Viscoelasticity of ionomer gels: 2. The elastic moduli

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The unusual viscoelastic properties of metal sulphonate- (or metal carboxylate-) containing ionomers in semidilute solutions with non-polar solvents are reexamined. At fairly low polymer concentration of relatively short chains, these ionomer solutions show, besides the extremely high-viscosity behaviour studied in an earlier paper, an extensive plateau in the storage modulus and a cusp in the loss modulus, both characteristic of a highly entangled polymer melt or concentrated solution.

We argue that, owing to the temporary crosslinks, the polymer chains are moving inside a network made up by the other crosslinked chains and hence undergo one-dimensional diffusional motions (reptation). The extensive plateau then arises from the disengagement of the chain from a deformed tube, as in the Doi–Edwards theory of melts and concentrationed solutions. We derive expressions for the storage and loss moduli which are in qualitative agreement with the experimental curves.

(Keywords: ionomer solutions; physical links; reversible gels; reptation; stress relaxation; dynamic moduli)

INTRODUCTION

In an earlier work by the author[1] we discussed the unusually high-voscisity behaviour exhibited by solutions of metal sulphonate (and metal carboxylate) ionomers, especially in solvents of low polarity. Further experimental studies[2,3] have shown that, at concentrations of only 2 to 10 wt% of relatively short chains, the ionomers exhibit viscoelastic properties which are characteristic of very high molecular weight polymers in the bulk state or in concentrated solutions. For example, a logarithmic plot[3] of the storage modulus (G') vs. frequency, for sulpho-EPDM of molecular weight $M_n \sim 40\,000$, exhibit an extensive rubbery plateay spanning four decades, at a concentration of only 5 wt% and room temperature. A similar plot[3] for the loss modulus (G'') shows a peak, which is again characteristic of a highly entangled polymer melt or concentrated solution. The corresponding plots for the base (non-sulphonated) polymer, under the same conditions, do not show even a hint of the plateau for G' or a cusp for G'', but a direct transition from the flow to the glassy regimes. All these results were interpreted[2,3] as arising from strong physical associations of the ion pairs, effectively crosslinking the different polymer chains in the solution and leading to gelation. Unlike strong (covalently crosslinked) gels[4], ionomer solutions flow over long periods of time, indicating that the bonds are not permanent but break easily after a certain characteristic lifetime.

Ionomers are hydrocarbon polymer chains containing relatively few metallic groups (usually sulphonated or carboxylated) on some of the monomers composing the chains. The fraction f of the sulphonated groups along the chains may be chemically controlled. Because of the attractive nature of the metal sulphonate groups, the corresponding monomers associate, crosslinking different chains for finite periods of time. The finite lifetime of the crosslinks arises from the fluctuations in the relative kinetic energy of the two corresponding monomers and is related to the escape of a particle in a thermal bath over a potential barrier. A rough estimate of this lifetime τ is given by the formula:[5]

$$\tau \sim \frac{1}{\omega_v} e^{u/k_B T}, \tag{1}$$

where ω_v is a characteristic vibrational frequency of two bonded monomers, u is the energy of interaction, k_B is the Boltzmann constant and T is the temperature.

The present work is concerned with the unusual viscoelastic properties of ionomer solutions at relatively low concentration of not very high molecular weight polymers, as exhibited in the storate and loss moduli, and one of the purposes is to give a derivation of both. In our calculations we will be inspired on early ideas of reptation of a chain inside a permanently crosslinked gel, by de Gennes[6], and on the computation of the stress relaxation tensor, by Doi and Edwards[7]. In the next section we give a derivation of the stress relaxation tensor for the ionomer system, starting from the corresponding expression for rubber elasticity and assuming one-dimensional diffusional motions for the primitive paths of the polymer chains. The following section will be employed to compute the storate and loss moduli and to make a logarithmic plot of both moduli vs. frequency, which will turn out to be in agreement with experiment. Finally, in

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the last section, we will discuss the conditions for the validity of the assumption of one-dimensional diffusion for the polymer chains, which is not trivial for systems with the stated conditions of concentration and molecular weight.

THE STRESS RELAXTION TENSOR

Let us consider a monodisperse ionomer solution of chains of polymerization index N, where a fraction f of the monomers are sulphonated. We will constantly assume a monomer concentration C above the overlap concentration C^*, for which the chains start to interpenetrate. This semidilute solution is often described in terms of 'blobs'[4,8,9]: each chain in the solution has a certain number of contacts with other chains: a blob is that part of the chain between two consecutive contacts. Indeed, the overlapped chains form a network of subchains and contacts, and the mesh size of the network ξ is precisely the blob distance. Each chain in this semidilute solution is also often described as trapped inside a tube of diameter ξ made up by the other chains. The walls of the tube correspond to the topological constraints (or noncrossability) between different polymer chains. The centre line of the tube was called the primitive path of Doi and Edwards[7].

