Appendix

The measured GPC spectra of the F40 and NBS samples are shown in Figures 23 and 24, respectively. The F40 sample has a width at half-height slightly greater than that of NBS, and both samples have a low-MW tail. See the text for their effects on the $G(t)$ line shape.

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(21) Lin, Y.-H., unpublished results. The blending law can be basically described by the following stress relaxation function for a blend system consisting of two monodisperse components which are far apart:

$$G(t) = G_N W_1[B_1\mu_B(t/\tau_{B1}) + C_1\mu_C(t/\tau_{C1})] + G_N W_2[W_1 T(t) + W_2][B_2\mu_B(t/\tau_{B2}) + C_2\mu_C(t/\tau_{C2})]$$

where W_1 and W_2 are the weight fractions of the low- and high-MW components, respectively, and $T(t)$ is a decaying function (for the tube-renewal process) with a characteristic time τ_T which is larger than the τ_{C1} value by about an order of magnitude. From analyzing the stress relaxation line shapes of nearly monodisperse MWD samples and the blend systems consisting of two components of such narrow MWD, it is suggested that the tube decaying function $T(t)$ for ideal monodispersity should be flat for a period $\tau_T \gg \tau_C$ and then decline quickly; i.e., the tube renewal process is negligible for ideal monodispersity. In a system where the high MW is 775 000 (the F80 polystyrene sample of TSK) and the low MW is 179 000 (the NBS sample), the τ_{C2} value is reduced to $0.85\tau_{C2}^0$ (τ_{C2}^0 is the τ_{C2} for $W_1 = 0$) at $W_1 = 0.25$, $0.7\tau_{C2}^0$ at $W_1 = 0.5$, and $0.5\tau_{C2}^0$ at $W_1 = 0.75$. With decreasing MW of the low-MW component, the effect of W_1 on the reduction of τ_{C2} increases. If the low MW is greater than ~400 000 estimated from extrapolation, τ_{C2} of F80 should not be reduced at $W_1 = 0.5$ (i.e., $\tau_{C2} = \tau_{C2}^0$). The physical meaning of the above equation for a blend system will be explained in detail in a future publication.
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Comparison of Experiment and the Proposed General Linear Viscoelastic Theory. 3. Zero-Shear Viscosity and Steady-State Compliance

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ABSTRACT: It was shown that the proposed general linear viscoelastic theory explained the molecular weight (MW) dependence of the zero-shear viscosity ($\eta_0 \propto M^{3.4}$ above M_c, $\eta_0 \propto M$ below M_c), the steady-state compliance, and the transition points M_c and M_c'. To do so, some information extracted from the short-time viscoelastic relaxation data in the MW region much higher than M_c was used. The reason the calculated and measured MW dependences of η_0 in the low-MW region agree so well was not evident. On the basis of the new insights obtained from the line shape analysis of the stress relaxation moduli reported in the accompanying report (paper 2), an explanation is given. Furthermore, it is shown that the proposed general linear viscoelastic theory is applicable above M_e, while the Rouse theory is applicable just below M_e. The transition point appears rather sharp. The result suggests that as far as the free volume distribution on the polymer chain is concerned, there is a "phase" transition point at $M_e(+)$ from "isotropic" to "anisotropic".

I. Introduction

Chain entanglement plays a very important role in the viscoelastic properties of concentrated polymer systems. One well-known example is the observed molecular weight (MW) dependence of the zero-shear viscosity $\eta_0 \propto M^{3.4}$, above the critical molecular weight (MW), M_c.[1,2] Empirically, the value of M_c is about twice the entanglement MW, M_e, which can be determined from the plateau modulus. Below M_c the viscosity increases linearly with M, as predicted by the Rouse theory. Similarly, the measured steady-state compliance J_e increases linearly with MW below M_c and is independent of MW above M_c'.[1,2]

The reptation model[3–7] predicted that the zero-shear viscosity scaled with MW as $\eta_0 \propto M^3$. In paper 1,[8] a general linear viscoelastic theory was developed from modifying the Doi–Edwards theory.[4–7] It was shown that the general theory explained the MW dependence of η_0 and J_e and the transition points M_c and M_c'. To do so, some information extracted from the short-time viscoelastic relaxation data in the MW region much higher than M_c was used. The reason the calculated and measured MW dependence of η_0 in the low-MW region agree so well was not evident.

In paper 2,[9] the viscoelastic relaxation spectra of narrow MWD polystyrene samples over a wide range of MW

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($31M_e$–$1.24M_e$) were measured and well analyzed in terms of the general theory. Two important observations were made:

(1) The K value (see eq 10, 12, and 13 in paper 2) is independent of MW to as low as MW = 16 700 ($1.24M_e$).

