Cross-Linking in Shear-Thickening Ionomers

T. A. Witten, Jr.*

Institute for Theoretical Physics, Santa Barbara, California 93106, and Exxon Research and Engineering Company, Linden, New Jersey 07036

M. H. Cohen

Exxon Research and Engineering Company, Linden, New Jersey 07036.
Received December 4, 1984

ABSTRACT: Ionic groups attached at wide intervals along nonpolar polymer chains produce strong associating interactions in solution. In certain cases, such solutions exhibit shear thickening; the viscosity increases with the flow rate. We sketch a mechanism for shear thickening in which the flow produces increased association between chains at the expense of associations within a chain. We calculate in a mean-field approximation how chain elongation produced by flow alters the balance between intra- and interchain associations. The effect is sufficiently large to account qualitatively for the observed dependence of viscosity on shear rate and on concentration. Surprisingly, the effect is maximized when the number of associating groups per chain is kept small.

I. Introduction

Ionomers like sulfonated polystyrene are flexible-chain macromolecules with widely spaced ionic groups that attract each other strongly. Solutions of these ionomers in nonpolar solvents have unusual rheological properties; in contrast to ordinary polymer solutions these have a viscosity in Couette flow that increases with increasing shear, attains a maximum, and then falls again at high shear rates.[1] The problem here is to understand microscopically how the associating groups produce the shear thickening. The discoverers[2] of the effect had a plausible qualitative picture of its origin. Shear flow is known to elongate polymers in solution. It seems reasonable that the elongation might increase the number of associations between chains—cross-links—thus forming larger temporary complexes. It is known that larger molecules are more effective at producing viscosity than are small ones. Thus, shear flow can lead to increased viscosity. The role of the associations in this scheme is to make links between chains and to make more of them when the chains are elongated. In this paper we use established statistical properties of polymers to show that this effect actually occurs. We infer how this cross-linking effect depends on molecular composition. Surprisingly, the cross-linking under shear is maximized with only a few associating groups per chain. We go on to study how much shear thickening is to be expected from this effect. We argue that a gel phase should be producible under shear.

We first review the nature of the associating interactions and the characteristic scales of energy, time, and distance. The sulfonated groups in ionomers tend to assemble into clusters, whose size is limited by mutual repulsion of the bulk of the monomers and by steric hindrance.[3] The clusters may contain only a handful of sulfonated groups each. For simplicity we shall assume that the groups may only associate in pairs. Each group is thus an associating site to which one other such site may be attached. A given site may stick to another site on the same chain or may cross-link two chains.

There are two important time scales in this system. The first is the mean lifetime of an associated pair. The pairs are held together strongly, with a binding energy U much larger than thermal energies kT. Thus, each pair remains attached for a time much longer than a local relaxation time. Indeed, the links must live a considerable time if they are to support shear stress in cooperation with the chains in solution. That is, if a cross-linked complex is to act rheologically as a single unit, the lifetime of the cross-link must be at least of the order of the hydrodynamic relaxation time of that unit. This hydrodynamic relaxation sets the second important time scale in the system. Qualitatively, this is of the order of a Zimm time for the chains;[4] this scales as the cube of the radius. Polymers in solution undergo elongation in a flowing solvent when the shear rates become comparable to the relaxation rate;[5] it is in shear flows of this magnitude that shear-dependent viscosity effects become apparent in ordinary polymer solutions. The same appears to be true for the associating polymers studied in ref 1. Both rates were of the order 10^{-2} s^{-1}. Thus, the shear-thickening effect does not appear to require large flow rates or extreme elongation. If the lifetime of a link is so long that it becomes comparable to the duration of an experiment—seconds—then hysteresis effects should become apparent in the rheological behavior.

The largest length scales in the system are set by the chain radius R and the mean volume per chain. The latter varies inversely with the concentration c. In order for the desired cross-linking to occur, the chains in solution must overlap. And indeed, solutions become shear thickening slightly above c^*, the concentration at which overlap becomes appreciable. For concentrations too far above c^* the viscosity becomes very large even without shear. Apparently in such cases the cross-linking has become extensive, so that a weak gel has formed. Two smaller length scales are the average distance between associating sites and the length of a statistical segment along the chain. The ratio of ionomeric groups to monomers is typically small, so that there are normally many statistical segments per associating site. Still, there are typically 10–30 sites per chain. Normally the solvent is a good one for the chains as a whole, so that all monomers that are not associating sites experience an effective mutual repulsion. Thus the chains are swollen[6] with end–end radius R varying with molecular weight to the ν power, where $\nu \simeq 0.6$ is the Flory exponent.

