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1990 J. Phys.: Condens. Matter 2 749

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LETTER TO THE EDITOR

‘Living trees’: dynamics at a reversible classical gel point

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Received 29 June 1989

Abstract. We discuss the effects of slow, reversible scission of cross-links in polymer networks very close to the ‘classical’ gel point in a densely pre-entangled system. We predict that for $k\beta\tau_x \gg 1$, reversible scission has a significant effect on the relaxation process, yielding a terminal time $\tau \approx k^{-1} \ln(\beta\tau_x k)$. In these expressions, k is the scission rate constant, β is a geometrical factor (proportional to the number of entanglements per chain in the precursor system), and τ_x is the disentanglement time for the irreversibly cross-linked system as calculated recently by M Rubinstein, S Zurek, T C B McLeish and R C Ball (to be published).

There has long been interest in the dynamics of physical sols and gels [1–5]. These contain polymeric units that cross-link reversibly with one another. If the cross-links are sufficiently long lived, then the relevant dynamics (e.g., for determining the viscoelastic properties of a sol) involve the diffusive motion of polymer clusters of complicated but *quenched* connectivity. However, if the lifetime of the cross-links is now decreased, a regime is soon encountered in which the polymeric motion of the cross-linked molecules, though not completely abolished, is strongly modified by the reversible scission and reconnection of the cross-links.

In the present note, we focus on this ‘slow breaking’ regime, as distinct from one in which cross-links break and recombine so rapidly that the coherent diffusion of large connected clusters may itself be ignored [6]. As in the case of reversibly breakable *linear* polymers [7], the slow breaking regime should be understandable by combining what we know about *quenched-connectivity* branched polymer dynamics, with simple kinetic models for cross-link scission and recombination. In what follows, we restrict attention to the case of ‘vulcanisation’: gel formation in a densely pre-entangled system. In this case the static properties of the system (i.e. the distribution of cluster sizes and connectivities) are especially simple, being governed by the Flory–Stockmayer theory [4].

For the case of quenched connectivities, the dynamics of highly entangled tree-molecules near the Flory–Stockmayer gel point were recently studied by Rubinstein, Zurek, McLeish and Ball (RZMB) [8]. Below we extend their new results to include the effects of slow reversible scission processes. A related discussion of reversible reaction effects in the case of percolation-type sols (formed by adding reversible cross-links to *unentangled* polymers or small molecules) is given in [9].

We will now consider *entangled trees*. Let us first recall the ingredients of the RZMB theory for such trees. We may designate the cross-link points as ‘sites’ on the tree with the original linear polymers as the connecting ‘bonds’. Now observe that a bond between sites i and j (say) on a branched polymer can be ranked according to its ‘seniority’ [8], which is defined as the minimum over i and j of the length of the longest chemical path (LCP) emanating from one and passing through the other. This is expected to be comparable to the ‘span’ of the smaller of the two trees that would be created by cutting the bond. (The span of a tree is the length of the longest LCP to be found anywhere upon it.) RZMB show that the concentration $C(m)$ of sites of seniority $\geq m$ scales as m^{-2} near the gel point. Note that very senior bonds are rather rare.

To predict viscoelastic properties we need to estimate the relaxation time $\tau(m)$ of a bond whose seniority is m . Treating the surrounding chains as a grid of topological constraints, the basic idea used by RZMB is that a given bond can only relax its orientation when the smaller of the LCPS in these two trees folds back on itself without enclosing any obstacles. (The idea originates in earlier work on the disentanglement of star polymers [10, 11].) This situation is extremely rare; the waiting time depends on the seniority of the bond and can be calculated recursively. For a branched polymer in a fixed network, the calculation is straightforward. Relaxation of a bond of seniority m must be preceded by that of the adjacent bond of seniority $m - 1$. The relaxation time τ_{m-1} for the latter determines the frequency with which the end of the retracting LCP attempts to overcome an entropic barrier to bring it the final step to the m -seniority bond. The probability of surmounting this barrier is [11, 8] $\exp(-\nu\bar{N})$, where ν is a geometrical constant (of order one) and \bar{N} is the average number of entanglements, with the fixed network, between one cross-link point on the tree and the next. (There is also a pre-exponential dependence of τ_m on \bar{N} which we may ignore at this level of approximation.) Thus in a fixed network

$$\tau_m = \tau_{m-1} \exp(\nu\bar{N}) \quad (1a)$$

which implies that

$$\tau_m = \tau_0 \exp(\nu m \bar{N}). \quad (1b)$$

In the gelling system, there is no fixed network of topological constraints; the entanglements are with other tree-like molecules. RZMB argue that, as far as the relaxation of a bond of seniority m is concerned, those parts of the surroundings of seniority less than m relax fast, and so do not contribute to the topological grid. The number of effective entanglements between cross-links is therefore not \bar{N} but $\bar{N}C(m)$ (since the molecular weight between entanglements scales roughly inversely with concentration [12]). As a result

