Role of Polymer Chain Flexibility on the Viscoelasticity of Amorphous Polymers around the Glass Transition Zone

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ABSTRACT: Young's modulus of amorphous polymers around the glass-to-rubber transition zone can be separated into two component functions (R and G) through a modified stress-optical rule (Inoue et al. *Macromolecules* **1991**, *24*, 5670) with the simultaneous measurements of the strain-induced birefringence and the stress. In the present study, the two component functions are compared among more than ten polymers, and their relation to chemical structure is investigated. The Rouse segment size is estimated from the limiting modulus at high frequencies of the R component, which can be related to the chain orientation. The molecular weight of the Rouse segment agreed with that of the geometrically evaluated Kuhn segment. The G component that originates the glassy nature of amorphous polymers is grossly similar among studied polymers but depends on chemical structure if compared in detail. The distinction found in shapes of the G component could be related to the number of effective bonds per Rouse segment. This result suggests that the shape of segmental dispersion (G component) is related to the distribution of internal modes of the Rouse segment.

I. Introduction

The mechanical properties such as Young's modulus of amorphous polymers vary with deformation rate as well as with temperature. For the case of oscillatory deformation, polymeric materials show liquid-like or rubber-like behaviors at the low-frequency region, and at high frequencies they exhibit glass-like properties. The frequency zone corresponding to the transition from rubber-like to glass-like behavior in the viscoelastic spectrum is called the glass-to-rubber transition zone.[1] This transition is deeply related to the glass transition as a function of temperature, although these two phenomena are distinct. The nature of viscoelasticity in the transition zone and related problems are recently reviewed by Ngai and Plazek, and a theoretical interpretation based on the coupling mode is presented.[2] The connection between chemical structure and viscoelasticity is one of the problems but it is still not understood well.

In theoretical descriptions of polymer viscoelasticity, the entropy spring concept and the associated Rouse model play a central role, in particular for low-frequency properties.[3] The Rouse segment is defined as a portion of polymer chain long enough for the separation of its ends to approximate a Gaussian probability distribution.[4] The Rouse model, which is developed for dilute solutions, is generally believed to be applicable to melts of low molecular weight polymers without entanglement and to the short time region of entangled polymers. However, the viscoelasticity in the transition zone cannot be perfectly understood by the Rouse chain concept. The shortcoming of the entropy spring concept in this zone has long been recognized by many investigators. For example, the configurational entropy has been regarded to have meaning only when referred to a time period in which the chain has been able to sample the various conformations available to it, and this requirement will not be satisfied for the short time dynamics of the polymer chain.[5] Another problem is that a calculation based on the Rouse model with reasonable segment size underestimates the glassy modulus by about 2 orders of magnitude. Because of these reasons and its original definition, the Rouse segment has been regarded as an artificial and arbitrary unit of polymer dynamics. Therefore, the relation between the Rouse segment size and chemical structure has not become an objective of polymer science. However, when we deal with chain dynamics in short time and short spacial scales, we cannot omit this problem. How short a portion of the chain can we regard as the Rouse segment? Can we predict this size from chemical structure?

In a series of recent experimental studies of dynamic birefringence of amorphous polymers,[6] our major attention has been given to the elucidation of the relation between birefringence and stress near the glass-to-rubber transition zone. Through the above studies, we have shown that the modulus in the transition region can be separated into two component functions *quantitatively* through a modified stress-optical rule, MSOR, with viscoelastic and birefringence data measured simultaneously. The separation into component functions is anticipated to be useful to interpret the relation between viscoelasticity and molecular motion, or chemical structure. According to a molecular interpretation, one component may correspond to the Rouse chain dynamic based on the entropy spring concept and the other to rotational motions of the main chain on the scale of repeating units.[7] The latter motion may be related to the segmental mode (note the distinction between the Rouse mode and the segmental mode). In the present paper, we discuss the relation between the Rouse segment size estimated from the former component and the chemical structure using the data for more than 10 polymer species. The relation between the segmental mode and chemical structure is also our interest.

