Macromolecules **1984,** *17,* 888–895

properties of PDMS in the temperature range 223–323 K.[7] As shown in ref 11, this is barely into the temperature interval where any deviation from a simple Arrhenius behavior is detected and surely cannot be used to estimate T_0. More recent attempts[13] to determine T_0 from viscosities produced even more outrageous results (T_0 = 67 K). The very rapid change in relaxation frequency with temperature near 150 K demands that T_0 be well above 81 K.

The empirical parameters in eq 10 can also be interpreted in terms of the free volume of the liquid according to the WLF[12] equation. PDMS was thought to have an unusually high fractional free volume at the glass transition.[12] The WLF parameters calculated from our results are c_1^g = 14.6 and c_2^g = 20 K. This leads to a calculated fractional free volume at the glass transition of f_g/B = 0.030. This is higher than some polymers, but well within the normal range.

The value of T_g listed in ref 12 is 150 K. It now appears that this value was obtained with semicrystalline PDMS. The value reported by Yim and St. Pierre[1] was obtained with shock-quenched amorphous PDMS. The difference can be rationalized by the results of Adachi et al.[9] obtained by dielectric relaxation on both amorphous and crystalline PDMS. The dielectric loss maximum shifts by approximately 2 orders of magnitude when the sample crystallizes. This corresponds to approximately 4 K in the region of T_g. The elevation of the glass transition temperature of the amorphous part in a semicrystalline polymer is a common phenomenon, but for PDMS little notice of this effect has been made. When the truly amorphous T_g is used for PDMS (146 K), the calculated freqency of maximum dielectric loss at the glass transition is approximately 0.02 Hz, which is quite reasonable.

Acknowledgment. We gratefully acknowledge many fruitful discussions with S. M. Lindsay.

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Viscoelastic Properties of Star-Shaped Polymers[†]

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ABSTRACT: A theory is presented to describe the viscoelastic properties of star-shaped polymers. Disentanglement processes are considered to be dominated by diffusion of the ends of the arms in a (free energy) potential field. The existence of the potential function is supported by recent work of Helfand and Pearson on random walks entangled with a fixed obstacle net. When compared with new and existing experimental data on well-characterized polymeric stars, the theory predicts the correct molecular weight dependence of the viscosity and the steady-state shear compliance, as well as the frequency dependence of the dynamic moduli, $G'(\omega)$ and $G''(\omega)$. Useful variables for plotting time- or frequency-dependent relaxation data of star polymers are suggested by the theory and are considered.

During the past few years important advances have been made in understanding the rheological properties of high molecular weight polymers. Using concepts originally suggested by Edwards[1] and de Gennes,[2] Doi and Edwards[3] developed a theory that describes the response of polymeric fluids when subjected to an external strain. Although improvements are still needed,[4,5] their theory has been remarkably successful in describing complex viscoelastic behavior.[6,7]

The theory, as originally presented, applies to concentrated solutions of linear molecules. For this case it is assumed that polymer chains are hemmed in by their neighbors and that they move by translating in a curvilinear fashion roughly paralleling their own contour. The time dependence of their escape from present surroundings to new surroundings can be obtained from a solution to the first-passage time problem[8] for a diffusing chain.[3] If the polymer molecule is branched, it is expected that this simple snake-like motion will be highly suppressed. The resulting change in the mechanism of diffusion will alter the rate of stress relaxation and, in general, all rheological properties.

The simplest type of branched polymer is the star-shaped molecule for which f chains are connected to a central point. Using small-strain deformation measurements, the time-dependent response of this type of polymer has been found to be quite different from linear polymer.[9-11] Approximate theories for describing the observed behavior were proposed by de Gennes,[12] Doi and Kuzuu,[13] and Graessley.[7]

[†] This paper is dedicated to Professor Walter H. Stockmayer on the occasion of his 70th birthday. We appreciate both the knowledge and the wisdom he has shared with us.

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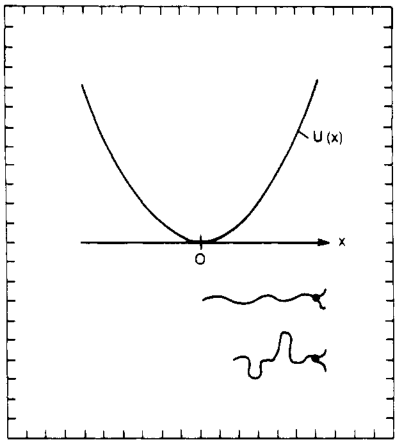

Figure 1. An arm of a star in two separate positions of escape. The probability of retracting a distance x along the tube is proportional to $\exp[-U(x)/k_BT]$.

In the first part of this paper we solve a modified first-passage time problem relevant to star molecules and use the answer to obtain various linear viscoelastic properties. Our model, although related to that of Doi and Kuzuu,[13] leads to results which are somewhat different from those obtained by them. In the second part we compare our theory with data in the literature on star polymers and with new data obtained on well-characterized polyisoprene star molecules. The agreement with experiment is gratifying. We conclude with a few remarks about other applications and possible extensions of our work.

I. Theory

In concentrated solutions or melts a polymer molecule is surrounded by other molecules which can be thought of as creating a constraining tube around it. A chain loses memory of its present configuration by diffusing out of this tube into a new one. For a linear polymer molecule this escape takes place by a translational diffusion process[2,14] along the tube, termed reptation. This type of motion will be prevented for star molecules because each arm is essentially fixed at one end by the branch point. However, stars can renew their configuration if the arms retract along their tube axes pushing out unentangled loops into the surrounding matrix.[12] The decrease in entropy involved in adopting such unlikely configurations (see Figure 1) can be thought of as creating a potential (actually a free energy), U, in which the end of the arm is diffusing. The lifetime of the tube is then related to the first-passage time problem for a particle moving in a potential well.[8]

In Figure 1 we show a diagram illustrating the model we are considering. Each arm of the star is made up of N segments, and each segment contains N_e monomers. N_e can be thought of as the number of monomers between entanglements and can be determined from measurements on linear polymers. There are $N_a = NN_e$ monomers per arm. Following Doi and Kuzuu[13] we assume the equilibrium contour length of an arm is

$$L_{eq} = \frac{N_a}{N_e}a \qquad \text{(I.1)}$$

The length of a segment, a, is related to N_e and the Kuhn monomer length b by $a = \nu b N_e^{1/2}$, where ν is a constant somewhat less than one. The potential function is taken to be[13] quadratic, i.e.

