Macromolecules **1985**, *18*, 1157–1162

friction coefficient increases more rapidly with concentration than is expected from the nondraining sphere of the blob for some still unclarified reason, such as the decrease of the free volume.[10] If this is the case, the blob-scaling result, eq 18, may hold valid at still lower concentrations or in some other (less viscous) solvent. An experiment at lower concentrations with a polymer of $M = 2.5 \times 10^7$ failed due to the degradation of the polymer. Measurements in less viscous solvents and higher frequencies will be valuable in elucidating the content of the parameter τ_s. Measurements at higher frequencies and lower concentrations may be valuable also for detecting the onset of entanglement in the semidilute solutions.

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Viscoelasticity of Randomly Cross-Linked Polymer Networks. Relaxation of Dangling Chains[†]

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ABSTRACT: A model based on the diffusion of dangling chains (in the presence of topological constraints) is used to predict the long-time, viscoelastic relaxation of randomly cross-linked polymer networks. In this calculation, the Pearson–Helfand theory for polymer stars is modified to account for the random distribution of chain lengths present in networks. An exact, numerical result is obtained which is found to agree with the previous Curro–Pincus theory at long times. In this limit, the theoretical relaxation modulus can be approximated by a power-law time dependence as in the phenomenological Thirion–Chasset equation. The cross-link density dependence of the exponent is in agreement with experimental data on natural rubber.

Introduction

Polymer networks typically exhibit exceedingly long viscoelastic relaxation times.[1] For example, it can take hundreds of hours for lightly cross-linked natural rubber to equilibrate in a stress relaxation or creep experiment.[2,3] Recently Curro and Pincus[4] developed a theory for this long-time viscoelastic behavior of networks which is in agreement with experimental observations. The Curro–Pincus theory is based on the ideas of de Gennes[5] regarding the reptation of branched polymer molecules in the presence of topological constraints. The purpose of the present investigation is to develop a more quantitative theory by extending the recent results of Pearson and Helfand[6] on star molecules to randomly cross-linked polymer networks.

A polymer network randomly cross-linked from polymer chains of finite molecular weight invariably contains network imperfections consisting of dangling chains ends.[7] Ferry[1] has postulated that the relaxation of these dangling ends, in the presence of entanglements, is responsible for the observed long relaxation times. The Curro–Pincus theory, as well as the present theory, employs a model based on the diffusion of dangling chains in the presence of topological constraints.

The diffusion of a linear polymer chain is strongly suppressed in a melt because of the presence of entanglements which act as topological constraints. The diffusion mechanism in this case is thought to consist of a reptation or "snakelike" motion of the chain.[8] The topological nature of a dangling chain or polymer star molecule, however, prevents the ordinary reptation process from occurring. De Gennes[5] has postulated that such a branched molecule relaxes to its equilibrium state by the branched chain retracing or retracting along its primitive path.

In the recent Pearson–Helfand theory[6] for polymer stars, the path retraction process is modeled by considering the chain end to be undergoing Brownian motion in a suitable

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[†] This paper is dedicated to Dr. Pierre Thirion on the occasion of his retirement.

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potential field. The probability distribution for branch retraction then is the solution of the Smoluchowski equation[9] for the probability of deepest penetration as a function of time. In the present theory, we take this penetration probability from the Pearson–Helfand theory and apply it to a randomly cross-linked polymer network. This is accomplished by performing a suitable averaging over the distribution of dangling-chain lengths.

Theoretical Background

From numerous experiments[1-3] on the long-term stress relaxation and creep of elastomers, it has been found that an excellent representation of the data in the long-time limit is given by the Thirion–Chasset equation[2]

$$E(t) = E_\infty[1 + (t/\tau_E)^{-m}], \qquad (t/\tau_E) \gg 1 \tag{1a}$$

for the tensile stress relaxation modulus $E(t)$ and the analogous expression

$$D(t) \cong 1/E(t), \qquad t \to \infty \tag{1b}$$

for the tensile creep compliance $D(t)$, for $m \ll 1$. E_∞ is the equilibrium tensile modulus and τ_E and m are material parameters. The Thirion–Chasset exponent m is typically found to be a smaller number in the range 0.1–0.3.

