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Miscibility-Induced Sequential Reordering in Random Copolyesters: A Monte Carlo Simulation

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ABSTRACT: Miscibility-induced sequential reordering (MISR) was investigated using a Monte Carlo simulation method in two systems, i.e., a ternary copolyester system and a binary copolyester system in the presence of a third noncondensation polymer. A homogeneous AB random copolymer/C homopolymer blend was used as an initial blend. Phase separation and ester-interchange reactions were performed simultaneously at a trial ratio of 100/1 using a one-site bond fluctuation model. MISR was monitored by calculating the number-average sequence length of each segment. In the case of the ternary copolyester system, ester-interchange reactions between segments A, B, and C were attempted under various attractive and repulsive interaction energies between the three. It was found that MISR of segment A was induced only when segment C was miscible with segment B. The more repulsive segments A and C are and the more attractive segments B and C are, the longer the sequence length of the segment A becomes. In the case of a binary copolyester system in the presence of a third noncondensation polymer, segment A or B is sequentially reordered, accompanied by phase separation of the blend, when segment C is miscible with either segment A or B, respectively. The more repulsive the interaction between segments A and C is and the more attractive the interaction between segments B and C is, the longer the sequence length of segments A and B becomes.

Introduction

It is generally well-known that ester-interchange reactions between homopolyesters in the melt produce first block copolymers and finally random copolymers.[1−6] The large increase in entropy which accompanies the transition of the block copolymer to a random copolymer is considered to be the main driving force. However, it has been reported that ester-interchange reactions can lead to sequential reordering of a random structure, i.e., the formation of block structures, under certain conditions. Lenz et al.[7−11] first reported the crystallization-induced sequential reordering (CISR) of random copolyesters via ester-interchange reactions below their melting temperatures. For example, the number-average sequence length of terephthalate units in poly(ethylene terephthalate-*co*-2-methyl succinate) containing 78.5% ethylene terephthalate units and 21.5% ethylene 2-methyl succinate units was increased from 5.3 to 6.8 when the copolymer was annealed at 220 °C for 30 h.[8] Fakirov et al.[12−14] also reported CISR in copolyesters prepared by immiscible and miscible polyester blends such as poly(ethylene terephthalate) (PET)/polycarbonate (PC), PET/polyarylate (PAr) (a copolymer of bisphenol A and an equimolar mixture of terephthalic and isophthalic acid), and poly(butylene terephthalate) (PBT)/PAr. Furthermore, they first proposed that PBT/PC/PAr and PBT/nylon 66 (PA66)/PAr terpolymers show miscibility-induced sequential reordering (MISR) when they were annealed above their melting temperature to exclude the possibility of CISR.[15]

In our previous study,[16,17] the effect of phase separation and ester-interchange reactions on the homogenization of immiscible polyester blends was investigated using a Monte Carlo simulation method. The results showed that the homogenization of the phase-separated structure of the immiscible polyester blend proceeds by ester-interchange reactions without a change in the domain size, while the concentration difference between the two phases becomes smaller. Also, when phase-separated structures were monitored until the degree of randomness (DR) reached 0.8 (DR is defined in the next section describing the model and simulation method), the results showed that the homogenization is accomplished via ester-interchange reactions over most of the polyester chains. Therefore, it is considered that the simulation method is suitable for the study of MISR in copolyesters. Fakirov et al.[12−15] used differential scanning calorimetry, X-ray measurements, and NMR[18] to monitor sequence reordering due to MISR. However, it is not always possible to systematically analyze the factors affecting the MISR in real systems, because experimental variables cannot be controlled precisely in the experiments. In this regard, computer simulation may provide a useful tool for analyzing such phenomena, because it can be carried out under controlled conditions in which experimental variables are readily factorized and can therefore yield useful results that cannot be obtained from experiment.

The purpose of the present study is to systematically analyze the conditions for MISR in a ternary copolyester system as well as a binary copolyester system in the presence of a third noncondensation polymer. To accomplish this, Monte Carlo simulations are performed using the model employed in our previous studies[16,17] under varying attractive and repulsive interaction energies. The rationale for MISR is also discussed thermodynamically.

