

Elastomeric Nanofibers of Styrene–Butadiene–Styrene Triblock Copolymer

HAO FONG, DARRELL H. RENEKER

The Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

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ABSTRACT: Nanofibers of a commercial styrene–butadiene–styrene triblock copolymer were electrospun from solution, and collected either as a nonwoven elastomeric fabric, or on a layer of graphite that was evaporated onto a glass microscope slide. The resulting nanofibers were elastic, birefringent, and most had diameters around 100 nm. A few thin, beaded fibers were found among the smooth nanofibers. The diameter of the fibers between the beads was as small as 3 nm. After staining with osmium tetroxide, the nanofibers were examined using transmission electron microscopy. Separated phases of styrene and butadiene blocks were observed. The single-phase domains were irregular in shape, but elongated along the axis of the fiber. Wide-angle X-ray diffraction patterns showed a weak indication of molecular orientation along the fiber axis, and the birefringence confirmed that such orientation was present. The single-phase domains grew larger in nanofibers that were held at room temperature ($\sim 25^\circ\text{C}$) for several days. Annealing at a temperature 70°C greatly accelerated the growth of the single-phase domains. The nanofibers softened and flattened on the evaporated graphite during annealing. © 1999 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 37: 3488–3493, 1999

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INTRODUCTION

As new technologies demand predictable performance of materials at all length scales between atoms and useful objects, it is necessary to control material properties that are associated with nanometer scale structures.^{1,2} Electrospinning provides a way to produce polymer fibers with diameters in the nanometer range.^{3,4}

Electrospinning occurs when the electrical forces at the surface of a polymer solution overcome the surface tension and cause an electrically charged jet of polymer solution to be ejected. Electrical forces also cause the jet to become thinner

as it travels. When the jet dries or solidifies, an electrically charged nanofiber remains.⁴

In the electrospinning process, solvent evaporation occurs on a millisecond time scale. The rapid removal of the solvent decreases the mobility of the polymer molecules and makes it more difficult for the polymer blocks to segregate into single phase domains. In this series of experiments, it is clear that the nanofibers, as they are formed, contain a nonequilibrium distribution of phase domains.

Electrospinning can produce fibers in the diameter range that overlaps textile fibers, but fibers with diameters ranging from 1000 nm downward are most interesting, because fibers with such small diameters are difficult to produce by conventional processes.⁵ Polymer nanofibers are transparent in an ordinary 100,000 electron volt transmission electron microscope. Nanofibers

Correspondence to: D. H. Reneker (E-mail: dhr@polymer.uakron.edu)

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have a very high ratio of surface area to mass. About 2% of the molecules in a fiber with a diameter of 100 nm and about half of the molecules in a nanofiber with a diameter of 3 or 4 nm are on the surface.

Styrene–butadiene–styrene (SBS) triblock copolymer is a typical microphase-separated thermoplastic elastomer. The copolymer molecules have a narrow molecular weight distribution ($M_w/M_n = 1.12$) in each block. When the polystyrene concentration is relatively low, the domains are spherical; with increasing concentration, the domains become cylindrical and then lamellar. Such well-developed morphology requires careful sample preparation. In general, the morphology is irregular and the complexity depends on the thermal and mechanical history of the preparation.⁶

Thermodynamic theories by, for example, Liebler,⁷ Matsen and Schick⁸ described miscibility of block copolymers and the resultant morphologies. It is the aim of this article to study the unusually thin fibers of an SBS triblock copolymer, prepared from solution and dried very rapidly.

EXPERIMENTAL

The styrene–butadiene–styrene triblock copolymer (SBS) used is a commercial product of Shell Chemical Co. (Kraton D1101), supplied in the form of rubbery pellets. Kraton D1101, which contains 31% polystyrene by weight, is a linear triblock copolymer. The weight average molecular weight (M_w) is 151,000 g/mol, the number average molecular weight (M_n) is 135,000 g/mol, and M_w/M_n of both blocks or of the entire molecule is 1.12.⁹ SBS was dissolved in a mixture, by weight, of 75% tetrahydrofuran and 25% dimethylformamide to form a solution that contained 14% polymer. Tetrahydrofuran is a good solvent for both polystyrene and polybutadiene blocks, and the addition of 25% dimethylformamide improved the stability of the electrospinning jet.

