Terminal and Segmental Relaxations in Epoxidized Polyisoprene

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Received July 13, 1992; Revised Manuscript Received September 14, 1992

ABSTRACT: The terminal and segmental dispersions in the dynamic mechanical spectra were measured for 1,4-polyisoprene (PIP) epoxidized to various levels. A systematic increase in the plateau modulus, arising from the transient entanglement network, is observed upon epoxidation. This increase is at odds with published correlations of the effect of chemical structure on chain entanglements. The segmental relaxation dispersion in the epoxidized polymers is broader and more sensitive to temperature than in the unmodified PIP, indicating enhanced intermolecular coupling of the segmental dynamics. The greater intermolecular cooperativity may reflect steric interactions promoted by the oxirane group.

Introduction

The chemical structure of a polymer chain has a profound influence on its relaxation behavior. Although there is a large difference in their relevant length scales and hence not necessarily any correlation between them, the terminal and segmental dynamics of polymers in the dense phase are both governed primarily by the uncrossability and the excluded volume of the polymer segments. Segmental relaxation, occurring in the vicinity of the glass transition temperature, involves correlated local motion of a few backbone bonds, and hence the shape of the corresponding viscoelastic dispersion reflects local molecular structure. Correlations of chemical structure with the glass transition temperature have been adduced.[1,2] The influence of chemical structure on the time dependence of the relaxation (that is, the shape of the segmental relaxation function) has received less attention. The terminal relaxation involves the longest-range molecular motions of polymers, and accordingly both the strength and shape of the terminal dispersion are less sensitive to local structure. This underlies the limited success of correlations which have been proposed between molecular structure and the terminal relaxation behavior.

The epoxidation of 1,4-polyisoprene (to form random copolymers of 2-methyl-1,2-epoxy-1,4-butanediyl and 2-methyl-1-butenylene) markedly alters the physical properties of the polymer. This has led to the commercial development of epoxidized natural rubber. Since conversion of the main-chain unsaturated carbons to oxirane moieties represents a significant chemical modification, the changes in physical properties accompanying epoxidation are unsurprising. This report describes a systematic study of the effect of epoxidation on the segmental and terminal dispersions in the viscoelastic spectrum of linear 1,4-polyisoprene.

Experimental Section

The polyisoprene, obtained from the Goodyear Tire and Rubber Co., was a random terpolymer of 77% *cis*- and 16% *trans*-1,4-polyisoprene and 7% 3,4-polyisoprene. The polymer was linear, with a weight-average molecular weight equal to 173 000 (polydispersity = 1.4). The epoxidation reaction was carried out using aqueous peracetic acid, with the polymer dissolved in dichloromethane at 0 °C. The epoxidized polymers, designated by their level of epoxidation in Table I, had from 15 to 50 mol % of the oxirane modification. The stability of the polymer is appreciably reduced beyond 50% epoxidation. The epoxidation reaction is random, specific for the 1,4 chain units, and maintains the stereochemistry.[3] The respective chemical structures of the 1,4-polyisoprene repeat unit and the oxirane moiety resulting from epoxidation are shown in Figure 1.

Dynamic mechanical data in the terminal zone were obtained with a Bohlin VOR rheometer using a parallel-plate geometry. Sample radii of 25 and 40 mm were used, with gaps in the range of 1.5–2 mm. The dynamic shear modulus was measured from 60 Hz down to as low as 1×10^{-5} Hz at temperatures between 25 and 30 °C. The broad range of experimental frequencies (6.3×10^{-5} to 380 rad/s) obviated the need for time–temperature superpositioning. Mechanical spectra in the vicinity of the glass transition were measured on strips (typically $24 \times 12 \times 1.5$ mm) in tension using an Imass Co. Dynastat Mark II mechanical spectrometer. The Dynastat has a frequency range of 0.01–100 Hz. For the segmental relaxation measurements, the temperature was adjusted according to the T_G of each polymer. Temperature control was usually better than ±0.1 °C.

