Macromolecules **1999,** *32,* 1679−1685

Effects of Ester Interchange Reactions on the Phase Behavior of an Immiscible Polyester Blend: Monte Carlo Simulation

Won Ho Jo,* Jong Geun Kim, Seung Soon Jang, and Ji Ho Youk

Department of Fiber and Polymer Science, Seoul National University, Seoul 151-742, Korea

Sang Cheol Lee

Department of Polymer Science and Engineering, Kumoh National University of Technology, Kumi 730-701, Korea

Received April 2, 1998; Revised Manuscript Received August 21, 1998

ABSTRACT: The effects of ester interchange reactions on the phase behavior of an immiscible polyester blend have been investigated using the Monte Carlo simulation method. Two kinds of ester interchange reactions such as alcoholysis (or acidolysis) and direct ester−ester interchange are simulated by end attack and bond flip, respectively. The chain movement is performed by the one-site bond fluctuation model. First, the phase-separated structure is prepared by introducing the pair interaction energy E_{AB} between segments A and B. As the ester interchange reactions at the interface between the two phases proceed, the degree of randomness increases and the maximum intensity of the collective structure factor decreases, whereas the peak position at which the structure factor has a maximum remains almost unchanged. These results indicate that the homogenization of the phase-separated structure of the immiscible polyester blend proceeds by the ester interchange reaction without a change in the domain size, while the concentration difference between the two phases becomes smaller. These results are also confirmed by analyzing the changes in concentration profiles.

Introduction

It is well-known that ester interchange reactions between two different polyesters in the melt produce copolyesters.[1−8] Particularly, it has been reported that, in immiscible polyester blends, these copolyesters formed by ester interchange reactions at the interface have a homogenizing effect on the phase-separated structure, leading to a single phase.[9−12] Although the extent of ester interchange reactions is a key factor in controlling the phase behavior of immiscible polyester blends, little information on such phenomena is available. To our knowledge, the mechanism for the homogenization process in immiscible polyester blends by the ester interchange reactions has not been reported because it is very difficult, if not impossible, to experimentally monitor the phase behavior during the ester interchange reactions in the melt.

Computer simulation using the Monte Carlo method may provide a powerful tool in monitoring the phase behavior because computer simulations can be carried out under controlled conditions in which the effects of experimental variables on the phase behavior are readily factorized. Sariban and Binder[13−18] have extensively studied the phase separation behavior of polymer blends using the Monte Carlo method. They have investigated spinodal decomposition by monitoring the collective structure factor and found that a model system with vacant sites enabling the chain to move can be used to study the binary system by the rescaling of parameters. Brown and Chakrabarti[19] have found that the asymptotic domain growth exponent is given by a modified Lifshitz−Slyozov law using Monte Carlo simulations. A point to be noted from their works is that phase separation is well described under the condition where only a repulsive interaction between different segments is adopted ($\epsilon_{AB} > 0$ and $\epsilon_{AA} = \epsilon_{BB} = 0$).

In our previous studies, the reorganization of the molecular weight distribution (MWD) in a polyester[20,21] and the formation of copolyesters by ester interchange reactions in miscible polyester blends[22] have successfully been studied using Monte Carlo simulations. These studies have motivated us to extend computer simulations to describe an immiscible polyester blend system. In this paper, ester interchange reactions in immiscible polyester blends are simulated using the Monte Carlo method in order to elucidate their effects on the phase behavior during the homogenization process. According to Tanaka et al.,[23] the homogenization of immiscible polyester blends is affected by two controlling factors: that is the rate of phase separation and that of ester interchange reaction. When the ester interchange reaction proceeds much faster than the phase separation, the system is homogenized before no distinct phase-separated structure is developed. On the other hand, when the phase separation proceeds much faster than the ester interchange reaction, a domain is first formed by the phase separation, and then the homogenization proceeds with the ester interchange reaction between different segments at the interface between two phases. In this study, we simulate the latter case because, from a practical point of view, most of immiscible polyester blends have phase-separated structures before ester interchange reaction begins. Therefore, the simulation is performed under the condition where the rate of phase separation proceeds much faster than that of ester interchange reaction.

Model and Simulation Method

Model Reactions for Ester Interchange. Four types of ester interchange reactions are implemented in our simulation: (1) homo-ester-interchange reaction

---

* To whom correspondence should be addressed. Tel +82−880−7192; Fax +885-1748; e-mail whjpoly@plaza.snu.ac.kr.

10.1021/ma980515z CCC: $18.00

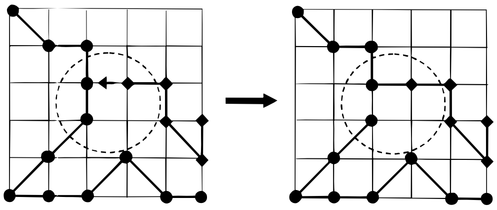
within the same chain (intrachain), (2) homo-ester-interchange reaction between two chains (interchain), (3) hetero-ester-interchange reaction within the same chain, and (4) hetero-ester-interchange between two chains. The homo- and hetero-ester-interchange reactions indicate the reaction between the same kind of segments (i.e., between segments A and A; between segments B and B) and the reaction between segments A and B, respectively. When the reaction 1 occurs, nothing is changed except chain conformation. When reaction 2 occurs, the molecular weights of the two chains are changed. Reaction 4 results in copolymer formation while reaction 3 yields a change in copolymer sequence.

