1172 *Macromolecules* **1994,** *27,* 1172–1176

Scattering and Phase Behavior of Cross-Linked Blends

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Received June 2, 1993; Revised Manuscript Received October 22, 1993[⊗]

ABSTRACT: The static scattering function is calculated for a cross-linked blend in the presence of a low molecular weight solvent. The idea suggested by de Gennes to treat analogously the effects of cross-links in a network and those of electric charges in a dielectric medium is generalized to include the concept of screening. It is argued that this generalization could help to resolve the discrepancy between the model and the neutron scattering data in the low q region. Other phenomena are also examined such as the enhancement of compatibility due to cross-links and the kinetics of the microphase separation transition.

1. Introduction

The scattering properties and phase behavior of blends in solution or in bulk are the subject of particular attention from both a theoretical[1–4] and an experimental[5–10] point of view. The random phase approximation (RPA)[11] and its extension by the renormalization group theory[12] to regions of strong fluctuations near the critical point are found to be successful[13] in describing experimental data in a wide range of relevant parameters such as the magnitude of the wave vector q, the temperature T, the mean polymer volume fraction (or concentration), ϕ, etc., as long as the system remains stable in a homogeneous state. The phase behavior is investigated by a number of techniques and, in particular, by radiation scattering, which is an indispensable tool in exploring the microphase separation transition (MST). The effects of cross-links on the phase behavior and the scattering properties have received only a limited attention for networks either in a dry state or in the presence of a low molecular weight solvent.

In view of the importance of blend systems for practical purposes and the recent progress in the understanding of their thermodynamic and structural behaviors, an attempt is made here to reexamine these systems in the presence of permanent or temporary cross-links. The complete theoretical formulation is not simple since it needs a generalization of the RPA, which in the present case may be too complicated by requiring advanced mathematical tools such as the replica formulation for cross-link constraints.[14,15] Instead, we adopt the simple model based on the analogy between a cross-linked blend and a dielectric medium as suggested by de Gennes.[16] The charges of opposite sign in the medium produce a local polarization field, inducing an electrostatic energy that can be identified with the elastic energy of a cross-linked network. The outcome of such an analogy is an enhanced compatibility of the two polymers in the thermodynamic limit (i.e., $q = 0$) and the emergence of a peak in the scattering function $S(q)$ at a finite wave vector $q = q_m$. Under certain conditions, the modes of wavelength $\lambda_m = 2\pi/q_m$ become unstable and the system undergoes MST. This transition has been studied theoretically by Bettachy et al.[17] for weakly cross-linked gels and experimentally by Briber and Bauer,[18] who reported small-angle neutron scattering data on blends of deuterated polystyrene and poly(vinyl methyl ether) at several degrees of cross-linking. These authors analyzed their data using de Gennes' model and found a good agreement, except in the small q range, where the extrapolation of $S(q)$ to $q = 0$ shows a finite value whereas the model predicts a zero limit.

In this paper, a model is proposed which intends to resolve this discrepancy and to improve de Gennes' analogy in this q range. For the sake of clarity, we present certain details of the model concerning the system of charges and use de Gennes' analogy to extend the results to a cross-linked blend in the presence of a low molecular weight solvent. We consider a symmetric mixture where the A and B polymers have the same degree of polymerization N, radius of gyration R_g, and volume of a unit segment σ^3. The composition of polymer A is $x = \phi_a/\phi$ and the Flory–Huggins[19] interaction parameter is χ. The volume fraction of the solvent is $\phi_s = 1 - \phi$ and its interaction parameter with the polymer is χ_{PS}.