The stress relaxation and creep rates are also known to depend strongly on cross-link density.[1-3] Plazek[3] found that relaxation curves could be shifted along the log time axis to form a type of master curve. The shift factor a_x associated with this shifting process has a power-law dependence on the cross-link density ρ_c:

$$a_x = (\rho_c/\rho_c^0)^{-x} \tag{2}$$

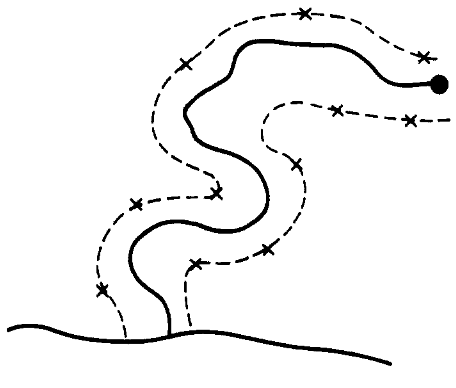
The Plazek exponent x is typically found to be a large number of order ~15.

We will assume that this long-term relaxation process is caused by simple branched chain structures containing single dangling ends. In principle more complicated structures in which the dangling chains themselves are branched can occur. For a randomly cross-linked network, however, Pearson and Graessley[10] have shown that the probability of occurrence of these complicated structures decreases very rapidly above the gel point.

We represent the dangling polymer chains as consisting of N segments with each segment containing N_e monomeric units. N_e can be considered to be the average number of monomer units between entanglements. The process by which a branched chain arm recovers its equilibrium conformation after a perturbation is by contraction along the primitive path. This occurs by the pushing out of unentangled loops[11,12] of greater than average extent, as is shown schematically in Figure 1.

Immediately following a perturbation of the dangling chain from its equilibrium state, as in a stress relaxation experiment, the chain can be considered to be trapped in a distorted, virtual tube (Figure 1a). As the chain end diffuses back along the tube *the first time*, that portion of the constraining tube vanishes since the chain end can reenter the surroundings at random (Figure 1b). De Gennes[5] argued that the time t_N required for the complete renewal of the tube would be inversely proportional to the probability of a random walk of N segments exactly retracing its path. On the basis of an approximate calculation de Gennes showed that this complete renewal time depends exponentially on the chain length N. A calculation performed by Pearson and Helfand[6] led to the result

$$t_N = \tau_0 N^{3/2} \exp(\alpha N) \tag{3}$$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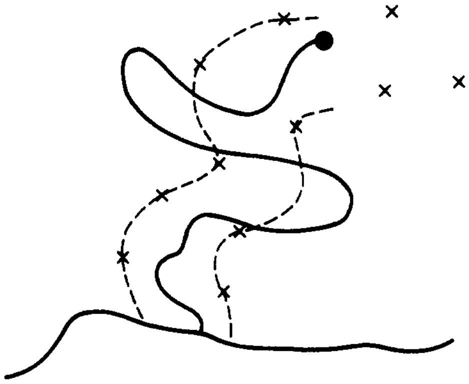
(b)

Figure 1. Schematic diagram of a chain trapped in a tube consisting of topological constraints. a represents the tube immediately following a perturbation of the chain from its equilibrium state. b is the situation after some time in which the chain has partially retracted within the tube. Note that the portion of the tube traversed by the chain end will disappear as a constraint since the chain end can reenter the surroundings at random.

For a lattice model they found α depends only on the coordination number of the lattice, q:[12]

$$\alpha = (1/2) \ln [q^2/4(q-1)] \tag{4}$$

It is expected that the relaxation time τ_0 would roughly correspond to the maximum Rouse relaxation time of a chain containing N_e monomers.

De Gennes also suggested that the *partial renewal time* for the fraction f_N of the original N segments to be retraced has the same form as eq 3 with N replaced by Nf_N. This leads to his conclusion that a dangling chain relaxes with an approximately logarithmic time dependence

$$f_N(t) \cong 1 - (\alpha N)^{-1} \ln (t/\tau_0) \tag{5}$$

This quantity is related to the stress on the network. As in the Doi–Edwards theory,[8] we take the contribution to the relaxation modulus from a particular chain to be proportional to Nf_N, the number of segments still trapped in the tube. Thus, the contribution E_N to the relaxation modulus from a single dangling chain containing exactly N segments can be written as

$$E_N(t) = KNf_N(t) \tag{6}$$

in the long-time limit, where K is a material constant.

