this choice, as is trivially shown[43] by using $(N_m/M)^{-1} = \exp[\ln(N_m/M)]$ and by choosing $M' = \exp(\sigma^2)M$ instead of M.
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Nonlinear Viscoelasticity of Semidilute Polystyrene Solutions. Effect of Molecular Weight Distribution

Kunihiro Osaki,* Eiichi Takatori, and Michio Kurata

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan.
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ABSTRACT: The nonlinear viscoelasticity of an entangled polymer may be represented by a function $h(t,\gamma) = G(t,\gamma)/G(t,0)$, where $G(t,\gamma)$ is the relaxation modulus at the magnitude of shear γ. The function $h(t,\gamma)$ is unity at $t = 0$, decreases with time, and levels off at a time τ_k independent of γ to a value $h(\gamma)$, which is well compared with the prediction of the tube model theory for polymers with sharp molecular weight distributions. Here we measured the function $h(t,\gamma)$ for semidilute polystyrene solutions containing polymers with molecular weights M_S and M_L ($>M_S$) by mass concentrations c_S and c_L, respectively; $10^{-4}M_L = 842$ or 448; $20 \leq 10^{-4}M_S \leq 289$; $c_L = 0.038$ g cm^{-3} and $1 \leq c_S/c_L \leq 2.6$. When $M_L \geq 4.7M_S$ the characteristic time τ_k was determined by M_L and the total concentration, $c_S + c_L$, and was independent of M_S or c_L/c_S. This result may be consistent with the prediction of the tube model theory. When M_S was smaller than the entanglement molecular weight corresponding to the total concentration, the nonlinear function $h(\gamma)$ was equal to that of monodisperse polymers. When M_S was larger, $h(\gamma)$ was larger than expected. The result may imply that the short chains have more effect than retarding the overall motion of long chains even at times much longer than the relaxation time of the short chains.

Introduction

The effect of molecular weight distribution (MWD) has long been one of the difficult problems in the study of polymer viscoelasticity.[1] Recent development in the theory of polymer chain entanglement based on the tube model[2-4] has given a big impact on this problem and the effect of MWD on linear viscoelasticity is now studied in connection with the molecular motion in entangled systems.[5-13] It is hoped that studies of polymers with a bimodal MWD (i.e., a blend of two samples with different molecular weights) may be used to assess the assumptions of the theoretical model of entangled polymer and to attain a better understanding of molecular motion. As for the nonlinear viscoelasticity, the tube model theory gives a simple description of the effect of varying strain on the relaxation modulus based on the molecular motion after an instantaneous deformation of the entangled polymer.[3,4] There are a few attempts to modify the theory to include the effect of MWD.[14,15] On the other hand, experimental studies have mostly been concerned with the flow properties at a constant rate of shear.[16] Even the result of elaborate studies on polymers with a bimodal MWD[17,18] is not very convenient for analysis under light of the new theory of entanglement. The purpose of the present study is to provide data of the strain-dependent relaxation modulus for solutions of polymers with a bimodal MWD. The strain-dependent relaxation modulus, $G(t,\gamma)$, is the ratio of the shear stress to the magnitude of shear, γ, applied to the material at time $t = 0$. The limit at $t \to 0$ of $G(t,\gamma)$ is the linear relaxation modulus, $G(t)$. We define two functions to represent the nonlinear behavior

$$h(t,\gamma) = G(t,\gamma)/G(t) \tag{1}$$

$$h(\gamma) = \lim_{t\to\infty} h(t,\gamma) \tag{2}$$

According to the tube model theory,[2-4] the gross shape of a polymer chain varies in two processes, the equilibration process of the fluctuation of chain contour length and the reptation process. The characteristic times, τ_B and τ_C, of the respective processes vary with the number of entanglement per chain, N, as follows:[2-4,19,20]

$$\tau_B \propto \tau_A N^2 \tag{3}$$

$$\tau_C \propto \tau_A N^{3.5} \tag{4}$$

where τ_A is the relaxation time of an entangled strand. In most cases, τ_C is much larger than τ_B. On application of a large strain to the material,[3,4] the chain is elongated and oriented to a certain direction on average. The tensile force along the chain relaxes as the contour length equilibrates and accordingly a large portion of stress relaxes with the characteristic time τ_B. At times sufficiently longer than τ_B, the relaxation modulus is predicted to be factored as

$$G(t,\gamma) = G(t)h(\gamma) \qquad (t \gg \tau_B) \tag{5}$$

The succeeding relaxation is caused by the reptation, or the disengagement of the chain from the oriented tube region, with the characteristic time τ_C. The function $h(\gamma)$ can be calculated from the increase of chain contour length on deformation of the material and is independent of the material. The predicitions are in good accord with the observation for polymer solutions with sharp MWD,[21-26] as explained below.

