Dynamics of Reversible Networks

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ABSTRACT: We present a model for dynamics of entangled networks made up of linear chains with many temporary cross-links. At times shorter than the lifetime of a cross-link such networks behave as elastic rubbers (gels). On longer time scales the successive breaking of only a few cross-links allows the chain to diffuse along its confining tube. The motion of a chain in this hindered reptation model is controlled by the concentration and lifetime of tie points. We calculate the self-diffusion coefficient and discuss the stress relaxation in terms of molecular parameters, including the chain length, the number of cross-linking groups per chain, and the lifetime and probability of formation of cross-links. We find good agreement with recent experiments by Stadler et al. on model thermoplastic elastomers.

1. Introduction

There is an important class of polymeric systems in which reversible cross-links are present.[1-3] Typical examples are biological macromolecules, with associations induced by hydrogen bonding, ion complexation, or crystallization. Another widely studied class is thermoplastic elastomers, where synthetic polymers are made with specific associating groups attached to obtain rubberlike systems which are moldable at elevated temperatures.

In this work we consider dynamics in temporary networks which have tie points with relatively weak binding energies, so that junctions break and form frequently on the time scale of experiments. At thermal equilibrium, a network with such truly reversible cross-links behaves like a viscoelastic liquid. The central problem is to relate the microscopic lifetime of a junction and the macroscopic stress relaxation time.

Indeed, the most salient feature of such reversible networks is their enhanced viscoelastic behavior compared with that of polymers which do not have associating groups. This enhancement shows up in a much longer relaxation time (slower diffusion) as well as an increase in modulus level in the rubbery plateau. For unentangled systems, the increase in the relaxation time can be described by a modified Rouse model, with the mobility controlled by the breaking time of a junction.[4-6] However, the more common case is the one in which entanglements are present and considerably hinder dynamics. This feature has been recognized by Gonzalez, who proposed to described diffusion[7] and stress relaxation[8] by a modified reptation model. Unfortunately, the Gonzalez model is based on a very restrictive assumption—the chain can only make a reptation step when it is simultaneously detached from all junctions. As a consequence, the relaxation time has an exponential dependence on the average number of tie points per chain. This model thus predicts an extremely fast crossover from a viscoelastic liquid to an essentially permanent network as tie points are added to the chain. Furthermore, the relaxation time of the reversible gel does not explicitly depend on the junction lifetime,[8,9] but rather there is only an implicit dependence through the probability of a sticker being free. Hence, there is no smooth crossover to the case of unentangled chains. This suggests the existence of a faster relaxation mechanism, which we investigate in the present work, culminating in a new model of dynamics of reversible networks.

In section 2 we show how, in a reversible gel, an entangled chain can move by coherent breaking of only a few cross-links. We calculate the self-diffusion coefficient which turns out to be much smaller than that obtained from the modified Rouse model[6] but significantly larger than predicted by Gonzalez. We discuss the time-dependent stress relaxation modulus in section 3 and compare our predictions with experiments in section 4.

2. Sticky Reptation

Consider a concentrated solution or melt of linear flexible chains with S specific units attached to each chain. These units, called stickers, can associate to form reversible cross-links. We assume that the stickers are at fixed positions along the chains, which is the typical situation for physical gels (e.g., ionomers and some biological macromolecules). We consider monodisperse chains of N monomers with end-to-end distance $R = bN^{1/2}$, b being the statistical segment (monomer) length. The average number of monomers along the chain between stickers is

$$N_s = N/(S+1)$$

A given sticker can exist in one of two states: either it is free (an open sticker) or it is associated and forms a cross-link with other stickers (a closed sticker). The simplest description on a microscopic level requires two parameters: the average fraction of stickers which are closed p and the average lifetime τ of a sticker in the associated state.

Furthermore, throughout this paper we only consider systems in thermal equilibrium with truly reversible cross-links. We assume that a free sticker can find many sites to attach to besides the one it was most recently associated with, and the association kinetics fulfill the detailed balance law for open and closed states. This implies, for instance, that the average lifetime of a free sticker $\tau_1 = \tau(1-p)/p$. In some cases these fundamental parameters p and τ can be directly measured by spectroscopy (e.g., NMR, IR) combined with a jump in temperature or pressure. At equilibrium they are related to reaction rates for association and dissociation. A particularly simple

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situation occurs when only two free stickers (A) can form a tie point (X).

$$A + A \underset{k_2}{\overset{k_1}{\rightleftarrows}} X$$

In this case, the lifetime of a cross-link is $\tau = 1/k_2$ and the fraction of free stickers is $1 - p = k_2/(k_2 + 2k_1c_A)$, where c_A denotes the concentration of free stickers.

