Concentration Dependence of Aggregation of Polyaniline in NMP Solution and Properties of Resulting Cast Films

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Introduction. The morphology of polyaniline films has been of recent interest as it has been clearly shown that the overall physical properties of the polymer including conductivity have a significant dependence on morphology.[1,2] The morphology in turn is dependent on the method by which the polymer is processed. It has been shown, for example, that partially crystalline doped polyaniline films can be obtained by processing in certain specific solvents. These films generally exhibit higher conductivity than do the corresponding amorphous films.[1] It is believed that the interchain electron mobility in a given polymer is significantly increased by having an ordered solid state structure such as crystalline domains which allow improved interchain electron coupling.[3,4] Thus, one method of achieving a higher level of conductivity in polyaniline films is to induce crystallinity. Films of polyaniline in the emeraldine base (EB) form, most commonly processed from solvents such as *N*-methyl-2-pyrrolidinone (NMP), are essentially amorphous.[5,6] Some crystallinity can be induced in these films by subsequent processing techniques such as mechanical orientation.[7] The crystallinity induced in the EB films has been found to be maintained to varying extents upon doping with protonic acids.[8]

The present communication examines the role of the properties of EB solutions on the properties of films cast from such solutions. In particular, we focus on understanding the relationship between the degree of aggregation of EB in NMP solution and the degree of crystallinity and conductivity in the film derived from this solution. Furthermore, a direct method of attaining partly crystalline EB films without the need for mechanical stretch orientation is reported.

Experimental Section. Polyaniline in the form of emeraldine base (EB) was synthesized by a standard method.[9] Solutions having different EB concentrations in NMP were prepared by slowly dissolving the appropriate amount of dry EB powder in ~10 mL of NMP with constant stirring for ~12−14 h. These solutions were then filtered through a 0.45 μm Spartan filter. Polyaniline in the form of a gel was prepared by placing ~10 ml of a ~12 wt % EB NMP solution in an aluminum dish in a sealed desiccator at room temperature for ~16 h. Free standing films of EB were cast from the above solutions and from the gel by placing them in an oven at ~60−70 °C in air for ~18 to 24 h to evaporate NMP. Films of EB were characterized by wide-angle X-ray scattering measurements using a Rigaku diffractometer via a transmission mode. X-ray diffraction patterns were taken with monochromatized Cu Kα (λ = 1.542 Å). The same EB films were then doped by immersion in 1 M aqueous HCl acid solution for ~55 h as previously described.[10] The conductivities of these films were measured by a standard four-probe method.

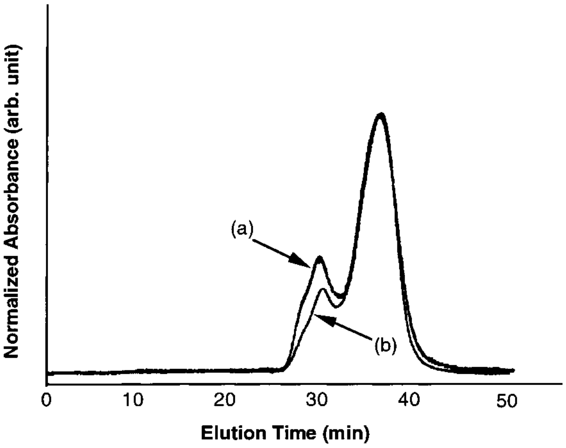

Figure 1. GPC chromatograms of (a) ~5.0 wt % EB/NMP solution that is diluted to ~0.5 wt % immediately before injection into the column and (b) ~0.5 wt % EB/NMP solution.

The infrared spectrum of EB powder was obtained from a mixture of EB powder with KBr powder using a diffuse reflectance mode. Thin films of EB were spin-cast onto KBr crystal plates from a ~5 wt % NMP solution. The residual NMP in the film was removed by methanol extraction. Infrared spectra of EB films were recorded using a Perkin-Elmer 1760x spectrometer in a transmittance mode. Samples for gel permeation chromatography (GPC) studies were made by preparing ~0.5 and ~5.0 wt % EB solutions in NMP. The 0.5 wt % solution was run without further dilution whereas the 5 wt % was diluted 10-fold to 0.5 wt % with NMP immediately prior to injection into the column. Both solutions were filtered through a 0.2 μm Spartan filter before injection. The GPC studies were carried out using a Waters ultrastyragel linear column operating at 85 °C. Polystyrene narrow molecular weight standards were employed, and the signal was detected using UV/vis absorption at ~660 nm.

