Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 8129–8137 **8129**
DOI: 10.1021/ma901560k

Polyaniline and Polypyrrole Templated on Self-Assembled Acidic Block Copolymers

Lynne A. McCullough, Bruno Dufour, and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15232

Received July 17, 2009; Revised Manuscript Received August 25, 2009

ABSTRACT: A method was developed for utilizing block copolymers that combine an acidic block, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), and an acrylate block, *n*-butyl, ethyl, or methyl acrylate, as templates for acid-doped conducting polymers such as polyaniline (PANI) or polypyrrole (PPY). PANI templated with diblock copolymers dissolved in dichloroacetic acid results in the formation of high-conductivity materials (30 S/cm) that possess a greater degree of flexibility than pure PANI (between 20% and 50% elongation at ~4 MPa). Triblock copolymers were used as templates for the oxidative polymerization of PANI and PPY to form *in situ* conducting polymer composites with conductivities of ~0.1 S/cm.

Introduction

Conjugated conducting polymers have been successfully used as components in anticorrosion coatings, charge-injection layers in organic light-emitting diodes, electromagnetic shielding, plastic circuitry, and biosensors due to their high conductivity, low density, and reasonably high processability.[1] Heteroatomic conducting polypyrrole (PPY) and polyaniline (PANI) are particularly suited to such applications, given their ease of synthesis, low cost, and high degree of environmental stability.[2] One drawback with these materials is the low solubility caused by π-stacking of the conjugation, resulting in poor processability in the finished polymers. Use of dopants such as HCl and H_2SO_4 in the case of PANI or PF_6^- or ClO_4^- for PPY[3] produces materials with several hundred S/cm conductivity[4] but does not interrupt intermolecular interactions and thus does not provide soluble doped materials. Replacing these small mineral dopants with larger functionalized organic dopants such as 10-camphorsulfonic acid (CSA),[5] 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA),[6] or dodecylbenezenesulfonic acid (DBSA)[7,8] increases the solubility of the conjugated polymers. This is due to both interfering with the polymer-to-polymer interactions and improving polymer–solvent interactions through the large organic functionalities attached to the inorganic moiety. Doping PANI with CSA and processing from a polar solvent such as *m*-cresol has resulted in films with conductivities as high as 400 S/cm,[5] while PPY processed from *m*-cresol with β-naphthalenesulfonic acid (NSA) has resulted in smooth films with conductivities up to ~30 S/cm.[9] Other sulfonic acids are effective as dopants, including polyelectrolytes,[10−14] diesters of sulfophthalic acid,[15] or sulfosuccinic acid.[16]

Another problem is the highly brittle nature of conducting polymers, which can be partially solved by preparing block copolymers with a conducting polymer segment and a low-T_g amorphous polymer segment. This approach is most successful with systems like poly(3-hexylthiophene), where the conducting polymer can be functionalized to provide end groups suitable for block extension.[17,18] Similar systems have proven applicable to PANI, though the conductivity of such materials was quite low (10^{-5} S/cm).[19,20] Segmented copolymers containing PPY are most often prepared by end-capping the low-T_g block or macromonomer with a pyrrole unit that can be chain extended via chemical or electrochemical polymerization, resulting in block and graft copolymers with moderate conductivities (10^{-2} S/cm).[21−23]

A second approach involves blending the conjugated polymer with matrix polymers exhibiting the desired mechanical properties.[24] Matrix polymers can include polypropylene,[25] poly(methyl methacrylate),[26,27] poly(vinyl alcohol),[28,29] and poly(*n*-butyl methacrylate).[30] However, all these matrices are insulating, and simple blending does not allow the degree of morphological control which would ensure continuity of the conjugated polymer phase necessary for good conductivity. Replacing these homopolymers with block copolymers containing one segment that exhibits an affinity for PANI or PPY creates a self-assembling phase-separated system that can serve as a template.[31−33] The block copolymer composition can be manipulated to control the connectivity of the conjugated polymer-containing phase, though conductivity is often significantly lower in blended systems. This is a side effect of varying percolation thresholds and poor chain planarity in the conducting polymer as a result of the insulating template material.[34]

Block copolymers can also be used as micellar templates for discrete conducting nano-objects.[35,36] Amphiphilic block copolymers containing hydrophobic polystyrene (PS)[37] or polycaprolactone (PCL)[38] segments combined with hydrophilic poly(ethylene oxide) (PEO) segments have been successfully used as templates for nanostructured PANI-based materials. However, these materials exhibited broad micelle size distributions and high degrees of aggregation due to the use of freely diffusing small molecule ionic dopants which were not effective in limiting the conducting polymer to the hydrophilic micellar corona. Similar behavior is observed when polystyrene and poly(2-vinylpyridine) (P2VP) are used to prepare micelles on surfaces that will preferentially template PPY-based nanostructures.[39,40] The morphological control of these nanostructures can be improved by the use of small molecule anionic surfactants that function both as a templating structure and as the dopant for PANI and PPY. Compounds such as bis(2-ethylhexyl sulfosuccinate) (AOT)[41] and DBSA[42] have been utilized successfully in creating spherical or cylindrical nanoparticles where control of the formed structure is based on the relative concentrations of the surfactant and the

---

*To whom correspondence should be addressed. E-mail: km3b@andrew.cmu.edu.

conducting polymer moiety.[43,44] Conductivities in these systems are generally significantly lower than in smooth films prepared from similar materials (10^{-3}−50 S/cm as opposed to 300−400 S/cm).[42−44] The combination of these two approaches has only recently been attempted for PANI-based systems. Loo utilized a diblock copolymer containing AMPSA as the acidic dopant block and methyl acrylate (MA) as templates for PANI-containing nanoparticles.[45] These templated nanostructures exhibited monodisperse size distributions, a function of the localization of doped PANI in the micellar corona.

The use of block copolymers as templates for conducting polymer materials most often centers around amphiphilic PEO-based materials[37,38] or styrene-based polymeric materials.[32] Recently, the incorporation of efficient small molecule dopants into the pendent functionalities of block copolymer has allowed for the preparation of amphiphilic molecules that function both as an organizing template and as a dopant for nitrogen-based conducting polymer materials such as PANI and PPY. AMPSA-based block copolymers have proven to be particularly effective as dopants and templating agents both in the solid state[46] and in micellar solutions.[45] These block copolymers are most frequently prepared using controlled/living radical polymerization techniques such as reversible addition−fragmentation chain transfer (RAFT),[47−49] which is tolerant of acidic functionalities, or atom transfer radical polymerization (ATRP).[50−54] It is also possible to prepare similar block copolymers by switching from one mechanism to another or by postpolymerization transformation of the end groups.[55−60]

We have utilized both approaches to prepare block copolymers that function as dual dopants and templating agents for PANI and PPY. In our previous work, we addressed the solubility issues by using diblock copolymers containing a hydrophobic soft methyl acrylate block and an acidic AMPSA hydrophilic block as templates for PANI dissolved in DCAA.[46] The nitrogen groups in the PANI backbone can be protonated by acids, and the resulting positively charged nitrogen in the conjugated polymer backbone can electrostatically interact with the deprotonated sulfonic acid in the block copolymer. This interaction results in the morphology of the conducting polymer being controlled by the morphology of the acidic segments. This morphology can be manipulated by changing the DP and molecular weight of the template block copolymers, thereby providing a method of controlling the connectivity and conductivity of the conducting polymer composites. Our current work involves broadening this method to encompass other low-T_g hydrophobic blocks. The goal is to maximize the conductivity and improve the mechanical properties by using flexible block copolymers as the templating material. The use of ATRP as a method for preparing low-polydispersity templates (PDI < 1.2) and the effect of PDI and block length on the properties of the final materials were also examined.