II. Statistics of Associations in Equilibrium

We first consider the associations in the absence of elongation. The solution contains a set $S = \{s_1,...,s_k\}$ of associating sites, which are in general associated in some pairing arrangement Y. Y is a list of specifications such as, e.g., s_1 paired with s_{223}, s_2 paired with s_{91}, s_3 unpaired, and so forth. The likelihood of a given state Y is determined by the partition function Z of the solution

$$Z \equiv \sum_{\{c\}} e^{-E(c)/kT} \tag{1}$$

where the sum is over all configurations c of the solution,

0024-9297/85/2218-1915$01.50/0

and $E(c)$ is the energy of that configuration. The probability $P(Y)$ of a particular pairing state Y is given by

$$P(Y) = \sum_{\{c\}(Y)} e^{-E(c)/kT}/Z \tag{2}$$

The numerator is the partition function with the sum restricted to those configurations compatible with the pairing state Y. Similarly, the probability B_i that sites s_0, and s_i are bound is given by

$$B_i = \sum_{\{c\}(s_0 s_i)} e^{-E(c)/kT}/Z \tag{3}$$

where the sum in the numberator is over configurations in which the sites s_0 and s_i are bound.

The exact calculation of B_i would be complicated and uninformative. The main dependence of B_i on the chemical distance between the associating sites can be deduced in a simple model. From this model we find that the pairing occurs predominantly between chemically adjacent sites, and we infer how cross-linking increases with concentration.

We first consider the pairing of site 0 with site i on the same chain a distance i statistical segments away. To see how B_i depends on i, we ignore the pairing of other sites. We may accomplish this by supposing that only site 0 attracts the others. The probability B_i can be expressed in terms of the pair distribution function $p_i(r)$, defined as the normalized probability per unit volume that the sites lie at displacement r in the absence of the attraction between sites. The r dependence of p_i is a known fundamental property of chain molecules.[7,8] This quantity falls to zero for distances r much greater than the average separation R_i. It peaks for distances of order R_i. For distances much smaller than R_i, $p_1 \sim r_\theta$, where θ is 0 for ideal chains and in the range 0.7–0.9 for excluded volume chains in three dimensions. Thus, close approaches are suppressed for the excluded volume segments. For small distances $r \ll R_i$, we infer

$$p_i(r) = K_1 R_i^{-d}[r/R_i]^\theta \tag{4}$$

where the R_i factors ensure normalization. We have written the formula for general dimension d of space. The constant K_1 is of order unity for a flexible chain in a good solvent and is independent of R_i and i. From $p_i(r)$ we may infer the partition function $Z_i(r)$; this is the partition function of the solution restricted to those configurations having the two sites at displacement r. Evidently $p_i(r) = Z_i(r)/Z$. In the presence of the interaction U the partition function $Z_i(r)$ is modified. For simplicity we treat $U(r)$ as a square well of depth $-ukT$ and range b. In the presence of interaction, the distribution function gains the Boltzmann factor $e^{-U(r)/kT}$; thus, $Z_1(r)$ gains the same factor. That is, $Z_i(r)$ is increased by a factor e^u for $r < b$ and is unchanged for $r > b$. From this Z_i we may calculate the probability B_i that a pair at chemical distance i is bound

$$B_i = \int_{r<b} d^d r \, \frac{Z_i(r)e^u}{Z(u)} = \frac{Ze^u}{Z(u)} \int_{r<b} d^d r \, p_i(r) = \frac{Ze^u}{Z(u)} K_1 \left(\frac{R_i}{b}\right)^{-d} \left(\frac{b}{R_i}\right)^\theta \tag{5}$$

where $Z(u)$ is the partition function of the solution. We shall treat only interactions short ranged on the scale of R_i. In this limit the binding ratio B_i/B_j for two pairs at different chemical distances can be written explicitly by using eq 5