2. On the Analogy with the Dielectric Medium

We proceed in the same way as in ref 20, including the solvent and writing the Flory–Huggins[19] free energy per site as

$$\frac{f}{kT} = \frac{\phi}{N}\ln\phi + \phi_s\ln\phi_s + \chi_{PS}\phi\phi_s + \phi\left[\frac{x\ln x + (1-x)\ln(1-x)}{N} + \chi x(1-x)\right] \quad (1)$$

where k is the Boltzmann constant and T is the absolute temperature. If the system undergoes local fluctuations, ϕ and ϕ_s become space dependent and the free energy functional per unit volume $\Delta\mathcal{F}$ is introduced by a Taylor expansion of eq 1:

$$\frac{\Delta\mathcal{F}}{kT} = \int\frac{d^3r}{\sigma^3}\left\{\frac{f[\phi(\mathbf{r})]}{kT} + \frac{\sigma^2}{36x(1-x)\phi^2}|\nabla\phi(\mathbf{r})|^2 + \frac{\mathcal{F}_{ex}[\phi(\mathbf{r})]}{kT}\right\} \quad (2)$$

where the segment length is assumed to be the same for both polymers. $\nabla\phi(\mathbf{r})$ represents the gradient of $\phi(\mathbf{r})$, and $\mathcal{F}_{ex}$ is the excess free energy. In the dielectric medium the latter quantity is expressed in terms of the local electric

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1994.

0024-9297/94/2227-1172$04.50/0

field **E** and the dielectric constant ϵ as

$$\mathcal{F}_{\mathrm{ex}} = \epsilon|\mathbf{E}|^2 \tag{3}$$

In de Gennes' analogy the excess free energy is expressed in terms of the local field of polarization **P** and the rigidity constant C:

$$\mathcal{F}_{\mathrm{ex}} = C|\mathbf{P}|^2 \tag{4}$$

In this analogy, the electric field **E** and the polarization **P** are conjugate to each other. They can be expressed in terms of the charge density $\rho(\mathbf{r})$ using Maxwell's equation:

$$\nabla\cdot\mathbf{E}(r) = \rho(\mathbf{r}) \tag{5}$$

Expressing the free energy in terms of the Fourier components of the density fluctuations $\phi(q)$, one finds that the excess part $\mathcal{F}_{\mathrm{ex}}$ shows a q^{-2} behavior describing a long-range $1/r$ potential. This interaction is due to the local charge separation inducing a local field. Moreover, it is known that each particle of a given sign, (+) for example, is surrounded by a cloud of charges (−), resulting in a significant screening of the electrostatic interactions. This means that the long-range $1/r$ potential should be modified as $e^{-\kappa r}/r$, where κ^{-1} is the classical Debye–Hückel screening length. The system should nonetheless satisfy the global electroneutrality condition. Locally, however, the latter condition may be violated, producing a local charge separation and hence a local electrostatic field $\delta\mathbf{E}(\mathbf{r})$. This is related to the electrostatic potential $\delta U(\mathbf{r})$ by the usual gradient operator ∇:

$$\delta\mathbf{E}(\mathbf{r}) = -\nabla\delta U(\mathbf{r}) \tag{6a}$$

$\delta U(\mathbf{r})$ is itself related to the density fluctuation $\delta\rho(\mathbf{r})$ by the Poisson equation:

$$\nabla^2\delta U(\mathbf{r}) = \delta\rho(\mathbf{r}) \tag{6b}$$

Writing $\delta\rho(\mathbf{r})$ in the form $\delta\rho^\circ(\mathbf{r})e^{-U(\mathbf{r})/kT}$ yields the classical Debye equation:

$$(\nabla^2 + K_g^{\,2})\delta\rho(\mathbf{r}) = 1 \tag{6c}$$

where $U(\mathbf{r})$ is assumed to be small compared to kT. In the analogy with the cross-linked blend, the inverse screening length is denoted K_g and is defined by

$$K_g^{\,2} \cong \frac{1}{N\sigma^2} \tag{7}$$

An alternative method of presenting this analogy is to examine the free energy of a mixture where the A polymer with volume fraction $x\phi$ carries a total charge $fx\phi$. The same amount of opposite charges is dispersed in the medium as counterions of mean volume fraction $\phi_{\mathrm{ci}} = fx\phi$. The local charge density fluctuation producing the local field is denoted $z(\mathbf{r})$:

$$e^{-1}z(\mathbf{r}) = \delta\rho(\mathbf{r}) = xf\delta\phi(\mathbf{r}) - \delta\phi_{\mathrm{ci}}(\mathbf{r}) \tag{8}$$

