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Terminal Relaxations in Linear and Three-Arm Star Polyisoprenes

C. A. Bero and C. M. Roland*

Chemistry Division, Code 6120, Naval Research Laboratory, Washington, D.C. 20375-5342

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ABSTRACT: Dynamic mechanical spectra were obtained for linear and three-arm star-branched polyisoprenes (PI) in the terminal region of the viscoelastic spectrum. Terminal relaxation times, defined from the peak frequency of the dispersion in the loss modulus, were found to be more sensitive to changes in temperature for the stars than for the linear polyisoprene. From Arrhenius plots of the ratio of the relaxation times for the star and linear polymers, an activation energy describing the excess temperature dependency of the stars was determined. The results were 2.3 and 3.2 kcal/mol for star PI with respective arm molecular weights equal to 18 and 44 times the molecular weight between entanglements. Unlike the linear PI, the star-branched polymers were thermorheologically complex. These results are very similar to the behavior of polybutadiene, hydrogenated polybutadiene, and hydrogenated polyisoprene. Nevertheless, they are unexpected, in that the existing hypothesis for the excess temperature dependence and thermorheological complexity of branched polymers should not apply to polyisoprene.

I. Introduction

The low-frequency dynamics of entangled chains are usually described in terms of the reptation model, whose simplicity and intuitive appeal have contributed to the theory's wide acceptance. Much experimental data is in agreement with the model's predictions.[1−3] Strict reptation theory, as embodied in the "tube model",[4] restricts the chain conformations to lie within a tube of entanglement constraints. This leads to discrepancies with experimental data regarding, for example, the molecular weight dependence of the terminal viscosity and relaxation time of entangled polymers,[4] the shape of the terminal relaxation function,[4,5−10] the dynamics of blends and polydisperse systems,[5,11] and the behavior of ring molecules[12] and microgels.[13] Such deviations of experiment from the predictions of the tube model do not invalidate its central premise that topological constraints cause motion along the chain contour to be more facile than lateral motions. They do indicate that reptation is not the only mechanism governing entangled chain dynamics and that perhaps the "tube" concept should not be taken too seriously.

One additional aspect of polymer melt rheology at variance with reptation theory is the differing temperature dependencies found for the terminal relaxation time of linear and branched polymers. The presence of long branches markedly alters the rheology of polymer liquids by suppressing molecular mobility. Strict reptation theory, however, predicts the temperature dependence of linear and branched chains to be the same, as governed by diffusion along the chain contour direction.[4] This prediction stems from the idea that the local environment (the "tube"), and hence the friction factor (which is just the Rouse friction), is the same for linear and branched chains.[2,14] However, experimentally it is found that branched chains usually are more sensitive to temperature than their linear counterparts, examples including commercial polyethylene,[15] polybutadiene,[16] hydrogenated polybutadiene,[16] and hydrogenated polyisoprene.[16] The differing temperature dependence of branched chains is accompanied by a breakdown of the time−temperature superposition principle.[16,17] This is quite unusual, since at frequencies below the softening dispersion, neat polymers are almost always thermorheologically simple.

One possible exception to the general observation of differing temperature dependencies for linear and branched chains is polystyrene. For polystyrene, the same temperature dependence has been reported for the linear polymer as for star and comb branched polystyrene.[18,19] However, none of the data for polystyrene with long branches extends into the terminal region. For this reason, the relative temperature dependence of branched and linear polystyrene is considered an open question.[20]

The hypothesis for the differing temperature dependence of branched and linear polymers is based on the idea that fluctuations in the contour length of the arms are necessary for a branched chain to withdraw from its "tube" of constraints.[21,22] As pointed out by Graessley,[17] such retraction of the arms produces a more compact transient structure, corresponding to a concentration of gauche conformers higher than at equilibrium. Often these gauche conformers have a higher energy than the trans states, whereby the activation barrier for the terminal relaxation time will be elevated. In this circumstance, branched chains will exhibit a stronger temperature dependence than their linear counterparts.[16,17] This hypothesis also accounts for the thermorheological complexity observed in branched polymers.[16,17]

In light of this hypothesis, the temperature dependence of branched and linear polyisoprene is intriguing because, distinct from polyethylene, high-vinyl polybutadiene, hydrogenated polybutadiene, and hydrogenated polyisoprene, the conformers of PI have the same energy.[17] Consequently, a changing population of trans and gauche states, as ostensibly occasioned by arm retraction, would not alter the energy. Hence, the reptation prediction from polyisoprene is that star-branched and linear chains will have the same temperature dependence.[16,17,23]

Experimentally, the situation for 1,4-polyisoprene is similar to that for polystyrene. An early study of linear and branched polyisoprene[24] noted the broadened terminal zone for the latter; however, no temperature dependencies were reported, in part because a distinct

