

X-ray Diffraction Study of Doped Polyaniline

H. K. CHAUDHARI and D. S. KELKAR*

Department of Physics, Institute of Science, Bombay 400032, India

SYNOPSIS

Polyaniline (PAn), an important conducting polymer, was synthesized chemically. Percentage crystallinity of PAn on doping with various dopants (viz., hydrochloric acid, formic acid, iodine, methylene blue) has been investigated using wide-angle X-ray diffraction analysis. It is observed that percentage crystallinity (X_c %) for PAn increases after doping, and it is different for different dopants. The electrical conductivity measurements of these samples show that there is an increase in electrical conductivity with an increase in crystallinity. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyaniline (PAn) has received great attention due to its good environmental stability and also due to its interesting electrochemical properties for the development of light-weight batteries and electrochromic display devices.¹

The synthesis and structure of PAn has been studied by various workers. Controversies have arisen about whether PAn is crystalline or amorphous. According to Wang et al.,² crystallinity of PAn decreases with increasing HCl concentration during synthesis over the whole range of 0.001–7 N. As pointed out in the report by Tang et al.,³ high HCl concentration in polymerization solution leads to the addition of Cl into the quinoid ring. Obviously, the introduction of Cl atoms into the orthoposition of the N— atom further increases the space hindrance to the internal rotation of the PAn chain. That is why the PAn prepared at high HCl concentration was entirely amorphous.

It has been shown that doped and undoped PAn have different crystalline contents.² It was reported that emeraldine salt (PAn–hydrochloride) was partly crystalline, while emeraldine base (undoped PAn) was essentially an amorphous polymer. It was also reported that *n*-methyl-2-pyrrolidone (NMP)-*p*-PAn films doped with 1M HCl were partly crystalline.⁴ The emeraldine base powder was up to ca. 50%

(orthorhombic) crystalline.^{5,6} The coherence lengths in the ordered regions were as large as ca. 150 Å perpendicular to the chain and ca. 150 Å in the chain direction when the film was oriented. These coherence lengths are similar to those in (CH_x).⁷

X-ray diffraction (XRD) patterns of the powdery PAn and NMP-*p*-PAn films at various NMP contents from 2.4 to 16 wt % were studied by Chen et al.,⁸ who found that the pattern of PAn powder exhibits a broad amorphous peak at $2\theta = 19^\circ$ and two weak crystalline peaks at $2\theta = 15^\circ$ and $2\theta = 24^\circ$. When the powdery PAn was doped with HCl, the PAn became more crystalline and was reflected in the presence of several diffraction peaks at $2\theta = 9^\circ$, 15° , 21° , and 26° . The author has also reported that due to NMP acting as a plasticizer, NMP cast PAn film has less crystallinity than the powdered samples.⁸ Wide-angle X-ray diffraction (WAXD), scans of undoped and doped PAn synthesized chemically in 1N H₂SO₄ solution showed that the undoped PAn was almost amorphous and that the doped PAn was remarkably crystalline.² It was shown that as the doping level increases, percentage crystallinity increases nearly proportional to the conductivity. This indicates that the dopant species (like a plasticizer) promote the movement of the PAn molecular chains and thus the crystalline regular arrangement can be more easily achieved. It was concluded that the dopant and oxidant of smaller molecular size lead to higher crystallinity.² Thus it appears that the existence of dopant species in PAn can have entirely opposite types of effects (i.e., it benefits movements of the PAn molecular chain, leading to more crys-

* To whom correspondence should be addressed.

talline structure, or may distort or destroy the crystalline lattice of the PAN structure). Hence, it was thought interesting to investigate the crystalline structure of PAN samples in powdered form doped with various dopants, like formic acid (HCOOH), iodine (I₂), and methylene blue (C₁₆H₁₈N₃SCl) along with HCl. Using the WAXD scans for samples, the percentage crystallinity is calculated and reported.

EXPERIMENTAL

Sample Preparation

Chemical polymerization of aniline was carried out using ammonium peroxodisulfate as an oxidizing agent.⁹ The temperature during the reaction was maintained low because the reaction is exothermic and also because at low temperature side reactions get depressed and hence the molecular weight of PAN can be increased. The details of synthesis of PAN are described herein.

