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Templating Conducting Polymers via Self-Assembly of Block Copolymers and Supramolecular Recognition

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The success of conjugated polymers as components in anticorrosion coatings, charge-injection layers in organic light-emitting diodes, electromagnetic shielding, plastic circuitry, and biosensors, among others, is due to their high conductivity, low density, and reasonably high processability.[1] Polyaniline (PANI) is particularly attractive because of its easy synthesis, low cost, and high degree of environmental stability in both the doped and undoped states. One drawback is its low solubility, caused by π-stacking of the highly conjugated backbone, resulting in low processability of the final materials. Replacing mineral acid dopants such as HCl or H_2SO_4 with functionalized organic acids such as 10-camphorsulfonic acid (CSA) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA)[2] increases the overall solubility by way of the large organic groups attached to the acidic 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.[3] Other sulfonic acids are effective as dopants, including polyelectrolytes such as polystyrenesulfonic acid,[4−6] diesters of sulfophthallic acid,[7] or sulfosuccinic acid,[8] particularly in association with polar solvents such as *m*-cresol or 2,2-dichloroacetic acid (DCAA).

A more difficult problem to address is the highly brittle nature of PANI. One solution to this problem is preparing block copolymers with a conducting polymer segment and a low-T_g amorphous polymer segment. Such attempts are most successful with systems like poly(3-hexylthiophene), where the conducting polymer can be functionalized to provide end groups suitable for block extension.[9] These systems have been extended to PANI, though the conductivity of such materials is quite low (10^{-5} S/cm).[10,11] Another approach, even more applicable to PANI, involves blending the conjugated polymer with matrix polymers exhibiting the desired mechanical properties.[12] Matrix polymers can include polypropylene,[13] poly(methyl methacrylate),[14] polyurethane,[15] cyanoresins,[16] and poly(butyl methacrylate).[17] However, all these matrices are insulating, and simple blending does not allow the degree of morphology control which would ensure the continuity of the PANI phase necessary for good conductivity. Replacing these homopolymers with block copolymers containing one segment that exhibits an affinity for PANI creates a self-assembling phase-separated system that can serve as a template. The block copolymer composition can be manipulated to control the connectivity of the PANI-containing phase, though conductivity remains low (<1 S/cm) for the styrene−butadiene−styrene system, a result of the weak preference of PANI for styrene.[18]

Herein we report a new approach to the preparation of templated flexible conducting polymer materials which employs block copolymers with both a soft hydrophobic segment and a segment containing a strongly acidic dopant moiety (i.e., poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA)) that actively interacts with polyaniline or oligoaniline, forming a dopant/conducting polymer complex. Acid−base interaction of PAMPSA with the imine group of the emeraldine base (EB) form of polyaniline, in combination with phase separation between incompatible segments, drives segregation of the conducting polymer into the hydrophilic phase and formation of morphologies assuring high conductivity. Block copolymers were synthesized by a reversible addition fragmentation chain transfer (RAFT)[19−23] process, using cumyl dithiobenzoate (CDB) and AIBN in methanol to prepare PAMPSA macroinitiators, as polymerizations in methanol were consistently better-controlled than those in DMF. These PAMPSA macroinitiators were then extended with methyl acrylate at 60 °C, as shown in Scheme 1. Chain extension allowed control of the composition and structures of the block copolymers, particularly the formation of a system with the hydrophilic block as a continuous matrix.

The use of cumyl dithiobenzoate as the RAFT agent resulted in PAMPSA macroinitiators with relatively low polydispersities (∼1.2) and controlled molecular weight, ranging from ∼4800 to ∼36 000 g/mol, as determined by ^{1}H NMR end-group analysis (Figure S1 of the Supporting Information). Gel permeation chromatography (GPC) traces were monomodal and cleanly shifted to higher molecular weight with the progress of polymerization (Figure S2). Block extension with acrylate monomers yielded block copolymers with monomodal GPC traces and controlled composition (PAMPSA weight fraction in the range of 10−50 wt % as determined by elemental analysis) and polydispersities below 1.4. These polymers were well-soluble in DCAA, allowing for the preparation of homogeneous solutions, which significantly facilitated the incorporation of the conducting aniline polymers and oligomers.