The electrospinning apparatus used a high voltage power supply (160 microamperes at 30 kilovolts, from Gamma High Voltage Research, Ormond Beach, Florida). A positive high voltage was applied, through a copper wire, to the SBS solution inside a glass pipette. A grounded copper sheet was placed 30 cm below the tip of the glass pipette. Several glass microscope slides covered by films of evaporated graphite were placed on the copper sheet. The pipette was tilted a few degrees from the horizontal so that surface ten-

sion maintained a small droplet of the solution at the tip without dripping. As the electrical potential was gradually increased to 24 kilovolts, a jet was created. The jet, formed by electrical forces, followed a complicated stretching and looping trajectory as it dried and solidified. The resulting electrically charged nanofibers were collected on films of graphite for electron microscopy, or on a rotating drum covered with aluminum foil to produce a nonwoven elastomeric fabric. The mass flow rate of the polymer solution, carried by the jet, was around 50 mg/min. The nanofibers were examined by both polarized optical microscopy and transmission electron microscopy. The diffraction of X-rays from a bundle of aligned nanofibers was also observed.

RESULTS AND DISCUSSION

The electrospun SBS nanofibers had diameters around 100 nm. A thin sheet of aligned nanofibers was elongated to more than three times its original length without breaking, although the individual nanofibers may have broken.

Figure 1 shows the appearance of the nanofibers as the sample was observed between crossed polarizers, and then rotated. In the upper picture, fibers A-A and B-B were bright. Turning the sample clockwise by about 45° caused these nanofibers to become dark, as shown in the bottom picture. The bright and dark segments in the looped nanofiber moved along the loops and remained approximately parallel to each other as the sample was rotated. These observations show that the electrospun nanofibers were birefringent. Both the elongational flow^{10,11} and the rubberlike strain of the molecular network may contribute to the birefringence.

Figure 2 shows bright field transmission electron micrographs of the electrospun SBS nanofibers. The nanofibers on the evaporated graphite were stained in osmium tetroxide (OsO_4) vapor by suspending them over a 1.0% aqueous solution of OsO_4 for 30 min. Osmium tetroxide is known to preferentially stain the polybutadiene phase so that the dark regions in the electron microphotographs are identified as polybutadiene domains. The lighter domains are polystyrene. After staining, the fibers were coated with a very thin layer of evaporated graphite to carry away electrical charge deposited on the nanofibers during examination in the transmission electron microscope.

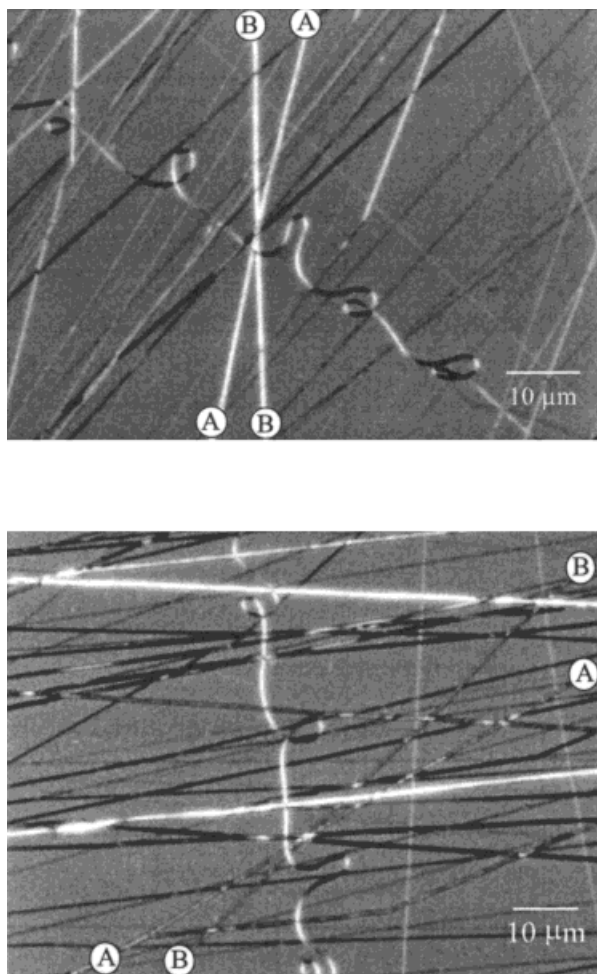


Figure 1. The birefringence of the electrospun SBS fibers.