$$U(s) = \alpha k_BT\left(1 - \frac{s}{L_{eq}}\right)^2 = \frac{\alpha k_BT}{L_{eq}^2}x^2 \qquad \text{(I.2)}$$

(Doi[14] has used a similar potential to discuss tube length fluctuations, and the resulting extra tube relaxation.) The distance s is measured along the contour of the tube from the branch point. It is more convenient to use the distance $x = L_{eq} - s$, such that when the end of the arm is at $x = L_{eq}$ it has completely escaped from the tube. The quantity

$$\alpha \equiv \nu'(N_a/N_e) = \nu' N \qquad \text{(I.3)}$$

of eq I.2 is the fundamental dimensionless parameter of the problem. For the most part it will be considered to be large; i.e., the arms will be regarded as being long. Estimation of the constant ν' will be discussed in section III. Some indication of the value of ν and the validity of eq I.2 as an approximation for U can be obtained from our previous work,[15] in which we studied random lattice walks entangled with fixed obstacles. In this case the constants ν and ν' can be related to the coordination number of the lattice.[16] Previously[3,14] it had been assumed that α could be related to the usual elastic constant for stretching a free chain (obtained from the probability of a Gaussian random walk having a given end-to-end distance). However, α should be related to the statistics of the tube length of walks which do not entangle with the other chains.[15]

A function which characterizes the statistics of escape from the tube is the probability density $p(x,t|x_0;y)$ that the end of the chain is at position x at time t, given that it was originally at x_0 at time 0 and that at no time between 0 and t did it move further toward the star junction than y. This probability density is the same as that of a diffusing particle in the potential U with an absorbing barrier at y. It can be obtained as a solution to the Smoluchowski equation[17]

$$\frac{\partial p}{\partial t} = \frac{k_BT}{\bar{\zeta}}\frac{\partial}{\partial x}\left(\frac{2\alpha}{L_{eq}^2}x + \frac{\partial}{\partial x}\right)p \qquad \text{(I.4)}$$

with boundary conditions

$$p(y,t|x_0;y) = 0$$
$$p(-\infty,t|x_0;y) = 0 \qquad \text{(I.5)}$$

and initial condition

$$p(x,0|x_0;y) = \delta(x - x_0) \qquad \text{(I.6)}$$

$\bar{\zeta}$ is the friction coefficient of the chain for this mode of contraction of the end toward the branch junction. It may be expected that $\bar{\zeta}$ is proportional to N_a.

As is discussed more fully in Appendix A, the solution of the Smoluchowski equation can be written in terms of the spectrum of eigenvalues and eigenfunctions of an operator $\mathbf{L}$

$$\mathbf{L}\psi_n \equiv -\frac{L_{eq}^2}{2\alpha}\frac{d^2}{dx^2}\psi_n - \frac{d}{dx}x\psi_n = \lambda_n\psi_n \qquad \text{(I.7)}$$

and the adjoint equation $\mathbf{L}^+\psi_n^+ = \lambda_n\psi_n^+$. The eigenfunctions are to vanish at $x = y$ and be well behaved at $-\infty$. They are related to parabolic cylinder functions (cf. Appendix A). The probability density, p, is given by

$$p(x,t|x_0;y) = \sum_{n=0}^{\infty}\psi_n(x)\psi_n^+(x_0)\exp\left(-\frac{2\alpha k_BT\lambda_n t}{\bar{\zeta}L_{eq}^2}\right) \qquad \text{(I.8)}$$

where the λ_n are functions of y.

Let us define x_e as the root-mean-squared fluctuations in the length of a tube containing an arm of length L_{eq}. It is given by

$$x_e \equiv L_{eq}/(2\alpha)^{1/2} \qquad \text{(I.9)}$$

The time

$$\tau_e \equiv \bar{\zeta} L_{eq}^2 / 2\alpha k_B T \propto N_a^2 \qquad \text{(I.10)}$$

is a measure of the time required for a chain to visit points with values of $x \geq x_e$; i.e., $\tau_e = x_e^2/D$, with $D = k_B T/\bar{\zeta}$. In Appendix A it is shown that for times $t \gg \tau_e$ and $y \gg x_e$ the solution may be approximated as

$$p(x,t|x_0;y) \sim \left(\frac{\alpha}{\pi L_{eq}^2}\right)^{1/2} \exp\left(-\frac{\alpha x^2}{L_{eq}^2}\right) \times \exp\left[-\frac{2\alpha k_B T}{\bar{\zeta} L_{eq}^2}\left(\frac{\alpha}{\pi}\right)^{1/2} \frac{y}{L_{eq}} \exp\left(-\frac{\alpha y^2}{L_{eq}^2}\right) t\right] \qquad \text{(I.11)}$$

Let $F(y,t)$ be the probability that the chain end has not penetrated to y at time t. It is given by

$$F(y,t) = \int_{-\infty}^{y} \mathrm{d}x \, p(x,t|x_0;y) \qquad \text{(I.12)}$$

$$\approx \exp\left[-\frac{2\alpha k_B T}{\bar{\zeta} L_{eq}^2}\left(\frac{\alpha}{\pi}\right)^{1/2} \frac{y}{L_{eq}} \exp\left(-\frac{\alpha y^2}{L_{eq}^2}\right) t\right] \qquad \text{(I.13)}$$

for $y \gg x_e$ and $t \gg \tau_e$. An alternative derivation of eq I.13 is presented in Appendix B, based on Kramers[17,19,20] approach to the rate of escape from a well over a cusp-shaped barrier. This derivation is also applied there to problems where U is not quadratic in x.