(2) The ratio K'/K (K' being the K value of eq 6 in paper 2) decreases from a plateau value of 3.3 (MW > $10M_e$) to a limiting value of 1 (M_c > MW > M_e) with decreasing MW.

The decrease of the K' value with decreasing MW was associated with the MW dependence of T_g or free volume in the polymer melt. On the basis of these new insights, an explanation to the question raised above is given in this report.

Furthermore, the viscoelastic relaxation of a polystyrene sample with MW slightly smaller than M_e (F1 sample, M_w = 10 300, obtained from TSK) is studied. The measured storage and loss moduli of the sample are analyzed in terms of the Rouse theory[10] and compared with those of the F2 sample (M_w = 16 700), which were analyzed in terms of the general linear viscoelastic theory in paper 2. The contrast between the general theory and the Rouse theory in comparison with the experimental results clearly shows that the constraint effect due to entanglement as described in the general theory is needed to describe satisfactorily the viscoelastic spectrum line shape in the MW region M_c > MW > M_e. This is a further illustration of the applicability of the general theory extending to this low-MW region, which we have concluded in paper 2. On the other hand, the Rouse theory is applicable just below M_e.

Just below M_e, we observe a sharp drop of the viscosity value. This is due to absence of entanglement for MW < M_e and the increase of free volume with decreasing MW. At ~ $M_e(+)$, the free volume in the polymer melt begins to show the anisotropic nature, as reflected in the friction coefficient for the polymer segment to move along the chain contour being different from that perpendicular to the chain contour.

II. Theory

In linear viscoelasticity, the zero-shear viscosity, η_0, and the steady-state compliance, J_e, are related to the stress relaxation modulus, $G(t)$, as

$$\eta_0 = \int_0^\infty G(t)\,dt \tag{1}$$

$$J_e = (1/\eta_0^2)\int_0^\infty G(t)t\,dt \tag{2}$$

In the high-MW region, both the $\mu_A(t)$ and $\mu_X(t)$ processes relax much faster than the $\mu_C(t)$ process. By the neglect of $\mu_A(t)$ and $\mu_X(t)$ in eq 4 of paper 2 (or eq 24 of paper 1), η_0 and J_e as a function of MW were derived as

$$\eta_0 = \frac{\rho RT\pi^2}{15}K\frac{M^3}{M_e^2}[(1 - (M_e/M)^{0.5})^3 + (1/3)(M_e/M)^{1.5}] \tag{3}$$

$$J_e = \frac{3M_e[(1 - (M_e/M)^{0.5})^5 + (1/9)(M_e/M)^{2.5}]}{2\rho RT[(1 - (M_e/M)^{0.5})^3 + (1/3)(M_e/M)^{1.5}]^2} \tag{4}$$

It was shown in paper 1 that the $\mu_A(t)$ and $\mu_X(t)$ processes contribute appreciably to the zero-shear viscosity and steady-state compliance values in the low-MW region (MW < $5M_e$ for η_0, and MW < $7M_e$ for J_e). By the inclusion of $\mu_A(t)$ and $\mu_X(t)$ into $G(t)$, the η_0 and J_e values, as given by eq 1 and 2, respectively, can be calculated numerically.

The Rouse theory was derived for a Gaussian chain without any specific interaction (such as entanglement) with neighboring chains. The interactions between statistical Kuhn segments (both intramolecular and intermolecular) are absorbed in the friction coefficient, ζ, which is identical with that in the Doi–Edwards theory and the general linear viscoelastic theory.

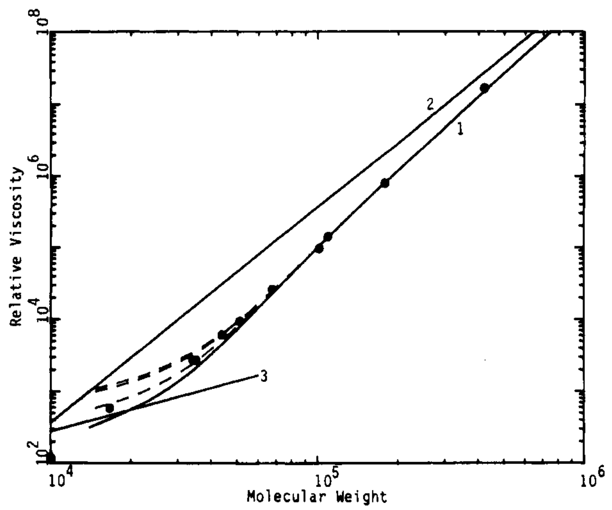

Figure 1. Comparison of the measured (●) viscosity values and the theoretical curves of eq 3 (curve 1), the Doi–Edwards theory (curve 2), the Rouse theory (curve 3), and the general linear viscoelastic theory with K'/K = 5.5 (top dashed line), K'/K = 3.3 (middle dashed line), and K'/K = 1 (bottom dashed line).