A randomly cross-linked network, of course, will in general contain a distribution of chain lengths. Thus, in order to obtain the complete relaxation modulus we need to average over all dangling chain lengths

$$E(t) = E_\infty + (E_0 - E_\infty)\langle Nf_N(t)\rangle/\langle N\rangle \tag{7}$$

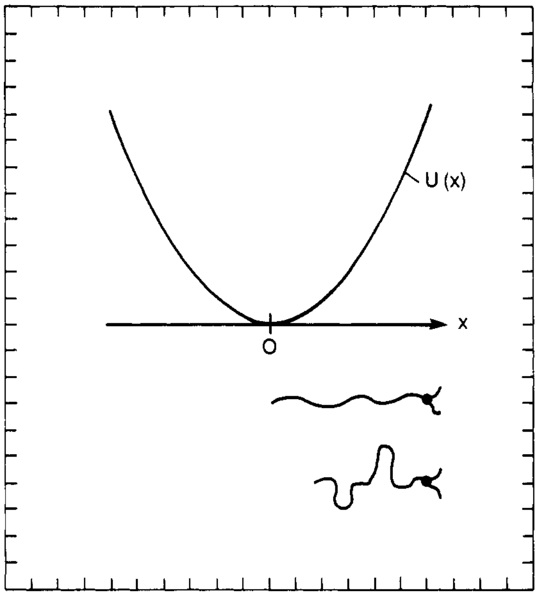

Figure 2. Dangling chain in two positions of escape from its constraining tube. The probability of retracting a distance x along the tube is proportional to $\exp[-U(x)/kT]$.

It is expected that $E_0 - E_\infty$ will be proportional to the volume fraction of dangling ends. $\langle N \rangle$ is the number-average degree of polymerization of dangling ends, and

$$\langle Nf_N \rangle = \int_0^\infty Nf_N(t)P_N \, dN \qquad (8)$$

is a tube renewal function; P_N is the probability of having a dangling end of exactly N segments. For a randomly cross-linked system of low cross-link density, the probability can be written as (see Appendix)

$$P_N = p \exp(-Np) \qquad (9)$$

Here p is the probability of a particular segment being cross-linked

$$p = N_e \rho_c / \rho_m \qquad (10)$$

where ρ_c/ρ_m is the cross-link/monomer density ratio. Note that $1/p$ is the number-average degree of polymerization $\langle N \rangle$.

Curro and Pincus[4] used de Gennes' approximate expression in eq 5 together with eq 6–10 to obtain the relaxation modulus. From this analysis they found that the relaxation modulus obeyed the phenomenological laws of eq 1. Furthermore, the Thirion–Chasset exponent m was predicted to depend on the cross-link density by the following relation:

$$m = N_e \rho_c / \alpha \rho_m \qquad (11)$$

A linear dependence of m on cross-link density is consistent with available experimental data on natural rubber.[13] Curro and Pincus[4] were also able to show that their theory is in approximate agreement with the Plazek phenomenological equation, eq 2, with the Plazek exponent having an order of magnitude

$$x \sim 2/m \qquad (12)$$

Although the Curro–Pincus theory gives results in good agreement with experiment, it is based on the premise in eq 5 that the chain relaxation is a simple logarithmic function of time. We will now address the problem of evaluating the relaxation modulus using the more rigorous theory of Pearson and Helfand.[6]

