Viscosity of ionomer gels

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We study the viscosity behaviour of metal sulphonate- (or metal carboxylate-) containing ionomers in solution with non-polar solvents; at relatively low polymer concentration these ionomer solutions show an unusually large thickening behaviour, due to the association of the metallic groups. By regarding the ionomer system as a polymer solution with transient crosslinks, an expression is derived from the viscosity of the sulphonated polymer in terms of the viscosity of the corresponding non-sulphonated polymer and the average number of crosslinks associated with any chain.

Keywords Ionomer solutions; physical links; maximum relaxation time; viscosity; time percolation; soil–gel transition

INTRODUCTION

Recently, there has been increased interest in the properties of metal sulphonated (and metal carboxylated) ionomers. Experimental studies[1–6] on the solution behaviour of these systems have shown them to exhibit unusually high viscosity behaviour, especially in solvents of low polarity. These results were interpreted[1–6] as arising from strong physical associations of the ion pairs, effectively crosslinking the different polymer chains in the solution and leading to gelation for certain conditions of concentration and temperature[7]. Unlike strong (covalently crosslinked) gels[8], ionomer solutions are highly viscous fluids, indicating weak bonds that are not permanent but fluctuate with time.

Ionomers are a distinct class of polymers containing relatively few metallic groups (usually sulphonated or carboxylated groups) on some of the monomers of a hydrocarbon polymer chain. The fraction f of metallic groups along the chains may be controlled chemically. The metal sulphonate (or metal carboxylate) groups act as electric dipoles when they are not dissociated; usually this occurs in the molten phase or in solution with a non-polar solvent. Because of the attractive nature of the dipole–dipole interaction[7], the metallic groups associate, crosslinking different chains for finite periods of time. The finite lifetime of the crosslinks is thought to arise from the fluctuations in the relative kinetic energy of the two corresponding monomers.

Two monomers carrying dipoles $\mathbf{p}_1$ and $\mathbf{p}_2$ have an energy of interaction u depending on their distance r apart:

$$u=\frac{1}{4\pi\varepsilon r^3}\left(\mathbf{p}_1\cdot\mathbf{p}_2-\frac{3}{r^2}(\mathbf{p}_1\cdot\mathbf{r})(\mathbf{p}_2\cdot\mathbf{r})\right) \qquad (1)$$

where ε is the dielectric constant of the medium.

We are interested in the range of interaction of the dipolar energy; that is, in the distance r_0 for which u is of the order of kT. This is calculated as

$$r_0\sim(\lambda)^{1/3}a \qquad (2)$$

where

$$\lambda\equiv\frac{p^2}{4\pi\varepsilon a^3kT} \qquad (3)$$

and where a is a characteristic monomer dimension. As explained in ref. 7, at room temperature λ is between 10 and 100; therefore, r_0 is between $2a$ and $5a$.

We are concerned here with the unusual behaviour of the viscosity of ionomers in semidilute solutions. The viscosity of the ionomer solution can be understood in terms of the viscosity of a corresponding non-ionic polymer solution, for which we know that viscosity is proportional to the maximum relaxation time of a polymer chain[8] (i.e. the time that it takes for a chain to renew completely its original conformation, by leaving the tube in which it is trapped). The proportionality factor is the elastic plateau modulus of the transient network[8]. We will see that the addition of a few physical crosslinks per chain leaves the plateau modulus almost unchanged but drastically quenches the diffusive reptating motions of the chain along its tube.

In the next section we will give an expression for the effective reptation time of a polymer chain carrying ion pairs in terms of the reptation time for a non-ionic polymer. The following section will be used to present an argument tending to show that the value of the plateau modulus is not altered much by the introduction of a few crosslinks per chain; in the same section, we will give the final expression for the viscosity of the ionomer in terms of the viscosity of the non-ionic polymer and the average number of crosslinks carried by any chain. Finally, this last expression will be computed as a function of concentration and temperature for some particular cases.

