Molecular Interpretation of Dynamic Birefringence and Viscoelasticity of Amorphous Polymers

Kunihiro Osaki,* Hirotaka Okamoto, Tadashi Inoue, and Eui-Jeong Hwang

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

Received December 8, 1994; Revised Manuscript Received March 1, 1995[⊗]

ABSTRACT: Published data of dynamic birefringence and viscoelasticity of amorphous polymers were compared with the molecular expression of stress proposed by Gao and Weiner. The theory states that the stress is composed of contributions from the chain orientation (orientation term), the monomer orientation around the chain axis (rotation term), and the fluctuation of the local stress tensor (fluctuation term); the birefringence is composed of only two terms corresponding to the first two of the stress. The experimental data indicate that in the glassy zone and the high-frequency region of the glass-to-rubber transition zone the stress is attributable to the rotation and the fluctuation terms and the degrees of contribution vary with polymer species. For polymers with flat units (like polycarbonate), the fluctuation term is negligible and the relaxation spectrum in the glassy zone is low. For polymers with thin axisymmetric units (like polyisobutylene) or bulky irregular units (like poly(2-vinylnaphthalene)), the relaxation spectrum in the glassy zone is enhanced by the fluctuation term. It is also argued that, for polymers with thin axisymmetric units, the relaxation spectrum for the rotation term resembles that of a dilute solution; the role of rotational barrier along the chain is relatively enhanced since the rotational barrier from the surrounding is low because of the symmetry of the unit and because of the high fluctuation of the local stress. Some experiments are proposed to verify the statements.

Introduction

The strain-induced birefringence of polymers is related to the stress. In the rubbery and terminal flow zones of the stress relaxation or dynamic mechanical measurements, the deviatoric component of the refractive index tensor, $\Delta\boldsymbol{n}$, is proportional to that of the stress tensor, $\boldsymbol{\sigma}$.

$$\Delta\boldsymbol{n} = C\boldsymbol{\sigma} \tag{1}$$

This relation is known as the stress-optical rule, SOR, and the coefficient, C, is called the stress-optical coefficient.[1,2] The relation does not hold valid in the glassy or glass-to-rubber transition zones.

The birefringence over a wider range of time scale can be expressed by a modified stress-optical rule, MSOR, for quite a number of polymers;[3–6]

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_A + \boldsymbol{\sigma}_B \tag{2a}$$

$$\Delta\boldsymbol{n} = C_A\boldsymbol{\sigma}_A + C_B\boldsymbol{\sigma}_B \tag{2b}$$

where $\boldsymbol{\sigma}_A$ and $\boldsymbol{\sigma}_B$ are functions of time and C_A and C_B are material constants. One of them, C_A, is equal to the ordinary stress-optical coefficient, C. The different definitions of the other coefficient, C_B, lead to different types of MSOR.[3–5] The MSOR states that the stress is composed of two components and the SOR can be applied to each component but with different coefficients; the ordinary SOR (eq 1) is recovered at long times where the contribution of $\boldsymbol{\sigma}_B$ to the stress becomes negligible.

The SOR is usually understood as due to the chain orientation. Thus the SOR is expected to hold valid provided that the rotational orientation of units is random around the chain axis, as is the case for polymers in the rubbery plateau or in the terminal flow zones. At short times after the deformation, the units may be oriented in a certain direction different from the deformation of the whole chain, giving rise to an extra birefringence. This contribution, which may relax rather rapidly as the unit rotates around the chain axis, may be a reasonable candidate for the origin of the second term of eq 2b.

On the other hand, it is not so easy to understand the first equation (eq 2a) for the stress. The birefringence can be directly related to the orientation of units because a definite polarizability tensor can be allotted to each unit. Since the stress is not directly connected to a "local stress tensor" corresponding to the polarizability tensor of the monomer unit, it is not likely to be expressed by two terms representing the orientation of the unit. Recently Gao and Weiner proposed an expression of stress similar to eq 2a but with three terms.[7] In the present paper, we try to interpret the observed results in terms of their expression. It seems that the behavior in accord with the MSOR as well as that in disagreement with the MSOR can be understood by varying degrees of contributions of three terms in the theory. Also, we believe that the degrees are related to the structure of the unit.

