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## Associating polymers and shear thickening

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**Résumé.** — On discute l'épaississement sous cisaillement des solutions d'ionomères. Les données de diffusion de rayonnement et les modules dynamiques suggèrent que les groupes ioniques s'agrègent en multiplets qui contrôlent la relaxation des contraintes. On décrit un mécanisme simple pour l'épaississement sous cisaillement ; ce mécanisme demande une énergie de liaison finie pour les agrégats. On montre que cette force d'association pose des problèmes graves pour la solubilité des polymères. Ces problèmes s'aggravent lorsque le nombre d'ions dans un multiplet augmente. On décrit la compétition des interactions qui détermine ce nombre d'agrégation.

**Abstract.** — The shear-thickening property observed in ionomer solutions is discussed. Scattering and dynamic modulus data suggest that the ionic groups cluster into multiplets and that these control the relaxation of stress. A simple mechanism for shear thickening is described ; it leads to the expectation that these clusters must be bound with a certain minimal strength. Associations with the strength required are argued to pose serious problems for solubility. These problems worsen with increasing number of ions in a multiplet. The competing interactions which determine this number are described.

### 1. Introduction.

Figure 1 illustrates a peculiar type of polymer solution. When it is rocked back and forth gently in its jar it flows with the consistency of motor oil. But if the jar is shaken or quickly inverted, the liquid becomes a weak gel, with the consistency of a half-cooled gelatin dessert. The liquid somehow becomes stronger under stress, instead of weaker like most materials. The molecular basis for this *shear thickening* property is the subject of this talk.

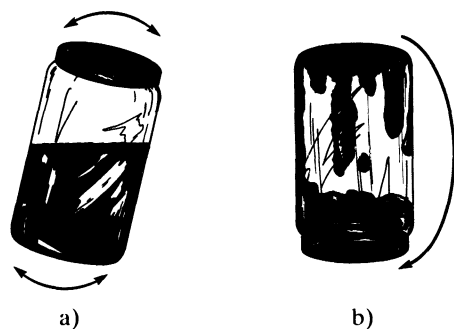


Fig. 1. — A jar of shear-thickening solution : (a) quiescent state ; (b) after rapidly inverting the jar.

Several kinds of polymers make shear-thickening solutions. One type especially familiar at the Exxon labs is known as an ionomer, such as sulfonated polystyrene [1, 2, 3]. This is an ordinary polystyrene chain, typically of molecular weight around  $10^5$ , with about thirty sulfonate groups attached randomly along the backbone. The sulfonate anions are neutralized by cations such as sodium or zinc. The solvent is a nonpolar hydrocarbon like xylene. The concentration is moderately greater than overlap concentration  $c^*$  ; the low-shear viscosity is typically 10-100 times that of the solvent.

When the viscosity of such a solution is measured in a Couette cell, the dependence of the stress  $\sigma$  on shear rate  $\dot{\gamma}$  is distinctly different from that of a solution of the unsulfonated parent polymer with similar viscosity, as shown in figure 2. This latter begins too thin when the shear rate exceeds a few hundred per second, and the viscosity  $\eta \equiv \sigma / \dot{\gamma}$  decreases progressively at higher shear rates. The sulfonated polymer solution, by contrast, begins to thicken at shear rates of the same order, and the viscosity may increase in two different ways, depending e.g. on the detailed geometry of the Couette cell. The typical behaviour is a severalfold increase in viscosity over a factor of 2-3 increase in shear rate,

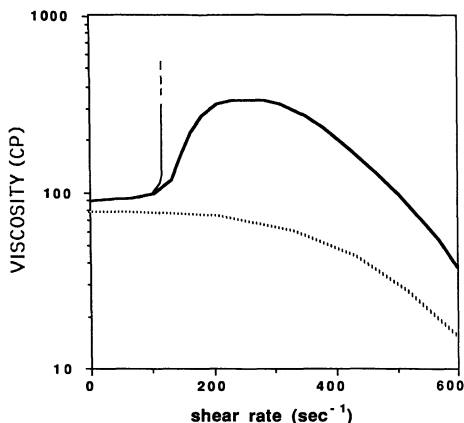


Fig. 2. — Schematic viscosity versus shear rate for two polymer solutions: (dashed line) ordinary linear polymers; (solid lines) sulfonated ionomers.

followed by a strong shear thinning at higher shear rates. Sometimes the thinning corresponds to a constant limiting stress, independent of shear rate. But the viscosity may also display an instability above a threshold shear rate. The viscosity increases slightly as the shear rate increases up to the threshold. For slightly greater shear rate, the viscosity rises spontaneously at fixed shear rate up to values beyond the range of the instrument, over a period of a minute or less.

