Rheological Behavior of Star-Shaped Polymers

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ABSTRACT: The rheological properties of star-shaped polyisoprenes having a wide range of arm numbers and arm molecular weights are reported. In contrast to linear polymers, stars have a broad relaxation spectrum and a viscosity that increases exponentially with arm molecular weight. A comparison of eight pairs of samples having 3 and 4 arms and identical arm molecular weights showed that the viscosity of 3-arm stars is approximately 20% lower. For higher degrees of functionality, $4 \leq f \leq 33$, the effect of functionality saturates and the viscosity is determined by arm molecular weight only. The nonlinear properties of one sample were studied using step-strain tests and found to be essentially identical to those of linear polymers. The predictions of a molecular theory for star polymers based on an extension of the reptation model are reviewed and shown to be in good agreement with the experimental data.

Introduction

The static and dynamic behavior of well-defined multi-armed star polymers has been extensively studied in recent years.[1-29] The interest that has been shown in these materials is due to their model nature. They are the simplest type of branched polymer that can be prepared with a uniform degree of branching and with branches (arms) that have essentially identical lengths. Although much of the work has been concerned with properties of dilute solutions of these materials,[2-13,28] the rheological behavior of concentrated solutions and melts has also been measured.[14-27,29] Topics of interest in the latter studies have been the concentration and molecular weight dependence of the zero shear rate viscosity as well as the time and frequency dependence of viscoelastic functions. A few studies have addressed the nonlinear properties that are observed when they are subjected to large strains or strain rates.[30-32]

The unique rheological properties of entangled stars is that the viscosity does not increase with a power law of the molecular weight as found for linear polymers but instead increases exponentially. This result was first reported by Kraus and Gruver[26] for 3- and 4-arm polybutadienes. Subsequently, Quack and Fetters[33] made the equally important observation that the viscosity of stars does not depend on the total molecular weight but only on the molecular weight of an arm. They showed, with data taken on stars having from 4 to 33 arms, that the viscosity could all be plotted on a single reduced curve if the independent variable was arm molecular weight.[34,35] This finding was subsequently confirmed by others[20,36] and fitted to an equation of the form

$$\eta_0 \sim (M_a/M_e)^b \exp(\nu' M_a/M_e) \qquad (1)$$

where M_e is the molecular weight between entanglements and M_a is the arm molecular weight. For uniform stars, the arm molecular weight is just equal to the total molecular weight, M, divided by the number of arms or functionality, f. Because the preexponential factor in eq 1 has only a small influence on the calculated viscosity, the exponent b is not determined from the experimental data. Instead, values of order 1 ($1/2 \leq b \leq 2$), consistent with theoretical work, are used.[20,36] When b is in this range, the experiments show that the constant ν' is approximately 0.5.

The reports cited above were convincing in their finding that the viscosity depends exponentially on M. No rheological studies, however, have explored a series of stars with the lowest degree of functionality, $f = 3$. Calculations by Klein[37] and Doi[38] indicate that trifunctional stars might have a lower viscosity than stars with $f \geq 4$. One purpose of this work is to present a more complete evaluation of the effect of functionality on the viscosity of stars. Although most of the data are on 3- and 4-arm stars, information on stars with values of f larger than in our previous papers is also reported.

In the sections that follow we provide further information on the derivation of eq 1 and on the value of the constants that appear in it. We also briefly describe the temperature dependence of viscoelastic properties, the effect of functionality on the diffusion coefficient, the rate of dielectric relaxation, and the nonlinear properties of stars at large strains. We conclude with some remarks on how the study of star-shaped molecules has made an important contribution to the development of structure–property relationships for polymeric materials.

Experimental Section

The methods used to prepare and characterize the stars have been previously published.[13,39-41] These papers can be summarized by stating that anionic polymerization techniques[42] were employed and that multifunctional chlorosilanes or divinylbenzene isomers were used as linking agents. The stars were fractionated repeatedly until size-exclusion chromatography measurements no longer detected any residual unlinked arms. The polyisoprene microstructure was typical of that found for organolithium-based polymerizations in hydrocarbon media, i.e., about 75% cis-1,4, 18% trans-1,4, and 7% 3,4.

The materials studied consisted of eight pairs of 3- and 4-arm stars, with the molecular weight of the arms varying from

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Table I
Molecular Characteristics of 3/4-Arm Polyisoprene Stars

no. of arms	M_w(arm), $\times 10^{-4}$	M_w(star), $\times 10^{-4}$	$[\eta]^{25°C}_{C_6H_{12}}$, dL g^{-1}	$A_2 \times 10^4$, mL md g^{-2}
3	1.14	3.52	0.354	0.33
4	1.14	4.65	0.376	0.35
3	1.70	5.06	0.450	0.33
4	1.70	6.80	0.480	0.36
3	3.67	11.1	0.803	0.42
4	3.67	14.8	0.869	0.37
3	4.40	13.7	0.958	0.36
4	4.40	17.3	0.973	0.34
3	4.75	13.9	0.979	0.40
4	4.75	18.8	1.03	0.41
3	7.22	21.1	1.34	0.38
4	7.22	28.0	1.45	0.39
3	9.50	27.8	1.65	0.36
4	9.50	38.0	1.74	0.37
3	10.5	32.2	1.85	0.40
4	10.5	41.0	1.95	0.46
4[a]	12.4	48.0		

[a] Used at 50% by weight in squalene for step-strain tests.