In Figure 2, the upper left image shows an as-spun nanofiber. In the as-spun fibers, the phase separated domains are small and irregular. The upper right image shows a nanofiber that was kept at 25 °C for 20 days. The phase separated domains are larger and more ordered. The fiber in the bottom left image was annealed at 70 °C for 30 min and the bottom right one was annealed at 70 °C for 1 h. The transverse width of the polystyrene domains increased from less than 10 nm in the as spun fiber to over 20 nm in the sample that was annealed at 70 °C for 24 h. Annealing the as-spun fibers at 70 °C greatly accelerated the growth rate of the domains. Thirty minutes at 70 °C are enough for the more ordered structure to appear.

Figure 2 also shows that the elongated single phase domains are oriented along the fiber axis by the electrospinning process. The edges of the fiber

in the upper left image of Figure 2 are well defined, showing the fiber has not flattened much. The more transparent edges of the nanofibers annealed at 70 °C indicate the nanofibers spread and flattened on the substrate. The nanofibers that were held at 25 °C for 20 days also spread and flattened, indicating that even at room temperature the SBS copolymer flowed a significant amount in 20 days. The attraction of the electrical charges carried by the fibers to the electrically conducting layer of graphite is estimated to generate an electrical pressure of about one atmosphere, which acts to spread and flatten the nanofibers during annealing.

In order to better understand the three-dimensional morphology of the phase separated SBS fiber, stereographically related images were obtained by tilting the sample in the transmission electron microscope. The same area of the sample is shown in both the images in Figure 3, but the left image was tilted 15° about the vertical axis. Stereoscopic viewing of these images shows the

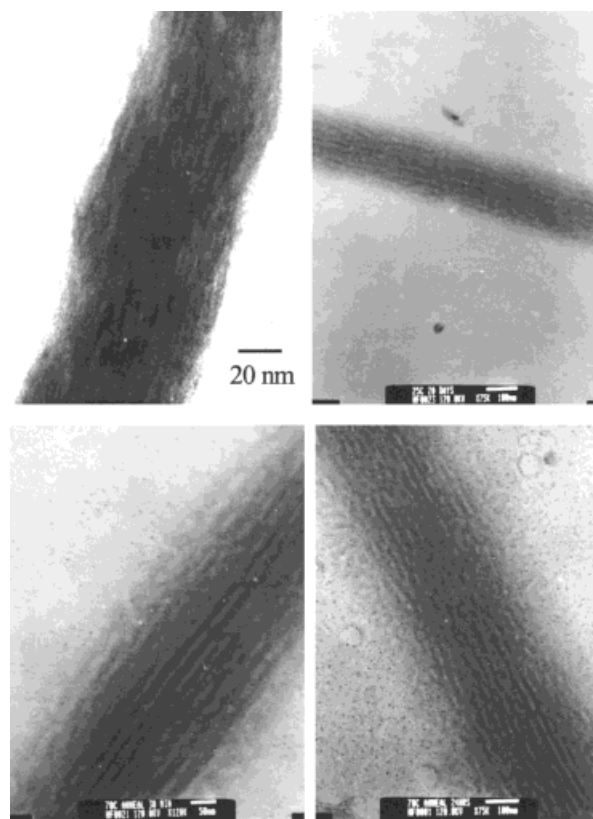


Figure 2. Transmission electron micrographs of electrospun SBS nanofibers. The diameter of the fibers in Figure 2 range from 70 nm (upper left) to 400 nm (bottom right).