Results and Discussion

Terminal Mode. In Figure 2 are displayed the plateau and terminal zones of the viscoelastic spectrum measured for each of the four polymers. The experimental frequencies are slow enough for entanglements to manifest themselves as a transient network.[5] However, since the molecular weights are not extremely large, the storage moduli, $G'(\omega)$, in the plateau region have some frequency dependence and cannot be used to quantify the modulus of the entanglement network, G_0. The dispersion in the loss modulus $G''(\omega)$, demarcating the onset of viscous flow, can provide a measure of the plateau modulus. Simple relationships, either empirically based[6] or obtained from phenomenological theory,[7,8] have been proposed between G_0 and the maximum in the loss modulus. Unfortunately, neither approach is useful for polydisperse polymers, wherein the dispersion is inhomogeneously broadened due to the distribution of terminal relaxation times.

A generally valid method, derived from the Kronig–Kramers relation, to extract the contribution of entanglements from the viscoelastic response is by integration over the dispersion in $G''(\omega)$[9,10]

$$G_0 = \frac{2}{\pi} \int_a^b G''(\omega) \, d \ln \omega \qquad (1)$$

G_0 for each polymer was obtained in this manner by numerical integration of the loss modulus data in Figure 2. The error in the determination of G_0 due to uncertainty in the application of eq 1 on the high-frequency side of the dispersion, where an extrapolation and termination are necessary to separate the partially overlapping transition zone, was no greater than the experimental error. The overall uncertainty in the obtained plateau moduli is less than 10%. The plateau modulus determined for the unmodified polyisoprene is within the range of previously reported values.[11-13] As seen in Figure 3 and listed in Table I, epoxidation causes a significant and systematic

Table I

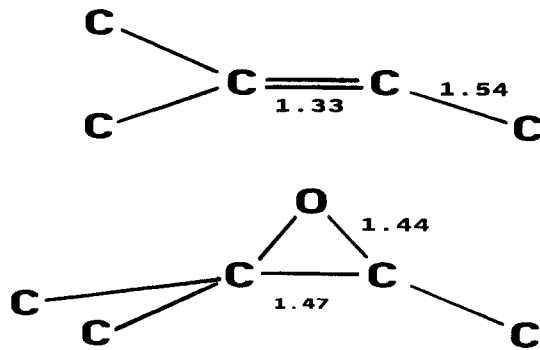| polymer	epoxide, mol %	ρ, g/cm^3	c, cm^{-3}	l, Å	G_0, MPa	T_G, C	n
PIP	0	0.894	0.0526	1.470	0.32	−65	0.48
EPIP-15	15	0.942	0.0535	1.478	0.38	−52	0.57
EPIP-30	30	0.972	0.0534	1.485	0.42	−36	0.68
EPIP-50	50	1.010	0.0532	1.495	0.53	−13	0.63

Figure 1. Repeat unit of PIP (upper) and that resulting from epoxidation (bottom). The bond distances (in angstroms) are as indicated. The O–C–C bond angle is 59.3°, with the plane formed by the carbons perpendicular to that of the ring.[4]

increase in G_0. At 50% epoxidation, the plateau modulus is more than 60% larger than G_0 of PIP.

There have been many attempts to relate the magnitude of the plateau modulus to chemical structure.[14-24] These correlations generally provide a trend about which experimental compilations of G_0 exhibit large scatter. From the idea that the density of entanglements is governed by the length of uncrossable chain contour per unit volume, Graessley and Edwards proposed[25]

$$G_0/RT \sim l_K^3 \, (\nu L l_K^2)^\alpha \qquad (2)$$

where ν is the number density of chains and l_K the Kuhn step length. The contour length of a chain, L, is the product of the number density of skeletal bonds, c, and their average length, l, divided by ν. From experimental data the exponent in eq 2 was deduced for flexible-chain polymers to lie in the range $2 \leq \alpha \leq 2.3$. For either empirical value ($\alpha = 2$ or 2.3 along with the corresponding proportionality factor), the predicted G_0 is more than a factor of 2 higher than the plateau modulus experimentally determined for PIP.

Equation 2 can be rewritten in terms of known quantities

$$G_0/RT \sim G_\infty^{2\alpha-3} l^{3\alpha-3} c^\alpha \qquad (3)$$

where the characteristic ratio $C_\infty = l_K/l$ and

$$c = \rho n_0/m \qquad (4)$$

In eq 4, ρ is the mass density, m is the monomer unit molecular weight, and, for the polymers studied herein, the number of backbone bonds per monomer unit $n_0 = 4$. It has been shown[26] that other scaling predictions can be cast in the form of eq 3, with different values for the exponent resulting from different concepts of chain entanglements. For example, the argument that the average number of polymer segments contributing to the formation of an entanglement is a universal constant yields $\alpha = 3$.[20,21] However, this approach overpredicts G_0 for PIP by as much as 100%. Indeed, the published correlations[14,18,19,27] generally predict larger entanglement effects in PIP than are ever found experimentally. As has previously been noted,[25] this seems to be a feature of 1,4-polyisoprene. Confronted with the problem that the entanglements in unmodified PIP are of lower abundance and/or effectiveness than theoretical expectations, inter-

pretation of changes in the plateau modulus arising from epoxidation is problematical.

