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Synthesis of Ribbon-like Nanopolymers by Crosslinking Reaction of Cylindrical Microdomains of Diblock Copolymer Films

(Running title: Ribbon-like nanopolymers)

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Abstract : The ribbon-like nanopolymers were prepared by the crosslinking reaction of poly(α -methylstyrene)-*block*-poly(4-vinylpyridine) (PMS-*block*-P4VP) diblock copolymer films exhibiting P4VP cylindrical microdomains, with the vapour of 1,4-dibromobutane in the solid state. It was indicated by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) that these crosslinked products had a structure of ribbon-like nanopolymers.

1. Introduction

Block and graft copolymers of incompatible block segments form microphase-separated structures in the solid state. We have established a novel synthesis method for core-shell polymer microspheres: crosslinking of segregated chains in spherical microdomains of diblock copolymers [1-7]. These microspheres were stabilized even in good solvents by multiarm chains.

More recently, Eisenberg and coworkers reported that aggregates of various morphologies can be prepared from amphiphilic block copolymers in solutions of small molecule solvents [8-11]. These aggregates are made from one family of highly asymmetric polystyrene-*block*-poly(acrylic acid) (PS-*block*-PAA) or PS-*block*-polyethylene oxide (PEO) diblock copolymer, in which the lengths of the insoluble PS blocks are much greater than those of the soluble PAA (or PEO) blocks. These aggregates are therefore described as "crew-cut". The observed morphologies include spheres, rods, vesicles, enlogated vesicles, lamellae, large-compound vesicles, large-compound micelles, and several others. Basically, the formation of the aggregates of different morphologies depends on the copolymer composition, the initial copolymer

concentration in solution, and the type and concentration of added ions.

As a matter of course, these aggregates lead to deformation in a dilute solution due to the equilibrium between micelle and unimer. Therefore, the microdomain locking of block copolymer films is one of the best methods for preparation of nanopolymers.

In this article, we carry out the crosslinking reaction of poly(α -methylstyrene)-*block*-poly(4-vinylpyridine) (PMS-*block*-P4VP) diblock copolymer films having P4VP cylindrical microdomains, with the vapour of 1,4-dibromobutane in the solid state to obtain the ribbon-like nanopolymers. The morphology and solution properties are studied in details by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS).

2. Experimental

2.1 Block Copolymer Synthesis and Characterization

The well-defined PMS-*block*-P4VP diblock copolymer was prepared by the usual sequential anionic addition polymerization using *n*-butyl lithium as an initiator in tetrahydrofuran (THF) at -78°C. The details concerning the synthesis, purification, and characterization of such block copolymer have been

given elsewhere [12]. Table 1 lists the characteristics of the monodisperse diblock copolymer MSV1 and the microdomain spacings of a specimen cast from 1,1,2-trichloroethane (TCE).

Table 1 Characteristics of poly(α -methylstyrene) block-poly (4-vinylpyridine) diblock copolymer and its domain spacings

Specimen code	Block copolymer			Shape of P4VP domain	Domain spacing	
	$10^{-4}\bar{M}_n^a$	$\bar{M}_w/\bar{M}_n^b$	P4VP ^c block (mol %)		$\bar{R}_{c,0}^d$ (nm)	$\bar{d}^e$ (nm)
MSV1	6.0	1.17	22	cylinder	7.9	22.3

^{a)}Determined by osmometry.

^{b)}Determined by gel permeation chromatography.

^{c)}Determined by ¹H n.m.r. in CDCl₃.

^{d)}Average radius of cylinder determined by TEM.

^{e)}Average nearest-neighbour distance between cylinders determined by TEM.

2.2 Crosslinking of Block Copolymer Films

The diblock copolymer film 50 μm thick was cast from a 0.03 g ml⁻¹ TCE solution on a Teflon sheet. The cast film was dried under vacuum for 2 days at room temperature. Crosslinking of the segregated P4VP chains in a cylindrical microdomain was carried out by using quaternization (reaction of tertiary amine with alkyl halide) with the vapour of 1,4-dibromobutane (DBB) at room temperature under a reduced pressure for 3 days. After crosslinking reaction, the films were washed with methanol and dried under high vacuum.

2.3 Morphological Observations

A film specimen of diblock copolymer for TEM observations was cast from a dilute solution of TCE on a Teflon sheet for 5 days and dried under vacuum. This film was embedded in an epoxy resin and cut into ultrathin sections (about 70–100 nm thick) using an ultramicrotome (Reichert-Nissei Co., Ultracut N). This specimen was exposed to the vapour of osmium tetroxide (OsO₄).

Ultrathin film specimens of ribbon-like nanopolymers were prepared by placing a drop of 0.01–1.0 wt% toluene solution on a TEM grid coated with a carbon film, and then evaporating the solvent as slowly as possible at 25°C. Morphological results were

obtained by TEM on a Hitachi H-500 operated at 75 kV.

2.4 SAXS measurements

A film specimen of the nanopolymer for SAXS measurements was cast from a dilute solution of TCE on a Teflon sheet for 5 days and dried under vacuum. This specimen was further annealed at 120°C for 1 week under vacuum so as to have a structure thermodynamically at equilibrium.

The SAXS intensity profile was measured with a rotating-anode X-ray generator (Rigaku Denki Rotaflex RTP 300RC) operated at 40 kV and 100 mA. The generated X-ray beam was monochromatized to Cu K α ($\lambda=1.5418\text{\AA}$) radiation. The SAXS patterns were taken with a fine-focused X-ray beam and a flat plate camera (Rigaku Denki, RU-100).