Preparation of Polyester Blends with Phase-Separated Structure. The simulation is performed on a simple cubic lattice of 60 × 60 × 60 ($L_x \times L_y \times L_z$) sites. Periodic boundary conditions[24] are imposed on all three directions to simulate a system with infinite size. To prepare the initial structure of phase-separated blend in which each polyester has polydisperse MWD, the following procedure is performed. First, the cubic lattice is filled with homopolyesters A and B at a blend ratio of 25/75 v/v, where 60% of the lattice sites are occupied by segments, which is known enough to properly describe the dense polymer melts.[25,26] The initial chain length is set at $N_A = N_B = 20$, and consequently the number of homopolyester chains A and B are 1620 and 4860, respectively. All the chains are arranged initially at randomly chosen positions with fully extended chain conformation. This initial structure is relaxed under athermal conditions through the bond diagonal method (BDM),[27] a kind of one-site bond fluctuation model, in a way of self- and mutual-avoiding walk on the lattice. In this method, the diagonals of squares and cubes as well as the edges of squares and cubes are used as bonds. An advantage to this method is being able to accommodate more chain conformations for dense polymer system than the conventional Verdier−Stockmayer method,[28] and hence the system could be relaxed more efficiently. Adjacent segments are connected via bonds taken from a given set of bond vectors. The set is built through **P** involving component permutations and sign inversions:

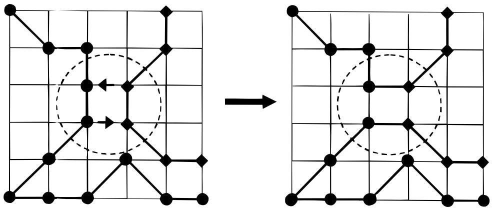
$$\mathbf{P}\,(1, 0, 0) \cup \mathbf{P}\,(1, 1, 0) \cup \mathbf{P}\,(1, 1, 1) \tag{1}$$

Thus, the bond length has values of 1, $\sqrt{2}$, and $\sqrt{3}$. Although this condition allowing the bond crossing during the chain movement seems unrealistic, it makes no critical error in the results for the following reasons. First, the chain in the melt as described by Flory[29] is the same as that of a phantom system.[27] Second, it is reported by Shaffer[30,31] that the dynamics of this model is consistent with that of the Rouse model. Details of chain movement are as follows. A segment is randomly chosen, and then an attempt is made to move the segment under the condition given in eq 1. If no other segment is present at the new location, and at the same time if the bond length of a new bond satisfies the bond length constraints, the movement is accepted. However, if the excluded volume conditions and the bond length constraints are not satisfied, the movement is rejected. In this study, time is measured in units of a Monte Carlo step (MCS). One MCS is defined as the time necessary for every segment to attempt to move once on average.

After the conformational state of polymer chains reaches an equilibrium, polyesters with polydisperse MWDs are prepared by executing the ester interchange reactions intra- or intermolecularly between the same kind of segments (i.e., between segments A and A; between segments B and B), the so-called homo-ester-interchange.



(a) end-attack



(b) bond-flip

Figure 1. Two kinds of ester interchange reactions schematically represented by 2-dimensional scheme of this bond diagonal model.

It is assumed that the ester interchange reactions take place by two mechanisms: end attack and bond flip, which correspond to alcoholysis (or acidolysis) and direct ester−ester interchange, respectively, as suggested by Mansfield.[32] The reaction by end attack occurs when a chain end contacts with the neighboring mid-segment of the same chain or another, as represented by the 2-dimensional scheme in Figure 1a, and the reaction by bond flip occurs under similar conditions as shown in Figure 1b. The trial of ester interchange reactions is rejected when the chosen segment has no neighboring segment or when the chosen segment and the neighboring one are all chain ends. In this study, it is assumed that the ester interchange reactions take place if the above-mentioned geometric condition is satisfied, even though the activation energy should be taken into account in a more realistic simulation. At this stage, the reaction between polyesters A and B, the so-called hetero-ester-interchange, is not executed. A chain movement using the BDM is attempted at every ester interchange reaction, so that only the MWD and the chain conformation are changed with the progress of ester interchange reactions.

After each polyester with polydisperse MWD is prepared, the phase separation is then induced by introducing the reduced pair interaction energy E_{AB} ($=\epsilon_{AB}/k_BT$ where ϵ_{AB} is a pair interaction energy parameter between segments A and B, k_B is the Boltzmann constant, and T is temperature). During phase separation, E_{AB} is set at 2.0, and the others such as $E_{\alpha\alpha}$ and $E_{\alpha v}$ (where α denotes A or B, and v denotes vacant site) are set to be all zero. From this stage, chain movement is governed by the pair interaction energy through the Metropolis sampling rule.[33] The movement decreasing the energy of system is accepted with a unit probability, whereas the movement increasing the energy of system is accepted with a probability of $\exp(-\Delta E/k_BT)$ where ΔE is the energy change before and after the movement.

