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Wang Fosong [a], Tang Jinsong [a], Wang Lixiang [a], Zhang Hongfang [a] & Mo Zhishen [a]

[a] Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin, P.R. China

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Study on the Crystallinity of Polyaniline

WANG FOSONG, TANG JINSONG, WANG LIXIANG, ZHANG HONGFANG and MO ZHISHEN

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin, P.R. China

WAXD, SEM, DSC and TGA were used to investigate the crystallinity of polyaniline (PAn). The results show that the crystallization behaviors of undoped PAn depend on its polymerization conditions. The crystallinity of undoped PAn decreases with the increasing acidity from 0.001 to 7N in polymerization solution. Doped PAn crystallizes more easily than undoped one and the crystallinity increases with increasing doping level. Appropriate heat treatment can enhance the crystallization ability of PAn.

INTRODUCTION

Polyaniline (PAn) is of considerable interest as one of conducting polymers. The synthesis, structure and properties have been described in previous papers.[1–4] But there are still controversies over its crystalline or amorphous nature. As early as the beginning of this century, Datta *et al.*[5] reported that PAn could crystallize, but some later studies showed that PAn was an amorphous solid.[6] Recently, Wessling[7] mentioned that PAn could become crystalline through some treatment, but he did not give the details. We have made preliminary studies on the crystallinity of PAn prepared under various conditions by using WAXD, SEM, DSC and TGA techniques.

EXPERIMENTAL

The PAn samples were chemically and electrochemically synthesized from 0.5 and 0.1 N aniline solution respectively as described in references (2) and (4). The molar ratio of the oxidant to aniline is 1:2 in the chemical synthesis. The sample thus obtained, which is doped PAn, was repeatedly washed with aqueous NH_4OH solution to obtain

the undoped PAn. The samples of different doping levels were prepared by saturating the undoped PAn with aqueous solution of different pH values. The samples were dried under a dynamic vacuum and ground in a mortar before examination. To carry out heat treatment, the samples were heated at 10°C/min to a desired temperature and kept at that temperature for 45 minutes under N_2 atmosphere, and then were made to cool naturally to room temperature.

WAXD spectra were taken on a Rigaku x-ray diffractometer, using CuKα radiation, Ni filter and continuous scan of 2°/min. Angle scale and recorder reading (2θ) were calibrated to an accuracy of ±0.01°. DSC and TGA measurements were carried out on Perkin-Elmer-DSC and TGS-2 respectively, under N_2 atmosphere and at a heating rate of 10°C/min. The SEM experiments were made on a JXA-840 scanning electron microscope. The conductivity was determined by the four-probe method.

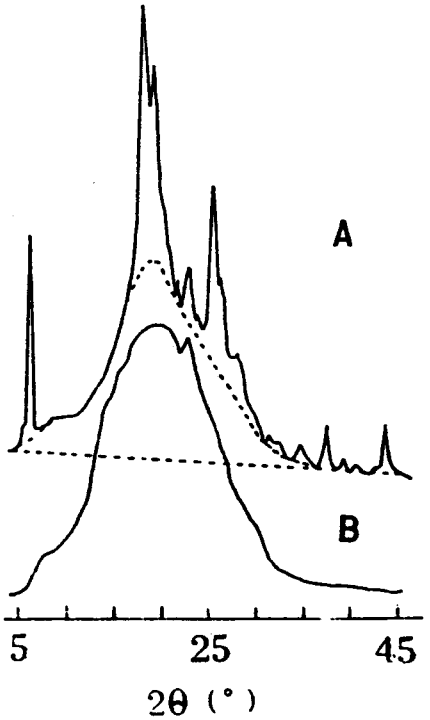


FIGURE 1 WAXD spectra of undoped PAn. HCl concentration in polymerization solution: (A) 0.001N; (B) 5N.

