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and a new approach to the study of entanglements and flow-induced chain scission.

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# Stress Relaxation and Chemical Kinetics in Pairwise Associating Polymers

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ABSTRACT: Within the framework of the tube model, a theoretical study is made of the dynamics of a concentrated system of long flexible macromolecules, each of which has a single functional end group that can associate with another such group to make a dimer. When the dissociation time of the dimer ($\tau_{\rm break}$) is very large compared with $T_{\rm d}$, the disengagement time of an undimerized chain (or "monomer"), the zero-shear viscosity of the system approaches $\eta = (16q + 1)\eta_0/(2q + 1)$, with $\eta_0$ the viscosity of pure monomers and $q$ the equilibrium ratio of dimers to monomers. In the opposite limit ($\tau_{\rm break}/T_{\rm d} \equiv \alpha \rightarrow 0$), the viscosity tends to $\eta = (2q + 1)\eta_0/(q + 1)$. For intermediate $\alpha$ (roughly $0.02 < \alpha < 50$), $\eta$ depends quite sensitively on $\alpha$ and $q$; the relevant behavior is studied numerically. The results may be useful in obtaining estimates of the dissociation rate from measurements of the static equilibrium constant and the zero-shear viscosity.

## Introduction

In recent years, there has been growing experimental and theoretical interest in associating polymers.[1-9] These are flexible chain molecules each containing one or more functional groups, which can form transient associations with one another. Such polymers frequently exhibit striking rheological behavior, such as shear thickening; they are of increasing technological importance as flow-modifying additives.[2-4] To be able to make best use of these materials, it is important to try to understand the relationship between the kinetics of association and dissociation and macroscopic flow properties. Conversely, one would like to be able to use rheological measurements on simple systems to obtain information concerning the underlying reaction kinetics.

Perhaps the simplest case of interest is when (i) the associating groups have a strong dimerizing interaction, such as occurs between carboxylic acid groups in a nonpolar solvent, and (ii) there is exactly one associating group, at one end, of every chain. In this case, there is a dynamic equilibrium between unassociated chains ("monomers") and 2-fold associates ("dimers"). Clearly, one expects the viscosity of the system to be higher than that of the unfunctionalized monomer. As emphasized by Worsfold and Bywater,[6] however, the magnitude of this viscosity enhancement can depend not only on the equilibrium constant for the dimerization but also on the reaction kinetics. These become relevant if the dissociation rate is high enough that significant rearrangement of the associations occurs on the characteristic time scale of stress relaxation (the terminal time).

In the present work, we assume that the equilibrium constant, or (equivalently) the ratio $q$ of the equilibrium number densities of dimers to monomers, is known:

$$q \equiv [\text{dimer}]/[\text{monomer}] \tag{1}$$

We then study theoretically the stress relaxation behavior as a function of the reaction rate for dissociation. We will assume throughout that the chains are long enough (and the concentration high enough) to be always in the strongly entangled regime, in which the viscosity is a rapidly increasing function of chain length. In this regime, the dynamics of stress relaxation in the absence of functional groups is understood semi-quantitatively in terms of the tube model;[10,11] it only remains to incorporate the effects of the associations. Earlier work by the author has focused on extending the tube model to the case of "living polymers"—chains which can break reversibly at any point in the chemical sequence.[12,13] The physics in the present case is rather different, since breakage of a dimer is only possible at the midpoint; nonetheless, several of the basic ideas can be taken over, with a minimum of modification, from ref 12.

## Reptation

In the tube model,[10,11] the dominant stress–relaxation pathway for an entangled polymer system is presumed to

