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Sequence-Length Segregation during Crystallization and Melting of a Model Homogeneous Copolymer

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Introduction

Experiments on the crystallization of ethylene-based copolymers indicate that comonomers tend to be excluded from crystalline regions formed during crystallization of statistical copolymers.[1−3] In a recent publication,[4] we have shown that this behavior can be reproduced in simulations using a simple lattice model for a statistical-copolymer system. The segregation manifests itself as a sequence segregation in homogeneous copolymers and a molecular segregation in heterogeneous copolymers. Nevertheless, it has been suggested that the segregation of monomers and comonomers during crystallization of a statistical copolymer actually reflects a segregation of monomer sequences of different *lengths*.[5,6] Possible implications of such sequence-length segregation for crystallization and melting of statistical copolymers have been widely discussed, for example in refs 7−9. We further proposed a pair of master cooling and heating curves of a statistical copolymer that reflect the characteristics of the monomer-sequence-length distribution.[4] However, thus far, there exists no direct experimental information concerning the length segregation during crystallization because it is not straightforward to measure the sequence-length distributions present in the crystalline and amorphous phases. In the present report, we focus our attention on the phenomenon of sequence-length segregation, using the same simulation approach by which the essential features of phase transitions of statistical copolymers have been reproduced.

Simulation Techniques

We chose a slightly alternating homogeneous copolymer system with the mole fraction of comonomers 0.24 from the copolymers studied in ref 4. This mole fraction is located in the middle of the comonomer-concentration range. The sequence-length distribution is expected to be wide in this system. In more details, the system was constructed with 1920 chainlike lattice polymers, each containing 128 units, in a cubic box with a linear size of 64. The total occupation density is as high as 0.9375 to represent a bulk polymer system. The sequence of monomers and comonomers along the chains was defined in analogy to a continuous copolymerization process of ethene and 1-octene using a vanadium-based Ziegler−Natta catalyst. Figure 1 shows the monomer-sequence-length distribution as a result of the simulated copolymerization process. The distribution agrees well with theoretical predictions for the specific set of chain-propagation parameters. The top of the sequence-length distribution belongs to single monomers, reflecting the tendency of slightly alternating. If the short noncrystallizable sequences containing one monomer (or less) are excluded in our estimation, the number-averaged length of crystallizable sequences will be 4.6. In our simulations, we employed the microrelaxation model, which performs single-site jumping accompanied by partial sliding diffusion of the chains in the cubic lattice with periodic boundary conditions. The jumps avoid both double occupancy and bond crossing, and in this way, the model accounts for the fact that polymer chains cannot intersect. The driving force for the crystallization of monomer sequences is the attraction E_p between adjacent (but nonbonded) parallel monomer−monomer bonds. Metropolis sampling was implemented with a potential energy penalty pE_p, where p is the net decrease in the number of parallel-packing pairs of monomer bonds. In general, other interactions could be included in the algorithm, such as a potential energy penalty for chain bending or a potential energy penalty to form adjacent monomer−comonomer site-to-site pairs. However, for the sake of simplicity, we assumed that the chains were fully flexible and that the mixing between monomers and comonomers was athermal. To mimic the behavior of ethylene-based copolymers with comonomers such as 1-octene, we assumed that comonomers are excluded from the crystallites during sliding diffusion of the chains. This implies that we reject sliding-diffusion trial moves that would result in a moving of a comonomer in the "crystalline" region (i.e., along a monomer bond that is adjacent to more than one parallel monomer bond).

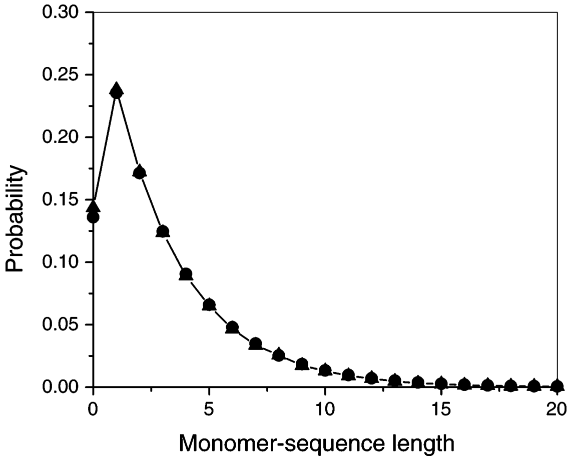

Figure 1. Number distributions of monomer-sequence length generated by a simulated copolymerization process (triangles) for a slightly alternating homogeneous copolymer with the comonomer mole fraction of 0.24, in comparison with the theoretical probabilities (spheres) of generating a monomer-sequence length of n given by $P_{21}P_{11}^{n-1}P_{12}$ for $n > 0$ and by P_{22} for $n = 0$. Here, $P_{11} = 0.727$, $P_{12} = 0.273$, $P_{21} = 0.864$, and $P_{22} = 0.136$ are the chain-propagation probabilities. See ref 4 for the details.