As seen in Figure 1, epoxidation increases the bond length of the vinyl carbons. Along with the increase in the number density of main-chain bonds (Table I), this augments the plateau modulus. The most important factor in eq 3 is the characteristic ratio. Since the oxirane ring has some torsional compliance, epoxidation is expected to increase the flexibility of PIP, in principle reducing C_∞ and thus G_0. However, correlation is not always observed between the magnitude of C_∞ and chain flexibility. For example, while hydrogenation of PIP presumably reduces the chain stiffness, the resulting polymer (an alternating ethylene–propylene copolymer) exhibits a larger characteristic ratio.[28] Accordingly, the effect of epoxidation on C_∞ must be deduced from measurements of the unperturbed dimensions of the respective chains. The intrinsic viscosity is proportional to the effective volume of the dissolved chains, and for PIP in THF at 40 °C it has been determined to vary as[29]

$$[\eta] = 1.09 \times 10^{-4} M^{0.79} \qquad (5)$$

where the units are dL/g and M represents the molecular weight. The corresponding relationship for EPIP-50 under the same conditions is[29]

$$[\eta] = 4.85 \times 10^{-5} M^{0.82} \qquad (6)$$

Using the weight-average molecular weights for M, $[\eta] = 1.50$ and 1.14 dl/g for PIP and EPIP-50, respectively, indicating a more convoluted configuration for EPIP-50. Since chain dimensions are affected by the thermodynamic affinity between the polymer and solvent, the lower $[\eta]$ of EPIP-50 does not necessarily imply an intrinsically more flexible macromolecule.[30,31] Epoxidation increases the solubility parameter of PIP from $\delta = 8.1$ to 8.9 cal/cm^3 at 50% epoxidation.[32] This means that THF, for which $\delta = 9.1$ cal/cm^3, is a better solvent for the epoxidized polyisoprene. Since a better solvent results in a higher value of $[\eta]$, the smaller intrinsic viscosity of EPIP-50 can only be due to the greater flexibility of its chain molecules.

A correction for the effect of the solvent power on chain dimensions can be estimated using the relation[33]

$$[\eta] = K_\Theta M^{1/2} + {}^1/_2 \phi M B \qquad (7)$$

where K_Θ is the Mark–Houwink coefficient under Θ conditions and ϕ is a universal constant ($=2.66 \times 10^{21}$ [34]). The quantity B is related to the polymer–solvent interaction parameter

$$B = (1 - 2\chi)/V_1 N_A \rho^2 \qquad (8)$$

where V_1 refers to the molar volume of the solvent ($=81.3$ cm^3/mol for THF) and N_A is Avogadro's number. The interaction parameter can be calculated from the solubility parameters