$$B_j = B_i[R_i/R_j]^{d+\theta} \tag{6}$$

Here the R_i and R_j are the noninteracting averages used previously. For excluded volume chains R_i varies[7] as i^ν; thus

$$B_j = B_i[i/j]^{(d+\theta)\nu} \tag{7}$$

The overall power is about 2 in three dimensions. Thus, the binding probability falls off rapidly with chemical distance. To illustrate this, we may consider a long chain with associating sites spaced at intervals of k statistical segments. Again site 0 interacts with all the others, but these are not allowed to interact among themselves. By summing the expression for B_j over all the distances k, $2k$, ..., one finds that the two adjacent sites, at distance k, account for nearly 70% of the binding.

Binding of different chains can be calculated by the same method used above. We denote the pair distribution function of the two sites fixed at distance r as $p_\infty(r)$. Without the sticking interaction, this $p_\infty(r)$ is suppressed at small r, with the same r^θ dependence as above. It becomes independent of r beyond the "static screening length" ξ of the solution. Thus, for $r < \xi$

$$p_\infty(r) = K_2/\Omega \, [r/\xi]^\theta \tag{8}$$

where K_2 is of order unity and Ω is the volume of the solution. Denoting the number of sites per unit volume by c_s, the probability B_∞ for binding of the given site with any other on another chain is evidently

$$B_\infty = K_2 c_s e^u b^{d+\theta} \xi^{-\theta} \frac{Z}{Z(u)} \tag{9}$$

From this we may find the ratio of binding between chains to binding with a site at a distance i segments within the chain.

$$B_\infty/B_i = K_2/K_1 c_s R^d{}_i [R_i/\xi]^\theta \tag{10}$$

We may find B_∞ more explicitly in the limit of strong binding. We take the sticking interaction to be so strong that the probability that the given site is unbound becomes vanishingly small. Then

$$\sum_i{}' B_i + B_\infty = 1 \tag{11}$$

where $\sum'$ runs over those values of i having associating sites. Using the illustrative case of many sites at positions 0, $\pm k$, $\pm 2k$, etc., we may express the $\sum'$ as DB_k, where D is a constant ≈ 2. Then

$$B_\infty = \frac{1}{1 + DB_k/B_\infty} \tag{12}$$

The concentration dependence of B_∞ is instructive. To discuss this, we suppose that the polymers have N statistical segments[4] and define R as the chain radius in the dilute limit. We denote c as the concentration of statistical segments in the solution. The polymer concentration is thus c/N; that of associating sites is $c_s = c/k$. In the dilute regime, defined by c/N less than or about equal to R^{-d}, the screening length ξ is of order R, and the mean distance between sites, $c_s^{-1/d}$ is much larger than R_k. Evidently, B_∞ is small; it can only become appreciable in the semidilute regime, where $\xi^{1/\nu-d} \sim c$. In this regime R_k/ξ and $c_s R_k{}^d$ are both measures of the chain overlap, and one is a simple power of the other

$$[\xi/R_k]^{1/\nu-d} = K_3 c_s R_k{}^d \tag{13}$$

Thus

$$B_\infty/B_k = \frac{K_2}{K_1 K_3}[R_k/\xi]^{\theta+d-1/\nu} \tag{14}$$

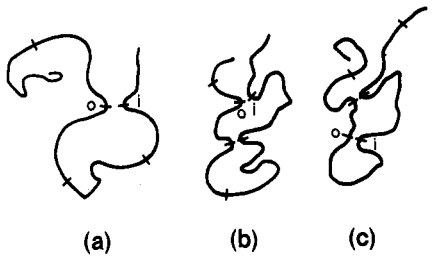

Figure 1. Pairing of stickers at segments 0 and i (a) without other pairing, (b) with additional pairing of two stickers between segments 0 and i, and (c) with additional pairing of stickers before segment 0 and beyond segment i.

in this regime. The power is about 2 in three dimensions. Thus, B_∞ increases with the concentration. The effects of cross-linking should become apparent when the number of cross-links per chain is of order 1. This number is roughly $(N/k)B_\infty$. Thus cross-linking is appreciable when

$$[\xi/R_k]^{\theta+d-1/\nu} \geq N/k \tag{15}$$

Thus, ξ is always larger than R_k for the marginally cross-linked solutions of interest. For higher concentrations, interchain cross-linking would be important and gelation would occur. The viscosity would become large even without shear as noted above.

