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Synthesis and Microphase Separation of Poly(styrene-*b*-acrylonitrile) Prepared by Sequential Anionic and ATRP Techniques

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ABSTRACT: Carbonaceous templates with nanopores <10 nm in diameter have been produced using low molecular weight diblock copolymers of poly(styrene-*b*-acrylonitrile). PS-*b*-PAN was synthesized using sequential living and controlled polymerization approaches, where the first block was anionically synthesized while the second block was added using atom transfer radical polymerization (ATRP). Polystyrene with a hydroxy end group was synthesized anionically and then reacted with 2-bromoisobutyryl bromide to create the ATRP macroinitiator. Acrylonitrile was polymerized using ATRP procedures. Polymer microphase separation, stabilization, and subsequent pyrolysis were characterized by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).

Introduction

The self-assembly of diblock copolymers into microphase-separated morphologies having structures on the nanometer size scale enables their potential use as scaffolds and templates for nanostructured devices. With the advent of atom transfer radical polymerization (ATRP), certain polar monomers that could not be polymerized using typical living anionic procedures can now be polymerized in a "controlled" fashion, allowing for the synthesis of multiblock materials. Acrylonitrile has been shown to polymerize under ATRP conditions yielding polymers with polydispersities as low as $M_w/M_n \sim 1.1$, with molecular weights ranging from 1000 to 10 000 g/mol.[1,2] Polyacrylonitrile (PAN) is of interest because of its use in the manufacture of carbon fibers (black Orlon) and in random copolymers to create acrylic (85% w/w PAN) and modacrylic (35−85% w/w PAN) fibers. When PAN is heated, it decomposes by cyclization and aromatization of the nitrile side groups, with some intermolecular cross-linking, to yield carbon fibers.[3] This cyclization is of interest since it can be used to "freeze in" a specific microstructure, in the case of a microphase-separated diblock copolymer. Further heating can be done to create nanostructured carbon arrays (see Figure 1). The creation of arrays of carbon nanodots, by using this method, has been shown by Kowalewski et al.[4,5] using poly(*n*-butyl acrylate-*b*-acrylonitrile).[6] Another clever method for the creation of nanoporous carbon structures was demonstrated by Dai et al.,[7] where a resorcinol−formaldehyde resin was polymerized within a microphase-separated PS-*b*-PVP template, and subsequent carbonization led to an ordered nanoporous carbon film. The approach described herein is to use microphase-separated PS-*b*-PAN diblock copolymers to create nanoporous carbon templates.

Previous attempts to synthesize poly(styrene-*b*-acrylonitrile) were done using anionic or free-radical methods using dialkylphosphines. These met with mixed results.[8−11] Poly(ethylene oxide-*b*-acrylonitrile),[12,13] poly(vinyl alcohol-*b*-acrylonitrile),[14] and poly(2-ethylhexyl methacrylate-*b*-acrylonitrile)[15] have also been synthesized using different polymerization methods. The synthesis of diblocks containing polyacrylonitrile is challenging due to the limited number of solvents that dissolve PAN. Controlled bulk polymerizations are difficult because PAN is not soluble in its own monomer, causing gelation and loss of control over the reaction. Bulk ATRP of PAN has been done to create diblocks, where PAN is the minor component (<10%) and has a molecular weight <3000 g/mol.[4] The reaction is usually aided by the addition of a solvent such as ethylene carbonate or dimethylformamide.[6,15] Recently, PAN-*b*-PS polymers were synthesized by ATRP techniques, using a polar aprotic solvent, to overcome the challenges associated with the instability of the propagating PS-Br end groups.[16] In the synthetic scheme described herein, the styryl bromide end group was avoided, allowing for the successful initiation of acrylonitrile by ATRP polymerization in a polar protic solvent.

Styrene and acrylonitrile random copolymers are made by emulsion polymerization on an industrial scale. The incorporation of acrylonitrile into the polymer imparts solvent resistance that opens a broad range of applications. It is interesting to note that these acrylonitrile-containing random copolymers cannot be pyrolyzed to graphitic structures. When acrylonitrile is copolymerized with styrene, it loses its ability to cross-link into a graphitic structure due to chain scission at the styrene−acrylonitrile bonds upon heating.[17] Therefore, attempts to pyrolyze the structure result in the decomposition of the polymer.

