Viscoelastic Properties of Solutions of Star-Branched Polystyrene

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ABSTRACT: The relaxation modulus, $G(t,\gamma)$, was measured for solutions of star-branched polystyrene with 4 arms in chlorinated biphenyl at magnitudes of shear, γ, ranging from 0.3 to 7. Molecular weights were 7.63×10^5, 1.24×10^6, and 2.65×10^6, and the concentration ranged from 0.076 to 0.25 g cm^{-3}. When the number of entanglements on the chain connecting two chain ends, M_A/M_e, was less than 4, the relaxation modulus at small strains, $G(t)$, agreed with that of a linear polymer having the same value of M_A/M_e. The maximum relaxation time increased in proportion to $(M_A/M_e)^{4.5}$. A function $h(t,\gamma) = G(t,\gamma)/G(t)$ leveled off at a certain time, τ_k, independent of γ. The characteristic time, τ_k, for the branched polymer was approximately equal to that of the linear polymer having the same M_A/M_e. The time-independent value of $h(t,\gamma)$ at long times, $h(\gamma)$, was slightly lower than that for the linear polymers and was in very good agreement with the prediction of the tube model theory. These features are in accord with the concept that the chain branching may hamper the reptational motion but may not affect the equilibration process of the chain contour length assigned as the origin of nonlinear viscoelasticity in the tube model theory.

Introduction

Owing to the technique of anionic polymerization, quite an amount of data have been piled up for the viscoelastic properties of well-characterized star-branched polymers.[1-10] Here the star-branched polymer is a substance of which a molecule is composed of f (>2) equal polymer chains, or arms, radiating out from one point. The molecular weight of an arm is denoted as M_b. The molecular weight, M, of the polymer is equal to fM_b. For a series of polymers with a fixed number of arms, f, the viscosity increases more rapidly with M than for the linear polymer. Compared at the same molecular weight, the viscosity of a branched polymer is lower than that of the linear polymer at relatively low molecular weights. The former increases more rapidly with increasing molecular weight and exceeds the latter at a certain M. This phenomenon is often called the viscosity enhancement of branched polymers. The relaxation spectrum of a branched polymer is more diffuse at the long time end than that of a linear polymer. The steady shear compliance is proportional to M^1c^{-1} instead of M^0c^{-2}, typical for highly entangled linear polymer. Here c represents the mass concentration of polymer. These features may be related to the restriction on the diffusional motion of polymer chain due to the branching and can be described, at least qualitatively, with the concept of restricted reptational motion.[2,6,8,10,12,13] Interesting features in nonlinear viscoelasticity as described later in this section are derived from the tube model theory for branched polymers.[12,13] However, experiments comparable with the theory are very scarce.[14,15]

In the present paper, we measure the viscoelasticity of solutions of star-branched polystyrenes to investigate the properties of branched polymers at relatively low degrees of entanglement. The study of solutions allows us to vary the number of entanglements per molecule, N, by changing the concentration as well as the molecular weight. The method has been employed to show that the ratios of the characteristic relaxation times, τ_1, τ_k, and τ_s, for linear polymers are unique functions of N independent of M, c, or the polymer species.[16] Here the maximum relaxation time, τ_1, characterizes the terminal flow region and is defined by an asymptotic form of the relaxation modulus, $G(t)$.

$$G(t) = G_1 \exp(-t/\tau_1) \tag{1}$$

The characteristic time for nonlinear viscoelasticity, τ_k, is defined as the time at which a function $h(t,\gamma)$ levels off where

$$h(t,\gamma) = G(t,\gamma)/G(t) \tag{2}$$

Here $G(t,\gamma)$ is the strain-dependent relaxation modulus measured at a shear strain, γ. The limiting value of $G(t,\gamma)$ at $\gamma \to 0$ is the linear relaxation modulus, $G(t)$. The quantity τ_s is the characteristic time for the glass-to-rubber transition region. The details of determination of τ_s and the rubbery plateau modulus, G_N, for semidilute polymer solutions were given elsewhere.[17] The entanglement molecular weight, M_e, is determined from G_N by

$$M_e = cRT/G_N \tag{3}$$

where R is the gas constant and T is the absolute temperature. The number of entanglements per molecule is the ratio M/M_e and varies with M as well as with c.