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terminal relaxation was not observed for the branched PI. Carella et al.[16] reported equivalent time–temperature shift factors for linear and star-branched PI; however, the rheology of the star-branched PIs was only measured over a 50 °C range of temperature. In the authors' words, this was "probably too small for that to be a satisfactory test" of the respective rheological responses to temperature. Additionally, the stars showed little viscosity enhancement over the linear PI, presumably due to the low molecular weights of the branches (the largest ratio of arm molecular weight, M_a, to the molecular weight between entanglements, M_e, was only 9.4).[16] Pearson et al.[23] asserted that the temperature dependence of star and linear PI were identical; however, no supporting data were given. Boese et al.[25,26] reported a "similar" temperature dependence for the dielectric normal mode relaxation of star and linear polyisoprenes; however, the arm molecular weights were low (<14 000), barely twice the entanglement molecular weight. For PI, this M_e is 6400 g/mol.[27,28] From studies on other polymers, the enhanced temperature dependence of branched chains is known to be an increasing function of the arm molecular weight.[16,17,29]

There is an alternative approach to the low-frequency dynamics of polymers which makes the opposite prediction concerning branched and linear polymer temperature dependences. The coupling model of relaxation focuses on general principles governing constraint dynamics in densely packed systems. Its application to the terminal relaxation process in polymers has been described, including a number of comparisons of the model's predictions to experimental data.[30–32] Two primary results of the coupling model are the prediction that the terminal relaxation function will have the Kohlrausch–Williams–Watts[33] form

$$G(t) = G_0 \exp\left[-\left(\frac{t}{\tau_{\mathrm{KWW}}}\right)^{\beta}\right] \tag{1}$$

The stretch exponent, β, is related to the coupling parameter n ($=1 - \beta$), whose magnitude ($0 \leq n < 1$) reflects the degree of intermolecular cooperativity of the relaxation. Sometimes employed only as an empirical fitting function, eq 1 is a popular choice for analyzing the terminal relaxation modulus[34,35] as well as the dielectric normal mode.[25,26]

The long-range topological interactions giving rise to the plateau modulus of a high molecular weight rubber should be essentially independent of chemical structure. This implies a fixed value of β (or n) for all linear, flexible polymers. For branched chains, however, the more severe entanglement constraints are expected to increase the coupling parameter (i.e., smaller β). Continuity of eq 1 with the Debye relaxation prevailing at short time gives the most important result of the coupling model, which for the present purposes can be expressed as

$$\frac{E_{\mathrm{star}}}{E_{\mathrm{linear}}} = \frac{\beta_{\mathrm{linear}}}{\beta_{\mathrm{star}}} \tag{2}$$

where E is the activation energy for the relaxation process. The stronger coupling in branched polymers is expected to reduce β, thus broadening the relaxation function and increasing the activation energy of the rheological properties. Thus, the coupling model makes an opposite prediction from reptation—that the temperature dependence of branched polymers (having smaller β) will *always* be stronger than that of the corresponding linear polymers (larger β). This prediction is independent of the particular conformational energies. Actually, it is an extant prediction of the coupling model that more intermolecularly cooperative motions will be more sensitive to temperature changes (larger activation energy). For segmental relaxation, this prediction is borne out by much experimental data.[36–40]

Table 1. Linear and Star-Branched Polyisoprenes

polyisoprene	structure	M_w	Mw/M_n	M_a/M_e	η_0 (Pa-s) at 30 °C
L145	linear	145000	1.06		4.7×10^4 [a]
L357	linear	357000	1.08		2.0×10^6 [a] 2.3×10^6 [b]
S342	3-arm star	342000[c]	1.10	18	1.3×10^7 [b]
S854	3-arm star	854000[c]	1.10	44	6.7×10^8 [b]

[a] From the low-frequency limit of $G''(\omega)/\omega$. [b] From the reciprocal of the long-time limit of $\mathrm{d}(J(t))/\mathrm{d}t$. [c] Calculated using M_w of the linear precursor; the listed polydispersity is the value measured for the star.

In this paper we describe dynamic mechanical spectroscopy of the terminal region of linear and star-branched 1,4-polyisoprene. The measurements allow assessment of the divergent predictions concerning its rheology.

II. Experimental Section

Two linear and two three-arm star-branched 1,4-polyisoprenes (high *cis*-1,4 microstructure) were obtained from Polymer Source, Inc. (Quebec, Canada). The linear polyisoprenes were anionically polymerized using *sec*-butyllithium as the initiator. Coupling of the linear precursor chains to form the three-arm stars was accomplished using a stoichiometric quantity of 2,4,6-tris(allyloxy)-1,3,5-triazine. Fractionation of the resulting star-branched polymers with benzene/methanol was carried out seven times to remove any low molecular weight residuals. Molecular weights and polydispersities, determined by size-exclusion chromatography calibrated for polyisoprene, are listed in Table 1. The arm lengths are more than an order of magnitude larger than the entanglement molecular weight, $M_e = 6400$ g/mol.[27,28]

Antioxidant, a mixture of 0.25 wt % zinc 2-mercaptotoluimidazole and 0.25 wt % octylated diphenylamine from R. T. Vanderbilt (Norwalk, CT), was added in solution prior to rheological measurements to minimize degradation.