The probability density of a chain penetrating to y is $\mathrm{d}F/\mathrm{d}y$. Thus the average fraction of tube not visited by the chain end (unrelaxed) at time t ($\gg \tau_e$) is

$$f(t) = \frac{1}{L_{eq}} \int_{x_e}^{L_{eq}} \mathrm{d}y \, (L_{eq} - y) \frac{\mathrm{d}F}{\mathrm{d}y} \qquad \text{(I.14)}$$

$$\approx \frac{1}{L_{eq}} \int_{x_e}^{L_{eq}} \mathrm{d}y \, F(y,t) \qquad \text{(I.15)}$$

A lower limit of x_e has been used as a cutoff on the integrals to avoid spurious singularities of the asymptotic form of the integrand. It introduces a negligible error for $t \gg \tau_e$ and large α, since F and $\mathrm{d}F/\mathrm{d}y$ are very small near x_e. Approximate evaluation of these integrals will be discussed below and in Appendix C.

If $\sigma(t)$ is the stress at time t after applying a small strain, γ, at time zero, then the stress relaxation modulus, $G(t)$, is defined as

$$G(t) = \sigma(t)/\gamma \qquad \text{(I.16)}$$

We follow the usual assumption[3] that the stress remaining at time t is proportional to the average length of the tube that has not relaxed (been visited by the free end of an arm); so

$$G(t) = G_0 f(t), \qquad t \gg \tau_e \qquad \text{(I.17)}$$

G_0 will be taken as the plateau modulus, which includes that part of the relaxation due to the small-scale fluctuations to x_e.

Various linear viscoelastic constants can be obtained from eq I.13 and I.15. The zero-shear-rate viscosity, η_0, is given by[22]

$$\eta_0 = \int_0^{\infty} G(t) \, \mathrm{d}t \qquad \text{(I.18)}$$

$$\sim \frac{G_0 \bar{\zeta} L_{eq}^2}{4\alpha^2 k_B T}\left(\frac{\pi}{\alpha}\right)^{1/2} e^{\alpha}, \qquad \alpha \gg 1 \qquad \text{(I.19)}$$

Since $\bar{\zeta}$, L_{eq}, and α are all proportional to the molecular weight of the arm, M_a, eq I.19 predicts that

$$\eta_0 \propto \left(\frac{M_a}{M_e}\right)^{1/2} \exp\left(\nu' \frac{M_a}{M_e}\right), \qquad \frac{M_a}{M_e} \gg 1 \qquad \text{(I.20)}$$

i.e., the viscosity of stars increases roughly exponentially with the molecular weight of the arms.

Another way of writing eq I.19 is

$$\eta_0 = G_0 \tau_m / (2\alpha) \qquad \text{(I.21)}$$

$$\tau_m \equiv \frac{\bar{\zeta} L_{eq}^2}{2\alpha k_B T}\left(\frac{\pi}{\alpha}\right)^{1/2} e^{\alpha} \qquad \text{(I.22)}$$

The relaxation time τ_m is, as will be shown, the characteristic time for complete escape of an arm from a tube. Equation I.21 can be understood by noting that most of the t integral comes from times of order τ_m where $G(t)$ has fallen to values of order G_0/α.

The steady-state shear compliance, J_e^0, can be obtained as[22]

$$J_e^0 = \int_0^{\infty} tG(t) \, \mathrm{d}t \Big/ \left[\int_0^{\infty} G(t) \, \mathrm{d}t\right]^2 \qquad \text{(I.23)}$$

$$= \alpha/G_0, \qquad \alpha \gg 1 \qquad \text{(I.24)}$$

or, equivalently

$$J_e^0 G_0 = \nu'(M_a/M_e) \qquad \text{(I.25)}$$

Equation I.24 is again understood on the basis of t and $\int_0^{\infty} ... \mathrm{d}t$ being $\mathcal{O}(\tau_m)$ and $G(\tau_m)$ being $\mathcal{O}(G_0/\alpha)$.

Let us return now to the evaluation of the integral of eq I.14 or I.15 for $f(t)$. Here the physical aspects, which are very important for understanding the remainder of the paper, will be emphasized, while in Appendix C the mathematical details will provided. The function $F(t,y)$ for $\tau_e \ll t \ll \tau_m$ looks very much like a step function. It undergoes a sharp transition from one to zero as the exponent (bracketed term) of eq I.13 passes through unity. This transition occurs over a range of values of y of $\mathcal{O}(\alpha^{-1})$ about $y = L_{eq}\xi(t)$, where $\xi(t)$ is defined as the solution of

$$t = \frac{\bar{\zeta} L_{eq}^2}{2\alpha k_B t}\left(\frac{\pi}{\alpha}\right)^{1/2} \frac{1}{\xi} \exp(\alpha \xi^2) \qquad \text{(I.26)}$$

To leading order in α^{-1} the functions $f(t)$ and, equivalently, $G(t)/G_0$ can be written as

$$G(t) = G_0[1 - \xi(t)] + \mathcal{O}(\alpha^{-1}) \qquad \text{(I.27)}$$

for $\tau_e \ll t \ll \tau_m$, which is the same as $x_e/L_{eq} < \xi(t) < 1 - \mathcal{O}(\alpha^{-1})$. The quantity $\xi(t)$ is a measure of the fraction of the tube which has been relaxed by passage of the end of the arm. It is very important to note that for each small increment ϵ of ξ, with $\alpha^{-1} \ll \epsilon \ll 1$, one gets a new hierarchy of times. Put another way, the time to escape to some value ξ is only a small fraction, $\mathcal{O}(e^{-2\alpha\xi\epsilon})$, of the time to escape to just a slightly larger value, $\xi + \epsilon$.

For $t > \tau_m$ another approach must be taken to evaluate eq I.14 as shown in Appendix C. The result is

$$G(t) = \frac{G_0}{2\alpha} E_1\left(\frac{t}{\tau_m}\right) + \mathcal{O}\left(\frac{1}{\alpha^2}\right), \qquad t > \tau_m \qquad \text{(I.28)}$$

$$\sim \frac{G_0}{2\alpha} \frac{\exp(-t/\tau_m)}{t/\tau_m}, \qquad t \gg \tau_m \qquad \text{(I.29)}$$

where E_1 is the exponential integral.[21]

In a similar way the frequency-dependent dynamic moduli can be obtained from the Fourier transform of $G(t)$ as

$$G^*(\omega) \equiv G'(\omega) + iG''(\omega) \qquad \text{(I.30)}$$

$$= G_0[1 - \xi(\omega^{-1})] + \mathcal{O}(\alpha^{-1}), \qquad \omega\tau_m \gg 1 \qquad \text{(I.31)}$$