Results and Discussion. We have shown previously that EB forms aggregates in NMP solution as evidenced by a bimodal molecular weight distribution in gel permeation chromatography studies.[2,11] This aggregation is the result of interchain hydrogen bonding between amine and imine nitrogen atoms in the polyaniline backbone.[12] We now find that the relative percentage of aggregation of EB in NMP is highly dependent on the concentration of polymer in solution.

Figure 1 shows the chromatographs characteristic of a ~0.5 wt % EB in NMP solution (b) and a ~5 wt % solution that is diluted to 0.5 wt % immediately before injection into the column (a). As can be seen, the area of the high molecular weight fraction which is due to chain aggregation is higher in the chromatograph obtained from the more concentrated solution even though this solution was diluted to the same concentration as that of solution b prior to injection into the column. Previously, we have shown that solvents having appropriate hydrogen bonding capability can disrupt some of the internal EB aggregation by preferentially hydrogen bonding with the polymer. For example, NMP was shown to hydrogen bond with EB via the carbonyl group of the NMP and the amine sites of

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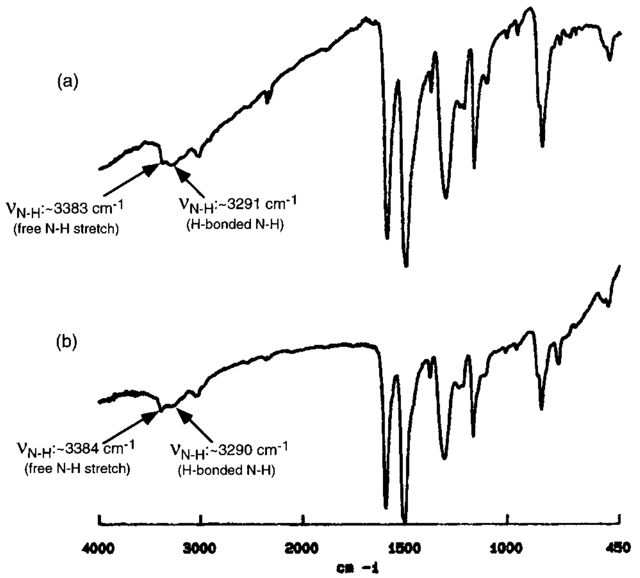

Figure 2. Infrared spectra of (a) EB powder and (b) an EB thin film cast from a ~5 wt % EB solution in NMP (residual NMP has been removed by methanol extraction).

EB (i.e., C=O···H—N), thereby reducing the extent of hydrogen bonding in the polymer in solution relative to the solid state powder form.[12] Thus, it is expected that the lower the polymer concentration in solution, the more effective will be the solvent at interacting with the polymer. As the concentration of polymer increases in a given solvent, the solvent—polymer interaction will decrease while the polymer—polymer interaction increases. The present GPC results are consistent with this argument as the chromatographs clearly show that the aggregation of the polymer increases with increasing concentration; i.e., NMP becomes less efficient at breaking up the aggregation as the concentration of polymer increases. The present results are also in agreement with recent reports indicating that the viscosity of EB solutions in NMP significantly increases with increasing EB concentration.[13]

The solution properties of EB in NMP are found to dramatically impact the properties of the polymer films derived from these solutions. In this respect, it is important to note that changes in conformation or changes in the interchain interactions in polymers are kinetic processes and as such are time dependent. This is well exemplified by the present GPC data. Dilution of the initial 5 wt % solution to 0.5 wt % did not result in the same chromatograph as that obtained from the 0.5 wt % solution that was initially prepared. The fact that the 5 wt % solution showed a significantly larger high molecular weight fraction points out that the interchain interactions of EB are not immediately disrupted upon dilution.

In a similar manner, the properties of a film cast from a concentrated polymer solution may not necessarily be expected to be identical to those obtained on evaporating the solvent from a more dilute solution, even though as solvent is evaporated from the dilute solution it will become a concentrated solution before the film is formed. Thus, the nature of a cast film will depend critically on the relative rate of solvent evaporation versus the rate at which changes in molecular interactions occur.

