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Functional Form for the Stress Relaxation Moduli of Binary Blends Consisting of Nearly Monodisperse Polymers and the Effect of Tube Size Enlargement. 1

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ABSTRACT: It has been concluded that the tube renewal process is negligible in (nearly) monodisperse polymers from the successful line-shape analyses of the viscoelastic spectra in terms of the proposed general theory (the monodisperse theory). In the case of binary blends, however, it is clearly visible in the measured spectra that the stress anisotropy in the regions of a long-chain tube, where entanglements with the short chains occur, relaxes as the short chains reptate away (referred to as the *regional* tube renewal or constraint release process). (Note: The word "regional" is added to distinguish the process considered here from the tube renewal or constraint release process, which involves the whole polymer chain and is often treated as a "Rouse tube" motion.[18-21]) A related phenomenon is the tube size enlargement effect, which can be observed very clearly in the terminal region of the long-chain component. Considering the regional constraint release process, a functional form for the stress relaxation moduli of binary blends (the binary theory) was previously proposed in brief. Here, the binary theory is described in detail. Specifically the effect of tube size enlargement is analyzed. The results of the analyses are in good agreement with the theoretical predictions. The relations between the monodisperse theory and the binary theory are discussed in light of the present and previous data analyses.

I. Introduction

On the basis of the Doi–Edwards theory,[1-4] a general linear viscoelastic theory for monodisperse flexible linear polymer melts and concentrated solutions (also referred to as the monodisperse theory below)[5] has been developed by including the chain contour length fluctuation effect and two additional relaxation processes: the Rouse motion of an entanglement strand (assuming the entanglement points are fixed in the short time region) and the chain slippage through entanglement links. The theory has been very successful in describing quantitatively the line shapes of the linear viscoelastic relaxation spectra of nearly monodisperse polystyrene melts[6,7] and concentrated solutions[8] and explaining the universal observations: the molecular weight (MW) dependence of the zero-shear viscosity and the steady-state compliance and their respective transition points, M_c and M_c'.[5-8] It has also been shown that the theory correlates quantitatively the viscoelasticity data and the diffusion data.[9]

An important conclusion derived from the successful comparisons of the monodisperse theory and the experimental results of polymer viscoelasticity is that the tube renewal (or constraint release) process is negligible in a monodisperse system to MW as low as $1.24M_e$. This conclusion has been physically explained by the fact that the number of entanglement strands per cubed tube diameter, n_t, which has been shown to be topologically a universal constant, is quite large ($\sim$17).[10]

In the case of binary blends consisting of two far separated monodisperse components, however, it is clearly visible in the measured spectra that the stress anisotropy in the region of a long-chain tube, where entanglements with the short chains occur, relaxes as the short chains reptate away (the regional constraint release process). As early as 1983,[11] we have recognized this effect and by including it proposed a functional form for the stress relaxation moduli, $G(t)$, for binary blends. Our functional form was published as a note in ref 6[12] with some preliminary experimental results. In the Appendix of ref 8, it was shown how the functional form can be reduced to that for a concentrated solution (denoted here as $G_s(t)$) consisting of a high MW polymer with MW $\gg M_e$ (as the polymer) and a low MW polymer with MW $< M_e$ (as the solvent). The high MW part of the $G_s(t)$ function is identical with that for the pure monodisperse melt as the MW is normalized with respect to the entanglement MW of the concentrated solution, M_e', given as

$$M_e' = M_e W_H^{-1} \tag{1}$$

where M_e is the entangle MW of the pure melt and W_H is the weight fraction of the high MW component. And the low MW part of $G_s(t)$ is described by the Rouse theory of a free chain.[13] The line shapes of the linear viscoelastic spectra of a series of concentrated polystyrene solutions have been very successfully analyzed in terms of the $G_s(t)$ function. It has been shown from the analyses that within experimental error the friction factor (K) in the Rouse part (for the low MW chains) and in the general theory part (for the high MW chains, with M_e' given by eq 1) are identical.[8] This strongly supports that the general theory has bridged the gap between the Rouse theory and the Doi–Edwards theory.

