

Nanohybrids of Metal Nanoparticles and Block Copolymers. Control of Spatial Distribution of the Nanoparticles in Microdomain Space

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As one of interesting themes in physical science of block copolymers, some groups of researchers have been exploring methods and principles of 'nanoprocessing' of block copolymer microdomain structures. The nanoprocessing involves processings of the microdomains formed in the block copolymers (i) to create 'nanochannels'¹ (holes created in one of the microdomain phase dispersed in the matrix of other microdomain phase) or 'nanotextures'² (created by selectively removing the matrix phase, while preserving the dispersed phase) and (ii) to create 'nanohybrids' by incorporating nanometal particles, organic or inorganic particles into desired parts of the microdomain space.^{3–5} The nanochannels and nanotextures can be coated with metals.¹ The nanoprocessing may involve a processing to create an oriented single grain of microdomain structures.^{6,7}

In this communication we present highlights of our work to create a nanohybrid composed of alternating lamellar microdomains of polyisoprene (PI) and poly(2-vinylpyridine) (P2VP) containing palladium nanoparticles (denoted hereafter by Pd for the sake of simplicity) of ca. 5 nm in diameter selectively in the P2VP lamellae. We will present a novel method to control a spatial distribution of Pd in the P2VP lamellae across the interface. This method, which has never been reported so far to our knowledge, involves firstly a preparation of Pd coordinated and stabilized by poly(2-vinylpyridine)-*block*-polyisoprene (Pd-(P2VP-*b*-PI)) and secondly induces self-assembling of Pd-(P2VP-*b*-PI) and poly(2-vinylpyridine)-*block*-polyisoprene (P2VP-*b*-PI) forming the matrix phase for Pd *via* solvent casting with benzene. In our earlier report⁸ we presented a method to prepare Pd-(P2VP-*b*-PI) of 4 to 6 nm in diameter. The self-assembly of Pd-(P2VP-*b*-PI) and P2VP-*b*-PI block copolymer with chloroform as a solvent was shown to create a nanohybrid in which Pd are selectively localized in the P2VP lamellae. However no methods have been so far proposed to control the location of Pd within the P2VP lamellae, *e.g.*, a uniform distribution of the particles across the interface, or controlled alignment of the particles along the interface or in the middle of the P2VP lamellae etc. This is a point which we would like to address in this paper.

A method similar to that described above was presented earlier by Schrock and his coworkers.⁴ They first prepared a block copolymer having a block which contains P(octyl)₂ side groups and CdSe nanoclusters stabilized by P(octyl)₃ or O=P(octyl)₃. The block copolymers and the CdSe nanoclusters were then solution-cast into films. The CdSe nanoclusters are selectively coordinated in the microdomains comprised of the block chains with P(octyl)₂ side groups. However the controlled spatial arrangement of the particles within the microdomains was not reported at all.

Here in this work we used the P2VP-*b*-PI block copolymers to stabilize Pd, instead of the low molecular weight compounds such as P(octyl)₃, and the same block copolymer P2VP-*b*-PI for providing the matrix for Pd-(P2VP-*b*-PI) to attain the controlled spatial arrangement of Pd within the P2VP lamellae. Needless to say that the controlled spatial arrangement of the nanoparticles is crucial for further applications of systems to some photonic devices.⁹

EXPERIMENTAL

Polymer Synthesis

P2VP-*b*-PI block copolymers used in this work were prepared by living anionic polymerization and were characterized as described in Table I. Further details have been described elsewhere.⁸ These two block copolymers listed in Table I were used not only for coordinating and stabilizing Pd but also for providing a matrix phase for Pd-(P2VP-*b*-PI), which is also a unique and novel point of this work.

