Macromolecules 1993, *26*, 6483-6488

Models of Shear-Thickening Behavior in Physically Cross-Linked Networks

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Received May 19, 1993; Revised Manuscript Received September 8, 1993[®]

ABSTRACT: Shear-thickening effects are often observed in physically cross-linked networks formed by polymeric chains having a few localized, energetically favored interactions. We find that a possible explanation for these effects is the non-Gaussian behavior of the chains stretched by the shear flow. Two network models for unentangled telechelic chains are proposed, which differ in the way unattached chains relax after deformation. One of the models correctly portrays the qualitative shear-thickening features commonly observed.

I. Introduction

There has been a growing interest in physically cross-linked polymer networks in recent years. Among the most intriguing systems are the ionomers,[1-6] which, in solutions of nonpolar organic solvents, often show shear-thickening behavior over a range of shear rates.[7-12] Other categories of modified polymeric systems can also exhibit similar phenomena.[13,15] An interpretation of the shear-thickening effect observed in ionomer solutions was advanced some years ago by Witten and Cohen.[15,16] Their proposal was that shear would increase the probability of the intermolecular associations of the ionic groups over that of the intramolecular ones, thus enhancing the effective molecular weight and the viscosity. In a somewhat similar vein, but in the context of temporary network theory, Wang[17] recently explained shear thickening in terms of shear-induced coagulation of free chains, leading to more chains participating in the network.

The idea pursued in this work is a different one; we want to explore the possibility that shear thickening is related to shear-induced chain stretching well inside the non-Gaussian range of chain behavior. The mechanism explored here is not alternative to that of Witten and Cohen nor to that of Wang; i.e., the effects might coexist. In this work, however, we will assume that the other mechanisms are inoperative, i.e., that the proportion of inter- and intramolecular associations stays constant. In the language of temporary, physically cross-linked networks, we assume a constant value for the concentration of "elastically active" chains in the network.

The dynamic behavior of physically cross-linked networks has been recently investigated by Tanaka and Edwards[18,19] in a systematic way. With the assumptions used by them, however, only shear-thinning behavior is predicted. Though inspired by their work, the approach taken here differs in that it is mainly focused on non-Gaussian chain behavior, a possibility only marginally considered by Tanaka and Edwards.

Two network models were explored in this work. One of them is very similar to that used by Tanaka and Edwards and will therefore be indicated as the TE model. As mentioned above, the approach followed here will nevertheless differ somewhat since the idea of non-Gaussian behavior is brought by us to its extreme consequences. As we shall see, a shear-thickening behavior is indeed found; yet it is too weak an effect to explain what has been observed in various systems.

A second model was examined in which a significant change in one of the physical assumptions was made. Since in this latter model there appears a new, concentration-dependent, characteristic length which has the meaning of a free path length, we will denote it as the FP model. Estimates based on such a model seem very promising insofar as they favorably compare with the rheological observations.

The paper is organized as follows. In section II, the assumptions of the TE model are reviewed and, under conditions which favor non-Gaussian behavior, an equation for the shear viscosity is derived, the predictions of which are worked out in some detail in section III. The FP model is introduced in section IV, and estimates based on that model are obtained. Finally, in section V the results are discussed and compared with the available evidence, including that reported by Pedley et al.,[10] who found no indication of shear-induced chain stretching.

II. The TE Model

As considered by Tanaka and Edwards,[18,19] the chains which form the network are taken to be ordinary polymers with "sticky" ends, like those of telechelic ionomer chains in organic solvents.[8] Under suitable concentration conditions, the chains will organize themselves in a network where the cross-links are small aggregates of these sticky ends. The network dynamics is controlled by the rates at which chains leave the network and join it again. It is assumed that no topological entanglement exist, i.e., that the molecular weight of the individual chains is below M_c, the critical value at the existing concentration.