A typical example of $G(t,\gamma)$ is shown in Figure 1 for a solution in Aroclor 1248 of a polystyrene with sharp MWD: $M = 2.89 \times 10^6$ and $c = 0.076$g cm^{-3} at 30 °C. The curves at the bottom represent the function $h(t,\gamma)$. The $G(t)$ values in the long-time range marked C can be fitted with an asymptotic equation

$$G(t) = G_1 \exp(-t/\tau_1) \tag{6}$$

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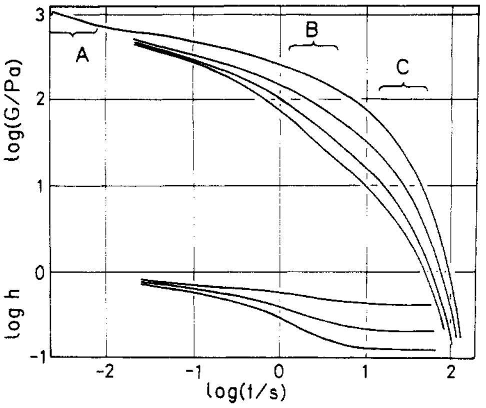

Figure 1. Strain-dependent relaxation modulus $G(t,\gamma)$ and function $h(t,\gamma)$ for the solution of polystyrene with a sharp MWD: $M = 2.89 \times 10^6$ and $c = 0.076$ g cm^{-3}.

wherefrom the longest relaxation time, τ_1, and the corresponding relaxation strength, G_1, may be evaluated. The function $h(t,\gamma)$ is independent of t at long times. Thus the same value of τ_1 is applicable to describe the relaxation at finite strains and this is factored as eq 5.[21] The development of nonlinearity is represented by the decrease of function $h(t,\gamma)$ in the range marked B. The time τ_k at which the function levels off marks the end of this process. This time is independent of γ. For solutions of polystyrene and poly(α-methylstyrene), with varying molecular weights, M, and concentrations, c, the function $h(t,\gamma)$ was found to be the same for all the solutions studied if it was regarded as a function of reduced time, t/τ_k.[25] The limiting value, $h(\gamma)$, of $h(t,\gamma)$ at long times was in good agreement with the theoretical value.[21] The characteristic times, τ_1 and τ_k, varied with M and c in the same manner as the theoretical quantities, τ_C and τ_B, do in the theory (eq 3 and 4).[22-24]

In this study, we investigate the properties of semidilute polystyrene solutions containing polymers with molecular weights M_S and M_L ($>M_S$) by mass concentrations c_S and c_L, respectively. Subscripts S and L imply short and long chains, respectively. The concentration c_L will be sufficiently high so that the solution of monodisperse polymer with molecular weight M_L at concentration c_L has the properties of a well-entangled system. The total concentration, $c_S + c_L$, is denoted as c. For melts and concentrated solutions,[7-12] it is well-known that, when M_L is much larger than M_S, the linear viscoelasticity at long times is very similar to that for the solution of monodisperse polymer of molecular weight M_L with concentration c_L. For example, the relaxation modulus, $G(t)$, for the bimodal polymer at long times agrees with that for the monodisperse polymer after the time scale is changed properly. This fact is believed to imply that at long times most of the stress is supported by the entanglement network of the longer chains with the concentration c_L; the short chains only retard the relaxation of long chains. We study the nonlinear viscoelasticity and investigate the effect of the M_S component. Preliminary results have been published elsewhere.[27]

Materials and Method

The nonlinear viscoelasticity was studied for polystyrene solutions in Aroclor 1248. Six polystyrene samples with a sharp MWD were employed (see Table I). The solvent, Arochor 1248, is a polychlorinated biphenyl from Monsanto Chemical Co. The viscosity and density of the solvent and details of sample preparation were described elsewhere.[24]

The bimodal polystyrene solutions are listed in Table II. The concentration c_L for the high M component is always 0.038 g cm^{-2}.

Table I
Polystyrene Samples

code	$10^{-4}M_w$[a]	M_w/M_n[a]
F850[b]	842	1.17
F450[b]	448	1.14
F288[b]	289	1.09
batch 61124[c]	180	1.3
batch 61208[c]	95	1.10
batch 1a[c]	20	1.06

[a] Supplier's data. [b] Supplied from Toyo Soda Manufacturing Co., Ltd. [c] Supplied from Pressure Chemical Co.

Table II
Characteristic Times for Bimodal Systems

code[a]	τ_{1L}/s	τ_{1S}/s
289/3.8-842/3.8	490	48
180/3.8-842/3.8	350	12
95/3.8-842/3.8	240	1.2
20/3.8-842/3.8		
95/3.8-448/3.8	48	1.2
95/6-842/3.8	500	2.8
20/10-842/3.8		

[a] The code implies $(10^{-4}M_S)/[10^2c_S/(\text{g cm}^{-3})] - (10^{-4}M_L)/[10^2c_L/(\text{g cm}^{-3})]$.

At this concentration, the solutions of polymers with $M = 8.42 \times 10^6$ or 4.48×10^6 exhibit the typical behavior of entangled systems.[24] The first four samples are such that only M_S is varied and other quantities are kept constant: $M_L = 8.42 \times 10^6$ and $c_S = c_L = 0.038$ g cm^{-3}. The fifth sample, as compared with the third, is to examine the effect of varying M_L when other parameters are kept constant. The last two samples are examples for which c_S is larger than c_L. The entanglement molecular weights M_e estimated at concentrations of 0.076, 0.098, and 0.138 g cm^{-3} (corresponding to $c_S + c_L$ for the samples in Table II) are respectively 2.7×10^5, 1.9×10^5, and 1.2×10^5.[24] The short chains in the samples 20/3.8-842/3.8 and 20/10-842/3.8 may be assumed not to form the part of the entanglement network since $M_S < 2M_e$. The short chains in the other samples satisfy the condition $M_S > 2M_e$.