THE EFFECTIVE REPTATION TIME

Let us consider a monodisperse ionomer solution of chains, where a fraction f of the monomers are sulphonated. We are interested in the behaviour of the

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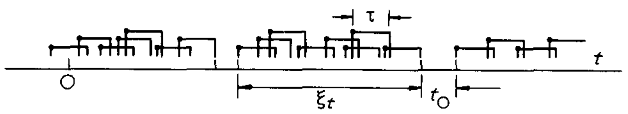

Figure 1 The history of a chain represented in a one-dimensional time diagram. Each segment indicates a crosslink, acquired at the time where the segment starts (filled circles) and broken at the time where it ends

ionomer in the semidilute regime; that is, at a concentration c above the overlap concentration c^* for which the chains start to interpenetrate. In this regime, the chains overlap and form a network made of chains and entanglements. This solution is often described in terms of 'blobs'[8,9]: each chain in the solution has a certain number of contacts with other chains, and a blob is that part of the chain between two consecutive contacts. The mean distance between two consecutive contacts is the correlation length ξ. Inside each blob there is single-chain behaviour (excluded volume or Gaussian, depending on temperature); however, the chain of blobs is Gaussian (the blobs are uncorrelated) on distance scales $r > \xi$.

The number of contacts per chain is estimated as[7,9]

$$n \simeq (c/c^*)^{5/4} \simeq Nc^{5/4} \tag{4a}$$

for excluded volume blobs

$$n \simeq (c/c^*)^2 \simeq Nc^2 \tag{4b}$$

for Gaussian blobs

Each contact has a certain number of monomers together, close enough to form a physical link if they were metal-sulphonated (see the discussion leading to equations (2) and (3)).

We are interested in the probability $P(\alpha)$ for a chain, picked at random at any instant of time, to have α crosslinks. Let $\mathscr{P}$ be the probability for a contact to be a physical link; as we will see in the last section, in the case of ionomer gels $\mathscr{P}$ is a number much smaller than unity. We can see that we have a set of n events (contacts per chain), each having a probability $\mathscr{P}$ to be a physical link. On the assumption that these events are uncorrelated, that is, that the probability $\mathscr{P}$ is independent of what is happening at any other contact of the chain, we would have the following binomial distribution:

$$P(\alpha) = \binom{n}{\alpha} \mathscr{P}^{\alpha} (1 - \mathscr{P})^{n-\alpha} \tag{5}$$

The average number of crosslinks per chain is then

$$\bar{\alpha} = \sum_{\alpha=0}^{n} \alpha P(\alpha) = n\mathscr{P} \tag{6}$$

All the above calculations are instantaneous, as if we were taking a snapshot of the solution. Actually we know (because the ionomer gel flows) that the crosslinks are not permanent, but that they fluctuate. We assume a lifetime τ per bond (which may depend on temperature); that is, the probability density for a crosslink to last a time t is a δ-function centred at τ.

Let us follow the history of a particular chain chosen at random and sketch a one-dimensional time diagram (cf. *Figure 1*). Each horizontal segment signifies a physical bond, acquired at the time where the segment starts (filled circles) and broken at the time where it ends. Every segment in this one-dimensional diagram is of size τ, due to the assumption of uniform lifetime for the physical links. If we pick any point on the time axis, the number of horizontal segments above the chosen point indicates the number of crosslinks that the chain has at the corresponding time. We know that there is a binomial probability (equation (5)) for any chain picked at random, at any instant of time, to have α crosslinks. This in turn means that the distribution of segments on the time axis should be binomial in the following sense: the probability for having α filled circles in any time interval of size τ follows the distribution (5), namely

$$\begin{aligned} P(\alpha,\tau) &\simeq \frac{n!}{\alpha!(n-\alpha)!}\mathscr{P}^{\alpha}\exp[-\mathscr{P}(n-\alpha)] \qquad (\alpha \leqslant n) \\ P(\alpha,\tau) &= 0 \qquad\qquad (\alpha > n) \end{aligned} \tag{7}$$

where we have used the fact that $\mathscr{P}$ is usually a very small number. For long chains, well inside the semidilute regime, n is usually very large; if we look at the probability $P(\alpha,\tau)$ for $\alpha \ll n$, we can write

$$\begin{aligned} P(\alpha,\tau) &\simeq \frac{1}{\alpha!}(n\mathscr{P})^{\alpha}\exp(-n\mathscr{P}) \\ &= \frac{1}{\alpha!}(\bar{\alpha})^{\alpha}e^{-\bar{\alpha}} \qquad (\alpha \ll n) \end{aligned} \tag{8}$$