Glass temperatures were obtained using differential scanning calorimetry (Perkin-Elmer System 7, Norwalk, CT) at a heating rate of 10 °C/min, which immediately followed cooling at the same rate.

Rheological measurements were carried out with both dynamic mechanical and constant-stress instrumentation. The complex modulus G^*, was measured with a Bohlin VOR rheometer (Bohlin Instruments, Cranbury, NJ) in the frequency range of 1×10^{-5} to 2 Hz. A parallel-plate geometry was used with sample diameter and height typically equal to 25 and 1.5 mm, respectively. Torsional creep and recovery at 30 °C were measured with a Plazek creep apparatus.[41] Sample diameters and heights were typically 6 and 1.5 mm, respectively. For both the dynamic and transient measurements, sample temperatures were maintained constant to within ±0.1 °C.

III. Results

A. Glass Transition Temperature. Interpretation of the rheological properties of linear and star PI in terms of their large-scale structure relies on the assumption that the local friction coefficient is independent of this structure. This is not necessarily true for stars of very high functionality, due to crowding near the branch site. In the present situation, however, there is only one branching point per 5700 and 14 200 repeat

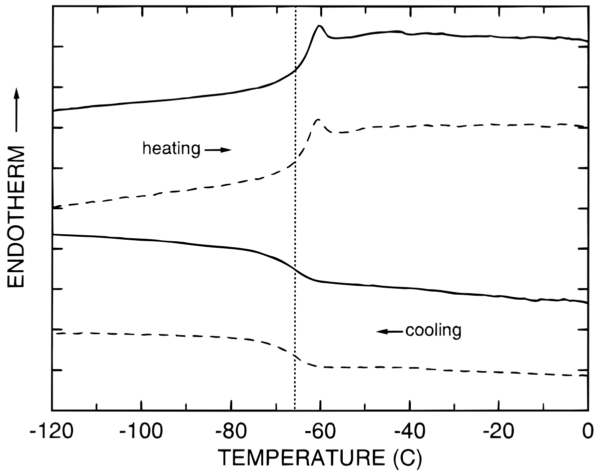

Figure 1. DSC data for L357 (- - -) and S854 (—) at 10 deg/min. "Fictive" glass transition temperatures were determined from the heating curves using the method of Plazek and Frund.[42]

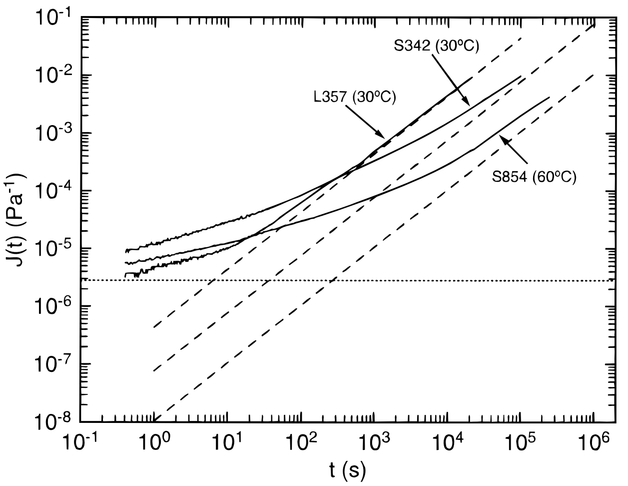

Figure 2. Creep compliance for the two stars and for one of the linear PI at the indicated temperatures. Terminal viscosities are obtained from the dashed lines (eq 3), which have a slope of unity on this double-logarithmic plot. The horizontal dotted line represents the plateau compliance associated with an entanglement network with $M_e = 6400$ g/mol.

units for S342 and S854, respectively. The expectation is that no difference exists in the local friction. This can be confirmed by comparing the glass transition temperatures of the polymers. As illustrated in Figure 1, the T_g's were equivalent for all samples, equal to -65.8 ± 0.6 °C. Note that this result is consistent with dielectric spectroscopy results showing identical segmental relaxation behavior for linear and star-branched PI.[25,26] Hence, we are justified in interpreting differences in rheological behavior in terms of the long-range structure.

