Influence of Nanoparticles on Miscibility of Polymer Blends. A Simple Theory

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ABSTRACT: We propose a simple theory describing the influence of nanoparticles on thermodynamics of binary polymer mixture. In particular, we consider the case in which nanoparticles preferentially segregate into one of the polymeric components. Depending on the particle radius R_p and the polymer degree of polymerization N, addition of nanoparticles can either promote or hinder mixing of the polymers. We calculate how the addition of nanoparticles shifts the spinodal of the polymer blend. These results help to improve understanding of recent simulations on the dynamics of polymer/particle mixtures.

Introduction

In recent years, there has been significant interest in the influence of nanoparticles on the behavior of polymeric systems (homopolymers, blends, or block copolymers).[1−20] This interest stems from the fact that nanoparticle addition can dramatically change various properties of the polymer (e.g., mechanical strength, modulus of elasticity, gas permeability, electrical conductivity, magnetic permittivity, etc.). One area which has come under intense scrutiny recently is the role of nanoparticles as potential compatibilizers for mixtures of immiscible polymers. Recent simulations by Ginzburg et al.,[1−3] Zhu and Ma,[4] and Laradji and McNevin[5,6] showed that nanoparticles slow the phase separation between the two polymers even when the particles themselves have a strong preference toward one of the two polymeric components. These results are in qualitative agreement with experiments of Tanaka et al.[7] and more recently Composto et al.,[8] although some uncertainty remains with regard to the specific rate of spinodal decomposition. However, these studies have not addressed the underlying thermodynamics of the system. Experimentally, Lipatov et al.[9−11] studied the influence of silica nanoparticles on the cloud point of the PVA/PMMA mixture. It was shown that the addition of nanoparticles shifted the location of the critical point and generally made the two polymers slightly more compatible. Lipatov et al.[11] postulated that nanoparticles could, under some conditions, play a role of compatibilizer in a binary polymer blend system and formulated a semiphenomenological theory aimed at explaining this phenomenon. However, this theory did not explicitly take into account the particle size or geometry and, in general, had somewhat limited predictive ability. There have been other experimental studies concerning the distribution of nanoparticles (e.g., carbon) in polymer blends,[12−14] but no theoretical analysis of the influence of particles on the phase behavior of the system. To our knowledge, to date there has been no comprehensive thermodynamic theory of polymer blend/nanoparticle mixtures.

It is important to note that thermodynamics of a closely related system, in which nanoparticles are added to the diblock copolymer, has also been studied extensively both theoretically and experimentally. Huh, Ginzburg, and Balazs[15] developed a simple strong-segregation mean-field theory predicting phase diagrams in AB-diblocks with nanoparticles preferentially attracted to the A-block. Subsequently, Thompson, Ginzburg, Matsen, and Balazs (TGMB) formulated a combined self-consistent field/density functional theory (SCF−DFT) general approach to describe the thermodynamics of block copolymer/nanoparticle mixtures.[16−17] Although in the original TGMB papers, the model was applied only to the nanoparticle/diblock systems, subsequent papers by Balazs et al.[18−20] significantly increased the applicability of this approach. In principle, one could use the SCF−DFT model to map out phase diagrams for any polymer/nanoparticle systems in a way similar to the use of a “classical” self-consistent field theory to describe phase behavior of any polymer system.[21−22]

Because of the “universality” of the SCF−DFT approach, one could potentially apply it to study thermodynamics of AB-blend/nanoparticle mixtures. However, such investigation would be computationally expensive. To map out the whole phase diagram, it would be necessary to perform a large number of simulations for various values of R_p (particle radius), ψ (particle volume fraction), ϕ (blend composition), and χN (degree of segregation). Thus, it would be useful to develop a simple analytical theory that would at least qualitatively indicate how the nanoparticles would influence the behavior of a polymer blend. Such a theory is formulated in this paper.

Theory

We consider a binary mixture of two homopolymers, A and B, with degrees of polymerization (number of monomer units) N_A and N_B. In the following, it will be assumed that $N_A = N_B = N$, but the theory can be easily applied to the more general case. The monomer radius is r_0 (usually $r_0 \sim 0.2-0.5$ nm). Into this system, we add spherical nanoparticles of radius R_p ($> r_0$) and volume $v_p = (4/3)\pi(R_p)^3$. We assume that nanoparticles have van der Waals interactions the same as the A-species (this could be the case, for example, if the nanoparticle surface is covered with short A-type ligands); then the Flory−Huggins interaction parameters are $\chi_{AP} = 0$ and $\chi_{BP} = \chi_{AB} = \chi$. The volume fraction of nanoparticles is denoted ψ. The volume fractions of two polymeric