As described before[1], the probability for a chain, picked at random at any instant of time, to have γ crosslinks is

$$P(\gamma)=\binom{n}{\gamma}\mathcal{P}^{\gamma}(1-\mathcal{P})^{n-\gamma}, \qquad (2)$$

where n is the number of contacts per chain and $\mathcal{P}$ is the probability for a contact to be a physical link. The average number of crosslinks per chain is then

$$\bar{\gamma}=\sum_{\gamma=0}^{n}\gamma P(\gamma)=n\mathcal{P}. \qquad (3)$$

We now assume the expression from rubber elasticity for the stress relaxation tensor[7]:

$$\sigma_{\alpha\beta}(t)=\frac{3k_{\mathrm{B}}T}{v}\left\langle\sum_{\gamma=0}^{n}x_{\gamma}\sum_{i=1}^{\gamma+1}\frac{r_{i\alpha}(t)r_{i\beta}(t)}{g_{\gamma}b^{2}}\right\rangle+p\delta_{\alpha\beta}. \qquad (4)$$

In this equation, v is the volume of the system, $\delta_{\alpha\beta}$ is the Kronecker delta, x_{γ} is the number of chains carrying γ crosslinks, $\mathbf{r}_i(t)$ is a vector joining two consecutive crosslinks of a polymer chain, $g_{\gamma}=N/(\gamma+1)$ is the number of monomers in the corresponding subchain*, b the bond length and p that part of the hydrostatic pressure not contained in the term between brackets. The angular brackets indicate an average over orientations of the vectors $\mathbf{r}_i(t)$. Note that we have assumed Gaussian statistics for the subchains.

Expression (4) can be rewritten as

$$\sigma_{\alpha\beta}(t)=\frac{3Ck_{\mathrm{B}}T}{N}\sum_{\gamma=1}^{n}P(\gamma)\left\langle\sum_{i=1}^{\gamma+1}\frac{\mathrm{r}_{i\alpha}(t)r_{i\beta}(t)}{g_{\gamma}b^{2}}\right\rangle+p\delta_{\alpha\beta}. \qquad (5)$$

To calculate the relaxation modulus we will follow the usual procedure[7] of suddenly deforming affinely the ionomer system at $t=0$, keeping the deformation constant and looking at the relaxation of the stress tensor. At times smaller than zero, that is, in equilibrium, we define $\mathbf{r}_i\equiv\mathbf{r}_i(t<0)$, and $\mathbf{r}_i$ is a vector of isotropic direction:

$$\left\langle\frac{r_{i\alpha}r_{i\beta}}{g_{\gamma}b^{2}}\right\rangle=\frac{1}{3}\delta_{\alpha\beta}. \qquad (6)$$

Let $\boldsymbol{\varepsilon}$ be the tensor describing the deformation. Then, the assumption of affine deformation at $t=0$ means that the isotropic vectors $\mathbf{r}_i$ transform, immediately after deformation, into

$$\mathbf{r}_i'=\boldsymbol{\varepsilon}\cdot\mathbf{r}_i. \qquad (7)$$

Hence, immediately after deformation, the stress tensor becomes

$$\sigma_{\alpha\beta}'=\frac{3Ck_{\mathrm{B}}T}{N}\sum_{\gamma=0}^{n}P(\gamma)\left\langle\sum_{i=1}^{\gamma+1}\frac{r_{i\alpha}'r_{i\beta}'}{g_{\gamma}b^{2}}\right\rangle+p\delta_{\alpha\beta}$$

$$=\frac{Ck_{\mathrm{B}}T}{N}(\bar{\gamma}+1)\varepsilon_{\alpha\eta}\varepsilon_{\beta\eta}+p\delta_{\alpha\beta}, \qquad (8)$$

where $\varepsilon_{\alpha\beta}$ represents the $\alpha\beta$ component of the strain tensor $\boldsymbol{\varepsilon}$. In this last expression and from now on, a repeated greek index indicates a sum over that index. We note that the vectors $\mathbf{r}_i'$ are stretched (or compressed) beyond the equilibrium length $g_{\gamma}^{1/2}b$ and then there is a force tending to restore them to equilibrium. Furthermore, the chain is now trapped inside a deformed tube, being no longer a random walk. If the crosslinks did not break, equation (8) would be the final expression for the stress. As the crosslinks break and reform, two relaxation processes occur. The first one is an equilibrium process inside the deformed tube, after which the subunit vectors (now called $\mathbf{r}_i''$) recover the equilibrium length $g_{\gamma}^{1/2}b$. Let τ_{R} be the equilibrium time[6,7] of a free, non-crosslinked chain. Then, three cases need to be mentioned.