This derivation of B_∞ assumes that the sticking interaction $U(r)$ only occurs between site 0 and the others. In the real solution all the sites interact. This alters B_∞, but only in a minor way. The main effect to be considered is the pairing of sites other than the pair in question. This alters the probability B_i of intrachain binding. Evidently, the B_i is increased if the average distance between the two sites is shortened by the binding of others, as in Figure 1. For a given state Y of the other sites one may readily work out the effect on B_i. Except for constants like K_1 and K_2, eq 5 for B_i is unaltered, except that the average R_i is to be taken with the other stickers paired as specified. Qualitatively this R_i varies as $(i')^\nu$, where i' is the *shortest* chemical distance between the given stickers. In examples like those in Figure 1 the qualitative behavior of the B_i is unaltered. A given sticker is still paired predominantly with the chemically nearest sticker. We expect the same to be true in general. The cross-linking of a given sticker to another is also enhanced by the pairing of other stickers between the same two chains. This cooperative effect may become important if B_∞ becomes large. We consider here the opposite regime, where the average number of cross-links between a chain and any other is small. Then the enhanced cross-linking should be small as well.

III. Statistics of Association in Flow

We expect the cross-linking rate B_∞ to increase when the chains are elongated in a velocity gradient. We describe how this increase occurs using a simple model for the elongation: a force $\mathbf{F}$ applied to the ends of the chain. The force $\mathbf{F}$ elongates the end–end distance in the direction of $\mathbf{F}$ by a factor denoted λ. We shall treat moderate elongations, for which $\lambda - 1 \approx \mathbf{F}\cdot(R/kT)$. This model is sufficiently realistic to describe the moderate elongations we wish to treat. The elongated chains attain a new thermal equilibrium state, which reflects the external force. The elongation may be treated here as an equilibrium process because any time dependence in the actual applied forces is no faster than the polymer relaxation times. In the new equilibrium state the pair distribution function $p_i(r)$ will be altered, and so will the probabilities B_i and B_∞. The changes come about because the average separation R_i is modified. This R_i appears in two places: the R_i^{-d} prefactor is essentially the inverse volume occupied by sticker i (with sticker 0 at the origin). With elongation this is replaced by $R_{\|i}^{-1} R_{\perp i}^{1-d}$. R_i also appears in the suppression factor $(r/R)^\theta$. This factor is due to the local repulsions between monomers whose average distance is of order r. The repulsive energies involved are of order kT or more. In contrast, the external tension $\mathbf{F}_i$ acting on the segment is less than kT/R_i, and the energy $\mathbf{F}_i\cdot r$ ($r \ll R_i$) competing with the local repulsive energy is minuscule. Thus, the suppression factor remains isotropic for the moderate elongations of interest. The suppression factor appearing in $p_i(r)$ is merely rescaled by replacing R_i by some other average $R^{ji}(\lambda)$, whose precise definition need not concern us.

With this information we can see how B_∞/B_i is modified by elongation

$$B_\infty/B_i = (K_2/K_1)c_s[R_{\perp i}(\lambda)]^{d-1}[R_{\|i}(\lambda)][R_{\theta i}(\lambda)/\xi]^\theta \tag{16}$$

We may estimate straightforwardly how the R's change under elongation and thereby calculate the change in B_∞. In the regime of interest the relative change of B_∞ under elongation will not be large, and it will be sufficient to consider a small elongation, which produces a change ΔB_∞. Using the saturation condition of eq 11, we find

$$\frac{\Delta B_\infty}{B_\infty} = \frac{1}{1+V}\frac{\Delta V}{V} \tag{17}$$

where $V \equiv B_\infty/\sum'_i B_i$.

We consider first our example of many associating sites per chain at intervals k, with $1 \ll k \ll N$. In this case $\sum'_i B_i$ is dominated by the adjacent sites, with $i \approx k$. This remains true with elongation, and again we may write $\sum'_i B_i(\lambda) = DB_k(\lambda)$, where D is constant of order unity. To find $\Delta V/V$, we need only consider B_∞/B_k, as given in eq 14. Evidently, $\Delta V/V \sim \Delta R_k/R_k$. But $\Delta R_k/R_k$ is very small if $k \ll N$, as we now show.