The stress relaxation was measured with a cone-and-plate relaxometer reported previously.[28] The linear relaxation modulus, $G(t)$, was evaluated from the data at the magnitude of shear, γ, less than 0.8. The strain-dependent relaxation modulus, $G(t,\gamma)$, was measured for $\gamma = 3$, 5, and 7. Measurements were performed at a few temperatures in the range from 10 to 30 °C, and the result was reduced to a reference temperature, 30 °C, with the method of reduced variables.[29] The dynamic complex modulus, $G^* = G'(\omega) + iG''(\omega)$, was measured with a cone-and-plate rheometer (Rheopexy Analyzer, Iwamoto Seisakusho Co., Kyoto). The magnitude of shear was 0.8 and the range of angular frequency, ω, was from 6.28×10^{-2} to 6.28 s^{-1}. Measurements were performed over the temperature range from 0 to 60 °C and the results were reduced to the reference temperature, 30 °C, with the method of reduced variables.

Linear Viscoelasticity Functions

The linear viscoelasticity functions are shown in Figures 2 and 3 for the series of solutions with varying M_S at constant M_L, c_S and c_L: the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, in Figure 2 and the relaxation modulus, $G(t)$, in Figure 3. The curves denoted a are for the solution with $M_S = M_L$, i.e., the 0.076 g cm^{-3} solution of the polymer with $M = 8.42 \times 10^6$. The curves a were obtained not by direct measurement but by changing the time (frequency) scale of the data for the 0.076 g cm^{-3} solution of the polymer with $M = 2.89 \times 10^6$ with the use of the relation that $\tau_1 \propto M^{3.5}$. The dashed curves are for the 0.038 g cm^{-3} solution of the polymer with $M = 8.42 \times 10^6$, i.e., $c_S = 0$.

The curves for bimodal systems exhibit the well-known features.[7-12] For example, the curve for the loss modulus

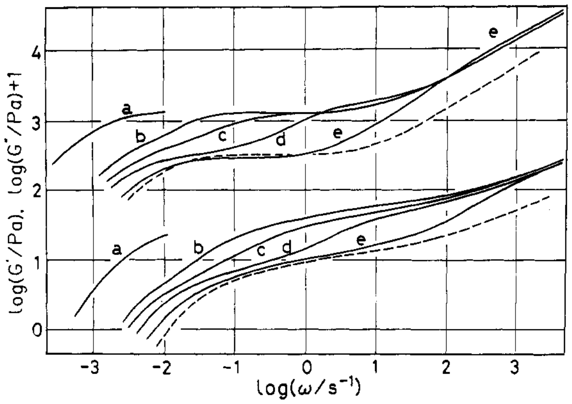

Figure 2. Real part G' and imaginary part G'' of complex modulus for solutions of polystyrene with a bimodal MWD: $M_L = 8.42 \times 10^6$ and $c_S = c_L = 0.038$ g cm^{-3}. $M_S/10^4 = 842$ (a), 289 (b), 180 (c), 95 (d), and 20 (e). Dashed lines are for solution of polystyrene with a sharp MWD: $M = 8.42 \times 10^6$ and $c = 0.038$ g cm^{-3}.

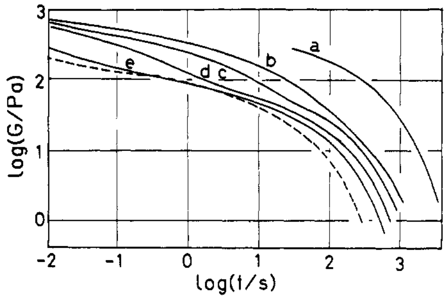

Figure 3. Linear relaxation modulus for the same polystyrene solutions as in Figure 2.

has an extra rise in the rubbery plateau region, and the rise moves to the higher frequency region as M_S decreases. In the case when $M_S = 2.0 \times 10^5$, the rise, if any, is not very clear because it is located in the glass-to-rubber transition region. Except for this sample, for which G'' is slightly higher than other samples, the G'' in the glass-to-rubber transition region is independent of M_S. Thus one can regard that the segmental friction coefficient for these samples is the same and that it is determined by the total concentration. Qualitatively the same features are observed also for the storage modulus and the relaxation modulus.

Considering the well-known results for melts as mentioned in the last paragraph of the Introduction, we decompose the linear viscoelasticity functions as follows:

$$G'(\omega) = G'_S(\omega) + G'_L(\omega) \quad (7)$$

$$G''(\omega) = G''_S(\omega) + G''_L(\omega) \quad (8)$$

$$G(t) = G_S(t) + G_L(t) \quad (9)$$

Here G'_L and G''_L (and G_L) are functions obtained from G' and G'' (and G) for the monodisperse polymer solution with $M = M_L$ and $c = c_L$ by changing the frequency (time) scale so that the values at low frequencies (long times) agree with those for the blend. In other words, G'_L and G''_L are obtained by shifting the dashed lines in Figure 2 to the left until they overlap with the curves for the bimodal system at the lowest frequency range. Then by subtraction, one can estimate G'_S and G''_S. The procedure is illustrated in Figure 4 for the case of the G'' component. The decomposition can be easily performed for all the bimodal solutions except for the two solutions with $M_S = 2.0 \times 10^5$. For these solutions, G' and G'' at long times are relatively low and the dashed lines cannot be superimposed on the G' and G'' curves at long times by the shift along the abscissa. The quantities G_S and G_L are determined through a similar procedure from the data shown in Figure 3. The dashed line must be shifted to the right in this case. The longest relaxation time, τ_{1L}, for the component $G_L(t)$ is evaluated from the amount of the shift and τ_1 for the monodisperse solution and is given in Table II.

