The theory of shear-thickening polymer solutions

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A theory that describes the rheological properties of shear-thickening polymer solutions has been developed. This theory comprises an extension of Flory's theory of the expansion parameter to the case where macromolecules contain segments that can associate in an intramolecular fashion. Analysis of experimental results using this theory enabled determination of the association constant. It is then proposed that, when macromolecules with associating groups are placed in an elongational flow field of sufficiently high strain rate, they extend, thereby breaking intramolecular associations and allowing the formation of intermolecular associations, to an extent dictated by the association constant. The quantitative predictions of this theory are then compared with rheological measurements on a well known shear-thickening polymer, ICI's FM9.

(Keywords: shear thickening; negative thixotropy; expansion parameter; FM9; anti-misting kerosene)

INTRODUCTION

In general, the viscosity of a polymer solution decreases as the shear strain rate is increased[1]. This effect is known as 'shear thinning', and it is thought to be due (*inter alia*) to the disentanglement of polymer chains under the influence of the flow field[2]. However, a small number of polymer solutions behave in precisely the opposite fashion. That is, the viscosity of the solution *increases* as the shear strain rate is increased[3]. Further, this increase can be smooth or abrupt, and may also be time-dependent[4].

Most, if not all, of these 'shear-thickening' polymers contain segments that are capable of association, through ionic or dipolar interactions, hydrogen bonding, insolubility in the medium and so on. This has led several authors[3,5] to speculate that the origin of 'shear thickening' lies in a change from primarily intramolecular to intermolecular associations, caused by the flow field. Recently, a semiquantitative theory based on these concepts has been proposed[6] for polymers with segments that associate very strongly. However, there is as yet no general theory that quantitatively predicts the behaviour of these unusual polymer solutions.

In this work we develop a fully quantitative theory for the phenomenon of shear-thickening polymer solutions. This theory is in two parts.

The first part is a thermodynamic description of the configuration of an isolated polymer chain that contains segments that are capable of association. There have already been two limited treatments of this problem. The first involved a perturbation treatment in the vicinity of the 'average' theta-point[7]. The conclusion was that associating polymers under near-theta conditions could have expansion parameters less than 1.0, but still have positive second virial coefficients. The second treatment[6,8] was limited to polymers with a small number of segments that associated very strongly. Unfortunately, this is not the case for most shear-thickening polymers. In the present paper we develop a general theory based on Flory's original approach[9] to the problem of the expansion parameter. While this will retain the problems inherent in Flory's approach, it is a general theory, it is conceptually very simple and it permits determination of the fundamental chemical parameters of the association.

The second part is a description of the dynamics of a polymer coil with associating segments, under the influence of a flow field. Of particular importance here is the pioneering work of Odell and Keller[10] on the behaviour of macromolecules in elongational flow fields. By consideration of what happens to an associating polymer coil in such flow fields, the mechanism of shear thickening is readily understood, and the equations that describe the process are easily written down. We then relate the behaviour of associating polymers in elongational flow fields to that in shear.

Finally, in order to test the validity of the theory proposed here, we compare its predictions with rheological measurements on what is probably the most well known shear-thickening polymer, ICI's proprietary anti-misting kerosene additive, FM9.

THE THERMODYNAMICS OF ASSOCIATING POLYMERS

The conformation of a polymer molecule in solution is described by the expansion parameter:

$$\alpha^2 = \langle r^2 \rangle / \langle r_\theta^2 \rangle \tag{1}$$

where $\langle r^2 \rangle$ is the mean-square radius of gyration and the subscript 'θ' denotes the theta (or unperturbed) state.

Flory[9] was the first to propose a theory of the expansion parameter. This theory was based upon the concept that the total free energy of the chain, ΔG, was the sum of the elastic (configurational entropy) free energy,

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ΔG_{el}, and the free energy of mixing, ΔG_m (the 'excluded-volume' effect). The chain then adopts the conformation of minimum free energy:

$$\partial \Delta G/\partial \alpha = \partial \Delta G_{el}/\partial \alpha + \partial \Delta G_m/\partial \alpha = 0 \tag{2}$$

In this section we derive an expression for the contribution of associations to the free energy, ΔG_a. We then use this to evaluate the expansion parameter of chains with associating segments.