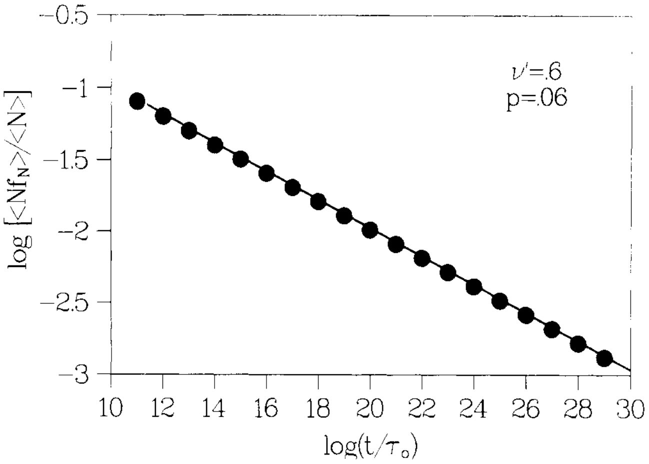

Figure 3. Tube renewal function for $\nu' = 0.6$ and $p = 0.06$. Points result from the numerical integration of eq 15, the curve the approximation in eq 30, and the Thirion–Chasset eq 31. In eq 31 A was chosen to agree with eq 30 at large t/τ_0. Only one curve was drawn for clarity since the two approximations gave essentially identical results.

General Analysis. Pearson and Helfand[6] modeled the relaxation of the arm of a polymer star molecule as a one-dimensional diffusion problem in a suitable potential field. The decrease in entropy associated with the retraction of the arm within its tube can be associated with an increase in a free energy acting as a potential. Pearson and Helfand approximated this potential as a quadratic function as is illustrated schematically in Figure 2. The probability of deepest penetration was calculated from the Smoluchowski equation.[9] For times $t >> \tau_e$, where τ_e is essentially the maximum Rouse relaxation time[1] of the chain

$$\tau_e = \left(\frac{\zeta_0 b^2 N_e^2 \nu^2}{2\nu' kT} \right) N^2 = \tau_0 (\nu'/\pi)^{1/2} N^2 \qquad (13)$$

this probability function can be approximated by a convenient analytical form. In eq 13 ζ_0 is proportional to the monomeric friction factor, b is the length of a monomer, and ν and ν' are material constants. ν is of order unity. ν' can be approximately identified with α in eq 4 and presumably depends on the effective coordination number of the lattice.

For our purposes the relevant quantity of interest is the function $f_N(t)$, the fraction of the tube not visited by the end of the chain having N segments. The de Gennes[5] approximation to this quantity is shown in eq 5. The Pearson–Helfand[6] result from the solution of the Smoluchowski equation accounts more accurately for the distribution of unentangled loops in the contracted chain. It can be written in the form

$$f_N(t) = \int_0^1 \exp[-zN^{-3/2}(t/\tau_0)e^{-\nu' N z^2}] \, dz \qquad (14)$$

where τ_0 is defined by eq 13 and is roughly the maximum Rouse relaxation time for a single subunit of N_e monomers.

In the present investigation, it is necessary to average Nf_N with respect to P_N according to eq 8–10. This leads to a general expression for the tube renewal function

$$\langle Nf_N \rangle = p \int_0^\infty N e^{-Np} \, dN \int_0^1 \exp[-(t/\tau_0) z N^{-3/2} e^{-\nu' N z^2}] \, dz \qquad (15)$$

Equation 15 together with eq 7 determines the time de-

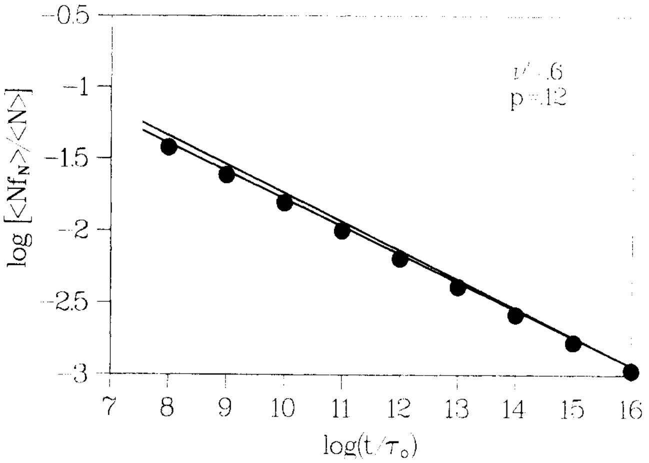

Figure 4. Tube renewal function for $\nu' = 0.6$ and $p = 0.12$. Points result from the numerical integration of eq 15, the lower curve the approximation in eq 30, and the upper curve is the Thirion–Chasset eq 31. In eq 31 A was chosen to agree with eq 30 at large t/τ_0.

