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L. Leibler, M. Rubinstein, R. Colby. Dynamics of telechelic ionomers. Can polymers diffuse large distances without relaxing stress?. Journal de Physique II, 1993, 3 (10), pp.1581-1590. 10.1051/jp2:1993219. jpa-00247926

HAL Id: jpa-00247926 https://hal.science/jpa-00247926

Submitted on 4 Feb 2008

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Dynamics of telechelic ionomers. Can polymers diffuse large distances without relaxing stress?

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(Received 8 April 1993, accepted 18 June 1993)

Abstract. — We consider dynamics of entangled telechelic ionomers in the limit of strong association, where there are no free chain ends. Stress relaxation occurs in such a system by an exchange between pairs of chain ends in the associated state. For complete relaxation of stress, an exchange event must **take** place on every entanglement strand. However, diffusion can occur on an arbitrarily shorter time scale, leading to the interesting result that chains can diffuse distances many times their coil size without relaxing stress.

Due to the relation between stress and orientational correlations in polymers [1], there is a general belief that diffusion and stress relaxation are coupled in polymer systems. There are examples where stress relaxation occurs much faster than diffusion, such as in a melt of star polymers [2], but the opposite case, where chains diffuse many times their sire without relaxing stress, is quite rare. One exception is semidilute solutions of disordered, rod-like polymers [1], for which translational diffusion is fast compared to rotational diffusion, which determines the time scale for stress relaxation. Due to the large aspect ratio of long rods, rotation through a small angle requires large translation. Another exception is a polydisperse system of flexible chains, where the measured diffusion coefficient reflects some average dominated by fast-moving (small) species, while the relaxation time is dictated by the slowest (largest) species. The question arises whether monodisperse flexible polymer chains can ever diffuse arbitrarily large distances without relaxing orientational correlations, and hence stress. The time scale for diffusion in polymers $au_{\rm diff}$ is defined as the time it takes for a chain to diffuse a distance of order of its coil size, which we take to be its end-to-end distance $R \simeq b N^{1/2}$, N being the number of monomers (Kuhn segments) and **b** being the monomer length

$$\tau_{\rm diff} \simeq \frac{R^2}{D} \,, \tag{1}$$

where D is the (three-dimensional) self-diffusion coefficient. Note that we drop numerical prefactors of order unity throughout the paper.

The relaxation time is typically associated with the longest mode encountered in a stress relaxation experiment. In other words, for times longer than the relaxation time, the stress u decays as a single exponential in time t

$$\sigma \sim \exp\left(-t/\tau_{\text{relax}}\right). \tag{2}$$

Experimentally, for monodisperse linear polymers τ_{relax} is slightly shorter [3, 4] than τ_{diff} , and for branched polymers τ_{relax} can be considerably smaller [2] than τ_{diff} . However, examples of monodisperse flexible polymer systems with $\tau_{\text{relax}} > \tau_{\text{diff}}$ are not found in the experimental literature. Here we develop a theory for stress relaxation and diffusion in concentrated solutions of monodisperse flexible linear telechelic polymers with no free chain ends. This situation could be realized in chains having opposite charger on each of their two ends [5] (with no unattached counter-ions) or in chains with singly-charged ionic groups of the same sign attached to each of their ends, in the presence of divalent counter-ions [6]. The ends of such chains exist solely in pairwise association states, due to strong ionic interaction. Pairs of chain ends are capable of forming reversible junctions through polar interactions. We show that in certain circumstances the chains comprising these reversible networks can indeed diffuse distances that are large compared to their size on time scales that are short compared to the stress relaxation time.

Consider a concentrated solution or melt of linear chains (with N monomers) with singly charged ionic groups at each of their ends. If the charges are of opposite sign, we have the telechelic ionomer shown schematically in figure la. In hydrocarbon media (low dielectric constant) the ends will be paired to minimize free energy, as shown in figure 1b. If the charges are of the same sign, we have the more conventional telechelic ionomer, schematically shown in figure 2a. For charge neutrality there must be oppositely charged counter-ions present. We focus on the case of divalent counter-ions. In low dielectric constant media, each divalent counter-ion will be strongly bound to two chain ends, shown in figure 2b.

In either case, the chain end pairs (hereafter called stickers) can lower their free energy further by associating to form larger groups of ions (so-called multiplets) through polar



Fig. 1. — Schematic representation of a telechelic chain with charges of opposite sign at its two ends : a) telechelic ionomer; b) ionic association of two chain ends; c) quadrupolar association state.



