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Crystallization Driven Formation of Conducting Polymer Networks in Polymer Blends

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ABSTRACT: Electrically conducting networks based on polyaniline−camphorsulfonic acid (PANI-HCSA), blended with crystalline and amorphous polyamides (nylon 6 and Selar), and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT-PSS), blended with poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA), were prepared from solution. These blends exhibited a conductivity that rises smoothly and rapidly from the insulating state with increasing conducting polymer content. When the conducting polymer salts are blended with insulating crystalline hosts, they show a more rapid increase in conductivity relative to blends prepared using amorphous hosts. This faster rise in electrical conduction stems from the presence of more developed conductive pathways in the crystalline host blends due primarily to the crystallization driven exclusion of the conducting polymer into the interspherultic region as seen by transmission electron microscopy (TEM). In the PANI-HCSA/nylon 6 blends conductivities of 1 S/cm are found at 10% loading (wt/wt), approximately 10 times higher than the conductivity observed using the amorphous Selar host. Similar conductivity differences are seen in comparing crystalline and amorphous hosts with PEDOT-PSS, though the magnitudes of the conductivities are lower.

Introduction

Blending of polymers offers a means of engineering into one material certain combinations of desired properties exhibited individually by the component polymers. In these blends, the two polymers composing the blend may be miscible and form one phase or they are immiscible and form two phases. The conditions that cause phase separation are due primarily to differences in molecular geometry, molecular weight, and functional group incompatibility.

Insulating polymers possessing many desirable technological properties may be rendered conductive by mixing with conductive particles such as carbon black, metal powders, flakes or fibers, and metal-coated particles. The level of electrical conductivity in these heterogeneous materials depends primarily on the concentration and geometry of the conductive filler particles. The observed critical filler content which marks the onset of discontinuous increase in conductivity (i.e., the percolation threshold) in the majority of these composites falls between 15 and 25% (vol/vol).[1] At such high filler concentrations, many of the desirable properties of the matrix polymer are either compromised or lost.

Recently it has been shown that highly conducting polymeric blends can be prepared by solution processing of insulating polymers and conductive polyaniline (PANI).[2] Electrical conductivities as high as 1 S/cm were obtained by solution processing to form a polyblend of PMMA containing only about 2% (wt/wt) of conductive PANI. High electrical conductivity of films cast from such solutions are obtained with as little as 1% (wt/wt) of the conducting component.

To account for the large difference in electrical conduction thresholds between metal-filled and organic conducting blend systems, Cao et al.[2,3] investigated the morphology of solution cast PANI blends. They reported[4] that the PANI-0.5-HCSA/PMMA blend, upon casting from *m*-cresol solution, forms a multiphase system. The low onset of electrical conductivity in the blend was apparently due to a fractal-like network formation of the phase-separated conducting polymer salt in the host PMMA during solvent (e.g., *m*-cresol) evaporation.[5,6] The formation of this network was confirmed by Reghu et al.[7] using transmission electron microscopy (TEM). These blends exhibit a pseudo-percolation conduction behavior in that no sharp increase in conductivity (e.g., no conventional percolation threshold) is observed. The conductivity rises smoothly from the insulating state with increasing PANI salt concentrations.

The “nonconventional” relationship between electrical conductivity and PANI salt content in the solution cast blend has been interpreted[8−11] as evidence for a phase-separated structure with conducting networks or pathways of pure PANI salt forming at low loading levels. It is difficult to pinpoint the conditions and molecular interactions that control the formation of the salt network. Interactions between solvent and polymer and between polymers, rate of crystallization of respective blend components, and kinetic effects of solvent evaporation from blend solution are all thought to be operative in forming these conductive pathways.

Recent attempts have been made to optimize the fractal nature of these conducting pathways by compatibilizing the host polymer with the functionalized dopant counteranion.[12] The geometry of the phase-separated salt in the host polymer was controlled by the polarity of the dopant counteranion. Using dopants with polar functionality in a polar host yielded a more fractal network than using a nonpolar dopant anion in the same host. These more developed pathways were thought to arise from a “semicompatiblization” between the PANI salt and host nylon.