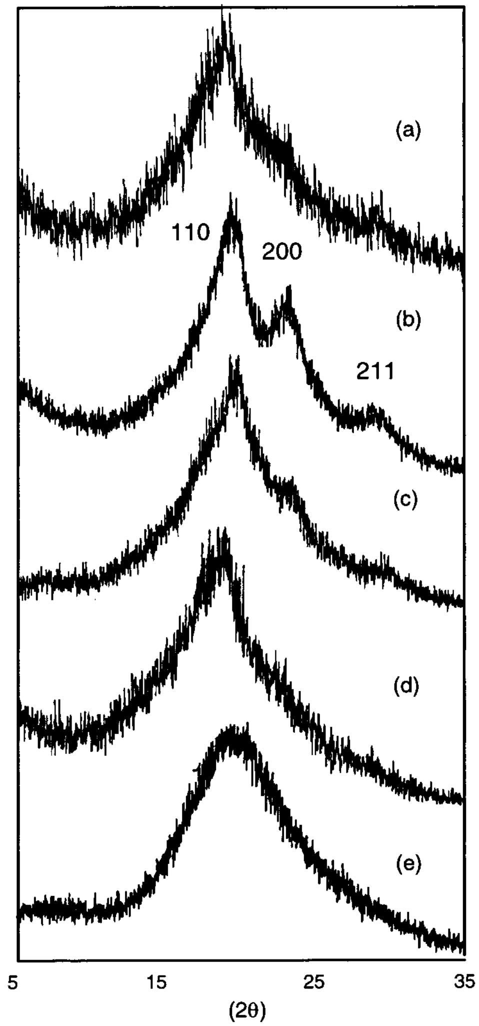

Figure 3. Wide-angle X-ray diffraction patterns of as-made EB films (a) cast from a ~1 wt % solution in NMP ($\Delta 2\theta_{110} \approx$ 4.1°), (b) cast from a ~3 wt % solution in NMP ($\Delta 2\theta_{110} \approx$ 2.8°), (c) cast from a ~5 wt % solution in NMP ($\Delta 2\theta_{110} \approx$ 4.0°), (d) cast from a ~10 wt % solution in NMP ($\Delta 2\theta_{110} \approx$ 4.6°), and (e) cast from a gel (~12 wt % solution in NMP) (amorphous).

The infrared data depicted in Figure 2 demonstrate the relatively slow change in inter-molecular interactions between EB chains especially in the solid state film form. In the as-made EB powder (Figure 2a) the hydrogen-bonded N—H stretching peak at ~3291 cm^{-1} is stronger than the free N—H stretching peak at ~3383 cm^{-1} indicating that the polymer is highly hydrogen bonded.[2,12] However, an EB film cast from NMP in which the residual NMP is removed from the film by extraction with methanol exhibits a significantly less intense hydrogen bonded N—H stretch (Figure 2b) than does the EB powder (Figure 2a). This suggests that upon dissolving EB powder in NMP, the solvent partially disrupts the interchain hydrogen bonding in the polymer. Once the hydrogen bonding between chains is disrupted, it does not completely re-form during the time needed for evaporation of the NMP during the film casting procedure.

Previous studies have reported that films of EB cast from NMP solutions without stretch-orientation are essentially amorphous.[5,6] It was therefore of considerable interest to find in the present study that under certain conditions crystallinity could be obtained in such films. The X-ray diffraction patterns for the as-made EB films cast from solutions with different polymer concentrations are shown in Figure 3. The Bragg diffraction peaks found in the X-ray spectra of as-made EB films (Figure 3) are the same diffraction peaks previously reported for partly crystalline stretch-

