

## Effect of added copolymer on the critical properties of polymer mixtures

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Monte Carlo simulation and finite-size analysis are used to determine the critical properties of a binary homopolymer blend and of a polymer blend that has been compatibilized with a random copolymer. Determination of  $\nu$ , the critical exponent for the correlation length, for the mixture of two homopolymers shows that the binary blend exhibits properties that are consistent with Ising behavior ( $\nu=0.63$ ). Similar results for the compatibilized blend show that the added copolymer acts very much like an impurity; lowering the mixing transition temperature and increasing the value of  $\nu$  to a value that is in qualitative agreement with Fisher renormalization ( $\nu=0.69$ ). These results are important as copolymers are often added to polymer blends to act as compatibilizers. These results, therefore, show that the analysis of the phase behavior of these mixtures must be analyzed with the understanding that its critical exponents differ from those of a binary polymer mixture. [S1063-651X(99)19310-3]

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### INTRODUCTION

The critical behavior and classification of the universality class of polymer mixtures has been an area of much attention recently [1–17]. This area is of interest from a fundamental point of view, but also has implications in the commercial use of polymer mixtures. It is well known that mixtures of two polymers obey the mean field approximation over a wide range of temperatures and concentrations [18]. However, it is expected [1,2], and has been confirmed experimentally [3,4,7–12], that near the critical point, binary polymer mixtures will crossover from mean field to three-dimensional (3D) Ising behavior. This crossover can result in an inaccurate determination of the critical temperature by extrapolation procedures assuming mean field behavior. The critical behavior of ternary polymer mixtures containing a copolymer and two homopolymers has been less studied. It is expected from Fisher renormalization [19–25] that a binary mixture that is diluted (and thus a ternary mixture) will have slightly higher critical exponents (for example,  $\nu' = 8/7\nu$ , where  $\nu'$  is the renormalized critical exponent for the correlation length) than the binary mixture. Fisher renormalization has been *qualitatively* verified for small molecule ternary mixtures [21–24] and polymer blends that have been diluted by a solvent [11,15,16]. It is not clear that a diluent that is polymeric in nature and consists of identical monomers as the homopolymers will alter the critical behavior of a “diluted” polymer blend in a similar way. This work seeks to answer that question and provide fundamental information on the critical behavior of a ternary polymer blend containing two homopolymers and a statistically random copolymer.

Monte Carlo methods have proven useful in determining the order and critical behavior of pure systems and mixtures, including polymer blends [26–31]. For example, Sariban and

Binder [26] have utilized Monte Carlo simulation and finite-size scaling techniques to obtain the critical exponents and critical amplitudes of the phase separation process of a lattice model and compared it to the Flory-Huggins theory. Their results confirm that a Monte Carlo lattice model exhibits critical exponents that are the same as those for the three-dimensional Ising model. They were not able to observe the expected transition to mean field critical behavior, which they attributed to the small chain lengths that were utilized in their study. These results do show, however, that a Monte Carlo model of a binary polymer blend can be expected to exhibit Ising behavior, much like a real system near the critical point and this can be verified using finite-size scaling techniques.

Industry has often utilized mixing of two (or more) polymers to develop new materials with targeted properties. By combining two polymers with diverse properties, it may be possible to create a new material that retains physical characteristics of both polymers. However, it is also well known that two long chain molecules will rarely mix on a thermodynamic level due to their low entropy of mixing. The resultant two-phase structure will have inferior properties to the initial components, primarily due to the presence of a sharp biphasic interface that does not provide entanglement between the polymers in the separate phases. This lack of entanglement across the interface results in poor transfer of stress, which in turn degrades the macroscopic properties of the mixture. Due to the importance of the presence of a biphasic interface on the ultimate properties of a polymer blend, the ability to improve and control that interface has been extensively examined [32–73]. In particular, the effect of adding a copolymer to act as an interfacial modifier has received abundant attention. Much of this work has centered on the ability of a copolymer to strengthen the biphasic interface, lower interfacial tension (to create a finer dispersion), and inhibit coalescence during processing. Each of these mechanisms apparently contributes to the improvement

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of macroscopic properties of biphasic polymer blends upon addition of a copolymer and the importance of each has been the subject of some debate in the literature.