$\delta\phi(\mathbf{r})$ and $\delta\phi_{\mathrm{ci}}(\mathbf{r})$ represent the fluctuations in the volume fractions of the polymer and the counterions, respectively, and e is the electron charge:

$$\delta\phi(\mathbf{r}) = \phi(\mathbf{r}) - \phi \tag{9a}$$

$$\delta\phi_{\mathrm{ci}}(\mathbf{r}) = \phi_{\mathrm{ci}}(\mathbf{r}) - \phi_{\mathrm{ci}} \tag{9b}$$

For convenience, the quantities appearing without the arguments **r** or q designate mean values and are constant in space. Expressing eq 2 in terms of $\delta\phi(\mathbf{r})$, keeping only terms proportional to $\delta\phi^2(\mathbf{r})$, and taking Fourier transforms yields[21]

$$\begin{aligned}\frac{\Delta\mathcal{F}}{kT} = \frac{1}{\sigma^3}\int \mathrm{d}^3q\, \Bigg\{&\left(\frac{1}{x\phi N} + \frac{\sigma^2\mathbf{q}^2}{18x\phi}\right)|\delta\phi_{\mathrm{a}}(\mathbf{q})|^2 + \left(\frac{1}{(1-x)\phi N} + \right.\\ &\left.\frac{\sigma^2\mathbf{q}^2}{18(1-x)\phi N}\right)|\delta\phi_{\mathrm{b}}(\mathbf{q})|^2 + \frac{|\delta\phi_{\mathrm{s}}(\mathbf{q})|^2}{\phi_{\mathrm{s}}} + \frac{|\delta\phi_{\mathrm{ci}}(\mathbf{q})|^2}{\phi_{\mathrm{ci}}} + \\ &2\chi\delta\phi_{\mathrm{a}}(\mathbf{q})\delta\phi_{\mathrm{b}}(-\mathbf{q}) + 2\chi_{\mathrm{PS}}[\delta\phi_{\mathrm{a}}(\mathbf{q}) + \delta\phi_{\mathrm{b}}(\mathbf{q})]\delta\phi_{\mathrm{s}}(-\mathbf{q}) + \\ &\frac{4\pi l}{q^2}|\delta\rho(\mathbf{q})|^2\Bigg\}\end{aligned} \tag{10}$$

where we have displayed explicitly the contribution from the three components a, b, and the solvent s and where l represents the Bjerrum length; i.e., $l = e^2/(\epsilon kT)$. The density fluctuations are subject to the incompressibility assumption $\delta\phi_{\mathrm{s}}(\mathbf{q}) = -\delta\phi_{\mathrm{a}}(\mathbf{q}) - \delta\phi_{\mathrm{b}}(\mathbf{q})$ and $\phi_{\mathrm{s}} = 1 - \phi$. From this result, one gets the useful correlation functions such as the structure factor $S(\mathbf{q}) = \langle|\delta\phi_{\mathrm{a}}(\mathbf{q})|^2\rangle$, which reflects the charged monomer correlations. This quantity is obtained as

$$S^{-1}(q) = [S^{-1}(q)]_0 + \frac{4\pi l f^2}{q^2 + K_g^{\,2}} \tag{11}$$

$[S^{-1}(q)]_0$ represents the static structure factor for the blend in the neutral limit (i.e., $f = 0$):

$$[S^{-1}(q)]_0 = G_x^{\,-1}(q) - \left(\frac{1}{\phi_{\mathrm{s}}} - 2\chi_{\mathrm{PS}} + \chi\right)^2 G_{1-x}(q) \tag{12a}$$

and

$$G_x^{\,-1}(q) = \frac{1}{x\phi NP(q)} + \frac{1}{\phi_{\mathrm{s}}} - 2\chi_{\mathrm{PS}} \tag{12b}$$

The form factor $P(q)$ can be approximated by the following expression,[22] which is more convenient if one seeks analytical results:

$$P(q) \cong (1 + u/2)^{-1} \tag{13a}$$

Equation 13a is only a few percent different from the classical Debye function $D(q)$ in the intermediate q range.