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consist of a gradual disengagement of each chain, by curvilinear diffusion along its own contour, from a tubelike environment. The tube represents the topological effects of neighboring chains, which inhibit diffusion normal to the chain contour. This snakelike disengagement process is known as "reptation". The curvilinear diffusion constant of a chain in its tube is $D_c(L) \propto 1/L$, where $L$ is the chain length. The time $T_d(L)$ for a chain to disengage from its tube obeys $D_cT_d \sim L^2$; more precisely, we define the disengagement time by[11]

$$T_d(L) = \frac{L^2}{\pi^2 D_c(L)} \tag{2}$$

The zero-shear viscosity of a system of unassociated chains of length $L$ may be written as

$$\eta(L) = G_e\tau(L) \tag{3}$$

where $G_e$, the plateau modulus, is independent of $L$ at fixed overall chain concentration, and where

$$\tau(L) = \frac{\pi^2}{12}T_d(L) \tag{4}$$

Hence the tube model predicts $\eta(L) \sim L^3$, as opposed to the empirically determined[14] law $\eta(L) \sim L^{3.4}$. (The distinction between these two results is presumably not crucial to the dimerization problem discussed here, in which $L$ varies by only a factor of 2.) Also of interest is the stress relaxation function $G(L,t) \equiv G_e\mu(L,t)$; here $\mu(L,t)$ is the fraction of shear stress remaining at time $t$ after a small step strain is applied at time zero. For a system of monodisperse chains, $\mu(L,t)$ shows a nearly pure exponential decay at all but the shortest times:[11]

$$\mu(t) = \frac{8}{\pi^2}\sum_{p\,\text{odd}} p^{-2}\exp[-p^2t/T_d(L)] \tag{5}$$

Note that the terminal time $\tau(L)$ is related to $\mu(L,t)$ by $\tau(L) = \int_0^\infty \mu(L,t)\,\mathrm{d}t$.

To see how these results arise, imagine an entangled polymer system to which a small strain applied at time $t = 0$. As time passes, each chain gradually reptates out of its original tube. When this occurs, a new tube is created that is in equilibrium in the strained environment, and hence carries no stress. Thus the stress relaxation function $\mu(t)$ is simply the fraction of the original tube still occupied at time $t$—that is, the average fraction of an original tube through which neither chain end has passed by this time. To compute this quantity, we focus attention on some randomly chosen portion of tube. Representing a chain as a line interval of length $L$, we can treat the tube segment as a particle launched at random on the line at time zero, which moves with diffusion constant $D_c(L)$. (We have chosen a reference frame in which the chain is stationary.) As soon as the "particle" reaches either end of the line interval, the stress associated with the corresponding tube segment is lost. Hence $\mu(L,t)$ is simply the *survival probability* to time $t$ of a particle of diffusion constant $D_c(L)$, launched at random on a line of length $L$, with absorbing boundary conditions at either end. Using this correspondence, it is straightforward[11] to derive the results (2)–(5).

## Effects of Associations

We now consider the effects of associations. For simplicity, we choose units of length so that $L = 1$ for an unassociated chain. Also, let us define a parameter

$$\alpha \equiv \tau_{\text{break}}/T_d(1) \tag{6}$$

where $\tau_{\text{break}}$ denotes the lifetime of a dimer before dissociating. It is easily checked that the lifetime of a monomer before recombining into a dimer is

$$\tau_{\text{rec}} = \tau_{\text{break}}/2q \tag{7}$$

We are interested in the behavior of the terminal time, $\tau(\alpha,q)$, as a function of $\alpha$, which measures the dissociation rate, and $q$, which measures the partition between dimers and monomers. Since $G_e$ is independent of the associations, we have for the viscosity simply

$$\eta(\alpha,q) = G_e\tau(\alpha,q) \tag{8}$$

In what follows, we will assume that, when a dimer dissociates, the subsequent recombination reactions of the two newly created monomers are typically with other nearby monomers, rather than with each other. This will hold so long as the volume explored by an associating group within its lifetime, $\tau_{\text{rec}}$, is large enough to contain many other such groups with which it could recombine. Presuming, for simplicity, that only unassociated groups are reactive (that is, neglecting recombination via interchange with a member of an existing dimer) and denoting the chain volume fraction by $\phi$, we find that, for concentrated chains, the condition for this mean-field assumption to hold is[12]

$$\alpha/q \gg \phi^{-4/3}(L/a)^{-2/3}(2q + 1)^{-4/3} \tag{9}$$

Here $a$ denotes a microscopic length comparable to the size of a repeat unit of the polymer chain. Since the factor $(L/a)^{-2/3}$ on the right is very small, we expect the condition (9) to be obeyed in most cases of interest (at least in concentrated systems).