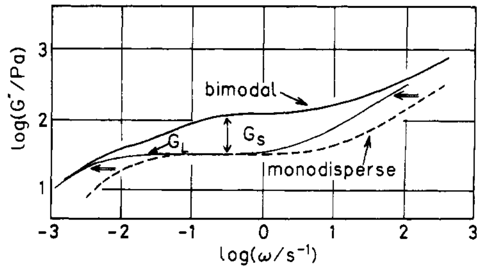

Figure 4. Procedure of estimating G''_S and G''_L. G'' curve for monodisperse system with $M = M_L$ and $c = c_L$ (dashed line) is shifted along the abscissa (as indicated by double arrows) until it overlaps the G'' curve for the bimodal system (thick solid line). The shifted curve (thin solid line) is taken as G''_L and the difference between solid lines (vertical arrow) as G''_S.

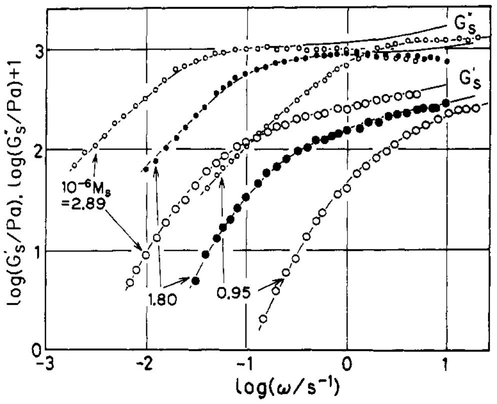

Figure 5. Quantities G'_S (large circles) and G''_S (small circles) for solutions of polystyrene with a bimodal MWD: $M_L = 8.42 \times 10^6$ and $c_S = c_L = 0.038$ g cm^{-3}. Values of $M_S/10^6$ are shown in figure.

As an example, the result of G'_S and G''_S for the series of systems with $M_L = 8.42 \times 10^6$ and $c_S = c_L = 0.038$ g cm^{-3} is shown in Figure 5. It may be noted that the quantities $G'_S(\omega)$ and $G''_S(\omega)$ on a log–log graph are very similar to $G'(\omega)$ and $G''(\omega)$, respectively, of well-entangled monodisperse polymers. The solid lines in Figure 5 were obtained from the complex modulus of the monodisperse polystyrene solution shown in Figure 1 by changing the scales appropriately. The longest relaxation times, τ_{1S}, corresponding to the solid lines are given in Table II. In the production of the solid curves in Figure 5, a factor of about 0.8 was multiplied to the data for the monodisperse solution of concentration $c = 0.076$ g cm^{-3}, which is equal to the total concentration, $c_S + c_L$, of the bimodal systems. Since the plateau modulus for the monodisperse solution varies as $c^{2.4}$,[24] the value 0.8 corresponds to the difference of the plateau moduli for monodisperse solutions of concentrations $c = c_S + c_L$ and c_L, respectively. The features seen in Figure 1 may be similar to those for undiluted polybutadiene.[12] For undiluted polystyrenes, more complex behavior was reported for $G'_S(\omega)$ and $G''_S(\omega)$ under certain conditions.[8]

Characteristic Times τ_{1S} and τ_{1L}

The characteristic time τ_{1S} is shown in Figure 6 for the solutions with $c_S = c_L = 0.038$ g cm^{-3}. The filled circles represent the maximum relaxation time, τ_1, plotted against the molecular weight, M, for solutions of sharp MWD polystyrene; the concentration is 0.076 g cm^{-3}, which is

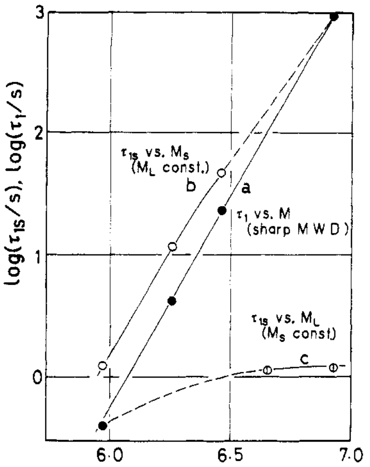

Figure 6. Maximum relaxation time τ_{1S} corresponding to quantitiy $G^*{}_S$: filled circles, τ_{1S} plotted against M_S for a series of bimodal systems with $M_L = 8.42 \times 10^6$ and $c_S = c_L = 0.038$ g cm^{-3}; slotted circles, τ_{1S} plotted against M_L for series with $M_S = 9.5 \times 10^5$ and $c_S = c_L = 0.038$ g cm^{-3}; filled circles, τ_1 plotted against M for sharp MWD systems with $c = 0.076$ g cm^{-3}.