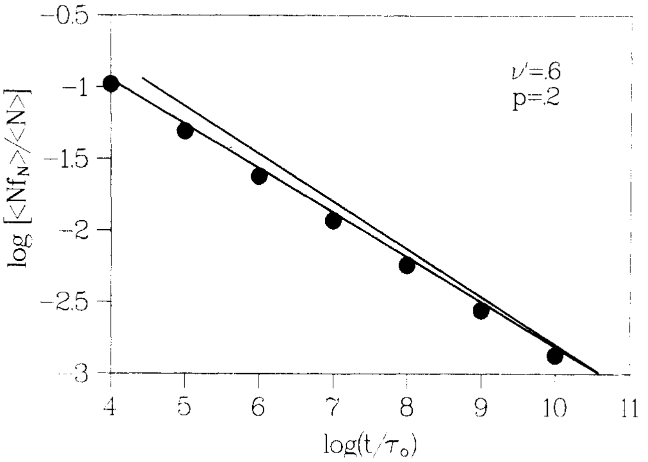

Figure 5. Tube renewal function for $\nu' = 0.6$ and $p = 0.20$. Points result from the numerical integration of eq 15, the lower curve from the approximation in eq 30, and the upper curve is the Thirion–Chasset eq 31. In eq 31 A was chosen to agree with eq 30 at large t/τ_0.

pendence of the relaxation modulus.

The double integral in eq 15 was performed numerically as a function of t/τ_0 for various choices of p and ν' using standard numerical quadrature techniques. These results are shown as the points in Figures 3–5.

Approximate Analytical Expressions. Approximate analytical expressions can be found for the general tube renewal function in eq 15. Pearson and Helfand[6] have shown that the single-chain relaxation function $f_N(t)$ can be approximated for various ranges of time t.

$$f_N(t) = 1 - \xi(t) \qquad \text{for } \tau_e \ll t \ll \tau_m \tag{16a}$$

$$f_N(t) = \frac{E_1(t/\tau_m)}{2\nu' N} \qquad \text{for } t \gg \tau_m \tag{16b}$$

τ_e is the Rouse relaxation time of the entire chain defined in eq 13, whereas τ_m can be considered to be the average retraction time or tube renewal time for the chain defined as

$$\tau_m = \tau_0 N^{3/2} \exp(\nu' N) \tag{17}$$

Note that eq 17 is identical with eq 3 if we identify ν' with α. $\xi(t)$ is given by the transcendental expression

$$t = \tau_0 N^{3/2} \xi^{-1} \exp(\nu' N \xi^2) \tag{18}$$

and $E_1(t/\tau_m)$ is the exponential integral

$$E_1(t/\tau_m) = \int_1^\infty \exp(-xt/\tau_m) \, d \ln x \tag{19}$$

Equations 16 suggest that the average tube renewal function in eq 15 can be divided into two parts

$$\langle N f_N \rangle = g_1 + g_2 \tag{20}$$

with

$$g_1 = (p/2\nu') \int_0^{n^*} \exp(-Np) E_1(t/\tau_m) \, dN \tag{21a}$$

$$g_2 = p \int_{n^*}^\infty N \exp(-Np)[1 - \xi(t,N)] \, dN \tag{21b}$$

The significance of $n^*(t)$ is that most dangling ends shorter than n^* have completely disentangled back to the branch point at time t. The few that have not give rise to g_1. On the other hand, most branches longer than $n^*(t)$ have not completely disentangled, and g_2 arises from the fraction of these chains which remains in the original tube. n^* can be obtained by simply setting $t = \tau_m$ in eq 8, which leads to

$$t = \tau_0 n^{*3/2} \exp(\nu' n^*) \tag{22}$$

From eq 17 and 22 it can be seen that $t < \tau_m$ corresponds to $N > n^*$ and $t > \tau_m$ implies $N < n^*$. Asymptotic expansions can be found separately for each of the integrals in eq 21 for large t. The solution of the transcendental equation for n^* in eq 22 can be approximated to second order by

$$n^* \cong \frac{1}{\nu'} \ln (t/\tau_0) - \frac{3}{2\nu'} \ln \frac{1}{\nu'}[\ln (t/\tau_0)] \tag{23}$$

for $t/\tau_0 \gg 1$.