The basic structure of PANI is a four-ring tetramer which, when it contains two imine and two amine groups, is known as emeraldine base (EB). Each imine nitrogen in this structure is a potential doping site for the acid; thus, the maximum effective dopant concentration is one sulfonic acid group for every two nitrogen atoms. As shown in Scheme 2, the complexes between PANI and PAMPSA block copolymer template were prepared in DCAA by mixing 1 wt % solution of PANI predoped with AMPSA monomer with 5 wt % solution of copolymer. The two solutions were mixed with different doping ratios between PAMPSA and the polyaniline (1:2, 1:4, 1:8, etc.) and were subsequently cast onto precleaned flexible polyethylene substrates and dried under vacuum at 75 °C for 24 h.

While tetrameric aniline is soluble in DCAA, undoped PANI is not. Direct addition of PANI allowed only small fractions of conducting polymer to complex with PAMPSA: about 1.2 wt % with respect to the PAMPSA block. However, it is well-known that AMPSA monomer-doped PANI exhibits good solubility in DCAA.[2] Therefore, in order to incorporate higher fractions of PANI and obtain good conductivity of the final material, AMPSA-doped PANI was mixed with PAMPSA-*b*-PMA block copolymers to produce a homogeneous solution. After casting the complexes onto substrates and evaporating the solvent, flexible films with a thickness ranging from 30 to 50

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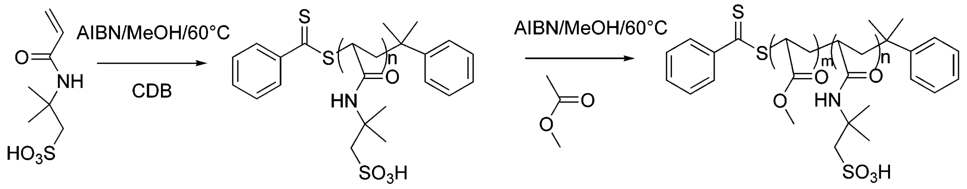
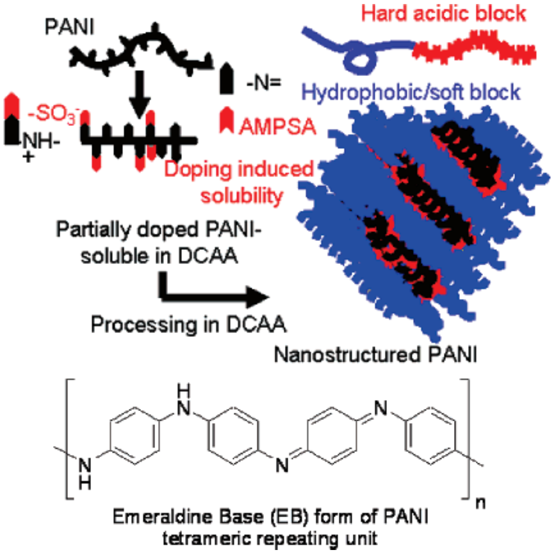
Scheme 1. Synthesis of AMPSA-*b*-MA Block Copolymers by RAFT with Cumyl Dithiobenzoate in Methanol ([M]:[CDB]:[AIBN] = 200:4:1, 60 °C)



Scheme 2. Preparation of Conducting Polymer Complexes with Sulfonic Acid-Containing Block Copolymers and Predoped Polyaniline in Dichloroacetic Acid



μm were formed, and conductivity was measured by a four-point probe.

The dependence of the macroscopic electrical conductivity on the composition of the diblock copolymer and the polyaniline content is shown in Figure 1. Each polymer system exhibited an increase in conductivity at ~10 wt % PANI, reaching conductivities as high as 30 S/cm, which may be the maximum achievable from these templates. However, as the amount of PAMPSA incorporated into the template decreased, the intensity of the increase in conductivity also increased. The most dramatic change of conductivity with composition was observed for block copolymers with 16 wt % PAMPSA. Upon doubling the PANI content, conductivity of these materials increased by 6 orders of magnitude.

