Controlled Alignments of Metal Nanoparticles in Polymer Matrix

Takeji Hashimoto and Hirokazu Hasegawa

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, 615-8510 Fax: 81-75-383-2623, e-mail: hashimoto@alloy.polym.kyoto-u.ac.jp

Some nanofabrication methods are discussed on the basis of block copolymer nanodomain structures as templates. They are ordered nanochannels and metal plating of the channel surface, ordered double Gyroid network texture containing metal nanoparticles, and controlled alignments of metal nanoparticles in nanodomain structures in block copolymers.

Key words: Nanoparticle, Block Copolymer, Palladium, Nanofabrication, Nanochannel, Gyroid

1. INTRODUCTION

Block copolymers are the chain molecules in which two or more polymer chains of different kinds are chemically linked together at their chain ends. In this paper, we would like to discuss how we control the alignments of metal nanoparticles by utilizing microdomain structures of block copolymers as templates.

In AB diblock copolymers, polymer A and polymer B are chemically connected. This single connection alters the physics of the two component systems of polymers A and B.¹³ Without the chemical bond, the two-component system is just a mixture and can achieve a phase separation into two phases of a macroscopic scale with a single interface at thermal equilibrium as shown in Figure 1a. We call this phase separation as macrophase separation. The important physics here is competing short-range interactions between A and A, B and B, and A and B segments.

AB diblock copolymers, on the other hand, cannot attain such macrophase separation because of the linkage, but can attain only so-called microphase separation. The chemical junctions are aligned along the interface, and A and B block chains segregate themselves into A and B microdomains as schematically illustrated in Figure 1b. Each domain has the molecular size of the order of 10 nm. Therefore, bulk block copolymers are nothing other than an assembly of interfaces made of the block copolymer monolayers. The connectivity in block copolymers involves long-range interactions of A and B block chains through a uniform packing of A and B block chains in the respective microphases under a



Figure 1 A/B blends vs A-b-B block copolymers

demand of incompressibility. The system still has the same short-range interactions as those in the mixture. The interplay of these two interactions, ⁴ short- and long-range interactions, yield unique periodic nanostructures with a long-range order with various symmetries³ as sketched in Figure 2.

We aim to explore the methods and principles of fabrication of nano-size domain structures to create new materials with interesting nanostructures and functionalities or properties. In this paper we present our works on (i) nanochannels and metal plating of them, (ii) metal nanoparticles coordinated and stabilized by block copolymers, and (iii) nanohybrids (metal nanoparticles arranged in polymer matrix).

2. NANOCHANNELS AND METAL PLATING

With increasing volume fraction of one of the components in block copolymers, the block copolymer nanostructure changes from spheres packed in a body-centered cubic (bcc) lattice, cylinders packed in a hexagonal lattice and alternating lamellae of A and B as schematically shown in Figure 2a. In a very narrow composition range between cylinders and lamellae, a bicontinuous structure of Double Gyroid Network Phase⁵ appears, as shown in Figure 2b, a computer graphic of one repeat unit of Double Gyroid Network with the



Figure 2 Microphase-separated domain structures of block copolymers

network volume fraction of 0.33. Their skeletal models are shown in Figures 2c and 2d: Double Gyroid Network (Figure 2c) consists of a set of two identical tripod networks, one of them being shown in Figure 2d, interlaced one another without touching. The minor component forms the networks and the major component forms the matrix.

One can selectively degrade one of the components of Double Gyroid Network, either the component forming the network or that forming the matrix. When the minor component forming the network is degraded, a set of two vacant channels is formed in the matrix of the major component.⁶ On the other hand, when the major component forming the matrix is selectively degraded, the double Gyroid texture freestanding in vacancy is resulted.^{7,8} We will first discuss below the nanofabrication leading to the ordered nanochannel network and subsequent metal plating of the channel surface.