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components (A and B) are given by $(1 - \psi)\phi$ and $(1 - \psi)(1 - \phi)$, respectively. The free energy per unit volume, $F = (F/k_BTV)$, can be written as

$$F = F_{\text{pol}} + F_{\text{part}} + F_{\text{int}} \tag{1}$$

where the three terms (polymer, particle, and polymer-particle interaction) can be written as

$$F_{\text{pol}} = \frac{(1-\psi)\phi}{N}\ln\left[\frac{(1-\psi)\phi}{N}\right] + \frac{(1-\psi)(1-\phi)}{N}\ln\left[\frac{(1-\psi)(1-\phi)}{N}\right] + \chi(1-\psi)^2\phi(1-\phi) \tag{2a}$$

$$F_{\text{part}} = \frac{\psi}{v_p}\left[\ln \psi + p\left(\frac{R_p}{r_0}\right)\frac{4\psi - 3\psi^2}{(1-\psi)^2}\right] \tag{2b}$$

$$F_{\text{int}} = \frac{\psi}{v_p}(1-\psi)p\left(\frac{R_p}{r_0}\right)\frac{3{R_p}^2}{2N{r_0}^2} + \chi\psi\left[\frac{r_0}{R_p}\right](1-\psi)(1-\phi) \tag{2c}$$

The derivation of the free energy expression of 2a–c has some similarities with earlier work on the nanoparticle/diblock copolymer systems,[15] but it has also some important differences. Let us discuss each term in detail.

The first term in eq 2, F_{pol}, given by eq 2a, is simply the Flory–Huggins[23–24] mixing free energy for a binary polymer blend (with appropriate corrections due to the fact that some volume in the system is occupied by nonpolymeric species).

The second term in eq 2, F_{part}, given by eq 2b, describes the contribution of the particles themselves and consists of the ideal and nonideal "entropic free energy" of hard spheres. We describe the nonideal contribution using the Carnahan–Starling[25] equation of state which is known to approximate the free energy of amorphous hard-sphere system with a very good accuracy. Note the appearance of the "interpolating factor" $p(R_p/r_0)$ in front of the nonideal term. In the limit $R_p/r_0 \to 1$, the "nanoparticles" would be equivalent to the A-monomers (or selective solvent molecules), and the nonideal term should not be present (since we do not introduce them for the polymeric components, using the incompressibility constraint instead). Thus, $p(x) \to 0$ as $x \to 1$, and $p(x) \to 1$ for $x \gg 1$. We use function $p(x) = \max(\tanh(x - 1),0)$ but any other reasonable choice of the interpolating function should yield results similar to those obtained here.[26]

The third term in eq 2, F_{int}, describes the interaction between particles and polymers. This interaction consists of two contributions—entropic and enthalpic. Entropic contribution is given by the first term in the rhs of eq 2c and is due to the fact that the particles cause stretching of polymer chains in their vicinity. The derivation of this term is similar to one in ref 15. On average, each polymer chain acquires stretching free energy of $h \sim 3R_p^2/2Nr_0^2$ every time it encounters a particle. Summing up these contributions in a unit volume, we obtain $\sim n_{\text{chains}}h\ [n_{\text{part}}/n_{\text{chains}}] \sim n_{\text{part}}\ h \sim (\psi/v_p)h$. Note that the entropic contribution is insensitive to the nature of the chain (whether it is A-homopolymer or B-homopolymer), it is only dependent on the chain length and the particle size. Note also that h plays a role of "entropic surface tension" for the polymer near the particle surface. Entropic surface tension increases as the particle radius (or the ratio of $R_p/[r_0N^{1/2}]$, to be more precise) is increased. Enthalpic contribution (second term in the rhs of eq 2c) to the interaction free energy is proportional to the number of contacts between the particle surfaces and the B-monomers. Note that this contribution is proportional to the surface-to-volume ratio of the particles and becomes smaller as one increases the particle radius.

Free energy (eq 2) describes only the homogeneous phase of the system. It neglects the possibility of nanoparticle positional ordering and also disregards potential effects of nanoparticle "crowding" on the polymer-particle interaction terms. Because of this, it is not possible to extend the use of this free energy to high (>0.3–0.4) nanoparticle volume fractions. At the same time, it is clear that elucidation of the full phase diagram of this system would require calculating phase equilibria between low-particle-concentration phases and high-particle-concentration phases. Thus, it would be difficult—if not impossible—to describe analytically the full phase diagram for this system. However, it is quite straightforward to analyze the spinodal curves for this system—and such an analysis could be very illuminating.