In this talk I will try to give you a feeling for our current understanding of these strange solutions. My understanding has leaned heavily on the help of many Exxon collaborators and senior colleagues, credited in the acknowledgements below. First I want to summarize what is known about the structure and rheology of ionomer solutions. As to the structure, inferred by scattering experiments, it seems that the ionic groups form small, robust multiplets, insensitive to perturbations of the solution. As to the rheology, the dynamic shear modulus suggests that these ionic groups control the relaxation of stress. But the nonlinear rheology of shear thickening is hard to characterize.

With these experimental clues we have evolved a theoretical picture of how shear thickening might work. I want to discuss this picture and its conclusion that the associations should be strong. The presence of such strong associations raises questions about the solubility of these polymers. But I will describe a way in which one may preserve both sufficient strength and solubility, if the associating multiplets are small. Finally, I will discuss the factors that control the size of a multiplet in solution, and compare with some recent experiments.

## 2. Structure.

To see the molecular structure responsible for the behavior of figure 1 is technically difficult. The ionic

groups are present in such small concentration that they scatter very weakly. Thus our main scattering information about ionomers comes from the melt state, with no solvent. MacKnight and Earnest [1] summarize this data.

The scattered intensity  $I(q)$  shows a peak in ionomers for wavevectors  $q$  in the range of  $(10 \text{ \AA})^{-1}$ , which is not present in the parent polymer melt. The peak position shifts as the cube root [4] of the concentration of ionic groups; i.e. it is proportional to the average distance between these groups. If we imagine that the groups are arranged in a close-packed lattice or a dense liquid, we may infer the nearest neighbour spacing  $d = (\text{Cst.})/q_{\text{max}}$ . Figure 3 shows the result [5]. A correlated liquid with the experimental concentration of groups would follow the dashed line. The observed  $d$ 's are too large. To understand this one may suppose that the ionic groups form clumps or multiplets. Then this data suggests that such multiplets must contain roughly three groups apiece, independent of the concentration of groups. Thus the  $d$  spacing grows substantially larger than the size of a multiplet. It is natural that the polar ionic groups should segregate in the nonpolar hydrocarbon melt. And it is interesting that these multiplets maintain their separation well enough to give a peak in  $I(q)$  even for volume fractions of ionic groups of only a few percent. A recent study [6] confirms this picture, and also shows that the number of groups  $f$  in a multiplet is insensitive to the addition of solvent. This study also indicates that the cations live in domains of radius 5-10  $\text{\AA}$ , consistent with the multiplicity  $f$  inferred above.

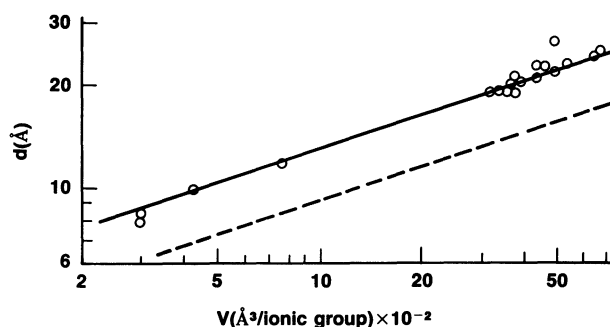


Fig. 3. —  $d$ -spacing versus volume fraction of methacrylic acid ionic groups, after reference [5]: (dashed line) expected  $d$  dependence for individual groups arranged in a close-packed lattice or dense-liquid arrangement, (solid line) best fit to scattering data, consistent with three-group multiplets.

## 3. Rheology.

The low-shear rheology of ionomeric solutions has been well studied. One instructive study is the extensive work of Jerome and Teyssie on end-

functionalized chains [7-10]. The polymers in their study have a carboxylate anion at each end of a linear chain such as polyisoprene. The carboxylate may be neutralized with various cations, such as (divalent) magnesium. The neutralized chains are prepared in dilute solution, and then concentrated to the desired point.

The viscosity of such a solution increases dramatically with concentration, as shown in figure 4a. The viscosity extrapolates to infinity at a concentration  $c_{gel}$  about equal to the overlap concentration  $c^*$ . The interchain distance at the gelation concentration was found to be the same as the root-mean-square end-to-end distance, within a constant numerical factor (Fig. 4b). This factor was independent of molecular weight and polymer type. Assuming that the end-end distance of the chains is equal to the nearest-

neighbour distance between multiplets at gelation, one gets an estimate of 6-7 groups per multiplet.