On the basis of the study, it was first pointed out[8] that in a binary blend consisting of a high MW (M_H) monodisperse component and a low MW (M_L) monodisperse component, both MWs being greater than M_e, tube size in the terminal region associated with the high MW component should enlarge gradually with decreasing M_L (at

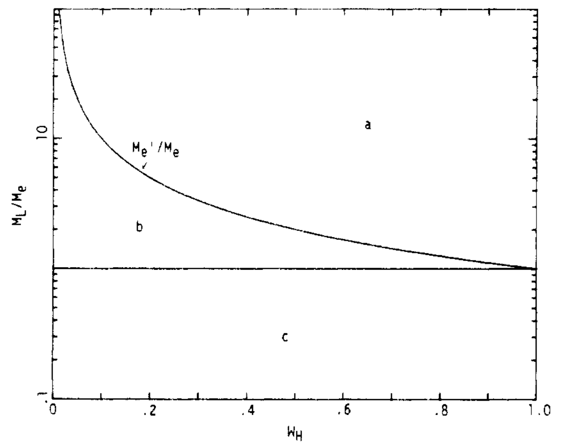

Figure 1. Boundaries of the three regions, a, b and c (see the text), in the plot of M_L/M_e vs W_H.

constant W_H) to a limiting value, namely, the value in a concentrated solution (i.e., M_e' given by eq 1, for the case of $M_L < M_e$).

Here the proposed functional form for the stress relaxation moduli of binary blends (referred to as the binary theory below) is described in detail. Specifically the effect of tube size enlargement is analyzed. The results of analyses are in good agreement with the theoretical predictions. The relations between the monodisperse theory and the binary theory are discussed in light of the previous and present data analyses.

II. $G(t)$ Functional Form for a Binary Blend

In order to extend our understanding of polymer dynamic behavior from the monodisperse case to the case of broad molecular weight distribution (MWD), we consider binary blend systems consisting of a high MW monodisperse component and a low MW monodisperse component. For our present discussion, depending on the values of M_L and W_H, three regions, a, b, and c, as shown in Figure 1 can be defined as (M_H is assumed to be very large)

(a) $M_H > M_L > M_e' > M_e$

(b) $M_H > M_e' > M_L > M_e$

(c) $M_H > M_e' > M_e > M_L$

where M_e' as given by eq 1 is the MW of the entanglement strand linking the high MW chains.

Now we are particularly interested in the cases of $M_H \gg M_L$, which occur in the a region. On the basis of the well-tested monodisperse theory, the conclusion that the tube renewal process is negligible in a monodisperse system, and the observation that in a binary blend the regional constraint release process occurring to the high MW component is caused by the relatively fast reptation motion of the low MW component, we have proposed a functional form of $G(t)$ for binary blends:

$$G(t) = G_N[1 + \mu_A(t/\tau_A)]\{W_L[1 + \tfrac{1}{4}\mu_X(t/\tau_X{}^L)] \times [B^L\mu_B(t/\tau_B{}^L) + C^L\mu_C(t/\tau_C{}^L)] + W_H[W_L\mu_T(t/\tau_T) + W_H][1 + \tfrac{1}{4}\mu_X(t/\tau_X{}^H)][B^H\mu_B(t/\tau_B{}^H) + C^H\mu_C(t/\tau_C{}^H)]\} \tag{2}$$

In eq 2, G_N is the plateau modulus of a monodisperse melt and is given as

$$G_N = 4\rho RT/5M_e \tag{3}$$

$\mu_A(t/\tau_A)$, shared by both the high and low MW components, is the Rouse motion of an entanglement strand (entanglement assumed fixed at $t < \tau_A$) and is given as[5,6,15]

$$\mu_A(t/\tau_A) = \sum_P^{N_e-1} \exp(-t/\tau_A{}^P) \tag{4}$$

with

$$\tau_A{}^P = \frac{K\pi^2}{24\sin^2(\pi P/2N_e)}\frac{M_e{}^2}{N_e{}^2} \tag{5}$$

and

$$K = \zeta b^2 N_0{}^2/kT\pi^2 M^2 \tag{6}$$

where N_e is the number of Kuhn segments of an entanglement strand and ζ, b, and M/N_0 ($=M_e/N_e$) are, respectively, the friction constant, length, and mass associated with each Kuhn segment.

The W_L-dependent term inside the braces of eq 2 represents the remaining (after the $\mu_A(t/\tau_A)$ process) three intrinsic relaxation processes associated with the low MW component: the chain slippage through entanglement links, $\mu_X(t/\tau_X)$: the chain contour length fluctuation, $\mu_B(t/\tau_B)$; and the reptational process corrected for the chain contour length fluctuation effect, $\mu_C(t/\tau_C)$. Because the tube renewal process is negligible in a monodisperse system, $\mu_X(t/\tau_X)$, $\mu_B(t/\tau_B)$, and $\mu_C(t/\tau_C)$ for the low MW component in a binary blend are the same as those for a monodisperse system.[5,6] The relaxation processes are given as (with the superscripts omitted)