Polybutadiene chains with attached urazole groups (which can form binary hydrogen-bonded cross-links) studied by Stadler and de Lucca Freitas[10-14] presumably correspond to this situation. For ionomers the situation can be more complex as ionic groups associate into larger clusters of various sizes and shapes.[15] The parameters p and τ are then more difficult to determine in practice. It is possible that a distribution of microscopic junction lifetimes may be needed in this case.

The motion of chain molecules, in general, is controlled by their conformation and topological constraints. It is important to realize that the formation of temporary cross-links is due to attraction between specific groups on the chains and may, therefore, lead to macroscopic phase separation or to formation of aggregates or mesophases.[16-19] Far from the demixing transition, however, the modification of chain conformation due to these attraction effects can presumably be neglected. We assume in what follows that the chain conformation and topological state are not significantly changed by the presence of the weakly binding stickers.

On time scales shorter than the average lifetime of a sticker in the associated state τ, the reversible gel is indistinguishable from a permanent network. However, for times longer than τ the structure of this network changes as stickers break away from one tie point (on time scale τ) and reassociate at another tie point (on time scale τ_1). Thus, we argue that, contrary to the permanent network, chains can diffuse in the reversible network and stress can relax.

In analogy with ordinary polymer liquids, we model the effect of topological constraints due to surrounding chains by a confining tube.[20,21] Chain motion transverse to the tube axis is restricted to a length scale a, called the tube diameter. The number of monomers in an entanglement strand, N_e, is determined from random walk statistics ($a \simeq bN_e^{1/2}$). The effective tube diameter may be decreased by the presence of the temporary cross-links. Here we only consider the case where $N_e < N_s < N$, so the presence of the stickers will not greatly affect N_e (the stickers will, however, affect the modulus level on some time scales, as discussed in section 3).

In concentrated solutions of unmodified linear polymers, the reptative motion of the chain is due to diffusion of unentangled loops of stored length along the contour of the tube.[22] When reversible cross-links are present, this diffusion is slowed down but still progresses. The motion of a tie point between two chains is restricted to the length scale a, since its motion is effectively constrained to the common volume of the tubes of both chains. This confinement is particular to entangled networks and is much stronger than the confinement in phantom networks which neglect entanglements,[23] where a cross-link can move distances of order of the distance between cross-links ($bN_s^{1/2}$).

Figure 1 illustrates an elementary step of chain diffusion in a reversible gel. A closed sticker belonging to cross-link i between chains P and P_1 can only move distances of order of the tube diameter a. Hence, cross-link i forbids diffusion of unentangled loops stored in the strand of chain

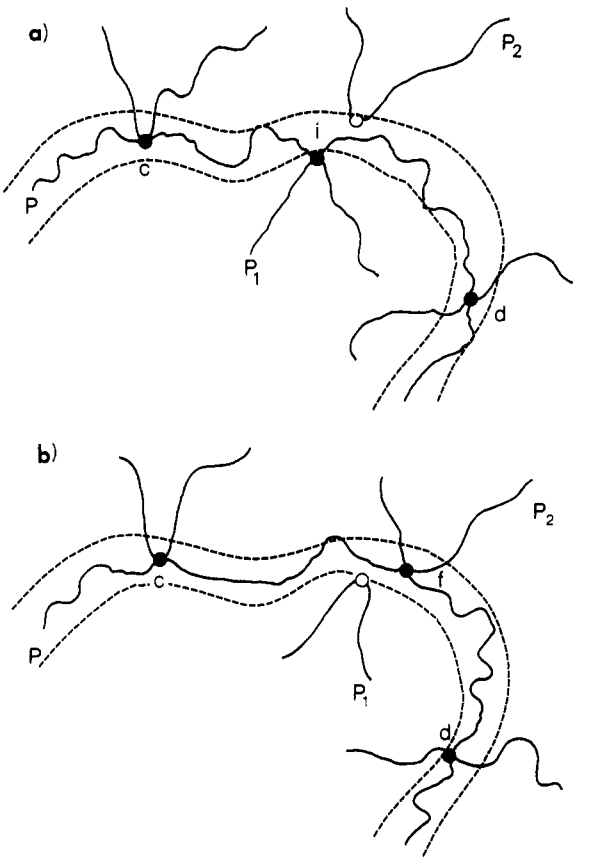

Figure 1. Schematic representation of an elementary step of chain diffusion. (a) Initial situation: the chain P has a cross-link i with chain P_1. (b) Final situation: the sticker forms a new cross-link f with another chain P_2. During this exchange the center of mass of the section cd of chain P is randomly displaced. For clarity, other chains and stickers are not shown. They effectively confine the chain P to a tube indicated by the dashed lines.

