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with this expression is in the range of the reported values.[9,11] Finally, the above discussion points out that c^* is not a sharp dividing line. It is therefore not physically meaningful to scale the concentration axis in a plot of D/D_0 vs. concentration divided by the crossover concentration. Equation 13 demonstrates that it is better to plot the relative diffusion coefficient vs. the weight concentration of the polymer, as was done by Munch et al.[9]

A similar decomposition of the diffusion coefficient into a linear relationship between the diffusion constant and the polymer concentration has been derived by Brochard et al.[12] While their equation was applied to diffusion in polymer–polymer melts it is applicable to polymer–simple molecular solvent systems if the degree of polymerization of one of the species is taken to be unity. While their result also predicts a linear relationship between the diffusion coefficient and the polymer concentration at concentrations well below and well above c^*, the same expression, but with different sets of constants, must be used. Our result is a single expression that is correct at all polymer concentrations.

Future work will involve comparison of eq 15 to measured diffusion coefficients for systems with a wide range of bond lengths and segmental molecular weights. Unfortunately, reliable data over a wide range of concentrations are difficult to obtain. We also hope to extend eq 13 to non-Θ conditions. At least superficially, eq 13 can be extended to non-Θ conditions by multiplying $\langle R_{ij} \rangle$ by an expansion parameter. Since it is known that the expansion parameter is greater than unity for good solvents and less than unity for poor solvents, eq 13 would predict that the slope of the D/D_0 vs. c_w line for $c_w > c^*$ would decrease in good solvents and increase in poor solvents, in agreement with predictions from scaling theory.[13] This is only superficial, since expansion parameters are functions of the polymer concentration and, therefore, for non-Θ solvents the diffusion coefficient curve at concentrations above the crossover concentration may no longer be linear.[14]

Acknowledgment. We thank one of the referees for pointing out the relation of this work to the result of Brochard et al.

Registry No. Polystyrene (homopolymer), 9003-53-6.

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Nonequilibrium Mechanical Response of a Cross-Linked Network

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Our understanding of the molecular mechanisms responsible for the nonequilibrium mechanical properties of a cross-linked network has recently been deepened by a theoretical model suggested by de Gennes.[1,2] In this analysis, each dangling chain and unattached chain in the network is confined by other chains in a virtual tube lying along the chain contour from which it is able to escape by a diffusion of its free end(s) along the chain contour. The escape of an unattached chain occurs by a "reptation" mechanism[1] involving the motion of both chain ends. The escape of a dangling chain occurs by a "retracing" mechanism[2] involving the motion of the free chain end toward the fixed chain end. In both cases, as a chain end passes out of a portion of the tube for the first time, that tube portion evaporates. The stress contribution of an unattached chain[3] or a dangling chain[4] is assumed to be proportional to the fraction of the tube that remains at time t.

When a cross-linked network is deformed, a dangling chain or an unattached chain deforms by virtue of its having distinct, localized entanglements at various positions along its chain contour. Using this picture, we can replace the evaporation of portions of the continuous tube in the de Gennes model by the dissolution of discrete entanglements as the free chain end(s) diffuse along the chain contour. Each disentanglement is obviously a barrier passage event, the precise nature of which depends on the specific character of the entanglement. The overall chain relaxation process is therefore a multiple barrier passage process.[5,6] This type of process has been modeled[7,8] in terms of a continuous-time random walk (CTRW) having a pausing-time distribution with a long time tail

$$\psi(t) \sim t^{-1-\alpha} \qquad 0 < \alpha \leqslant 1 \tag{1}$$

In the following sections, we will examine both the reptation and retracing mechanisms in terms of this CTRW model.

Reptation of an Unattached Chain

We have recently shown[9] that in the reptation process, the fraction of tube that has evaporated at time t equals the span at time t of a one-dimensional nearest-neighbor random walk and that the stress relaxation function at time t is given by

$$\phi(t) = f(L,t) = \int_0^L \left(1 - \frac{s}{L}\right) p(s,t)\, \mathrm{d}s \tag{2}$$

where $f(L,t)$ is the fraction of the tube that remains at time t, L is the chain contour length, and $p(s,t)$ is the probability density for the random walk to achieve a span s at time t.

We can rewrite eq 2 in the form

$$f(L,t) = \frac{1}{L} \int_0^L P(s,t)\, \mathrm{d}s \tag{3}$$

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0024-9297/86/2219-0927$01.50/0

where $P(s,t) = \int_0^s p(\xi,t)\,d\xi$ is the probability that the span is less than or equal to s at time t.

