Cocrystallization in Binary Blends of Crystalline-amorphous Diblock Copolymers

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It is well known that homopolymer mixtures from the same homologous series, differing sufficiently in length, undergo fractionated crystallization. In some instances, however, the long and short chains crystallize into the same crystalline lamellae leading to cocrystallization. The cocrystallization observed in such homopolymer mixtures is a kinetically driven process which takes place under nonequilibrium conditions.

Recently we observed that PEO blocks of different molecular weight in PEO-b-PB diblock copolymer blends undergo cocrystallization irrespective of degree of undercooling *(Macromolecules 2004, 37, 8175).* The cocrystallization process in the PEO-b-PB diblock blends is favored since it gives rise to a structure having lowest free energy under the given crystallization conditions. Nevertheless, the diblock copolymer chains being of higher molecular weight will have slower diffusion under a given crystallization condition and hence question arises as to whether the cocrystallization process is driven thermodynamically or is it simply a kinetically controlled process. In the present study we investigate whether the cocrystallization in our previous diblock system was a result of favorable conformational entropy of longer PB blocks. Our present system again consists of a diblock mixture of symmetric and asymmetric PEO-b-PB diblock copolymers but here the PB blocks in both the diblocks are of almost similar molecular weight.

The symmetric PEO-*b*-PB has the molecular weight of the respective block of $M_{b,PEO}$ = 7500 and $M_{b,PB}$ = 5500 (denoted by $E_{170}B_{102}$) while the highly asymmetric PEO-*b*-PB has $M_{b,PEO}$ = 23500 and $M_{b,PB}$ = 5000 (denoted by $E_{534}B_{93}$). The microphase-separated structures in the melt of $E_{170}B_{102}$ and $E_{534}B_{93}$ are 1-D stacked lamellae and hexagonally packed PB cylinders, respectively. The microphase-separated $E_{534}B_{93}/E_{170}B_{102}$ blends were prepared by solution casting using toluene as the solvent, followed by removing the residual solvent in vacuo at 80 ^{o}C. The compositions of the blends denoted by the weight ratio of $E_{534}B_{93}$ to $E_{170}B_{102}$ are 0/100, 20/80, 40/60, 50/50 and 60/40.

Figure 1 shows Lorentz corrected SAXS profiles of $E_{534}B_{93}/E_{170}B_{102}$ mixtures collected at 90^{o}C (> T_m^{PEO}). It can be seen that all the samples display multiple scattering peaks with the peak positions relative to the first-order maximum following the ratios of 1: 2: 3: 4. This attests that all the blends display a 1-D stacked lamellar morphology consiting of alternating PEO and PB lamellae in the melt state. In this case, both the long and short PEO (PB) chains mix uniformly in the lamellar microdomains.

Figure 2 shows SAXS profiles of the diblock blends slowly crystallized from the melt state. It can be observed that the SAXS profiles of diblock mixtures are very different than that in the melt state as it no longer shows peaks in integral ratios.

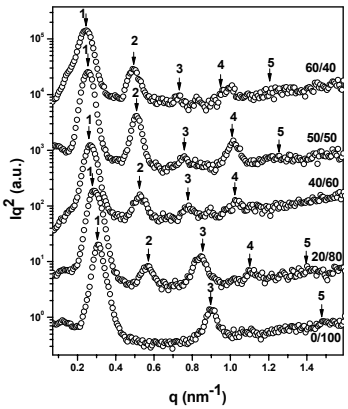

Figure 1. Lorentz-corrected SAXS profiles (Iq^2 vs. q) of binary $E_{534}B_{93}/E_{170}B_{102}$ mixtures in the melt.

This is evidently more clear from the SAXS profiles of compositions 40/60, 50/50, and 60/40. The higher order peaks may correspond to higher order lattice peaks corresponding to a structure on different and smaller length scale then the original one. The primary peak of the smaller length scale structure in this case may be superimposed on that of the larger length scale structure. Nevertheless the structure in the crystallized state at present is not very clear but evidently the crystallization behavior of diblock mixture in this case is different from that observed in our previous system where the SAXS profile after crystallization where found to retain the structural characteristic of the melt state. Further work will be required to resolve the self-assembled structure of the diblock mixtures and nature of crystallization in the present diblock blend system.

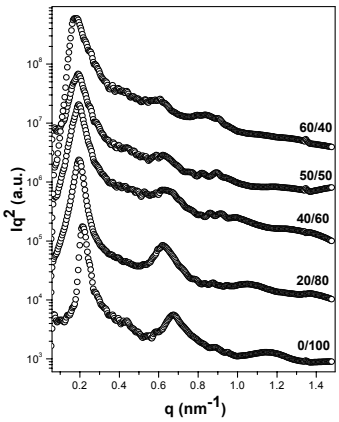

Figure 2. Lorentz-corrected SAXS profiles (Iq^2 vs. q) of binary $E_{534}B_{93}/E_{170}B_{102}$ mixtures in the crystallized state.