Let us recall the criteria of the stability of the homogeneous phase (with respect to phase separation). The spinodal stability of the homogeneous phase means that free energy should be a positive definite quadratic form with respect to any density fluctuations near the uniform state. Thus, in our case, it reduces to the following criteria:

$$\frac{\partial^2 F}{\partial \phi^2} > 0 \tag{3a}$$

$$\frac{\partial^2 F}{\partial \psi^2} > 0 \tag{3b}$$

$$J = \det\left\|\begin{matrix} \dfrac{\partial^2 F}{\partial \phi^2} & \dfrac{\partial^2 F}{\partial \phi \partial \psi} \\ \dfrac{\partial^2 F}{\partial \phi \partial \psi} & \dfrac{\partial^2 F}{\partial \psi^2} \end{matrix}\right\| = \left[\frac{\partial^2 F}{\partial \phi^2}\right]\left[\frac{\partial^2 F}{\partial \psi^2}\right] - \left[\frac{\partial^2 F}{\partial \phi \partial \psi}\right]^2 > 0 \tag{3c}$$

For any given ϕ and ψ, system is homogeneous at low enough χN (high temperatures), and goes through the spinodal once any of the three conditions (eq 3a, 3b, or 3c) is no longer fulfilled. For all χN below the spinodal, the homogeneous phase is stable with respect to the long-wavelength density fluctuations; for all χN above the spinodal, it is unstable with respect to such fluctuations and undergoes the so-called spinodal decomposition.[26] In the following section, we will describe how the addition of particles influences the location of the spinodal compared to the pure polymer blend.

Results and Discussion

In our calculations, we vary two parameters: polymer chain length N and particle radius R_p. (Below, we will take r_0 to be the unit of length and express R_p in units of r_0). For each pair (N, R_p) we calculate spinodal curves as a function of ϕ while varying the particle volume fraction ψ from 0 to 0.2. The particles influence the shape and location of the spinodal curve in several ways:

I. As the particle concentration increases, the mixture becomes more "A-like", and therefore, the spinodal curve is moving left (toward lower ϕ).