This gelation phenomenon suggests that the chains associate with one another to form a macroscopic network when they reach a concentration near  $c^*$ . Multiplets with half-a-dozen chains emerging from them would be expected to be connected with several other nearby multiplets at this concentration. Thus the network picture is intuitively appealing.

The dynamics of this network are important for its mechanical properties. These properties were studied [10] by measuring the *dynamic moduli*  $G'(\omega)$  and  $G''(\omega)$ , i.e. the ratio of in-phase and out-of-phase stress to strain when the system is subjected to a small oscillating strain. The moduli show the same magnitude and frequency dependence as an ordinary semidilute polymer solution of the same concentration, but much higher molecular weight. As shown in figure 5a, there is a peak in the loss modulus  $G''$ , whose position gives the characteristic stress relaxation time of the system. The same time scale is seen when the steady-shear viscosity is measured as a function of shear rate. This system showed a mild shear thickening, with onset at a shear rate roughly equal to the peak frequency in  $G''$ .

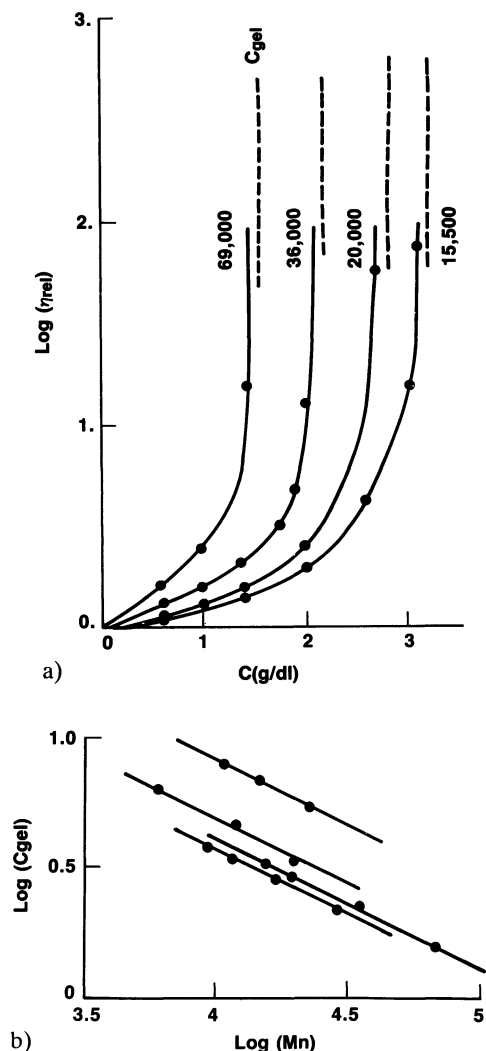


Fig. 4. — (a) Low-shear viscosity *versus* concentration for end-functionalized polymers of various molecular weights as indicated. The polymers are polyisoprene with a magnesium-neutralized carboxylate group at each end; (b) dependence of apparent gel concentration  $c_{gel}$  on molecular weight for various polymers. Redrawn from reference [8].

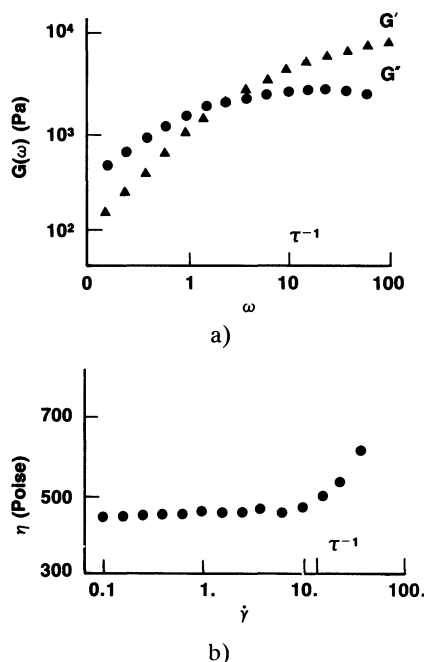


Fig. 5. — (a) Reactive and dissipative parts  $G'$  and  $G''$  of the dynamic modulus *versus* angular oscillation frequency  $\omega$  for a 10 g/deciliter solution of 4,600-molecular-weight poly-butadiene chains functionalized as described under figure 4. Peak angular frequency in  $G''$  is indicated as  $\tau^{-1}$ ; (b) steady-shear viscosity of the solution in (a). Redrawn from reference [10].