2.1. Selective Degradation of Gyroid Network by Ozonolysis

Double Gyroid Network Phase was prepared by casting a mixture of polystyrene-block-polyisoprene diblock copolymer (SI) and polystyrene homopolymer (HS) having an overall volume fraction of polystyrene (PS) component of 0.66 from ca. 5 wt% solution in toluene. The number average molecular weights of SI and HS are 8.8×10^4 and 7.5×10^3 , respectively, and the volume fraction of polystyrene component in SI is 0.51. The cast film was subjected to ozonolysis and subsequent rinsing with water, which selectively degraded the polyisoprene (PI) phase and transformed it into a vacant channel phase almost completely, leaving some functional group such as ketone on the channel surface.⁶ Figure 3a shows a field-emission scanning electron micrograph of the freeze-fractured surface of the SI/HS film after ozonolysis of the PI network phase. A regular pattern, which we call a double wave pattern, with periodically arranged large-amplitude and smallamplitude bright waves as well as dark holes is seen. The bright region is undegraded PS matrix, while the dark and gray regions are the degraded vacant channel phase. Figure 3b shows a 3D computer graphics of the solid matrix phase of mathematically constructed Double Gyroid Network Phase where the network phase was made empty.⁶ Figure 3c is the cross-sectional view of the same model as shown in Figure 3b, which appears on a particular plane cut parallel to the (211) plane of the Double Gyroid lattice that has a cubic unit cell with Ia3d



Figure 3 Double Gyroid Network Phase and nanochannels



Figure 4 TEM image of Ni-plated nanochannels.

symmetry. The cross-sectional surface appearing bright shows a double wave pattern consisting of a set of a large-amplitude wave and a small-amplitude wave arranged periodically. Here again the bright and gray regions correspond to the matrix phase and empty channel phase, respectively. The pattern is exactly identical to that shown in Figure 3a. Thus, it was confirmed that the ordered nanochannel network was successfully produced from Double Gyroid Network Phase of SI/HS by the selective degradation of the PI networks. According to numerical analysis, this particular plane parallel to (211) plane is one of cleavage planes where the area fraction of matrix phase becomes minimum.⁹

2.2. Metal Plating of Nanochannel Surface

The nanochannel surface prepared above can be plated with Ni metal by nonelectrolytic metal plating. In the nonelectrolytic metal plating, Sn^{2+} was first introduced on the nanochannel surface, then exchanged to Pd⁰ upon a further introduction of Pd²⁺ and resulting redox reaction with Sn^{2+} , which was used as the catalyst to reduce Ni²⁺. Figure 4a shows a TEM image of the ultrathin section of the Ni-plated nanochannel specimen obtained without staining. The Ni metal plated on the nanochannel surface gives a dark contrast for the TEM image, and the PS phase having the double wave pattern appears bright as highlighted in Figure 4b. 2.3. Double Gyroid Texture

By degrading the matrix phase of Double Gyroid Network Phase of block copolymers, freestanding Double Gyroid Network Texture or nanoporous



Figure 5 Pd nanoparticles coordinated by polymers.

materials with pore volume fraction of 67% can be Poly(2-vinylpyridine-block-polyisoprene) created. diblock copolymer (P2VP-b-PI), in which poly-2vinylpyridine (P2VP) phase forms double Gyroid networks, was used for this purpose. The P2VP network phase was first cross-linked with diiodobutane, and subsequently the PI matrix phase was degraded by ozonolysis. We call this texture as the double Gyroid texture. The texture was further soaked into a toluene solution containing Pd2+ ions and 1-propanol as a reductant. The Pd²⁺ ions were reduced to form Pd nanoparticles of the average size in the range of 5-10 nm in the double Gyroid texture. The size and the amount of Pd nanoparticles increase with the reduction time of Pd²⁺ ions. In this way, a large amount of Pd nanoparticles can be introduced into the Double Gyroid texture. More details will be reported elsewhere.10

3. COORDINATION AND STABILIZATION OF METAL NANOPARTICLES BY BLOCK COPOLYMER

Metal nanoparticles are not stable by themselves but coagulate into large clusters with time. Some polymers are good as coordinating and stabilizing agents for metal nanoparticles.^{7,11-16} We will discuss coordination and stabilization of Pd nanoparticles by P2VP homopolymer as well as P2VP-*b*-PI diblock copolymer.

A dilute benzene solution of P2VP or P2VP-*b*-PI containing Pd^{2+} ions was prepared. The reduction of Pd^{2+} ions was done by adding 1-propanol as a reducing agent and heating the solution at 85°C. Figure 5 shows typical TEM images of the Pd nanoparticles thus obtained. The average size of the Pd particles is 4-5 nm. An elemental analysis of the Pd nanoparticles separated from the polymer solution indicated that less than 5 polymer chains are coordinating per single Pd particle. The details were described elsewhere.¹⁷ Important problems to be solved are: (i) how many chains are coordinating to a single metal particle, and (ii) what kind of configurations the coordinating chains are taking. One



Figure 6 Nanohybrids: Process (1)

possible example is schematically illustrated in the bottom part of Figure 5. Of course, it is just a schematic model and the coordinating polymer chains themselves cannot be directly observed by TEM. We shall discuss this issue later.

