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Small Angle Neutron Scattering (SANS) and  
Small Angle X-ray Scattering (SAXS) Analysis of  
Polyaniline Salts and Blends.

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### Introduction

Doped polyaniline emeraldine salts (PANI-ES) exhibit good environmental stability with a high level of conductivity (1 to 300 S/cm). However, they suffer from the fact that they have poor mechanical properties and must be blended with an insulating host polymer to be useful in industrial applications. Polyaniline blends are a new type of conducting material that typically show very low onsets of conductivity unlike that of metal filled blends. This is primarily due to the unique cellular geometry of the PANI-ES that is formed within the insulating host polymer.<sup>1</sup> The formation of this immiscible polymer network may be due in part to *structural* and *conformational* differences in the blend components.

Electron microscopy (i.e. tunneling electron microscopy (TEM))<sup>1</sup> has been extensively used to characterize the geometric details of the fibrils that make up the web-like network morphology in polyaniline blends. These qualitative results define the blends as a two-phase polymer blends with semi-crystalline PANI-ES rich fibrils intermingled in the host polymer.

Often the SANS technique is a more powerful quantitative tool for evaluating domain dimensions of polymer blends in the bulk state. It takes advantage of the large difference in coherent scattering lengths between deuterium and hydrogen atoms and therefore a large contrast can be generated by dispersing a small concentration of fully deuterated polymer in a polymer matrix or *vice versa*.<sup>2</sup> In addition, the contrast deuteration approach does not markedly influence the thermodynamic properties of the polymer.<sup>2</sup> Since previous electron micrographs suggested that blends of PANI-ES and insulating polymers form a dual phase in the host polymer, the SANS technique was used to allow further insight into the phase separated geometry. Specifically in this study, the morphology of deuterated polyaniline emeraldine salt fully doped with camphor sulfonic acid (i.e. *d*-

PANI-HCSA) and polycaprolactam blends were investigated. The differences in scattering length densities between the labeled salt and matrix give rise to the necessary contrast to allow characterization of domain sizes. A Debye-Bueche treatment of the absolute differential scattering data was employed to elucidate the multi-component nature of the blend. In addition, morphology information extracted from SAXS scattering can be used to compliment SANS data.

The present work is part of a larger study to understand what effect the polyaniline sulfonate counter-anion has on the molecular structure and morphological features of the dual phase blend.

### Experimental

**Procedure:** Polymerized *d*-PANI-EB was formed as follows: In an argon gas filled glove box, approximately 5 mL of *d*-5 aniline and 50 mL of deuterium oxide were added to a three-neck flask (immersed in a 35 °C oil bath) and vigorously stirred for 10 minutes with a mechanical stirrer. After 10 minutes of stirring, 50 mL of a 2.65 M ferric chloride in D<sub>2</sub>O was drop-wise added over a 50 minute period. Solution was stirred for 12 hours. The precipitated polymer was subsequently washed twice with 1.0 M HCl and then with 1.0 M NH<sub>4</sub>OH. Finally, the wash was carried out with distilled water, methanol and diethyl ether in the order mentioned. The resulting dark, free flowing PANI-EB powder was then dried at 70 °C for 12 hours to remove remaining moisture and solvent. X-ray photoelectron spectroscopy, elemental analysis and FTIR confirmed the polyaniline in the EB oxidation state (i.e. x ≈ 0.5) and NMR (<sup>1</sup>H and <sup>13</sup>C) confirmed the PANI-EB was ≈ 95 % deuterated.

Doped *d*-PANI-HCSA solutions were prepared in HFIP by a solution doping method.

All filtered, fully doped PANI-HCSA salt and blend solutions were solution cast onto a Teflon coated glass substrate and covered with a glass dish to allow for a slow evaporation at room temperature. All films were subsequently peeled off the Teflon substrate and dried in a dynamic vacuum oven at 75 °C for approximately 24 hours. From fluorine elemental analysis, percent residual HFIP solvent in films was less than 0.5% (wt/wt). This cast process from HFIP produced robust, free standing and solvent free PANI-HCSA and PANI-HCSA / polycaprolactam films.

