Macromolecules **1994**, *27*, 5037–5042

Bridging by Reversibly Adsorbed Telechelic Polymers: A Transient "Network"

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Received February 28, 1994; Revised Manuscript Received May 24, 1994®

ABSTRACT: In this work we study a model "network" formed by the reversible adsorption of telechelic polymers between two flat surfaces using the dynamic Monte Carlo technique on a cubic lattice. Chains of 50 segments are studied in an athermal solvent and in the weak overlap limit. The parameters varied are the end-adsorption energy (ϵ/kT) and separation of the surfaces (L). We investigate the effect of the adsorption energy and the surface separation upon the equilibrium bridging fraction and on the lifetime distribution of the bridges. The bridging fraction is seen to increase monotonically with adsorption energy and reaches a limiting value for strong adsorption; the bridging fraction decreases monotonically with increasing surface separation. The average bridging time increases exponentially, without limit, with the adsorption energy. The average bridging time is relatively insensitive to the spacing of the surfaces if the bridges are not stretched strongly compared to the rms end-to-end distance of free chains, and drops off steeply above a critical stretching rate. The fraction of bridges of a given lifetime falls exponentially with the lifetime. Accordingly the stress decay in the system after unit shear strain is also exponential. While the stress decay time is rather insensitive to the surface separation (below a critical stretch) the plateau modulus depends both upon the binding energy and the surface separation. The exponential dependence of the bridging lifetime allows a simple scaling of the time axis so that the normalized stress relaxation data for different binding energies fall on the same curve.

1. Introduction

Adsorption of polymers on colloidal particles controls the stability of colloidal suspensions.[1] Advances in the understanding of the thermodynamics of polymers at interfaces have been motivated in part by the quest for a better understanding of steric colloid control.[2,3] A major effect of the surface polymer layer, apart from colloid control, is the modification of the suspension rheology.[4] The tailoring of the viscoelastic properties of the suspension through polymer adsorption is a major application of polymers at interfaces. Reversible bridging of colloidal particles by randomly adsorbed or telechelic chains would form transient networks with interesting rheology. Indeed transient networks arising from the self-association of block polymers or polymers with "sticky" groups are known to dramatically affect the viscoelastic properties of polymer solutions (the "stickiness" could arise from dispersion forces, hydrogen bonding, ionic interactions, etc.).[5-8] These rheological applications depend not only upon the thermodynamics of the polymer chains at interfaces but also on the chain dynamics in the vicinity of the interface. In view of these exciting applications of polymers with sticky ends, recent theoretical works have focused upon elucidating the nature of transient networks formed by these chains.

In what follows we shall focus solely on telechelic polymer chains tethered by both ends to surfaces. (The situation is qualitatively similar to that obtained by the self-association of polymers with sticky ends.) Recently we have reported the results for strongly adsorbed and reversibly adsorbed telechelic polymer chains between two flat surfaces.[9] Lamellar systems of irreversibly adsorbed telechelic chains have also been addressed theoretically.[10-14] Lamellar systems, while providing a model for studying transient networks, in general, differ in some respects from transient networks formed by self-association of telechelic chains. The former have a far higher functionality; their compression and expansion are asymmetric and the shear and longitudinal moduli are no longer proportional to one another.

The *transient* response however of weakly adsorbed telechelic chains has not yet been addressed; in these systems, unlike permanent networks, stress can decay due to breakage of bridges. Reversible adsorption of telechelic polymers between two surfaces leads to a dynamic thermodynamic equilibrium between chains that are in the following four states: (i) free, (ii) dangling (having only one adsorbed end), (iii) loops (having both ends adsorbed to the same surface), and (iv) bridges (which are adsorbed by both ends to two surfaces). We reported the variation in the equilibrium populations of these chains as a function of the separation between the adsorbing surfaces as well as that of the end adsorption energy. The dynamic response of the system is also of interest, given that the bridging chains break off and new bridging chains are formed on finite time scales that depend upon factors like the adsorption energy, chain length, and the surface separation. After the application of a step shear strain, the stress would relax gradually as some of the bridges present at the beginning are converted to dangling ends or even free chains (Figure 1), through thermal fluctuations and fluctuations in the stretching of the chain. In this work we focus on the dynamic exchange of these chains from one state to another and the implications of such exchange for the stress relaxation in the system. In particular we are interested in looking explicitly at the relaxation spectrum of bridges and the manner in which it is affected by the binding energy and separation of the surfaces (inversely related to the cube root of the particle density in the suspension) as well as its implications for the stress relaxation in such systems. The motivation for these calculations also arises from some recent theoretical advances in transient network theories; the system under investigation is similar in many respects to some of the self-associated structures investigated theoretically. This computational model could possibly be mimicked by surface force apparatus (SFA). Longitudinal forces between surfaces coated with reversibly adsorbed triblock

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® Abstract published in *Advance ACS Abstracts*, July 15, 1994.