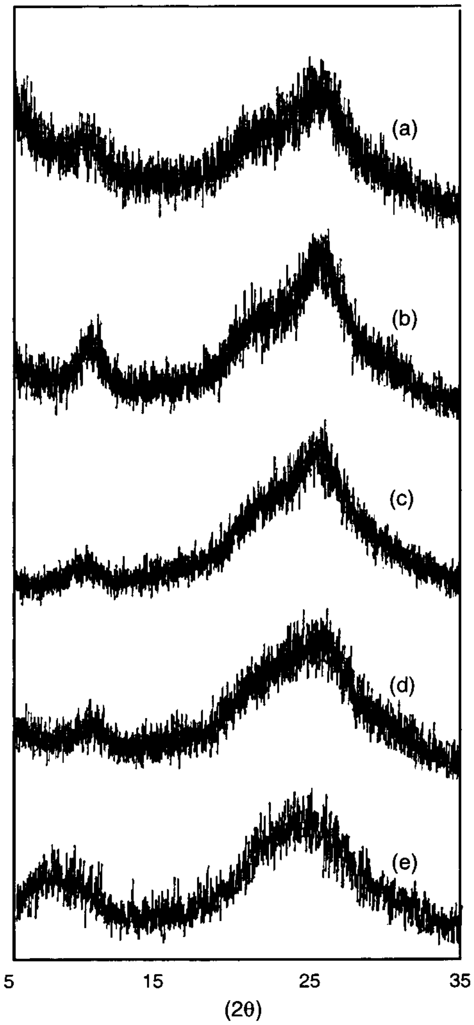

Figure 4. Wide-angle X-ray diffraction patterns of doped[14] polyaniline films (a) cast from a ~1 wt % solution ($\sigma = 8$; 13 S/cm) (b) cast from a ~3 wt % solution ($\sigma = 25$; 30 S/cm), (c) cast from a ~5 wt % solution ($\sigma = 10$; 16 S/cm), (d) cast from a ~10 wt % solution ($\sigma = 9$; 13 S/cm), and (e) cast from a gel ($\sigma = 7$; 10 S/cm).

oriented EB films.[8] As can be seen, the degree of crystallinity in the films is significantly dependent on the initial polymer concentration in NMP solution. EB films cast from more dilute solutions are partially crystalline and have basically the same 2θ values of ~19.3, 23.1, and 29.5° for the 110, 200, and 211 diffraction peaks respectively. They differ significantly from EB films prepared from the gel which exhibit amorphous diffuse scattering at $2\theta \approx 20°$. As shown above, the degree of aggregation in solution increases with increasing concentration. The increase in aggregation, in turn, limits the mobility of the chains to allow a crystalline state to be achieved. Thus, the more crystalline EB films are attained from the less concentrated solutions as shown in Figure 3.

It is interesting to note that in the EB films cast from > ~3 wt % solutions, the 200 and 211 diffraction peaks start to diminish as the concentration increases, and the 110 peak becomes significantly broader as can be seen from the peak width at half-intensity ($\Delta 2\theta$) given in Figure 3. The above three major Bragg diffraction peaks completely disappear and are replaced by amorphous scattering in EB films cast from the gel. This strongly indicates that as the concentration of EB is increased above ~3 wt %, the degree of order in the as-made EB films significantly decreases. One may have expected that films cast from the ~1 wt % solution might have exhibited the greatest crystallinity. However, in three separate experiments, the ~3 wt % solution consistently gave the greatest crystallinity. It is possible that the longer time required for evaporation of the solvent from the very dilute ~1 wt % solution may have been sufficient to permit some agglomeration during the time needed for solvent evaporation with concomitant reduction in crystallinity.

Upon doping the various EB films with aqueous HCl acid, the crystallinity of the EB does not appear to be significantly perturbed. As shown in Figure 4, the partially crystalline EB films remain crystalline upon doping while the amorphous films remains amorphous. The degree of crystallinity in EB impacts the properties of the doped polymer in that the conductivity of the various doped EB films (see Figure 4) parallels their degree of crystallinity. This is consistent with our previous observation that enhanced crystallinity is generally accompanied by enhanced conductivity.[1,3,4]

Conclusion. It has been shown that the degree of aggregation of EB in NMP solution significantly increases as the concentration of polymer increases. The solution properties of EB are found to dramatically impact the properties, in particular, the degree of crystallinity, of the resulting cast films. More concentrated solutions, which contain a higher proportion of aggregated polymer chains, result in the formation of less crystalline material. More dilute solutions which contain a smaller percentage of aggregated polymer chains results in more crystalline films. The most crystalline EB films are attained from a ~3% solution.

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