$$\mu_X(t/\tau_X) = \exp(-t/\tau_X) \tag{7}$$

with

$$\tau_X = 0.55KM_eM \tag{8}$$

$$B = (M_e/M)^{1/2} \tag{9}$$

$$C = 1 - B \tag{10}$$

$$\mu_B(t/\tau_B) = \sum_{P_{\text{odd}}} \frac{8}{\pi^2P^2}\exp(-P^2t/\tau_B) \tag{11}$$

with

$$\tau_B = (1/3)KM^2 \tag{12}$$

and

$$\mu_C(t/\tau_C) = \sum_{P_{\text{odd}}} \frac{8}{\pi^2P^2}\exp(-P^2t/\tau_C) \tag{13}$$

with

$$\tau_C = K(M^3/M_e)[1 - (M_e/M)^{1/2}]^2 \tag{14}$$

Although the intrinsic relaxation of a low MW chain is not affected by the presence of the high MW component in a blend, the reverse is not so. For an easy explanation, we can assume that the long (high MW) chains are basically immobile in the reptational time frame of the short (low MW) chains in the case of $M_H \gg M_L$. In a step strain stress relaxation process, as short chains disentangle and reptate away from a long chain, the stress anisotropy on the long-chain tube in the regions entangled with the short chains will be relaxed (the regional constraint release process) before the long chain by reptation completes the relaxation of its entire tube stress anisotropy at $t > \tau_C{}^H$. The sum of the regions on a long chain that entangle with other long chains is statistically proportional to the weight fraction (equivalent to the volume fraction here) of the high MW component (W_H). Thus, at the end of the regional constraint release process caused by disentanglement of the short chains, the remaining stress anisotropy distributed over a long-chain tube is proportional to W_H.

At this point, the bulk (plateau) modulus (associated with the high MW component) is reduced to $G_N W_H^2$. The $W_L W_H$-dependent term (the $\mu_T(t/\tau_T)$ process) in eq 2 represents the stress relaxation associated with the regional constraint release process on the long-chain tube. Here the relaxation form for $\mu_T(t/\tau_T)$ is phenomenologically assumed to be a single-exponential decay (see the Appendix of paper 2)

$$\mu_T(t/\tau_T) = \exp(-t/\tau_T) \tag{15}$$

with a characteristic time τ_T, which should be proportional to the reptation time of the low MW component:

$$\tau_T = S\tau_C^L \tag{16}$$

In comparing the theoretical $G(t)$ form with the measured spectrum line shapes as done in paper 2, S is used as an adjustable parameter. Theoretically, S should be greater than one.

At $t > \tau_T$, the remaining stress (anisotropy) on a long-chain tube (proportional to W_H) is to be relaxed *mainly* by the intrinsic $\mu_C(t/\tau_C^H)$ process of the long chain (inside the W_H^2-dependent term of eq 2). If there is not the tube size enlargement effect as described in the following section, τ_C^H is given by eq 14 with $M = M_H$. As we shall see, the tube size enlargement effect occurs for $M_H \gg M_L$. In this case, eq 13 and 14 can still describe the terminal relaxation of the high MW component, if M_e is replaced by an effective M_e'' value, which is larger than M_e.

While the above-described relaxation processes are occurring, the other intrinsic relaxation processes of the long chains, $\mu_X(t/\tau_X^H)$ and $\mu_B(t/\tau_B^H)$, are also taking place. $\mu_X(t/\tau_X^H)$ and $\mu_B(t/\tau_B^H)$ are given by eq 7–9, 11, and 12 with M replaced by M_H. Note that the relaxation time τ_X and the relaxation strength B (and C) can be affected by the tube size enlargement effect but not the relaxation time τ_B (see eq 12). For all the data analyses below and in paper 2, the tube size enlargement effect in the $\mu_X(t/\tau_X^H)$ region is assumed not occurring. For the M_H/M_L ratios (large but not extremely large) of the systems under study, this should be a good assumption.

In the c region, M_L is smaller than M_e. Because it experiences no entanglement, the molecular dynamics of the low MW component is best described by the Rouse theory for a free chain.[8] And $\mu_T(t/\tau_T)$ decays to zero very quickly and merges into the $\mu_A(t/\tau_A)$ process. As shown in the Appendix of ref 8, eq 2 can be reduced to the $G(t)$ form for a monodisperse concentrated solution, which is identical with that for a monodisperse melt, as the MW is normalized with respect to M_e' as given by eq 1. In the c region, as well supported by the quantitative line-shape analyses of the measured linear viscoelastic spectra, the relaxation process of an entanglement strand linking long chains can be described in terms of the Rouse motion ($\mu_A(t/\tau_A)$). But not so for $\mu_T(t)$ in the a and b regions. We have found a box-type relaxation function for $\mu_T(t)$ similar to eq 15 works best (see the Appendix of paper 2).