We begin with the chemistry of the association of small molecules. Let us assume that such association is a chemical reaction:

$$\mathrm{m} + \mathrm{m} \rightleftharpoons \mathrm{d}$$

where 'm' denotes monomers, or unassociated molecules, and 'd' denotes dimers. The equilibrium constant for the reaction is:

$$K = [\mathrm{d}]/[\mathrm{m}]^2 \tag{3}$$

and the free energy of association is:

$$\Delta G_a^\circ = -RT \ln K \tag{4}$$

The concentration of dimers is then:

$$[\mathrm{d}] = \{4K[\mathrm{m}]_0 + 1 - (8K[\mathrm{m}]_0 + 1)^{1/2}\}/8K \tag{5a}$$

$$\simeq K[\mathrm{m}]_0^2 \tag{5b}$$

where $[\mathrm{m}]_0$ is the initial concentration. Equation (5a) is exact, and equation (5b) is an approximation that is valid for low degrees of association.

We now make a second important assumption: that the association of segments of a polymer chain can be described within the same framework. Thus given a Gaussian distribution of chain segments:

$$x(r) = N(\beta_\theta/\pi^{1/2})^3 \exp(-\beta_\theta^2 r^2) \tag{6}$$

where N is the number of segments, r is the radius and β_θ is related to the mean-square radius of gyration in the theta state by:

$$\beta_\theta = (1.5/\langle r_\theta^2 \rangle)^{1/2} \tag{7}$$

the distribution of associating segments is:

$$[\mathrm{m}]_0 = f x(r)/N_A \tag{8}$$

where f is the mol fraction of segments in the polymer that are capable of association, and N_A is Avogadro's number. The distribution of dimers is then given by substituting equation (8) into equations (5); if we use the approximate result for simplicity then:

$$[\mathrm{d}] = K f^2 x^2(r)/N_A^2 \tag{9}$$

The contribution of associations to the free energy is just the number of associations times the free-energy change per association (using equation (9)):

$$\Delta G_a = \Delta G_a^\circ \int_0^\infty [\mathrm{d}] 4\pi r^2 \, \mathrm{d}r$$
$$= -2kTC_m(\mathrm{d}_p^2 V_1 f^2 K \ln K/M_s^2) M^{1/2} \alpha^{-3} \tag{10}$$

where d_p is the density of polymer, V_1 is the molar volume of solvent, M_s is the average segment molecular weight, M is the molecular weight of the chain and C_m is the usual constant:

$$C_m = (27/2^{2.5}\pi^{1.5})(1/\mathrm{d}_p^2 N_A V_1)(M/6\langle r_\theta^2 \rangle)^{1.5} \tag{11}$$

The associative free-energy gradient can then be derived from equation (10), and, when combined with the elastic and mixing free-energy gradients, yields:

$$\alpha^5 - \alpha^3 = 2C_m(0.5 - \chi - f^2 d_p^2 V_1 K \ln K/M_s^2) M^{1/2} \tag{12}$$

where χ is Flory's polymer–solvent interaction parameter. This equation is the main result of this section. Except for the third term in the parentheses, it is identical to Flory's original result. Physically, it means that associations make macromolecules contract in size and decrease in solvency to an extent dictated (*inter alia*) by the number of associating segments in the chain and the equilibrium constant for their association. This behaviour has been observed experimentally[11].

Equation (12) is an approximate result that is valid for small degrees of association. The exact expression for the associative free energy is:

$$\Delta G_a = kT \ln K \sum_{i=2}^{\infty} 3^{3(i-1)} i^{-1.5} \pi^{1.5(1-i)}$$
$$\left(\prod_{j=1}^{i} (0.5 - j + 1)\right)(1/i!)$$
$$\times (8K)^{i-1} f^i (M/M_s)^i (6^{1.5} N_A \langle r^2 \rangle^{1.5}) \alpha^{3(1-i)} \tag{13}$$

Unfortunately, one cannot obtain an analytical expression for the expansion parameter from this result. However, a value for the expansion parameter can be calculated by numerical evaluation of equation (13) and its derivative. In practice, with physically reasonable degrees of association, this value is identical to that obtained with equation (12).

THE DYNAMICS OF ASSOCIATING CHAINS

Odell and Keller[10] have found that in an elongational flow field a macromolecule undergoes a transition from the random coil to the fully extended state at a sufficiently high strain rate (see *Figure 1*). This extension occurs at a strain rate given by the Zimm, non-free-draining relaxation time. When the strain is switched off, the extended macromolecule returns to the more thermodynamically stable coil state. It does this slowly because the extended chain experiences the full viscous drag of the solvent, and so it behaves as a Rouse free-draining chain.

