Conducting Polyaniline Nanoparticle Blends with Extremely Low Percolation Thresholds

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ABSTRACT: Blends of HCl-doped polyaniline (PANI·HCl) nanoparticles with the following conventional polymers, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), poly(vinyl acetate), and poly(vinyl alcohol) (PVA), were prepared by suspending preformed submicronic PANI·HCl particles in the solutions of the matrix polymers and sonicating the suspension for 1.5 h. The submicronic PANI·HCl particles were prepared by oxidative dispersion polymerization using poly(vinyl methyl ether) (PVME) stabilizer. The particles contained 4.4 wt % PVME and had a conductivity of 4.96 S/cm. They had an oblong shape (250 nm × 190 nm). Sonication breaks the particles to sizes less than 20 nm. The blend films exhibit an extremly low percolation threshold (f_p) in every case. The volume fraction of PANI·HCl at the percolation threshold for the above mentioned matrices lies in the range 2.5×10^{-4} to 4×10^{-4}. Transmission electron microscoopy of PANI·HCl−PVA blend films directly cast on carbon-coated TEM grids reveals connectivity at compositions close to f_p. Self-assembly of the nanoparticles is evident from the TEM pictures.

Introduction

There has been considerable interest in recent years on conducting polymer blends with low percolation thresholds.[1−8] These materials, besides being conductive, processable, technologically attractive by virtue of being transparent, cost effective, and mechanically as strong as the matrix polymer, have been subjects of scientific curiosity with regard to their morphology and electron transport properties. The classical percolation theory predicts the percolation threshold at a volume fraction $f_p = 0.16$ for conducting particles dispersed in an insulating matrix in three dimensions.[9] This prediction is found to be true with some conducting polymer blends.[10−12] However, of late, some success in making conducting polymer blends with $f_p \ll 0.16$ has been reported to be achieved.[4−7] Features like molecular self-assembly of the disperse conducting polymer molecules,[4,5] a nano-sized disperse phase,[6] multiple percolation,[7] etc. have led to such blends.

Ordinarily, most conducting polymers in the doped state are intractable, being difficult to dissolve or melt. Morphology regulation in blends involving such polymers remains therefore a difficult problem. In the case of polyaniline (PANI) Heeger et al. have shown that the use of dopants having sizable organic structures such as camphor sulfonic acid (CSA) makes the polymer soluble in some common solvents so that blends with conventional polymers can be solution cast.[4,5,13] Blends of PANI·CSA and poly(methyl methacrylate) (PMMA) so prepared showed a very low $f_p \simeq 0.01$, which was attributed to the self-assembly of PANI·CSA molecules into a fibrillar network morphology during liquid−liquid phase separation.[5] However, very recently, Reghu et al. reported f_p as low as 3×10^{-3} for the same blend system.[14] In this paper we report for the first time blends of HCl-doped PANI (PANI·HCl) with a number of common polymers such as polystyrene (PS), poly(vinyl chloride) (PVC), PMMA, poly(vinyl acetate) (PVAc), and poly(vinyl alcohol) (PVA) which have f_p values in the range $(2.1−4.2) \times 10^{-4}$. A study of the morphology of the PANI·HCl−PVA blend is also included.

Experimental Section

The blends were prepared by dispersing preformed submicronic PANI·HCl particles with surface-adsorbed poly(vinyl methyl ether) (PVME) in solutions of the matrix polymers using ultrasonics for 1.5 h. The dispersion medium must be a good solvent for PVME which acts as the steric stabilizer for the dispersion. Tetrahydrofuran (THF) was used as a solvent for all the matrix polymers except PVA, for which acidic water (1.25 M HCl) replaced THF. The dispersions so prepared obeyed Beer's law in the studied concentration range 0.025−0.9 g/dm^3 PANI·HCl at the latter's absorption maximum at 800 nm. The dispersions of lower PANI·HCl concentrations prepared by diluting a dispersion containing higher PANI·HCl concentrations showed the same absorbances as those prepared independently using the required amount of PANI·HCl and matrix polymer. The blend films were cast from the dispersions. The PANI·HCl content in the blend films except for those with the lowest PANI·HCl loading was determined from the reduced nitrogen content of the dried blends relative to pure PANI·HCl. The blends with the lowest PANI·HCl loading were prepared by diluting dispersions of blends with higher loadings by means of the matrix polymer solution and subsequently casting films.

