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Anomalies in morphological behaviours of microphase separation in S_1BS_2 Asymmetric triblock copolymers having different lengths of end-block chains

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Introduction

We report experimental results on relationship between primary (chemical) structures and morphology of microdomains of block copolymers. For this purpose, we prepared various asymmetric styrene-butadiene-styrene (SBS) triblock copolymers having different lengths of end blocks. The morphology was examined by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).

Experimental

The SBS samples have Mn of about 4.7×10^4 for Group 1 (six samples) and about 7.1×10^4 for Group 2 (five samples). The values of Mw/Mn are about 1.05 and ϕ_{PS} of about 0.67 for all samples.

The solution cast of the SBS triblock copolymer using a neutral solvent (toluene) was conducted to prepare equilibrium microdomain structure. The as-cast samples were then thermally annealed at 170˚C for 2 hours. The SAXS measurements were conducted to reveal microdomain morphology in the annealed samples.

Results and Discussion

Although total molecular weight, composition, and temperature were kept constant, the morphology was found to change with a degree of difference in length of end blocks. One typical example exhibits a morphological change as cylinder → lamella → cylinder with a decrease of length of one polystyrene (PS) end block, while keeping the total PS composition constant. This curious morphological behavior exhibiting a re-entrant type change is qualitatively in good accord with the theoretical result presented by Matsen [1], as shown in Fig 1(a) for Group 1 and in Fig. 1(b) for Group 2 samples. Here, the parameter τ denotes the degree of asymmetry, as defined by $\tau = M_S / (M_L + M_S)$, where M_S and M_L stand for shorter and longer PS end-block chains, respectively. Namely, $\tau = 0.5$ is for symmetric triblock copolymer SBS, and $\tau = 0$ is for diblock copolymer SB. Abbreviations L, G, C, and PL designate lamella, gyroid, cylinder and perforated lamella, respectively. The dotted curve divides lamellar and gyroid phases in Group 1, or it divides lamellar and cylinder phases in Group 2.

If pulling-out of the shorter PS end block from a PS microdomain takes place, the shorter PS end block is solubilized in polybutadiene (PB) microdomains. As a result, the effective PB composition is increased. This kind of mechanism may be relevant to the re-entrant type change of morphology with the degree of difference in length of end blocks.

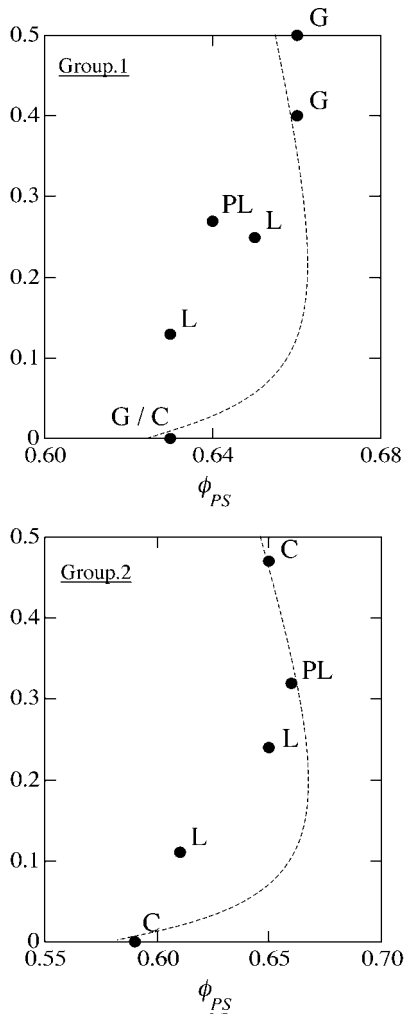

Figure 1 Phase diagram of the microdomain morphology showing in the τ–ϕ_{PS} space for (a) Group 1 and (b) Group 2, where τ and ϕ_{PS} stand for the asymmetric parameter and the volume fraction of the triblock copolymers, respectively.

References

[1] M. W. Matsen, J. Chem. Phys. 113, 13 (2000)

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