$$\chi = V_1(\delta_1 - \delta_2)^2/RT \qquad (9)$$

giving $\chi = 1.4 \times 10^{-1}$ and 6.1×10^{-3} for PIP and EPIP-50, respectively. Employing these values together with eqs 7 and 8, K_Θ is calculated to be 40% larger for PIP than for
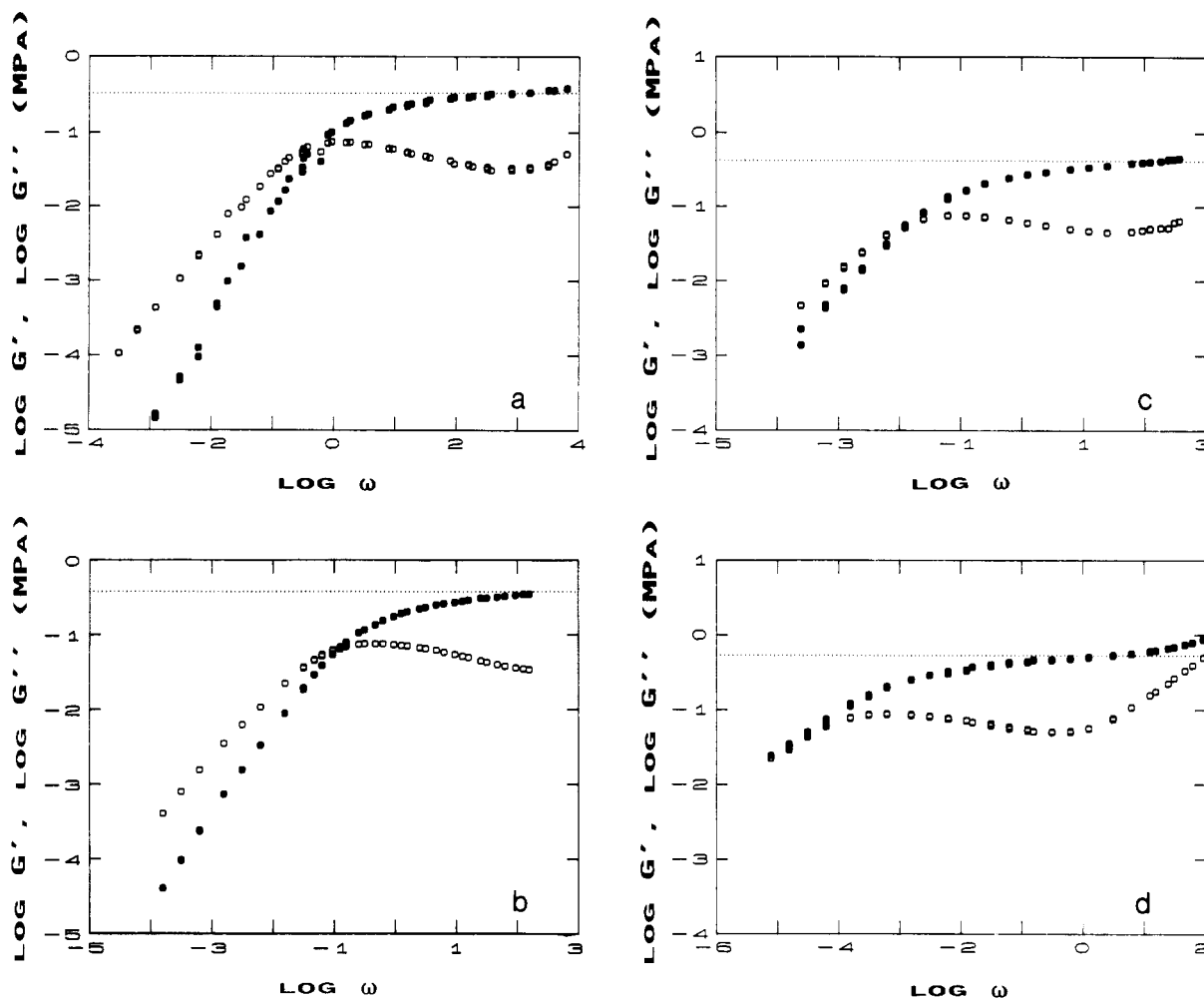
Figure 2. Storage (●) and loss (O) moduli versus angular frequency for (a) PIP at 25 °C, (b) EPIP-15 at 25 °C, (c) EPIP-30 at 30 °C, and (d) EPIP-50 at 25 °C. The magnitude of the plateau modulus obtained using eq 1 is indicated by the dotted line.
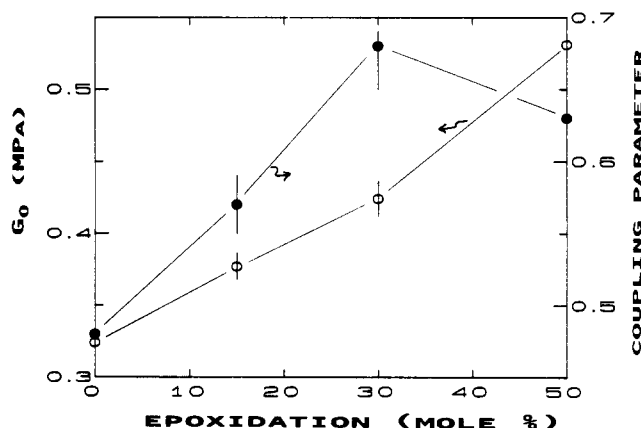

Figure 3. Variation in the plateau modulus (O) and in the coupling parameter for segmental relaxation (●) for PIP epoxidized to the indicated level. The uncertainties in the determinations are indicated by the vertical lines through the points.