The basic physical picture we originated in proposing the $G(t)$ functional form for binary blends has been used by Struglinski and Graessley[11] to explain their experimental results of binary blends of linear polybutadiene and later by Doi et al.[14] and Pearson[17] in considering the dynamics of polymers in polydisperse melts. This basic picture is obviously very different from the tube renewal models proposed earlier by several people.[18–21] Those tube renewal models basically assumed that each disentanglement randomized *right away* the orientation of a primitive path step of the tube and that the whole tube behaved as a "Rouse tube". The validity of those models has been questioned on the grounds that the number of entanglement strands per cubed tube diameter, n_t (which has been shown to be a universal constant), is quite large (~17).[10] Furthermore, those models do not appear capable of describing the line shapes of the linear viscoelastic spectra of monodisperse melts and binary blends as we have done previously[5–8] and in paper 2. Struglinski and Graessley,[11,16] Doi et al.[14] and Pearson,[17] while adopting the present basic picture, on which the $G(t)$ functional form for binary blends is based, have described the constraint release process (caused by the low MW component) between two adjacent entanglement points linking long chains as a Rouse-like process, whose basical mechanism is similar to that in the "Rouse tube" models. In paper 2, we shall show the reasons why we do not take this view of a Rouse tube process for $\mu_T(t)$ in the W_H range of the samples under study ($W_H \geq 0.25$).

III. Tube Size Enlargement

The linear viscoelastic relaxation spectra of an extensive series of blend samples in the c region (equivalent to concentrated solutions) have been well analyzed quantitatively in terms of a combination of the Rouse theory for the low MW component (free chains)[13] and the general linear viscoelastic theory for the high MW component.[8]

An important result from that study was the proposal of the tube size enlargement effect, which had a strong implication in the blending law (in the a and b regions). The basic idea of the tube size enlargement effect, mainly occurring in the terminal region associated with the high MW component, was derived by considering the tube sizes in the two limiting cases: the monodisperse melt[5–7] and concentrated solution.[8]

In the c region, because of dilution by the low MW component, the MW of an entanglement strand (M_e') linking the high MW chains increases. For polystyrene, it has been shown that eq 1 is well followed. As M_L increases beyond M_e, the system transits from the c region to the b region. The short chains begin to have entanglement with the long chains and among themselves. Here, there should be at least a subregion close to the crossover line, where, because the MW of the low MW component is sufficiently low, it basically serves as a solvent to the high MW component in its terminal region. And the MW of an entanglement strand linking the high MW chains is basically given by eq 1. In another extreme, when the low MW component converges into the high MW component (i.e., becoming a monodisperse system consisting of the high MW component only), the regional constraint release effect that could be caused by the low MW component disappears. This has been well concluded in the study of the monodisperse systems as reported previously.[5–7] In between, the entanglement MW at a certain W_H value (denoted as M_e'' here) in the terminal region associated with the high MW component should have a value between M_e and M_e' and increases gradually to M_e' with decreasing M_L.[8]

If M_H is sufficiently higher than M_L, it is conceivable that M_e'' being greater than M_e should have an effect to the quantities B^H and C^H and the relaxation time τ_C^H. Consider a blend consisting of two nearly monodisperse components: F80 and F4 (F80 M_w = 775 000 and F4 M_w = 44 900), which are used in the experimental work of this paper. The theoretical ratios between the relaxation times (before the tube size enlargement effect caused by F4 is included) are $\tau_C(\text{F80}):\tau_B(\text{F80}):\tau_C(\text{F4}) = 1.9 \times 10^4:1.5 \times 10^2:1$. In other words, on the time scales of the $\mu_B(t/\tau_B)$ and $\mu_C(t/\tau_C)$ processes of F80, the F4 chains have already disentangled from and reentangled with the F80 chains many many times. In such a case, the mobility of the F4

