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Kinetics of Microphase Separation in Cross-Linked Polymer Blends

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ABSTRACT: We study the early kinetics of the microphase separation that occurs in cross-linked polymer blends. For strong gels, when the distance between cross-links is small, this is dominated by the Rouse modes. We find a characteristic growth rate $\Omega(q)$ dependence on temperature and wavenumber q for the unstable modes $\Omega_q \sim q^4(\chi_s - \chi)$, where the Flory monomer–monomer interaction parameter χ is inversely proportional to temperature and χ_s its value at spinodal. We discuss briefly the cross-over to the kinetics of phase separating blends as cross-linking density is decreased.

1. Introduction

Polymer mixtures were usually phase separated. When the chains are large, their translational entropy is small, and a small chemical mismatch between the monomers is considerably amplified. In a temperature–composition diagram, a lower or a higher critical separation temperature[1-3] is however observed in some cases. In the vicinity of such temperature, fluctuations in composition are important, and there is a divergence of the correlation length that characterizes the spatial extent of these fluctuations. One way of preventing the phase separation is to chemically cross-link the mixture in its one phase region. When such a permanently cross-linked mixture is brought into the coexistence region, although it has a natural tendency for phase separation, elastic forces due to the presence of the cross-links prevent it from doing so. As a result of this competition, there is a local microphase separation.[4-6] This was studied theoretically by de Gennes[1] in a mean field approach. He showed that the size of the microphases is dependent on the amount of cross-linking, and corresponds, in a rough approximation, to the average distance between cross-links. A second important effect of cross-linking is to make the mixture more compatible: there is a shift in the critical temperature that also depends on the cross-linking density. This was also found experimentally by Briber and Bauer[7] who used neutron small angle scattering to study the structure of the microphases in a polystyrene–poly(vinyl methyl ether) mixture. In what follows, we will consider mainly tight gels, with a high density of cross-links. Therefore the typical distance scale for microphase separation is much smaller than the radius of a chain and the distances over which phase separation takes place when the mixture is not cross-linked. Thus, we expect the kinetics also to be different in both cases. Un-cross-linked, blends were studied by de Gennes,[1] Pincus,[2] and Binder.[3] They showed that reptation contributes significantly to the kinetics of phase separation. In the present case, we expect the typical time scale to be significantly smaller because the large scale motions of the chains are frozen by the cross-links. We therefore anticipate that only a Rouse type of motion is important for the system that we are considering. It was shown that the dynamical structure factor of a phase separating mixture may be split into two components,[2,8] namely a fast, small amplitude contribution and a slow, large amplitude one. The former corresponds to the local motion, whereas the latter is related to the large scale creep of the chains. In a cross-linked system, above the gel point, we do not expect any creep because of the constraints. This is why one expects only local, Rouse type motion to be responsible for the kinetics of the microphase separation. This Rouse time corresponds to the very early motion in the case of an un-cross-linked mixture and is discussed only very briefly by the authors mentioned above.

In what follows, we will first recall the main equilibrium results for the microphase separation. Section 3 is devoted to the kinetics. In the final section, we discuss our results and compare them with those for un-cross-linked mixtures. We also critically discuss the various approximations that are made in the present study.

2. The Microphase Separation

Consider a mixture of two large polymer chains of different chemical species A and B made of the same number N of monomers which is initially in the single phase region of its phase diagram. Because of the symmetry, we choose the composition Φ in monomer A to be $^1/_2$. We assume that the polymers are randomly mixed and that no fluctuations in composition are present. This is a high-temperature approximation which implies that the system is far from its critical point. This mixture is now densely cross-linked. Then the temperature is changed and the resulting gel brought into the two-phase region. Following de Gennes,[4] the free energy of such a system may be written in a Landau approximation as

$$F = \int \{[\chi_c - \chi]\,\rho(\mathbf{r})^2 + a^2|\nabla\rho(\mathbf{r})|^2 + C\,P(\mathbf{r})^2\}\,d\mathbf{r} \quad (1)$$

where χ is the Flory monomer–monomer interaction and is inversely proportional to temperature, χ_c its value at the critical point of the un-cross-linked mixture, $\rho(\mathbf{r})$ is the local fluctuation in the composition $\Phi(\mathbf{r})$:$\rho(\mathbf{r}) = \Phi(\mathbf{r}) - \Phi_c$, where Φ_c is the critical composition of the un-cross-linked mixture. The gradient term takes into account the spatial variations of the fluctuations,[10] and the last term, to be discussed below is the elastic contribution due to cross-linking. Both $\chi_c = 2/N$ and $\Phi_c = {}^1/_2$ are determined in a Flory–Huggins (FH) approximation.[9] Note that relation 1 may be considered as the sum of the expansion

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of the FH free energy in the vicinity of its critical point and of the elastic term. On the other hand, solving eq 1 is equivalent to determining the effect of the perturbation to a critical point. We know from previous studies in critical phenomena that this effect may either be small, giving a simple perturbation, or be dramatic, leading to a change in the universality class of the problem. This will be the case in the following.