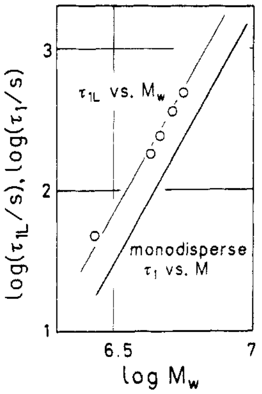

Figure 7. Maximum relaxation time τ_{1L} corresponding to the quantity $G^*{}_L$ plotted against the weight-average molecular weight M_w for bimodal systems with $c_S = c_L = 0.038$ g cm^{-3}. The thick line represents the maximum relaxation time τ_1 for monodisperse polymers at $c = 0.076$ g cm^{-3} plotted against molecular weight.

equal to the total concentration of the bimodal systems shown in the same figure. The slope of line a is 3.5. Curve b represents how τ_{1S} varies with M_S at constant M_L. Curve c shows its variation with M_L at constant M_S. The dashed lines are drawn under an assumption that τ_{1S} approaches τ_1 for the sharp MWD solution when M_S approaches M_L. From the solid portions of lines b and c, one obtains for $M_L \gg M_S$ an expression

$$\tau_{1S} \propto M_S{}^{3.5} M_L{}^0 \qquad (10)$$

The properties of τ_{1S} seem to be similar to those for undiluted polybutadiene with $M_L \gg M_S \gg M_e$.[12]

For the series of samples with $M_L = 8.42 \times 10^6$ and $c_S = c_L = 0.038$ g cm^{-3}, the characteristic time τ_{1L} given in Table II increases slightly with increasing M_S. For undiluted polybutadiene and polystyrene,[8,12] the relaxation time is reported to be independent of M_S provided $M_L \gg M_S \gg M_e$. The present solutions may not fill the condition that $M_L \gg M_S$ stated in these cases. The maximum relaxation time is plotted against the weight-average molecular weight, M_w, in Figure 7 for the 0.076 g cm^{-3} solutions. The maximum relaxation time, τ_{1L}, for the bimodal solutions with $c_S = c_L = 0.038$ g cm^{-3} may be approximated by a simple relation

$$\tau_{1L}/\mathrm{s} = 1.2\ (M_w/10^6)^{3.5} \qquad (11)$$

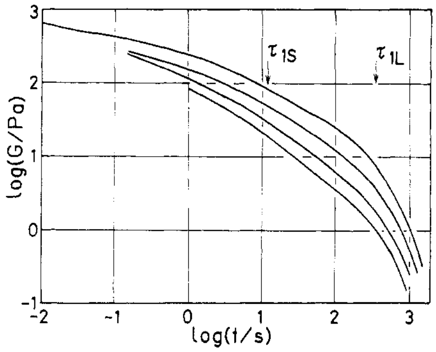

Figure 8. Relaxation modulus for bimodal system 180/3.8-842/3.8. Magnitudes of shear are ≤ 0.8, 3.0, 5.0, and 7.0 from top to bottom.

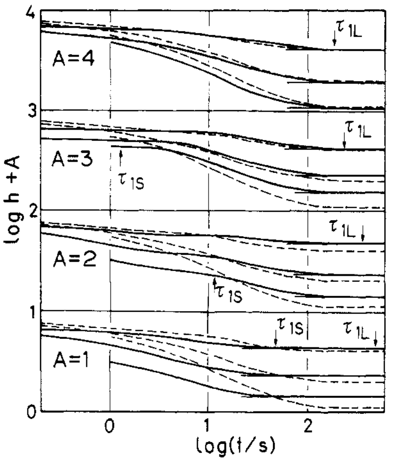

Figure 9. Function $h(t,\gamma)$ for bimodal systems (solid lines) with $M_L = 8.42 \times 10^6$ and $c_S = c_L = 0.038$ g cm^{-3}. Results for four solutions are shown in different scales represented by constants A; $M_S/10^4$ = 20, 95, 180, and 289 from top to bottom. For each solution, three lines represent results for γ = 3, 5, and 7 from top to bottom. Dashed lines are for a monodisperse system with $M = 8.42 \times 10^6$ and $c = 0.076$ g cm^{-3}.

However, this is not a general relation of wide applicability; the maximum relaxation time, τ_1, of the 0.076 g cm^{-3} solutions of monodisperse polymers are approximately 1/2 of the value given by eq 11. Evidently our data are not sufficient to extract a general rule for the maximum relaxation time.

Strain-Dependent Relaxation Modulus

The strain-dependent relaxation modulus $G(t,\gamma)$ is shown in Figure 8 for the bimodal system with $M_S = 1.80 \times 10^6$, $M_L = 8.42 \times 10^6$, and $c_S = c_L = 0.038$ g cm^{-3}. The curve at the top represents the linear relaxation modulus $G(t)$. One can see two relaxation modes characterized by time constants τ_{1S} and τ_{1L}, respectively. The relaxation modulus decreases with increasing shear strain. Due to the different degrees of decrease at different time scales, the wavy feature of the curve attributable to the two relaxation modes becomes less clear with increasing shear. The relaxation moduli for other bimodal solutions carry similar features.

