

TUNABLE DOMAIN SPACING OF MICROPHASE-SEPARATED STRUCTURES BY SOLVENTS MIXTURES

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ABSTRACT

Diblock copolymers form various periodic nanostructures by self-assembly. The domain spacing is determined by segment length, degree of polymerization, incompatibility of constituent blocks, etc. It is reported that selective solvents are partitioned into preferred domains and enhance the incompatibility of two domains while a common solvent exhibit no preferential partitioning and decrease the incompatibility¹. In this report, we explore the behavior of three polystyrene-*b*-polyisoprene (SI) diblock copolymers listed in table 1, designated as SI-lam, SI-cyl, and SI-sph, in the mixture of a styrene-selective solvent, dimethyl phthalate (DMP), an isoprene-selective solvent, *n*-tetradecane (C14), and a common solvent, dioctyl phthalate (DOP). The structures of solutions were measured by Small-angle X-ray scattering (SAXS) at BL40B2 in SPring-8, BL8S3 in Aichi SR, Japan and by NANO-Viewer (Rigaku Corp.). In Fig. 1, domain spacings (D) of the SI-cyl solutions at the polymer concentrations (ϕ_{pol}) of 20, 30, 40, 50 vol.% and neat SI-cyl are plotted as a function of a DOP fraction (f_{DOP}). The ratio of DMP and C14 is fixed at 30:70. Most of the solutions formed hexagonally packed cylinders. It is clearly seen that D increased with the decrease of f_{DOP} and that the solutions at lower polymer concentrations show larger change of D . More interestingly, the four curves cross at $f_{\text{DOP}} = 30\%$, and D decrease/increase at f_{DOP} smaller/larger than the crossover point with increasing ϕ_{pol} . Additionally volume fractions of polystyrene domain (ϕ_{PS}) estimated by curve-fittings of the SAXS profiles with those calculated on

the basis of paracrystal theory drastically increased with decrease of f_{DOP} in the range from 0 to 30% while nearly constant above 30%. These tendencies of D and ϕ_{PS} can be attributed to the quality of solvent mixtures. Actually, the three solvents are homogeneously miscible at $f_{\text{DOP}} > 30\%$ while immiscible and separate into two phases at $f_{\text{DOP}} < 30\%$. The results on the other two SIs will be shown on site. The tendencies mentioned above give us the fascinating techniques² to fabricate tunable photonic crystals with large refractive indices.

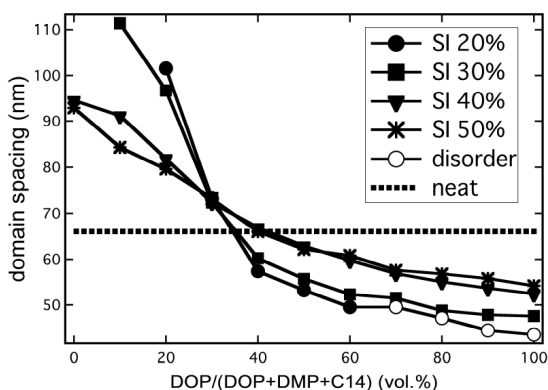


Fig. 1: Domain spacing versus f_{DOP} of SI-cyl solutions at ϕ_{pol} of 20, 30, 40, 50 vol.% and neat SI-cyl. Note that the solutions at small f_{DOP} and low polymer concentration, i.e., at $f_{\text{DOP}} < 30\%$ and $\phi_{\text{pol}} = 20\%$, and at $f_{\text{DOP}} < 20\%$ and $\phi_{\text{pol}} = 30\%$, macro-phase separated.

Table.1: Characteristics of SI.

SI code	M_n (g/mol)	M_w/M_n	f_{PS} (vol.%)
SI-lam	6.0×10^4	1.03	54
SI-cyl	1.5×10^5	1.03	25
SI-sph	2.1×10^5	1.08	11

References

¹ Hanely, K. J.; M. D.; Lodge, T.P.; Huang, C-I. *Macromolecules*. **2000**, *33*, 5918.

² Ando, K.; Yamanaka, T.; Okamoto, S.; Inoue, T.; Sakamoto, N.; Yamaguchi, D.; Koizumi, S.; Hasegawa H.; Koshikawa, N. *IOP Conf. Series: Mater. Sci. and Eng.* **2010**, *14*, 012012.