These concepts of network formation in conducting polymer blends were extended beyond the PANI-based systems as demonstrated by studies of PEDOT-PSS in a series of polar polymer hosts that were processed from aqueous solutions.[13] In these blends, ionic interactions

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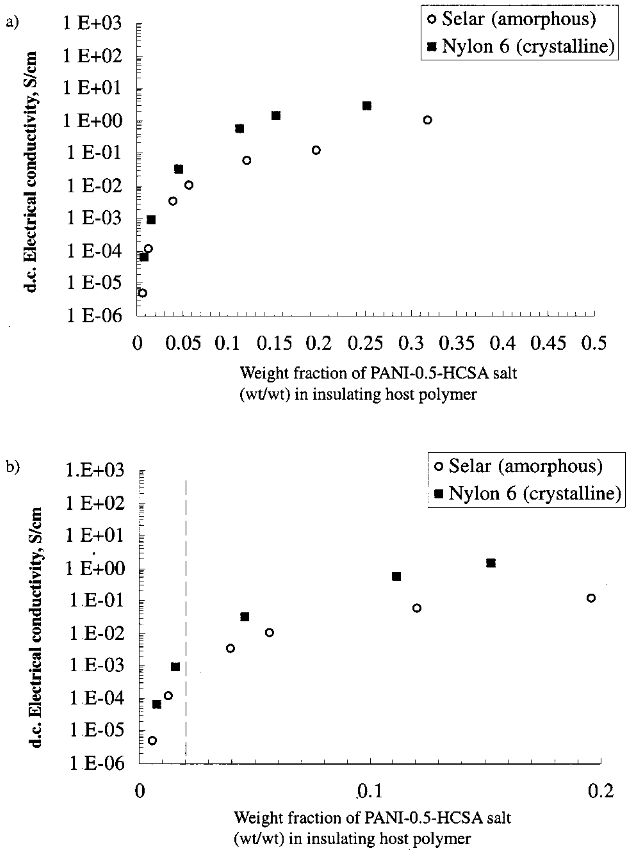

Figure 1. Conductivity as a function of PANI-HCSA salt loading fraction in host polyamide. Blend concentration range of (a) 0−0.35 (wt/wt) and (b) 0−0.2 (wt/wt). Dashed line indicates salt concentration where conductivity profiles change between the two blend systems.

were found to play a strong role in determining morphology and conductivity composition profiles.

In this work, we have utilized the ability of a host polymer to crystallize which excludes a conducting polymer into interspherulitic domains to modify the morphology of the conducting pathways that form. Specifically, we employed two polyamides: nylon 6 (crystalline) and a polyamide copolymer, Selar (amorphous), which were solution blended with PANI optimally doped with camphorsulfonic acid (PANI-HCSA) as the conducting polymer. In addition, poly(ethylene oxide) (PEO, crystalline) and poly(vinyl alcohol) (PVA, amorphous) were solution blended with conducting poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT-PSS). Transmission electron microscopy (TEM) and dc electrical conductivity were used as tools to probe the nature of the conducting pathways.

Experimental Section

Materials. Nylon 6 (Aldrich Chemical Co), Selar (Dupont, a copolymer of isophthalic acid, terephthalic acid, and hexamethylenediamine), and camphorsulfonic acid (Aldrich Chemical Co.) were vacuum-dried at 70 °C for 24 h before use. PEDOT-PSS was obtained from AG-Bayer as an aqueous dispersion. Hexafluoro-2-propanol (HFIP, Aldrich Chemical Co.), poly(vinyl alcohol) (PVA, Aldrich Chemical Co.), and poly(ethylene oxide) (PEO, Polysciences) were used as received.