Experimental observations are reviewed first, and then the expression of Gao and Weiner is introduced before the discussion. Finally we propose a few predictions concerning the viscoelasticity and the structure of the unit to be examined experimentally.

Experimental Observations

Modified Stress-Optical Rule (Type I Polymers). The time variation of birefringence can be studied in terms of the complex strain-optical ratio, $O^* = O' + iO''$. This is defined as the ratio of the birefringence, Δn, to the strain, e, in an oscillatory elongational deformation of radian frequency, ω, just as the complex Young's modulus, $E^* = E' + iE''$, is defined as the ratio of the tensile stress, σ, to the strain.[4–6] The relation between the birefringence and the stress can be expressed by a modified stress-optical rule, MSOR, proposed by the present authors for a number of polymers (type I) listed in Table 1.[5–14] We avoid the use of the lengthy rigorous names of polymers, which may be found in the original papers, and

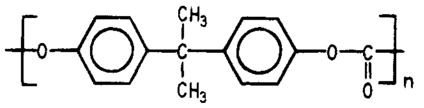
---

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1995.

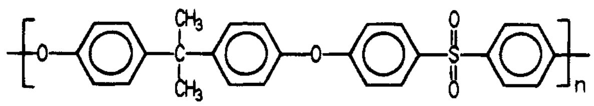
0024-9297/95/2228-3625$09.00/0 © 1995 American Chemical Society

Table 1. Type I Polymers

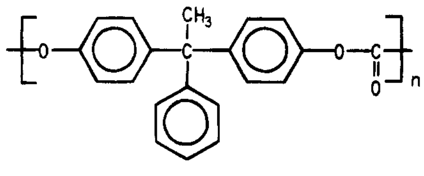
PC (8)



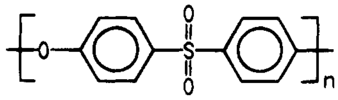
PSF (12)



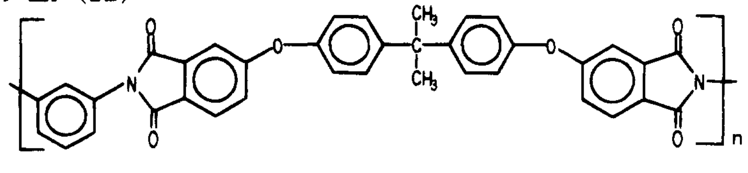
PCAP (9)



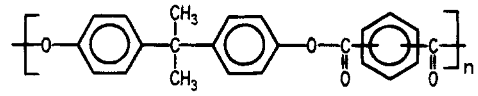
PES (12)



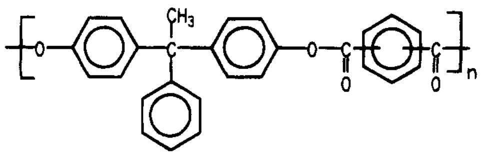
PEI (12)



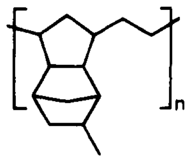
UP (10)



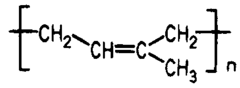
UPAP (11)



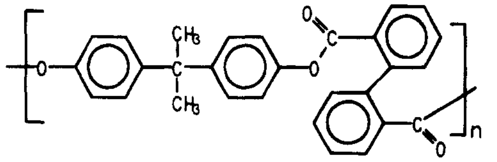
APO1 (13)



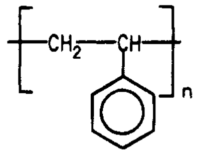
PIP (14)



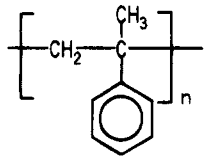
PAr1 (11)



PS (5)



PMS (8)



use abbreviations in this paper.

$$E^* = E^*_{\mathrm{R}} + E^*_{\mathrm{G}} \tag{3a}$$

$$O^* = C_{\mathrm{R}}E^*_{\mathrm{R}} + C_{\mathrm{G}}E^*_{\mathrm{G}} \tag{3b}$$

