Confined Assembly of Asymmetric Block-Copolymer Nanofibers via Multiaxial Jet Electrospinning

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Multiaxial (triaxial/coaxial) electrospinning is utilized to fabricate block copolymer (poly(styrene-b-isoprene), PS-b-PI) nanofibers covered with a silica shell. The thermally stable silica shell allows post-fabrication annealing of the fibers to obtain equilibrium self-assembly. For the case of coaxial nanofibers, block copolymers with different isoprene volume fractions are studied to understand the effect of physical confinement and interfacial interaction on self-assembled structures. Various confined assemblies such as co-existing cylinders and concentric lamellar rings are obtained with the styrene domain next to the silica shell. This confined assembly is then utilized as a template to guide the placement of functional nanoparticles such as magnetite selectively into the PI domain in self-assembled nanofibers. To further investigate the effect of interfacial interaction and frustration due to the physically confined environment, triaxial configuration is used where the middle layer of the self-assembling material is sandwiched between the innermost and outermost silica layers. The results reveal that confined block-copolymer assembly is significantly altered by the presence and interaction with both inner and outer silica layers. When nanoparticles are incorporated into PS-b-PI and placed as the middle layer, the PI phase with magnetite nanoparticles migrates next to the silica layers. The migration of the PI phase to the silica layers is also observed for the blend of PS and PS-b-PI as the middle layer. These materials not only provide a platform to further study the effect of confinement and wall interactions on self-assembly but can also help develop an approach to fabricate multilayered, multistructured nanofibers for high-end applications such as drug delivery.

1. Introduction

Electrospinning is a simple, top-down method that has earned enormous attention due to its versatility and capability to produce continuous nanofibers. Typically, a strong electric field is applied on a droplet of polymer solution/melt. When the electrostatic forces on the polymer liquid surface exceed surface tension, a thin polymer jet is ejected. The charged jet undergoes strong deformation (strain (extension) rate $\approx 10000 \text{ s}^{-1}$) and fast solvent evaporation ($\approx 200 \text{nL s}^{-1}$) and gets deposited on a grounded collector placed $\approx 4-6$ inches away as a random non-woven mat. We refer the reader to recent reviews that elaborate on the versatility and promise of this distinctive process. Owing to the ultrathin diameters, these fiber mats exhibit large surface-area-to-mass ratios and are attractive materials for high-performance separation, sensing, and filtration devices, to name a few. Specific surface-area ranges from $10 \text{ m}^2 \text{ g}^{-1}$ to as high as $1000 \text{ m}^2 \text{ g}^{-1}$.
Recently, some work has been done to fabricate core/sheath nanofibers by coaxially electrospinning two different immiscible liquids through a coaxial spinneret system. Using ethylene glycol and photopolymer as inner and outer jets, Loscertales et al. demonstrated the principles and design of stable, coaxial, electrified liquid nanojets toward the production of nanocapsules and nanofibers. Sun et al. described the processing of core/shell nano/mesofibers by coaxial electrospinning of polymer solutions or a combination of polymer solution and melt. They demonstrated that undesirable mixing of the core and shell material can be prevented by slow diffusion rates of the polymer chains as compared to the fast solidification of the polymer jet in the electrospinning process. In the coaxial electrospinning process, the shell serves as a template for formation of fibers from the core material. Therefore, as demonstrated by Yu et al., this process is particularly advantageous for core materials that are not viscoelastic enough to form fibers by themselves. Using coaxial electrospinning, Li and Xia produced hollow nanofibers with walls made of titanium oxide/poly(vinyl pyrrolidone) (TiO$_2$/PVP) composite or pure titania. Recently, melt coaxial electrospinning has been demonstrated as a versatile method for the encapsulation of solid materials and fabrication of phase-change nanofibers.