Synthesis. PANI was made using a method similar to that reported by Yasuda and Shimidzu.[14] The precipitated polymer was washed twice with 1.0 M HCl and then with 1.0 M NH_4OH. This protonation/deprotonation step promotes the breakup of physical cross-links in the PANI chains and improves solubility. Finally, the insulating polymer was washed with distilled water, methanol, and diethyl ether. Each wash step was carried out until the filtrate became clear and colorless. The resulting dark, free-flowing PANI-EB powder was placed in a vacuum oven at 70 °C for 12 h to remove any remaining moisture and solvent. PANI-EB powder made using this methodology has been fully characterized previously.[15]

To dope the PANI, 6.55 mmol of powdered HCSA was added to 68 mL of hexafluoro-2-propanol[16] and magnetically stirred for 10 min. This 2% (wt/wt) acidic solution was then added to 10.9 mmol of PANI-EB and vigorously stirred for 48 h at room temperature to yield a ≈2% (wt/wt) salt solution. The dark green/blue solution was then filtered through a 0.50 μm metal Waters filter. Very little, if any, insoluble PANI-HCSA material was left. Optimal protonation was achieved in HFIP solution to yield the optimal molar doping ratio (i.e., sulfonic acid dopant to PANI = y = 0.5) as seen qualitatively by the dark forest-green color.

Blending. Starting with 2% (wt/wt) solution of each polymer, blends of varied compositions of conductive salt relative to the respective host polymer used were prepared in order to determine the percolation behavior of the conducting blend. Blends were magnetically stirred for 24 h and subsequently cast from their respective solution.

Film Preparation. Using filtered solutions, conductive polymer salt films were cast onto a glass substrate and subsequently covered with a recrystallization dish to allow for a slow evaporation (at room temperature) of solvent for a period of approximately 24 h. Subsequently, these films were placed in a vacuum oven at 80 °C for 12 h to remove remaining solvent.

Characterization. *Transmission Electron Microscopy (TEM).* TEM was used for morphological observations of the conducting polymer blends. A typical sample was prepared by embedding multiple films in a 24 h curing epoxy resin. Microtoming was performed normal to the film surface (at room temperature) so that a cross section of the film could be observed under the TEM. A Riechhart E Ultracut microtome and a DuPont diamond knife were used to obtain sections of ca. 100 nm. All blend samples were stained by RuO_4[17] (Polysciences) for 1.2 h prior to sectioning. The TEM used to capture the morphology was a Hitachi H7000 electron microscope operated at 100 keV.

dc Electrical Conductivity. Polymer blends were coated with four parallel gold strips 1 μm apart by a vapor deposition method. A Keithley 224 current source and a Keithley 181 nanovolt meter were hooked up to a four-point-in-line dc electrical conductivity apparatus. For conductivities of less than 1×10^{-2} S/cm, a two-point probe was employed as the sample resistance exceeded ca. 10 MΩ. Polymer samples were cast onto an ITO plate, and a 1 cm^2 diameter gold contact was deposited on both the polymer surface and ITO to ensure good contact with sample. A Keithley 610 C solid-state electrometer was used to measure resistance of the blend.

The thickness of PANI-ES films was determined using a Sloan Dektak II surface profilometer. Several scratches in the film were scribed by a razor blade, and the 12 mg stylus was traced perpendicularly across the series of scratches. Average step height was calculated and used as the thickness of the film. Solution cast films were ≈4−5 μm thick.

Results and Discussion

Electrical conductivity has been shown to be sensitive to the morphology of a conducting polymer.[18] To determine the dependence on conductivity of adding conducting polymers into host polymers, we have examined blends over the full range of composition. Figure 1a shows electrical conductivity as a function of volume fraction of the PANI-HCSA in blends with nylon 6 and Selar up to ca. 35% (wt/wt) PANI-HCSA loading. Beyond this level, the conductivity was independent of PANI-HCSA composition. It is seen that the rate of increase in conductivity varies depending on the composition of