The relaxation time in ordinary semidilute solutions [11] is the time for the interpenetrating chains

to disentangle. The relaxation seen in ionomer solutions appears to have a different origin. The temperature dependence of the relaxation time shows this. Figure 6 shows that this time, corrected for the viscosity of the solvent [11], varies exponentially in the inverse temperature, so that the relaxation is characterized by an activation energy. By contrast, the relaxation time in normal polymer solutions, similarly corrected, shows practically no temperature dependence.

The origin of the activation energy in the ionomers appears to be the ionic multiplets themselves. This is because of the way the relaxation time varies with the neutralizing cation. There is an important variation, as figure 6 shows, and it depends monotonically on the ionic radius. Agarwal *et al.* [12] found similar behaviour of the dynamic modulus in randomly sulfonated chains like those of figure 1, with various cations.

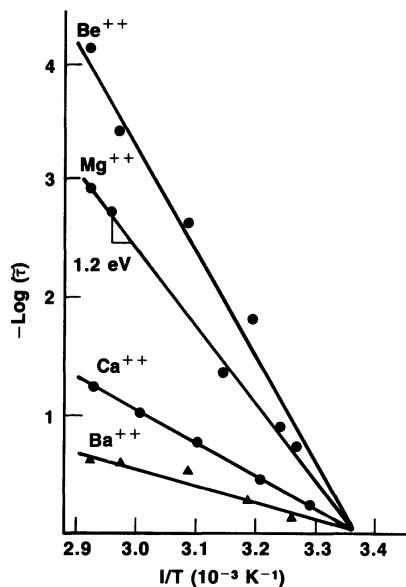


Fig. 6. — Dependence of inverse relaxation time  $\tilde{\tau}$  on inverse temperature for the solution in figure 5 and solutions with other neutralizing cations as indicated. The times  $\tilde{\tau}$  have been scaled to compensate for the variation in viscosity of the solvent with temperature. The lines correspond to Arrhenius behaviour. The activation energy for the Mg salt is indicated. Redrawn from reference [10].

Since the stress relaxation is so sensitive to this minor component in the solution (the cations), it seems clear that the multiplet that contains these is the place where the stress relaxes. This suggests that the time for stress to relax in these solutions is simply the time for an ionic group to dissociate from a multiplet. If so, dynamic modulus measurements can also tell us something about the strength of the multiplets.

The activation energies  $E$  obtained from figure 6

suggest rather strong binding, of order an electron volt (23 kcal/mol) or more. We may check this by using a simple Eyring [13] argument to estimate the relaxation time  $\tau$ :  $\tau = \tau_0 \exp(E/(kT))$ , where the attempt time  $\tau_0$  is no shorter than about  $10^{-12}$  s (typical liquid relaxation times [14] are of the order  $10^{-11}$  s). The value of  $E$  for magnesium cations from figure 6 gives a predicted relaxation time of more than a million seconds, a factor of  $10^8$  slower than the observed relaxation (Fig. 5).

A likely source of this discrepancy is that the dissociation energy is temperature dependent. If this (free) energy  $E$  had the form  $A + BT$ , the slope in figure 6 would give only the constant part  $A$ . The real energy  $E$  could thus be appreciably less than this slope suggests. The binding energy might decrease at higher temperature e.g. because of increasing dielectric constant of the solvent, leading to increased solubility of the ionic groups. To show directly the connection between the stress relaxation rate and a measured free energy of binding would be an important step in understanding ionomers.

Ionomers with many groups per chain show a low-shear rheology like the end-functionalized chains discussed above [12]. A distinct gelation concentration has not, however, been reported for these polymers (cf. Fig. 4). This may be due to weaker association in the sulfonate system used [15]. It could also be due to polydispersity effects, which could smear out the gelation transition. These many-group polymers show stronger shear thickening than that shown in figure 5b for the end-carboxylated chains. The shear thickening is most dramatic near the overlap concentration  $c^*$ , suggesting that the chains must interact, but need not interpenetrate strongly. The thickening sets in at shear rates of the order of the inverse relaxation time of the system, suggesting that the shear is strong enough to perturb the chains appreciably.

To study this shear thickening more quantitatively has proven surprisingly difficult. I was unable to document my description of shear thickening in ionomers with any published reports! The origin of these difficulties is probably important both for understanding and for using these solutions. Thus I will try to summarize the some of the problems encountered.