The phase separation is confirmed by calculating the collective structure factor,[34] which has often been used to investigate the time evolution of the long-range ordering, as described in our previous papers.[35−37] The time-dependent collective structure factor of an $L_x \times L_y \times L_z$ ($L = L_x = L_y = L_z$) lattice with periodic boundary conditions is given by

$$S(\mathbf{q},t) = \langle \sum_{r_i} \sum_{r_j} \exp(i\mathbf{q}\cdot\mathbf{r}_{ij})(\xi^i \xi^j - \langle \xi \rangle^2) \rangle / L^3 \qquad (2)$$

where $\langle\ \rangle$ denotes a thermal statistical average, ξ^j represents ($\phi_A{}^j - \phi_B{}^j$), and $\mathbf{r}_{ij}$ is the vector between the lattice sites i and j. The local concentration variable $\phi_A{}^j$ is equal to 1 if the lattice site j is occupied by an A segment, but otherwise equal to zero, and $\phi_B{}^j$ is equal to 1 if the lattice site is occupied by a B segment, but otherwise equal to zero. The quantity $S(\mathbf{q},t)$ represents the Fourier transform of the pair correlation function and is spherically averaged as follows:

$$S(q,t) = \sum_{|\mathbf{q}|} S(\mathbf{q},t) / \sum_{|\mathbf{q}|} 1 \qquad (3)$$

with $q = (2\pi/L)n$, where $n = 1, 2, 3, ...$ denotes that, for a given n, a spherical shell is taken as $n - {}^1\!/_2 \le qL/2\pi \le n + {}^1\!/_2$. For all the samples, phase separation is implemented up to 3×10^4 MCS. The phase-separated structure at 3×10^4 MCS is used as an initial structure for ester interchange reaction, although the structure may not be in an equilibrium state.

Simulation of Hetero-Ester-Interchange Reactions. The hetero-ester-interchange is allowed to take place as well as homo-ester-interchange in the sample with the phase-separated structure previously obtained. Several values of E_{AB} (=0.05, 0.10, 0.15, and 0.20) are used for simulation in order to examine the effect of temperature on the ester interchange reaction, since the change in E_{AB} value reflects the temperature change through the relation $E_{AB} = \epsilon_{AB}/k_B T$ where ϵ_{AB} is constant. Since activation energy is not taken into account in this simulation, the homo- and hetero-ester-interchange have the same probability of occurring only if the geometric condition is satisfied. To trace the progress by the hetero-ester-interchange, the degree of randomness (DR) is calculated, and at the same time the effects of copolymerization on the phase behavior are investigated by monitoring $S(q,t)$. The DR is given by the following relation:[38]

$$\mathrm{DR} = \frac{1}{\langle l \rangle_{n,A}} + \frac{1}{\langle l \rangle_{n,B}} \qquad (4)$$

where $\langle l \rangle_{n,A}$ and $\langle l \rangle_{n,B}$ are the number-average sequence lengths of blocks A and B, respectively.

To more clearly observe the change in concentration profile at the interface during the phase homogenization by the ester interchange reaction, a supplementary simulation is carried out as follows. In the cubic lattice with periodic boundary conditions, the polyesters A and B are placed at $1 \le Z \le 20$ and $21 \le Z \le 60$, respectively, resulting in the formation of sharp interfaces between A and B. Generally, the lamellar pattern formation has never been observed in polyester blends. However, the system having artificial lamellar morphology with flat interface is prepared in our simulation in order to observe more clearly the effect of ester interchange reaction on concentration profiles at the interface. After equilibrating the chain conformation by the BDM and then making each polyester polydisperse by homo-ester-interchange in each region, the system is equilibrated sufficiently by the BDM with $E_{AB} = 0.20$. Finally, one makes the hetero- and homo-ester interchange reactions at the interface to occur, and the change in concentration profiles with the extent of interchange reaction is observed. To enhance the statistics of results, five independent runs are performed for each case, and all the results are reported by averaging the data from the five independent runs.

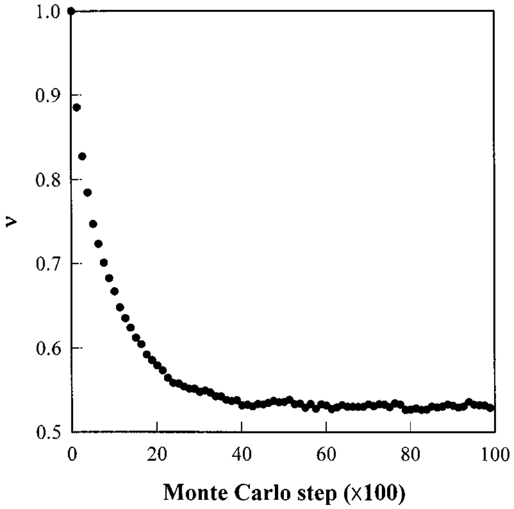


Figure 2. Change of scaling exponent (ν) with Monte Carlo step during the chain relaxation.