4. NANOHYBRIDS OF METAL NANOPARTICLES AND BLOCK COPOLYMERS

Among many ways of creating the nanohybrids of metal nanoparticles and block copolymers, two of them are presented below.

We can think about a system comprised of A-B block copolymers and metal nanoparticles, and let the system self-assemble into a nanodomain structure in which the particles are aligned selectively in one of the domains. Let us define this process as process (1). For this purpose, we can use the nanoparticles coordinated and stabilized by the A-B block copolymers that are prepared by the method that we have just discussed in Section 3.

Alternatively we prepare a system containing A-B block copolymer and metal ions and let the system form nanodomain structures containing metal ions. The metal ions are then reduced into metals that selectively cluster into nanoparticles in one of the nanodomains. In the previous case of the Double Gyroid texture containing Pd nanoparticles, this process was employed.

4.1. Nanohybrid: Process (1)

First we will consider a self-assembly of a mixture containing a small amount of Pd particles coordinated and stabilized by P2VP-*b*-PI block copolymers (designated hereafter as Pd-P2VP-*b*-PI) and a large amount of the same block copolymers which form lamellar nanodomains and serve as a template for the nanoparticles (designated hereafteras T_p -P2VP-*b*-PI) as schematically shown in Figure 6a.

Figure 6b shows a typical TEM image of the unstained specimen of such a system where the dark and



Figure 7 Possible configuration of PI-*b*-P2VP block copolymer chains adhered to Pd nanoparticles.

bright lamellae are P2VP and PI lamellae, respectively, and the dark dots are the Pd nanoparticles. Interestingly enough we found that Pd nanoparticles are more or less uniformly distributed in the lamellae. What does this mean? Figure 6c schematically represents a part of Pd-P2VP-*b*-PI in the PI and P2VP lamellae formed by the Tp-P2VP-*b*-PI. We highlight below interactions between Pd particles and the block copolymer in Figure 7.

It is known that Pd likes P2VP more than PI. If Pd particles are heavily adsorbed by many P2VP block chains as illustrated in part a of Figure 7, so that P2VP blocks cover the particles and PI blocks emanate as a brush, then the Pd nanoparticles should be incorporated into PI lamellae rather than P2VP lamellae. We have never found this case. Thus this is not the case.

Part b of Figure 7 represents the case where the Pd nanoparticles adsorb only a small number of the block copolymer chains, e.g., only one chain here. Then the P2VP block segments are extensively adsorbed to the Pd nanoparticles so that the subchains of P2VP free from the particles are short and hence have such a configuration as one end of the PI chain being fixed to the Pd nanoparticle but the rest of it being free from the particle, as shown in Figure 7b because P2VP and PI chains repel each other. If this were the case the particles should have aligned preferentially near the interface of P2VP lamellar nonodomains. This is not the case either.

The more or less uniform distribution of the particles in the P2VP lamellar nanodomains should infer that the Pd nanoparticles adsorb only a small number of P2VP chains, moreover only a small fraction of segments per single P2VP chains (Figure 7c). Furthermore, the Pd nanoparticles adsorb uniformly any parts of the P2VP



Figure 8 Mixtures of long and short block copolymers.

chains, at the end, middle, and junction point (Figure 7d). This implication is quite interesting and will leads us to an idea to control location of the metal nanoparticles across the interface, as shown schematically in Figure 8.

To control the location of the particles across the interface physically, we can use physics of block copolymer mixtures.^{18,19} Part a in Figure 8 exaggerates the chain conformation of a small amount of larger-molecular-weight block copolymers mixed in the matrix of smaller-molecular-weight block copolymers, while part b exaggerates that of a small amount of smaller-molecular-weight block copolymers. If a part of larger-molecular-weight block copolymers. If a part of the chains shown by the thick lines coordinate Pd nanoparticles with equal probability along the chains, then the Pd particles will be localized preferentially in the middle or near the interface in the case (a) and (b), respectively.