Experimental Section

Materials. The aniline, AMPSA, *n*-butyl acrylate, methyl acrylate, ethyl acrylate, methanol, 2,2′-bipyridine, ethyl 2-bromoisobutyrate, CuCl, $CuCl_2$, and dichloroacetic acid were purchased from Aldrich. CuCl was purified by stirring in glacial acetic acid for several hours, followed by washing with ether and ethanol. Aniline and pyrrole were distilled under vacuum before use, while acrylates were passed through basic alumna to remove the radical inhibitor. All other compounds were used as received.

PANI Base Preparation. Aniline (30 mL), LiCl (48 g), ethanol (285 mL), and HCl (3 M, 355 mL) were mixed together and cooled to −15 °C. After 3 h, ammonium persulfate (18.75 g), LiCl (24 g), and HCl (2 M, 180 mL) were added and stirred for 16 h. The reaction temperature was raised to 5 °C before polyaniline was collected and filtered by vacuum, washed with 1 L of HCl (3 M) and 2 L of water, stirred for 2 days in 2 L of NH_4OH (0.1 M), washed with methanol until the liquid was no longer a dark purple, washed with 200 mL, and dried under vacuum.

Synthesis of Poly(acrylamido-2-methyl-*N*-propanesulfonic acid) by RAFT. AMPSA (10 g), degassed methanol (40 mL), and cumyl dithiobenzoate (71 mg) were added to a degassed Schlenk flask. After overnight stirring to solubilize the monomer, azoisobutyronitrile (8.1 mg) was added and degassed, and then the flask was lowered into a thermostated oil bath (60 °C). The reaction was stopped when the mixture turned from cloudy to clear (60% conversion by NMR). The solvent was removed by rotary evaporation, and the polymer was purified by dialysis. ^{1}H NMR and aqueous GPC were used to determine the MW and PDI (14 500 g/mol, $M_w/M_n = 1.36$).

PAMPSA Block Extension with Methyl Acrylate. PAMPSA (0.8065 g) was added to a Schlenk flask and degassed for 30 min. Degassed methanol (6 mL), methyl acrylate (4 mL), anisole (1 mL), and AIBN (1.1 mg) were then added, and the flask was heated to 60 °C in an oil bath. The reaction was monitored by GC, and the final composition was determined by elemental analysis.

Preparation of a Poly(*n*-butyl acrylate) Macroinitiator by ATRP. 37 μL of dimethyl 2,6-dibromoheptanedioate or methyl 2-bromopropionate (MBP) (0.17 mmol) and 34 μL of *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 0.34 mmol) were dissolved in 20 mL of deoxygenated *n*-butyl acrylate and 2 mL of deoxygenated anisole in a Schlenk flask. 24.4 mg CuBr (0.34 mmol) were then added. The reaction was carried out at 70 °C for 18 h. The resulting polymer was diluted with THF, passed through a neutral alumina column, and dried under vacuum until constant weight, M_n = 59 900 g/mol, and PDI = 1.15.

Block Extension of Polyacrylates with AMPSA Using AGET ATRP. AMPSA (16.6 g) was added to a Schlenk flask, along with 8.2 g of PBA macroinitiator (MW 59 900 g/mol), and degassed. Degassed tri(*n*-butyl)amine (19.2 mL) and degassed DMF (48 mL) were added. Copper chloride (79.2 mg), ascorbic acid (47 mg), and 2,2′-bipyridine (bpy) (87.6 mg) were added to a separate Schlenk flask and deoxygenated by three cycles of vacuum pumping and N_2 purging. Degassed DMF (3 mL) was added, and a 1 mL aliquot was added to the reaction flask. The flask was lowered into a 60 °C oil bath for 18 h and purified by dialysis.

Preparation of PANI/Block Copolymer Composite. A 1 wt % solution of PANI/AMPSA2 in dichloroacetic acid was prepared by mixing PANI (1 g), AMPSA (1.144 g), and dichloroacetic acid (100 g) in a flask. When the mixture turned a uniform dark green, the polyaniline was both doped and solubilized and could be used to prepare the PANI /block copolymer composites. A 5 wt % solution of the block copolymer was also prepared in dichloroacetic acid. Portions of the PANI solution were pipeted into the block copolymer solution, and the mixtures were stirred in order to facilitate formation of the composites.

***In Situ* Synthesis of Polyaniline or Polypyrrole Using Micellar Triblock Copolymer Templates.** The solution of micellized triblock copolymer (5 mg/mL, 5 mL) was placed in a round-bottom flask and cooled to 0 °C. Aniline or pyrrole (30 μL) equivalent to 5−30 wt % of the polymer was added and stirred for 30 min to allow monomers to self-assemble in the acidic corona of the micelles. A solution of ammonium persulfate (APS) was prepared by dissolving the APS (55 mg) in 1 mL of water, and a 0.5 mL aliquot was added dropwise to the reaction flask and the reaction was allowed to stir overnight. *N*-Methylpyrrolidone (NMP) was added, and the water was removed by rotary evaporation prior to film processing.

Film Preparation. A clean Petri dish was lined with polyethylene film, fastened in place by double-sided tape. The polyaniline (or polypyrrole) block copolymer composite was dropped onto

Table 1. Block Copolymer Templates with AMPSA and Acrylates Prepared by RAFT and ATRP[a]

	polymer	polym method	CTA or catalyst	MW (g/mol)	PDI	wt % AMPSA
1	$AMPSA_{72}MA_{460}$	RAFT	CDB	54 500	1.52	27
2	$AMPSA_{72}MA_{2150}$	RAFT	CDB	199 900	1.75	7
3	$AMPSA_{172}BA_{775}$	RAFT	CDB	134 900	1.63	26
4	$AMPSA_{72}BA_{255}$	RAFT	CDB	47 600	1.56	31
5	$BA_{195}AMPSA_{61}$	ATRP	$CuCl_2$/bpy	32 300	1.08	22
6	$EA_{225}AMPSA_{68}$	ATRP	$CuCl_2$/bpy	36 600	1.10	38
7	$MA_{162}AMPSA_{81}$	ATRP	$CuCl_2$/bpy	30 700	1.21	55
8	$AMPSA_{27}BA_{468}AMPSA_{27}$	ATRP	CuCl/bpy	71 100	1.19	16
9	$AMPSA_{30}BA_{156}AMPSA_{30}$	ATRP	CuCl/bpy	32 400	1.17	38
10	$AMPSA_{29}EA_{260}AMPSA_{29}$	ATRP	CuCl/bpy	38 000	1.13	31

[a] All RAFT reactions were in methanol at 60 °C with cumyldithiobenzoate as chain transfer agent and AIBN as radical source ([M]:[I]:[CTA] = 300:1:4). All AGET ATRP reactions were in DMF with 5 mol % excess TBA using $CuCl_2$/bpy and ascorbic acid (AA) ([M]:[I]:[$CuCl_2$]:[bpy]:[AA] = 300:1:1:2:0.8).

the central flat portion and dried under vacuum for 2 h at 90 °C and then overnight at 50 °C.

Characterization and Analysis. Monomer conversions were determined by gas chromatography (GC) with a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector and using a capillary column (CEC-Wax, 30 m × 0.53 mm × 1.0 μm, Chrom Expert Co.). The NMR spectra (in D_2O or DMSO-d_6 with tetramethylsilane as the reference) were recorded on a Bruker instrument operating at 300 MHz. Template molecular weights were determined by size exclusion chromatography (SEC) using 50 mM solution of LiBr in DMF (flow rate 1 mL/min, 50 °C) with a series of three Styragel columns (10^5 Å, 10^3 Å, 100 Å; Polymer Standard Services) and a Waters 2410 differential refractometer as the detector. Calibration based on polystyrene standards was used with toluene as the elution volume marker. The polymer solutions were filtered through neutral alumina columns attached to a 0.2 μm PTFE filter prior to the analysis.