The PANI·HCl colloid particles with surface-adsorbed PVME were prepared by oxidative dispersion polymerization of aniline in acidic (1.25 M HCl) water at ~0 °C using ammonium persulfate as the oxidant and PVME as the steric stabilizer.[15] The oblong-shaped particles (250 × 190 nm) were sedimented by centrifugation and redispersed in acidic (HCl) water. The particles were sedimented again and washed with hot water. The particles used in the present work contained 4.4 wt % PVME with a conductivity of 4.96 S cm^{-1} in the pressed pellet form. PVME being soluble in a variety of solvents, both aqueous and nonaqueous, PANI·HCl colloid particles coated with it can be redispersed in these liquids which can be solvents for many polymers so that blends with a great variety of polymers can be prepared by this method, as is done here.

The conductivity of the films was measured by the usual four-probe method using free-standing films. For transmission electron micrography (TEM) of the blend films the latter were

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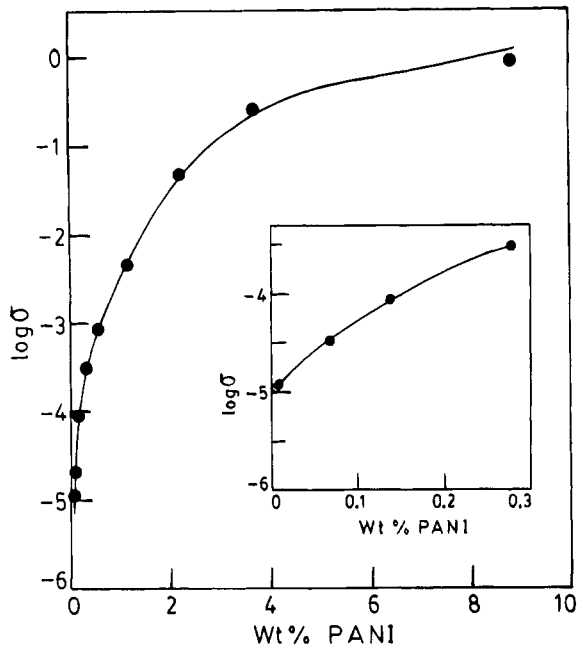

Figure 1. Plot of log electrical conductivity vs PANI·HCl concentration in PANI·HCl–PVA blend films. The inset shows an enlarged view for the low PANI·HCl concentration region.

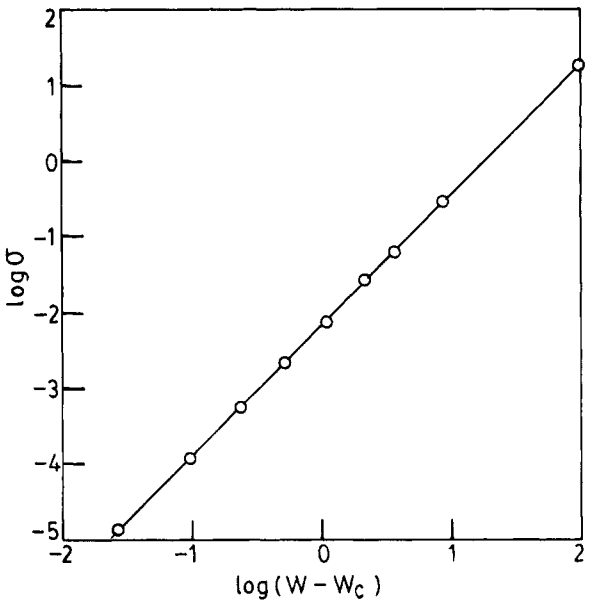

Figure 2. Plot of log(conductivity) vs $\log(W - W_c)$.

cast directly on carbon-coated copper grids from dispersions containing 0.75–1.75% blends. The lower concentrations were used for the blend with higher PANI·HCl loadings, viz. 0.5%.

