Nanoprocessing Based on Bicontinuous Microdomains of Block Copolymers: Nanochannels Coated with Metals

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Abstract: The bicontinuous microdomain phase of microphase separated block copolymer was subjected to selective degradation to create a continuous, tortuous hole. Nickel metal was introduced on the surface of the hole by nonelectrolytic plating.

Introduction

It is well-known that block copolymers form ordered nanostructures such as spheres, cylinders, bicontinuous structures, lamellae, and their phase-inverted structures[1-4]. The size and shape of the structures can be "tailor-made" by their molecular weights and compositions. The structure units and their spacings are of the order of the radii of gyrations of block copolymers and of nanometer scale.

In this symposium, we will report the creation of a "nanochannel" through processing of a bicontinuous structure formed by microphase separation of block copolymer. The processing involves a selective degradation of one of the bicontinuous microdomain phases to create a continuous, tortuous hole having a diameter of nanometer scale (designated as "nanochannel") and the plating of the surfaces of the nanochannel with nickel metal. The nanochannel and the metal plating were confirmed by the transmission and scanning electron microscopies.

Experimental

Synthesis of Polymers. We used a block copolymer system composed of binary mixture of poly(styrene-*block*-isoprene) (SI) and homopolystyrene

(HPS). These polymers were synthesized by living anionic polymerization technique.

Preparation of Thin Film having bicontinuous microdomain. Thin film was prepared by slowly evaporating solvent from the toluene solution of the mixture of SI and HPS having an overall volume fraction of styrene units of 0.66. The microdomain structure in the as-cast film was observed under a transmission electron microscope (TEM) operated at 160kV on the ultrathin sections stained with OsO_4 vapor.

Ozonolysis. The as-cast film was subjected to the ozonolysis, by which the PI domains were selectively degraded and transformed into holes. To cleave the carbon-carbon double bond of PI, the film was exposed to ozone, soaked in trimethyl phosphite, and then, soaked in methanol. The film subjected to the ozonolysis was freeze-fractured and the fractured surface was investigated under a scanning electron microscope (SEM) operated at 20kV.

Nonelectrolytic Plating. The material with the nanochannels was then subjected to nonelectrolytic plating with nickel metal. All the commercial solutions were diluted with water to avoid rapidly clogging of the nanochannels by the metal. The materials having the nanochannels whose surfaces are coated with nickel metal were subjected to the ultrathin sectioning and to the TEM observations without staining.

Results and Discussions

Figure 1 shows the TEM micrograph of the as-cast specimen stained with OsO_4 in which the dark and bright phases correspond, respectively, to the stained PI and unstained PS phases[5]. The micrograph shows the ordered bicontinuous phases with the spacing of 50 to 60 nm.

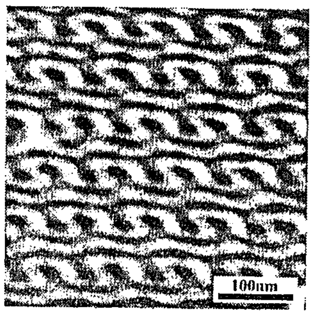

Fig.1 TEM micrograph showing the bicontinuous microdomain structure of a SI/HPS mixture cast from toluene solution[5].

Figures 2(a) and (b) show the SEM micrographs of the freeze-fractured specimens after ozonolysis[5]. The micrographs revealed a characteristic topological feature of the regularly spaced nanochannels with diameter of 20 to 30 nm, essentially identical to the features seen in the TEM micrograph of as-cast film. This result suggests that the PI phase is selectively degraded into the nanochannel in the PS matrix without significant perturbations of original symmetry of the structure in the as-cast films. To the best of our knowledge, it is for the first time that the three dimensionally continuous and periodic nanochannels with long-range spatial order are created in the polymer matrix by selective degradation of the gyroid phase and observed by the SEM method, though there have been a report of selective degradation of one of the microdomain phases with some discrete morphologies such as lamellae or cylinder[6].