Sample Preparation

Pd-(P2VP-*b*-PI) were prepared by reducing Pd²⁺ ions (Pd(II)) with 1-propanol at 85°C for 48 h in a dilute homogeneous solution of P2VP-*b*-PI and palladium acetylacetonate, Pd(acac)₂. For this purpose 0.05 g of P2VP-*b*-PI, 0.12 g of Pd(acac)₂, and 10 mL 1-propanol were dissolved into 70 mL of benzene, and a homogeneous solution was prepared by stirring. The reduction was conducted by refluxing the solution under nitrogen gas at-

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Table I. Block copolymers (BCP, P2VP-*b*-PI) used in this work

BCP	M_n^a	M_w/M_n^b	W_{P2VP}^c
P2VP- <i>b</i> -PI1	100- <i>b</i> -45	1.86	69.0
P2VP- <i>b</i> -PI2	441- <i>b</i> -102	1.18	81.2

^a Number average molecular weight determined by the molecular weight of PI block precursor determined by GPC and the molar ratio of 2-vinylpyridine and isoprene monomer units determined by ¹H NMR. In X-*b*-Y, X and Y designates number average molecular weights of P2VP block and PI block, respectively, in unit of thousand. ^b Heterogeneity index determined by GPC with a standard polystyrene calibration. ^c Weight fraction of P2VP in the block copolymer determined by the molar ratio of 2-vinylpyridine and isoprene monomer units determined by ¹H NMR.

Table II. Three self-assembled systems studied in this work

System	Pd-(P2VP- <i>b</i> -PI)	P2VP- <i>b</i> -PI forming a matrix	No. of free P2VP- <i>b</i> -PI per a single Pd-(P2VP- <i>b</i> -PI)
A	Pd-(P2VP- <i>b</i> -PI 1) ^a (100- <i>b</i> -45) ^b	P2VP- <i>b</i> -PI2 (441- <i>b</i> -102)	110
B	Pd-(P2VP- <i>b</i> -PI 1) (100- <i>b</i> -45)	P2VP- <i>b</i> -PI1 (100- <i>b</i> -45)	410
C	Pd-(P2VP- <i>b</i> -PI 2) ^a (441- <i>b</i> -102) ^b	P2VP- <i>b</i> -PI1 (100- <i>b</i> -45)	1080

^a Pd-(P2VP-*b*-PI1) and Pd-(P2VP-*b*-PI2) denote the palladium nanoparticles coordinated by P2VP-*b*-PI1 and P2VP-*b*-PI2, respectively. ^b X and Y in X-*b*-Y denote, respectively, number average molecular weight of P2VP blocks and PI blocks in P2VP-*b*-PI1 or P2VP-*b*-PI2 in unit of thousand.

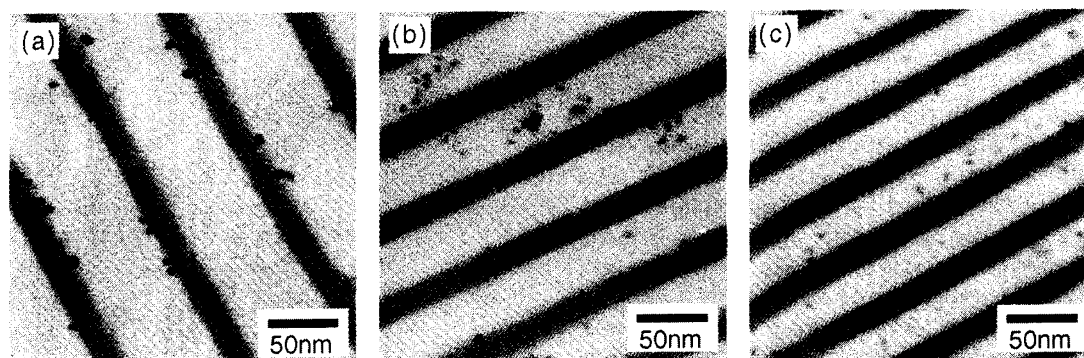


Figure 1. TEM of microphase-separated structures as observed in thin films cast from benzene solution of P2VP-*b*-PI_{*i*} mixed with Pd-(P2VP-*b*-PI_{*i*}) (*i* = 1 or 2) (a) system A (P2VP-*b*-PI₂ with Pd-(P2VP-*b*-PI₁)), (b) system B (P2VP-*b*-PI₁ with Pd-(P2VP-*b*-PI₁)), and (c) system C (P2VP-*b*-PI₁ with Pd-(P2VP-*b*-PI₂)). Ultramicrotomed thin specimens were stained with OsO₄.