Tapping mode atomic force microscopy (TMAFM) studies were carried out with the aid of a NanoScope III-M system (Veeco Corp., Santa Barbara, CA), equipped with a J-type vertical engage scanner. The AFM observations were performed at room temperature under air using silicon cantilevers with nominal spring constant of 40 N/m and nominal resonance frequency of 300 kHz (standard silicon TESP probes). Typically, the cantilever was oscillated at the frequency at which the oscillation amplitude was equal to 10−20% of amplitude on resonance.

Electrical conductivity measurements were conducted on free-standing polymer films by the standard spring-loaded pressure-contact four-point probe method in ambient conditions. Six repeated measurements were taken from 1 cm by 1 cm samples of uniform area. The conductivity σ (S/cm) was calculated according to the following equation: $\sigma = 1/(4.53Rl)$, where R is the resistance ($R = V/I$) [Ω] and l is the film thickness (cm).

Micelle size and size distribution were measured by dynamic light scattering (DLS) on a Model HP5001 high performance particle sizer, from Malvern Instruments, Ltd. DLS measurement provides average diameter, D_{av}, and size distribution index, CV (coefficient of variation), which is defined as follows: $D_{av} = \sum_{i=1}^{n} D_i/n$; $S = [\sum_{i=1}^{n}(D_i - D_{av})^2/(n-1)]^{1/2}$; $CV = S/D_{av}$, where D_i is the diameter of the particle i, n is the total number counted, and S is the size standard deviation. In this paper, particle sizes are expressed as ($D_{av} \pm S$) nm.

Transmission SAXS images were taken at Cornell High Energy Synchrotron Source (CHESS) D1 station. A wide-bandpass (1.47%) double-bounce multilayer monochromator supplied an intense beam of 10.1 keV photons which impinged onto thick sample thin film. Transmission SAXS scattering intensities were recorded with an area detector (Medoptics) with a resolution of 47.19 μm per pixel and a total area of about 50 mm by 50 mm at a distance of 1210 mm from the sample. The intense scattering was blocked with a 1.5 mm wide tantalum rod. Exposures times ranged from 10 to 30 s depending on contrast and sample quality.

Results and Discussion

Preparation of Block Copolymer Templates. Diblock copolymers containing PAMPSA and either poly(methyl acrylate) (PMA) or poly(*n*-butyl acrylate) (PBA) were prepared using cumyl dithiobenzoate as the RAFT agent and azobis(isobutyronitrile) (AIBN) as the initiator (4:1 [CTA]:[I]) in methanol, as described previously.[46] Polydispersities (M_w/M_n) for these block copolymers were high (>1.6) despite monomodal GPC traces, while PAMPSA macroinitiators exhibited M_w/M_n of ~1.3. The composition of these polymers was easily controlled by varying the length of both the PAMPSA and polyacrylate blocks, resulting in preparation of block copolymers with high and low molecular weights as seen in Table 1, **1**−**4**. The preparation of block copolymers using ATRP[52−54,61] was more challenging due to the sulfonic acid group on AMPSA which could protonate the nitrogen-based ligands and thus poison the copper catalyst, preventing polymerization. However, using tri(*n*-butylamine) (TBA) in 5% excess as an *in situ* acid neutralizing agent, with CuCl/bpy as the catalyst and mono- or difunctional polyacrylate macroinitiators (AMPSA: macroinitiator:CuCl:bpy = 200:1:1:2), resulted in block copolymers with $M_w/M_n < 1.2$.[62] AMPSA conversion in these systems was relatively low, but composition could be easily controlled by varying the molecular weights of the polyacrylate macroinitiators (Table 1, **8** and **9**). Using activators generated by electron transfer (AGET) ATRP[63−66] in place of regular ATRP, with $CuCl_2$/bpy as the catalyst and ascorbic acid (AA) as the reducing agent, improved both the rate of AMPSA polymerization and the maximum conversion (~48% 0.8 AA:Cu(II)), providing greater molecular weight control in the block copolymers.

PANI/Diblock Copolymer Composite Preparation. PANI/block copolymer composites were prepared by dissolving PAMPSA-*b*-PMA and PAMPSA-*b*-PBA diblock copolymers **1**−**4** in dichloroacetic acid (DCAA) to (5 wt % of the template) and mixing this with a 1 wt % solution of emeraldine base (EB) PANI doped with 2 equiv of AMPSA monomer per PANI tetramer (Scheme 1). Doping ratios between the sulfonic acid content of the template copolymers and the imine nitrogens in the PANI backbone were 1:2 and 1:4 for the templated copolymer composites. UV−vis absorption spectra for these composites were characteristic of the doped emeraldine base form of polyaniline, with a $\pi-\pi^*$ transition from benzene ring excitations at ~340 nm and a localized polaron peak at 800 nm (Figure 1), as well as an absorbance tail that indicates the presence of delocalized polarons. The lack of a characteristic quinoid shift for undoped EB at ~600 nm supports that the solubilized PANI is doped to the emeraldine salt (ES).

Conductivity of PANI/Block Copolymer Composites. Solid films of these composites were cast from solution onto

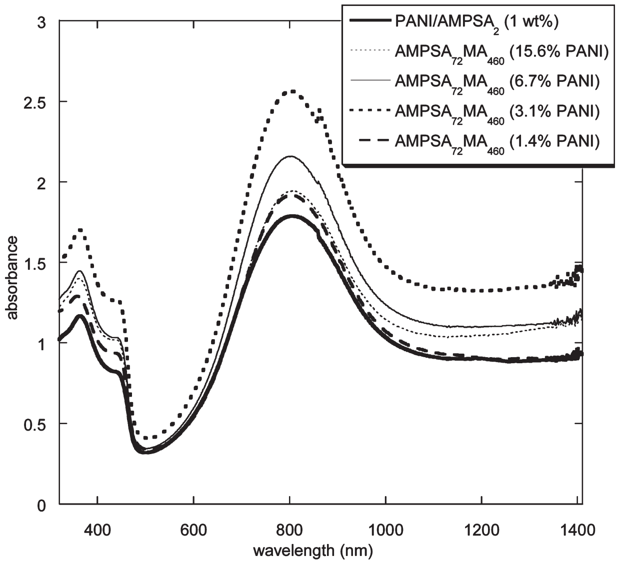
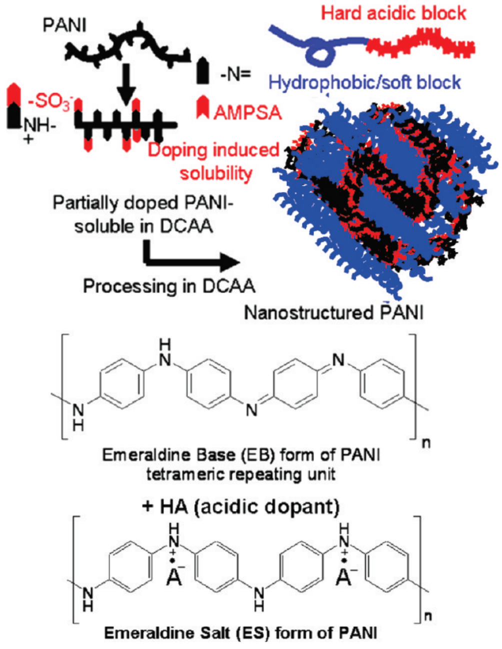


Figure 1. UV–vis spectra of PANI/AMPSA$_2$ in DCAA (1 wt %) and PANI/AMPSA$_2$ templated on AMPSA$_{72}$MA$_{460}$ (5 wt % in DCAA) with ratios of PANI tetramer:SO$_3$ 1:2, 1:4, 1:8, and 1:16.