But $\bar{\alpha} = \rho\tau$, where ρ is the average density of segments on the time axis. Hence

$$P(\alpha,\tau) = \frac{1}{\alpha!}(\rho\tau)^{\alpha}e^{-\rho\tau} \qquad (\alpha \ll n) \tag{9}$$

which means that the probability for having α filled circles in any arbitrary time interval of size Δt is

$$P(\alpha,\Delta t) = \frac{1}{\alpha!}(\rho\Delta t)^{\alpha}e^{-\rho\Delta t} \qquad (\alpha \ll n) \tag{10}$$

This Poisson distribution, without any restriction in α, is the probability that one would have for a random distribution of points on a one-dimensional axis, when the average density of these points is ρ. This means in our case that the distribution of filled circles on the one-dimensional time axis is, approximately, a random distribution.

Next, we consider the one-dimensional, continuum percolation problem[10] that results when we look at the segments as percolating units. We say that two segments belong to the same cluster if they are connected through overlapped segments. The connectedness 'length' ξ_t, which is the size of an average cluster (cf. *Figure 1*), has been calculated, in the case of random distribution of percolating units, as[10]

$$\xi_t^2 = \frac{e^{\rho\tau}[2e^{2\rho\tau} - (2 + 4\rho\tau)e^{\rho\tau} + 2\rho\tau + (\rho\tau)^2]}{\rho^2(e^{\rho\tau} - 1)} \tag{11}$$

Let us call t_0 the average time interval for which the chain is free, with no crosslinks. The fraction of time spent free by the chain is

$$\frac{t_0}{t_0+\xi_t}$$

This last expression is equal to the probability for any point, picked at random on the one-dimensional time axis, not to be covered by a percolating segment. According to equations (7), this is precisely* $P(0,\tau)$:

$$\frac{t_0}{t_0+\xi_t}=P(0,\tau)\simeq\exp(-n\mathscr{P})=\mathrm{e}^{-\rho\tau} \qquad (12\mathrm{a})$$

Hence

$$t_0=\frac{P(0,\tau)}{1-P(0,\tau)}\xi_t \qquad (12\mathrm{b})$$

As we can see, we have now three quantities $P(0,\tau)$, ξ_t and t_0 as functions of the average number of crosslinks per chain $n\mathscr{P}=\rho\tau$. Let us now look at some limiting cases:

(i) At high temperatures, when the average number of crosslinks per chain is almost zero,

$$\begin{aligned} P(0,\tau)&\simeq 1\\ \xi_t&\simeq\tau \qquad (13)\\ t_0&\simeq\infty \end{aligned}$$

(ii) At low temperatures, when there are on average several crosslinks per chain,

$$\begin{aligned} P(0,\tau)&\simeq\exp(-n\mathscr{P})\\ \xi_t&\simeq 2^{1/2}\tau\frac{\exp(n\mathscr{P})}{n\mathscr{P}} \qquad (14)\\ t_0&\simeq\frac{2^{1/2}\tau}{n\mathscr{P}} \end{aligned}$$

As mentioned in the introduction, we are interested in the reptation time T_{rep}, which essentially measures the time that it takes for a chain to renew completely the tube it is trapped in. For a non-ionic polymer solution, this time has been calculated as[8]

$$T_{\mathrm{rep}}\simeq\tau_1 N^3 \qquad (15)$$

where τ_1 is some microscopic time and N is the polymerization index of the chains.

It has also been noted that the reptation time for a branched chain becomes exponentially long with the degree of polymerization[8], and thus all reptation processes are almost quenched for crosslinked polymers. We will assume, for simplicity, that a chain only diffuses (reptates) if it is completely free of crosslinks. In this way, the effective time T_{eff} taken by a chain to diffuse its own length is T_{rep} divided by the fraction of time that the chain spends free, with no crosslinks. According to equation (12a), this is precisely $P(0,\tau)$. Hence

$$T_{\mathrm{eff}}=T_{\mathrm{rep}}/P(0,\tau)\simeq\exp(n\mathscr{P})T_{\mathrm{rep}} \qquad (16)$$

This last formula may not be valid well inside the gel phase, when each chain carries on average many crosslinks. In this case $t_0 \ll \xi_t$ (cf. equation (14)), and the chains may move further away during the long times that they spend crosslinked than during the very short times that they spend free.