The chain detachment rate under equilibrium conditions, called β_0, depends on the "stickiness" of the junctions, i.e., on the energy barrier that the functional groups at the chain ends must overcome to set themselves free from an aggregate. We will assume that, in a given system at equilibrium at a given temperature, β_0 is a constant independent of chain extension. There follows that the "lifetime" distribution function of the network chains at equilibrium, $\psi_0(t)$, is given by

$$\psi_0(t) = \beta_0 \exp(-\beta_0 t) \qquad (1)$$

Here, t is the time a chain spends attached to the network, and $\psi_0(t)\,dt$ gives the probability that such a time falls between t and $t + dt$. The average lifetime of the chains in the equilibrium network is β_0^{-1}.

It is to be expected that a flow process, by stretching the chains out, will alter the lifetime distribution function. It

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[®] Abstract published in *Advance ACS Abstracts*, October 15, 1993.

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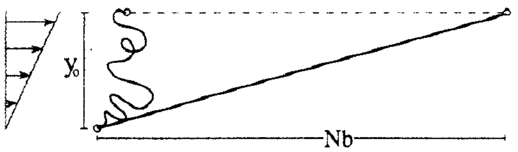

Figure 1. Affine kinematics of a chain in a shear flow, which is used to relate the chain end-to-end distance R to the time t measured from the moment the chain joined the network.

is well known that, as long as the chain remains Gaussian, the tension F in the chain is related to the end-to-end distance R by the linear relationship

$$F = \frac{3kT}{Nb^2}R \tag{2}$$

where N is the number of "monomers" in the chain, and b their length. Equation 2 shows that, unless the chain becomes fully stretched, the tension is always smaller than kT/b. Now, since the energy barrier that the chain end must overcome to exit an aggregate is estimated to be several times kT,[15,16] it follows that, to a good approximation, we can ignore the effect of chain stretching on the detachment rate up to the point when the chain is fully stretched. As the chain approaches the fully stretched state, the tension in the chain shoots up to unbounded values and detachment will take place instantly.

We will therefore assume (somewhat differently from Tanaka and Edwards[18,19]) that the lifetime distribution function under flow conditions, $\psi(t)$, is modified with respect to equilibrium simply as a result of the following "cutoff" scheme:

$$\begin{aligned} &\text{for } t \le t_{\max} \quad \psi(t) \propto \exp(-\beta_0 t) \\ &\text{for } t > t_{\max} \quad \psi(t) = 0 \end{aligned} \tag{3}$$

where $t_{\max}$ is the time required for a chain attached to the network to become fully extended.

It should be noted that $t_{\max}$ is not a constant in a given flow; rather, it depends on the value taken by the end-to-end vector at the moment the chain joins the network. For example, in a steady shear flow (the only flow considered in this work), $t_{\max}$ is given by

$$t_{\max} = \frac{Nb}{\dot\gamma|y_0|} \tag{4}$$

where $\dot\gamma$ is the shear rate and $|y_0|$ is the projection of the end-to-end vector along the velocity gradient direction (see Figure 1) "at time zero", i.e., when the chain joins the network and the stretching process begins.

Equation 4 embodies two assumptions. One of them is that the end-to-end vector of a chain attached to the network deforms affinely. The second is that the end-to-end chain distance at time zero is much smaller than the fully extended length Nb. In other words, no matter how large R was at the previous detachment event, the chain has relaxed before joining the network. Both these assumptions are classical ones in temporary network theory and are also used by Tanaka and Edwards.[18,19] As regards the second of these two assumptions, we will take a different viewpoint when considering the FP model later on.

Although $t_{\max}$ depends on $|y_0|$, we will temporarily view it as a constant and calculate two relevant time averages on the basis of eq 3. The first of them is the average lifetime of a chain in the network under flow conditions, indicated as β^{-1}, which is given by

$$\beta^{-1} = \frac{\int_0^{t_{\max}} t \exp(-\beta_0 t)\,\mathrm{d}t}{\int_0^{t_{\max}} \exp(-\beta_0 t)\,\mathrm{d}t} \tag{5}$$

From eq 5, it is apparent that, for any finite value of the cutoff time $t_{\max}$, the detachment rate under flow conditions, β, is larger than β_0, as it should be.