Therefore, the effect of an added copolymer on the properties of a polymer mixture is of current interest. This paper reports results of an investigation which utilize finite-size analysis and Monte Carlo simulation to determine the critical exponents of the phase separation transition that occurs in binary (two homopolymers) and ternary (two homopolymers and a statistically random copolymer) polymer mixtures on a cubic lattice. These results will determine how the addition of the copolymer alters the critical exponents of the phase separation process. This, in turn, provides fundamental information that can be utilized in the analysis of the phase separation of a polymer blend that has been compatibilized with a copolymer.

### MODEL AND SIMULATION METHOD

The model system consists of  $N_p$  chains of length  $N = 10$  confined to a cubic lattice. This length was chosen to maximize computational efficiency, while still providing behavior that has been shown in previous simulations to emulate polymers. To simulate an infinite set of chains, the system is approximated as a set of infinitely many identical cells of length  $L$  with periodic boundary conditions in all three orthogonal directions ( $x, y, z$ ). In this study, the only interaction energy is a nearest neighbor monomer-monomer interaction  $\varepsilon_{A-B}$ . This energy is positive if two neighboring monomers are of different type ( $A-B$ ) and is zero otherwise. In other words,  $A-A$ ,  $B-B$ ,  $A$ -void, or  $B$ -void arrangements have a zero energy while  $A-B$  alignments contribute a positive energy.  $\varepsilon_{A-B}$  applies to any two adjacent monomers, whether a bond connects them or not. Steric interactions are included as excluded volume; simultaneous occupation of a given lattice site by more than one monomer is prohibited. The density of the system is held constant for all lattice sizes and is calculated as the fraction of occupied lattice sites,  $\rho = N_p N / L^3$ .  $N_p$  and  $N$  are defined as above and  $L$  is the size of the cubic lattice. In the present study,  $N_p$  and  $L$  are varied such that  $\rho = 81.25 \pm 0.04\%$  and  $L$  ranges from 16 to 30.

Adding the polymers to the lattice in a completely ordered state creates the initial configuration. One half of the homopolymers are of type  $A$  and half are type  $B$ . The percent copolymer present ranges from 0 to 10%. The composition of the copolymer is 50%  $A$  and 50%  $B$ . It is interesting that given this model, the number of  $A$  and  $B$  monomers in the system does not change as a copolymer is added, just the way that they are bonded together is altered. The sequence distribution of the copolymer is parametrized by  $P$  [74], defined as the percentage of the neighboring monomers along the copolymer chain which are of the same type. This results in the correlation between  $P$  and the copolymer structure as listed in Table I.

Once the initial configuration is created, applying a modified reptation technique [75] to the chains creates various chain configurations. In this modified reptation technique, a void on the lattice is chosen at random. A direction from that void is then selected randomly. If the end of a chain resides on that lattice point, the polymer chain is reptated into the void and the other end of the chain is vacated. In this way the

TABLE I. Correlation between  $P$  and copolymer sequence distribution.  $N$  denotes molecular weight of the copolymer.

Copolymer sequence distribution	$P$
Block copolymer	$N/(N-1) \approx 1$
Random copolymer	0.5
Alternating copolymer	0

configuration of the polymer chain changes and the void is displaced. The new configuration is accepted according to the Metropolis sampling technique [76]. To ensure there is no bias due to the initially ordered state, the system is equilibrated through 10 000 system configurations before statistics for the system characterization is calculated.

The phase behavior of the mixtures is characterized by the heat capacity,  $C_v$  and the reduced fourth-order cumulant  $U_L$  of the system. The heat capacity is calculated as the fluctuation in the total energy of the system:

$$C_v = [\langle E^2 \rangle - \langle E \rangle^2], \quad (1)$$

where  $\langle \rangle$  denotes the ensemble average.  $E$  is the energy of the system and is equal to the number of neighboring monomers that are of different type. The miscible-immiscible transition temperature is determined as the temperature at which the heat capacity peaks in a plot of heat capacity vs temperature. The reduced fourth-order cumulant of the order parameter is defined as

$$U_L = 1 - \langle M^4 \rangle / (3 \langle M^2 \rangle^2). \quad (2)$$

In this equation,  $M$  is the order parameter, which in a mixture of two types of molecules can be defined as the difference between the percentage of neighboring lattice site pairs that contain the same types of monomers and the percentage of neighboring lattice site pairs that contain different types of monomers.