This suggests the following qualitative model for the phenomenon of shear thickening, shown stylistically in *Figure 2*. At rest, associating macromolecules are in solution in the random coil state, and have a number of transient intramolecular associations. When a sufficiently large elongational strain rate is applied, the macromolecules will extend, thereby breaking these intramolecular associations. After some time, shear, turbulence and Brownian motion will entangle the

Figure 1 Transition from the coil to the extended state

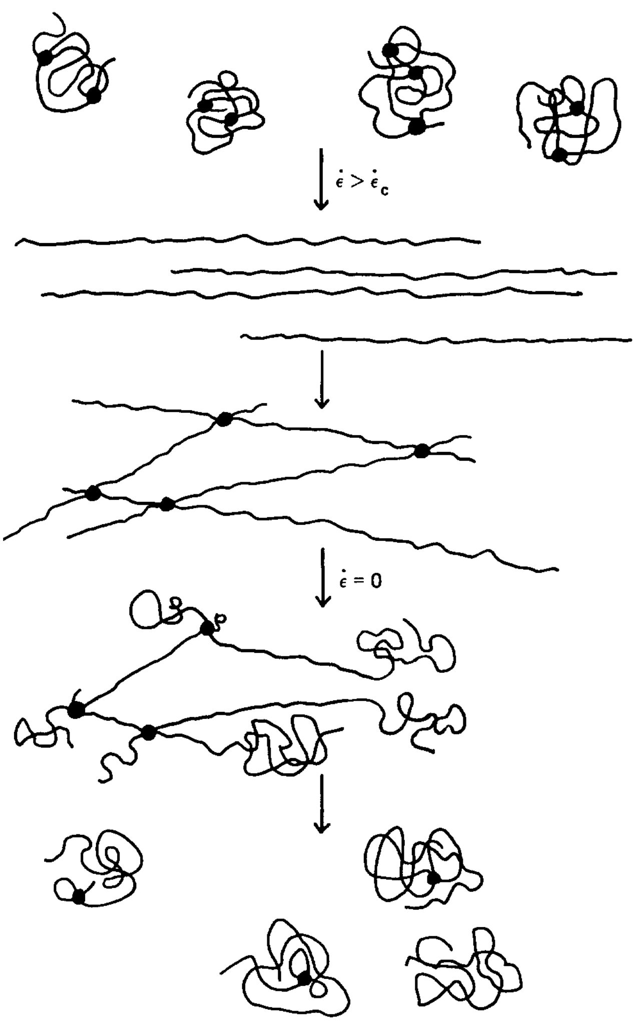

Figure 2 A qualitative model for thickening in elongational flow

extended chains, and associations will re-form, but in an intermolecular fashion because each chain is extended. These intermolecular associations act as physical crosslinks, thereby creating a gel network. Because these associations are transient in nature, this gel is not a true gel: it does have a finite, if large, viscosity. Finally, if the strain is switched off, the gel will decay as the chains return to the more thermodynamically stable coil state.

Thus, in summary, high strain rates extend macromolecules: this breaks intramolecular associations and allows the formation of intermolecular associations, thereby creating a gel network and giving rise to an increase in viscosity. We now proceed to quantify this process.

The critical elongational strain rate at which a macromolecule extends is[10]:

$$\dot{\varepsilon}_c = C/\eta M^{1.5} \propto 1/\eta\langle r^2\rangle^{1.5} \qquad (14)$$

where C is a constant for a given polymer. Thus for any given strain rate $\dot{\varepsilon}$, macromolecules of molecular weight M_c and above will extend:

$$M_c = (C/\eta\dot{\varepsilon})^{2/3} \qquad (15)$$

Now, since polymer samples are often polydisperse in molecular weight, we wish to know how much of a particular sample will be extended by a given strain rate. To do this we consider the molecular-weight distribution $N(M)$: the number of macromolecules of molecular weight M. The weight fraction of chains that are extended by a strain rate of $\dot{\varepsilon}$ is then:

$$\phi_w = \int_{M_c}^{\infty} MN(M)\,dM \Big/ \int_{0}^{\infty} MN(M)\,dM \qquad (16)$$

Note that since M_c depends on both the strain rate and the viscosity, so too does ϕ_w. Further the number-average molecular weight of those extended chains is:

$$M_n^e = \int_{M_c}^{\infty} MN(M)\,dM \Big/ \int_{M_c}^{\infty} N(M)\,dM \qquad (17)$$