B. Viscosities. The zero-shear viscosities of the linear polymers were obtained from the creep compliance at long times (Figure 2)

$$\eta_0 = \lim_{t\to\infty}\left(\frac{\mathrm{d}J(t)}{\mathrm{d}t}\right)^{-1} \tag{3}$$

as well as dynamically, from the loss modulus at low frequencies

$$\eta_0 = \lim_{\omega\to 0}\frac{G''(\omega)}{\omega} \tag{4}$$

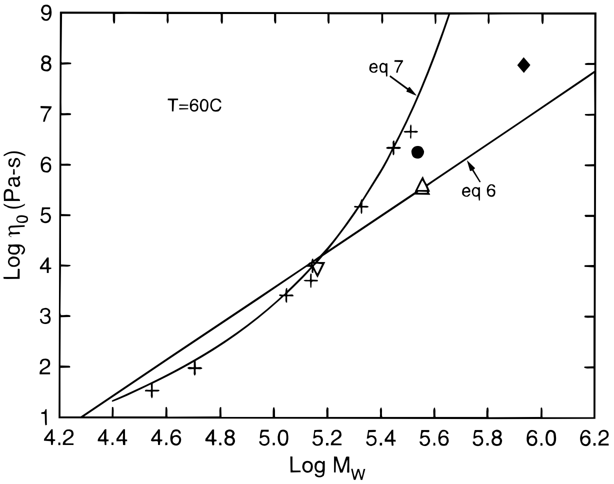

Figure 3. Terminal viscosities measured herein (L145 (▽), L357 (△), S342 (●), S854 (◆)), along with data for three-arm star PI taken from ref 23.

The results were equivalent (see Table 1) and also consistent with two empirical relations[24]

$$\eta_0 = 9.38 \times 10^{-15} M_w^{3.66} \tag{5}$$

in units of Pa-s at 25 °C and[23]

$$\eta_0 = 5.26 \times 10^{-15} M_w^{3.57} \tag{6}$$

in units of Pa-s at 60 °C. The dielectric normal mode relaxation time of PI has been reported[25,26] to vary as the 3.7 power of molecular weight, which is not significantly different from the viscosity results. Evidently PI has a somewhat stronger molecular weight dependence than other linear polymers, for which this exponent is typically about 3.4.[14] The viscosity data for the linear PI are shown in Figure 3, along with eq 6.

For star polymers, the viscosity is dependent primarily on the molecular weight of the arms, rather than the total molecular weight.[43−45] Except for very high functionality stars (more than 200 arms), in which the arms mutually interact, leading to very high viscosities,[46,47] the viscosity of short-armed stars is less than that of an equal molecular weight linear polymer, due to the smaller coil size of the branched molecule.[14] However, when the length of the arms becomes substantially greater than the molecular weight between entanglements, the branches cause the viscosity to exceed that of the corresponding linear polymer.[2]

The terminal viscosities of the three-arm star polyisoprenes were deduced from creep experiments using eq 3 and the method of Ninomiya[48] (Figure 2). The results, listed in Table 1, indicate that the star viscosities are significantly enhanced over the linear polymer values, consistent with the high molecular weights of the arms ($M_a/M_e = 18$ and 44). In Figure 3 we compare the present data with results for three-arm star PI reported by Fetters et al.[23] Those polymers had significantly shorter arm lengths than herein; nevertheless, there is good agreement between the viscosities. From the earlier study,[23] it was determined that the terminal viscosities for three- and four-arm polyisoprenes could be described by (in units of Pa-s)

$$\eta = (4.47)\left(\frac{M_a}{M_e}\right)^{3/2}\exp\left(0.47\frac{M_a}{M_e}\right) \tag{7}$$

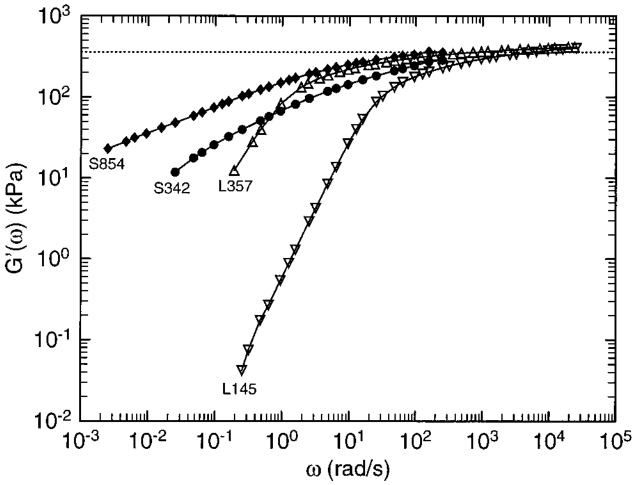

Figure 4. Representative measurements of the storage modulus for the three-arm star PI at 60 °C (S342) and 70 °C (S854), respectively, as well as a master curve for the linear polyisoprenes reduced to 60 °C. The horizontal dotted line represents the plateau modulus corresponding to an $M_e = 6400$ g/mol.