mosphere. After the alcohol reduction, benzene and 1-propanol were evaporated. Thus obtained Pd-(P2VP-*b*-PI) were then dissolved into chloroform solution and precipitated into acetone to remove unreacted salt. The precipitates were again dissolved by benzene and purified by centrifugation three times to remove free P2VP-*b*-PI. Finally black powders of Pd-(P2VP-*b*-PI) were obtained by freeze-drying of the benzene solution. Two kinds of Pd-(P2VP-*b*-PI), *i.e.*, Pd-(P2VP-*b*-PI₁) and Pd-(P2VP-*b*-PI₂), the Palladium nanoparticles coordinated by P2VP-*b*-PI₁ and P2VP-*b*-PI₂, respectively, were prepared (Table II). The resultant Pd-(P2VP-*b*-PI) were reported to coordinate approximately equal to or less than five block copolymer chains per a single Pd nanoparticle on average as analyzed previously.⁸ The Pd nanoparticles used in the present study, however, were found to be stabilized by about 1.1 block copolymer chains from the elemental analysis. The Pd-(P2VP-*b*-PI_{*i*}) (*i* = 1 or 2) obtained were mixed with P2VP-*b*-PI_{*i*} (*i* = 1 or 2) with a composition of Pd-(P2VP-*b*-PI_{*i*}) of 2 wt% and dissolved into a homogeneous solution with benzene containing 0.5 wt% of Pd-(P2VP-*b*-PI_{*i*}) and P2VP-*b*-PI_{*j*} (*i, j* = 1 or 2) in total. The dilute homogeneous solution was cast into films in petri dish made of Teflon at room temperature by slowly evaporating solvent until a constant weight was attained. The cast-films were further dried under vacuum at 60°C for 24 h. In this way we obtained three types of specimens as summarized in Table II: system A comprised of Pd-(P2VP-*b*-PI₁)/P2VP-*b*-PI₂, system B comprised of Pd-(P2VP-*b*-PI₁)/P2VP-*b*-PI₁ and system C

comprised of Pd-(P2VP-*b*-PI₂)/P2VP-*b*-PI₁.

TEM Observation

These specimens were microtomed into ultrathin sections of about 50 nm in thickness with Reichert-Nissei Ultracut-S Ultramicrotome. The ultrathin sections were stained with OsO₄ vapor for 30 min and then subjected to morphological studies under transmission electron microscopy with JEOL JEM-2000 FXZ operated at 120 kV.

RESULTS AND DISCUSSION

Figure 1 shows transmission electron micrographs (TEM) for (a) system A, (b) system B, and (c) system C. In each image, the dark phases, the bright phases, and the small black dots are lamellae composed of PI blocks stained by OsO₄, lamellae composed of P2VP blocks unstained by OsO₄, and Pd-(P2VP-*b*-PI_{*i*}) (*i* = 1 or 2), respectively. Note that the observed lamellae morphology may not be necessarily an equilibrium structure, expected from the composition of the P2VP-*b*-PI block copolymer. The Pd nanoparticles are localized in the P2VP lamellae in all the cases. However interestingly enough their locations in the P2VP lamellae are different: they locate near the interfaces between the P2VP and PI lamellae in system A (part a), more or less uniformly across the interface in system B (part b) and likely in the middle of the P2VP lamellae in system C (part c). The average size of Pd was about 5 nm in all the cases. There is a size dis-

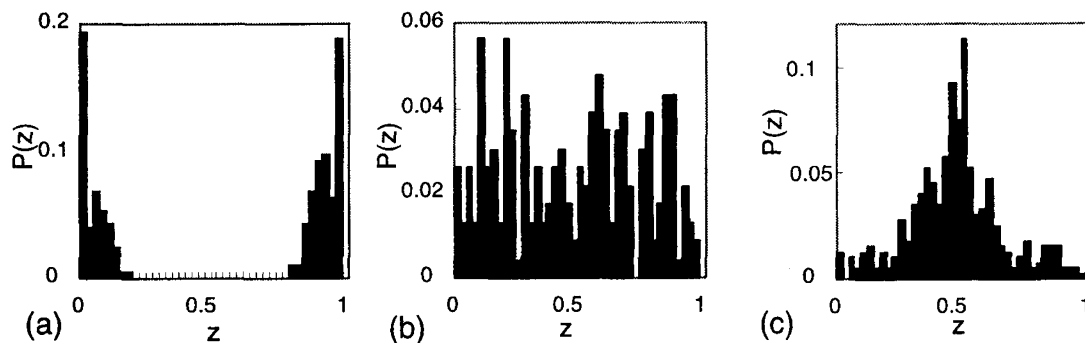


Figure 2. Histogram $P(z)$ on a spatial distribution of Pd nanoparticles across the interface in the P2VP phase for system A(a), system B(b) and for system C(c). $z = d/D$, a distance between center of the Pd particles and interface normalized by the P2VP lamellar thickness D . $P(z)$ satisfies $\int_0^1 P(z) dz = 1$.