$$M = \Sigma - \Delta, \quad (3)$$

where  $\Sigma$  is the percentage of neighboring sites on the lattice that contain monomers of the same type and  $\Delta$  is the percentage of neighboring sites on the lattice that contain monomers that are different. Examination of this equation shows that in the phase-separated state, most neighboring monomers will be of the same type,  $\Sigma$  will approach 1 and  $\Delta$  will approach 0. This gives a value of the order parameter approaching 1. In the miscible state, there is equal probability that neighboring sites will hold similar or different monomers, and therefore  $\Sigma \rightarrow 0.5$  and  $\Delta \rightarrow 0.5$ , thus  $M$  goes to zero.

In a small molecule mixture, this order parameter will provide accurate information on the mixing process. However, with polymers, the connectivity of the polymer chain will bias this calculation. For a homopolymer chain, two of the neighboring lattice sites must contain monomers of the same type because they are the next and previous monomers along the chain (except for chain ends). Therefore, to overcome this bias, Eq. (3) is still used, however, the definition of  $\Sigma$  and  $\Delta$  is altered. Rather than utilize the nearest neighbor lattice sites to compare monomer types, the calculation is

based on two lattice sites that are slightly farther apart. The choice of the distance between the two lattice sites is a balance between wanting a larger distance to minimize effects of chain connectivity versus needing a smaller distance to minimize the effect of the biphasic interface on the calculation. Essentially, when the system is phase separated, the biphasic interface in the phase separated system limits  $M$  to values less than 1. Increasing the distance between the compared sites effectively broadens the interface and exacerbates this problem. In this study, it was found that a distance of five lattice sites between compared lattice sites offered a good compromise of these two factors and was thus used in the calculations of the following results.

To minimize statistical deviation, each point in the following figures is an average of at least  $7.5 \times 10^6$  Monte Carlo steps per chain in the vicinity of the phase transition and at least  $2.0 \times 10^6$  Monte Carlo steps per chain far from the phase transition. This simulation was completed on many computers including a DEC Alpha 400/266 in the Chemistry Department at the University of Tennessee, two Silicon Graphics Indigo2 computers in the Chemistry Department at Pacific Lutheran University, and an IBM SP/2 at the Joint Institute of Computer Science at the University of Tennessee. The program was run with vector processing when possible and maximum optimization on all machines.

## RESULTS

In recent publications [74,77], one of us utilized this Monte Carlo model to examine the effect of the copolymer sequence distribution on the phase behavior and interfacial structure of a ternary blend containing a copolymer and two homopolymers. The results generally show that, to strengthen the biphasic interface, it is preferable that the copolymer be "blocky" rather than random or alternating in nature. It was also seen that the phase transition temperature for the ternary mixture did not depend on the sequence distribution of the added copolymer, merely on the amount. More exactly, the temperature at which demixing occurs decreases with an increase in copolymer concentration, however, at a given copolymer loading there was no observable difference between the different copolymer structures (block, random, or alternating). This trend is shown in Fig. 1 which plots the heat capacity vs reduced temperature,  $\tau = k_b T / \epsilon_{A-B}$  for the blend of the two homopolymers and the ternary mixtures which contain 1, 5, 7.5, and 10% random copolymer. The lines in this figure are included to guide the eye. Inspection of this figure shows that as the concentration of the copolymer increases, the peak maximum of the heat capacity and transition temperature both decrease.

From the data in Fig. 1, a plot of the transition temperature as a function of copolymer concentration can be created, as shown in Fig. 2. This figure shows that the decrease in phase transition temperature decreases linearly with increased copolymer concentration, much as an added inert impurity (i.e., dilution) will alter the phase transition temperature of a pure sample. This result is interesting, however, it does not provide information on how the copolymer affects the *nature* of the phase transition. For this, finite-size analysis is needed.

