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# Dynamics of Reversibly Cross-Linked Chains

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ABSTRACT: The dynamics and viscoelastic response of a polymer chain bound by reversible cross-links to a (phantom) network are considered in a mean-field picture. A reversible cross-link is presumed to act like a classical cross-link in binding a segment of polymer to a fixed point in space. However, unlike the permanent cross-link which always remains intact, the reversible cross-link may spontaneously break away and then reattach to allow the bound segment and hence the polymer to move. The motion of such a bound segment is taken to be entropically controlled, i.e., the probability distribution for the position of the rebound segment is that appropriate to (local) equilibrium. It is shown how chains with such dynamical cross-links exhibit (self-)diffusion and a spectrum of relaxation processes. The dependence of $D$, the diffusion constant, on the number of reversible cross-links, $N$, and their distribution along the chain is given and the relaxation spectra of the dumbbell ($N = 2$) and the trumbbell ($N = 3$) explicitly calculated. The relaxation spectrum of the general linear chain is approximated and the dynamics of a chain with regularly spaced cross-links shown to be essentially Rouse-like.

## I. Introduction

The idea of transient networks in which cross-link sites undergo continuous rupture and reformation thereby relaxing stress in strained systems has long been known.[1,2] The simplest theory of Lodge[2] predicts just one relaxation mode for each section of chain between such cross-links. A spectrum of relaxation modes derives from a spectrum of lifetimes for the reversible cross-links.

With the advent of ionomer gels[3] and controlled synthesis of chains with well-characterized reversible cross-link sites along the backbone has come the ability to probe directly the dynamics and viscoelasticity of chains with such reversible cross-links. In what follows we consider the dynamics of one such chain binding and disassociating either to a permanent gelled network[4,5] or to other such chains in a melt.[3]

In studying the dynamics of reversibly cross-linked chains we specifically separate out the dynamics due to cross-link reorganization (breakage and reformation) and local Brownian motion between cross-link sites and focus on the former. This separation is realized in practice when $1/\mu$, the characteristic time for reorganization of a cross-link far exceeds the maximum equilibration time of a section of polymer between cross-links, the situation pertaining in ionomer gels.

We may make several general statements about the dynamics conferred by the reversible cross-links on the chain. First, since no permanent constraints (cross-links) act on the chain, the chain is not localized and is therefore free to move throughout the network. Such motion given the random nature of the breakage and subsequent reformation of the cross-links will clearly be diffusive. Second, the continual reorganization of the cross-links allows relaxation of internal chain configurations to some equilibrium form. This relaxation will exhibit a spectrum of exponential decay processes, as do other models for polymer internal relaxation,[6–8] which show up as a viscoelastic response to mechanical deformation of the chain.

The dynamics of the reversibly cross-linked chain should therefore show both diffusive and relaxation response. What follows seeks to illustrate both these effects.

## II. The Basic Model

We consider the polymer chain to consist of an arc of length $L$ with reversible cross-link sites along its arc separated by lengths $s_1, s_2, ..., s_{N-1}$ (Figure 1). Such cross-link sites bind the polymer to the host network and are presumed to be fixed along the arc; i.e., they do not migrate down to chain. The dynamical reversible character of the cross-links is modeled by associating a breakage rate $\mu$ with each cross-link. The probability of a particular cross-link remaining intact over a time $t$ is therefore $e^{-\mu t}$. Once broken, the reversible cross-link is presumed to rebind to the host network, the position at which it rebinds assuming local equilibrium.

In following the dynamics of such a chain we focus on the configuration probability distribution function $P(\mathbf{R}_1, ..., \mathbf{R}_N)$ or $P(\mathbf{R}_C, \rho_1, ..., \rho_{N-1})$. The coordinates $\rho_i = \mathbf{R}_{i+1} - \mathbf{R}_i$ here characterize internal motions of the chain, while

$$\mathbf{R}_C = \sum_{i=1}^{N} \alpha_i \boldsymbol{R}_i, \qquad \sum_{i=1}^{N} \alpha_i = 1 \tag{II.1}$$

characterizes the translational bulk chain motion and will be termed the chain center coordinate. For $\alpha_i = 1/N \; \forall \; i$, this center $\mathbf{R}_C$ is the center of mass; for $\alpha_i = (1/s_{i-1} + 1/s_i)/2\sum_{i=1}^{N-1} s_i$, $\mathbf{R}_C$ is, as shown later, an effective center of friction. Clearly at equilibrium $P$ takes the form

$$P(\mathbf{R}_C, \rho_1, ..., \rho_{N-1}) = G_0(\rho_1, s_1) \; ... \; G_0(\rho_{N-1}, s_{N-1})/V \tag{II.2}$$

where

$$G_0(\rho_i, s_i) = \left[\frac{3}{2\pi l s_i}\right] \exp\left[\frac{-3}{2 l s_i} \rho_i \cdot \rho_i\right] \tag{II.3}$$

and where we take the chain center to be randomly positioned throughout the (macroscopic) network of volume $V$. $l$ here is the Kuhn length, the effective persistence length.

For an ensemble of chains initially not at equilibrium, $P$ will naturally change with time, as cross-link sites break away and reattach to the host network, evolving toward $P_0$. This evolution is controlled by the dynamics of the cross-link reorganization—breakage and reattachment. We take the breakage to be random, each cross-link survives without breakage over time $t$ with probability $e^{-\mu t}$. The reformation process is taken to allow the new cross-link to be in local thermodynamic equilibrium (Figure 2). If the $k$th cross-link is reformed at $\mathbf{R}_k'$ when its neighboring cross-links are at $\mathbf{R}_{k-1}$ and $\mathbf{R}_{k+1}$, then

$$P(\mathbf{R}_k') = N_k^{-1} G_0(\mathbf{R}_k' - \mathbf{R}_{k-1}, s_{k-1}) \; G_0(\mathbf{R}_{k+1} - \mathbf{R}_k', s_k) \tag{II.4}$$

where $N_k$ the normalization coefficient is given by

$$\int \mathrm{d}\mathbf{R}_k' \; G_0(\mathbf{R}_k' - \mathbf{R}_{k-1}, s_{k-1}) \; G_0(\mathbf{R}_{k+1} - \mathbf{R}_k', s_k) = G_0(\mathbf{R}_{k+1} - \mathbf{R}_{k-1}, s_{k-1} + s_k) \tag{II.5}$$

The effect of a cross-link reorganization on say the $k$th cross-link is therefore to change an original distribution

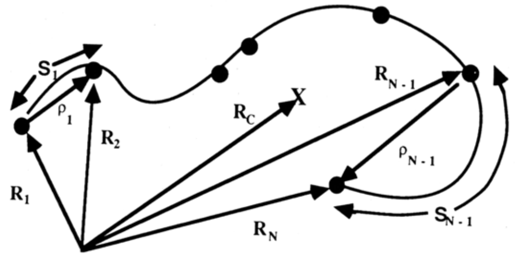

**Figure 1.** Reversible cross-link chain. A chain of length $L = \sum s_i$ with $N$ reversible cross-link sites (●), the $i$th cross-link, at position $\mathbf{R}_i$, located an arc length $s_{i-1}$ and displacement $\rho_{i-1} = \mathbf{R}_i - \mathbf{R}_{i-1}$ from the $(i-1)$th.