**SANS and SAXS data acquisition.** SANS data were obtained on the 30 m instrument<sup>3</sup> at the W.C. Koehler facility of Oak Ridge National Laboratory (ORNL) via a 64 X 64 cm<sup>2</sup> area detector with element size ≈ 1 cm<sup>2</sup>. The range of the momentum transfer or wave vector, Q, was 0.040 - 4.0 nm<sup>-1</sup> where  $Q = (4\pi/\lambda) \cdot \sin\theta$  with  $\lambda = 0.475$  nm, the neutron wavelength, and  $\theta$ , one half the scattering angle. Standard corrections for detector efficiency, background, empty cell scattering and sample transmission were applied. Free standing isotropic film samples of ≈ 0.5 mm diameter were cut and stacked to achieve a sample thickness of ≈ 1 mm. The data were then converted to an absolute scale by comparison with secondary standards<sup>4</sup> and reported as differential cross sections per unit volume of sample, (dΣ/dΩ), with units of cm<sup>-1</sup>. This quantity expresses the neutron scattering power of a sample. No corrections were made for incoherent scattering. Typically, this is on the order of 1.

The SAXS measurements were conducted at both the 10 m facility<sup>5</sup> and ORNL. The incident radiation was copper K<sub>α</sub> ( $\lambda = 0.154$  nm) from a rotating anode source equipped with a monochromator, and a Q range of 0.05 - 4.5 nm<sup>-1</sup> was used. For comparison with wide angle X-ray scattering (WAXS) (at the same  $\lambda$ ) this corresponds to a 2θ range of 0.07 - 6.3 °. Here also standard corrections were applied and the data converted to an absolute differential scattering cross sections.<sup>6</sup>

### Results and Discussion

**Scattering by salts.** Reference to the SAXS data in Figure 1 shows an intense scattering below  $Q = 1$  nm<sup>-1</sup> for PANI-HCSA, *d*-PANI-HCSA and a 50 % (wt/wt) blend of the respective deuterated and hydrogenated salts. This

upswing in scattering intensity implies the presence of another component in the films such as small solvent voids. At  $Q = 2.5 \text{ nm}^{-1}$ , a large broad peak is seen for all three salt samples but not in the PANI-EB sample which implies that the scattering is due to the doped salt which has a periodicity of about 2.5 nm. For comparison with WAXS scattering, this peak corresponds to  $\sim 3.5^\circ$  on a  $2\theta$  scale. Interestingly, the WAXS diffractogram of PANI-HCSA has shown a sharp diffraction peak at  $\sim 4.5^\circ$  ( $2\theta$  scale). Since this diffraction peak corresponds to such a large periodicity (i.e.  $\sim 2.5 \text{ nm}$ ), we suggest that the charged polyaniline chains pack back-to-back with the CSA sulfonate counter-anions facing outward, as depicted in Figure 2. This type of behavior has been proposed before by Jarvinen *et. al.*<sup>7</sup> and Kim *et. al.*<sup>8</sup> Both these groups report a very sharp Bragg peak at approximately  $\sim 3^\circ$  for polyaniline salt fully doped with dodecyl benzene sulfonic acid (HDBSA). Furthermore, a very similar type of WAXS diffractogram was seen by Kricheldorf *et. al.*<sup>9</sup> using  $C_{15}H_{31}$  alkyl substituted terephthalic acid rigid rod polyesters. These reports attributed the strong, single Bragg diffraction peak at  $\sim 3^\circ$  (which corresponds to a d-spacing of  $\sim 3.1 \text{ nm}$ ) to back-to-back chain packing of rigid chains with respective sulfonate counter-anions / substituent groups radiating outward.