In a theoretical infinite system a first order phase transi-

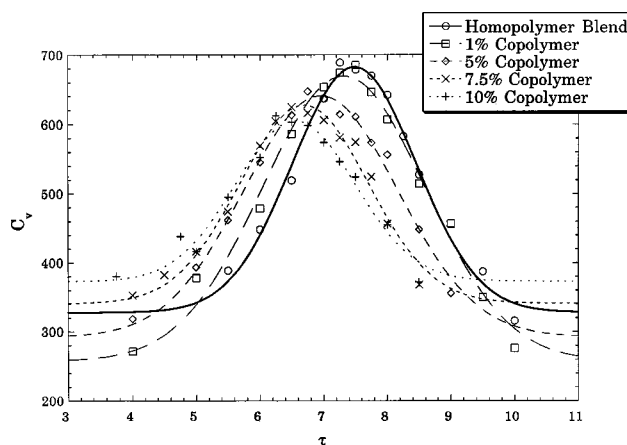


FIG. 1. The effect of a copolymer loading on the heat capacity peak for the mixing-demixing transition of a compatibilized polymer blend.

tion is characterized by a discontinuity in the first derivative of the free energy. This results in a  $\delta$  function singularity in the heat capacity, the second derivative of the free energy. This divergence is a consequence of the coexistence of two phases. The system does not anticipate the transition and there is no critical region or critical exponents. In second order phase transitions, there is a power law divergence in the heat capacity, but this divergence is a consequence of the correlation length becoming infinite. The system anticipates the transition and a critical region and critical exponents are found. In real finite systems this divergence does not occur. Finite-size effects cause the divergence to become a finite peak. There are two effects, a rounding of the peak with decreasing sample size and a shifting of the peak with a change in sample size. In second order phase transitions the shift of heat capacity peak is due to the limitation of the correlation length to the lattice size,  $L$ . Scaling theory [78,79] therefore predicts that the heat capacity maximum  $C_v^{\max}$  will diverge as  $L^{\alpha/\nu}$  while the transition temperature will shift as

$$(T_c^* - T_c) / T_c^* \sim L^{1/\nu}, \quad (4)$$

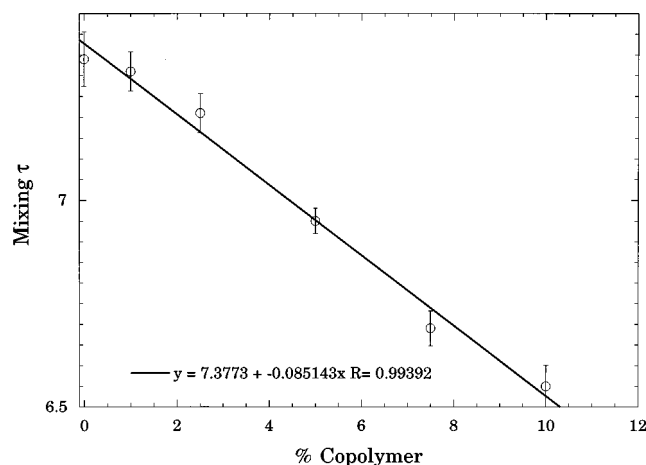


FIG. 2. The change in the mixing-demixing transition temperature with copolymer concentration in a compatibilized polymer blend.

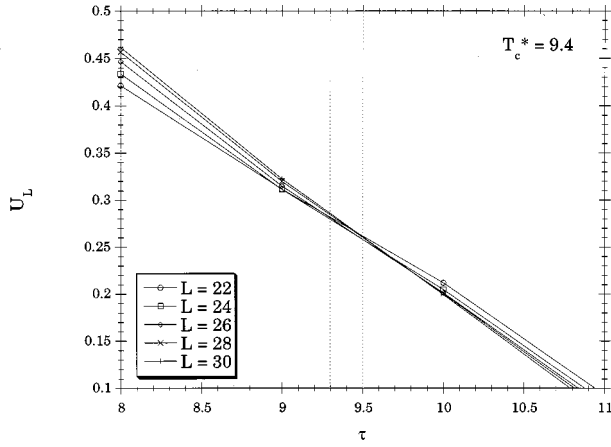


FIG. 3. The behavior of the fourth-order cumulant  $U_L$  near the transition temperature of the infinite system  $T_c^*$  for the binary homopolymer blend.

where  $T_c$  is the transition temperature of the finite system,  $T_c^*$  is the transition temperature of the infinite system,  $\alpha$  is the heat capacity critical exponent, and  $\nu$  is the correlation length critical exponent.