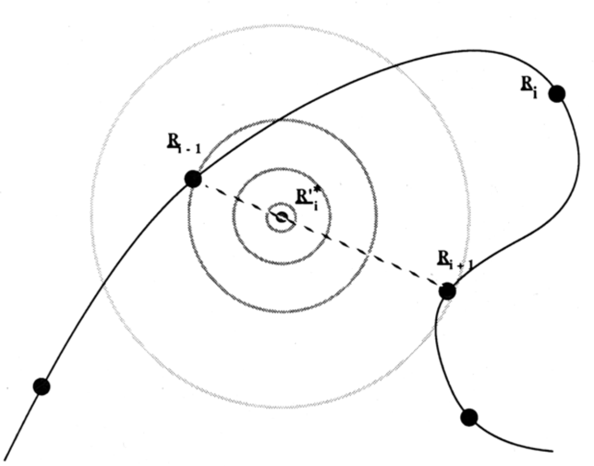

**Figure 2.** Reorganization of a cross-link. The cross-link originally located at $\mathbf{R}_i$ is reattached at $\mathbf{R}_i'$ so as to assume local equilibrium. Density of contours represents probability of reformation, eq II.4, the most probable point $\mathbf{R}_i'^*$ at $\mathbf{R}_i'^* = \mathbf{R}_{i-1} + s_{i-1}(\mathbf{R}_{i+1} - \mathbf{R}_{i-1})/(s_{i-1} + s_i)$.

function $P(\mathbf{R}_1, ..., \mathbf{R}_k, ..., \mathbf{R}_{N-1})$ to $P'(\mathbf{R}_1, ..., \mathbf{R}_k', ..., \mathbf{R}_{N-1})$ given by

$$P'(\mathbf{R}_1, ..., \mathbf{R}_k', ..., \mathbf{R}_{N-1}) = \frac{G_0(\mathbf{R}_k' - \mathbf{R}_{k-1}, s_{k-1})\, G_0(\mathbf{R}_{k+1} - \mathbf{R}_k', s_k)}{G_0(\mathbf{R}_{k+1} - \mathbf{R}_{k-1}, s_{k-1} + s_k)} \times \int \mathrm{d}\mathbf{R}_k\, P(\mathbf{R}_1, ..., \mathbf{R}_k, ..., \mathbf{R}_{N-1}) \quad \text{(II.6)}$$

Appendix A shows how under such reorganizations $P = P'$ when $P = P_0$, that is $P_0$ is the equilibrium distribution.

A generalization of this to an *ordered* sequence of cross-link reorganizations (e.g., the $k$th cross-link followed by the $j$th followed by ...) is obvious, $P'$ of the previous reorganization playing the role of $P$ above for the next reorganization. Using this generalization to the dynamical evolution of $P$, $P(t)$ may now be followed by averaging $P$ over all possible ordered sequences of cross-link reorganizations in time $t$. The probability of a particular ordered sequence of $n$ reorganizations (a Poisson process) is clearly

$$\frac{1}{n!}(\mu t)^n e^{-N\mu t} \quad \text{(II.7)}$$

so that

$$P(t) = e^{-N\mu t}\sum_{n=0}^{\infty}\frac{1}{n!}(\mu t)^n \sum_{m=0}^{N^n} P_n^{\ m} \quad \text{(II.8)}$$

where $P_n^{\ m}$ is the probability distribution for $n$ reorganizations in a particular sequence $m$. $P'$ of eq II.6 would be $P_1^{\ k}$, there being $N$ possible sequences of single reorganizations, each corresponding to a particular cross-link site.

Equation II.8 now contains all the information necessary to probe any dynamical property of the chain, e.g., the dynamical structure factor, the center of mass motion, or the viscoelastic response. If we know the value of the property, $A[\mathbf{R}]$, for a particular configuration $[\mathbf{R}]$ of the chain then we simply have

$$\langle A\rangle_t = \int \mathrm{d}[\mathbf{R}]\, P([\mathbf{R}], t)\, \mathrm{A}([\mathbf{R}]) = e^{-N\mu t}\sum_{n=0}^{\infty}\frac{1}{n!}(\mu t)^n \sum_{m=0}^{N^n}\langle A\rangle_n^{\ m} \quad \text{(II.9)}$$

where $\langle A\rangle_n^{\ m}$ denotes the average of $A$ over the configuration probability distribution function $P_n^{\ m}$.

In what follows we look at two particular dynamical properties, center of chain motion and response to step strain of the host network. For the former we consider

$$A = \sum_{i=1}^{N}\alpha_i\mathbf{R}_i\cdot\sum_{i=1}^{N}\alpha_i\mathbf{R}_i = R_\mathrm{C}^{\ 2} \quad \text{(II.10)}$$

the square of the chain center coordinate, and for the latter

$$A = \frac{3kT}{L}\sum_{i=1}^{(N-1)}\frac{1}{s_i}\rho_{i\alpha}\rho_{i\beta} = \sigma_{\alpha\beta} \quad \text{(II.11)}$$

which is well-known form for the stress tensor of a Gaussian polymer chain. $\alpha$ and $\beta$ here denote Cartesian components of the second-rank stress tensor.

For the former case we consider an initial ensemble of chains equilibrated in cross-link site separations ($\{\rho_i\}$) but not in the chain center coordinate. In particular we take the center of each chain to be initially fixed at the origin

$$P_{t=0} = G_0(\rho_1, s_1)\ ...\ G_0(\rho_{N-1}, s_{N-1})\ \delta(\mathbf{R}_\mathrm{C}) \quad \text{(II.12)}$$

If the chain is to exhibit diffusion and relaxation processes, $\langle R_\mathrm{C}^{\ 2}\rangle$ must evolve as

$$\langle R_\mathrm{C}^{\ 2}\rangle = 6Dt + \sum a_i(1 - e^{-\mu_i t}) \quad \text{(II.13)}$$

where $a_i$ are positive semidefinite coefficients, dependent on $\{\alpha_i\}$, and where the summation runs over the internal relaxation processes. Further there must exist a choice of $\{\alpha_i\}$ for which $a_i = 0\ \forall\ i$ and the internal relaxation processes decouple from the translational diffusive term. The coordinate thus defined is called the center of friction.