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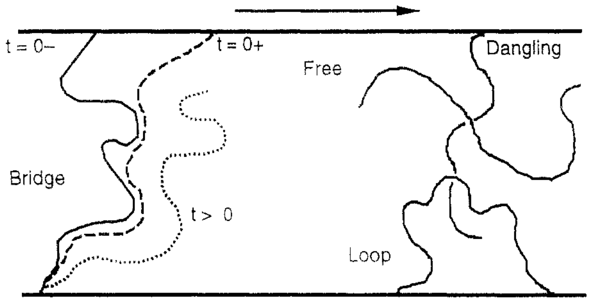

Figure 1. A schematic of telechelic polymers confined between two surfaces. The upper surface is sheared instantaneously at time t = 0. A bridge at time t = 0– (solid line) also stretches instantaneously to a new conformation at t = 0+, producing stress in the system. At some later time $t > 0$ thermal energy overcomes the binding energy, allowing the bridge to relax to a dangling chain (dotted line), thus reducing the stress. The dangling chains, loops, and free chains do not contribute to stress due to the lack of entanglements.

copolymers have been measured by Dai and Toprackcioglu,[15-16] however, the transient nature of the response is not fully addressed even though the reversibility of adsorption is evident from the difference in forces between compression and stretching cycles. For an experimental evaluation of the transient shear response, which is discussed in this study, we have in mind the modified SFA used by Klein et al. whereby the opposing surfaces can be made to undergo a sinusoidal shear motion with respect to each other.[17]

Earlier theories of transient networks were motivated by the need to explain stress relaxation in polymeric media that exhibit both elastic and viscous behavior.[18-21] These theories were limited by the lack of understanding of the detailed mechanism of the creation/annihilation of cross-links and of entanglements. More recently theories have appeared that reexamine the stress relaxation in chains participating in temporary cross-links. Broadly speaking, transient networks can be of the unentangled type if the chain length connecting two cross-links (N) is less than the entanglement chain length (N_e), i.e. $N < N_e$, or the entangled type if $N > N_e$.[22] In the former the chain dynamics is essentially Rouse-like and the stress relaxation depends only upon the dynamics of chains joining and breaking from cross-linking sites after the strain has been applied. In the latter, entanglements produce a confinement that leads to hindered reptation-like movement for the chain. In addition to the dynamics of cross-link breakage the stress relaxation also depends upon the disengagement of the entanglements of the chains. Recent theoretical work can also be broadly classified along those lines.

Tanaka and Edwards (TE) have presented a model that looks at stress relaxation in unentangled transient networks formed by telechelic chains with sticky ends.[22] The chains are assumed to be Gaussian and the deformation experienced by the network is affine. The model does not consider free chains in the system and thus cannot explain the shear-thickening behavior observed in associated polymers. Wang's extension of the TE model considers the dynamic exchange between bridges, dangling, and free chains.[23] This model shows that the shear-thickening phenomenon is governed by both the free chain number density and the rate of formation of network chains from free chains. This model is reduced to the TE model in the limit where dangling chains can no longer become free. Both theories address the time evolution of stress after a step strain has been applied to the network.

Baxandall introduced a model,[24] more appropriate for the system under investigation, for chain motion in a phantom network where tubelike confinement effects are absent. The stress in the chain, after the network is strained, relaxes as the reversible cross-links between the chain and the network break and remake. In general the length of the chain sections between cross-links is taken be a variable with a spectrum of relaxation times associated with each section. This is a refinement over the simple theory of Lodge which assumes only one relaxation mode for each chain section between the cross-links.[19] Baxandall specializes his model to chains with cross-links only at the two ends, a situation similar to the present study. Further the motion of the probe chain is shown to be Rouse-like with no confinement effects. This is also closely related to the system under study where entanglement effects are negligible, due to negligible chain overlap.