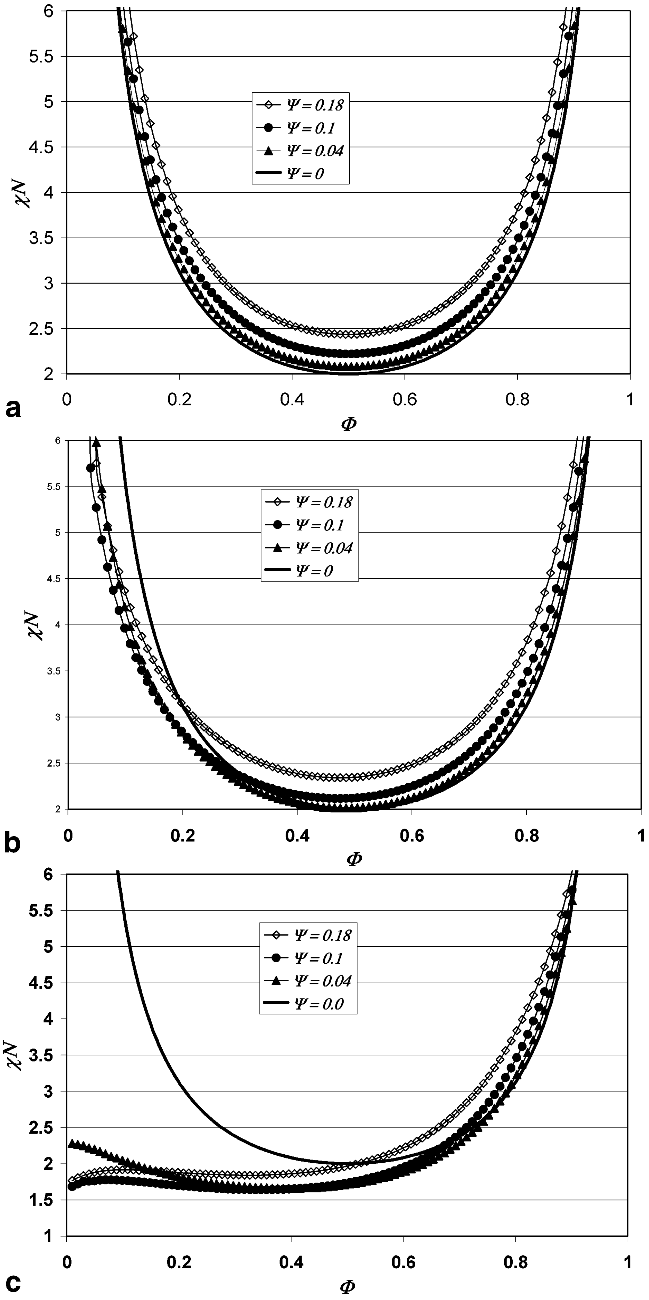

Figure 1. Calculated spinodals for polymer/nanoparticle mixture with $N_A = N_B = N = 100$. Particle radius R_p (in lattice units r_0): (a) $R_p = 1$; (b) $R_p = 5$; (c) $R_p = 10$. Here, ϕ is the volume fraction of A-homopolymer in the blend, and ψ is the volume fraction of nanoparticles.

II. If nanoparticles are more compatible with B than the A-polymers, the spinodal curve moves up upon the increase in the particle concentration; if nanoparticles are less compatible with B than the A-polymers, the spinodal curve moves down.

III. Since addition of nanoparticles leads to the overall decrease of the total amount of B-polymers in the systems, spinodal curve moves slightly up independently of all other factors.

Let us now observe how all these factors influence the spinodal curves for various systems. In Figure 1, we plot spinodals for mixtures with $N = 100$ for $R_p = 1$ (a), 5 (b), and 10 (c) lattice units. It can be clearly seen that for the smallest particles (Figure 1a), the curves move up upon increase in particle concentration, indicating that particles act as compatibilizers. As R_p is increased, however, the miscibility between the particles and the polymers begins to worsen. Figure 1b illustrates that for the "intermediate" particle size ($R_p = 5$), the effective "upward" shift in the spinodal becomes less pronounced, and the actual shape of spinodal curve becomes influenced by all three factors discussed above. Finally, once $R_p \sim N^{1/2}$, entropic surface tension for particles in the polymer melt becomes quite substantial, depressing the stability of the homogeneous phase with respect to the nanoparticle density fluctuations. Thus, at larger particle radii, the spinodal is determined not by the polymer−polymer phase separation, but by the polymer−nanoparticle phase separation. This can be seen indeed in Figure 1c, where the spinodal curves for the polymer−nanoparticle blends have *lower* critical points than that of a pure polymer blend. Further increase in R_p would depress the critical point toward the $\chi = 0$ line and even to the negative χ region. Indeed, for large R_p, the main mode for the phase separation would be the segregation between particle-rich and polymer-rich regions, typical for colloid−polymer mixtures.

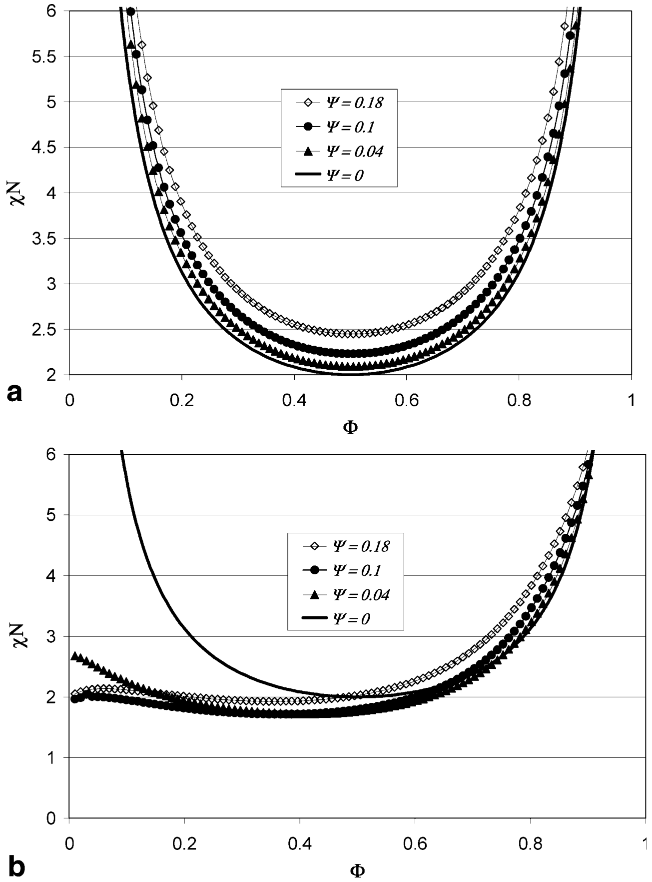

Figure 2. Calculated spinodals for polymer/nanoparticle mixture with $N_A = N_B = N = 1000$. Particle radius R_p (in lattice units r_0): (a) $R_p = 10$; (b) $R_p = 20$. Here, ϕ is the volume fraction of A-homopolymer in the blend, and ψ is the volume fraction of nanoparticles.

