Effects of Reaction Condition on Microphase-Separated Structure in Sequential IPN : A Monte Carlo Approach

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INTRODUCTION

Generally polymer blends show multiphase morphology due to the well-known thermodynamic incompatibility. In the case of IPN, however, phase separation is not as extensive as other multicomponent materials, since the phase separation resulting from chain growing is restricted by cross-linking. The micro phase structure of IPN depends on both the thermodynamic miscibility of constituent networks and the kinetic condition of cross-linking reaction[1]. Since it is not easy to control kinetic parameters for network formation, systematic study on the effect of cross-linking condition on micro-structure of IPN is difficult. In our previous work,[2] using computer simulation technique, we found that the phase separation is more restriced as the cross-linking reaction rate increases, under the condition that the cross-linking rate is lower than polymerization rate. In the early stage of reaction, however, the system which has higher cross-linking reaction rate shows more phase-separated sturcture. In this study, we investigate how the reactivity of cross-linking agent affects the micro-phase separated structure of sequential IPN, with various reaction condition using Monte Carlo technique.

MODEL AND SIMULATION METHOD

The systems considered in our simulation are 3D simple cubic lattice with size L×L×L, L=50, filled with chains of two species called A and B at a volume fraction of 0.46. The composition ratio of A and B in the mixture are fixed at 50/50 and the interaction between A and B is repulsive(ε_{AB} = 0.2). The interaction energies between the same molecules are assumed to be zero. The bond fluctuation algorithm[3] has been used for the simulation of polymer chain dynamics. In this lattice Monte Carlo simulation, each effective monomer occupies all eight corners of a unit cell of the simple cubic lattice. The bond length between consecutive mononers varies from 2 to $\sqrt{10}$ out of $\sqrt{8}$.

To describe the formation process of sequential IPN, we start from polymer network A swollen by monomer B with cross-linking agents randomly distributed at the mixture. Polymerization and cross-linking reaction proceed simultaneously. In the case of polymerization, a fixed number of monomer sites is activated. When activated monomer site contacts with a non-activated monomer site a new bond is formed between the activated monomer site and the non-activated monomer site with probability P_{poly}. The activated monomer loses activity at the same time the non-activated monomer gains activity. In the case of cross-linking reaction, a cross-linking agent forms new bond with monomer site in one of the six nearest coordinates with probability P_{cross}.

To investigate the evolution of the long range ordering, the collective structure factor of an L×L×L lattice is calculated. To improve the statistics of the structure factor we perform the standard spherical average in $\vec{q}$ space[4].

RESULTS AND DISCUSSION

In this simulation, we fixed the total number of cross-linking agents at 4 per 30 monomer sites and polymerization probability P_{poly} at 0.002. Figure 1 shows that the collective structure factor profiles for the simulated model with various cross-linking reaction probability. It is observed that the maximum peak of structure factor appears for all the case at 150000 MCS after the reaction beginning. It is also observed that in the cases of lower cross-linking rate, structure factor maximum increases with decreasing the cross-linking reaction probability, and that the wave vector, q for maximum structure factor shifts lower with decreasing the cross-linking reaction probability. When cross-linking rate is higher than polymeriztion rate, however, structure factor profiles show similar shape.

To investigate the effect of cross-linking on the phase separation, we start cross-linking reatction with delayed time, t_{cross}, after polymerization begins. The result is shown in Figure 2. It is observed that when t_{cross} exceeds the critical time the structure factor maximum does not decrease any more. From this result, it is concluded that the cross-linking facilitate the phase separtion in the early stage of reaction.

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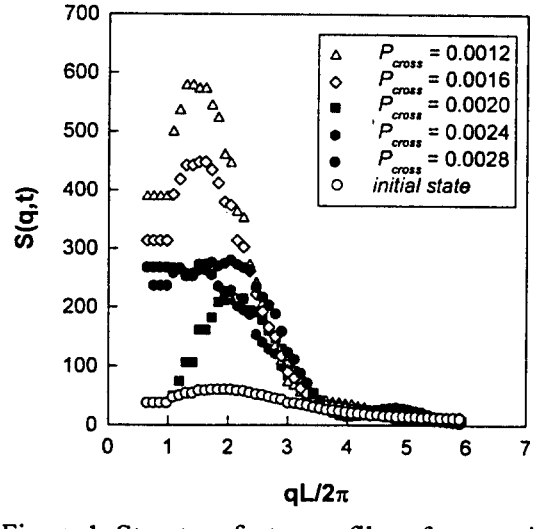

Figure 1. Structure factor profiles of sequential IPN(A/B) model for various cross-linking reaction probability.

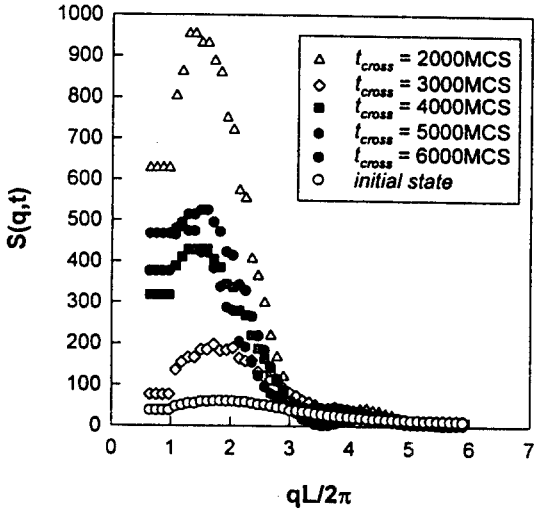

Figure 2. Structure factor profiles of sequential IPN model ,where the cross-linking reaction starts at t_{cross}.