The second time average of interest has to do with the work done in stretching the chain out. Because the chains may elongate considerably under flow conditions, well inside the non-Gaussian range, we need to replace eq 2 with some appropriate nonlinear force law. We will use here the classical inverse Langevin function, though other choices can be accommodated as well. Thus

$$r(f) = \coth f - 1/f \tag{6}$$

where r and f are the nondimensional end-to-end distance and the nondimensional chain tension, respectively

$$r = R/Nb; \quad f = Fb/kT \tag{7}$$

From eq 6, the nondimensional work w done in elongating the chain from a zero length up to when the force has attained a value f is obtained as

$$w(f) = f \coth f - 1 - \ln(\sinh f/f) \tag{8}$$

The actual work, W, averaged over the life span of chains, is then given by

$$W = NkT\frac{\int_0^{t_{\max}} w \exp(-\beta_0 t)\,\mathrm{d}t}{\int_0^{t_{\max}} \exp(-\beta_0 t)\,\mathrm{d}t} \tag{9}$$

where the link between t and r, hence between t and w, is obtained by the same kinematic arguments illustrated in Figure 1 and used previously to derive eq 4, i.e.

$$t = \frac{Nb}{\dot\gamma|y_0|}r \tag{10}$$

We can then write

$$\int_0^{t_{\max}} w \exp(-\beta_0 t)\,\mathrm{d}t = \frac{Nb}{\dot\gamma|y_0|}I \tag{11}$$

where I is the nondimensional integral

$$I(G) = \int_0^1 w(r) \exp(-r/G)\,\mathrm{d}r \tag{12}$$

or, since the function $w(r)$ is not explicit while $w(f)$ is,

$$I(G) = \int_0^\infty w(f)\, c(f) \exp[-r(f)/G]\,\mathrm{d}f \tag{12'}$$

Here, $c(f)$ is the "chain compliance"; i.e.

$$c(f) = \mathrm{d}r/\mathrm{d}f = 1/f^2 - 1/\sinh^2 f \tag{13}$$

In eqs 12 and 12′, G is the group

$$G = \frac{\dot\gamma|y_0|}{\beta_0 Nb} \tag{14}$$

representing a nondimensional shear rate. Equation 12′ shows that the I integral is well defined because, although $w(f)$ diverges logarithmically as $f \to \infty$, the chain compliance $c(f)$ goes to zero as $1/f^2$ in the same limit.

We now have all the ingredients required to calculate the viscosity. Indeed, the average of the product $W\beta$ gives the rate of energy dissipation per active chain. Thus, if the number of active chains per unit volume of network is indicated by ν, $\nu\langle W\beta\rangle$ gives the rate of energy dissipation per unit volume. The viscosity is then obtained as

$$\eta = \frac{\nu\langle W\beta\rangle}{\dot{\gamma}^2} \tag{15}$$

where the average $\langle ...\rangle$ is over the configurations of the chains when they join the network, i.e., over the possible values of $|y_0|$. As suggested by Tanaka and Edwards,[18,19] we will take the distribution of chain conformations at "birth" to be the equilibrium Gaussian. As mentioned in the Introduction, we will also take ν to be a constant, independent of shear rate.

Substituting for W and β in eq 15, the following viscosity formula is obtained:

$$\frac{\eta}{\eta_0} = \frac{\langle {y_0}^2 Y(G)\rangle}{\langle {y_0}^2\rangle}; \qquad Y(G) = \frac{\dfrac{I(G)}{3G^3}}{1-\left(1+\dfrac{1}{G}\right)\exp\left(-\dfrac{1}{G}\right)} \tag{16}$$

where we have replaced $Nb^2/3$ with $\langle {y_0}^2\rangle$ to better emphasize the role played by the "viscosity function" $Y(G)$, and we have set

$$\eta_0 = \nu kT/\beta_0 \tag{17}$$

to be soon recognized as the zero-shear viscosity. The averaging over y_0 in the numerator of eq 16 cannot be readily made since y_0 enters $Y(G)$ in a complex way.