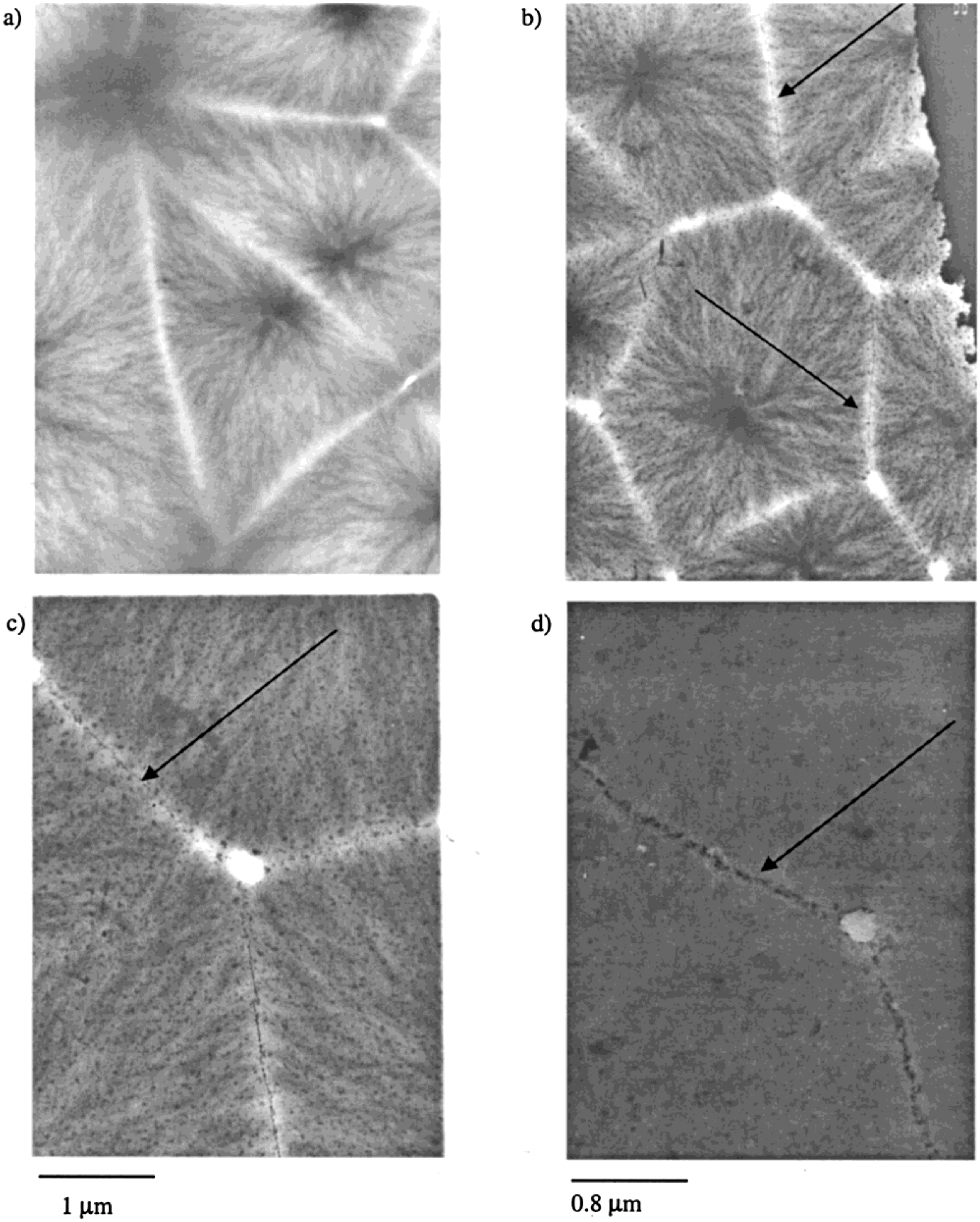

Figure 2. TEM micrographs of (a) 100% nylon 6 (10 000 magnification) and 2% (wt/wt) PANI-HCSA/nylon 6 blend with magnifications of (b) 20 000, (c) 30 000, and (d) 50 000. Dark areas in micrographs represent stained PANI salt imbedded in host nylon 6.