Results and Discussion

Preparation of Polyester Blends with Phase-Separated Structure. Chain dimensions in the melt state can be characterized by the following relation:[29,39]

$$\sqrt{\langle r^2 \rangle} \propto N^{\nu} \sqrt{\langle l^2 \rangle} \qquad (5)$$

where r is the end-to-end distance, N is the number of mer units, ν is the scaling exponent, and l is the bond length. It has been confirmed experimentally[40,41] that an ideal chain in the melt state has a value of $\nu = 0.5$ owing to the screening of the excluded volume effect by other chains. During the chain relaxation process, the change of ν for polyester A with MCS is shown in Figure 2 (the change of ν for polyester B is the same). The value of ν decreases with MCS and approaches an equilibrium value of 0.53. This value is slightly higher than the ideal value of 0.5. This discrepancy may arise from the excluded volume effect that cannot be completely removed in the lattice model. This excluded volume effect results in chain expansion so that all the values of ν obtained by the Monte Carlo method become slightly larger than 0.5.[21,22,42]

Figure 3 shows the change in MWD of polyester A with MCS. As the homo-ester-interchange reactions proceed, the MWD approaches an equilibrium state, i.e., the most probable MWD proposed by Flory.[29] Since this system starts from the monodisperse MWD with DP = 20 for both polyesters, the number fraction at DP = 20 appears above the curve, as can be seen in Figure 3a,b. This protruding point disappears as the ester interchange reactions proceeds in Figure 3c,d. The MWD after 1.5 MCS was in good agreement with the most probable MWD. To analyze the MWD more quantitatively, the polydispersity index (PI) was calculated by the following relation:

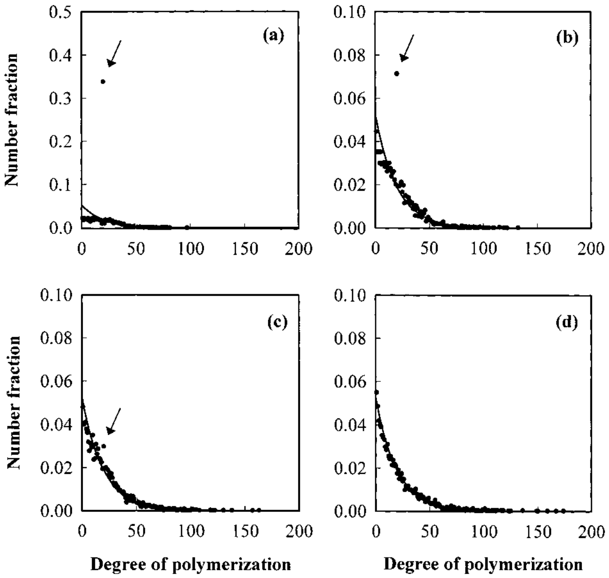


Figure 3. Molecular weight distribution after (a) 0.1 MCS, (b) 0.3 MCS, (c) 0.5 MCS, and (d) 1.5 MCS. The solid line represents the most probable distribution predicted by Flory.[29]

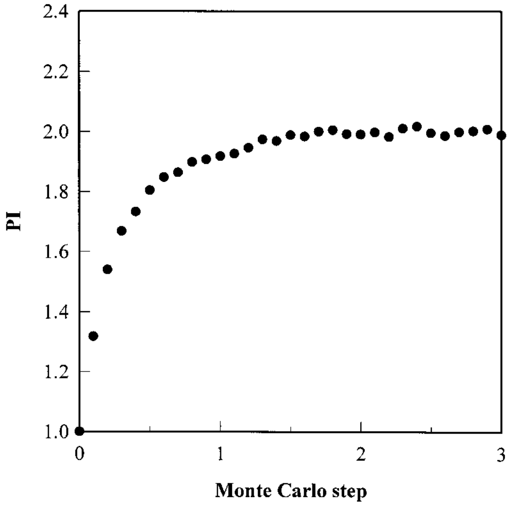


Figure 4. Change of polydispersity index (PI) with Monte Carlo step.

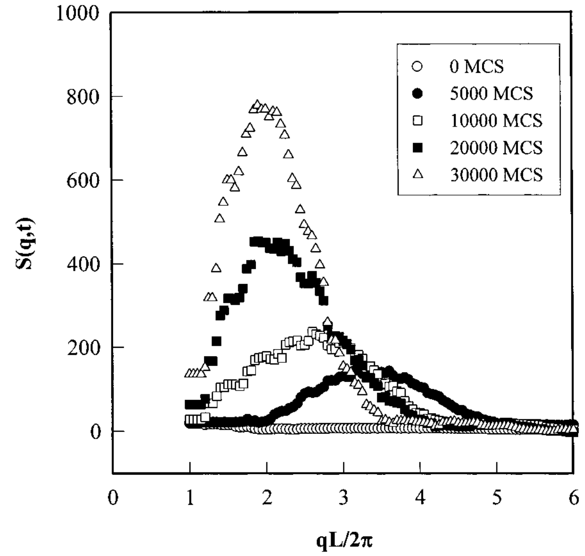


Figure 5. Time evolution of collective structure factor $S(q,t)$ during the phase separation when $E_{\mathrm{AB}} = 0.20$ is given.