P between closed stickers c and d. Sections of chain P between closed stickers (i.e., ci and id) still undergo Rouse-like motions with nearly fixed ends, so their centers of mass fluctuate around their average positions. When cross-link i opens, the free sticker is allowed to move. The equilibration time of the strand cd is simply the Rouse time of a strand of $2N_s$ monomers. For the moment, we will assume that this equilibration time is shorter than the lifetime of the open sticker [$\tau_R(2N_s) < \tau_1$] and that the stickers c and d remain closed (both of these assumptions will later be released). The entire strand cd undergoes Rouse-like motions until one of two events occurs. The sticker either recombines with chain P_1 at cross-link i (in which case no net displacement occurs)[24] or associates with a different chain P_2 and forms cross-link f (see Figure 1b). During this elementary step from cross-link i to cross-link f, the centers of mass of the segments of chain P displace to new average positions [assuming that the stickers remain stuck on the time scale required for the strands to equilibrate, i.e., $\tau > \tau_R(N_s)$]. This corresponds to a motion of the center of mass of chain P along its tube. A sequence of such random elementary steps results in a reptation-like diffusion of the chain P.

When cross-link i breaks, the strand between cross-links c and d undergoes Rouse-like motion. The mean-square curvilinear displacement of the free sticker along the tube during time t is[20]

$$l^2(t) \simeq b^2N_e[t/\tau_e]^{1/2} \qquad t < \tau_R(2N_s) \tag{1}$$

for time t smaller than the Rouse time of the strand

$$\tau_R(2N_s) \cong \tau_e(2N_s/N_e)^2 \quad (2)$$

Here τ_e is the Rouse time of an entanglement strand. For times longer than the Rouse time of the strand cd, the displacement is constrained by the cross-links c and d, and the mean-square curvilinear displacement of the free sticker is

$$l^2(t) \cong \langle l^2 \rangle \cong b^2(2N_s) \qquad t > \tau_R(2N_s) \quad (3)$$

which is of the order of the mean-square end-to-end distance of the free strand[20] (of $2N_s$ monomers). On average, after time τ_1, the sticker closes to form a new cross-link f such that the curvilinear displacement of the sticker is $l(\tau_1)$. If the cross-links c, d, and f do not open during the equilibration time $\tau_R(N_s)$, i.e., if $\tau > \tau_R(N_s)$, the curvilinear displacement of the center of mass of the section cd is $l(\tau_1)/2$. The center of mass of the chain moves by $\Delta_1 \cong l(\tau_1)/(S+1)$ along the tube, since only a fraction $2/(S+1)$ of the chain is between cross-links c and d. Hence, a random sequence of such elementary steps is the proposed mechanism of chain diffusion.

Of course, a more general situation must be considered when during some period of time several neighboring stickers are open. We call a succession of k open stickers a k strand. A k strand can be created by either a sticker separating two smaller strands opening (with the two smaller strands having a combined total of $k-1$ free stickers) or a sticker on a larger strand closing to make the k strand. This section of $(k+1)N_s$ monomers undergoes Rouse-like motion inside its tube until either one of the k stickers closes or one of the two closed stickers at the ends of the strand opens. We need to discriminate between these two cases because displacement of the center of mass of the chain along the tube only locks in through the action of a sticker closing.

Thus, a k step ends when one of the stickers of a k strand closes. The average duration of this k step is $\tau_k = \tau_1/k$. The mean-square curvilinear displacement along the tube of a typical sticker in the k strand during the k step is

$$l_k^2 \cong \begin{cases} b^2(k+1)N_s & \tau_k > \tau_R((k+1)N_s) \\ b^2N_e[\tau_k/\tau_e]^{1/2} & \tau_k < \tau_R((k+1)N_s) \end{cases} \quad (4)$$

The two different cases in eq 4 arise because the k strand only completely equilibrates if its Rouse time is shorter than the duration of the k step. In general, for a given sample, there will be a maximum value of $k = k_{max}$ for which this criterion holds.

$$\frac{\tau_1}{k_{max}} \cong (k_{max}+1)^2\left(\frac{N_s}{N_e}\right)^2\tau_e \quad (5)$$

We can now write eq 4 in terms of k_{max}.

$$l_k^2 \cong \begin{cases} b^2(k+1)N_s & k < k_{max} \\ b^2(k_{max}+1)N_s\left(\frac{k_{max}}{k}\right)^{1/2} & k > k_{max} \end{cases} \quad (6)$$

Note that the conditions $k = k_{max}$ and $\tau_k = \tau_R((k+1)N_s)$ are identical. The root-mean-square curvilinear displacement of the center of mass of the chain along the tube after a k step is

$$\Delta_k \cong \begin{cases} \frac{1}{2}\left(\frac{k+1}{S+1}\right)l_k & k < k_{max} \\ \frac{1}{2}\left(\frac{k_{max}+1}{S+1}\right)l_k & k > k_{max} \end{cases} \quad (7)$$

since, for $k < k_{max}$, the fraction of the chain participating in the k step is $(k+1)/(S+1)$ and for $k > k_{max}$ only k_{max} stickers are displaced coherently before another sticker closes.