Table II
Molecular Characteristics of Multiarm ($f > 4$) Polyisoprene Stars

no. of arms	M_w(arm), $\times 10^{-4}$	M_w(star), $\times 10^{-4}$	$[\eta]^{25°C}_{Tol}$, dL g^{-1}	$A_2 \times 10^4$, mL md g^{-2}
5	3.00	15.0	0.77	7.5
5	5.1	25.0	1.03	6.5
8	0.51	4.1	0.250	7.4
8	1.4	11.0	0.420	6.8
8	3.7	27.6	0.875	5.9
8	9.8	79.5	1.84	4.5
12	0.35	4.1	0.225	9.4
12	0.83	9.6	0.280	5.5
12	2.1	25.0	0.580	4.5
12	3.6	41.2	0.800	3.9
12	6.9	81.0	1.36	3.4
12	12.0	144	2.14	3.0
18	1.1	19.7	0.351	4.4
18	2.1	38.4	0.529	3.2
18	4.6	80.0	1.02	2.7
18	8.2	148	1.62	2.3
27	3.9	102	0.820	1.9
33	5.1	167	0.926	1.5

approximately 10^4 to 10^5. Each pair was made by dividing the same batch of arms and then linking half with trichloromethylsilane and the other half with tetrachlorosilane. This assured that the polymers differed only in functionality and not in the molecular weight or molecular weight distribution of the arms. Other stars with functionalities of 5, 8, 12, and 18 were made with other chlorosilanes, and two stars with average functionalities of 27 and 33 were made with divinylbenzene as the linking agent.

These polymers were part of an extensive study of chain dimensions of stars in dilute solutions.[13] Static and dynamic light scattering and measurements of the intrinsic viscosity were used for molecular characterization. The details of how the measurements were done are summarized in ref 13. Results pertinent to this study are reproduced in Tables I ($f = 3$ and 4) and II ($f > 4$).

The rheological measurements were carried out with either a Mechanical spectrometer or System 4 instrument obtained from Rheometrics, Inc. Both instruments were equipped with 25-cm-diameter parallel disks and a 2000 g cm torque transducer. The dynamic moduli, $G'(\omega)$ and $G''(\omega)$, were determined as a function of frequency, ω, by subjecting the samples to small sinusoidal strains (1–10%). For the studies done as a function of temperature, a range of at least 0–75 °C was covered and in some cases the lowest temperature was −35 °C. The frequency range was sufficiently large so that data were obtained from the high-frequency transition region down to the low-frequency terminal region. For all polymers, the data extend to low enough frequencies so that the viscosity attains a constant value of η_0 and in some cases so did the value of the steady-state linear compliance J_e^0.

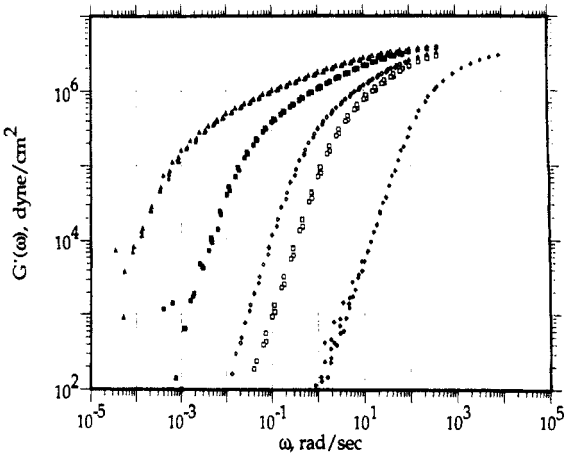

Figure 1. In-phase component of the dynamic shear modulus, $G'(\omega)$, as a function of frequency for five of the 4-arm star polymers in Table III. Samples are labeled by their total molecular weight: (◆) 68K, (□) 148K, (◇) 188K, (■) 280K, (▲) 380K. Data are reduced to a reference temperature of 25 °C.

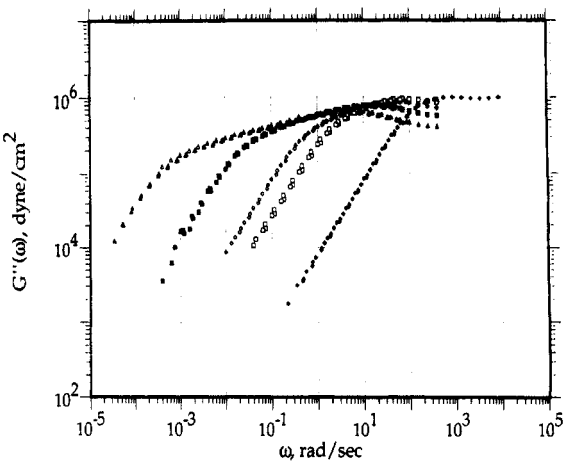

Figure 2. Out-of-phase component of the dynamic shear modulus, $G''(\omega)$, as a function of frequency for five of the 4-arm star polymers in Table III. Samples are labeled by their total molecular weight: (◆) 68K, (□) 148K, (◇) 188K, (■) 280K, (△) 380K. Data are reduced to a reference temperature of 25 °C.