$$D(q) = \frac{2}{u^2}(\mathrm{e}^{-u} + u - 1) \tag{13b}$$

where u is defined by

$$u = q^2R_g^{\,2} \tag{14a}$$

and

$$R_g^{\,2} = N\sigma^2/6 \tag{14b}$$

In the absence of solvent $\phi_{\mathrm{s}} = 0$, $\phi = 1$, one recovers a result similar to eq 11 where $[S^{-1}(q)]_0$ has the form[11]

$$[S^{-1}(q)]_0 = \frac{1}{x(1-x)NP(q)} - 2\chi \tag{15}$$

The analogy suggested by de Gennes and the results obtained here indicate that the extension of eq 11 to the cross-linked blend is implemented by writing

$$S^{-1}(q) = [S^{-1}(q)]_0 + \frac{C}{q^2 + K_g^{\,2}} \tag{16}$$

This equation shows that if K_g is larger than q, the effect of cross-linking is reduced, whereas if K_g is smaller, the strong gel limit described by de Gennes is recovered. To elucidate this behavior further, let us consider first the case of a dry blend.

3. Cross-Linked Blend without Solvent

It is useful to reexamine this system not only because it is simple but also because it contains the essential features of the model. The scattering function $S(q)$ is given by eq 16, where the form factor $P(q)$ is approximated by eq 13a. The result is

$$S^{-1}(q) = \frac{1}{x(1-x)N} - 2\chi + q^2\frac{R_g^{\,2}}{2x(1-x)N} + \frac{C}{q^2 + K_g^{\,2}} \tag{17}$$

which is to be compared with eq 11 of ref 17a. The critical parameter for spinodal decomposition at $q = 0$ is increased by a finite value whereas in de Gennes' model, one obtains a cross-linking term proportional to $1/q^2$, which goes to infinity as q goes to zero. Therefore, the critical parameter for the network is found as

$$\chi_c(\text{network}) = \frac{2}{N} + \frac{C}{2K_g^{\,2}} \tag{18}$$

The first term on the right-hand side corresponds to a mixture of free chains whereas the second term represents the enhancement of compatibility due to the cross-links. This increased stability toward phase separation is accompanied by the emergence of a peak at a finite wave vector q_m which signals a microphase separation transition (MST). This transition takes place within the system if the fluctuations of wavelength $\lambda_m = 2\pi/q_m$ are strong enough to drive it beyond its stability limit. Such a limit is obtained by setting to zero the derivative of eq 16 with respect to q^2. This operation gives the position of the maximum q_m as

$$q_m^{\,2} = \left(\frac{12x(1-x)C}{\sigma^2}\right)^{1/2} + K_g^{\,2} \tag{19a}$$

For a symmetric blend, $x = {}^1/_2$, one obtains

$$q_m^{\,2} = \left(\frac{3C}{\sigma^2}\right)^{1/2} + K_g^{\,2} \tag{19b}$$

Furthermore, de Gennes proposed the following relationship between the rigidity constant C and n:

$$C = \frac{1}{3n^2\sigma^2} = \frac{\sigma^2}{3\xi^4} \tag{20}$$

where the proportionality constant is introduced for convenience and $\xi^2 = n\sigma^2$ represents the square end-to-end distance between two consecutive cross-links. Combining eqs 19 and 20 yields

$$q_m^{\,2} = \frac{1}{\xi^2} - K_g^{\,2} \tag{21}$$

In the end-linking limit, the number of segments between two consecutive cross-links is of the order of the initial chain length N (i.e., $n \approx N$), q_m goes to zero, and the microphase structure disappears. This is expected since the system behaves as a mixture of interacting free chains. The case of a strongly cross-linked, highly elastic network ($n \ll N$) is treated within the framework of de Gennes' analogy which predicts that $q_m \approx 1/n^{1/2}$. This also suggests that the screening length K_g^{-1} should be proportional to the end-to-end distance of the chain as described by eq 7. Therefore, q_m is obtained as

$$q_m^{\,2}\sigma^2 = \frac{1}{n} - \frac{1}{N}; \quad n \le N \tag{22a}$$

and

$$q_m^{\,2}\sigma^2 = 0; \quad n > N \tag{22b}$$

Obviously, for $n > N$, the network is made of free chains and the cross-linking contribution disappears. Furthermore, a rough estimate of the extent of compatibility enhancement can be made from eqs 7, 18, and 20:

$$\chi_c(\text{network}) = \frac{2}{N} + \frac{N}{6n^2}; \quad n \le N \tag{23a}$$

$$\chi_c = \frac{2}{N}; \quad n > N \tag{23b}$$

The scattering in the forward direction $S(q{=}0)$ can be obtained from eq 17:

$$\frac{1}{2S(q{=}0)} = \frac{2}{N} - \chi + \frac{N}{6n^2}; \quad n \le N \tag{24a}$$

$$= \frac{2}{N} - \chi; \quad n > N \tag{24b}$$

The critical parameter for MST, χ_m, can be obtained from the stability condition $S^{-1}(q{=}q_m) = 0$ and eq 17. The result is

$$\chi_m(\text{network}) = \frac{2}{N} + \frac{1}{6}q_m^{\,2}\sigma^2 + \frac{C}{2(q_m^{\,2} + K_g^{\,2})} \tag{24c}$$

This result is in good qualitative agreement with the experimental observations[18] for various cross-linking densities.

4. Effects of Solvent

Equations 10–16 define the scattering function $S(q)$ for a cross-linked blend in the presence of a low molecular weight solvent. For simplicity, we consider the case of a symmetric mixture where the composition $x = {}^1/_2$. The structure factor can also be written in the form of eq 16, where the bare structure factor $[S(q)]_0$ is given by

$$2[S(q)]_0 = \frac{\phi NP(q)}{2}\left\{\left[1 - \frac{\chi}{2}\phi NP(q)\right]^{-1} + \left[1 + \left(v + \frac{\chi}{2}\right)\phi NP(q)\right]^{-1}\right\} \tag{25}$$

The variation of $S(q)$ as a function of q shows a broad maximum at a small polymer content but this maximum becomes sharper as ϕ increases. In good solvent conditions the network is swollen and the incompatibility of the two polymers is increased. This compatibility is even more enhanced when the blend is cross-linked.[23,24] To estimate this enhancement, one can derive the critical parameter χ_c from eqs 16 and 25 using the condition of the stability limit $S^{-1}(q{=}0) = 0$:

$$\chi_c = \left(\frac{2}{\phi N} + \frac{1}{\phi_s} - 2\chi_{PS}\right)^{1/2}\left[\frac{2}{\phi N} + \frac{1}{\phi_s} - 2\chi_{PS} + \frac{C}{K_g^{\,2}}\right]^{1/2} - \frac{1}{\phi_s} + 2\chi_{PS} \tag{26}$$

This expression clearly shows that χ_c increases with decreasing ϕ and increasing C. The stability condition for microphase separation transition yields the corresponding critical parameter χ_m. Introducing the quantity P_m

$$P_m = \left(1 + q_m^{\,2}\frac{N\sigma^2}{12}\right)^{-1} \tag{27}$$

into eqs 16 and 25 and the condition $S^{-1}(q_m{=}q) = 0$ yields

$$\chi_{\mathrm{m}} = \left(\frac{2}{\phi N P_{\mathrm{m}}} + \frac{1}{\phi_{\mathrm{s}}} - 2\chi_{\mathrm{PS}}\right)^{1/2}\left[\frac{2}{\phi N P_{\mathrm{m}}} + \frac{1}{\phi_{\mathrm{s}}} - 2\chi_{\mathrm{PS}} + \frac{C}{{q_{\mathrm{m}}}^2 + {K_{\mathrm{g}}}^2}\right]^{1/2} - \frac{1}{\phi_{\mathrm{s}}} + 2\chi_{\mathrm{PS}} \quad (28)$$

This equation shows that the critical parameter for microphase transition has a behavior similar to that of the corresponding parameter for the ordinary macrophase transition except that it depends on the location of the maximum q_{m}. The thermodynamic behavior is related to the scattering in the forward direction, and therefore it is useful to have the expression of $S(q{=}0)$ which is obtained from eqs 16 and 25.