The frequency of the elementary k step, ν_k, is the ratio of the probability p_k to find a sequence of exactly k open stickers

$$p_k = (S-k-1)p^2(1-p)^k \quad (8)$$

and the duration of this k step $\tau_k = \tau_1/k$ (the average time before one of the k open stickers closes):

$$\nu_k = p_k/\tau_k = (S-k-1)kp^3(1-p)^{k-1}/\tau \quad (9)$$

During a long time span T there will be, on average, $\nu_k T$ of these k steps per chain. Each k step randomly displaces the center of mass of the chain a distance of order Δ_k along the contour of the tube. Therefore, the total mean-square curvilinear displacement of the center of mass of the chain along the tube during time span T is

$$\Delta^2 = \sum_{k=1}^{S-2}\nu_k\Delta_k^2T + \sum_{k=1}^{S-1}\nu_k^{end}(\Delta_k^{end})^2T + \nu_S\Delta_S^2T \quad (10)$$

where we have summed the contributions of all the possible k steps in a chain of S stickers (the first term) and added two terms. The second term describes the displacement due to open stickers at the ends of the chain (discussed below). The contribution Δ_S^2 comes from completely free chains ($k = S$). For $S < k_{max}$ [or, equivalently $\tau_S > \tau_R(N)$]

$$\Delta_S^2 \cong l_S^2 \cong b^2N[\tau_S/\tau_R(N)] \quad (11)$$

and for $S > k_{max}$ [$\tau_S < \tau_R(N)$]

$$\Delta_S^2 \cong \left(\frac{k_{max}+1}{S+1}\right)^2 l_S^2 \cong b^2N\left(\frac{k_{max}+1}{S+1}\right)^2[\tau_S/\tau_R(N)]^{1/2} \quad (12)$$

The frequency of steps involving such completely free chains is

$$\nu_S = (1-p)^S/\tau_S \quad (13)$$

In eq 10 we also separated the contribution coming from steps involving chain ends. The frequency of occurrence of a strand with k open stickers at an end of the chain is

$$\nu_k^{end} = 2p(1-p)^k/\tau_k \quad (14)$$

In a k step involving the chain ends, the displacement of the center of mass of the chain depends on which of the stickers closes to end the k step. After averaging over all possible situations, we get

$$\Delta_k^{end} = \frac{3}{2}\Delta_k$$

where Δ_k is given by eq 7.

The curvilinear diffusion coefficient of the chain along its tube is

$$D_c \cong \Delta^2/T \quad (15)$$

Aside from the slower motion along the tube, diffusion of chains in a reversible gel is completely analogous to ordinary reptation of linear polymers. The three-dimensional self-diffusion coefficient is

$$D_{self} \cong Nb^2/T_d \quad (16)$$

where $T_d = (Na/N_e)^2/D_c$ is the time required for the chain to escape from its tube by curvilinear diffusion.[20,22]

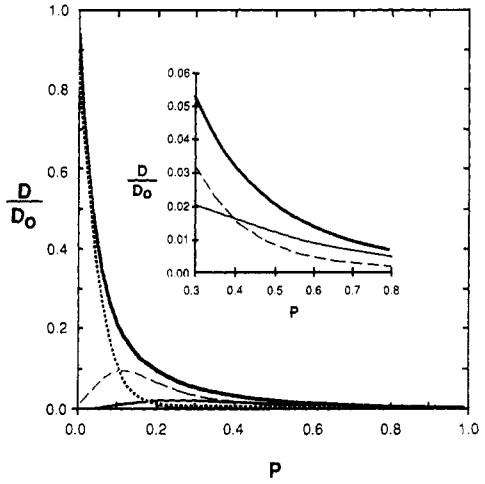

Figure 2. Self-diffusion coefficient D_{self} (thick line) as a function of the fraction of closed stickers p for typical molecular parameters: number of stickers per chain $S = 20$, number of entanglements per chain $N/N_e = 100$, and the lifetime of a cross-link $\tau = 16000\tau_e$. Various contributions to D_{self} are also illustrated: $\sum D_k$ (thin line), $\sum D_k^{end}$ (dashed line), and D_S (dotted line). All are normalized by D_0, the self-diffusion coefficient of the chain without stickers.