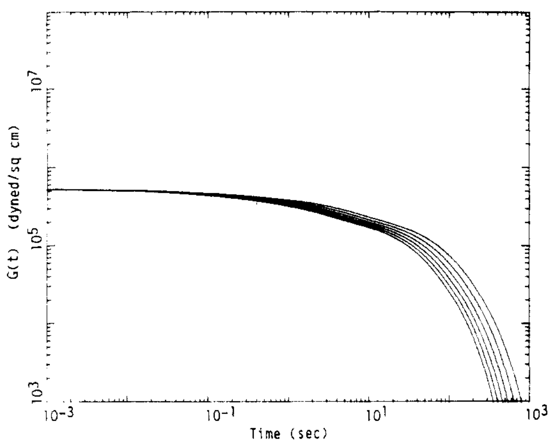

Figure 2. $G(t)$ curves calculated for F80/Y = 50/50 (convoluted with the three-component MWD of F80 as extracted from the line-shape analysis of its linear viscoelastic spectrum in the pure melt state; see Figure 7 of ref 5) from only the $W_H{}^2$ term of eq 2 with M_e replaced by $M_e'' = 1M_e$, $1.2M_e$, $1.4M_e$, $1.6M_e$, $1.8M_e$, and $2M_e$ to show the effect of tube size enlargement.

chains causes the MW of the entanglement strands on the F80 chains to increase to a certain effective value, M_e'' (a value "averaged" over the contributions from entanglement with other F80 chains and F4 chains). Phenomenologically, we can treat M_e'' as a parameter with some effective value to substitute for M_e in eq 9, 10, and 14. Note that $\tau_B{}^H$ is independent of the entanglement MW (see eq 12).

To show how the tube size enlargement effect causes the $G(t)$ line shape of a F80/Y = 50/50 blend sample (Y is a monodisperse sample with a MW sufficiently smaller than that of F80 and greater than M_e) to change in the long-time region, we calculate the $G(t)$ curves using only the $W_H{}^2$ term of eq 2 (without $\mu_A(t/\tau_A)$ and convoluted by the three-component MWD shown in Figure 7 of ref 5) with M_e replaced by $M_e'' = 1M_e$, $1.2M_e$, $1.4M_e$, $1.6M_e$, $1.8M_e$, and $2M_e$ (used in eq 9, 10, and 14). According to eq 1, $2M_e$ is the maximum M_e'' value allowed for a 50/50 blend. As shown in Figure 2, one observes a gradual shift of the terminal relaxation zone to the shorter time corresponding to the increase of the M_e'' value. The effective M_e'' value increases as the MW of Y decreases. Clearly we should be interested in the magnitude of shifting of the terminal relaxation zone to the shorter time as the MW of Y decreases. Note that the plateau modulus in Figure 2 is reduced by a factor of 4 ($=W_H{}^2$) from its value in the pure monodisperse state.

We have measured the linear viscoelastic relaxation spectra of the blend samples: F80/NBS (NBS M_w = 179000), F80/F10 (F10 M_w = 100000), F80/F4, F35/F10 (F35 M_w = 355000), F35/S8 (S8 M_w = 83000), F35/S6 (S6 M_w = 60400), and F35/F4 at two different concentrations (F80/Y or F35/Y = 75/25 and 50/50). All the polymer components have nearly monodisperse MWDs. Either right before or right after the measurement of a blend sample, the pure sample of the high MW component (F80 or F35) in the blend was also measured under the same condition. Thus, the small drift of the controlled temperature from day to day can be eliminated. From such pairs of experimental results, we can determine the time (or frequency) shifting factors by superposing the two $G(t)$ (or $G'(\omega)$ and $G''(\omega)$) curves of a pair in the terminal region. In such a superposition between a pure melt sample and a blend sample, the shifting factors along the modulus coordinate remain well equal to $W_H{}^2$. The $W_H{}^2$ dependence of the modulus is also well obeyed in the concentrated solution systems of polystyrene (region c) as reported previously.[8]

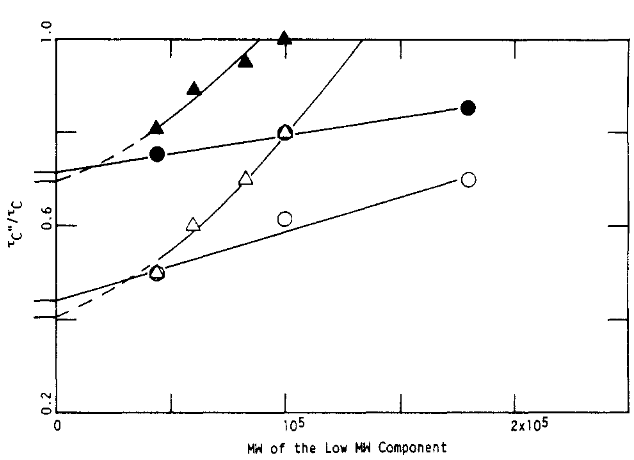

Figure 3. Time shifting factor, τ_C''/τ_C, as a function of the MW of the low MW components in the binary blends: F80/Y = 75/25 (●); F80/Y = 50/50 (○); F35/Y = 75/25 (▲); F35/Y = 50/50 (△). The horizontal lines on the vertical axis indicate the theoretical τ_C'/τ_C values calculated from eq 17 corresponding to the four series of blend samples.