tribution in Pd as will be detailed elsewhere.¹⁰ However we could hardly observe the traces of coalescence of the particles themselves. In each image, the P2VP lamellae are thicker than PI lamellae as expected from the composition of P2VP-*b*-PI_{*i*} (*i* = 1 or 2) (Tables I and II). The lamellae spacing determined by total molecular weight of P2VP-*b*-PI_{*i*} (*i* = 1 or 2) is larger for system A (part a, 100 nm) than that for system B (part b, 45 nm) and system C (part c, 55 nm), again as expected.

A spatial distribution of Pd across the interface was more quantitatively studied by measuring a histogram for the location of Pd. The histogram, $P(z)$, was obtained for about 200 Pd and plotted as a function of a reduced distance $z = d/D$ in Figure 2, where d is the distance between the center of Pd and the interface and D is the thickness of the P2VP lamellae. The histogram is normalized such that $\int_0^1 P(z) dz = 1$. The results clearly re-

veal that Pd are localized in the P2VP lamellae in all the cases but in a narrow region near the interface for system A(a), more or less uniformly in whole region in the lamellae for system B(b) and more likely in the middle region for system C(c).

The experimental evidence shown in Figures 1 and 2 further infers the following possible model for a coordination mechanism of Pd by P2VP-*b*-PI block chains: (1) The Pd nanoparticles are selectively coordinated by P2VP block chains in P2VP-*b*-PI but not by PI blocks; (2) only a few P2VP-*b*-PI chains are coordinating Pd so that the PI blocks are not isotropically shielding Pd and the P2VP blocks and Pd as schematically shown in Figures 3a to 3c. This particular configurations of Pd-(P2VP-*b*-PI) allow the PI blocks of Pd-(P2VP-*b*-PI) to segregate into the PI lamellae and Pd coordinated by the P2VP blocks of Pd-(P2VP-*b*-PI) segregate in the P2VP lamellae. Interestingly enough those results in Figures 1 and 2 further infer the following important aspects, as shown schematically in parts a to c of Figure 3; (3) a whole part of the P2VP block of Pd-(P2VP-*b*-PI) is not coordinating to Pd but rather only a part of the P2VP block is coordinating so that scheme (c) is more probable than scheme (a); (4) Pd may be coordinated at any parts of the P2VP block such that the coordination at the location 1 to 3 in scheme (b) is equally probable; (5) Pd nanoparticles do not easily change their coordinating position within the same P2VP block, *e.g.*, from place 1 to 2 or 3

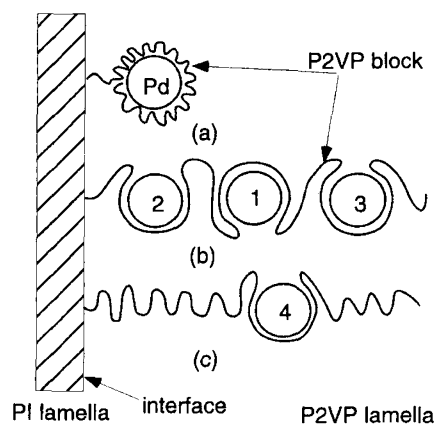


Figure 3. Schematic representation of the Pd nanoparticles and P2VP block chains coordinating the Pd nanoparticles.

in scheme (b), and between different P2VP blocks, *e.g.*, from place 1 in scheme (b) to place 4 in scheme (c) over the time scale of observation covered in the present study (for 13 months at room temperature and 2 days at 140°C).

In the above arguments, the statements (1) and (2) are reduced from the piece of evidence that the Pd nanoparticles are localized in the P2VP lamellae but not in the PI lamellae in all the cases. The statement (3) is reduced from evidence that the Pd nanoparticles are not necessarily localized near the interface. If scheme (a) were correct, Pd should be always localized near interface for all the three systems A to C. The statement (4) is reduced from the uniform distribution of Pd in the P2VP lamellae for the case of system B. Finally the statement (5) is reduced from existence of the difference in the spatial distribution of Pd for the three different systems even after the long annealing processes as described above.