$$S^{-1}(q{=}0) = \frac{\left(1 - \frac{\chi\phi N}{2}\right)\left[1 + \left(\upsilon + \frac{\chi}{2}\right)\phi N\right]}{\frac{\phi N}{2}\left[1 + \frac{\upsilon\phi N}{2}\right]} + \frac{C}{{K_{\mathrm{g}}}^2} \quad (29)$$

The first term on the right-hand side is simply $[S(q{=}0)]_0^{-1}$, whereas the second term represents the effect of cross-linking. As the rigidity constant C increases, $S(q{=}0)$ decreases, consistent with the previous findings in this paper describing an increased compatibility of the mixture toward phase separation.

5. On the Kinetics of the MST

Suppose that the cross-linked blend is initially at a temperature T_{i} in the equilibrium one-phase region. By a sudden drop of temperature $|\Delta T| = T_{\mathrm{i}} - T_{\mathrm{f}}$, it is brought into the region of microphase separation at the final temperature T_{f}, where the mixture experiences an interaction exceeding χ_{m}. In the early stages of MST, the scattering intensity will grow exponentially:

$$S(t,q) = S_{\mathrm{i}}(q)\mathrm{e}^{2\gamma_{\mathrm{f}}(q)t} \quad (30)$$

where $S_{\mathrm{i}}(q)$ is the structure factor at the temperature T_{i} and $\gamma_{\mathrm{f}}(q)$ is the growth rate of the concentration fluctuations at the temperature T_{f}. In the early stages of microphase transition where the new structures have not been fully developed, $\gamma_{\mathrm{f}}(q)$ can be estimated from an extension of the theory in the one-phase region:[22]

$$\gamma_{\mathrm{f}}(q) = q^2 kT_{\mathrm{f}}\frac{M_{\mathrm{f}}(q)}{\beta_{\mathrm{f}}(q)} \quad (31)$$

$M_{\mathrm{f}}(q)$ and $\beta_{\mathrm{f}}(q)$ are the generalized mobility (or the Onsager kinetic coefficient) and the fictitious structure factor in the final state. In the bulk limit, assuming that the final interaction parameter χ_{f} is higher than both χ_{m} and χ_{c}, eq 17 yields

$$[\beta_{\mathrm{f}}(q)]^{-1} = \chi_{\mathrm{f}} - \chi_{\mathrm{c}} - q^2\sigma^2/6 - \frac{C}{2(q^2 + {K_{\mathrm{g}}}^2)} \quad (32)$$

Using the expressions for C and ${K_{\mathrm{g}}}^2$ given by eqs 20 and 17, respectively, yields

$$[\beta_{\mathrm{f}}(q)]^{-1} = \chi_{\mathrm{f}} - \chi_{\mathrm{c}} - q^2\sigma^2/6 - \frac{1}{6(q^2\xi^2 + n/N)n}; \quad n \le N \quad (33a)$$

and

$$[\beta_{\mathrm{f}}(q)]^{-1} = \chi_{\mathrm{f}} - \chi_{\mathrm{c}} - q^2\sigma^2/6; \quad n > N \quad (33b)$$

To proceed further with the description of the kinetics of the system, one needs to examine the quantity $M_{\mathrm{f}}(q)$. The dynamical model which will be used neglects reptation and uses Rouse modes but distinguishes between the friction coefficient of monomers at the cross-links $\zeta = 2\zeta_0/f$, where f is their functionality and should not be confused with the subscript f, the free energy in eq 1, or the charge parameter in eq 11. ζ_0 is the friction coefficient of the free monomers. The monomers contributing to cross-links constitute only a small fraction of the total number of monomers but they are characterized by a higher mobility. Therefore, choosing the model of additive mobilities, which favors the component with a higher mobility, one has

$$M = M(\text{cross}) + M(\text{free}) \quad (34a)$$

where M(cross) is the contribution of cross-links

$$M(\text{cross}) = f/2n\zeta_0; \quad n \le N \quad (34b)$$

f is the cross-link functionality and M(free) is the contribution of free monomers:

$$M(\text{free}) = \frac{1}{\zeta_0}\left(1 - \frac{1}{n}\right); \quad n \le N \quad (34c)$$

