

Acrylic Acid-Doped Polyaniline Sensitive to Ammonia Vapors

ANJALI A. ATHAWALE, V. V. CHABUKSWAR

Department of Chemistry, University of Pune, Pune 411 007, India

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ABSTRACT: Acrylic acid and HCl-doped polyanilines were synthesized by chemical oxidative polymerization. The synthesized materials were used as sensors for ammonia. Comparison of the responses of the two polymers reveal that the acrylic acid-doped polymer exhibits higher sensitivity and reversibility. Further, the resistance is observed to decrease on exposing the acrylic acid-doped polyaniline to saturated ammonia vapors. A reversed trend is observed in the case of HCl-doped polyaniline. The results are explained in terms of the differences in the chemical interactions of the two polymers with respect to ammonia vapors. The proposed mechanism is further supported by the X-ray diffraction and FTIR analysis. The X-ray diffractogram of acrylic acid-doped polymer shows an enhancement in the crystallinity on exposure to ammonia vapors, while the HCl-doped polymer exhibits a loss in crystallinity. The FTIR spectra shows a higher doping level in acrylic acid doped polymer as observed from the intense peak of the dopant ion at 1158 cm^{-1} , which is seen to be shifted to a lower wavenumber i.e. $\sim 1128\text{ cm}^{-1}$ on exposing the polymer to ammonia vapors. On the other hand, in HCl-doped polyaniline, the peak of the dopant ion $\sim 1120\text{ cm}^{-1}$ is initially less intense, which is further suppressed on exposure to ammonia. Conductivity measurements show a large vapor-induced increase in conductivity, in the case of ammonia-exposed acrylic acid-doped polyaniline, which results in the formation of a more crystalline-conducting phase. Exactly the opposite results were obtained in the case of HCl-doped polyaniline exposed to ammonia. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1994–1998, 2001

Key words: ammonia vapor sensor; acrylic acid-doped polyaniline; HCl-doped polyaniline; chemical synthesis; crystallinity; conductivity

INTRODUCTION

Electronically conducting aromatic polymers have been the object of extensive research in recent years, for example, polypyrrole, polythiophene, polyphenylene, polyaniline etc.¹ In particular, polyaniline has attracted considerable attention because of its use in commercial

applications related to rechargeable batteries, electrochromic windows, biosensor and antistatic coating materials.^{2,3} Recently, synthetic routes have been developed for obtaining soluble conducting polymers by introducing a substituent⁴ or use of functional dopant such as polymeric acids.^{5,6} The incorporation of functional dopants in electronically conducting polymers is found to enhance its solubility, processibility, and conductivity, which can be attributed to the conformational changes of the polymer chain. In the present study, we have synthesized conducting acrylic acid-doped polyaniline, which provides an improved

Correspondence to: A. A. Athawale.
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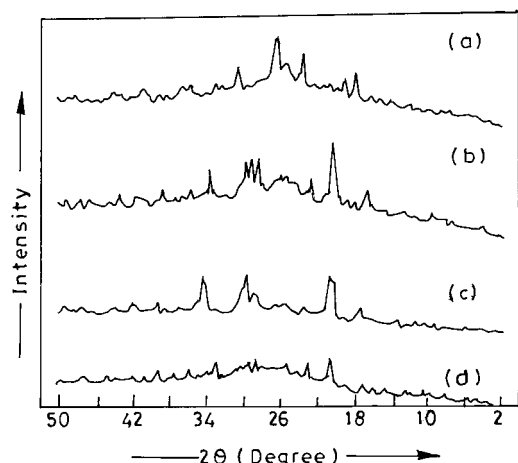


Figure 2 X-ray diffraction patterns of acrylic acid and HCl-doped polyaniline: (a) acrylic acid-doped polyaniline; (b) acrylic acid-doped polyaniline exposed to ammonia; (c) HCl-doped polyaniline; (d) HCl-doped polyaniline exposed to ammonia.

line decreases when exposed to ammonia because it reacts with the polymer such that neutralization occurs and the H^+ over the polymer chain would tend to accumulate on the δ^- side, i.e., on the outside of the polymer at the polymer/gas interface rather than on the δ^+ side, i.e., inside of the polymer. Further, the Cl^- ions tend to migrate from the solid polymer surface towards NH_4^+ to maintain neutrality, i.e. conversion of the conducting salt form of the polymer undergoes transition to the insulating basic form contributing to a decrease in conductivity.¹¹ These results are supported by the X-ray studies of these polymers.

