# Diblock Copolymer Nanofibers

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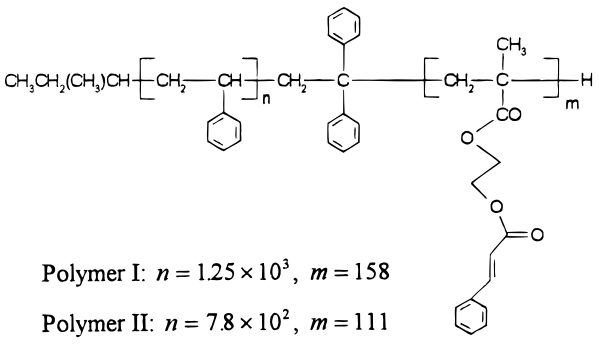
A diblock copolymer, e.g. $(A)_n-(B)_m$, in bulk may form an ordered phase, in which microdomains of B are uniformly distributed in the matrix of A, if A is in excess. The size of the B domains should be similar to that of the individual B coil, i.e. on the nanometer scale. The domain structures vary depending on the composition or the relative *n* and *m* values. At a volume fraction below roughly 17% for B, B will exist as spheres dispersed in the continuous A phase. As the B content is gradually increased to 60% by volume, the B domain successively changes its shape from spheres to cylinders, double diamonds, and lamellae. The phase transitions of block copolymers with their composition have been studied extensively,[1] and factors affecting the domain size and spacing have been elucidated both experimentally[2,3] and theoretically.[4,5]

Despite well-established evidence for microdomain formation from block copolymers in the bulk state, full advantage of the self-assembling property of diblock copolymers has not been taken of for nanostructure preparation. We prepared diblock copolymers with photo-cross-linkable blocks.[6,7] Utilizing the self-assembling properties of the diblocks, we prepared polymer brushes or monolayers at solid and polymer solution interfaces,[8] and star and crew-cut micelles[9] in the solution phase. The subsequent photo-cross-linking of these self-assembled structures led to our preparation of cross-linked polymer brushes,[10] star polymers,[11] and nanospheres.[11] In this paper, we report the preparation of diblock copolymer nanofibers by taking advantage of the diblock domain formation property in bulk.

A diblock nanofiber is defined as a cylindrically shaped aggregate of a diblock copolymer. In an isolated nanofiber in the solvent-free state, one block constitutes the cross-linked core and the other block forms the concentric shell. When dissolved in a good solvent, chains of the shell block would swell and stretch out into the solution phase.

Our strategy to make nanofibers was to prepare bulk samples from a diblock copolymer with a cross-linkable block as the cylindrical phase. Then the cylindrical phase was cross-linked. The dissolution of the continuous un-cross-linked phase led to disentanglement of different nanofibers.

The diblock copolymers used in this study were



Polymer I: $n = 1.25 \times 10^3$, $m = 158$

Polymer II: $n = 7.8 \times 10^2$, $m = 111$

where the poly(2-cinnamoylethyl methacrylate) or PCEMA block is photo-cross-linkable. The procedure for synthesizing these polymers has been reported elsewhere.[12] The samples were carefully characterized by static light scattering, NMR, and GPC and possessed polydispersity indices below 1.10 in terms of polystyrene standards. The details of characterization results have been reported elsewhere.[13]