3. Results and Discussion

3.1 Synthesis and Morphology of Ribbon-like Nanopolymers

Fig. 1 shows a TEM photograph of the MSV1 diblock copolymer specimen cast from TCE. The dark portions are selectively stained P4VP blocks. This specimen shows a texture of hexagonally packed P4VP cylinders in a continuous PMS matrix. On the other hand, the thermal equilibrium morphology of the MSV1 specimen (cast from toluene and annealed at 120°C) was a texture of dispersed P4VP spheres in a PMS matrix [12]. Therefore, the as-cast film from TCE was found to have the metastable morphology. The absolute values of cylinder radius ($R_{c,0}=7.9\text{ nm}$) and the nearest-neighbour distance between P4VP cylinders ($d=22.3\text{ nm}$) are also listed in Table 1.

Fig. 1 TEM photograph of diblock copolymer MSV1.

The segregated P4VP cylindrical domains were crosslinked by using the DBB vapour in the solid state. It was made clear from our previous results [13-15] that the films having both P4VP spherical and lamellar shapes, which consist of continuous polystyrene segment phases, were quaternized with DBB (the degree of quaternization = 40~100 mol%) under such reaction conditions. It was also found from Volhard's titration that the crosslink densities (intermolecular and intramolecular crosslinkings) were in the range of 36~42 mol%. Therefore, it can be judged that the crosslinked products prepared from films with cylindrical microdomains will have similar values of crosslink density. The crosslinked product (MSV1-N) was freely dissolved in organic solvents such as benzene, toluene, THF and TCE. In order to investigate a morphology of the crosslinked products, TEM observations of the products which had been stained with OsO_4 were carried out.

Fig.2 shows typical TEM photographs of MSV1-N, cast from 0.01~1.0 wt% toluene solutions. First, Fig.2(a) shows a TEM photograph of the MSV1-N cast from a 1.0 wt% toluene solution. This specimen corresponds to the restructured film from nanopolymers. This morphology seems to be apparently PMS/P4VP alternating lamellae. Fig.2(b) and 2(c) show TEM photographs of MSV1-N, cast from 0.1 and 0.01 wt% toluene solutions, respectively. Under the preparation conditions of these specimens, the nanopolymers are frozen with a state of the unimolecule on the carbon substrate. The structure recognized in Fig.2(b) and 2(c) shows the ribbon-like morphology. Then, the morphology shown in Fig.2(a) can be judged to be the P4VP cylinders in a PMS matrix. That is to say, the crosslinked P4VP domains are not able to interpenetrate each other and the ribbon-like nanopolymers are compatible with only the portion of PMS branches. The P4VP cylinders in an MSV1 film are locked with being of almost the same size²⁰ (P4VP cylinder radius, $R_{c,1} = 7.6$ nm) by crosslinking reaction, judging from TEM photographs. It is clear that these nanopolymers have only a narrow radius distribution for the crosslinked P4VP cylinders. The lengths of major axis (cylinder length) of the crosslinked P4VP cylinders were in the range of 2040~6490 nm (average value = 3670 nm), by surveying the

Fig. 2 TEM photographs of nanopolymer MSV1-N, cast from toluene solutions of different concentration: (a) cast from 1.0 wt%; (b) cast from 0.1 wt%; (c) cast from 0.01 wt%.

structures observed by TEM.

3.2 SAXS Measurements

Fig.3 shows the SAXS intensity profile of the as-cast film of MSV1-N nanopolymer in the edge view, where $q [= (4\pi/\lambda)\sin\theta]$ is the magnitude of scattering vector. The arrows show the scattering maxima (q_i) and the values in the parentheses indicate the relative q positions (q_i/q_1). The first four peaks appear closely

Fig. 3 SAXS intensity profile of the as-cast nanopolymer MSV1-N film (edge view).

at the relative q positions of $1:\sqrt{3}:2:\sqrt{7}$ as shown by arrows. This packing pattern is identical to the interplanar spacing of a hexagonally packed cylinder structure. The interplanar spacing d_1 corresponding to the innermost intense reflection was estimated to be 24.2 nm from the SAXS data. It is also noticed that the observed d_1 is almost identical to the nearest-neighbour distance of cylinders ($d = 22.3$ nm: see Table 1) in the MSV1 film before the domain locking. On the other hand, the weight-average molecular weight ($\bar{M}_w$) of the nanopolymer MSV1-N was determined to be 1.93×10^8 by static light scattering in benzene. It is found that this nanopolymer is composed of MSV1 diblock copolymers of aggregation number $f = 3230$.

4. Conclusion

The nanopolymers were prepared by the crosslinking reaction of PMS-*block*-P4VP diblock copolymer films exhibiting P4VP cylindrical microdomains, with the vapour of 1,4-dibromotutane in the solid state. It was indicated from TEM and SAXS measurements that

these nanopolymers had a structure of ribbon-like morphology. The degree of crosslinking (especially, intermolecular crosslinking) in the P4VP microdomains may influence strongly not only on the molecular weight but also on the molecular conformation of the nanopolymers in solution. Moreover, the degree of crosslinking may effect on the rigidity of P4VP cylinder backbone. So, it is necessary to study the crosslinking reaction of P4VP microdomains in detail. The results obtained from such a study will be reported in the near future.

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