As one increases polymer chain length N, the condition $R_p \sim N^{1/2}$ means that the larger particles can still exert compatibilizing effect on polymer mixtures. This is illustrated in Figure 2, where polymer chain length N is set to 1000. For $R_p = 10$ (Figure 2a), addition of nanoparticles always improves miscibility compared to pure polymers. Once again, however, at very large R_p, macrophase separation between the particles and the

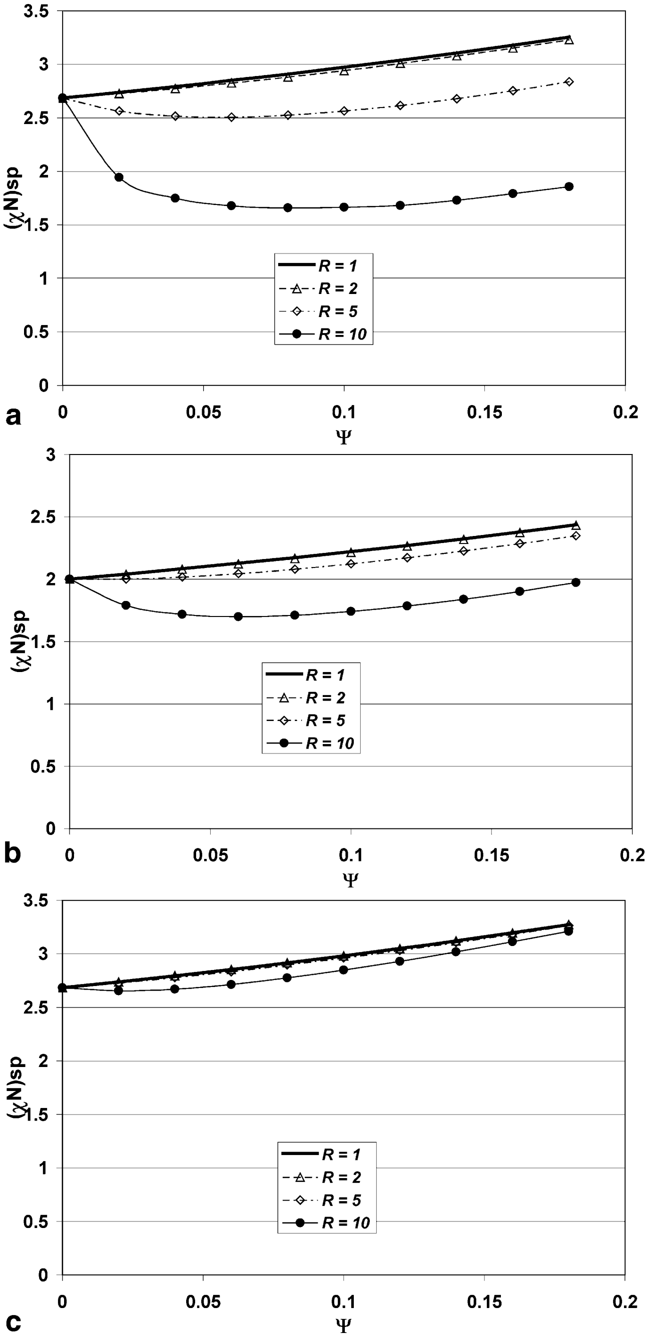

Figure 3. Dependence of the onset of spinodal decomposition $(\chi N)_{sp}$ on the nanoparticle volume fraction ψ for given $\phi = 0.25$ (a), 0.50 (b), and 0.75 (c). Homopolymer degree of polymerization $N_A = N_B = N = 100$.