The plan of this paper is as follows: In section II we present a brief description of viscoelasticity and birefringence and how they correlate to each other around the glass transition zone. The characteristic behavior of the two component functions that are determined through the MSOR is explained. In section III we estimate the Rouse segment size by using the above experimental results and discuss its relation to the

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chemical structure. It will be shown that the Rouse segment size is in accord with the Kuhn segment size which is calculated from chain dimensions. We also discuss the relation between chemical structures, specifically chain flexibility, and the segmental motion that is responsible for the viscoelasticity in short times in the transition zone. We show that the broadening of the segment mode can be related to the number of internal motions of the Rouse segment. Finally, a summary of this study is presented in section IV.

II. Birefringence and Viscoelasticity around the Glass Transition Zone

Modified Stress-Optical Rule. The refractive index tensor of amorphous polymers becomes anisotropic, i.e. the material becomes birefringent, under deformations. In the rubbery plateau or in the terminal flow zones of the viscoelastic spectrum, the deviatory component of the refractive index tensor is proportional to that of the stress. This relation is called the stress-optical rule, SOR, and it has extensively been employed in rheological studies of polymeric liquids in steady flow[8,9] as well as in nonsteady flow.[10,11] For the case of oscillatory elongation, SOR can be written as follows.

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

Here, $O^*(\omega)$ is the complex strain-optical ratio which is defined as the oscillatory birefringence divided by the strain, and $E^*(\omega)$ is the complex Young's modulus. The frequency-independent coefficient, C, called the stress-optical coefficient, is essentially determined by the polymer structure and is rather insensitive to the temperature, the solvent species, and the polymer concentration. The stress-optical rule is interpreted in terms of deformation of the Gauss segment for flexible polymers.[8,9,12]

However, SOR does not hold well in the vicinity of the rubber-to-glass transition zone and the glassy zone. We have shown that the relation between the birefringence and the stress in these zones can be classified into three types.[7] For type I polymers the modified stress-optical rule, MSOR, holds well.[6] MSOR for a sinusoidal tensile strain can be written as follows:

$$E^*(\omega) = E^*_{\mathrm{G}}(\omega) + E^*_{\mathrm{R}}(\omega)$$

$$O^*(\omega) = C_{\mathrm{G}}E^*_{\mathrm{G}}(\omega) + C_{\mathrm{R}}E^*_{\mathrm{R}}(\omega) \tag{2}$$

Here, $E^*_{\mathrm{G}}(\omega)$ and $E^*_{\mathrm{R}}(\omega)$ are two component functions of Young's modulus, and C_{R} and C_{G} are the respective associated stress-optical coefficients. MSOR is based on two experimental observations: the validity of the ordinary stress-optical rule, $O^*(\omega) = C_{\mathrm{R}}E^*(\omega)$, in the rubbery plateau and terminal flow zones and the proportionality of $O''(\omega)$ to $E''(\omega)$ in the glassy zone over a wide frequency region.[6] Therefore, C_{R} and C_{G} can be determined experimentally, and hence eq 2 can be solved for E^*_{R} and E^*_{G}.

MSOR holds well for most of the studied polymers (type I polymers) and exceptions are few: For poly(2-vinylnaphthalene), PVN (type II),[13] and polyisobutylene, PIB (type III),[14] $O''(\omega)$ is not proportional to $E''(\omega)$ in the glassy zone. This feature can be explained by the existence of an additional relaxation mechanism in the glassy zone,[14] and a theoretical interpretation of this third term has been proposed.[7] PIB is different from PVN and type I polymers in the frequency dependence of the G component in the low-frequency region and is then categorized as a type III group. In addition, MSOR is not applicable for polymers like poly(alkyl methacrylate)s[15] which show a subrelaxation in the glassy zone due to the side chain motion.

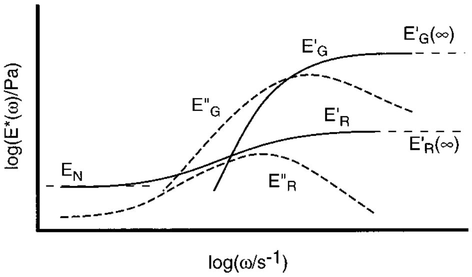

Figure 1. Characteristic behavior of the MSOR component functions.