(a) $\tau\gg\tau_{\mathrm{R}}$. In this case all chain subunits equilibrate almost immediately after a crosslink is broken or reformed. If we regard the chain made of $\bar{\gamma}+1$ subunits as a Rouse[10] chain, the equilibration time for the whole chain should be[10]:

$$\tau_{\mathrm{eq}}\sim\tau(\bar{\gamma}+1)^{2}.$$

(b) $\tau\ll\tau_{\mathrm{R}}$. In this other case, the crosslinks break and reform in a time much shorter than that taken by the subunits to equilibrate. Hence, the crosslinks are not really felt, with the exception of an added increase in the friction coefficient. The equilibration time should follow the pattern of that of a free Rouse chain[10], with a renormalized friction coefficient ζ':

$$\tau_{\mathrm{eq}}\sim\frac{N^{2}b^{2}\zeta^{1}}{6\pi^{2}k_{\mathrm{B}}T}.$$

(c) $\tau\sim\tau_{\mathrm{R}}$. In this last case the crosslinks act as constraints on the chain diffusion and at the same time increase the friction. One then has a complicated dynamic problem whose solution is not attempted here. In any case, it will be argued in the discussion section that, in order to have one-dimensional diffusion, we need to be in the former case (a). According to equation (1), this clearly can be achieved by picking an ionomer system with a high

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*We have assumed that the γ crosslinks carried by a chain are equally spaced along its length. A distribution of subchain lengths can be taken into account with more effort, leading to no interesting changes in the final result.

energy of interaction. From now on we will restrict ourselves to case (a).

After the first relaxation process has been settled, the stress tensor transforms into

$$\sigma''_{\alpha\beta}=\frac{3Ck_{\mathrm{B}}T}{N}\sum_{\gamma=0}^{n}P(\gamma)\left\langle\sum_{i=1}^{\gamma+1}\frac{r''_{i\alpha}r''_{i\mathrm{B}}}{g_\gamma b^2}\right\rangle+p\delta_{\alpha\beta}, \tag{9}$$

where $\mathbf{r}''_i$ is an anisotropic vector of magnitude $g_\gamma^{1/2}b$. In Appendix A we show that

$$\left\langle\frac{r''_\alpha r''_\beta}{g_\gamma b^2}\right\rangle\simeq\frac{\varepsilon_{\alpha\mu}\varepsilon_{\beta\mu}}{\varepsilon_{\eta\theta}\varepsilon_{\eta\theta}}. \tag{10}$$

Hence

$$\sigma''_{\alpha\beta}=\frac{3Ck_{\mathrm{B}}T}{N}(\bar{\gamma}+1)\frac{\varepsilon_{\alpha\mu}\varepsilon_{\beta\mu}}{\varepsilon_{\eta\theta}\varepsilon_{\eta\theta}}+p\delta_{\alpha\beta}. \tag{11}$$

As usual[7], the second relaxation process is disengagement from the deformed tube. At any instant of time during this process, the stress tensor reads

$$\sigma_{\alpha\beta}(t)=\frac{3Ck_{\mathrm{B}}T}{N}\sum_{\gamma=0}^{n}P(\gamma)$$

$$\times\left\langle\sum_{d=0}^{\gamma+1}P_\gamma(d,t)\left([(\gamma+1)-d]\frac{r_\alpha r_\beta}{g_\gamma b^2}+d\frac{r''_\alpha r''_\beta}{g_\gamma b}\right)\right\rangle+p\delta_{\alpha\beta}, \tag{12}$$

where $P_\gamma(d,t)$ is the probability at time t for a chain to have d deformed subunits inside the original tube*, out of a total of $\gamma+1$. We can recast (12) in the following form:

$$\sigma_{\alpha\beta}(t)=\frac{3Ck_{\mathrm{B}}T}{N}\sum_{\gamma=0}^{n}P(\gamma)\bar{d}_{\gamma+1}(t)\left(\frac{\varepsilon_{\alpha\mu}\varepsilon_{\beta\mu}}{\varepsilon_{\eta\theta}\varepsilon_{\eta\theta}}-\frac{\delta_{\alpha\beta}}{3}\right)+p'\delta_{\alpha\beta}, \tag{13}$$

where

$$\bar{d}_{\gamma+1}(t)=\sum_{d=0}^{\gamma+1}P_\gamma(d,t)\cdot d, \tag{14}$$

$$p'=p+\frac{(\bar{\gamma}+1)Ck_{\mathrm{B}}T}{N}. \tag{15}$$

We now make the following plausible assumption:

$$\frac{\bar{d}_{\gamma+1}(t)}{\gamma+1}=\frac{\bar{L}_d(t)}{L}, \tag{16}$$

independent of the number γ of crosslinks that the chain has. Here $\bar{L}_d(t)$ is the average portion of the primitive length still inside the deformed tube at time t and L is the total primitive length. The quantity $\bar{L}_d(t)/L$ has been calculated several times[6,7]. For completeness we give a derivation in Appendix B, based on the concept of the range of a one-dimensional random walk. The result for the case we are considering here is:

$$\frac{\bar{L}_d(t)}{L}=\frac{8}{\pi^2}\sum_{l=1,3,5,\ldots}^{\infty}\frac{1}{l^2}\exp\left(-\frac{\pi^2D_c l^2 t}{L^2 e^{\bar{\gamma}}}\right), \tag{17}$$

wher D_{c} is the curvilinear diffusion coefficient for a chain free of sulphonated monomers. The quantity L^2/π^2D_{c} was called the reptation time (denoted here by T_{r}^0) by de Gennes[6]. Hence

$$\frac{L_d(t)}{L}=\frac{8}{\pi^2}\sum_{l=1,3,5,\ldots}^{\infty}\frac{1}{l^2}\exp\left(-\frac{l^2t}{T_{\mathrm{r}}^0 e^{\bar{\gamma}}}\right). \tag{18}$$

In the case of the ionomers, we found[1] that the effective reptation time (T_{r}) for a sulphonated chain can be written as:

$$T_{\mathrm{r}}=T_{\mathrm{r}}^0 e^{\bar{\gamma}}, \tag{19}$$

where $\bar{\gamma}$ is given by (3). This formula was proposed to be valid provided that we are in a regime in which there are not too many crosslinks per chain, and was obtained on the assumption that a chain diffuses much faster when it is free of crosslinks. These points will be clarified, we hope, in the discussion section.

Using (3), (13), (16), (18) and (19), the stress tensor can be put in the final form:

$$\sigma_{\alpha\beta}(t)=\frac{24(\bar{\gamma}+1)Ck_{\mathrm{B}}T}{\pi^2N}\left(\sum_{l=1,3,5,\ldots}^{\infty}\frac{1}{l^2}e^{-l^2t/T_{\mathrm{r}}}\right)$$

$$\times\left\{\frac{\varepsilon_{\alpha\mu}\varepsilon_{\beta\mu}}{\varepsilon_{\eta\theta}\varepsilon_{\eta\theta}}-\frac{\delta_{\alpha\beta}}{3}\right\}+p'\delta_{\alpha\beta}. \tag{20}$$

THE STORAGE AND LOSS MODULI

The shear relaxation modulus, $G(t)$, is defined[11] as the ratio of the shear stress relaxation to an applied small shear deformation ε_0 at $t=0$. In this case, the deformation tensor $\boldsymbol{\varepsilon}$ is[12]:

$$\boldsymbol{\varepsilon}=\begin{pmatrix}1 & \varepsilon_0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}. \tag{21}$$

With this tensor, the quantity between curly brackets in (20), to first order in ε_0, becomes

$$\frac{\varepsilon_{\alpha\mu}\varepsilon_{\beta\mu}}{\varepsilon_{\eta\theta}\varepsilon_{\eta\theta}}-\frac{\delta_{\alpha\beta}}{3}=\frac{1}{3}\begin{pmatrix}0 & \varepsilon_0 & 0\\ \varepsilon_0 & 0 & 0\\ 0 & 0 & 0\end{pmatrix}. \tag{22}$$

Hence, the shear relaxation modulus is

$$G(t)=\frac{8(\bar{\gamma}+1)Ck_{\mathrm{B}}T}{\pi^2N}\sum_{l=1,3,5,\ldots}^{\infty}\frac{1}{l^2}e^{-l^2t/T_{\mathrm{r}}}. \tag{23}$$

From this last expression we can compute the dynamic storage modulus, G', and loss modulus, G'', using the well known formula[11]:

$$G'(\omega)=\omega\int_0^\infty G(t)\sin\omega t\,\mathrm{d}t \tag{24}$$

and

$$G''(\omega)=\omega\int_0^\infty G(t)\cos\omega t\,\mathrm{d}t. \tag{25}$$

A substitution of (23) in (24) and (25) gives:

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* We note that no problem arises due to the fact that part of a subchain can be in the original tube and part outside it. We count a subchain as part of the original tube when more than half of it is inside.

$$G'(\omega)=\frac{8(\bar{\gamma}+1)Ck_BT}{\pi^2N}$$

$$\times\left[\sum_{l=1,3,5,\ldots}^{\infty}\frac{1}{l^2}-\sum_{l=1,3,5,\ldots}^{\infty}\frac{l^2}{l^4}+\omega^2T_r^2\right], \qquad (26)$$

and

$$G''(\omega)=\frac{8(\bar{\gamma}+1)Ck_BT}{\pi^2N}(\omega T_r)\sum_{l=1,3,5,\ldots}^{\infty}\frac{1}{l^4+\omega^2T_r^2}. \qquad (27)$$