Good dissolution is difficult with these polymers. Sometimes the samples swell as a gel instead of dissolving. Even when the polymers dissolve, they may take many weeks to equilibrate; viscosity continues to change over this time scale. The diluted chains can be aggregated in clusters of 3-5 chains [16]. The ionic groups can absorb water, changing the associations significantly. The viscosity under steady, moderate shear has been observed to increase gradually over many days without apparent limit.

#### 4. A proposed mechanism for shear thickening.

A theory of shear thickening should justify why associating polymers shear thicken while ordinary polymers do not. It should give some insight about what properties the associating groups must have in order to achieve the most shear thickening. It should also be consistent with the observed concentration and shear-rate dependence. Several years ago, Cohen and I [17] proposed a mechanism for shear thickening. The qualitative ideas behind the mechanism are taken from the conventional wisdom [18]. But the development of these ideas leads to some clear suggestions about how the associating groups must act: they must be strong in a specific sense to be discussed below.

For simplicity, we consider the polymers as structureless self-avoiding walks. Each chain has a number of associating groups, which we model as binary *stickers*. For definiteness we imagine 2-3 stickers per chain [19]. The extension to many stickers per chain is discussed in reference [17]. Each sticker can bind to a single other sticker, either on the same chain or on another. We shall assume that the associations are strong, so that every sticker *must* be paired with one other. In this limit, the free energy of sticking is irrelevant for our purposes, since all the configurations of the solution considered have the same number of pairs, hence the same sticking energy.

An equilibrium solution of such chains has some evident properties. At concentrations far below  $c^*$  every chain is paired to itself [20]. Interchain pairing costs translational entropy and gains no sticking energy. As the concentration is raised above  $c^*$ , interchain pairing becomes more and more common, and many of the chains are bound in aggregates or clusters of many chains. Somewhere near  $c^*$  paired aggregates of extensive size appear; the system gels.

The time for the chains to attain their equilibrium state depends on the binding energy of the stickers: stronger binding means slower equilibration. In what follows we assume that the pairs are long-lived on the scale of any shear rate, so that the aggregates look virtually permanent to the flow. But we suppose that the duration of our experiments is many times the lifetime of a pair, so that equilibrium between interchain and intrachain pairing is established.

We expect moderate shear to alter the pairing of chains. In a solution just below the gel concentration, a shear rate comparable to the inverse hydrodynamic relaxation time of a chain will distort the chains (and aggregates) appreciably. They become somewhat elongated in the flow, as do ordinary polymers under similar conditions [21]. An elongation by a factor of order unity stores very little energy in the polymers; each chain gains of order [21]  $kT$ . (We note that this

would not introduce enough stress in the stickers to alter their binding energy appreciably.) But the elongation does lead to a statistical bias against intrachain pairing, as one may estimate quantitatively. Since all stickers are paired, the reduction of intrachain pairing leads to an increase in interchain pairing. Thus the sheared solution is expected to have larger aggregates and to attain gelation at lower concentration than the same solution without shear. It is natural then for the sheared solution to have an increased viscosity. But this occurs only because the interchain pairing increased. And this increase in turn occurs only because the pairing was strong, so that lost intrachain pairs had to be replaced.

More quantitatively, we consider the double-line chain in figure 7. This chain may either be self-paired (Fig. 7a) or cross-paired (Fig. 7b). We wish to see how an imposed elongation of this chain alters its cross-pairing probability  $p_x$ . It is simple to compute the ratio of the self-paired to cross-paired probabilities for, say, the left-hand sticker on our chain. This ratio may be determined by considering the system in which the pairing interaction of this sticker with all others is turned off. Then we can compute the probability that this sticker touches another from the theory of ordinary polymer solutions [22]. The probability of touching a sticker from another chain is evidently proportional to the concentration of stickers in the solution, but independent of any elongation of our chain (or the others). On the other hand the probability that this sticker touches the other on the same chain is sensitive to elongation. It falls off as a power of the elongated radius; the specific power depends on whether good-solvent swelling effects are important [23].

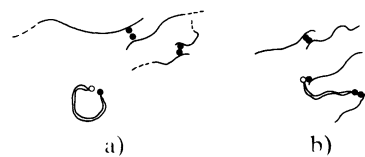


Fig. 7. — Typical configurations of model associating polymer solution. The thick chain is self-paired in a; cross paired in b.

