A SIMPLE TECHNIQUE OF PRODUCING A NOVEL NETWORK MORPHOLOGY: GUIDED SELF-ASSEMBLY OF TRIBLOCK TERPOLYMERS

Hirokazu Hasegawa

Research Administration Center, Graduate School of Engineering, Kyoto University (Nishikyo-ku, Kyoto, Japan 615-8245, hasegawa.hirokazu.3v@kyoto-u.ac.jp)

ABSTRACT

ABC triblock terpolymers tend to undergo two-step microphase separation when they are cast from solution in selective solvent. The resulted microdomain morphology is not in equilibrium. However, the non-equilibrium process can lead to a variety of unexpected morphology including unusual network morphologies.

We investigated the microdomain morphologies of the as-cast films of polystyrene-*block*-polyisoprene-*block*-poly-1,4-dimethylsiloxane linear triblock terpolymer (PS-*b*-PI-*b*-PDMS) with various compositions synthesized via sequential living anionic polymerization. Since the films were cast from solution in toluene, which is selective to PS and PI and poor to PDMS component, two-step microphase separationtook place during solvent evaporation, i.e., PDMS microphase separates first from the other two components. We call this process “guided self-assembly” because the PDMS microdomains regularly arranged in space should acta s the guids and direct the subsequent microphase separation of PS and PI components. The PI-PDMS junction points are fixed on the microdomain interfaces and it restricts the second-step microphase separation between PS and PI components. The resulting microdomain structures are non-equilibrium structures, some of which exhibit unusual network morphologies of core-shell types. The structure of the as-cast films was analyzed by 3D electron tomography (3D-TEM) and small-angle X-ray scattering (SAXS) with synchrotron radiation source (Spring8). Unexpectedly from the non-equilibrium structures, some of the as-cast films exhibited very well-defined SAXS patterns with extremely regular structures. In addition to the well-known equilibrium cubic morphology of double Gyroid networks (or I$a\bar{3}d$), we found two different double network morphologies with non-cubic unit cells and PDMS-PI core-shell networks. One has an orthorhombic unit cell with the symmetry of space group F*ddd*, which is different from the F*ddd* single network structure found in the triblock terpolymers or in the weakly-segregated PS-*b*-PI diblock copolymer. The other one has a tetragonal unit cell and is considered as an elongated P-surface (or Plumber’s Nightmare) network structure. Both of them have the core-shell type networks with double-network structures as revealed by 3D TEM. In addition, we have observed double diamond (or D-surface) network structure of the core-shell type as well as the single-diamond network structure by 3D TEM. In the latter network structure, PS network and PDMS-PI core-shell network have almost the same volume and divide the space into two halves having the mirror images. Thus, we found five different network morphologies out of ten samples with different compositions in the limited composition range of f_{PS} between 0.33 and 0.41. This range resembles to the composition range of double Gyroid morphology ($0.33 \leq f_{PI} \leq 0.37$) in PS-*b*-PI diblock copolymer.

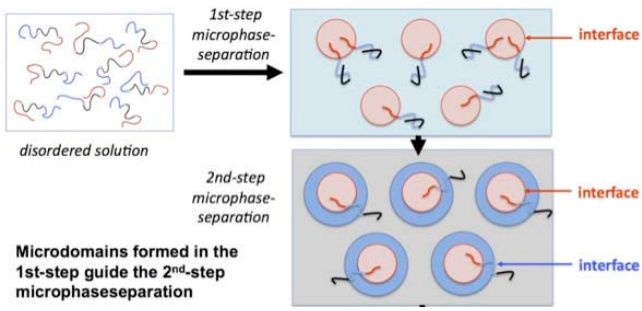

Fig.1 Two-step microphase separation.