It was revealed that for solutions of linear polystyrene and poly(α-methylstyrene)[16]

$$\tau_1/\tau_s = 1.3N^{3.5} \tag{4}$$

$$\tau_k/\tau_s = 28N^{2.0} \tag{5}$$

These relations are in semiquantitative agreement with the prediction of the tube model theory[18] if τ_1 is regarded as the reptation time and τ_k as the time in which the fluctuation of chain contour length completely equilibrates in entangled systems. The property of τ_k as well as the limiting value, $h(\gamma)$, of the function $h(t,\gamma)$ at long times strongly supports the idea of the tube model theory that the nonlinear behavior is due to the shrink of an extended chain along the tube.

For a series of branched polymers with a fixed value of f, we still expect that the ratios τ_1/τ_s and τ_k/τ_s are functions only of N.[12] In view of the viscosity enhancement, we

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Table I
Star-Branched Polystyrene Samples

code	$M_b/10^4$	$M_w/10^4$	M_w/M_n	$M_A/10^4$
4S662	66.2	265	1.06	132.5
4S310	31.0	124	1.06	62.0
4S184	18.4	73.6	1.05	36.8

Table II
Viscoelastic Parameters at 30 °C

code	$c/10^{-2}$ g cm^{-3}	M_A/M_e	$\tau_s/10^{-3}$ s	τ_k/s	τ_1/s
4S662	15.0	11	2.6	11.9	61.7
	12.0	8.0	2.7	6.6	18.4
	9.0	5.5	4.3	4.38	4.0
	7.6	4.4	4.4	2.38	1.8
4S310	20.0	7.3	2.5	4.45	6.1
	16.0	5.5	2.9	2.36	2.0
	15.0	5.0	2.6	1.47	1.4
	12.0	3.8	2.7	0.66	0.40
4S184	30.0	7.3	5.3	15.2	12.9
	25.0	5.8	3.8	3.3	3.53

expect that the quantity τ_1/τ_s is much larger than that for the linear polymer if the comparison is made for polymers with the same value of span molecular weight, M_A ($=2M_b$); $M = M_A$ for linear polymers. On the other hand, the branch point at the center of molecule would not affect the shrink of chain envisaged as the origin of the nonlinear viscoelasticity in the tube model theory. Thus we may expect that the nonlinear function, $h(t,\gamma)$, for a star-branched polymer is essentially the same as that of the linear polymer, which has the same value of M_A. We here compare the viscoelastic properties of star-branched and linear polymers and investigate the differences in the relaxation modulus, $G(t)$, the nonlinear function, $h(t,\gamma)$, and the characteristic times, τ_1 and τ_k.

Experimental Section

Materials. Three samples of star-branched polystyrene with $f = 4$ were synthesized by coupling polystyryl anion with 1,2-bis(trichlorosilyl)ethane.[19] The solvent was benzene, and the initiator for the anionic polymerization was *sec*-butyllithium. The crude product was fractionated through repeated precipitation in a benzene–methanol system until the gel permeation chromatogram became sufficiently sharp. The weight-average molecular weights of the precursor polystyrene before coupling, M_b, and of the final product, M_w, were determined by gel permeation chromatography and the light-scattering method. These values are given in Table I together with the ratio of the weight-average to the number-average molecular weights. More details of synthesis and characterization were given in a previous report.[19] The quantity M_A in the table is equal to $M_w/2$ and represents the molecular weight of the chain connecting two ends of the star-branched polymer.

The solvent was Aroclor 1248, a polychlorinated biphenyl supplied from Monsanto Chemical Co. For preparation of the test solution, weighed amounts of the polymer sample and the solvent were mixed with dichloromethane and the latter was evaporated after homogenization. Test solutions are listed in Table II.

Apparatuses. The stress relaxation after an instantaneous shear deformation of magnitude γ was measured with an apparatus of the cone-and-plate type.[20] The strain-dependent relaxation modulus, $G(t,\gamma)$, was obtained as the ratio of the shear stress to γ. The function $G(t,\gamma)$ was independent of γ when γ was less than 0.7. The value of $G(t,\gamma)$ in this range was taken as the linear relaxation modulus, $G(t)$. Measurements were performed at several temperatures in the range of 5–60 °C, and the result was reduced to a reference temperature, 30 °C, with the method of reduced variables.

The storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, were measured with a rheometer of the cone-and-plate type, Rheopexy analyzer (Iwamoto Seisakusho Co., Ltd., Kyoto, Japan). The range of angular frequency, ω, was from 0.0628 to 6.28 s^{-1}. Results at several temperatures ranging from 5 to 60 °C were reduced to the reference temperature, 30 °C, with the method of reduced variables.