In order to examine the nonlinear effect in more details, we employ the function $h(t,\gamma)$ defined by eq 1. The results for all the bimodal systems studied are shown in Figures 9 and 10. Figure 9 gives the results for the solutions with $M_L = 8.42 \times 10^6$ and $c_S = c_L = 0.038$ g cm^{-3}. The dashed lines are the $h(t,\gamma)$ for the 0.076 g cm^{-3} solution of monodisperse polymer with $M = M_L$. These are derived from curves at the bottom of Figure 1 with the assumption that the functions for sharp MWD samples of various M are

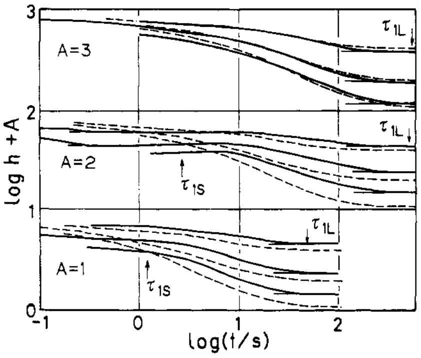

Figure 10. Function $h(t,\gamma)$ for bimodal systems (solid lines): 20/10-842-3.8, 95/6-842/3.8, and 95/3.8-448/3.8 from top to bottom. For each solution, three lines represent results for γ = 3, 5, and 7 from top to bottom. Dashed lines are for a monodisperse system with $M = M_L$ and $c = c_S + c_L$.

identical in reduced time scales, t/τ_k; the τ_k value for the monodisperse solution was estimated from the result of a previous study.[23-25] Figure 10 represents the rest of the bimodal solutions. The dashed lines are for monodisperse systems with $M = M_L$ and $c = c_S + c_L$ and are derived from the result for a 0.1 g cm^{-3} solution (upper two sets) and 0.076 g cm^{-3} solution (set at the bottom) of polystyrene with $M = 2.89 \times 10^6$.

The following features may be noticed. For the bimodal systems with $M_S = 2.0 \times 10^5$ (Figure 9, A = 4; Figure 10, A = 3), the h function is very similar to that for the monodisperse system with $M = M_L$ and $c = c_S + c_L$ (dashed line); the gross shape of the curve is similar and the limiting value, $h(\gamma)$, of $h(t,\gamma)$ at long times is approximately equal to that of the monodisperse system. For other bimodal systems, in which the short chains are supposed to form a part of the entangled network, the limiting value, $h(\gamma)$, is higher than that for the monodisperse system. For the systems with $M_S = 9.5 \times 10^5$ (Figure 9, A = 3; Figure 10, A = 1 and 2) or $M_S = 1.80 \times 10^6$ (Figure 9, A = 2), the function $h(t,\gamma)$ remains almost constant or decreases very slowly over a certain range of relatively short times. In the case of $M_S = 2.89 \times 10^6$ (Figure 9, A = 1), the $h(t,\gamma)$ decreases rather continously over the whole range of time studied.

Characteristic Time τ_k

In Figures 9 and 10 the time τ_k, at which the function $h(t,\gamma)$ levels off, is approximately independent of γ for each sample. It may also be noted that the solid lines and the dashed lines level off at approximately the same time in each panel but one with $M_S = 2.89 \times 10^6$ (Figure 9, A = 1). Thus we may say that the τ_k for the bimodal system with $M_L \gg M_S$ is approximately equal to that for the monodisperse system with $M = M_L$ and $c = c_S + c_L$. In Figure 9, the maximum relaxation time for the monodisperse system (dashed lines) is 950 s. The maximum relaxation time for the bimodal system at the top of Figure 9 is 180 s. So the τ_k remains the same while the maximum relaxation time decreases by 5 times on replacing 1/2 by the weight of the long chains with short ones. One exception is the system with $M_S = 2.89 \times 10^6$ and $M_L = 8.42 \times 10^6$ (Figure 9, A = 1). In this case, the function $h(t,\gamma)$ levels off approximately at $t = \tau_{1S}$.

For three cases with $M_L \gg M_S \gg M_e$ (Figure 9, A = 2; Figure 10, A = 1 and 2), the function $h(t,\gamma)$ decreases relatively rapidly at short times and then remains constant over a certain range of intermediate times. The relatively rapid decrease of $h(t,\gamma)$ at short times may be associated with the contour length equilibration of the short chains as discussed below.

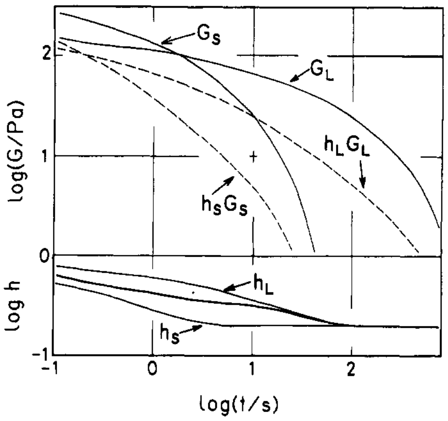

Figure 11. Model calculation on $h(t,\gamma)$ for sample 180/3.8-842/3.8 at γ = 5. G_S and G_L are derived from the linear relaxation modulus $G(t)$ for a bimodal system as described following eq 9. h_S and h_L are $h(t,\gamma)$ functions for monodisperse systems with $M = M_S$ and M_L, respectively, and $c = c_S + c_L$. These are obtained from the h function of Figure 1 by appropriately modifying the abscissa scale. The nonlinear relaxation modulus $G(t,\gamma)$ for the bimodal system is assumed to be the sum of products h_SG_S and h_LG_L (dashed lines). The thick solid line represents the estimate of $h(t,\gamma)$ for the bimodal system, i.e., a quantity $(h_SG_S + h_LG_L)/(G_S + G_L)$.