Model and Simulation Method

The model and simulation method used in this study are detailed in our previous papers,[16,17] so only the main

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points are summarized here. The simulations were performed on a simple cubic lattice of 50 × 50 × 50 ($L_x \times L_y \times L_z$) sites with periodic boundary conditions.[19] The cubic lattice was filled with homopolymers A, B, and C at a blend ratio of 1/1/1 (v/v/v), where 60% of the lattice sites were occupied by segments. For convenience, we assume that a segment in the lattice corresponds to one Kuhn segment. The initial chain length was set at $N_A = N_B = N_C = 20$, and consequently 1250 chains of each homopolymer A, B, and C were present on the lattice. All the chains were arranged initially at randomly chosen positions with fully extended chain conformations. This initial structure was then relaxed under athermal conditions through the bond diagonal method,[20] generating self- and mutual-avoiding walks on the lattice. After the conformational state of the polymer chains reached equilibrium, ester-interchange reactions between the same kind of segments (homo-ester-interchange) were executed to prepare polymers with polydisperse molecular weight distributions (MWD). The polydispersity index of each chain was 2.0 after the system reached equilibrium. In this work, two kinds of ester-interchange reactions (i.e., end attack and bond flip) corresponding to alcoholysis (or acidolysis) and to a direct ester−ester interchange reaction, respectively, were executed as suggested by Mansfield.[21]

After polydisperse polymer blends were prepared, hetero-ester-interchange reactions between polymers A and B were performed to prepare AB random copolymers (A-*r*-B) under the condition of $E_{AB} = 0.15$, $E_{AC} = 0$, and $E_{BC} = 0$ ($E_{ij} = \epsilon_{ij}/k_BT$ where ϵ_{ij} is a pair interaction energy between segments i and j, k_B is the Boltzmann constant, and T is the absolute temperature). Although polymers A and B are now immiscible, they were homogenized by ester-interchange reactions as shown in our previous study,[17] which will be discussed in detail later. This A-*r*-B/C blend was used as an initial blend. An ester-interchange reaction was then attempted once every 100 segment movements on average, and homo- and hetero-ester-interchange reactions were assumed to have the same probability of occurring as long as the geometric condition was satisfied.

The sequential reordering of each type of segment was evaluated by calculating its number-average sequence length, i.e., $\langle L_A \rangle$, $\langle L_B \rangle$, and $\langle L_C \rangle$, which denote the number-average sequence length of segments A, B, and C, respectively. The degree of randomness (DR) of the A-*r*-B copolymer was calculated by using the following relation:[22]

$$\mathrm{DR} = 1/\langle L_A \rangle + 1/\langle L_B \rangle \qquad (1)$$

Theoretically, the values of the DR vary from 0 for a homopolymer with infinite chain length to 1.0 for completely random copolymer. As the time unit, a Monte Carlo step (MCS) was defined as one attempted trial per segment to move or to react on the average. Phase separation was monitored by calculating the collective structure factor $S(q,t)$, which has often been used to investigate the time evolution of long-range ordering. To monitor the phase separation in the A-*r*-B/C blend, the time-dependent collective structure factors $S(q,t)$ were calculated at equal time intervals and spherically averaged as described in our previous papers.[16,17] To improve the statistics of the results, three independent runs were performed for each case, and the results were reported by averaging the data from three independent runs.

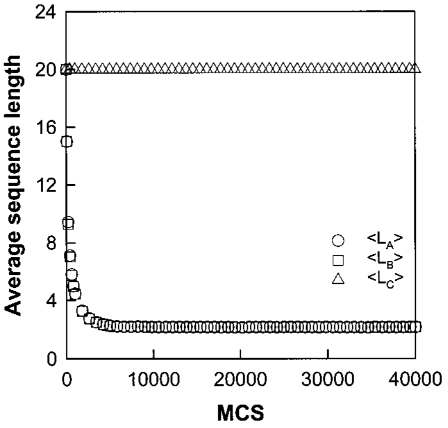

Figure 1. Changes of $\langle L_A \rangle$ and $\langle L_B \rangle$ with Monte Carlo step during the preparation of an initial A-*r*-B/C blend.

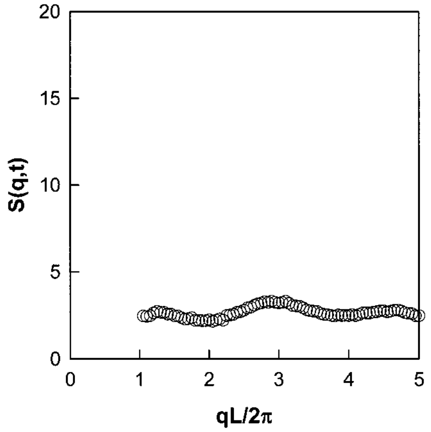

Figure 2. Collective structure factor $S(q,t)$ of an A-*r*-B/C blend prepared with $E_{AB} = 0.15$, $E_{AC} = 0$, and $E_{BC} = 0$.