Another set of theories examine the motion of a probe chain with sites that bind reversibly with a host network that itself is permanent—the entanglement effects are incorporated in these works. Gonzalez has modeled the motion of a chain within the network as reptation which includes reversibly bonded sites along the tube.[25] The Gonzalez model assumes that reptation is possible when all the stickers along the chain are free; a constraint that is severe and overestimates the terminal relaxation times. This condition was relaxed by Leibler, Rubinstein, and Colby (LRC) who showed that with the breaking of only a few bonding sites the chain can relax substantially.[26] The experimental work of Stadler and de Lucca Freitas[27] also confirms that while the Gonzalez model overestimates the relaxation time for chains with a large number of stickers, the LRC model is closer to reality; at least as far as systems with strong confinement constraints, like melts or permanent gels, are concerned. With regard to the telechelic polymer between two surfaces, these theories would be applicable to the case where chain lengths and the grafting density are high enough for entanglements to occur between dangling ends from the opposing surfaces. (Entangled loops from the opposing surfaces act essentially as bridges; through a visual inspection of loops in our simulations we did not observe any such entanglements.)

In section 2 the ranges of parameters employed in the simulations are presented as are the details on how the equilibrium ensembles of chains were generated and how the dynamics of the chains was followed. In section 3 the equilibrium properties of the system as obtained in the current simulations, viz. the chain populations as a function of the adsorption energy and the separation of the adsorbing surfaces, are highlighted. This is followed, also in section 3, by the results of the chain dynamics with focus on the effects of surface separation and adsorption energy not only on the average lifetimes of temporary bridges but also on the distribution of lifetimes. The bridge lifetime distributions are used to predict the shear stress relaxation modulus for the system, in the linear response regime. It is shown that the exponential dependence of the relaxation time upon the adsorption energy leads to a convenient scaling of different relaxation moduli for different binding energies onto a single curve. Conclusions are presented in section 4.

2. Simulation Details

Simulation Parameters. The Monte Carlo simulations for generating ensembles of equilibrium configurations were performed on a cubic lattice. The basis and the mechanics of the Monte Carlo method for polymers are amply documented (see for example ref 28). The impenetrable adsorbing surfaces were placed at $z = 0$ and $z = L$. The lateral dimensions of the simulation box (x and y) were both 30 units. Periodic boundary conditions were imposed in x and y directions. All simulations were performed with 20 chains of 50 segments in the simulation box. L took on values of 11, 14, 15, 17, 19, and 21. The average polymer volume fraction in the box, $\langle \Phi \rangle$, thus varied between 0.051 and 0.093. The rms end to end distance of a free chain, $\langle r^2 \rangle^{1/2}$, of 50 segments on a cubic lattice was also estimated by simulation to be 9.04, which is reasonable for a self-avoiding walk of this length.[9] The threshold overlap polymer volume fraction Φ^*, estimated as $N\langle r^2 \rangle^{-3/2}$, is 0.068. The average polymer volume fraction inside the simulation boxes is thus near or below the overlap concentration. Indeed, as shown in previous work, at these concentrations interchain interactions play a negligible role in defining the chain conformations.[9] The solvent was taken to be athermal and the only nonzero energy parameter in the simulation was the binding energy, $\beta\epsilon$ (where, $\beta = 1/kT$), of the chain ends with the adsorbing surfaces. Simulations were performed with $\beta\epsilon = 0, -1, -2, -3$, and -5 for each value of surfaces separation (L). This is a typical range of values reported in a recent experimental work on the binding of single end-functionalized chains to colloidal particles.[29]

Equilibrium Ensemble. These ensembles were generated in the previous work to study equilibrium properties of the system.[9] The equilibrium ensembles provide a starting point for the current dynamics simulation and also a benchmark against which some of the results from the dynamics study can be cross-checked. We recount the generation of the equilibrium ensembles briefly (details are available elsewhere[9]). Twenty self and mutually avoiding chains in each simulation box were equilibrated for various pairs of $\{\beta\epsilon, L\}$ using 10^7 attempted moves. The Monte Carlo algorithm cycled between reptation of a randomly picked chain followed by either a kink–jump or crankshaft move (whichever was applicable) on a randomly chosen segment on that chain. Three hundred configurations were chosen at regular intervals from the last 3×10^6 moves of a given trajectory and averages were performed on these. The equilibrium results from these ensembles were reported in a previous work[9] and provide an independent test for the dynamics algorithm which is discussed next.