$$\tau_m = \tau_{m-1} \exp(\nu' \bar{N}/m^2) \quad (2a)$$

with $\nu'/\nu \approx 1$, which implies

$$\tau_m = \tau_1 \exp[\nu' \bar{N}(1 - 1/m)]. \quad (2b)$$

The stress relaxation function $G(t)$ is the effective elastic modulus of the unrelaxed part of the network at time t ; at the gel point, this is found to be [8]

$$G(t) \approx (1 - \log(t/\tau_1)/\nu' \bar{N})^4. \quad (3)$$

Here τ_1 is the relaxation time for a bond of seniority one, which in the tube model of

linear chain disentanglement scales as $\bar{N}^2 \exp(\nu \bar{N})$. The longest relaxation time as the gel point is approached from below is

$$\tau_\infty = \tau_1 \exp(\nu' \bar{N}) \quad (4)$$

which is finite. For incomplete gelation, the longest time corresponds to τ_M where M is a characteristic cut-off scale for the distribution of bond seniorities (so that $C(m) \sim m^{-2} f(m/M)$); M diverges in a known manner as the gel point is approached [8].

It is notable that this self-consistent treatment of entanglements predicts complete relaxation of stress in a finite time τ_∞ . Hence eventually there must be a crossover to unentangled motion of the largest trees; this is considered in [8] and we discuss the effect at the end of this paper.

We now go on to consider *reversible scission of cross-links*. The RZMB theory predicts a hierarchy of relaxation times for bonds according to their seniority. The rate limiting step for relaxation of a given bond is the return to the origin of the shorter of its LCPs without enclosing any obstacles of the (dynamically diluted) topological network.

Consider now the relaxation rate at the gel point for a bond of seniority m , in the presence of slow reversible scission reactions. Clearly there is no direct effect on the relaxation of this bond unless (i) the LCP in the smaller of the two trees emanating from the bond (this is the LCP that has to return to the origin) breaks somewhere along its length m ; or (ii) the tree containing this LCP undergoes a cross-linking reaction, leaving it with an LCP larger than m ; or (iii) the LCP in the larger tree breaks within a distance m of the bond (so that this becomes the shorter of the two LCPs).

Suppose we consider simple kinetics with a scission rate k per unit time the same for all cross-links. (In the regime of linear response, there is negligible correlation between the scission rate at a given bond, and its orientation.) In this case it is clear that the characteristic waiting time for process (i), in which the LCP of length m breaks somewhat along its length, is

$$\mathcal{T}_m \approx 1/km. \quad (5)$$

Clearly, this is also the waiting time for process (iii). Perhaps less obviously, the characteristic time for process (ii) is also the same (to which a factor of order unity), as may be inferred by applying the principle of detailed balance to a master equation for the evolution of the length of the LCP in a tree. To illustrate this, we may for example assume that the rate for formation of a cross-link between two clusters is proportional to the product of their masses (in keeping with the mean-field approach). The rate constant k' for this process is proportional to k/ρ , with ρ the number density of precursor chains, as may be confirmed, e.g., by applying detailed balance to the equilibrium between monomers and dimers only. The rate for process (ii) may then be approximated as the sum over all reactions in which any bond in the tree combines with one on a tree whose span m' is comparable to or larger than m . Converting from m' to cluster mass $\mu \sim (m')^2$, we find that process (ii) occurs at a rate

$$k' m^2 \rho \int_{m^2}^{\infty} \mu^{1-\tau} d\mu$$

where $\tau = 2.5$ is the cluster size distribution exponent [4, 8]. Performing this integral gives a rate of order km , implying a characteristic lifetime for process (ii) that obeys equation (5), as stated above. Hence all the scission and recombination processes in the system, in so far as they influence the relaxation of a bond of seniority m , are characterised by a single time scale \mathcal{T}_m .

If \mathcal{T}_m (equation (5)) is long compared with τ_m obeying equation (2), then relaxation of the bond by the hierarchical retraction process is rapid on the scale of \mathcal{T}_m , and the scission processes only weakly perturb the process. On the other hand, for $\mathcal{T}_m \ll \tau_m$, there is a strong effect. Before the LCP of length m can return to the origin, it will break somewhere along its length. We now argue that there is a maximum effective value m^* of m , fixed by the criterion

$$\mathcal{T}_{m^*} \simeq \tau_{m^*} \equiv \tau^*. \quad (6)$$

Note that the seniority of any bond undergoes random and discontinuous changes on the time scale τ^* .

We therefore expect that all bonds that are more senior than m^* should relax uniformly (i.e. with a single exponential decay) with time constant τ^* . To justify this, note that a slower relaxation (say with time $\tau_{m'} \gg \tau^*$) requires that the bond retains a seniority that is large compared with m' throughout the time interval $\tau_{m'}$. The equilibrium probability that $m \geq m'$ at an instant varies as $C(m') \sim (m')^{-2}$; with of the order of $t_{m'}/t^*$ independent trials taking place, the chances of a bond retaining a high seniority throughout this period are slight indeed.