In this study we demonstrate the use of the sol–gel technique to produce polymer–ceramic functional nanofibers. Silica sol–gel is prepared by a combination of hydrolysis and condensation reactions in a precursor solution formed with carefully chosen compositions of tetraethyl orthosilicate (TEOS), distilled water, ethanol, and HCl. The solution gels over time due to the formation of linear networked structures rendering it spinnable at a viscosity of about 10 poise. The presence of linear structures increases the extensional viscosity of these materials. The viscosity along with the high electric conductivity of the solvent helps the formation of very stable liquid jets in the presence of electric field and robust nanofibers. Moreover, as we will see in the remaining part of the paper, the thermal stability of silica offers a useful means to induce self-assembly of block copolymers during high-temperature annealing. In this work, we wish to combine the advantages of nanofiber mats (e.g., high surface area, open pore structure, ability to be woven into a fabric) with the functionalities of block-copolymer self-assembly to greatly widen the scope of potential applications.

Block-copolymer (BCP) solutions and melts are known to self-assemble into a variety of nanoscale morphologies including spheres, rods, micelles, lamellae, vesicle tubules, and cylinders (typically in the size range of few tens of nanometers) depending on the volume fraction and interaction parameter between different blocks. This phenomenon has been extensively studied for both solution and melt in bulk systems via theory, experiments, and simulations. BCP self-assembly has attracted increasing interest in recent years for applications in nanotechnology. Precise control over the size, shape, and periodicity of these nanoscale microdomains is the key factor in providing opportunities for realization of nanoscale systems.

In order to combine the two systems, we develop nanofibers using block copolymers. The main limitation in fabricating such materials is the inability to form ordered self-assembly in situ due to the fast solvent evaporation and strong deformation during electrospinning. Furthermore, post-annealing treatment so as to preserve the fiber morphology is also difficult.

To overcome this limitation, we fabricate polymer nanofibers with silica as a protective shell using multiaxial (coaxial/triaxial) electrospinning (Figure 1). The silica shell (synthesized using the sol–gel technique) provides thermal stability to the fibers and helps to anneal the materials at temperatures higher than the core polymer glass transition to obtain equilibrium self-assembly without destroying the fiber morphology. It also serves as a process aid for low-molecular-weight unentangled polymers that are difficult or impossible to electrospin. Most of this paper is dedicated to our results on coaxial electrospinning with a silica shell and block-copolymer core. Towards the end, we present our recent work on triaxial electrospinning, also with silica as the outermost shell and different combinations of materials for the innermost and middle layers.

As shown in our previous study, the silica layer is later etched using HF solution to obtain continuous nanofibers (100–400-nm diameter) with periodic internal mesostructures. Furthermore, with selective removal of one of the BCP
domains, mesoporous nanofibers can be fabricated with the ability to tailor the size and shape of the pores by using different-molecular-weight BCPs and block volume ratios, respectively. Porous nanofibers can be very advantageous in applications such as tissue engineering, catalysis, filtration, and drug delivery. For example, internal fiber mesopores act as anchoring points for cells in tissue engineering. For filtration, catalysis, or sensing applications, the mesopores increase the surface area, while the external large pores in fiber mats provide an open structure and prevent any mass flow restrictions of the inlet fluid. The walls of the pores can be functionalized for catalytic, sensing, and separation applications by tailoring the location of nanoparticles such that they selectively wet only one of the BCP domains.

Our methodology provides an easy template to study the effect of cylindrical confinement or shell–core interaction on self-assembly compared to nanotubes/nanorods. Nanorods are discontinuous objects and are therefore difficult to align, assemble, and process. We had recently reported the effect of cylindrical confinement on bulk lamellar forming poly(styrene-b-isoprene) using the procedure mentioned above. Ma et al. had independently demonstrated a similar procedure using high-molecular-weight PMMA as the shell of silica and a relatively low-molecular-weight core polymer so that its relaxation temperature and time remains lower than the glass transition of the shell polymer.