Table I
Molecular Characteristics and Viscosity of Polyisoprene Melts

sample	M_w(arm)[a] $\times 10^{-3}$	M_n(arm)[b] $\times 10^{-3}$	M_w(star)[a] $\times 10^{-3}$	M_n(star)[b] $\times 10^{-3}$	$\bar{f}$[d]	η_0, P 60 °C
5S17	3.4		17		5	1.1×10^4
5S27	5.5		27		4.9	2.5×10^5
8S41		5.1	41	40	7.8	5.0×10^1
8S110		14.0	110	104	7.4	3.5×10^2
8S276	39.0[c]	37.4	276	270	7.1	3.3×10^4
8S795	100	98.0	795		8.0	3.5×10^7
12S41	3.5		41	40	11.7	3.6×10^1
12S96	8.3		96	100	11.6	1.5×10^2
12S250	21.0[c]	21.8	250	247	11.9	1.8×10^3
12S412	35.6[c]	36.0	412	415	11.6	2.0×10^4
12S810	68.9[c]	69.0	810		11.8	1.2×10^6
12S1440	112	120	1440		12.9	2.2×10^8

[a] Light scattering, except where noted. [b] Membrane osmometry. [c] Gel permeation chromatography. [d] $\bar{f} = M_w(\text{star})/M_w(\text{arm})$ or when not available, $M_n(\text{star})/M_n(\text{arm})$.

The term of $\mathcal{O}(\alpha^{-1})$ is given in Appendix C, and this includes the leading contribution to the loss modulus. Note that, to leading order, the approximation $G(t) = G'(\omega = 1/t)$ holds. For $\omega < \tau_m$ one finds

$$G^*(\omega) = \frac{G_0}{2\alpha} \ln (1 + i\omega\tau_m) + \mathcal{O}(\alpha^{-1}), \qquad \omega\tau_m < 1 \qquad \text{(I.32)}$$

The steady-state compliance, J_e^0, the viscosity, η_0, and the dynamic shear moduli are the experimental quantites which we will compare with our theory in the discussion which follows.

II. Experimental Section

The polyisoprenes used in this study were synthesized by L. J. Fetters. The method, which involved anionic polymerization initiated by *sec*-butyllithium, is described in ref 23. Multiple-arm stars with functionalities (f) of 5, 8, and 12 were prepared by adding an f-functional chlorosilane to an excess of polyisoprenyllithium. Unreacted arms were removed by fractional precipitation from a benzene–methanol mixture.

The number- and weight-average molecular weights of the arms and the weight-average molecular weights of the stars were measured (see Table I). In all cases the average functionality of the stars calculated by $\bar{f} = M_w\,(\text{star})/M_w\,(\text{arm})$ was within 10% of the functionality of the silane coupling agent (Table I).

Rheological measurements on the polyisoprene melts were performed with a Rheometrics System Four rheometer equipped with cone-and-plate test fixtures. The dynamic moduli of linear viscoelasticity were measured at 60 °C by subjecting the samples to a sinusoidal strain. The zero-shear-rate viscosity was obtained from the limiting behavior of $G''(\omega)$

$$\eta_0 = \lim_{\omega \to 0}\, [G''(\omega)/\omega] \qquad \text{(II.1)}$$

However, experiments were usually not carried to low enough frequencies to obtain values of

$$J_e^0 = \lim_{\omega \to 0}\, \{G'(\omega)/[G''(\omega)]^2\} \qquad \text{(II.2)}$$

The viscosities of some of the low molecular weight polyisoprene star molecules were measured by Mr. F. J. Vitus[24] at the University of Akron using a Rheometrics dynamic spectrometer.

Values of η_0 and J_e^0 for polybutadiene star solutions, polyisoprene star solutions, and polystyrene melts were obtained from the literature. Correlating those data with the ratio M_a/M_e required values of the plateau modulus, G_N^0. M_e is given by

$$M_e = \rho\phi RT/G_N^0 \qquad \text{(II.3)}$$

where ρ is the polymer density and ϕ is the volume fraction of polymer. The expressions used were

$G_N^0 = 1.18 \times 10^7 \phi^{2.26}$ dyn/cm² for polybutadiene[11]

$G_N^0 = 4.35 \times 10^6 \phi^{2.21}$ dyn/cm² for polyisoprene[25]

$G_N^0 = 2.1 \times 10^6$ dyn/cm² for polystyrene at $\phi = 1$[10]

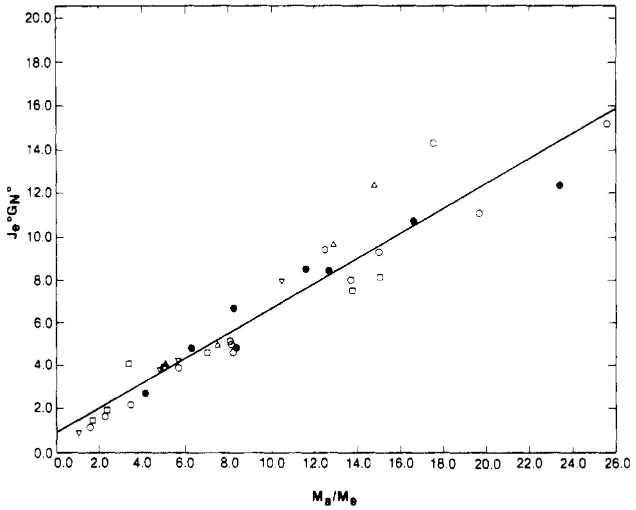

Figure 2. Product of the steady-state compliance, J_e^0, and the plateau modulus, G_N^0, for a series of star-shaped molecules. The symbols indicate polybutadiene solution,[11] 4 arm (○); polystyrene melts,[10] 4 arm (△) and 6 arm (▽); and polyisoprene solutions,[9] 4 arm (●) and 6 arm (□). Values of M_e were calculated from eq II.3 as described in the Experimental Section.

III. Discussion

1. Determination of the Constant ν'. The reptation model for linear polymers contains two parameters: ζ, the friction factor for the chain, and M_e, the molecular weight between entanglements. Extension of this theory to include star-shaped molecules introduces an additional parameter, ν', which is associated with the potential function, U, influencing the retraction of the chain end along the axis of the tube.

