same relaxation behavior? More specifically, can MR explain how the dielectric segmental dispersion is related to the mechanical properties? In any case, we admit that MR have a right to propose a new stress–optical relationship if it is reasonable, and we will examine what they have proposed.

MR Hypothesis. MR start from an expression for the complex compliance

$$D^*(\omega) = D_r^*(\omega) + D_g^*(\omega) \qquad (5a)$$

They employed uppercase R and G for the subscripts in their paper, but we employ lowercase r and g here to distinguish the two hypotheses. $D^*(\omega)$ is the response function for strain when stress is stimulus. A simple way to compare the birefringence with $D^*(\omega)$ would be to regard it as a response to given stress and employ the corresponding response function, $C^*(\omega)$, the ratio of birefringence to stress. The present authors were once obliged, in response to a reviewer of their previous paper,[10] to examine the possibility of expressing birefringence using the form of eq 5a and wrote $C^*(\omega)$ as a linear combination of $D_r^*(\omega)$ and $D_g^*(\omega)$ to yield a set of simultaneous equations analogous to eq 5a. This hypothesis did not lead to any reasonable description of observed strain–birefringence behavior.

MR proposed a rather complicated expression for the birefringence.

$$\frac{1}{O^*(\omega)} = \frac{D_g^*(\omega)}{C_g} + \frac{D_r^*(\omega)}{C_r} \qquad (5b)$$

Here C_r and C_g are constants which are different than the C_R and C_G used by IO. MR say that, "in fact, they have no a priori values other than the requirement of yielding agreement with the experimental data of E^* and O^*". If we regard eq 5a and 5b as a set of simultaneous equations, we have two unknown functions, $D_r^*(\omega)$ and $D_g^*(\omega)$, and two adjustable parameters, C_r and C_g.

The first reaction of the present authors to the MR hypothesis was to apply it to the data of other polymers such as polystyrene and polycarbonate and to see what derived functions $D_r^*(\omega)$ and $D_g^*(\omega)$ looked like. It was soon found that this was impossible. MR wrote that the parameters C_r and C_g were determined through "curve fitting". However, no criterion for the curve fitting was described. One could choose any values for the parameters C_r and C_g and then solve for $D_r^*(\omega)$ and $D_g^*(\omega)$. In other words, the curve fitting given as the criterion for determining the parameters, C_r and C_g, can be carried out with complete accuracy for any choice of the parameters. MR do not provide readers, in our opinion, with any clear method for evaluating the adjustable parameters in their scheme.

We therefore abandoned the application of the MR method to other polymers. Since MR gave parameters for polyisoprene,[11] we used these to derive the functions $D_r^*(\omega)$ and $D_g^*(\omega)$, which were not explicitly given in the MR paper. The result is shown in Figure 1, where the imaginary parts of E^*, E_R^*, and E_G^*, and complex compliance D^*, D_r^*, and D_g^* are shown. The derived functions D_r^* and D_g^* have some interesting features. First, D_r^* and D_g^* vary with frequency in a similar manner over a wide range of low frequencies. Actually $D_r^* = (^1/_4)D^*$ and $D_g^* = (^3/_4)D^*$ at frequencies lower than the low-frequency end of glass-to-rubber transition zone, $\omega a_T < 10^{-1}s^{-1}$. This means that the plateau value of D' in the rubbery zone is mostly originated by the glassy component, D_g', and therefore, it is not likely due to chain entanglements as usually believed. On the contrary, the plateau value of D' at high frequencies is originated by the rubbery component, D_r'. In addition, in the low-frequency region, D_g'' is still far from proportional to ω^{-1}; D_g'' is associated with relaxation modes having these long times. This result seems contradictory because according to the original points of the MR criticism they must have tried to find a D_g'' that would not have relaxation or retardation mechanisms in the long time region. The criticism of MR against the IO model of E_G^* may therefore be applied also to their function, D_g^*.

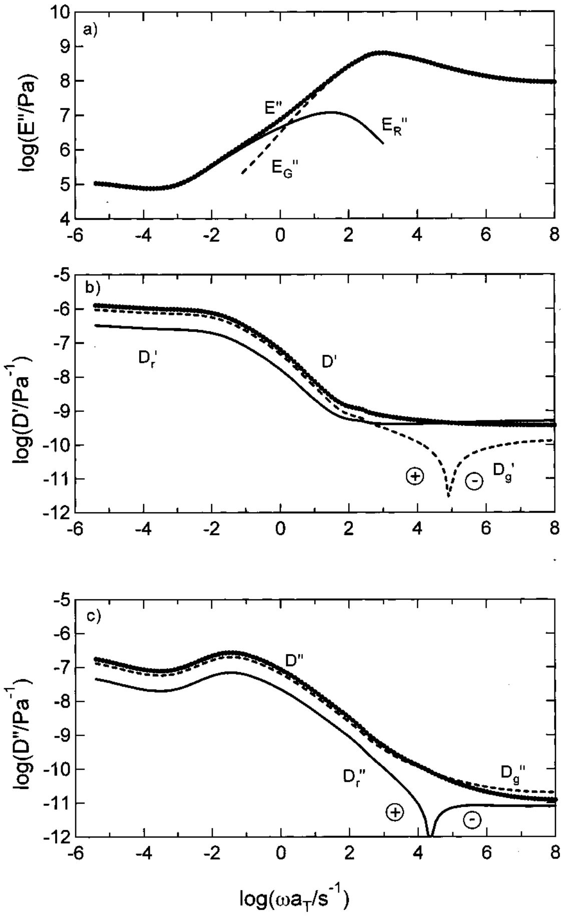

Figure 1. Loss modulus, complex compliance, and their component functions for polyisoprene. (a) E_R'', E_G'', and E''. (b) D_r', D_g', and D'. (c) D_r'', D_g'', and D''.

According to the MR hypothesis, one can show that the ratio D_g''/D'' is only a function of C_r and C_g at low frequencies, where eq 1 is applicable. The loss compliance, D'', varies with molecular weight at low frequencies. Then, D_g'' must vary with molecular weight unless the parameters C_r or C_g also vary with molecular weight in some special way. On the other hand, if one allows a molecular weight dependence of the C_r and C_g parameters, then one finds a molecular weight dependence of D_g^* at high frequencies. This predicted variation with molecular weight is probably a more serious defect for a function representing glassy nature than the problem raised by MR against E_G^* is. Incidentally, the IO function E_G^*, as well as the parameters C_R and C_G, are all independent of molecular weight.

Another interesting feature is that D_g'' and D_r' are negative at high frequencies. The implication of such a curious feature should have been more fully discussed in the MR paper.

In summary the MR hypothesis includes a few unexpected features and may not even be consistent with the MR criticisms against the IO hypothesis. Within the range of detail provided in the paper, the MR hypothesis cannot be followed or even applied to other data. We really expect that hypotheses or theorems which are presented in *Macromolecules* will have sufficient explanation and detail provided so that scientists can follow the logic necessary to examine them.

References and Notes

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