Therefore

$$D_{self} \cong \frac{N_e}{N}\frac{\Delta^2}{T} \cong \sum_{k=1}^{S-2} D_k + \sum_{k=1}^{S-1} D_k^{end} + D_S \qquad (17)$$

where

$$D_k = \nu_k \Delta_k^2 (N_e/N)$$

$$= \frac{a^2}{4\tau} p^3 (1-p)^{k-1} k \frac{(S-k-1)}{(S+1)^3} \times \begin{cases} (k+1)^3 & k < k_{max} \\ (k_{max}+1)^3 \left(\frac{k_{max}}{k}\right)^{1/2} & k > k_{max} \end{cases} \qquad (18)$$

The k steps involving end stickers contribute to the diffusion constant by

$$D_k^{end} = \frac{9D_k}{2p(S-k-1)} \qquad (19)$$

The contribution to the diffusion coefficient from the S steps (with all stickers on the chain open) is

$$D_S = \left(\frac{a^2}{\tau_e}\right)\left(\frac{N_e}{N}\right)^2 \begin{cases} (1-p)^S & \tau_S > \tau_R(N) \\ (1-p)^S \left(\frac{k_{max}+1}{S+1}\right)\left(\frac{S}{k_{max}}\right)^{1/2} & \tau_S < \tau_R(N) \end{cases} \qquad (20)$$

The relative contributions of the three terms in eq 17 to the self-diffusion coefficient are plotted as a function of p in Figure 2. Our theory only treats thermal equilibrium, where a free sticker can find other sites to associate with inside the volume it samples by Rouse-like fluctuations (roughly $a^3[2N_s/N_e]^{1/2}$).[20] In the specific case of only pairwise associations between stickers, this requires $p \lesssim 1 - (N_s/2)^{1/2}/N_e$, which means that $p \lesssim 0.8$ for the example considered in Figure 2. At small p the D_S term dominates, and at large p the $\sum D_k$ terms dominate. At intermediate p (in this example, $p \cong 0.2$) the $\sum D_k^{end}$ terms contribute the most to the diffusion. Therefore, to be completely general, we must include all three terms in eq 17 to describe self-diffusion in reversible gels. We will now consider some interesting limits of this general result.

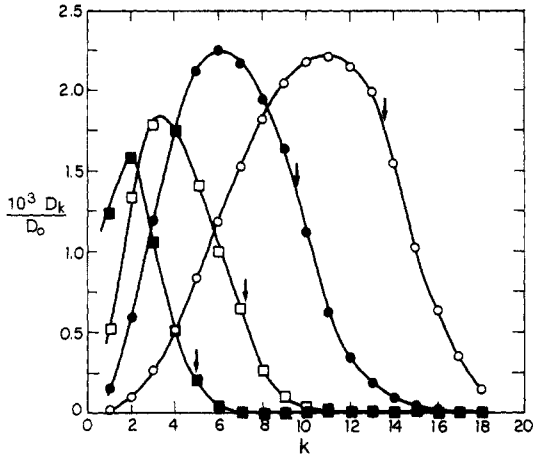

Figure 3. Contribution to the diffusion coefficient D_k from different k steps for several fractions of closed stickers: $p = 0.2$, open circles, $p = 0.4$, solid circles, $p = 0.6$ open squares, $p = 0.8$ solid squares. Molecular parameters are the same as in Figure 2. Arrows indicate values of k_{max}.

In the limit $p \to 0$, all terms for D_{self} in eq 17 vanish except for the D_s term (see Figure 2). This term [for $\tau_s > \tau_R(N)$] is exactly the Gonzalez result[7] and assures the proper crossover to the standard reptation result as $p \to 0$. However, reversible gels are generally truly connected ($pS \gg 1$), and the probability of all stickers on a given chain being simultaneously open is exponentially small $(1-p)^S$. The contribution of the D_s term to the self-diffusion coefficient is, therefore, usually negligible.

Steps with many open stickers (large k) are not very probable, but during these large k steps the center of mass of the chain is displaced by a large curvilinear distance. On the other hand, steps with small k are more frequent, but each small k step results in only a small displacement of the chain. Due to this trade-off, there is an optimum value of k (which depends on the fraction of free stickers) that contributes the most to the diffusion process. Figure 3 shows the contribution to the self-diffusion coefficient from different k steps, D_k, for several values of p. Clearly, for networks which are strongly stuck (those in which most stickers are closed, or p near 1) the dominant process is the elementary $k = 1$ step that was described in detail above. Values of k_{max} for each p are indicated by the arrows in Figure 3. For $p \gtrsim 0.6$, the terms with $k > k_{max}$ make a comparatively small contribution to D_{self}.