Now our sticker is again allowed to interact. This increases the self- and cross-contact probabilities greatly. Specifically, each is multiplied by a large Boltzmann factor exponential in the binding energy  $E$ . But this factor cancels out in the ratio  $T$  of self-pairing to cross-pairing probabilities. Thus the ratio is independent of the strength of associations. Since the ratio  $T$  depends on concentration and elongation in a known way, we can use it to predict the cross-pairing probability  $p_x$  itself in the strongly associated

limit. In this limit the cross-pairing and self-pairing probabilities must sum to unity, so that  $p_x = (1 + T)^{-1}$ . Cross-pairing increases with elongation, as anticipated above.

Without strong association, i.e. when  $E \leq kT$ , the elongation of a chain has much weaker impact on cross-pairing. Thus in the limit of weak association, we may neglect the Boltzmann factor in  $E$ , so that the cross-pairing probability is directly the cross-contact probability in the absence of sticking. There is no need to compute the ratio  $T$ . As discussed above, this cross-contact probability does not depend on elongation. Thus the shear-thickening mechanism fails in this limit. Although the flow decreases the probability of intra-chain pairing, the cross-pairing need not increase to compensate; instead the total number of paired stickers can simply decrease. Evidently to give an appreciable effect, the associations must be strong enough that a substantial fraction of the stickers are bound.

Given the increased cross-pairing due to flow, one may estimate how the viscosity might increase. The size distribution of the cross-linked aggregates can be found using percolation theory [24]. Since the mean volume-per-polymer of the aggregates increases with shear, the solution of aggregates is at a higher concentration relative to its  $c^*$ . We may use empirical expressions [25] for the viscosity as a function of  $c/c^*$  to estimate the increase of viscosity under shear. Typical behaviour is shown in figure 8. Apparently a mild elongation, and a moderate change in cross-pairing, can lead to a large change in viscosity, if one operates close to the gel concentration.

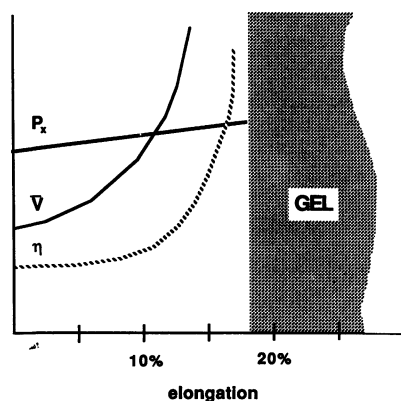


Fig. 8. — Schematic plot illustrating how elongation influences aggregates in model associating polymer solution. As the cross-pairing probability  $p_x$  increases slightly, the average cluster volume  $\bar{V}$  diverges at a particular elongation. The viscosity  $\eta$  also diverges.

This viscosity dependence has certainly not been confirmed quantitatively; indeed our model is only applicable qualitatively, since real ionomers as-

sociate into larger multiplets. Still, the principles discussed here seem to offer a plausible explanation of shear thickening, which could be tested.

### 5. Association and solubility.

Associations are a form of attraction of polymer chains for themselves. Usually such attraction, if it is strong, leads to collapse of individual polymers and phase separation of solutions. This, plus the practical solvation problems that I mentioned above, lead to the alarming possibility that good shear-thickening properties are inherently *incompatible* with good solvation properties. I discuss that possibility in this section.

Recently Agarwal, Garner and Graessley [26] of our laboratory have studied the solubility question experimentally. They measured the hydrodynamic volume per chain of dilute polystyrene sulfonate in toluene using viscosity measurements. As figure 9 shows, the chains appear to collapse progressively with increased sulfonation. The reduction in volume-per-chain follows the same functional dependence on amount of sulfonation with a variety of different cations and temperatures, when suitably scaled [26]. This collapse behavior is a disturbing sign of solubility problems.

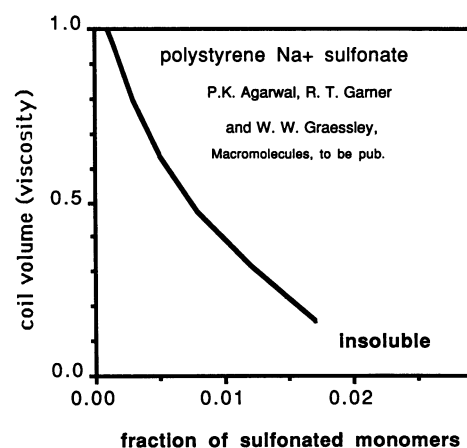


Fig. 9. — Hydrodynamic volume of sulfonated polymers relative to that of the unsulfonated precursor, after reference [26]. Horizontal axis is fractional sulfonation. The cation was sodium.