The stress relaxation modulus for a Rouse chain is given as

$$G(t) = (\rho RT/M)\sum_{P=1}^{N_0-1}\exp(-t/\tau_P) \tag{5}$$

with

$$\tau_P = \frac{K\pi^2}{24\sin^2(\pi P/2N_0)}\frac{M^2}{N_0^2} \tag{6}$$

where the notations are the same as in papers 1 and 2.

The η_0 and J_e values as a function of MW for a Rouse chain polymer are given as

$$\eta_0 = (\rho RT\pi^2/36)KM \tag{7}$$

$$J_e = 2M/5\rho RT \tag{8}$$

The Rouse theory, eq 5 and 6, will be used to analyze the viscoelastic results of the F1 sample and compared with the general linear viscoelastic theory in analyzing those of the F2 sample.

III. Zero-Shear Viscosity

The $G(t)$'s of F40, NBS, L11, F10, P7, P5, F4, L3, P3, and F2 reported in paper 2 are integrated according to eq 1 to obtain their zero-shear viscosity values (see ref 11). The results are shown and compared with the theoretical curves in Figure 1.

The experimental points agree very well with the curve calculated with eq 3 in the high-MW region (MW > 68000). Below MW ~ 68000, the experimental values are higher than those of eq 3. This is due to neglecting the $\mu_A(t)$ and $\mu_X(t)$ contributions to η_0 in eq 3.

As shown in paper 2, K'/K transits from a plateau value of 3.3 (after 30% correction to K'/K = 4.2) to a limiting value of 1 as MW decreases. In Figure 1, the theoretical curves including the $\mu_A(t)$ and $\mu_X(t)$ contributions with K'/K = 3.3 and 1 are also shown. Indeed, the experimental points fall between these two curves and transit from the curve of K'/K = 3.3 to the curve of K'/K = 1 with decreasing MW. Since, as reported in paper 2, the viscoe-

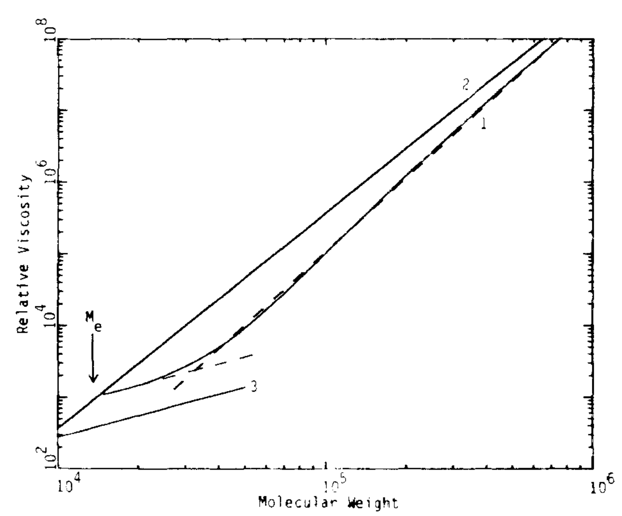

Figure 2. Comparison of the theoretical curve (curve 1) of the general linear viscoelastic theory with $K'/K = 5.5$ and the power-law relations $\eta_0 \propto M^{3.4}$ above M_c and $\eta_0 \propto M$ below M_c (the dashed lines). Also shown are the curves of the Doi-Edwards theory (curve 2) and the Rouse theory (curve 3): $M_e = 13\,500$; $M_c = 33\,000$.

lastic relaxation spectra of these samples were well analyzed and the obtained K values are independent of MW, the good agreement between the theoretical and experimental η_0 values is expected (see paper 2 for the explanation of a 30% deficiency of the K values of the NBS and F40 samples).