EPIP-50. Using the relationship[34]

$$C_\infty = (m/n_0 l^2)(K/\phi)^{2/3} \qquad (10)$$

this implies that the characteristic ratio of EPIP-50 is about 10% lower than C_∞ of the unepoxidized polyisoprene. This result is only approximate given the error in calculating χ, as well as the fact that polymers are not monodisperse (using the number-average molecular weights in eqs 5–7 would suggest a reduction in C_∞ at 50% epoxidation of almost 20%).

The important point is that the flexibility of polyisoprene is somewhat increased by epoxidation, which

according to eq 3 can only serve to reduce the plateau modulus. When any effect of chain stiffness is neglected, the increase in G_0 due to the changes in l and c upon epoxidation can be estimated from eq 3. As indicated above, the appropriate value for α is uncertain. Consideration of the number of binary contacts required for an entanglement[23,35] or the number per entanglement volume[24] gives $\alpha = 2$ and $\alpha = 7/3$, respectively. These correspond to the original empirical bounds on the exponent in eq 2.[25] From a recent compilation of experimental data, a mean value of $\alpha = 2.45 \pm 0.22$ has been deduced.[26] The greatest predicted enhancement in G_0 upon epoxidation of PIP would be obtained using $\alpha = 3$.[20,21] Using this value for the exponent, eq 3 predicts that epoxidation of half the PIP chain units will effect a 14% increase in the plateau modulus. This is an upper bound due to the neglect of the decrease in chain stiffness upon epoxidation. In fact, even a 10% reduction in C_∞ would result in a net reduction in G_0. The experimentally measured increase in G_0 notwithstanding, any of the possible values for α predicts a reduction in G_0 upon epoxidation.

From a statistical analysis of experimental data, Aharoni has criticized the correlation expressed in eq 2, proposing a strictly empirical alternative[19]

$$G_N = 0.4096(C_\infty l/A^{1/2}) - 0.2961 \qquad (11)$$

where A, the cross-sectional area of a chain, is determined from crystallography to equal 28 Å² for PIP.[36] This is the only published correlation that does not substantially overestimate entanglement effects in 1,4-polyisoprene. In

fact, eq 11 predicts almost exactly the G_0 given in Table I for PIP. However, eq 11 fails utterly in describing the effect of epoxidation on the plateau modulus. Since the cross-sectional area of PIP chains is increased by epoxidation (see Figure 1) while the characteristic ratio decreases, eq 11 is unable to predict even the direction of the change in G_0 upon epoxidation.

To summarize, epoxidation is expected to decrease the plateau modulus of PIP due to a decrease in the chain contour length per unit volume. However, G_0 is found experimentally to increase at all levels of epoxidation. A characteristic of the unmodified PIP seems to be a plateau modulus anomalously smaller than predictions derived from scaling arguments. The latter's underestimation of the increase in G_0 accompanying epoxidation may simply reflect the polymer's departure from the structure provoking this anomaly.

Segmental Mode. There are two perspectives when considering the segmental relaxation behavior of polymers. For an isolated chain it is established that the segmental dynamics can be well described in terms of intramolecularly correlated, skeletal bond conformational transitions.[37-41] The correlations preclude motion over long length scales, since this would encounter prohibitive frictional resistance. Focusing solely on this intramolecular cooperativity, forms obtained for the relaxation function, reflecting the spectrum of conformational transition modes, are in good agreement with simulations[42,43] and experiments on dilute solutions.[44,45] In dense phase there exist intermolecular constraints on segmental relaxation, in the form of density fluctuations in the local environment. These can be represented as a mean-field frictional resistance,[41] which broadens the computed correlation function to obtain improved agreement with experiments on polymers in dense phase.

In these models of segmental relaxation, the consequences of intramolecular cooperativity are rigorously treated in the calculation of the orientational correlation function. For an isolated chain, chemical structure determines the conformational transition rates, and hence the segmental relaxation. There is no a priori expectation concerning how the segmental relaxation of a given structure will be altered by some modification of the structure. On the other hand, it might be expected that random copolymers, by virtue of their heterogeneous chain structure and consequent distribution of segmental relaxation times, might exhibit broader dispersions than homopolymers.

