

Dynamics of Pd Cluster Formation in Microphase-separated Structures of Block Copolymers

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The formation of the palladium (Pd) clusters with nanometer scale in microphase-separated structures of block copolymers was investigated *in situ* by time-resolved small angle X-ray scattering. The Pd clusters were produced by reducing Pd ions dissolved in concentrated polyisoprene-*block*-poly(2-vinylpyridine) diblock copolymer solution in benzyl alcohol. We could observe that the SAXS intensity corresponding to the Pd clusters increases with the formation of the Pd clusters proceeding.

Introduction

The introduction of the metal clusters with the diameter less than 10 nm into microphase-separated structures of block copolymers has been intensively investigated. Recently we found that the palladium (Pd) clusters can be introduced selectively in poly(2-vinylpyridine)(P2VP)-phase in microphase-separated structures of polyisoprene(PI)-*block*-P2VP diblock copolymers by reducing Pd ions dissolved in the concentrated PI-*block*-P2VP diblock copolymer solution in benzyl alcohol. The Pd clusters in P2VP-phase are produced via P2VP-Pd ion (or P2VP-Pd atom) complexes in reduction.

In this work, we will present the dynamics of the formation of Pd clusters in microphase-separated structures of PI-*block*-P2VP diblock copolymers investigated by time-resolved small angle X-ray scattering (SAXS).

Experimental

The PI-*block*-P2VP diblock copolymer solution in benzyl alcohol containing palladium(II) acetylacetonate ($\text{Pd}(\text{acac})_2$) was employed in this work. The M_n , f_{PI} , and M_w/M_n of this PI-*block*-P2VP diblock copolymer, coded as PI(18000)-*b*-P2VP(12600), are 3.06×10^4 , 0.64, and 1.04, respectively. The specimen contained 29 wt% PI(18000)-*b*-P2VP(12600), 59 wt% benzyl alcohol, and 12 % $\text{Pd}(\text{acac})_2$, i.e., $\text{Pd}(\text{acac})_2/\text{PI}(18000)\text{-}b\text{-P2VP}(12600) = 0.40$ (wt/wt). The Pd ions are reduced by heating the specimen above 80 °C.

The time-resolved SAXS measurement was performed as follows; (i) the specimen was put in the heater block controlled at a particular temperature above 80 °C (T-jump); (ii) the time-resolved SAXS measurements were started and time t was set zero at the time when the specimen was put into the heater block.

Results and Discussion

Figure 1 gives the SAXS profiles at various time after T-jump to 80 °C. The SAXS intensity in the q -region larger than 0.22 nm^{-1} clearly increases with time, and reaches equilibrium at 120 min. Moreover the SAXS intensity, increasing after T-jump, can be expressed by the theoretical scattering profile from isolated spherical particles with the diameter of 3.0 ~ 4.5 nm, though it is not presented here. These results indicate that the spherical Pd clusters were produced after T-jump and the conversion from Pd ion to Pd clusters completed within 120 min. With precise analyses on these SAXS profiles, we could obtain the time-evolution of the diameter of the Pd clusters and conversion rate at 80 °C.

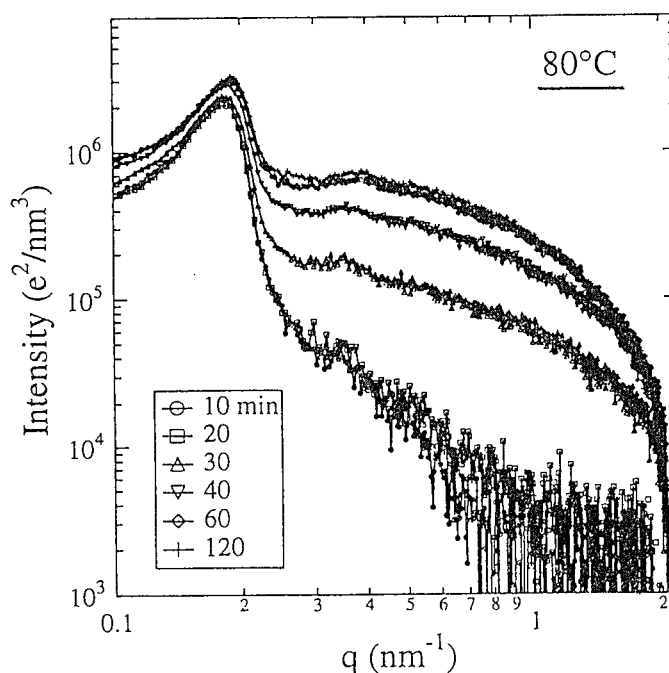


Figure 1 Time-changes in SAXS profiles after T-jump to 80 °C.