These series can be summed in closed form, using a lengthy but straightforward procedure[13], with the results:

$$G'(\omega)=G_N^0\left[1-\frac{1}{\sqrt{(\frac{1}{2}\pi^2\omega T_r)}}\right.$$

$$\left.\times\frac{\sinh\sqrt{(\frac{1}{2}\pi^2\omega T_r)}+\sin\sqrt{(\frac{1}{2}\pi^2 T_r)}}{\cosh\sqrt{(\frac{1}{2}\pi^2\omega T_r)}+\cos\sqrt{(\frac{1}{2}\pi^2\omega T_r)}}\right], \qquad (28)$$

and

$$G''(\omega)=G_N^0\frac{1}{\sqrt{(\frac{1}{2}\pi^2\omega T_r)}}$$

$$\times\left[\frac{\sinh\sqrt{(\frac{1}{2}\pi^2\omega T_r)}-\sin\sqrt{(\frac{1}{2}\pi^2\omega T_r)}}{\cosh\sqrt{(\frac{1}{2}\pi^2\omega T_r)}+\cos\sqrt{(\frac{1}{2}\pi^2\omega T_r)}}\right], \qquad (29)$$

where we have defined the elastic plateau modulus of the ionomer system as

$$G_N^0\equiv\frac{(\bar{\gamma}+1)Ck_BT}{N}. \qquad (30)$$

This result corrects an assumption made earlier[1], which is wrong for the system with the stated conditions of concentration and molecular weight that we are considering here. A logarithmic plot of the dynamic moduli (28) and (29) vs. frequency is shown in *Figure 1*, which compares well with the experimental curves[3] in a qualitative sense. A cumbersome fitting procedure was avoided.

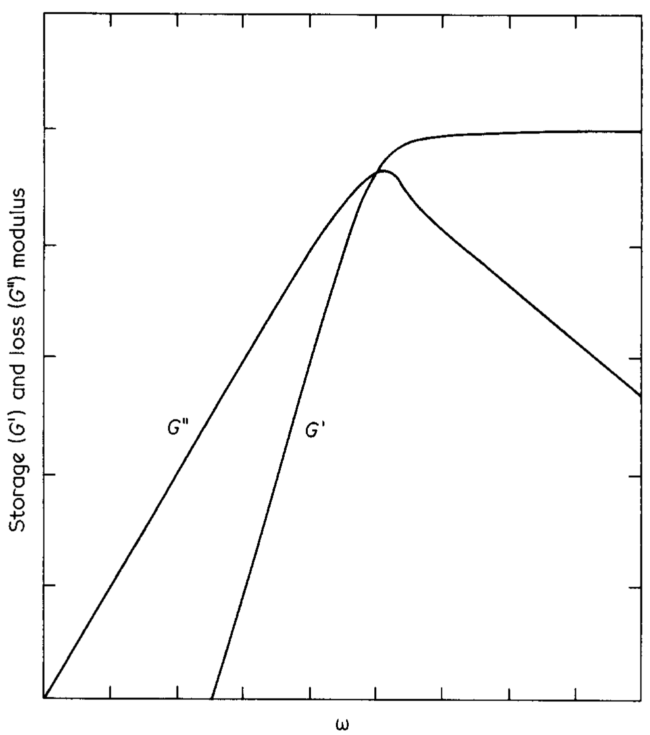

Figure 1 A double logarithmic plot of the storage modulus (G') and the loss modulus (G'') vs. frequency, from equations (28) and (29)

DISCUSSION

It is well known[11] that some dynamic quantities of concentrated solutions and melts undergo a transition as a function of molecular weight and concentration. The zero shear viscosity as a function of molecular weight is an example of this: below the transition, the viscosity is proportional to the polymerization index N, and above is proportional to the 3.4 power of N. It has been argued[14] that the transition point, called the onset of entangled behaviour in polymer solutions, corresponds to the point where polymer diffusion becomes restricted to reptation alone; that is, the primitive chain is capable of undergoing one-dimensional diffusion only. Below the transition point the Rouse theory gives a fairly good description of the dynamic properties. The transition point N_c for undiluted polymers is observed to be of the order of 300–600 backbone units, depending on the polymer under consideration. For diluted polymers the data conform more or less to the equation[15]:

$$N_c(\text{soln})\sim N_cC^{-5/4}. \qquad (31)$$

In our case of relatively low concentration of not very high molecular weight polymers, we would expect not to be in the entangled regime and hence one-dimensional diffusion would play a minor role. However, we have assumed one-dimensional diffusion for the primitive chain in the calculation of the stress tensor. This is the question we want to address in this section.