III. Predictions of the TE Model

For vanishing shear rates, as G approaches zero the integral defined by eq 12 can be calculated by taking the small-r approximation of the work term, which is $w = 3r^2/2$. Hence

$$\dot{\gamma} \to 0; \quad I(G) \to 3G^3; \quad Y(G) \to 1; \quad \eta \to \eta_0 \tag{18}$$

The expression for the zero-shear viscosity, eq 17, coincides with that obtained by Tanaka and Edwards[19] and is in fact generated by all classical models of temporary networks. The zero-shear viscosity is directly proportional to the equilibrium network connectivity ν and is inversely proportional to the thermal rate of junction renewal β_0. Further comments on η_0 are postponed to the discussion section.

Next, we consider the limit $G \to \infty$, i.e., the high shear rate range. As regards the denominator of $Y(G)$, it is found to approach $1/(2G^2)$ in such a limit. On the other hand, the function $I(G)$ approaches a constant value K given by

$$K = \int_0^\infty w(f)\, c(f)\, \mathrm{d}f \approx 0.766 \tag{19}$$

Hence we find

$$\frac{\eta}{\eta_0} = 2K\frac{\langle {y_0}^2/G\rangle}{\langle {y_0}^2\rangle} = 2(3^{1/2})K\frac{\langle |y_0|\rangle}{\langle {y_0}^2\rangle^{1/2}}\frac{\beta_0 N^{1/2}}{\dot{\gamma}} \tag{20}$$

where we have used again the equality $\langle {y_0}^2\rangle = Nb^2/3$. Since the front factor in the last expression of eq 20 is a numerical constant of order unity (ratio of the two averages included), the high shear rate result essentially reduces to

$$\dot{\gamma} \to \infty; \quad \eta/\eta_0 \to \sim\beta_0 N^{1/2}/\dot{\gamma} \tag{21}$$

Equation 21 shows that the material becomes shear thinning at high shear rates. In a log-log plot, the ultimate slope of the viscosity curve is predicted to become −1. The intercept of such an asymptote with the Newtonian zero-shear plateau occurs at a value of the shear rate given by

$$\dot{\gamma}_{\text{crossover}} \approx \beta_0 N^{1/2} \tag{22}$$

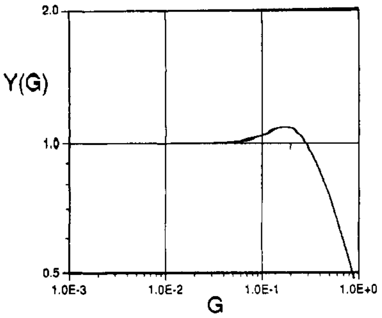

Figure 2. Nondimensional, universal, viscosity function $Y(G)$ defined in eq 16.

Equation 22 shows that the crossover value of shear rate depends, through β_0, on ion type as well as on temperature. However, if the shear stress at crossover is considered, which is

$$\sigma_{\text{crossover}} = \eta_0\dot{\gamma}_{\text{crossover}} \approx \nu kTN^{1/2} \tag{23}$$

$\sigma_{\text{crossover}}$ is found to be independent of ion type and, virtually, of temperature, to depend only on chain molecular weight and concentration.

Before the shear thinning described by eq 21 sets in at large shear rates, a region of shear thickening is predicted by the model. To see this analytically, we need to expand eq 16 in powers of $\dot{\gamma}$, i.e., in powers of G. To do so, we start from the small-f expansions of $r(f)$ and $w(f)$, which are

$$r(f) = \frac{f}{3} - \frac{f^3}{45} + ... \tag{24}$$

$$w(f) = \frac{f^2}{6} - \frac{f^4}{60} + ... \tag{25}$$

Inversion of eq 24 and substitution into eq 25 then give

$$w(r) = \frac{3}{2}r^2 + \frac{9}{20}r^4 + ... \tag{26}$$

so that, from eq 12, we obtain

$$I(G) = 3G^3 + \frac{54}{5}G^5 + ... \tag{27}$$

and, finally, from eq 16

$$\frac{\eta}{\eta_0} = 1 + \frac{6}{5}\frac{\langle {y_0}^4\rangle}{\langle {y_0}^2\rangle^2}\frac{\dot{\gamma}^2}{N{\beta_0}^2} + ... \tag{28}$$

Equation 28 shows that the first deviation from the Newtonian plateau at low shear rates is upward, demonstrating the shear-thickening effect. However, eq 28 also shows that, in order to obtain a significant effect, $\dot{\gamma}$ must reach values of order $\beta_0 N^{1/2}$, which is the same order of magnitude of the crossover value in eq 22. Thus, shear thickening and shear thinning are in conflict with one another, and no large shear-thickening effect is anticipated from this model.