Figure 9 shows a histogram P(z) of Pd nanoparticles across the interface for the three systems as indicated in the figure where z indicates location of Pd nanoparticles



Figure 9 Self-assembly of Pd-P2VP-b-PI/T_p-P2VP-b-PI

in the P2VP lamellae renormalized by thicknesses of the lamellae. In the case when the P2VP blocks in Pd-P2VP*b*-PI have the molecular weight much smaller than the matrix-forming P2VP blocks in T_p -P2VP-*b*-PI, the Pd nanoparticles are localized near the interface (part a). If the two P2VP blocks have the same molecular weight, the Pd nanoparticles are more or less uniformly distributed (part b). If the P2VP block in Pd-P2VP-*b*-PI have the molecular weight much larger than the P2VP blocks in T_p -P2VP-*b*-PI, the Pd nanoparticles are localized in the middle of the P2VP lamellae (part c). Thus our intuition was experimentally verified. The details should be referred to elsewhere.²⁰

4.2. Chain Conformation of Coordinating Block Copolymer

In order to confirm the assumption concerning the conformation of P2VP block chains coordinating Pd nanoparticles as discussed in Sections 3 and 4.1, atomic force microscopy (AFM) studies were conducted.



Figure 10 AFM image of P2VP-*b*-PI block copolymers coordinating to a Pd nanoparticle

The chain conformation of isolated P2VP-*b*-PI block copolymer chains coordinating Pd nanoparticles was explored. For the AFM observation, the block copolymer chains were transferred onto a freshly cleaved mica surface by dipping the mica into extremely dilute solution of the block copolymer coordinating Pd nanoparticles. Further details of the method should be referred to elsewhere.²¹

Figure 10 shows an AFM image of P2VP-*b*-PI block copolymer chains coordinating a Pd nanoparticle (top) and a corresponding sketch (bottom). In this case, two block copolymer chains are coordinating one Pd nanoparticle whose height is 7 nm, consistent with the average diameter of the Pd nanoparticles observed by TEM.²¹ Those two chains have contour lengths of 380 nm and 400 nm, which are consistent with the contour length of 700 nm expected from the molecular weight of the P2VP block. A free chain can be observed as well. In another case, a single block copolymer chain was observed to be coordinating two Pd nanoparticles.

The important conclusions obtained by this study are the following: (i) Only a small fraction of segments in a polymer chain is adsorbed to the metal nanoparticles and, moreover, only a small number of chains are adhering. (ii) The adsorbed polymer chains have long subchains free from the metal nanoparticles and, therefore, stabilize the particles against coalescence and aggregate formation due to entropic repulsions of the subchains. (iii) Finally, the metal nanoparticles have a large free surface area, assuring the surface activities of the particles.

4.3. Nanohybrids: Process (2)

Next we will consider a way to create nanohybrids by a single-step process as schematically illustrated in Figure 11. In this case, P2VP-*b*-PI diblock copolymer and palladium acetylacetonate, Pd(acac)₂, were dissolved into a dilute solution of benzyl alcohol and chloroform as a mixed solvent. Chloroform was first evaporated at room temperature to obtain a concentrated solution of



Figure 11 Nanohybrids: Process (2)

the block copolymer in benzyl alcohol in which the nanodomain structures were already self-organized but Pd ions are not yet reduced and uniformly distributed in both PI and P2VP lamellae. Then temperature was raised to 140°C where Pd^{2+} ions were reduced into metals, the metals were aggregated into nanoparticles, and benzyl alcohol was simultaneously evaporated. In this way the films in which Pd nanoparticles were selectively aligned in P2VP nanodomain structures were obtained.

Figure 12a shows a typical TEM image of the microphase-separated structure observed for an unstained ultrathin section of thus obtained films. The dark dots are Pd clusters. They are aligned in a raw with a spacing of about 40 nm perpendicular to the raw. The image obtained with the OsO_4 stained specimen (not shown here) indicated dark lamellae comprised of selectively stained PI phase and bright lamellae comprised of unstained P2VP phase. The Pd nanoparticles were selectively localized in the P2VP lamellae.²²

In this way, we can create hybrids of metal nanoparticles aligned selectively in a raw in one of the lamellae with a controlled spacing between the raw. Figure 12b shows a sketch of block copolymer chains and metal nanoparticles which are to be driven toward middle of the nanodomain due to the elastic force of the polymer chains. We can have a dense nanoparticles with increasing concentration of Pd²⁺ ions.

5. CONCLUSIONS

We discussed some nanofabrication methods based upon block copolymer nanodomain structures as templates. These are (i) ordered nanochannels and metal plating of the channel surface, (ii) ordered double Gyroid network texture containing metal nanoparticles, and (iii) controlled alignments of metal nanoparticles in nanodomain structures in block copolymers.

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Figure 12 Microphase-separated structure containing Pd clusters obtained by the single-step process as schematically shown in Figure 11.

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