Therefore, one way to determine the critical exponents of a model phase transition is to perform finite-size analysis on the system by determining how the heat capacity peak and the transition temperature change with lattice size. Using the change in the heat capacity maximum is not feasible in this study due to the significant error in determining the heat capacity maximum. Additionally, in completion of this analysis using the transition temperature, it becomes necessary to determine the transition temperature at infinite size ( $T_c^*$ ). In practice,  $T_c^*$  is often determined using finite-size analysis, i.e., the transition temperature is determined as a function of lattice size,  $T_c$  is plotted vs  $1/L^\nu$ , and extrapolated to  $1/L^\nu \rightarrow 0 \equiv L \rightarrow \infty$ . Thus, we are left with the chicken and the egg problem;  $\nu$  is required to determine  $T_c^*$  and  $T_c^*$  is also needed to determine  $\nu$ . Fortunately, there exist other methods by which  $T_c^*$  can be evaluated. The most straightforward is using the reduced fourth-order cumulant [26,29–31]. It can be shown [26,30] that  $U_L$  scales with  $(1 - T/T_c^*)$  and  $L^{1/\nu}$  as

$$U_L \propto (1 - T/T_c^*) L^{1/\nu}; T \rightarrow T_c^*, L \rightarrow \infty \quad (5)$$

which implies that  $U_L(T = T_c^*) = U^*$  which is independent of  $L$ . Therefore a plot of  $U_L$  vs temperature for different lattice sizes,  $L$ , will produce a series of curves which intersect at  $T_c^*$ , the transition temperature for an infinite system.

Figure 3 shows the plot of  $U_L$  vs  $\tau$  for a 50/50 binary blend of the two homopolymers (A and B) while Fig. 4 shows the same plot for a ternary blend containing a  $2.5 \pm 0.08\%$  random ( $P=0.5$ ) copolymer and an equimolar mixture of homopolymers A and B. On first inspection it is evident that the curves for different lattice sizes do not all intersect at a single point. This is due to a number of reasons, but most importantly that the scaling denoted in Eq. (5) only holds for  $L \rightarrow \infty$ . The lattice sizes that were examined here obviously do not approach this limit. Nevertheless,  $T_c^*$  can

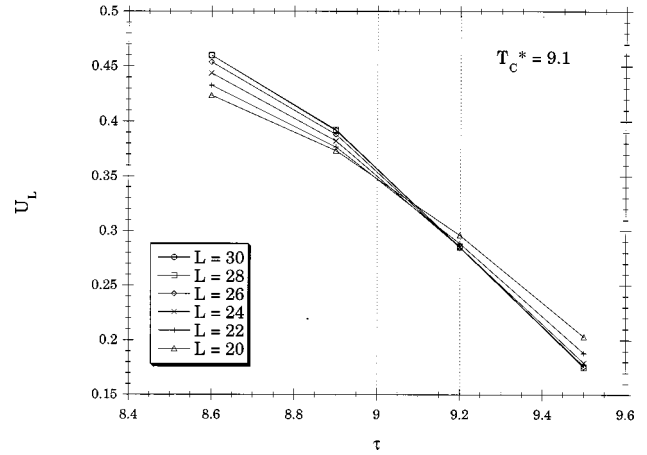


FIG. 4. The behavior of the fourth-order cumulant  $U_L$  near the transition temperature of the infinite system  $T_c^*$  for the ternary (compatibilized) polymer blend.

be estimated with modest error to be  $9.4 \pm 0.1$  for the binary system and  $9.1 \pm 0.1$  for the ternary system from the data in both plots.