Diblock copolymers of PS and PAN are particularly interesting due to the strong nonfavorable segmental interactions, χ, between styrene and acrylonitrile. Since the order-to-disorder transition depends on the product χN, where N is the total number of segments in the copolymer, then N can be made small while maintaining the block copolymer in the microphase-separated state. This, of course, means that the microdomains and resulting carbonaceous structures can be made smaller, with dimensions of ∼10 nm readily achieved.

Experimental Section

Materials. Styrene (Fluka) was distilled over calcium hydride and stored under nitrogen immediately before polymerization. *sec*-Butyllithium (1.4 M in hexanes) and ethylene oxide were obtained from Aldrich and used without further purification. Benzene was distilled over sodium/benzophenone. Acrylonitrile (AN) (Aldrich, 99+%) was passed over a column of basic alumina prior to use. Dimethylformamide (DMF) was distilled under reduced pressure over magnesium sulfate. Copper(I) bromide (Aldrich, 99.999%) and

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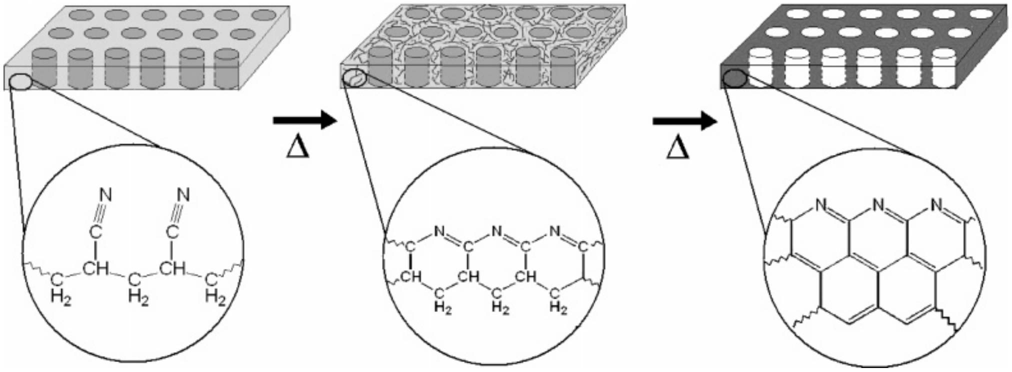

Figure 1. Carbonaceous template formation via stabilization and subsequent pyrolysis of PAN-containing diblock copolymers. PAN is shown as the matrix in this diagram; the minor component is a sacrificial nongraphitic forming polymer which is removed during the pyrolysis step.

Table 1. PS-*b*-PAN Samples Used in the Microphase Separation Studies

polymer	reaction time (min)	total M_n	M_n PAN (NMR)[a]	conv[b]	vol % PAN[c]	PDI[e]
SANb3	30	4200	2200	30.5	49.9	1.30
SANb5	50	4650	2650	36.4	54.6	1.34
SANb6	60	5300	3300	N/A[d]	59.9	1.26
SANa2	60	4607	2610	37.9	54.1	N/A[d]
SANa3	180	5668	3670	54.1	62.4	N/A[d]

[a] M_n was determined by NMR using the dried polymer sample in DMSO-d_6. [b] Conversion was measured using aliquots of the reactions (a, b, c) at different times and using the integration of the DMF peak at 7.95 ppm as an internal standard to measure the disappearance of the monomer peaks. [c] Volume fraction was calculated from the NMR data using $d_{PS} = 1.06$ g/mL and $d_{PAN} = 1.17$ g/mL. [d] Data are not available due to limited quantities of material. [e] No correction was done to account for peak tailing from instrument, which may account for a broadening in PDI (see Supporting Information).

4,4′-dinonyl-2,2′-dipyridyl (dNbpy) (Aldrich, 97%) were used as received.