In the current study, we present how the interfacial interaction and frustration due to physically confined environment affects the morphology of the bulk-cylinder- and sphere-forming block copolymers. The effect is particularly prominent in cylinder-forming block copolymers; the cylinders tend to bend around the fiber axis due to stresses created at the outer BCP domains due to the physical confinement of the shell creating mixtures of hexagonal cylinders and concentric lamellar layers. The confinement effect is even more drastic and interesting in triaxial nanofibers with block copolymer as the middle layer and silica as the outermost and innermost layers. Finally, to incorporate functionalities into such self-assembled materials, we have incorporated nanoparticles (NPs) into the PS-b-PI core material. Magnetite nanoparticles coated with oleic acid are selectively dispersed in the isoprene domain of PS-b-PI nanofibers (with silica shell). This provides a comprehensive approach for the fabrication of high-performance multifunctional nanomaterials. For instance, nanofiber mats with both magnetic and fluorescent functionalities can combine size exclusion with magnetic interaction for collecting and separating proteins present in blood in small amounts that may have diagnostic value for early detection of diseases. The presence of fluorescent nanoparticles will provide a sensitive marker for counting the separated cells using fluorescence imaging.

2. Results and Discussions

2.1. Study of Confined Block-Copolymer Self-Assembly via Coaxially Electrospun Nanofibers

To justify the use of coaxial electrospinning and the silica shell in this work, we first show the transmission electron microscopy (TEM) image of a cross section of an as-made monaxial SI-33 fiber in Figure 2a. Although the structures are microphase-separated, they remain disordered due to the fast solvent evaporation and strong deformation during the electrospinning process. In Figure 2b, we show a scanning electron microscopy (SEM) image of the monaxial fibers annealed above the polymer glass-transition temperature ($T_g$) in an attempt to obtain ordered internal self-assembly and, as expected, the fibers melt. In coaxial fibers the silica shell allows us to anneal the samples at high temperatures to obtain equilibrium morphology. Figure 3a shows the SEM image of a typical electrospun coaxial fiber. Figure 3b and c shows the SEM images of coaxial fibers annealed at temperatures well above the $T_g$ ($\approx$100°C). These figures show no leakage of the polymer, indicating a good cover of the silica around the block-copolymer fibers providing thermal stability.

All coaxial nanofiber samples shown in this paper were annealed at 175°C for 2 days (post fabrication) to obtain equilibrium morphology. Figure 4 shows the annealed fibers spun using SI-09 as the core material. The block copolymer has 0.09 volume fraction of isoprene and forms a body-centered cubic (bcc) lattice of isoprene spheres in styrene matrix in the bulk (not shown). Figure 4 clearly shows the formation of isoprene spheres in styrene in the annealed nanofiber section. As seen from this image and other images shown later, it appears that the matrix domain, styrene, has favorable
interaction with the silica shell and therefore prefers to stay close to the interface between core and shell layers. Therefore, we do not see the isoprene spheres lining up close to the silica shell, unlike the TEM images obtained by Ma et al.\cite{24}

We then studied the effect of cylindrical confinement on diblock copolymers that form hexagonal cylinders in the bulk. We use two polymers, SI-33 and SI-31 with 0.33 L and 0.3 L isoprene volume fractions, respectively. For all SI-33 nanofiber TEM images (Figures 5 and 6), the structures at the outer edges close to the core–shell interface are lamellar layers (in the form of concentric layers due to cylindrical confinement\cite{21}) with the styrene domain next to the silica shell in both cross sections (Figure 5) and longitudinal sections (Figure 6). In some fiber cross sections, as seen in Figure 5a, we see hexagonal cylinders as the inner structures (along with the lamellar layers close to the polymer–silica interface, as mentioned above). It is worth noting that this polymer, SI-33, forms pure cylindrical morphology in the bulk (see Table 1). Li et al.\cite{25} recently studied different self-assembled structures formed by a diblock copolymer in a cylindrical nanopore. They mapped out a phase diagram using real-space self-consistent field theory. They also found mixtures of lamellae and cylinders for volume fractions that lie within the cylindrical regime in a bulk-phase diagram. In addition, they found that most of such intermediate structures were formed for the case where the majority block is attracted to the nanopore wall similar to our system. The mixture of lamellae and cylindrical structures formed in our fibers are consistent with the results they found. (For example, Figure 5a is similar to the structure $LC_{1+}$ in Li et al., also formed for volume fractions between 0.3 and 0.4\cite{25}).