The elastic contribution in (1) was introduced by de Gennes[4] by analogy with the polarization of a dielectric medium. C is a rigidity constant that was related to the number n of monomers between consecutive cross-links

$$C \sim n^{-2} \tag{2}$$

P is the average displacement between the center of masses of A and B strands. Polarization in the dielectric problem is equivalent to the distance between centers of masses of different strands in the polymer problem, and the charge fluctuations correspond to the fluctuations in composition. This implies that P and Φ are not independent but are related by div $\mathbf{P} = -\rho$, or, in reciprocal space by

$$i\mathbf{q}\cdot\mathbf{P}(q) = -\rho(q) \tag{3}$$

where the Fourier transform $\rho(q)$ of the composition fluctuation is defined below. We are then led to consider only longitudinal modes, and the free energy may be written in the following form

$$F = \sum_q \left\{ \chi_c - \chi + q^2 + \frac{C}{q^2} \right\} |\rho_q|^2 \tag{4}$$

where ρ_q is the Fourier transform of the composition fluctuation

$$\rho_q = \int [\Phi(\mathbf{r}) - \Phi c] \exp(i\mathbf{q}\cdot\mathbf{r})\, d\mathbf{r} \tag{5}$$

The scattered intensity $S(q)$ in a neutron or light scattering experiment is

$$S(q) \sim \langle |\rho_q|^2 \rangle = \left\{ \chi_c - \chi + q^2 + \frac{C}{q^2} \right\}^{-1} \tag{6}$$

it exhibits a maximum for

$$q^* \sim C^{1/4} \sim n^{-1/2} \tag{7}$$

The value of this maximum diverges at the spinodal, for

$$\chi_c - \chi_s \sim -C^{1/2} \tag{8}$$

Thus the divergence occurs for a nonzero value of q, and this is interpreted as a microphase separation. There is also a shift in the critical temperature; the cross-linked system is more miscible than the un-cross-linked one. We consider now the kinetics of the microphase separation.

3. Kinetics

As mentioned above, the main difference between the demixing of a tightly cross-linked blend and of an un-cross-linked polymer mixture is that the distance scales under investigation are very different. Whereas the former case involves motions of chains on large distances by reptation, the latter is dealing with local rearrangements over distances on the order of the mesh size. For an un-cross-linked mixture, de Gennes[8] and Pincus[2] showed that the time-dependent scattered intensity is the sum of two contributions. The first one is a fast mode and corresponds to "local" reptation. The second one, which has a larger amplitude and is much slower, corresponds to "creep" of the polymer chains and allows the disentanglement of the various species. In the present case, because of the presence of permanent cross-links, one does not expect the latter to contribute, and the long time motions are frozen. The local dynamics was not considered in previous studies because it corresponds to the very early kinetics of phase separation in a blend. It is the only type of motion present here. It is a local Rouse[1] dynamics inside the tube made by the other chains.[11] This will appear in the expressions for the Onsager coefficient that will be introduced below. Formally however, one has to write the same kind of equations as for a blend;[12] we look for the time evolution of a fluctuation with fixed wavevector **q**. We will follow a standard procedure which is carefully discussed by Binder.[3] The time evolution is found by introducing a current **j** for species A. The continuity equation is

$$\frac{\partial\Phi}{\partial t} + \operatorname{div}\mathbf{j} = 0 \tag{9}$$

where t is time. The current **j** is related to a potential $\mu(r) = \partial F/\partial\Phi(r)$

$$\mathbf{j}(\mathbf{r}) = \int \Lambda(\mathbf{r} - \mathbf{r}')\nabla\mu(\mathbf{r})\, d\mathbf{r} \tag{10}$$