We discuss these problems by considering a solution of strongly associating chains. For convenience we take them to be end-functionalized. But for realism, we allow them to form not simply pairs, but multiplets of  $f$  stickers apiece. As before, we take these multiplets to be strongly associated, so that all the stickers are in these multiplets. Our question is whether the chains will dissolve well with these strong associations or whether they will stay together as a gel.

The issue is whether two multiplets, with their associated chains, have a lower free energy apart or together in a good solvent. If the two multiplets are apart, each is the center of a *flower* of  $f/2$  chains. When brought to a separation comparable to their size, these chains experience the usual excluded-volume repulsion of polymers in a good solvent. At such separations the excluded volume free energy is of order  $kT$  (see Ref. [27]). Countering this excluded-volume repulsion is the extra freedom that stickers have when two multiplets are nearby (Fig. 10). The *two flower* configuration is no longer required; chains may link one multiplet with the other. This freedom adds an entropy of up to  $kT(f \log 2)$  to the two nearby multiplets, and constitutes an effective attractive free energy of up to about  $fkT$ . Based on this upper bound, it appears plausible that the pairing free energy increases with  $f$ .

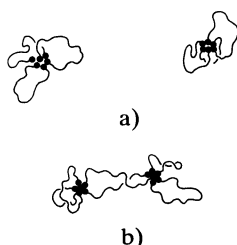


Fig. 10. — Two  $f$ -multiplets far apart (a) and close together (b). In (a) both multiplets must adopt the *flower* configuration, in which both ends of a chain are in the same multiplet; in (b) the two ends of a chain may be in the same or in different multiplets.

Comparing the attractive and repulsive energies, it appears that the attraction must dominate for sufficiently large  $f$ . If the net energy is more attractive than about  $kT$ , the solution must phase separate in some range of concentrations. Thus large multiplets, with large  $f$ , imply bad solubility.

How small must  $f$  be to allow good solvation? We can get some information about this by going back to the pairing model:  $f = 2$ . Here the *flowers* reduce to simple loops, and there is only one type of chain re-arrangement, which itself forms a loop. Much is known about the interaction of a self-avoiding loop with itself and with other loops. Because of this Cates and I [23] were able to evaluate the net interaction energy in spatial dimensions  $d$  approaching 4. The result, found to first order in  $(4-d)$  and extrapolated to three dimensions is that the attractive effect is substantially stronger. According to this approximate (though systematic) calculation, even  $f = 2$  is too large to give good solubility!

This prediction that strongly associating end-functionalized ionomers are insoluble has not been explicitly tested to my knowledge. A natural case in

point would be the carboxylate-tipped polymers of Teyssie and Jerome. The papers of these authors suggest that these chains, once concentrated, cannot be rediluted. This gives some support for the prediction. Fetters *et al.* [28] found similarly that their both-end functionalized chains were insoluble unless the associations were weakened substantially.

The bad solubility of the end-functionalized chains can be overcome by modifying the chain architecture [23]. If the two stickers are placed not at the ends of a polymer, but partway towards the center, the freedom gained from re-pairing is reduced, while the excluded-volume repulsion is left essentially unchanged. This improvement can again be estimated using scaling properties of excluded-volume chains, and  $(4-d)$  expansion methods. Cates's and my estimates to first order in  $4-d$  are shown in figure 11. Here the interaction energy is expressed as a second virial coefficient for the chains. According to this estimate, the polymers become soluble if the stickers are placed less than about halfway in from the ends. We expect this trick of placing the stickers unevenly along the chains to work for higher multiplicities  $f$  and for chains with many stickers. It appears that the attainment of solubility and shear-thickening poses important problems, but that there is good hope for solving them.

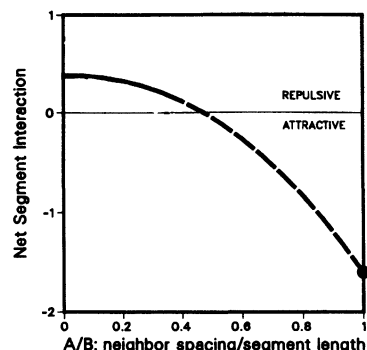


Fig. 11. — Estimate of the net mutual excluded volume for two associating segments of  $B$  monomers, each with a pair of stickers separated by  $A$  monomers in a good solvent with  $A$  and  $B$  much greater than 1. Excluded volume is scaled by cubed end-end distance. After reference [23].