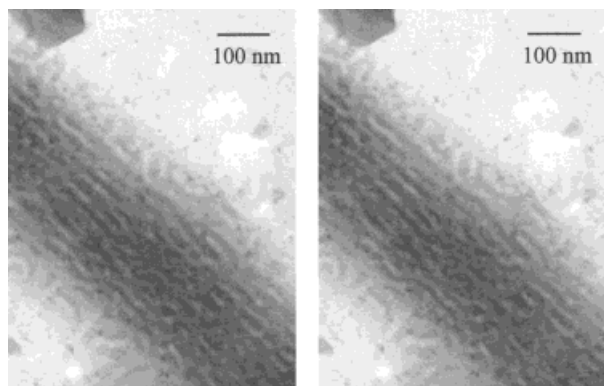


Figure 3. TEM images for stereographic observation. The tilt axis was parallel to the longer edge of the images. The tilt angle is 15° .

fiber became flattened and that the stained regions are somewhat above the small particles lying directly on the film of evaporated graphite. The stained regions only penetrate a short distance into the nanofiber, consistent with the reported¹² penetration depth of 3 nm. In these micrographs, cylindrical domains of polystyrene at the surface of the nanofibers cannot be distinguished from lamellar domains of polystyrene that extend from the central region and intersect the surface.

Since both polystyrene and polybutadiene are amorphous polymers, wide-angle X-ray diffraction produced only diffuse rings. Figure 4(a) shows the intensity as a function of azimuthal angle in the equatorial plane using radiation of wavelength 0.154 nm from a copper target. Two broad peaks were observed. The more intense peak is centered at $2\theta = 20^\circ$, and the weaker one is centered around 10° . Glassy atactic polystyrene usually shows a scattering peak centered at $2\theta = 10^\circ$ in addition to the main amorphous halo ($2\theta \approx 20^\circ$).¹³ Amorphous polybutadiene shows a single peak centered at 19.5° .¹⁴ The wide-angle X-ray diffraction pattern in Figure 4(a) is consistent with that expected from a mixture of amorphous polystyrene and polybutadiene.

An indication of the distances between molecules can be obtained by employing the Bragg equation: $n\lambda = 2d \sin \theta$, where n is the order of reflection ($n = 1$ in these data), λ is the wavelength of radiation ($\lambda = 0.154$ nm), d is a distance, and 2θ is the angle of diffraction. The distance related to the strong peak near 20° is 0.44 nm, and the distance related to the weak peak near 10° is 0.88 nm.

Figure 4(b) shows the intensity of the diffuse ring integrated between $2\theta = 17.5^\circ$ and 22.5° as a function of the azimuthal angle β . The fiber axis was assigned $\beta = 180^\circ$. The small peaks in the integrated intensity near 90° and 270° indicate a small increase in scattering at the equator, which, together with the observed optical birefringence, indicates that the molecules were somewhat extended along the fiber axis.

In addition to the smooth nanofibers, very thin nanofibers with small beads are sometimes found. Beads form, while the jet is still fluid, if the force that tends to extend the nanofiber is reduced, for example, by the neutralization of the excess charge on the fibers with ions created in air by a