For the latter case consider an initial ensemble of chains equilibrated and then stretched by a step strain $\lambda_{\alpha\beta}$ imposed on the host network

$$P_{t=0} = G_0(\lambda_{\alpha\beta}^{\ -1}\rho_{1\beta}, s_1)\ ...\ G_0(\lambda_{\alpha\beta}^{\ -1}\rho_{N-1}\beta, s_{N-1})/V \quad \text{(II.14)}$$

Again with diffusive/relaxation response we expect

$$\langle\sigma_{\alpha\beta}\rangle_t - \langle\sigma_{\alpha\beta}\rangle_{t\to\infty} = (\langle\sigma_{\alpha\beta}\rangle_{t=0} - \langle\sigma_{\alpha\beta}\rangle_{t\to\infty})\sum b_i(1 - e^{-\mu_i t}) \quad \text{(II.15)}$$

where in the principal axes of strain

$$\langle\sigma_{\alpha\beta}\rangle_t - \langle\sigma_{\alpha\beta}\rangle_{t\to\infty} = (N-1)kT\delta_{\alpha\beta}(\lambda_\alpha^{\ 2} - 1) \quad \text{(II.16)}$$

and $\sum b_i = 1$.

In the next section we show how for the simplest reversible cross-link chain, the "dumbbell", the suppositions of (II.13) and (II.15) are indeed correct.

## III. The Reversible Cross-Link Dumbbell

The dumbbell consists of a chian of length $L = s_1$ with a reversible cross-link site at each end. $P_0$ the equilibrium distribution for such a chain is clearly

$$P_0 = G_0(\rho_1, s_1)/V \quad \text{(III.1)}$$

With two reversible cross-links ("1" and "2") there are also clearly $2^n$ possible orderings for $n$ cross-link reorganizations. The probability of such an ordering occurring in time $t$ is $(\mu t)^n e^{-2\mu t}/n!$. For any $n$, however, there are only $2n$ different probability distributions $P_n^{\ m}$, since sequences of successive one-cross-link reorganizations have the same effect as a single such cross-link reorganization, e.g., for $n = 4$, $P_4(1222) = P_2(12)$. Further each of these $2n$ distributions corresponds to a sequence of $j$ alternating (first 1, then 2, then 1, ...) cross-link reorganizations where $n \geq j \geq 1$ and either 1 or 2 may be reorganized first. We may therefore replace the summation over $P_n{}^m$ of (II.7) by a summation over $P_n{}^{*1}$ ($P_n{}^{*2}$) where $P_n{}^{*1}$ ($P_n{}^{*2}$) is the distribution after $n$ alternating reorganizations, 1 (2) being the first reorganized cross-link, to give

$$P(t) = e^{-2\mu t}\sum_{\nu=1}^{2}\sum_{n=1}^{\infty}(-1)^n[1 - e^{\mu t}\sum_{m=0}^{(n-1)}(-\mu t)^m]P_n{}^{*\nu} + e^{-2\mu t}P_0{}^* \tag{III.2}$$

where $P_0{}^*$ is the initial distribution. In terms of some property $A$

$$\langle A\rangle_t = e^{-2\mu t}\sum_{\nu=1}^{2}\sum_{n=1}^{\infty}(-1)^n[1 - e^{\mu t}\sum(-\mu t)^m]\langle A\rangle_m{}^{*n} + e^{-2\mu t}\langle A\rangle_0{}^* \tag{III.3}$$

For the step–strain relaxation

$$P_0 = G_0(\lambda_{\alpha\beta}{}^{-1}\rho_{1\beta}, s_1)/V \tag{III.4}$$

and

$$P_n{}^{*\nu} = G_0(\rho_{1\alpha}, s_1)/V \ \forall\ \nu, n \tag{III.5}$$

Evaluating

$$\langle\sigma_{\alpha\beta}\rangle = \frac{3kT}{L}\frac{1}{s_1}\rho_{1\alpha}\rho_{1\beta} = \langle A\rangle$$

therefore gives

$$\langle A\rangle_0{}^* = kT\delta_{\alpha\beta}\lambda_\alpha{}^2 \tag{III.6}$$

and

$$\langle A\rangle_n{}^{*1} = \langle A\rangle_n{}^{*2} = kT\delta_{\alpha\beta} \tag{III.7}$$

so that

$$\langle\sigma_{\alpha\beta}\rangle = kTe^{-2\mu t}\delta_{\alpha\beta}(\lambda_\alpha{}^2 + (e^{2\mu t} - 1)) \tag{III.8}$$

or

$$\langle\sigma_{\alpha\beta}\rangle_t - \langle\sigma_{\alpha\beta}\rangle_{t\to\infty} = kTe^{-2\mu t}\delta_{\alpha\beta}(\lambda_\alpha{}^2 - 1) \tag{III.9}$$

which is of the form of (II.15).

For center of chain motion

$$P_0{}^* = \delta(\mathbf{R}_\mathrm{C})G_0(\rho_1, s_1) \tag{III.10}$$

$$P_n{}^{*1} = G_0(\rho_1, s_1)\ G_0(\mathbf{R}_\mathrm{C} + (\alpha - 1/2 - (-1)^n/2)\rho_1, s_1(n - 1 + \alpha^2)) \tag{III.11}$$

$$P_n{}^{*2} = G_0(\rho_1, s_1)\ G_0(\mathbf{R}_\mathrm{C} + (\alpha - 1/2 + (-1)^n/2)\rho_1, s_1(n - 1 + (1 - \alpha)^2)) \tag{III.12}$$

and for $A = R_\mathrm{C}{}^2$ we have

$$\langle A\rangle_0{}^* = 0 \tag{III.13}$$

$$\langle A\rangle_n{}^{*1} = (n - 1 + \alpha^2 + (\alpha - 1/2 - (-1)^n/2)^2)s_1 \tag{III.14a}$$

and

$$\langle A\rangle_n{}^{*2} = (n - 1 + (1 - \alpha)^2 + (\alpha - 1/2 + (-1)^n/2)^2)s_1 \tag{III.14b}$$

so that

$$\langle R_\mathrm{C}{}^2\rangle = 6(s_1l\mu/6)t + 2(\alpha - 1/2)^2(1 - e^{-2\mu t}) \tag{III.15}$$

which is of the form (II.13), with $D = s_1l\mu/6$ and $a_1 = 2(\alpha - 1/2)^2$.