This expectation is confirmed by the numerical results shown in Figure 2. The curve $Y(G)$ shows a bump in the neighborhood of $G = 0.2$, which corresponds to a viscosity increment of only about 9% over the zero-shear viscosity value, much too small in comparison with the observations.[8-14] It is likely that this value would be even further reduced as a consequence of the averaging over y_0 indicated in eq 16, though the shear-thickening effect cannot vanish completely, as proved by eq 28.

Furthermore, the viscosity function $Y(G)$ is system independent, and therefore eq 16 predicts that η/η_0 is a

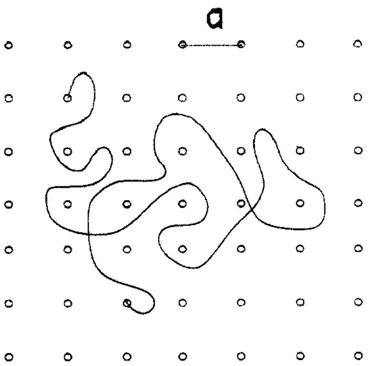

Figure 3. The chain attached with its end points to the "lattice" of ion aggregates. The real lattice is not regular as depicted. The characteristic lattice spacing is smaller than the chain dimension.

universal function of $\dot{\gamma}/\beta_0 N^{1/2}$. Thus, even if the shear thickening in Figure 2 was more pronounced, the prediction would have not compared favorably with data that show a bump "height" which in fact varies significantly with the type of ion.[12]

We conclude this section by emphasizing the positive aspects of the model so far considered. They are at least two. On the one hand, the model correctly predicts that all the "excitement" in the viscosity curve must occur at a value of stress which is independent of the junction "stickiness", i.e., of the type of ion (compare eq 23). This prediction is in good agreement with the observations[12] and must therefore be conserved in any evolution of the model. The second positive aspect is that shear thickening, tiny as it was found to be in this case, can indeed result from non-Gaussian chain behavior. This encouraged us to look into the matter further.

IV. The FP Model

In the previous model, it was assumed that after a chain has detached itself from the network it would relax entirely before joining the network again. That assumption is now put under closer scrutiny. To do so, we define the average spatial distance (called a) among neighboring aggregates, such that a^3 is the volume containing, on average, a single aggregate. Since, by definition of ν, this volume will also contain νa^3 active chains each carrying two ions, a is related to ν as

$$a = (z/2\nu)^{1/3} \approx \nu^{-1/3} \tag{29}$$

where z is the average number of ions (belonging to active chains) per aggregate, and the latter approximate equality holds if z is a constant not very much larger than 2. The very existence of the network implies that the chain concentration be such that the distance a obeys the following inequality, possibly in a strong form

$$a^2 < Nb^2 \tag{30}$$

The geometrical relationship between a chain and the "lattice" of aggregates is illustrated schematically in Figure 3.

When a chain detaches itself from the network, the ion at the chain end starts moving about and ends up "captured" by some other aggregate (or even by the previous one again). In view of the fact that ion aggregates are favored energetically over isolated ions, it is expected that the probability of being recaptured very soon is high, i.e., that the collision diameter of this absorption event is large. Generally, the mean distance traveled by a "free" ion before being captured will depend on the ratio of such collision diameter to the distance a between neighboring absorbers, a limiting situation being that such "mean free path" is of the order of a itself. In view of the inequality in eq 30, it would follow that a detached chain generally rejoins the network before it has completely relaxed the previous deformation, if any was present. It should be emphasized that this "incomplete relaxation" concept only relates to "length scales", as depicted in Figure 3, and not at all to time scales. Indeed, we maintain the assumption that the motion of a free chain, as determined by its "intrinsic" relaxation time, is much faster than the network kinetics, as measured by β_0. Yet, no matter how fast the chain end travels when it is free, it will not go any farther than some distance which can be as small as a. This limiting situation is the new assumption adopted here; the FP model considered in this section represents the opposite extreme from the complete-relaxation assumption of the TE model. Intermediate situations would be obtained by varying the ratio of the collision diameter to the distance a.