Results and Discussion

The variation of room temperature conductivity of the blend films with PANI·HCl loading is shown in Figure 1 with PVA used as the matrix, as an example. The blends exhibit reasonably good conductivity even at very low PANI·HCl loading. Thus, at the lowest loading used, viz. 0.007 wt %, the conductivity is 1.12×10^{-5} S cm^{-1}. Figure 1 does not show any well-defined percolation threshold. However, the data of Figure 1 have been fitted to the scaling law of percolation theory (Figure 2)

$$\sigma(f) = c(f - f_p)^t \quad (1)$$

where c is a constant, t is the critical exponent, and f is the volume fraction of the filler particles. The method yields a value of 3.60×10^{-4} for f_p and 1.96 for t. Treatment of σ, f data for all the other blends according to eq 1 yields f_p,t values for the corresponding blends. The values are given in Table 1. The f_p's are unusually low for all the systems, falling in the range $(2-4) \times 10^{-4}$. Earlier, Heeger et al. reported such a low f_p ($<2.5 \times 10^{-4}$) for conducting gels of polyethylene (PE) which contain poly(3-octylthiophene) (P30T) as the conducting filler. It has been postulated that in these systems the latter merely decorates the connecting paths of the PE gel network, hence yielding such low f_p.[1,2] The values of t are in good agreement with the theoretical value of $\simeq$1.87 calculated from the percolation theory by assuming an idealized fractal structure near the percolation threshold for a three-dimensional system.[16] For the PANI·CSA–PMMA system Heeger et al. obtained a value of 1.97 for t.[5]

Parts a–d of Figure 3 show the TEM images of the PANI·HCl–PVA blend films respectively containing 0.035, 0.045, 0.05, and 0.5 wt % PANI·HCl. The contrast

Table 1. f_p and t Data for Various Blends of PANI·HCl with Conventional Polymers

matrix	$10^4 f_p$	t
PVC	4.02	1.87
PS	4.19	1.91
PVAc	3.18	1.94
PMMA	2.14	1.89
PVA	3.60	1.96

in the images is good enough so that unlike the PMMA–PANI·CSA blend films investigated by Heeger et al. the matrix polymer in the present study was not required to be extracted; also the films were neither stained nor shadow-coated with Pt–C. The electron micrographs show a fibrillar morphology of the disperse PANI·HCl. At the lowest PANI·HCl loading (0.035%) the dispersed PANI·HCl phase appears to exist in isolated clusters (Figure 3a). As the loading is increased to 0.045%, the clusters appear to have become weakly interconnected, indicating that at least some of them have grown to infinite clusters (Figure 3b). The system is thus on the verge of percolation at this point. As the PANI·HCl loading is increased further to 0.05%, the fibrous structures are clearly found to exist in the form of both bounded clusters and an interconnected network (Figure 3c). The structure is very stringy and tenuous, which is characteristic of clusters near percolation.[9] Thus, the TEM study reveals that the percolation threshold is somewhere around 0.045%. This result is in good agreement with the f_p value calculated using eq 1 from the conductivity data at various PANI·HCl loadings, which are given in Table 1. The value is $f_p = 3.6 \times 10^{-4}$, which corresponds to 0.043 wt % PANI·HCl.

As the loading is increased further above the percolation threshold to 0.5%, a thick network with wide nets (bold impressions in Figure 3d) coexisting with tenuous clusters develops. The formation of a thick network of a particular pattern rather than an increase of network density over the whole area of the film suggests the self-assembled ordering of the network. Figure 4 is a TEM image of the same film as was used in Figure 3d but from a different area. Here the thick network is seen to be present along with an insignificant amount of small clusters. This picture indicates nearly complete