Now, if the concentration of polymer in solution is c, then the concentration of polymer in the extended state is:

$$c_e = c\phi_w \qquad (18)$$

so the concentration of segments capable of association in extended polymer chains is:

$$[m_e] = fc_e/M_s \qquad (19)$$

Next, we assume that an equilibrium degree of association occurs between segments in the extended chains, and that these associations are intermolecular in nature because the chains are extended. The concentration of intermolecular dimers is thus:

$$[d_e] = \{4K[m_e] + 1 - (8K[m_e] + 1)^{1/2}\}/8K \qquad (20)$$

Since the molar concentration of extended chains is c_e/M_n^e, the average number of associative crosslinks per extended macromolecule is:

$$X = 2[d_e]M_n^e/c_e \qquad (21)$$

The factor of 2 arises because every single crosslink is present in two different macromolecules. Since there are X crosslinks per extended chain, there are $(X+1)$ subchains per extended chain. The molar concentration of these subchains involved in network formation is thus:

$$c_X = (X + 1)c_e/M_n^e \qquad (22)$$

We now apply the theory of rubber elasticity in its earliest form[9] in order to calculate the shear modulus G. While the modulus predicted by Flory's theory is not very accurate (it is generally about 30% too low), this is a minor flaw in comparison with the assumption that the extended subchains can be described by Gaussian statistics. Bearing these limitations in mind, the predicted modulus of the gel is:

$$G = c_X RT \qquad (23)$$

In order to calculate the increase in viscosity we start with the reptation theory[12] of Doi and Edwards[13,14]. Their expression for the viscosity of a polymer solution is[13]:

$$\eta = \pi^2 G\tau/60 \qquad (24)$$

where τ is the reptation time, so the increase in viscosity upon strain is:

$$\eta_X/\eta_0 = (G_X/G_0)(\tau_X/\tau_0) \qquad (25)$$

The increase in modulus is given by equations (22) and (23), and so the unknown in equation (25) is the reptation time, and how it changes upon the formation of transient associations.

The question of the reptation time of chains with associating groups (e.g. ionomers) has been studied by Gonzalez[15]. He presented a model in which transient associations were continually breaking and re-forming, but in which reptation of a chain could only occur if all of its associations were broken. This model leads to an exponential increase in the reptation time with the average number of associations per chain. This is probably an overestimate of the effect of associations upon the reptation time, as it predicts that solutions of macromolecules with about a dozen or more associations would effectively have infinite viscosity. Further, the theory itself is somewhat unphysical, as it does not take the strength of the association into account.

The origin of these two problems lies in the assumption that reptation can only occur if all associations are broken. A more plausible postulate is that chain motion is impossible only near the association, and that the motion of the bulk of the chain is relatively unaffected. The best analogy is that of a centipede: most of its legs are stuck to the ground (by gravity) at any given time, but it moves quite quickly by detaching one leg from one spot and re-attaching it somewhere else. A chain with associative crosslinks moves in a similar fashion: as it reptates, single associations decay in one place and re-form somewhere else, and so it maintains an equilibrium number of crosslinks.

This model of the motion of a chain with associations suggests that its reptation time is only slightly greater than that of a chain without associations. To a rough approximation the increase in reptation time will just be the time taken for all of the associations to decay:

$$\tau_X = \tau_0 + X\tau_a \tag{26}$$

When we combine equations (22), (23), (25) and (26), and recognize that there are three contributions to the viscosity (solvent, coiled chains and extended, crosslinked chains) we obtain:

$$\eta/\eta_0 = 1 - (\eta_r - 1)(1 - \phi_w) + (\eta_r - 1)\phi_w(1 + X)(1 + X\tau_a/\tau_0) \tag{27}$$

where η_0 is the solvent viscosity and η_r the relative viscosity.

In order to calculate this viscosity rise, we adopt an iterative procedure. For any given strain rate and initial viscosity, we calculate a critical molecular weight, M_c, and then calculate ϕ_w, M_n^e, $[m_e]$, $[d_e]$, X and the viscosity rise η/η_0 from equations (15) to (27). We then recalculate M_c with the new viscosity, and proceed through the calculations again to give a new viscosity rise. We then iterate until the viscosity rise converges, up to a maximum of 100 iterations. This procedure directly reflects the fact that shear thickening is a positive-feedback process, as noted by Witten and Cohen[6].

Finally, we come to the question of how the behaviour in shear flow relates to that in elongational flow. Rather than propose an explicit model to relate the two, we instead note that while FM9 in decalin at 0.5% concentration has a critical elongational strain rate of[10] $\dot{\varepsilon}_c = 232\,\mathrm{s}^{-1}$ (at half the viscosity maximum), FM9 in kerosene at the same concentration has a critical shear strain rate of $\dot{\gamma}_c = 505\,\mathrm{s}^{-1}$ (see *Figure 4*). Given the difference in viscosities of the two solvents (kerosene, $\eta_0 = 1.15$ mPa s; decalin, $\eta_0 = 2.46$ mPa s[16]) one would predict using equation (16) that FM9 in kerosene would have a critical elongational strain rate of $\dot{\varepsilon}_c = 496\,\mathrm{s}^{-1}$. The similarity of these two values for FM9 in kerosene suggests that shear and elongation are equivalent insofar as the critical strain rate is concerned. However, the elongational viscosity is likely to be much higher than that predicted by Trouton's rule[17], and so equation (27) should only be regarded as giving the shear viscosity.