The asymptotic expansion for g_1 can be found by first interchanging the order of integration in eq 21a.

$$g_1 = \frac{p}{2\nu'} \int_1^\infty \frac{du}{u} \int_0^{n^*} e^{-Np} \exp\left[-u\left(\frac{n^*}{N}\right)^{3/2} e^{\nu'(n^*-N)}\right] dN \tag{24a}$$

We note that the integrand of the inner integral in eq 24a is a strongly peaked function of N at $N = n^*$. Taking advantage of this fact, we expand this integrand to first order in a Taylor series about $N = n^*$. The inner integral can then be evaluated, which leads to the approximation for small p

$$g_1 \sim (1/2p) e^{-n^* p} E_2(1) \, (p/\nu')^2 \tag{24b}$$

where E_2 is a second-order exponential integral.

Turning our attention to g_2, we note that the integrand in eq 21b is a rapidly decreasing function of N with a maximum at $N = n^*$, the lower limit of integration. In the range of N near n^*, eq 18 and 22 can be used to show

$$\xi \cong (n^*/N)^{1/2} \tag{25}$$

so that eq 21b now becomes

$$g_2 = p \int_{n^*}^\infty \exp(-Np) N [1 - (n^*/N)^{1/2}] \, dN \tag{26}$$

Equation 26 can be expressed in terms of the incomplete Γ function[15] as

$$g_2 = (1/p)[\exp(-n^* p)(1 + n^* p) - (n^* p)^{1/2} \Gamma(3/2, n^* p)] \tag{27}$$

Using the continued fraction representation for the incomplete Γ function leads to the asymptotic expansion

$$g_2 \sim B(n^* p) \exp(-n^* p)/2p \tag{28}$$

where the coefficient B is defined as

$$B(n^*p) = [1 + 3/2n^*p - 1/2(n^*p)^2]/[1 + 1/n^*p - 1/4(n^*p)^2] \quad (29)$$

large n^*p $(=n^*/\langle N\rangle)$ means that, at the time t, most of the dangling ends have completely relaxed.

Equations 24b and 28 can now be combined to give an asymptotic expansion for the tube renewal function

$$\langle Nf_N\rangle \sim (1/2p)[B(n^*p) + (p/\nu')^2E_2(1)]e^{-n^*p} \quad (30)$$

Note that the contribution from g_1 is proportional to p^2 and hence is small compared with g_2. Equations 23 and 30 can be used to approximate the dangling-chain relaxation for $t/\tau_0 \gg 1$.

A further approximation can be developed by using eq 23 and 30 to give

$$\langle Nf_N\rangle \sim A(p,\nu')(t/\tau_0)^{-p/\nu'} \quad (31a)$$

where the coefficient A is given by

$$A = (1/2p)[B(n^*p) + (p/\nu')^2E_2(1)](n^*)^{3p/2\nu'} \quad (31b)$$

It can be shown that A is a weak function of time compared to the remaining power-law time dependence in eq 31. We can, therefore, approximately consider A to be a constant. The value of A can be chosen so that the approximation in eq 31 agrees with eq 24 and 30 at some arbitrary time.

Discussion

In the present investigation we have related the relaxation modulus of a network to a tube renewal function $\langle Nf_N\rangle$. The exact expression for $\langle Nf_N\rangle$ is shown in eq 15 with two approximations given in eq 30 and 31. The approximation in eq 31 is identical with the result of Curro and Pincus[4] and agrees with the phenomenological equation of Thirion and Chasset in eq 1. From eq 7 and 31 we can write

$$E = E_\infty[1 + (t/\tau_E)^{-p/\nu'}] \quad (32)$$

in which use was made of the rubber elasticity result[16] for the equilibrium modulus and

$$\tau_E = \tau_0[(E_0 - E_\infty)Ap/E_\infty]^{\nu'/p} \quad (33)$$

By comparing eq 32 with eq 1 we see that the Thirion–Chasset exponent m is given by

$$m = p/\nu' = N_e\rho_c/\rho_m\nu' \quad (34)$$

Note that this is identical with the Curro–Pincus result[4] if we identify ν' with α in eq 34.

