

# Novel Tricontinuous Microphase-Separated Structures formed from ABC Triblock Terpolymer Blends

A. Takano<sup>1\*</sup>, A. Kitahara<sup>2</sup>, and J. Suzuki<sup>3</sup>

<sup>1</sup> Research Institute for Quantum and Chemical Innovation, Nagoya University, Nagoya, Japan

<sup>2</sup> Department of Molecular & Macromolecular Chemistry, Nagoya University, Nagoya, Japan.

<sup>3</sup> High Energy Accelerator Research Organization, Tsukuba, Japan

\*email : atakano@chembio.nagoya-u.ac.jp

It is well-known that non-gyroid cocontinuous structures is hardly constructed in block copolymer system, and a lot of investigation were carried out experimentally and theoretically so far.[1, 2] In this study, a double-primitive (DP) tricontinuous structure has been observed in a quaternary blend system consisting of two kinds of ABC triblock terpolymers and A and C homopolymers (ABC'/A'BC/A/C) as illustrated in Figure 1. The two ABC triblock terpolymers have a chain length difference in the end block components, and the A/C homopolymers have comparable chain lengths with the longer A/C blocks of ABC triblock terpolymers.



**Figure 1.** Schematic illustrations of the two ISP triblock terpolymers, I- and P-homopolymer investigated. Black, dashed and gray chains represent I, S, and P, respectively.

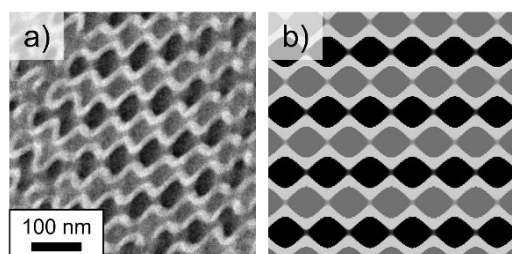
Polyisoprene-*b*-polystyrene-*b*-poly(2-vinyl pyridine) (ISP) triblock terpolymers and I, P homopolymers were synthesized by a living anionic polymerization. The two ISP triblock terpolymers are approximately equal in total molecular weight ( $M_w \approx 120k$ ) and volume fraction of the middle block component ( $\phi_S \approx 0.6$ ). The two end block components I and P have a chain length difference of 5.8 and 6.8 folds, respectively.

**Table 1.** Molecular characteristics of samples

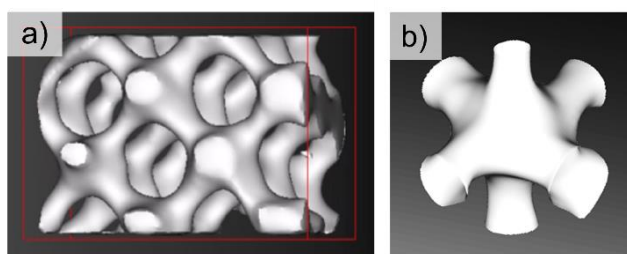
Sample	$10^{-4} M_n^a$	$M_w/M_n^a$	$\phi_I:\phi_S:\phi_P^b$
ISP- $\alpha$	10.9	1.02	0.35:0.60:0.05
ISP- $\beta$	12.2	1.02	0.06:0.62:0.32
I	4.9	1.05	-
P	4.1	1.05	-
ISP- $\alpha/\beta$ /I/P	-	-	0.31:0.42:0.26

<sup>a</sup>Determined by GPC and GPC-MALS, <sup>b</sup>by <sup>1</sup>H NMR.

Figure 2(a) shows the transmission electron microscopy (TEM) image of the blend sample, ISP- $\alpha/\beta$ /I/P (0.31/0.42/0.26). This observed image was in good agreement with the simulated image for DP structure as shown in Figure 2(b). Furthermore, three-dimensional reconstructed image from TEM tomography (TEMT) showed a clear network structure of 6-fold branching as shown in Figure 3.



**Figure 2.** (a)TEM image of ISP'/I'SP//P, and (b)simulated image of DP(011).



**Figure 3.** (a)3D reconstructed image of ISP'/I'SP//P, and (b)6-fold branching point.

[1] Asai, Y. et al. *Macromolecules*, **50**, 5402-5411(2017)

[2] Dotera, T. *Phys. Rev. Lett.*, **89**, 205502(2002)