Such structures are not formed in the bulk systems and, to the best of our knowledge, this is the first time these structures have been found experimentally. Interestingly, we found a few SI-33 fiber with pure lamellar rings (Figure 5b) and a morphology similar to $L_{C_{1+}}$\cite{25} (Figure 5c). It is very interesting to note how the confinement created by a nanopore can force a pure cylindrical structure in the bulk into a concentric lamellar ring morphology. Although it is hard to provide to concrete explanation of how the same polymer gives different
morphologies under cylindrical confinement in the present study, we believe it is the effect of variations in the fiber diameter and the actual temperature conditions each individual fiber is exposed to. One thing consistent in all of these results for SI-33 fibers is the formation of at least some lamellar rings. We anticipate that first the outermost layer coalesces into a single domain of PS due to favorable interactions between the PS domain and the silica wall, then due to the covalent bond between the two blocks the other domain just follows. However, the presence of multiple lamellar rings shows that the lamellar morphology also has lower free energy in the confined state and is not a mere effect of wall interactions. We expect the formation of pure lamellar rings to be more prevalent in smaller pore diameters, as we anticipate that the inner structures in a large-diameter fiber would not feel any effect of the confinement and will exhibit bulk morphology.

In the fiber sections along the axis (Figure 6), we see isoprene cylinder cross sections instead of the long cylinders, which indicates the presence of bent isoprene cylinders or helices formed due to the confinement of the silica shell. The helical structure is much clearer in the images we obtained for the annealed SI-31 polymer. In Figure 7a, we see pure cylindrical morphology in SI-31 nanofibers. Pure cylindrical structures are not found in any SI-33 fibers probably due to the higher PI volume fraction in SI-33 than in SI-31. If we look at

Table 1. Details of all PS-b-PI block co-polymers used in this study.

<table>
<thead>
<tr>
<th>Name</th>
<th>Total MW</th>
<th>PI Vol. fraction</th>
<th>Bulk morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI-09</td>
<td>56200</td>
<td>0.09</td>
<td>Sphere (BCC)</td>
</tr>
<tr>
<td>SI-19</td>
<td>45750</td>
<td>0.19</td>
<td>Hexagonal cylinders</td>
</tr>
<tr>
<td>SI-28</td>
<td>45800</td>
<td>0.28</td>
<td>Hexagonal cylinders</td>
</tr>
<tr>
<td>SI-31</td>
<td>41800</td>
<td>0.31</td>
<td>Hexagonal cylinders</td>
</tr>
<tr>
<td>SI-33</td>
<td>45000</td>
<td>0.33</td>
<td>Hexagonal cylinders</td>
</tr>
<tr>
<td>SI-74</td>
<td>34100</td>
<td>0.74</td>
<td>Inverse hexagonal cylinders</td>
</tr>
</tbody>
</table>
Figure 7a more closely, we find that isoprene cylinders form a pentagon (not hexagon), a structure absent from any bulk-phase diagram. Again, this is an effect of the cylindrical confinement and is also seen in the phase diagram as $L_{C_{1.5}}$ by Li and Wickham.[25] We do find some SI-31 fibers with mixtures of lamellar and cylindrical morphology as well, though pure lamellar rings are not seen, unlike SI-33 fibers, demonstrating how the increasing volume fraction of isoprene in SI-33 compared to SI-31 favors lower-curvature structures.[25] Figure 7b and c shows the intermediate structures similar to $L_{C_{4}}$ (with only 4 isoprene cylinders) and $L_{C_{1.5}}$ in Li and Wickham[25] phase diagram, respectively. The SI-31 fiber sections cut along the axis in Figure 8 show mixtures of straight and curved cylinders. In a study done by Wu et al.,[26] it was found that the stresses imposed by confinement cause the cylinders to bend around the pore axis and form helices and donut-type structures. Our longitudinal self-assembly structures match very well with the images shown by Wu et al.[26] Previous studies where helices have been found due to cylindrical confinement have used a much smaller pore size than our fibers. Our study shows that cylindrical pores even as large as 8–10 times the lamellar spacing can impose large enough stresses to significantly affect the self-assembly of block copolymers. This work demonstrates that electrospun fibers provide a good template to study the effects of cylindrical confinement.