Given that these sharp increases in conductivity correspond to decreasing amounts of dopant in the block copolymers, it is likely that template morphology plays an important role in the conductivity of these systems. The evolution of nanoscale morphology with the introduction of oligoaniline and polyaniline was investigated for the block copolymer with 16 wt % PAMPSA using a combination of AFM and SAXS. As commonly observed in classical diblock copolymers,[24] the nanostructures were strongly dependent on the weight fractions of each block. The AFM surface morphology of films of PAMPSA-*b*-PMA processed from DCAA is presented in Figure 2, which combines AFM images (a−c) with their azimuthally averaged radial profiles of 2-D Fourier transforms overlaid with similarly averaged SAXS scattering patterns (d). For block copolymer (PAMPSA)$_{23}$-*b*-(PMA)$_{290}$ with 16 wt % of PAMPSA, a dispersed morphology was observed, with the hard PAMPSA phase scattered in the softer PMA matrix (Figure 2a). Upon addition of tetrameric aniline into block copolymers for the maximum degree of doping, i.e., one sulfonic acid group for one imine group, the color of the reaction mixture changed from light pink to dark green. The thin-film morphology changed as shown in Figure 2b. Because of the complexation between tetrameric aniline and AMPSA, the fraction of hard

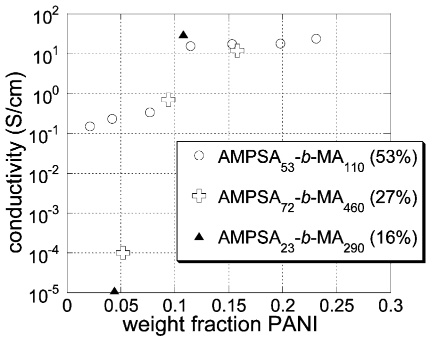


Figure 1. Dependence of conductivity on block composition and polyaniline content as measured by a four-point probe in ambient conditions from 1 cm × 1 cm films (30−50 μm thick).

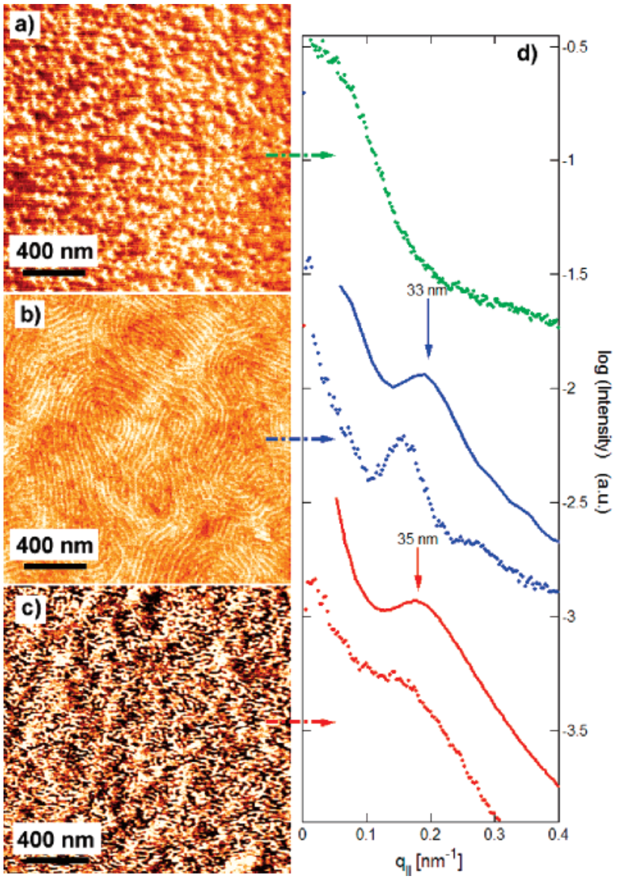


Figure 2. Left: phase contrast TMAFM images (a) (AMPSA)$_{23}$-*b*-(MA)$_{290}$, (b) 4EB$_{11.5}$/(AMPSA)$_{23}$-*b*-(MA)$_{290}$, and (c) PANI(AMPSA)$_1$)$_{2.3}$/(AMPSA)$_{23}$-*b*-(MA)$_{290}$. Right: (d) azimuthally averaged SAXS scattering profiles (solid lines) with superimposed azimuthally averaged radial profiles of 2D Fourier transforms (dotted lines) from the AFM images on the left.

phase increased to 31 wt %, yielding lamellar-like morphology observed by AFM (Figure 2b), with similar periodicity evident in SAXS (Figure 2d).

An AFM image of PANI(AMPSA)$_1$)$_{2.3}$/(PAMPSA)$_{23}$-*b*-(PMA)$_{290}$ (one PANI represents a tetrameric repeating unit) is shown in Figure 2c. Assuming complete incorporation of doped polyaniline in the "hard" PAMPSA phase, the content of this phase should increase to ~20 wt % with the addition of AMPSA-doped PANI. A complex branched structure manifested by distinct peaks in SAXS and the AFM image Fourier transforms was now observed (Figure 2d). The overall agreement between AFM and SAXS periodicities (Figure 2d) is an indication that surface morphologies observed by AFM, at least to some extent, reflected the bulk organization within thin films.