In Figure 3, we show the time shifting factor in the terminal region (dominated by the $\mu_C(t/\tau_C)$ process; the time shifting factor is equivalent to the apparent ratio of the relaxation times of the $\mu_C(t/\tau_C)$ process, denoted as τ_C''/τ_C, where τ_C'' is for the binary blend and τ_C for the pure monodisperse component) as a function of the MW of Y at blend percentage ratio of F80/Y = 75/25 and 50/50. Indeed the τ_C''/τ_C ratio decreases in an orderly way as the MW of Y decreases. Very significantly, the extrapolated values of τ_C''/τ_C to the zero MW of Y (denoted as τ_C'/τ_C) are in close agreement with the ratio values between the two terminal relaxation times associated with a concentrated solution (τ_C') and a pure melt (τ_C), which can be calculated from the following equation:

$$\tau_C'/\tau_C = M_e[1 - (M_e'/M)^{0.5}]^2/M_e'[1 - (M_e/M)^{0.5}]^2 \quad (17)$$

Equation 17 results from eq 14 being applied to a pure melt and a concentrated solution (see eq 1). Note that the values of τ_C'/τ_C obtained from the extrapolation correspond to the case where the frictional factor, K, of eq 14 is not affected by the presence of the low MW component in region c (i.e., the case of constant free volume).

The close agreement between the calculated τ_C'/τ_C values and those obtained from the extrapolation of the measured τ_C''/τ_C values joins the previous data analyses supporting the quantitative correctness of the theoretical forms for τ_C' and τ_C (eq 14).[5-9]

In Figure 4, we compare the measured $G(t)$ curves of F80, F80/NBS = 50/50, F80/F10 = 50/50, and F80/F4 = 50/50 with the calculated $G(t)$ curves of the pure melt and concentrated solution (at 50/50) of F80. Both the calculated and measured $G(t)$ curves of F80 have been reduced by a factor of 4 in the modulus coordinate so that they can be readily compared with the results of the blend samples. By superposing Figure 4 on Figure 2 in the terminal region, we can estimate the effective M_e'' values for different MWs of Y. The obtained results are shown in Figure 5. The M_e' value obtained by extrapolating the M_e'' values to the zero MW of Y is in good agreement with the expected value: $2M_e$.

The tube size enlargement effect mainly occurs in the long-time region associated with the high MW component. Note that a constant M_e'' value is used over the entire time domain in the calculation of each theoretical curve shown in Figure 2. Apparently this is a good approximation, as it can be seen that the $G(t)$ values in the short-time region

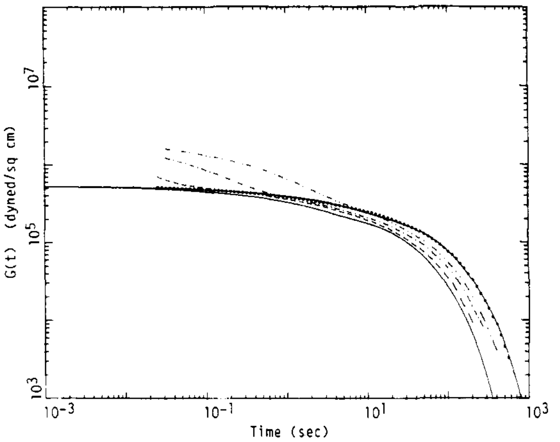

Figure 4. Comparison of the calculated and measured $G(t)$ curves: (a) upper solid line, calculated for the F80 melt; the modulus is reduced by a factor of 4 for comparison purpose; (b) lower solid line, calculated for the F80/Y = 50/50 concentrated solution; (c) (···) measured results of the F80 melt, the modulus is reduced by a factor of 4 for comparison purpose; (d) (–···–) measured results of the F80/NBS = 50/50 blend; (e) (–··–) measured results of the F80/F10 = 50/50 blend; (f) (- - -) measured results of the F80/F4 = 50/50 blend.