$\Lambda(\mathbf{r})$ is an Onsager coefficient to be discussed below. Assume an exponential decay for the fluctuation with wavevector **q**

$$\delta\,\Phi(q,t) = \delta\,\Phi(q,0)\, e^{-t/\tau_q} \tag{11}$$

where τ_q is the characteristic decay time. Using relations 9 to 11 and keeping only linear terms in the composition fluctuations,[13] we get

$$\tau^{-1}(q) = -\frac{1}{\delta\Phi_q}\frac{\partial(\delta\Phi_q)}{\partial T} = q^2\,\Lambda(q)\left[\chi_c - \chi + q^2 + \frac{C}{q^2}\right] \tag{12}$$

Equation 12 gives the relaxation rates for early times, when the linearization procedure is valid. Positive rates correspond to stable cases where a fluctuation decays with time. Negative rates are unstable modes. Any such fluctuation grows with time.[14] In order to determine completely the relaxation rate, we need to know the Onsager transport coefficient $\Lambda(q)$, and therefore the nature of the motion of the strands. The form of eq 12 indicates that the product of the last two terms is a diffusion coefficient. As usual, it is the ratio of a mobility μ and the correlation function

$$D(q) = \mu(q)/S(q) \tag{13}$$

Comparing with eq 6, we find that the Onsager coefficient is interpreted as the mobility of the strands. In a highly cross-linked system such as considered here, the motion to be considered is the local one within a distance $d \sim n^{1/2}a$, where a is the monomer length and n the contour length between successive cross-links. Because we are considering tightly cross-linked systems, with $n \ll N_e$, where N_e is the distance between entanglements, only a Rouse motion is to be considered. Thus the transport coefficient $\Lambda(q)$ is proportional to a Rouse mobility. We will consider the case $n \gg N_e$ in the discussion of next section. Because we are dealing with a melt, the number $n(q)$ of monomers in a strand within a distance q^{-1} is proportional to q^{-2}. In a Rouse approximation, the mobility is

$$\Lambda(q) \sim n^{-1}(q) \sim (qa)^2 \tag{14}$$

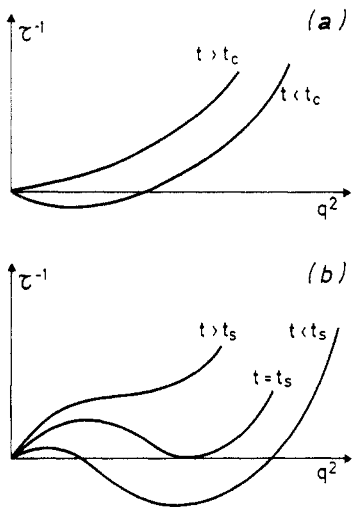

Figure 1. (a) Relaxation rate as a function of wavenumber for an un-cross-linked mixture. For $\chi > \chi_c$, low q modes are unstable. (b) Relaxation rates for a cross-linked mixture. For $\chi_c > \chi > \chi_s$ the minimum is positive and no instabilities are present. Above χ_s the minimum is negative and modes are instable in a range of q.

and thus we have

$$\tau^{-1}(q) = q^4 \left[\chi_c - \chi + q^2 + \frac{C}{q^2}\right] \tag{15}$$

Figure 1 shows the various cases that may be obtained for the characteristic frequency $\Omega_1(q) = \tau^{-1}(q)/q^4$. Figure 1a shows the case when no cross-links are present and for very early stages. For $\chi < \chi_c$ (or $T > T_c$) all frequencies are positive and no instabilities are present. In the opposite case, $T < T_c$, we find that all modes with

$$q > q_c \sim (\chi - \chi_c)^{1/2} \tag{16}$$

are stable whereas the large wavelength modes with $q < q_c$ are unstable: Any fluctuation with such wavelength grows with time: for a cross-linked mixture, $C \neq 0$, Figure 1b, the situation is somewhat different. For $\chi > \chi_c$, the curves exhibit a minimum which may be positive or negative. For $\chi < \chi_s$ all frequencies are positive, and there is no instability. We remind that

$$\chi_c - \chi_s \sim -C^{1/2} \tag{17}$$

For $\chi = \chi_s$ the minimum vanishes, and this corresponds to the microphase separation. For lower temperatures, $\Omega_1(q)$ has a negative part corresponding to the presence of instabilities in a finite q range. The fastest growing instability corresponds to the minimum of the curve, for

$$q^2_{\min} \sim \chi - \chi_c + [(\chi - \chi_c)^2 - 3C]^{1/2} \tag{18}$$

For $\chi \sim \chi_s$ this corresponds to the size q^* of the microdomains. As shown previously, this may be written in the scaled form