The reversible cross-link dynamics of the dumbbell thus exhibits diffusive/relaxation response, diffusing with $D = s_1l\mu/6$ and relaxing with a single relaxation mode of rate $2\mu$. The relaxation term disappears for $\alpha = {}^1/_2$; the center of friction coincides with the center of mass. It is not difficult to show further that if the cross-links break at different rates $\mu_0$ and $\mu_1$, (III.15) and (III.9) then become

$$\langle\sigma_{\alpha\beta}\rangle_t - \langle\sigma_{\alpha\beta}\rangle_{t\to\infty} = kTe^{-(\mu_0+\mu_1)t}\delta_{\alpha\beta}(\lambda_\alpha{}^2 - 1) \tag{III.16}$$

and

$$\langle R_\mathrm{C}{}^2\rangle = \frac{1}{6}(12s_1l\mu_\mathrm{eff})t + s_1\frac{(\mu_0 - \mu_1)^2}{(\mu_0 + \mu_1)^2}(1 - e^{-(\mu_0+\mu_1)t}) \tag{III.17}$$

where $1/\mu_\mathrm{eff} = 1/\mu_0 + 1/\mu_1$. The relaxation mode now has rate $\mu_0 + \mu_1$ and the diffusion constant $6s_1l2\mu_\mathrm{eff}$. Note how if $\mu_0 \to 0$ and $\mu_1 = \mu$, the relaxation rate $= \mu$ and the diffusion constant $\to 0$. Such a limit is appropriate to a dumbbell with a fixed cross-link at one end and a reversible one at the other.

Having illustrated the general method for elucidating the dynamics of a reversible cross-link chain with the dumbbell, we now move up one stage in complexity to the trumbbell (three reversible cross-link chain) before considering the general reversible cross-link chain in section V.

## IV. The Reversible Cross-Link Trumbbell[9]

The trumbbell[9] consists of a chain with three reversible cross-links, two at the ends and one between located an arc length $s_1$ from one end and $s_2$ from the other. With three reversible cross-links the probability of a particular ordered sequence of reorganizations in time $t$ is $(\mu t)^ne^{-3\mu t}/n!$.

To determine the internal relaxation processes and the diffusive contribution to the dynamics of the chain we follow the program already outlined. However, in determining the center of friction and the diffusion constant we may make use of a variational procedure which only requires knowledge of one and two cross-link reorganization processes.

Accepting the form of (II.13) and expanding to $O(t^2)$, we have

$$\langle R_\mathrm{C}{}^2\rangle_t = (6D + \sum a_i\mu_i)t - \sum a_i\mu_i{}^2t^2/2 + O(t^3), \quad \mu_i, a_i \geq 0\ \forall\ i \tag{IV.1}$$

For $\{\alpha\}$ corresponding to the center of friction $a_i = 0\ \forall\ i$, providing an upper bound (of zero) on the $O(t^2)$ term and a lower bound (of $6D$) on the $O(t)$ term. This variational character is sufficient to determine the $\{\alpha\}$ for the center of friction and hence $D$. Since the lowest order contribution from an $n$ cross-link reorganization is $n$ (eq II.6) this procedure simply requires evaluation of the three one-cross-link and nine double-cross-link reorganization terms.

Evaluating $\langle R_\mathrm{C}{}^2\rangle_n{}^m$ for the $n = 1$, $m = 1, 3$ and the $n = 2$, $m = 1, 9$ reorganizations given

$$\langle R_\mathrm{C}{}^2\rangle = \mu te^{-3\mu t}\{2\alpha_1{}^2s_1 + 2\alpha_3{}^2s_2 + 2\alpha_2{}^2s_2s_1/(s_1 + s_2)\} + \frac{(\mu^2t^2)}{2}e^{-3\mu t}\{10\alpha_1{}^2s_1 + 10\alpha_3{}^2s_2 + (10\alpha_2{}^2 + 4\alpha_2\alpha_3 + 4\alpha_1\alpha_2)s_2s_1/(s_1 + s_2)\} + O(t^3) \tag{IV.2}$$

On maximizing the $O(t^2)$ term of (IV.2) subject to $\sum_{i=1}^{N}\alpha_i = 1$, we find

$$\alpha_i = \frac{\frac{1}{2}\left(\frac{1}{s_{i-1}} + \frac{1}{s_i}\right)}{\sum_{i=0}^{3}\frac{1}{s_i}} \tag{IV.3}$$

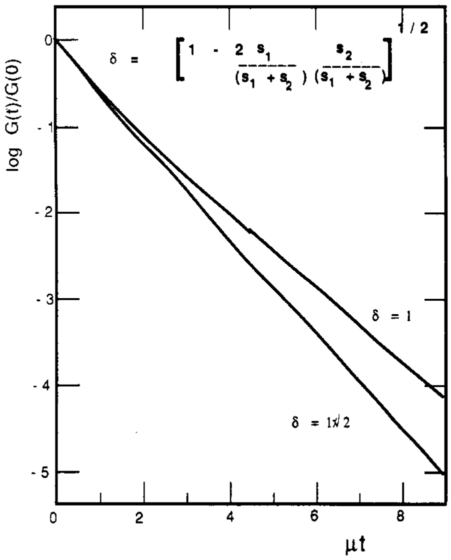

**Figure 3.** Normalized relaxation modulus, $G(t)/G(0)$, for the trumbbell. Relaxation is fastest for the interior cross-link midway between the ends, $\delta = 1/2^{1/2}$, eq VI.2b, and slowest, $G(t) = kT(e^{-\mu t} + e^{-2\mu t})$, when located at either end, $\delta = 1$. Relaxation for intermediate values of $\delta$ lie within these bounds.

where $1/s_0$ and $1/s_3$ are both 0 and are introduced purely for ease of representing $\alpha_i$. For $\alpha_i$ defined by (IV.3) we have

$$\langle R_C^2\rangle_t = 6\frac{\mu l t}{6\sum_{i=1}^{2}\frac{1}{s_i}} \tag{IV.4}$$

which gives $D$, the diffusion constant, as

$$D = \mu s_1 s_2 l/6(s_1 + s_2) \tag{IV.5}$$

For the relaxation modes we have

$$\langle\sigma_{\alpha\beta}\rangle_n^{\{m\}} = kT(s_2/(s_1+s_2))^{m_1}(s_1/(s_1+s_2))^{m_2}(0)^{m_3}\delta_{\alpha\beta}\lambda_\alpha^{\,2} + kT(1-(s_2/(s_1+s_2))^{m_1}(s_1/(s_1+s_2))^{m_2}(0)^{m_3})\delta_{\alpha\beta} \tag{IV.6}$$