To prepare the initial simulation system, we let the polymer chains relax to random coils at the infinite temperature ($1/T = 0$). Subsequently, we initiated the cooling process from $T/E_p/k_B = 3.0$ to 1.0 and then the heating process back to 3.24. The temperature-scanning program was steps of 0.02, each step having a "duration"

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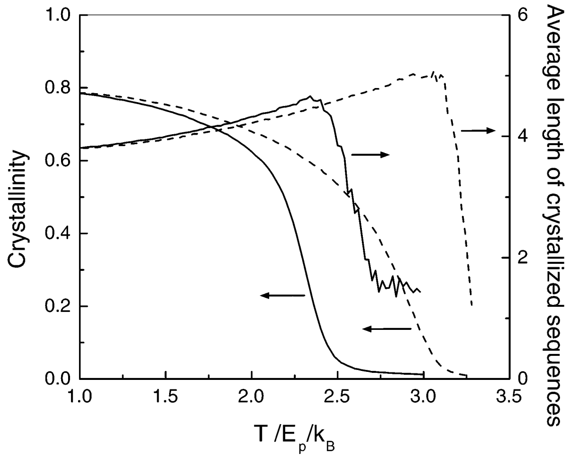

Figure 2. Crystallinities and average lengths of crystallized sequences as a function of reduced temperature on cooling (solid lines) and subsequent heating (dashed lines) for a slightly alternating copolymer with the comonomer mole fraction of 0.24.

of 300 Monte Carlo (MC) cycles. Here, one MC cycle is a trial move per chain unit summed over the whole system. At each temperature step, the first 100 MC cycles were discarded to eliminate fast transient effects. The reported data were averaged over the remaining 200 MC cycles. To monitor phase transitions, we traced the crystallinity during temperature scanning. The crystallinity was defined as the fraction of monomer bonds having more than five parallel neighbors of monomer bonds. The total number of monomer bonds in the system is 134 806. This definition of crystallinity leads to higher values than found in experiments.[4,10] Furthermore, a monomer sequence was considered to be crystalline if more than half of its monomer bonds were satisfying the crystallinity criterion defined above. During cooling and subsequent heating, we traced the number-averaged length of crystallized sequences to detect the possible sequence-length segregation.

Results and Discussion

Figure 2 shows the results of both the crystallinity and the average length of crystallized sequences. The crystallinity curves indicate a significant hysteresis between crystallization and melting. The average length of crystallized sequences decreases with the temperature when $T/E_p/k_B < 2.4$. It increases back as the temperature is increased until $T/E_p/k_B \simeq 3.1$. At high temperatures, where the crystallinity is appreciable, the average lengths of crystallized sequences are larger than the value of 4.6, which is the mean value of all the crystallizable sequences. At low temperatures, shorter crystallized sequences dominate in phase transitions. These results clearly demonstrate a reversing sequence-length selection during crystallization and melting.

We note, however, that at the early stage of crystallization (crystallinity less than 20%) the average sequence length rises but not as sharp as expected. The slowdown can be attributed to the criterion of half sequence length applied to the crystallized sequences. At an early stage of crystallization, relatively short sequences have priority to satisfy this criterion and result in a gradual increase in the average length of crystallized sequences. The similar reason also holds true for the gradual drop-off at the end of melting during heating.