Here E^*_{R} and E^*_{G} are complex functions of ω and C_{R} and C_{G} are material constants. The former, C_{R}, is defined as equal to the ordinary stress-optical coefficient, C, and the latter as equal to the ratio of the imaginary parts, O''/E'', in the glassy zone, *i.e.*, at high frequencies and low temperatures. The ratio has been found to be a monotonic function of ω and to become, in the glassy zone, a constant over a wide range of ω for all the polymers of Table 1, in spite of the wide variety of O'' with occasional change of signs. As an example, the result for polyisoprene[14] is shown in the upper panel of Figure 1. The ratio is independent of the frequency at the low- and high-frequency limits. The low-frequency limiting value, being equal to the limiting value of O'/E', is the ordinary stress-optical coefficient, C_{R}. The high-frequency limiting value, C_{G}, is not equal to O'/E' in general.

Equation 3 can be solved for E^*_{R} and E^*_{G} if measured values of E^* and O^* are substituted on the left-hand sides. E^*_{R} and E^*_{G} were found to be dominant components of E^* in the rubbery zone and the glassy zone, respectively. In most cases, E^*_{G} varied more strongly with temperature than E^*_{R}. The function E^*_{G} was approximately common to the polymers of Table 1 in the sense that in the log–log plots of E'_{G} and E''_{G} vs ω the shapes of the curves were almost universal.[14] In particular, the slope for the imaginary part, d log E''_{G}/d log ω, at high frequencies is approximately the same for all the polymers of type I; the relaxation spectrum in the glassy zone is common to these polymers (except for the scale units). The function E^*_{R} was approximately described with the bead–spring model theory,[15,16] and the curve fitting gave a reasonable size for a Rouse segment.[5,6,14]

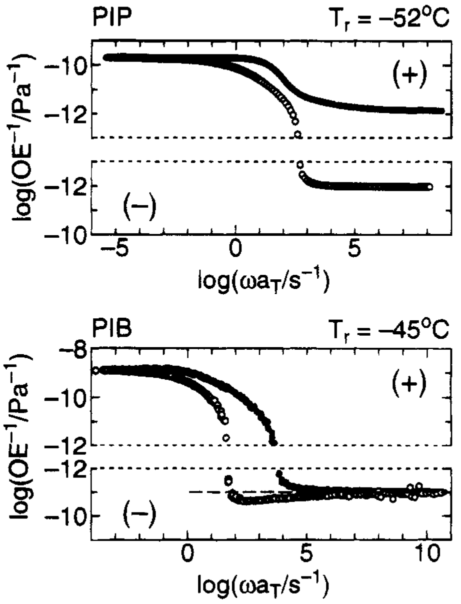


Figure 1. Ratios O'/E' (filled marks) and O''/E'' (unfilled marks) for polyisoprene[14] (PIP) and polyisobutylene (PIB).[19]

The MSOR states that the stress is composed of two components and the SOR can be applied to each component but with different coefficients; the SOR is recovered at long

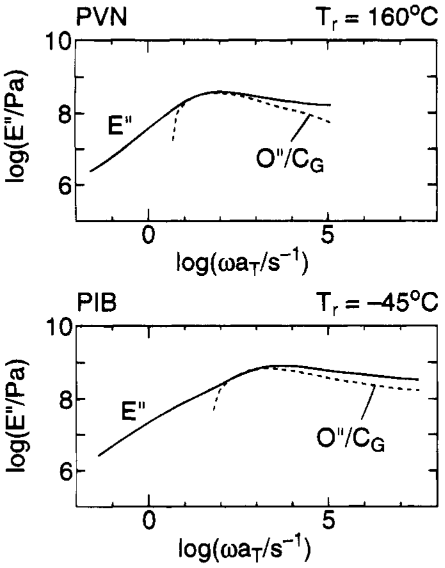


Figure 2. Comparison of E'' and O'' in the glassy zone for poly(2-vinylnaphthalene)[18] (PVN) and polyisobutylene[19] (PIB). $C_G/10^{-11}$ Pa^{-1} = 16 for PVN and −2.4 for PIB.

times where the contribution of the G component becomes negligible. Obviously the R component is associated with the chain orientation.