In the long chain (large N, S) limit, the self-diffusion coefficient is dominated by the first term in eq 17, since the end terms are smaller by a factor of S (see eq 19) and the D_S term is negligible due to the exponentially small chance of finding a completely free chain (see eq 20). When the chains are strongly stuck ($p \cong 1$) the $k < k_{max}$ part of eq 18 dominates, and the D_{self} prediction is particularly simple

$$D_{self} \cong \frac{a^2}{4\tau}\frac{p^3}{S^2}\sum_{k=1}^{\infty}(1-p)^{k-1}k(k+1)^3 \cong \frac{a^2}{2\tau S^2}\left(1 - \frac{9}{p} + \frac{12}{p^2}\right) \qquad (21)$$

For $S = 20$, $N/N_e = 100$, $\tau/\tau_e = 16\,000$, and $p \geq 0.6$, D_{self} estimated from eq 21 is within 10% of the full prediction of eq 17. Apart from the p dependence of eq 21 and neglected numerical prefactors, the prediction of the self-diffusion coefficient is quite similar to the result for reptation of ordinary polymers without stickers [$D_0 \cong (a^2/\tau_e)(N_e/N)^2$]. In our model of reversible gels, the time that

the sticker is stuck, τ, plays the role of the equilibration time of an entanglement strand τ_e, and the number of stickers per chain, S, plays the role of the number of entanglements per chain N/N_e.

3. Stress Relaxation

We now calculate the linear viscoelastic response of reversible gels, using the sticky reptation model presented above. Consider a step shear strain γ applied to the sample at time $t = 0$. The time-dependent stress relaxation is described by the shear relaxation modulus,[20,25] which is defined as the ratio of the stress $\sigma(t)$ and the strain γ.

$$G(t) = \sigma(t)/\gamma \tag{22}$$

There are four time regimes that are important for the stress relaxation modulus of reversible gels. At times shorter than the Rouse time of an entanglement strand τ_e, relaxation is indistinguishable from that in the polymer without stickers. Since we consider only the case $N_s > N_e$, Rouse motions of the entanglement strands are unaffected by the presence of the stickers (except possibly for a small time shift due to a change in the glass transition temperature). On time scales $\tau_e < t < \tau$, there will be a rubbery plateau analogous to that observed in permanently cross-linked networks,[25] with a modulus which has contributions from both cross-links and entanglements. The modulus is the product of the number density of elastically active network strands and the stored energy per strand, kT. We make the simplest possible assumption here, that the number densities of entanglements and cross-links add together without any synergistic effects

$$G_1 \cong cRT\left[\frac{p}{N_s} + \frac{1}{N_e}\right] \tag{23}$$

where c is the number concentration of monomers. On the time scale where the stickers open, τ, the stress held by the stickers relaxes, and the modulus drops to the level of the identical linear chain system without stickers.

$$G_2 \cong cRT\left[\frac{1}{N_e}\right] \tag{24}$$

This second plateau persists until the terminal relaxation time of the reversible gel, T_d, which we calculate from the diffusion coefficient using eq 16. For long chains that are strongly stuck together, using the approximate eq 21 for D_{self}, we get

$$T_d \cong \frac{Nb^2}{D_{self}} \cong \left(\frac{N}{N_e}\right)\frac{2S^2\tau}{1 - 9/p + 12/p^2} \tag{25}$$

The overall schematic representation of $G(t)$ for a reversible gel is compared with that of an identical linear polymer without stickers in Figure 4. The four regimes of stress relaxation, discussed above, are clearly delineated in Figure 4, separated by the three important time scales in the reversible gel: τ_e, τ, and T_d.

So far we have intentionally left out relaxation mechanisms other than the main one (reptation) to emphasize concepts unique to reversible gels. In reality, relaxation mechanisms such as fluctuations in tube length[26] and constraint release,[27] known to be important for stress relaxation in ordinary linear polymers, will be needed for a full quantitative prediction of $G(t)$. These relaxation processes in reversible gels should be completely analogous to those in ordinary linear polymers (the details of both relaxation processes are still the subject of considerable debate in the literature). These secondary relaxation processes act to lower the modulus level at a given time