One sample was subjected to large step-strain experiments using the same equipment with cone and disk fixtures in place of parallel disks. To avoid overloading the rheometer transducer, the experiments were conducted with a 50 wt % solution of polymer in squalene. The solvent was a low molecular weight, naturally occurring 1,4-polyisoprene. The concentration and molecular weight ($M = 480\,000$) of the star were sufficiently high so that the molecules overlapped with each other. Strains up to 5 were used.

Results

Figures 1 and 2 show the dynamic moduli, $G'(\omega)$ and $G''(\omega)$, of the 4-arm stars. To prevent excessive overlap, data from only five of the eight samples are shown. Although the measurements include data taken over a wide range of temperatures, they are reduced to a common reference temperature of 25 °C using time–temperature superposition.[43] From this procedure it was determined that the temperature dependence of polyisoprene stars is identical to that of linear polyisoprene, a result that agrees with earlier findings of Graessley.[44,45] This similarity is in contrast to that found for stars of hydrogenated polybutadiene and polyisoprene that have a temperature dependence different from linear species and more like that of polyethylene containing long branches. Further

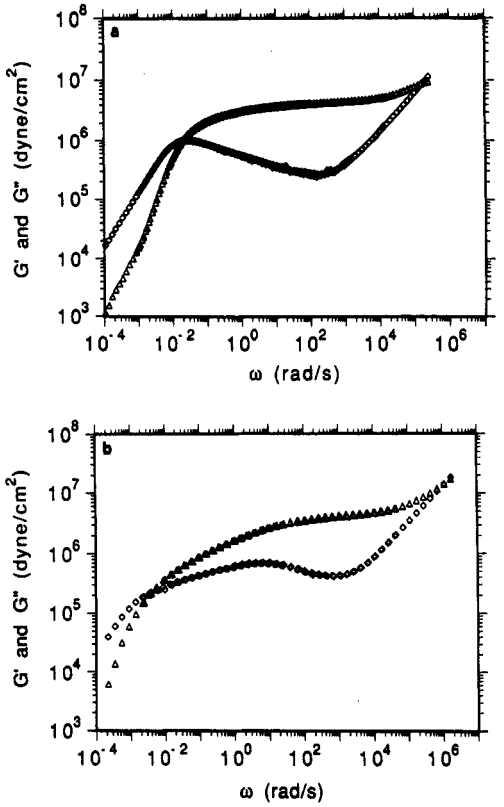

Figure 3. Comparison of the dynamic moduli of a linear and a 4-arm star polymer having similar viscosities. (a) Linear polymer with $M = 5.0 \times 10^5$ and $\eta_0 = 1 \times 10^8$ P. (b) Star polymer (4-arm) with $M_a = 9.5 \times 10^4$ and $\eta_0 = 1.8 \times 10^8$.

discussion on the temperature dependence is delayed until after the theoretical models of star relaxation have been reviewed.

The most important feature of the frequency response is the distinctively different shape of the star polymer data when compared to that of linear polymers. This is shown by comparing linear and star polymers with similar viscosities (see Figure 3a,b). For both polymers the frequency (ω_c) at which $G'(\omega)$ crosses $G''(\omega)$ is approximately the reciprocal of the longest relaxation time, τ_m. At frequencies higher than ω_c, the value of G'' decreases for linear polymers, or equivalently the slope of the dynamic viscosity, d ln $\eta'(\omega)$/d ln ω, is less than −1. In contrast to this behavior, star polymers have a dynamic loss modulus that continues to increase for frequencies greater than ω_c. Therefore, the logarithmic derivative of the viscosity in this region is greater than −1. At still higher frequences $G''(\omega)$ for stars finally reaches a maximum at ω_{max}. The quantity ω_{max}^{-1} has been shown by Roovers[20] to be proportional to M^2 which is the expected Rouse relaxation time of an arm, τ_{eq}. Our own data shown in Figure 4 indicate the molecular weight dependence is somewhat stronger ($\omega_{max}^{-1} \sim M^{2.6}$). Because ω_c^{-1} is proportional to the longest relaxation time which increases exponentially with the arm molecular weight and ω_{max}^{-1} increases as a power law, the region between ω_c^{-1} and ω_{max}^{-1} becomes larger as the arm molecular weight goes up. This can be seen by comparing Figures 1 and 2.