The complex modulus of an unattached chain is therefore

$$G^*(\omega) = i\omega G_N{}^0 \int_0^\infty f(L,t)e^{-i\omega t}\,dt = \frac{i\omega G_N{}^0}{L}\int_0^L \hat{P}(s,i\omega)\,ds \tag{4}$$

where $G_N{}^0$ is the plateau modulus and $\hat{P}(s,u)$ is the Laplace transform with respect to time of $P(s,t)$. The quantity $P(s,t)$ can also be written[10] as

$$P(s,t) = \sum_{n=1}^{\infty} P(s,n)\int_0^t \psi_n(\tau)\Psi(t-\tau)\,d\tau \tag{5}$$

where $P(s,n)$ is the probability that the span of an n-step random walk is less than or equal to s, $\psi_n(t)$ is the probability density for the sum of n pausing times, and $\Psi(t) = \int_0^t \psi_1(\tau)\,d\tau$. The Laplace transform of eq 5 is

$$\hat{P}(s,u) = \sum_{n=1}^{\infty} P(s,n)\hat{\psi}^n(u)\frac{[1-\hat{\psi}(u)]}{u} \tag{6}$$

The combination of eq 4 and 6 gives

$$G^*(\omega) = \frac{G_N{}^0}{L}\int_0^L ds\,\{[1-\hat{\psi}(i\omega)]\sum_{n=1}^{\infty} P(s,n)\hat{\psi}^n(i\omega)\} \tag{7}$$

The bracketed quantity in eq 7 has been previously evaluated[11] in our calculation of the first passage time probability density for a span. Using the result obtained in the limit where the standard deviation of a single step, σ, is much less than L, we have

$$G^*(\omega) = \frac{G_N{}^0}{L}\hat{\psi}(i\omega)\int_0^L ds\left\{1 - \operatorname{sech}^2\left[\frac{s}{\sigma}\left\{\frac{1-\hat{\psi}(i\omega)}{2}\right\}^{1/2}\right]\right\} \tag{8}$$

Performing the integration, we obtain

$$G^*(\omega) = G_N{}^0\hat{\psi}(i\omega) \times \left\{1 - \frac{\sigma}{L}\left[\frac{1-\hat{\psi}(i\omega)}{2}\right]^{-1/2} \tanh\left(\frac{L}{\sigma}\left[\frac{1-\hat{\psi}(i\omega)}{2}\right]^{1/2}\right)\right\} \tag{9}$$

The Laplace transform of eq 1 has the property $\hat{\psi}(u) \sim 1 - (uT)^\alpha$ as $|u| \to 0$, where T is a parameter with the dimensions of time. Consequently, eq 9 is, to lowest order in $(i\omega)$

$$G^*(\omega) = G_N{}^0\left[\frac{L^2}{6\sigma^2}\right]T^\alpha[i\omega]^\alpha \tag{10}$$

Retracing of a Dangling Chain

In the retracing process, the stress relaxation function is given by

$$\phi(t) = g(L,t) = \int_0^L \left(1 - \frac{y}{L}\right)q(y,t)\,dy \tag{11}$$

where $g(L,t)$ is the fraction of the tube that remains at time t, L is the chain contour length, and $q(y,t)$ is the probability density for the maximum displacement of a one-dimensional nearest-neighbor random walk that starts at the origin where a reflecting barrier is located.

We can rewrite eq 11 in the form

$$g(L,t) = \frac{1}{L}\int_0^L Q(y,t)\,dy \tag{12}$$

where $Q(y,t) = \int_0^y q(\xi,t)\,d\xi$ is the probability that the maximum displacement is less than or equal to y at time t.

The complex modulus of a dangling chain is therefore

$$G^*(\omega) = i\omega G_N{}^0\int_0^\infty g(L,t)e^{-i\omega t}\,dt = \frac{i\omega G_N{}^0}{L}\int_0^L \hat{Q}(y,i\omega)\,dy \tag{13}$$

where $\hat{Q}(y,u)$ is the Laplace transform of $Q(y,t)$. The quantity $\hat{Q}(y,u)$ can be written, by analogy to eq 6, as

$$\hat{Q}(y,u) = \sum_{n=1}^{\infty} Q(y,n)\hat{\psi}^n(u)\frac{[1-\hat{\psi}(u)]}{u} \tag{14}$$

where $Q(y,n)$ is the probability that the maximum displacement of an n-step random walk that starts at the origin where a reflecting barrier is located is less than or equal to y. This quantity is calculated by using[12] the eigenfunction expansion method to be

$$Q(y,n) = \frac{4}{\pi}\sum_{j=0}^{\infty}\frac{(-1)^j}{(2j+1)}\exp\left\{\frac{-\pi^2(2j+1)^2\sigma^2 n}{4y^2}\right\} \tag{15}$$