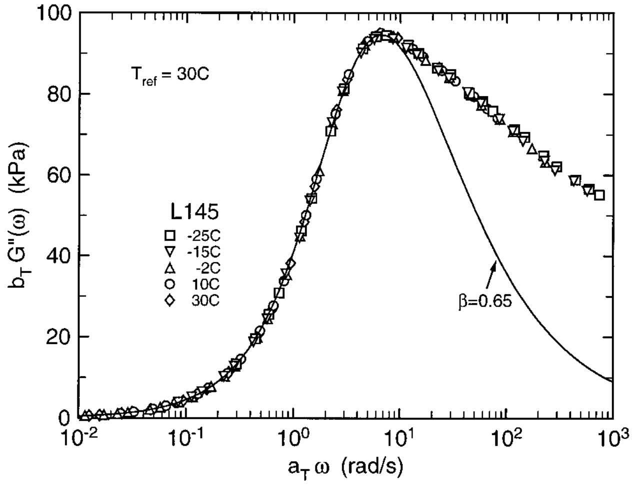

Figure 5. Terminal dispersion in the loss modulus measured at the indicated temperatures for the linear polyisoprene of M_w = 145 000, reduced to T = 30 °C. The solid line corresponds to the best fit to eq 1.

(Note that the numerical coefficients in eq 7 correspond to $M_e = 6400$ g/mol, rather than the value of 5000 used in ref 23.) This relationship emphasizes the fact that the viscosity of stars depends primarily on the molecular weight of the arms, not the total molecular weight. Interestingly, as seen in Figure 3, the higher molecular weight star has a viscosity that is substantially smaller than the prediction from eq 7. While there is agreement for the shorter arm stars, the viscosity apparently does not continue to increase exponentially when M_a/M_e is as high as 44.

C. Terminal Relaxation Function. Figure 4 shows the storage modulus for the four polyisoprenes. The plateau modulus, reflecting the transient entanglement network, is independent of branch structure and comparable to previously reported values for PI.[27,28] The obvious effect of branching is the smearing out of the terminal zone. To quantitatively investigate this, we analyze the loss modulus spectrum.

Representative measurements of the terminal dispersion in the loss modulus of the linear polyisoprenes are given in Figures 5 and 6. The spectra are superpositions of measurements obtained at various temperatures, with a reference temperature of 30 °C. The peak is slightly broader for the higher molecular weight L357. Fits of the data to the Fourier transform of eq 1 are also given in the figures. The experimental relaxation function deviates significantly from the KWW form at high frequencies. From the perspective of the coupling model, this would indicate a contribution from other modes or mechanisms.[38,49,50] Such deviation introduces some uncertainty in the fitting; the best-fit β is determined to be $\beta = 0.63 \pm 0.03$.

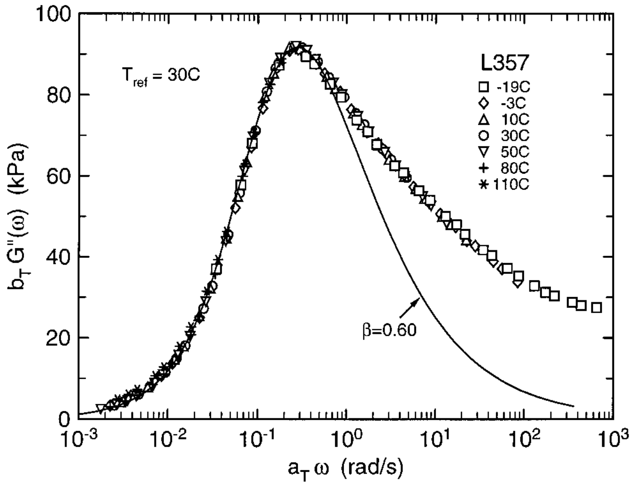

Figure 6. Terminal dispersion in the loss modulus measured at the indicated temperatures for the linear polyisoprene of M_w = 357 000, reduced to T = 30 °C. The solid line corresponds to the best fit to eq 1.

As is well-known, the shape of the terminal relaxation function is broader than expected from strict reptation prediction theory, which predicts[4]

$$G_{\text{reptation}}(t) = G_0 \sum_{p}^{\infty} (2p-1)^{-2} \exp\left(-\frac{(2p-1)^2 t}{\tau}\right) \quad (8)$$

This function yields essentially exponential decay (eq 1 with $\beta = 1$). Modifications of the basic theory have been proposed to account for the discrepancy with experiment[4,5,10] although these extensions of the theory still do not yield a relaxation function in complete agreement with experiment.