Figure 7. TEM images of microtomed cross sections of annealed (180 °C, 2 days) fibers electrospun using SI-31 as the core material. All scale bars are 100 nm. The outermost gray region in each image is the silica skin layer.

Figure 8. TEM images of microtomed longitudinal sections of annealed (180 °C, 2 days) fibers electrospun using SI-31 as the core material. All scale bars are 200 nm.
confinement on self-assembling materials such as block copolymers.

2.2. Using Block-Copolymer Assembly as a Template to Guide Nanoparticle Location Within Nanofibers

To provide functionality to such self-assembled materials, we incorporated magnetite nanoparticles into the PS-\(b\)-PI core. In addition, this study serves as a method to understand the effects of processing conditions during electrospinning on nanoparticle (NP) location and to explore if these effects can be used to an advantage for tailoring nanoparticle placement within nanofibers. Monodisperse magnetite NPs (4 nm) were synthesized and surface coated with oleic acid to provide slight selectivity towards isoprene domain, while preserving their magnetic properties.\[^{27,28}\] Magnetite nanoparticles have been shown to display superparamagnetic behavior due to their small size, making them ideal for magnetic-field-driven transport of drugs and bioseparations. Figure 9 shows TEM images of sections cut perpendicular to and along the axis of a fiber electrospun using SI-19 with 0.05 weight fraction of magnetite nanoparticles. For the nanocomposite fiber study, we only use SI-19, which has a pure cylindrical morphology in both the bulk and nanofibers. The nanoparticles (black dots in TEM images) are selectively and uniformly dispersed in the PI phase. As suggested by previous work and solubility analysis,\[^{27,28}\] the selectivity is due to the presence of oleyl groups on the particle surface. No evidence of magnetic particle aggregation was found in the TEM images. Previous studies on films of the same system have shown that aggregates of nanoparticles form beyond a weight fraction of 0.02.\[^{28}\] We anticipate that the strong deformation and fast solvent evaporation during the electrospinning process prevent the aggregation of magnetite nanoparticles even at such high particle loadings. We refer the reader to our recent publications for discussion of the effect of electrospinning conditions on nanoparticle dispersion and selectivity.\[^{27,29}\] Although it is not shown here, similar experiments with 0.1 weight fraction of quantum dots (cadmium sulphide, also coated with oleic acid) produced similar self-assembly with NPs uniformly dispersed in the isoprene domain.

With the freedom to vary nanoparticle surface coating, block-copolymer self-assembly, processing conditions (e.g., deformation rate), and nanoparticle size, among other parameters, these results demonstrate the possibility of developing an entire spectrum of multifunctional materials with precisely controlled self-assembly. This work provides a robust methodology to fabricate high-surface-area multifunctional nanocomposites including cases where particle–particle interactions are dominant. This would be particularly helpful in cases where surface functionalization of nanoparticles can lead to loss of material properties, such as catalytic particles or carbon nanotubes (for electrical-property enhancement). The success of alternate methods such as deformation in preventing NP aggregation will lead towards next-generation functional materials.