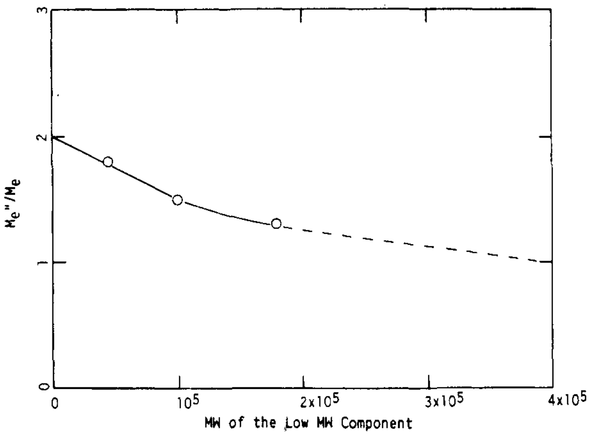

Figure 5. M_e''/M_e values as a function of the MW of the low MW component in the F80/Y = 50/50 blends, obtained from comparison of Figures 2 and 4.

are virtually not affected by the change of the M_e'' value and that in the long-time region the measured curves in Figure 4 can be described very well by theoretical curves calculated this way. More about this is described in the line-shape analyses of the viscoelastic spectra in paper 2.

The relaxation time ratios (τ_C''/τ_C) of F35/Y at concentrations of F35/Y = 75/25 and 50/50 vs the MW of Y are also shown in Figure 3. At F35/F10 = 75/25 no shifting in time is observed. Based on the data of F35/Y = 50/50, no shifting in time is expected if the MW of Y is greater than 130 000 ($\ll$MW of F35). In the case of F80/Y = 50/50 as shown in Figure 3, the τ_C''/τ_C ratio is one when the MW of Y is greater than ~400 000 ($\ll$MW of F80). In a monodisperse system, if the tube renewal process affected the terminal relaxation as proposed in several "Rouse tube" models,[18-21] the τ_C''/τ_C ratio would be dependent on the MW of Y regardless of the region of the MW of Y. Here we have observed that in a X/Y blend (X being the high MW component) there is a MW region of Y smaller than the MW of X, in which the τ_C''/τ_C ratio is equal to 1 and independent of the MW of Y. We notice that the τ_C''/τ_C ratios of the F35/Y systems rise much faster to reach the value of 1 with increasing MW of Y than those of the F80/Y systems. This is expected because the F35/Y systems approach monodispersity (at which the constraint release effect is negligible) earlier with increasing MW of Y than the F80/Y systems.

IV. The Relations to the Monodisperse Theory

The blending law as expressed by eq 2 has been proposed on the basis of the monodisperse theory, which has been extensively well tested by the experimental results. Here and in paper 2, eq 2 has been successfully used to analyze the experimental results of binary blends in which the MW of the high MW component is considerably larger than that of the low MW component. Equation 2 should converge to the monodisperse theory as the binary blend approaches monodispersity. Theoretically, the binary blend can approach monodispersity in three different ways. (1) $W_L \rightarrow 0$: In this case, eq 2 reduces to the form of the monodisperse theory. (2) $W_H \rightarrow 0$: As in case 1, eq 2 reduces to the form of the monodisperse theory. (3) $M_H \rightarrow M_L$ (or $M_L \rightarrow M_H$): Equation 2 reduces to the form of the monodisperse theory, as $\mu_T(t/\tau_T)$ becomes equal to 1 and independent of time.

The first two ways are obvious. However, in the second way, one should recognize that the system will go through a state where there is no direct entanglement among the high MW chains in the dilute regime ($W_H < M_e/M_H$). The relaxation functional form in the long-time region associated with the high MW component should change to a form to reflect this expectation. Literature data suggest that in the long-time region the high MW chain behaves as a Rouse chain.[22] Even in the concentrated regime ($W_H > M_e/M_H$) of the case $M_H \gg M_L$, we have already observed the evolution of the relaxation functional form in the terminal region associated with the high MW component through replacing M_e in eq 9, 10, and 14 with an effective value, M_e''.

The third way requires some explanations. If the binary blend theory (eq 2) is valid, it has to become independent of W_H (or W_L) when $M_H = M_L$. This can only occur if $\mu_T(t/\tau_T)$ becomes independent of time and equal to 1. Hence, the binary blend theory and the monodisperse theory have to be consistent in the third way. $\mu_T(t/\tau_T)$ becoming 1 as $M_H = M_L$ suggests that when M_H and M_L are sufficiently close to each other, the linear additivity law for the contributions from the two components becomes applicable (put $W_L\mu_T(t/\tau_T) + W_H = 1$ in eq 2). This has been our conclusion based on extensive quantitative line-shape analyses of the linear viscoelastic spectra of nearly monodisperse samples in terms of the monodisperse theory.[5-8] As we have shown previously, here and in paper 2, the validity of the monodisperse theory and the binary blend theory is well supported by the experimental results. It is dictated that $\mu_T(t/\tau_T)$ becomes a constant (equal to one) as $M_H \rightarrow M_L$ (or $M_L \rightarrow M_H$). Therefore, there is a transition of $\mu_T(t/\tau_T)$ from being time dependent to being time independent. This transition corresponds to the observations (or conclusions) that the tube renewal process is negligible in a monodisperse system and that the regional constraint release process is effective in a binary blend, which we have pointed out early on.[5-7] Watanabe et al.,[22] on the basis of their analyses of relaxation times, have suggested a transition equivalent (or similar) to this.