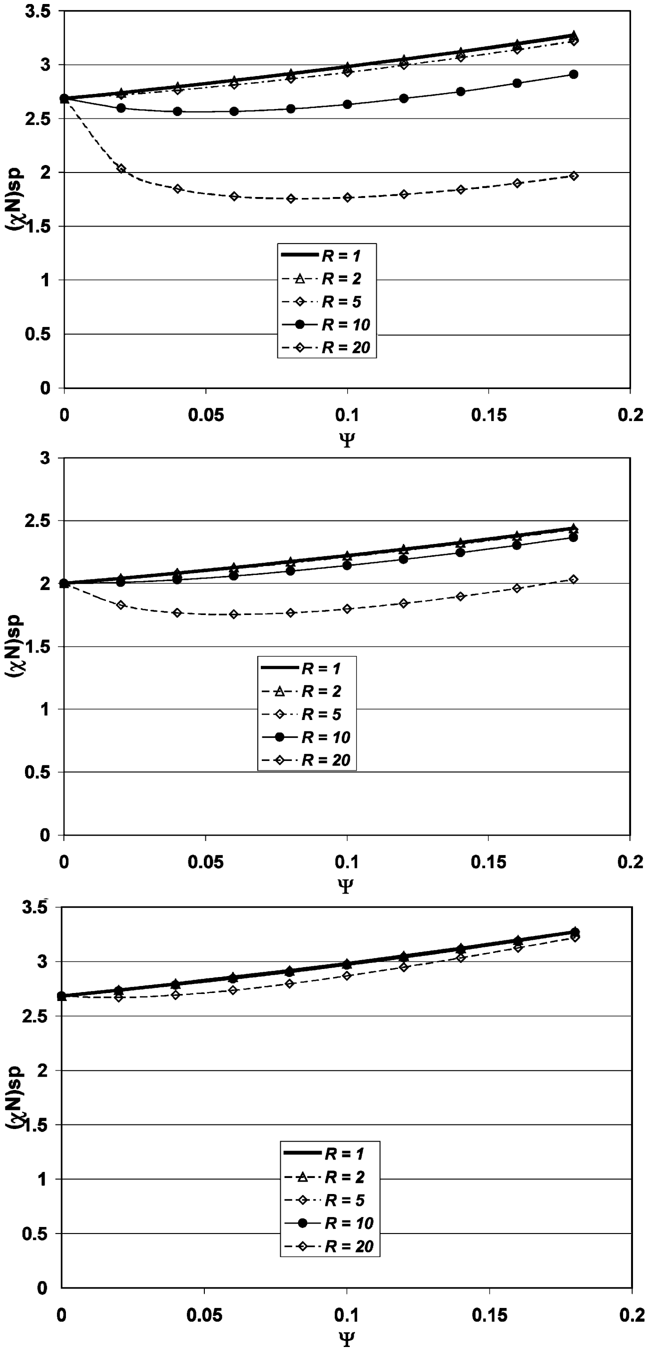

Figure 4. Same as Figure 3, but for $N_A = N_B = N = 1000$.

polymers sets in and reverses the trend. Thus, for $R_p = 20$ (Figure 2b), we observe the decrease in the critical point upon nanoparticle addition (compare to Figure 1c).

We can also look at the results from a different perspective by plotting the dependence of the spinodal on the nanoparticle volume fraction ψ for given polymer composition ϕ. In Figure 3, we plot this dependence for $N = 100$ and $\phi = 0.25$ (a), 0.5 (b), and 0.75 (c). Similar plots in Figure 4 are depicted for $N = 1000$. Interestingly enough, these results have qualitative similarity to the analysis of Semenov et al.[28] for the behavior of the order−disorder transition (ODT) in block copolymer/homopolymer mixtures as a function of homopolymer volume fraction and degree of polymerization. This similarity is well-justified since ODT in block copolymers and spinodal transition in polymer blends are closely related, and the "additive" (homopolymer or nanoparticle) modifies the mixture composition in the same way in both cases. Another system where a similar effect is observed is that of weakly charged polyelectrolyte blends.[29] In those blends, translational entropy of counterions leads to improved compatibility compared to uncharged polymers with the same values of χ and N.

Detailed examination of Figures 3 and 4 shows that the dependence of $(\chi N)_{sp}$ on ψ strongly depends on whether the polymer mixture is symmetric (b) or nanoparticles prefer the minority component (a) or the majority component (c). In case a (nanoparticles prefer the minority component), the addition of nanoparticles makes the mixture more symmetric; such a change would normally lead to the decrease in $(\chi N)_{sp}$. This decrease, for small nanoparticles, is counterbalanced by the increase in $(\chi N)_{sp}$ due to the factors discussed earlier. However, once $R_p \sim N^{1/2}$, the particle/polymer miscibility worsens, and the overall trend is dominated by the decrease in $(\chi N)_{sp}$. In case b, and especially in case c, the addition of nanoparticles drives the system away from symmetric composition, thereby shifting $(\chi N)_{sp}$ upward. For the 50−50 mixture (b), this shift is relatively small, but for the 75−25 mixture (c) it is dominant. Thus, we can see that while for the 50−50 mixture with $N = 1000$ (Figure 4b), the addition of $R_p = 20$ nanoparticles leads to the decrease in $(\chi N)_{sp}$, for the 75−25 mixture the addition of the same nanoparticles have compatibilizing effect (i.e., $(\chi N)_{sp}$ increases monotonically with increasing ψ).