COMPARISON OF THEORY AND EXPERIMENT

Physical properties of FM9

In this section we review the physical properties of the FM9 macromolecule, in particular the solution properties. This information will be used in the subsequent two sections on the thermodynamics and dynamics of the molecule.

FM9 is a polymer from t-butylstyrene and methacrylic acid and contains 11.6 mol% carboxyl groups. Light scattering in a variety of solvents[18] suggested a molecular weight of $M_w = (10 \pm 2) \times 10^6\,\mathrm{g\,mol^{-1}}$. While excess scattering is often a problem with copolymers[19], it is an unlikely source of error here as FM9 is chemically very homogeneous[20], and because it showed no systematic variation of molecular weight with the refractive index of solvent. As far as other techniques are concerned, sedimentation studies[21] gave a value of $M_w = (6\text{–}13) \times 10^6\,\mathrm{g\,mol^{-1}}$, and when polystyrene was synthesized by the same route as FM9 it had an intrinsic viscosity[18] that suggested a degree of polymerization equivalent to $M_w = (8.7\text{–}10.2) \times 10^6\,\mathrm{g\,mol^{-1}}$. The average segment molecular weight is $M_s = 149.05\,\mathrm{g\,mol^{-1}}$, and the density of polymer is $1028\,\mathrm{g\,dm^{-3}}$.

The dimensions of FM9 in the theta-state are unknown. However, Kucukyavuz and Kucukyavuz[22] have studied the dilute-solution behaviour of poly(t-butylstyrene). In nitropropane at 31°C (a theta-solvent) they found $\langle r_\theta^2 \rangle / M = 6.6 \times 10^{-18}\,\mathrm{cm^2\,mol\,g^{-1}}$, from which we calculate a value of $\langle r_\theta^2 \rangle^{0.5} = 81.2$ nm for a chain of molecular weight $10 \times 10^6\,\mathrm{g\,mol^{-1}}$. The measured value of the radius of gyration of FM9 in kerosene is 82 nm[18], which suggests that in kerosene FM9 is close to its theta dimensions, i.e. $\alpha = 1$. In kerosene/butanol (95/5) mixtures the radius by light scattering is 107 nm[18], which suggests that $\alpha = 1.30$ in this solvent. The ratio of the intrinsic viscosities of FM9 in these two solvents is 2.74, which (assuming $[\eta] \propto \alpha^3$) suggests that $\alpha = 1.40$ in kerosene/butanol. We therefore adopt values of $\alpha = 1.0$ in kerosene and $\alpha = 1.35$ in kerosene/butanol.

Kerosene itself has a density of $780\,\mathrm{g\,dm^{-3}}$ and a 'molar' volume of approximately $0.218\,\mathrm{dm^3\,mol^{-1}}$. FM9 is normally used at a concentration of 0.3% w/w ($2.4\,\mathrm{g\,dm^{-3}}$), giving a low shear viscosity of 1.67 mPa s, and hence a reduced viscosity of $\eta_r = 1.45$.

When FM9 is dissolved in decalin/acetic acid (97/3), the latter to suppress hydrogen bonding, and subjected to an elongational flow field, it has a relaxation time of 620 μs[23]. This corresponds to a strain rate of $1613\,\mathrm{s}^{-1}$. However, what we wish to know is the critical strain rate of hydrogen-bonded FM9 in kerosene. This differs in two major ways from the measurement quoted above. First, hydrogen-bonded FM9 has a smaller expansion factor: $\alpha = 1.0$ instead of $\alpha = 1.35$. Second, decalin is a more viscous solvent than kerosene. When both effects are taken into account, we predict (through equation (16)) that hydrogen-bonded FM9 in kerosene should have a critical elongational strain rate of $\dot{\varepsilon}_c = 8490\,\mathrm{s}^{-1}$. A further minor difference is that kerosene and decalin are slightly different in solvency, but this is a relatively small effect.

Finally, when the relaxation spectrum of FM9 in an elongational flow field is measured in order to obtain the molecular-weight distribution, the peak (number-average) molecular weight is $5 \times 10^6\,\mathrm{g\,mol^{-1}}$ (polystyrene equivalent) with a polydispersity index of $M_w/M_n = 2.0$. We therefore assume that FM9 has a Flory 'most probable' molecular-weight distribution:

$$N(M) = M_n^{-1}\exp(-M/M_n) \qquad (28)$$

The thermodynamics of FM9

In this section we use the theory of the expansion parameter, and the physical properties of the FM9 molecule, in order to deduce a value for the association constant. We then use this value in the following section to predict the rheological properties of solutions of FM9.