With this knowledge of  $T_c^*$ , the data can be analyzed to determine the critical exponent  $\nu$  for the two systems and thus the nature of the phase demixing transition that occurs in a blend with and without added copolymer compatibilizer. Figure 5 is a plot of  $\ln[(T_c^*(L) - T_c^*)/T_c^*]$  vs  $\ln(1/L)$ , where values of 9.4 and 9.1 for  $T_c^*$  were used in the binary and ternary polymer blend, respectively. Examination of Eq. (4) shows that the slope of this plot is equal to  $1/\nu$ . This analysis provides a value of  $\nu=0.63$  for the binary and  $\nu=0.69$  the ternary mixture (see Table II).

It should be noted that the value of  $\nu$  that is determined from Fig. 5 is very sensitive to the value of  $T_c^*$  that is used. Plots similar to Fig. 5 can be produced using values of  $T_c^*$  which range from 9.0 to 9.5. Completing this analysis using values of  $T_c^*$  within the ranged delimited by the vertical dashed lines in Fig. 3 and 4 demonstrates that the error that exists in determining  $T_c^*$  propagates to an error of  $\pm 0.02$  in the value of  $\nu$ .

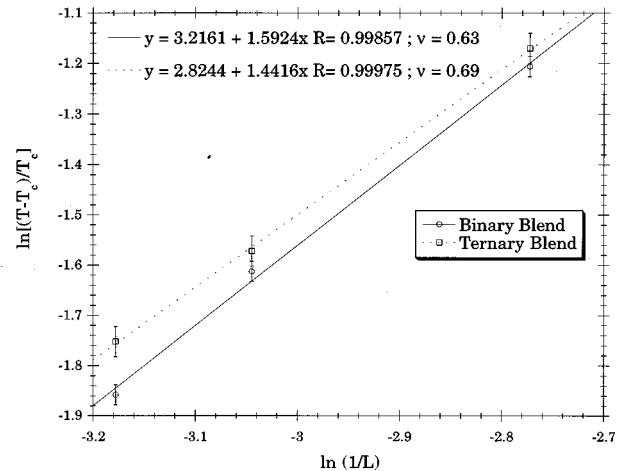


FIG. 5. The finite-size analysis plot. The slope of this plot of  $\ln[(T_c^*(L) - T_c^*)/T_c^*]$  vs  $\ln(1/L)$  is equal to  $1/\nu$ , where  $\nu$  is the critical exponent for the correlation length.



TABLE II. Predicted and observed values for  $\nu$ .

Correlation length Critical Exponent $\nu$	Binary system	Ternary system (Fisher renormalization)
This study	0.63 ( $\pm 0.02$ )	0.69 ( $\pm 0.02$ )
Theory (Ising behavior)	0.63	0.72
experimental	0.63 [80]	0.68 ( $\pm 0.2$ ) [11]

Thus, the addition of a copolymer does change the critical exponents of the miscible-immiscible phase transition in a binary polymer blend. The change is in qualitative agreement with Fisher renormalization, though is slightly lower than the predicted value. Renormalization predicts that the exponent will increase by a factor of 1/7, which would result in a value of  $\nu=0.72$ .

Interestingly, the value determined in this study is very close to the experimental value of  $\nu=0.68$  found by Hair *et al.* for a polymer blend that was diluted by a small molecule [11]. Finally, these results also emphasize that the phase separation behavior of a ternary polymer mixture containing two homopolymers and a copolymer must be analyzed with the knowledge that its critical exponents differ from those of a binary polymer blend.

## CONCLUSION

Finite-size analysis and Monte Carlo simulation have been completed to determine the critical exponent  $\nu$ , of the demixing phase transition in a binary mixture of two homopolymers as well as a ternary mixture of two homopolymers and a copolymer. A copolymer is often added to a polymer mixture to improve the miscibility and ultimate properties of the resultant blend. The analysis shows that the critical exponent  $\nu$  of the binary blend is compatible with Ising-like behavior ( $\nu=0.63$ ). However the critical exponent  $\nu$  of the ternary mixture is slightly higher than that of the binary blend ( $\nu=0.69$ ) in qualitative agreement with Fisher renormalization. These results suggest that the addition of a copolymer to a polymer mixture slightly changes the nature of the phase decomposition process of that mixture and must be analyzed accordingly.

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