Formation of Pd Clusters into Microphase-separated Structures of Block Copolymers and Their Controlled Arrangements.

Masafumi Harada and Takeji Hashimoto
Hashimoto Polymer Phasing Project, ERATO, JST
Keihanna Plaza, 1-7 Hikari-dai, Seika,
Kyoto 619-0237, Japan

Polyisoprene-*block*-poly(2-vinylpyridine) (PI-*b*-P2VP) films containing palladium clusters (diameters less than 10 nm) were obtained by preparing the concentrated PI-*b*-P2VP solutions (33 wt%) in benzyl alcohol with palladium(II) acetylacetonate and quickly evaporating benzyl alcohol solvent at ca. 140 °C. Block copolymers (PI-*b*-P2VP) having different volume fractions of polyisoprene(PI) formed their corresponding microphase-separated structures in benzyl alcohol solutions as well as in cast films. Pd cluster formations in the microphase-separated structure occurred in the P2VP phase through producing P2VP-Pd ion (or P2VP-Pd atom) complexes in reduction.

Introduction

Nanocomposite materials like nanometer-sized particles of metals and semiconductors in polymer matrix have been intensively investigated with respect to the development of their novel electronic, optical, and magnetic properties.[1] Formation of metal clusters in polymer thin films has been carried out by some of the techniques, such as ionized-cluster-beam deposition, chemical vapor deposition, etc., which result in a rather broad size distribution of metal clusters and have difficulty in manipulating a well-controlled structure.

It has been well known that diblock copolymer spontaneously formed microphase-separated structures in cast film, and metal clusters could be prepared selectively into one block section of diblock copolymer[2-5] through the formation of polymer-metal ion complexes,[6] because the metal ions were bound preferentially to the functional block having strong interaction with metal ions. For their applications, considering the influences of formation of metal clusters to the microphase-separated structure of diblock copolymer when the load of metal clusters increases, we can explore the possibilities to obtain prospective devices such as quantum wires, quantum wells and quantum dots.

In this work we investigated morphologies and domain sizes of the microphase-separated structures of PI-*b*-P2VP cast films after the formation of

Pd clusters and those of PI-*b*-P2VP in concentrated benzyl alcohol solutions before reduction by means of transmission electron microscopy (TEM) as well as small-angle X-ray scattering (SAXS) measurements. We also attempted to prepare polymer films with monodisperse regularly distributed Pd clusters for the purpose of structural control of well-defined self-assemblies.

Experimental

Sample preparation. Polyisoprene-*block*-poly(2-vinylpyridine),PI-*b*-P2VP, was synthesized by sequential anionic polymerization. The PI-*b*-P2VP samples used in this experiment are listed in Table 1. PI(18000)-*b*-P2VP(12600), PI(76000)-*b*-P2VP(23500), and PI(220000)-*b*-P2VP(21500) were purchased from Polymer Source, Inc., for the convenience. PI-*b*-P2VP (300 mg) concentrated solutions (33 weight%) in benzyl alcohol (0.6 mL) containing palladium(II) acetylacetonate [$Pd(acac)_2$], which have already formed microphase-separated structures, were prepared by slowly evaporating the only chloroform solvent (5.4 mL) at room temperature from a mixed solution of benzyl alcohol / chloroform (0.6 mL / 5.4 mL v/v) dissolving the designed amount of $Pd(acac)_2$. The initial polymer concentrations before evaporating the chloroform were ca. 5 weight%. In this case, $Pd(acac)_2$ was added to the mixed solution, according to the weighting ratio of $Pd(acac)_2$ / PI-*b*-P2VP, i. e., $Pd(acac)_2$ / PI-*b*-P2VP = 0, 0.04, 0.08, 0.20, 0.40, and 0.80. Following the evaporation of chloroform, PI-*b*-P2VP films containing Pd clusters were prepared by quickly evaporating the benzyl alcohol solvent at ca. 140 °C on hotplate from the concentrated PI-*b*-P2VP solutions (33 wt%) including $Pd(acac)_2$ in benzyl alcohol. This procedure was carried out for about 8 - 10 hours in order to make the evaporation of benzyl alcohol completed. The obtained films were dried under vacuum at room temperature for 1 day before characterization by means of TEM and SAXS measurements.