First, we note from equation (11) that $C_m = 0.024\,10$. Secondly, when FM9 is dissolved in kerosene/butanol the hydrogen-bond associations are 'switched off', and $\alpha = 1.35$. Inversion of Flory's original equation gives a value for the mixing parameter of $\chi = 0.4867$. Thirdly, when FM9 is dissolved in kerosene alone, the hydrogen bonds are 'switched on', and the chains have contracted to an expansion parameter of $\alpha = 1.0$. Given the values of C_m and χ determined above, the value of the association constant that produces this value of α is $K = 1.0945\,\mathrm{dm^3\,mol^{-1}}$. This corresponds to 23.2 associations per macromolecule.

Zimm and Stockmayer[24] showed that, if an ensemble of chains has on average n branches of functionality 4 (i.e. crosslinks), then the ratio of the intrinsic viscosity of these chains to that of linear chains of the same molecular weight is:

$$[\eta]_{\mathrm{branched}}/[\eta]_{\mathrm{linear}} = [(1/n)\ln(1+n)]^{1/2} \qquad (29)$$

Given the ratio of intrinsic viscosities reported above, this yields $n = 24.3$ associations per chain. If we use the more well known expression of Zimm and Kilb[25] for monodisperse star-branched macromolecules we obtain $n = 21.8$. Thus the number of associations predicted by the theory of the expansion parameter is in good agreement with the number of crosslinks estimated from theories of the intrinsic viscosity.

On the other hand, the value of the association constant does not agree with values in the literature for small hydrogen-bonding molecules in non-polar solvents. These latter values[26,27] are typically of order $K = 1000\,\mathrm{dm^3\,mol^{-1}}$. We interpret this apparent disagreement to be due to the loss of configurational entropy upon the formation of associative crosslinks. A crude but realistic model is as follows (I. Miles, private communications). Consider the formation of a single associative crosslink (see *Figure 3*). Before crosslink formation, the segments adjacent to the carboxyl groups could be in any one of three sites, based on a tetrahedral lattice. However, after crosslink formation only one or at most two sites are allowed. The next segments are also restricted in the number of sites they can occupy, albeit to a lesser degree, and this restriction persists for a number of segments m away from the crosslink in both directions on both chains. The change in entropy caused by this restriction in the number of available sites is:

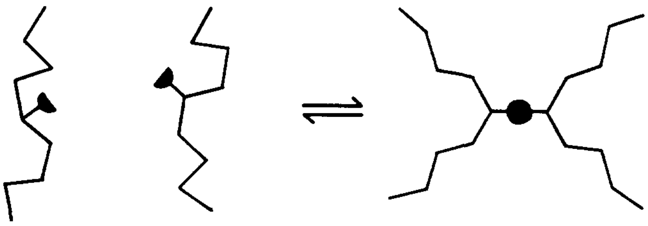

Figure 3 The formation of a single crosslink

$$\Delta S = R\ln(s/s_0)^{4m} \qquad (30)$$

where s is the number of sites available out of a possible s_0 sites. Thus if K_s is the equilibrium constant for the association of small molecules:

$$\Delta G_a = -RT\ln K = -RT\ln K_s - T\Delta S \qquad (31)$$

When we substitute equation (30) into (31) and rearrange, we obtain:

$$m = \ln(K/K_s)/4\ln(s/s_0) \qquad (32)$$

Taking the values of K and K_s discussed earlier, a restriction to one out of a possible three sites on a tetrahedral lattice gives a value of $m = 1.6$. Restriction to two out of three sites gives a value of $m = 4.2$. That is, the lower value of the association constant for carboxyl groups in polymers is consistent with a reduction in conformational freedom for two to four segments away from the association.

Thus the theory of the expansion parameter accounts for the loss in configurational entropy upon crosslink formation in two ways. First, the loss in volume caused by chain contraction is explicitly accounted for with the Flory term. Secondly, the conformational restriction of segments near a crosslink is implicitly accounted for with an effective association constant that includes the effect of crosslinks upon the local configurational entropy. This approach has the advantage that the same restriction in configurational entropy will occur with intermolecular associations in the gel state, and so the effective intramolecular association constant, determined through the expansion parameter, is also appropriate for describing intermolecular associations.

The major source of error in the above analysis is the lack of an accurate value for the radius of gyration in the theta-state. While we have assumed a value of $\langle r_\theta^2\rangle^{0.5} = 82\,\mathrm{nm}$, which gives $\alpha = 1$ for FM9 in kerosene, the true value may be somewhat lower. We therefore assume a much lower value of 60 nm, and repeat the analysis. This gives $\alpha = 1.367$ for FM9 in kerosene, and 1.845 in kerosene/butanol, from which we calculate $K = 1.2154\,\mathrm{dm^3\,mol^{-1}}$ and 26.0 associations per macromolecule. That is, the results are fairly insensitive to the value of the radius of gyration in the theta-state, and really only depend on the change in expansion parameter upon the formation of associations.