RESULTS AND DISCUSSION

Two typical WAXD spectra of PAn are shown in Figure 1. Spectrum B looks like amorphous and spectrum A contains crystalline defraction peaks. The two samples were prepared in 5N and 0.001N HCl solutions respectively. The maximum of spectrum B is located at about $2\theta = 19.5°$. An amorphous peak was thus taken as shown by the dotted line in Figure 1 with its apex at $2\theta = 19.5°$. The crystallinity (Xc) of partially crystalline sample is calculated according to reference (8).

1. Effect of molecular structure

Figure 2 shows the effects of the concentration of hydrochloric acid in the synthesis solution on the Xc of the undoped PAn. It can be seen that the Xc decreases with increasing HCl concentration over the whole range of 0.001–7N examined. Corresponding conductivity is shown by the other curve in Figure 2. The variation of the conductivity as a function of HCl concentration in polymerization solution has been explained in the previous paper.[2] At very low HCl concentration, formation of azo-group was verified.[2] The PAn prepared at low HCl concentration shows a very strong WAXD peak, the position of which is very close to that of poly-*p*-phenyldiamine

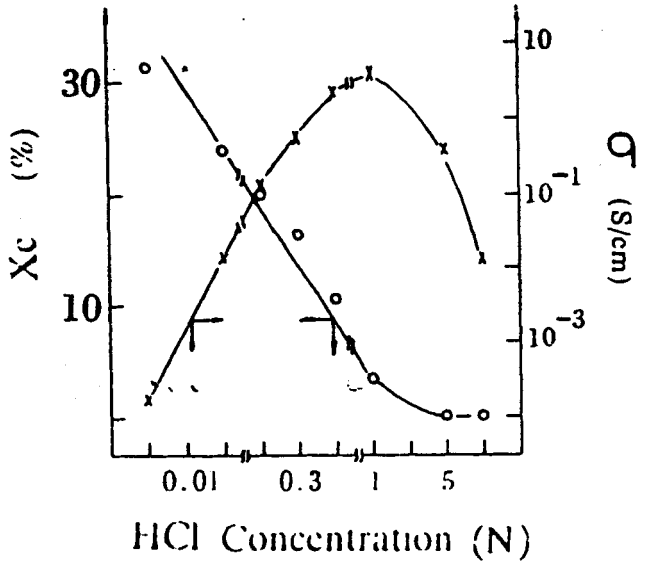


FIGURE 2 Effect of the HCl concentration in the polymerization solution on Xc of the undoped PAn and the conductivity of the doped PAn.

prepared under similar conditions.[9] Therefore, the higher X_c may be ascribed to the existence of azo-groups in the molecular chains of PAn obtained. The normal 1,4-coupled polyaniline shows very high conductivity but a few percent of Xc as shown in Figure 2. This is because there are both benzoid and quonoid structure units in a molecular chain and dihedral angle between these two units is close to 80–90°.[10] Thus the molecular chain is very stiff and is difficult to move to achieve regular crystalline arrangement.

As pointed out in reference (2), high HCl concentration in polymerization solution leads to the addition of Cl into the quonoid ring. Obviously, the introduction of Cl atoms into the orth-position 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 is entirely amorphous.

2. Effect of doping

Figure 3 gives WAXD spectra of doped and undoped PAn synthesized chemically in 1N H_2SO_4 solution. It is seen that the undoped PAn is almost amorphous and the doped PAn is remarkably crystalline.