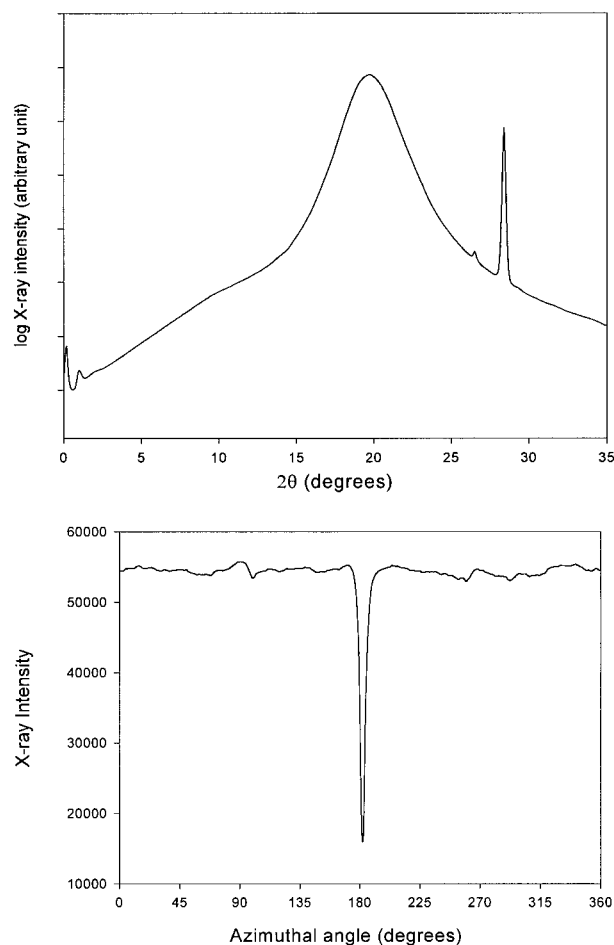


Figure 4. (a) Wide-angle X-ray diffraction plot of SBS nanofibers (the sharp peak at $2\theta = 28.5^\circ$ is from a silicon calibration material, and the small peak at $2\theta = 26^\circ$ is a crystalline impurity in the sample or solvent); (b) intensity of the diffuse ring, integrated between $2\theta = 17.5^\circ$ and 22.5° , as a function of azimuthal angle. The low intensity at 180° is caused by the support for the beam stop.

corona discharge. Then surface tension in the small fiber creates a pressure, which forces the solution into the beads.^{15,16} An electron micrograph of a beaded fiber found in this experiment is shown in Figure 5. The ratio of the volume of the fibers to the volume of the beads is less than 5%, whereas in the SBS used here, the volume ratio of PS to PB is greater than 30%. Therefore, a mixture of PS blocks and PB blocks must be present in each bead. The fibers between the beads had diameters as small as 3 nm. Since the average distance between the molecules is around 0.5 nm, there are fewer than 50 molecular chains in a typical cross section of such a thin fiber. The beads had diameters of about 60 nm and were elongated in the direction of the fiber axis. The number average molecular weight of the SBS used is around 135,000, so that the total length of an extended SBS molecule is around 2000 nm. This is much longer than the bead diameter (around 60 nm) or the distance between the beads (around 100 nm). It is therefore likely that both PS and PB blocks are present in both the fibers and the beads, although the osmium stain produced no contrast inside the fibers.

The osmium stain shows contrast between polystyrene and polybutadiene domains inside the small beads. In Figure 6, the contrast was increased to emphasize the domains. The darker single-phase domains inside the beads have a "diameter" of about 8 nm. The cube drawn in near the scale bar of Figure 6(a), with edges 6.8 nm long, has a volume equal to the volume of a typical SBS molecule. The white section of the cube has a volume equal to the volume of the polystyrene block of a typical

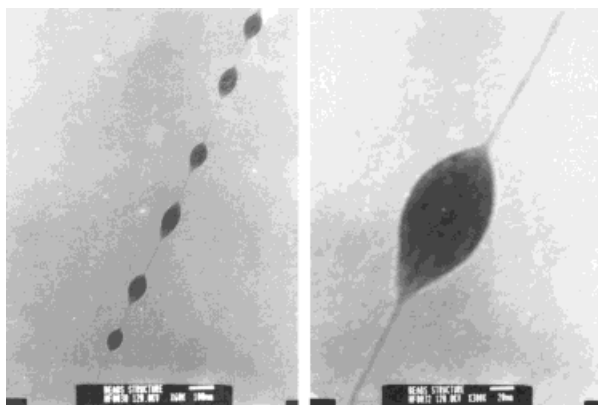


Figure 5. Beaded nanofiber of SBS copolymer, stained with osmium.