Fig. 2. — Schematic representation of a telechelic chain with like charges at its two ends : a) telechelic ionomer; b) ionic association of **two** chain ends with a divalent counter-ion; c) polar association state.

interactions. For simplicity we focus on the strongest of these interactions, shown schematically in figures 1c and 2c. These polar interaction energies are considerably weaker than the ionic ones of figures 1b and 2b (of order a few kT at room temperature), and thus these polar associations are reversible junctions. We define p to he the probability of a sticker to be in a multiplet, and thus the probability of a sticker to he free from multiplets (i.e. the simple chainend pair states of Figs. 1b, 2b) is 1 - p. We define the lifetime of the sticker in the associated State (multiplet) to he T. The situation is very similar to that discussed in reference [7]. The polar associations act as temporary crosslinks and the system as a whole is a reversible network. The strong pairwise association of chain ends causes formation of trains of chains between multiplets, hereafter called superchains, with effective degree of polymerization that can be much larger than N. Thus the system is usually highly entangled even when $N < N_{s}$, the number of monomers in an entanglement strand. The effect of surrounding chains is modeled by a tube of diameter $a = bN_e^{1/2}$. The details of the multiplet state are not important for dynamics — any sticker in the associated state is confined to a volume of roughly a^3 , from which it cannot move until it leaves the associated state.

We assume there is a thermal equilibrium between the associated and free states of stickers. As discussed in reference [7], the two parameters p and τ are sufficient to fully describe the kinetics of association and dissociation of the stickers. For example, the average duration of a single sticker free from the multiplets is $\tau_1 = \tau (1 - p)/p$.

We consider the dynamics of a labeled telechelic chain in this reversible network. The situation is analogous to reversible networks made up of long chains with stickers regularly spaced along the chain [7], with the main difference now being that the effective chain length is infinite (no free ends). At short times the curvilinear motion of the labeled chain along its tube is subdiffusive. In contrast to the standard situation of entangled polymers, the effective friction for times longer than τ is controlled by the opening and closing of reversible junctions. The time dependence of the mean-square curvilinear displacement of a monomer along the tube is still

$$\Delta^{2}(t) = a^{2} \left(t / \tau_{\rm eff} \right)^{1/2}, \tag{3}$$

but with τ_{eff} being the effective Rouse time of an entanglement strand, modified by the presence of the stickers. The detailed mechanism of motion of a chain of S stickers and finite number of monomers M = N (S + 1j was discussed in reference [7]. Since τ_{eff} measures local chain dynamics, it does not depend on the overall chain length in the multisticker problem. On short time scales chain motion is Rouse-like, with

$$\Delta^{2}(t) = \frac{M}{m} a^{2} (t/T_{\text{Rouse}})^{1/2} ,$$

where the effective Rouse time of the chain is proportional to the square of the number of stickers in the limit of large M, S, and $p \approx 1$.

$$T_{\text{Rouse}} \simeq \tau S^2 . \tag{5}$$

Hence, the effective Rouse time of an entanglement strand scales like

$$\tau_{\rm eff} \simeq \tau \left(N_{\rm e}/N \right)^2 \,. \tag{6}$$

This simple result is only valid when the majority of junctions are closed ($p \approx 1j$). The more general situation has a friction that depends on p, the average fraction of closed junctions

$$\tau_{\rm eff} \simeq \tau \left(N_{\rm e}/N\right)^2 / f\left(p, \, k_{\rm max}\right) \,. \tag{7}$$

The function $f(p, k_{\text{max}})$ was derived in reference [7].

$$f(p, k_{\max}) = \frac{p^3}{4} \sum_{k=1}^{\infty} (1-p)^{k-1} k \begin{cases} (k+1)^3 \\ (k_{\max}+1)^3 (\frac{k_{\max}}{k}) \end{cases}$$

where we have summed the contributions from the various k-strands (successions of k open stickers) weighted by their probabilities of occurence, whereas only the k = 1 process is active when $p \cong 1$ (cf. Eq. (6)). The sum is split into two parts : for $k < k_{max}$ the strand of k open stickers can equilibrate by Rouse motions during the lifetime of the k-strand, while for $k > k_{max}$ the equilibration is incomplete. The parameter k_{max} was thus evaluated by matching the Rouse time of the k-strand with the lifetime of the k-strand [7], resulting in

$$\left[(k_{\max} + 1) \frac{N}{N_e} \right]^2 \tau_e = \frac{\tau_1}{k_{\max}},$$

where τ_1 is the lifetime of a single open sticker and τ_e is the Rouse time of a chain of N_e monomers.