## 6. Nature of the multiplets.

From the discussion above, it is clear that the multiplicity  $f$  is important in controlling the properties of ionomers. Recently some experimental [28] and theoretical [29] work at Exxon addressed the factors that control  $f$ . This work deals with solutions of chains with ionic groups on one end only.

Qualitatively, the energy balance which determines the multiplicity  $f$  can be discussed in three



parts. The driving force for forming multiplets is the electrostatic dipole-dipole attraction between the ionic groups. For typical ionomers in simple hydrocarbon solvents, this energy could easily amount to 10-20  $kT$  of energy. In packing together to maximize this electrostatic energy, the ionic groups and the nearby monomers lose some configurational energy. The exclusion of solvent from this region can cost substantial energy, as can the packing constraints on the chain segments. These energies are important for the local region around the multiplet where the volume fraction of chain segments is high. Unless  $f$  is quite large, this concentrated region extends no more than a few monomers from the center.

These two contributions, which involve the immediate vicinity of the multiplet, are independent of the molecular weight  $N$  of the  $f$  chains. In addition the  $f$  chains extending from a multiplet contribute a repulsive (excluded-volume) free energy that grows with molecular weight  $N$  of a chain. This energy behaves the same as that of a star polymer. Pincus and I [27] have worked out the scaling of this energy using the Daoud-Cotton [30] picture of starlike polymers. This picture treats the polymer as a semidilute solution, exploiting the fact that the local concentration changes slowly on the scale of a correlation length. As in a semidilute solution, the tail free energy is of order  $kT$  per correlation volume, and scales as  $f^{3/2} \log(N)$ .

Since the free energy depends so weakly on the molecular weight  $N$ , the arm number  $f$  of lowest free energy should in general also vary weakly with  $N$ . The behaviour of ionomer multiplets discussed above is consistent with this idea. The multiplicity is not observed to vary much with the molecular weight between ionic groups. Recently this expectation was examined more directly at Exxon [28], using chains with ionic groups at one end. These were not the neutralized organic anions discussed above, but bulky zwitterions, with three carbons linking the two ions.

These zwitterionic chains behave counter to the expectations expressed above. The multiplicity  $f$  determined by light scattering and osmometry sometimes varied from 30 to one as the molecular weight per chain varied between 20,000 and 200,000. Evidently the weakly-varying tail energy is nevertheless sufficient to destabilize these multiplets. We believe this means that the attractive and repulsive contributions to the micelle energy are closely balanced. Further evidence for this balance is that the multiplets are strongly influenced by small changes in the solvent, even among good solvents for the tails. It seems likely that there are significant differences between these zwitterion multiplets and those made with simple ions and counterions.

## 7. Conclusion.

The first part of this talk reviewed some experimental findings on polymer solutions that show shear thickening. These suggest that shear thickening arises from the tendency of the functional groups to stick to one another in small clusters or multiplets. In the second part of the talk I considered how far these sticking properties were needed for shear thickening. To this end I suggested a specific mechanism for shear thickening. For the mechanism to work effectively, I concluded that the associations must be strong-strong enough that the removal of one associating group from a multiplet makes it probable that another one will take its place. This strength requirement creates serious difficulties with regards to solubility. In simplified associating systems we saw that the entropy associated with the exchange of associating groups between multiplets can easily produce sufficient attraction to cause phase separation. There are two ways to minimize this attraction. One is to use associations that make small multiplets rather than large ones. The other is to distribute the associating groups unevenly along the chains.

To address what controls the multiplicity  $f$ , one can identify several types of interaction which produce the multiplets and limit their size. But we have not yet achieved a satisfying understanding of the multiplicity.

I hope this talk persuades you that these associating-polymer solutions, apparently so dirty and ill-behaved, have a fundamental interest. Like many statistical systems with competing interactions, associating polymers show properties qualitatively different than either of the competing interactions alone would give. Shear thickening is such a property. This thickening may result from a network structure whose organization is sensitive to the state of flow. But beyond this primitive suggestion, the understanding of associating polymer rheology has barely begun. The molecular events leading to mechanical relaxation of the associated network are surely much different from those in a gel or a solution. The inhomogeneous flow states that such solutions may exhibit and the range of rheologies achievable by changing the molecular composition raise exciting questions to be tackled in the next few years.

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