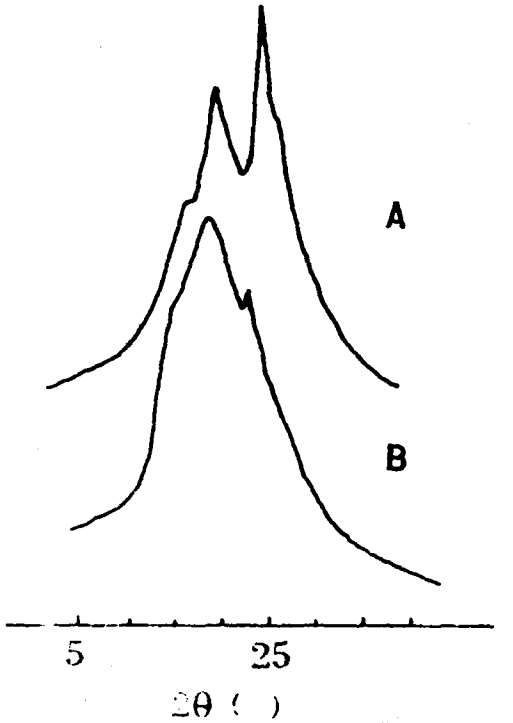


FIGURE 3 WAXD spectra of doped(A) and undoped(B) PAn synthesized chemically in 1N H_2SO_4.

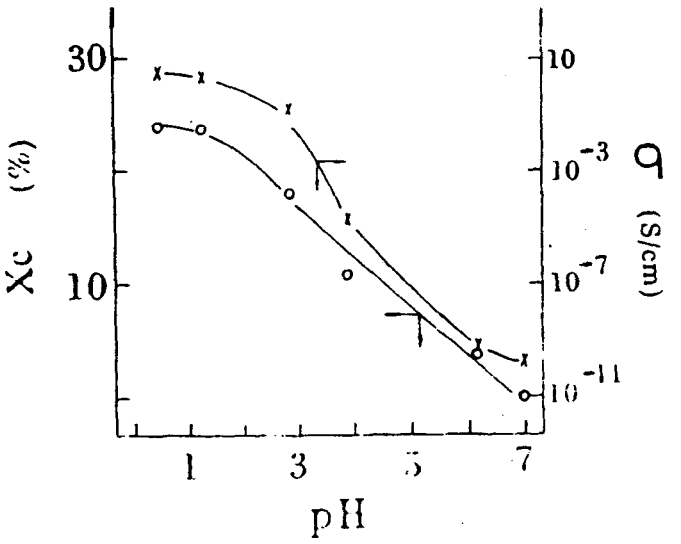
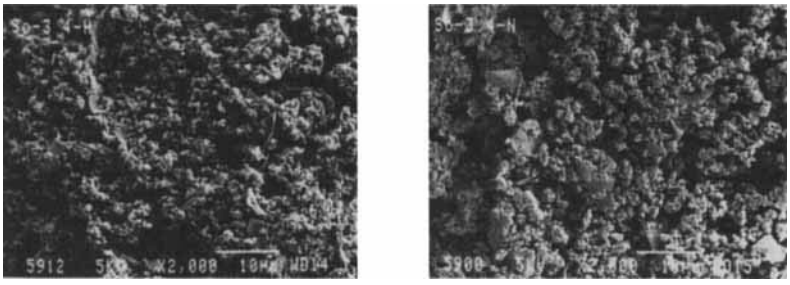


FIGURE 4 Relationship between the doping level and Xc.

Figure 4 shows the relationship between the crystallinity and the doping level. It can be seen that as the equilibrium pH of aqueous HCl solution decreases, that is, as the doping level increases, Xc increases nearly proportionally to the conductivity. This indicates that the dopant species (like a "plasticizer") promote the movement of the PAn molecular chains and the crystalline regular arrangement can be more easily achieved.

SEM photographs of doped and undoped PAn obtained under the above condition are shown in Figure 5. Obviously, the doped PAn has a continuous surface and larger grains whereas the undoped PAn is composed of smaller grains separated by "honeycombs."



(a) (b)

FIGURE 5 SEM photographs of doped(a) and undoped(b) PAn obtained in 1N H_2SO_4.

