Which is More Efficient as Compatibilizer: Di-block or Multiblock Copolymer?

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Monte Carlo simulations were used to investigate the compatibilizing behaviors of multi-block copolymers with different architectures in A/B/(block copolymer) ternary blends. The volume fraction of homopolymer A, employed as the dispersed phase, was 19%. The simulations illustrate how a di- or multi-block copolymer aggregates at the interfaces and influences the phase behaviour of such incompatible polymer blends. The di-block copolymer chains tend to “stand” on the interface whereas the multi-block chains lie on the interface. In comparison with the di-block copolymer, the block copolymers with 4, or 10 blocks can occupy more areas on the interface, and thus the multi-block copolymers have higher efficiency for the retardation of the phase separation.

\textbf{Key words:} Monte Carlo simulation, Compatibilizer, Phase interface

\section{I. INTRODUCTION}

Most polymeric materials used today are the polymer alloy that is made by chemically or physically mixing two or more unlike polymers. Because of the large entropy of high macromolecular chain, these unlike polymers are usually incompatible. As a result, these incompatible blends usually exhibit poor mechanical properties because of weak interactions at the interfaces between phases. Some efforts have been devoted in the past years to improving the compatibility of incompatible polymer blends. One of the successful methods is to add a few percent of block copolymers into the mixture of homopolymers A and B, in which one component is miscible with polymer A and the other is miscible with polymer B. It has been demonstrated experimentally and theoretically that the copolymer chains are located at the interface and act as a compatibilizer \cite{1-8}. Considerable efforts have been devoted in recent years to understanding the performance of block copolymers in such blends. Noolandi \textit{et al.} proposed a statistical thermodynamic theory to describe the copolymer emulsification in an A/B/A-B ternary melt blend \cite{9-12}. Laradji \textit{et al.} investigated the phase separation of binary mixtures containing surfactants by means of a time-dependent Ginzburg-Landau model \cite{13}. Jo \textit{et al.} have carried out detail studies on the phase separation dynamics of polymer blends in the presence of di-block copolymers \cite{14-16}. They concluded that the rate of the phase separation process is significantly suppressed by the addition of block copolymers because of the reduction of the interfacial tension. This retardation effect is very dependent on the chain lengths of the block copolymer and on the interaction energies between the copolymer blocks and their corresponding homopolymers. Liang \textit{et al.} showed that the di-block copolymer chains located at the interfaces, acting as a compatibilizer in such A/B/copolymer ternary blends \cite{17,18}. Below the critical copolymer concentration, the domain size of the dispersed phase decreased linearly with increasing copolymer concentration. When homopolymer A is the dispersed phase in such blends, B-A-B type tri-block copolymers are more efficient compatibilizers than A-B-A and A-B type copolymers \cite{18,19}. Although we have gotten some insights in understanding the performance of block copolymers as the compatibilizer, there are still several problems remaining. For example, one problem is: which is more efficient, di-block or multi-block copolymers? We will answer this question by means of computer simulations in the present work.

\section{II. SIMULATION}

A two-dimensional simulation was used to provide a direct inspection of polymer configuration and the coarsening of the phase-separated structure. Cifra \textit{et al.} showed that there is no essential difference in the phase behavior between a two-dimensional and a three-dimensional simulation \cite{20}. Multiple-chain configurations were generated on a planar square with 420 × 420 lattices. The system contained 8400 linear chains and each chain had 20 seg-
ments, resulting in a polymer concentration of 0.95, thus it could be regarded as being in the bulk state. The remaining 0.05 unfilled space is handled as free volume. A standard periodic boundary condition was imposed on the lattice to mimic an infinite-size system [21]. Considering that the polymer concentration was high, we adopted the “single-site bond fluctuation” model proposed by Larson et al. [22,23] and Carmesin et al. [24] and the “vacancy diffusion” algorithm suggested by Lu et al. [25] to improve the Monte Carlo simulation efficiency. A schematic of the model and the corresponding micro-relaxation modes can be found elsewhere [26]. The evolution of the chain configuration in the simulation was achieved by the random displacement of single vacancy site to one of its eight nearest neighbouring sites on the lattice. Each attempted move changes the bond length, but the chain connectivity restricts the bond length to 1 and \( \sqrt{2} \). The excluded volume interaction ensures no more than one bead per lattice site. If one attempted move violates either the excluded volume or the bond length restriction, it is rejected. The acceptance or rejection of one attempted move which satisfies both the excluded volume and the bond length conditions is further governed by the Metropolis rule [27]. Namely, it is accepted if the energy change, \( \Delta E = (N_{AB}^0 - N_{AB}^0) \varepsilon \), is negative. Otherwise, it is accepted with a probability of \( \rho = \exp(-\Delta E/kT) \), where \( N_{AB}^0 \) and \( N_{AB}^0 \), respectively, are the numbers of the nearest-neighbouring pairs of sites taken by the pair of beads (or segments) after and before the attempted move. \( \varepsilon \) is the interaction energy gained when two different kinds of repeat units occupy two neighbouring lattice sites. The negative and positive \( \tau = \varepsilon/kT \), respectively, correspond to a homogeneous and a heterogeneous state.

In the simulation, we first let \( \tau = -1 \). After a long Monte Carlo time, the system reaches a completely compatible state. Then let \( \tau = 1 \), so that the change of domain structures in the phase separation process can be observed.