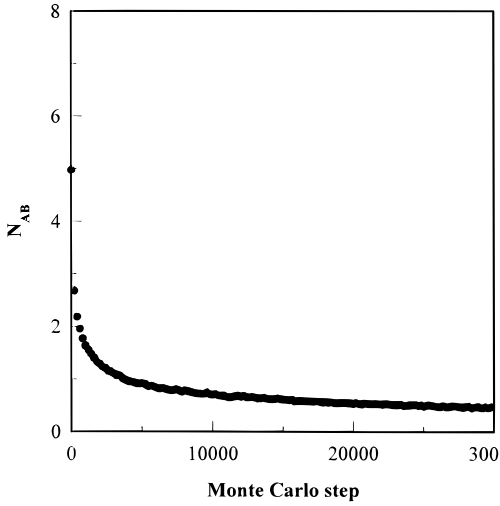


Figure 6. Change of the number of hetero-pair contact (N_{AB}) during the phase separation.

$$\mathrm{PI} = \frac{\langle M \rangle_{\mathrm{w}}}{\langle M \rangle_{\mathrm{n}}} = 1 + P \tag{6}$$

where $\langle M \rangle_{\mathrm{w}}$ and $\langle M \rangle_{\mathrm{n}}$ is the weight-average and the number-average molecular weight, respectively, and P is the extent of reaction. At $P = 1.0$, the theoretical value of PI is 2.0. As shown in Figure 4, the PI approaches the equilibrium value of 2.0 after 3.0 MCS. This indicates that the homogeneous mixture of polyesters A and B with each polyester having a polydispersity was successfully prepared.

The next step is to prepare the phase-separated structure of polyesters A and B by introducing the pair interaction energy E_{AB} between them. In an immiscible polyester blend, the blends already have a phase-separated structure before ester interchange reactions begin. To simulate this situation, the system is first quenched and then phase-separated until phase-separated structures are fully developed. Figure 5 shows the time evolution of collective structure factor $S(q,t)$ during the phase separation with $E_{\mathrm{AB}} = 0.20$. Since the initial mixture of polyesters A and B is homogeneous, a maximum of $S(q,t)$ is not observed at 0 MCS. As the phase separation proceeds, a distinct maximum of structure factor appears, and its value $S_{\max}$ increases while the scattering vector $q_{\max}$ at $S_{\max}$ shifts toward a smaller q. This behavior indicates that the periodic concentration fluctuation grows, and concurrently the coarsening process occurs during phase separation. Figure 6 shows that the number of hetero-pair contacts per segment (N_{AB}) decreases with increasing MCS. This also indicates that the polyester blends with phase-separated structure were successfully prepared by the procedure mentioned above.

Effect of Ester Interchange on the Phase Behavior. The resultant structure, obtained after a sufficient phase separation time (3×10^4 MCS is taken from the result shown in Figure 6) elapses, is used as an initial structure of the next procedure, which allows the hetero-ester-interchange reactions. As shown in Figure 7, a phase-separated structure with several domains is well developed in the simulation box when the snapshot is taken after 3×10^4 MCS. The variation of DR with MCS at various E_{AB}'s is shown in Figure 8. The more repulsive the pair interaction, the slower the increasing rate of DR and the lower the value of DR.

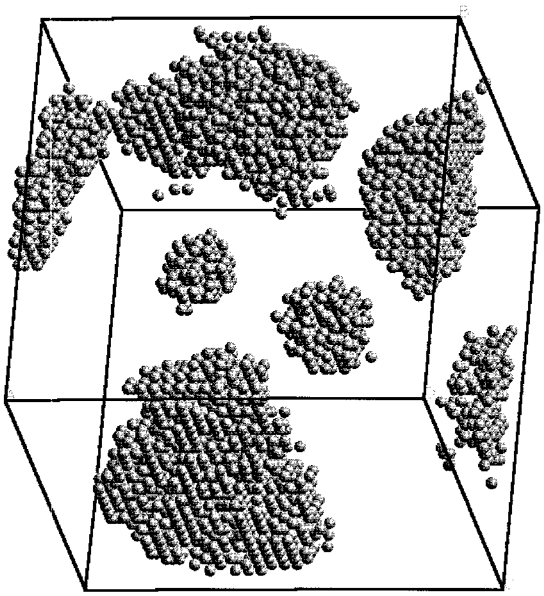


Figure 7. Snapshot of a phase-separated structure obtained at $E_{AB} = 0.20$. For visualization, only domain structures are presented.