High positive C_G values on the order of 3×10^{-11} Pa^{-1} were obtained for polymers which contained many benzene rings.[6] This was irrespective of whether the benzene ring was located in the chain backbone or in the chain side group. Some correlation was seen between C_G and the content of the benzene ring. The values for polyisoprene (PIP)[14] and APO1[13] were negative and the absolute values were low. These observations seem to imply that the G component of stress is associated with the anisotropy of local structures.

Failure of the MSOR (Types II and III Polymers). It is expected that the MSOR fails for polymers that exhibit β-relaxation of viscoelasticity due to the side-chain motion in the frequency range close to the main dispersion. This is the case with poly(alkyl methacrylate)s. The birefringence as well as the viscoelasticity is complicated in the glassy zone.[17]

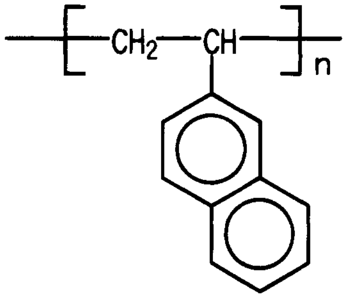
On the other hand, the MSOR was found to fail for a few polymers for which no extra viscoelastic relaxation has been reported in the range close to the main dispersion.[18,19] The failure is such that the ratio O''/E'' is not a monotonic function of ω but exhibits a minimum as exemplified for polyisobutylene (PIB)[19] in Figure 1; the agreement of O''/E'' with O'/E' at high frequencies is fortuitous. Direct comparisons of E'' and O'' are given in Figure 2 for poly(2-vinylnaphthalene) (PVN)[18] and PIB.[19] Here E'' is compared with a constant multiple of O'' in the glassy zone. Obviously, E'' varies more slowly than O'' does for these polymers. In such a case, the assumption of eq 3 is impossible as far as one allows only simple functions for E^*_R and E^*_G, of always positive values of the imaginary parts, for example. At least three components are needed if an MSOR of the same type is sought.

For the case of PVN (we call a type II polymer; Table 2) the behavior is markedly different from that of type I polymers only in the glassy zone; in the transition zone, the behavior is similar to that of type I. A very slight tendency of the same behavior, overlooked at the early stage of study, was detected also for polystyrene (PS) and poly(α-methylstyrene) (PMS).[11,19] The effect was very small and would not have affected the earlier analysis significantly.

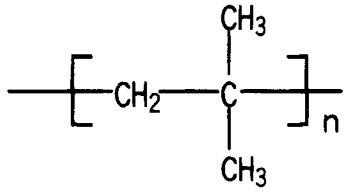
For PIB, which we call the type III polymer, the difference is not limited to the glassy zone. A power law dependence of the loss modulus, $E'' \propto \omega^{0.55}$, was observed over about 3 decades of frequency range just below the maximum of E'' in the glass-to-rubber transition zone (see Figure 2).[19] This is in contrast with other polymers, for which log E'' is a sigmoidal function of log ω in the corresponding region. A tendency similar to that of PIB, the failure of MSOR at high frequencies and a power law variation of E'' in the transition zone, was observed for an ethylene−propylene rubber (EPR).[20]

Table 2. Types II and III Polymers

PVN (18)



PIB (19)



Molecular Expression of Birefringence and Stress

Birefringence. In order to understand the observed features of the birefringence and the stress, we consider a simplified model. Suppose the polymer is composed of identical units that do not change the shape over the time scale to be investigated; the shape of the polymer chain is due exclusively to the rotation of the units around the connecting bonds. This model is a generalization of that employed by Gao and Weiner[7] in their molecular dynamics simulation of a polyethylene-like free rotation chain. We assume that the polarizability tensor of the unit is diagonal with respect to the local frame fixed to the unit (molecular frame) for simplicity, and the deviatoric (traceless) components are α_1, α_2, and α_3, where the subscripts represent 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 in simple elongation is written as follows.

$$\Delta n \propto \alpha_1\langle 3a_1^2 - 1\rangle + (\alpha_2 - \alpha_3)\langle a_2^2 - a_3^2\rangle \qquad (4)$$

The quantity $a_j(t)$ represents the direction cosine of the j axis of the molecular frame with respect to the stretch direction and varies with time and from unit to unit. The bracket implies the average over all the units in the system and over an ensemble of systems of the same deformation state.