In conclusion, we have successfully demonstrated a facile route toward preparing flexible conductive polymer films by templating the conducting polymer with block copolymers containing both flexible insulating segments and segments containing a sulfonic acid group as dopant moiety. These complexes were processed by casting from acidic solvents such as dichloroacetic acid, forming films whose conductivity varied with the composition, reflecting the changes in morphology and connectivity of the conductive phase. Conductivities as high as 30 S/cm were achieved, significantly higher than those of previous templated or polymer-doped PANI systems. Owing to the combination of mechanical properties of the soft matrix and rigid phase-separated domains, the films exhibited high mechanical flexibility and durability and were in this regard superior to brittle films formed by the homopolymer PANI.

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Supporting Information Available: Experimental procedures, tables of all prepared polymers, and ^{1}H NMR, GPC, AFM, and SAXS data. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Pron, A.; Rannou, P. *Prog. Polym. Sci.* **2001**, *27*, 135−190.

(2) Adams, P. N.; Devasagayam, P.; Pomfret, S. J.; Abell, L.; Monkman, A. P. *J. Phys.: Condens. Matter* **1998**, *10*, 8293−8303.

(3) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91−97.

(4) 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.

(5) Ding, S.-J.; Zhang, C.-L.; Yang, M.; Qu, X.-Z.; Lu, Y.-F.; Yang, Z.-Z. *Polymer* **2006**, *47*, 8360−8366.

(6) Zhang, F.; Halverson, P. A.; Lunt, B.; Linford, M. R. *Synth. Met.* **2006**, *156*, 932−937.

(7) Dufour, B.; Rannou, P.; Fedorko, P.; Djurado, D.; Travers, J.-P.; Pron, A. *Chem. Mater.* **2001**, *13*, 4032−4040.

(8) Dufour, B.; Rannou, P.; Djurado, D.; Janeczek, H.; Zagorska, M.; de Geyer, A.; Travers, J.-P.; Pron, A. *Chem. Mater.* **2003**, *15*, 1587−1592.

(9) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 329−332.

(10) Kinlen, P. J.; Frushour, B. G.; Ding, Y.; Menon, V. *Synth. Met.* **1999**, *101*, 758−761.

(11) Asawapirom, U.; Guentner, R.; Forster, M.; Scherf, U. *Thin Solid Films* **2005**, *477*, 48−52.

(12) Anand, J.; Palaniappan, S.; Sathyanarayana, D. N. *Prog. Polym. Sci.* **1998**, *23*, 993−1018.

(13) Fryczkowski, R.; Slusarczyk, C.; Fabia, J. *Synth. Met.* **2006**, *156*, 310−317.

(14) Mezzenga, R.; Ruokolainen, J.; Fredrickson, G. H.; Kramer, E. J.; Moses, D.; Heeger, A. J.; Ikkala, O. *Science* **2003**, *299*, 1872−1874.

(15) Chiou, W.-C.; Yang, D.-Y.; Han, J.-L.; Lee, S.-N. *Polym. Int.* **2006**, *55*, 1222−1229.

(16) Choi, J. H.; Kim, S. H.; Oh, K. W. *Mol. Cryst. Liq. Cryst.* **2007**, *464*, 863−871.

(17) Han, M. G.; Sperry, J.; Gupta, A.; Huebner, C. F.; Ingram, S. T.; Foulger, S. H. *J. Mater. Chem.* **2007**, *17*, 1347−1352.

(18) Soares, B. G.; Leyva, M. E. *Macromol. Mater. Eng.* **2007**, *292*, 354−361.

(19) Sumerlin, B. S.; Lowe, A. B.; Thomas, D. B.; McCormick, C. L. *Macromolecules* **2003**, *36*, 5982−5987.

(20) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 6977−6980.

(21) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.

(22) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93−146.

(23) Davis, K. A.; Matyjaszewski, K. *Adv. Polym. Sci.* **2002**, *159*, 2−166.

(24) Fredrickson, G. H.; Bates, F. S. *Annu. Rev. Mater. Sci.* **1996**, *26*, 501−550.

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