Characterization. TEM was performed at 200 keV (bright field images) on a JEOL JEM-2000FXZ instruments. For the TEM observation, an ultrathin film specimen of PI-*b*-P2VP containing Pd clusters was prepared by cutting the obtained film with a cryomicrotome (Reichert-Nissei, Ultracut-S) (film thickness, ca. 30 nm), and the microtomed sample was then mounted on a PVF-supported copper grid. Additionally, in order to clearly observe a microphase-separated structure of PI-*b*-P2VP formed during the casting, the mounted ultrathin film was stained by osmium tetroxide (OsO_4) vapor for 2-3 hours to enhance a contrast of brightness between PI and P2VP phases. SAXS experiment of PI-*b*-P2VP samples was carried out at room temperature.

Table 1. Characteristics of PI-*b*-P2VP samples

Sample	Mn(PI)	Mn(P2VP)	Mw / Mn
PI(20000)-*b*-P2VP(44300)	20000	44300	1.53
PI(17100)-*b*-P2VP(23200)	17100	23200	1.03
PI(13400)-*b*-P2VP(17600)	13400	17600	1.03
PI(18000)-*b*-P2VP(12600)	18000	12600	1.04
PI(76000)-*b*-P2VP(23500)	76000	23500	1.04
PI(220000)-*b*-P2VP(21500)	220000	21500	1.05

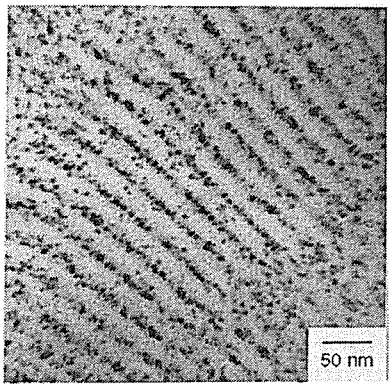

Fig. 1 24.1 mg $Pd(acac)_2$ added. (not stained)

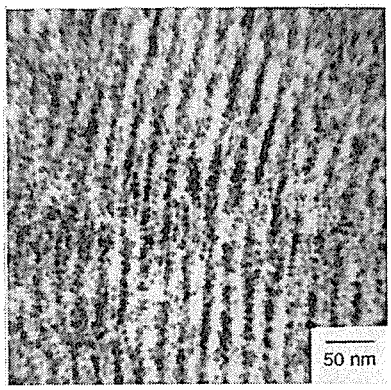

Fig. 2 120.5 mg $Pd(acac)_2$ added. (not stained)

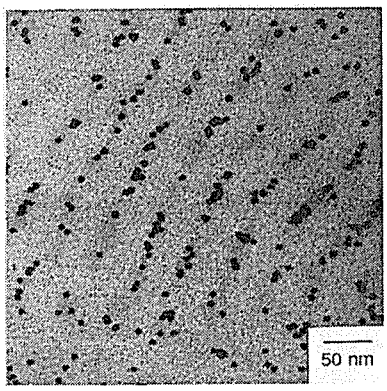

Fig. 3 PI(76000)-*b*-P2VP(23500). (not stained)

Results and Discussion

In the sample preparation, cast films turned from (transparent) yellow-orange to dark-brown in color during the first 10 min of the evaporation of benzyl alcohol at 140 °C. The consecutive 8 - 10 hours evaporation is enough long to reduce Pd ions to metals completely. Thus the color change indicated that the formation of metal clusters in PI-*b*-P2VP films was achieved obviously.