All of the dynamic data on the stars continue into the low-frequency range where G'' is proportional to ω. The Newtonian viscosities obtained in this region from the

$$\lim_{\omega \to 0} G''(\omega)/\omega = \eta_0 \qquad (2)$$

are plotted in Figures 5 (for $f \geq 4$) and 6 (for $f = 3$ and 4) as a function of the span molecular weights, M_s. M_s is the molecular weight of the longest linear span in the molecule,

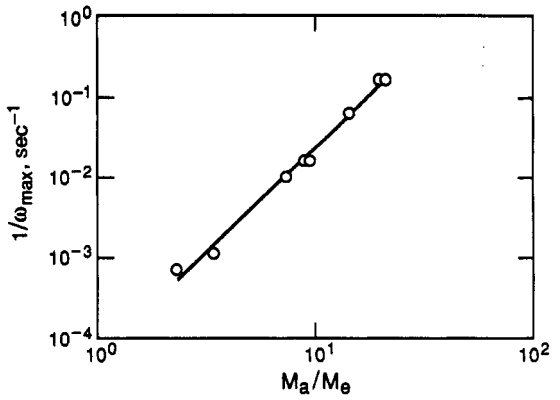

Figure 4. Reciprocal of the frequency at the peak of G'' for the all of the 4-arm star polymers vs M_a/M_e. The slope of the line is 2.6.

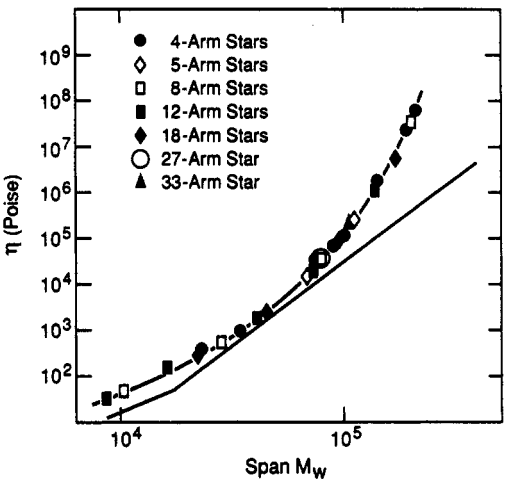

Figure 5. Logarithmic plot of the viscosity of star polymers with functionalities of 4 or more verses span molecular weight. The lower line applies to linear polymers.

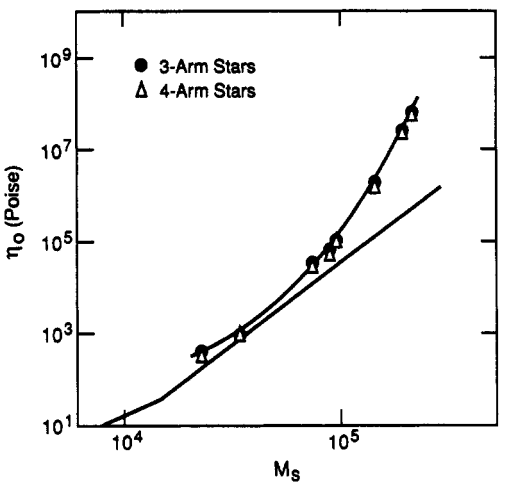

Figure 6. Logarithmic plot of the viscosity of star polymers with functionalities of 3 and 4 verses span molecular weight. The lower line applies to linear polymers.

and it is equal to the total molecular weight of a linear molecule or to twice the arm molecular weight of a star, $M_s = 2M_a$. The figures also contain a line showing the viscosity of linear polyisoprenes. The viscosity of the linear polymers in poise follows power laws in the molecular weight given by the expressions[46]

$$\eta_0 = 2.16 \times 10^{-7} M^{1.98} \qquad M < M_c = 15\,000 \qquad (3a)$$

$$\eta_0 = 5.26 \times 10^{-14} M^{3.57} \qquad M > M_c \qquad (3b)$$

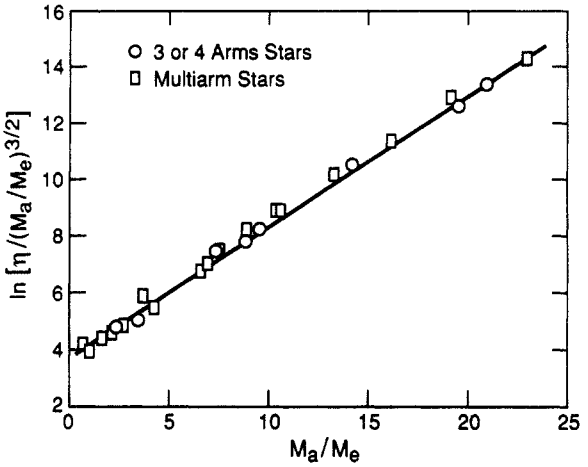

Figure 7. Semilogarithmic plot of the log of the viscosity of star polymers divided by $(M_a/M_e)^{3/2}$ verses M_a/M_e. The slope of the line is $\nu' = 0.47$.

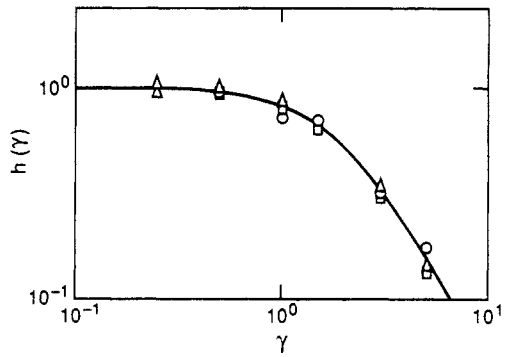

Figure 8. Function $h(\gamma)$ characterizing the nonlinear response to a step strain of star polymers. Data were obtained in triplicate at each strain.

which have coefficients and exponents valid at 60 °C. From these figures, it is clear that the viscosity of the star molecules is increasing *faster* than a power law.