Combining eq 13, 14, and 15, we can perform the summation over n exactly, yielding

$$G^*(\omega) = G_N{}^0\{1-\hat{\psi}(i\omega)\}\left[\frac{4}{\pi L}\sum_{j=0}^{\infty}\frac{(-1)^j}{(2j+1)}\int_0^L dy \bigg/ \left(1 - \hat{\psi}(i\omega)\exp\left\{\frac{-\pi^2(2j+1)^2\sigma^2}{4y^2}\right\}\right)\right] \tag{16}$$

Using $\hat{\psi}(u) \sim 1 - (uT)^\alpha$ in eq 16, we find, to lowest order in $(i\omega)$ and (σ^2/y^2), that

$$G^*(\omega) = G_N{}^0 l(i\omega T)T^\alpha[i\omega]^\alpha \tag{17}$$

where $l(i\omega T)$ is the square bracketed quantity in eq 16. Since, as $\omega T \to 0$, $l(i\omega T) \to L^2/18\sigma^2$, the complex modulus goes as $\omega T \to 0$ as

$$G^*(\omega) = G_N{}^0[L^2/18\sigma^2]T^\alpha[i\omega]^\alpha \tag{18}$$

Discussion

In both the retracing and reptation processes, we find that $G^*(\omega) \sim (i\omega)^\alpha$, where $0 < \alpha < 1$. We expect the value of α to differ for the two mechanisms (we note that if we introduce a distribution of chain contour lengths into our calculations, the results are changed in only a trival fashion with the factor L^2 becoming $\langle L^2\rangle$ in the $G^*(\omega)$ expressions). It follows that the loss modulus, $G''(\omega)$, is proportional to ω^α as $\omega \to 0$. This corresponds to the relaxation function, $\phi(t)$, varying as $t^{-\alpha}$ as $t \to \infty$. These two relationships[13] have previously been found[6] to compare favorably with published experimental data on the stress relaxation and loss modulus behaviors of cross-linked natural rubber.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation, Division of Materials Research, Polymers Program.

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(13) Gaylord, R. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26* (2), 41 and ref 6 have also obtained these $\phi(t)$, $G''(\omega)$ relations using a different approach in which $\phi(t)$ is given by the probability function $[\int_t^\infty F(t)\,dt]$ where $F(t)$is the first-passage time probability density for a CTRW.

Communications to the Editor

Simple Criterion of the Applicability of the Hoffman–Lauritzen Theory of Crystal Growth: A Comment on Hoffman's Paper (*Macromolecules* 1985, *18*, 772)

Five years ago, in a paper with Kovacs[1] on the kinetics of growth of extended-chain and folded-chain crystals of poly(ethylene oxide) fractions, we showed that one cannot consider the deposition of the first stem of a secondary nucleus as a single stage. There are major objections[2] to such a postulate; the large free energy barrier pertaining to the deposition of a full first stem, well illustrated in Figure 1 of Hoffman's paper,[3] leads to an overestimate of both the kinetic length[4] $(2g/i)^{1/2}$ and the substrate completion rate g.

In his paper,[3] Hoffman makes the suggestion of the "presence in poly(ethylene oxide) of a mode of growth very different from that which occurs in the corresponding hydrocarbons", and in his analysis of the data of Leung, Manley, and Panaras[5a] for polyethylene fractions he reaches conclusions quite different from the above, despite the fact that, for the samples studied, molecular weight and polydispersity of both the poly(ethylene oxide) fractions and the polyethylene fractions were quite similar.