To see this, we write the elongational energy of the chain as $\mathbf{F}\cdot R = \mathbf{F}\cdot\sum_{i=1}^N \mathbf{a}_i$, where the $\mathbf{a}_i$ are the random vectors defining the chain. The effect of the force $\mathbf{F}$ on the segment 0–k can be separated into two contributions. The simpler is the direct perturbation $\sum_{i=0}^k \mathbf{F}\cdot\mathbf{a}_i$ on the links within the segment itself. This effect causes a ΔR_k of order $R_k[\mathbf{F}\cdot R_k/kT]$.

Since F/kT is of order $(\lambda - 1)/R$, we have

$$\Delta R_k/R_k \sim (\lambda - 1)[R_k/R] \tag{18}$$

There is another contribution to ΔR_k. The force $\mathbf{F}$ elongates the tails connected to either end of the segment. There is less overlap between these tails when the segment is oriented along $\mathbf{F}$. The repulsive energy is comparable to the direct energy $\mathbf{F}\cdot R_k$. We conclude that the net elongation of the segment is comparable to that due to the direct effect alone. From this, recalling eq 17 for ΔB_∞, we obtain

$$\Delta B_\infty/B_\infty \sim (\lambda - 1)[R_k/R] \tag{19}$$

so that B_∞ can only change by a small percentage under moderate elongation, $\lambda \approx 1$. The same is true of the average number of cross-links per chain, $(N/k)B_\infty$. Since the cross-linking does not increase appreciably, the viscosity cannot increase appreciably.

In the opposite limit of a *small* number of sites per chain, the cross-linking rate is much more sensitive to elongation. Again ΔB_∞ may be calculated via eq 17. In this limit the distance k between adjacent sites is of order N, and thus in eq 18, R_k/R is no longer as small as before.

Moderate elongations now produce an appreciable change in cross-linking rate.

IV. Cross-Linking Enhances Viscosity

We have established that elongation can affect cross-linking substantially. We now show qualitatively that this cross-linking should increase the viscosity η of the solution. We assume that the complexes formed by cross-linking act as a unit in the velocity gradient. These complexes have various radii R_a, with some well-defined average $\bar{R}$. The clusters are composed of various numbers of chains, which also have a well-defined average $\bar{s}$. We may treat the viscosity qualitatively by replacing each cluster by a sphere whose radius is of order R_a. Thus, in the dilute limit[9]

$$\eta = \eta_s\left[1 + D_2\sum_a \frac{R_a{}^d}{\Omega}\right] = \eta_s\left[1 + D_2\frac{c\overline{R^d}}{N\bar{s}}\right] \quad (20)$$

Here η_s is the viscosity of the solvent, Ω is the volume of the solution, and D_2 is a numerical constant. This dilute-limit formula underestimates the viscosity somewhat at the concentrations of interest. First we rewrite the formula to give the relative change $\Delta\eta/\eta$ under an incremental change in cross-linking

$$\frac{\Delta\eta}{\eta} = \frac{D_2[c\overline{R^d}/N\bar{s}]}{1 + D_2[c\overline{R^d}/N\bar{s}]}\frac{\Delta[\overline{R^d}/\bar{s}]}{\overline{R^d}/\bar{s}} \quad (21)$$

At the concentrations of interest, we may ignore the prefactor, since it is of order 1.

The change of $\overline{R^d}/\bar{s}$ with cross-linking can be estimated with the classical gelation theory of Flory and Stockmayer.[6] In this theory the clusters are treated as random tree structures. When the cross-linking rate B_∞ exceeds a critical value B_c of order $(N/k - 1)^{-1}$, a gel forms. The average $\bar{s}$ diverges near the threshold as $(B_c - B_\infty)^{-1}$, and the average radius $\bar{R}$ diverges as $(B_c - B_\infty)^{-1/2}$. This leads to

$$\Delta\eta/\eta \sim \Delta B_\infty/(B_c - B_\infty) \quad (22)$$

Thus, the viscosity changes by an appreciable factor whenever B_∞ does. Further, if B_∞ approaches the gelation threshold, the viscosity becomes increasingly sensitive to changes in B_∞. Thus, e.g., if B_∞ varies from $^1/_2B_c$ to B_c, the viscosity should increase from near that of un-cross-linked chains to a large value characteristic of a weak gel.