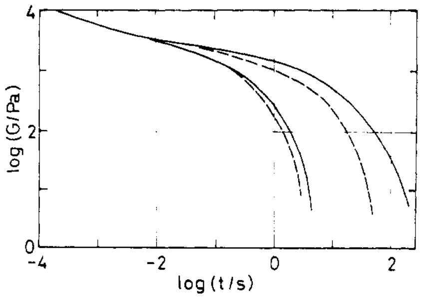

Figure 1. Relaxation modulus, $G(t)$, for polystyrene solutions at $c = 0.15$ g cm^{-3}. Solid lines are for branched polymers 4S662 (right) and 4S310 (left). Dashed lines are for linear polymers with molecular weights 1.26×10^6 (right) and 5.91×10^5 (left).

The linear relaxation modulus, $G(t)$, was derived from the dynamic data through a phenomenological relation[21]

$$G(t) = G'(\omega) - 0.4G''(0.4\omega) + 0.016G''(10\omega)_{\omega=1/t} \tag{6}$$

The values of $G(t)$ thus obtained were in good agreement with the directly measured values when the ranges of t for the two methods overlap with each other. The linear relaxation modulus over quite a wide range of time was available by the combination of data of two origins.

Results and Discussion

Linear Viscoelasticity. The relative moduli, $G(t)$, for solutions at $c = 0.15$ g cm^{-3} are shown in Figure 1. Solid lines represent branched polymers, and dashed lines, linear polymers. The relaxation modulus at very short times, $t < 10^{-2}$ s, is evidently independent of the geometry and the molecular weight of the chain. For upper two curves, a slight symptom of the plateau region is observed in the range $10^{-2} < t/\mathrm{s} < 10^{-1}$, and the modulus in this range is not likely to be affected by the geometry of chain. These features are in accord with the earlier observations that the glass-to-rubber transition zone and the rubbery plateau zone are not changed by the introduction of branching.

At long times, the relaxation modulus varies much with the geometry and the molecular weight. The upper two lines represent relatively high M_A, approximately 1.3×10^6. In this case the relaxation modulus of the branched polymer extends to a range of longer times than those for the linear polymer. The curve in the terminal region for the branched polymer cannot be produced by parallel horizontal shift of the curve for the linear polymer; one may note the difference of the slope at a certain level, say, $G = 10$ Pa. Thus if eq 1 is fitted to the curve, the value of G_1 will be very low and τ_1 will be high for the branched polymer with relatively high M_A. For the samples with a relatively low M_A value, approximately 6.1×10^5, the difference of $G(t)$ for the branched and linear polymers is relatively small.

In order to examine the difference between branched and linear polymers in a more systematic manner, we compare the relaxation modulus at the same value of M_A/M_e. In Figure 2, reduced relaxation moduli, $G(t)/G_N$, are plotted against a reduced time, t/τ_s, for solutions with M_A/M_e = 3.8, 7.3, and 11. The curves for linear polymers (dashed lines) were produced through interpolation from the group of curves published previously.[16] The rubbery plateau modulus, G_N, was evaluated from the previous result

$$G_N = 2.4 \times 10^5 c^{2.3} \text{ Pa} \tag{7}$$

obtained for solutions of linear polystyrene in Aroclor 1248

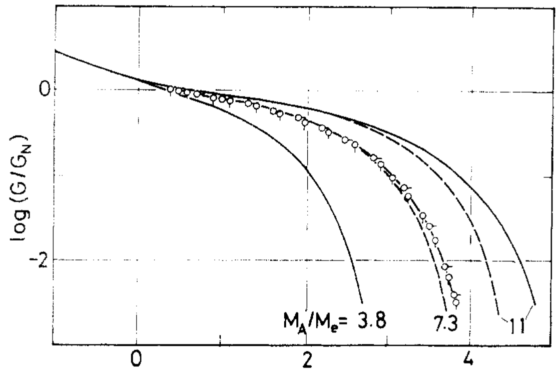

Figure 2. Relaxation moduli, $G(t)$, of star-branched (solid lines) and linear (dashed line) polystyrenes: M_A/M_e = 3.8 (4S310 at 0.12 g cm^{-3}); M_A/M_e = 7.3 (4S310 at 0.20 g cm^{-3} (pip right) and 4S184 at 0.30 g cm^{-3} (pip down)); M_A/M_e = 11 (4S662 at 0.15 g cm^{-3}). The dashed line for M_A/M_e = 3.8 overlaps with the solid line.