Thus the relaxation time for all bonds of $m \geq m^*$ is simply τ^* as defined in equation (6). Inserting into equation (6) the RZMB result (equation (2)) for τ_m and that of equation (5) for \mathcal{T}_m , we find the self-consistent equation

$$\tau^*/\tau_\infty \simeq \exp(-\beta k \tau^*) \quad (7)$$

with $\beta \equiv \nu' \bar{N}$. Introducing a characteristic scission rate

$$k_c \equiv 1/\beta \tau_\infty \quad (8)$$

equation (7) becomes

$$\hat{\tau}^* = \exp(-\hat{k} \hat{\tau}^*) \quad (9)$$

where $\hat{\tau}^* \equiv \tau^*/\tau_\infty$ and $\hat{k} \equiv k/k_c$.

We see that for $k/k_c \ll 1$ the longest relaxation time τ^* at the gel point is only weakly perturbed from the RZMB prediction: $\tau^* = \tau_\infty(1 - \beta k \tau_\infty)$. For $k \gg k_c$, however, there is a strong effect, with the leading behaviour $\hat{\tau}^* \simeq \ln(\hat{k})/\hat{k}$. (This may be found by rewriting equation (9) as $\hat{\tau}^* \simeq -\ln \hat{\tau}^*/\hat{k}$ and iterating once with respect to $\hat{\tau}^*$.) Equivalently

$$\tau^* = k^{-1} \ln(\beta \tau_\infty k). \quad (10)$$

Note that apart from the logarithmic factor, this is the same as the waiting time for a break to occur within a fixed (i.e. k -independent) distance of a given bond on the tree. For practical purposes, the viscoelastic response function $G(t)$ should be well approximated by

$$G(t) \simeq (1 - \log(t/\tau_1)/\nu' \bar{N})^4 \quad t \leq \tau^* \quad (11a)$$

$$G(t) \simeq (1 - \log(\tau^*/\tau_1)/\nu' \bar{N})^4 \exp(-t/\tau^*) \quad t > \tau^*. \quad (11b)$$

The second form reflects the crossover to single-exponential decay, corresponding to the fact that all bonds of seniority $\geq m^*$ have essentially the same relaxation time.

We now discuss our results. Clearly, if we are not at, but below the gel point, the above arguments carry-over so long as the RZMB relaxation time τ_M for the most senior bonds present is long compared with τ^* ; otherwise, of course, relaxation is completed before scission processes come into play and the original RZMB analysis is adequate.

We may also discuss the response of the system above the gel point. In the quenched system, there are bonds of infinite seniority (the backbone of the infinite cluster) presumably with infinite relaxation times. However, with reversible reactions present, no bond is likely to remain in this state for a long time compared with τ^* . Thus our prediction for the longest relaxation time and for $G(t)$ should remain valid in a finite interval above the gelation threshold. (Indeed, this threshold may be very difficult to identify precisely.) Our arguments finally break down when the assumption of a tree-like molecular structure ceases to be valid on the scale of the characteristic chemical path length m^* . This is when the characteristic span of the largest finite clusters present, which varies [8] as $(p - p_c)^{-1}$, is of order m^* .

Finally, we may consider the crossover to unentangled motion which occurs for the largest clusters very close to the gel point. It is known [4] that there exists a characteristic cluster span $m_x \sim N^{5/6}$ beyond which the static exponents of Flory–Stockmayer theory cross over to those of percolation. According to [8], this is the first way in which the hierarchical disengagement model breaks down (i.e. it occurs before the nominal onset of disentangled dynamics for the largest trees). Clearly, the arguments we have given for the case of reversibly breakable cross-links continue to apply so long as $m^* \leq m_x$. If breaking is so slow that $m^* \geq m_x$, one should consider motion of breakable clusters of the percolation type, as discussed in [9].

In summary, we have extended recent work on the entangled motion of branched polymers close to the classical gel point, so as to allow for the effects of slow, reversible scission of cross-links. The main effect is to cut off the relaxation spectrum at a characteristic time τ^* which depends on the scission rate constant k according to equation (10). We hope that our predictions will stimulate new experiments on reversibly cross-linking, densely entangled systems, close to the gel threshold. At present the main data, e.g., for end-linking ionomeric materials, concern systems in the well-gelled regime [5]. It should be possible to decrease the connectivity deliberately, for example by mixing telechelic ionomers with various proportions of monofunctional chains.

One of us (MEC) wishes to thank Professor Fyl Pincus, whose lectures at Geilo provided a stimulating working environment in which to study this problem. He also thanks Dr Moti Lal for a stimulating discussion. TCBM is supported by ICI plc.

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