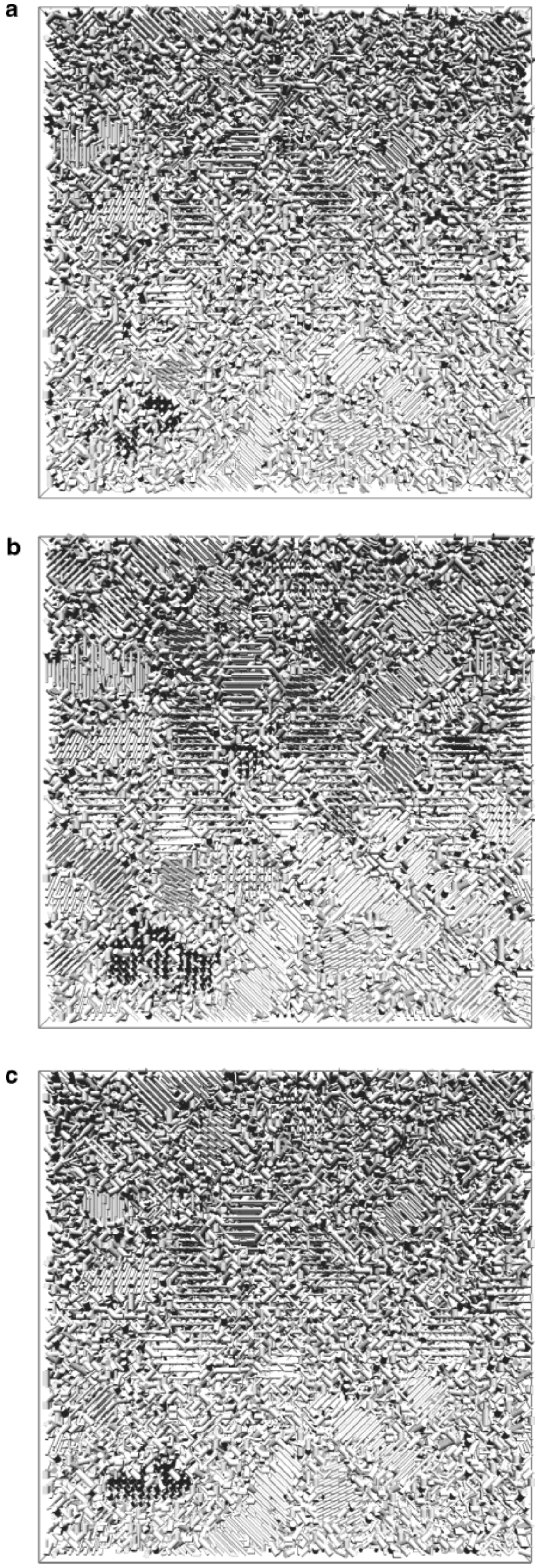

Figure 3. Snapshots of crystallite morphologies of the slightly alternating copolymer in a cubic lattice with periodic boundary conditions at the reduced temperatures of (a) 2.3 on cooling, (b) 1 after cooling, and (c) 2.8 on the subsequent heating. The sample and the temperature scanning program are the same as in Figure 2. All the polymer bonds are drawn in cylinders, and the bonds containing comonomer units have double thickness.

The morphological evolution of polymer crystallites during these crystallization and melting was further studied. We found that the crystallites that form at an early stage of cooling (see Figure 3a) are almost the same as those surviving the longest on heating (see Figure 3c). This result becomes more clear if we compare them with the crystal morphology at the lowest temperature (see Figure 3b). New crystallites that formed at a late stage of cooling disappear at an early stage of heating. Since longer sequences tend to crystallize and melt at relatively high temperatures, this result implies that the sequences with different lengths distribute in separable regions of crystallites. This observation evidences our proposition about the master melting and crystallization curves of statistical copolymers reflecting the sequence-length distribution. In addition, we found that, during heating, there is no significant thickening of surviving crystallites. This agrees with the experimental observations about constant thickness on heating[11] and about local annealing[12] of copolymer crystallites. The absence of thickening suggests that the thickness of lamellae is constrained by the presence of comonomers on the polymer chains and implies that the annealing effect should be attributed to the perfection of poorly developed crystallites.

Several books offer reviews on the existing equilibrium theories of sequence-length segregation.[13,14] Flory-type theories assumed an equilibrium selection of randomly distributed crystallizable sequences in the liquid phase. A one-to-one correspondence of crystallite thickness to a critical sequence length was implied, depending only on the crystallization temperature. Sequences of the lengths longer than the critical value were supposed to crystallize without chain folding.[15,16] However, the diffusion of polymer chains is difficult in a viscous and crystallizing liquid. Therefore, a complete selection of sequence lengths at the crystal growth front will never be realized. In addition, chain folding has hardly been considered in the crystallization theories of statistical copolymers. Actually, to conserve the lamellar morphology, chain folds must coexist with dangling ends (loops, tied molecules, cilia) on the lamellar surfaces, especially when the dangling ends are constrained to crystallize by the comonomers. This is because those dangling ends creat an overcrowding problem on the lamellar surface. This problem also exists in our simulations because each dangling end occupies more than one lattice site in the section area of crystalline stems, while the connecting crystalline stem occupies only one lattice site in this area. In Figure 3a, the lengths of crystalline stems are fairly constant around 4.7 chain units, close to the mean value of crystallizable sequences. This implies that the crystallized sequences of their lengths longer than the average may perform chain folding and hence serve to the occurrence of the lamellar morphology. The lamellar crystallites still occur at low temperatures (see Figure 3b), implying the residue of long sequences in the liquid and the incompleteness of sequence-length segregation.

In summary, on the basis of molecular simulations, we showed a direct evidence of sequence-length segregation during crystallization and melting of a homogeneous copolymer. Such a segregation is driven by the crystallization but cannot be completed due to the kinetic and morphological restrictions, reflecting the irreversible nature in the behaviors of (co)polymer crystallization.

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