Subject to this assumption, it remains true that the stress associated with any particular tube-segment will relax as soon as an unassociated chain end passes through that segment. This enables us to include the effects of associations, with only a small modification to the tube model. We can again represent a randomly chosen tube segment as a diffusing particle on a line but must now allow for the fact that the line itself can undergo discrete changes in length (by virtue of dissociation and recombination reactions) with corresponding changes in the diffusion constant of the particle. The elementary processes to be considered are shown schematically in Figure 1.

We start our discussion with the limit $\alpha \to \infty$, in which the problem becomes trivial. Recall that $\mu(t)$ is the survival probability of a randomly chosen segment of tube. Such a segment starts on a dimer or monomer with probability $p_d \equiv 2q/(2q + 1)$ or $p_m \equiv 1/(2q + 1)$, respectively. Since no rearrangement of the associations occurs on the time scale of relaxation, $\mu(t)$ is just the weighted average

$$\mu(t) = p_d\mu(2,t) + p_m\mu(1,t) \tag{10}$$

Correspondingly the terminal time is

$$\tau(\alpha{\to}\infty,q) = p_d8\tau_0 + p_m\tau_0 = \frac{16q+ 1}{2q + 1}\tau_0 \tag{11}$$

Here $\tau_0 \equiv \pi^2T_d(1)/12$ denotes the terminal time of the corresponding system of unassociated monomers.

A little less obviously, the behavior also becomes simple in the opposite limit of $\alpha \to 0$. In this case, the diffusing particle moves on a line that fluctuates rapidly between length 2 and length 1; the fraction of time spent in each of these two states is, respectively, $p_d$ and $p_m$. We now argue that, for $\alpha \to 0$, the particle will be absorbed ("fall off the line") as soon as it reaches either end of the *monomer* it is on. In other words, if it is on a dimer, and

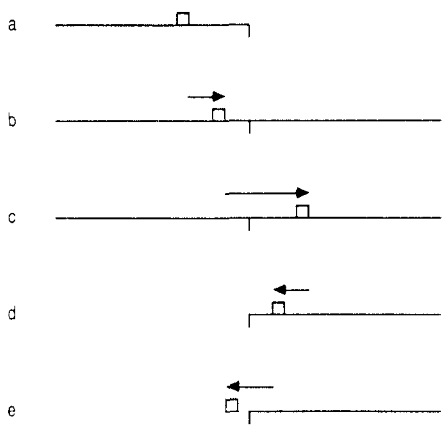

**Figure 1.** Typical sequence illustrating the coupled polymer diffusion and dissociation/recombination processes. An unassociated chain (a) is represented by a line of unit length, upon which a particle (representing a tube segment) can diffuse with diffusion constant $D_c(1)$. Such a chain can dimerize (a → b); the particle now has diffusion constant $D_c(2)$ and can, in principle, diffuse across the central juntion point, as in (c). The dimer can dissociate (d), leaving the particle on either one of its constituent monomers. The diffusing particle is lost when it reaches an unassociated chain end, such as in (e).

reaches the central junction point, it is virtually certain to "fall off" during one of the frequent (although very brief) intervals during which the dimer is temporarily dissociated. In this case, one might expect[7] $\tau \to \tau_0$; but that is not correct, since the average curvilinear diffusion constant is still affected by the associations.

Specifically, when breaking and recombination are both frequent, the diffusion constant with which the particle moves is the time average

$$D_c = p_d D_c(2) + p_m D_c(1) = \frac{q+1}{2q+1} D_c(1) \qquad (12)$$

The corresponding terminal time is therefore

$$\tau(\alpha \to 0; q) = \frac{2q+1}{q+1} \tau_0 \qquad (13)$$

The stress relaxation spectrum in this limit should be of the same form as for a pure system of unassociated chains (eq 5), but with a shifted time scale corresponding to the new value of the curvilinear diffusion constant, eq 12.