Dynamics of Chains. Once equilibrium ensembles for each pair $\{\beta\epsilon, L\}$ were generated the configuration sampled last was chosen as the initial configuration of the dynamics trajectory. In the dynamics run three moves were allowed: end flip, kink–jump, and crankshaft. Reptation produces unrealistically fast relaxation and therefore while it is suitable for generating equilibrium ensembles it is not appropriate for studying the dynamic properties of the system. In the dynamics run each chain was visited sequentially (from 1 to m) and on each chain a move was attempted sequentially for each segment (from 1 to N). The moves were accepted if they satisfied mutual and self avoidance as well as the Metropolis rule.[30] According to this rule a move, with an associated energy change of ΔE, is accepted with a probability $P = \min[1, \exp(-\beta\Delta E)]$. The sequential approach to moving segments was also taken by Sariban and Binder to study polymer chain dynamics in another context.[31] They found that the dynamics were unaffected whether one chose segments randomly or sequentially; the latter however resulted in faster algorithms. In some control runs we also followed dynamics of the system by choosing segments at random—the results were identical to those obtained by moving segments sequentially. The Metropolis rule was followed in accepting or rejecting a move. In this process segments 1 and N experienced end-flip moves while the internal segments were either kink–jumped or crankshafted. Configurations were stored every Monte Carlo time step, Δt, in which a move was attempted once on every segment in the system. Thus $m \times N = 20 \times 50$, or 1000, attempted moves constituted one Monte Carlo time step. The simulation box for each pair $\{\beta\epsilon, L\}$ was subjected to a dynamic run of 5000 time steps (or 5×10^6 attempted moves). The state of each chain (viz. bridge, loop, etc.) was stored at each time step. We thus had the history of each chain as a linear sequence of states from which the lifetime spectrum of any state could be extracted.

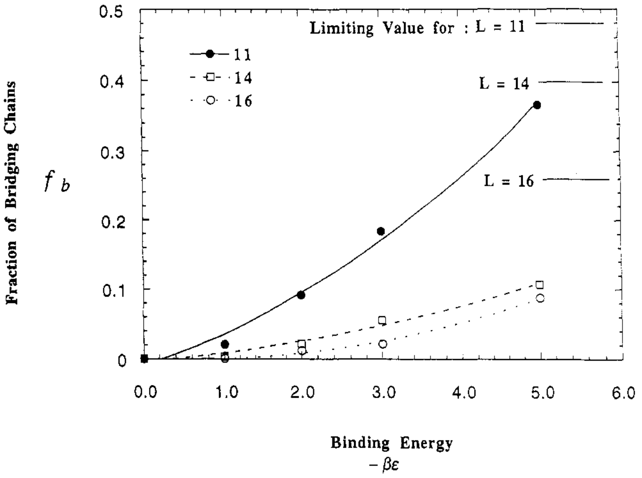

Figure 2. Bridging fraction, f_b, as a function of the binding energy, $\beta\epsilon$, of the chain end to the surface, for various values of surface separation. The curves in this and other figures are meant as a guide to the eye unless stated otherwise. The solid horizontal line segments denote the asymptotic limit as $-\beta\epsilon \rightarrow \infty$.

3. Results and Discussion

Equilibrium Properties. The equilibrium populations of different states were reported in an earlier work using ensembles generated by a different approach. However some of these results are directly relevant to the interpretation of the stress–relaxation response of the system and so we revisit the salient results on the bridging fraction. The data reported below are extracted from the current dynamics runs and are in complete agreement with the previously reported results.[9]

In Figure 2 we examine the bridging fraction as a function of the energy of interaction, $\beta\epsilon$, for various values of the surface separation, L. Indeed as expected the bridging fraction rises monotonically with increasing binding energy (since it is energetically more favorable for dangling ends or free chains to bind to surfaces). It was shown previously that as the value of the binding energy increases, more dangling ends and free chains are converted to loops and bridges, until finally all chains occupy only these two states. For each value of L the bridging fractions will reach previously determined asymptotic limits[9] (shown on the Figure 2 as solid horizontal lines). The rise toward the asymptotic value is faster for small surface separations.