X-ray Diffraction Studies

The X-ray diffraction patterns of acrylic acid and HCl-doped polyaniline are shown in Figure 2(a) and (c). Several sharp peaks are observed in both the polymers at 2θ of 17, 20, 25, 26, and 28°, indicating the presence of a rigid chain and ordered structure resulting in partial crystallinity.^{12,13} Apart from this, some additional peaks are observed in acrylic acid-doped polymer at 18, 19, 24, 30, 33, 36, and 41°. The HCl-doped polymer shows peaks at 17, 20, 28, 29, and 34.8°, of which the two at 17.5 and 18.4° demonstrate a partially amorphous nature due to short range order.¹⁴ However, the degree of crystallinity in acrylic acid-doped polymer is greater than the HCl-doped polymer, as observed from the inten-

sity of the peaks, which is consistent with the conformational changes of the polymer chain in acrylic acid-doped polymer together with the increased sharpness in the amorphous scattering at 2θ of 20°.¹⁵ This is further manifested by a remarkable increase in crystalline peaks at 26 and 28° compared to amorphous peaks in HCl-doped polymer.

Upon exposing the polymer to ammonia vapors, a drastic change is observed in the X-ray patterns, as depicted in Figure 2(b) and (d). The crystallinity is enhanced in acrylic acid-doped polymer with additional sharp peaks at 28, 29, and 30°, indicating improved subchain alignment because these peaks are usually observed for crystalline polyaniline.¹⁵ The reflections at higher angles, i.e., 23.2 and 33°, above the background amorphous scattering, is a good indication that the dopant counter anion undergoes secondary interaction, with the ammonia vapors inducing higher degree of crystallinity.¹³ This can be evaluated by considering the polymer system as a polymer cation–anion complex where polyaniline could be treated as a polycation while acrylic acid acts as an anion that allows an increase in inter-chain packing and thus induces higher structural order in the solid state. Further, it implies that the initially rigid polymer becomes still more rigid on exposure to ammonia, which is obvious from the increase in the volume fraction because ionic species are known to be formed on exposing the polymer to ammonia vapors.

Contrary to this, HCl-doped polyaniline exhibits an appreciable loss in crystallinity, as observed from Figure 2(d). The peaks present at 2θ of 17, 20, 28, 29, and 34° in unexposed polymer are lost or broadened, implying a decrease in the rigidity of the polymer, i.e., there is a loss in the dopant ion concentration and protons in polyaniline. Further, the Cl^- ion, being smaller in size, would only act as an inert spacer, because it provides little or no secondary interaction with the polymer chain.

FTIR Studies

These results are also in agreement with the IR spectra obtained for the two polymers. Figure 3(a) and (c) show the IR spectra of the two polymers. The major absorption bands having usual significance are quoted in Table I. However, differences are observed in the spectra in terms of specific bands and shifts in the two polymers.

The broad and intense bands at 3400–3300 and 1150–1120 cm^{-1} in acrylic acid-doped poly-

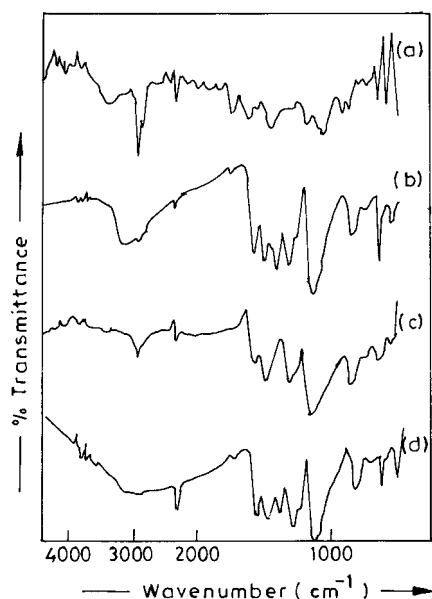


Figure 3 FTIR absorption spectra of acrylic acid and HCl-doped polyaniline: (a) acrylic acid-doped polyaniline; (b) acrylic acid-doped polyaniline exposed to ammonia; (c) HCl-doped polyaniline; (d) HCl-doped polyaniline exposed to ammonia.

mer account for the higher degree of doping and protonation of amine and imine nitrogens. In HCl-doped polymer these bands are relatively sharp and narrow, indicating a lower degree of protonation and doping. However, both the polymers exist in conductive form. The presence of sharp peaks at 2900 and 2800 cm^{-1} can be attrib-

uted to the C—H stretching vibration of aromatic ring and acrylic acid, which is less conspicuous in HCl-doped polyaniline. Further, broad absorption bands $\sim 2500 \text{ cm}^{-1}$, along with a shoulder $\sim 2700 \text{ cm}^{-1}$, are clearly observed in acrylic acid-doped polymer, which can be attributed to the various stretching vibrations of protonated amine and imine N atoms.¹⁶ These are relatively weak in HCl-doped polymer. Apart from this, the acrylic acid-doped polymer shows a peak $\sim 1610 \text{ cm}^{-1}$, which could be the convolution of the bending vibration $\delta(\text{OH})$ of the water molecule and the asymmetrical stretching of carboxylate group ($-\text{COO}^-$)¹⁷ resulting from acid base reaction between acrylic acid and polyaniline. It is important to note the presence of nonprotonated $-\text{COO}$ groups as a stretching band at $\sim 1720\text{--}1740 \text{ cm}^{-1}$. Strong peaks at 1238 and 1410 cm^{-1} for C—O stretching, and $-\text{C}-\text{OH}$ in-plane bending, reveal the presence of free acrylic acid in the polymer matrix. The quinoid and benzenoid bands are observed at 1560 and 1480 cm^{-1} in HCl-doped polymer.¹⁸ These peaks are seen to be broadened and shifted to lower wave number, i.e., 1573 and 1488 cm^{-1} . Also, the spectral intensity of these bands is comparably typical of a highly doped emeraldine salt form of polymer.