It is instructive at this point to plot the data in a manner suggested by eq 1. For reasons explained below, we choose a value of $b = 3/2$. The linear behavior of this semilogarithmic plot (Figure 7) shows that the viscosity is increasing exponentially with the molecular weight of the arm. The slope of the line is equal to the parameter ν' that appears within the exponential of eq 1. It has a value of 0.47, which is similar to our earlier findings[32] and those of others.[20]

An examination of Figure 6 indicates that the difference between the viscosity of 3- and 4-arm stars is hardly noticeable. Direct numerical comparison nevertheless shows (see Tables III and IV) that the viscosity of 4-arm stars is always slightly larger than that of 3-arm stars. Although the average difference for the eight pairs of polymers is small (21%), it is real because the comparison is between materials that have identical arm molecular weights. Our data also agree with those of Hadjichristidis and Roovers,[19] who found a difference of 20% using one pair of stars having 3 and 4 arms. The effect of functionality on viscosity does saturate. If the comparison is between stars having $f = 4$ and, say, $f \geq 8$, the difference is negligible (see Figure 5).

A molecular explanation for the difference in behavior between 3- and 4-arm stars is given in the Discussion.

Data on the nonlinear properties of star-shaped molecules are extremely limited, although a few reports have appeard.[30-32] We describe some new results taken from step strain tests where the strain, γ, is large enough to be far out of the linear viscoelastic regime ($1 < \gamma < 5$). For star molecules it is found that the shear modulus, $G(t,\gamma)$, given by the ratio of shear stress, $\sigma(t,\gamma)$, to γ, has the same time dependence at long times regardless of the initial strain. This implies that $G(t,\gamma)$ can be factored into two functions, one depending on time and equal to the linear viscoelastic shear modulus, $G(t)$, and the other depending on strain, $h(\gamma)$. The same factorability is observed for linear molecules as well.[32] As expected from the differences in dynamic moduli described above, the shapes of $G(t)$ for linear and star molecules are different.[47] However, the function $h(\gamma)$ shown in Figure 7 is the same.

The molecular theory given in the next section attributes the nonlinear properties of $h(\gamma)$ to the contraction of molecules that have been stretched. Because star molecules are connected at only one end to a branch point, it is expected that they can contract back just like linear polymers and therefore have the same nonlinear strain dependence. Our data support this idea.

Discussion

The viscoelastic properties of entangled polymers have received considerable theoretical attention.[1,48-56] The most successful model for describing the relaxation of entangled *linear* polymers assumes that the motion proceeds by "reptation" which involves translation of each molecule along a tubelike region created by the surrounding polymers.[1,54-56] An essential assumption made in adapting these models to entangled *stars* is that the central branch point suppresses the translational motion of the arms and therefore another mode of arm motion is needed. The proposed process involves retraction of the end of the arm along its average contour with the simultaneous projection of unentangled loops into the surrounding matrix.[48-53] This mechanism could in principle proceed without any diffusive motion of the star's center of mass as expected, for example, in the relaxation of dangling strands that are anchored to junctions in a rubber network.[57]

As the arm retracts the free energy increases due to the loss in configurational entropy. de Gennes[48] was the first to explore this problem, and using a lattice model, he calculated the number of walks for each tube length and concluded that the time required to retract completely and therefore the viscosity would increase exponentially with the arm length, M_a. In a related approach, Doi and Kuzuu[49] showed how to obtain the time dependence of star relaxation. They calculated the probability that the end of an arm of a star polymer has partially retracted toward the branch point from an analysis of diffusion in a potential field, U. An approximation for U given by the quadratic function[36,49,50]

$$U = \alpha kT[(L - L_{eq})/L_{eq}]^2 \qquad (4)$$

was used. Here L is the position of the tip of the arm and L_{eq} is its equilibrium position. The height of the potential barrier in units of kT is $\alpha = \nu'(M_a/M_e)$ where ν' is the same order 1 numerical constant given in eq 1. For typical stars, α is much larger than 1, and under these conditions the Doi–Kuzuu theory predicts that the viscosity increases exponentially with the molecular weight and has a power law prefactor, $(M_a)^b$ with $b = 2$. This agrees with eq 1.

As is well-known,[56] the de Gennes entropy calculation contained an error that was later corrected by Helfand and Pearson,[58] by Needs and Edwards,[59] and by Nechaev, Semenov, and Koleva.[60] The problem has been studied further by Khoklov, Ternovsky, and Zheligovskaya[61] and by Mehta, Needs, and Thouless.[62] For large L and for values of L that are not to far removed from L_{eq}, these