In Figure 3, similar data is shown in a different form. The bridging fraction is depicted as a function of the surface separation. Again, as expected, the bridging fraction drops monotonically as the surface separation increases since it becomes entropically more favorable to bind as a loop to decrease stretching, or as a dangling end or free chain, both of which have a higher translational entropy.

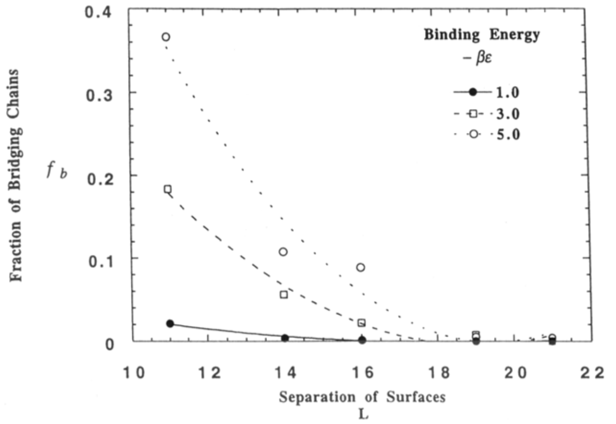

Figure 3. Bridging fraction, f_b, as a function of the surface separation, L, for various values of $\beta\epsilon$.

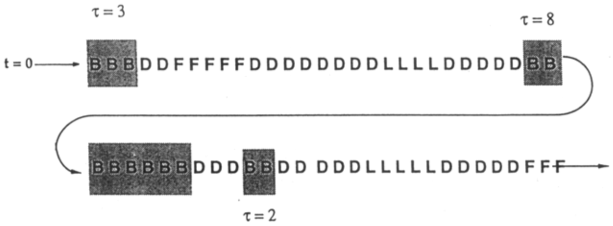

Figure 4. The history of a chain as a linear sequence of states. At each Monte Carlo time step the chain is in one of the following states: bridge (B), loop (L), dangling end (D), or a free chain (F). Sequences of continuous bridging define a bridging event and the number of steps in the sequence defines a bridging time, τ.

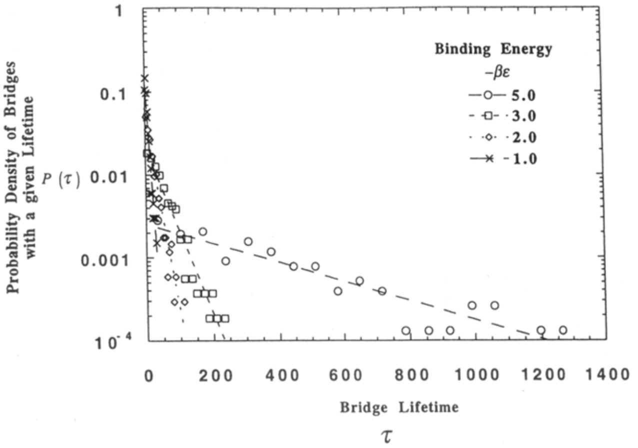

Figure 5. Normalized probability density, $P(\tau)$, of a bridge with a given lifetime τ. $L = 11$ and different values of $\beta\epsilon$. The lines are the best exponential fits.

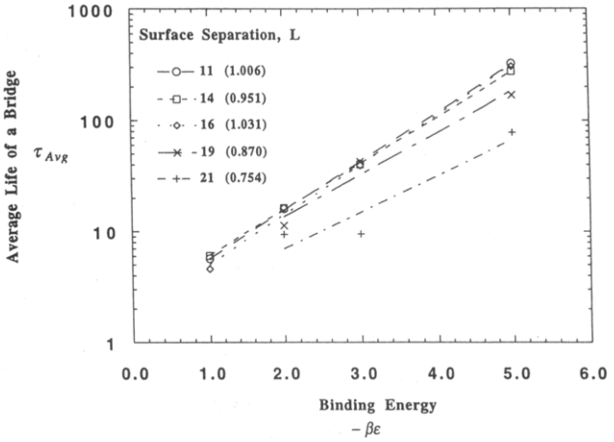

Figure 6. Average bridge lifetimes, τ_{avg}, as a function of the binding energy, $\beta\epsilon$, for various values of surface separation. The lines are the best exponential fits to the data (the numbers in the parentheses are the slopes of the lines).