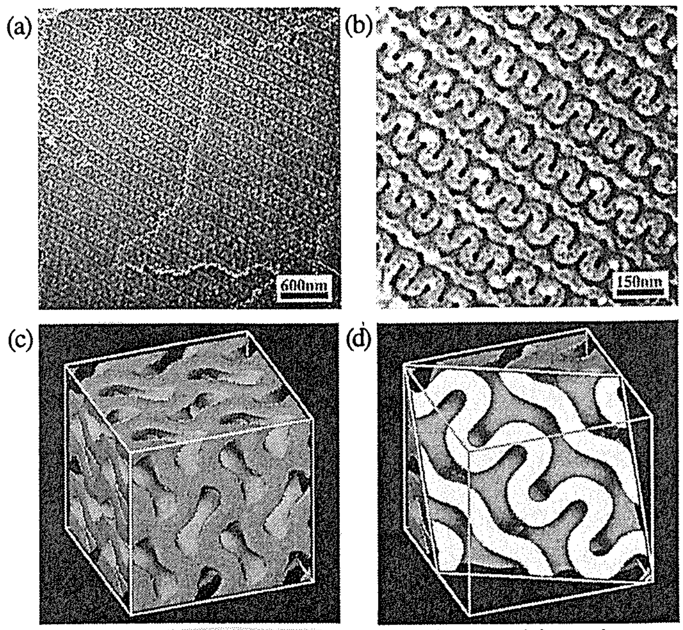

Fig. 2 SEM micrographs showing a bicontinuous nanochannel in the matrix of PS with two different magnifications (parts a and b), and computer graphics of a double gyroid network (parts c and d): (c) a three dimensional view and (d) a two dimensional intersection cut along the (211) direction[5]. Part c and d shows a solid model in which only the matrix phase, corresponding to the PS matrix in our specimens.

The micrograph (b) with a higher magnification shows that the fracture surface corresponds approximately to (211) plane of the double network of the gyroid structure whose three dimensional (3d) computer graphic and a sliced section are shown, respectively, in parts (c) and (d). The selective etching of one of the phase is proposed here to be quite useful for exploration of 3d structures of the bicontinuous phases.

Figure 3 shows the TEM micrograph of the ultrathin sections of the PS specimens having 3d continuous nanochannels whose surfaces (or interfaces) are plated with nickel metal[5]. It should be noted that the TEM was observed with the specimens unstained by OsO_4: the metal-coating of the channel surfaces give rise to the absorption contrast for the TEM without staining. A comparison between

Figures 1 and 3 clearly reveals that the symmetry, image contrast, and size of the nanopattern observed after the nanoprocessing are in complete agreement with those of the nanopattern observed in the as-cast specimens: the dark PI phase stained with OsO_4 in Figure 1 corresponds to the dark channels phase in Figure 3 whose surface is coated with nickel metal. This evidence shows a conservation of the nanostructure through the nano-processing and the fact that the PI phase is transformed into a channel with its surface coated by the metal.

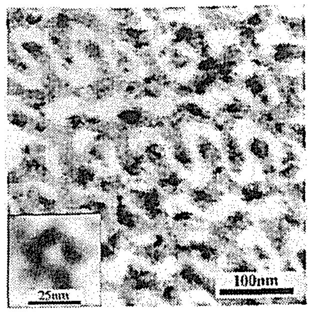

Fig. 3 TEM micrograph showing a continuous, regular nanochannel plated with nickel metal. Ultrathin section was not stained. The nanochannel appears dark in the micrograph due to the nickel metal[5].

Conclusion

We were able to prepare nanochannels regularly spaced in a glassy polymer matrix whose surfaces are coated by nickel metals. This nanohybrid is expected to be useful as a high performance membrane reactor because of the high surface area of the metal nanoparticles and the easy handling of the polymer films.

References

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