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# Physical Origin of the Anomalous Temperature Dependence of the Steady-State Compliance of Low Molecular Weight Polystyrene

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ABSTRACT: In an earlier detailed study of viscoelastic behavior of low molecular weight polystyrenes by Plazek and O'Rourke, an anomalous temperature variation of the steady-state compliance, $J_e$, was established. At high temperatures, $J_e$ was sensibly independent of temperature, but it decreased markedly with temperature as $T_g$ was approached from above. This anomalous temperature dependence of $J_e$ has been confirmed by dynamic viscoelastic measurements of Gray, Harrison, and Lamb. Although $J_e$ for samples of molecular weights higher than the critical value for entanglement is more difficult to measure in the neighborhood of $T_g$, a similar decrease of $J_e$ with falling temperature was observed in narrow molecular weight distribution samples with molecular weight up to $9.4 \times 10^4$. The low molecular weight polystyrenes used in these previous measurements had high molecular weight tails. We present additional measurements in a polystyrene sample of narrower molecular weight distribution. These minimize any contribution to recoverable compliance from the high molecular weight tail. The strong temperature dependence of $J_e$ near $T_g$ is confirmed. The marked decrease in $J_e$ of low molecular weight polystyrenes with decreasing temperature near $T_g$ is not in accordance with predictions from the Rouse model. We find the predictions from the coupling model of Ngai and co-workers applied to the local segmental relaxation when considered in conjunction with the Rouse modes of the unentangled polymer chain can give an explanation of the anomalous viscoelastic behavior in low molecular weight polystyrenes.

## Introduction

One of us in collaboration with O'Rourke[1] carried out detailed measurements of the shear creep and creep recovery of narrow molecular weight distribution polystyrene samples of low molecular weight, $1.1 \times 10^3$, $3.4 \times 10^3$, and $1.57 \times 10^4$, as a function of temperature near and above the glass temperature $T_g$. Time–temperature equivalence for the total creep compliance was found to be nonapplicable, and in fact the steady-state recoverable compliance, $J_e$, was a strong function of temperature. This most startling feature was observed as a marked decrease in recoverable deformation as the temperature of measurement approaches $T_g$ from above. Far above $T_g$ the steady-state compliance $J_e$ approached a fairly constant asymptotic value which is similar in magnitude to the prediction of the Rouse model[2] modified for an undiluted polymer:[3]

$$J_e = (M/\rho RT)S_2/S_1^2 \qquad (1)$$

where $M$ is the molecular weight, $\rho$ is the density, $R$ is the gas constant, $T$ is the temperature, $S_1 = 1.645$, and $S_2/S_1^2 = 0.40$. The asymptote was approached in an increasingly smaller temperature interval as the molecular weight increases. For example, in the interval between 100 and 70 °C the $J_e$ for the 3400 molecular weight species having a $T_g$ of 70 °C decreased by thirtyfold.

The decrease of $J_e$ as $T_g$ was approached from above was observed[1] also in narrow molecular weight distribution samples with molecular weights of $4.7 \times 10^4$ and $9.4 \times 10^4$. These molecular weights are above the critical molecular weight of entanglement $M_c$, 17 000 for polystyrene. The $J_e$ for samples with higher molecular weights are more difficult to measure in the neighborhood of $T_g$ because of the excessively long times required to achieve steady-state creep. It is evident that many mechanisms contributing to the retarded deformation are lost as the temperature of measurement approaches $T_g$. This loss of mechanisms is biased toward those with larger retardation times. That is,[1] long-time retardation mechanisms are preferentially being lost with decreasing temperature. Thus, the shape of the curve is maintained at relatively short times and the time-scale shifts obtained reflect the temperature dependence of all the mechanisms operative at the temperature of measurement. All of the viscoelastic mechanisms which contribute to the recoverable deformation reflect molecular orientation.

The published data of Plazek and O'Rourke[1] that have demonstrated this anomalous strong temperature dependence of $J_e$ were obtained from samples which apparently had small high molecular weight tails (i.e., small concentrations of high molecular weight species). The creep compliance obtained by them as a function of the time $t$ were analyzed according to the classic representation:[3]

$$J(t) = J_g + J_d\psi(t) + t/\eta \qquad (2)$$

where the total creep compliance, $J(t)$ (in cm$^2$/dyn), is the sum of the recoverable contributions $J_g + J_d\psi(t)$ and that representing the permanent viscous deformation, $t/\eta$. $J_g$ is the glassy compliance which is the long-time steady-state value for relaxations occurring at very short times. $\psi(t)$, the normalized retardation function for the primary dispersion, increases monotonically with time from zero at $t = 0$ to one at $t = \infty$. The steady-state compliance is $J_e = J_g + J_d$, where $J_d$ is the steady-state delayed compliance. The recoverable compliance is identified as $J_r(t) = J(t) - t/\eta$, where $\eta$ is the viscosity. The terminal zone response has been found to be enormously sensitive to molecular weight dispersity. A small concentration of a high molecular weight species can increase $J_e$ by orders of magnitude. These effects are clearly evident in 3400 molecular weight sample PC11-2 (see Figures 5 and 7 of ref 1). At each temperature the recoverable creep compliance $J_r(t)$ has a plateau but, on further increase of time, it continues to increase until reaching a steady-state value. At temperatures sufficiently high above $T_g$, the first plateau has a value slightly lower than the steady-state recoverable compliance $J_e = 2M/5\rho RT$ predicted by the modified Rouse theory, eq 1 (see Figures 10–14 of ref 3). Thus, it

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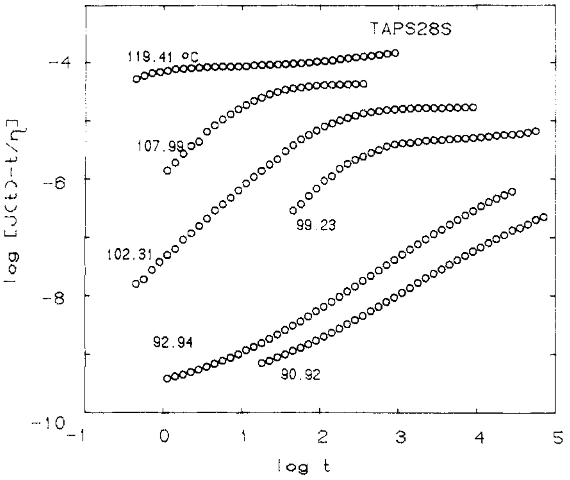

**Figure 1.** Recoverable compliance (open circles) of a TAPS-28S sample of polystyrene plotted against time at temperatures between 90 and 120 °C.

is reasonable to assume that the first plateau is the steady-state compliance of the predominant species in the sample. If the sample were ideally monodisperse, $J_r(t)$ would have remained at this plateau value. The observed increase in $J_r(t)$ beyond the steady-state recoverable compliance for the predominant species present in the distribution has been attributed to the presence of a high molecular weight tail.