The dynamics of FM9

In this section we use the theory of shear thickening in combination with the physical parameters of FM9 and the value of the association constant in order to predict the rheological properties of solutions of the polymer. In particular, we first calculate the viscosity rise and the modulus for complete extension. Next, we calculate the viscosity as a function of strain rate at three polymer concentrations, and compare the results with experiment. We then predict the time dependence of the thickening process and compare it with experiment. Finally, we compare theory and experiment on the existence of a universal 'critical stress'.

Consider FM9 dissolved in kerosene at a concentration of 0.3 % w/w. If the strain rate is sufficiently high to extend all macromolecules, then $M_c=0$, $\phi_w=1$, $M_n^e=M_n$ and $c_e=c$. The concentration of segments that can associate is $[m_e]=1.87\times10^{-3}$ mol dm^{-3}, so the concentration of associations is $[d_e]=3.80\times10^{-6}$ mol dm^{-3}. The average number of crosslinks per chain is $X=15.8$, so the modulus is $G=20.0$ Pa. For the moment, let us assume that the chemical relaxation time $\tau_a \gg \tau_0$, the reptation time; the viscosity in the gel state is then $\eta=9.84$ mPa s. While this value is somewhat lower than that observed experimentally (to be discussed shortly), it is in reasonable agreement.

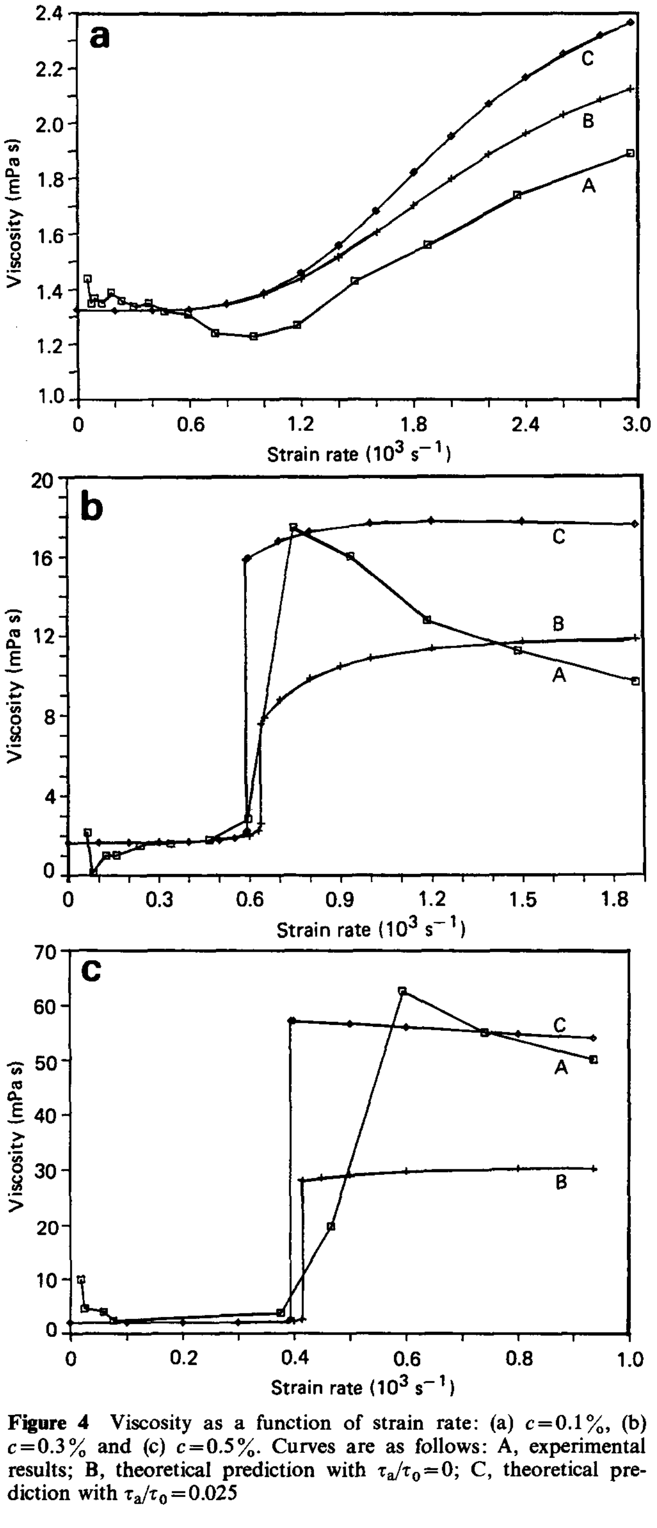

Figure 4 Viscosity as a function of strain rate: (a) $c=0.1\%$, (b) $c=0.3\%$ and (c) $c=0.5\%$. Curves are as follows: A, experimental results; B, theoretical prediction with $\tau_a/\tau_0=0$; C, theoretical prediction with $\tau_a/\tau_0=0.025$