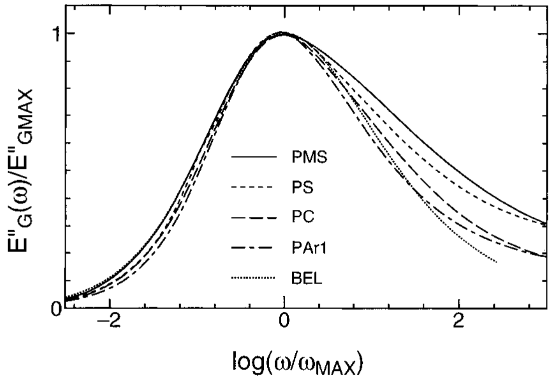

Figure 2. Comparison of the G component of PS, PMS, PC, and PAr1.

Viscoelastic Spectrum and Component Functions. In the following discussion we limit our attention to type I polymers, since the exceptions are few. Figure 1 shows the characteristic behavior of the viscoelastic spectrum of type I polymers. In the rubbery plateau zone, the R component is a dominant component of the Young's modulus; the contribution of the G component to the modulus is negligibly small. Since the ordinary stress-optical rule holds well for the R component, the concept of the Rouse segment and associated coarse-grained theories may be applicable to describe the R component. Actually, in the glass-to-rubber transition zone, the frequency dependence of $E_{\mathrm{R}}^*(\omega)$ of some polymers agrees well with the prediction of the bead−spring theory. This is obvious for PS, PMS, and PIP which show the characteristic frequency dependence of the Rouse model, $E_{\mathrm{R}}'' \propto \omega^{1/2}$, over three decades of frequency in the transition zone (see the Appendix for abbreviation of polymers). For the polymers which have a relatively high rubbery plateau modulus, E_{N}, such as PC, the corresponding frequency range is very limited and is not sufficient for appraisal of the theory.

On the other hand, the high glassy modulus is supported by the G component. The molecular motions corresponding to the relaxation of the G component may be the so-called segmental motion, molecular motions of the main chain on a scale of repeating units. In a previous study, Osaki et al. have proposed a rotational motion of subunits about the main chain as a candidate for the relaxation mode of the G component.[7] Figure 2 shows some examples of $E''_{\mathrm{G}}(\omega)$ of type I polymers for which the modified stress-optical rule holds well. Here, the curves are normalized by a maximum value of $E''_{\mathrm{G}}(\omega)$ and the frequency where $E''_{\mathrm{G}}(\omega)$ takes the maximum. The curves are fairly similar to each other, but the broadness of the dispersion slightly varies with the

Table 1. Characteristic Parameters of Polymers

polymer	T_r, °C	$E_R'(\infty)$, MPa	$E_G'(\infty)$, MPa	$\langle R^2\rangle/M$, 10^{-3}nm^2	R_m/M, 10^{-3}nm	M_0	n_b	M_S	M_K	κ'
PC	160	26	1500	13.2[a]	4.51	254	4	490	650	7.6
PCAP	188	21	1350			316	4	640		8.0
PSF	193	27	1800	7.06[b]	4.33	442	4	520	380	4.7
PES	230	26	1900	5.67[c]	4.22	232	2	640	320	5.6
PEI	222	24	1700	10.5[d]	4.54	592	6	630	510	6.4
UP	202	27	1120	8.3[d]	3.88	358	5.5	510	550	7.9
PAr1	182	53	1150			428	7.5	250		4.1
PS	116	12	2500	4.76[c]	2.38	104	2	850	840	16
PMS	176	16	2300	4.23[c]	2.10	118	2	730	960	12
PIP	−52	35	2700	7.17[c]	6.45	68	3	190	170	6.6
PEMOMID	165	13	1130			176	3	800		14
PVN[e]	160	(8)	1400	3.54[c]	1.61	154	2	1420	1370	18
PIB[f]	−51	(30)	(3000)	4.90[c]	4.34	56	2	200	260	6.9