To confirm this we have carried out additional measurements in a polystyrene sample of narrower molecular weight distribution. The sample TAPS-28S was prepared by the anionic polymerization of styrene. Its molecular weight as determined by gel permeation chromatographic measurement[4] is 12 300. The original 28S[14] sample had a heterogeneity index $M_w/M_n < 1.06$. It was subsequently fractioned by means of coevacuation by using benzene–methanol mixtures into 20 cuts. Fraction 14 was used in the currently reported study. The glass temperature of the sample was calculated to be 89.7 °C by using the empirical equation $T_g = 98.0 - 1.02 \times 10^5 M^{-1}$.[1] The creep and recovery measurements were made with a magnetic bearing torsional creep apparatus.[5] Constant torques were induced in the rotor by means of a drag cup motor, and angles reflecting the torsional deformation in the cylinderical samples were monitored with a laser light lever and a Beckman photopen recorder. Cylinderical samples were prepared in a vacuum mold at about 150 °C. Temperatures of measurements were between 90 and 120 °C are were held constant to within 0.04 °C.

Although the recoverable compliance has been denoted on the figures by $[J(t) - t/\eta]$, it was measured directly after steady-state flow in creep had $\rho$ obtained. When long time was required for steady-state flow (as, for example, at temperatures near $T_g$), a technique suggested by Leaderman et al.[6] and described in ref 1 was used to attain steady-state flow in a relatively short time. The measured recoverable compliance is shown in Figure 1.

The shear viscosity $\eta$ was determined also within a temperature range 89.6–167.0 °C. The results are shown in Figure 2. Over this temperature span the viscosity $\eta$ decreases nearly 10 orders of magnitude from $1.26 \times 10^{12}$ to $9.15 \times 10^2$ P.

The data of Figure 1 had been shifted horizontally to the temperature-reduced time $t/a_T$. Shift factors $a_T$ were determined by its empirical equation $\log a_T = -13.46 + 389/(T - T_g)$ as suggested by Plazek and O'Rourke.[1] The result of the reduction effected by such a simple logarithmic time axis shift is presented in Figure 3. At each temperature the recoverable compliance $J(t) - t/\eta$ levels off rather sharply to a steady-state recoverable compliance value $J_e$. In contrast to previous results[1] obtained from samples with suspected high molecular weight tails, there is no further increase in the recoverable compliance after attainment of the steady-state value. Again $J_e$ decreases with decreasing temperature. The temperature dependence of $J_e$ is particularly strong as the temperature of measurement approaches $T_g$. These measurements on an essentially monodisperse angle TAPS-28S support our suspicion of the presence of a high molecular tail in samples used in previous measurements. The further rise of $J_r(t)$ from the plateau seen in samples studied in ref 1 is now eliminated in the present sample, but the strong temperature dependence of $J_e$ is still seen. Therefore, it is certain the latter is a real anomalous viscoelastic phenomenon that needs an explanation. Additional independent evidence for the anomalous decrease in $J_e$ has been reported by Gray, Harrison, and Lamb.[7] Their results on polystyrenes with molecular weights of 3500 and 10 200 were obtained by means of dynamic mechanical measurements.

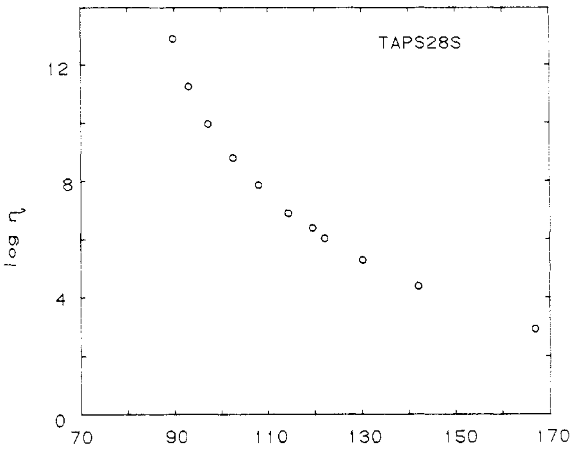

**Figure 2.** Zero-shear viscosity $\eta$ of a TAPS-28S sample of polystyrene (open circles) measured within a temperature range of 89.6–167.0 °C.

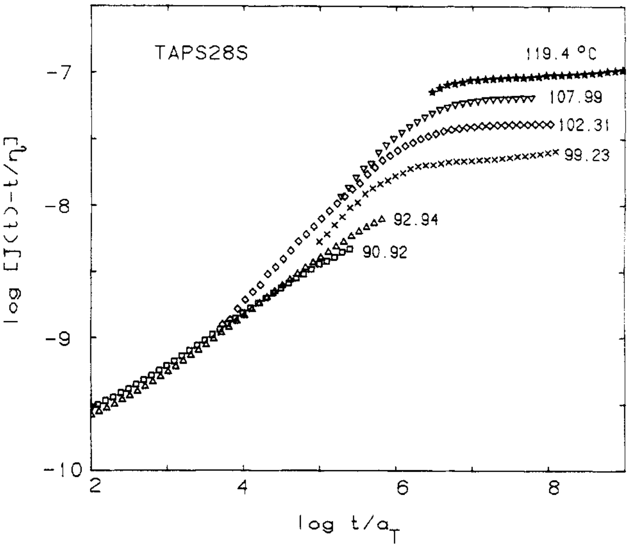

**Figure 3.** Recoverable compliance at different temperatures of TAPS-28S plotted against reduced time $t/a_T$ by the use of empirical horizontal shift factor $a_T$ given in the text.

The retardation spectra $L(t)$ defined by the relation

$$J(t) = J_g + \int_{-\infty}^{\infty} L(1 - e^{-t/\tau})\, d \ln t + t/\eta \qquad (3)$$

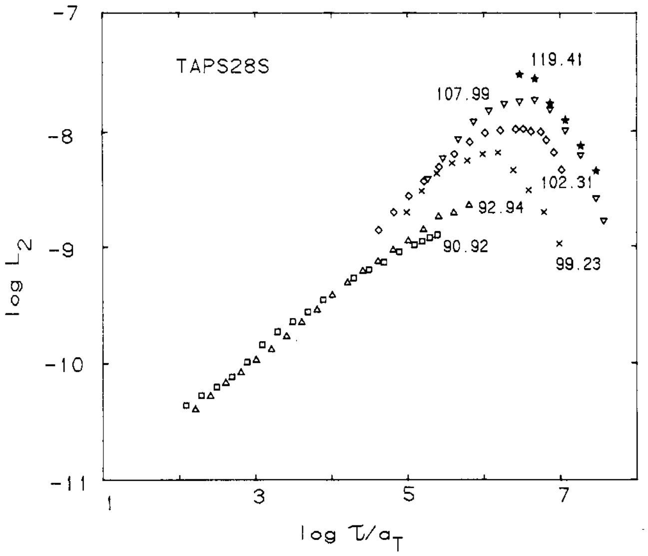

**Figure 4.** Retardation spectrum $L(\tau)$ of TAPS-28S polystyrene calculated from the recoverable compliance data of Figure 3 at different temperatures by the second approximation method of Schwarzl and Staverman.[3,8] Points are the $L(\tau)$ data calculated this way.