The above calculations show that nanoparticles can indeed act as compatibilizers in the binary polymer melts provided that the following points are true: (i) nanoparticle radius $R_p \leq R_g$(A,B) (polymer radius of gyration); (ii) polymers are relatively close to the spinodal point (quench is shallow, not deep). In particular, we find that

$$\frac{(\chi N)_{\rm sp}(\psi)}{(\chi N)_{\rm sp}(0)} \leq \frac{1}{1-\psi} \approx 1 + \psi \tag{4}$$

Assuming that $\chi \sim B/T$, we can recast eq 4 to describe the effective decrease in the spinodal temperature for a binary blend upon addition of nanoparticles:

$$\left[\frac{\Delta T}{T}\right]_{\rm sp} = -\left[\frac{\Delta(\chi N)}{\chi N}\right]_{\rm sp} \approx -\psi \tag{5}$$

From eq 5, it follows that for a binary blend with $T_{cr} = 400$ K, addition of 10 vol % nanoparticles can reduce the critical temperature up to 40 deg. This reduction can be quite important in industrial polymer processing. However, to achieve this reduction, one also needs to have sufficiently small nanoparticles. For example, if we take $r_0 = 0.5$ nm and $N = 1000$, then nanoparticle radius should be roughly $r_0 N^{1/2} \sim 15$ nm.

While it is difficult at this time to make quantitative comparison with experiments (experimental data are scarce, and there is always uncertainty in the determination of interaction parameters and nanoparticle size), we can compare our results qualitatively with recent data on the cloud point of PVA/PMMA blend with and without fumed silica.[11] Such a comparison is shown in Figure 5, where both experimental cloud point curves and calculated spinodals are plotted. Model parameters used in the calculation are described in the figure caption. Note that our goal is not to describe the phase behavior quantitatively (as we do not know precisely all the details about the experimental system) but rather to show that the model successfully reproduces main features of the phase diagram in the presence of the fillers. At low PMMA content, particles have adverse effect on polymer miscibility, but for high PMMA content, they can actually help to compatibilize the two polymers, shifting the spinodal toward higher temperatures (or higher χN since the PVA/PMMA system has the LCST-type behavior). Perhaps if one knew exactly the molecular weight ratio of the two polymers and the effective χ-parameters of the silica with both polymers, the agreement between theory and experiment could have been further improved.

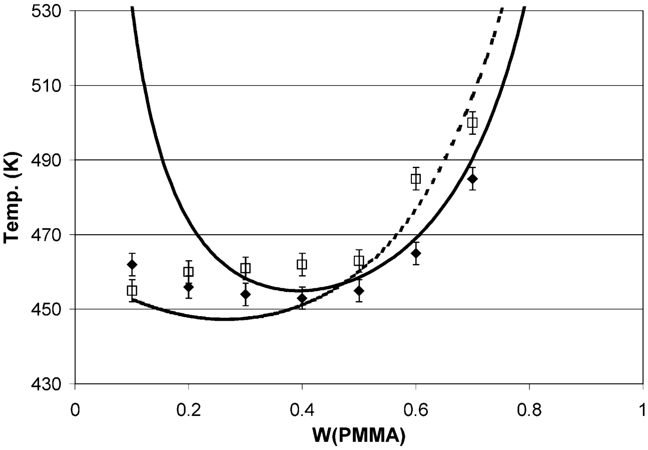

Figure 5. Qualitative comparison between the theory and the experimental phase diagram (cloud points) for the PVA/PMMA polymer blend without fillers (filled diamonds) and with 10 wt % fumed silica (open squares)[11]. The two curves correspond to the spinodals calculated using eqs 1−6 of this paper. We assumed that both PVA and PMMA had degrees of polymerization $N = 1000$, and that $\chi N = a + bT$, with $a = -10.0$, $b = 0.026374$. Finally, we assumed that $\rho_{PMMA}/\rho_{PVA} = 0.65$. For the filled system, we took nanoparticle loading of 14 vol %, with the dimensionless particle radius $R = 20$ (corresponding to the "real" particle radius of ∼ 10 nm).

Finally, one can now comment on the relationship between thermodynamics and dynamics of phase separation in such polymer/nanoparticle mixtures. Previous modeling studies[1−3,5,6] described two distinctly different scenarios of phase separation in the AB binary blend quenched into spinodal region when A-type nanoparticles are added. In one case (denoted "weak coupling case[3]), nanoparticles move at random throughout the system. Such motion disrupts domain growth that ordinarily would have led to the macrophase separation between A-rich and B-rich regions. Instead, effective domain size saturates at some finite value which depends on the particle concentration and particle diffusion constant.[2] In the second scenario (denoted "strong coupling case"[3]), nanoparticles are driven into the bulk of A-rich regions, and domain growth is slowed but not arrested.[6] The actual regions of applicability—or boundaries between—these two scenarios have not been well understood up to date.