THE ELASTIC MODULUS

The elastic plateau modulus E of a polymer solution relates the strain induced during short times to an applied small perturbative stress. The elastic properties of a polymer solution originate from the usual elasticity of single chains between entanglements. During the short times over which we measure the strain, the chains cannot disentangle and the modulus remains essentially constant. In this sense, the entanglements act as links of a rubbery network and the plateau modulus should be proportional to the density of the entanglements[8]. The width of the plateau measures the time taken for the chains to disentangle.

For long chains, well inside the semidilute solution, there are many entanglement points per chain. In equation (4) we gave an expression for the number of contacts per chain; however, not every contact is an entanglement, as *Figure 2* shows. The addition of crosslinks to contact points, which are already entanglements, does not alter the high-frequency modulus at all; however, if the crosslinks fall in contacts which are not entanglements, the plateau modulus will be altered. As we are interested in a regime not well inside the gel phase, when each chain carries a few crosslinks at most and such that equation (16) is still valid, the plateau modulus should not be greatly altered; notwithstanding this, the width of the plateau broadens due to the fact that it takes longer for crosslinked chains to disentangle[11].

We now regard the ionomer solution as a polymer solution for which the dynamics of each chain has been slowed down, according to equation (16). The viscosity of the ionomer solution can then be written as

$$\eta\simeq ET_{\mathrm{eff}}=\exp(n\mathscr{P})ET_{\mathrm{rep}}=\exp(n\mathscr{P})\eta_0 \qquad (17)$$

where η_0 is the viscosity of the non-sulphonated polymer solution, at the same concentration and same temperature.

COMPUTATION OF THE AVERAGE NUMBER OF CROSSLINKS

We now attempt to give an expression for the probability $\mathscr{P}$ for a contact to be a physical link, for some particular cases. Each contact means a set of pairs of monomers, the two monomers of each pair belonging to different chains (or to different parts of the same chain). Let A be this number of pairs. The probability for the first monomer of each pair to be sulphonated is f. In a non-correlated case ($T\rightarrow\infty$), the probability for the second monomer to be sulphonated is also f. The probability for two sulphonated monomers, in the range of interaction of each other, to form a physical link has been calculated as[7]

$$\mathscr{P}(T)=\frac{1}{1+\mathrm{e}^{u/kT}}\frac{\Gamma(\frac{3}{2}-u/kT}{\Gamma(\frac{3}{2})} \qquad (18)$$

where $\Gamma(a,x)$ is the incomplete Γ-function and u is the

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* It should be noted that equation (12a) is equivalent to the ergodic assumption that the fraction of time that a chain spends free is equal to the fraction of chains, in the sample, carrying no crosslinks.