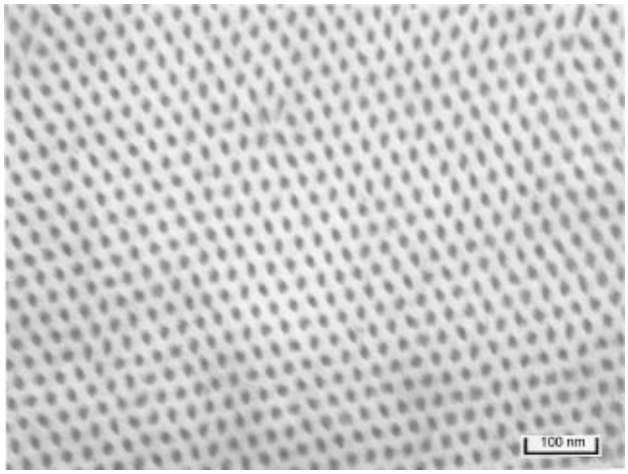



**Figure 1.** Ordered domain structures of polymer I. The dark regions represent PCEMA cylinders pointing toward us.

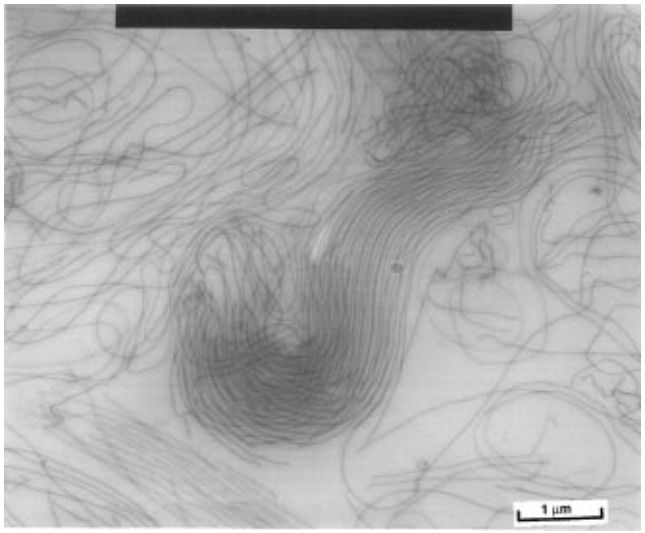



**Figure 2.** TEM micrograph of nanofibers. The TEM sample was prepared by transferring a thin film, formed on a water surface after the dispensing of a drop of a THF nanofiber solution, onto a copper grid.

In our study, transmission electron microscopy (TEM) was used to demonstrate cylindrical phase formation from the PCEMA block. Solid samples of polymer I or II were prepared by evaporating ~0.30 mL of ~10% (by volume) polymer I or II in toluene in polyethylene capsules over a 3−4 day period. The samples were further dried and annealed under 30 cmHg pressure at 65 ± 5 °C for 3 days and 90 ± 5 °C for a week before they were sectioned by ultramicrotomy (Ultracut-E, Reichert-Jung) to slices with a thickness ~50 nm. The microtomed samples were viewed with a Hitachi-7000 electron microscope operated at 100 kV.

Shown in Figure 1 are the ordered domain structures formed from polymer II. The hexagonally packed dark ovals represent PCEMA cylinders pointing toward us. The PCEMA domains are dark as they were preferentially stained by $OsO_4$ vapor. From Figure 1, the