Table 1. Effect of Interaction Energies on $\langle L_A \rangle$, $\langle L_B \rangle$, and $\langle L_C \rangle$ When Ester-Interchange Reactions between A, B, and C Segments Are Attempted; Number-Average Sequence Length of Each Segment Is Taken after 30 000 MCS

interaction energies				
E_{AC}	E_{BC}	$\langle L_A \rangle$	$\langle L_B \rangle$	$\langle L_C \rangle$
0.15	0.15	1.60	1.60	1.60
−0.15	−0.15	1.52	1.52	1.39
0.15	0.0	1.75	1.53	1.53
0.15	−0.05	2.02	1.55	1.55
0.15	−0.15	3.05	1.63	1.63
0.15	−0.20	3.75	1.65	1.65
0.20	−0.20	4.55	1.66	1.71

Results and Discussion

Preparation of a Miscible A-*r*-B/C Blend. Fakirov et al.[15] reported that randomized PBT/PC/PAr and PBT/PA66/PAr ternary copolymers were sequentially reordered due to transreactions in the direction of an entropy decrease when these copolymers were annealed for a prolonged period in the melt state. Those ternary copolymers were prepared by adding PBT and PAr to PC/PAr and PBT/PA66 random copolymers as the third polymer, respectively. They concluded that the driving force for reordering is related to the miscibility of PBT and PAr in any composition. In these two systems, both PC/PAr and PBT/PA66 were immiscible. In this study, the conditions for MISR in a ternary copolyester system and in a binary copolyester system in the presence of a third noncondensation polymer were investigated using the Monte Carlo simulation. The interaction energies

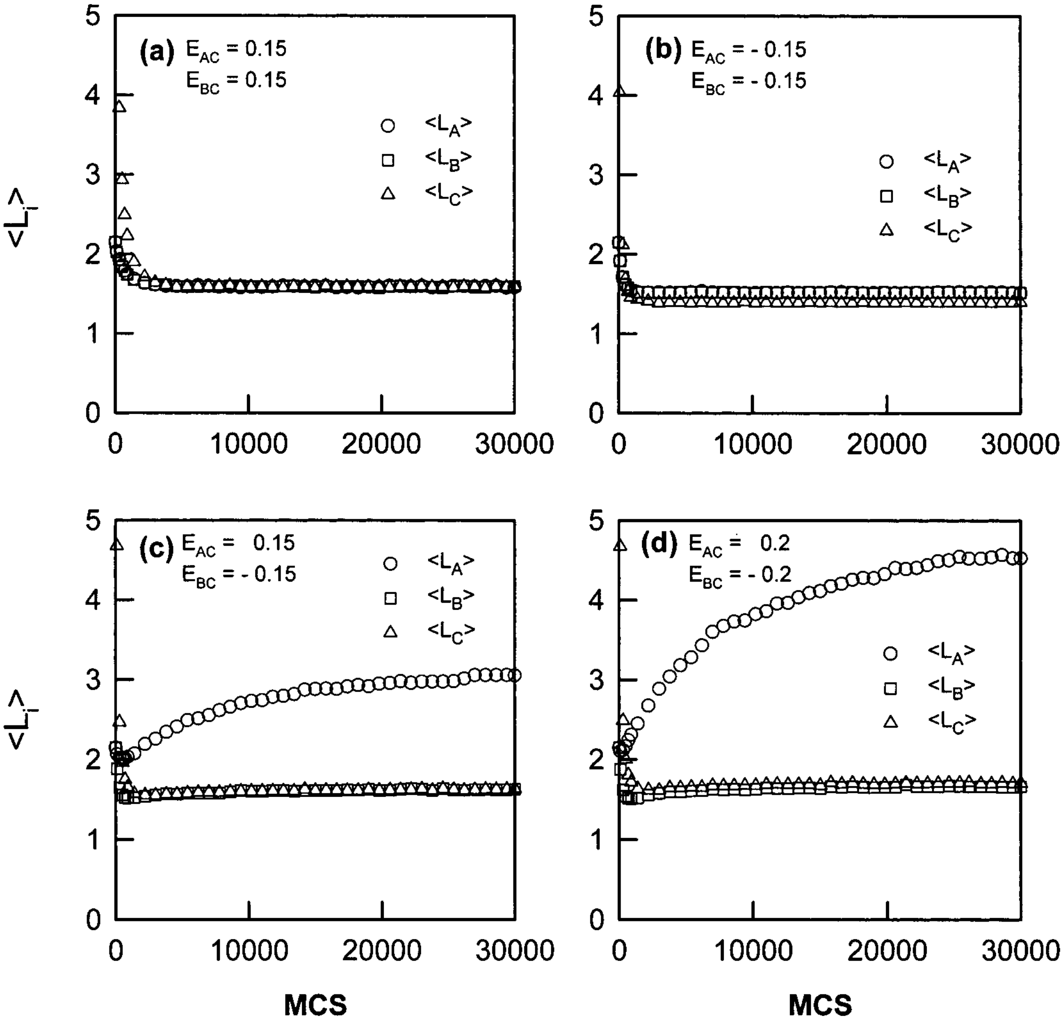

Figure 3. Change of the number-average sequence length $\langle L_i \rangle$ in an A-*r*-B/C blend with Monte Carlo step when ester-interchange reactions between A, B, and C segments are performed under various interaction energies.