Scheme 1. Polyaniline Templated with Functionalized Acidic Block Copolymers[a]



[a] The imine nitrogens on the emeraldine base (EB) form are protonated by acidic protons to give a positively charged emeraldine salt (ES).

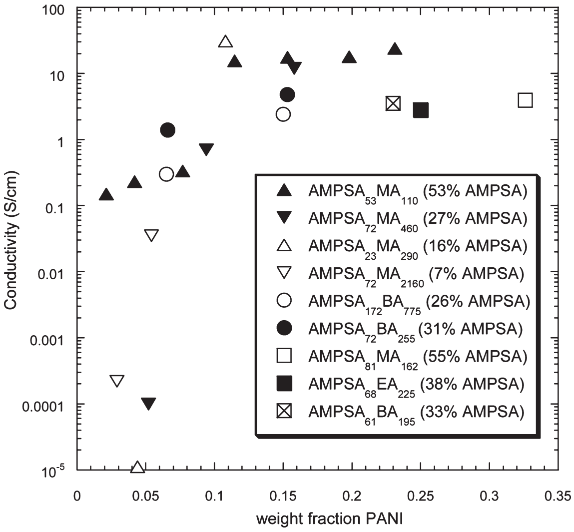


Figure 2. Conductivity of PANI/AMPSA$_2$ templated on diblock copolymers as measured by four-point probe from 1 cm^2 films cast from DCAA solution and dried under vacuum.

polyethylene backing and dried under vacuum for 2 h at 90 °C and then for 24 h at 50 °C. Films were easily removed from the substrate as free-standing films with thicknesses of 20–30 μm. Conductivities reached a maximum of 30 S/cm for low molecular weight block copolymers. Materials with higher molecular weights reached conductivities as high as 15 S/cm for templates containing MA and 5 S/cm for templates containing BA, even with composites containing similar AMPSA content by weight (Figure 2). Increasing AMPSA content (52 wt %), on the other hand, resulted in composites with much higher conductivities at low PANI incorporation (~0.1 S/cm at 2.5 wt % vs 10^{-4} at 5 wt % for 30% AMPSA) but similar conductivities when greater amounts of PANI were added (~10–15 S/cm above 10 wt %). Additionally, given that the ratio of PANI tetramer (Scheme 1) to dopant was 1:2 for each case of high conductivity, it is likely that the differences in maximum conductivity were due to morphology differences between the phase separated composites. Highly conductive materials are more likely to exhibit continuous or bicontinuous phases such as lamellae or gyroidal phases, while materials with lower conductivity may exhibit isolated cylindrical structures. Percolation thresholds were between 5 and 8 wt %, significantly lower than the 16% expected for the general model of spheres distributed in a background matrix. This is most likely the result of the morphology constraints exerted by the templating block copolymers.[46]

Analysis of Composite Morphology by AFM. Phase-separated morphologies of the PANI/block copolymer composites were determined by AFM from thin films cast on silica substrates and dried under vacuum first for 2 h at 90 °C and then overnight at room temperature. The morphologies of the block copolymers differ significantly between the high PDI samples prepared by RAFT (M_w/M_n ~ 1.6) and the lower PDI materials prepared by RAFT (M_w/M_n ~ 1.3) (Figure 3a) and ATRP (M_w/M_n ~ 1.2). Addition of the polyaniline/AMPSA$_2$ solution to the high-PDI materials prepared by RAFT resulted in disordered phase separation and a significant amount of precipitation of the PANI materials (Figure 3b). This may be due to an additive effect on the PDI of the system once PANI is incorporated, as the oxidative polymerization of aniline produces polymers with high polydispersities.[67] Addition of this material to the block copolymers will increase the PDI of the templating acidic block and thus increase the overall PDI of the system. This type of increase can result in a wider variety of morphologies than is classically considered “available” to a particular weight and composition of block copolymers, while too great an increase will result in the loss of ordered morphologies entirely.[68]

In the lower PDI materials prepared by ATRP, however, a lamellar/branched phase separation was seen for the BA$_{195}$AMPSA$_{61}$ block copolymer after the addition of 14.9 wt % PANI (Figure 3c). A more disordered phase separation was seen for MA$_{162}$AMPSA$_{81}$ with 15.2 wt % PANI (Figure 3d) due to the low molecular weight of the block copolymer template.[69] The relative conductivities of these two sets of materials differ by a factor of 2−3, with higher conductivities (12−7 S/cm) for the higher molecular weight and higher PDI materials vs the 2−3 S/cm for the low MW and PDI materials prepared by ATRP. This difference could result from the larger size of the conducting domains; the higher MW materials have a greater interpenetration of conducting polymer due to the lack of phase separation, and thus charge carriers do not pass through insulating domains as frequently. Additionally, variation of morphology can have origins in the higher polydispersity of polymers prepared by RAFT.[70,71]

Mechanical Properties of PANI/Block Copolymer Composites. The mechanical properties of the polymer composites also vary significantly with molecular weight. For example, the breaking stress for the RAFT-prepared polymers reached as high as 5 MPa, with extension of up to 20% for MA-containing block copolymers and 50% for polymers containing BA. The films prepared by ATRP, however, exhibited ultimate stress only as high as 11.5 kPa, with extensions of 33% for MA-containing films, and 1.76 kPA, with an extension of 34% in the PEA films. This could be a result of the lower molecular weight and lower polydispersity of the ATRP-derived block copolymers as compared to those prepared by RAFT. When block lengths are near or below the entanglement lengths for each polymer segment, good mechanical robustness and strength are difficult to achieve.[72]

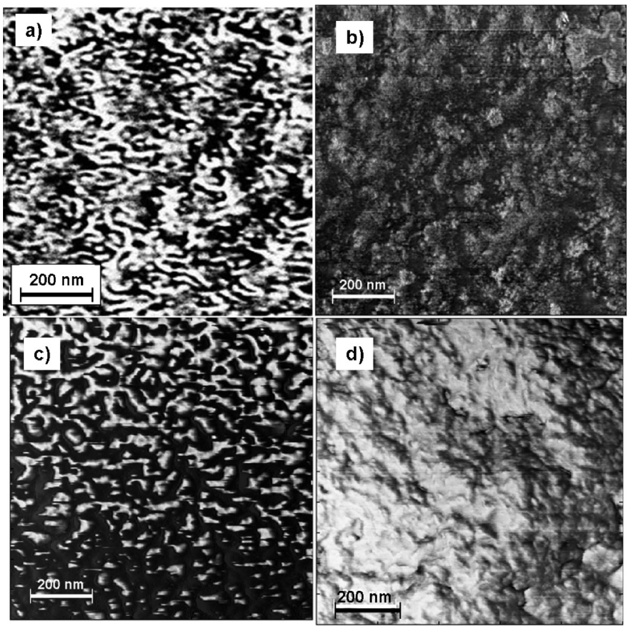


Figure 3. AFM phase images of PANI/block copolymer composites: (a) $AMPSA_{23}MA_{290}$ prepared by RAFT (PDI 1.3) with 12.3 wt % PANI; (b) $AMPSA_{72}MA_{460}$ prepared by RAFT (PDI 1.52) with 15.6 wt % PANI; (c) $AMPSA_{61}BA_{195}$ prepared by ATRP (PDI 1.08) with 14.9 wt % PANI; (d) $AMPSA_{81}MA_{162}$ prepared by ATRP (PDI 1.21) with 15.2 wt % PANI. These films were cast from 2 wt % DCAA solutions onto 1 cm^2 silica substrates and dried 48 h under vacuum.