It was determined above that the product of the steady-state compliance and the initial modulus, $J_e^0 G_0$, is given by

$$J_e^0 G_0 \approx \nu'(M_a/M_e) \qquad \text{(I.25)}$$

In Figure 2 data are presented in accordance with this equation for 4- and 6-arm polyisoprene solutions,[9] for 4- and 6-arm polystyrene melts,[10] and for 4-arm polybutadiene solutions.[11] A reasonably linear relationship is obtained, which by least-squares analysis fixes the value of ν' at approximately 0.6.

The connection between the viscosity of star polymers and their molecular weight also involves the parameter ν'. According to eq I.19 and I.20, a plot of the logarithm of $\eta_0(M_a/M_e)^{-1/2}$ vs. M_a/M_e should be linear at high molecular weights, with a slope of ν'. In Figure 3 we show data on

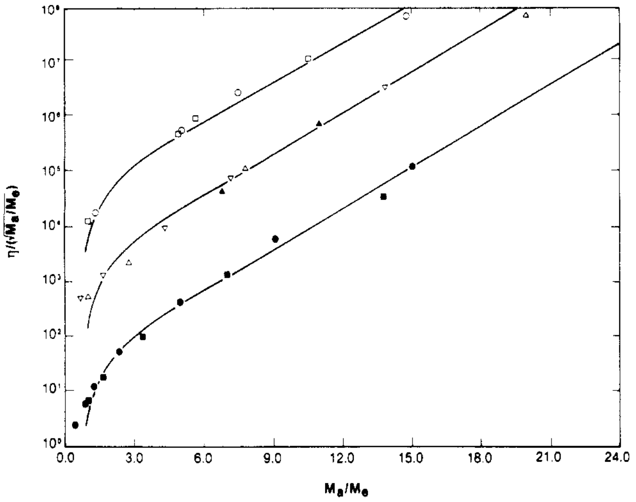

Figure 3. Steady-state viscosity, η_0, divided by $(M_a/M_e)^{1/2}$ for three types of star polymers: polyisoprene solutions, 4 arm (●) and 6 arm (■); polyisoprene melts, 5 arm (▲), 8 arm (△), and 12 arm (▽); and polystyrene melts, 4 arm (○) and 6 arm (□). To separate the curves the polyisoprene melt viscosities have been multiplied by 10.

polyisoprene solutions, polystyrene melts, and 5-, 8-, and 12-arm polyisoprene melts.[24] At values of $M_a/M_e \gg 1$ lines with a slope of 0.6 fit all of the data well. The full curves were calculated by numerical evaluation of the integral in eq I.15 using eq I.13 and I.18 and not just from the asymptotic result given by eq I.19.

2. Molecular Weight of the Arm as the Proper Variable. A basic premise of the model we have used is that each of the arms of a star polymer relaxes independently of the others. Hence the linear viscoelastic properties depend on the arm molecular weight and not the total molecular weight of the star. Support for this assumption is evident in Figures 2 and 3, where data on different functionality stars are all reduced by the common variable M_a/M_e.

3. Frequency-Dependent Behavior. The dynamic moduli, $G'(\omega)$ and $G''(\omega)$, for star polymers depend on frequency in a way which is quite different from that of linear polymers. This is demonstrated in Figure 4, where we compare theoretical predictions for the two types of polymers. At low frequency $G'(\omega)$ is less than $G''(\omega)$ and the moduli attain their usual[22] limiting values proportional to ω and ω^2:

$$G'(\omega) \approx \omega^2 \eta_0^2 J_e, \qquad \omega\tau_d \ll 1 \tag{III.1}$$

$$G''(\omega) \approx \omega\eta_0, \qquad \omega\tau_d \ll 1 \tag{III.2}$$

The terminal relaxation time, τ_d, for star polymers is given by τ_m, eq I.22, and for linear polymers is the reptation time[26] given by $\tau_R = \zeta L_{eq}^2/\pi^2 k_B T \propto M^3$.

As the frequency increases, the value of $G'(\omega)$ crosses above $G''(\omega)$. For linear polymers this occurs when $\omega\tau_d \approx 1$ and for stars when $\omega\tau_d \approx 4$. Near the point where $G'(\omega) = G''(\omega)$, $G''(\omega)$ for linear polymers passes through a maximum which is approximately equal to $0.4G_0$. However, for star polymers the value of $G''(\omega)$ continues to increase after the crossing point (see Figure 4b,c). The magnitude of G' when $G'(\omega) = G''(\omega)$ is independent of molecular weight for linear polymers whereas for star polymers it decreases approximately with the reciprocal of the arm molecular weight.[27] The latter observation serves to point out that the dynamic moduli of linear polymers in the terminal region are universal functions of a single variable, $\omega\tau_d$, whereas for star polymers they are functions of both $\omega\tau_d$ and α ($\alpha = \nu' M_a/M_e$).

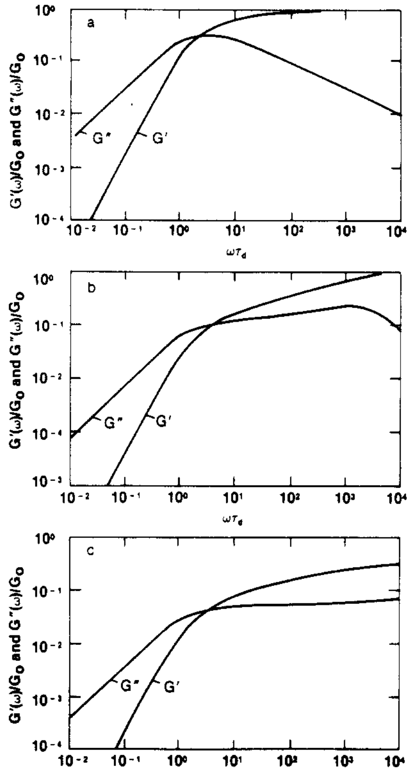

Figure 4. Dynamic moduli, $G'(\omega)$ and $G''(\omega)$, as a function of reduced frequency: (a) linear polymer; (b) star polymer with $\alpha = 10$; (c) star polymer with $\alpha = 20$.