at 30 °C. Here the units for c are grams per cubic centimeters. The entanglement molecular weight, M_e, was calculated from G_N by eq 3. The characteristic time τ_s was determined by comparison of the relaxation modulus with the standard system given in the previous paper. The difference between the branched and linear polymers as observed in Figure 1 is clearly seen in the case of M_A/M_e = 11 in Figure 2. The difference becomes smaller but still exists at M_A/M_e = 7.3. The relaxation modulus for the branched polymer decreases more slowly than that for the linear polymer at long times, $t/\tau_s > 10^3$. The difference is not seen at any times when M_A/M_e is as small as 3.8; the reduced relaxation modulus $G(t)/G_N$ as a function of a reduced time t/τ_s for a branched polymer is equal to that of a linear polymer whose molecular weight is half of that of the branched polymer. As the number of entanglement, M_A/M_e, increases, the equality breaks down at long reduced times; a long time tail appears in the relaxation modulus for the branched polymer and the longest relaxation time increases more rapidly with molecular weight than for the linear polymer.

Longest Relaxation Time. For linear polymers, the longest relaxation time can easily be evaluated from the relaxation modulus because the reduced relaxation modulus, $G(t)/G_N$, as a function of a reduced time, t/τ_1, is the same for any system at long times. Thus once the τ_1 value is determined for one standard sample, the value for other samples can be obtained by plotting log $[G(t)/G_N]$ against log t and measuring how much shift along the abscissa is required to superimpose the graph on that of the standard sample. This procedure is much easier than fitting eq 1 to the data at long times but is not applicable for branched polymers.

It is well-established that the steady shear compliance, J_e, is proportional to M_A/cRT for a series of star-branched polymers with a fixed number of branches, f. Therefore one expects that a reduced relaxation modulus, $G(t)M_A/cRT$, is a unique function of a reduced time, t/τ_1, at long times. We plotted the reduced quantity, $G(t)M_A/cRT$, against time, t, on double-logarithmic scales for the branched polymers and shifted the graph along the abscissa and confirmed that the curves for all the solutions superimposed on each other at long times. The result is shown in Figure 3 for a few typical samples. The superposition at long times is good. At short times, $t < \tau_1/2$, the shape of relaxation curves depends on the molecular weight and concentration and the superposition is not good. The deviation is more marked than for linear polymers.[16] However, agreement at long times is good enough to allow us to estimate the maximum relaxation time as follows. The solid line is the result for the solution of a linear polymer with M_A/M_e = 3.8. This line corresponds to the line for M_A/M_e = 3.8 in Figure 2 and agrees well with the reduced data for branched polymers at long times. The scale of the abscissa, τ_1, was chosen to suit the data for the linear polymer. The longest relaxation time, τ_1, for the branched polymers was determined from the shift factor in the making of Figure 3 and is listed in Table II.

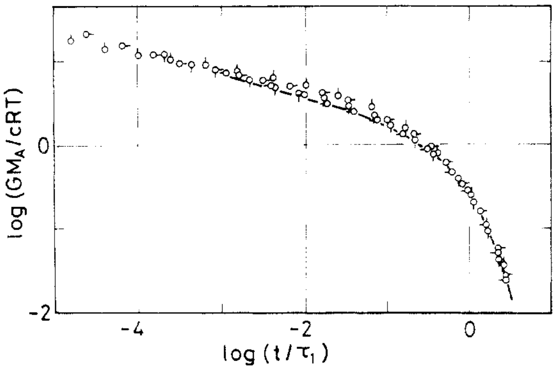

Figure 3. Reduced relaxation modulus, $G(t)M_A/cRT$, plotted against reduced time, t/τ_1. The line is for the linear polymer with M_A/M_e = 3.8. Circles are for branched polymers; pip up is for 4S662 at 0.15 g cm^{-3}; pip right, down, and left are for 4S310 at 0.20, 0.15, and 0.12 g cm^{-3}, respectively.