Alternative descriptions of segmental dynamics focus on the consequences of intermolecular cooperativity.[46-49] According to the coupling model of relaxation[48,49] as segments in dense phase try to relax, interchain interactions and correlations among the segments cause some of the attempted conformational transitions to fail. The resulting variations in the success rate for conformational transitions by the segments slow down the relaxation of macroscopic variables such as stress. Intermolecular cooperativity is accounted for in the coupling model by the introduction of a factor $(t\omega_c)^{-n}$ into the relaxation rate for the isolated chain. With the latter described by the Hall–Helfand model,[37] at times longer than some characteristic time $(\omega_c^{-1} \sim 10^{-10} s^{48})$, the relaxation modulus is given by[49]

$$E(t) = E(0) \exp(-[t/\tau^*]^{1-n}) \qquad (12)$$

The quantity n in this expression is a measure of the capacity of the segments to couple to neighboring nonbonded chain units. It is invariably found that, at the
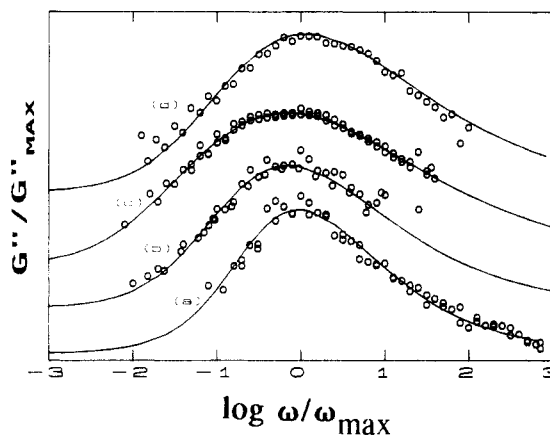

Figure 4. Semilogarithmic plot of the loss moduli measured for (a) PIP at −65 °C, (b) EPIP-15 at −45 °C, (c) EPIP-30 at −32 °C, and (d) EPIP-50 at −11 °C. The values have been normalized by the maximum in G'' occurring at ω_{max}. The solid curve is the best fit of eq 12.

times appropriate for mechanical results $(t \gg \omega_c^{-1})$, the relaxation modulus of neat polymers exhibits the form of eq 12. The effective relaxation time τ^* is related to the relaxation time in the absence of intermolecular coupling according to[48]

$$\tau^* = ([1 - n]\omega_c^n \tau_0)^{1/(1-n)} \qquad (13)$$

where τ_0 may be identified with the Hall–Helfand uncorrelated relaxation time.[37,49] It is expected that the value of n will depend on chemical structure; however, given the complexity of the dynamics of undiluted polymers, this coupling parameter cannot be calculated directly. It must be deduced from experiment.

Shown in Figure 4 is the segmental relaxation dispersions in the dynamic mechanical spectra measured for the four polymers. All are well described by eq 12. The n for PIP is in agreement with the value previously determined from mechanical data on natural rubber (i.e., *cis*-1,4-polyisoprene).[50] The best-fit value of n is significantly larger for the epoxidized polymers in comparison to the unmodified PIP (Figure 3), indicating an enhanced capacity for intermolecular coupling in the former.

An increasing coupling parameter upon epoxidation suggests that the oxirane groups enhance the cooperativity of the segmental relaxation process. As illustrated in Figure 1, this moiety projects more than 1 Å from the chain backbone. A larger volume is therefore swept out during the course of conformational transitions by the polymer backbone, so that mutual encounters of the chain segments become more probable. These steric interferences inhibit the segmental motions, retarding the relaxation and hence increasing the breadth of the mechanical dispersion.

This interpretation is similar to earlier findings[50] that the presence of pendant vinyl groups in polybutadiene increases the intermolecular coupling of the neat polymer's segmental relaxation. Also, simulations of the dynamics in dense systems of complex molecules[51] reveal that the transition from short to long time behavior is predicted to broaden as the structural irregularity of the segments increases. At least for systematic alterations of chemical structure, structural irregularities, in the form of less compact or more irregular structure, enhance interparticle interactions. These steric hindrances increase the cooperativity of the local motions, homogeneously broadening the segmental dispersion.

