LiCl Induced Morphological Changes in Polyaniline Base and Their Effect on the Electronic Properties of the Doped Form

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Introduction. Considerable evidence has recently indicated that the conductivity of polyaniline (pani) salts can vary significantly depending on the morphology of the polymer.[1−4] Morphology is a generic term which encompasses various levels of structure including molecular chain conformation, intermolecular chain-to-chain configuration depending on the presence or absence of interchain interactions, degree of order, crystallinity, etc. Of particular recent scrutiny has been the chain conformation of the doped pani and its role on the conductivity.[3] Pani salts processed from solvents such as *m*-cresol exhibit conductivity 2 to 4 orders of magnitude higher than do corresponding salts processed from solvents such as *N*-methylpyrrolidinone (NMP).[1,3,4] It has been proposed that salts processed from *m*-cresol exist in an expanded coil conformation whereas salts processed from NMP exist in a compact coil conformation.[3] The expanded coil conformation allows increased intrachain carrier mobility and thus higher conductivity results. The effect of the solvent on the interchain interactions has not been sufficiently investigated.

The pani in the non-doped or base form generally exhibits better solubility than does the conducting salt form and thus, in most cases, the base is the starting point for processing and doping.[5] It may not be surprising, therefore, to expect that the conductivity of the salt may be strongly influenced by the method in which the base is processed and, thus, on the morphology of the base material.[6,7] The present communication examines the morphology of pani in the base form as processed from NMP and from NMP containing LiCl. LiCl is found to induce an *intermolecular* as well as an *intramolecular* structural change in the polymer as evidenced by dramatic changes in the bulk properties such as molecular weight distribution, glass transition temperature, and optical absorbance as well as on the surface structure properties. The effect of these structural changes on the conductivity of the polymer upon doping with a protonic acid will be discussed.

Experimental Procedures. Pani was synthesized in a manner similar to that previously described.[8] The base form of the polymer was dissolved to 5% in NMP and in NMP containing various amounts of LiCl. All concentrations of the polymer are given as percent by weight; the LiCl content is weight percent relative to NMP. The solutions were filtered through 0.2 μm Millipore filters. Free-standing films on the order of 150 μm were made by solution-casting techniques. Thin films ($\simeq$0.5 μm) were made by spin-coating onto quartz wafers.

Surface structure was measured using a Topometrix TMX2000 scanning probe microscope. Topography measurements were obtained using force microscopy operating in the repulsive mode, a high aspect ratio "super tip", and a low force to minimize any tip-induced modification of the pani. Samples consisted of free-standing films mounted onto a metal disk. In addition, freshly cleaved highly oriented pyrolytic graphite (HOPG) substrates were dip-coated with dilute solutions (0.1%) of pani in NMP and NMP/0.5% LiCl.

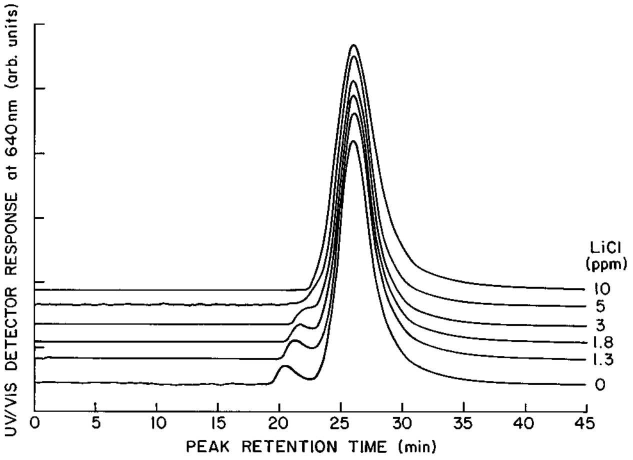

Figure 1. Gel permeation chromatographs of pani base in NMP containing various amounts of LiCl.

Molecular weight measurements were done by gel permeation chromatography (GPC) using polystyrene as a standard. An Ultrastyragel column was used operating at 85 °C. The concentration of the pani solution was 0.1% in NMP and in NMP/LiCl.

