The sisters of phase-separated structures with triply periodic minimal surfaces (G-, D-, and P-surfaces) in block copolymer/homopolymer blend systems

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A diblock copolymer, in which two immiscible polymer chains are covalently bonded at their ends, forms a bicontinuous network structure when the volume fraction of one of the polymer components is approximately 35%. In most cases, it forms a Double Gyroid (G) structure. However, in recent years, it has been confirmed that blending the minor component of the diblock copolymer with the same homopolymer under dry brush conditions leads to the formation of a Double Diamond (D) structure[1]. Nevertheless, the formation of the P-surface (P), which is predicted theoretically for this blend system[2], has not been confirmed. In this study, we investigated the formation of the P-surface in two types of blend systems: polystyrene-*b*-poly(methyl acrylate) (SMA)/polystyrene (hPS) and SMA/poly(methyl acrylate) (hPMA).

SMA, hPS, and hPMA were synthesized via atom transfer radical polymerization. For the preparation of SMA/hPS blend samples, a toluene solution was prepared by blending SMA (M_n = 16,400, M_w/M_n = 1.11, v_{PS} = 32.6 vol.%) and hPS (M_n = 5,500, M_w/M_n = 1.05) in the desired ratios. The films were prepared from solution casting at room temperature for a week. The samples were then thermally annealed at 120–160°C under vacuum. The microphase-separated structures formed by these samples were observed using small-angle X-ray scattering (SAXS) at KEK-PF.

The SAXS results of the SMA/hPS blend samples are shown in Figure 1. The four lower profiles represent samples annealed at 120°C and then quenched to room temperature with hPS blending ratios (f_{hPS} = 0, 10, 30, and 35 wt%). The two upper profiles represent the SAXS results for f_{PS} = 35 wt% samples that were first heat-treated at 120°C (quenched to room temperature), then re-heat-treated at 160°C (quenched to room temperature), and finally re-heat-treated again at 140°C (quenched to room temperature). The relative peak positions to the primary diffraction peak are indicated above each profile. From the ratio of these peaks, structural transitions from Cylinder → G → D → P+D were confirmed as f_{hPS} increased. For the sample with f_{hPS} = 35 wt% that formed the P structure, a phase transition from D at higher annealing temperatures to P at lower temperatures was observed. This indicates that P is a thermodynamically stable structure, forming the D (with four branches) at higher temperatures and the P (with six branches) at lower temperatures. Similar trends were observed in the SMA/hPMA blend samples.

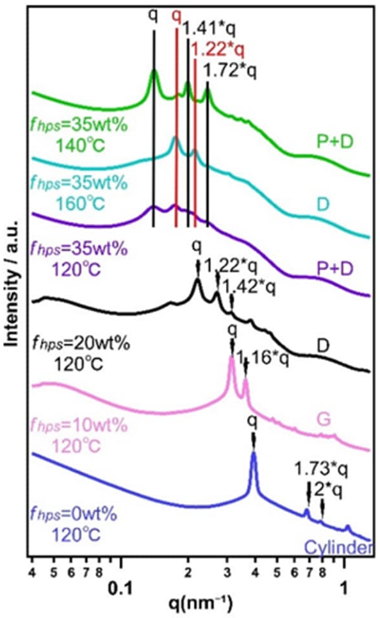

Fig1. SAXS profiles of SMA/PS

References

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