the blend. The conductivity for all PANI/polyamide blends increases at a fast rate as the concentration of conducting PANI increases above the value marking the onset of conductivity. Furthermore, the blend systems show monotonic behavior over a large salt concentration and have conductivities approaching that of the neat PANI-HCSA by 10−15%. As seen in Figure 1b, the ≈2% (wt/wt) loading level marks the point where the rate of increase in conductivity grows higher for the crystalline host than that of the amorphous host. It should be noted, even at such low PANI-HCSA contents of 1−5% (wt/wt), that the conductivities are in useful ranges for applications which include electromagentic shielding and static charge dissipation.

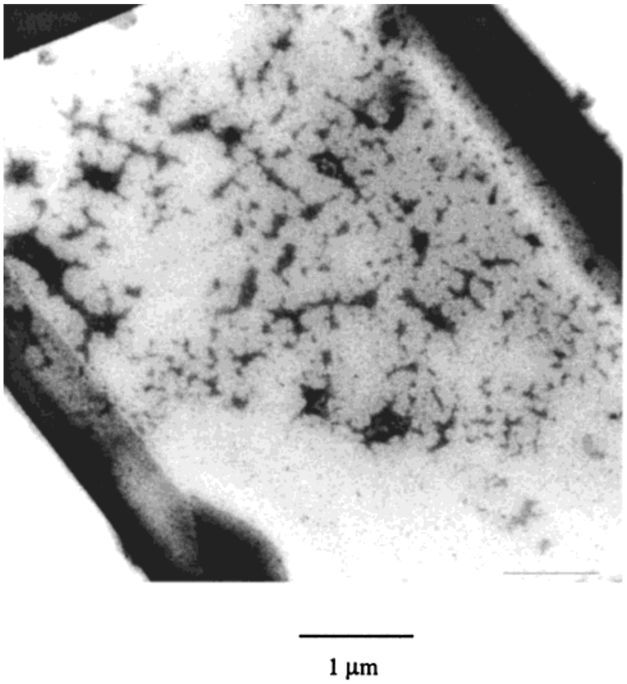

Figure 3. TEM micrograph of 2% (wt/wt) PANI-HCSA/Selar blend with magnification of 50 000. Dark areas in micrograph represent stained PANI salt imbedded in host Selar.

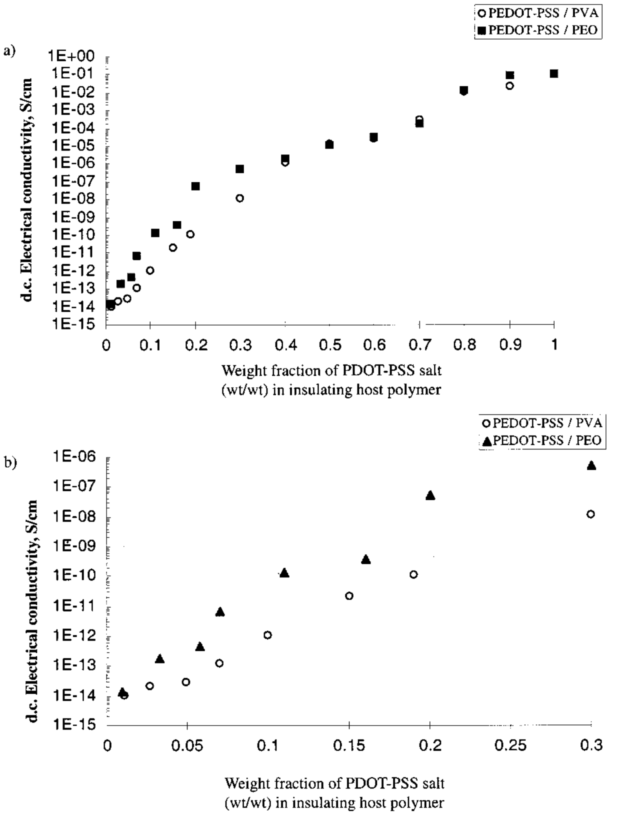

Figure 4. Conductivity as a function of PEDOT-PSS salt loading fraction in host PVA and PEO. Blend concentration range of (a) 0−1 (wt/wt) and (b) 0−0.3 (wt/wt).