The statements (1) and (2) are consistent with the conclusion elucidated from the previous study.⁸ The statements (3) to (5) are newly obtained from the present study and provide fundamental bases for the novel, controlled alignments of Pd within the P2VP lamellae. The prediction that only a part of the block copolymer chains and only a small number of chains (up to three chains) are coordinating single Pd was directly proved recently under atomic force microscopy (AFM).¹¹ Moreover we

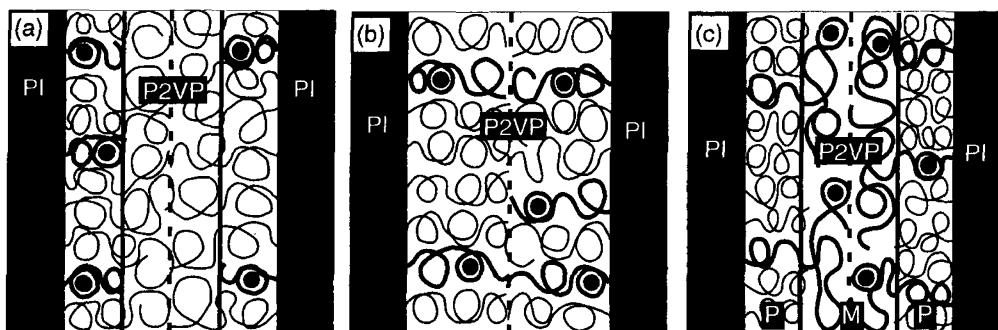


Figure 4. Schematic model for the distribution of the P2VP chains of Pd-(P2VP-*b*-PI) (—●—) and P2VP-*b*-PI (—) in the P2VP phase of the microphase-separated structure for system A(a), for B(b), and C(c). PI and P2VP are the PI and P2VP lamellae, respectively. Only P2VP blocks are schematically drawn, and PI blocks are not drawn.

can conclude that the previous result⁸ corresponds to the case of system A, *i.e.*, only one of the three cases of the present study and hence the present study is of value in generalizing the method for the controlled incorporation of the metal nanoparticles in the microdomain spacing.

Figure 4 schematically presents possible models describing the location of Pd in the P2VP lamellae. The P2VP and PI lamellae are drawn by bright and dark phases, respectively, and the center of the P2VP lamellae are drawn by dashed lines. In all the cases of system A to C, chemical junctions between the P2VP and PI blocks in both P2VP-*b*-PI and Pd-(P2VP-*b*-PI) are assumed to share common interface. The PI blocks and P2VP blocks or those coordinating Pd are assumed to segregate into the PI and P2VP lamellae, respectively, as in the case of mixtures of two miscible block copolymers of (A-B)_α and (A-B)_β.^{12,13} Moreover in all the cases, the thickness of the P2VP lamellae is essentially and explicitly controlled by the P2VP blocks free from Pd and forming the matrix.

In the case of system A shown in part (a), Pd are naturally confined near the interface, simply because P2VP chains coordinating Pd is much shorter than the P2VP blocks of the metal-free P2VP-*b*-PI which control the thickness of the P2VP lamellae. In the case of system B shown in part (b), Pd distributed uniformly across the interface due to scheme (b) shown in Figure 3. In the case of the system C shown in the part (c), (i) the chain ends of the long P2VP blocks carrying Pd and those of the short P2VP blocks free from Pd segregate into respective spaces¹⁴ designated by M and P in Figure 4 which are separated by straight lines, and (ii) the contour length of the long P2VP blocks in the space M may be longer than that in the space P. These two factors (i) and (ii) may account for the experimental finding of the localization of Pd in the middle of the P2VP lamellae as shown in Figures 1 and 2.

In summary we succeeded in controlling the location of the Pd nanoparticles in the microdomain space by con-

trolling relative molecular weights of the free block copolymers P2VP-*b*-PI forming the microdomains and the block copolymers P2VP-*b*-PI coordinating the Pd nanoparticles. The control of the location of the Pd nanoparticles presumably depends on the particular preparation method of Pd-(P2VP-*b*-PI) employed in this study and hence the particular configurations of the P2VP-*b*-PI coordinating the Pd nanoparticles. Further investigation along this line deserves future works.

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