where for any ordering $\{m\}$, $m_1$ is the number of 12 or 21 pairs, $m_2$ is the number of 23 or 32 pairs, and $m_3$ is the number of 13 or 31 pairs. If $m_3 \neq 0$ then $\langle\sigma_{\alpha\beta}\rangle = kT\delta_{\alpha\beta}$. The sequence 122323212 for instance has $m_1 = 3$, $m_2 = 4$, and $m_3 = 0$ while 122323122 has $m_3 = 1$ and therefore $\langle\sigma_{\alpha\beta}\rangle = kT\delta_{\alpha\beta}$. Summing $\langle\sigma_{\alpha\beta}\rangle_n^{\{m\}}$ over the cross-link ordering probability according to (II.9) gives

$$\langle\sigma_{\alpha\beta}\rangle_t - \langle\sigma_{\alpha\beta}\rangle_{t\to\infty} = \delta_{\alpha\beta}(\lambda_\alpha^{\,2} - 1)G(t)$$

where $G(t)$ the relaxation modulus is given by

$$G(t) = kT\left[\frac{(1-\delta)}{2\delta^2}e^{-(2+\delta)\mu t} + \frac{(2\delta^2-1)}{\delta^2}e^{-2\mu t} + \frac{(1+\delta)}{2\delta^2}e^{-(2-\delta)\mu t}\right] \tag{IV.7}$$

where $\delta = [1 - 2s_1s_2/(s_1+s_2)^2]^{1/2}$ and is bounded by $[1/2^{1/2}, 1]$. $\delta$ is a measure of the relative values of $s_1$ and $s_2$, a minimum of $1/2^{1/2}$ for $s_1 = s_2$ and a maximum of 1 for $s_1/s_2$ (or $s_2/s_1$) → ∞. The relaxation and its dependence on $\delta$ are plotted in Figure 3.

From (IV.4) and (IV.7) it is clear that the trumbbell exhibits relaxation response and diffusion in the manner of the dumbbell. It may be noted, however, that three relaxation terms appear rather than two if each term were attributable to a mode. We return to this point in the next section when we consider the relaxation spectrum of the general reversible cross-link chain.

## V. The General Reversible Cross-Link Chain

For the general chain of Figure 1 we may determine $D$ the diffusion constant by the method of the last section, calculating $\langle R_C^2\rangle_n^m$ for 1 and 2 cross-link reorganizations. We find

$$\langle R_C^2\rangle = \mu t e^{-N\mu t}\sum_{i=1}^{N}2\alpha_i^{\,2}(1/s_{i-1} + 1/s_i)^{-1} + (\mu^2t^2)e^{-N\mu t}\sum 2(N-1)\alpha_i^{\,2}(1/s_{i-1} + 1/s_i)^{-1} + 2\alpha_i\alpha_{i+1}(1/s_{i-1} + 1/s_i)^{-1}(1/s_i + 1/s_{i+1})^{-1}s_i^{-1} + O(t^3) \tag{V.1}$$

where $\{\alpha\}$ are defined in (II.1).

Maximizing the $O(t^2)$ term with respect to $\alpha_j$, $N \geq j \geq 0$ subject to $\sum_{j=1}^{N}\alpha_j = 1$ gives

$$\alpha_j = \frac{\frac{1}{2}\left(\frac{1}{s_{j-1}} + \frac{1}{s_j}\right)}{\sum_{i=0}^{N}\frac{1}{s_i}} \tag{V.2}$$

where as in (IV.3), $1/s_0 = 1/s_N = 0$, and then finally

$$D = \frac{\mu L}{6\sum_{i=1}^{(N-1)}\frac{1}{s_i}} \tag{V.3}$$

The general chain thus shows the diffusive character anticipated.

The identification of relaxation processes in the general chain is not so simple, the method as presented requiring the evaulation of all $n!$ diagrams (contributions from specific ordered sequences of $n$ cross-link reorganizations) to all orders in $n$ and their summation. It might be thought that each exponential contribution in the relaxation would be attributable to a mode or normal coordinate, with the form[10]

$$\langle X_{i\alpha}X_{i\beta}\rangle_t - \langle X_{i\alpha}X_{i\beta}\rangle_{t\to\infty} = A_i\delta_{\alpha\beta}(\lambda_\alpha^{\,2} - 1)e^{-\mu_i t} \tag{V.4}$$

where $X_{i\alpha} = \sum_{j=1}^{N-1}\beta_j\rho_{j\alpha}$. If such were the case, then a variational procedure for trial $\beta_j$, involving the calculation of one and two cross-link terms along the lines for the $\alpha_i$ of (V.1) and (V.2), would suffice to identify the $X_i$ and hence $\mu_i$. However, such modes do *not* exist. A full evaluation of $\langle X_{i\alpha}X_{i\beta}\rangle_t$ for the trumbbell gives

$$\langle X_{i\alpha}X_{i\beta}\rangle_t - \langle X_{i\alpha}X_{i\beta}\rangle_{t\to\infty} = 2kT\delta_{\alpha\beta}(\lambda_\alpha^{\,2} - 1)[A_1e^{-(2+\delta)\mu t} + A_2e^{-2\mu t} + A_3e^{-(2-\delta)\mu t}] \tag{V.5}$$

where

$$A_1 = \frac{(1-\delta)}{2\delta^2}(s_1\beta_1 + s_2\beta_2)^2/(s_1+s_2) - \frac{1}{\delta^2}s_1s_2\beta_1\beta_2/(s_1+s_2) \tag{V.6a}$$

$$A_2 = \frac{(2\delta^2-1)}{\delta^2}(s_1\beta_1^{\,2} + s_2\beta_2^{\,2}) + \frac{1}{2\delta^2}(s_1 - s_2)(s_1\beta_1^{\,2} - s_2\beta_2^{\,2}) \tag{V.6b}$$

$$A_3 = \frac{(1+\delta)}{2\delta^2}(s_1\beta_1 + s_2\beta_2)^2/(s_1+s_2) - \frac{1}{\delta^2}s_1s_2\beta_1\beta_2/(s_1+s_2) \tag{V.6c}$$

for which there exist *no* choices of $\{\beta\}$ in which two of $A_1$, $A_2$, and $A_3$ vanish.

A further indication of the lack of modes comes from the number of exponential terms. For a linear problem, with Cartesian component degeneracy as here, the number of nondegenerate modes is $N$. With the existence of the diffusive center of friction as one normal coordinate, this leaves $N-1$ potential different values of $\mu_i$. However for the trumbbell ($N = 3$) equation (IV.7), it is clear that such is not the case since *three*, not two, values of $\mu_i$ exist.