Bridging Lifetime Distributions. In the previous section it was pointed out that the state of each chain was recorded at each time step. We thus have a linear history of states, for each chain, which could be scanned for sequences of consecutive bridging states (see Figure 4). Each such sequence corresponds to a bridging event, i.e. a chain forming a bridge and existing as a bridge for some time before disengaging from one or both surfaces. For each pair $\{\beta\epsilon,L\}$ one can obtain a set of bridging events of different time lengths. From these one can deduce the spectrum of lifetimes of bridges, i.e. the probability distribution of finding a bridge with a particular lifetime. Additionally one can estimate the average bridging time as a function of these parameters. A similar analysis of dangling ends and free chains shows that the lifetime of bridges is longer than the lifetime of the other two configurations.

In Figure 5 the normalized probability density, $P(\tau)$, of finding a bridge with lifetime τ is shown as a function of different energies for $L = 11$. In order to display the data for each energy, the bridging events were assigned to 20 equal bins between $\tau = 0$ and $\tau = \tau_{\max}$ (the largest bridging time observed for that set of parameters). It is possible to fit the lifetime distribution to a single exponential decay function, in accordance with the dumbbell model of Baxandall[24] (corresponding to the relaxation of a telechelic chain in a phantom host network). Similar fits can be obtained for $L = 14$ and 16, although for larger values of L there are fewer bridging events and the fits have higher uncertainty.

In Figure 6 are shown the average bridging lifetimes, for various values of the surface separation, as a function of the binding energy. For $L = 11$, 14, and 16 (i.e. bridges that are stretched not more than twice the end-to-end distance of a free chain, 9.04), the average bridging lifetime increases exponentially with the binding energy. In other words

$$\tau_{\text{avg}} = \int_0^\infty \tau P(\tau)\,\mathrm{d}\tau \approx \mathrm{e}^{-\beta\epsilon} \tag{1}$$

This result agrees with the formula given by Chandrashekhar.[32] However for higher stretching the elastic energy also plays a role in the breaking of bridges. The elastic energy stored in the stretched bridges causes them to break off sooner than compared to less stretched bridges of the same binding energy.

Figure 7 explicitly depicts the dependence of the bridging lifetime on the separation of the surfaces (i.e. as a function of the stretching of the bridges). It appears that for $L < 2\langle r^2\rangle^{1/2}$ the bridging lifetime is more or less independent of the stretching of the bridges. Once past that threshold, the lifetimes drop off rapidly due to the stretching of the bridges. Approximately then one could decouple the energy and the stretching effect on the bridging lifetime as follows

$$\tau_{\text{avg}} \approx \theta(L_{\text{crit}} - L)\mathrm{e}^{-\beta\epsilon} \tag{2}$$

where θ the Heavyside function is defined as, $\theta(X) = 1, X > 0$ and $\theta(X) = 0, X < 0$. In this case $L_{\text{crit}} \approx 2\langle r^2\rangle^{1/2}$. The Tanaka and Edwards model[22] makes an assumption about the effect of stretch rate upon bridging that has an effect similar to that of eq 2. They assume that below a critical end to end distance the bridging lifetime is independent

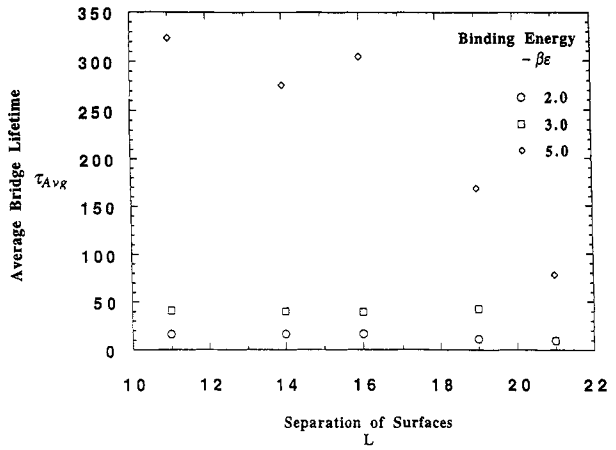

Figure 7. The average bridge lifetime, τ_{avg}, as a function of the surface separation, L. (The points for $\beta\epsilon = -2$ and 3 overlap at $L = 21$).