(E_{AB}, E_{AC}, and E_{BC}) between segments A, B, and C were systematically varied in order to examine the effect of interaction energy on the MISR. To directly compare simulation results with experimental ones, a homogeneous blend of polydisperse homopolymers A, B, and C at a blend ratio of 1/1/1 (v/v/v) was first prepared, and then ester-interchange reactions between homopolymers A and B were allowed to occur under the condition of $E_{AB} = 0.15$, $E_{AC} = 0$, and $E_{BC} = 0$, resulting in a blend of A-*r*-B/C. The values of $\langle L_A \rangle$ and $\langle L_B \rangle$ decreased rapidly with MCS while the value of $\langle L_C \rangle$ remained constant at 20, because ester-interchange reactions between homopolymers A and B were only allowed to occur, as shown in Figure 1. After 40 000 MCS, the values of $\langle L_A \rangle$ and $\langle L_B \rangle$ reached 2.15 and the DR was 0.93. When $S(q,t)$ was plotted against the scattering vector for the A-*r*-B/C blend taken after 40 000 MCS, it revealed that the scattering intensity did not show q dependence, indicating the initial blend was a homogeneous mixture, as shown in Figure 2.

According to the Flory–Huggins theory,[23] the free energy of mixing per unit volume of a binary polymer system is described by the well-known relation

$$\Delta G/RT = (\phi_1/n_1) \ln \phi_1 + (\phi_2/n_2) \ln \phi_2 + \chi_{\text{blend}}\phi_1\phi_2 \quad (2)$$

where ϕ_i and n_i are the volume fraction and the degree of polymerization of components i, respectively. For the case of an A_y-*r*-B_{1-y}/C binary system, where A_y-*r*-B_{1-y} is a copolymer with the composition y of A monomer, and C is a homopolymer, the net interaction parameter χ_{blend} is given by the following relation:[24–26]

$$\chi_{\text{blend}} = y\chi_{AC} + (1 - y)\chi_{BC} - y(1 - y)\chi_{AB} \quad (3)$$

where y is the volume fraction of segment A in the A-*r*-B copolymer and χ_{ij} is the interaction parameter between segments i and j. Examination of eq 3 tells us that it is possible for χ_{blend} to become negative under a proper condition even if all segmental interaction parameters are positive. Therefore, the miscibility of the A-*r*-B/C blend prepared under the condition of $E_{AB} = 0.15$, $E_{AC} = 0$, and $E_{BC} = 0$ can also be explained by eq 3.

MISR in a Ternary Copolyester System. Ester-interchange reactions between segments A, B, and C were then allowed to occur in the A-*r*-B/C blend under various attractive and/or repulsive interaction energies. It was assumed that all of the homo- and hetero-ester-interchange reactions occur with the same probability. When segments B and C experience an attractive interaction, the blend becomes more miscible, as can be seen from eq 3. However, since all types of ester-interchange reactions between segments A, B, and C had the same probability, it is expected that the blend would be homogenized irrespective of the interaction energies.