With this lack of identification of modes arising from the local constraints (fixed adjacent cross-links) of the equilibrating step (II.4) and an inability to sum all diagrams in the general case, one cannot find the exact general relaxation spectrum. On the assumption that modes exist, however, we can find a variational approximation for the relaxation spectrum. Appendix B details the general calculation. For a regular linear chain ($s_j = s \ \forall \ j$)

$$G(t) = \sum_{j=1}^{(N-1)} e^{-2\mu \sin^2[j\pi/2(N-1)]t} \tag{V.7}$$

with $\mu_j = {}^1/_2[4 \sin^2 (j\pi/2(N-1))]$, the eigenvalues of a matrix identical to the Rouse[6] matrix except in that corner elements are 3 rather than 2.

For $N = 3$ this gives

$$G(t) = e^{-\mu t} + e^{-2\mu t} \tag{V.8}$$

Figure 3 compares this prediction (corresponding to $\delta = 1$ in (IV.7)) with the true nonmodal relaxaton, $\delta = 1/2^{1/2}$, of (IV.7). The relaxations are of similar form, the modal relaxation providing an upper bound on the true relaxation. An upper bound will be found for general $N$, a consequence of the fact that the true relaxation with local constraints allows for $\mu_i > 2$ whereas the mode picture does not. For increasing $N$ a mode picture becomes increasingly valid, the global relaxations (Appendix B) for which $\mu_i \ll \mu$ dominating the relaxation.

The modal approximation of (V.7) may be compared with a true modal polymer chain, the Rouse chain. The Rouse[6] chain with $N$ beads of drag $\zeta$ separated by Gaussian sections of chain of length $s$ exhibits modal response with

$$G(t) = \sum_{j=1}^{(N-1)} e^{-2[12kT/ls\zeta]\sin 2[j\pi/2N]t} \tag{V.9}$$

The two models exhibit the same form of relaxation dynamics, with $\mu = 12kT/ls\zeta$, to within $O(1/N)$ corrections. Comparison of the diffusion mode for the regular linear chain

$$D = ls\mu/6(N-1) \tag{V.10}$$

and the Rouse chain

$$D_R = kT/N\zeta \tag{V.11}$$

again exhibits the same scaling structure, $D \propto 1/N$ with $O(1/N)$ corrections. These corrections essentially arise from end effects clear from (IV.3) where $\alpha_i = 1/N$ for $2 \le i \le N-1$ (the interior cross-links) but $1/2N$ for $i = 1$ and $N$ (the end cross-links). Such end effects in computer realizations of the Rouse chain (lattice Rouse dynamics[11]) are well-known, the representation adopted there of chain dynamics which involves random selection of bonds and their local reorientation strongly resembling the model (section II) used here.

The introduction of irregularity, $s_j \neq s \ \forall \ j$, will in general slow down relaxation as it does for diffusion, eq V.3, the smaller segments acting as pinning points. Equations B.2 and B.8 provide the modal prediction. The Rouse chain, with irregularity, gives $G(t)$ of the form (B.8) with $\mu_{iR} = (6kT/l\langle s\rangle\zeta)\lambda_i$ and $\lambda_i$ eigenvalues of the matrix $A_{jk} = (2\delta_{kj}\langle s\rangle/s_j - \delta_{kj+1}\langle s\rangle/s_{j+1} - \delta_{kj-1}\langle s\rangle/s_{j-1})$ where $\langle s\rangle = \sum_{i=1}^{(N-1)} s_i/(N-1)$. Since $\lambda_i < 4$, $\forall \ i$, the effect of pinning points does not appear for the Rouse chain. A full treatment of the general reversible cross-link chain will clearly elicit some interesting effects arising from such pinning features.

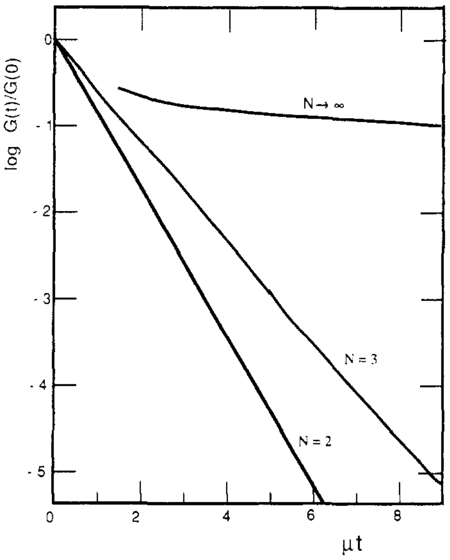

**Figure 4.** Relaxation modulus (normalized to 1 at $t = 0$) for regular (cross-links evenly distributed) chains, the dumbbell, and the trumbbell and the modal prediction for $N \to \infty$ (Rouse, $\mu = 12kT/(1s\zeta)$) chain. As $N$ increases relaxation slows and the behavior becomes Rouse-like, at least for $t > 1/\mu$.

## VI. Discussion and Conclusion

The reversible cross-link chain model presented here purports to represent the dynamics of a polymer chain continually attaching and breaking away from a host network, whether the host network be a melt of such polymers or a permanent gelled network. An important point to note about the model is the absence of topological or tubelike effects. It is not surprising therefore that the dynamics of the chain resembles closely (section V) that of the Rouse bead–spring chain rather than the reptation chain which is the basis for alternative treatments of polymer dynamics in gels.[5,12,13] In reality the degree of freedom for reattachment in an ionomer gel is likely to be restricted by tube effects and local clustering, neither of which are dealt with here.

Calculations with the model indicate that the chain exhibits diffusive/relaxation behavior. The chain diffuses with a diffusion constant $D$ given by

$$D = \frac{\mu l}{6 \sum_{i=1}^{(N-1)} 1/s_i} \tag{VI.1}$$

a result which for a chain with a uniform line density of reversible cross-links has the same scaling with molecular weight (polymer length), $D \propto 1/M$ as a Rouse chain.

The chain relaxes under step strain. The relaxation moduli, $G(t)$, for chains of length $L$ with two and three reversible cross-links separated by $L$ and $L/2$, respectively, are

$$G(t) = kTe^{-2\mu t} \tag{VI.2a}$$

$$G(t) = kTe^{-2\mu t}[(1 - 1/2^{1/2})e^{-\mu t/2^{1/2}} + (1 + 1/2^{1/2})e^{\mu t/2^{1/2}}] \tag{VI.2b}$$

$G(t)/G(0)$ is plotted in Figure 4.

A modal prediction for the relaxation gives

$$G(t) = \sum_{j=1}^{(N-1)} e^{-2\mu \sin^2[j\pi/2(N-1)]t} \tag{VI.3}$$

a relaxation Rouse-like in form with $\mu = 12kT/l s\zeta$. The modal prediction will be exact in the limit of $N \rightarrow \infty$, suggesting that the regular reversible cross-link chain exhibits Rouse dynamics with an effective drag at each reversible cross-link site of $12kT/l s\zeta$. The modal prediction for $N \rightarrow \infty$ is plotted in Figure 4.