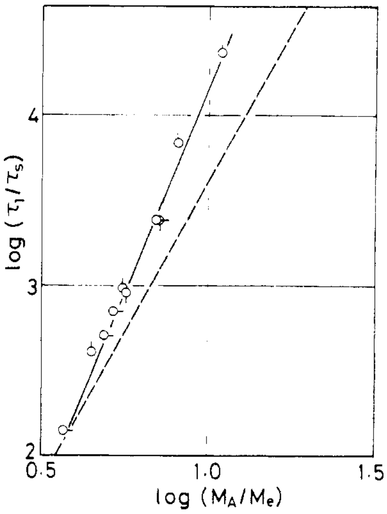

Figure 4. Reduced relaxation time, τ_1/τ_s, plotted against M_A/M_e. Circles represent branched polymers; pip up, 4S662; pip right, 4S310; pip down, 4S184. The dashed line represents eq 4 for linear polymers.

The ratio τ_1/τ_s is plotted against M_A/M_e in Figure 4. The dashed line represents eq 4 for the linear polymer. Obviously, the reduced relaxation time, τ_1/τ_s, of the branched polymer is higher and increases more rapidly with M_A/M_e than that of the corresponding linear polymer. The solid line to approximately represent the points for branched polymers can be expressed as

$$\tau_1/\tau_s = 0.24(M_A/M_e)^{4.8} \tag{8}$$

The strong molecular weight dependent is in accord with the viscosity enhancement. The data may also be expressed by a formula including the well-known factor, $\exp(M_A/M_e)$, and may be understood with the concept of hampered reptational motion.

One may note that the dashed line and the solid line meet at M_A/M_e = 3.8. Thus the effect of branch points becomes noticeable when the number of entanglements

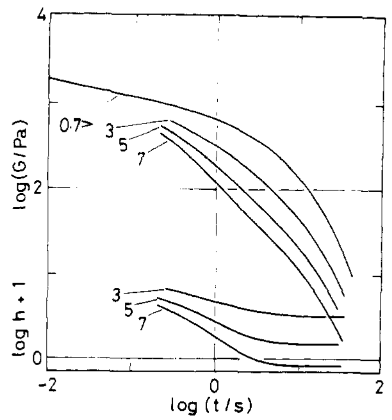

Figure 5. Strain-dependent relaxation modulus, $G(t,\gamma)$ (upper four curves), and nonlinear function, $h(t,\gamma)$ (lower three curves) for a 0.12 g cm^{-3} solution of 4S662. The number on each curve indicates the magnitude of shear, γ.

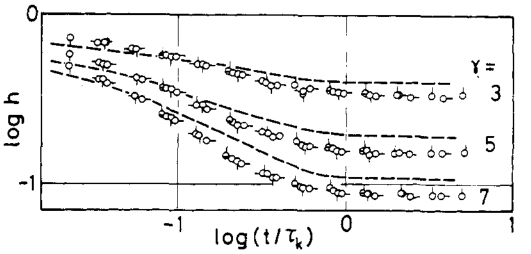

Figure 6. Function $h(t,\gamma)$ plotted against reduced time t/τ_k for branched polymers (circles); pip up, right, and left represent 4S662 at c/g cm^{-3} = 0.15, 0.12, and 0.09, respectively, and pip down represents 4S310 at c/g cm^{-3} = 0.16. Magnitudes of shear, γ, are 3, 5, and 7 from top to bottom. Dashed lines represent results for linear polymers.

on each branch exceeds about 2. This statement is valid also for the shape of the relaxation modulus shown in Figure 2. Since the reptational motion should be hampered by a branch point, one may conjecture that the reptational motion becomes of some importance for the relaxation of chain orientation for linear chains only when the number of entanglements per chain exceeds 4.

Strain-Dependent Relaxation Modulus. The strain-dependent relaxation modulus, $G(t,\gamma)$, for a 0.12 g cm^{-3} solution of 4S662 is shown in Figure 5. The curve at the top represents $G(t)$ obtained at magnitudes of shear, γ, less than 0.7, and the following three represent $G(t,\gamma)$ at γ = 3, 5, and 7, respectively. The relaxation modulus decreases with increasing magnitude of shear. The effect of large strain at various times is more clearly seen in the function $h(t,\gamma)$ shown at the bottom of Figure 5. This is a decreasing function of time, t, and levels off at a certain time, denoted as τ_k in the following. These features are qualitatively the same as those of linear polymers. The characteristic time, τ_k, is listed in Table II. The function $h(t,\gamma)$ is plotted against a reduced time, t/τ_k, in Figure 6. Data for various solutions superimpose on one another and support a common curve at each magnitude of shear. The same was true for other solutions omitted in Figure 6 to avoid complication in drawing. Thus the function $h(t,\gamma)$ representing the nonlinear viscoelasticity is a universal function of the reduced time t/τ_k for 4-armed star-branched polystyrene solutions with various molecular weights and concentrations. This result may be in contrast with the result at small strains that the reduced relaxation modulus, $G(t)/G_N$, is not a unique function of t/τ_1 for branched polymers.