Synthesis: (a) Polystyrene Macroinitiator. Benzene (300 mL) was added to a flame-dried flask equipped with glass stir bar, nitrogen inlet/outlet, and Teflon stopcock. Addition of reagents was done under a positive nitrogen flow. *sec*-Butyllithium solution (actual 1.2 M, 0.75 mL) was added via syringe to the stirring solution. Styrene (20.0 mL) was added via syringe to the reaction flask that was cooled in an ice bath due to exothermic initiation. After 10 min the ice bath was removed to prevent benzene freezing. The reaction flask was sealed, and the reaction was allowed to proceed for 3 h at room temperature. Ethylene oxide was bubbled through the reaction until the color associated with the living anion vanished (∼5 min). [*Caution: ethylene oxide is very toxic*!] The reaction flask was then sealed and stirred overnight (∼16 h). An excess of 2-bromoisobutyryl bromide (1.6 mL) was added to the reaction flask, and the polymer was precipitated in methanol and dried under vacuum overnight. The macroinitiator was characterized by SEC in THF with $M_w = 2.1 \times 10^3$, $M_n = 2.0 \times 10^3$, and a PDI $= 1.09$. ^{1}H NMR (in $CDCl_3$) end-group analysis: PS$-CH_2-C\mathbf{H}_2-$OH (br m, 3.30 ppm, from aliquot before acid halide addition); PS$-CH_2-C\mathbf{H}_2-O-CO-C(CH_3)_2-$Br (br m, 3.73 ppm), PS$-CH_2-CH_2-O-CO-C(C\mathbf{H}_3)_2-$Br (br m, 3.93 ppm).

(b) Poly(styrene-*b*-acrylonitrile) (PS-*b*-PAN). The polystyrene macroinitiator (0.50 g), CuBr (0.030 g), and dNbpy (0.160 g) were added to an oven-dried polymerization tube equipped with a Teflon stir bar. The polymerization tube was back-flushed with nitrogen three times, and then DMF (4.0 mL) and AN (2.0 mL) were added. The tube was then freeze/pump/thawed three times, backfilled with nitrogen, and reacted at 70 °C for varying times (see Table 1).

Characterization. Number-average molecular weights (M_n) were determined by ^{1}H NMR in $CDCl_3$ (for polystyrene samples) and DMSO-d_6 (for diblock samples) using a 300 MHz Bruker spectrometer. Monomer (acrylonitrile) conversion was determined by taking aliquots of the reaction at different times and measuring the DMF to acrylonitrile peak ratio. M_w, M_n, and PDI were measured via SEC against PS standards using two Polymer Laboratories PLGel 5 μm Mixed-D and one PLGel 5 μm 50A columns (see Supporting Information for a complete description of the SEC data). Polystyrene samples were run using a Knauer K-501 HPLC pump, and Knauer K-2301 RI detector, in THF at 1.0 mL/min flow rate. Diblock copolymers were run using a Hewlitt Packard (HP) series 1050 HPLC pump and a HP series 1047A RI detector in DMF (0.01 M LiCl) at 0.5 mL/min flow rate.

Thin Film and Bulk Sample Microphase Characterization. Bulk samples were prepared by drop casting from 5% DMF solutions onto a Kapton film and heating on a hot plate at 120 °C for several minutes. The film was removed from the hot plate and further dried in a vacuum oven overnight prior to the SAXS measurements. SAXS measurements were done under vacuum using an Osmic MaxFlux X-ray (Cu Kα, 1.54 Å) source with a Molecular Metrology, Inc., camera consisting of a three-pinhole collimation system, 150 cm sample-to-detector distance (calibrated using silver behenate), and a 2-dimensional, multiwire proportional detector (Molecular Metrology, Inc.).

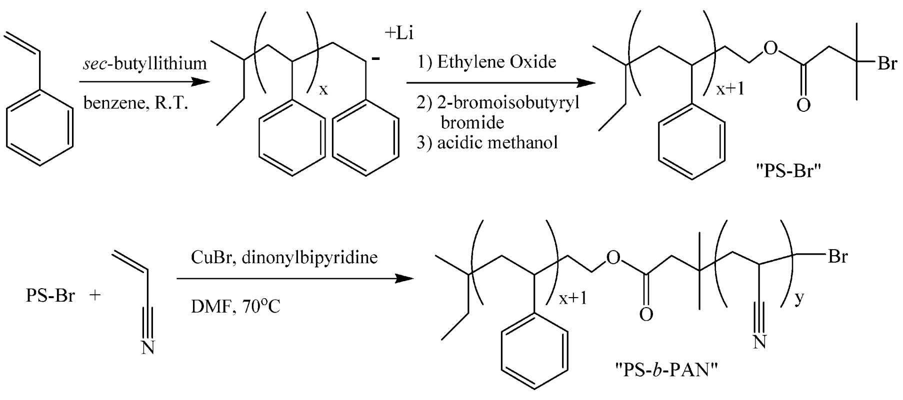

Figure 2. Synthetic scheme for PS-*b*-PAN polymers.