Model Calculations

The linear relaxation modulus for a bimodal system could be decomposed to two components, $G_S(t)$ and $G_L(t)$; see eq 9. Now we try to estimate the strain-dependent relaxation modulus with the use of these functions. We assume that the strain-dependent relaxation modulus can be written as

$$G(t,\gamma) = G_S(t)h_S(t,\gamma) + G_L(t)h_L(t,\gamma) \qquad (12)$$

where the nonlinear functions h_S and h_L are equal to those for monodisperse systems with $M = M_S$ and $M = M_L$, respectively, with $c = c_S + c_L$. The assumptions on the nonlinear functions are based on the conjecture that the contour length equilibration time, τ_B, for a polymer in the bimodal system is determined by its molecular weight and the total concentration. This conjecture may be partly supported by the observation on τ_k in the preceding section. All the quantities on the right-hand side of eq 12 can be derived from the data of linear viscoelasticity for the bimodal system and the nonlinear function $h(t,\gamma)$ for monodisperse systems.

The procedure of calculation is shown in Figure 11 for the case of sample 180/3.8-842/3.8 and γ = 5 (the third line from the top in Figure 8). The quantities G_S and G_L are derived from the linear relaxation modulus, $G(t)$, for the bimodal system through the procedure described below eq 9. The nonlinearity functions h_S and h_L at γ = 5 are just those for monodisperse systems with $M = 1.80 \times 10^6$ and 8.42×10^6, respectively, with c = 0.076 g cm^{-3}. The quantities h_SG_S and h_LG_L are derived from these ingredients. The predicted value of $h(t,\gamma)$ for the bimodal system, obtained as the ratio of $h_SG_S + h_LG_L$ to $G_S + G_L$, is represented by the thick line. This is to be compared with the data shown in Figure 9.

The comparison is made in Figure 12 for the results at γ = 5 for all the samples for which the linear relaxation modulus could be separated according to eq 9. It is seen that the calculated curve well represents the qualitative features of time variation of the observed in each panel. For all the cases except the one at the bottom (A = 1; 95/3.8-448/3.8), the calculated results are in excellent agreement with the observed at relatively short times (<10 s). Significant deviation is observed over relatively long

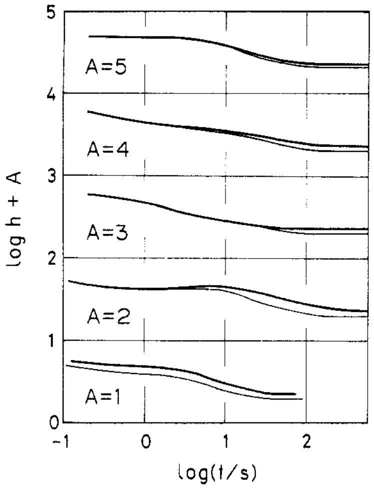

Figure 12. Comparison of predicted (thick line) and observed (thin line) values of $h(t,\gamma)$ at $\gamma = 5$ for bimodal solutions: 95/3.8-842/3.8, 180/3.8-842/3.8, 289/3.8-842/3.8, 95/6-842/3.8, and 95/3.8-448/3.8, from top to bottom.

time ranges where the last decay and leveling off of $h(t,\gamma)$ are involved. The agreement at short and intermediate times may imply that the assumption concerning the function $h_S(t,\gamma)$ may not be too bad. The first decrease of $h(t,\gamma)$ may be associated with the contour length equilibration of the short chains. We cannot locate the origin of the discrepancy at relatively short times for the case of the bottom panel ($A = 1$) at the moment.

Summary and Speculations

The nonlinear viscoelasticity, as represented by the function $h(t,\gamma)$, for bimodal polystyrene solutions may be classified in three types according to the combination of M_S and M_L.

Type I is the case where M_S is lower than twice the entanglement molecular weight, $2M_e$, corresponding to the total concentration, $c_S + c_L$. The function $h(t,\gamma)$ is similar to that for the monodisperse system with $M = M_L$ and $c = c_S + c_L$.

Type II is the case where $M_L \gg M_S > 2M_e$. The function $h(t,\gamma)$ decreases in two steps, probably corresponding to the contour length equilibration of chains of different lengths. The time τ_k at which h levels off is equal to that for the monodisperse system with $M = M_L$ and $c = c_S + c_L$. The final value, $h(\gamma)$, of the function $h(t,\gamma)$ is higher than that for the monodisperse system.

Type III is the case where M_S is not much smaller than M_L. The function $h(t,\gamma)$ does not show doulbe-step decreases. The time τ_k is significantly smaller than that for the monodisperse system with $M = M_L$ and $c = c_S + c_L$. The function $h(\gamma)$ is higher than that for the monodisperse system.

The result of type I implies the following. Suppose that some of the polymer chains in a system with a sharp MWD are replaced with shorter chains. The contour length equilibration process of the longer chains are not affected provided that the total concentration is kept constant and that the shorter chains are shorter than the entanglement strand. It may be noted that the quantity τ_k remains constant while the maximum relaxation time of the system decreases considerably on replacing long chains with short ones. This fact may support the prediction of the tube model theory that the contour length equilibration time, τ_B, is independent of the mesh size of entanglement.