Because of the MW dependence of T_g or free volume in the polymer melt, the measured isothermal viscosity data at different MW's need be corrected to a common temperature of equal distance away from individual T_g. After the T_g correction, the MW dependence of viscosity has the relation $\eta_0 \propto M^{3.4}$ above M_c and $\eta_0 \propto M$ below M_c.[12,13]

It was concluded in paper 2 that the MW dependence of the K' value must be associated with the MW dependence of T_g or free volume. Although the K' value decreases by a factor greater than 3 as MW decreases from the high value ($>10M_e$) to the low value ($M_c > M > M_e$), because the $\mu_A(t)$ process only contributes a fraction to the total viscosity value at most in the low-MW region, its effect on the MW dependence of T_g as observed in the temperature dependence of viscosity is not as great (a buffering effect due to K being independent of MW). The theoretical viscosity curve that has taken the T_g or free volume effect into account would be equivalent to the curve calculated with $K'/K = 3.3$.

The glassy relaxation process would also contribute an appreciable small amount to the total viscosity in the low-MW region ($4M_e > \text{MW} > M_e$). To take this effect into account in the viscosity calculation, we calculate an effective K'/K, whose value is such that the area between the measured $G(t)$ values and line X shown in Figures 4 and 5 of paper 2 is equal to the theoretical $\mu_A(t)$ area using the effective K' value in the calculation (the K value remains the same). The estimated effective K'/K value is 5.5. In the estimation, the effect of the compliance of the transducer on the measured glassy relaxation is secondary and neglected.

In Figure 1, the viscosity curve calculated with $K'/K = 5.5$ is also shown, which only differs from the curve of $K'/K = 3.3$ by a small amount in the low MW region. Both curves of $K'/K = 5.5$ and $K'/K = 3.3$ can be extremely closely approximated by the relation $\eta_0 \propto M^{3.4}$ above M_c and $\eta_0 \propto M$ below M_c. However, the M_c values for these two curves are, of course, slightly different. Within experimental error, both the M_c values of these two curves are in good agreement with the M_c literature value.[1,2] The viscosity curve calculated with $K'/K = 5.5$ is compared with the relation $\eta_0 \propto M^{3.4}$ for $M > M_c$ and $\eta_0 \propto M$ for $M < M_c$ in Figure 2.

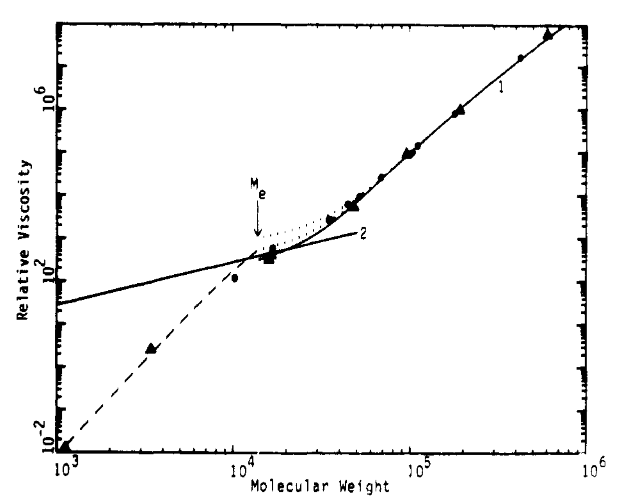

Figure 3. The present data (●) and the data of Plazek and O'Rourke ((▲) at 130 °C, obtained though interpolation with the WLF relation and the experimental values at other temperatures) are compared with the theoretical curves of eq 3 (curve 1), the Rouse theory (curve 2), and the general linear viscoelastic theory with $K'/K = 5.5$ (the upper dotted line) and $K'/K = 1$ (the lower dotted line).

In paper 1, $K'/K = 5$ was obtained, where the glassy relaxation process did not appear in the measured $G(t)$ curves, because a soft transducer was used (see section III of paper 2). The value of $K'/K = 5$ differs about 20% from $K'/K = 4.2$ obtained in paper 2. This difference is in part due to using different transducers and in part due to some difference in the ways of matching the calculated $\mu_A(t)$ curve to the measured $G(t)$ line shape. Fortuitously the K'/K (=5) value obtained in paper 1 differs only slightly from the calculated effective K'/K (=5.5) value. Thus, the viscosity curve calculated with $K'/K = 5$ in raper 1 had taken both T_g correction and the glassy relaxation process into account.

Also shown in Figure 1 is the viscosity value of F1 obtained with the oscillatory measurement. We notice that viscosity value has a precipitous drop below M_e. The value of F1 is below the theoretical Rouse curve. To further illustrate this, the data of Plazek and O'Rourke[14] are shown together with the present data in Figure 3. Apparently, the precipitous drop of the η_0 value is due to the absence of the entanglement effect and the increase of free volume with decreasing MW. In other words, the buffering effect of K being independent of MW is absent for MW $< M_e$. This effect was also quite noticeable in the viscosity data of Allen and Fox, as shown in Figure 2 of ref 12.