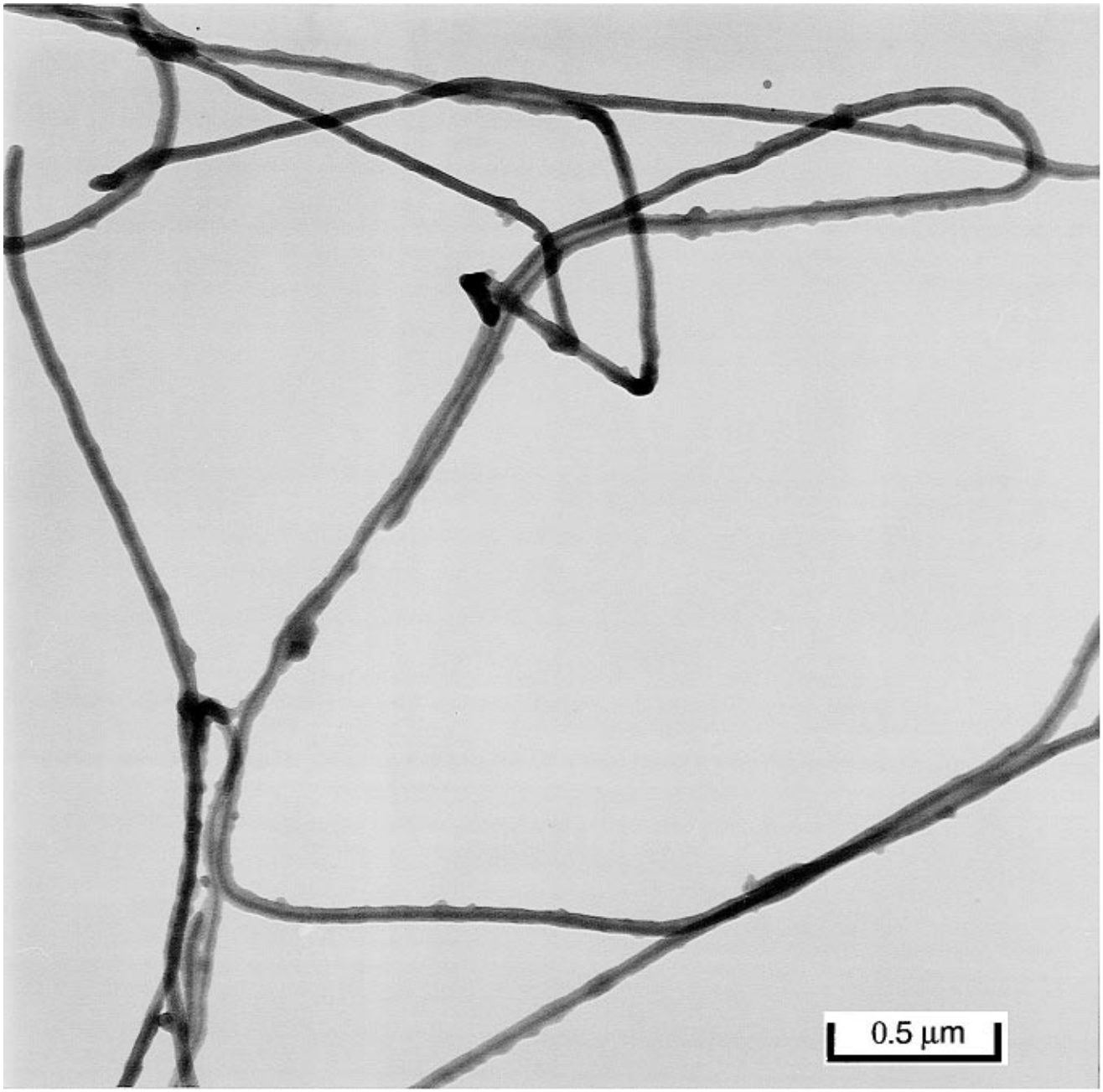



**Figure 3.** TEM micrograph of nanofibers. The TEM sample was prepared by freeze-drying a benzene solution of nanofibers on a copper grid.

dimension of the PCEMA phase along the long axis of the oval was estimated to be between 15 and 17.5 nm and that along the short axis is between 7.5 and 10 nm. Similarly sized PCEMA cylindrical phases were also observed for polymer I.

Upon establishing the conditions for cylindrical phase formation from PCEMA, we proceeded to prepare nanofibers. Disks of polymers I and II, ~1.0 mm thick and weighing ~0.040 g, were prepared by casting and evaporating ~5% toluene solutions of them on water. The disks were then annealed under identical conditions as described for the samples used for their morphology studies by TEM. After irradiating a polymer I disk for 0.5 h on each side, half of it was stirred in 60 mL of THF for ~20 h. Upon centrifugation, a supernatant with a bluish tinge typical of a diblock copolymer micellar solution was separated from 11 mg of powdery precipitate. After removing ~0.1 mL for TEM analysis, the rest of the supernatant was pored into excess methanol to produce 10 mg of THF-soluble product as a precipitant, yield 48%.

The 0.1 mL of THF supernatant was diluted before two drops of it were dispensed on water to produce a thin film. The film was transferred onto a copper grid for viewing by TEM. According to Figure 2, the THF-soluble product consisted of isolated, highly uniform nanofibers ~25 nm thick and thousands of nanometers long. In addition, some nanofiber bundles were also observed. They could have been present in the original sample or have been formed due to the self-assembly of individual nanofibers on water when preparing samples for TEM analysis.

The core−shell structure of these nanofibers was not seen even upon further magnification. We do not know the exact reason for this. The expected core−shell structure was seen in Figure 3, when we prepared TEM samples using a freeze-drying method. In this method, a small amount of the solid nanofiber sample, prepared

by drying the precipitant from methanol, was stirred with benzene for some 60 h and a drop of the benzene solution was then dispensed on a copper grid cooled to −78 °C. Benzene was sublimed at this temperature to leave the nanofibers for viewing by TEM. The outer diameter of the nanofibers in Figure 3 is ∼60 nm.

We also carried out TEM studies of the THF-insoluble product following the freeze-drying method and similar results were observed for both the THF-soluble and -insoluble products. Thus, the initially THF-insoluble portion also consisted of nanofibers. They are probably more entangled than the soluble portion. With longer stirring and the use of more solvent, we were able to extract more soluble product from the initially insoluble portion.

As anticipated, nanofibers can be prepared by selectively cross-linking the cylindrical domains of a bulk block copolymer. We are currently experimenting with the preparation of nanofibers from a polymer melt. Since microdomain formation occurs in most block copolymers, this represents a general method for preparing uniform nanofibers from a wide range of polymers with various diameters. We expect this method to be useful in producing precursor fibers which can be pyrolyzed to make carbon or metal carbide nanofibers.[15] Carbon or silicon carbide nanofibers may be used in the manufacturing of nanocomposites.[16] Or this method can be tailored for making nanowires by replacing the core block with a conductive polymer. In that case, the outer block will function as the insulating plastic layer. Nanowires will be useful in constructing molecular electronic and optical devices.[17]

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