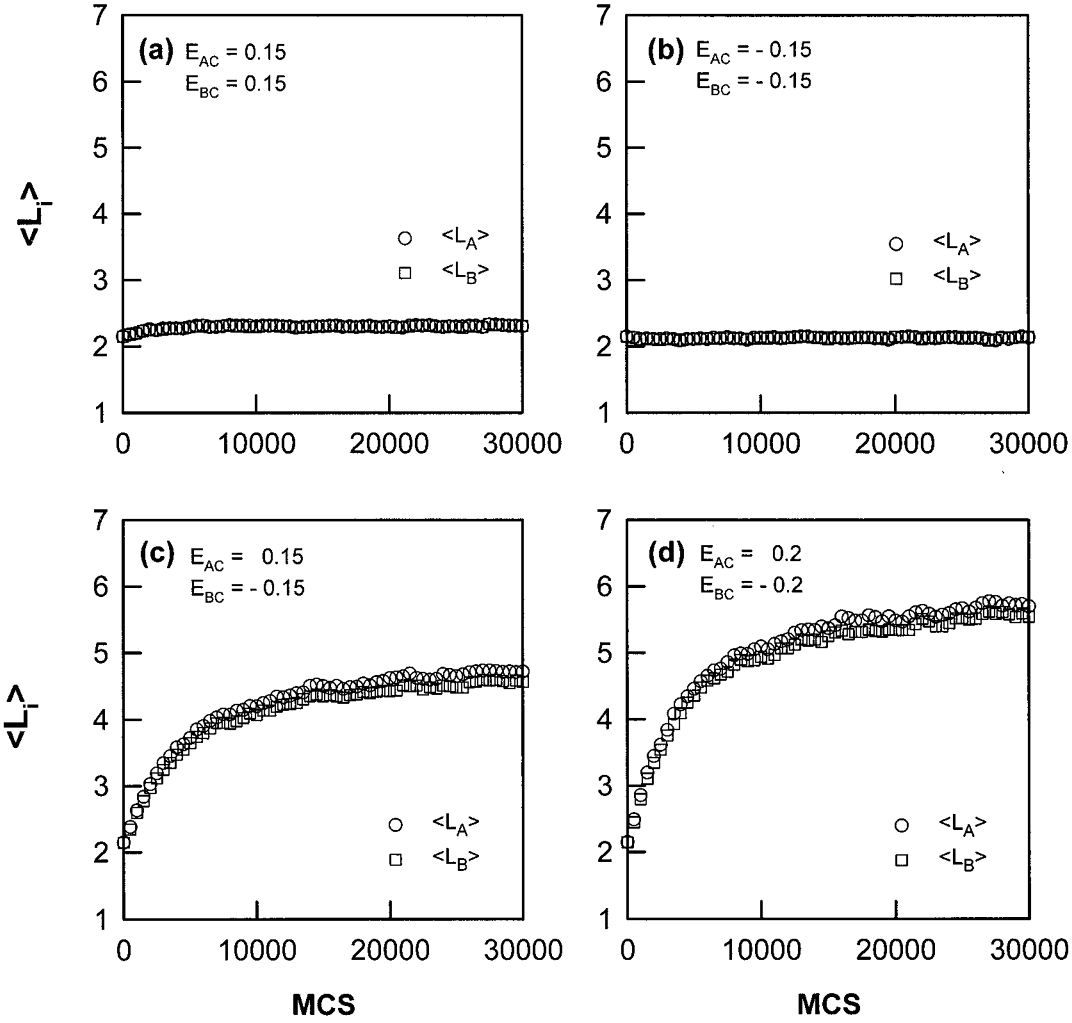

Figure 4. Change of the number-average sequence length in an A-*r*-B/C $\langle L_i \rangle$ blend with Monte Carlo step when ester-interchange reactions between A and B segments are performed under various interaction energies.

When segment C is miscible only with segment B, $\langle L_A \rangle$ increases while $\langle L_B \rangle$ and $\langle L_C \rangle$ decrease rapidly and level off with time, as shown in Figure 3c,d, indicating that only segment A is sequentially reordered. The number-average sequence lengths taken after 30 000 MCS are listed in Table 1. When the values of E_{AC} and E_{BC} are both positive (repulsive) or both negative (attractive), the ternary copolymers are randomized, as shown in Figure 3a,b. The more repulsive the interaction between segments A and C is and the more attractive interaction between segments B and C is, the longer the sequence length of segment A becomes. It is concluded that the attractive interaction energy between segments B and C is a driving force for MISR. However, Fakirov et al.[15] observed that all of components were sequentially reordered in the randomized PBT/PC/PAr and PBT/PA66/PAr ternary copolymers, when annealed at high temperature for longer than 20 h, although the glass transition of PAr was not observed. Here PC, PAr, and PBT in PBT/PC/PAr ternary copolymer correspond to A, B, and C, respectively, and PA66, PBT, and PAr in PBT/PA66/PAr ternary copolymer correspond to A, B, and C, respectively. In our simulation, however, when segment C is miscible only with segment B, $\langle L_B \rangle$ and $\langle L_C \rangle$ increased slightly after a rapid decrease at the initial stage and then leveled off with time. This slight increase is not sufficient to completely explain sequential reordering of segments B and C observed in Fakirov et al.'s experiment.

The discrepancy between the simulations and experiment may arise from other factors ignored in simulation. In the randomized PBT/PC/PAr ternary copolymers, PBT/PAr and PC/PAr have a common chemical moiety in their repeating units. The repeating unit of PAr can be formed via interchange reactions between PBT and PC units. As a result, in the experiment a blocky structure can be induced via interchange reactions in the PBT/PC/PAr ternary copolymer irrespective of MISR. Moreover, in the case of the PBT/PA66/PAr ternary copolymer, new repeating units, such as butylene adipate and hexamethylene terephthalamide units, are formed by interchange reactions, which can affect MISR. However, in the simulations these segmental changes were not considered while only the miscibility effect was taken into account.