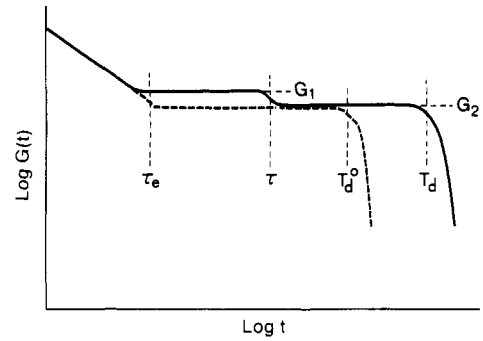

Figure 4. Schematic comparison of the time-dependent relaxation moduli for reversible networks comprising linear chains with stickers (solid line) and linear chains without stickers (dashed line). See text for explanation of times and modulus levels.

and broaden the spectrum of relaxation times but will not change the qualitative aspects of Figure 4. Here we employ a phenomenological approach—the commonly used expression for the terminal relaxation time of ordinary linear polymers is

$$T_d^0 = \tau_e\left(\frac{N}{N_e}\right)^{3.5} = \tau_R(N)\left(\frac{N}{N_e}\right)^{1.5}$$

with $\tau_R(N)$ being the Rouse time of a chain of N monomers. We adopt an analogous approach for the relaxation time of reversible gels, based on eq 25:

$$T_d \cong \left(\frac{N}{N_e}\right)^{1.5}\frac{2S^2\tau}{1 - 9/p + 12/p^2} \tag{26}$$

It is also important to note that in practice the number of stickers varies about some mean value for different chains. These fluctuations in the number of stickers per chain depend on how the functionalized chains were synthesized, and these fluctuations may considerably influence the stress relaxation. Moreover, the number of monomers in an entanglement strand, N_e, may be affected by the presence of the reversible cross-links on time scales smaller than τ. This means that the value of N_e used in eq 23 for the short time plateau modulus G_1 may be slightly smaller than that used in eq 24 for the long time plateau level G_2. If we ignore this complication, eqs 23 and 24 can be subtracted to get p from viscoelastic measurements.

$$p \cong N_s(G_1 - G_2)/cRT \tag{27}$$

To sum up, the most striking feature of truly reversible networks should be the existence of two maxima in the loss modulus function $G''(\omega)$ measured by the oscillatory shear technique[25] above the glass transition temperature. There should be a high-frequency peak at a frequency $1/\tau$ which is independent of other molecular parameters (N and S). On the other hand, the low-frequency peak occurs at a frequency $1/T_d$ which depends on chain length and degree of substitution as well as τ (see eqs 25 and 26). The relaxation time T_d is significantly enhanced relative to that of unmodified polymers due to the fact that for $\tau > \tau_e$ the stickers retard the reptation process. This will also manifest itself in an increase in the viscosity of reversible gels which can be approximated by the product of T_d and the plateau modulus G_2:

$$\eta \cong G_2T_d \cong \frac{cRT}{N_e}\left(\frac{N}{N_e}\right)^{1.5}\frac{2S^2\tau}{1 - 9/p + 12/p^2} \tag{28}$$

4. Discussion

A number of measurements of linear viscoelastic properties of reversible gels have been reported in the literature.

Table I
Experimental Parameters[a] for Urazole-Modified Polybutadienes at 0 °C

sample	T_d, s	N/N_e	S	p
PB26-0.5	0.001	15	2.5	0.68
PB26-2	0.01	15	10	0.75
PB26-5	0.3	15	25	0.81
PB26-7.5	3	15	38	0.84
PB35-1	0.02	20	6.9	0.71
PB50-1	0.2	28	9.5	0.71
PB50-2	2	28	19	0.75
PB200-1	20	120	43	0.71

[a] Parameters were determined from data in refs 10–12 and 30 as described in the text.

We can make a quantitative comparison of our theory with the experiments on monodisperse polybutadiene chains with randomly attached urazole groups studied by Stadler and de Lucca Freitas.[10-14] This system seems to be in thermal equilibrium and thus should correspond to our theory. Each urazole group is capable of forming a doubly hydrogen bonded complex with a single other urazole group.[10,11] Since polybutadiene has a very low glass transition temperature (~−100 °C), the modified polymers form reversible gels which can be studied near room temperature.

There are two maxima in the loss modulus $G''(\omega)$ for urazole-modified polybutadiene.[10,11] The low-frequency maximum corresponds to the longest relaxation time and decreases in frequency as the degree of modification increases. The high-frequency maximum appears at a frequency of roughly 2×10^4 rad/s (at 0 °C), independent of the degree of substitution.[10] While Stadler and de Lucca Freitas do not report data on the unmodified polymer at this high frequency, polybutadiene of this microstructure and chain length does not have any maxima in the loss modulus in the vicinity of this frequency at 0 °C.[28] The high-frequency peak increases in magnitude as the degree of substitution increases.[10] All of these observations are, at least qualitatively, consistent with our theory.