The two terms on the right-hand side are due to optical anisotropies of the unit in two directions, respectively. The first term obviously represent the orientation of the chain axis and corresponds to the birefringence described with the ordinary SOR.[1,2] The second term is due to the anisotropy of the unit in the directions perpendicular to the chain axis. This term must be small for polymers with axisymmetric units. It disappears as the unit rotates around the chain axis and is expected to be associated with a shorter relaxation time than the first term.

We hope that the model picks up important characteristics of the chain, at least of polymers with many benzene rings and some other polymers treated in this paper, although real polymers are not composed of identical units and have delicate differences in the rotation of units. It may be obvious that the above statement is not valid if the unit changes its shape in the frequency range concerned, as is the case with methacrylate polymers. On the other hand, a very rapid motion of the part of the unit, like the rapid rotation of methyl side groups in some polymers, may not affect the argument provided that the quantities α_1, α_2, and α_3 are regarded as averages over an appropriate time span. For definite conclusions in the future, it is necessary to confirm that the state of motion of the pendant group does not change in the frequency range concerned.

Stress (Gao–Weiner Expression). Gao and Weiner defined a local stress tensor with which the tensile stress in simple elongation can be written as

$$\sigma \propto \langle \sigma_1(3a_1^2 - 1) + (\sigma_2 - \sigma_3)(a_2^2 - a_3^2)\rangle \tag{5}$$

where $\sigma_j(t)$ is the deviatoric (traceless) component in the molecular frame of the local stress tensor, assumed diagonal for simplicity.[7] The local stress tensor for each unit is defined as follows. The statistical mechanical expression of the stress can be derived from the gradient of the potential energy at each atom composing the system. The local stress of a unit in the molecular frame may be defined by grouping the stress terms for the atoms composing the unit. It depends on the packing state of the surrounding units and so varies with time and from unit to unit. Thus it has to be included inside the bracket representing the ensemble average. 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. On writing σ_j as the sum of the constant and the deviation therefrom (or the fluctuation), they derived an expression for stress which includes terms corresponding to eq 4 and an additional term due to the fluctuation of σ_j.

Here we write the local stress tensor as the sum of the equilibrium average over time and over all the units, σ_j^0, and the deviation from the equilibrium average, $\delta\sigma_j$, which may vary with time and from unit to unit.

$$\sigma_j(t) = \sigma_j^0 + \delta\sigma_j(t) \tag{6}$$

The equilibrium average over all the units must be equal to the constant value meant by Gao and Weiner provided that the chain is long. Then the stress can be written as

$$\sigma \propto \sigma_1^0\langle 3a_1^2 - 1\rangle + (\sigma_2^0 - \sigma_3^0)\langle a_2^2 - a_3^2\rangle + \langle\delta\sigma\rangle \tag{7}$$

The first two terms on the right-hand side varies in the same manner as the two terms of eq 4. An explicit form of the last term of eq 7, due to the fluctuation of the local stress, is given in the paper of Gao and Weiner. It may vary rapidly as guessed from its origin and from the result of simulation by Gao and Weiner. They showed that this term was quite large at short times for the polyethylene-like model. The first two terms were not separately evaluated in their paper. Obviously the second terms disappear provided that the unit is axisymmetric or that the units are rapidly rotating around the chain axis.

It is obvious that eqs 4 and 7 do not tell much about the relaxation process until the quantities in the brackets are explicitly evaluated. On the other hand, the equations are of simple and clear forms and are fairly rigorous. Therefore, we would like to examine how far and how reasonably they could be compared with the experimental results. The first terms of eqs 4 and 7, which we call the orientation terms for short, are obviously due to the chain orientation and already discussed in the theories of SOR for rubbers.[1,2] We mainly discuss the rest of the terms. We call the second terms "the rotation terms" and $\langle\delta\sigma\rangle$, "the fluctuation term".