TABLE I

Relationship between the dopants and oxidants and the crystallinity of doped PAn

Method	Oxidant	System	Dopant	Xc (%)	Conductivity (S/cm)
chemical	$K_2Cr_2O_7$	1N HCl	HCl	11.5	2.3×10^{-3}
	$(NH_4)_2S_2O_8$	1N HCl	HI[a]	20.9	2.0×10^{-2}
	$KClO_3$	1N HCl	HCl[b]	23.7	1.9
	$(NH_4)_2S_2O_8$	1N H_2SO_4	H_2SO_4	23.9	6.9
	H_2O_2	1N HCl	HCl	27.9	2.2×10^{-1}
	$(NH_4)_2S_2O_8$	1N HCl	HCl	31.9	5.5
electro-chemical	constant potential (0.8V vs. SCE)	0.1N $HClO_4$	$HClO_4$	13.7	4.5
		0.1N H_3PO_4	H_3PO_4	14.6	2.8
		0.1N H_2SO_4	H_2SO_4	21.6	6.7
		0.1N HCl	HCl	22.3	3.2

[a]Synthesized in 1N HCl and the undoped sample doping with 1N HI.
[b](oxidant)/(aniline) = 1:1.

Table I shows the dependence of the Xc of the doped PAn prepared by chemically or electrochemically on the dopants and oxidants used in the preparation. Of all dopants, HCl gives the highest Xc if same oxidant is used or for the electrochemically prepared samples. With HCl as dopent, H_2O_2 results in higher Xc than $KClO_3$ or $K_2Cr_2O_7$ does. It seems that dopant and oxidant of smaller molecular size lead to higher crystallinity. This implies that small dopant species like Cl^- can enter the PAn lattice, bulk dopants may distort or even destroy the lattice and reduce Xc. Actually, the spectrum B in Figure 3 gives interplanar spacings of 4.5 Å and 3.9 Å. Therefore, the existence of dopant species has two consequences, it benefits movements of PAn molecular chain on the one hand, and may distort or destroy crystalline lattice on the other hand. The observed Xc is determined by the competition between these two factors.

3. Effect of heat treatment

Figure 6 gives the WAXD curves of undoped PAn synthesized in 0.1 N H_2SO_4 by $(NH_4)_2S_2O_8$, as a function of heat treatment temperature. It can be seen that Xc increases with increasing heat treatment temperature, but decreases after 150°C. Finally, PAn becomes amorphous after 300°C treatment. The relationship between Xc and heat treatment temperature depend on the preparation conditions of the samples as shown in Figure 7. It can be seen that four samples get their maximum Xc values at about 150°C. Over the range of 30–

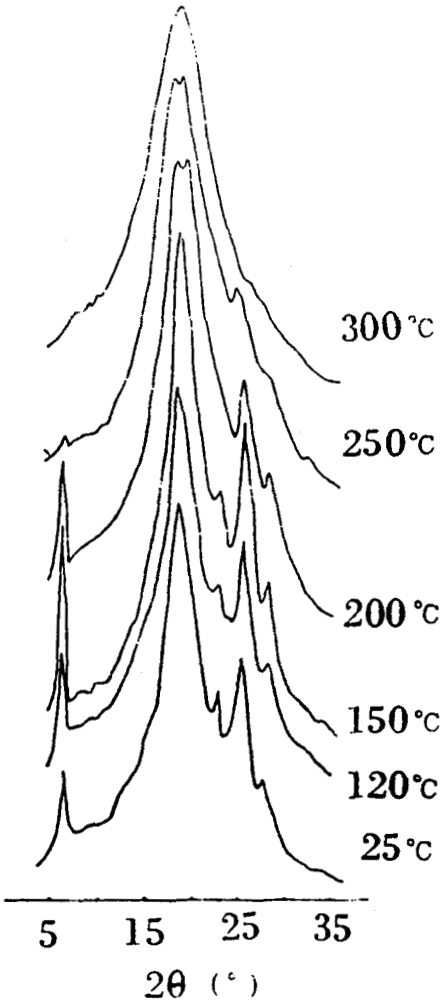


FIGURE 6 Relationship between the heat treatment temperature and the WAXD intensity of undoped PAn obtained in 0.1N H_2SO_4.