It seems that the essence of the problem is intimately related to the nature and stability of the constraints forming the tube. The notion of a tube formed by the topological constraints arising from the other molecules seems to be a plausible idea, even in semidilute solution (not very near C^*). *With fixed constraints* the primitive chain would have no other choice but to reptate along the tube in which it is trapped[6], and numerical simulations have confirmed this[16]. However, if the original constraints disappear to be replaced by new ones with a different topology, before the chain has the opportunity to reptate along them, we cannot really talk about one-dimensional diffusion.

In a one-dimensional diffusion process (as well as in higher dimensions), there is a characteristic step time and step length such that, for times and lengths smaller than those, the diffusion law $\langle R^2\rangle\sim t$ is not obeyed. We would like to propose now that, in the case of a free chain, this time should be the Rouse or equilibration time along the tube, as explained in *Figure 2*. This is because we cannot really say that the chain has been displaced to the right or to the left until the primitive path recovers its equilibrium length. If $\tau\gg\tau_R$, as we are considering her, then the time that a chain spends free is also greater than τ_R as found before[1], and this free chain has the capability of undergoing many steps in its one-dimensional diffusion along the tube formed by crosslinked chains (as well as by some free ones). In this sense our chain is moving inside fixed constraints (herefore reptating) until it gets caught by a crosslink and becomes part of the infinite network. Then, the primitive path of the chain becomes more or less static,

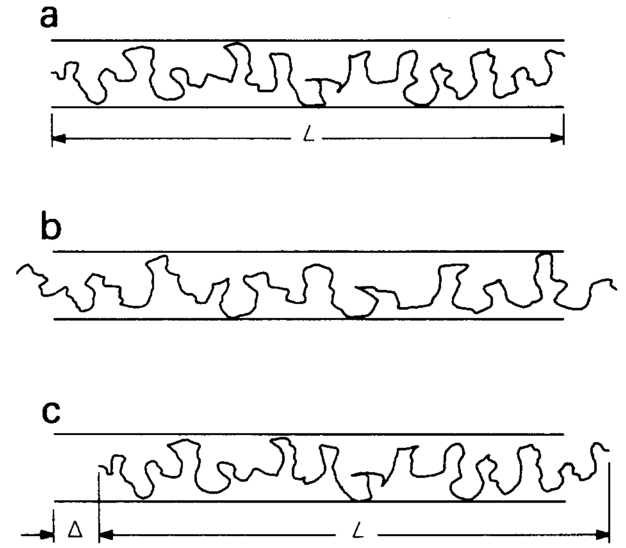

Figure 2 (a) A polymeric chain inside a tube with an equilibrium primitive length equal to L. (b) The same chain after a time shorter than the equilibrium time τ_R; the length of the primitive path is no longer L. (c) After a time τ_R the chain recovers its equilibrium length and finds itself displaced by an amount Δ

particularly when it has acquired more than one crosslink along its length. We acknowledge that when the system is very crosslinked, a chain in the infinite network has to wait for a time exponentially long to be free of crosslinks[1]; in this case some other processes, like dangling ends retracing their steps[17], could occur before it gets free, and reptation would not be the only mechanism for the long-time stress relaxation.

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REFERENCES

1 González, A. E. *Polymer* 1983, **24**, 77
2 Agarwal, P. K., Makowski, H. S. and Lundberg, R. D. *Macromolecules* 1980, **13**, 1679
3 Agarwal, P. K. and Lundberg, R. D. *Polym. Prepr.* 1982, **23**, No. 1, 58
4 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, NY, 1979
5 Chandrasekhar, S. *Rev. Mod. Phys.* 1943, **15**, 1
6 de Gennes, P. G. *J. Chem. Phys.* 1971, **55**, 572
7 Doi, M. and Edwards, S. F. *J. Chem. Soc. Faraday Trans. II* 1978, **74**, 1802
8 Daoud, M., Cotton, J. P., Farnoux, B., Jannik, G., Sarma, G., Benoit, H., Duplessix, R., Picot, C. and de Gennes, P. G. *Macromolecules* 1975, **8**, 804
9 Joanny, J. F. *Polymer* 1980, **21**, 71
10 Rouse, P. E. *J. Chem. Phys.* 1953, **21**, 1272
11 Graessley, W. W. *Adv. Polym. Sci.* 1974, **16**, 1
12 Bird, R. B., Hassager, O., Armstrong, R. C. and Curtiss, C. F., 'Dynamics of Polymeric Liquids', Wiley, New York, 1977
13 See, for example, Morse, P. M. and Feshbach, H. 'Methods of Theoretical Physics', McGraw-Hill, New York, 1953, Vol. 1, p 413
14 Klein, J. *Macromolecules* 1978, **11**, 852
15 Schurz, J. and Hochberger, H. *Makromol. Chem.* 1966, **96**, 141
16 Richter, D., Baumgärtner, A., Binder, K., Ewen, B. and Hayter, J. B. *Phys. Rev. Lett.* 1981, **47**, 109; Baumgärtner, A. and Binder, K. *J. Chem. Phys.* 1981, **75**, 2994
17 de Gennes, P. G. *J. Phys. (Paris)* 1975, **36**, 1199
18 Feller, W. *Ann. Math. Statist.* 1951, **22**, 427