It is also possible that different reaction conditions may be one of the reasons for the discrepancies. In the experiment, PBT was mixed with PC/PAr random copolymer to prepare the PBT/PC/PAr ternary copolymer, but PBT was not completely randomized even after annealing for 500 min at 280 °C, whereas segment C, corresponding to PBT, was completely randomized in the simulations. In the case of PBT/PA66/PAr ternary copolymer, there are ester and amide bonds in the

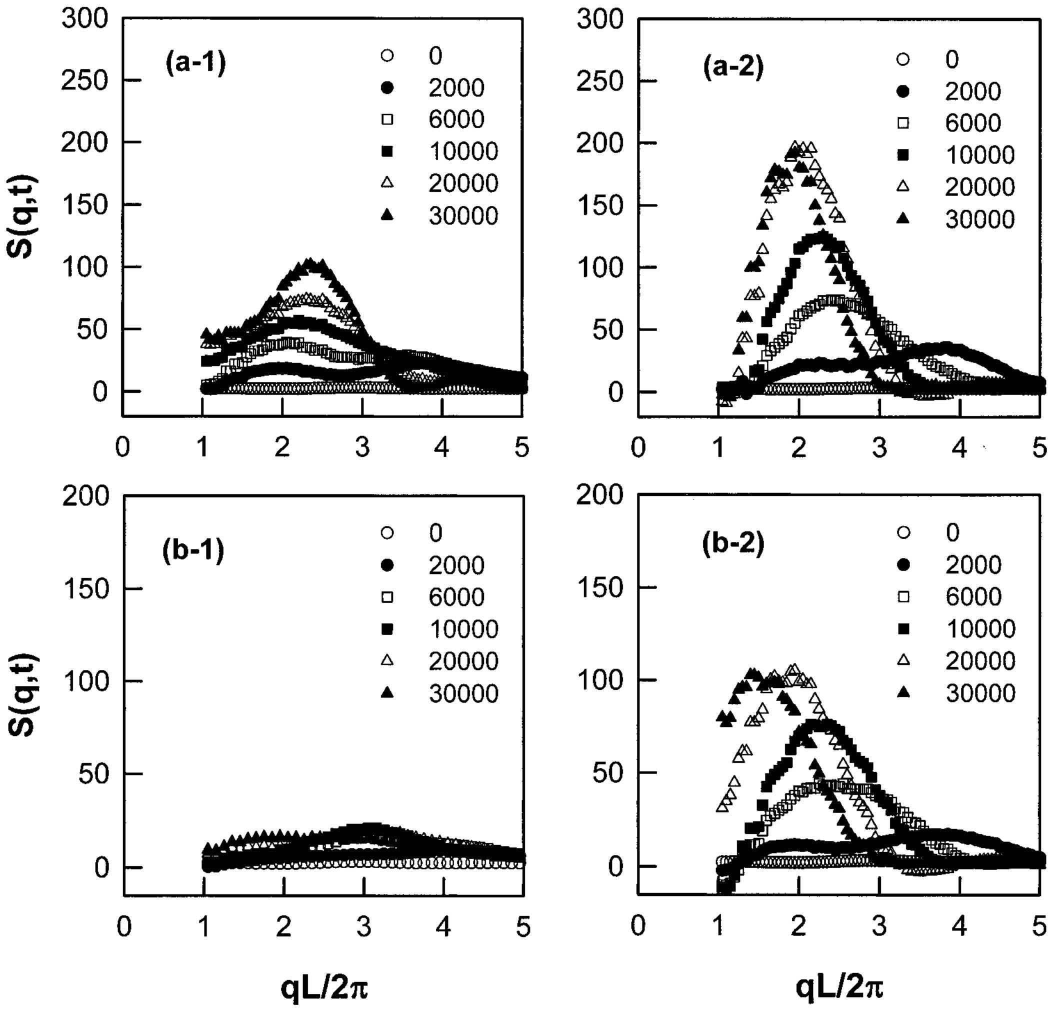

Figure 5. Time evolution of collective structure factor $S(q,t)$. The interaction energies of $E_{AC} = 0.15$ and $E_{BC} = -0.05$ are given for (a-1) and (a-2), and the energies of $E_{AC} = 0.15$ and $E_{BC} = -0.15$ are given for (b-1) and (b-2). The numbers 1 and 2 behind a and b in figure numbering denote the case without (1) and with (2) ester interchange reactions between segments A and B.

random copolymer. In the simulations, all segments had the same reactivity, but in the experiment, the reactivity of interchange reactions may be different from one another. Indeed, we showed in a previous report that differences in reactivities of ester-interchange reactions between segments can induce a blocky structure in even miscible polyester blends.[27]

MISR in a Binary Copolyester in the Presence of a Third Noncondensation Polymer. The MISR in an A-*r*-B copolyester in the presence of a third noncondensation polymer (homopolymer C) was also simulated under various attractive and repulsive interaction energies. Since the third component was not a condensation polymer, no ester-interchange reactions between segments C and A and between C and B are allowed. Ester-interchange reactions between segments A and B were performed with the same probability.