Discussion

On the Modified Stress-Optical Rule for Type I Polymers. The good applicability of the MSOR as shown above implies that the fluctuation term is much smaller than the rotation term for the type I polymers. This hypothesis may be supported by the fact that the monomer units of the type I polymers are mostly flat. This is true at least for polymers containing a phenylene group in the main chain in Table 1. The flatness means that the rotation term is large because the factor $\sigma_2^0 - \sigma_3^0$ is likely to be large. Also, we may claim that the fluctuation of local stress, $\delta\sigma_j$, must be smaller for flatter units than for symmetric thin units or irregular bulky ones. The local stress of a certain unit is determined by the packing of neighboring units around it. The flatter units may tend to pack more regularly in equilibrium as well as in the deformed state and so the deviation from the equilibrium average must be small in any state.

One may say that *cis*-PIP has a relatively flat rigid unit; all the carbon atoms in a monomer unit lie on one plane. APO1 also contains a rigid portion included in the main chain. The units of PS and PMS may not be very flat as dicsussed in the following section.

The assignment of the G component to the rotation terms may be in accord with the result of a two-dimensional infrared dichroism study by Noda for polystyrene:[21] the phenyl residue is aligned in the stretch direction on average at temperature and frequency where the contribution of the G component is large in the present study; they align perpendicularly to the stretch direction at a high temperature where the G component vanishes. The correlation observed for C_G and the content of the benzene ring may also imply the strong relation of the G component to the rotation terms. In view of the present expression, C_G should be proportional to the ratio of $\alpha_2 - \alpha_3$ to $\sigma_2^0 - \sigma_3^0$. For flat units the latter may be positive. The former may be positive for units composed mainly of benzene rings. The estimation of $\alpha_2 - \alpha_3$, even only up to the sign, for PIP and APO1 seems very difficult.

Failure of the MSOR for Types II and III Polymers. In Figure 2, the loss modulus, E'', is compared with the corresponding component of birefringence, O'', for poly(2-vinylnaphthalene)[18] and polyisobutylene[19] in the glassy zone. It may be noted that E'' decreases more slowly than O'' with increasing frequency. One remarkable fact is that the slope of the (almost straight) curve for O'' at high frequencies is approximately the same for all the polymers referred to in this paper: The relaxation spectrum in the glassy zone derived from O'' is common to these polymers (except for the scale units).

On the other hand, the relaxation spectrum from E'' includes an extra short time mode in the case of polymers shown in Figure 2. This result is consistent with the statement of eqs 4 and 7 that the stress includes a relaxation mode with short relaxation times that is not included in the birefringence. It also implies that the relaxation spectrum due to the rotation term is approximately common to all the polymers in the glassy zone. The variation in the behavior of E'' in the glassy zone is due to varying contributions of the fluctuation term for different polymers.

The monomer unit of PIB is similar to the polyethylene-like model adopted by Gao and Weiner in the sense that it is fairly axisymmetric and relatively thin. One may expect that the factor $\sigma_2{}^0-\sigma_3{}^0$ is small. Also, the fluctuation of local stress, $\delta\sigma_i$, may not be small; the units may be packed in a relatively random manner even in equilibrium, and the fluctuation of local stress, i.e., the deviation from the equilibrium average, must be large.

The fluctuation term could be large for PVN for which the unit is bulky and not flat. The unit may be anisotropic in the 2−3 direction but it may not be regarded as a flat unit included in the main chain because the naphthyl group must be rotating rapidly. The monomer units do not have to be packed as regularly and tightly as flatter units of the type I polymers do and the packing in equilibrium could be looser. This means that the fluctuation is likely to be larger. The phenyl group of PS and PMS sticks out of the main structure as the naphthyl group of PVN and may be the origin of the slight deviation from the type I behavior.