at different temperatures are calculated from the reduced recoverable compliance data in Figure 3 by using the second approximation method of Schwarzl and Staverman.[3,8] The results of the calculation are shown in Figure 4. The results shown in the figure clearly demonstrate that the population of retardation mechanisms diminishes with decreasing temperature. This depletion of mechanisms is biased toward those with large retardation times. It is worthwhile to point out that a similar marked decrease of $J_e$ with decreasing temperature within 15 K above the glass transition temperature has been found also in 4000 molecular weight poly(propylene glycol) in shear creep and creep recoverey measurements by Cochrane, Harrison, Lamb, and Phillips.[9] The anomalous temperature dependence of $J_e$ seems to be rather general.

This rather distinctive viscoelastic behavior of low molecular weight polystyrene has remained unexplained to this date. There is another fundamental viscoelastic behavior first observed more than 20 years ago in high molecular weight entangled linear polymer systems including polystyrene that is closely related to the present problem.[10] It was found that there is a lack of thermorheological simplicity in the viscoelastic behavior. Near $T_g$, the glass to rubber softening dispersion (which includes the segmental or $\alpha$ relaxation) moves toward long times more rapidly with temperature decreases than does the terminal dispersion or the viscous flow contribution to the total measured compliance. More recently measurements on poly(vinyl acetate)[11] and polypropylene[12] have indicated this phenomenon to be general for linear amorphous polymers. A coupling model of relaxation[13,14] that already accounted for viscoelastic properties in *both* the softening and terminal dispersions[15-17] (the $M^{3.4}$ dependence of $\eta$ and the $M^{-2}$ dependence of the self-diffusion coefficient $D$, etc.) has been found to explain quantitatively their different temperature dependences.[18,19] In view of these successes, it is natural for us to examine whether the coupling model can explain also the viscoelastic behavior observed in low molecular weight polystyrenes. One can view this work as another stringent test of the probity of the coupling model.

The basic idea behind the coupling model is that for a molecular relaxation process which is constrained by others and requires some degree of cooperativity, the relaxation rate $W_0$ in general will not remain a constant with time. The interaction with others will slow down its initial (primitive) relaxation rate $W_0$. The effective relaxation rate $W(t)$ is reduced[20-23] from $W_0$ by a factor $f(t)$ and is now a function of time. We found that the slowing down of the rate can be modeled by some generic features common to most complex Hamiltonian systems. Considerations of the coupling of the molecular relaxation process to these generic features enables us to calculate its actual form of the slowing down function $f(t)$. The result is that there is a characteristic time scale $t_c$ such that $f(t) = 1$ for $t/t_c < 1$ and $f(t) = (t/t_c)^{-n}$ for $t/t_c > 1$. Hence $n$, a fraction of unity $0 < n < 1$, is a measure of the rate of slowing down caused by the coupling of the primitive relaxation process to other molecular units.

Approaches[22,23] developed within the context of classical Hamiltonian mechanics and statistical mechanics of irreversible processes are now available. One approach modeled the interaction of the relaxing molecular unit with others, as time-dependent Dirac[24] constraints imposed on its phase space coordinates. Another approach has exploited some generic properties of chaotic (nonintegrable) Hamiltonians[23] that govern realistic interacting molecular systems and deduced the effects they have on the relaxation rate. The conclusion reached in these different yet related approaches is the same. That is, the coupling of the relaxation process to other molecular units causes the relaxation rate to slow down and acquire the time-dependent form $W_0f(t)$. Hence, we have called this class of related models the coupling model.

In any version of the coupling model, we have traced the time dependence, $W_0(\omega_c t)^{-n}$ where $\omega_c = 1/t_c$, of the rate of slowing down to some fundamental property of complex interacting molecular systems. The technical procedures used to derive it are not the familiar ones encountered in polymer physics. This situation may impose a barrier to others to achieve a thorough understanding without some degree of mastery of concepts and techniques initially foreign. There is a line of thought that may impart some familiarity with the coupling model at little cost of investment in time. This goes as follows. First, it is not difficult to accept the proposal that the relaxation rate is in general time dependent if cooperativity with or constraints by its environment are important. In fact, we should question why, in a complex system, the relaxation rate has to be always a constant $W_0$ at all times leading to exponential decay $\exp(-W_0t)$ of a dynamic variable. We can construct simple models to bring out the concept of a time-dependent relaxation rate. A similar concept of time-dependent friction was proposed by Anderson and Ullman.[25] Second, it is physically reasonable that the time-dependent $W(t)$ corresponds to a slowing down of the initial rate $W_0$ caused by constraints of, or coupling with, the environment. In general, there is a time scale $t_c$ characteristic of the molecular interactions in the system for the onset of the slowing down of the initial rate $W_o$. Third, of all possible choice of the slowing down function $f(t)$ defined by $W(t) = W_0f(t)$ for $t > t_c$, only one choice

$$f(t) = (\omega_c t)^{-n}, \qquad 0 < n < 1 \tag{4}$$

is both reasonable[14] and acceptable.[22] It is reasonable because the function is self-similar in time development, i.e.,

$$dW/W = -n(dt/t) \tag{5}$$

such that there is no time that distinguishes itself from others after $t_c$. The choice of $f(t)$ given by eq 4 is the only acceptable one if we want the relaxation function $\phi(t)$ obtained by solving the master or rate equation

$$d\phi/dt = -W_0 f(t)\phi \tag{6}$$

to be thermorheologically simple.[26] Ngai, Rajagopal, and Teitler[22] have proved that no other choice of $f(t)$ will give a relaxation function $\phi(t)$ that can be written as a function of the reduced time $(t/\tau^*)$ only. The latter condition when satisified is equivalent to being thermorheologically simple. Moreover, this choice of $f(t)$ will lead to the Kohlrausch[27]–Williams–Watts[28] (KWW) relaxation function

$$\phi(t) = \exp[-(t/\tau^*)^{1-n}] \tag{7}$$

where $\tau^*$ is given by the second relation[14]

$$\tau^* = [(1-n)\omega_c{}^n\tau_0]^{1/(1-n)} \tag{8}$$

and $\tau_0 = W_0{}^{-1}$. The rather general success of the KWW function in describing various relaxations in polymers[29] provides an additional endorsement for eq 4. In another connection of the Kohlrausch function with probability distribution of the frequency spectrum obtained by its Fourier transforms, it has been shown[30] that the Kohlrausch functions, eq 7, are the characteristic functions of stable superposable probability distributions. Actually, the Kohlrausch function does not satisfy the requirement for a relaxation function for all times. Generalization to k-dominance stability is required[30] and the results again point to the choice of $f(t) = (\omega_c t)^{-n}$. Stability of probability distribution upon superposition is relevant to the relaxation frequency spectrum since we do not expect the latter to change if we, say, double the size of the sample.