Equation 34 predicts a linear dependence of the Thirion–Chasset exponent with cross-link density. This prediction is consistent[4] with the data on natural rubber obtained by Dickie and Ferry.[13]

In Figures 3–5 we compare the two approximations in eq 30 and 31 with the numerical integration of the general formula, eq 15. The comparisons are shown for typical values of p and ν' fixed at 0.6. This value of ν' is predicted on the basis of eq 4 for a coordination number of 12, making the identification of ν' with α. It can be seen from these figures that the tube renewal function relaxes to zero very slowly. The two approximations give good agreement with the numerical calculations at large values of t/τ_0.

The cross-link density dependence of the viscoelastic relaxation at long times can be found by examining the tube renewal function in eq 15. According to Plazek,[3] the viscoelastic curves should shift along the log t axis with a shift factor a_x given by eq 2. Superposition of the theoretical relaxation curves to obtain a master curve is shown in Figure 6. These curves were obtained from eq 7 and 15 for $\nu' = 0.6$ and various values of p, which is proportional to cross-link density. It can be seen that superposition of these various curves is obtained only at large times. As pointed out by Curro and Pincus,[4] exact superposition would not be expected since the Thirion–Chasset exponent in eq 1 is predicted to depend on cross-link density. It should be mentioned that the relaxation curves for polymer star molecules were also found not to be superposable except at long times.[6]

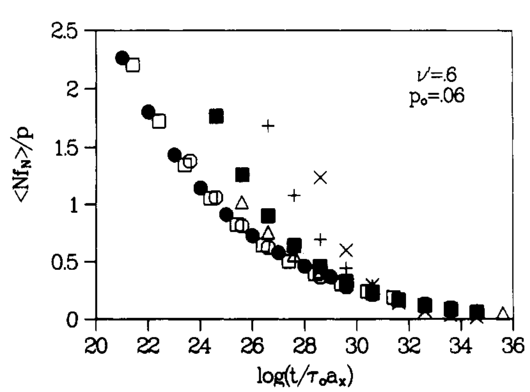

Figure 6. An attempt to obtain a master curve from the numerical solution of eq 15 for $\nu' = 0.6$ for various values of p: (filled circles) $p = 0.06$, (open squares) $p = 0.065$, (open circles) $p = 0.07$, (open triangles) $p = 0.08$, (filled squares) $p = 0.09$, (pluses) $p = 0.12$, and (x's) $p = 0.2$. The curves are shifted to the reference state $p_0 = 0.06$. The ordinate can be shown to be proportional to log (E/E_∞).

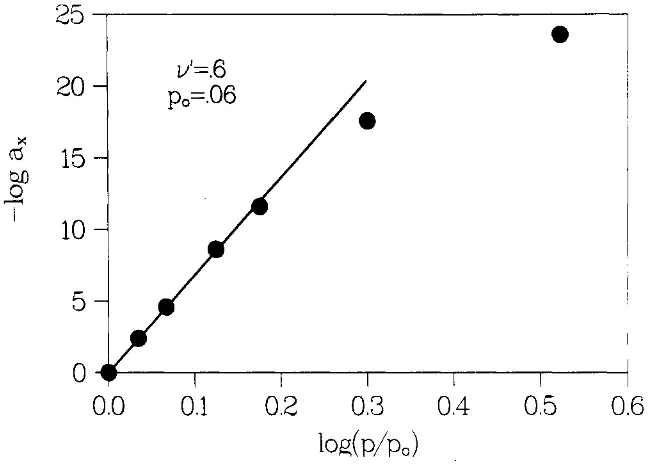

Figure 7. Shift factors obtained for the master curve in Figure 6 for $\nu' = 0.6$ and $p_0 = 0.6$. The straight line shown through the points having small log (p/p_0) has a slope of 68.