The monomer displacement remains subdiffusive (with $\Delta^2 \sim t^{1/2}$) as long as the chains are confined to their original tubes. Since we consider the limit with no free ends, the only way for a chain to get out of its original superchain tube is by a *multiplet exchange* [8]. This exchange process is shown schematically in figure 3 for the simplest association of chain-end pairs. We demonstrate the exchange process for the case of a conventional telechelic ionomer with divalent counter-ions, hut the case of telechelic ionomers with opposite charges at their two enda (Fig. 1) is perfectly analogous. Initially (Fig. 3a) the two chains are confined to their original tubes. Through subdiffusive motion, their sticker pairs meet and form a polar association (Fig. 3b). After time τ the polar association breaks, and the chains can either recombine in their previous pairs (Fig. 3a) or they can exchange in the associated state and



Fig. 3. — The quadrapolar exchange process : a) initial state showing two chains trapped inside their tubes; b) the quadrapolar association; c) final state showing chains moving into new tubes after the **exchange**.

emerge in new pairs (Fig. 3c). Notice that after the exchange occurs, the chains can diffuse into new tubes.

The multiplet exchange process is described by the characteristic time τ^* , which is the average time between exchange events **for** a given chain end. The probability **of** a given sticker to be unexchanged after **a** time t is

$$Q(t) = \exp\left(-t/\tau^*\right). \tag{9}$$

We need to calculate the (time-dependent) average contour length between exchanged chain end pairs, $L(t) = \langle X(t) \rangle aN/N_e$. The average number of primary chains between exchanged chain end pairs is given by one-dimensional percolation [9]

$$\langle X(t) \rangle = \frac{1+Q(t)}{1-Q(t)},$$
 (10)

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$$L(t) = a \frac{N}{N_e} \frac{1 + Q(t)}{1 - Q(t)} = a \frac{N}{N_e} \frac{1 + \exp(-t/\tau^*)}{1 - \exp(-t/\tau^*)} = a \frac{N}{N_e} \coth(t/2\tau^*).$$
(11)

The subdiffusive monomer motion described by equation (3) ends at time scale T_1 , when the typical monomer's motion begins to be influenced by exchange events (when the Rouse time of the chain between exchange events is reached). Thus $T_1 \equiv (L(T_1)/a)^2 \tau_{eff}$ and using equation (11), we obtain the equation for time scale T,

$$(T_1/\tau_{\rm eff})^{1/2} \simeq \frac{N}{N_{\rm e}} \coth (T_1/2\tau^*)$$
 (12)

This time criterion corresponds to a mean-square curvilinear displacement $\Delta^2(T_1) \cong aL(T_1)$. In the limit where subdiffusive motion is fast compared with exchange events $(T_1 \ll \tau^*)$, coth $(T_1/2\tau^*) \cong 2\tau^*/T_1$, and we get

$$T_{\rm I} \simeq \left(2 \frac{N}{m} \tau^* \right)$$

On time scales beyond T, the curvilinear displacement of a monomer along the tube is diffusive, with a curvilinear diffusion coefficient

$$D_1 \equiv aL(T_1)/T_1 \simeq a^2/(T_1 \tau_{\text{eff}})^{1/2} .$$
(14)

The three-dimensional monomer motion remains subdiffusive until the curvilinear monomer fluctuations reach the coherence length between exchange events. This time scale is T_2 , determined by $\Delta^2(T_2) \cong D_1 T_2 \cong L^2(T_2)$, which leads to

$$\left(\frac{N}{N_{\rm e}}\right)^2 \coth^2(T_2/2\tau^*) = \frac{T_2}{(T_1 \ \tau_{\rm eff})^{1/2}}$$

In the slow exchange limit $(T_2 \ll 2\tau^*)$, this reduces to

$$T_2 \simeq \left(2\frac{N}{N_e}\tau^*\right)^{7/9}\tau_{\rm eff}^{2/9} \tag{16}$$