## Numerical Calculation for Intermediate $\alpha$

When $\alpha$ is of order unity, the problem of computing the terminal time is no longer analytically tractable. However, given our previous assumptions, it is straightforward to implement numerically the coupled stochastic processes of polymer diffusion and chemical kinetics, as depicted in Figure 1. The computation of $\tau(\alpha,q)$ was performed with a Monte Carlo algorithm closely related to that described in detail in ref 12. The diffusion of the particle is allowed to take place in discrete steps, which are short compared to the length of the line segment (in all cases the ratio being less than 0.02); at each time step, dimerization (of a monomer) or dissociation (of a dimer) is allowed to occur, with the appropriate probability.

Values of the terminal time, $\tau$, were computed for seven values of $q$ (with $0.2 \le q \le 20$) and six values of $\alpha$ (with $0.02 \le \alpha \le 50$). To obtain good statistics, between 2000 and 5000 runs were required for each of these 42 grid points. An estimate of the remaining (statistical and discretization) errors suggests that the computed values of $\tau(\alpha,q)$ are probably accurate to within a few percent; errors of this order are certainly not significant when compared with the contributions of alternative relaxation pathways, such as tube renewal,[15] that are present in any real polymer system but are completely omitted from our simplified treatment.

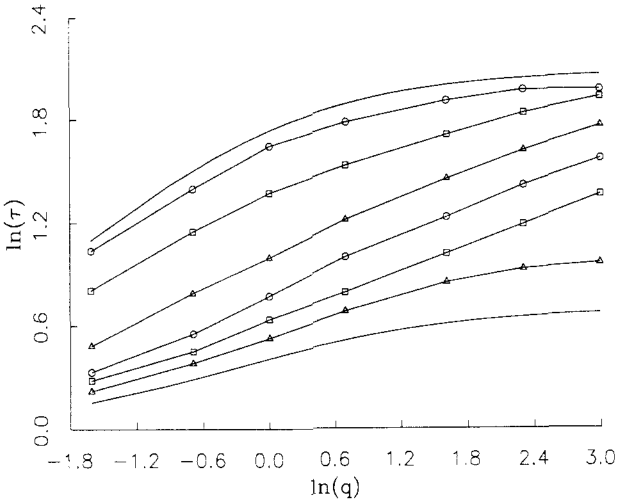

**Figure 2.** log–log plot of the terminal time $\tau(\alpha,q)$ versus the equilibrium ratio $q$ for various $\alpha$; $\tau$ is measured in units of $\tau_0$, the terminal time for a system of unfunctionalized monomers. The upper curve ($\alpha = \infty$) and the lower curve ($\alpha = 0$) are given by eq 11 and 13. The symbols denote computed values; from the bottom, these are for $\alpha$ = 0.02 (triangles), 0.1 (squares), 0.5 (circles), 2 (triangles), 10 (squares), and 50 (circles). The interpolating lines are to guide the eye.

The terminal time data are shown in log–log form in Figure 2. As might be expected, these show a smooth interpolation between the two limiting curves (given in eq 11 and 13 respectively for $\alpha \to \infty$ and $\alpha \to 0$). To see significant departures from either asymptote, one requires $50 > \alpha > {}^1/_{50}$, roughly speaking. Hence measurements of the viscosity can yield useful information on the dissociation rate constant so long as $\tau_{\text{break}}$ is within an order of magnitude or two either side of $T_d(1)$, the disengagement time of a monomer. To make best use of the predictions it is necessary to know to reasonable accuracy (by some other means) the equilibrium ratio $q$; then $\alpha$ may be estimated by comparing the measured ratio of the terminal times for the functionalized and unfunctionalized systems, $\tau/\tau_0$, with those of Figure 2. (Since, for long chains, $G_e$ is not affected by associations, $\tau/\tau_0$ is also equal to the ratio of the viscosities, $\eta/\eta_0$, of the two systems; compare eq 8.)

In the course of the simulation, data on the stress relaxation function $\mu(t)$ were also obtained. However, except for rather small values of $q$ and large values of $\alpha$, the behavior of $\mu(t)$ was in all cases quite close to a pure exponential decay; since the plots show no unusual features, we do not present them here. It appears that, for the purposes of estimating the dissociation rate, there is little to be gained by measuring the full relaxation function, $\mu(t)$, rather than simply the zero-shear viscosity, $\eta$.