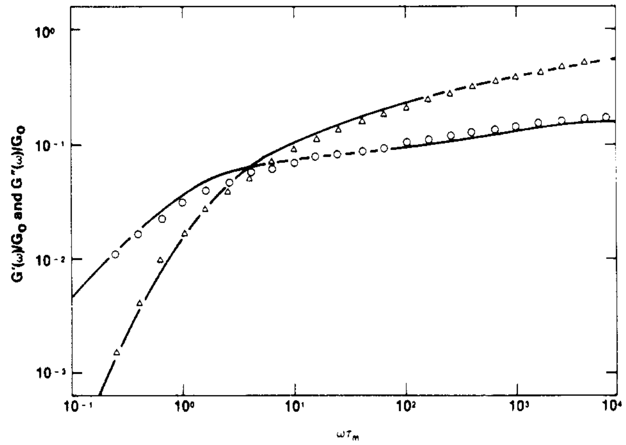

Figure 5. Dynamic storage modulus (△) and dynamic loss modulus (○) for sample 8S795 at 25 °C. Experimental values of $\alpha = 12$ and $\tau_m = 1600$ s are used. The parameter G_0, obtained by superimposing the theoretical curves on the data, is 4.1×10^6 dyn/cm^2, which is within 5% of the reported plateau modulus (4.35×10^6 dyn/cm^2).[25]

In Figure 5 we compare our theory with experimental data on an 8-arm-star polyisoprene (see Table I, sample 8S795). The solid lines were calculated from the theory using a value of $\nu' = 0.6$.

A potentially more useful way of presenting experimental data was introduced above. Because of the nature of the relaxation process of star molecules, the variable $\xi(t)$ is equal [with fluctuations only of $\mathcal{O}(\alpha^{-1})$] to the amount of arm which has disengaged from the original tube. Therefore

$$f(t) = G(t)/G_0 \approx 1 - \xi(t) \tag{I.27}$$

In a similar fashion the dynamic storage modulus, $G'(\omega)$, is given by

$$G'(\omega)/G_0 \approx 1 - \xi(\omega^{-1}) \tag{I.31}$$

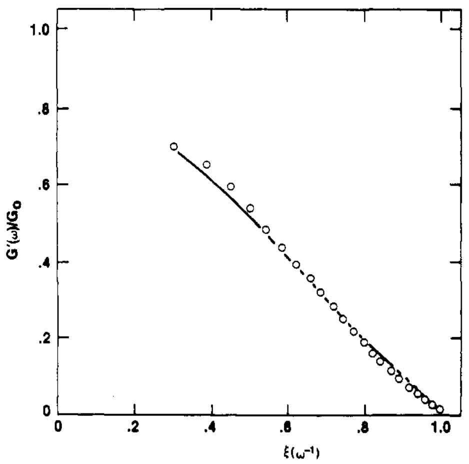

Figure 6. Dynamic storage modulus (○) as a function of ξ for sample 8S795. The values of ξ is from eq III.3 and the full curve was calculated with eq C.12. A straight line, as indicated by eq I.31, would fit the data almost as well.

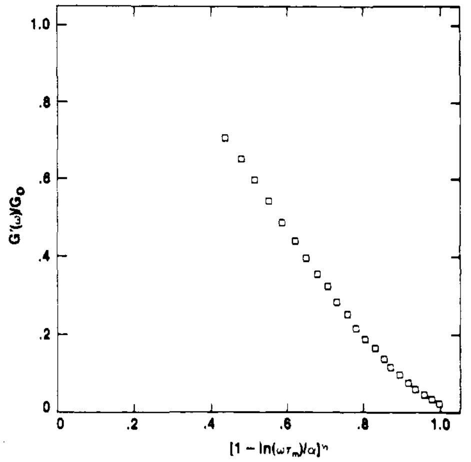

Figure 7. Storage modulus (□) as a function of an approximate value of ξ. $\xi \approx [1 - \alpha^{-1} \ln (\omega\tau_m)]^{1/2}$ (eq III.5). One notes that the deviation from a straight line increases as ξ becomes small.

Using the data shown in Figure 5 we have determined $\xi(\omega^{-1})$ by solving eq I.26 in the form

$$\frac{1}{\omega\tau_m} = \frac{1}{\xi} \exp(\alpha\xi^2 - \alpha) \tag{III.3}$$

with τ_m determined by

$$\eta_0 J_e^0 = \tau_m/2 \tag{III.4}$$

Figure 6 shows $G'(\omega)/G_0$ as a function of $\xi(\omega^{-1})$. The nearly linear relationship is apparent. The full curve was calculated using eqs C.12. Another way to present the data is to use an approximate solution of eq III.3

$$\xi \approx [1 - \alpha^{-1} \ln (\omega\tau_m)]^{1/2} \tag{III.5}$$

although this approximation is very bad for $\xi^2 \lesssim \alpha^{-1}$. One then plots

$$G'(\omega) \text{ vs. } [1 - \alpha^{-1} \ln (\omega\tau_m)]^{1/2}$$

The result is shown in Figure 7. A final means of graphing, suggested by the theory, is to plot

$$[1 - G'(\omega)/G_0]^2 \text{ vs. } \ln \omega$$

as shown in Figure 8.

IV. Concluding Remarks

While the experiments discussed in this paper have been on star polymers and the theory has also been couched in these terms, one would believe that the results are applicable to the relaxation of other branched structures. This would include the branches (but not the backbone) of the usual branched molecules and dangling ends in cross-linked networks. For the latter system Dr. J. G. Curro and the authors are examining the effects of polydispersity on relaxation, following ideas previously discussed by Curro and Pincus.[28]

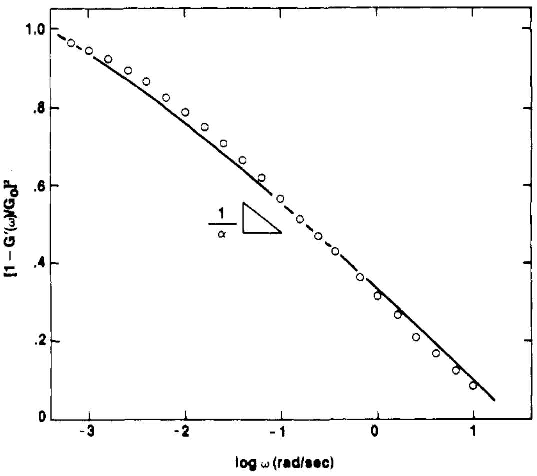

Figure 8. Plot of $[1 - G'(\omega)/G_0]^2$ as a function of logarithmic frequency. The slope is somewhat larger than α^{-1}, the deviations being due to the approximate nature of eq III.5. The solid curve was calculated with eq C.12.