150°C, two curves for doped PAn and two curves for undoped samples are parallel respectively and latter look steeper than the former two, showing more temperature dependence. HCl doped sample gives higher Xc than H_2SO_4 doped one as shown by curves with symbols × and ◐. This is in agreement with Table I.

Above 150°C, the Xc of all tested samples decrease with increasing treatment temperature. In order to examine the reason for the de-

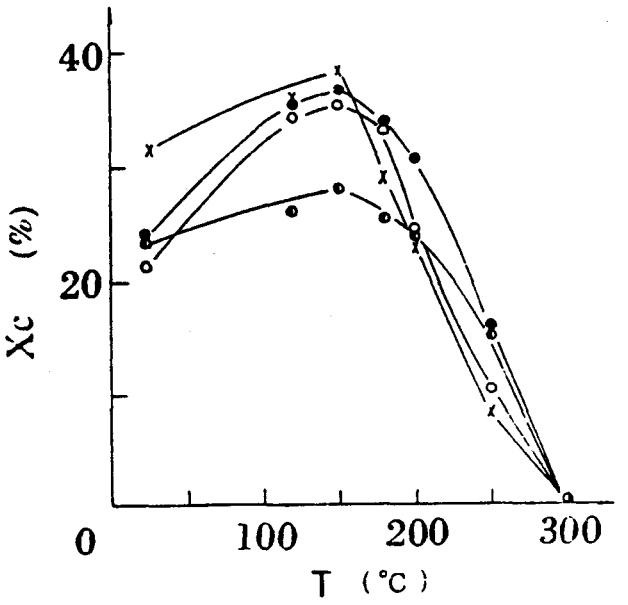


FIGURE 7 Relationship between Xc and the heat treatment temperature of different samples: (1) ● synthesized in 0.1N HCl and undoped by NH_4OH; (2) ○ synthesized in 0.1N H_2SO_4 and undoped by NH_4OH; (3) ◐ synthesized in 1N H_2SO_4; (4) × synthesized in 1N HCl.

crease in crystallinity, DSC and TGA measurements were carried out. The sample gives an endothermic peak at about 270°C during the first heating but does not show any endo- or exo-thermic effect during subsequent cooling and heating circles as shown in Figure 8. Therefore the endothermic peak at 270°C corresponds both the melting of PAn crystallinity and a certain chemical change. It is this chemical change that is responsible for the irreversibility. Because the weight loss determined by TGA up to 300°C was only 7% as shown in Figure 8(d), crosslinking or dehydrogenating may be more probable than decomposition of the molecular chain.[11]

Figure 9 consists of three scanning electron micrographs, showing the morphology of PAn after the heat treatments. At 150°C, PAn exhibits grain-like morphology and has larger grain size than at room temperature. The morphology is changed by the 300°C treatment as shown in Figure 9(c). It is lack of fine structure, indicating its amorphous nature.

In summary, normal PAn shows low crystallinity when it is polymerized and doped in an acidic (~1N) solution. Xc is dependent on

