Phase diagram for irregular and non-symmetric cross-linked polymer blends

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Abstract

We consider a blend made of two types of polymers, *A* and *B*, of different chemical nature. At high temperature, the homogeneous mixture is cross-linked. As the temperature is lowered, the two species try to segregate but are kept together by the cross-links. We show that for inhomogeneous, non-regular and non-permanent cross-links, there is a complete segregation at low temperatures, if the system is just weakly cross-linked, and partial segregation otherwise. We also demonstrate that there is no phase transition between the homogeneous phase and the microphase for non-symmetric systems. Our analysis is checked with the experiment. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The phase separation of polymer blends is an interesting problem for practical [1,2] and fundamental reasons [3–7]. Polymers are present in many materials and the understanding of their behavior under changes in temperature, pressure or magnetic field becomes quite important. An interesting case is the mixture of two types of polymers, *A* and *B*, forming a gel. Usually, chemically different species are not compatible in the molten state and, consequently, at low temperature this system segregates in two regions, one rich in *A* and another rich in *B*. This actually happens for some polymer mixtures where the chemical groups forming one polymer do not react with the compounds forming the monomers of the other. However, for most mixtures this is not the case. If the two types of polymers are brought into contact at high temperatures where the entropic free energy guarantee their coexistence, the

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monomers of polymer A react with the monomers of B forming cross-links [1,2]. When this system is cooled, a competition between the natural tendency for phase separation and the elasticity of the network that resists this separation is established. As a result of this competition, there is a formation of microdomains alternatively rich in A and in B, which is called a microphase [4]. The case of a regular and strongly cross-linked mixture of two species of polymers, A and B, where the polymers are considered to be symmetric and with the same degree of polymerization, N (the number of monomers in each chain), was studied by de Gennes [4]. He found that the size of each domain is given by $\xi \propto a\sqrt{n}$ where n is the number of monomers between two successive cross-links and where a is the size of each monomer. In his approach, the position of each cross-link does not fluctuate in space. Besides, since they were homogeneously distributed, n is fixed for the whole gel. From his analysis, one obtains that the transition between the homogeneous phase and the microphase occurs at a critical temperature given by $T_c = T_0/(1 + \sqrt{6}N/n)$ that is lower than the temperature T_0 where complete segregation would have taken place [3,4]. For weakly cross-linked mixtures, the trapped entanglements have to be taken into account [5]. When the number of monomers between two successive cross-links becomes greater than the number of monomers between two successive entanglements, n_e, it is the repetition mechanism that leads to the critical behavior and, consequently, the size of the microphase is given by $\xi \propto a\sqrt{n_e}$ [5].

This is the scenario for the phase behavior of these mixtures when the cross-links are *permanent*, *regularly distributed* and *fixed* in space. In this paper, we will consider a mixture of *two chemically different* polymers, A and B, *not compatible* in the molten state and forming *non-permanent*, *not regularly distributed* and *mobile* cross-links. The chemical differences between monomers A and B means that regions rich in A and regions rich in B are not symmetric and that the two species exhibit different chemical potentials. In usual critical systems, this does not significantly change the phase diagram. However, in this particular case, it leads to the formation of two distinct microphases and to the absence of a phase transition between the homogeneous and the microphases. Another effect that we are also taking into account is that the cross-links are not permanent. Physically, this is relevant for interpenetrating gels where the chemical bonds open and reconnect again. In this sense, the cross-links do not differ from the entanglements that control the physics of non-cross-linked mixtures. Indeed the mobility of the cross-links weakens the elasticity of the network and increases the overall tendency for phase-separation. We will also relax the constraint of regularity. A uniform distribution of cross-links is a good approximation just for very strong gels, where almost all the monomers are cross-linked [4,5]. In real systems, the cross-links are not uniformly distributed along the gel but according to a distribution that differs from system to system. We will represent these inhomogeneities in the cross-links using a Poisson distribution. In the next section, we obtain the phase diagram associated with our model (that represents a generalization of de Gennes's approach).