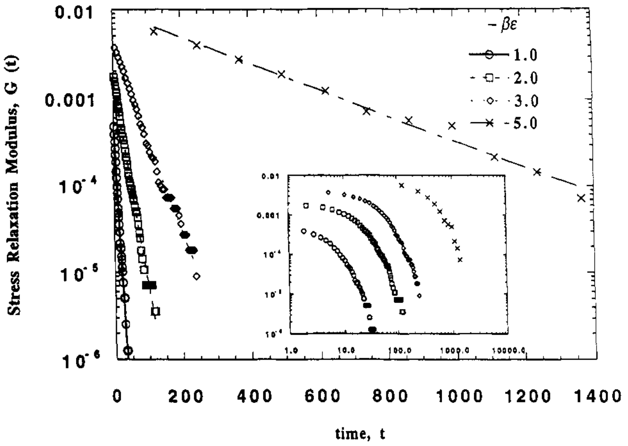

Figure 8. Stress relaxation moduli after unit strain has been applied at $t = 0$. The surface separation is 11 and the lines are the best exponential fits to the data. The inset shows the same data on a log–log plot.

of stretching while no bridges above that critical end to end distance are allowed. The present simulation shows that such an assumption which neglects bridges above a certain critical stretching is quite appropriate.

Stress Relaxation after Step Strain. We now discuss the consequences of the bridging lifetime distributions on the shear stress relaxation after one of the surfaces is sheared with respect to the other. In this process we assume that the dangling chains or free chains play no role through entanglements, since the polymer concentrations are below or close to the chain overlap concentration. In other words the stress in the system is totally due to the bridges. We also assume that the strain deformation is small (linear response) and that the strain rate itself is not too large (so as to affect the breakage of bridges). After the strain has been applied, at time $t = 0$, the bridges that were present at $t = 0$ break off and are converted to either dangling chains (or with a much lower probability to free chains). The fraction of the original stress that remains after time t is just the fraction of chains (which were active at $t = 0$) which still remain active. (Of course, in keeping with the equilibrium population of the bridges, new bridges are continuously formed as old ones are destroyed but these do not contribute to the stress in the system since they were formed after the application of stress and hence are at equilibrium.) One can write thus

$$\frac{\sigma(t)}{\sigma_0} = \int_t^\infty P(\tau)\,\mathrm{d}\tau \qquad (3)$$

where $\sigma(t)$ is the stress remaining in the system after time t has elapsed and σ_0 is the stress in the system at time $t = 0$. The stress at time $t = 0$ is proportional to the equilibrium bridging density. Assuming that bridges are linear springs one can write (for strain γ)

$$\frac{\sigma_0}{kT} = f_b \Sigma \gamma \qquad (4)$$

where Σ is the area available on either surface per chain in the system. (In the present simulations with 20 chains and a surface area of 30 × 30, we have $\Sigma = 20/900 = 0.022$. The right-hand side of the equation is divided by the segment length, unity in the present dimensionless case, to give proper dimensions to the equation.) It is important to note that since $f_b = f_b(\beta\epsilon, L)$ also, the relaxation modulus depends upon the system parameters through both the relaxation time as well as the zero time stress in the system. Given that $P(t) \approx e^{-t/\tau_C}$ (τ_C being the characteristic relaxation time of the bridges) one would also expect an exponential decay for the stress. Analytically one can write the stress relaxation modulus as

$$G(t) = f_b \Sigma \exp(t/\tau_C) \qquad (5)$$

In Figure 8 are shown the time-dependent stress relaxation moduli for various values of the binding energy at a given surface separation ($L = 11$). For each set of parameters $\{\beta\epsilon, L\}$ the time τ_{max} was divided into n equal time intervals such that, on an average, 10 bridging events were observed for each interval. The fractional stress remaining at the end of a given time interval was just the fraction of bridging events that were of larger lifetimes, according to eq 3. The data are shown on a semi log plot along with single exponential fits to each data set. Indeed a single exponential decay represents the stress relaxation very well and is good agreement with the model of Baxandall for a dumbbell[24] (a Rouse chain with two beads connected by a single spring) inside a phantom network. The present system is therefore well represented by a single Maxwell element (see for example ref 33). As expected from the bridge lifetime distributions, the stress decay is on a longer time scale as the binding energy increases. The inset depicts the same data on a log–log plot and shows clearly that this time, after which the plateau modulus decays and the system starts to flow, is a strong function of the binding energy. As to the absolute value of the plateau modulus, this increases with increasing binding energy as well (though not exponentially fast), as shown in Figure 2.

