Morphology and Crystallization Behavior of the Binary Blend of Crystalline-Amorphous Diblock Copolymers

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The melt morphology and crystallization behavior of PS-b-PEO (SEO)/PS-b-PLLA (SLLA) blends have been investigated. The X-ray diffraction data were collected using synchrotron radiations at NSRRC BL 17A1 and BL17B3 beam lines.

Fig. 1 shows the SAXS profiles of SEO, SLLA and their blends collected in the melt state. The PS blocks from these two copolymers mixed intimately in the PS lamellar microdomains in the melt. Furthermore, PLLA and PEO also formed a miscible mixture in the lamellar microdomains.

To examine the arrangement of the crystallites in the blend, the oriented sample of SEO/SLLA 20/80 blend was prepared by large amplitude oscillatory shear (LAOS). In Fig. 2(a)-(c) the presences of arc in the 2-D SAXS patterns indicate that large-scale orientations of the microdomains are attained by LAOS. The SAXS patterns are almost identical along the x and y directions, corresponding to a distinct lamellar morphology. The fact that the diffraction arcs are located at the meridians, indicating that the lamellar microdomains stack along the z direction. By contrast, only a weak isotropic pattern is observed in the 2-D pattern along the z direction. These results suggest that the macroscopically aligned sample, where the normal of the lamellar domains is parallel to z direction, has been obtained even though the orientation is not perfect. Fig. 2(d)-(f) show the corresponding 2-D WAXS patterns along z, y, and z direction, respectively. The new species contributes predominately to the crystalline phase in this sample, because the crystallization temperature (30℃) is so low, that PLLA blocks cannot crystallize significantly. It can be seen that the new species exhibits two arcs in the equator in the tangential and radial views. However, only an isotropic ring is observed in the normal view. These results indicate that the crystallites of the new species are highly oriented when viewing along x and y directions, but the orientation is rather random when looking through the z direction (i.e. the system displays the in-plane orientation).

With the development of pure PLLA crystallites, the strong diffractions of PLLA crystals are discernible in the 2-D WAXS patterns. Fig. 5(g)-(i) show the resultant 2-D WAXS patterns. Four PLLA diffractions, i.e., (010), (200)/(110), (203), and (015), appear clearly. For the tangential and radial views, it can be seen that the (200) arcs appear at the equator, meaning that the crystalline peaks of PLLA align normal to the lamellar interface. The lamellar organization is however isotropic when views through the z direction, as the corresponding WAXS pattern displays a ring.

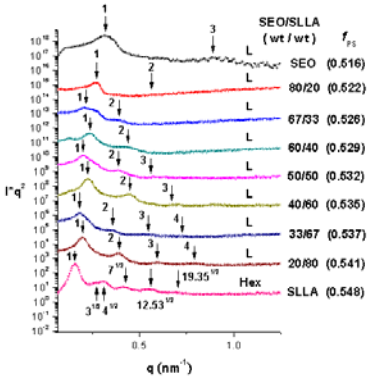

Figure 1. Lorenty-corrected SAXS profiles of SEO, SLLA and SEO/SLLA blends collected at melt state (190℃).

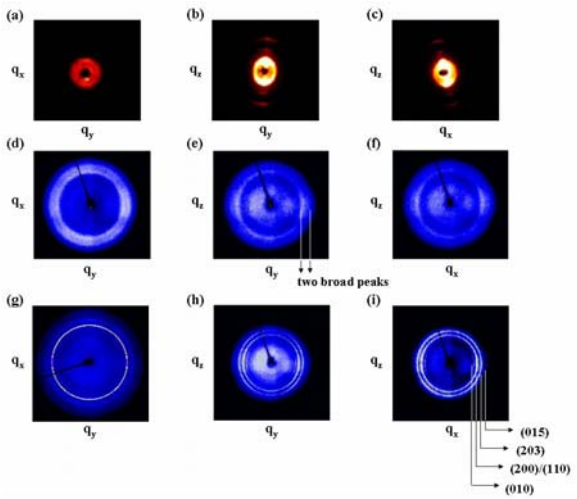

Figure 2. X-ray scattering patterns of oriented SEO/SLLA 20/80 blend isothermally crystallized at 30℃ for 24hrs. The sheared lamellar geometry is shown on the top. (a) 2-D SAXS pattern obtained when the X-ray beam is parallel to z-direction; (b) 2-D SAXS pattern along x-direction; (c) 2-D SAXS pattern along y-direction; (d) 2-D WAXS pattern along z-direction; (e) 2-D WAXS pattern along x-direction; (f) 2-D WAXS pattern along y-direction. (g)(h)(i) 2-D WAXS patterns of the oriented crystalline SEO/SLLA 20/80 blend.