Following the above argument, we propose a modified stress-optical rule appropriate for types II and III polymers.

$$E^* = E^*_{\rm R} + E^*_{\rm G} + E^*_{\rm F} \qquad (8a)$$

$$O^* = C_{\rm R}E^*_{\rm R} + C_{\rm G}E^*_{\rm G} \qquad (8b)$$

The only difference from eq 3 is an additional term in E^* representing the fluctuation term of stress. The term $E^*_{\rm F}$ can easily be evaluated from the data of E^* and O^*. For example, $E''_{\rm F}$ can be obtained as the difference of the solid curve and the dashed curve of Figure 2. The quantities $E^* - E^*_{\rm F}$ and O^* are similar to E^* and O^* of type I polymers and so $E^*_{\rm R}$ and $E^*_{\rm G}$ can be evaluated with an appropriate choice of the $C_{\rm G}$ value. The imaginary parts of $E^*_{\rm R}$, $E^*_{\rm G}$, and $E^*_{\rm F}$ for PIB and PVN are shown in Figure 3. The fluctuation term is of the same order of magnitude as the rotation term in the glassy zone and relaxes rapidly before the glass-to-rubber transition begins.

The values of $C_{\rm G}$ are obtained in the above procedure. They were -2.4×10^{-11} Pa^{-1} for PIB and 1.6×10^{-10} Pa^{-1} for PVN. The large positive value for PVN may be consistent with the argument for type I polymers in view of the large anisotropy of the naphthyl group. The value for PIB is more negative than that for PIP, -1.1×10^{-11} Pa^{-1}. This again seems reasonable because the unit of PIB is less flat than that of PIP.

Speculation on the Power Law Frequency Dependence of E'' for PIB. The loss modulus of PIB varies like $E'' \propto \omega^{0.55}$ over more than 3 decades of frequency on the low-frequency side of the maximum. This means that the relaxation spectrum is represented by a power of relaxation time. The power law behavior is similar to that observed for dilute polymer solutions. The power law spectrum in this case is a result of the motion of linearly connected units in an isotropic frictional resistance of the solvent.

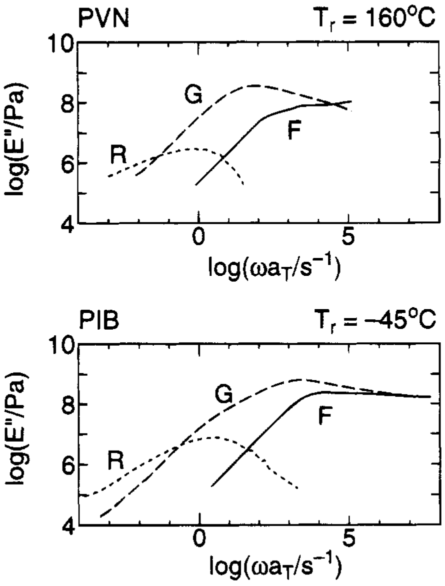


Figure 3. Components of loss moduli, $E_{\rm R}''$, $E_{\rm G}''$, and $E_{\rm F}''$, obtained from the data of Figure 2 with eq 8 for PVN and PIB.

We would like to claim that the chain connectivity is relatively important in the rotation term for PIB; it is not so important for other polymers, for which the rotational barrier of the surrounding medium is relatively large. One reason is that the fluctuation term is large for PIB, and in the time range where the fluctuation term has relaxed, the surrounding medium is more uniform and liquidlike compared with that of other polymers. Second, the unit itself is relatively thin and close to axisymmetric. These two factors would make the surrounding medium act like an isotropic liquid in the rotational motion of the unit. In such a case, the rotational motion would be largely affected by the rotational barrier along the chain, and the chain connectivity becomes important in determining the relaxation spectrum.

In fact, Ferry et al. has pointed out the importance of the rotational barrier for PIB, which they attributed to the two methyl groups on one carbon atom in the main chain.[22]

Conclusion

Published data of dynamic birefringence and viscoelasticity of amorphous polymers can be classified into three groups: type I described by a modified stress-optical rule of eq 3, types II and III with an additional relaxation mode in the glassy zone, which contributes to the stress but not to the birefringence. Type III is characterized by the relaxation spectrum of a power law type in the glass-to-rubber transition zone. The characteristic features of various types are shown in Figure 4. The type I behavior is observed for polymers with flat monomer units, type II for those with bulky irregular units, and type III for those with thin and axisymmetric units.

The additional relaxation mode for types II and III is suggested to be due to the fluctuation term proposed by Gao and Weiner. It is also suggested that the power law behavior of type III is due to the relatively high importance of the role of the rotational barrier in each chain for thin and axisymmetric units, for which the barrier due to the surroundings is low.