The variations of $\langle L_A \rangle$ and $\langle L_B \rangle$ with time for various interaction energies are shown in Figure 4, and the number-average sequence lengths taken after 30 000 MCS are listed in Table 2. Since the homopolymer C is not a condensation polymer, the value of $\langle L_C \rangle$ remains constant at 20. When segment C is miscible only with segment B, the values of $\langle L_A \rangle$ and $\langle L_B \rangle$ increase rapidly with time and then level off after 30 000 MCS, as shown in Figure 4c,d, indicating that both segments A and B were sequentially reordered. The value of $\langle L_A \rangle$ was slightly larger than that of $\langle L_B \rangle$, because segment B was miscible with segment C. As the interaction between segments A and C becomes more repulsive while the interaction between segments B and C becomes more attractive, the sequence length of segments A and B becomes longer.

Table 2. Effect of Interaction Energies on $\langle L_A \rangle$ and $\langle L_B \rangle$ When Ester-Interchange Reactions between A and B Segments Are Attempted; Number-Average Sequence Length of Each Segment Is Taken after 30 000 MCS

interaction energies			
E_{AC}	E_{BC}	$\langle L_A \rangle$	$\langle L_B \rangle$
0.15	0.15	2.31	2.31
−0.15	−0.15	2.13	2.13
0.15	0.0	2.70	2.63
0.15	−0.05	3.38	3.26
0.15	−0.15	4.73	4.58
0.15	−0.20	5.31	5.25
0.20	−0.20	5.71	5.58

When segment C is miscible with either segment A or B, the A-*r*-B/C blend becomes more miscible, as expected from eq 3. Parts a-1 and a-2 of Figure 5 show the time evolution of $S(q,t)$ plotted against the scattering vector at given interaction energies of $E_{AC} = 0.15$ and $E_{BC} = -0.05$ and $E_{AC} = 0.15$ and $E_{BC} = -0.15$, respectively, when ester-interchange reactions between segments A and B are not allowed to occur. In the case of $E_{BC} = -0.05$, a distinct maximum of $S(q,t)$ was observed, indicating a phase-separated structure was developed. However, in the case of $E_{BC} = -0.15$, the scattering intensity does not show a q dependence, indicating that the blend is almost a homogeneous mixture. On the other hand, when ester-interchange reactions between segments A and B are allowed to occur under the conditions of $E_{AC} = 0.15$ and $E_{BC} = -0.05$ and $E_{AC} = 0.15$ and $E_{BC} = -0.15$, as shown in parts b-1 and b-2 of Figure 5, respectively, a scattering maximum (S_{max}) is distinctly observed in both cases, and its value increases with time. When Figure 4c is compared with Figure 5b-2, it is realized that S_{max} reaches a maximum as the value of $\langle L_A \rangle$ and $\langle L_B \rangle$ approaches respective equilibrium value. This indicates that phase separation is induced as the structure of copolymer changes from random copolymer to block copolymer.

It is clearly shown in this study that the attractive interaction energy between segments B and C is a driving force for MISR in both cases. To more clearly understand this phenomenon, χ_{blend} was monitored as a function of time in a binary copolyester in the presence of a third noncondensation polymer with/without ester-interchange reactions between segments A and B. According to the mean-field approximation, the χ_{blend} for a A_y-r-B_{1-y}/C blend can be related to the reduced interaction energies as follows:[28,29]

$$\chi_{blend}\phi_1\phi_2 = (1/N)\{E_{AB}N_{AB} + E_{AC}N_{AC} + E_{BC}N_{BC} - \phi_1 E_{AB}(N_{AB})_{co,y}\} \quad (4)$$

where the subscripts 1 and 2 designate the A-r-B and C polymers in the mixture, respectively, and N_{ij} is the equilibrium overall number of heterocontacts between segments i and j. The average number of heterocontacts $N_{ij}(E_{ij})$ is a function of the reduced interaction energy E_{ij}. The first three terms on the right-hand side of eq 4 are accounted for by interactions between segments in the mixture, while the last negative term is taken into account by considering the reference state of the pure copolymer on a lattice under the same condition as used in the mixture. In eq 4, $(N_{AB})_{co,y}$ is the number of heterocontacts in the copolymer with the copolymer composition y, and N is the total number of sites in the system.