This Rouse chain interpretation has perhaps an application for transient network theories in which cross-link sites undergo continuous rupture and reformation thereby relaxing stress in strained systems.

In the simplest of such theories, due to Lodge,[2] each segment between cross-links relaxes independently with a single relaxation rate—a network of reversible cross-link dumbbells. As the trumbbell case shows, however, correlations exist between the relaxation of adjacent segments of a polymer chain inducing slower relaxation (Figure 4). Taking into account such adjacent segment correlations would predict a relaxation modulus of the form (VI.2b) rather than (VI.2a). In a true network, correlations would exist along the entire backbone, $N \rightarrow \infty$ segments, of the network. Such correlations are accounted for in the reversible cross-link chain in the same limit, suggesting that a true transient network is essentially a macroscopic Rouse chain.

Flory[14] and subsequently Fricker[15] have attempted to include the network correlations in a transient network, both predicting $G(t) \propto t^{-1}$ for a large range of time. The above model would predict power law behavior, but rather $G(t) \propto t^{-1/2}$, the well-known result for the Rouse chain.

Chains with cross-links irregularly distributed along the backbone exhibit effects qualitatively different from those for a Rouse chain with unevenly distributed drag. Equation VI.1 and Figure 3 illustrate the general feature of uneven distributions—namely, to slow both diffusion and relaxation. For a chain of given length and number of cross-links, $D$ is a maximum for a regular distribution, $s_i = L/(N-1)\ \forall\ i$, and for the trumbbell $G(t)$ is a minimum (the relaxation a maximum) for $\delta = 1/2^{1/2}$, $s_1 = s_2$.

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### Appendix A: Maintenance of Equilibrium under Cross-Link Reorganization

We consider here how $P(\mathbf{R}_1, ..., \mathbf{R}_N)$ or $P(\mathbf{R}_C, \rho_1, ..., \rho_{N-1})$, the configuration probability distribution function, evolves from $P_0 = G_0(\rho_1, s_1) \ldots G_0(\rho_{N-1}, s_{N-1})/V$ under reorganization (breakage and reformation) of cross-links which attain local equilibrium, (II.4). In particular consider the reorganization of the $k$th cross-link from $\mathbf{R}_k$ to $\mathbf{R}_k'$.

Following (II.6) we have $P(\mathbf{R}_1, ..., \mathbf{R}_N) \rightarrow P'(\mathbf{R}_1, ..., \mathbf{R}_k', ..., \mathbf{R}_N)$, where

$$P'(\mathbf{R}_1, ..., \mathbf{R}_k', ..., \mathbf{R}_N) = P(\mathbf{R}_C, \rho_1, ..., \rho_{k-1}', \rho_k', ..., \rho_{N-1}) = G_0(-s_{k-1}/(s_{k-1}+s_k)\rho_k' + s_k/(s_{k-1}+s_k)\rho_{k-1}', s_{k-1}s_k/(s_{k-1}+s_k)) \int \mathrm{d}\mathbf{r}_k\, G_0(\rho_1, s_1)\, G_0(\rho_2, s_2) \ldots G_0(\rho_{k-1}' + \mathbf{r}_k, s_{k-1})\, G_0(\rho_k' - \mathbf{r}_k, s_k) \ldots G_0(\rho_{N-1}, s_{N-1})/V \quad \text{(A.1)}$$

where $'$ denotes replacement of $\mathbf{R}_k$ by $\mathbf{R}_k'$ and $\mathbf{r}_k = \mathbf{R}_k - \mathbf{R}_k'$. Performing the integration over $\mathbf{r}_k$ and noting that

$$G_0(-s_{k-1}/(s_{k-1}+s_k)\rho_k' + s_k/(s_{k-1}+s_k)\rho_{k-1}', s_{k-1}s_k/(s_{k-1}+s_k))\, G_0(\rho_{k-1}' + \rho_k', s_{k-1}+s_k) = G_0(\rho_{k-1}', s_{k-1})\, G_0(\rho_k, s_k) \quad \text{(A.2)}$$

give $P' = P_0$. Reorganization thus preserves the configuration equilibrium distribution function.

### Appendix B: Variational (Mode) Calculation for the Relaxation Spectrum of the General Linear Chain

The discretized jump processes for the dynamics of the general linear chain allow for relaxation which is nonlocal in character (section V). Such nonmodal character arises from the local constraints (fixed adjacent cross-links) imposed at each jump.

On the assumption that relaxation modes do indeed exist, they may be determined variationally, in the manner of the diffusive mode of sections IV and V, and the relaxation spectrum/modulus determined. "Modes", of relaxation $e^{-\mu_i t}$, identified by such means will fall into two categories. Global relaxations for which $N_i = \mu/\mu_i \gg 1$, involving typically $N_i$ jumps, will be truly modal relaxations in which local constraints are unimportant. Local relaxations, for which $\mu/\mu_i = 1$, will be modal approximants for the nonmodal local relaxation processes.

In general the modal decomposition of the relaxation will serve as an approximation, exact for $N \rightarrow \infty$ where global modes dominate and at its worst for $N = 3$ ($N = 2$ is trivial and exact) for local relaxation. The main text returns to the assessment of the approximation; the modes are determined in what follows.

Consider a trial function $X_\alpha = \sum_{j=1}^{(N-1)} (\alpha_j/s_j^{1/2})\rho_{j\alpha}$. Expanding to $O(t^2)$ by summing over 0 and 1 cross-link reorganizations gives

$$\langle X_\alpha X_\beta \rangle_t = \lambda_\alpha^2 e^{-N\mu t} \delta_{\alpha\beta} \sum_{i=1}^{(N-1)} \alpha_i^2 + (\mu t) e^{-N\mu t} \delta_{\alpha\beta} \left[ N \sum_{i=1}^{(N-1)} \lambda_\alpha^2 \alpha_i^2 + (\lambda_\alpha^2 - 1) \sum_{i=1}^{N} \frac{s_{i-1}s_i}{(s_{i-1}+s_i)} \left[ \frac{\alpha_i}{s_i^{1/2}} - \frac{\alpha_{i-1}}{s_{i-1}^{1/2}} \right]^2 \right] + O(t^2) \quad \text{(B.1a)}$$

with (defined for convenience) $s_0 = s_N \rightarrow \infty$ and $\alpha_0 = \alpha_N = 0$

$$= \delta_{\alpha\beta}[\lambda_\alpha^2 \alpha^{\mathrm{T}} \cdot \boldsymbol{I} \cdot \alpha + (1 - \lambda_\alpha^2) \alpha^{\mathrm{T}} \cdot \boldsymbol{M} \cdot \alpha + O(t^2)] \quad \text{(B.1b)}$$

where $\alpha^{\mathrm{T}} = (\alpha_1, ..., \alpha_{N-1})$, $\boldsymbol{I} = \delta_{ij}$ is the identity matrix, and $\boldsymbol{M}$ is given by

$$M_{ij} = \mu \left[ \frac{s_{i-1}}{(s_{i-1}+s_i)} + \frac{s_{i+1}}{(s_i+s_{i+1})} \right] \delta_{ij} - \mu \frac{s_i^{1/2} s_{i-1}^{1/2}}{(s_{i-1}+s_i)} \delta_{i-1j} - \mu \frac{s_i^{1/2} s_{i+1}^{1/2}}{(s_i+s_{i+1})} \delta_{i+1j} \quad \text{(B.2)}$$