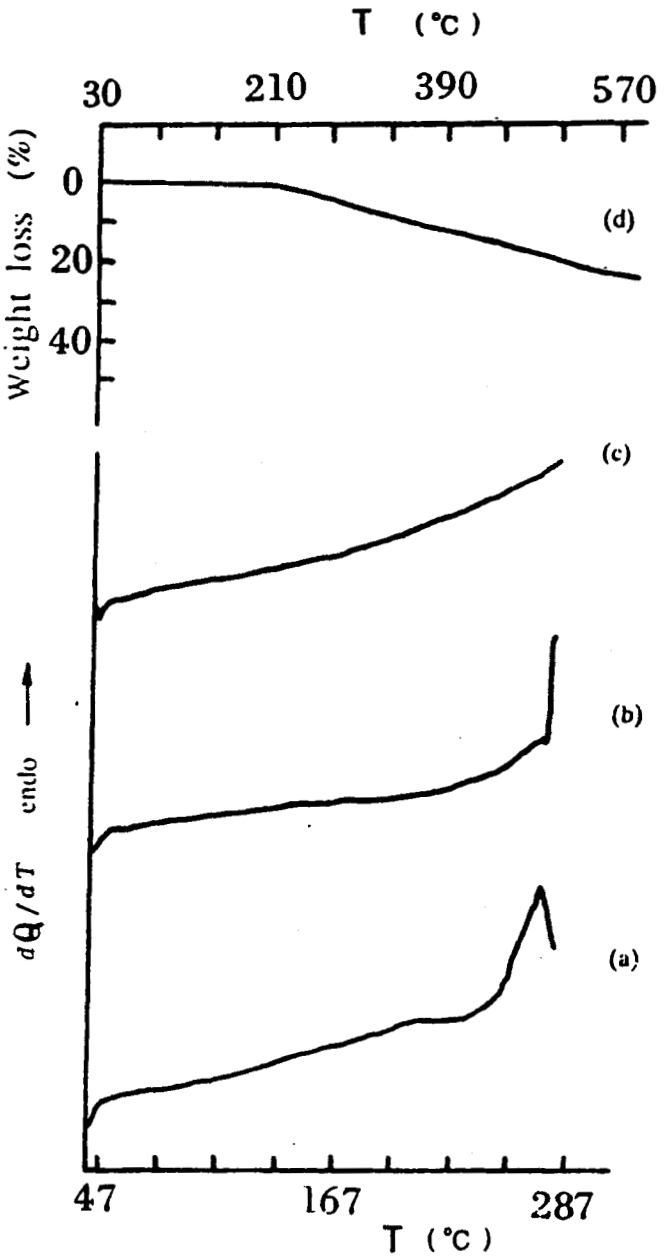


FIGURE 8 DSC and TGA curves of undoped PAn obtained in 0.1N HCl: (a) the first heating; (b) cooling; (c) the second heating.

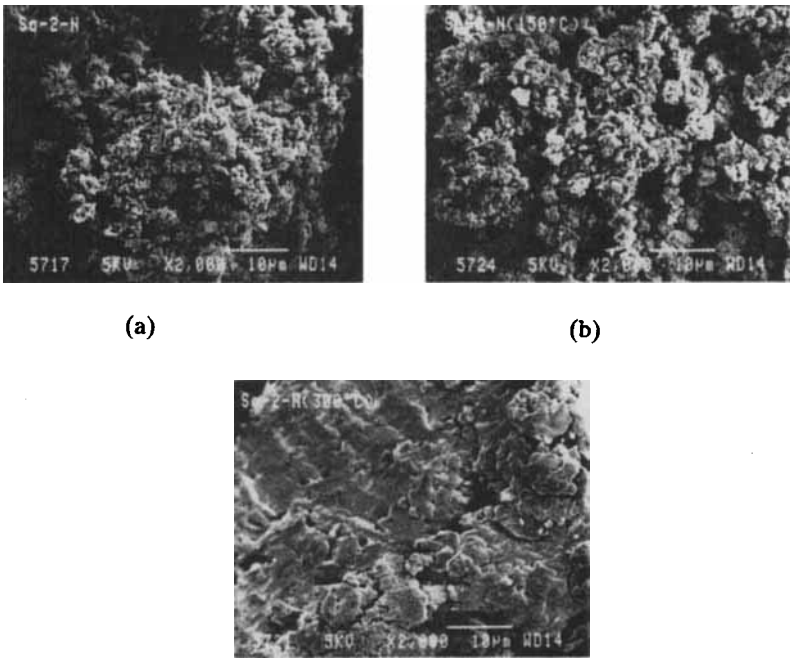


FIGURE 9 Effect of heat treatment temperature on the morphology of PAn obtained in 0.1N H_2SO_4.

the doping level. It becomes almost amorphous when it is undoped with NH_4OH. Heat treatment at up to 150°C is favorable to the crystallization of both doped and undoped PAn and heating at higher temperatures destroy its crystalline structure.

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