*Scattering by d-PANI-HCSA / polycaprolactam blends.* Figure 3 shows SAXS from *d*-PANI-HCSA / polycaprolactam blends. At the lowest values of  $Q$  (i.e.  $< 0.5 \text{ nm}^{-1}$ ) intense scattering again indicates the presence of some additional component (i.e. perhaps small voids) in 100 % polycaprolactam, salts and respective blends. Figure 3-d shows that the nylon 6 matrix has a shoulder that corresponds to a spacing of about 8 nm and implies that the material is semicrystalline when cast from HFIP solvent. The same feature is found in the curves for the 5 % *d*-PANI-HCSA / polycaprolactam but is not apparent in the 25 % and 46 % blends (i.e. Figures 3-a, b and c respectively). This suggests that the *d*-PANI-HCSA salt is interacting with the polycaprolactam on a molecular scale and suppressing lamellar development at the high salt concentration. Furthermore, the structure that causes the peak at  $Q \sim 2.5 \text{ nm}^{-1}$  remains in the blends.

The SANS cross section for the two deuterated blends, salts and polycaprolactam host polymer is seen in Figure 4. As expected, the scattering is flat (i.e. Figure 4-c) for the non-deuterated polycaprolactam sample and is consistent with the fact that there is little scattering contrast in this host polymer. At lowest  $Q$ -values, the scattering from the 5 % *d*-PANI-HCSA / polycaprolactam (Figure 4-a) is nearly an order of magnitude greater than that for the host polymer (Figure 4-c). If the blend components were uniformly dispersed, the difference in scattering would be much less.

Consequently, most of the neutron scattering from the 5 % deuterated blend must come from a phase separated morphology.

It is surprising that in Figures 4-a and b the 25 % blend with 5 times more deuterated material does not scatter more than the 5 % blend. This result may indicate a change in blend morphology. As indicated in Figure 3, the SAXS lamellar peak at  $Q \approx 0.8 \text{ nm}^{-1}$  gradually dissipates as more *d*-PANI-HCSA is incorporated into the blend, indicating that the polycaprolactam lamellae are no longer present. This indicates that the blend components might be more intermixed, explaining the lower SANS intensity seen in Figure 4-b.

A widely used formalism for analyzing small angle scattering data to characterize the inhomogeneities (i.e. domain sizes) present in a random two-phase material is the Debye-Bueche model<sup>10</sup> which is based on a single exponential correlation function. Figure 5 shows the fit of this model to the 5 % deuterated blend at a low Q range (i.e. 0.5 to  $1.5 \text{ nm}^{-1}$ ) by plotting  $(d\Sigma/d\Omega)^{1/2}$  vs. Q. Over this limited Q range, the correlation length,  $a$ , evaluated from the ratio of the slope to the intercept of this plot indicates that the size of the PANI-HCSA domain in the blend is roughly 15.3 nm. However, only a small Q range could be fitted to the Debye-Bueche model. The nonlinear behavior over the large Q range of Figure 5 suggests that the *d*-PANI-HCSA / polycaprolactam blend cannot be treated as a simple random dual phase system.

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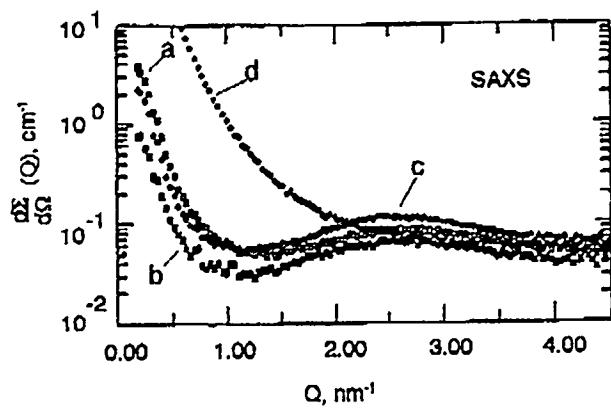


Figure 1.  $d\Sigma(Q)/d\Omega$  vs.  $Q$  for: (a) PANI-HCSA, (b) *d*-PANI-HCSA, (c) blend of 50 % PANI-HCSA / 50 % *d*-PANI-HCSA and (d) PANI-EB