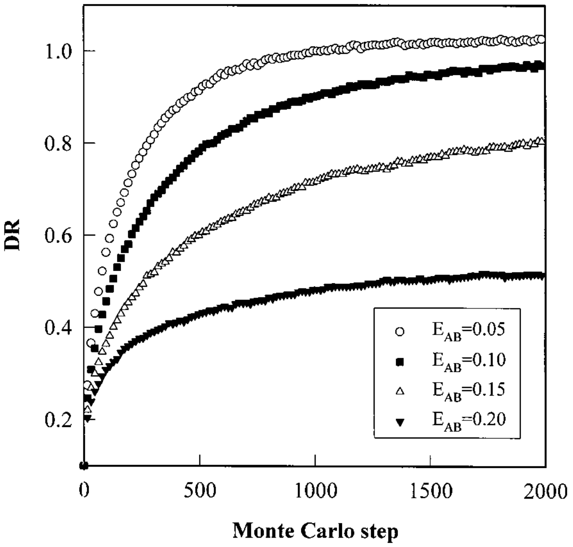


Figure 8. Change of the degree of randomness with Monte Carlo step at various E_{AB}'s.

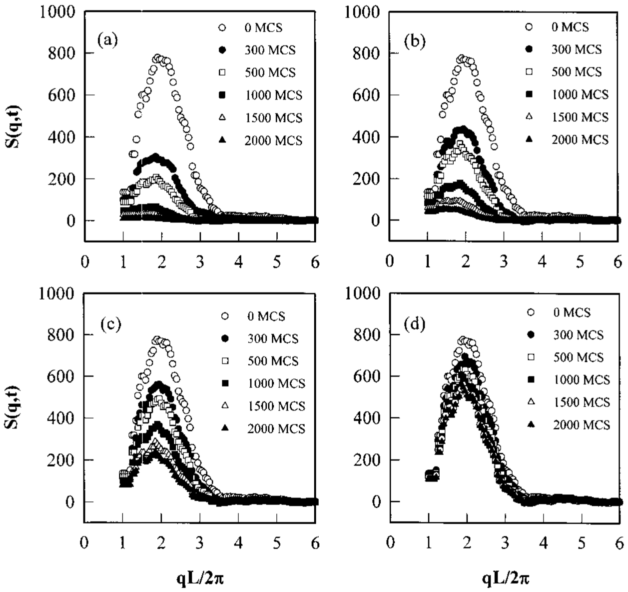


Figure 9. Time evolution of collective structure factor $S(q,t)$ at various E_{AB}'s: (a) $E_{AB} = 0.05$, (b) $E_{AB} = 0.10$, (c) $E_{AB} = 0.15$, (d) $E_{AB} = 0.20$.

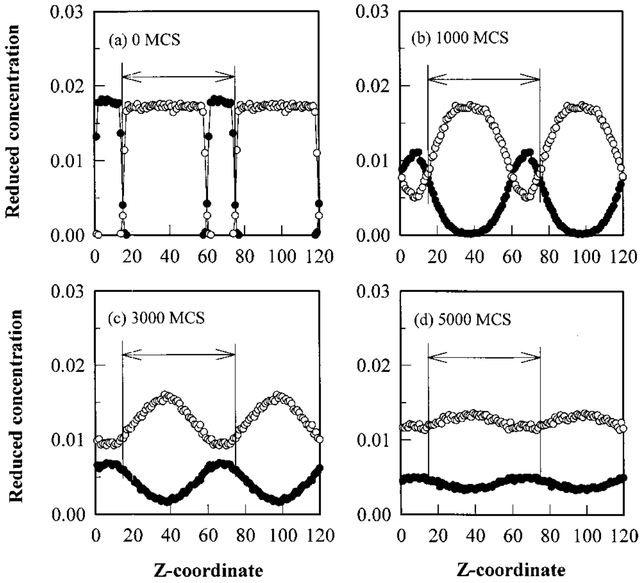


Figure 10. Time evolution of concentration profile when $E_{AB} = 0.05$ is given: (●) polyester A, (○) polyester B.

The copolyester formed after 2×10^3 MCS at $E_{AB} = 0.05$ is nearly a random copolymer whereas the copolyester formed at $E_{AB} = 0.20$ has a blocky structure. The change of phase structure with ester interchange reactions at various E_{AB}'s was monitored by the time evolution of $S(q,t)$, as shown in Figure 9. In all cases, the S_{max} value decreases with increasing interchange reaction time, and the more repulsive the pair interaction is, the slower the decreasing rate of S_{max} is. These results indicate that the magnitude of E_{AB} is an important factor for controlling the rate of homogenization. Since the value of S_{max} reflects the composition difference between two phases, a decrease in S_{max} indicates the homogenization of phase-separated structure. Another important feature to note from Figure 9 is that the q_{max} value remains nearly unchanged during the homogenization process. This result indicates that the domain size does not significantly change during homogenization process because the value of q_{max} is inversely proportional to the domain size ($\Lambda = 2\pi/q_{max}$, where Λ denotes the periodicity of concentration fluctuation related to the domain size[43]).