It follows from this line of reasoning that the strongest intermolecular coupling might then be associated with
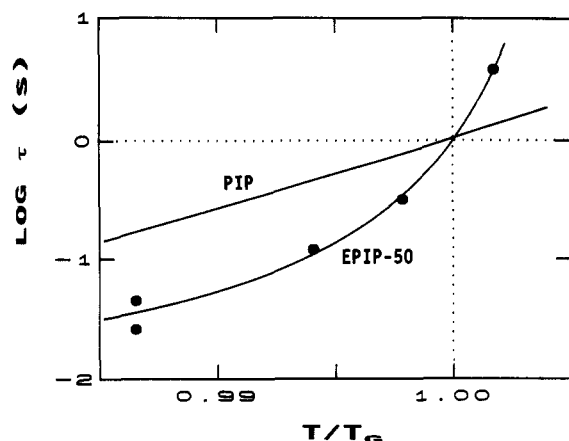
Figure 5. T_G-normalized Arrhenius plots of the segmental relaxation time measured for EPIP-50, along with results reported[50] for unmodified *cis*-1,4-polyisoprene. The curves represent the best fit to the Volger–Fulcher equation.[10] The more marked dependence on temperature exhibited by the epoxidized polymer reflects a more intermolecularly cooperative segmental relaxation, consistent with the larger n in Figure 4.

the highest concentration of oxirane groups in the PIP chain. However, there is a maximum in the curve in Figure 3. We tentatively ascribe this to a copolymer effect, whereby the heterogeneous chain structure imparts inhomogeneous broadening (a distribution in the intramolecularly correlated conformational transition rates). In the presence of the intermolecular coupling arising in dense phase, the net result can be a maximum in the breadth of the dispersion versus the copolymer composition. This phenomenon is anticipated for copolymers comprised of chain units with vastly different conformation transition rates. This likely pertains to epoxidized polyisoprene, given the large change in T_G upon epoxidation (Table I), and hence the large difference in τ_0 (eq 13) for the isoprene and oxirane moieties.

The inference that the increased breadth of the dispersion observed for the epoxidized polymers reflects primarily enhanced intermolecular coupling can be corroborated by examination of the temperature dependence of the segmental relaxation time. It has been established that a correlation exists between time and temperature dependencies of segmental dynamics.[50,52–55] Specifically, polymer chains whose relaxation is characterized by stronger intermolecular coupling (larger n) exhibit a more marked dependence on temperature. Over the range of most experimental measurements, however, temperature dependencies are non-Arrhenius. Some normalization scheme must be invoked to allow comparisons among different polymers of the effect of temperature on the measured relaxation times. Angel[52,53] proposed a normalization scheme employing T_G-scaled Arrenhius plots of segmental relaxation times; that is, τ^* is plotted as a function of the inverse temperature normalized by the glass transition temperature. The validity of T_G-scaled Arrhenius plots has recently been demonstrated by comparison of the data from polymers differing only in molecular weight.[55]

The segmental relaxation dispersion of EPIP-50 was measured at several temperatures and τ^* obtained by application of eq 12. The Volger–Fulcher equation[10] was used to interpolate the data and provide a determination of the glass transition temperature, taken to be the temperature at which $\tau^* = 1$ s. (As far as dynamics are concerned, T_G is arbitrary, so that any convenient operational definition suffices.[55]) In Figure 5 the results are displayed in the T_G-normalized Arrhenius form, along with

corresponding results previously reported for PIP.[50] The data for EPIP-50 cover only a limited temperature range, due to the limited range of experimental frequencies (4 decades). Nevertheless, it is apparent that the segmental relaxation time of EPIP-50 has a stronger temperature dependence than is observed for the unmodified PIP. This is consistent with the idea that epoxidation of polyisoprene amplifies the degree of intermolecular cooperativity of the segmental relaxation.

Summary

The epoxidation of polyisoprene significantly alters both the short and long time viscoelastic behavior. Greater cooperativity (entanglements in the case of the terminal relaxation and intermolecular coupling for the segmental relaxation) is observed in the epoxidized polymers. The plateau modulus of PIP is lower than theoretical predictions; the unexpectedly large increase in G_0 upon epoxidation is perhaps a consequence thereof. The broadened segmental relaxation of the epoxidized PIP suggests enhancement in intermolecular cooperativity due to steric interactions promoted by the oxirane group. The enhanced intermolecular coupling increases the temperature sensitivity of the segmental relaxation time. The breadth of the segmental dispersion exhibits a maximum versus epoxidation level, which may be a consequence of the very different conformational transition rates of the isoprene and oxirane chain units.

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