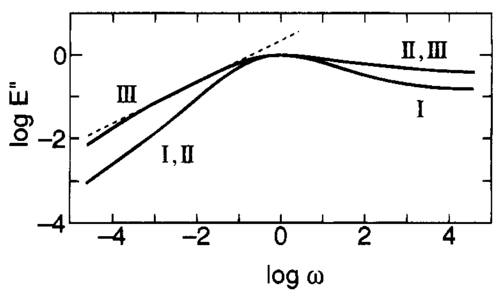


Figure 4. Illustration of the three types of loss moduli, E'', proposed in this paper. The units of E'' and ω are arbitrary.

These statements could be verified by measurements of dynamic birefringence and viscoelasticity for other polymers. We believe that the data for type I polymers are ample. As an example of type III polymer, we propose dimethylsiloxane. The present authors cannot handle this polymer at this moment because of its low glass transition temperature. Polypropylene may behave in a similar manner if a stable amorphous sample is available. The measurements would be easy for any type II polymers with bulky and irregular units. We appreciate any proposal of such a material.

Acknowledgment. This study was supported by a Grant-in-Aid for Scientific Research (02453101) of the Ministry of Culture, Science, and Education of Japan. H.O. was supported by Fellowships of the Japan Society for the Promotion of Science for Japanese Junior Scientists.

References and Notes

(1) Treloar, L. R. G. *The Physics of Rubber Elasticity*, 2nd ed.; Oxford University Press: Oxford, 1958.
(2) Janeschitz-Kriegl, H. *Polymer Melt Rheology and Flow Birefringence*; Springer-Verlag: Berlin, 1983.
(3) Read, B. E. *Polym. Eng. Sci.* **1983**, *23*, 835.
(4) Priss, L. S.; Vishnyakovm, I. I.; Pavlova, I. P. *Int. J. Polym. Mater.* **1980**, *8*, 85.
(5) Inoue, T.; Okamoto, H.; Osaki, K. *Macromolecules* **1991**, *24*, 5670.
(6) Osaki, K.; Inoue, T.; Hwang, E. J.; Okamoto, H.; Takiguchi, O. *J. Non-Cryst. Solids* **1994**, *172–174*, 838.
(7) Gao, J.; Weiner, J. H. *Macromolecules* **1994**, *27*, 1201.
(8) Inoue, T.; Hwang, E. J.; Osaki, K. *J. Rheol.* **1992**, *36*, 1737.
(9) Inoue, T.; Hwang, E. J.; Osaki, K. *Bull. Inst. Chem. Res., Kyoto Univ.* **1992**, *70*, 161.
(10) Hwang, E. J.; Inoue, T.; Osaki, K. *Polymer (Korea)* **1993**, *17*, 249.
(11) Hwang, E. J. Doctoral Thesis, Kyoto University, 1994.
(12) Hwang, E. J.; Inoue, T.; Osaki, K. *Polym. Eng. Sci.* **1994**, *34*, 135.
(13) Inoue, T.; Takiguchi, O.; Osaki, K.; Kohara, T.; Natsuume, T. *Polym. J. (Tokyo)* **1994**, *26*, 133.
(14) Okamoto, H.; Inoue, T.; Osaki, K. *J. Polym. Sci., Polym. Phys. Ed.* **1995**, *33*, 417.
(15) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(16) Mooney, M. *J. Polym. Sci.* **1959**, *34*, 599.
(17) Takiguchi, O.; Inoue, T.; Osaki, K. *Nihon Reoroji Gakkaishi* **1995**, *23*, 13.
(18) Hwang, E. J.; Inoue, T.; Osaki, K.; Takano, A. *Nihon Reoroji Gakkaishi* **1994**, *22*, 129.
(19) Okamoto, H.; Inoue, T.; Osaki, K. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(20) Okamoto, H.; Inoue, T.; Osaki, K., to be published.
(21) Noda, I. *Appl. Spectrosc.* **1990**, *44*, 550.
(22) Ferry, J. D.; Landel, R. F. *Kolloid Z.* **1956**, *148*, 1.

MA946152U