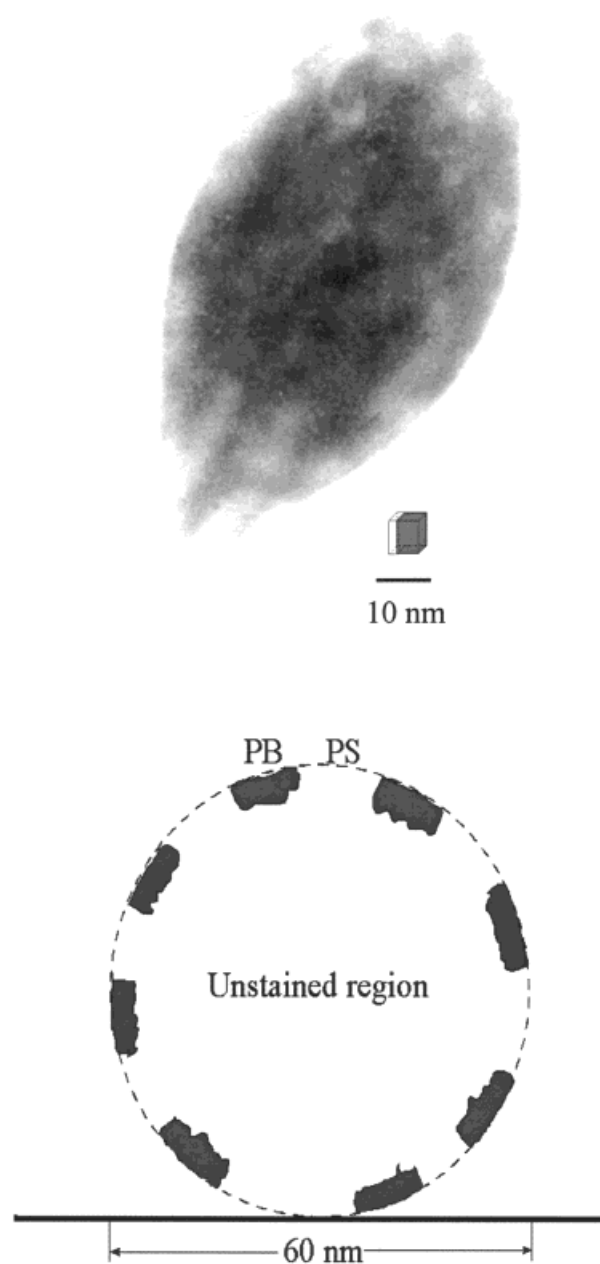


Figure 6. (a) Phase separation in a bead, with a cube showing the volume of an SBS molecule on the same scale; (b) schematic diagram of a representative cross section of a bead.

molecule. Figure 6 indicates that phase separation occurs on a scale of two or three typical SBS molecules. The osmium stain penetrates only about 3 nm from the surface,⁹ so only the parts of the PB phase near the surface are stained. Figure 6(b) is a diagram showing where the stain is observed. Possible flattening of the bead is ignored in this diagram.

CONCLUSION

SBS nanofibers produced by electrospinning have diameters around 100 nm, which is 10 to 100 times smaller than that of conventional textile fibers. Nanofibers with a diameter of 100 nm have a ratio of geometrical surface area to mass of around 100 m²/g. In the electrospinning process, the rapid stretching and the fast solvent evaporation rate allows the polymer blocks only a short time to segregate. In the as-spun fibers, the single-phase domains were small, irregular and somewhat elongated (see Fig. 2, upper left). As-spun SBS nanofibers were found to be birefringent.

In electrospinning, even though the fiber diameters were small and the solvent evaporation rate was fast, microphase separation was observed in the as spun fibers. The morphology of the separated microphases was irregular. Keeping the fibers at 25 °C for 20 days allowed the single phase domains to become larger. Annealing at 70 °C accelerated the ordering progress and allowed trapped stresses to relax. This experiment did not distinguish between rodlike or lamella-like shapes of the polystyrene domains because the stain only penetrated about 3 nm. The PS domains were elongated in the direction of the fiber axis and were around 10 nm in the transverse direction. Increasing the annealing temperature and the annealing time made the scale of the phase separation more uniform. The fibers flattened onto the substrate during annealing, probably with help from electrical forces associated with the charge carried by the fibers.

Very thin fibers with many 60-nm-diameter beads were also produced. Because the diameter of the fibers between the beads is as small as 3 nm, the number of molecular chains in a cross section of the fibers is less than 50. The stained domains in the beads have widths on the scale of

8 nm, suggesting that segregation of PS and PB blocks occurs on the scale of 2 or 3 copolymer molecules.

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