III. RESULTS AND DISCUSSION

In this simulation, each polymer chain has 20 segments. The volume fractions of homopolymer A, the dispersed phase, and block copolymers were fixed at 0.19 and 0.10, respectively. As a result, the sum of the volume fractions of homopolymer B and block copolymer was 0.66. The performances of di- and multi-block copolymers as compatibilizer in A/B/(block copolymers) ternary mixtures will be given in details as following.

In order to investigate the influence of the block number of the multi-block copolymers on the phase behavior of blends during the phase separation, the multi-block copolymers with 2, 4, 10 and 20 blocks, each of which is with the equivalent block length, were chosen as the compatibilizer. Figure 1 shows that the domain size of the dispersed phase increases with Monte Carlo steps during phase separation for different kinds of block copolymers as the compatibilizer. The domain size \( (D) \) is defined as \( N/N_d \), where \( N \) and \( N_d \) are the lattice numbers and the dispersed phase numbers on the lines drawn parallel to the borderline. (The way of the measurement of dispersed phase used here is analogous to that of experimental measurement of domain size from Scanning electron microscopy). From Fig.1, we observed that the dispersed phase size formed by the homopolymer A grows up with Monte Carlo steps because of the occurrence of phase separation. In principle, the block copolymers acting as the compatibilizer in the system should reside on the interface and avoid the collision among the separated phases, thus resulting in the smaller domain size of dispersed phase. The more efficient the block copolymers as the compatibilizer, the smaller the size of dispersed phase. As indicated by Fig.1, we can concluded that the multi-block copolymers, i.e. 4, 10 and 20 blocks, are more efficient than the di-block copolymer. For clarity, the domain sizes of the dispersed phase A after different Monte Carlo steps as a function of block numbers are plotted in Fig.2. From this figure, it is clear that, when the block number is less than 10, the size of the dispersed phase decreases with the increase of the block number. But the size of the dispersed phase becomes larger for the 20-block copolymer than those for the 4-block and 10-block copolymers, implying the existence

![FIG. 1 Monte Carlo steps dependence of the domain size (D) of dispersed phase for di-block copolymers with different block number, where the dispersed phase concentration and the block copolymer concentration were kept at 0.19 and 0.10, respectively.](image-url)
of an optimal block number.

![FIG. 2](image1.png)  
**FIG. 2** Block number of multi-block copolymer dependence of domain size of dispersed phase at different Monte Carlo steps.

![FIG. 3](image2.png)  
**FIG. 3** Block number of multiblock copolymer dependence of domain size of block copolymer phase at different Monte Carlo steps.

In general, as a higher efficient compatibilizer, more block copolymers should be expected to reside and align along the interface. So the block copolymers should distribute homogeneously in the system rather than aggregate each other to form some bigger domain. Keep this in mind, the domain sizes of the block copolymers after different Monte Carlo steps are plotted as a function of block numbers in Fig.3. As expected, the most efficient compatibilizer, i.e. block copolymer with 10 blocks, corresponds to the smallest domain size of block copolymers.

For a clear presentation, we give the typical pattern of A/B/(block copolymer) ternary mixtures for the block copolymers with different molecular architectures as the compatibilizer in Fig.4. As shown in Fig.4(a), as expected, the di-block copolymers indeed distribute on the interface. However, a further examination of the conformation of the di-block copolymers on the interfaces reveals that these di-block copolymers “stand” on the interface, i.e. the di-block copolymers tend to align per-

![FIG. 4](image3.png)  
**FIG. 4** Typical configuration pattern of A/B/(block copolymer) ternary polymer blends after 1200 Monte Carlo steps. Where the dispersed phase concentration and the block copolymer concentration were kept at 0.19 and 0.10, respectively. –, •, ○ represent homopolymer A, B-block, and A-block of the copolymer, respectively, and white color represent homopolymer B. a: di-block block copolymer; b: 10-block copolymer; c: 20-block copolymer.
perpendicularly to the interface because both of blocks are adsorbed into their individual phase. On the contrary, we can see from Fig.4(b) that the 10-block copolymers tend to lie on the interface. By comparison of Fig.4 (a) with (b), it is reasonable that the copolymer with 10 blocks should occupy more area than the di-block copolymer, and thus are efficient for the retardation of phase separation. But with further increase of the block number, as in the case of 20 blocks, the retardation efficient for the phase separation become a little lower in comparison of the case 10 blocks. Combining of Fig.3 and Fig.4(c), although the copolymers with 20 blocks also tend to lie on the interface, these copolymers have some tendency to aggregate each other on the matrix, homopolymer B phase, when they are on the interface, therefore not acting as the compatibilizer.

IV. CONCLUSIONS

The computer simulations have given insights into the influence of the block number of multi-block copolymers on A/B/(block copolymer) ternary blends. A direct observation of the morphology of the dispersed phase and the matrix phase, and of the configuration of the block copolymer chains reveals that the phase behavior of blend significantly depends on the architecture of multi-block copolymer chains. In the A/B/di-block copolymers ternary mixtures system, the di-block copolymer is less efficient as the compatibilizer than the multi-block copolymer, such as 4, 10 blocks. This is mainly because the di-block copolymer chains tend to “stand” on the interface, which occupy less area. In contrary, the multi-block copolymer chains have the tendency to lie on the interface and occupy more area, which results in higher efficiency for the retardation of the phase separation.

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