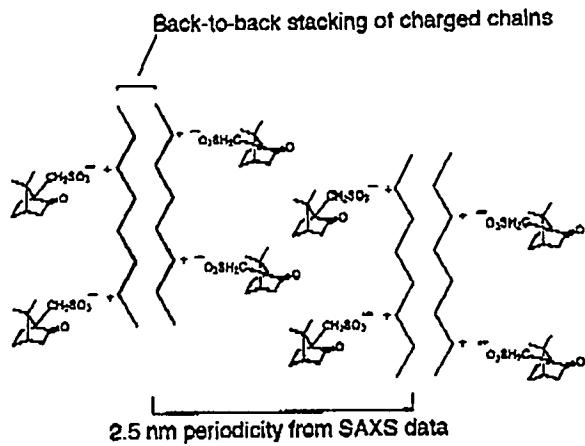


Figure 2. Proposed stacking of PANI-HCSA chains from SAXS data.

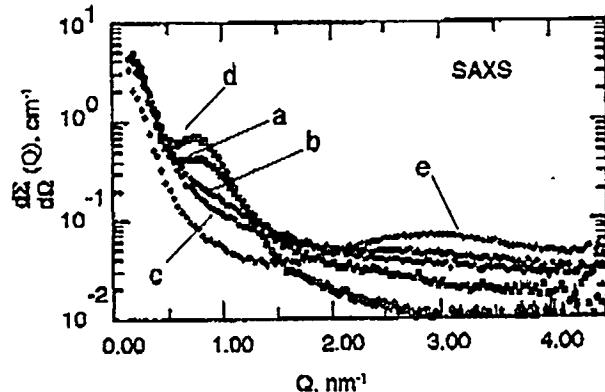


Figure 3.  $d\Sigma(Q)/d\Omega$  vs.  $Q$  for: (a) 5%, (b) 25%, (c) 46 % (wt/wt) *d*-PANI-HCSA / polycaprolactam. (d) is 100 % polycaprolactam and (e) is 100 % *d*-PANI-HCSA.

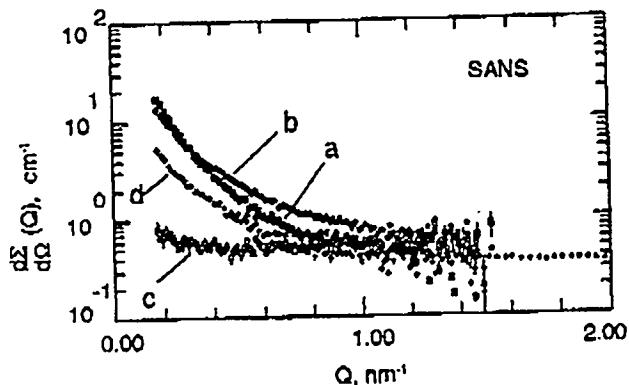


Figure 4.  $d\Sigma(Q)/d\Omega$  vs  $Q$  for: (a) 5 % and (b) 25 % (wt/wt)  $d$ -PANI-HCSA / polycaprolactam. (c) is 100 % polycaprolactam and (d) is 100 %  $d$ -PANI-HCSA.

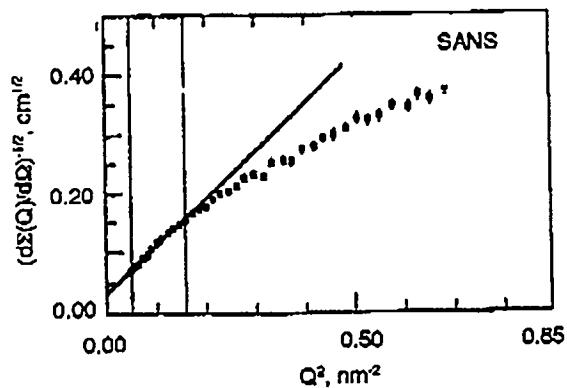


Figure 5. Debye-Bueche plot of scattering data for 5 % (wt/wt)  $d$ -PANI-HCSA / polycaprolactam blend.

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