While smaller than the strict reptation prediction, the experimental value of β is larger than that deduced from the coupling model. Since the coupling model predicts that the exponent in the molecular weight dependence of the viscosity is equal to $2/\beta$,[32,51] eqs 5 and 6 for PI would yield $\beta = 0.55 \pm 0.01$. However, this value gives a noticeably poorer fit to the experimental spectra.

The β determined for the L357 was slightly less than β for L145 (cf. Figures 5 and 6). A similar weak dependence of the terminal peak's shape was previously seen by Boese and Kremer in dielectric loss data on polyisoprenes of similar microstructure.[25] The β determined dielectrically differ significantly from the present mechanical results; however, the two spectroscopies yield different relaxation functions. A detailed study of the dielectric behavior of linear and star PI will be reported elsewhere.[52]

In accord with previous studies, the terminal zones for the three-arm star-branched PI are significantly broader than for the linear polyisoprene. The terminal peak in the loss modulus is shown for the two star PI in Figures 7 and 8. Apparent in the data for the stars is a modest but definite breakdown of time–tempera-

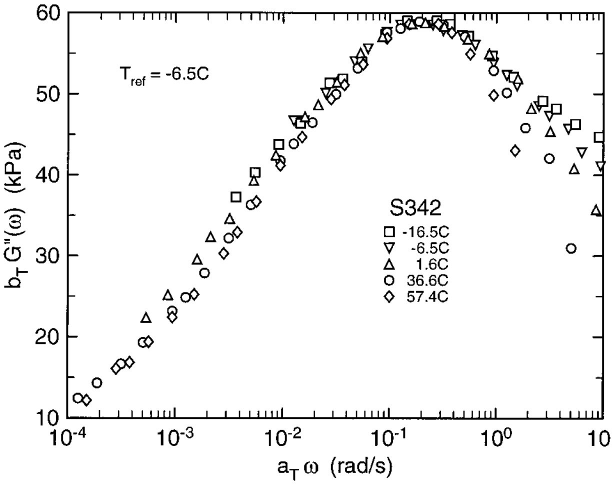

Figure 7. Dispersion in the terminal zone for the three-arm star PI(M_w = 342000). The spectra were measured at the indicated temperatures and then shifted to a reference temperature of −6.5 °C.

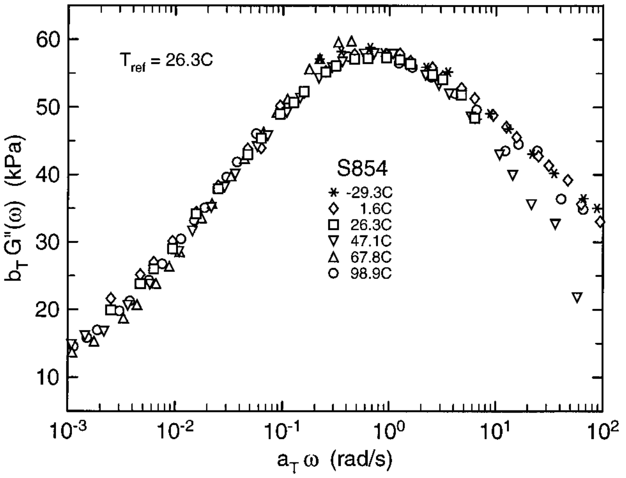

Figure 8. Dispersion in the terminal zone for the three-arm star PI(M_w = 854000). The spectra were measured at the indicated temperatures and then shifted to a reference temperature of 26.3 °C.

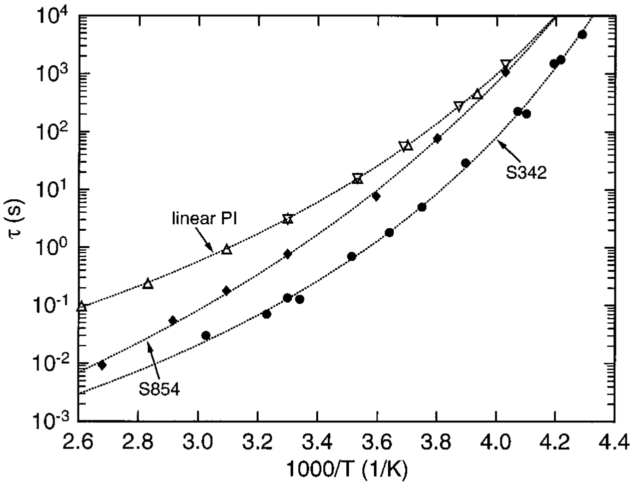

Figure 9. Terminal relaxation times, determined as $1/\omega_{\max}$, for the linear PI (L145 (▽) and L357 (△)), with the values for the lower molecular weight shifted vertically by a factor of 24, and for the two star-branched polyisoprenes. The solid lines are the best fits to eq 9.