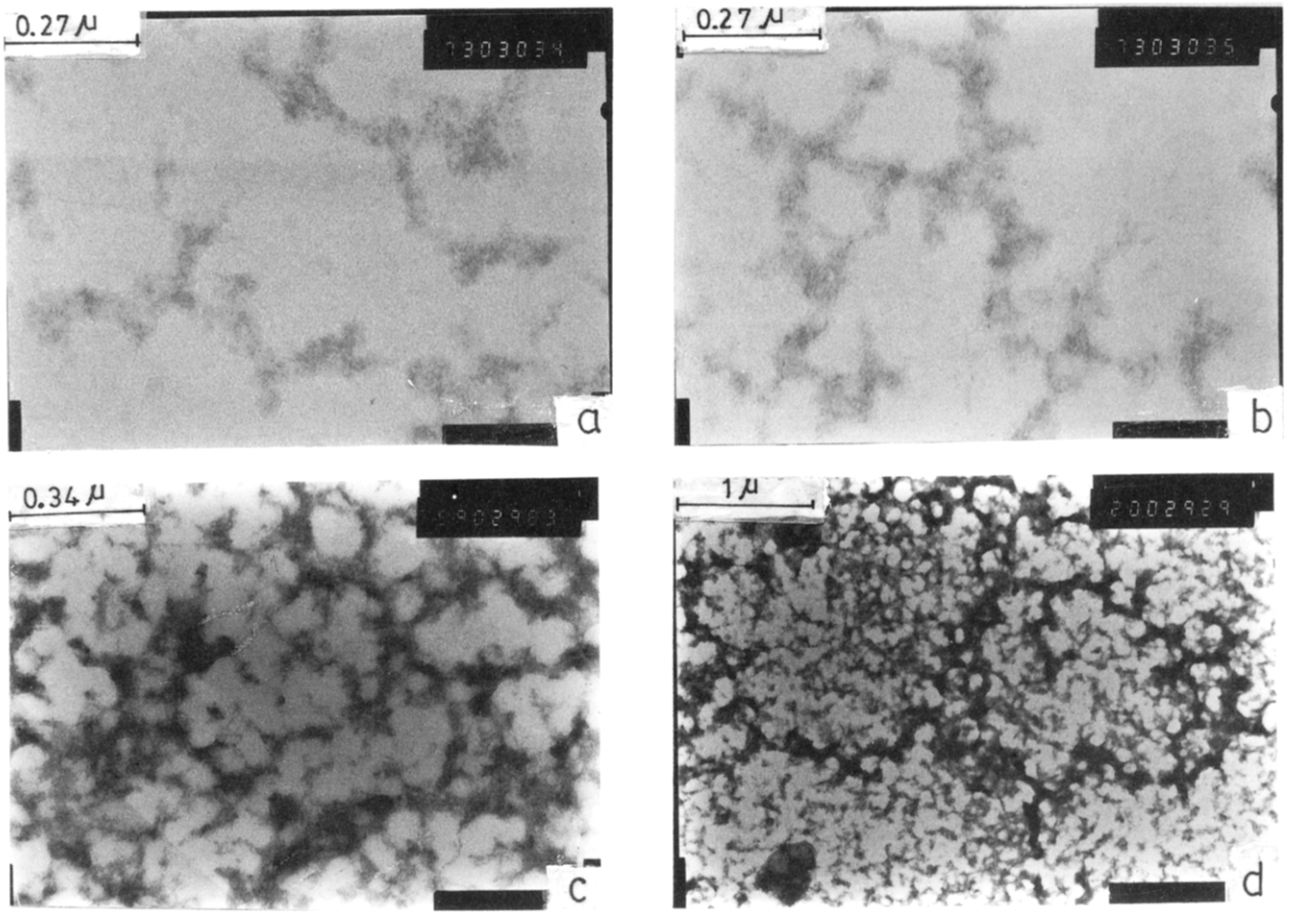

Figure 3. Transmission electron micrograph of PANI·HCl–PVA blend films containing different amounts (in wt %) of PANI·HCl: (a) 0.035%, (b) 0.045%, (c) 0.05%, (d) 0.5%.

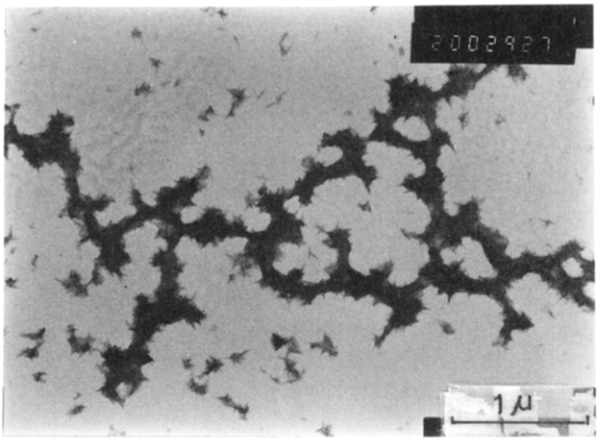

Figure 4. Transmission electron micrograph of a PANI·HCl–PVA blend film containing 0.5% PANI·HCl. This is the same film as was used for Figure 3d but from a different area.

self-assembled network formation. The difference in the two images (Figure 3d vs 4) probably arises from different rates of solvent evaporation from the two areas of the same film. In Figure 4 the evaporation rate is presumably slower so that the fluidity of the matrix is maintained for a long enough time to allow the ordering of the associating clusters to near completion, while in the situation depicted in Figure 3d the process was arrested before the completion of the ordering due to quick evaporation of the solvent.