Results. (a) Effect of LiCl on the Properties of Pani Base. A number of authors have previously reported that the GPC of pani base in NMP exhibits a bimodal distribution[9−11] similar to that shown in the bottom curve of Figure 1. The chromatograph consists of a major peak having a weight-average molecular weight (M_w) on the order of 26K and a minor peak of very high molecular weight (MW), M_w in this case on the order of 550K. The area of the minor peak in Figure 1 is 4%. It has also been noted that the addition of 0.5% LiCl to the NMP eliminates the high MW fraction, resulting in a single peak.[9,11] Various explanations have been offered for this observation. In general, it is believed that some form of "aggregation" or "clumping" occurs in the base polymer, accounting for the high MW fraction.[11−14] The aggregation is believed to be due to interchain interactions such as physical entanglements[12] or hydrogen bonding (H-bonding).[11,13,14] The LiCl apparently eliminates the aggregation. This study probes the nature of the high MW fraction further as well as the mechanism by which LiCl eliminates the aggregation. We have recently observed that the area of the high MW peak or the degree of aggregation significantly varies, in certain cases exceeding 50%, depending on the prior history of the base polymer powder as well as on the processing parameters, such as solvent, concentration, and temperature. In addition, in certain instances, additional peaks are observed having M_w in excess of 1000K. In all cases, the addition of LiCl eliminates the high MW fractions. Full details of this study will be published in the near future.[15] To examine the effect of LiCl more closely, GPC was performed with LiCl loadings ranging from 0 to 0.5%. Figure 1 depicts the chromatographs in which the LiCl ranged from 0 to 10 ppm or 0.001%. As can be seen, elimination of the high MW fraction is a gradual process. The high MW peak continually shifts to lower MW and the area decreases as the LiCl content is increased. The LiCl appears to be gradually breaking

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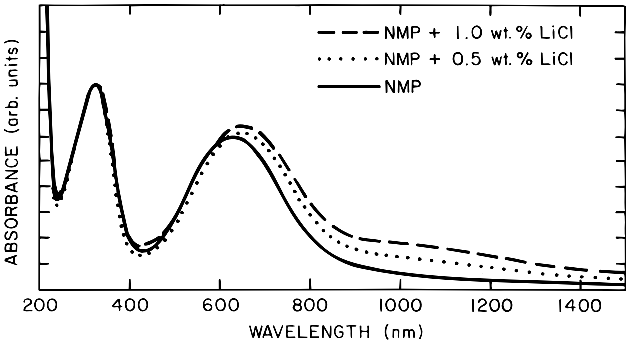

Figure 2. UV/vis/near-IR absorbance spectra for pani base films processed from NMP and NMP/LiCl combinations.

up the high MW material into lower MW. At 0.001%, no sign of the high MW fraction is observed. At higher LiCl loadings, no significant change is observed in the MW distribution. At levels approaching 0.5%, some increase in the MW ($M_w = 33$ K) is observed indicative of higher hydrodynamic volume.

In addition to the molecular weight, LiCl is also found to change the optical properties of the polymer. Figure 2 depicts the changes that are observed in the UV/vis/near-IR absorbance for pani base as increasing amounts of LiCl are added to the NMP solution from which the film is processed. A significant red shift (620 to 648 nm) is observed in the exciton peak[16] with increasing LiCl content. We have previously reported that this peak is sensitive and quite dependent on the morphology of the base polymer.[14] In addition, a weak polaron[16] absorption, generally characteristic of doped pani, emerges at ≃1000−1100 nm. The presence of the weak polaron peak indicates that LiCl is inducing some level of doping in the polymer. The changes in the optical absorbance are reversible. If LiCl is removed from the film with a water wash, the polaron peak is eliminated and the exciton peak is blue shifted.

The glass transition temperature (T_g) of pani base is also dramatically impacted by the presence of LiCl. We previously reported an extensive investigation on the mechanical properties of pani base.[6] The T_g of the polymer processed from NMP was measured to be 250 °C. This T_g is that measured on the second scan (the film was previously scanned to 300 °C under N_2) and thus reflects the T_g for the solvent-free polymer. The T_g for a pani base processed from NMP/0.5% LiCl is 180 °C. This T_g is again that measured on the second scan, and thus no residual solvent is in the film. LiCl reduces the T_g of the polymer by ≃70 °C.

In addition to the macroscopic properties discussed above, the surface structure properties of pani base are also dramatically influenced by the presence of LiCl. Figure 3 shows the atomic force micrographs (AFMs) for a pani base film processed from NMP and for one processed from NMP/0.5% LiCl. The polymer cast from NMP exhibits significant surface morphology, consisting of 100 nm phases which appear to be clusters or bundles. Clusters have also been previously observed in evaporated pani films.[17] The surface structure for pani base processed with LiCl appears to be smooth and more homogeneous. The clusters are not present. Figure 4 shows a high-resolution scan of the polymer processed with LiCl on HOPG. An ordered pattern of what appears to be pani chains (superimposed lines) is observed. The spacing along the chain between neighboring bright dots is ≃0.5 nm or 5 Å. This is in excellent agreement with previous calculated reports,[18] scanning tunneling microscopy data,[19] and X-ray diffraction measurements[20] for the spacing between the C_6H_4 rings along the chain. Interchain spacings are on the order of 1.8 nm or 18 Å, higher than previously reported spacings for proton-doped pani (≃11 Å).[19] High-resolution structure was not resolved for pani base deposited from NMP alone.