If one has now accepted the arguments and rationales outlined by the three steps as discussed above, then a reasonable familiarity of the coupling model can be achieved. The principal result of the coupling model is the time-dependent slowed down relaxation rate

$$\begin{aligned} W(t) &= W_0 \qquad \omega_c t < 1 \\ &= W_0(\omega_c t)^{-n} \qquad \omega_c t > 1 \end{aligned} \tag{9}$$

where $0 < n < 1$. Three coupled predictions follow immediately from this $W(t)$. Two of these three have already been displayed by eq 7 and 8. The utility of the three coupled predictions to relaxation phenomena and interpretation of experimental data have been reviewed in ref 14. We shall exploit these coupled predictions to explain the temperature dependence of $J_e$ of low molecular weight polystyrenes.

## Preliminaries

In a paper[18] published earlier we have dealt with a similar problem in amorphous polymers of high molecular weight well above $M_c$ which have a zone of rubberlike behavior separating the terminal relaxation of steady flow from the segmental or $\alpha$ relaxation. In polymers of low molecular weight below the minimum for entanglement coupling, there is no intermediate rubber range. The transition goes directly from the glassy zone, sequentially through local segmental ($\alpha$) relaxation and polymer chain relaxations, to the terminal zone of steady flow. Segmental relaxation reflects the motion of chemical groups rotating about single covalent bonds in the chain backbone. The exact nature of the motion is still not known and is still a subject for research. The general view is that the local motion of a segment of the polymer chain can be described in terms of a combination of torsional–vibrational motions and rotational conformation changes that involve only a few monomers. Segmental ($\alpha$) relaxation associated with noncorrelated motions of localized chain segments is seen[29] in undiluted polymers by dielectric relaxation, photon correlation spectroscopy, stress relaxation, and creep compliance measurements usually at temperatures above $T_g$.

The polymer chain relaxation in undiluted polymer can be rather well described by the bead-spring theory of Rouse[2] when appropriately modified,[3] as long as the molecular weight is sufficiently low so that the coupling entanglements do not occur. For example, the measured viscosity $\eta_0$ and recoverable compliance $J_e$ have magnitudes and molecular weight dependences as predicted by the Rouse theory, in accordance with the principle proposed by Bueche and explained by Ferry.[3] An essential feature of the normal-coordinate treatments is the division of the chain into a number of Gaussian subunits. As stated by Ferry, a number of chain atoms are required to define a Gaussian subunit. The bead-spring model has assumed that, in the time scales of the normal modes, the polymer chain is flexible and can be represented as a chain of $N$ Gaussian submolecules. The $N + 1$ ends of the submolecules, called beads, can execute jumps and the motion of the polymer chain can be expressed in terms of normal coordinates. The normal modes relax according to the time dependence of $\exp(-t/\tau_k)$ where[3]

$$\tau_k = \eta_0 M/\pi^2 k^2 \rho RT, \qquad k = 1, ..., N \tag{10}$$

and from these it follows that the viscosity is given by

$$\eta_0 = (\rho RT/M)\tau_1 S_1 \tag{11}$$

and $J_e$ by eq 1. The requirement of the Rouse model is that all subunits be Gaussian and hence flexible. Obviously only complete relaxation of any localized chain segment within the subunit can bring about this condition. If $\tau^*_\alpha$ denotes the time scale of the local segmental relaxation, then the logical basis of the Rouse model requires that

$$\tau^*_\alpha \ll \tau_N, \tau_{N-1}, ..., \tau_1 \tag{12}$$

Equation 12 is verified by various measurements in flexible and semiflexible polymers in solution or undiluted polymers[1,3,18,19,31] at temperatures *far above* $T_g$ which show the normal-mode contribution occurs at much lower frequencies (or longer times) than that of the local segmental motion. This is also the case for the creep measurements on low molecular weight polystyrenes addressed in this work. Far above $T_g$, not only does the steady-state compliance $J_e{}^0$ agree rather well with the Rouse prediction[3] (indicating all the normal modes are present and contributing), but also the peak of the retardation spectrum of these normal modes is located at a time much longer than the effective relaxation time of the local segmental motion. In the next section we shall show, as a consequence of one of the three predictions, eq 8, of the coupling model[14,20-23] discussed in the previous section, the condition, eq 12, can be violated at temperatures near $T_g$. When eq 12 is violated, some normal modes of chains are arrested, and there is a loss of mechanisms contributing to the retarded deformation. This continued loss of mechanisms with decreasing temperature is biased toward those with larger relaxation times $\tau_k$'s on the right-hand side of eq 12. Thus the coupling model provides a physical explanation for the anomalous viscoelastic behavior.

## Theoretical Development

The coupling model[14,20-23] on which our explanation of the strong temperature dependence of $J_e$ is based has been discussed in a previous section. The application of the coupling model here is particularly closely related to those in the two latest works.[18,19] In these applications the viscoelastic properties of both the local segmental mode (also referred to as the primary $\alpha$ relaxation mode) and the polymer-chain normal modes responsible for viscous flow and self-diffusion are addressed in light of the coupling model. The essence of the coupling model and its three predictions have been summarized in eq 5–9 of ref 19 and in eq 2–5 of ref 18. For economy of space we shall not repeat the discussions of the utility of these predictions here. The reader is asked to consult these two references together with ref 14 for details. Two of the three predictions have been reproduced here as eq 7 and 8 for clarity. Applying these to the local segmental ($\alpha$) relaxation, the first prediction for the time dependence of its normalized relaxation function $\phi_\alpha(t)$ is

$$\phi_\alpha(t) = \exp[-(t/\tau^*_\alpha)^{1-n_\alpha}] \qquad (13)$$

provided the condition $\omega_c\tau_\alpha \gg 1$ is satisfied by the crossover frequency $\omega_c$ and the primitive relaxation time $\tau_\alpha$ of the $\alpha$ relaxation mode. The quantity $n_\alpha$ is the coupling parameter of the local segmental relaxation. The second prediction relates the effective relaxation time $\tau^*_\alpha$ in eq 13 to the primitive relaxation time $\tau_\alpha$ by the equation