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polymer species. Since the G component relates to the glassy nature of polymers, it may be worthwhile to compare the G component with viscoelastic properties of other glass-forming materials. In very extensive measurements by Lam, Barlow, and collaborators, shear viscoelastic properties of low molecular weight organic glass formers were studied at very high frequencies from T_g to about 50 deg above. The character of the frequency dependence is the same for 11 liquids of moderately complex but widely differing structures. The frequency dependence can be described by the equations of Barlow, Erginsav, and Lamb (BEL).[16,17]

$$G'/G_\infty = \frac{4(\omega\eta/2G_\infty)^{3/2}[1 + (\omega\eta/2G_\infty)^{1/2}]}{[(1 + (\omega\eta/2G_\infty)^{1/2})^2 + \omega\eta/2G_\infty]^2}$$

$$G''/G_\infty = \frac{4(\omega\eta/2G_\infty)[1 + (\omega\eta/2G_\infty)^{1/2}]}{[(1 + (\omega\eta/2G_\infty)^{1/2})^2 + \omega\eta/2G_\infty]^2} \qquad (3)$$

The dotted line in Figure 2 indicates the BEL equation. The frequency dependence of the G component of polymers is similar to viscoelastic properties of supercooled liquids. The BEL equation appears to be the narrowest limit of the glassy dispersion. The similarity to the supercooled liquids indicates the importance of the nonbonded interaction for understanding the relaxation mechanism in dense systems including polymeric systems. For most of polymers, the G component has a stronger temperature dependence than the R component. This result relates to the failure of the time−temperature superposition scheme for the complex modulus, which is a sum of G and R components, around the glass transition zone. The characteristic times of each component of some polymers at the glass transition temperature were compared to discuss the relative position of two component functions.[18] The characteristic time of the G component was nearly constant at T_g while that of the R component depended on the polymer species. This result could be attributed to the distinction of the characteristic spacial scales of the two components. MSOR is also applied to nonlinear viscoelastic behaviors around the glass transition zone.[19,20]

III. Results and Discussion

Size of Rouse Segment and Comparison to Kuhn Segment. Since the R component is in accord with the concept of the Rouse segment, as seen before, it may be worthwhile to calculate the molecular weight of the segment, M_S, from the limiting modulus of the R component at high frequencies, $E_R'(\infty)$.[21]

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

Here, ρ is the density and R is the gas constant. The quantity M_S may be called the molecular weight of the Rouse segment. Note that eq 4 is essentially consistent with the estimation of submolecules with bead−spring theories for polymers in dilute solution by using dynamic viscoelasticity[22] and oscillatory flow birefringence measurements.[23]

In order to examine the utility of eq 4, we compare M_S with the Kuhn segment size that can be estimated from chain dimensions. The gross shape of a flexible polymer chain can be mimicked by a simplified model composed of N_K Kuhn steps with Kuhn step length b_K connected in series with free joints.[24] The unperturbed mean-square end-to-end distance, $\langle \boldsymbol{R}^2\rangle$, and the fully extended end-to-end distance, R_m, of the chain can be related to N_K and b_K.[25]

$$\langle \boldsymbol{R}^2\rangle = N_K {b_K}^2$$

$$R_m = N_K b_K \qquad (5)$$

The molecular weight of the Kuhn segment, M_K, can be written as follows.

$$M_K = \frac{M}{N_K} = \frac{\langle \boldsymbol{R}^2\rangle}{M}\left(\frac{M}{R_m}\right)^2 \qquad (6)$$

where M is the molecular weight of the chain. Since $\langle \boldsymbol{R}^2\rangle/M$ data of many polymers are available in the literature, M_K can be easily calculated.

The values of M_S and M_K are summarized in Table 1. Abbreviations used for polymer identification are given in the Appendix together with the reference for the viscoelasticity and birefringence data. The number of data is limited due to the lack of $\langle \mathbf{R}^2\rangle/M$ data in the literature. Also included are the data for type II (PIB) and III (PVN) polymers.

Figure 3 shows a comparison between M_S and M_K. The figure indicates that a good correlation is obtained between the two segment sizes. M_S, estimated through the MSOR is nearly equal to the Kuhn segment size. In other words, M_S is determined by the traditional chain flexibility concept. Note that the Kuhn segment is calculated from the equilibrium property while M_S is estimated from the relaxation phenomena.