A solution of aniline (0.1M) in diluted (dil.) HCl was maintained at low temperature. To this solution 0.1M ammonium peroxodisulfate [(NH₄)₂S₂O₈] solution in dil.HCl was added dropwise for about 1 h under vigorous stirring. After 8 h the dark green precipitate that had formed was collected by filtration and then washed repeatedly with distilled water. PAN-hydrochloride thus obtained was converted into PAN-base by treatment of aqueous ammonia. This powder was then dried under dynamic vacuum for at least 48 h.

Doping of PAN

Undoped PAN powder was doped by immersion in various dopant solutions, such as 1M aqueous HCl, 10% aqueous formic acid, 1% iodine solution in acetone, or 1% aqueous methylene blue solution, for 24 h, followed by drying under dynamic vacuum at room temperature and then pressing to form pellets. The thickness of pellets was about 1–2 mm.

WAXRD

WAXD scans for undoped and doped powders were obtained using a JEOL JDX-8030 X-ray diffractometer model. Nickel-filtered copper radiation (K_α) was incident on the sample, which was scanned at the rate of 1°/min in the reflection mode over a range of 2θ from 5–35°. From the radial scans of intensity versus 2θ, the crystallinity index of the sample was calculated using Manjunath et al.'s formula.¹⁰

According to the method suggested by authors¹⁰ for any polymer, the resolution of the peak *R* is given by

$$R = \frac{m_1 + 2m_2 + \dots + m_{n-1}}{h_1 + h_2 + \dots + h_n}$$

where *m*₁, *m*₂ . . . are the heights of minima between two peaks, and *h*₁, *h*₂ . . . are the heights of peaks from the base line.

Then (1 - *R*) gives the lateral order or the index of crystallinity. Figures 1 and 2 indicate that all the peaks are quite sharp and well resolved; hence for calculating percentage crystallinity, all the peaks were considered.

Conductivity Measurements

The two-probe method was used to measure the electrical conductivity of the samples in the sandwich configuration.

RESULTS AND DISCUSSION

The XRD scans for the undoped and various doped samples of PAN are depicted in Figures 1 and 2.

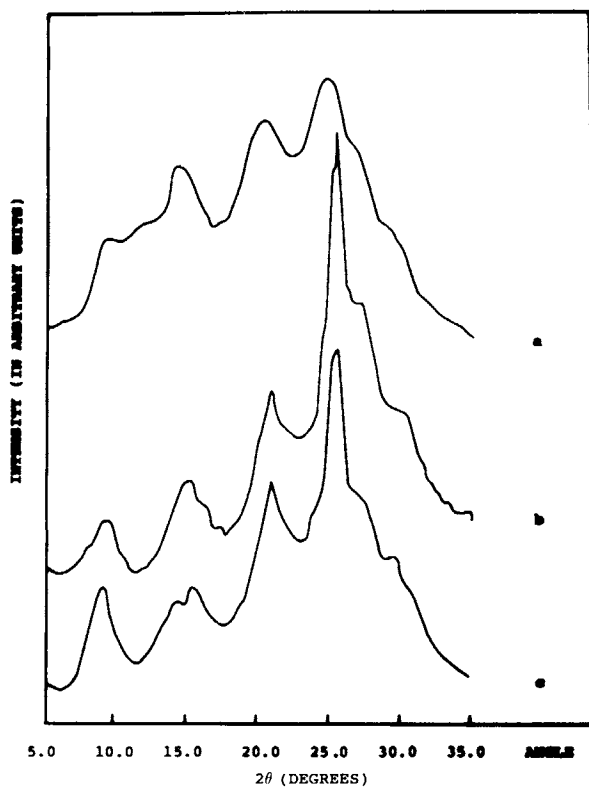


Figure 1 WAXRD scans of PAN in powder form: (a) undoped, (b) HCl doped, (c) formic acid doped.