V. Discussion

We have shown that moderate elongation of ionomeric chains can produce large increases in viscosity and can even cause gelation. The reasoning has been kept as simple as possible and has thus ignored several important effects. Chief among these is a cooperative effect relating viscosity to elongation. When the solution viscosity increases in a given shear, the relaxation time of the clusters increases. This makes the given shear more effective in producing elongation. The increased elongation produces additional viscosity, forming a positive-feedback cycle. As the shear increases, this effect should lead to an instability of the system against an abrupt, first-order gelation above some threshold value of the shear rate. In this regime a given shear rate may be compatible with two different elongations λ and with two different viscosities η; one might then see coexistence of a fluid phase with a gel phase. A further cooperative effect would enhance this positive feedback. This is the dependence of the viscosity on volume fraction of complexes, mentioned above. As the volume fraction $(c/N)(\bar{R}^d/\bar{s})$ increases, the viscosity rises progressively beyond the dilute-limit formula of eq 20.[9] This only augments the positive-feedback cycle described above.

Another effect limits the increase of viscosity seen above. Even in the gel phase the viscosity is limited by the relaxation of the sticker bonds themselves. The limiting viscosity is roughly the elastic modulus G of the gel, supposing the cross-links permanent, times the relaxation rate of a bond. A further effect inhibits the thickening mechanism treated here. This is the well-known shear thinning of polymer solutions in shears larger than the chain relaxation rate. This effect is thought to arise because of the alignment of the molecules in the flow, so that they avoid one another. This effect could wipe out the abrupt gelation if the latter requires too great elongation.

To treat these cooperative effects on a quantitative theoretical basis is a difficult problem. However, these effects—viscosity → elongation and overlap → viscosity—are not peculiar to ionomers but are common to all polymer solutions. One may thus use the well-studied phenomenology of ordinary polymers to treat these effects. The effect of elongation on cross-linking rate—unique to ionomers—appears to be a simple one where cooperative effects are not crucial. Thus, it seems that shear thickening in ionomers can be understood on a simple basis. It may even give rise to dramatic effects like first-order gelation, which had not been anticipated.

The effects predicted here are in qualitative agreement[10] with experiments on ionomers such as those studied in ref 1. The shear-thickening effect is observed maximal near concentratins of order the marginal overlap concentration c^*. The abrupt gelation anticipated above is also observed. The dependence of shear thickening on the number and fraction of associating groups is in rough accord with experiment. These qualitative observations are not sufficiently detailed to test the theory stringently. Such a test would require direct measurements of the relationship between elongation and complex size. Optical birefringence and dynamic light scattering offer potential means of probing this relationship. In ionomers the number of associating groups in a cluster is expected to depend on the proportion of the groups along the chain. This effect must be measured and accounted for to make detailed predictions of shear thickening.

Acknowledgment. We are grateful to R. D. Lundberg, I. Duvdevani, and P. Pincus for helpful discussions.

References and Notes

(1) Duvdevani, I.; Agarwal, P. K.; Lundberg, R. D. *Polym. Eng. Sci.* **1982** *22*, 499.
(2) Lundberg, R. D.; Duvdevani, I., private communication.
(3) Eisenberg, A. *Macromolecules* **1970** *3*, 147. MacKnight, W. J.; Earnest, T. R. *Macromol. Rev.* **1981** *16*, 41.
(4) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(5) Zimm, B. *J. Chem. Phys.* **1956** *24*, 269.
(6) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1971; Chapter XII.
(7) des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1980** *41*, 223.
(8) Witten, T. A., Jr.; Prentis, J. J. *J. Chem. Phys.* **1982** *77*, 4253.
(9) Bird, R. B. "Dynamics of Polymeric Liquids"; Wiley: New York, 1977.
(10) Duvdevani, I.; Lundberg, R. D., private communication.