Mechanical stretching also exhibits an effect on the electrical properties of conducting polymer-based materials, particularly when the stretching is applied along the backbone of the polymer chain. This results in increased linearity and planarity in conducting polymer chains, thereby improving the mobility of the charge carriers along the polymer backbone.[73] The conductivity of both the PMA ($AMPSA_{81}MA_{162}$) and PEA ($AMPSA_{68}EA_{225}$) templated conducting polymer composites approximately doubled after applied stretching (PMA: 6.13 S/cm vs 3.95 S/cm; PEA: 6.07 S/cm vs 2.82 S/cm). A similar increase in conductivity was not in evidence perpendicular to the stretching direction, a common occurrence in stretched conducting materials.[74] This suggests that physical processing of these conducting copolymer composites may offer a route to enhanced conductivities beyond those allowed by pure solution processing.

Solvent Processing. Because of the highly corrosive nature and low volatility of DCAA, the potential of using more volatile solvents to process these templated PANI materials was investigated. Methanol, chloroform, and *m*-cresol were used to dissolve the block copolymer $AMPSA_{23}MA_{290}$ (5 wt % solutions) prior to addition of the PANI/$AMPSA_2$ dissolved in DCAA (1 wt %) and subsequent processing as before. AFM images of the as-cast thin films are shown in Figure 4. Processing from chloroform resulted in rough films full of large holes, which lowered the film conductivity to 5×10^{-5} S/cm. Methanol-processed films exhibited particulates embedded in the block copolymer film; these

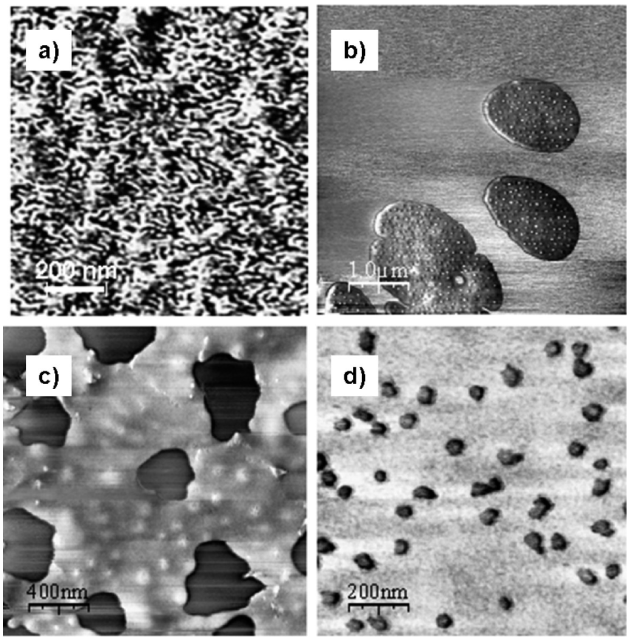
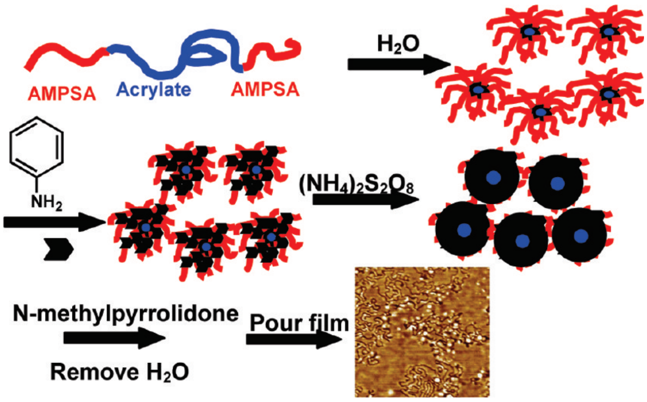


Figure 4. AFM images of PANI/$AMPSA_{23}MA_{290}$ cast from (a) DCAA, (b) *m*-cresol, (c) chloroform, and (d) methanol. Thin films were cast from 2 wt % solutions onto 1 cm^2 silica substrates and dried under vacuum for 48 h.

Table 2. Mechanical Properties of PANI Templated on Block Copolymers Containing Polyacrylates

template	PANI content (%)	% extension	stress (MPa)	conductivity (S/cm)	stretched (S/cm)
$AMPSA_{72}MA_{460}$	15.6	23	5.01	12.1	
	6.7	31	1.61	0.7	
	3.1	54	0.87	10^{-4}	
$AMPSA_{172}BA_{775}$	23.2	20	3.54	2.4	
$AMPSA_{81}MA_{162}$	33.1	33	0.0115	3.95	6.07
$AMPSA_{68}EA_{225}$	25.4	34	0.0018	2.82	6.13

Scheme 2. Triblock Copolymers as Templates for *In Situ* Preparation of PANI (and Also PPY)



particulates were likely precipitated PANI particles, as is often the case with PANI suspended in a water/methanol system.[75] *m*-Cresol, an effective solvent for organic acid-doped PANI, exhibited poor compatibility with the initial block copolymer templates, resulting in formation of a patchy film. Conductivities for both the methanol and the *m*-cresol-processed films were low, but still significant, for processable composite PANI systems (1×10^{-3} S/cm for methanol and 4×10^{-3} S/cm for *m*-cresol).[24,25,76] Given that identical templates exhibited 30 S/cm conductivities when processed from pure DCAA, it seems clear that the morphology of the films, as well as the orientation and configuration of the PANI chains, is the primary agent controlling conductivity in these templated materials.

***In situ* Preparation of Conducting Polymer Composites on Triblock Copolymers.** When triblock copolymers with a central hydrophobic block and outer acidic/hydrophilic blocks were used as templates for PANI/$AMPSA_2$ in DCAA, the film quality was very poor. Macrophase separation was observed in each case, regardless of the PANI content. The large sizes of the central hydrophobic block (40 000−60 000 g/mol) may have been the cause of this increased segregation. However, when dialyzed in DMF against water, these triblock copolymers formed micelles that could be used as *in situ* templates for acid-dopable conducting polymers such as polyaniline. The overall scheme for the preparation of these conducting nanoparticles is shown in Scheme 2. Triblock copolymers were dialyzed against water to form micelles with a hydrophobic core and acidic corona; the basic monomers would be protonated by the sulfonic acid groups after addition and "trapped" in the corona.[45] After oxidative polymerization using ammonium persulfate (APS) at 0 °C, the polymer composites could be cast as thin films either from water or from an organic solvent like *N*-methylpyrrolidone (NMP) after removal of water.

Micellar Aggregation of Triblock Copolymers. The dimensions of the micelles formed by the AMPSA-containing triblock copolymers was determined by dynamic light scattering (DLS) to be in the range of 60−150 nm, varying primarily by the composition and block length of the hydrophobic acrylate block. The ethyl acrylate-containing triblock copolymer $AMPSA_{29}EA_{260}AMPSA_{29}$ (M_n = 38 000 g/mol) showed the presence of micelles with $D_H = 66 \pm 4$ nm and a moderate size distribution (CV ~ 0.25). Similar results were observed for $AMPSA_{30}BA_{156}AMPSA_{30}$ ($D_H = 77 \pm 4$ nm, CV ~ 0.44) and $AMPSA_{27}BA_{468}AMPSA_{27}$ ($D_H = 145 \pm 3$ nm, CV ~ 0.065). The smaller micelle size of block copolymers with ethyl acrylate was most likely a result of smaller hydrocarbon pendent groups in ethyl acrylate, leading to improved compressability and a smaller hydrophobic core than in the butyl acrylate copolymers. The micelles exhibited swelling after addition of the aniline or pyrrole monomer, up to a maximum value of ~10 nm at ~15 wt %. Micelle size increased further after oxidative polymerization of the templated monomer, resulting in particles with a diameter D_H ~ 520 nm and a CV of 0.60 with ~20 wt % conducting polymer. This size increase was due to a combination of aggregation resulting from charge shielding of the sulfonic acid groups by doped PANI or PPY and cross-linking between particles during polymerization.