$$q^2 \sim (\chi_c - \chi)\, f[C/(\chi_c - \chi)^2] \tag{19}$$

Let us point out that the fact that the very small q part of the curves vanishes is a consequence of the vanishing of $S(q)$ for $q = 0$. This was recently shown to be at variance with neutron scattering results by Briber and Bauer. Thus one does not expect the above considerations to be valid in this region. We will return to this point in the next section. Finally, in the vicinity of the characteristic size q^{*-1}, the characteristic frequency varies as

$$\Omega(q^*) \approx q^{*4}[\chi_s - \chi] \tag{20}$$

with

$$\chi_s = \chi_c + q^{*2} \tag{21}$$

and vanishes as χ approaches χ_s. That the modes are slower than the equivalent Rouse ones for a free chain is not surprising and may be related to the critical slowing down[1] that is usually present near a critical point. Note that relation 15 also implies that for $\chi \approx \chi_c$, the characteristic frequencies varies as

$$\Omega(q) \sim q^6 \tag{22}$$

A similar result was found earlier for a binary mixture and was interpreted as a weighted average of two characteristic rates, namely the local and the creep motions of a long chain. In the present case however, the interpretation is quite different. Part of this behavior is related to the local Rouse motion of a chain. The remaining part corresponds to a slowing down related to the presence of a spinodal decomposition.

4. Discussion

We discussed the kinetics of the early stages of the microphase separation that appears when a system of two chemically different linear polymers is tightly cross-linked in the single phase region and subsequently brought into the demixing zone. We argued that because only local motions are permitted by the constraints, a Rouse motion is responsible of the kinetics of the phase separation. The former is further slowed down by the presence of the latter. There results a typical q^6 dependence of the characteristic rate at the spinodal temperature. Further in the one-phase region the instabilities increase with a characteristic time $\Omega_q \sim q^4(\chi_s - \chi)$, where χ is the monomer interaction parameter, usually inversely proportional to temperature, and χ_s its value at the spinodal.

Our main approximation is that we assumed, as in previous work, that there is only one temperature in the problem. More precisely, the random mixing of the polymer species when cross-linking is performed implies that this is done at high temperature, far from a critical point. Thus the only temperature that comes into play is the one where the system is brought subsequently. As mentioned above, there was some discrepancy between the theoretical and experimental results, which we briefly discuss here in order to make clear the approximation that we used in this paper. Indeed, it was predicted that the zero angle scattered intensity should vanish, and this was at variance with the neutron scattering results of Briber and Bauer. The reason for this is, in our opinion, related to the fact that in an actual un-cross-linked mixture, for a finite temperature, fluctuations in composition are present. They are more important and extended as the blend is closer to its critical temperature. They are frozen in by cross-linking. Therefore, in a scattering experiment, one should still observe them for low wavevectors. This implies that there is not only one but two temperatures in the problem, namely the one where cross-linking is performed, and the one where the system is brought after quench. This will be discussed elsewhere.

Finally, one may extend the above considerations to the case of less tightly bound blends and look how one recovers the kinetics for un-cross-linked mixtures. For large chains and a less tightly bound mixture, when the contour length n between successive cross-links is larger than the length N_e between entanglements, the kinetics involves local reptation in tube portions between cross-links. Therefore the early stages we are discussing are going to take place at longer times than the ones that were discussed above.

The Onsager coefficient $\Lambda(q)$ corresponds no longer to a Rouse dynamics, but to the local reptation of the strands inside the tube portions. It was shown recently by Pincus[2] that such motion implies

$$\Lambda(q) \sim (qn)^{-2} \tag{23}$$

and therefore

$$\tau^{-1}(q) \sim n^{-2}(\chi_c - \chi + q^2 + C/q^2) \tag{24}$$

the cross-over between relations 24 and 15 occurring for $n \sim N_e$. Relation 24 implies that the fastest growing instability is for $q \sim q^*$ and grows as

$$\tau^{-1}(q^*) \sim n^{-2}(\chi_s - \chi) \tag{25}$$

Note that when C goes to zero, the latter relation crosses over smoothly to the Pincus[2] result for an un-cross-linked mixture undergoing phase separation

$$\tau^{-1}(q^*) \sim N^{-2}(\chi_c - \chi) \sim N^{-3}t$$

with

$$t = (\chi_c - \chi)/\chi_c$$

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