In the free-chain limit, there are no cross-links, $n > N$, and $M = 1/\zeta_0 = M(\text{free})$. In the high cross-linking density limit, $n = 1$, the contribution of free monomers vanishes. For intermediate values of n, one has

$$M = \frac{1}{\zeta_0} + \frac{1}{n}\left(\frac{1}{\zeta} - \frac{1}{\zeta_0}\right) \equiv \frac{1}{\zeta_0}\left(1 + \frac{1}{n}\left(\frac{2}{f} - 1\right)\right); \quad n \le N \quad (35a)$$

$$M = \frac{1}{\zeta_0}; \quad n > N \quad (35b)$$

One should note that the mobilities are normalized by a factor N for reasons of consistency with the normalization of the structure factors. Therefore, combining eqs 31–35 yields the growth rate of the composition fluctuations:

$$\gamma(q) = q^2\frac{kT}{N}\left\{\frac{1}{\zeta_0} + \frac{1}{n}\left(\frac{1}{\zeta} - \frac{1}{\zeta_0}\right)\right\}\left\{\frac{\chi_{\mathrm{f}}}{\chi_{\mathrm{c}}} - 1 - q^2\frac{N\sigma^2}{12} - \frac{N}{12n[q^2\xi^2 + n/N]}\right\}, \quad n \le N \quad (36a)$$

$$\gamma(q) = q^2\frac{kT}{N\zeta_0}\left\{\frac{\chi_{\mathrm{f}}}{\chi_{\mathrm{c}}} - 1 - q^2\frac{N\sigma^2}{12}\right\}, \quad n > N \quad (36b)$$

where we have used $\chi_{\mathrm{c}} = 2/N$. The free-chain limit for $n > N$ reduces to the classical Cahn–Hilliard–Cook[25] equation:

$$\gamma(q) = q^2 D_{\mathrm{s}}\left[-\frac{\delta^2 f}{\delta\phi^2} - 2k_{\mathrm{f}}q^2\right] \quad (37a)$$

with the following identification of terms:

$$D_{\mathrm{s}} = \frac{kT}{N\zeta_0}; \quad -\frac{\delta^2 f}{\delta\phi^2} = \frac{\chi_{\mathrm{f}}}{\chi_{\mathrm{c}}} - 1; \quad k_{\mathrm{f}} = \frac{N\sigma^2}{24} \quad (37b)$$

The extrapolation of this model to the strong cross-linking limit (i.e., $n \ll N$) gives the growth rate:

$$\gamma(q) = q^2\frac{kT}{N\zeta}\left\{\frac{\chi_{\mathrm{f}}}{\chi_{\mathrm{c}}} - 1 - q^2\frac{N\sigma^2}{12} - \frac{N}{12nq^2\xi^2}\right\} \quad (38)$$

where several q regimes can be distinguished. In the regime of high q's, one has $\gamma \approx q^2$ if $qR_{\mathrm{g}} < 1$, corresponding to a kinetics of phase separation by an interdiffusion process. If $qR_{\mathrm{g}} > 1$, one obtains a stable Rouse contribution which behaves like $\gamma \approx q^4$, reflecting the internal modes. In the small q limit, one has a peculiar behavior corresponding to a finite value of $\gamma(q{=}0)$. This behavior is observed in charged systems, where it is known as the plasmon mode. It may mean that the gel is in a quasi-frozen state and its cross-links move harmonically around their mean position.[26] Likewise, in charged systems, small ions follow the motion of polyions in an attempt to ensure the screening of their electrostatic forces and the electroneutrality condition.

In the presence of a low molecular weight solvent, one may need to include the hydrodynamic interaction in the mobility using the Oseen tensor. In the presence of cross-links, such interaction is expected to be screened due to the local concentration of monomers which is enhanced. If the cross-linking density is weak and the polymer concentration is low, the hydrodynamic interaction should be included, and this can be implemented in the same way as described in various papers dealing with free chains.[11,22]

Acknowledgment. This work was accomplished while the first author was a guest of the MPI-P (Mainz). He thanks Professor E. W. Fischer for his kind invitation and the MPI-P for hospitality.