$$\tau^*_\alpha = [(1 - n_\alpha)\omega_c^{n_\alpha}\tau_\alpha]^{1/(1-n_\alpha)} \qquad (14)$$

with the *same* $n_\alpha$ as appears in eq 13. This additional relation between $\tau^*_\alpha$ and $\tau_\alpha$ when rewritten as

$$\tau^*_\alpha = \tau_\alpha[[(1 - n_\alpha)^{1/n_\alpha}\omega_c\tau_\alpha]^{n_\alpha/(1-n_\alpha)}] \equiv a_\alpha\tau_\alpha, \qquad \omega_c\tau_\alpha > 1 \qquad (15)$$

yields additional physical weight. The slowing down of the relaxation rate by coupling of the relaxation process to its complex environment, the essential piece of physics of the coupling model, leads not only to the Kohlrausch–Williams–Watts[28] time dependence, eq 13, but *also* a shift of the primitive $\tau_\alpha$ to a longer effective $\tau^*_\alpha$ by a multiplicative factor $a_\alpha$ which is the term inside the square brackets in eq 15. The magnitude of this shift factor $a_\alpha$ depends on $n_\alpha$ and the product $\omega_c\tau_\alpha$. The coupling parameter $n_\alpha$ here has been determined for the $\alpha$-relaxation of polystyrene by best fit of theoretical creep compliance functions $J_n(t)$[18] to experimental data. The theoretical $J_n(t)$ is derived from a stress-relaxation function that has the Kohlrausch form eq 13 by deconvolution of linear viscoelastic relation.[3,18] The values of $n_\alpha$ obtained this way[18] for samples with different molecular weights fall in the range $0.62 \le n_\alpha \le 0.65$.

It is easy to verify from eq 15 that for such sizeable values of $n_\alpha$, the shift factor $a_\alpha$ is a very rapid increasing function of the product $\omega_c\tau_\alpha$. Starting from above $T_g$, as the temperature of measurement is lowered to approached $T_g$, the primitive $\tau_\alpha$ increases. The product $\omega_c\tau_\alpha$ increases accordingly since the crossover frequency $\omega_c$ is not expected to be a sensitive function of temperature. Rapid increases of the shift factor $a_\alpha$ and of the effective relaxation time $\tau^*_\alpha$ follow as consequences of eq 15. As a result, $\tau^*_\alpha$ can be orders of magnitude longer than $\tau_\alpha$ as $T$ approaches $T_g$ such that, although in principle the primitive $\tau_\alpha$ satisfies all the conditions of eq 12, $\tau^*_\alpha$ may become comparable to or even exceed some of the $\tau_k$'s of the chain normal modes. The latter is an untenable situation because the bead–spring normal modes are based on Gaussian submolecules and any of their relaxation times $\tau_k$ cannot have relaxation times shorter than $\tau^*_\alpha$, the effective relaxation time of a local segment *within* any Gaussian submolecule. Otherwise at a time of the order of $\tau_k$, a local segment *within* a submolecule would not have yet relaxed contradicting the assumption of a flexible chain made up of Gaussian submolecules. This argument which follows as a consequence of the *second* relation, eq 14, of the coupling model signals the possible breakdown of the Rouse theory for undiluted polymers[3] of low molecular weight when $T$ approaches $T_g$. Some of the bead–spring chain normal modes which contribute to recoverable deformation at higher temperatures are lost as the temperature is lowered as a consequence of greater molecular crowding leading to a larger shift factor $a_\alpha$ caused by coupling.

The above discussion is now expanded to incorporate the approach and methods used in several related works into our consideration of the present problem. Before we start let us briefly review the chain normal modes in connection with the coupling model. For a normal mode relaxation, coupling occurs through interaction with other chains and is significant in the terminal zone of response only if the chains are entangled. In the entanglement regime, the natural choice of the size of the Gaussian submolecule for the flexible chain is the molecular chain between entanglements with a molecular weight of $M_e$. The strength of entanglement coupling is maximum for the most cooperative mode corresponding to $k = 1$, decreasing rapidly for higher modes with greater mode numbers or shorter "wavelengths". For systems of linear flexible molecules the entanglement coupling for the $k = 1$ mode with coupling parameter $n$ causes its relaxation function to be modified from its primitive time dependence $\exp(-t/\tau_1)$ to have the Kohlrausch form $\exp(-t/\tau^*_1)^{1-n_1}$, where $\tau^*_1 = [(1 - n_1)\omega_c^{n_1}\tau_1]^{1/(1-n_1)}$. From fits of viscoelastic data of the terminal zone in monodisperse linear polymers,[14–18] we have found $n_1$ to lie within the range $0.40 \le n_1 \le 0.45$. Although high-order modes other than $k = 1$ are present in the viscoelastic response, according to the superlinear dependence of the effective $\tau^*_k$ on $\tau_k$ and the smaller $n_k$ for larger $k$, they contribute little to the terminal zone and the shear viscosity. In some of the previous works[14,17,18] where we have to distinguish the coupling parameter for the $k = 1$ mode from that of the segmental $\alpha$ relaxation mode, we have replaced the notation $n_1$ by $n_\eta$. The subscript $\eta$ reminds us that the coupling parameter is for the mode primarily responsible for viscous flow. For low molecular weight polymers that are not entangled, the coupling parameter $n_\eta$ is reduced to zero. When $n_\eta$ is zero, the Kohlrausch function becomes the exponential function $\exp(-t/\tau_1)$, and $\tau^*_1$ becomes $\tau_1$. The coupling model of the chain modes reduces to be the same as the modified Rouse model for undiluted polymers.

In ref 18 we considered the different temperature dependences of the segmental $\alpha$ relaxation and the terminal relaxation in entangled linear polymers.[10–12] The occurrence of these two different temperature dependences is explained in the coupling model by the difference of $n_\alpha$ and $n_\eta$. The two coupling strengths lead to two different temperature shift factors, $a_{T\eta} = [\zeta_0(T)/\zeta_0(T_0)]^{1/(1-n_\eta)}$ and $a_{T\alpha} = [\zeta_0(T)/\zeta_0(T_0)]^{1/(1-n_\alpha)}$ respectively for viscous deformation and local segmental relaxation from a reference temperature $T_0$. Here $\zeta_0(T)$ denotes the *primitive* (i.e., before coupling is taken into account) friction factor which has been assumed to be the same for both. It has been further shown that this difference in temperature dependence can be explained quantitatively with values of $n_\alpha$ and $n_\eta$ determined independently from recoverable and permanent creep deformation. For polystyrene we[18] have found $0.62 \le n_\alpha \le 0.65$ and $0.40 \le n_\eta \le 0.45$.