2. Phase diagram

In order to investigate the melt of a non-compatible and *non-cross-linked* mixture of polymers A and B, one can use the Landau–Ginsburg–Wilson–de Gennes Hamiltonian that contains the entropic free energy associated with the mixing of the two species and a term related to the repulsion between the two types of polymers [3,4,8–10]

$$\beta H_0 = \int d^3r \left\{ a^2 \frac{(\nabla \phi(\mathbf{r}))^2}{48} + \frac{t}{2} \phi(\mathbf{r})^2 + u\phi(\mathbf{r})^4 - h(\mathbf{r})\phi(\mathbf{r}) \right\}, \tag{1}$$

where a is the size of one monomer. In the network, the average concentrations of the two species, $\langle \phi_A(\mathbf{r}) \rangle = 0.5 + \langle l(\mathbf{r}) \rangle$ and $\langle \phi_B(\mathbf{r}) \rangle = 0.5 - \langle l(\mathbf{r}) \rangle$ are fixed but can have local fluctuations associated with $\phi(\mathbf{r})$ by

$$\phi_A(\mathbf{r}) = \tfrac{1}{2}(1 + l(\mathbf{r}) + \phi(\mathbf{r})) \tag{2}$$

and

$$\phi_B(\mathbf{r}) = \tfrac{1}{2}(1 - l(\mathbf{r}) - \phi(\mathbf{r})). \tag{3}$$

For a symmetric medium, $l(\mathbf{r}) = 0$, the difference between the chemical potentials of the two species also vanishes and, since the linear term in Eq. (1) does depend on $l(\mathbf{r})$ and on the chemical potentials, $h(\mathbf{r}) = 0$. In this case, the phase diagram exhibits a high temperature disordered phase where $\phi(\mathbf{r}) = 0$, which means that the two species are mixed at a low-temperature ordered phase, where $\phi(\mathbf{r}) \neq 0$, which means that the two species are separated. We are going to consider a non-symmetric medium for which $\langle l(\mathbf{r}) \rangle \neq 0$ and where the two chemical potentials differ and so $h(\mathbf{r}) \neq 0$.

Despite the chemical differences between the two species, we allow the A and B polymers to make cross-links. To account for the elastic forces due to the cross-links, besides the terms in Eq. (1), one has to introduce one new term in Eq. (1). For finding this contribution, we will use the electrostatic description proposed by de Gennes [4] that goes as follows. In a dielectric the negative and positive charges are tied together but can be displaced. This leads to the appearance of a polarization. Similarly, in polymer mixtures, the monomers A and B are linked but when they are not fixed, a small displacement of their center of masses leads to an elastic "polarization" given by

$$\mathbf{P} = \frac{1}{V} \left(\sum_{i \in A} \mathbf{r}_i - \sum_{j \in j} \mathbf{r}_j \right), \tag{4}$$

where $\mathbf{r}_i$ is the position of the ith monomer at a polymer of type A, $\mathbf{r}_j$ is the position of the jth monomer of type B, and V is the total volume of the system. As in the electrostatic case, polarization and charge are not independent quantities. Then elasticity and volume fraction of each species are also related by

$$\nabla \cdot \mathbf{P} = \phi(\mathbf{r}) + l(\mathbf{r}). \tag{5}$$

Now, using the above description, one has to add to the Hamiltonian Eq. (1) an elastic contribution associated with the cross-links. For simplicity, we assume that this term has a quadratic form that resembles the energy of a spring system, namely,

$$\beta H_p = \int d^3r \frac{C(r)P(r)^2}{2} ,$$

(6)

where here $C(r)$ is the internal rigidity. Within de Gennes approach, this quantity is a constant and given by $C = 36/(na^2)$. In our model, however, the cross-links are not homogeneous. Inhomogeneities in the cross-links can be taken into account by assuming that the elastic constant is a function of the position [8,9], given by

$$C(r) = C_0 \sum_{r_i} \delta(r - r_i),$$

(7)

where the vectors $\{r_i\}$ correspond to coordinates of N_c particles randomly distributed in the volume V. These N_c particles are actually the number of cross-links that are so far distributed according to a Poisson distribution characterized by

$$\langle C(r_1)C(r_2) \rangle = C_0 \langle C(r_1) . \rangle \delta(r_1 - r_2).$$

(8)