(b) Effect of LiCl on Doped Pani. Pani base doped with camphorsulfonic acid (CSA) in NMP exhibits a conductivity on the order of 10^{-2} S/cm. The UV/vis/near-IR absorbance of this doped polymer is shown in Figure 5 (bottom curve). A localized polaron absorption is observed at 850 nm. Doping pani base in NMP containing various levels of LiCl results in higher conductivity. As the LiCl content is increased from 0 to 1%, the conductivity increases by 2 orders of magnitude, saturating at 10^0 S/cm at 0.75% LiCl. In addition, as the LiCl content is increased, a delocalized free-carrier tail absorption extending to 2500 nm forms (Figure 5), similar to that previously observed with *m*-cresol cast films and characteristic of doped panis with an expanded coil conformation.[3] The above results are those observed when the CSA dopant is added to a pani base solution in NMP/LiCl. If the LiCl is added secondary, that is to an NMP solution of the CSA doped pani, it is less effective at enhancing the conductivity. Conductivity on the order of 10^{-1} S/cm is attained at 0.75% LiCl.

To confirm that the above observations were due to LiCl and not to water which may have been introduced into the film as a result of the hygroscopic nature of LiCl, water (0.5−20% relative to solvent) was deliberately added to the doping reaction. At no point did the materials doped in this fashion exhibit a free-carrier tail. The conductivity was 10^{-2} S/cm, identical to that exhibited by pani CSA cast from NMP alone. At the high water content, the pani CSA precipitated from solution. Water was also added to the corresponding doping reaction in NMP/LiCl. No further enhancements were observed in the conductivity as a result of the added water.

The effect of LiCl on HCl doping of pani was also studied. HCl vapor doping of thin pani base films cast from NMP/0.75% LiCl results in a conductivity of 60 S/cm, whereas corresponding samples without LiCl exhibit conductivity of 10 S/cm.

Discussion. A number of experimental results presented in this communication clearly show that LiCl dramatically impacts the properties of pani base and induces higher conductivity upon doping. All of the results are consistent with a significant change in the morphology of the polymer induced by the LiCl.

As discussed above, pani base has a tendency to aggregate as a result of intermolecular H-bonding. The aggregation accounts for the high MW fractions observed in the GPC. There is also a possibility of intramolecular H-bonding; however, such interactions could not realistically account for the high MWs. LiCl interacts with pani base via a "pseudo-doping" process[21] in which the imine site of the polymer reacts with Li^+. Thus, some degree of doping of the polymer is induced by LiCl as evidenced by the weak polaron peak which is observed in Figure 2. Further evidence for this doping reaction will be published in the near future.[22] As LiCl reacts with pani base, the internal polymer chain interactions are disrupted and thus LiCl deaggregates the polymer, consistent with the gradual breakup of the high MW fraction observed in the GPC studies

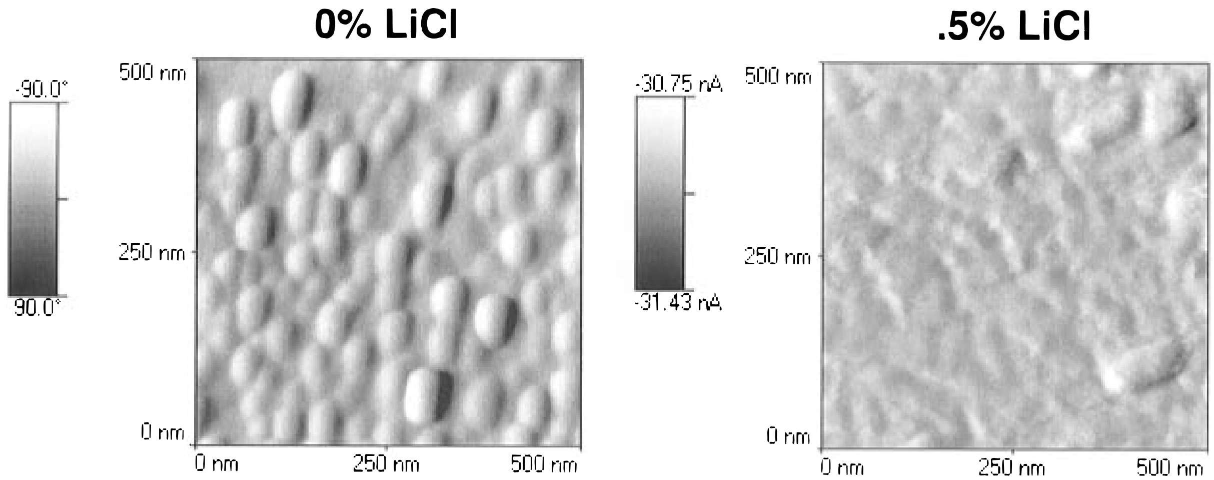

Figure 3. AFM scans of pani base films cast from NMP and from NMP/0.5 wt % LiCl.