Parts a and b of Figure 6 show the changes of homo- and heterocontacts per segment without and with ester-interchange reactions between segments A and B, respectively, at a given value of $E_{AC} = 0.15$ and $E_{BC} = -0.15$. When MISR was induced via ester-interchange reactions, larger values of N_{AA}, N_{BC}, and N_{BB} and smaller values of N_{AB} and N_{AC} were obtained, as shown in Figure 6b. In this case, the value of χ_{blend} calculated from eq 4 is much smaller than that obtained in the case where ester-interchange reactions do not occur. Since ester-interchange reactions do not change the degree of polymerization, the free energy of mixing calculated from eq 2 decreases as the MISR proceeds. This is because the number of homocontacts per segment increases as the MISR proceeds, indicating that homo-ester-interchange reactions become more favorable. Consequently, MISR is induced by a decrease in the free energy of mixing, and as a result phase separation occurs in the blend.

Conclusions

Conditions for MISR were investigated using a Monte Carlo simulation method in two cases: one is a ternary copolymer system, and the other is a binary copolyester in the presence of a third noncondensation polymer. In the case of a ternary copolyester system, when segment C is miscible only with segment B, the value of $\langle L_A \rangle$ increases while the values of $\langle L_B \rangle$ and $\langle L_C \rangle$ decrease rapidly and level off with MCS, indicating that only segment A is sequentially reordered. The more repulsive the interaction between segments A and C is and/or the more attractive the interaction between segments B and C is, the longer the sequence length of segment A becomes. In the case of a binary copolyester system in the presence of a third noncondensation polymer, where segment C is miscible with either segment A or B, the values of $\langle L_A \rangle$ and $\langle L_B \rangle$ increase rapidly and level off after 30 000 MCS, indicating that both segments A and B are sequentially reordered. This reordering is accompanied by phase separation of the blend. The more repulsive segments A and C are and the more attractive segments B and C are, the longer the sequence lengths of the segments A and B are. Under these conditions, the number of homocontacts increases, and therefore homo-ester-interchange reactions contribute to decrease the free energy of mixing. It is concluded that MISR in this case is induced by a decrease in the free energy of mixing in the system.

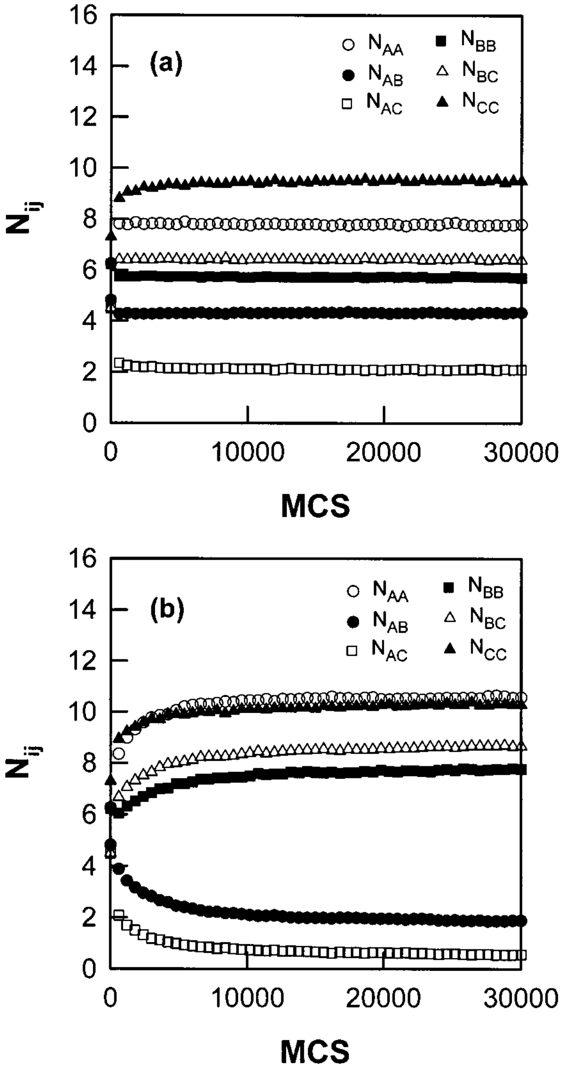

Figure 6. Changes of homo- and heterocontacts per segment as a function of time (a) without and (b) with ester-interchange reactions between A and B segments, when $E_{AC} = 0.15$ and $E_{BC} = -0.15$ are given.

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