Table III
Newtonian Viscosities for 3/4-Arm Polyisoprene

no. of arms	M_w(arm), $\times 10^{-3}$	M_w(star), $\times 10^{-3}$	M_a/M_e[a]	Newtonian viscosities, P				
				0 °C	25 °C	50 °C	60 °C	75 °C
3	11.4	35.2	2.3	5.3×10^4	2.9×10^3	5.5×10^2	3.4×10^2	1.8×10^2
4	11.4	46.5	2.3	6.4×10^4	3.5×10^3	6.8×10^2	4.2×10^2	2.3×10^2
3	17.0	50.6	3.4	1.2×10^5	8.3×10^3	1.6×10^3	9.5×10^2	5.1×10^2
4	17.0	68.0	3.4	1.5×10^5	8.6×10^3	1.7×10^3	9.6×10^2	5.1×10^2
3	36.7	111	7.3	2.0×10^6	2.1×10^5	4.5×10^4	2.6×10^4	1.4×10^4
4	36.7	148	7.3	3.0×10^6	2.7×10^5	5.5×10^4	3.3×10^4	1.7×10^4
3	44.0	137	8.8	5.2×10^6	4.4×10^5	8.8×10^4	5.1×10^4	2.7×10^4
4	44.0	173	8.8	6.8×10^6	5.5×10^5	1.1×10^5	6.3×10^4	3.3×10^4
3	47.5	139	9.5		7.6×10^5	1.7×10^5	1.0×10^5	5.3×10^4
4	47.5	188	9.5		8.7×10^5	2.0×10^5	1.1×10^5	6.0×10^4
3	72.2	211	14.2		1.0×10^7	2.5×10^6	1.5×10^6	8.2×10^5
4	72.2	280	14.2		1.3×10^7	3.2×10^6	1.9×10^6	1.0×10^6
3	95	278	19.6		1.5×10^8	4.2×10^7	2.2×10^7	1.0×10^7
4	95	380	19.6		1.75×10^8		2.5×10^7	1.3×10^6
3	105	322	21.0			8.6×10^7	4.6×10^7	2.6×10^7
4	105	410	21.0			1.0×10^8	6.1×10^7	3.0×10^7

[a] M_a = arm molecular weight; $M_e = 5 \times 10^3$, the entanglement molecular weight.

Table IV
Newtonian Viscosities for Multiarm Polyisoprene Stars

no. of arms	M_w(arm), $\times 10^{-3}$	M_w(star), $\times 10^{-3}$	M_a/M_e	Newtonian viscosities at 60 °C, P
5	30.0	150	6.54	1.40×10^4
5	51.0	250	10.58	2.50×10^5
8	5.1	40.8	0.98	5.0×10^1
8	14.0	111	2.69	5.60×10^2
8	37.0	276	7.50	3.60×10^4
8	98.0	795	19.23	3.3×10^7
12	3.5	40.9	0.67	3.6×10^1
12	8.3	96.3	1.60	1.65×10^2
12	21.0	250	4.19	2.0×10^3
12	36.0	412	6.92	2.0×10^4
12	69.0	810	13.27	1.2×10^6
12	122	1440	23.08	1.7×10^8 [a]
18	10.9	197	2.10	3.0×10^2
18	21.0	384	3.65	2.5×10^3
18	46.0	800	8.84	9.9×10^4
18	82.0	1480	16.14	5.45×10^6
27	38.9	1020	7.50	3.60×10^4
33	53.5	1670	10.29	2.4×10^5

[a] Extrapolated value.

theories predict that

$$p(L) = (\alpha/\pi L_{eq}^2)^{1/2} \exp\{-\alpha[(L - L_{eq})/L_{eq}]^2\} \quad (5)$$

is the probability density that the end of the arm is between L and $L + dL$. Apart from terms that depend only on L_{eq}, the logarithm of eq 5 multiplied by $-kT$ gives the potential (free energy) U shown in eq 2.

The diffusion problem for the motion of the end of the arm was further developed by Pearson and Helfand.[50] If U is derived from eq 3, they showed that the constant b in eq 1 is equal to 1. However, for values of L near the branch point of the star, the more accurate forms of U given in the original papers[58,62] should be used. When this is done, the exponent b increases to $^3/_2$, which is the value used in this paper. Details on the derivation of these results are given in the appendix.[63]

The value of the constant ν' can be estimated from the lattice models, but it also can be related to the elastic modulus, G_N, of the polymer in the plateau region. According to the Doi–Kuzuu[49] and Pearson–Helfand[50] models (see the appendix),

$$\alpha = \frac{15}{8}\frac{G_N M}{\rho RT} \quad (6)$$

If the definition of M_e is the conventional one of the plateau modulus, G_N, divided by ρRT, then $\nu' = {}^{15}/_8$.

Because the experimentally measured value of ν' is only about 0.5, the difference between theory and experiment is enormous. In fact the discrepancy is larger than the much discussed case of linear polymers for which the theoretical and experimental power law exponents for viscosity are 3 and 3.4, respectively.[1]

One method for decreasing the coefficient ν' is to use a more general form for the potential U. When U is obtained from a lattice model and a reasonable estimate of the lattice coordination number ($6 < q < 12$) is used, the factor ν' is lowered by a factor between 1.3 and 2.25 (see the appendix).