ture superposition. As seen in these two figures, the terminal peak broadens as temperature is lowered. This is quite distinct from the results on the linear PI, which were thermorheologically simple (Figures 5 and 6). This was also observed by Nemoto in creep experiments on a series of linear polyisoprenes.[53]

The spectra for the star-branched PI do not conform particularly well to the KWW form (eq 1), in part due to polydispersity (Table 1). Any residual polydispersity in the linear precursor PI is amplified when the coupling reaction is carried out to make the three-arm stars. Besides this complication from polydispersity, analysis of the star data is difficult because the thermorheologically complex data cannot be reduced to a single master curve. The fitting must be carried out on the peak as measured at a single temperature, which is ambiguous due to its substantial breadth and the finite experimental range of frequencies. We estimate that for the three-arm stars $\beta = 0.26 \pm 0.06$.

D. Temperature Dependence. There are various methods to assess the temperature dependence of the terminal relaxation, since, at least for linear polymers, the zero-shear viscosity, the crossover frequency (at which $G'(\omega) = G''(\omega)$), and the various viscoelastic functions such as the terminal loss modulus have the same temperature dependence. Herein we focus on the terminal relaxation time, defined as $\tau = \omega_{\max}{}^{-1}$, where $\omega_{\max}$ is the frequency of the maximum in the loss modulus, $G''(\omega)$ (note that $\omega_{\max}{}^{-1}$ is somewhat larger than the τ_{KWW} in eq 1). Compared to the use of viscosities, there is greater accuracy in determining a peak frequency, which is insensitive to absolute errors in torque and angle measurement as well as sample loading. Terminal relaxation times are also preferred over terminal viscosities since degradation is a concern with unsaturated polymers such as PI. The zero-shear limiting viscosity is attained at frequencies lower than the maximum in the loss modulus, whereby higher temperatures are required to bring the terminal flow region into the experimentally accessible range of frequencies.

The relaxation times measured mechanically for the polyisoprenes at a series of temperatures are shown in Figure 9. We can superpose the results for the two linear PI by vertically shifting the data for L145 by a factor of 24. Within the uncertainties in the molecular weights of the polymers, this factor of 24 is in accord with the power dependence on molecular weight given above by eq 5 or 6. The relaxation times at the various measurement temperatures can be well represented by the Vogel−Fulcher−Tamman−Hesse equation[54−56]

$$\tau = A \exp\left(\frac{B}{T - T_\infty}\right) \qquad (9)$$

which is equivalent to the WLF equation.

A confirmation of the thermorheological complexity suggested by Figures 7 and 8 can be obtained by comparing for S342 the temperature dependence of $\omega_{\max}$ with that of the crossover frequency (Figure 10). The data for the latter are more limited, since for the star polymers $G'(\omega) = G''(\omega)$ at frequencies much lower than those associated with the maximum in $G''(\omega)$. Figure 10 shows that, unlike the behavior of linear PI, the separation between the loss modulus peak and the crossover frequency increases substantially for the star as temperature is lowered. This is thermorheological complexity.

An implication of the argument advanced concerning the origin of the differing temperature dependence of star and linear polymers is that the activation energy

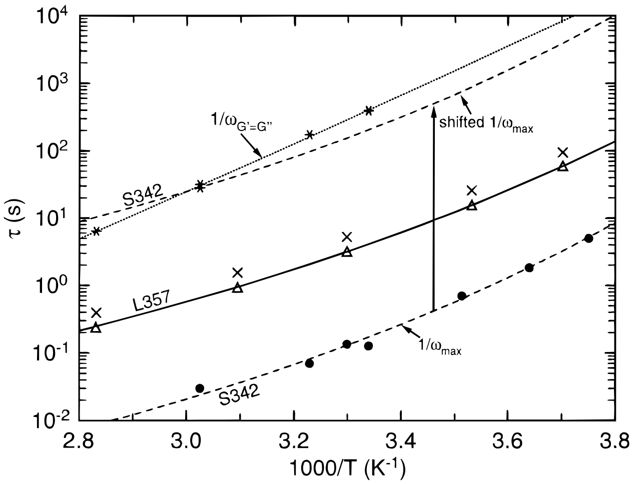

Figure 10. Terminal relaxation times for linear PI determined from the maximum in the loss modulus (▽) and from the frequency at which $G'(\omega) = G''(\omega)$ (×) and for star PI from the maximum in $G''(\omega)$ (●) and from the crossover frequency (*). The $\omega_{\max}{}^{-1}$ data for the star are also shown after vertical shifting by a factor of 1200. This comparison with the crossover frequency results makes clear the greater temperature sensitivity of the latter.