To account for this difference between the PANI-HCSA/nylon 6 and Selar conductivity profiles, we suggest that a crystallization-induced phase separation is occurring in the crystalline nylon host. TEM was employed to capture the phase-separated morphology of these blends. As seen in the TEM micrographs in Figure 2, the nylon 6 blends clearly shows spherulitic formation. For the 2% (wt/wt) PANI-HCSA, the conducting polymer is concentrated in the interspherulitic regions (Figure 2b−d) as seen by the dark regions in the micrographs. The crystallization of nylon 6 forces the salt to be excluded from the host polymer. This crystallization-induced phase separation of salt behavior has been previously observed using small-angle X-ray scattering (SAXS) in PANI-HCSA/nylon 6 systems.[12] It was reported that the salt component was being rejected from the interlamellar regions, and the salt mainly resided in the interspherulitic regions.

As seen in Figure 3, again for 2% (wt/wt) PANI-HCSA now blended with the amorphous nylon (Selar), the connectivity of the salt network is not as developed as that observed for the crystalline blend in Figure 2d. The diffusion of the salt component away from the developing nylon crystal is thought to be a contributing factor to network formation. This more developed network contributes to the more rapid rise in conductivity observed using the crystalline host. Compared with the crystalline blends, the absence of a well-developed and connected network is consistent with the observed (Figure 1b) slower increase in conductivity in the amorphous blends. This behavior is consistent with the results of Du et al.,[19] who reported on the charge transport of a series of HCSA-doped polyaniline composite systems in a nylon 12 host. The charge transport studies reported for these composite systems showed a dependence on the formation of ordered regions or “metallic islands” in the blends. Du et al. suggested that a more ordered orientation of the polyaniline composite within the insulating nylon 12 host enhanced the percolation of the metallic islands which would yield higher electrical conduction in the blend. This network ordering is analogous to our blend systems where the connectivity of the conducting salt becomes more ordered due to the crystallization of host polymer which yields higher conductivity values versus the amorphous nylon. The use of temperature dependence results to probe the differences in the local order of these nylon blends would be useful but these measurements are outside the scope of this work.

To test whether or not this hypothesis was specific only to PANI blends, we subsequently investigated a series of blends of PEDOT-PSS in amorphous PVA and crystalline PEO. PEDOT-PSS was chosen for its high conductivity, ambient stability, aqueous compatibility, and commercial importance as a relatively transmissive coating material.

As shown in Figure 4, PEDOT-PSS/PVA blends show a monotonic behavior of the conductivity over the 1−50% (wt/wt) interval with no sharp indication of a percolation threshold. These blends, when solution cast from water, are transparent at loading fractions less than 20% (wt/wt). In addition, these films are robust and do not show signs of any phase separation. Making a comparison of the blends of PEDOT-PSS with PANI-HCSA with the amorphous hosts shows the latter to develop higher conductivities more rapidly. This reduced sensitivity of conductivity of the PEDOT-PSS blends may prove useful for fine conductivity control at relatively low values. Certain applications such as cladding electrode materials in NLO devices can benefit from this effect.[20]