An additional explanation for the low value of ν' has been given by Ball and McLeish.[53] They reason that during the long period required for an arm to retract back to the origin the surrounding constraints made up of arms of other stars are also retracting back. This allows each arm to relax its orientation by a process of tube renewal.[64] The effect of this process is included by assuming that the value of M_e increases in inverse proportion to the amount of polymer that has not relaxed. A mechanism like this has been presented previously for linear polymers by Marrucci,[65] Viovy,[66] and des Cloizeaux.[67] Pursuing this idea in an approximate way, they find that the value of ν' is decreased by a factor of 3 in good agreement with experiment.

Pearson and Helfand[50] showed that the frequency dependence of G' and G'' was described well by the diffusion model. The Ball–McLeish tube renewal mechanism causes some changes in the shape of G' and G'' that further improve the agreement with data. A more refined version of their model could be obtained by using the potential derived from the lattice model.[58,62]

Stress relaxation for entangled polymers is achieved by a process of disorientation involving diffusion out of a tube or tube renewal. Klein[37] and Doi[38] have both suggested that 3-arm stars have an additional mechanism of relaxation that higher arm stars do not have. They propose that an arm can vacate its tube if the branch point of a 3-arm star diffuses down one of the tubes. This motion requires one of the tubes to be occupied by $f - 1$ arms and would have an extremely low probability for higher functionality stars. Using an approximate potential field, Klein predicts a viscosity lowering of 33% for 3-arm stars that is in reasonable accord with the results reported above.

Graessley[44] has made an important connection between relaxation in stars and the temperature dependence of their viscoelastic properties. If stars relax by chain

retraction, then the chain must pass through transition states with much more compact configurations than the ones near the average. The longest relaxation times should be associated with the most compact configurations since complete disengagement requires the chain to retract a distance proportional to the whole length of an arm. On average, retracted polymer chains will have a larger fraction of gauche states. If the gauche configuration has a higher energy, the activation barrier for the longest relaxation time should increase in a roughly linear manner with the length of the arm. The faster relaxation times will be proportionally less affected. Behavior like this is found for hydrogenated polybutadiene stars and hydrogenated polyisoprene stars,[44,45] but not for polystyrene, polybutadiene, and polyisoprene stars.[44] Data on the chain dimensions of polyisoprene suggest that they are independent of temperature,[68] which implies that the trans and gauche minima have essentially the same energy. With no energy difference between contracted configurations and expanded ones, the temperature dependence of star and linear polyisoprene should be the same. This agrees with our findings.

Even though the temperature dependence of high molecular weight entangled star polymers is not always larger than that of linear polymers, the width of the relaxation spectra is. This suggests that coupling theories that predict a direct connection between the shape of the relaxation spectra and the temperature dependence are not correct.[69]

Step-strain experiments are a conceptually simple test for determining nonlinear response. At time $t = 0$, a large strain is rapidly imposed on the sample and the resulting stress is measured until it relaxes to zero. The ratio of stress to strain, the stress relaxation modulus ($G(t,\gamma)$, is normally a function of strain. However, the well-known Rouse and Zimm models[1] predict that $G(t,\gamma)$ is independent of strain and equal to $G(t)$, the relaxation modulus of linear viscoelasticity. This result is consistent with a microscopic model containing linear Brownian springs that are stretched and oriented by the strain. $G(t,\gamma)$ for the reptation model is strain dependent and decreases as $1/\gamma^2$ for large strains. This behavior is consistent with a model containing Brownian springs that have relaxed to their rest length but are still oriented by the strain. More precisely the reptation model predicts that

$$G(t,\gamma) \cong G(t)/(1 + \gamma^2/5) \quad (7)$$

where again $G(t)$ is the linear viscoelastic shear modulus (see the appendix). Since the polymer retracts on a time scale much faster than it loses its orientation, the function $h(\gamma)$ plotted in Figure 7 should be approximately $1/(1 + \gamma^2/5)$. This separation of time scales for retraction and disorientation is expected for both linear and star-shaped polymers. The experimental data on stars shown in Figure 7 are very similar to those reported for linear polymers. Results similar to these have been previously reported by Osaki et al.[32] Other types of branched polymers often show values of $h(\gamma)$ between the predictions of the Rouse and reptation models,[70,71] and it is reasonable to expect that time-scale separation may break down for highly branched polymers.[72]

Another important nonlinear test is to determine the shear rate dependence of the viscosity at high shear rates. The reptation model predicts the shear rate dependent viscosity, $\eta(\dot{\gamma})$, is essentially equal to the frequency-dependent dynamic viscosity, $\eta'(\omega)$, in agreement with the so-called Cox–Merz relationship.[73] Furthermore, for shear rates greater than $1/\tau_m$, linear polymers are predicted to have a maximum in the steady shearing stress which may cause the onset of an unstable flow.[1] According to the Cox–Merz relationship, the maximum in σ should correspond to a maximum in $\eta'(\omega)\ \omega = G''(\omega)$. As noted in the Results section, star polymers do not have a maximum in $G''(\omega)$ near $\omega\tau_m = 1$. Hence, it may be possible to sustain steady flow deep into the non-Newtonian region while avoiding the onset of flow instabilities. There are a few studies on steady shearing behavior of stars,[30] but probably because the range of shear rates between $1/\tau_m$ and $1/\tau_{eq}$ was not large, no differences between stars and linear polymers were noted.