The experimental results of viscosity *versus* strain rate for FM9 concentrations of 0.1%, 0.3% and 0.5% in kerosene are shown in *Figure 4*. These were measured with concentric cylinders on a Bohlin rheometer. Also shown are the theoretical predictions, both with $\tau_a/\tau_0=0$ and with an arbitrarily chosen value of $\tau_a/\tau_0=0.025$. As can be seen, the overall agreement between theory and experiment is excellent. The critical strain rates are correctly predicted, within ±20% at all three polymer concentrations. In particular, note that while the critical strain rate of an isolated molecule is about 8000 s^{-1}, at finite polymer concentrations the critical strain rates are around an order of magnitude lower. This is due to the positive-feedback process mentioned earlier: chains of high molecular weight extend first and form a gel network that increases the viscosity, and this increased viscosity induces the extension of chains of lower molecular weight. The viscosity rises predicted by the theory are somewhat low; however, they can be brought into good agreement with experiment by suitable choice of the ratio of association to reptation times. Further, the theory correctly predicts the transition from smooth shear thickening at low polymer concentration to abrupt thickening at high concentrations.

The only area of disagreement is the gradual decrease in viscosity with strain rate in the gel region. While the theory does predict a very slight degree of thinning at high shear rates, the substantial decrease observed experimentally is more likely to be due to slippage at the walls of the rheometer, or to the disentanglement of chains and dissociation of crosslinks under the influence of the flow field, effects that the theory does not attempt to encompass.

It is not possible to predict quantitatively the time dependence of the thickening process. However, it is possible to predict it in a qualitative fashion by recognizing that the number of iterations of equations (15) to (27) is a direct measure of the time. The resulting predicted time dependence is shown in *Figure 5*. This predicted qualitative behaviour is the same as that observed experimentally[4].

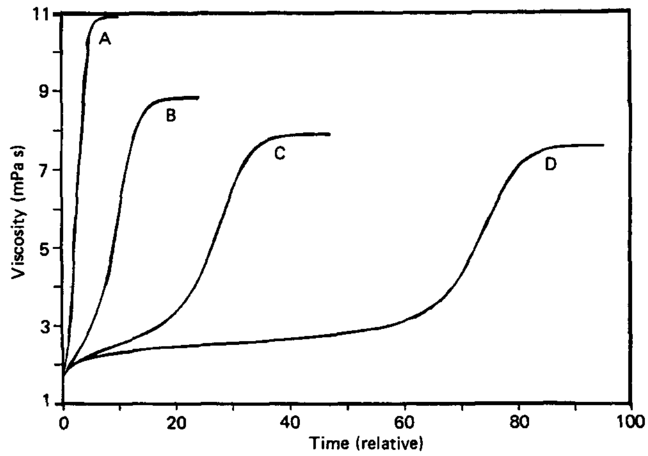

Figure 5 Time dependence of the viscosity rise; strain rates are 1000, 700, 650 and 637 s^{-1} from left to right (A to D)

Table 1 The critical stress

c	η	$\dot{\gamma}$ (s^{-1})		σ_c (Pa)	
(%)	(mPa s)	Expt	Theory	Expt	Theory
0.2	1.47	2000	1102	0.55	0.35
0.3	1.64	1200	637	0.53	0.34
0.4	1.8	780	498	0.47	0.32
0.5	2.1	560	415	0.51	0.39
				0.52±0.03	0.35±0.03

Finally, Peng and Landel[4] noted that solutions of FM9 thickened at the same 'critical stress' due to polymer, $\dot{\gamma}_c(\eta-\eta_0)$, independent of the polymer concentration. Their results, and our predictions, are summarized in *Table 1*. Thus theory agrees with experiment on the constancy of the critical stress. The difference between the values is due to different definitions of the critical strain rate. Peng and Landel defined it as the strain rate at which gelation happened instantaneously; we have defined it as the strain rate at which gelation happens eventually (within 100 iterations). Given the time dependence of the thickening discussed above, it is not surprising that our critical strain rates and stresses are lower than those of Peng and Landel.

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