For aqueous compatibility and processing, we chose

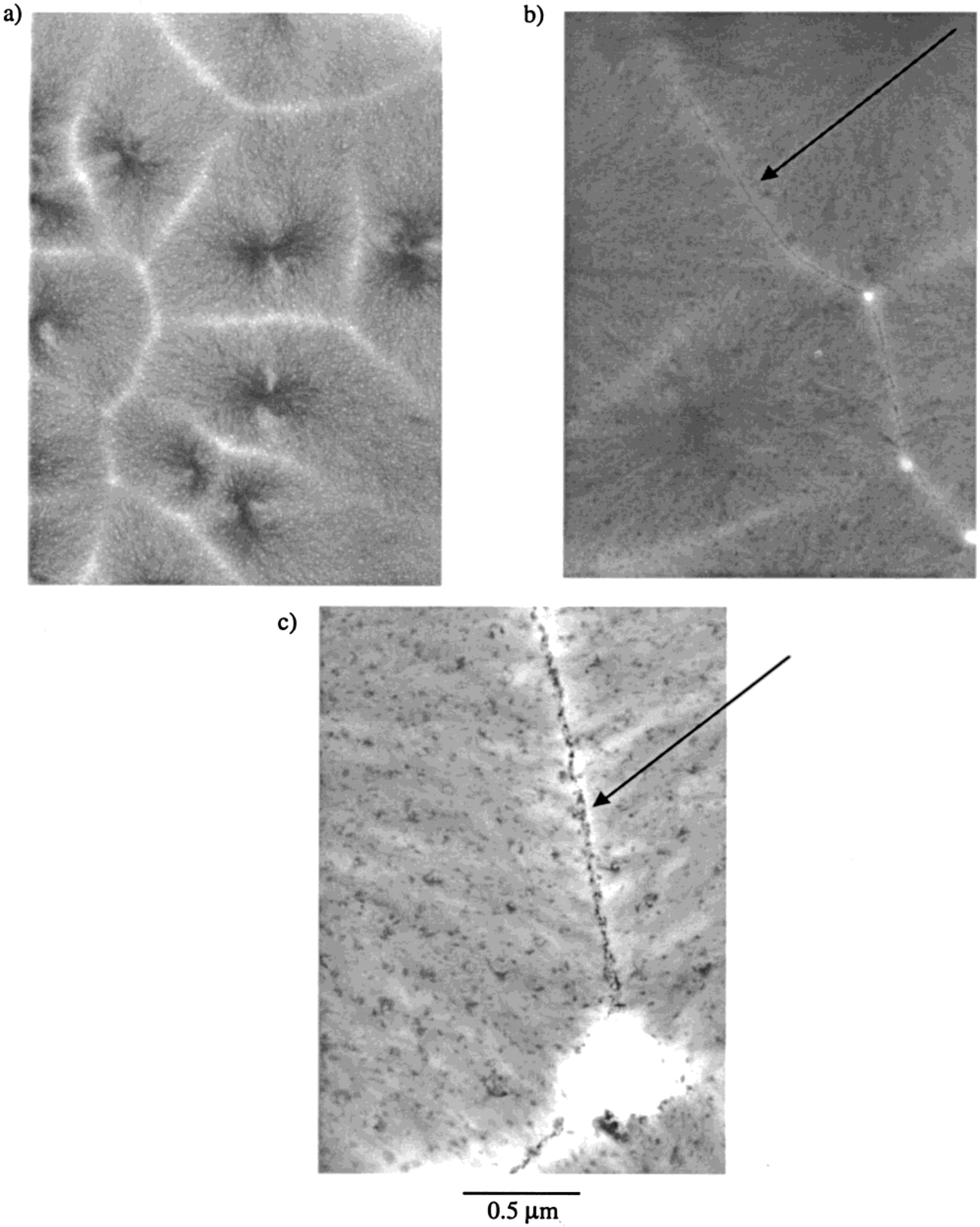

Figure 5. TEM micrographs of (a) 100% PEO (10 000 magnification) and 2% (wt/wt) PEDOT-PSS/PEO blend with magnifications of (b) 30 000 and (c) 70 000. Dark areas in micrographs represent stained PEDOT-PSS salt imbedded in host PEO.