The results presented here are also adaptable, in a fairly straightforward manner, to the interpretation of double-step-strain experiments. Indeed the sharpness of the distribution of fractional relaxation of an arm produces a picture of the process which is simpler than for linear polymers.[29] Preliminary measurements on double-step-strain relaxation of stars has been reported earlier by Pearson.[30] Further results and the theoretical framework for their interpretation will be reported subsequently.

Acknowledgment. We gratefully acknowledge the contribution of Lewis J. Fetters, who provided the polyisoprene star samples and who first suggested to us that viscosity data on concentrated solutions of different functionality stars could all be reduced to a common curve by plotting viscosity vs. the arm molecular weight. We also thank F. Jerome Vitus for the use of data he obtained on the viscosity of the polyisoprene melts.

Appendix A. Solution for $p(x,t|x_0;y)$

The eigenfunctions ψ_n and ψ_n^+ of L are

$$\psi_n(x) = N_n \exp(-x^2/4x_e^2) D_\lambda(-x/x_e) \tag{A.1}$$

$$\psi_n^+(x) = N_n \exp(+x^2/4x_e^2) D_\lambda(-x/x_e) \tag{A.2}$$

where the normalization constants, N_n, are such that ψ_n and ψ_n^+ form orthonormal sets. The D_λ are the parabolic cylinder functions. The eigenvalues λ_n are determined by the boundary condition in the form

$$D_\lambda(-y/x_e) = 0 \tag{A.3}$$

For large argument the asymptotic form of D_λ, as given by Miller and Good,[31] may be used to determine an asymptotic expression for the smallest eigenvalue

$$\lambda_0 \sim \left(\frac{\alpha}{\pi}\right)^{1/2} \frac{y}{L_{eq}} \exp\left(-\frac{\alpha y^2}{L_{eq}^2}\right) \tag{A.4}$$

The higher eigenvalues are

$$\lambda_n = n + \mathcal{O}(\lambda_0) \tag{A.5}$$

Therefore, after a time $t \gg \tau_e$ and for $y \gg x_e$, only the $n = 0$ term of eq I.8 for $p(x,t|x_0;y)$ is significant. In regions of $x/x_e = \mathcal{O}(1)$, one can show that

$$D_{\lambda_0}(-x/x_e) = \exp(-x^2/4x_e^2) + \mathcal{O}(\lambda_0) \tag{A.6}$$

$$N_0^2 \approx (2\pi x_e^2)^{-1/2} \tag{A.7}$$

It is because of eq A.6 that $p(x,t|x_0;y)$ is essentially independent of x_0 for the most likely range of values of x_0, i.e., those within the thermal fluctuation range, x_e. Physically, this is because the arm end rapidly equilibrates, on the time scale τ_e of eq I.10, within a range of order x_e.

Appendix B. Rate Expression for $F(y,t)$

The quantity $F(y,t)$ is analogous to the probability that a particle undergoing Brownian motion (high-friction limit) in the field $U(x)$ will not have escaped past the point y. Thus $F(y,t)$ is given as

$$F(y,t) = \exp[-r(y)t] \tag{B.1}$$

with $r(y)$ being the rate constant for escape from a well $U(x)$ over a cusp-shaped barrier at y [i.e., motion of a particle in the potential $U(x)$ for $x \leqslant y$ and $-\infty$ for $x > y$]. Kramers[17,19,20] has discussed the diffusive passage over barriers. The formula for $r(y)$ is (Kramers[19] does not give this explicitly, but it is easily derived)

$$r(y) = \frac{[U''(0)U''(y)]^{1/2}}{\zeta}\left[\frac{U(y)}{\pi k_B T}\right]^{1/2} \exp\left[-\frac{U(y)}{k_B T}\right] \tag{B.2}$$

Equation I.13 for $F(y,t)$ clearly follows for the quadratic potential. On the other hand, one could use a more general U, in which case eq I.27 for $G(t)$ and eq I.31 for $G^*(\omega)$ would still apply. However, $\xi(t)$ would be determined by solving the equation

$$r(\xi L_{eq}) = 1/t \tag{B.3}$$

Appendix C. Evaluation of Intergrals for $G(t)$ and $G^*(\omega)$

In this appendix we will provide more mathematical detail on the problem of evaluating the integrals for $G(t)$ and $G^*(\omega)$. Consider first for $t \gg \tau_e$

$$G(t)/G_0 \approx \int_{x_e/L_{eq}}^{1} F(zL_{eq},t)\,dz \tag{C.1}$$

$$F(zL_{eq},t) = \exp\left[-\frac{2\alpha k_B T}{\zeta L_{eq}^2}\left(\frac{\alpha}{\pi}\right) z e^{-\alpha z^2} t\right] \tag{C.2}$$

It is convenient to write F in terms of ξ defined by eq I.26

$$F(zL_{eq},t) = \exp\left[-\frac{z}{\xi} e^{-\alpha(z^2-\xi^2)}\right] \tag{C.3}$$

Because of the large α which appears in the inner exponential, F passes very quickly from 0 to 1 as z passes through ξ. It is clear that eq I.27 follows, but to make this more quantitative consider the change of variables

$$z = \xi(1 + q/\alpha) \tag{C.4}$$

in eq I.14 for $G(t)/G_0$. One can then write

$$\frac{G(t)}{G_0} \approx \int_{-\alpha(1-x_e/L_{eq}\xi)}^{\alpha(\xi^{-1}-1)} dq\,(1-\xi)\,\frac{dF}{dq} \tag{C.5}$$

$$-\frac{1}{\alpha}\xi \int_{-\alpha(1-x_e/L_{eq}\xi)}^{\alpha(\xi^{-1}-1)} dq\,q\,\frac{dF}{dq} \tag{C.6}$$