Since the cross-links can open and close, the disorder is assumed to be annealed. Consequently, the resulting effective Hamiltonian $\beta H_{eff} \equiv \beta H_0 + \langle \beta H_p \rangle$ is given by

$$\beta H_{eff} = \beta H_0 + g^{-1} \int d^3r [1 - e^{C_0 P(r)^2/2}],$$

(9)

where $g^{-1} = N_c/V$. Then, one has to use the constraint, Eq. (5), in order to eliminate P from the above Hamiltonian. Since $l(r)$ is assumed to be small, its contribution in Eq. (5) just leads to a shift in the linear term h_q in the expression for H_{eff}. Then, the thermodynamic behavior of the system is all contained in the Helmoltz free energy, $\beta F_{eff} = -\ln Z_{eff}$, where Z_{eff} is the partition function associated with the effective Hamiltonian H_{eff}. The expression for F_{eff} can be evaluated at the mean-field level by taking the saddle-point approximation of the integral related to the partition function. This approximation leads to an effective free energy given by

$$\beta F_{eff} = \frac{1}{2} \left[t + \frac{(q_c a)^2}{24} \right] \psi_{q_c}\psi_{-q_c} + u\psi_{q_c}^2\psi_{-q_c}^2 - h_{-q_c}\psi_{q_c} + g[1 - e^{-cg\psi_{q_c}\psi_{-q_c}/(2q_c^2)}],$$

(10)

where we have Fourier transformed Z_{eff}. The expressions for ψ_{q_c} and q_c are given by the saddle-point equations

$$\left. \frac{\partial \beta H_{eff}}{\partial \phi(q)} \right|_{\phi_q = \psi_{q_c}, q = q_c} = \left[t + \frac{(q_c a)^2}{24} \right] \psi_{-q_c} + 4u\psi_{-q_c}^2\psi_{q_c} - h_{-q_c}$$
$$+ \frac{c}{q_c^2}\psi_{-q_c}e^{-cg\psi_{q_c}\psi_{-q_c}/(2q_c^2)},$$

(11)

and

$$\frac{\partial \beta H_{eff}}{\partial q}\bigg|_{\phi_q = \psi_{q_c}, q = q_c} = a^2 \frac{q_c}{24}\psi_{q_c}\psi_{-q_c} - \frac{c}{q_c^3}e^{-cg\psi_{q_c}\psi_{-q_c}/(2q_c^2)}, \tag{12}$$

and where $c = g^{-1}C_0$. From the above equations we can see that the system exhibits four possible phases:

(a) *phase* I, a *homogeneous phase* where $\psi_I \to 0$ as $h_{q_c} \to 0$ and where $q_c = q_I \neq 0$;

(b) *phase* II, a *complete segregated phase*, where $\psi_{II} \not\to 0$ as $h_{q_c} \to 0$ and where $q_c = q_{II} = 0$;

(c) *phases* III$_+$ and III$_-$, two microphases where *partial segregation* occurs, where $\psi_{III} \not\to 0$ as $h_{q_c} \to 0$ and where $q_c = q_{III} \neq 0$.

The free energy associated with each one of these phases is given by

$$\beta F_I = \frac{1}{2}\left[t + \frac{(aq_I)^2}{24}\right]\psi_I^2 + u\psi_I^4 + g^{-1}[1 - e^{-[cg\psi_I^2/(2q_I)]}] - h_{-q_I}\psi_I \tag{13}$$

for phase I,

$$\beta F_{II} = \frac{t}{2}\psi_I^2 + \frac{u}{4}\psi_I^4 + g^{-1} \tag{14}$$

for phase II and

$$\beta F_{III} = \frac{1}{2}\left[t + \frac{(aq_{III})^2}{24}\right]\psi_{III}^2 + u\psi_{III}^4 + g^{-1}[1 - e^{-[cg\psi_{III}^2/(2q_{III})]}] - h_{-q_{III}}\psi_{III} \tag{15}$$

for phases III$\pm$. The values of $\psi_I, \psi_{II}, \psi_{III}, q_I,$ and q_{III}, are given by the saddle-point solutions of Eqs. (11) and (12).