PANI Templated on Triblock Copolymers. Films were cast from the micellar triblock composite suspensions after addition of an organic solvent, *N*-methylpyrrolidone (NMP), and evaporation of water. Copolymers processed from pure water exhibited cracked films with significant bubbling and formation of macroscopic holes. The use of NMP resulted in formation of regular thick films at higher concentrations of the conducting polymer. This solvent improved the solubility of the various micelle components and provided an avenue for reorganization of the micelles into well-ordered domains. The conductivities were determined by the four-point probe technique on 1 cm^2 samples. PANI templated on $AMPSA_{29}EA_{260}AMPSA_{29}$ exhibited very low conductivities even at high PANI wt % (10^{-4} S/cm) with a percolation threshold roughly in line with the theory of distribution of spherical particles (16%) (Figure 5). This low conductivity was attributed to the fact that the full number of dopable nitrogens on the PANI backbone was not accessible to the sulfonic acid groups in the dopant, and vice versa. This observation is supported by the increase in conductivity by 3 orders of magnitude (approaching 10^{-1} S/cm) when the composite was dialyzed against 0.1 M HCl for an hour.

Additional support for the existence of inaccessible dopant moieties is demonstrated by UV−vis spectroscopy. The expected UV−vis spectra for doped EB PANI exhibited a $\pi-\pi^*$ transition from benzene ring excitations at ~340 nm and a localized polaron peak at 800 nm. However, composites with PANI content >10 wt % also exhibited the quinoid excitation peak at 600 nm corresponding to undoped EB (Figure 5), indicative of a lack of full doping in the templated system arising from the inaccessibility of all sulfonic acid moieties to the conducting polymer in the solvent-constrained micelles. Given the maximum doping ratio is 2 acid units to 1 PANI tetramer, undoped PANI should not be present with <16 wt % PANI in the system.

Polypyrrole Templated on Triblock Copolymers. Since polypyrrole (PPY) often exhibits higher conductivity than PANI, PPY was also templated on triblock copolymer micelles. The conductivities of PPY templated on $AMPSA_{29}EA_{260}AMPSA_{29}$ were significantly improved from those obtained with PANI, with values as high as 10^{-3} S/cm at low PPY content (<10 wt % PPY), though further increases with the addition of PPY were modest, leveling off to ~10^{-2} S/cm at 20 wt %. This may be the result of significant distribution of the conducting phase even at low PPY content (percolation threshold <5 wt %), though it may also be the result of ionic conductivity in the acidic block. The conductivity obtained by polymeric proton conductors is $10^{-5}-10^{-2}$ S/cm, which falls neatly within this range.[77,78] Conductivities for the block copolymer with the highest molecular weight central block ($AMPSA_{27}BA_{468}AMPSA_{27}$) were uniformly low, even for the composite structure with 25 wt % PPY ($<10^{-9}$ S/cm). Decreasing the size of the insulating block (and thus increasing the proportion of acidic dopant in the polymer) resulted in a

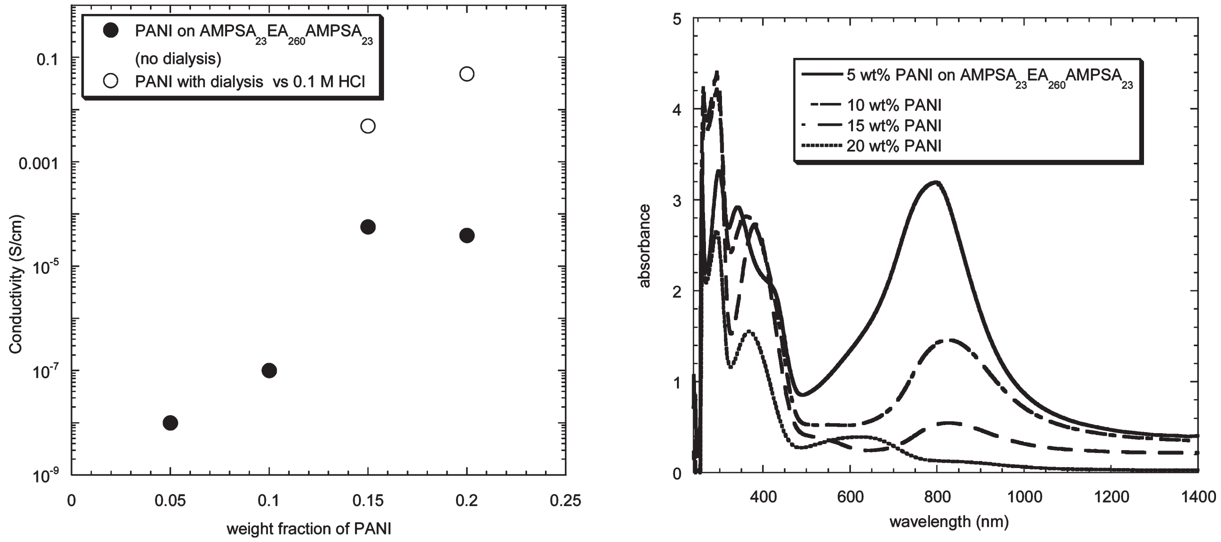


Figure 5. (left) Conductivities of PANI templated on $AMPSA_{23}EA_{260}AMPSA_{23}$ with varying wt %. Dialysis was carried out for 1 h vs 0.1 M HCl. Conductivities were measured by four-point probe from free-standing 1 cm^2 films of 10 μm thickness. (right) UV−vis PANI templated on micelles of $AMPSA_{23}EA_{260}AMPSA_{23}$ with varying conducting polymer wt % (0.1 mg/mL).

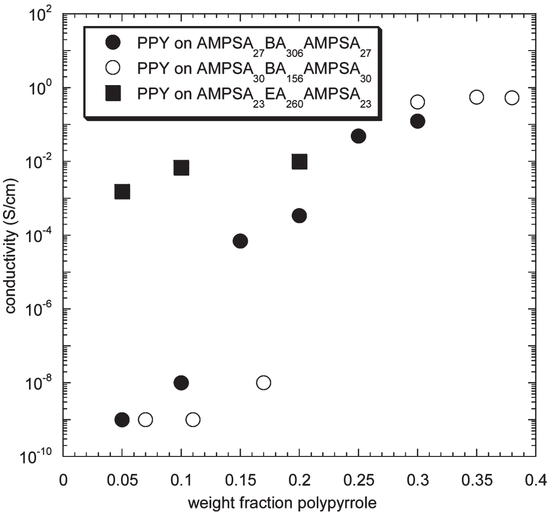


Figure 6. Conductivities of varying wt % PPY templated on triblock copolymers. Conductivities were determined by four-point probe technique from 10 μm free-standing films of 1 cm^2.