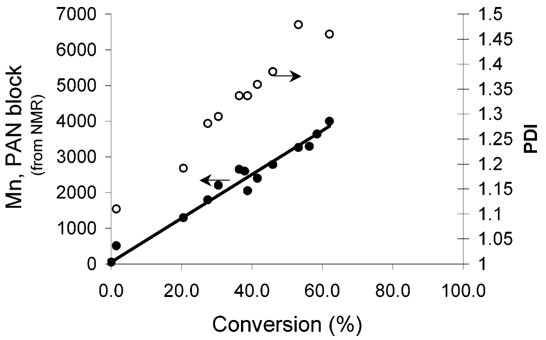

Figure 3. Number-average molecular weight and polydispersity as a function of conversion for the growth of the PAN block (see also Supporting Information).

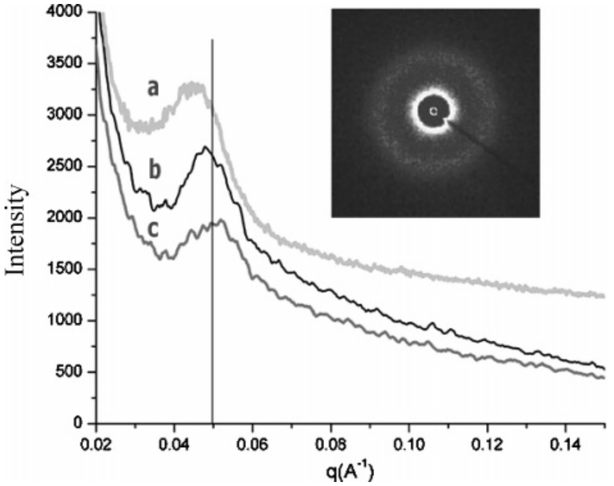

Figure 4. Overlay of SAXS patterns for various PS-*b*-PAN diblocks: (a) SANa3, *d* spacing = 14.2 ± 0.2 nm; (b) SANb6, *d* spacing = 13.1 ± 0.1 nm; (c) SANb3, *d* spacing = 12.5 ± 0.4 nm. Curves are offset for clarity. Inset is sample of 2D SAXS scattering pattern. The range of uncertainty in the *d* spacing values results from variations in the curve fitting used to determine the *d* spacing.

Thin films were spin-coated at 1000−3000 rpm from either 1% or 5% w/w DMF, DMAc, or DMSO solutions onto silicon wafers having a 200 nm silicon oxide layer. The wafer was heated using a hot air gun just prior to spin-coating to facilitate the evaporation of the solvent. An alternate method that proved to be equally effective was to pass a light stream of dry nitrogen over the wafer during the spin-coating process. Sample thicknesses before stabilization and pyrolysis ranged from 18 to 46 nm (depending on the spinning speed) for the 1% solutions and ~100 nm for the 5% solutions (3000 rpm), as was measured with a Filmetrics interferometer using a silicon oxide calibration wafer and also by scanning force microscopy. TEM samples were prepared by floating the films onto copper grids using 5% HF(aq) to dissolve the silicon oxide layer. Unstabilized samples were stained with ruthenium tetraoxide for 30 min. Stabilized and pyrolyzed samples had larger contrast so no stain was needed. TEM was done using a JEOL2000FX transmission electron microscope, with a tungsten filament, with an accelerating voltage of 200 kV.

Carbonaceous Film Formation. Thin films of PS-*b*-PAN were heated at 250 °C under air for 2 h on a hot plate, then cooled, and placed into a TGA furnace. A TA Instruments Series 2050 thermogravimetric analyzer with a quartz furnace was used for thin film pyrolysis. Films were pyrolyzed by heating at 20 °C/min from room temperature to 600 °C and held at 600 °C for 10 min under nitrogen. TEM preparation of these films was the same as above.

Results and Discussion

A series of low molecular weight (<4000 g/mol total) diblock copolymers were synthesized, using bromine-functionalized PS to grow PAN by ATRP using a copper catalyst (see Figure 2).

Multiple reactions were done using the same starting PS-Br (2.0 kg/mol), and aliquots were taken to monitor the growth of the PAN for reaction times up to 4 h and 62% conversion. The kinetics data for the ATRP polymerization of the PAN block are given in Figure 3, and a summary of conversion and molecular weights for representative diblock copolymers is given in Table 1.