The (three-dimensional) self-diffusion coefficient of the primary chains is

$$D \simeq \frac{a}{L(T_2)} D_1 \simeq \frac{aL(T_2)}{T_2} \simeq \frac{a^2}{T_2} \frac{N}{N_e} \operatorname{coth} (T_2/2\tau^*)$$
(17)

In the slow exchange limit $(T_2 \ll 2\tau^*)$ the self-diffusion coefficient is

$$D \simeq 2 a^2 \frac{N}{N_e} \frac{\tau^*}{T_2^2} \simeq a^2 \left(2 \frac{N}{N_e} \tau^*\right)^{-5/9} \tau_{\text{eff}}^{-4/9},$$
(18)

and the time required for a chain to diffuse a distance of order of its size is

$$\tau_{\rm diff} \simeq \left(\frac{N}{N_e}\right) 14/9 \ (27^*)^{5/9} \ \tau_{\rm eff}^{4/9} \tag{19}$$

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N° 10

The three-dimensional mean-square monomer displacement $\Phi(t)$ is calculated from the mean-square curvilinear displacement $\Delta^2(t)$ along the tube in the usual manner [I], remembering that the tube itself is a random walk. $\Phi(t)$ and $\Delta^2(t)$ are plotted in figure 4 and the relevant time scales are summarized in table I. This plot is very similar to that for simple reptation of flexible linear polymers [1]. Up to the Rouse time of the average chain strand between closed stickers, T_s the dynamics are identical to those of a linear chain on time scales less than its Rouse time. Between T_s and the lifetime of a sticker τ , no net monomer displacement occurs, as the Rouse modes of a strand between closed stickers have completed, and further displacement must await the opening of the associations (on time scale τ). The curvilinear monomer displacement at τ is $\Delta^2(\tau) \approx az$ where $z \approx a (T_s/\tau_e)^{1/2} = a(\tau/\tau_{eff})^{1/2}$ and the three-dimensional displacement is $\Phi(\tau) \neq a^{3/2} z^{1/2}$. Between τ and T, (the time where exchange events start to influence monomer displacement) the curvilinear displacement is subdiffusive ($\Delta^2 \sim t^{1/2}$ and thus $\Phi \sim t^{1/4}$). As discussed before, τ_{eff} is the effective Rouse time of an entanglement strand, determined by extrapolation of the subdiffusive motion between τ and T, back to the tube diameter (see Fig. 4). T_1 is the Rouse time of the largest portion of chain or string of chains that moves without knowledge of exchange events. The curvilinear monomer displacement at T_1 is $\Delta^2(T_1) = \mathcal{L}(T_1)$ and the three-dimensional displacement is $\Phi(T_1) = a^{3/2} [L(T_1)]^{1/2}$. T_2 is the time where exchange events allow the monomer motion to no longer be confined to the original tube. Between T, and T_2 the curvilinear displacement is diffusive, but the three-dimensional displacement is not $(\Phi \sim t^{1/2})$, in exact analogy with normal linear polymers between the Rouse and reptation times of the chain. Beyond T_2 the three-dimensional monomer displacement is diffusive. The diffusion time $\tau_{\rm diff}$ is determined by extrapolation of the three-dimensional mean-square displacement in the diffusive regime $(t > T_2)$ back to the end-to-end distance of a single chain *R*', as shown in figure 4.



Fig. 4. — Three-dimensional mean-square displacement of a monomer Φ (solid curve) and mean-square curvilinear displacement of a monomer along the tube Δ^2 (dashed curve) as functions of time. Logarithmic scales. See table I for an explanation of time scaler.

Table	Ι.	- Summary	o£ rimes	scales f	for te.	lechelic	ionomers.
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τ	duration of a temporary association of chain end pairs				
	closed sticker lifetime)				
τ1	duration of the unassociated state for a chain end pair				
	(open sticker lifetime).				
τ _e	Rouse time of an entanglement strand without association				
⁷ eff	effective Rouse time of an entanglement strand with				
	association				
τs	Kouse time of a strand between closed stickers				
τ1	time scale when exchange events begin to influence				
monomer motion					
	(curvilinear monomer displacement becomes diffusive)				
τ_2	time scale when monomer displacement becomes diffusive				
⊄diff	diffusion time of a single chain				
τ*·	time between exchange events for a given chain end				
[∵] relax	stress relaxation time				