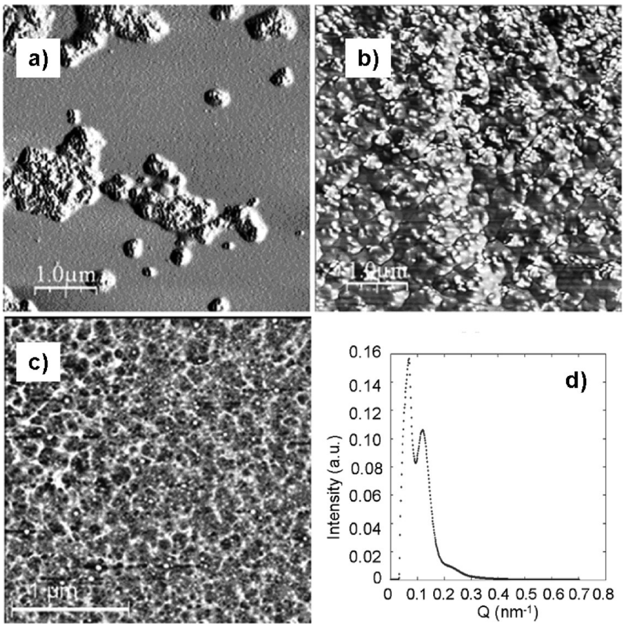


Figure 7. AFM images (1 μm scale) of $AMPSA_{30}BA_{156}AMPSA_{30}$ with (a) 5 wt % polypyrrole and (b) 25 wt % polypyrrole cast from 0.5 mg/mL DMF solution onto silica substrates. (c) AFM image of $AMPSA_{30}BA_{468}AMPSA_{30}$ (9 wt % PPY). (d) SAXS profile of (c) (spacing ~ 50 nm).

significant increase in conductivity, particularly with PPY >20 wt % (Figure 5). Lower BA content also resulted in polymers with much later, sharper percolation thresholds: 23 wt % for $AMPSA_{30}BA_{156}AMPSA_{30}$ and 19 wt % for $AMPSA_{27}BA_{306}AMPSA_{27}$. Both values are close to the 16% demonstrated by spherical particles in a matrix. While the experimental percolation thresholds do not confirm the retention of the spherical micelle shape during processing, they do support the possibility of a spherical shape after polymerization and film processing.

As-Cast Morphology. Thin films were cast from 0.5 mg/mL solutions of the polymer composites onto silica substrates and dried under vacuum for 24 h. All films exhibited regions of aggregated spherical particles regardless of concentration of the conducting polymer (Figure 7). The particles were all <100 nm in diameter, corresponding roughly to the D_H indicated for the block copolymer templates (65−100 nm) without the conducting polymer. This indicates that the immense size increases for the micelles postpolymerization result from aggregation and cross-linking, not swelled micelles. Samples cast with low-to-moderate PPY content templated on $AMPSA_{30}BA_{468}AMPSA_{30}$ exhibited similar behavior in AFM (Figure 7c), but small-angle X-ray scattering (SAXS) measurements demonstrated some evidence of longer-range order in the high-MW system (Figure 7d) with spacing of ~50 nm. Films processed from this high molecular weight template exhibited greater smoothness and cohesiveness than those prepared from lower molecular weight materials, indicating either a different micelle shape or more well-defined micelles that allowed greater connectivity between the acrylate domains during processing. The higher BA content in this polymer might also make the micelles more susceptible to disruption and solvation by NMP.

Table 3. Effect of Small Molecule Dopants and Sulfonate Counterions on the Conductivity of PPY/Block Copolymer Templated Composites

copolymer template	counterion	wt % PPY	dopant	conductivity (S/cm)
$AMPSA_{30}BA_{156}AMPSA_{30}$	H^+	16		0.16
	H^+	16	AOT	0.75
	H^+	16	$HClO_4$	0.25
	H^+	38		0.54
	Na^+	38		0.357
	TBA^+	38		0.01
$AMPSA_{27}BA_{468}AMPSA_{27}$	H^+	17		10^{-9}
	H^+	17	AOT	2×10^{-4}
	H^+	17	$HClO_4$	6×10^{-4}
	H^+	17	AMPSA	10^{-6}

Effect of Small Molecule Dopants on Conductivity. The use of small molecule dopants as a means to improve the conductivity of our materials was examined. Dried thin films were dipped into aqueous solutions of 0.1 M of AOT, $HClO_4$, and monomeric AMPSA for ~1 h before being dried under vacuum prior to conductivity measurements (Table 3). Films of $AMPSA_{30}BA_{156}AMPSA_{30}$ with 16 wt % PPY exhibited doubled or quadrupled conductivities of 0.25 and 0.75 S/cm after exposure to solutions of $HClO_4$ and AOT, respectively. Similar results were seen for exposure of 17 wt % PPY composites with $AMPSA_{30}BA_{468}AMPSA_{30}$, where conductivity increased from 10^{-9} up to 10^{-4} S/cm. This 5 order of magnitude increase in conductivity to a value which remained low indicated that morphology constraints and poor connectivity between the PPY domains contribute more to the poor conductivity than insufficient doping. Effects of sulfonic acid counterions were also determined (Table 3), with protonated acid exhibiting more effective doping than the sodium salt, both of which were more effective than the tributylammonium salt. This result is not unsurprising given that protonation of the nitrogen groups is the basis for conductivity in the system, though size of the counterion and its effect on planarity of the conducting polymer chain could also be a significantly contributing factor.[79]

Conclusions

We have investigated the effects of various hydrophobic blocks on the conductivity of PANI templated on block copolymers, both with preprepared conducting polymers and with materials prepared *in situ*. Conductivity is controlled by a combination of hard phase composition, conducting polymer content, polydispersity, and block size, with higher conductivity materials possessing smaller block sizes and lower PDI. The identity of the insulating block is also a contributing factor, with longer alkyl pendant groups producing materials with lower conductivities for similar PANI compositions. *In situ* polymerization of conducting polymers on dopant-containing block copolymer-derived micellar templates is an effective method of preparing nanostructured conducting materials in aqueous and noncorrosive solvents. The relative flexibility of PPY vs PANI affects the accessibility of the template dopant functionalities and thus limits the maximum conductivity of the system without further small molecule doping which may be accomplished via pre- or postprocess doping.

Acknowledgment. The financial support of DMR-05-49353 is gratefully acknowledged. Acknowledgments are also extended to Rui Zhang, John McGann, and Tomasz Kowalewski for AFM and SAXS analysis.