The manner in which this relaxation time depends upon the binding energy (or inversely on the temperature) is of importance. We have some insight from the fact that the average bridge lifetime depends exponentially on the binding energy. In Figure 9, as in Figure 8, we show the fractional stress remaining in the system after time t for various values of the binding energy (for $L = 11$). The time in this figure is scaled by $e^{-\beta\epsilon}$. The stress relaxation curves line up very nicely, indicating that the characteristic stress relaxation time also increases exponentially with the binding energy.

Figure 10 examines the effect of the separation of the surfaces on stress relaxation for a given binding energy ($\beta\epsilon = -3$). The bridging time was shown to be rather insensitive to the stretching of bridges below a critical surface separation. On the other hand the bridging fraction is a strong function of the surface separation. Therefore, as

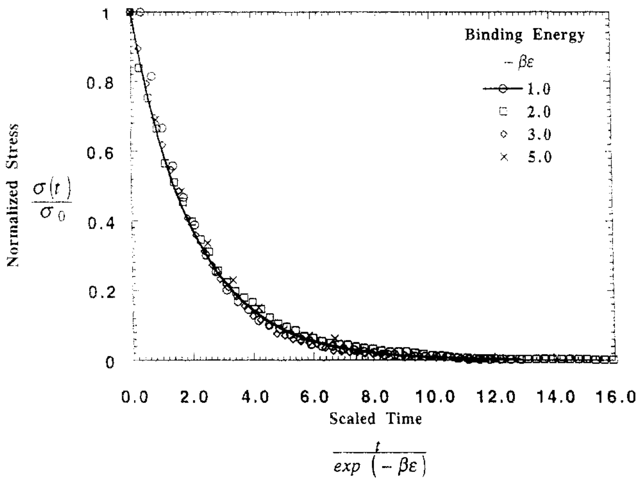

Figure 9. Normalized moduli of Figure 8 with a time axis scaled by $e^{-\beta\epsilon}$. The surface separation is 11.

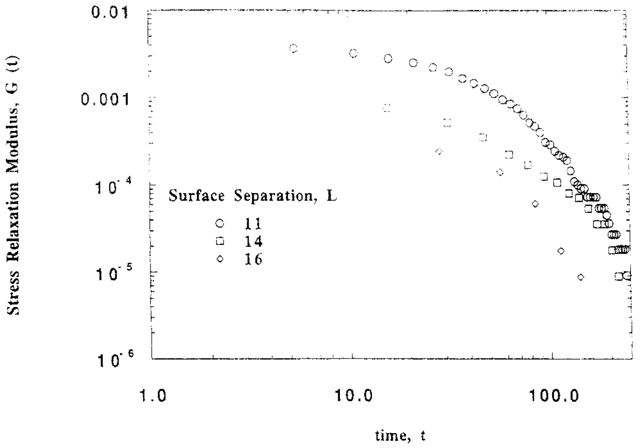

Figure 10. Stress relaxation moduli as a function of the surface separation. The binding energy is $\beta\epsilon = -3$.

seen in Figure 10, while the values of the plateau moduli depend upon the surface separation the time at which the system starts to flow does not depend significantly upon the surface separation.

4. Conclusions

In this work we have looked at the dynamics of telechelic chains of 50 segments confined between two parallel surfaces, in a concentration regime where there is little overlap between chains. The situation is similar to the unentangled network models and especially close to the model due to Baxandall.[24] For given surface separation and binding energy, the lifetimes of the elastically active chains, the bridges, are found to be distributed exponentially. The average bridge lifetime grows exponentially with the binding energy. However the bridge lifetime is rather insensitive to the separation of the surfaces up to a certain critical surface separation after which it drops off rapidly. This observation provides some support for a similar assumption in the TE model.[22] These observations on the bridging lifetime yield that the stress decay in the system after step strain is also exponential, like a single Maxwell element. The characteristic relaxation time grows exponentially with the binding energy but is insensitive to the surface separation. The plateau modulus however depends strongly both on the surface separation as well as the binding energy.

Acknowledgment. This work was supported by NSF grant DMR 92-20369.

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