The conversion was measured using ^{1}H NMR, by monitoring the disappearance of the monomer peaks. The molecular weight is shown to be linear as a function of conversion, one indication of a controlled reaction, and typical for an ATRP polymerization. The PDI increases as a function of conversion, possibly due to deactivation of the copper catalyst by the DMF, as suggested by Matyjaszewski et al.[1] Even with this increase in PDI, the diblock copolymers were shown to phase separate in bulk and in thin films.

SAXS and TEM were used to study the microphase separation behavior of the PS-*b*-PAN samples listed in Table 1. SAXS was performed on three representative samples: SANb3,

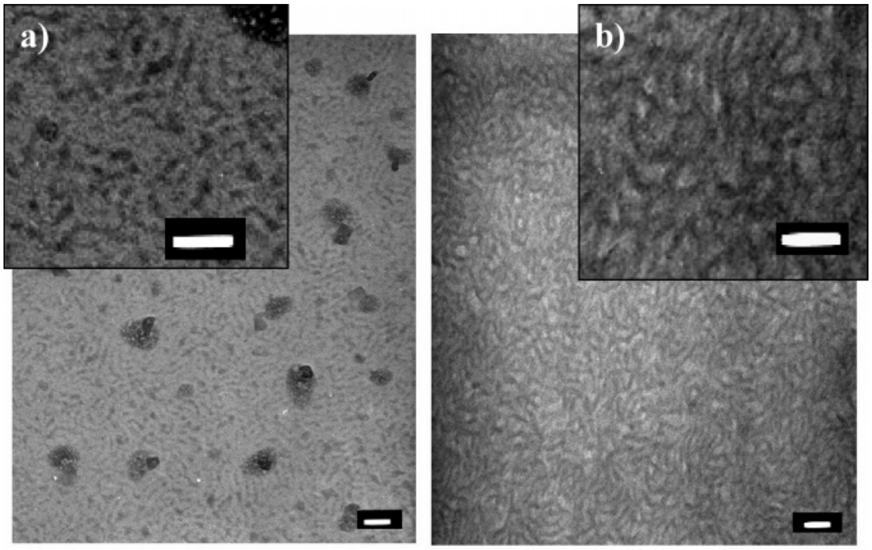

Figure 5. TEM images looking down through films of PS-*b*-PAN (SANa3) (a) as cast from DMF then stained with RuO_4 and (b) stabilized at 250 °C. The stained sample shows PS as the dark regions, and the stabilized sample shows PAN as the dark regions. Large dark spots are from contamination during the RuO_4 staining process. (a) and (b) are "zoomed in" regions of the underlying TEM images. Scale bars = 50 nm.

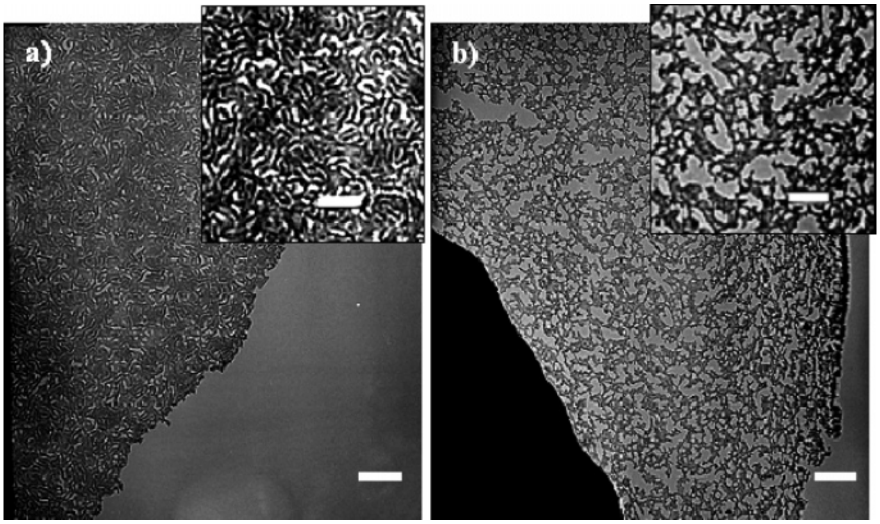

Figure 6. Carbonaceous film formation using thin films of SANa2 cast from DMF (a) stabilized and pyrolyzed and (b) unstabilized and pyrolyzed. (a) and (b) are "zoomed in" regions of the underlying TEM images. Scale bars = 200 nm; inset scale bars = 100 nm.