The morphology of the PANI·HCl–PVA blend shown in Figure 3a–c is similar to that reported by Heeger et al. for the PANI·CSA–PMMA blend system. This may indicate that in the two systems PANI is at similar level of dispersion in the solution of the matrix polymer. However, in the process of preparation of the blend PANI·CSA was in solution to start with. This was not so with the PANI·HCl. However, the following observations and the discussion reveal that although the preformed PANI·HCl particles used in preparing the dispersion have a size ~250 × 190 nm to start with, they break down to nano sizes when they are sonicated even in the absence of any polymer Thus, it was found that the particle size is reduced to ~20 nm when the particles are suspended in THF and sonicated for 1.5 h (compare Figure 5a,b). Additionally, parts of some of the particles are found to be smeared out, indicating that particles of size lower than ~20 nm are also present.[17] The disintegration of the particles could be facilitated when sonication is performed using the solutions of the matrix polymers as the dispersion media. The greater viscosity of these solutions compared to the pure solvent would generate a greater shearing force which should help in disintegrating the particles. The breaking of the original bigger size PANI·HCl colloid particles into nano sizes is consistent with the observation of Armes et al. who showed by using scanning tunneling microscopy that the colloid particles of PANI·HCl or polypyrrole (~100 nm) prepared by the dispersion polymerization route are composed of particles of very small size, ca. 5–10 nm.[18] The dispersion of PANI·HCl in the solution of the matrix polymer in THF effected by sonication is very homogeneous, as is evidenced by their adherence to Beer's law

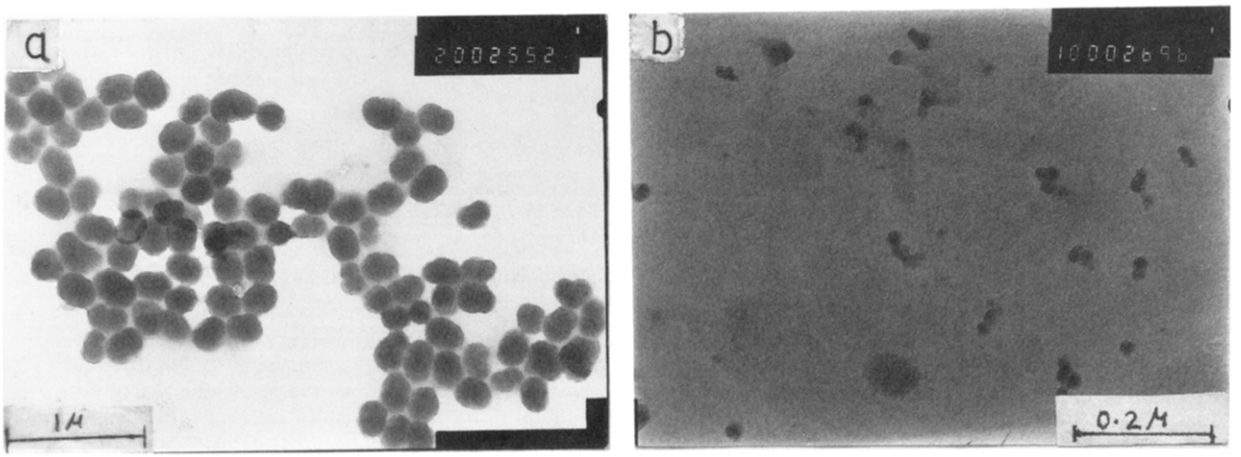

Figure 5. Transmission electron micrograph of PANI·HCl colloid particles (a) prior to sonication and (b) after 1.5 h sonication in THF.

(not shown). The dispersions are sterically stabilized. The THF medium offers a good solvent environment for the PVME stabilizer which is adsorbed on the PANI·HCl particles. Flocculation of the particles is prevented due to the excluded volume effect of the stabilizer adsorbed on the particle surface. When the solvent is evaporated off, the stabilizer finds itself in a bad solvent environment in PVA, with which PVME is not miscible. The particles broken to molecular or nano size during sonication therefore undergo aggregation when the solvent is removed. The aggregation has self-assembly character which helps to reach percolation at the extremely low PANI·HCl loading.