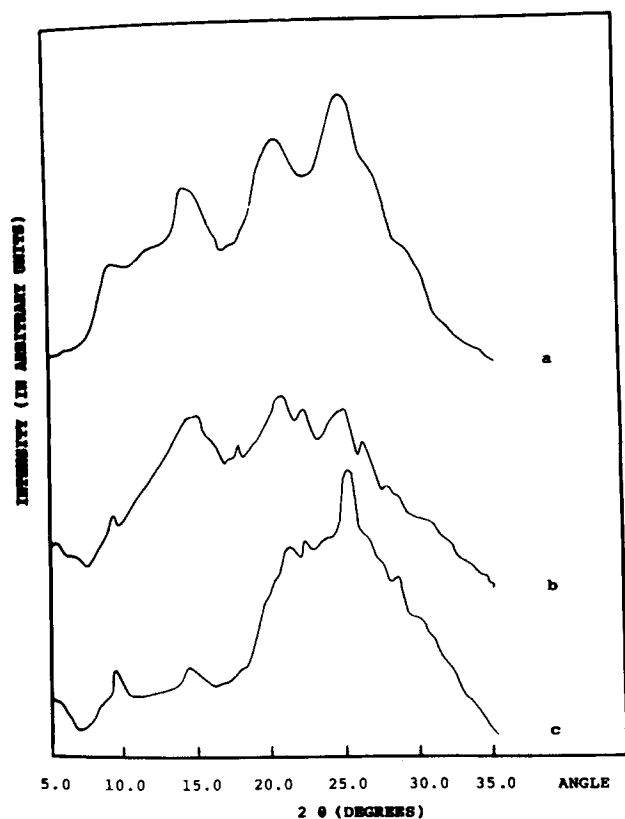


Figure 2 WAXRD scans of PAN in powder form: (a) undoped, (b) iodine doped, (c) methylene blue doped.

The WAXD pattern of undoped PAN powder [Fig. 1(a)] shows peaks at $2\theta = 9.5^\circ$, 14.7° , 20.4° , and 25.1° , and its percentage crystallinity is 45%. It indicates that complete amorphous form is not obtained using this method. It has also been reported that crystallinity of PAN depends on the conditions used during synthesis of the polymer.² The crystalline peak at $2\theta = 25.1^\circ$ is more prominent than the amorphous peak, which is reported at $2\theta = 19.5^\circ$.

After doping with HCl, PAN became more crystalline. Its XRD pattern [Fig. 1(b)] shows peaks with increasing intensity. For HCl-doped PAN powder, the XRD pattern shows a sharp crystalline diffraction peak at $2\theta = 25.6^\circ$; and several other diffraction peaks at $2\theta = 9.5^\circ$, 15° , and 21° are obtained (i.e., peaks are only slightly shifted from their position in the XRD scans of undoped PAN). Percentage crystallinity (X_c %), as shown in Table I, increases remarkably for HCl-doped PAN. After doping with formic acid, the XRD pattern [Fig. 1(c)] remains almost the same as that for HCl-doped PAN. The crystallinity index, however, reduces compared to the HCl-doped sample. This

sample exhibits the XRD pattern with the diffraction peaks at $2\theta = 9^\circ$, 15.2° , 21° , and 25.5° with X_c % of 65% (Table I).

Figure 2(b) shows XRD scans of iodine doped PAN. It is very interesting to note that here the peaks are not as distinct and sharp as they are for the undoped one. Further, the peak at $2\theta = 19.5^\circ$ (amorphous peak) is more intense than the peak at $2\theta = 25.1^\circ$, which corresponds to the crystalline peak. In the case of undoped PAN and other doped PAN samples, the crystalline peak at $2\theta = 25.1^\circ$ is much sharper than the amorphous peak. Another interesting observation is that a crystalline peak appearing at $2\theta = 14^\circ$ for this (iodine-doped PAN) sample is much distinct and prominent than that in the case of other samples. These features in the XRD pattern of iodine-doped PAN lead to the conclusion that there is a possibility of a different crystalline form for the sample. It is also observed that the X_c % reduces to 35%, which is even less than the undoped PAN. This indicates that after iodine doping, PAN becomes more amorphous. However, the appearance of an appreciably sharp crystalline peak at $2\theta = 14^\circ$ for iodine-doped PAN with a weak crystalline peak at $2\theta = 25.1^\circ$ also may be due to the change in the crystalline form of the sample. To confirm this, a detailed study of WAXRD patterns of iodine-doped PAN with varying iodine concentrations should be carried out and will be undertaken in near future.