## Discussion

The results given above provide a way of estimating the dissociation rate of (pairwise) associating polymers from measurements of their zero-shear viscosity and the static equilibrium constant for association. This information is potentially relevant to studies of any associating polymer in which the functional groups have a strong preference for 2-fold associations. The main assumptions are (i) that the chains are at high enough concentration for the tube model to offer an appropriate description of their dynamics and (ii) that successive dissociation and recombination reactions are uncorrelated, in the sense discussed above in connection with eq 9.

A system to which our new results are relevant is that studied experimentally by Worsfold.[7] He gives data for concentrated solutions of nitrophenol-capped polystyrenes, dissolved in diethylbenzene with a tertiary amine as linking agent. (Similar measurements on polymers end capped with carboxylic acid groups are currently in progress.[16]) For chains in the fully entangled regime (his polymer PS-S), Worsfold gives $q$ values in the range 0.3–0.5. The measured viscosities are of order $\eta/\eta_0 \simeq 1.21\text{–}1.35$; while there is considerable scatter, these results appear to be broadly consistent with eq 13. The indication is that, in this particular system, the dissociation time of a dimer may be very short compared to the disengagement time of a chain ($\alpha < 0.02$). If so, the observed viscosity enhancement can be attributed solely to the shift in the curvilinear diffusion constant $D_c$, as described by eq 10. It is interesting to find a rheological experiment in which the chain-length dependence of $D_c$ is, apparently, manifested in isolation from the other factors that determine the viscosity.

More generally, one can expect to find other systems for which the calculated curves of Figure 2 will yield semiquantitative estimates for $\alpha$, rather than just a bound as in this particular example. Certainly there are ion-containing polymers which undergo rather long-lived pairwise associations;[8] moreover the shear-rate-dependent rheological activity of other associating polymers[2–4] is an indication that the time scales for rearrangement of the associations, and for stress relaxation, are comparable in many cases of interest.

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# Electron Microscopy Studies of the Cofacial Phthalocyanine Polymers $(AlPcF)_n$ and $(SiPcO)_n$

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ABSTRACT: $(AlPcF)_n$ and $(SiPcO)_n$ (Pc = phthalocyanine ligand), both of which are cofacial polymers, have been studied by electron microscopy. $(AlPcF)_n$ has been examined after being sublimed onto glass or KCl. $(SiPcO)_n$ has been examined as synthesized. Films formed by heating $(SiPcO)_n$ and condensing the resulting vapors on KCl have also been studied. It is concluded that some of the molecules in $(AlPcF)_n$ have molecular weights in the range 18 000–23 000 and that the rings in the molecules are eclipsed. It is also concluded that the molecules in $(SiPcO)_n$ have quite variable molecular weights. Electron diffraction data indicate that the $(AlPcF)_n$ crystallites from both types of sublimations are tetragonal with $a = b = 13.37$ Å and $c = 3.6$ Å.

## Introduction

The first linear, cofacial phthalocyanine polymer reported was $(GePcO)_n$[1] (Pc = phthalocyanine ligand). Others that have been reported since are $(SiPcO)_n$,[2] $(SnPcO)_n$,[3] $(AlPcF)_n$,[4,5] $(GaPcF)_n$,[5] $(CrPcF)_n$,[6] and $(GePcS)_n$[7] (Figure 1).

A number of studies have been done on members of this family. A study of $(AlPcF)_n$ based on X-ray powder and other techniques[5] has led to the conclusion that its chains are packed parallel to each other and has yielded interring spacing data for it.[8] Results from an electron microscopy study of $(AlPcF)_n$[9] have been interpreted as providing data on the lengths of the chains. A single-crystal X-ray study of $(GaPcF)_n$[10] has shown that its chains are truly linear and its rings are eclipsed. It also has provided confirmation of the conclusion, derived in an earlier study based partly on powder data,[5] that its chains are packed parallel to each other. In addition, it has provided confirmation for and refinement of interring spacing data from the earlier study.[5] A powder study of $(SiPcO)_n$, $(GePcO)_n$, and

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