The entanglement MW not only plays an important role in the topological constraint as described in the general linear viscoelastic theory but also is much related to the MW dependence of free volume. Above M_e, the change of the free volume or friction coefficient with MW is limited to segmental movement in the direction perpendicular to the chain contour. For the chain motions along the chain contour, the friction coefficient does not change with MW. On the other hand, below M_e, the polymer linear viscoelastic spectrum is well described by the Rouse theory, as shown in section V; the change of the free volume with MW is homogeneous and isotropic. This result suggests that as far as the free volume distribution on the polymer chain is concerned, there is a "phase" transition point at MW $\sim M_e(+)$, i.e., from "isotropic" to "anisotropic".

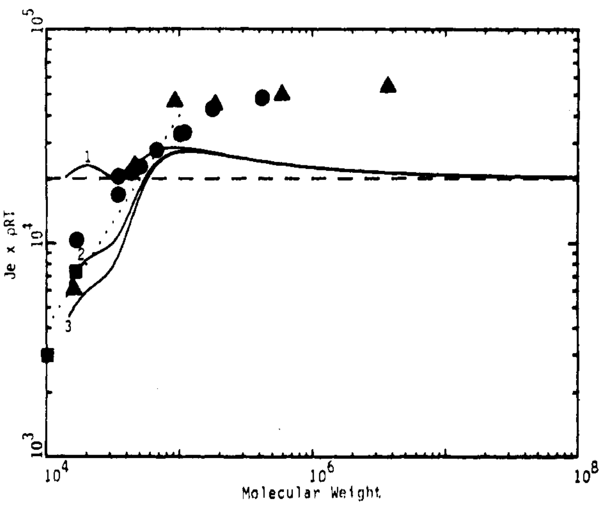

Figure 4. The experimental J_e values of the present study ((●) obtained from integrating $G(t)$ curves; (■) obtained from oscillatory measurements) and of Plazek and O'Rourke (▲) are compared with the theoretical curves of eq 4 (curve 1) and the general linear viscoleastic theory with $K'/K = 1$ (curve 2) and $K'/K = 3.3$ (curve 3). Also shown are the Doi-Edwards (the dashed line) and the Rouse (the dotted line) curves.

IV. Steady-State Compliance

In Figure 4, the experimental values of the steady-state compliance, J_e, of the studied samples are compared with the theoretical curves. The experimental J_e values were obtained by substituting the $G(t)$'s of the samples into eq 2 (see ref 11). The theoretical curve of eq 4 does not decline in the low-MW region ($<7M_e$), as the experimental data do, due to neglecting the $\mu_A(t)$ and $\mu_X(t)$ contributions. By the inclusion of the $\mu_A(t)$ and $\mu_X(t)$ processes, two curves with $K'/K = 3.3$ and 1 are calculated numerically. These curves converge with eq 4 in the high-MW region. In the MW region MW $< 8M_e$, the actual theoretical curve should transit gradually from the curve of $K'/K = 3.3$ to that of $K'/K = 1$ with decreasing MW. The effect of the glassy relaxation process on J_e, expected to be small, has not been taken into account in the calculation of the J_e values.

J_e values are highly sensitive to the MWD of the samples. Thus, the experimental points are above the theoretical curve because of their finite MWD. Also shown in Figure 4 are the data of Plazek et al.[14] The points for F1 and F2 obtained from the oscillatory measurements include the effect of the glassy relaxation, which makes the J_e values smaller. Overall, the experimental J_e values of the samples in the high-MW region ($>8M_e$) differ from the theoretical curve more than those in the low-MW region because of their broader MWD's. The gradual decline of the theoretical J_e curve in the high-MW region MW $>$ $10M_e$ with increasing MW is not observed in the experimental data. Since, as a characteristic of the anionic polymerization process, it is generally true that MWD is broader at higher MW, the flatness of the J_e values vs. MW in the high-MW region actually supports that the true theoretical curve should decline. Furthermore, the theoretical curve correctly predicts the transition point M_c', which is about $7M_e$.

V. Comparison of the General Linear Viscoelastic Theory and the Rouse Theory in the Low-MW Region: MW < M_c

It is generally believed that at low MW (MW $< M_c$) the polymer molecular dynamics is described by the Rouse theory. This belief is mainly based on the observed MW dependence of zero-shear viscosity ($\eta_0 \propto M$) below M_c. On the other hand, the entanglement MW, M_e, calculated from the plateau modulus with eq 23 of paper 1 (the conventional way of calculating M_e) is about half the M_c value. The relation between M_e and M_c and the role of entanglement in the MW region $M_c >$ MW $> M_e$ has never been discerned until the present study. From the line shape analysis of the measured $G(t)$, $G'(\omega)$, and $G''(\omega)$ reported in paper 2 and the comparison of the theoretical and experimental η_0 and J_e values described above, it is already very clear that the constraint effect due to entanglement as described by the general linear viscoelastic theory persists to this low-MW region ($M_c >$ MW $> M_e$). Nevertheless, it is illustrative to compare the general theory with the Rouse theory in the context of analyzing the viscoelastic relaxation spectra of the samples in this low-MW region.