2.3. Triaxial Electrospinning

As mentioned before, we conducted a new study on the fabrication of triaxial nanofibers, with silica in both the innermost and outermost shells/layers and a self-assembling polymeric material in the middle layer. We considered two cases with different materials in the middle layer. In the first, we fabricated nanofibers with block copolymer and nanoparticles in the middle layer. With this type of system, we hope to study the effect of confinement (on both sides, unlike coaxial nanofibers) on block-copolymer self-assembly and the effect of the presence of nanoparticles on block-copolymer assembly within nanofibers. Figure 10a–c shows the cross sections of annealed triaxial nanofibers using SI-28 as the block copolymer with increasing magnetite nanoparticle loading. TEM images show the formation of triaxial nanofibers with silica as the innermost and outermost layers and block copolymer with magnetite as the middle layer. These results also demonstrate the incorporation of magnetite nanoparticles (coated with oleic acid) selectively into the isoprene domain in the block-copolymer layer. Here, the BCP layer thickness is only \(\approx\)40 nm and is indeed comparable to the block-copolymer domain size, therefore only a single domain fits into the...
available confined space. It appears that the isoprene phase with magnetite shows a preference to the silica walls, and thus most of the isoprene and magnetite migrate to both inner and outer interfaces with silica. This is opposite to what we observe in the case of pure block copolymers, where styrene shows a preference for the wall. This aspect needs to be studied in more detail to understand the specific interactions of different blocks with the silica wall and how these interactions change with the presence of nanoparticles. A further study of these aspects is underway.

In the second case, the PS-\(b\)-PI block copolymer (SI-74) with PS hexagonal cylinder morphology (in the bulk) was mixed with polystyrene homopolymer (\(M_w = 13,000\)) (PS-\(b\)-PI:PS = 65:35), and was placed as the middle layer in triaxial electrospinning. In this system the PS domain in the block copolymer is the cylinder-forming minor phase, and the addition of PS homopolymer leads to a symmetric composition. The questions that can be raised here are i) can the cylinder-forming PS-\(b\)-PI and PS homopolymer blend system form the confined assembly structures similar to symmetric block copolymers in electrospun nanofibers and ii) how does the presence of PS homopolymer affect the interactions with the silica wall? Again, the presence of the silica shell allows us to anneal the materials and investigate the formation of equilibrium structures. Figure 11 shows TEM images of microtomed triaxial fiber sections. Again, the middle layer thickness is only \(\approx 40 \text{ nm}\) and is indeed comparable to the block-copolymer domain size and only a single domain fits into the available confined space. These TEM images suggest that the isoprene phase prefers the silica walls, and most of the isoprene migrates to both the inner and outer interfaces with silica, while the styrene phase resides between the isoprene phases. This is opposite to what we observe in the case of symmetric copolymers, where styrene shows a preference for the silica wall in the concentric-ring morphology.[20,27] This aspect needs to be studied in more detail to understand the specific interactions of different blocks with the silica wall and how these interactions change with the presence of nanoparticles or the PS homopolymer. Further study of these aspects is also underway. Nonetheless, block-copolymer/homopolymer systems offer a useful means to alter the confined assembly in nanofibers.

Through our work on triaxial electrospinning, we have demonstrated the ability to develop multiaxial nanofibers with
different combinations of materials. A more detailed and systematic study of the effect of fiber diameter, wall interactions, nanoparticle inclusion, and so on is underway. Such multilayered materials provide a unique platform to study the effect of confinement and wall interactions on self-assembly. Furthermore, hollow porous nanofibers with potential applications in drug delivery can be formed after the dissolution of silica layers and the minor BCP phase. With the use of cylinder-forming block copolymers, multichannel nanotubes can also be developed. Compared to single-channel structures, multi-channel structures may possess considerable advantages such as independent addressable channels, mechanical stability, and larger surface-to-volume ratios (biomimetic). Potential applications of such materials include biomimetic superlightweight thermoinsulated textiles, vessels for nanofluidic devices, and multicomponent drug delivery. Moreover, the use of block copolymers to fabricate these multistructured materials allows for unprecedented control of pore/channel size and shape or of nanoparticle location in the case of composites.

3. Conclusions

In this work, we have presented a systematic methodology to develop multiaxial block-copolymer nanofibers with confined self-assembly. The effect of cylindrical confinement was first studied on the self-assembly of asymmetric PS-b-PI with varying volume fractions of isoprene using coaxial electrospinning. A rich series of hybrid, confined structures were obtained. These materials provide a great platform to control nanoparticle location within nanofibers for effective utilization in applications such as catalysis, sensing, and smart textiles. One such example has been demonstrated by selectively placing magnetite nanoparticles in the isoprene domain of PS-b-PI nanofibers. Through this work, we demonstrated a novel methodology to combine the functionalities of block-copolymer self-assembly with the advantages of nanofiber mats (e.g., high surface area, open pore structure, ability to be woven into a fabric) to widen the scope of potential applications. Furthermore, we found that the strong deformation and fast solvent evaporation during electrospinning helps prevent nanoparticle aggregates. Good control over location of magnetic nanoparticles at such high loading opens up a plethora of potential future applications including electromagnetic shielding, high density memory, magnetic recording, drug delivery and separation aids. Further addition of quantum dots can be potentially helpful in bioseparation applications.

