

**Phase Separation of Block Copolymer
Containing Metal Nanoparticles.
Influence of Molecular Weight of Copolymer.**

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Abstract: Structure based on the self organization of block copolymer containing metal nanoparticles was investigated. Films consisting of block copolymer and metal nanoparticles stabilized by block copolymer were observed by transmission electron microscopy (TEM), for various molecular weights of the polymer. The location of the metal introduced into the microphase structure was influenced by a combination of the molecular weight of the matrix polymer and that of stabilizing polymer.

Introduction

Noble metal nanoparticles of well defined size are expected to be useful for optical applications and catalysis. Recently our project succeeded in synthesizing palladium (Pd) nanoparticles stabilized by poly(2-vinylpyridine) homopolymer (P2VP) (designated as "Pd-(P2VP)") and those stabilized by polyisoprene/poly(2-vinylpyridine) block copolymer (PI-P2VP) (designated as "Pd-(PI-P2VP)") by reduction of palladium acetylacetonate ($\text{Pd}(\text{acac})_2$) in homogeneous polymer solution. These particles were introduced into the P2VP phase or near the interface between the PI and P2VP phase of the microphase separated structure of the PI-P2VP matrix, by using a mixture of PI-P2VP and Pd-(P2VP) or of PI-P2VP and Pd-(PI-P2VP), respectively.¹⁾ In this study, we

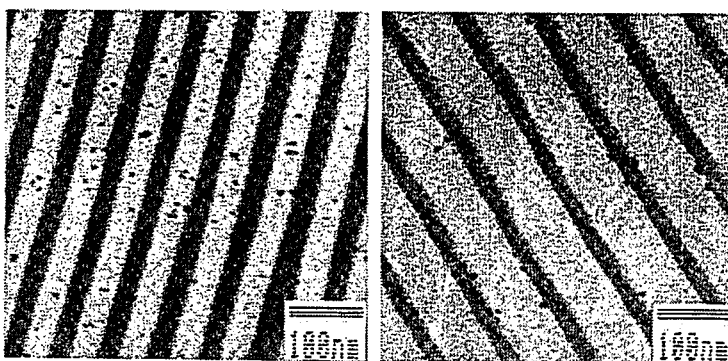
examined the influence of the molecular weight of the block copolymer.

Experimental

PI-P2VP was synthesized by living anionic polymerization in tetrahydrofuran. Pd nanoparticles stabilized by PI-P2VP were synthesized as follows. PI-P2VP (0.05g) and Pd(acac)₂ (0.12g) were dissolved in a mixed solvent of benzene(70ml) and 1-propanol(5ml). Refluxing of the resulting solution under N₂ on an oil bath at 85°C for 48 hours gave a homogeneous colloidal dispersion of Pd nanoparticles. The particles were purified by precipitation in acetone and then centrifugation in benzene. Cast films were prepared by solvent-casting from benzene solution at 30°C. The phase structure in the as-cast film was observed by TEM at 120KV on the ultrathin sections stained with OsO₄ vaper.

Results and Discussion

Fig. 1 shows TEM images of the micro structure of the cast film consisting of PI-P2VP and Pd-(PI-P2VP); molecular weight of PI-P2VP



used for the matrix is lower(Fig. 1(a)) and higher(Fig. 1(b)) than that for stabilizing the Pd

nanoparticles. The particles (black dots) exist only in the P2VP phase (white phase) of the lamella structure. But on close observation,we observe that the location of the particles in the P2VP phase changes according to a combination of the moleclar weight of the matrix polymer and that of the stabilizing polymer. Next, we discuss the relation between the molecular weight of the copolymer and location of the particles in detail.

(a) (b)
Fig. 1. TEM of the film consisting of PI-P2VP and Pd-(PI-P2VP)(OsO₄ stained). Molecular weight of polymer is (a)45K-100K and 102K-441K (b)102K-441K and 45K-100K, respectively.

Fig. 2 shows the distribution of the particles in the P2VP phase as a function of the distance from the interface of the microdomain calculated from Fig. 1. In Fig 2(a) the particles exist mainly

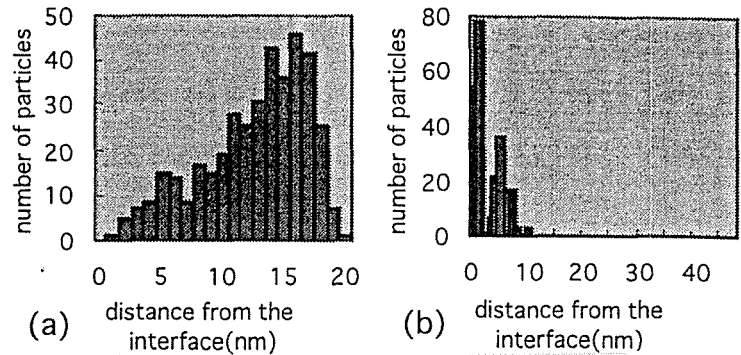


Fig. 2. A distribution of the particles in the P2VP phase as a function of the distance from the interface of the microdomain calculated from Fig. 1. (a) calculated from Fig. 1(a), (b) from Fig. 1(b)

around 16nm away from the interface, which is the center of the P2VP phase having a thickness of about 40nm. In this case, the stabilizing copolymer, of which the P2VP chain can spread to about 50nm²⁾ was added to the matrix copolymer forming a 30nm thick P2VP lamella phase. Thus the part of the P2VP chain stabilizing the particles, which is more than 15nm from the junction of PI and P2VP block, may be distributed around the center of the P2VP phase. Then the particles stabilized by that part of the chain must also be distributed around the center of the P2VP phase. In Fig. 2(b), the particles exist in the range of 10nm away from the interface. In this case, the P2VP chain for stabilizing the Pd particles could only exist in the range of less than 15nm away from the interface.³⁾ Thus the particles could be introduced only in the range where the polymer for stabilizing can exist.

In conclusion, we could control the location of the introduced Pd nanoparticles in the P2VP phase by changing the combination of the molecular weight of the matrix copolymer and that of the stabilizing copolymer.

References and Notes

- 1) Y. Funaki, HPPP News, **5**, 27(1997).
- 2) The microphase separated structure of this polymer for stabilizing is about 100nm thick P2VP lamella.
- 3) The microphase separated structure of this polymer for stabilizing is about 30nm thick P2VP lamella.