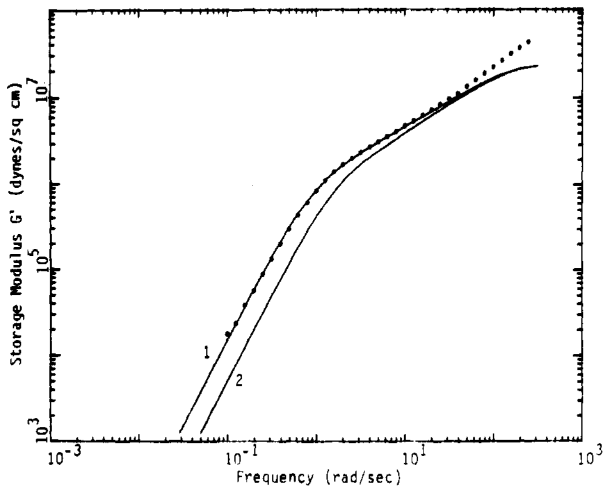

Figure 5. Comparison of the measured (●) and the calculated storage moduli using the general linear viscoelastic theory (line 1) and the Rouse theory (line 2) for the F2 sample (see the text).

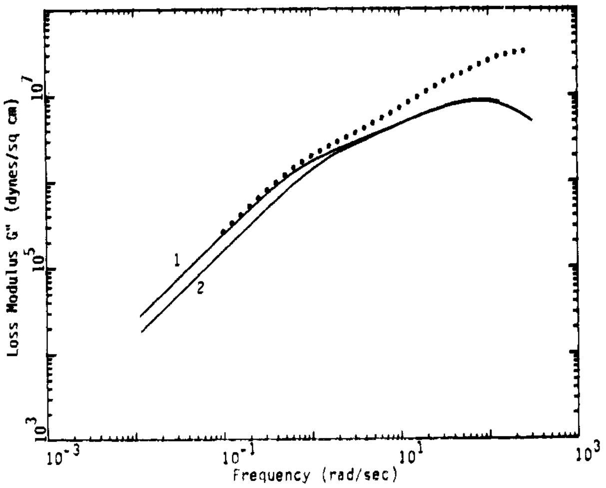

Figure 6. Comparison of the measured (●) and the calculated loss moduli using the general linear viscoelastic theory (line 1) and the Rouse theory (line 2) for the F2 sample (see the text).

Shown in Figures 5 and 6 is the comparison of the calculated and measured $G'(\omega)$ and $G''(\omega)$ of the F2 sample as reported in paper 2. Also shown in these figures are the Rouse curves calculated from convoluting eq 5 (in combination with eq 6) with the Schulz MWD using the same K and Z values. The number of segments, N_0, per molecule in eq 5 and 6 is chosen to be 13 (for $M_w = 16\,700$) corresponding to $N_e = 10$ for $M_e = 13\,500$. Increasing the N_0 value will only affect the calculated $G'(\omega)$ values in the high-frequency region, where the glassy relaxation process

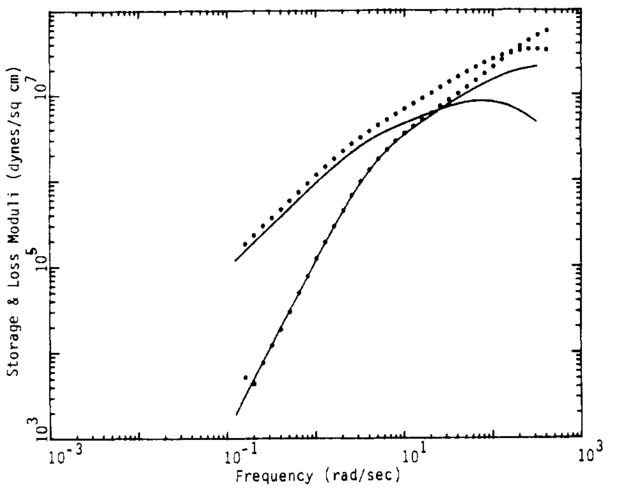

Figure 7. Comparison of the measured (●) and the calculated storage and loss moduli (—) using the Rouse theory for the F1 sample.

is important. The $G'(\omega)$ value in the frequency region of our interest is independent of the choice of N_0 as long as it is sufficiently large.