For example, with selective dissolution of the styrene domain and fluorescent (quantum dots) and magnetic nanoparticles incorporated into the walls of the fiber structure can help fabricate next generation bioseparation devices for early detection of diseases. Here, dissolution of styrene domain will increase the functional surface area of the nanofiber mats by many folds, the magnetic nanoparticles will allow more sensitive magnetically assisted separation of biomolecules and the fluorescent nanoparticles will provide a sensitive marker for counting the separated cells using fluorescence imaging. In addition, we demonstrated the ability to fabricate triaxial nanofibers, where different self-assembling polymeric materials are confined on both sides by silica layers. Interesting self-assembly has been observed due to the small width of the middle layer and presence of silica on both sides. This methodology can serve as a simpler and more controlled way to produce biomimetic multichannel microtubes. Our study on triaxial nanofibers raises some intriguing questions regarding interaction effects in confined blends and composites and further work to understand these systems is underway.

4. Experimental Section

Material fabrication: Tetra(ethyl) ortho silicate (TEOS) was supplied by Aldrich. To produce the sol–gel solution, a molar ratio of TEOS:EtOH:H2O:HCl of 1:2.2:2:0.01 was used. After vigorous mixing to produce a homogeneous solution, the solution was placed in a 50 °C oven to accelerate the sol–gel transition. After ripening for 3–5 h, the solution is ready to be electrospun. An applied voltage of 20 kV was used. The outer jet flow rate was 0.03 mL min−1 and the inner jet flow rate was 0.02 mL min−1, and the tip to collector distance was 4.5 inches. The polymer solution concentration (≈0.1–0.15 weight fraction) and the above spinning conditions were carefully chosen to obtain a continuous production of submicrometer-scale coaxial fibers. For triaxial electrospinning, the flow rates used were 0.02, 0.015, 0.02 mL min−1, for innermost, middle and outermost layers, respectively. The rest of the conditions were same as above. The electrosun fibers were annealed at temperatures in the range of 150 °C to 180 °C (>polymer glass transition of 100 °C) to obtain equilibrium self-assembly structures. Six different PS-b-PI polymers with asymmetric compositions were used in this study, with isoprene volume fraction of 0.09, 0.19, 0.28, 0.31, 0.33, and 0.74. They are denoted as SI-09, SI-19, SI-28, SI-31, SI-33, and SI-74, respectively, and have total molecular weights of 56200, 45750, 45800, 41800, 45000, and 34100 respectively. SI-09 forms spherical structures of the isoprene phase arranged in a BCC lattice in the bulk. SI-19, SI-28, SI-31 and SI-33 form hexagonal isoprene cylinders in the bulk while SI-74 forms hexagonal cylinders of the styrene in accordance with the PS-b-PI melt phase diagram, and also as seen in our TEM studies. The information on various PS-b-PI used in this study is tabulated in Table 1. The polydispersity of these block copolymers determined by NMR and GPC is less than 1.04.

Figure 1 shows the coaxial and triaxial arrangements used with a standard electrospinning set-up for this work. We refer the reader to our recent publications for a detailed overview of the electrospinning setup and conditions. Characterization: SEM was conducted using the LEICA 440, for which the samples were coated with Au-Pd. TEM was conducted using the Tecnai T-12. For the TEM images, the nanofibers were sliced into ≈60-nm-thick sections using an ultramicrotome along the fiber axis and perpendicular to the axis to view internal structures. All samples were stained with osmium tetroxide to differentiate between isoprene (dark regions) and styrene (light regions) domains.

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