On the basis of our analysis, it seems that the "weak coupling" scenario is appropriate in the region between the spinodal point for a pure AB-blend and the spinodal point for a polymer−nanoparticle mixture, *provided that nanoparticles are small enough so that the spinodal χN is increased by their presence.* Under these conditions, addition of nanoparticles changes the system morphology from macrophase-separated (although the two phases are not very dissimilar since the system is close to the critical point) to the homogeneous one. The mechanism of this change is indeed similar to that described by Ginzburg et al.,[1−3] i.e., that nanoparticles "stir" the system and disrupt any attempts at domain formation and growth. For all other situations—especially in all cases of deep quench—the "strong coupling" scenario is appropriate (as suggested by Laradji[6]). In those cases, particles are unable to stir the system enough to prevent domain growth and/or are strongly driven into the bulk of A-rich domains, away from the interfaces. It is most likely that in such systems, particles do not influence the domain growth exponent ($n = 1/3$ for pure diffusive case). Further systematic exploration of the dynamics of polymer blend/nanoparticle systems remains a challenge for the future research.

Conclusions

We developed a simple model to study thermodynamics of polymer/nanoparticle mixtures. For the mixture of A−B binary polymer blend with spherical nanoparticles, the free energy is written by combining Flory−Huggins free energy of mixing for the polymers with Carnahan−Starling equation of state for the nanoparticles. While the exploration of the full phase diagram is very complicated and is beyond the scope of the current work, it is possible to study the influence of nanoparticles on the stability of the homogeneous uniform phase. We calculate the shift in the spinodal as a function of the mixture composition, nanoparticle radius, and homopolymer degree of polymerization for the case in which particles are attracted to one of the two components (e.g., when nanoparticles are coated by A-type ligands).

It is found that, as expected, when nanoparticle radius is smaller than polymer radius of gyration, the addition of nanoparticles increases the critical value of χN and stabilizes the homogeneous phase. The reason for that is that the replacement of some A-homopolymers with nanoparticles reduces the number of unfavorable AB-interactions and therefore decreases the enthalpic portion of the free energy. In addition, the translational entropy of such small particles is larger than that of a polymer. The effect, in general, is similar to the addition of a short A-homopolymer or even A-monomer—the spinodal shifts toward higher χN as the concentration of the additive is increased.

Once particle radius becomes comparable to the polymer R_g, the particles begin to influence the configurational entropy of the chains. This entropic penalty can be thought of as an "entropic surface tension" between particles and polymers (this is in addition to the enthalpic surface tension existing between particles and the B-homopolymer). As particle radius is increased, the role of entropic surface tension becomes stronger. Finally, for large particle radii ($R_p \gg R_g$), the particle-rich phase would segregate from the polymer at very low particle concentrations regardless of the polymer composition. Since we assumed that the particle is "A-like", this shift would manifest itself in the effective downward shift in the spinodal toward lower χN. Now, however, the phase separation would be not between the A-rich (homopolymer + nanoparticles) and B-rich phases, but likely between three phases − particle-rich, A-homopolymer-rich, and B-homopolymer-rich.

This thermodynamic analysis helps us to clarify earlier simulations of dynamics of phase separation in binary polymer blends with nanoparticles. If small nanoparticles are added to the binary AB-blend weakly quenched into spinodal region, the addition of nanoparticles can block domain growth and lead to the saturation of domain size (so-called "weak coupling model"). On the other hand, for the cases of large nanoparticles and/or strong quenches, nanoparticles cannot block domain growth, and the dynamics of phase separation is likely to remain generally the same as for the pure polymer system (so-called "strong coupling model"). Better understanding of these boundaries remains a challenge for the future.

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(26) Due to the scaling nature of eq 2c and specifically, the function $p(R_p/r_0)$, the agreement between theory and experiment could worsen somewhat in the "intermediate" region ($R_p/r_0 \geq 1$). The "steric penalty" term, which depends on $p(x)$, makes particles and polymer less compatible and promotes phase separation between them. We note, however, that for long-chain polymers ($N \gg 1$), when the steric term becomes sufficiently large ($R_p \geq r_0 N^{1/2}$), the scaling function $p(R_p/r_0)$ should be already equal to unity. Thus, we expect that in the limit of long chains, the actual choice of $p(R_p/r_0)$ (subject to constraints discussed in the text) has very little influence on the final phase diagrams.
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