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Gradual Changes in Microphase-Separated Structures of Poly(4-*tert*-butylstyrene-*block*-4-*tert*-butoxystyrene) Through Hydrolysis Reaction

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Introduction

Microphase-separated structures of block copolymers have potentials in applications such as nanoporous materials, templates of nanoparticles, high conductivity nanocomposite, and dye-sensitized solar cell *etc*. In order to have flexible access in controlling microphase-separated structures, understanding the thermodynamics of block copolymers is crucial. In this study, we investigate the changes in microphase-separated structures of poly(4-*tert*-butylstyrene-*block*-4-*tert*-butoxystyrene) (BO) upon hydrolysis reaction. Poly(4-*tert*-butoxystyrene) (O) can be easily converted into poly(4-hydroxystyrene) (H) through hydrolysis reaction. Since O is a non-polar polymer and H is a polar one, the conversion of O into H should sensitively change the segregation strength in the copolymer thus, altering its aggregation state.

Experiments

Three BOs having different molecular weights were prepared by sequential living anionic polymerizations. The molecular weights of the samples are 67k, 98k and 148k and their volume fractions are ca. 0.5. Hydrolysis reactions were conducted by heating 5 wt% of 1,4-dioxane solutions of BOs under the presence of concentrated hydrochloric acid (HCl). The conversion from O into H, f_H, was controlled by reaction time, temperature and HCl concentration. f_H was measured by ^{1}H NMR at 500 MHz[1]. The morphologies were evaluated by transmission electron microscopic (TEM) observations and small-angle X-ray scattering (SAXS) measurements.

Results and Discussion

The morphologies of the hydrolyzed BO98k are represented in Figures 1. The non-hydrolyzed BO (f_H=0) was transparent under TEM and its SAXS profile showed only correlation hole peaks. These results imply that it is in disordered states. In contrast, lamellar structures were mainly observed in the hydrolyzed samples, which were guaranteed by the integer order peaks in the SAXS profiles. The domain spacings increase with increasing f_H.

Figure 2 depicts the relationship between D/D_0 and χN for BO67k, BO98k and BO148k where D/D_0 indicates the degree of stretch of a chain compared to its random coil state and χN is segregation strength. D/D_0 values from three different BOs overlap each other within the whole range of χN signifying that the changes in D/D_0 for all hydrolyzed BOs are scaled by χN. Three regimes can be distinguished in Figure 2: (I) $D/D_0 \sim 1$, (II) D/D_0 is

proportional to $(\chi N)^{0.34}$, (III) D/D_0 is constant to be 2.3. This means that the chains initially adopt Gaussian conformation in regime (I) and stretch gradually with increasing χN in regime (II), and finally reach an equilibrium stretched state in regime (III). It should be noted that the D/D_0 values are constant in two regimes of (I) and (III), reflecting that the structural similarity of chain conformation are maintained and the scaling laws can be applied in each regime. However, it is worth noting that the scaling law can be applied in the regime (II) in a strict sense of only χN.[2]
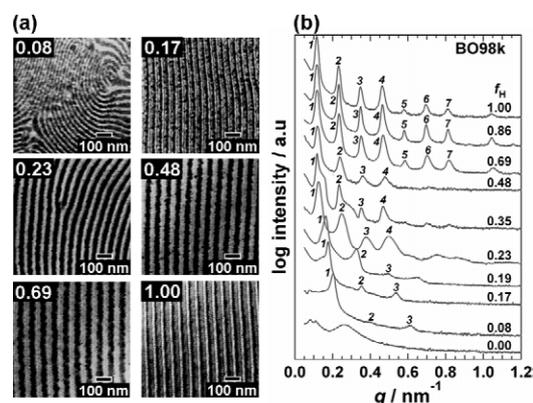

Figure 1. (a) TEM micrographs and (b) SAXS profiles of BO98k having various f_H values. The numbers at the upper left-hand of each TEM micrograph represent f_H.
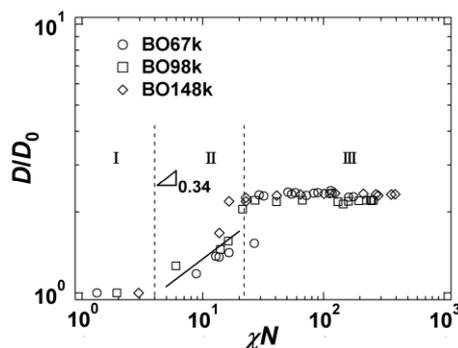

Figure 2. Relationship between D/D_0 and χN for BO67k (○), BO98k (□) and BO148k (◊). D_0 is the correlation length obtained from the non-hydrolyzed sample.

References

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[2] Rahman et al., Macromolecules, 44, 2799 (2011).

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