Stress relaxation in ordinary linear polymers (without ionic groups) occurs by chain ends abandoning entanglements as the chain diffuses out of its original confining tube [1]. Since we consider the limiting case of no free ends in these telechelic ionomers, one may wonder whether stress will relax at all in these systems. However, stress can relax by the mechanism of multiplet exchange [8]. As can be seen in figure 3, multiplet exchange events change the topology of the system. For complete stress relaxation, all entanglements along a given chain must be abandoned. Hence, to relax completely by multiplet exchange, an exchange event must occur in each tube section [10]. Since we are focusing on the limit where exchange events are rare, each tube section has chain end pairs visiting it many times before an exchange event occurs. Therefore, the stress relaxation time is simply the product of the average time between exchanges and the number of entanglement strands per chain

$$\tau_{\rm relax} = \tau * N/N_{\rm e} \,. \tag{20}$$

We are now in a position to compare time scales for diffusion and stress relaxation. Their ratio can he made arbitrarily large by choosing $\tau^* \ge \tau_{eff}$.

$$\frac{\tau_{\text{relax}}}{\tau_{\text{diff}}} \cong \left(\frac{2N}{N_{\text{e}}}\right)^{-5/9} \left(\frac{\tau^*}{\tau_{\text{eff}}}\right)^{4/9} \tag{21}$$

We therefore predict that it is indeed possible to have a situation where chains diffuse many times their size without relaxing stress. An example of this prediction is shown in figure 5 for



Fig. 5. — p-Dependence of the ratio of relaxation time and diffusion time fur a specific example with $N = N_{r}$, $\tau = 100 \tau_{e}$ and E = 2/3. The ordinate is the square of the number of coil sizes chains diffuse before relaxing stress. The solid curve is the prediction of equation (21). The dashed line is the asymptotic (low p) expansion result (Eq. (22)).

 $N = N_e$ and $\tau = 100 \tau_e$ (in this case equation (21) is it very good approximation to the full prediction). When the probability of polar association, p, is small, the chains diffuse many times their coil size during the stress relaxation time. Also shown in figure 5 as a dashed curve is the asymptotic behavior for small p, obtained by expanding equation (8)

$$\lim_{p \to 0} \frac{\tau_{\rm relax}}{\tau_{\rm diff}} \simeq \frac{\pi^{2/9}}{2^{17/9} E^{4/9}} \left(\frac{N}{N_{\rm e}}\right)^{-19/27} \left(\frac{\tau}{\tau_{\rm e}}\right)^{14/27} p^{-8/27} , \qquad (22)$$

where we have used the expression $\tau^* = (\tau + \tau_1 j/E \equiv \tau/(pEj (E \text{ is the efficiency factor for exchange, taken to he 213 in Fig. 5).$

Whether this situation can be experimentally realized with conventional telechelic ionomers is not known. Telechelic ionomers are synthesized by neutralizing acidic groups at the chain ends with inorganic salts. In order to avoid free ends in the system, one needs to neutralize all acidic groups. In practice this is never achieved, possibly due to an equilibrium being reached short of 100 % neutralization or a kinetic problem of chain ends finding each other as the neutralization nears completion. Complete substitution is essential for the limit we consider (no free chain ends). Thus new methods of making more perfect telechelic ionomers may need to he developed to test the interesting prediction that relaxation can be slow compared to diffusion. Another possibility for avoiding free ends is to use a positive charge on one end of the chain. and a negative charge on the other end, with no counter-ions (see Fig. 1). Studies on such materials have recently been started [5]. It is important to recognize that real systems may have some small number of chain ends at equilibrium. In this case, stress relaxation and diffusion will he slowed by electrostatic associations, hut the distinction between diffusion time and relaxation time rapidly disappears as free chain ends are introduced.

Experimentally, telechelic ionomers have been of interest for over a decade [6]. Although the details of the ionic association states are not yet understood, structural studies on telechelic

ionomers indicate that chain dimensions are not affected by association of the ends [11, 12]. Recent viscoelastic experiments on telechelic ionomers with divalent counter-ions [13, 14] (i.e. calcium, copper) indicate a very pronounced plateau, with an extremely long relaxation time. However, diffusion measurements have not been made for these systems. On the practical side, these materials may have potential application in synthetic biological tissue, where both structural integrity and global rearrangements are required.

Acknowledgements.

The financial support and hospitality of Eastman Kodak Company while Ludwik Leibler was a visiting scientist are acknowledged with gratitude.

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