For a mode (eq V.4) $X_{i\alpha} = \sum_{j=1}^{N-1} (\alpha_j^i/s_j^{1/2})\rho_{j\alpha}$

$$\langle X_{i\alpha} X_{i\beta} \rangle_t = \delta_{ik}\delta_{\alpha\beta}[1 + (\lambda_\alpha^2 - 1)e^{-\mu_i t}] = \delta_{ik}\delta_{\alpha\beta}[\lambda_\alpha^2 + (1 - \lambda_\alpha^2)(\mu_i t) + O(t^2)] \quad \text{(B.3)}$$

For general $\alpha$ we have, by expansion in modes

$$\langle X_\alpha X_\beta \rangle = \delta_{\alpha\beta} \sum_{i=1}^{(N-1)} a_i^2 (\lambda_\alpha^2 + (1 - \lambda_\alpha^2)(\mu_i t) + O(t^2)) \quad \text{(B.4)}$$

where the weight of each mode is $a_i$. Comparing (B.1) and (B.4) by takin ratios of $O(t)$ and constant terms, we have

$$\frac{\sum_{i=1}^{(N-1)} a_i^2 \mu_i}{\sum_{i=1}^{(N-1)} a_i^2} = \frac{\alpha^{\mathrm{T}} \cdot \boldsymbol{M} \cdot \alpha}{\alpha^{\mathrm{T}} \cdot \boldsymbol{I} \cdot \alpha} \quad \text{(B.5)}$$

from which it is clear that the relaxation rates are variational maxima of the right-hand side, that is, eigenvalues of the matrix $\boldsymbol{M}$. Modes are the eignevectors of $\boldsymbol{M}$.

The weights, $a_i$, of each mode in general require knowledge of the eigenvectors of $\boldsymbol{M}$. For the relaxation modulus defined by

$$\sum_{i=1}^{(N=1)} \frac{\langle \rho_{i\alpha}\rho_{i\beta}\rangle}{s_i} = [(N-1) + (\lambda_\alpha{}^2 - 1)G(t)]\delta_{\alpha\beta} \quad \text{(B.6)}$$

with

$$G(t) = \sum_{i=1}^{(N-1)} w_i e^{-\mu_i t} \quad \text{(B.7)}$$

then since

$$\frac{\langle \rho_{i\alpha}\rho_{i\beta}\rangle}{s_i} = \delta_{\alpha\beta}[\lambda_\alpha{}^2 + (1 - \lambda_\alpha{}^2)\mu t M_{ii} + O(t^2)]$$

and $\sum_{i=1}^{(N-1)} M_{ii} = \sum_{(i=1}^{(N-1)} \mu_i$, we have $w_i = 1$.

Finally we therefore have that a mode approximation to the relaxation gives

$$G(t) = \sum_{i=1}^{(N-1)} e^{-\mu_i t} \quad \text{(B.8)}$$

where $\mu_i$ are eigenvalues of $\boldsymbol{M}$ defined by (B.2).

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# Theory of Thermoreversible Gelation

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ABSTRACT: A simple model is introduced to describe observed coexistence of gelation and phase demixing in atactic polystyrene solutions. Our theory demonstrates that the multiple-equilibria conditions for molecular clustering caused by physical cross-linking can describe the characteristic features of the temperature–concentration phase diagram. Detailed calculations are made for the concentration dependence of the gelation curve, the spinodal curve, the mean cluster size, and the osmotic pressure under the assumption that intracluster association is negligible. Effect of molecular weight and functionality is examined. Our results show reasonable agreement with experimental data obtained for atactic polystyrene in carbon disulfide. The condition for the gelation line to pass over the critical demixing point is clarified.

## 1. Introduction

Since the discovery[1] that certain chemically inactive atactic polystyrene (at-PS) solutions can exhibit gelation, there has been a growing interest[2-6] in the phenomena of physical gelation. Recent experimental studies[2,3] have furnished strong evidence that the gelation is thermally reversible and a fairly universal phenomenon that takes place in a wide variety of solvents. Although the origin of associative interchain interaction has not been clarified, the binding energy connecting a pair of polymer segments is expected to be of the order of thermal energy, so that bonding–unbonding equilibrium is easily attained. The current understanding of the experimental observations is based on the co-occurrence[2] of sol–gel transition and two-phase separation on the temperature–concentration phase diagram. Effect of the molecular weight of at-PS and of solvent species has been examined[2,3] in detail. Although quantitatively different, the essential characteristics of the phase behavior are found to be preserved regardless of these substitutions.

Only few attempts have been made to develop theories that would describe such phase behavior, and they are highly qualitative. For example, de Gennes[7] presented an overall picture about the competition between gelation and segregation in some polymeric solutions. As the molecular origin of the phase behavior was not sufficiently elucidated in this study, neither the precise position of the phase boundary nor any solution properties were calculated.

Coniglio et al.[8] proposed a microscopic model on the basis of the original classic ideas of gelation developed by Flory[9-11] and Stockmayer.[12] Though there were some findings on the relationship between the gelation line and the coexistence curve, it was impossible to relate a model parameter $p$ (percolation probability) with the solute concentration without ambiguity. Hence, they did not calculate physical quantities, such as mean cluster size or osmotic pressure, *as a function of the concentration.*

Some computer simulations[13] were attempted in relation to the lattice percolation theory. Because the molecular basis of the percolation model is not clear, difficulty remains in interpreting the model parameters in terms of the system quantities on which the real solution will depend.

Although these researches have thrown much useful light on many aspects of the general problem, it is the purpose of this paper to establish a microscopic foundation for the study of associating solutions and to give a complete picture to the important case of thermoreversible gelation.

We start with the lattice theory of polydisperse solutions originally developed by Flory[14,15] and Huggins[16] and in-

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