PEO as the crystalline host polymer with the hope that exclusion of the conducting polymer from the crystalline domains would force the PEDOT-PSS into a continuous fractal network. As seen in Figure 4b, the PEDOT-PSS/PEO blends show lower onsets of electrical conductivity compared to PEDOT-PSS/PVA. The conductivity in these crystalline blends are more conductive than the amorphous blends up to 30−40% (wt/wt) loading of the conductive component. Again, we suggest that a crystallization-induced phase separation is occurring in the PEO host. The crystallization of PEO forces the salt to be excluded from the host polymer. The PEDOT-PSS is thus expected to be concentrated in the interspherulitic regions.

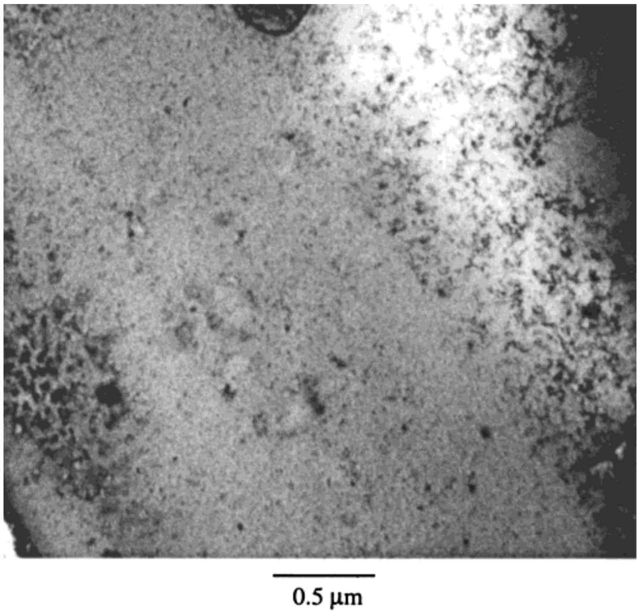

Figure 6. TEM micrograph of 2% (wt/wt) PEDOT-PSS/PVA blend with magnification of 50 000. Dark areas in micrograph represent stained PEDOT-PSS salt imbedded in host PVA.

While the PEDOT-PSS/PEO blends show higher levels of conductivity compared to that of PEDOT-PSS/PVA, they are optically opaque due to scattering by the PEO crystals. Optical microscopy of the PEDOT-PSS/PVA blends, on the other hand, showed a continuous morphology and did not show any visible signs of phase separation. This may prove important in applications where optical clarity is necessary, and conductivity is retained.

Using TEM, neat PEO and blends at low salt concentrations were shown to form spherulites. As the concentration of the salt is increased to 10−15% (wt/wt), spherulitic growth is not inhibited. However, most notably, the number of these spherulites in a given region decreases with a concurrent increase in their size with increasing salt content. We speculate that, at low salt concentrations, the spherulites are nucleated by the PEDOT-PSS which is highly dispersed in the blend. As the concentration of the salt increases, the salt aggregates into larger domains and acts as large sites for nucleating PEO crystals.

It is evident from the TEM results shown in Figure 5 that the PEDOT-PSS is being excluded from the growing spherulites, concentrated in the interspherulitic region, and forming a continuous pathway of conducting PEDOT-PSS, while the PEDOT-PSS blended with the amorphous PVA host shows a rather undeveloped network as seen in Figure 6. Comparing the PEDOT-PSS and PANI-HCSA systems blended with the crystalline hosts shows them to both have very similar network structures. However, the conductivities of the two systems vary significantly at these low concentrations, which is likely due to the inherent electrical properties of the conducting polymer and the micromorphology within the conducting network. The use of crystallization-induced phase separation as a method for controlling morphology and tuning the ultimate electrical properties of conducting polymer blends will likely prove useful for many systems beyond those reported here.

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(16) Safety information: Although HFIP is not identified as a carcinogen or teratogen, its solvent power toward skin, mucous membranes of the eyes and nose, combined with its high volatility, requires that it be handled with considerable caution. See standard safety data tabulations such as MSDS or similar for details.
(17) Ruthenium tetroxide, RuO_4, attacks and fuses organic material (i.e., skin, corneas, membranes, etc.) and should always be handled in a hood with strong ventilation.
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