A very similar effect has been found by light scattering techniques in *low* molecular weight unentangled poly(phenylmethylsiloxane) (PPMS). Ngai and Fytas[19] have extended the work of Ngai and Plazek to this case where $n_\alpha = 0.56$ and $n_\eta = 0$. Again, the differences in both the temperature and pressure dependences of the local segmental $\alpha$ relaxation and the chain normal modes can be explained quantitatively by the difference in size of their coupling parameters. The chain modes shift as $\zeta_0(T,P)/\zeta_0(T_0,P_0)$ because there is no entanglement with other chains, and the coupling parameter $n$ vanishes. On the other hand, the $\alpha$ relaxation shifts as $[\zeta_0(T,P)/\zeta_0(T_0,P_0)]^{1/(1-n_\alpha)}$. For $n_\alpha = 0.56$, the exponent $(1 - n_\alpha)^{-1}$ is larger than two. This causes a much more rapid increase of the relaxation time $\tau^*_\alpha$ of the local segmental $\alpha$ relaxation than that of the chain normal modes as $T$ is decreased to approach $T_g$ or as $P$ is increased.

A similar behavior to that in PPMS has been observed in low molecular weight dry samples of poly(propylene glycol) P4000 by Cochrane et al.[9] The recoverable compliance data measured at temperatures −68 °C and below reflect, in the main, the contributions from the local segmental relaxation. The time shift factors $a_T$ obtained by superposition of the creep recovery curves in this temperature range of $-68.0 \leq T \leq -76.0$ °C has a more rapid variation with temperature than that of the shift factors $a$ for the Maxwell relaxation time $\tau_m = \eta J_g$ defined by the ratio $a = (\tau_m)_T/(\tau_m)_{-68\,°C}$. This difference in temperature dependence is consistent with that observed for local segmental relaxation and chain normal modes in PPMS by photon correlation spectroscopy.[19,33]

The origin of the strong temperature dependence of $J_e$ in low molecular weight polystyrene and poly(propylene glycol) is the difference between the temperature dependences of the local segmental relaxation and the chain Rouse modes. In polystyrene the coupling parameter $n_\alpha$ is even larger than the corresponding quantity in PPMS ($n_\alpha = 0.56$), and the relaxation time $\tau^*_\alpha$ will increase so rapidly when $T$ approaches $T_g$ that it can catch up with the relaxation times $\tau_k$ of the chain normal modes. As has been discussed above, this is catastrophic for the chain bead–spring normal modes. Obviously a monomeric friction coefficient cannot be greater than that of an entire submolecule. Therefore, the response of the entire molecule becomes prohibited leading to the long-time reduction of the number of effective modes which decreases $J_e$.

## Model Description

The discussions in the last section give a physical picture of how an effect predicted by the coupling model[14,20-23] on the segmental $\alpha$ relaxation can cause depletion of the normal modes of the chain. The discussions also tie together the various works published recently[14-19] that have given satisfactory explanations to several previously puzzling problems in polymer physics. In this section, we introduce the theoretical framework for an explanation of the present problem sketched above.

The segmental relaxation time $\tau^*_\alpha$ is a measure of the least time that is needed to meet the requirement to have a flexible chain of $N$ Gaussian submolecules. The chain normal mode with index $k$ equal to $N$ has relaxation time $\tau_N$ which is shortest among all the $\tau_k$'s. The normal coordinates describing the beads $0, ..., j, ..., N$ for the $k$th mode are given by[2,3]

$$Q_{kj} = (2/N)^{1/2} \cos (jk\pi/N) \qquad (16)$$

The $k = N$ mode has the beads at the two ends of a submolecular unit having maximum amplitude of displacement in the opposite directions. Its relaxation time $\tau_N$ gives a typical time scale of relaxation of the Gaussian submolecular unit. If $\tau^*_\alpha \ll \tau_N$, any segment within the submolecule is always relaxed on a time scale of the order of $\tau_N$ and the requirement of complete flexibility for a Gaussian submolecule is satisfied. If $\tau^*_\alpha$ for some physical reason (as provided by the coupling model) becomes comparable to $\tau_N$, then in a fraction of time $\tau^*_\alpha$ out of $\tau_N$ the segment has not been fully relaxed, and the submolecule is not Gaussian. Hence the ratio $\tau^*_\alpha/\tau_N$ can be considered as a measure of the probability of not having the condition of a Gaussian submolecule satisfied because one of its segments may not have been fully relaxed. Let $P$ be the number of monomers in the chain, then the number of monomer units in a submolecule is $q = P/N$. If the local segmental relaxation involves $q_\alpha$ continguous monomers, then there are approximately $q$ possible and distinguishable local segments to consider within a submolecule provided $q_\alpha \ll q$. Ignoring correlations of more than one local segmental motion within a submolecule, the probability of the submolecule not being Gaussian is $q\tau^*_\alpha/\tau_N$. By inspection of the displacement pattern of the normal modes for the linear chain (see Figure 5 of Stockmayer[2]) we find the entire $N$ units are involved to define the elementary displacement pattern for the $k = 1$ mode. For the $k = 2$ mode, only $N/2$ units are needed to define the elementary displacement pattern which is repeated once more in the other half of the chain. In general for the $k$th mode, only $N/k$ units are necessary to define the elementary displacement pattern which is then repeated $k$ more times down the chain. Thus, fewer Gaussian submolecular units are required to define a repeated elementary displacement pattern for normal modes with increasing mode number $k$. Each submolecule within a repeat unit has the probability of $(1 - q\tau^*_\alpha/\tau_N)$ of being Gaussian. Therefore the probability of survival $F_k$ of the repeated elementary displacement pattern for the $k$th mode is given by