As shown in Figure 5, the experimental $G'(\omega)$ data are clearly incapable of fitting the Rouse curve. This is mainly due to some additional modes of motion existing in the low-frequency region (dominated by the $\mu_B(t)$ process, see Figure 22a of paper 2), which are, however, properly described by the general linear viscoelastic theory.

Although the $G''(\omega)$ data can fit the Rouse curve better, if we shift the Rouse curve in the frequency coordinate in Figure 6, this agreement has no physical basis, because the $G''(\omega)$ values are bound to be affected by the high-frequency glassy relaxation process, which is not included in the calculation of the Rouse curve. The agreement between experiment and the general theory in the low-frequency region is good. The difference between experiment and the general theory in the intermediate frequency region (1–10 rad/s) being due to the high-frequency glassy relaxation process is the same as in the cases of higher MW samples reported in paper 2.

Below M_e, the entanglement effect should be absent. In Figure 7, the measured $G'(\omega)$ and $G''(\omega)$ values of F1 are compared with curves calculated from the Rouse theory. The theoretical curves were calculated with $N_0 = 8$ (for $M_w = 10\,300$) and $Z = 120$ for the Schulz MWD. The calculated and measured $G'(\omega)$ values agree well over the entire frequency range except for the expected difference in the high-frequency glassy relaxation region. On the other hand, the difference between the calculated and measured $G''(\omega)$ values due to the glassy relaxation process extends over the entire frequency range, as shown in Figure 7.

Because of the good agreement between the calculated and measured $G'(\omega)$ values for the F1 sample, we can conclude that the Rouse theory is valid for MW $\sim 10\,000 < M_e$. This narrow MW range is very likely the only region where the Rouse theory can be expected to be valid because the entanglement effect is absent and the MW is still high enough for the polymer molecule to be modeled as a Rouse chain.

VI. Discussion and Conclusion

In paper 1, it was shown that the proposed general linear viscoelastic theory explained very well the MW dependence of the zero-shear viscosity and steady-state compliance and their respective transition points, M_c and M_c'. These results are confirmed in this report.

On the basis of the new insights obtained from the line shape analysis of the linear viscoelastic relaxation spectra in paper 2, the physical basis for the good agreement between the theoretical and experimental viscosity values (after the T_g correction) in the low-MW region $5M_e >$ MW $> M_e$ is given. Two factors affect the viscosity values in this low-MW region: (1) the MW dependence of the K' value, which is related to the T_g correction, and (2) contribution from the glassy relaxation process. It is shown that the calculation of the MW dependence of the zero-shear viscosity in paper 1 had in effect taken these two effects into account.

From the line shape analysis of the linear viscoeastic relaxation spectra of the polystyrene samples of MW's just above and below the entanglement MW, it is shown that the Rouse theory is valid just below M_e while the general linear viscoelastic theory is valid above M_e. This suggests that there is a clear correlation length given by $a = bN_e^{1/2}$ (b is the segment length)[4,5] existing in the polymer melt. If the end-to-end distance, R, of the polymer molecule is smaller than a, the motions of all the segments of the molecule are correlated and described by the normal modes of the Rouse theory. If R is greater than a, the interaction (entanglement) between polymer chain screens out some of the dynamic correlation between two segments separated beyond the distance a along the chain contour. The modes of the Rouse motions that are screened are the motions in the direction perpendicular to the chain contour and are contained within a section of N_e segments. On the other hand, the different modes of the Rouse motions along the chain contour extend over the entire molecule. The screening point M_e, which separates the applicability of the general linear viscoelastic theory and the Rouse theory, appears quite sharp.

The interaction (entanglement) between polymer chains that occurs for MW $> M_e$ (or $R > a$) can also be relaxed by the diffusion motion of the polymer molecule (in addition to the intramolecular Rouse motions) since the interaction is intermolecular. Below MW $\sim M_c$, the diffusion (reptation) motion plays only a minor role in relaxing the interchain interaction because $C < B$ (see eq 7 and 8 of paper 2). With increasing MW, τ_C and C become greater than τ_B and B at MW $= 2.49M_e$ and MW $= 4M_e$, respectively. In other words, at MW $\sim M_c$, the reptation motion begins to play an important role, and, as a result, the viscosity starts to rise sharply as MW increases.