For the cast film of PI(18000)-*b*-P2VP(12600) containing Pd clusters [$Pd(acac)_2$ / PI-*b*-P2VP = 0.08], lamellar microdomains with the domain spacing of ca. 30 - 35 nm and linear alignments of separate Pd clusters (diameter of ca. 4 nm) located in the center of P2VP microdomains could be observed from TEM, as shown in Figure 1. SAXS profile also indicated the first scattering maximum at q=0.171 nm^{-1}, corresponding to the domain spacing of about 35 nm. On the other hand, in the case of cast films containing the large amount of Pd clusters [$Pd(acac)_2$ / PI-*b*-P2VP = 0.40], lamellar microdomains with the domain spacing of ca. 25 - 30 nm were kept in structure and aggregates (or flocculates) of Pd clusters (each diameter of 6 - 8 nm) were aligned, which looks like nanometer-sized wires, inside the P2VP microdomains.(Figure 2) There has shown to be a possibility to form nanometer-sized wires in the microphase-separated structure of diblock copolymer films in this method or improved one in near future.

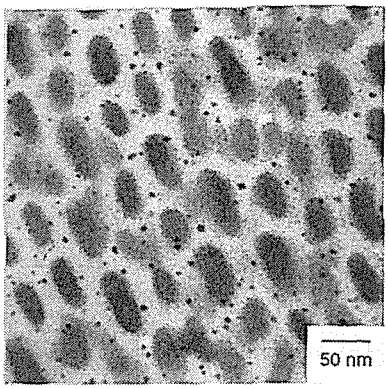

Fig. 4 PI(17100)-*b*-P2VP(23200). (stained with OsO_4)

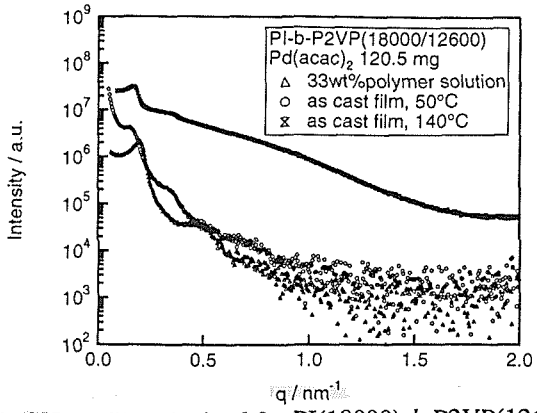

Fig. 5 SAXS profiles obtained for PI(18000)-*b*-P2VP(12600). The cast at 50 °C does not allow Pd ions to be reduced.

In order to investigate the morphologies of microphase-separated structure of PI-*b*-P2VP against the formation of Pd clusters in difference of P2VP microdomains in shape, some PI-*b*-P2VP listed in Table 1 were employed. Figures 3 and 4 show TEM images of PI(76000)-*b*-P2VP(23500) and PI(17100)-*b*-P2VP(23200) cast films containing Pd clusters [$Pd(acac)_2$ / PI-*b*-P2VP = 0.08], prepared as the same procedure as in the case of PI(18000)-*b*-P2VP(12600), respectively. In these films, the former has a cylindrical P2VP phase and the latter a spherical PI phase, and the Pd clusters are also selectively located in the P2VP phase.

Figure 5 shows SAXS profiles obtained for the films of PI(18000)-*b*-P2VP(12600) cast from benzyl alcohol containing 120.5 mg $Pd(acac)_2$ [$Pd(acac)_2$ / PI-*b*-P2VP = 0.40]. The scattering intensity of film prepared at 140 °C is much larger than that prepared at 50 °C, owing to the formation of Pd clusters at 140 °C. The detailed analysis will be discussed at the symposium.

References

(1) D. Yu. Godovski, Adv. Polym. Sci. **119**, 79 (1995).

(2) Y. Ng Cheong Chan, R. R. Schrock, and R. E. Cohen, J. Am. Chem. Soc. **114**, 7295 (1992).

(3) R. Saito, S. Okamura, and K. Ishizu, Polymer **33**, 1099 (1992).

(4) D. E. Fogg, L. H. Radzilowski, R. Blanski, R. R. Schrock, and E. L. Thomas, Macromolecules **30**, 417 (1997).

(5) R. W. Zehner, W. A. Lopes, T. L. Morkved, H. Jaeger, and L. R. Sita, Langmuir **14**, 241 (1998).

(6) J. P. Spatz, A. Roescher, and M. Möller, Adv. Mater. **8**, 337 (1996).