In an attempt to more clearly observe the homogenization process by the ester interchange reaction, a supplementary simulation was carried out on an artificial lamellar morphology with a flat interface prepared in the simulation box. The concentration profiles obtained under the condition of $E_{AB} = 0.05$ and 0.20 through the supplementary simulation are shown in Figures 10 and 11, respectively. The reduced concentration of the y-axis is the quantity that the number of segments A or B on the xy-plane at each z-coordinate is normalized by the total number of segments existing in the system. At $E_{AB} = 0.05$, the sharp interface becomes gradually broader, and the concentration difference between the two phases becomes smaller until the concentration of each segment A and B becomes constant on an overall range of z-coordinate, as the ester interchange reactions proceed. It is noteworthy that the

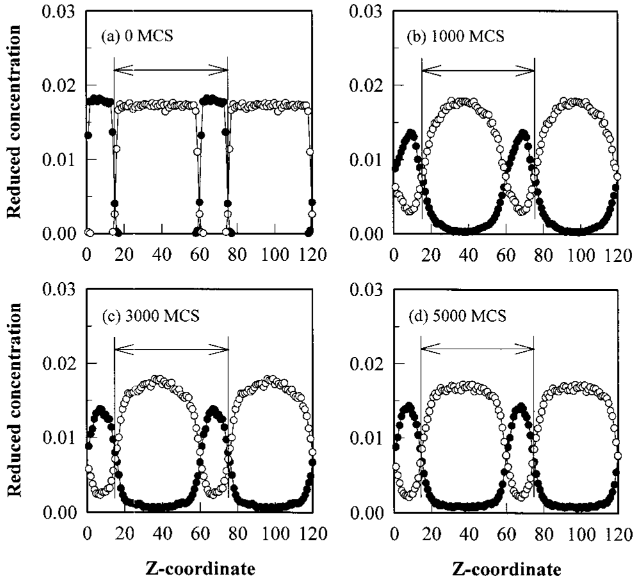


Figure 11. Time evolution of concentration profile when $E_{AB} = 0.20$ is given: (●) polyester A, (○) polyester B.

periodicity of the concentration fluctuation remains unchanged during the homogenization process, indicating that the domain size does not change during the homogenization process. This result is very consistent with the time evolution of the collective structure factor in Figure 9. Unlike the case with $E_{AB} = 0.05$, the concentration profile with $E_{AB} = 0.20$ does not show a significant change, as shown in Figure 11. This is because the repulsive interaction between different segments is too strong for segments to interdiffuse with each other for homogenization. These results in Figures 10 and 11 are also consistent with the time evolution of the collective structure factor.

From the simulation results, the mechanism of the homogenization process by ester interchange reactions in an immiscible polyester blend can be proposed as follows. In the first step of ester interchange reactions, the reactions take place at the interface between phases A and B to produce copolymers. In the second step, some thus-formed copolymers, containing the A unit as a major component, penetrate into the B phase. Similarly, the copolymers with the B unit as a major component diffuse into the A phase. This mutual solubility results in a reduction of the concentration difference of both phases and finally transforms a heterogeneous system into a homogeneous one. In this step, the rate of mutual diffusion depends strongly on the magnitude of the E_{AB} value. The larger E_{AB} value retards the mutual diffusion, thus leading to a delay in the copolymerization process and consequently the homogenization.

Conclusions

In this study, the effects of ester interchange reactions on the phase behavior in an immiscible polyester blend were investigated using the Monte Carlo method. An immiscible polyester blend with polydisperse polyester was successfully prepared by using the bond diagonal method and homo-ester-interchange reactions. After hetero-ester-interchange reactions were allowed to take place in the immiscible polyester blend, the formation of copolyester was examined by calculating the degree of randomness. When the degree of randomness was plotted against time at various phase separation conditions (E_{AB} = 0.05, 0.10, 0.15, and 0.20), it was revealed that the rate of copolymerization is dependent upon the magnitude of E_{AB}; i.e., at small E_{AB}, the degree of randomness increases up to unity, indicative of the formation of random copolymer, whereas the increase of the degree of randomness is stagnated at large E_{AB}. It was observed that the maximum value of $S(q,t)$ decreases with MCS, when hetero-ester-interchange reactions between two polyesters are allowed to take place. This indicates that the copolyesters formed during the ester interchange reactions have a homogenizing effect on the immiscible polyester blend. Another important feature of note is that q_{max}, where $S(q,t)$ is maximized, remains unchanged with MCS regardless of the magnitude of E_{AB}. This result indicates that the domain size does not change during the homogenization process, which has also been confirmed by the analysis of concentration profiles. Consequently, it is concluded that the homogenization of phase-separated polyester blends proceeds through the reduction of the concentration difference between two phases by ester interchange reaction without changing the domain size.