References and Notes

(1) Pron, A.; Rannou, P. *Prog. Polym. Sci.* **2001**, *27*, 135–190.
(2) Ansari, R. *Eur. J. Chem.* **2006**, *3*, 186–201.
(3) Zang, J.; Li, C. M.; Bao, S.-J.; Cui, X.; Bao, Q.; Sun, C. Q. *Macromolecules* **2008**, *41*, 7053–7057.
(4) Whang, Y. E.; Han, J. H.; Nalwa, H. S.; Watanabe, T.; Miyata, S. *Synth. Met.* **1991**, *43*, 3043–3048.
(5) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91–97.
(6) Adams, P. N.; Devasagayam, P.; Pomfret, S. J.; Abell, L.; Monkman, A. P. *J. Phys.: Condens. Matter* **1998**, *10*, 8293–8303.
(7) Jang, K. S.; Lee, H.; Moon, B. *Synth. Met.* **2004**, *143*, 289–294.
(8) Lee, J. Y.; Kim, D. Y.; Kim, C. Y. *Synth. Met.* **1995**, *74*, 103–106.
(9) Shen, Y.; Wan, M. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3689–3695.
(10) Baker, C. K.; Qiu, Y. J.; Reynolds, J. R. *J. Phys. Chem.* **1991**, *95*, 4446–4452.
(11) Prezyna, L. A.; Qiu, Y. J.; Reynolds, J. R.; Wnek, G. E. *Macromolecules* **1991**, *24*, 5283–5287.
(12) Glatzhofer, D. T.; Ulanski, J.; Wegner, G. *Polymer* **1987**, *28*, 449–453.
(13) Yoo, J. E.; Cross, J. L.; Bucholz, T. L.; Lee, K. S.; Espe, M. P.; Loo, Y.-L. *J. Mater. Chem.* **2007**, *17*, 1268–1275.
(14) Zhang, F.; Halverson, P. A.; Lunt, B.; Linford, M. R. *Synth. Met.* **2006**, *156*, 932–937.
(15) Dufour, B.; Rannou, P.; Fedorko, P.; Djurado, D.; Travers, J.-P.; Pron, A. *Chem. Mater.* **2001**, *13*, 4032–4040.
(16) Dufour, B.; Rannou, P.; Djurado, D.; Janeczek, H.; Zagorska, M.; de Geyer, A.; Travers, J.-P.; Pron, A. *Chem. Mater.* **2003**, *15*, 1587–1592.
(17) Kowalewski, T.; McCullough, R. D.; Matyjaszewski, K. *Eur. Phys. J. E* **2003**, *10*, 5–16.
(18) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 329–332.
(19) Kinlen, P. J.; Frushour, B. G.; Ding, Y.; Menon, V. *Synth. Met.* **1999**, *101*, 758–761.
(20) Asawapirom, U.; Guentner, R.; Forster, M.; Scherf, U. *Thin Solid Films* **2005**, *477*, 48–52.
(21) Yildiz, H. B.; Kiralp, S.; Toppare, L.; Yagci, Y. *J. Appl. Polym. Sci.* **2005**, *96*, 502–507.
(22) Oztemiz, S.; Toppare, L.; Onen, A.; Yagci, Y. *J. Macromol. Sci., Pure Appl. Chem.* **2000**, *A37*, 277–291.
(23) Street, G. B.; Lindsey, S. E.; Nazzal, A. I.; Wynne, K. J. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 137–148.
(24) Anand, J.; Palaniappan, S.; Sathyanarayana, D. N. *Prog. Polym. Sci.* **1998**, *23*, 993–1018.
(25) Fryczkowski, R.; Slusarczyk, C.; Fabia, J. *Synth. Met.* **2006**, *156*, 310–317.
(26) Jang, J.; Oh, J. H. *Adv. Funct. Mater.* **2005**, *15*, 494–502.
(27) Mezzenga, R.; Ruokolainen, J.; Fredrickson, G. H.; Kramer, E. J.; Moses, D.; Heeger, A. J.; Ikkala, O. *Science* **2003**, *299*, 1872–1874.
(28) Chattopadhyay, D.; Bain, M. K. *J. Appl. Polym. Sci.* **2008**, *110*, 2849–2853.
(29) Heng, L.; Wang, X.; Zhai, J.; Sun, Z.; Jiang, L. *ChemPhysChem* **2008**, *9*, 1559–1563.
(30) Han, M. G.; Sperry, J.; Gupta, A.; Huebner, C. F.; Ingram, S. T.; Foulger, S. H. *J. Mater. Chem.* **2007**, *17*, 1347–1352.
(31) Radhakrishnan, S.; Saini, D. R. *Polym. Int.* **1994**, *34*, 111–117.
(32) Ruckenstein, E.; Sun, Y. *Synth. Met.* **1995**, *74*, 107–113.
(33) Ruckenstein, E.; Hong, L. *Synth. Met.* **1994**, *66*, 249–256.
(34) Lee, D. H.; Chang, J. A.; Kim, J. K. *J. Mater. Chem.* **2006**, *16*, 4575–4580.
(35) Carswell, A. D. W.; O'Rear, E. A.; Grady, B. P. *J. Am. Chem. Soc.* **2003**, *125*, 14793–14800.
(36) Wang, M.; Kumar, S.; Lee, A.; Felorzabihi, N.; Shen, L.; Zhao, F.; Froimowicz, P.; Scholes, G. D.; Winnik, M. A. *J. Am. Chem. Soc.* **2008**, *130*, 9481–9491.
(37) Sapurina, I.; Stejskal, J.; Tuzar, Z. *Colloids Surf., A* **2001**, *180*, 193–198.

(38) Cheng, D.; Ng, S.-C.; Chan, H. S. O. *Thin Solid Films* **2005**, *477*, 19–23.
(39) Goren, M.; Lennox, R. B. *Nano Lett.* **2001**, *1*, 735–738.
(40) Yoo, S. I.; Sohn, B.-H.; Zin, W.-C.; Jung, J. C. *Langmuir* **2004**, *20*, 10734–10736.
(41) Jang, J.; Yoon, H. *Langmuir* **2005**, *21*, 11484–11489.
(42) Stejskal, J.; Omastova, M.; Fedorova, S.; Prokes, J.; Trchova, M. *Polymer* **2003**, *44*, 1353–1358.
(43) Antony, M. J.; Jayakannan, M. *J. Polym. Sci., Part B: Polym. Phys.* **2009**, *47*, 830–846.
(44) Son, A. J. R.; Lee, H.; Moon, B. *Synth. Met.* **2007**, *157*, 597–602.
(45) Bucholz, T.; Sun, Y.; Loo, Y.-L. *J. Mater. Chem.* **2008**, *18*, 5835–5842.
(46) McCullough, L. A.; Dufour, B.; Tang, C.; Zhang, R.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 7745–7747.
(47) Sumerlin, B. S.; Donovan, M. S.; Mitsukami, Y.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2001**, *34*, 6561–6564.
(48) Sumerlin, B. S.; Lowe, A. B.; Thomas, D. B.; McCormick, C. L. *Macromolecules* **2003**, *36*, 5982–5987.
(49) Lowe, A. B.; McCormick, C. L. *Prog. Polym. Sci.* **2007**, *32*, 283–351.
(50) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614–5615.
(51) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901–7910.
(52) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990.
(53) Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107*, 2270–2299.
(54) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93–146.
(55) Coca, S.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 2808–2810.
(56) Coca, S.; Paik, H.-j.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 6513–6516.
(57) Davis, K. A.; Charleux, B.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2274–2283.
(58) Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 4241–4243.
(59) Kajiwara, A.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 3489–3493.
(60) Yagci, Y.; Tasdelen, M. A. *Prog. Polym. Sci.* **2006**, *31*, 1133–1170.
(61) Davis, K. A.; Matyjaszewski, K. *Adv. Polym. Sci.* **2002**, *159*, 2–166.
(62) McCullough, L. A.; Dufour, B.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, in press.
(63) Min, K.; Gao, H.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 10521–10526.
(64) Min, K.; Jakubowski, W.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2006**, *27*, 594–598.
(65) Min, K.; Gao, H.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2005**, *127*, 3825–3830.
(66) Jakubowski, W.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 4139–4146.
(67) Mattoso, L. H. C.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1994**, *68*, 1–11.
(68) Bendejacq, D.; Ponsinet, V.; Joanicot, M.; Loo, Y. L.; Register, R. A. *Macromolecules* **2002**, *35*, 6645–6649.
(69) Fredrickson, G. H.; Bates, F. S. *Annu. Rev. Mater. Sci.* **1996**, *26*, 501–550.
(70) Listak, J.; Jakubowski, W.; Mueller, L.; Plichta, A.; Matyjaszewski, K.; Bockstaller, M. R. *Macromolecules* **2008**, *41*, 5919–5927.
(71) Lynd, N. A.; Meuler, A. J.; Hillmyer, M. A. *Prog. Polym. Sci.* **2008**, *33*, 875–893.
(72) Ward, I. M. *An Introduction to the Mechanical Properties of Solid Polymers*, 2nd ed.; Wiley: Chichester, England, 2004.
(73) Abell, L.; Pomfret, S. J.; Adams, P. N.; Middleton, A. C.; Monkman, A. P. *Synth. Met.* **1997**, *84*, 803–804.
(74) Adams, P. N.; Devasagayam, P.; Pomfret, S. J.; Abell, L.; Monkman, A. P. *J. Phys.: Condens. Matter* **1998**, *10*, 8293–8303.
(75) Haba, Y.; Segal, E.; Narkis, M.; Titelman, G. I.; Siegmann, A. *Synth. Met.* **1999**, *106*, 59–66.
(76) Soares, B. G.; Leyva, M. E. *Macromol. Mater. Eng.* **2007**, *292*, 354–361.
(77) Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463–1502.
(78) Przyluski, J.; Wieczorek, W. *Synth. Met.* **1991**, *45*, 323–333.
(79) Shen, Y.; Wan, M. *Synth. Met.* **1998**, *96*, 127–132.