$$F_k = (1 - q\tau^*_\alpha/\tau_N)^{N/k} \qquad (17)$$

For large $N/k$, $F_k$ can be approximated by

$$F_k \simeq \exp(-P\tau^*_\alpha/k\tau_N) \qquad (18)$$

It may be noted that $F_k$ decreases rapidly with decreasing $k$ if $\tau^*_\alpha/\tau_N$ is fixed. Also, as the temperature is decreased to approach $T_g$, the ratio $\tau^*_\alpha/\tau_N$ will increase because $\tau^*_\alpha$ shifts to longer times much faster than $\tau_N$. The cause of this effect, as explained by the coupling model, is the large size of the coupling parameter $n_\alpha$ for the segmental motion compared with vanishing coupling parameter $n_\eta$ for the chain normal modes in unentangled chains. These dependences of $F_k$ on $k$ and $T$ enable the following conclusions to be drawn. At temperatures high above $T_g$, the $\omega_c\tau_\alpha$ product in eq 15 is not that large, and it follows from the same equation $\tau^*_\alpha$ will not be much larger than $\tau_\alpha$ such that the condition $P\tau^*_\alpha/\tau_N \ll 1$ is satisfied, and $F_k = 1$ for all $k$'s. All modes from $k = 1$ to $k = N$ are fully populated and contribute fully to the viscoelastic response and $J_e$ in accordance with the Rouse theory modified for undiluted polymers.[3] On decreasing $T$ at the point that $P\tau^*_\alpha/\tau_N$ is no longer negligible, the population of the bead–spring normal modes are all diminished. Diminishing population causes the loss of retardation mechanisms in creep compliance. From the dependence of $F_k$ on $k$ given by eq 18, this loss of retardation mechanisms is more severe for normal modes with smaller $k$ and large retardation times. Further decrease in temperature makes $P\tau^*_\alpha/\tau_N$ even larger. Populations of all modes are diminished according to eq 18 to a greater extent. Higher $k$-modes will also now be depopulated and lost. The result is an increasing depletion of the retardation spectrum (see Figure 4) and a rapid drop of the recoverable compliance (See Figure 1) as $T$ approaches $T_g$ as observed in shear creep and creep recovery measurements. The coupling model gives a physical basis for this peculiar decrease in the contribution of the bead–spring modes to retardation mechanisms as $T$ approaches $T_g$. The cause of this effect is the tendency of the effective local segmental relaxation time $\tau^*_\alpha$ to encroach on the time domain of the relaxation times $\tau_k$'s of the bead–spring modes. This encroachment means each submolecule and hence the entire chain become effectively more rigid and enables the chains to store more energy, but it also diminishes their contributions to dissipation and hence the recoverable compliance.

Molecular motions which are described by modes that involve segmental cooperation over large distances have larger retardation times. Local segmental modes which involve more local or short-range cooperative motions have shorter retardation times. The former modes contribute dominantly to viscous flow and the approach to $J_e$. The latter contribute additively to recoverable deformation in the softening dispersion. As mentioned above the former modes slow down less rapidly with temperature than the latter, reflecting a coupling constant $n_\eta$ which is zero at low molecular weights, $M < M_c$. The local segmental mode is highly coupled with $n_\alpha \simeq 0.65$ having smaller retardation times which increase more rapidly with decreasing temperature and approach the levels of the retardation times of the more loosely coupled long-range motions. As a consequence the long-range coordinated motions cease to be possible with a further decrease in temperature since long-range coordinated motions cannot take place faster than local motions. The rate of deformation of polymers and other supercooled liquids is known to be predominantly determined by the free volume available for the involved molecular motions. One of us[10] has noted previously that the free volume parameters derived for the softening dispersion and for viscous flow indicate that the occupied volume for the molecular motions contributing to the softening dispersion (presumed to be the local segmented motion) is higher than that for the motions which contribute to viscous flow. This reflects the fact that the local mobility involved in short-time motion in the softening dispersion decreases more rapidly than the global mobility involved in the relative displacement of entire molecule predominantly in the axial direction of the chain backbone.

If we presume that normal mode motions which produce contributions to the recoverable deformation require local rarefactions above some minimum for the polymer chain segment involved (i.e., a given segmental jump unit requires a large enough hole), then such a motion will not be possible if the required decrease in the local density does not occur. And if we further presume that the size as well as the frequency of hole sizes diminishes with temperature, at low enough temperatures (close to $T_g$) large enough holes for a given size jumping unit will never occur and modes of motion will not be possible starting from those with the longest relative retardation times. Flow, the accumulation of permanent deformation, continues as a result of contributions from more local motions. These crude notions are not inconsistent with the coupling model.

The method used in this section to calculate the survival probability of the Gaussian nature of the submolecule is rather crude. A more formal mathematical analysis of the survival probability of a chain normal mode is needed for an entirely satisfactory discussion of this problem. In spite of this crudeness, the essential features of experimental data appear to be explained by the coupling model. The emphasis of the present work is on the search of the physical origin of the effect that causes the anomalous viscoelastic behavior of low molecular weight polystyrene. We have found the predictions of the coupling model provide an explanation of the effect. No attempt of actually calculating the recoverable compliance or the retardation spectrum as a function of temperature is made at this time. It will be an interesting problem to pursue in the future.

The strong temperature dependence of $J_e$ is observed also in high molecular weight ($M > M_c$) samples. In a previous work,[1] evidence of this behavior has been found in 94 000 molecular weight polystyrene. The drop in the recoverable compliance starts in an increasingly smaller neighborhood of $T_g$ as the molecular weight increases. This feature follows from the presence of entanglement coupling for high molecular weight samples. The entanglement coupling gives rise to a finite coupling parameter $n_\eta$ for the terminal dispersion and shifts the first few chain modes and particularly the $k = 1$ mode to longer times according[15-18] to eq 8. The shift has the $M^{3.4}$ molecular weight dependence of course. As $T$ is lower toward $T_g$, this shift delays the onset of the effect on the terminal zone caused by the intrusion in time scale of the local segmental relaxation into that of the chain modes. The coupling parameter $n_\alpha$ for the $\alpha$-relaxation being larger[18,19] than $n_\eta$ for polystyrene and other vinyl polymers ensures the same effect discussed for low molecular weight polystyrenes will be observed also for high molecular weight samples. There is a delay due to the shift of the terminal zone to longer times by entanglement coupling. This delay causes the drop in $J_e$ to start much closer to $T_g$ as observed. Recent measurement[32] of recoverable creep compliance of 200 000 polystyrene at temperatures much closer to $T_g$ indeed has revealed the same behavior. As a consequence, any theory of entangled polymer melts is not satisfactory unless it has a prediction that is consistent with this observed viscoelastic property.

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## References and Notes

(1) Plazek, D. J.; O'Rourke, V. M. *J. Polym. Sci., Polym. Phys. Ed.* **1971**, *9*, 209.

(2) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272. Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269. Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.

(3) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.

(4) This result is supplied through the kindness of Prof. Guy C. Berry.

(5) Plazek, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 621.

(6) Leaderman, H.; Smith, R. G.; Williams, L. C. *J. Polym. Sci.* **1959**, *36*, 233.

(7) Gray, R. W.; Harrison, G.; Lamb *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1361; *Proc. R. Soc. London* **1977**, *356*, 77.

(8) Schwarzl, F.; Staverman, A. J. *Appl. Sci. Res., Sect. A* **1953**, *4*, 127.

(9) Cochrane, J.; Harrison, G.; Lamb, J.; Phillips, D. W. *Polymer* **1980**, *21*, 837.

(10) Plazek, D. J. *J. Phys. Chem.* **1965**, *69*, 3480; *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 621; *Polym. J.* **1980**, *12*, 43.

(11) Plazek, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 729.

(12) Plazek, D. L.; Plazek, D. J. *Macromolecules* **1983**, *16*, 1469.

