Self-Assembled Structures Through Triblock Terpolymers Forming Gyroid Structures

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Abstract:

Gyroid, which is one of the three-dimensional continuous network structures, is a promising structure. Gyroid structures were achieved by the use of block copolymers that show micro-phase separated structures through a self-assembly process. We fabricated a template of gyroid structures by blending triblock terpolymers and homopolymers. After self-assembled structures were prepared, homopolymers were removed by solvents, so that porous structures were obtained. Structures were evaluated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

Introduction:

The colors of morpho butterfly's wings are derived from their wing's structure, the so called 'structural color' [1]. It has been ascertained that one of the structures is gyroid, which is a 3D continuous network structure. This structure has been and is expected to be used in many fields, for example fuel cells, solar cells, metamaterials, etc., so it is important to be able to fabricate gyroid structures easily.

Gyroid structures were achieved by the use of block copolymers. Block copolymers consist of chemically distinct components that show immiscibility due to their different chemical affinities. Since they are covalently bonded to each other, they show various micro-phase separated structures through a self-assembly process. Gyroid is one of the micro-phase separated structures, but gyroid areas on a phase diagram of diblock copolymers are generally small. We used triblock terpolymers to extend the gyroid areas because gyroid areas on a phase diagram of triblock terpolymer become larger.

Our plan to fabricate gyroid structures was to use triblock terpolymers as a template [2]. After one component of triblock terpolymer was removed by selective etching, porous structures for templates could be obtained. Our strategy for the selective etching was to blend triblock terpolymers and oligomers, which are supposed to be miscible with one component of triblock terpolymers. Because oligomers are easily removed by solvents, selective etching could be achieved. We used poly(isoprene-*block*-styrene-*block*-glycidyl methacrylate) (PI-PS-PGMA; ISG) and 1,2-polybutadiene (B), which was supposed to be miscible with polyisoprene block. And poly(glycidyl methacrylate) (PGMA) was also blended to tune the volume fractions of samples. PGMA components would keep their structure after crosslinked by acid.
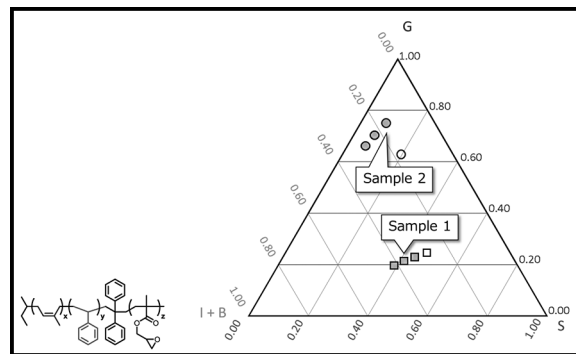

Figure 1: Chemical structure of ISG and volume fractions of each samples on phase diagram. Open square indicates ISG [1] and black squares indicate ISG [1] + B in different compositions. Open circle indicates ISG [2] and black circles indicate ISG [2] + B in different compositions.

Experimental Procedure:

ISGs (ISG [1]: $M_n(I)$ = 10.5 kg/mol, $M_n(S)$ = 21.3 kg/mol, $M_n(G)$ = 40.7 kg/mol, ISG [2]: $M_n(I)$ = 4.9 kg/mol, $M_n(S)$ = 6.2 kg/mol, $M_n(G)$ = 13.9 kg/mol), homopolymers B (M_n = 3.0 kg/mol) and/or poly(glycidyl methacrylate) (PGMA) were dissolved into tetrahydrofuran (THF) in different compositions (10 wt%) (Figure 1). Then photoacid generator (Irgacure PAG 290) was added to the solutions (1 wt% of total solute). After they were poured in aluminum dishes, they were kept overnight at 50°C during which time THF evaporated from the solutions. After light irradiation for 15 minutes to cross link the PGMA component, samples were observed by transmission electron microscopy (TEM). In preparation for TEM, specimens were
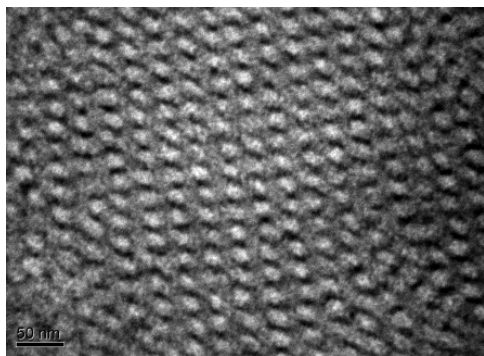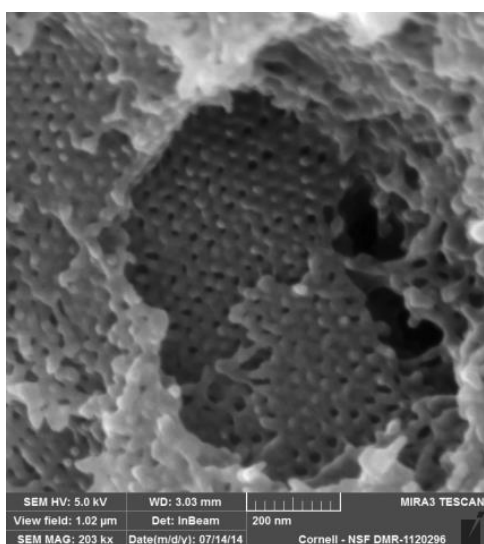
Figure 2: TEM image of Sample 1.

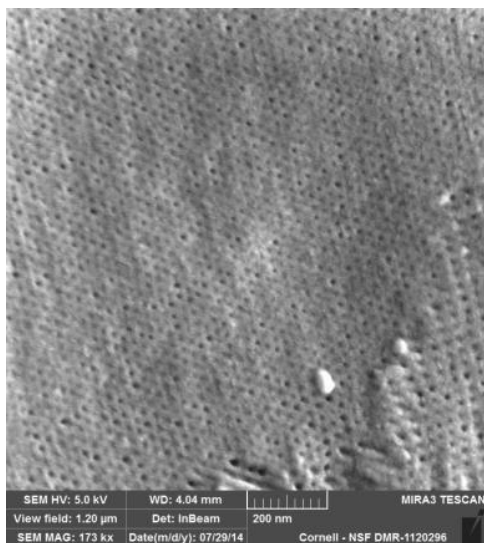*Figure 3: SEM image of Sample 1 after immersed in hexane to remove B.*

Figure 4: SEM image of Sample 2 after immersed in hexane to remove B.

cut with a cryomicrotome at -60°C, then exposed to osmium tetraoxide vapor to stain I component. After samples were immersed in hexane to remove B, they were observed by SEM.

Results and Conclusions:

ISG [1] + B (square). Micro-phase separated structures were found in each sample by TEM measurement, and especially the sample shown as the middle one of black squares in the phase diagram (Figure 1) showed the most ordered self-assembled structure (Sample 1, Figure 2). This structure might be gyroid or cylinder, but it was difficult to determine its structure because the intensity of small angle x-ray scattering (SAXS) — which could identify their structures — was too weak. After it was immersed in hexane to remove B, Sample 1 was observed by SEM (Figure 3). Porous structure was found and its diameter was 15-20 nm.

ISG [2] + B + G (circle). ISG [2], B and homopolymer G were blended to fabricate samples with high G ratio. Micro-phase separated structures were found in each samples by TEM measurement, and especially the sample that is shown as the top one of the black circles in the phase diagram (Sample 2) (Figure 1) showed the most ordered self-assembled structure, which was hexagonal-packed cylinder. And then Sample 2 was immersed in hexane to remove B, followed by SEM measurements of the structure (Figure 4). Porous structure was found and its diameter was below 10 nm.

In conclusion, we could achieved the selective etching of B component from self-assembled structures. We fabricated two porous samples in different compositions and pore diameters were also different, which indicates that we could control the pore size by control the ratios of homopolmer B.

Future Work:

Future research is needed to optimize the etching conditions; temperatures, solvents, immersing time, etc. After that, porous structures will be used as a template to be replicated with functional materials by deposition of other materials.

Acknowledgments:

References:

[1]   R. O. Prum, et al., PNAS 2010, 107, 11676.

[2]   K. Hur, et al., Angew. Chem. Int. Ed. 2011, 50, 11985.