In both integrals the limits can be written as $-\infty$ to $+\infty$ with errors that are exponentially small. The first term gives eq I.27, and from the second term corrections beginning with $\mathcal{O}(\alpha^{-1})$ can be obtained. We will not present details of the calculation of these corrections but merely indicate the route. One makes the further change to a variable p defined by

$$p = -\ln F\left[\xi L_{eq}\left(1 + \frac{q}{\alpha}\right)\right] \tag{C.7}$$

$$= \left(1 + \frac{q}{\alpha}\right)\exp\left(-2\xi^2 q - \frac{\xi^2 q^2}{\alpha}\right) \tag{C.8}$$

Then solve for q as a function of p in a power series in $1/\alpha$. The result is

$$\frac{G(t)}{G_0} = (1-\xi) - \frac{C}{2\alpha\xi} + \mathcal{O}(\alpha^{-2}) \tag{C.9}$$

where $C = 0.5772...$ is Euler's constant. One caution in applying this formula is that, to be consistent, the formula for λ_0 should also be carried to higher order in $1/\alpha$, which will produce corrections of this order to the value of ξ. The steps are easily generalized to a nonquadratic $U(x)$.

For times $t > \tau_m$ a different procedure must be used. The integrand of eq C.1 is only significant for z within $\mathcal{O}(\alpha^{-1})$ for unity, so one makes the change of variables from z to r defined by

$$z = 1 - \frac{1}{2\alpha}\ln\frac{r\tau_m}{t} \tag{C.10}$$

The result is eq I.28 to leading order in $1/\alpha$.

A quite similar procedure may be used to find the dynamic modulus

$$G^*(\omega) \equiv i\omega\int_0^\infty dt\, e^{-i\omega t}G(t) \tag{C.11}$$

$$\approx G_0\int_{x_e/L_{eq}}^{1} dz\,(1-z)\,\frac{d}{dz}\,\frac{1}{1 - i(z/\xi)\exp[-\alpha(z^2-\xi^2)]} \tag{C.12}$$

where ξ is defined by eq I.26 with $1/\omega$ replacing t. For $\omega\tau_m \gg 1$, one makes the substitutions defined by eq C.4, C.7, and C.8. The result is

$$\frac{G^*(\omega)}{G^0} \approx 1 - \xi(1/\omega) + \frac{i\pi}{4\alpha\xi(1/\omega)} + \mathcal{O}(\alpha^{-2})$$

This goes beyond eq I.31 in that it gives the leading term of $G''(\omega)$, which is small like $1/\alpha$. For $\omega\tau_m < 1$ the change of variables defined by eq C.10 is what yields eq I.32.

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Effect of Molecular Weight Distribution on Viscoelastic Properties of Polymers. 2. Terminal Relaxation Time and Steady-State Compliance[†]

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ABSTRACT: The mole-basis blending law for the relaxation spectrum, $H(\tau) = \sum_i x_i H_i(\tau/\lambda_i)$, is presented, which gives better predictions of the terminal viscoelastic properties of polymer blends in the entangled state than does the weight-basis blending law. x_i is the mole fraction of the ith component, $H_i(\tau)$ the relaxation spectrum of the individual pure component i, and λ_i the shift factor of the time scale. The theoretical basis of this law is studied with partial success in the light of the tube model theory by Doi and Edwards. It has been reconfirmed that the lower molecular weight polymers in a binary blend behave like simple solvent molecules against the motion of the higher molecular weight polymers after the disengagement time of the former polymers elapsed.

Introduction

Doi and Edwards[1-3] have recently derived a rheological constitutive equation for highly entangled polymers from the primitive chain model and suggested that, for a mixture of a certain number of components, the memory function $\mu(t)$ involved in the constitutive equation obeys the weight-basis additivity[2]

$$\mu(t) = \sum_i w_i \mu_i(t) \tag{1}$$

Here, w_i is the weight fraction of the ith component polymer in the mixture and $\mu_i(t)$ is the memory function of the polymer i in the individual pure state. The effect of polydispersity on the steady-state compliance J_e can be estimated from the Doi–Edwards constitutive equation with eq 1 as[4]

$$J_e = C(M_{z+2}M_{z+3}M_{z+4})/(M_w M_z M_{z+1}) \tag{2}$$

where M's are the average molecular weights of indicated orders and C is a function of the polymer mass per unit volume, ρ, only. Thus J_e is independent of molecular weight for a monodisperse polymer but strongly dependent on the distribution of molecular weight. These are in accord with experiments, at least qualitatively.

Closer inspection, however, reveals a marked discrepancy between the theoretical prediction (2) and the experimental results. For example, let us consider the case in which the molecular weight distribution is represented by the logarithmic-normal distribution. Then we can rewrite eq 2 as

$$J_e = C(M_z/M_w)^9 \tag{3}$$

with the aid of the well-known relations

$$M_w/M_n = M_z/M_w = M_{z+1}/M_z = M_{z+2}/M_{z+1} = \ldots \tag{4}$$

On the other hand, the experimental data obtained by various investigators since Leaderman and associates[5,6] are fairly well represented by the empirical equation of Mills[7,8]

$$J_e = C(M_z/M_w)^{3.7} \tag{5}$$

or by the empirical equation of Agarwal[9]

$$J_e = C(M_z M_{z+1})/(M_n M_w) \tag{6}$$

The latter equation reduces to $J_e = C(M_z/M_w)^4$ for the logarithmic-normal distribution. Thus the two equations (5) and (6) give practically the same prediction not only for the case of binary blends but also for the continuous broad distribution.

The purpose of this paper is to bridge the existing gap between theory and experiment as exemplified by eq 3 and 5 and to afford a better understanding of the effect of molecular weight distribution on the terminal-zone behavior of highly entangled systems.

Phenomenological Linear-Blending Laws

We start with the classical linear blending law of Ninomiya[10] for a mixture of two monodisperse polymers with molecular weights M_1 and M_2, which may be written as

$$H(\tau) = w_1 H_1(\tau/\lambda_1) + w_2 H_2(\tau/\lambda_2) \tag{7}$$

Here, $H(\tau)$ is the relaxation spectrum of the mixture, $H_1(\tau)$ and $H_2(\tau)$ are those of the individual pure components, and w_1 and w_2 are the weight fractions. The quantity λ_i (i =

[†] This paper is dedicated to Professor Walter H. Stockmayer on his 70th birthday.

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