Exposure to ammonia reveals differences in specific bands, which are more significant in acrylic acid-doped polymer compared to HCl-doped polymer. The band $\sim 3300 \text{ cm}^{-1}$ is shifted to a lower wave number $\sim 3200 \text{ cm}^{-1}$ together with the peak at 1158 cm^{-1} shifting to 1111 cm^{-1} in acrylic acid-

Table I Characteristic Frequencies of Acrylic Acid and HCl-Doped Polyaniline

Polyaniline (Acrylic Acid) cm^{-1}	Polyaniline (HCl) cm^{-1}	Polyaniline (Acrylic Acid) NH_3 Exposed cm^{-1}	Polyaniline (HCl) NH_3 Exposed cm^{-1}	Peak Assignment
698–749	700–750	615–702	617–708	Out of plane C—H bending vibration
824	811	823	819	<i>Para</i> disubstituted benzene ring
1158	1118	1111	1120	Vibration band of dopant anion
1284	1290	1275	1244	Secondary (C—N) stretching band
1340	1320	1304	1300	Aromatic (C—N) ⁺ stretching band
1490	1480	1499	1488	Benzenoid rings stretching band
1577	1560	1580	1573	Quinoid ring stretching band
1730	—	1744	—	Carbonyl (C=O) stretching band
1620	—	1610	—	$\nu(\text{COO})$ antisymmetrical stretching band
2338	2314	2356	2358	$\nu(\text{NH}_2)^+$ saturated amine
2505	2500	2498	2502	$\nu(\text{N}-\text{H})^+$ unsaturated amine
2920	2918	2915	2916	C—H aromatic stretching band
3405	3410	~ 3130	~ 3200	N—H stretching band

Table II Conductivity Values of Acrylic Acid and HCl-Doped Polyaniline

Species	Conductivity S cm ⁻¹	
	Before Exposing the Polymer to Ammonia Vapors	After Exposing the Polymer to Ammonia Vapors
Acrylic acid-doped polyaniline	4.8×10^{-6}	2.5×10^{-4}
HCl-doped polyaniline	1.785×10^{-6}	3.38×10^{-7}

doped polymer, implying that the doping level is maintained in the sample even after exposing to ammonia vapors. Conversely, in HCl doped polymer, the characteristic peak for dopant ion ~ 1118 cm⁻¹ is shifted to a higher wave number and gets narrower, while the band at ~ 3200 cm⁻¹ is broadened, indicating oxidation of nitrogen of the polymer chain.¹² Similarly, the peaks at ~ 2500 and 2700 cm⁻¹ are affected significantly in HCl-doped polymer, while acrylic-acid doped polymer shows a negligible effect. So also the peak ~ 1480 cm⁻¹ is sharpened and blue-shifted, suggesting enhancement in the quinoid form. In acrylic acid-doped polymer the bands at 1238 and 1410 cm⁻¹ are affected appreciably, implying partial neutralization of acrylic acid via formation of ionic salt species. However, doping is maintained by free acrylic acid molecules, as observed from the peaks at 1158 and 1125 cm⁻¹. Hence, there is an increase in conductivity as well as crystallinity.

Electrical Conductivity

These results are well supported by the conductivity data (Table II) obtained for both the polymers. The conductivity in acrylic acid doped polyaniline is seen to increase upon exposure to ammonia vapors. This can be attributed to the presence of large concentration of $-\text{COO}^-$ ions serving as a dopant alongwith few HCl-doped sites and trapped $-\text{COOH}$ molecules present in the polymer matrix. When exposed to ammonia, some molecules of ammonia are adsorbed while some interact with the Cl^- ions present in the polymer forming NH_4Cl . As a result, there is a loss of the Cl^- ions together with the charge imbalance caused over the polymer chain. These effects are neutralized by the trapped $-\text{COOH}$ molecules, which may occupy the free dopant sites, thereby increasing the carrier concentra-

tion and, hence, the conductivity. In contrast with this, in HCl-doped polyaniline, the conductivity is seen to decrease on exposure to ammonia vapors. This is because the ammonia molecules interact with the polymer chains, thereby converting the conducting salt phase of the polymer to insulating emeraldine base form.¹⁰

CONCLUSION

Acrylic acid-doped polyaniline serves as a superior material for sensing ammonia vapors compared to HCl-doped polyaniline. The conductivity and crystallinity of acrylic acid-doped polyaniline increase upon exposing to ammonia vapors, while HCl-doped polyaniline shows a reverse trend.

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