The dashed lines in Figure 6 represent the function $h(t,\gamma)$ for linear polymers. The result for branched polymers is similar to that for linear polymers. However, the function for the branched polymer decreases more sharply with time and levels off to a lower value than that for the linear polymers.

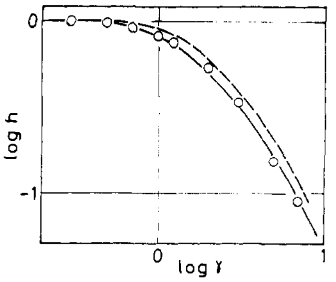

Figure 7. Function $h(\gamma)$ for branched polymers (circles) and linear polymers (dashed line). The solid line represents the result of the Doi–Edwards theory with independent alignment approximation.

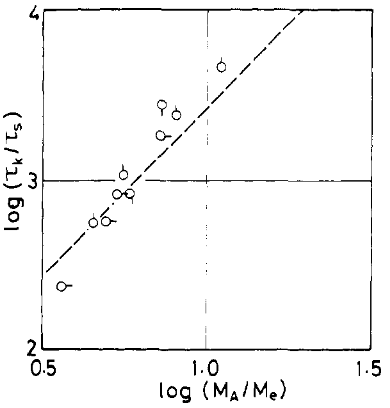

Figure 8. Reduced characteristic time, τ_k/τ_s, for branched polymers (unfilled circles; for pips, see the caption to Figure 4). The dashed line represents eq 5 for linear polymers.

Parameters of Nonlinear Viscoelasticity. The limiting value of the function $h(t,\gamma)$ at long times, $h(\gamma)$, for branched polymers is shown in Figure 7. The circles represent the average values for all the solutions studied. The dashed line represents the average for solutions of linear polystyrene and poly(α-methylstyrene). As noted above, the $h(\gamma)$ values for branched polymers are lower than those for linear polymers. The data for branched polymers are in excellent agreement with the theoretical result of Doi and Edwards.

A reduced characteristic time, τ_k/τ_s, is plotted against M_A/M_e in Figure 8. In contrast with the case of τ_1/τ_s shown in Figure 4, the points for branched polymers (circles) are not especially higher than those for linear polymers (dashed line) represented by eq 5.

Discussion

Concerning the stress relaxation at small strains, an enhancement of the longest relaxation time due to the chain branching was observed in two ways. First, the relaxation spectrum at long times became more diffuse with an increasing number of entanglements. Thus the reduced relaxation modulus, $G(t)/G_N$, was not a unique function of the reduced time, t/τ_1, at long times in contrast with the case of linear polymers. Second, the ratio τ_1/τ_s increased more rapidly with M_A/M_e than that for linear polymers. In either of the senses, the effect of branching began to show up only when M_A/M_e exceeded 4. Up to this number of entanglement, the stress relaxation of a linear polymer should proceed through the same mechanism as a branched polymer does. Thus the reptation is not likely to be the main process of stress relaxation in this range.

Concerning the stress relaxation at large strains, the behavior of branched polymers was similar to that of linear polymers in two senses. First, the function $h(t,\gamma)$ representing the nonlinearity was a unique function of the reduced time t/τ_k for a series of solutions of branched polymers. Second, the reduced characteristic time τ_k/τ_s was approximately the same function of M_A/M_e as that for linear polymers. The similarity between branched and linear polymers may be remarkable if compared with the marked difference observed at small deformations. The result is consistent with the conjecture that the reptation may be hampered by branching but the equilibration of fluctuation of contour length may not be. Thus the present result strongly supports the tube model theory assigning the rapid shrink of an extended chain as the origin of nonlinear viscoelasticity.

The limiting value of $h(t,\gamma)$ at long times, $h(\gamma)$, for branched polymers was in very good agreement with the prediction of the tube model theory. The agreement was better than that for linear polymers. The difference between branched and linear polymers is not insignificant and may indicate some additional effect, such as the coupling between the reptation and the shrink in linear polymers, that has not been included in the tube model theory.

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