In contradistinction, on the basis of a comprehensive analysis of the data of Leung et al., we maintain the need to postulate a surface nucleation model where the surface nucleus builds up piecemeal by successive addition of parts of stems of molecules. Such models have been described previously.[9,10]

We suggest here a definitive scheme of coordinate experiments and calculations to decide in any circumstance the applicability of the Hoffman–Lauritzen (H–L) theory, and we illustrate this option in a new analysis of the data of Leung et al.[5a] When extended-chain growth rate data are considered, Hoffman[3] bases his conclusion solely on a numerical agreement between predicted and experimental values of G. In contradistinction, we propose to calculate also the initiation rate i, the rate of lateral spreading of a secondary nucleus g, the kinetic length $L_k = (2g/i)^{1/2}$, and the area A_n of the nucleation site for a full stem. Then we recall that not only G but also the kinetic length $L_k = (2g/i)^{1/2}$ may be measured[8] (or at least bounded) by a study of the dependence of the growth rate on the size of the involved facet. Finally we propose to compare the theoretical estimates of G and L_k with the experimental vallues (or bounds) for these quantities and in addition to discuss if both the values of g (see also Simon et al.[11]) and A_n are reasonable or unrealistic. The most innovative part of our proposal is a critical comparison of the experimental value of L_k (or of experimental bounds for this quantity) with its theoretical estimate. The way to measure L_k is fully discussed elsewhere[8] and a way to bound it is given below. Clearly, an efficiently decisive criterion for the validity of the theory is obtained when data pertaining to different chain lengths are available, as shown in our paper with Kovacs.[1]

We apply now our procedure to an analysis of the data of Leung et al.[5a] on a polyethylene fraction (denoted 3100) whose number-average molar mass, 2.9×10^3, corresponds to C-207 and where $M_w/M_n = 1.07$. Our analysis is in fact an extension of that given by Hoffman[3] but includes the calculation and examination of the values obtained for L_k, g, and A_n. The calculation of L_k is made from eq 42.c and 13 of Hoffman's paper

$$iL_p{}^2/4g = C_0ns^2/4[A_0/A]$$

$$L_p = n_sa_0$$

from the expressions for A_0 and A (footnote 11 of the same paper), and from the following figures: $C_0 = 10^4$, $\sigma'_1 = 0$, $\sigma = 76$ erg/cm^2, $l_x = 2.629 \times 10^{-6}$ cm, $\sigma(1 - \gamma) = 10.52$ errg/cm^2, and $T_0 = 86.6$ °C. From the inequality $\psi\gamma W\Delta T > 0$, we obtain for $T_c = 81$ °C

$$L_k = (2g/i)^{1/2} > [2a_0{}^2/C_0\{\exp(-2a_0b_0\sigma'/kT)\} \times \exp(2b\sigma(1-\gamma)l_x/kT)]^{1/2} = 0.55\text{ cm} \quad (1)$$

We conclude, as Hoffman did, that his theory implies that crystallization occurs definitively in regime I. The calculation of i and g is performed from the experimental value[5] for the growth rate at 81 °C ($G = 1.25 \times 10^{-7}$ cm/s) and from Hoffman's estimate of the persistence length L_p:

$$i = G/bL_p = 3 \times 10^4\text{ cm}^{-1}\text{ s}^{-1} \quad (2)$$

$$g = iL_k{}^2/2 > 4.58 \times 10^3\text{ cm/s} \quad (3)$$

The value of A_n area of a nucleation site for a full stem comes from the C_0 value:

$$A_n = a_0l_x/C_0 = 1.2 \times 10^{-17}\text{ cm}^2$$

The experimental bounds for L_k and L_p are obtained from the following consideration. As widely recognized[6] and discussed extensively elsewhere,[8] the growth rate of crystals smaller than both the persistence length and the kinetic length cannot be a constant. But Leung et al.[5] find for crystal size smaller than 1000 nm a *decrease* of the growth rate. We are, thus, forced to conclude that either $L_k \ll 10^{-4}$ cm or $L_p \ll 10^{-4}$ cm or both. Hoffman's analysis performed on the basis of the H–L theory leads to $G_{\text{calcd}} = G_{\text{exptl}}$, $L_p = 10^{-4}$ cm, $L_k = 0.55$ cm, $g > 4.58\ 10^3$ cm/s, and $A_n = 1.2 \times 10^{-17}$ cm^2; then L_p or L_k or both are too large. The value of A_n is much too small and the value of g is far too large to be credible.[7] Let us consider this last point in some detail. According to Hoffman, when crystallization at 81 °C from the 0.001 wt % solution is considered, coverage of the hypothetical persistence length by *attachment* of 2200 molecules would occur in 0.14 μs. But in this time interval, even *in a gas phase* (with the same number of molecules per unit volume) only 82 molecules *hit* the concerned part of the surface of the crystal. This

0024-9297/86/2219-0929$01.50/0