References and Notes

(1) Yamadera, R.; Murano, M. *J. Polym. Sci.* **1967**, *5*, 2259.
(2) Kotliar, A. M. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 367.
(3) Devaux, J.; Godard, P.; Mercier, J. P. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1901.
(4) McAlea, K. P.; Schults, J. M.; Gardner, K. H.; Wignall, G. D. *Polymer* **1986**, *27*, 1581.
(5) Kugler, J.; Gilmer, J. W.; Wiswe, D.; Zachmann, H.-G.; Hahan, K.; Fisher, E. W. *Macromolecules* **1987**, *20*, 1116.
(6) Montaudo, G.; Montaudo, M. S.; Scamporrino, E.; Vitalini, D. *Macromolecules* **1992**, *25*, 5099.
(7) Fernandez-Berridi, M. J.; Iruin, J. J.; Maiza, I. *Polymer* **1995**, *36*, 1357.
(8) Ha, W. S.; Chun, Y. K.; Jang, S. S.; Rhee, D. M.; Park, C. R. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 309.
(9) Birley, A. W.; Chen, X. Y. *Br. Polym. J.* **1984**, *16*, 77.
(10) Kimura, M.; Porter, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 367.
(11) Suzuki, T.; Tanaka, H.; Nishi, T. *Polymer* **1989**, *30*, 1287.
(12) Robenson, L. M. *J. Appl. Polym. Sci.* **1985**, *30*, 4081.
(13) Sariban, A.; Binder, K. *J. Chem. Phys.* **1987**, *86*, 5859.
(14) Sariban, A.; Binder, K. *Macromolecules* **1988**, *21*, 711.
(15) Sariban, A.; Binder, K. *Colloid Polym. Sci.* **1988**, *266*, 389.
(16) Sariban, A.; Binder, K. *Makromol. Chem.* **1988**, *189*, 2357.
(17) Sariban, A.; Binder, K. *Colloid Polym. Sci.* **1989**, *267*, 469.
(18) Sariban, A.; Binder, K. *Macromolecules* **1991**, *24*, 578.
(19) Brown, G.; Chakrabarti, A. *Phys. Rev. E* **1993**, *48*, 3705.
(20) Jo, W. H.; Kwon, I. H.; Huh, J.; Kim, C. Y. *Eur. Polym. J.* **1992**, *28*, 1411.
(21) Jo, W. H.; Lee, J. W.; Lee, M. S.; Kim, C. Y. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 725.
(22) Jang, S. S.; Ha, W. S.; Jo, W. H.; Youk, J. H.; Kim, J. H.; Park, C. R. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1637.
(23) Tanaka, H.; Suzuki, T.; Hayashi, T.; Nishi, T. *Macromolecules* **1992**, *25*, 4453.
(24) Binder, K.; Heermann, D. W. *Monte Carlo Simulation in Statistical Physics*, 2nd ed.; Springer-Verlag: New York, 1992.
(25) Paul, W.; Binder, K.; Heermann, D. W.; Kremer, K. *J. Chem. Phys.* **1991**, *95*, 7726.
(26) Binder, K.; Paul, W. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 1.
(27) Dotera, T.; Hatano, A. *J. Chem. Phys.* **1996**, *105*, 8413.
(28) Deutsch, H. P.; Binder, K. *J. Chem. Phys.* **1992**, *96*, 6291.
(29) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1979.
(30) Shaffer, J. S. *J. Chem. Phys.* **1994**, *101*, 4205.
(31) Shaffer, J. S. *J. Chem. Phys.* **1995**, *103*, 761.
(32) Mansfield, M. L. *J. Chem. Phys.* **1982**, *77*, 1554.
(33) Metropolis, N.; Rosenbluth, A. N.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.

(34) Chakrabarti, A.; Toral, R.; Gonton, J. D.; Muthukumar, M. *J. Chem. Phys.* **1990**, *92*, 6899.

(35) Jo, W. H.; Kim, S. H. *Macromolecules* **1996**, *29*, 7204.

(36) Kim, S. H.; Jo, W. H. *Macromolecules* **1996**, *29*, 6933.

(37) Kim, S. H.; Jo, W. H.; Kim, J. *Macromolecules* **1997**, *30*, 3910.

(38) Koenig, J. L. *Chemical Microstructure of Polymer Chains*; John Wiley and Sons: New York, 1980.

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

(40) Cotton, J. P.; Decker, H.; Benoit, B.; Farnoux, B.; Higgins, J.; Jannink, G.; Ober, R.; Picot, C.; des Cloiseaux, J. *Macromolecules* **1974**, *7*, 863.

(41) Kirste, R. G.; Kruse, W. A.; Ibel, K. *Polymer* **1975**, *16*, 120.

(42) de Vos, E.; Bellamans, A. *Macromolecules* **1975**, *8*, 651.

(43) Hashimoto, T. In *Material Science and Technology*; Cahn, R. W., Haasen, P., Kramer, E. J., Eds.; VCH: Weinheim, 1993; Vol. 12, p 251.

MA980515Z