Under equilibrium conditions, and if, as we assume here, the chain end is endowed with an effective diffusion coefficient D given by

$$D \approx a^2 \beta_0 \tag{31}$$

the "effective" relaxation time of the chain, due to the presence of the network, becomes

$$\tau \approx \frac{Nb^2}{a^2} \beta_0^{-1} \tag{32}$$

Since τ also represents the relaxation time of the network in this case (instead of β_0^{-1} of the previous model), the zero-shear viscosity is now given by

$$\eta_0 = \nu kT\tau = \frac{\nu kT}{\beta_0} \frac{Nb^2}{a^2} \propto \nu^{5/3} \tag{33}$$

where the augmented dependence on concentration should be noted.

As regards shear thickening and shear thinning, the following argument provides estimates which should give us the essential predictions. We start by noting that, as long as the chains remain Gaussian and the detachment rate remains β_0, the dynamic behavior of the network is exactly described by an elastic dumbbell model in which the "spring" elasticity obeys eq 2 and the friction coefficient of the end beads is given by kT/D, where D is the diffusion coefficient defined by eq 31. As a consequence, the shear viscosity remains constant with increasing $\dot{\gamma}$. However, the chains become progressively stretched out in the shear direction with increasing $\dot{\gamma}$, following the quadratic law

$$\langle x^2 \rangle = \langle x_0^{\,2} \rangle (1 + 2\tau^2\dot{\gamma}^2) \tag{34}$$

where $\langle x^2 \rangle$ is the mean square projection of the chain dimension in the shear direction and $\langle x_0^{\,2} \rangle = Nb^2/3$ is that same quantity at equilibrium. Therefore, the chains will become fully stretched at a value of $\dot{\gamma}$ which makes the factor in brackets of the order of N, i.e., approximately at

$$\dot{\gamma} \approx N^{1/2}/\tau \tag{35}$$

When the chains are close to being fully stretched, the detachment rate dramatically increases with respect to β_0. Indeed, the rate of detachment increases significantly when the force in the stretched chain becomes of the order of E/b, where E is the energy of the barrier. Under such conditions, the shear stress is approximately given by

$$\sigma \approx \nu \langle |y| \rangle \frac{E}{b} \tag{36}$$

where $\langle |y| \rangle$ is the mean projection of the chains in the

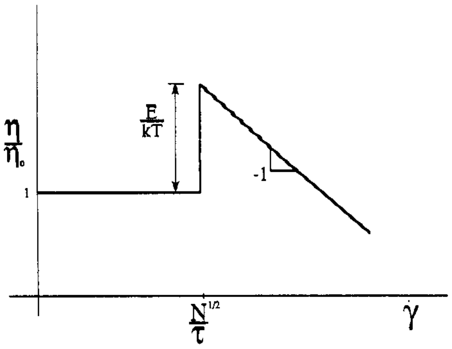

Figure 4. Logarithmic plot of the viscosity curve according to the crude estimates based on the FP model. More detailed calculations are expected to "round off" the jump, thus producing curves very similar to those observed.

gradient direction and is probably not very different from the equilibrium value $bN^{1/2}$. Since all terms in eq 36 remain constant when the shear rate is further increased (the chains just cannot be stretched any further), the viscosity will henceforth decrease inversely with the shear rate

$$\eta = \frac{\sigma}{\dot{\gamma}} \approx \frac{\nu N^{1/2} E}{\dot{\gamma}} \tag{37}$$

The shear-thinning behavior described by eq 37 starts at the value of $\dot{\gamma}$ given by eq 35, which suggests the viscosity attains a maximum value given by

$$\eta_{\max} \approx \nu E \tau = \frac{E}{kT}\eta_0 \tag{38}$$

Here, the last equality is obtained by using the first expression of η_0 in eq 33.