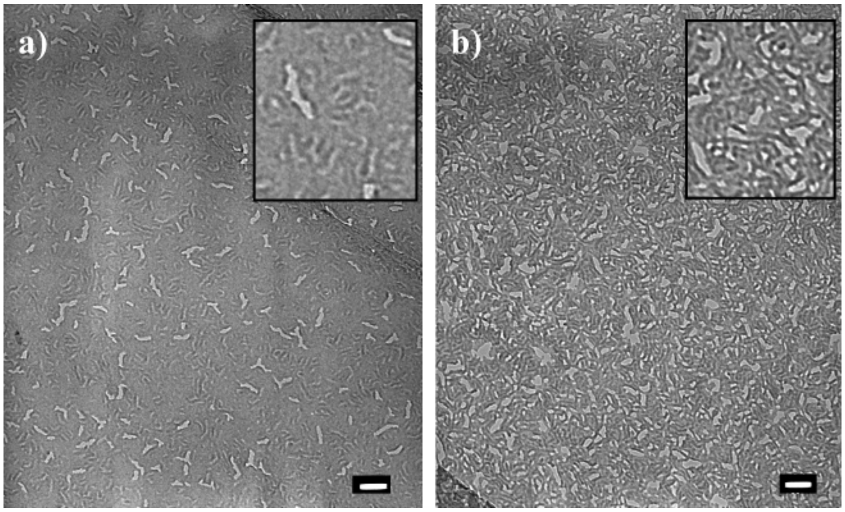

Figure 7. Effect of different casting solvents on the morphology of the carbonaceous films. Thin films spin-coated using SANb5 from (a) DMAc and (b) DMSO solutions, stabilized at 250 °C and then pyrolyzed at 600 °C. A similar DMF film is shown in Figure 6. Scale bar = 100 nm.

SANa3, and SANb6. The scattering peak in SAXS yields a d spacing ranging from 12.5 nm (for sample SANb3) to 14.2 nm (for sample SANa3). No preferred orientation or long-range order of the microphase-separated domains was seen in the data (see Figure 4). The SAXS data alone does not prove microphase separation, and TEM was needed to confirm microphase separation. It is important to note that the samples used for the TEM and SAXS studies were slightly different, with the exception of SANa3. The reason for using the different samples was due to the limited supply of SANb3 and SANb6. Consequently, diblock copolymers with similar volume fractions were chosen to complete the studies. TEM yielded reproducible results for the PS-*b*-PAN polymers studied, and the values for the domain spacing agreed with the SAXS measurements.

The phase separation and pyrolysis behavior of thin films of three of the PS-*b*-PAN diblock copolymers were studied in detail: SANa2 and SANb5 (54% v/v PAN) and SANa3 (62% v/v PAN). Microphase separation occurs on the <10 nm size scale due to the large value of χ and low molecular weight.

Stabilization of the Morphology. The microphase-separated morphology in thin films of PS-*b*-PAN was monitored throughout the stabilization process using TEM. There was not sufficient electron density contrast to see the morphology in the unstabilized (as cast) PS-*b*-PAN thin films (~30 nm), and ruthenium tetraoxide was needed to selectively stain the PS domains.[18] However, after the PAN was stabilized (250 °C for 2 h in air), the cyclization reaction of the nitrile groups, and initial degradation of the PS domains, provided enough electron density contrast to see the morphology clearly (see Figure 5).

This stabilization step starts the intra- and intermolecular reactions that are needed to stabilize the structure prior to pyrolysis. Without this initial stabilization step, the competition between chain scission and cyclization during the pyrolysis step (at 600° C under nitrogen) would lead to the destruction of the thin film. This can be seen in Figure 6, where a thin film sample (~30 nm) of SANa2 (54% PAN) was broken into two pieces: one-half was stabilized then pyrolyzed, and another half was just pyrolyzed. The sample that was quickly heated to 600 °C shows gaping holes in the film and no preservation of the microphase-separated morphology. The stabilized, then pyrolyzed samples, however, show that the morphology remains, now in a carbonaceous form, and the sacrificial PS domains have been removed.