APPENDIX A

In this appendix we show that, when the first relaxation process finishes:

$$\left\langle \frac{r''_\alpha r''_\beta}{g_\gamma b^2} \right\rangle \cong \frac{\varepsilon_{\alpha\mu}\varepsilon_{\beta\mu}}{\varepsilon_{\eta\theta}\varepsilon_{\eta\theta}}. \qquad (32)$$

We assume that the $\mathbf{r}''$ are vectors of magnitude $g_\gamma^{1/2} b$ joining successive points on the deformed primitive path. Of course, in the real system these vectors do not have to start and end at points on the primitive path but anywhere inside the tube; so, the better the approximation the longer and thinner the tube is.

Let us start with the end-to-end vector:

$$\mathbf{R} = \sum_{i=1}^{\gamma+1} \mathbf{r}_i. \qquad (33)$$

Then

$$\boldsymbol{\varepsilon} \cdot \mathbf{R} = \sum_{i=1}^{\gamma+1} \boldsymbol{\varepsilon} \cdot \mathbf{r}_i = \sum_{i=1}^{\gamma'+1} \mathbf{r}''_i. \qquad (34)$$

We observe that we need more than $\gamma+1$ vectors to span the deformed primitive length. So

$$\left\langle \left(\sum_{i=1}^{\gamma+1} \boldsymbol{\varepsilon} \cdot \mathbf{r}_i \right)_\alpha \left(\sum_{j=1}^{\gamma+1} \boldsymbol{\varepsilon} \cdot \mathbf{r}_j \right)_\beta \right\rangle = \left\langle \left(\sum_{i=1}^{\gamma'+1} \mathbf{r}''_i \right)_\alpha \left(\sum_{j=1}^{\gamma'+1} \mathbf{r}''_j \right)_\beta \right\rangle,$$

or

$$\sum_{i,j=1}^{\gamma+1} \varepsilon_{\alpha\theta}\varepsilon_{\beta\eta} \langle r_{i\theta} r_{j\eta} \rangle = \sum_{i,j=1}^{\gamma'+1} \langle r''_{i\alpha} r''_{j\beta} \rangle. \qquad (35)$$

Now, obviously:

$$\langle r_{i\theta} r_{j\eta} \rangle = \tfrac{1}{3} \delta_{ij} \delta_{\theta\eta} g_\gamma b^2. \qquad (36)$$

Also, for the physically interesting cases of elongation and shear deformation, we have:

$$\langle r''_{i\alpha} r''_{j\beta} \rangle = \delta_{ij} \langle r''_\alpha r''_\beta \rangle. \qquad (37)$$

On substituting (36) and (37) into (35), we get:

$$\left\langle \frac{r''_\alpha r''_\beta}{g_\gamma b^2} \right\rangle = \frac{(\gamma+1)}{3(\gamma'+1)} \varepsilon_{\alpha\eta}\varepsilon_{\beta\eta}. \qquad (38)$$

Putting $\alpha = \beta$ and summing over the index leads to:

$$1 = \frac{\gamma+1}{3(\gamma'+1)} \varepsilon_{\alpha\eta}\varepsilon_{\alpha\eta}. \qquad (39)$$

A substitution of this last equation back into (38) gives the desired result.

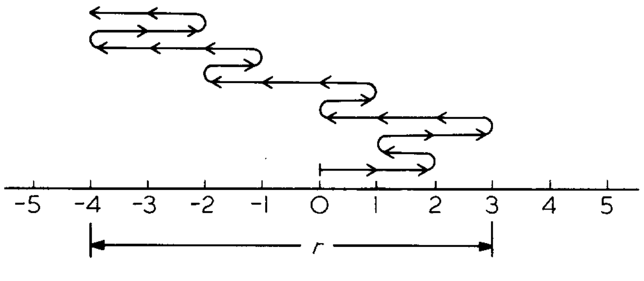

Figure 3 A random walk of 20 steps with a range, *r*, equal to 7

APPENDIX B

In this appendix we want to show that the ratio of the average primitive length still inside the deformed tube to the total primitive length is given by (17). Therefore it is enough to show that:

$$\frac{\bar{L}_{\mathrm{out}}(t)}{L}=1-\frac{8}{\pi^2}\sum_{l=1,3,5,\ldots}\frac{1}{l^2}\exp\left(-\frac{\pi^2 D_{\mathrm{c}} l^2 t}{L^2 \mathrm{e}^{\bar{\gamma}}}\right), \tag{40}$$

where

$$\bar{L}_{\mathrm{out}}(t)=L-\bar{L}_d(t). \tag{41}$$

We know that the primitive path of a free chain is performing a one-dimensional random walk while it is more or less static when the chain is crosslinked. A moment of reflection shows that the portion of the primitive length that left the deformed tube is precisely the range of the random walk[18], *r*, depicted in *Figure 3*; hence, it is our aim to get the probability distribution for the range of a random walk. We begin with a free random walker starting at the origin at $t=0$, with absorbing barriers at $\chi=-Q$ and $\chi=R$. The probability density $\omega_t(\chi)$ for the walker to be at χ after a time t satisfies the following set of equations:

$$\begin{gathered}\frac{\partial w_t(\chi)}{\partial t}=D_{\mathrm{c}}\frac{\partial^2 w_t(\chi)}{\partial \chi^2}\\ w_i(\chi)=0 \qquad \text{if} \quad \chi=-Q \quad \text{or} \quad R \\ w_{t=0}(\chi)=\delta(\chi).\end{gathered} \tag{42}$$

The solution of this set is given by:

$$w_t(\chi)=\frac{2}{R+Q}\sum_{l=1}^{\infty}\exp\left(-\frac{D_{\mathrm{c}}\pi^2 l^2 t}{(R+Q)^2}\right) \sin\left[l\pi\left(\frac{\chi+Q}{R+Q}\right)\right]\sin\left(\frac{l\pi Q}{R+Q}\right). \tag{43}$$

Then, the probability that, at the time t, the walker has not been caught by the barriers at $-Q$ and R is:

$$\begin{aligned}F(t;Q,R)&=\int_{-Q}^{R} w_t(\chi)\,\mathrm{d}\chi\\ &=\frac{4}{\pi}\sum_{l=1,3,5,\ldots}\frac{1}{l}\exp\left(-\frac{\pi^2 D_{\mathrm{c}} l^2 t}{(R+Q)^2}\right)\sin\left(\frac{l\pi Q}{R+Q}\right).\end{aligned} \tag{44}$$

We note that this is also the probability for a random walker with no absorbing barriers, starting at the origin at $t=0$, not to have left the interval $(-Q, R)$ at the time t. If we let

$$f(t;Q,R)\equiv\frac{\partial}{\partial R}\frac{\partial}{\partial Q}F(t;Q,R), \tag{45}$$

then the probability density for a random walker to have a range between r and $r+\mathrm{d}r$ is:

$$\delta(t,r)=\int_0^r f(t;Q,r-Q)\mathrm{d}Q. \tag{46}$$

After performing the calculations indicated in (45) and (46) we get:

$$\delta(t,r)=4\sum_{l=1,3,5,\ldots}^{\infty}\exp\left(-\frac{\pi^2 D_{\mathrm{c}} l^2 t}{r^2}\right)\cdot\left(\frac{8\pi^2 D_{\mathrm{c}}^2 l^2 t^2}{r^5}-\frac{4D_{\mathrm{c}}t}{r^3}\right). \tag{47}$$

$\bar{L}_{\mathrm{out}}(t)$ is given by

$$\bar{L}_{\mathrm{out}}(t)=\int_0^L r\delta(t,r)\,\mathrm{d}r+L\int_L^{\infty}\delta(t,r)\,\mathrm{d}r; \tag{48}$$

that is, a walker whose range is between 0 and L contributes that amount to the length that left the tube, but a walker whose range is greater than L only contributes L to the length that left the tube. A substitution of (47) into (48) gives:

$$\frac{\bar{L}_{\mathrm{out}}(t)}{L}=1-\frac{8}{\pi^2}\sum_{l=1,3,5,\ldots}^{\infty}\frac{1}{l^2}\exp\left(-\frac{\pi^2 D_{\mathrm{c}} l^2 t}{L^2}\right). \tag{49}$$

As explained before[1], the fraction of time that a chain spends free, with no crosslinks, is $\mathrm{e}^{-\bar{\gamma}}$; therefore, the effective time in which a sulphonated chain behaves as a random walker is $\mathrm{e}^{-\bar{\gamma}}t$. A replacement of t by $\mathrm{e}^{-\bar{\gamma}}t$ in (49) leads to (40), as desired.