In the reptation regime ($M > M_c$), because the importance of the $\mu_C(t)$ process increases while that of the $\mu_B(t)$ process decreases with increasing MW, the slope of log η_0 vs. log M is greater than the prediction of the pure reptation model. At extremely high MW, the relation $\eta_0 \propto M^3$ of the pure reptation model should emerge as the $\mu_B(t)$ process becomes negligible.

In the reptation regime, because of the topological constraint effect due to entanglement and the fact that extra local free volume is associated with the free chain end, the free volume distribution is not uniform between the ends and the rest of a chain. This results in a larger friction coefficient for polymer segments to move in the direction perpendicular to the chain contour vs. that for motion along the chain contour. This "anisotropy" of the free volume distribution on the polymer chain begins to appear at $\sim M_e(+)$ like a "phase" transition. Below M_e, the viscosity of the polymer melt drops precipitously with decreasing MW. This is mainly due to absence of entanglement for MW $< M_e$, where the increase of the free volume with decreasing MW has a direct effect on viscosity. For MW $> M_e$, the K value being independent of

MW has a buffering effect on the free volume and T_g change with MW, as observed in the zero-shear viscosity measurements.

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Enhanced Low-Angle Scattering from Moderately Concentrated Solutions of Atactic Polystyrene and Its Relation to Physical Gelation

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ABSTRACT: The enhanced low-angle scattering (ELAS) observed in moderately concentrated solutions of atactic polystyrene is examined in the light of its possible correlation with physical gelation. This paper deals with several points: (i) This correlation is again tested by means of light scattering with solvents of very low freezing points ($T_m \simeq -100$ °C). Results show that ELAS is observable in THF (gelation solvent) but absent in methylene chloride (nongelation solvent). (ii) The vanishing of ELAS is studied as a function of temperature and solution preparation (centrifugation). It is shown that the ELAS disappears at a well-defined temperature on heating and then reappears on cooling. Identical intensity patterns recorded after a heating and cooling cycle attest to the perfect reversibility of the phenomenon. Concerning centrifugation, it is pointed out that for solvents wherein ELAS is evidenced, a gradient of concentration is created unlike for solvents wherein ELAS is absent. (iii) The thermal properties (melting enthalpy and melting point) of the solvents in polymer solutions are examined by differential scanning calorimetry. These investigations reveal that paradoxically the more solvating diluents give rise to ELAS. In addition, it is found that the solvent melting temperature does not vary significantly for solvents wherein ELAS is observed, while it exhibits a rapid falloff in the other ones. These results suggest the existence of a kind of solvent-polymer complex. Light scattering results are further analyzed. It is shown that in all the systems investigated the larger angle data are consistent with $I \sim (q^2 + \xi^{-2})^{-1}$. Determination of ξ^{-1} gives $\xi \sim C^{-3/4}$ in all cases. In solvents where ELAS is observed, the smaller angles are analyzed in terms of the Debye-Bueche scattering function $I \sim (q^2 + a^{-2})^{-2}$. The correlation length a varies as C^{-1}, which suggests that long-range fluctuations are determined by three-body interactions. Finally, all these results are discussed in the light of the different views expressed hitherto on physical gelation of atactic polymers.

Introduction

Solution properties of amorphous polymers have received a renewal of attention the past few years thanks to the theoretical breakthrough of scaling laws.[1] Different studies by scattering techniques have shown that such a theoretical approach accounts for chain behavior in a wide range of concentration and temperature. Yet for semidilute or moderately concentrated solutions, the theory pertains only as long as dimensions smaller than chain dimensions are dealt with. For distances of the order of the chain radius of gyration, light scattering experiments surprisingly reveal in some systems an enhanced low-angle effect that all the theories have failed to predict.[2-8] The appearance of this effect seems to depend on the method used for preparation of the solutions[5] and on the nature of the solvent.[9] Until recently, two major explanations have been put forward. On one hand, it has been claimed that this abnormal scattering could be due to the presence of islands of pure polymer in solution. This explanation is in conflict with the fact that the effect exists in very good solvents.[2] On the other hand, density fluctuations due to chain reptation have been taken into consideration. This statement cannot account for the total absence of effect in some solvents.[9]

While heterogeneities undoubtedly exist and are solvent-dependent, their origin is still puzzling when only considering a completely disordered polymer.

In the light of the discovery by Tan el al.[10] of atactic polystyrene's (aPS) ability to form physical gels, Guenet et al.[9] have suggested that enhanced low-angle scattering and gelation would be different manifestations of the same phenomenon. They have in particular shown that when a polymer-solvent couple can physically gel, the enhanced low-angle scattering is observable at room temperature and

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