The value of the viscosity predicted by eq 38 is larger than η_0 inasmuch as E/kT is larger than unity. In other words, the shear-thickening behavior predicted by this model is due to the fact that the energy barrier is larger than kT, so that the chains are forced to become fully extended at large enough shear rates. The viscosity enhancement factor is of the order of E/kT; i.e., it is directly proportional to the value of the energy barrier.

The overall behavior of the viscosity predicted by the model (or, rather, by these first crude estimates based on the model) is schematically represented in Figure 4. The abrupt jump upward which takes place at the value of the shear rate given by eq 35 is not realistic, of course. A somewhat smoother transition is expected from a more exact treatment of the model. It is worth noting that, although the magnitude of the jump depends on the activation energy E, the location of the jump (predicted by eq 35) remains independent of E (as in the previous model) once such location is expressed in terms of stress rather than shear rate. This "critical" stress is found by combining eqs 33 and 35

$$\sigma_{\text{crit}} = \nu kTN^{1/2} \tag{39}$$

which exactly coincides with eq 23. Differently from the previous model, however, the value of the stress in eq 39 does not represent the crossover to shear thinning. The latter occurs at a larger, and E-dependent, value of stress, given by eq 36.

V. Discussion

At first sight, it may appear surprising that the shear-thickening effects predicted by the two models, both based on non-Gaussian behavior of the chains, differ so markedly. In the TE model, the predicted bump is E-independent and very small; in the FP model, it is significant and proportional to E. To understand how this difference arises, we use again a "work" argument. As shown explicitly by the calculations in section II, in the TE model the relevant work term is that required to stretch the chain from an essentially zero length all the way up to detachment which, under limiting conditions, occurs when the tension in the chain is of the order of E/b, i.e., when the chain is virtually fully stretched. The work made under those limiting conditions therefore consists of a fixed dominant part plus a small additional contribution which only grows logarithmically with E/b, i.e., very weakly. In fact, in the calculations made in section II, even that weak dependence was ignored, and the time average of the work was calculated by assuming a fixed renewal frequency β_0, up to a full extension of the chain (so as to obtain the maximum conceivable viscosity).

A very different situation is that pertaining to the FP model. Here, when the shear rate is large enough for the chains to become nearly fully stretched, the elementary dynamics of a chain can roughly be described as follows. Under the combined action of temperature and of a tension value close to E/b, the chain end detaches itself from the network and moves "back" a distance of the order of a. It then is captured again and moves "forward" a similar distance (one should in fact remember that a steady state of the system is being considered). Then the cycle repeats itself. Now, since a is much smaller than Nb, the tension in the chain remains of the order of E/b all the time, and the work per cycle is therefore roughly aE/b; i.e., it is directly proportional to E. The maximum in the viscosity will occur when the ratio of the detachment frequency to the shear rate (which decreases monotonically with increasing shear rate) has not yet dropped to its asymptotic lower bound ($\sim bN^{1/2}/a$), and yet the chain tension is already close to that large value (nearly E/b) which makes detachment virtually instantaneous.

As regards comparison with the observations, we will first consider the rheological experiments and, subsequently, the direct measurements of the chain radius of gyration.[10] With respect to the former, the FP model seems to predict correctly several significant features shown by the experiments. The data reported by Ketz et al.,[12] for example, clearly indicate that the value of the shear stress at which the shear-thickening effect first becomes apparent is independent of the type of counterion, while the zero-shear viscosity definitely is not. At a fixed concentration of the sulfonated copolymer used by them,[12] η_0 is found to increase with the ion sequence Zn, Cd, Ni, Na by more than a factor of 10. The critical shear rate at which shear thickening first appears is found to scale in the inverse direction, and therefore the critical shear stress stays roughly constant, just as predicted by the model.

The second important feature of shear thickening, i.e., the "height" $\eta_{\max}/\eta_0$ of the viscosity bump, also seems to be predicted correctly by the FP model, i.e., by eq 38. Indeed, with reference to the same data,[12] the sequence of increasing values of the zero-shear viscosity with the type of ion, from Zn to Na, implies that the energy barrier E also grows in the same order. Therefore, from eq 38, the bump height is predicted to increase from Zn to Na, which is in fact observed.