Remarks

Although this paper is concerned with the rheological properties of multiarm stars, it is appropriate to comment on the diffusion coefficient of these materials. In the early models of star diffusion,[37,51] it was assumed that all but two of the arms of the star would have to retract simultaneously to the central branch point before it could jump a distance on the order of the tube diameter. But, recent experiments[74] show that the diffusion of stars is almost independent of f, similar to the viscoelastic properties. The mode of diffusion requiring the coordinated retraction of the arms[37,51] must not be the dominant one, a result also suggested by the recent work of Rubinstein.[75]

An important tool for studying the dynamics of polymeric materials is dielectric relaxation. For polymers like polyisoprene that have dipoles oriented along the chain direction, the longest relaxation time will be related to the relaxation of the end-to-end vector of the polymer chain. The model described here would predict that this time will increase exponentially with the molecular weight. Two groups[76,77] have reported dielectric data on polyisoprene stars. When their results on the longest relaxation time are shown on a logarithmic plot, the evidence for an exponential molecular weight dependence is not as clear as in our work. This is most likely due to the restricted range of molecular weights that were covered. The highest molecular weight sample had a M_a/M_e of 4 compared to 24 in this work.

Perhaps the experimental results on stars have their greatest value in the role they have played in the development of molecular theory. Although melts of linear and star polymers are both entangled and have similar high-frequency properties, their behavior at low frequency is entirely different. We have shown that models can very accurately describe the experimental observations if they consider how molecular motion is affected by structure. From this it seems that other theories for polymer relaxation which do not include microscopic predictions on the chain motion are not likely to be successful.

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Appendix. The Longest Relaxation Time

Pearson and Helfand[50] have shown how an expression for the time required for the arm of a star to relax partially can be obtained by solving the Smoluchowski equation for the probability that the chain end has not penetrated past y at time t, $F(y,t)$. The function F is equal to $\exp[-t/\tau(y)]$, where is τ the average time to reach y. F also can be obtained from the following Kramers type formula

for diffusion over a potential barrier:[50]

$$\frac{1}{\tau(y)} = (D_c/a^2kT)[U''(0)\ U''(y)]^{1/2}[U(y)/\pi kT]^{1/2} \times \exp[-U(y)/kT] \quad \text{(A1)}$$

Here U describes the shape of the potential barrier, D_c is the diffusion coefficient for the chain in the tube, and a is the characteristic step length along the tube. The coordinate $y = L_{eq} - L$ is measured along the chain from its average position at L_{eq}. When $y = L_{eq}$, the chain has reached the branch point, and the time $\tau(L_{eq})$ is equal to the longest relaxation time, τ_m.

Helfand and Pearson[58] obtained an expression for U valid over the entire range of y as well as an approximation valid near $y = 0$ given by eq 4. When the general expression for U is used, the longest relaxation time is

$$\tau_m = \frac{aL_{eq}}{D_c}(q-1)\left(\frac{\pi^2}{2\nu'_{genl}}\frac{M_a}{M_e}\right)^{1/2}\exp\left(\nu'_{genl}\frac{M_a}{M_e}\right), \quad \text{(A2)}$$

where ν'_{genl} is $\ln [q^2/4(q-1)]/2$ and q is the coordination number of the lattice. If the quadratic approximation to U (eq 4) is used, the resulting expression for τ_m is

$$\tau_m = \frac{aL_{eq}}{D_c}\frac{4(q-1)}{q^2}\left(\frac{\pi}{\nu'_{quad}}\right)\exp\left(\nu'_{quad}\frac{M_a}{M_e}\right) \quad \text{(A3)}$$

where ν'_{quad} is $(q-2)^2/8(q-1)$. Note that the molecular weight dependence of the prefactor in eq A2 is $M_a^{5/2}$, whereas in eq A3 it is M_a^{2}.[63] Also the ratio ν'_{quad}/ν'_{genl} varies from 1.3 to 2.25 as the lattice coordination number changes from 6 to 12.

If the stress is calculated using the usual Kramers formula,[78] the plateau modulus can be expressed as

$$G_N = \frac{4}{15}\nu F_{eq}L_{eq} \quad \text{(A4)}$$

where ν is the number of chains per unit volume, L_{eq} is the equilibrium length of the chain in its tube, and F_{eq} is a fictitious force required to maintain the chain at length L_{eq}. F_{eq} can be obtained from U, and if the quadratic approximation given by eq 4 is used, we find that $F_{eq}L_{eq}$ is equal to $2\alpha kT$. Using the usual definition, $G_N = \rho RT/M_e$, we find that ν' is $^{15}/_{8}$.

The modulus G_N applies at $t \cong 0$, but the complete stress relaxation modulus for a star is $G(t) = G_N f(t)$ where $f(t)$ is equal to the fraction of the star arm that has not relaxed at time t. It can be obtained from $F(t,y)$ as[50]

$$f(t) = \frac{1}{L_{eq}}\int_0^{L_{eq}} dy\,(L_{eq} - y)\frac{dF(t,y)}{dt} \quad \text{(A5a)}$$

or

$$f(t) \cong \frac{1}{L_{eq}}\int_0^{L_{eq}} dy\,F(t,y) \quad \text{(A5b)}$$

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