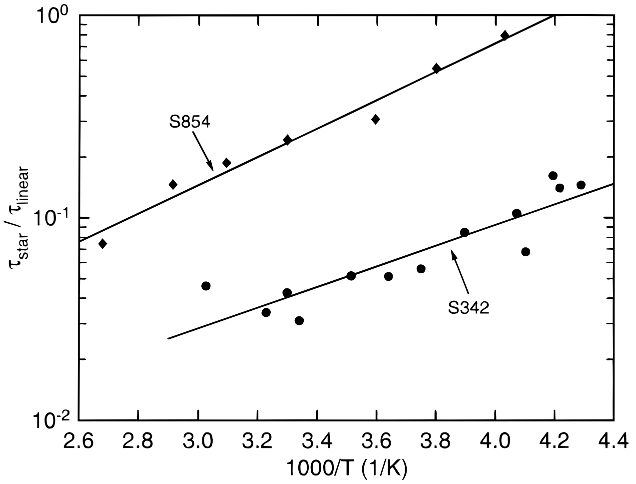

Figure 11. Arrhenius plots of the ratio of the terminal relaxation times for the three-arm star polyisoprenes and the linear PI (see Figure 6). The slopes yield values for the excess activation energy of 3.2 kcal/mol for S854 and 2.3 kcal/mol for S342.

will be proportional to arm length.[16,17,29] This would preclude superpositioning of the data for S342 (M_a = 91 000) on to that for S854 (M_a = 228 000). Indeed, there are differences between the curves in Figure 9 for the two star-branched polyisoprenes. Since these Arrhenius plots are not linear, we assess the star and linear temperature dependencies in the manner suggested by Graessley.[16] The relaxation times for the stars are normalized by the relaxation time for the linear polymer at the same temperature. For the latter we use the Vogel function for interpolation. The results, plotted in Figure 11, clearly demonstrate that the three-arm stars exhibit a stronger temperature dependence than the linear polyisoprene. Also note that if the terminal relaxation time were defined as the reciprocal of the crossover frequency, rather than as the reciprocal of $\omega_{\max}$, the excess temperature sensitivity of the stars would be magnified because of the crossover frequency's steeper slope in Figure 10. Hence, the stronger temperature dependence of the stars seen in Figure 11 is not qualitatively dependent on the manner in which τ is defined.

This excess temperature dependence can be quantified by the activation energy deduced from the data in Figure 11. The result is 3.2 kcal/mol for S854 and 2.3 kcal/mol for S342. These activation energies are of the same magnitude as found for hydrogenated polyisoprene, polybutadiene, and hydrogenated polybutadiene.[16,17,29] The enhancement of the temperature dependence due to branching is amplified for the PI having longer arms, in agreement with results on other polymers.[16] This likely explains why earlier studies on star polyisoprenes with smaller M_a/M_e did not observe any difference between the linear and branched temperature dependencies.[16,24,25] For PI this difference in temperature dependence between the stars and linear polymer is contrary to reptation theory, since the two architectures are associated with the same local friction coefficient. Moreover, the rationale suggested by Graessley[16,17] to explain similar results on other polymers does not apply to polyisoprene, since its conformers have equivalent energies.[57]

The present results are qualitatively congruent with the coupling model, which predits that any homogeneously broadened relaxation (i.e., involving only a single relaxing species) will have a temperature dependence that is directly correlated with the breadth of the relaxation function. Although Arrhenius behavior is not obtained in the terminal zone at temperatures as low as those of the present measurements, we can apply eq 2 to obtain an order of magnitude estimate of the flow activation energy of linear polyisoprene.

As reported above, $\beta_{\text{linear}} = 0.63 \pm 0.03$ and $\beta_{\text{star}} = 0.26 \pm 0.06$. Ascribing a portion of the breadth of the star polymers' terminal spectrum to polydispersity, we choose a higher value of $\beta_{\text{star}} = 0.32$ and thus deduce from eq 2 that $E_{\text{star}}/E_{\text{linear}} \geq 2$. From Figure 11 the difference in E_{star} and E_{linear} was found to be 3.2 and 2.3 kcal/mol for S854 and S342, respectively; thus, the flow activation energy for linear polyisoprene is on the order of 3 kcal/mol. This value, at best only a crude estimate, is nevertheless comparable to flow activation energies reported for other polymers.[29,58] The fact that the result is reasonable gives credence to the coupling model approach.

IV. Summary

Quantitatively describing the dynamics of entangled chains presents a major challenge. Although considerable progress has been made, results such as those presented herein make clear that work remains. The clarity and intuitive appeal of single chain theories such as reptation have much to offer; nevertheless, some problems, such as the temperature dependence of relaxation, may be better addressed by more general approaches such as the coupling model. It is certainly true that lacking modifications and additional parameters, neither reptation theory nor the coupling model offers a completely satisfactory accounting of the low-frequency dynamics of polymer melts.

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