The type II behavior is similar to that of type I as far as the time constant τ_k is concerned. However, the nonlinearity at long times is weaker. Suppose that all the entanglements along each chain are disentangled or the tube wall disappears before the extended chain shrinks through the equilibration process of contour length. In such a case, the relaxation modulus would not depend on the strain and so $h(\gamma) = 1$. Thus the weakening of nonlinearity may be associated with partial tube renewal caused by the diffusion of shorter chains. On the other hand, the weakening of nonlinearity is not expected to occur if the entanglement points are regularly placed along the chain and that a portion of the entanglement points are homogeneously (every two, say) removed at a certain moment in the stress relaxation process. An existing theory[15] for the nonlinearity of bimodal systems does not predict the weakening of nonlinearity at long times. Graessley[30] argues that, for monodisperse systems, the nonlinearity will be more marked than in the original Doi–Edwards theory if the effect of constraint release, or the tube renewal due to the motion of neighboring chains, is taken into account.

The type III behavior is probably associated with the fact that the characteristic time τ_{1S}, presumably the reptation time of the short chains in the bimodal system, is comparable with the contour length equilibration time, τ_B, of the long chains. The function $h(t,\gamma)$ levels off at a time close to τ_{1S} and no decrease is detected at longer times. The tension of long chains may relax to a large extent in the partial tube renewal when τ_{1S} is not much smaller than τ_B.

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Lattice Walk Models of Uniform Star Polymers with Many Arms

A. J. Barrett* and D. L. Tremain

Department of Mathematics and Computer Science, Royal Military College of Canada, Kingston, Ontario K7K 5L0, Canada. Received October 30, 1986

ABSTRACT: A high coordination random lattice walk serves as the basis of a model of a uniform star polymer with from 1 to 24 branches. Monte Carlo results are presented for two classes of walk which exhibit significantly different excluded volume characteristics. The effects of excluded volume and functionality on stars and star fragments are observed and interpreted in light of theoretical predictions and experiment. Results provide a fairly complete picture of excluded volume effects in uniform stars, in partial agreement with the scaling results of Daoud and Cotton. The success of the Zimm–Stockmayer equation in describing real stars is discussed.

1. Introduction

When several linear polymers are brought together at a point, called the *branch point*, a star polymer is formed. If each of the branches or arms of the star has the same chemical length, then the star is said to be *uniform*. Stars are fascinating objects. Within the same molecule one finds compact, highly structured fragments and extended, linear ones. A star is dense near the branch point and dilute far from the branch point. Polymer dimensions are known to be dependent on concentration; the dimensions of stars and fragments of stars depend on the concentration profile within the star. At the same time, uniform stars have an idealized structure. They are far simpler than almost all natural and synthetic branched polymers and provide a natural framework for the study of the physics of large molecules.

Following some notable studies of stars over many years,[1-3] several recent works have considered the effects of excluded volume[4-8] and have furnished a number of intriguing predictions. Many of these can only be adequately tested on stars with many arms. Some fascinating experimental work on such stars has been done by Fetters and his associates,[9,10] who have produced uniform polystyrene stars with as many as 18 branches. Theorists too have sought to confirm scaling and renormalization group predictions by numerical means, and results are now available for stars with up to 12 arms.[11-17]

In the present work, a non-nearest-neighbor lattice walk[18] is used to model uniform star polymers with up to 24 branches, using Monte Carlo techniques. Both self-avoiding (SA) and neighbor-avoiding (NA) walks, which differ considerably in their excluded volume properties, are simulated. It is hoped that by observing stars with a larger number of branches, using models with widely disparate excluded volume characteristics, it will be possible to learn enough about the effects of excluded volume in stars to permit intelligent assessment of the arguments which have been put forward. It is further hoped that some conclusions might be drawn concerning the significance of the various concentration regimes within the star.

2. Theory

Configurational properties of particular interest include the mean square radius of gyration $\langle S_N^2(f)\rangle$ of the star, the mean square end-to-end length of a single branch or arm $\langle R_n^2(f)\rangle$, and the mean square distance $\langle R_{ij}^2(f)\rangle$ between two sites i and j within the star. Also of interest is the number of configurations of uniform stars s_N. Here n is the number of monomer units or segments per branch, N is the number of monomer units in the star, and f is the *functionality* or number of branches. Clearly $N = nf$. If N is large, then these quantities are expected to satisfy relations of the form

$$\langle S_N^2\rangle \sim A(f)N^{2\nu} \qquad (1)$$

$$\langle R_n^2\rangle \sim B(f)n^{2\nu} \qquad (2)$$

and

$$s_N \sim \lambda(f)^N N^{\gamma(f)-1} \qquad (3)$$

It is expected that $\langle R_{ij}^2\rangle$ obeys a law similar to eq 2. The analogy with scaling laws for isolated, linear chains is clear. Power laws such as eq 1 and 2 display both an exponent and a prefactor or amplitude. The exponent is characteristic of a fundamental physical process and therefore universal. This means that the same exponent ν should apply to all equations relating to chain dimensions. Numerous studies put the value of ν close to the Flory value: $^3/_5$. Recent renormalization group analysis yields a value of 0.588.[19]

The amplitude on the other hand is characteristic of functionality and such model-dependent details as monomer structure, permitted bond angles, and short-range interaction. It is possible to eliminate these model-dependent details by forming the ratios

$$g(f) = \frac{A(f)}{A(1)}$$

and

$$g'(f) = \frac{B(f)}{B(1)}$$

One expects then that both g and g' will be universal functions of f. We will assume that for large f, the prefactors $A(f)$ and $B(f)$ can be described by power laws:

$$A(f) \sim f^{\delta} \qquad B(f) \sim f^{\delta}$$

It is especially important to note that these equations

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