V. Conclusion

This paper brings forth in more detail the description of the proposed $G(t)$ functional form for binary blends and its comparison with experimental results than was presented previously as a note in ref 6[12] and in the Appendix of ref 8.

On the one hand, as M_L becomes smaller than M_e, the $G(t)$ functional form reduces to that for a concentrated solution, which is identical with the monodisperse theory (the general linear viscoelastic theory), as MW is normalized with respect to M_e' given by eq 1.[8]

On the other hand, as a binary blend becomes monodisperse in three ways, the $G(t)$ functional form transforms into the monodisperse theory (for a melt). For $M_H \rightarrow M_L$ or $M_L \rightarrow M_H$, a transition of $\mu_T(t/\tau_T)$ from being time dependent to being time independent is indicated. This transition corresponds to the conclusion that the tube renewal process is negligible in a monodisperse system and the regional constraint release process is effective in a binary blend.

In a previous report,[8] based on the tube sizes in monodisperse melts and concentrated solutions, we have proposed the tube size enlargement effect, which mainly occurs in the terminal region associated with the high MW component in a binary blend. Here, the experimental results of binary blends in the terminal region of the high MW component are compared with the calculated $G(t)$ curves by using different M_e'' values and the measured spectra of the pure monodisperse melts of the high MW components. The comparison allows us to quantify the tube size enlargement effect. The τ_C'/τ_C and M_e'/M_e values obtained from extrapolating the obtained τ_C''/τ_C and M_e''/M_e values as M_L becomes zero are in good agreement with the theoretical values. These results join the previous studies supporting the validity of the general linear viscoelastic theory as applied to monodisperse melts and concentrated solutions and justifies the phenomenological description of the tube size enlargement effect occurring in binary blends.

The proposed $G(t)$ functional form (the blending law) greatly advances our understanding of the polymer dynamics in binary blends. This will be further demonstrated in the line-shape analyses of the linear viscoelastic spectra of binary blends as reported in the accompanying paper.

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Line-Shape Analyses of the Linear Viscoelastic Spectra of Binary Blends in Terms of the Proposed $G(t)$ Functional Form. 2

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ABSTRACT: The linear viscoelastic spectra of a series of binary blends consisting of nearly monodisperse polymers have been measured and analyzed in terms of the proposed binary theory. The unique features of the line shapes of the spectra are quantitatively described by the proposed theory in a consistent manner. Very significantly, it is shown that the reptation time of the low molecular weight (MW) component in a binary blend is identical with that in its pure melt state. This is in agreement with the expectation from the conclusion that the tube renewal process is negligible in a monodisperse polymer. The characteristic time associated with the regional constraint release process, $\mu_T(t/\tau_T)$, is about seven times larger than the reptation time of the low MW component regardless of the MWs and weight fractions of the components. This indicates that the $\mu_T(t/\tau_T)$ process should not be described by the "Rouse tube" motion. In the terminal region of the high MW component, the tube size enlargement effect is included in the line-shape analyses by using an effective entanglement MW (M_e''). The extrapolated values of M_e'' to the concentrated solution cases ($M_L \rightarrow 0$) are in good agreement with the theoretical values ($M_e' = M_e W_H^{-1}$).

I. Introduction

A functional form for the stress relaxation moduli $G(t)$ of blends consisting of two (nearly) monodisperse polymers has been proposed[1] (referred to as the binary theory below). This functional form is built upon the monodisperse theory,[2] which has been extensively and quantitatively tested with experimental results.[3-8] Along with the proposition of the binary theory, specifically we have pointed out the following three effects, which were described in paper 1:[1] the relative fast reptation motion of the low molecular weight (MW) component causes the regional constraint release process on the high MW chain tube; tube size enlargement occurs (mainly) in the terminal region associated with the high MW component; transition of $\mu_T(t/\tau_T)$ from being time dependent to being time independent takes place as $M_H \rightarrow M_L$ or $M_L \rightarrow M_H$.

Polymer dynamics in a binary blend are much more complicated than those in a monodisperse system. In a

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