The ordering of the network into a thick structure above the percolation threshold was also observed by Heeger et al.[4,5] for PANI·CSA–PMMA systems, in which case the conductivity systematically increases to 200–300 S cm^{-1} upon increasing the PANI·CSA concentration.[14,19] On the other hand, in PANI·HCl–PVA blends under study the conductivity seems to saturate at ~1 S cm^{-1} above 10 wt % PANI·HCl.

Finally, we note that in carbon black–polymer blends carbon black particles of a diameter of a few tens of nanometers have been used earlier which resulted in very low f_p values, ca. 0.1 vol %.[20,21] However, the present work reports for the first time conducting polymer nanoparticle blends which have a percolation threshold as low as $f_p \simeq 3 \times 10^{-4}$.

Detailed studies on the electron transport properties and morphology of the various blends prepared by the present method are in progress in our laboratory. The present method of blending is versatile in the sense that a great variety of polymer matrix can be used to form the blends.

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References and Notes

(1) Fiazi, A.; Moulton, J.; Pakbaz, K.; Rughooputh, S. D. D. V.; Smith, P.; Heeger, A. J. *Phys. Rev. Lett.* **1990**, *64*, 2180.
(2) Heeger, A. J.; Smith, P.; Fiazi, A.; Moulton, J.; Pakbaz, K.; Rughooputh, S. *Synth. Met.* **1991**, *41–43*, 1027.
(3) Suzuki, Y. Y.; Heeger, A. J.; Pincus, P. *Macromolecules* **1990**, *23*, 4730.
(4) Yang, C. Y.; Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1993**, *53*, 293.
(5) Reghu, M.; Yoon, C. O.; Yang, C. Y.; Moses, D.; Heeger, A. J.; Cao, Y. *Macromolecules* **1993**, *26*, 7245.
(6) Wang, Y.; Rubner, M. F. *Macromolecules* **1992**, *25*, 3284.
(7) Levon, K.; Margolina, A.; Patashinsky, A. Z. *Macromolecules* **1993**, *26*, 4061.
(8) Makhlouki, M.; Morsli, M.; Bonnet, A.; Conan, A.; Pron, A.; Lefrant, S. *J. Appl. Polym. Sci.* **1992**, *44*, 443.
(9) Zallen, R. *The Physics of Amorphous Solids*; John Wiley: New York, 1983; Chapter 4.
(10) Hotta, S.; Rughooputh, S.; Heeger, A. J. *Synth. Met.* **1987**, *22*, 79.
(11) Aldissi, M.; Bishop, A. R. *Polymer* **1985**, *26*, 622.
(12) Aldissi, M. *Synth. Met.* **1986**, *13*, 87.
(13) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91.
(14) Reghu, M.; Yoon, C. O.; Yang, C. Y.; Moses, D.; Smith, P.; Cao, Y.; Heeger, A. J. *Phys. Rev. B* **1994**, *50*, 13931.
(15) Banerjee, P.; Digar, M. L.; Bhattacharyya, S. N.; Mandal, B. M. *Eur. Polym. J.* **1994**, *30*, 499.
(16) Clerc, J. P.; Giraud, G.; Laugier, J. M.; Luck, J. M. *J. Phys. A.* **1985**, *18*, 2565.
(17) The progress of disintegration of the particles with sonication time was monitored by observing the blend films under an optical microscope (magnification ×800) at various time intervals. No macroparticles (particle lumps) could be seen after ~1 h of sonication. Sonication times lower than 1 h yield blends with higher f_p values. For example, a 0.5 h sonication yields blends with $f_p = 0.007$. Heeger et al. also sonicated their system for a long period of 48 h in order to take PANI·CSA into solution. See, for example: Reghu, M.; Cao, Y.; Moses, D.; Heeger, A. J. *Phys. Rev. B* **1993**, *47*, 1758.
(18) Armes, S. P.; Aldissi, M.; Hawley, M.; Beery, J. G.; Gottesfeld, S. *Langmuir* **1991**, *7*, 1447.
(19) Yoon, C. O.; Reghu, M.; Moses, D.; Heeger, A. J.; Cao, Y. *Synth. Met.* **1994**, *63*, 47.
(20) Michels, M. A. J.; Brokken-Zijp, J. C. M.; Groenewoud, W. M.; Knoester, A. *Physica (Amsterdam)* **1989**, *157A*, 529.
(21) van der Putten, D.; Moonen, J. T.; Brom, H. B.; Broken-Zijp, J. C. M.; Michels, M. A. J. *Phys. Rev. Lett.* **1992**, *69*, 494.

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