A third significant feature of the model which appears to agree with experiment is the prediction of eq 35 that the shear rate at which the shear thickening occurs is not of the order of $1/\tau$ but, rather, $N^{1/2}$ times as much. Indeed, the data reported by Broze et al.[7] for a solution of a telechelic polymer show the following: (i) The viscosity stays constant up to a value of the shear rate $\dot{\gamma} = 6\ \mathrm{s}^{-1}$ (their Figure 3), where shear thickening begins. (ii) From the storage and loss moduli as a function of frequency (their Figure 2), $1/\tau$ can be estimated as the frequency at which $G''(\omega)$ and $G'(\omega)$ depart from their limiting low-ω behavior (a linear and a quadratic law, respectively). The data indicate a value of the order of $0.1\ \mathrm{s}^{-1}$; Broze et al.[7] themselves indicate $0.45\ \mathrm{s}^{-1}$ as the frequency value below which "the system behaves as a viscous liquid". (iii) According to eq 35, one would then estimate $N^{1/2} = \dot{\gamma}\tau = 6/0.45 = 13$, which is not inconsistent with the molecular weight $M_n = 4600$ of the polybutadiene chains used by Broze et al.[7]

Still on the rheological evidence, an alarming note is signaled by the dependence of the relevant quantities on concentration. Indeed, if the concentration ν of elastically active chains is taken to be representative of the overall chain concentration, then we must conclude that eq 33 (not to speak of eq 17) strongly underestimates the concentration dependence of the zero-shear viscosity as shown by the data.[12] One way out of this difficulty could be to go from a model of telechelic unentangled chains, as considered in this work, to one of entangled polyion chains. Such a case could be treated along lines similar to those followed by Leibler et al.,[20] while also accounting for the fact that the basic friction coefficient kT/D is itself concentration-dependent, D being given by eq 31.

However, a different, and perhaps more attractive way of accounting for the discrepancy might be that of drawing a sharp distinction between elastically active chains and total chains. Indeed, from the critical value of stress where shear thickening begins (compare, e.g., Ketz et al.[12]), an estimate for ν can be obtained by using eq 39. The value of ν calculated this way is found to be dramatically smaller (by as much as a factor of about 10^3) than the ion concentration. This result links the rheological evidence to that of chain extension, which is discussed next.

The most disturbing observation which, seemingly, speaks against the idea followed in this paper (as well as against the suggestion of Witten and Cohen) was obtained, in one case at least, by Pedley et al.[10] From a neutron scattering experiment on labeled chains, they found that the shear-thickening effect was not accompanied by any appreciable stretching of the chains in the shear direction. They then proposed a mechanism based on larger structural units, consisting of aggregates of many chains.

Following up on their idea, the model presented in this paper could perhaps be reconciled with their evidence, as well as with the ν value calculated above, if one assumes that these multichain aggregates are attached to one another by a few chains (or pieces thereof) to form a continuous network. The rheological predictions would not change in any essential way with respect to the model considered here since the connecting chains would still be stretched in the way described and would provide the prevailing contribution to the stress tensor. Yet the proportion of these chains with respect to the virtually unstretched ones in the aggregates would be small enough to possibly escape detection in the neutron scattering experiment. More detailed modeling of this complex situation will be attempted in a future work.

It appears that it is still too early to draw definitive conclusions. Going back to our model as it now stands, a final remark regards the crudeness of the estimates obtained here for the case of the FP model. We tend to believe that, in order to improve on the quality of the predictions, one must either solve a nontrivial Smoluchowski equation or else perform Brownian dynamics simulations. Should the ideas expounded here prove to be worth further pursuit, both of these options can be explored.

Acknowledgment. G.M. gratefully acknowledges the hospitality of the Department of Chemical Engineering of the University of Delaware, where this work was carried out. S.B. and S.L.C. wish to thank the U.S. Department of Energy through Grant DE-FG02-88ER45370 for support of their research on ion-containing polymers.

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