The shift factors used in Figure 6 were obtained by visual examination of the individual curves at various values of p ranging from 0.06 to 0.2. These estimated shift factors are plotted in Figure 7 in a log–log plot. A least-squares straight line for p near p_0 gives a Plazek[3] exponent x of 68 for ν' chosen to be 0.6. It can be seen from this figure, however, that a straight line does not fit the results over the entire range of log (p/p_0). On the basis of the crude approximation, $x \sim 2/m$, given by Curro and Pincus[4] we would expect a smaller exponent of $x \sim 20$.

The present theory is based on the hypothesis that long-term viscoelastic processes in polymer networks are controlled by Brownian motion of dangling chain ends in the presence of entanglements which act as topological constraints. The calculations presented here give results which are consistent with phenomenological observations on polymer networks. Further experiments on well-characterized samples are needed to test the generality of the theoretical predictions. In particular, relaxation experiments on networks in which the dangling-end distribution is known would be of significant interest.

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Appendix: Distribution of Chain Lengths

For a randomly cross-linked system, the probability Q_n of having a dangling chain end of exactly n monomers is given by[4]

$$Q_n = q(1-q)^{n-1} \tag{1A}$$

For a lightly cross-linked system, q is simply the ratio of the cross-link density to the monomer density. In eq 8 we require the probability P_N of having a chain of $N = n/N_e$ segments. From eq 1A we can write

$$P_N = Cq(1-q)^{N_eN-1} \tag{2A}$$

where C is a normalization constant to ensure that

$$\sum_{N=1}^{\infty} P_N = 1 \tag{3A}$$

From eq 3A we find that

$$C = [1-(1-q)^{N_e}]/q(1-q)^{N_e-1} \tag{4A}$$

We now write

$$(1-q)^{N_e} = \exp[N_e \ln(1-q)] \cong \exp(-N_eq) \tag{5A}$$

where we have used the fact that $q << 1$. Substituting eq 5A into eq 4A and 2A leads to the desired result for large N

$$P_N \cong (e^p - 1)\exp(-Np) \tag{6A}$$

with p defined as

$$p = N_eq = N_e\rho_c/\rho_m \tag{7A}$$

For small p one can substitute integrals for summations on N and write

$$P_N \cong p\exp(-Np) \tag{8A}$$

References and Notes

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Self-Diffusion of Polystyrene Chains in Networks

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ABSTRACT: A holographic grating technique was applied to measuring self-diffusion coefficients D of polystyrene (PS) chains in PS networks. Friedel–Crafts cross-linking with *p*-dichloroxylylene was performed in concentrated and dilute solutions, the latter resulting in microgels of self-cross-linked macromolecules. The average number P_c of monomer units between cross-links was varied from 16 to 400. Mixtures of photolabeled linear PS and small particles of dry cross-linked PS were annealed in order to obtain dilute solutions of chains in network systems. The D values of PS chains measured in cross-linked PS at 177, 185, and 194 °C are found to be reduced by factors less than 4 relative to those in the un-cross-linked PS. The dependence of D upon the degree of polymerization P_n of the labeled PS could be described by a power law, $D \sim P_n^{-\alpha}$, where α depends somewhat upon the network preparation conditions. $\alpha = 2.07$ was found at 194 °C for $177 \leq P_n \leq 990$ in a microgel system having a network chain length P_c of 33.

Introduction

The reptation model of polymer chain motion[1] has been generally supported by self-diffusion[2-7] and dynamic mechanical[8] experiments. Inelastic neutron scattering data could be analyzed in terms of the Rouse model.[9] However, due to the limited space and time ranges accessible to this method, it is difficult to obtain sensible information upon slow whole chain motion. Numerical simulations of many-chain model systems[10] leave no doubt about reptation of a single chain in a "frozen" environment, but no reptation was found if all chains are free to move. Our current work on polystyrene (PS) chain diffusion as a function of the chain length of the surrounding matrix indicates that "tube renewal" effects are important even for chain lengths much longer than that of a relatively long diffusing chain. In order to clarify the tube concept, experiments where "fixed obstacles" are successively introduced by cross-linking should certainly be helpful. In particular, one can vary the number P_c of monomer units between cross-links and can thus test whether the number $P_e \sim 300$ of monomers between entanglements is related with the tube diameter in un-cross-linked entangled melts.