After methylene blue doping [Fig. 2(d)], the crystallinity of the sample does not show much improvement, as is shown by HCl and formic acid doped samples. The crystallinity of this sample is more than the undoped one and is about 52%. Its XRD pattern is similar to that of the undoped, HCl doped, and formic acid doped samples, with a reduction in the intensity of crystalline peaks. The diffraction peaks are not well resolved, while peaks are obtained at $2\theta = 9^\circ$, 14° , 20° , and 25.4° .

Table I Percentage Crystallinity, X_c (%), and Electrical Conductivity (Measured at Room Temperature) of PAN in Powdered Form

PAN Powder	X_c (%)	Conductivity ($S\ cm^{-1}$)
Undoped	45	5.27×10^{-7}
HCl doped	74	6.0×10^{-2}
Formic acid doped	65	1.0×10^{-1}
Iodine doped	35	3.68×10^{-4}
Methylene blue doped	52	7.18×10^{-7}

Table I shows the percentage crystallinity X_c (%) and electrical conductivity (measured at room temperature) of variously doped PAN samples. From Table I it can also be observed that even if the X_c (%) of the iodine-doped sample is less than the undoped sample, its electrical conductivity is still more than the undoped one. For other doped samples, it is found that in general as X_c (%) increases, its electrical conductivity also increases. It may be concluded that iodine has helped for electrical conduction in spite of its smaller X_c %. Hence it may be concluded that electrical conductivity not only depends on the crystallinity of the sample but also on the dopant species.

CONCLUSION

The results of the X-ray diffraction analysis point out that dopant species affect the structure and also the crystallinity of PAN. Table I lists the electrical conductivities for all samples along with their respective values of percentage crystallinity. From this it can be concluded that, in general, electrical conductivity increases as the crystallinity of the sample increases. The conductivity also depends on the type of dopant species.

REFERENCES

1. M. G. Kantizidis, *Chem. and Eng. News*, **3**, 36 (1990).
2. F. S. Wang, J. S. Tang, L. Wang, H. F. Zhang, and Z. Mo, *Mol. Cryst. Liq. Cryst.*, **160**, 175 (1988).
3. J. S. Tang, X. B. Jing, B. C. Wang, and F. S. Wang, *Synth. Met.*, **24**, 231 (1988).
4. A. G. MacDiarmid and A. J. Epstein, *J. Faraday Diss. Chem. Soc.*, **88**, 317 (1989).
5. M. E. Jozefowicz, R. Laversane, H. H. S. Javadi, A. J. Epstein, J. P. Pouget, X. Tang, and A. G. MacDiarmid, *Phys. Rev. B, Rapid Commun.*, **39**, 12958 (1989).
6. A. J. Epstein and A. G. MacDiarmid, in *Electronic Properties of Conjugated Polymers*, H. Kuzmany, M. M. Mehring, and S. Roth, Eds., Springer-Verlag, Berlin, 1989.
7. P. Robin, J. P. Pouget, R. Comes, H. W. Gibson, and A. J. Epstein, *Phys. Rev. B.*, **27**, 3938 (1983).
8. S. A. Chen and H. T. Lee, *Macromolecules*, **26**, 3254 (1993).
9. M. Angelopoulos, G. E. Aaturious, S. P. Ermer, A. Ray, E. M. Scherr, A. G. MacDiarmid, M. Khhtar, Z. Kiss, and A. J. Epstein, *Mol. Cryst. Liq. Cryst.*, **160**, 151 (1988).
10. B. R. Manjunath, A. Venketraman, and T. Stephen, *J. Appl. Polym. Sci.*, **17**, 1091 (1973).

Received October 30, 1995

Accepted March 6, 1995