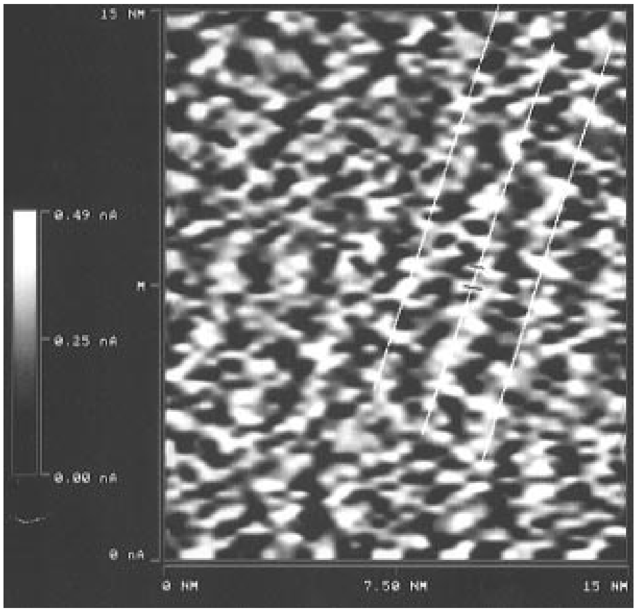

Figure 4. High-resolution AFM scan of a pani base film deposited on HOPG from an NMP/0.5 wt % LiCl solution.

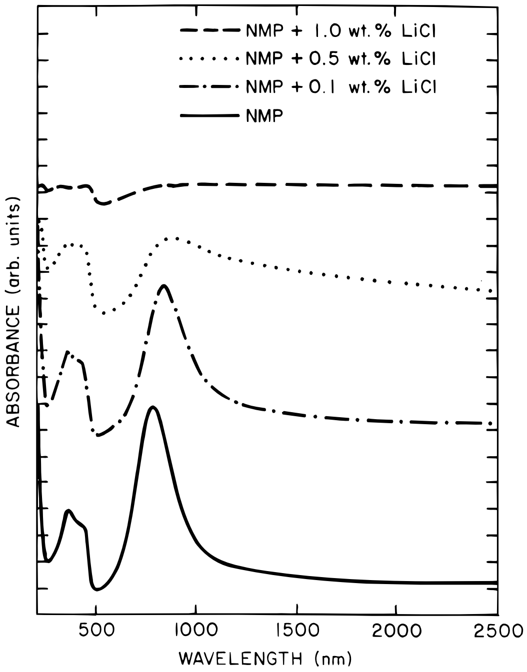

Figure 5. UV/vis/near-IR absorbance spectra for CSA-doped pani films processed from NMP and NMP/LiCl combinations.

(Figure 1). Pani base films, therefore, processed from NMP have more interchain interactions and aggregation as compared to films processed from NMP/LiCl. The T_g and AFM measurements reflect these structural changes. The T_g of a polymer generally increases with increased interchain interactions. Thus, pani films made from NMP exhibit a very high T_g ($\simeq$250 °C) as compared to films made from NMP/LiCl ($\simeq$170 °C). The surface structure of the polymer processed from NMP is composed of clusters which may represent the aggregates. LiCl eliminates the clusters, yielding a smoother, more uniform structure. The high-resolution AFM scan delineates a relatively large interchain spacing for films processed with LiCl, consistent with the model that LiCl is complexed to the polymer and acts as a spacer between chains. The especially large spacing may imply that the LiCl doped pani chains are hydrated.

In addition to the intermolecular structural change, LiCl induces an intramolecular conformational change in the polymer as well. As the polymer interacts with LiCl and becomes deaggregated, the disentangled chains can now be better solvated and thus adopt a more expanded coil conformation. In addition, the pseudo-doping process itself induces a more polar chain; the electrostatic repulsion of the ions can cause an expansion of the chain. Lastly, any intramolecular H-bonding would also be disrupted by the LiCl, allowing the chain to expand.

The deaggregation and subsequent chain expansion increase the degree of delocalization in the pani base as evidenced by a red shift in the exciton absorption of the polymer processed with LiCl. The morphological changes induced by LiCl in the base polymer are in turn reflected in the doped, protonated form. The protonated salts exhibit higher conductivity than those isolated from NMP and they also exhibit a delocalized free-carrier tail indicative of increased delocalization of the electrons in the polaron conduction band, similar to salts processed from *m*-cresol.[3] The conductivity of salts processed from NMP/LiCl, however, is not as high as that of salts processed from *m*-cresol. This observation may imply that LiCl may be too effective at deaggregating the pani base and that the interchain spacing may be too enlarged for high interchain carrier mobility. This point will be further discussed in the future.

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