References and Notes

(1) Benmouna, M.; Benoit, H.; Duval, M.; Akcasu, A. Z. *Macromolecules* **1987**, *20*, 1107.

(2) Roby, R.; Joanny, J. F. *Macromolecules* **1992**, *25*, 4612.

(3) Brosetta, D.; Leibler, L.; Joanny, J. F. *Macromolecules* **1987**, *20*, 1937.

(4) Akcasu, A. Z. *Dynamic Light Scattering: The Method and Some Applications*; Brown, W., Ed.; Oxford University Press: Oxford, 1993.

(5) Giebel, L.; Borsali, R.; Fischer, E. W.; Meier, G. *Macromolecules* **1990**, *23*, 4054.

(6) (a) Ould Kaddour, L.; Strazielle, C. *Polymer* **1987**, *28*, 459. (b) Kent, M. S.; Tirrell, M.; Lodge, T. P. Solution Properties of Polymer Mixtures (preprint).

(7) Aven, M. R.; Cohen, C. *Macromolecules* **1990**, *23*, 476.

(8) Csiba, T.; Jannink, G.; Durand, D.; Papoular, R.; Lapp, A.; Auvray, L.; Boué, F.; Cotton, J. P.; Borsali, R. *J. Phys. (Fr.)* **1991**, *1*, 381.

(9) Borsali, R.; Duval, M.; Benmouna, M. *Macromolecules* **1989**, *22*, 816.

(10) Daivis, P. J.; Pinder, D. N.; Callaghan, P. T. *Macromolecules* **1992**, *25*, 170.

(11) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(12) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev.* **1991**, *B21*, 3976.

(13) (a) Schäfer, L.; Kappeler, Ch. *J. Phys.* **1985**, *46*, 1853. (b) Kappeler, Ch.; Schäfer, L.; Fukuda, T. *Macromolecules* **1991**, *24*, 2715.

(14) (a) Vilgis, T. A. *J. Phys. II (Fr.)* **1992**, *2*, 581. (b) Brereton, M. G.; Vilgis, T. A. *J. Phys. I (Fr.)* **1992**, *2*, 581.

(15) (a) Edwards, S. F.; Vilgis, T. A. *Rep. Prog. Phys.* **1988**, *51*, 243. (b) Vilgis, T. A. *Prog. Colloid Polym. Sci.*, in press. Vilgis, T. A. in *Synthesis, Characterization, and Theory of Polymeric Networks and Gels*; Aharoni, S. M., Ed.; Plenum Press: New York, 1992.

(16) de Gennes, P.-G. *Phys. Lett.* **1979**, *40*, L-69.

(17) (a) Bettachy, A.; Derouiche, A.; Benhamou, M.; Daoud, M. *J. Phys. I (Fr.)* **1991**, *1*, 153. (b) Derouiche, A.; Bettachy, A.; Benhamou, M.; Daoud, M. Kinetics of MST in Cross-Linked Polymer Blends (submitted).

(18) Briber, R. M.; Bauer, B. J. *Macromolecules* **1988**, *21*, 3296.

(19) (a) Flory, P. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1965. (b) Huggins, M. *J. Chem. Phys.* **1941**, *9*, 440.

(20) Vilgis, T. A.; Benmouna, M.; Daoud, M.; Bettachy, A.; Derouiche, A.; Benhamou, M. *Polym. Network Blends* **1993**, *3*, 59.

(21) Khokhlov, A. R.; Nyrkova, I. A. *Macromolecules* **1992**, *25*, 1493.

(22) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.

(23) Brereton, M. G.; Vilgis, T. A. *Macromolecules* **1990**, *23*, 2044.

(24) Brereton, M. G.; Vilgis, T. A.; Boue, F. *Macromolecules* **1989**, *22*, 4051.

(25) (a) Cahn, J. W. *Acta Metall.* **1961**, *9*, 796. (b) Cook, H. E. *Acta Metall.* **1970**, *18*, 297. (c) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.

(26) Vilgis, T. A.; Boue, F. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 2291.