The reciprocal of the frequency at which the high-frequency peak occurs is identified with the average duration of an association, τ. From the data in refs 10 and 11 we estimate this cross-link lifetime to be $\tau \cong 5 \times 10^{-5}$ s at 0 °C. This seems to be an acceptable value, because if we assume a microscopic time of 10^{-11} s, we get an activation energy for dissociation of ~15 kT, which is reasonable for a pair of hydrogen bonds at 0 °C. Unfortunately, many of the experiments reported in refs 10–12 did not extend to high enough frequency to determine whether the high-frequency maximum in $G''(\omega)$ depends on molecular parameters.

To compare our theory (and the theory of Gonzalez[7,8]) with the data on urazole modified polybutadiene, one additional piece of information is required which is not available[29] in refs 10–14, the fraction of complexed urazole groups, p. In her thesis, however, de Lucca Freitas[30] measured p as a function of temperature (between 20 and 100 °C) for three samples. Such data for two samples with 1 mol % urazole groups extrapolated to $p = 0.71$ at 0 °C, and the other for 5 mol % urazole groups extrapolated to $p = 0.81$. Values of p for other samples (with 0.5, 2.0, and 7.5 mol % urazole groups) were estimated by interpolation and extrapolation based on our assumed second-order kinetics (see section 2), i.e., overall urazole group concentration being proportional to $p/(1-p)^2$.

The necessary data for their eight samples are summarized in Table I, which includes estimates of the longest relaxation time T_d at 0 °C obtained as the reciprocal of the frequency at which $G''(\omega)$ has its terminal maximum. Due to the breadth of the peak in $G''(\omega)$, the values of T_d are only estimated to one significant figure. The theoretical predictions of the Gonzalez model,[7,8] $T_d = T_d^0 \exp(Sp) = \tau_e(N/N_e)^{3.5}\exp(Sp)$, and eq 26 for the longest relaxation time are plotted against the experimental values in Figure 5 (τ_e for polybutadiene of this microstructure was estimated to be 2×10^{-7} s at 0 °C from the data in ref 28). The solid line in Figure 5 is the one-to-one correspondence expected. Both the data and the prediction of eq 26 span a range of roughly 4 orders of magnitude in time. The Gonzalez prediction, on the other hand, spans a range of over 15 orders of magnitude—the exponential dependence on S, due to the requirement that all stickers be simultaneously free for a reptation step, is much too strong. We conclude from Figure 5 that our predictions are in good agreement with the data of Stadler and de Lucca Freitas.

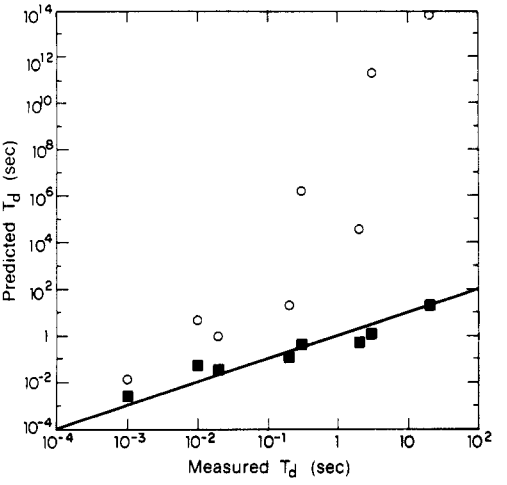

Figure 5. Comparison of predicted and measured values of terminal relaxation time for the urazole-modified polybutadienes of refs 10–14 (see Table I). Open circles are predictions of Gonzalez;[8,9] solid squares are predictions of eq 26. The line is the expected one-to-one correspondence.

The numerical agreement between the predictions of our model and the data shown in Figure 5 is somewhat surprising, considering the lack of precision in extracting relaxation times from the $G''(\omega)$ data (particularly for τ) and the fact that the numerical prefactor in eq 26 is not exact. However, we are encouraged that the model developed here may provide a useful insight into relaxation processes in reversible gels. First, linear viscoelastic measurements at high frequencies may provide a direct measure of the lifetime of a cross-link. In this context, a comparison with other spectroscopic studies would be very interesting. Second, the model can be used to predict the enhancement of viscosity and the slowing of diffusion in reversible gels.

Ionomer melts and concentrated solutions certainly exhibit enhanced viscoelastic response compared to that of ordinary polymers.[31] However, experiments on such systems are mostly still in the preliminary stages—careful linear viscoelastic measurements on well-characterized ionomers are sorely needed. Such studies have commenced with telechelic ionomers,[32] and these actually exhibit two maxima in the loss modulus function above the glass transition. A detailed theoretical description of dynamics for telechelic ionomers will be the subject of a future publication.[33]

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