(13) Ngai, K. L. *Comments Solid State Phys.* **1979**, *9*, 127; **1980**, *9*, 141.

(14) For recent reviews of the coupling model, see: Ngai, K. L.; Rajagopal, A. K.; Rendell, R. W.; Teitler, S. *IEEE Trans. Electr. Insul.* **1986**, *EI-21*, 313. Ngai, K. L.; Rendell, R. W.; Rajagopal, A. K.; Teitler, S.*Ann. N. Y. Acad. Sci.* **1986**, *484*, 150, 321.

(15) Ngai, K. L.; Rendell, R. W. *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23*, 46.

(16) Ngai, K. L.; Plazek, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2159.

(17) McKenna, G. B.; Ngai, K. L.; Plazek, D. J. *Polymer* **1985**, *26*, 1651.

(18) Ngai, K. L.; Plazek, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 619.

(19) Ngai, K. L.; Fytas, G. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1683.

(20) Ngai, K. L. *Comments Solid State Phys.* **1979**, *9*, 127; **1980**, *9*, 141.

3054 *Macromolecules* **1987**, *20*, 3054-3059

(21) Rajagopal, A. K.; Teitler, S.; Ngai, K. L. *J. Phys.* **1984**, *17*, 6611.

(22) Ngai, K. L.; Rajagopal, A. K.; Teitler, S., submitted for publication in *J. Chem. Phys.*

(23) Rendell, R. W.; Ngai, K. L., unpublished results. See pp 181–182 of second article of ref 14.

(24) Sudarshan, E. C. G.; Makunda, N. *Classical Dynamics: A Modern Perspective*: Wiley: New York, 1974.

(25) Anderson, J.; Ullman, R. *J. Chem. Phys.* **1967**, *47*, 2178. Ullman, R. *J. Chem. Phys.* **1968**, *49*, 831.

(26) We borrow the phrase "thermorheologically simple" and use it in a restricted meaning only, i.e., "rigidity" of relaxation spectrum for a *single* relaxation process. The conventional use of the phrase usually implies the successful reduction to a master curve of measurements made at different temperatures in an experimental time or frequency window and may involve more than one relaxation process, e.g., a local segmental relaxation and the terminal relaxation in a polymer liquid as studied in this work.

(27) Kohlrausch, R. *Prog. Ann. Phys.* **1847** *12*, 393; **1854**, *1*, 56, 179.

(28) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1971**, *66*, 80.

(29) Ngai, K. L., Wright, G. B., Ed. *Relaxations in Complex Systems*; U.S. Government Printing Office: Washington, DC, 1985 (available from the National Technical Information Service, Springfield, VA 22161).

(30) Ngai, K. L.; Rajagopal, A. K.; Teitler, S. *Physics*, **1985**, *133A*, 213.

(31) Baur, M. E.; Stockmayer, W. H. *J. Chem. Phys.* **1965**, *43*, 4319.

(32) Cox, J. R.; Plazek, D. J., unpublished results.

(33) Fytas, G.; Dorfmuller, Th.; Chiu, B. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1471.

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# Loop Entanglement in a Constrained Liquid Region: Simulation Data, Simplified Models, and General Measurement Heuristics

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ABSTRACT: Complete entanglement measurement data from a computer simulation of the random walk model of a liquid region in a semicrystalline polymer is presented for plane separations out to 54 units. These data are compared with the same measures calculated analytically in a simplified model of the simulation. A case is presented for validation of the simplified model measurements as heuristics for the more complicated calculations used in the simulation. The model simplification process is general enough to apply to any model that contains loops and ties as chains between parallel planes. The heuristics may be applied directly from knowledge of single-chain statistics. As an example application, the heuristics are calculated for a model recently introduced by Marqusee and Dill, where it is found that both physical ties and loop entanglements are more likely than in the random case.

## Introduction

The extent and complexity of loop entanglement in long molecules, along with the significance of entanglement in determining chemical and physical properties, has been a subject of interest probably since long molecules were discovered.[1] In particular, there is considerable current research activity which directly or tangentially bears on such questions in the amorphous region of semicrystalline polymer. Various models of the intercrystalline region have been proposed, and most of these relate in some way to the entanglement question. The entanglement question is persistent, at least in part, because measures of entanglement are very difficult to calculate analytically[2] and very expensive to calculate numerically.[3]

The paper begins with a full report on the data from a computer simulation (announced in Lacher et al.[4]) calculating entanglement measures for the random walk/cubical lattice model. Three statistical measures are reported: link probability $P_{\rm link}$ (the probability of a chain linking one from the opposing plane), link density $D_{\rm link}$ (the expected number of opposing chains linked by a given chain), and total Gauss winding $W_1$ (the expected value of total winding of a chain about opposing chains). (Complete definitions are given in later sections.) These data cover plane separations out to 54 units and show that loop entanglements in the random walk model are significantly more prevalent than physical ties for separations greater than 20 units and, according $D_{\rm link}$ and $W_1$, for separations greater than 14 units. This is a complex simulation that actually generates random walks from opposing planes in space, calculates Gauss linking numbers for opposing loops, and combines these calculations into measures of loop entanglement, all in sufficient quantity to assure stable statistical estimates.

Next the simplified model of Lacher, Bryant, and Howard[5] is considered. This is a general model in which counterparts of link probability and link density, $P^{s}_{\rm link}$ and $D^{s}_{\rm link}$, respectively, can be defined and calculated analytically. The simulation data are compared with the calculations in the simplified model. In the case of link density, where the asymptotics of $D^{s}_{\rm link}$ are known,[5] the simulation data fit the asymptotic curve type with root-mean-square error on the order of 0.05 standard deviation in the data; the predicted limiting value of $D_{\rm link}$ is the same as that of $D^{s}_{\rm link}$ to within similar error. In the case of link probability, comparison of the $P_{\rm link}$ data with the $P^{s}_{\rm link}$ curve shows the two functions have the same discernible qualitative features and are in reasonable quantitative agreement.

The simplification process may be applied to any model whose basic components are loops and ties that are chains in the region between two parallel planes in space. The formulae derived for $D^{s}_{\rm link}$ and $P^{s}_{\rm link}$ are equally general, depending only on single-chain statistics (and not on interaction of two or more chains). Thus $P^{s}_{\rm link}$ and $D^{s}_{\rm link}$ can be calculated as entanglement measurement heuristics for any model in which these single-chain statistics are known. The paper concludes with calculations of these entanglement heuristics for the model recently introduced by Marqusee and Dill,[6] where it was found that introduction of a tendency to order near crystal faces significantly increases the likelihood of tie chains over that expected in the random walk model. These calculations show that in spite of a decrease in the number of loops, the likelihood of links connecting lamellar crystals is also higher than that for the random case, so that a tendency to order near

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