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Features of microphase - separated structures in S_1BS_2 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]. Fig. 1 shows changes in SAXS profiles with τ where ones in red are for Group 1samples and ones in blue are for Group 2 samples. Here, the parameter τ denotes the degree of asymmetry, as defined by $M_S / (M_L + M_S)$, where M_S and M_L stand for shorter and longer PS end-block chains, respectively. Namely, τ = 0.5 for a symmetric triblock copolymer SBS, and τ = 0 for a diblock copolymer SB. Abbreviations L, G, C, and PL designate lamella, gyroid, cylinder and perforated lamella, respectively.

References

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

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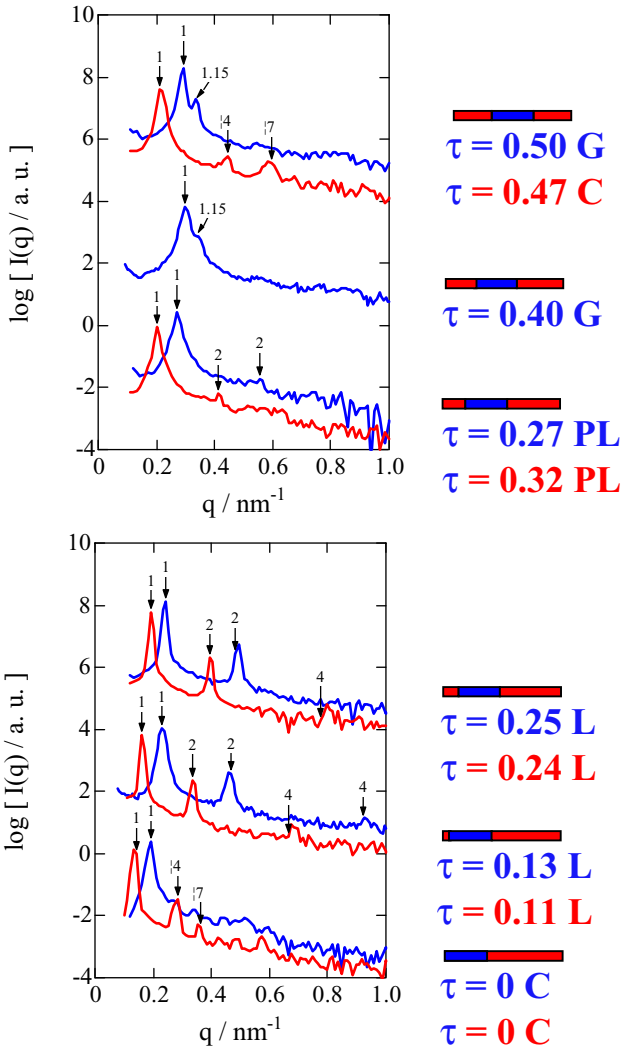

Fig. 1 Changes in SAXS profiles with τ wnere ones ın red are for larger molecular weight samples and ones in blue are for shorter molecular weight samples with a similar degree of asymmetry, τ. Abbreviations L, G, C, and PL designate lamella, gyroid, cylinder and perforated lamella, respectively.