Effect of Different Casting Solvents on Morphology. The solubility of PAN is a limiting factor in the number of solvents that can be used for casting thin films. Typical solvents that can be used are DMF, DMSO, and DMAc. All three solvents have varying polarities and vapor pressures but, under the same

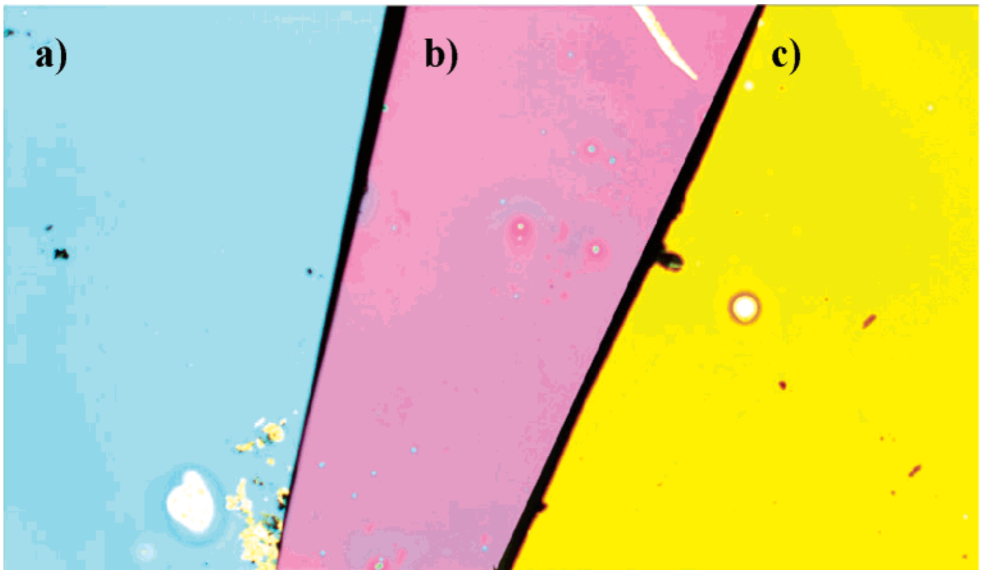

Figure 8. Optical microscopy images of thicker films of SANa2 cast from DMF onto 200 nm SiO: (a) as cast, (b) stabilized at 250 °C for 2 h under air, and (c) pyrolyzed at 600 °C under nitrogen. Image shows a distinct color change due to the change in film thickness and no cracking of the films upon heating.

casting conditions, give similar results. Several films were spin-coated onto silicon wafers having a 200 nm layer of oxide, stabilized, and then pyrolyzed (see Figure 7).

For all the solvents used, the morphology does not appear to orient in a preferred direction. Further studies need to be done to optimize the casting and stabilization conditions to afford an ordered array of microphase-separated polymer domains with preferred orientation either perpendicular or parallel to the substrate.

Thickness Changes upon Carbonaceous Film Formation. The thin films that were studied all show the presence of a few “holes” or voids after stabilization and pyrolysis, as can be seen in the TEM images (see Figures 6 and 7). While some of these holes can be attributed to the removal of the PS sacrificial block, larger holes are more likely due to volume contraction of the film after stabilization and pyrolysis. Studies on the pyrolysis of PAN to create carbon films and fibers have shown that ~50% of the polymer weight is lost during the carbonization process, two-thirds of which is lost during the initial stabilization process.[3,19,20] This loss of weight also corresponds to a significant volume change for the carbon fibers and films, with a volume shrinkage of ~25% between 200 and 300 °C.[21] PS-*b*-PAN thin films coated on 200 nm SiO substrates also undergo a change in volume. During this volume shrinkage, the film remains adhered to the substrate, so that only the thickness of the film changes. Optical microscopy was used to study this thickness change after stabilization and pyrolysis (see Figure 8). The films in Figure 8 were lightly scratched, and SFM measurements were done to monitor the change in thickness. The “as-cast” sample was 100 nm and after stabilization at 250 °C was 70 nm. After the final pyrolysis step, the resulting film was 32 nm thick. These volume shrinkages are larger than what has been seen for PAN, which may be due to additional volume contraction from the removal of the PS domains.

Conclusions

A diblock copolymer containing PS-*b*-PAN was synthesized via ATRP and ring-opening polymerizations and was shown to phase separate for low molecular weights. SAXS and TEM data indicate poor lateral ordering, but distinctive phase separation. This is a promising method to obtain nanoporous (<10 nm) carbonaceous films using diblock copolymers that have strong phase separation behavior.

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Supporting Information Available: Representative SEC data and molecular weight trends. This material is available free of charge via the Internet at http://pubs.acs.org.

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