Then, by comparing the free energies associated with each one of the phases, we find [10] the phase diagram illustrated in Fig. 1. At high temperatures, only the homogeneous phase is present. For strong gels (low g), as the temperature is decreased, the microphases predicted by de Gennes appear. However, contrary to his analysis, there is *no* transition between phase I and phases III$_+$ or III$_-$. As the temperature is decreased even further, the system segregates completely. The transition between phases III$_\pm$ and II is of first-order. For weak gels, the microphase is not present. Indeed, there is a first-order phase transition between the homogeneous phase, I, and the completely segregated phase, II. In our phase diagram, de Gennes model corresponds to the continuous transition at ($g = 0$, $h = 0$). At the plane $h = 0$, the critical line, λ meets the first-order phase boundaries, $\sigma_\pm$, at the end point e [6,8].

Recently, it was suggested that for any system that has an end point, the phase boundaries near this region should exhibit universal features related to the nonanalytical behavior of the thermodynamic functions near the critical λ-line [11]. We also confirmed this prediction in our model for cross-linked polymer blends [10].
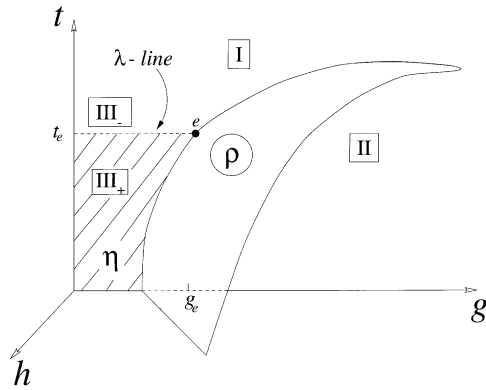
Fig. 1. Phase diagram $t \times g \times h$ for an A–B polymer blend. Phase I is a homogeneous phase, phase II is completely segregated, and phases III$_\pm$ are the microphases. The dashed line, is a continuous λ-line of transitions, the planes ρ and η are first-order phase boundaries and e locates the end point. The first-order lines, $\sigma_\pm$, are the intersection of the surface ρ with the plane $h = 0$.

3. Discussions and conclusions

We have generalized de Gennes–Schulz's model [4,8] for microphase separation in cross-linked polymer mixtures by taking into account the asymmetry between the two species of polymers, A and B, and by considering a non-homogeneous distribution of cross-links that are also not fixed in space.

Our main results are summarized in the phase diagram illustrated in Fig. 1. We found that a mixture of two chemically different polymers at high temperatures is in an homogeneous phase. If the system is strongly cross-linked (high values of g), as the temperature is decreased, there is the formation of two possible partial segregated phases or microphases. These phases are characterized by forming small domains rich in one type of polymer, A, followed by domains rich in the other species, B, and vice versa. The symmetry between the two microphases is broken by the difference in chemical potential, for example, or any "field" that would prefer one phase over the other. In this asymmetric case, there is no phase transition between the homogeneous and one of the microphases. If, however, the temperature is decreased even further, one finds a first-order phase transition from partial to complete segregation. On the other hand, if g is large, the polymers are just weakly cross-linked and, as the temperature is decreased, the system segregates in two regions, one rich in A and another rich in B. This transition between the homogeneous phase and the complete segregated phase is of first-order.

The microphases, III$_-$ and III$_+$, are characterized by an average domain size that is proportional to $\xi \propto 1/q_{\text{III}}$. Close to the critical line, the wave vector q_{III} is related to the elastic constant c by $q_{\text{III}} \approx (24c/a^2)^{1/4}$. If the number of monomers between two cross-links is fixed and given by n, one finds that the coefficient of internal rigidity is given by $c = 36/(na)^2$ [4] and, consequently, $q_{\text{III}} = 5.42/(an^{1/2})$. However, if we assume that the number of monomers between two cross-links is not fixed but given by a

distribution of sizes $\{n^{\alpha}\}$, then $q_{III} = 5.42\varrho/a(\langle n\rangle)^{1/2}$ where $\langle n\rangle$ is the average distance between two cross-links and where $\varrho = (\langle n\rangle \langle 1/n\rangle)^{1/4}$ is a parameter that depends on the distribution. Experimental results gives $q_{III} = 2.30/(\langle n\rangle)^{1/2}$ [1], that agrees qualitatively with de Gennes calculation, and is in good agreement with our analysis if the distribution $\{n^{\alpha}\}$ is such that $1/\varrho = 2.36$.

Another interesting result is that for weaker gels the microphase disappears and the phases of the system separate as observed in real systems [1,2].

Acknowledgements

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