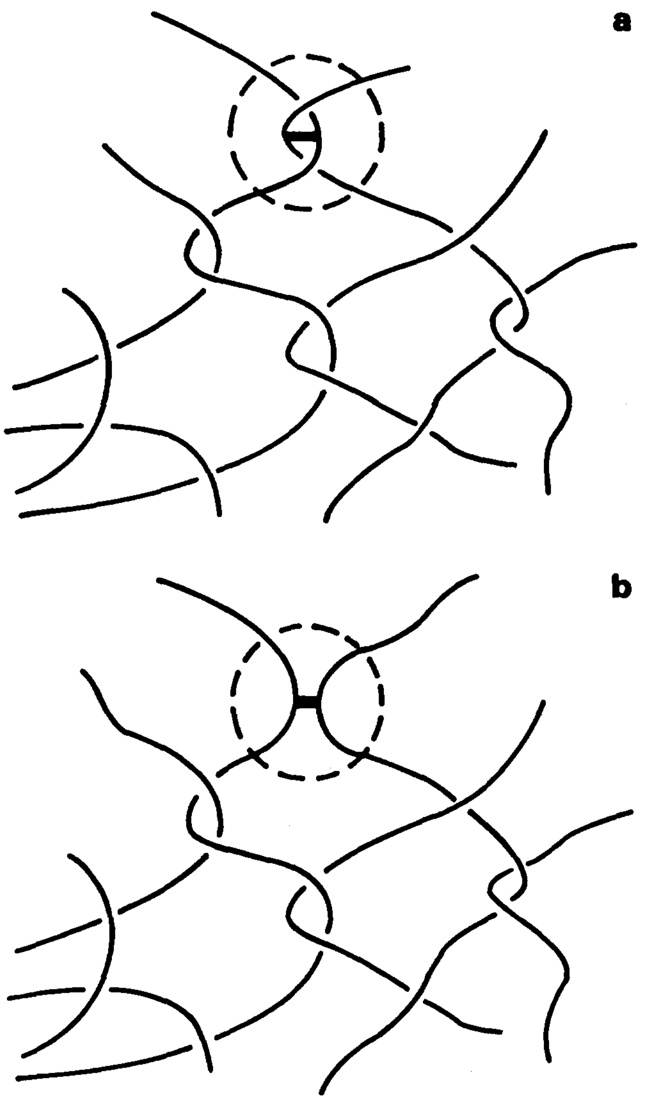

Figure 2 (a) The addition of a crosslink to a contact, which is already an entanglement, does not contribute to elasticity. (b) The addition of a crosslink to a contact, which is not an entanglement, contributes to elasticity

(intrinsically negative) energy of the dipole–dipole interaction. The probability for a contact to be a physical link, in this non-correlated case, is then

$$\mathscr{P} = Af^2 \nearrow(T) \qquad (19)$$

The average number of crosslinks per chain can then be written as[7]

$$n\mathscr{P} = Nc^y Af^2 \nearrow(T) \qquad (20)$$

where y is $\frac{5}{4}$ or 2 depending on whether we are in the excluded volume regime or in the theta regime. In *Figure 3* we sketch the concentration dependence on the ratio η/η_0, for this high-temperature regime.

In a melt, each monomer is in the range of interaction of $r_0^3/(\frac{1}{2}a)^3 \sim 80$–800 other monomers (cf. equation (2)), assuming a complete packing of the monomers. Under these conditions, each sulphonated monomer is very likely to find another sulphonated monomer within the range of interaction. The average number of crosslinks per chain should be written in this case as

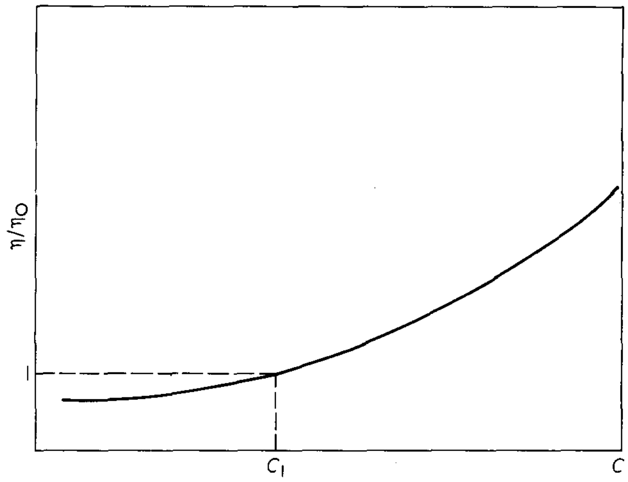

Figure 3 A plot of η/η_0 as a function of concentration for a high (constant) value of the temperature. c_1 is the concentration for which the effects on the viscosity of the intramolecular and intermolecular links just balance, and is of the order of c^*

$$n\mathscr{P} = NA'f \nearrow(T)\,. \qquad (21)$$

Thus, there should be a crossover from an f^2 law to an f law, when we increase concentration at high temperature.

As a final comment, we would like to point out that some enlightenment could be obtained for the correct expression of $n\mathscr{P}$, for T different from infinity and c different from the melt concentration, by measuring the shape of the gelation curve. As explained in ref. 7, the gelation curve is given by the condition $n\mathscr{P} \sim 1$. Experimentally, the gelation curve can be located by measuring the viscosity of the sulphonated polymer and checking that it coincides with e times the viscosity of the non-sulphonated one, for the same values of T and c, according to equation (17).

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