Two comments may need to be noted in relation to Figure 3. Firstly, the result $M_S \approx M_K$ suggests that the

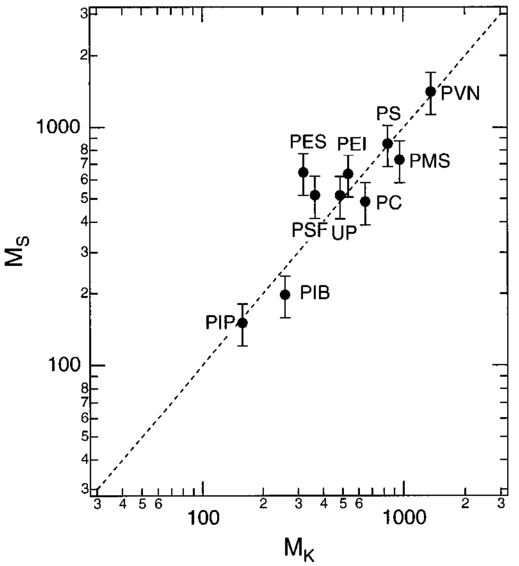

Figure 3. Comparison of the Gaussian segment size, M_S, estimated by rheo-optical measurements to M_K by geometrical measurements.

meaning of M_S may differ from the original definition of the Rouse segment. Since the Rouse segment is defined in theories as a portion of polymer chain long enough for the separation of its ends to approximate a Gaussian probability distribution,[4] it would be impossible for M_S to equal M_K. Therefore, M_S likely includes contributions from molecular motions that would not be included in the Rouse chain as originally developed. Thus, molecular interpretation of M_S might be complicated, but the result of $M_S \approx M_K$ indicates the utility of eq 4.

Secondly, M_S is a concept of the dynamics, and therefore it is a very intricate question whether it should agree with the Kuhn segment size. On the other hand, according to the interpretation of the preceding paper, $E^*_R(\infty)$ would represent the stress due to the orientation of the chain contour if all the rotational anisotropy around the axis is virtually removed without changing the chain contour.[7] Thus, $E^*_R(\infty)$ would be related to the contour expressed in terms of the Kuhn segment. Note that this interpretation is not directly connected to the concept of the configurational entropy, on which eq 4 is based. As a result of molecular simulation studies, Gao and Weiner conjectured that the stress with long relaxation times might correspond to the entropic force similar to that of rubber.[26] A theory based on a similar viewpoint hopefully can derive eq 4, in accord with the concept of the configurational entropy.

Effect of Chain Flexibility on the Primary Dispersion. According to the molecular interpretation of MSOR, the G component is related to rotational motions of the segment or the repeating unit about the main chain. It is a natural conjecture that the G component reflects the polymer chain structure. In order to examine this idea, we define a new parameter, κ, which is the number of effective bonds per the Rouse segment.

$$\kappa = \frac{M_S n_b}{M_0} \tag{7}$$

Here, M_0 is the molecular weight of the repeating unit and n_b is the bond number per repeating unit. κ is a flexibility parameter determined by viscoelastic measurements and represents the strength of intrachain interaction.

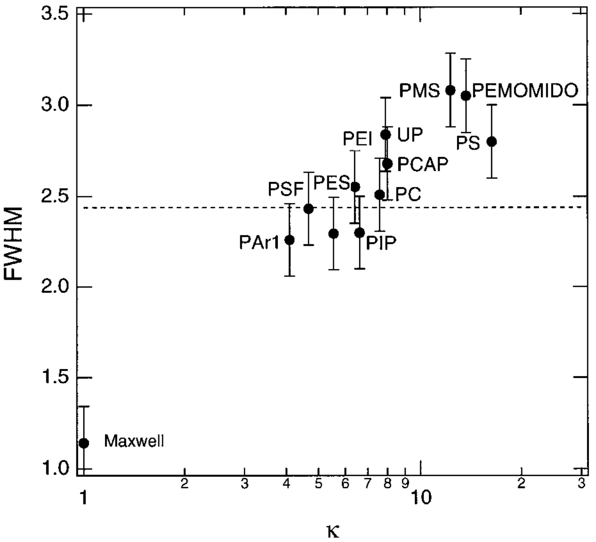

Figure 4. Relation between the broadness of the G component and chain flexibility.

In order to characterize the shape of the G component, we use the full width at half-maximum of $E''_G(\omega)$ in logarithmic frequency scale.

$$\mathrm{FWHM}(\log \omega) = \log E''_G(\omega_1) - \log E''_G(\omega_2)$$

$$\log E''_G(\omega_1) = \log E''_G(\omega_2) = \frac{1}{2} \log E''^{\mathrm{MAX}}_G \tag{8}$$

Here, E''^{MAX}_G is the maximum value of $E''_G(\omega)$.

In Figure 4, FWHM is plotted against κ. The mark on the $\kappa = 1$ indicates the FWHM of the Maxwell model with a single relaxation mode. There is a strong correlation between the chain flexibility, κ, and the shape of the G component. The more flexible chain has the narrower G component. Since κ is the number of bonds per Rouse segment, κ may reflect the variety of internal motions of the Rouse segment. Note that the minimum value of FWHM of the polymers is close to the dashed line for supercooled liquids which have no or less internal motions. Thus, *the broadening of the G component can be attributed to the increase of internal modes included in the Rouse segment.*

The above observation may be in accord with dielectric relaxation measurements. Recently, Ngai and Roland have discussed the relation between the segmental motion and chemical structure.[27] They have found that polymers with less flexible backbones and/or sterically-hindering pendent groups exhibit broader segmental dispersions.

IV. Concluding Remarks

In this work we have investigated the relation between molecular structures and viscoelasticity in the vicinity of the glass transition zone. The stress in the transition zone is decomposed into two components of distinct origins through the modified stress-optical rule applied to simultaneously measured stress and birefringence. For one component, which is a dominant component for the rubbery stress, the Rouse picture is satisfactory, including the segment size: The Rouse segment size which was estimated from the limiting modulus at high frequencies of the R component is very close to the Kuhn segment size. The Rouse picture holds quantitatively if applied to the R component of the stress and thus represents well the viscoelastic behavior at the low-frequency end of the glass-to-rubber transition zone.

The G component which is related to the glassy nature exhibits approximately similar dispersions in shape among various polymers. The slight variation in broadness of the dispersion curves of the loss modulus showed a strong correlation with the number of effective bonds per the Rouse segment derived from $E'_{R}(\infty)$, a new parameter characterizing the chain flexibility. This result may imply that the increase of the internal motions of the Rouse segment gives rise to broadening of the mode of the segmental motion.

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Appendix. Abbreviations Used for Polymer Identification (References for Physical Properties of Each Polymer Are Given)

PS	polystyrene[6]
PMS	poly(α-methylstyrene)[28]
PC	Bisphenol A polycarbonate, poly(oxycarbonyloxy-1,4-phenylenedimethylmethylene-1,4-phenylene)[28,30]
PCAP	Bisphenol AP polycarbonate, poly(oxycarbonyloxy-1,4-phenylenemethylphenylmethylene-1,4-phenylene)[29]
PES	poly(ether sulfone), poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene)[30]
PSF	Bisphenol A polysulfone, poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene)[30]
PEI	Bisphenol A poly(ether imide)[30]
UP	polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A)[31]
UPAP	polyarylate from tere- and isophthalic acids (mole ratio is 1:1) and 2,2,2-tris(4-hydroxyphenyl)phenylethane (Bisphenol AP)[32]
PAr1	polyarylate from 2,2′-dicarboxybiphenyl and 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A)[32]
cis-PIP	1,4-polyisoprene, 98% cis content[33]
PVN	poly(2-vinylnaphthalene)[13]
PIB	polyisobutylene[14]
PEMOMID	amorphous polyolefin, poly[1-ethyl-5-methyloctahydro-4,7-methano-1*H*-indene-1^{2}, 3-diyl][34]

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