

# Synthesis and Properties of Novel Conducting Polyaniline Copolymers

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**ABSTRACT:** A novel copolymer based on aniline and *N*- $\beta$ -cyanoethylaniline was chemically prepared and characterized by a number of techniques including UV-vis, FTIR, ESR, XRD, and TGA. According to the systematic studies on the physical properties, it was found that the copolymers had excellent solubility in common organic solvents especially in DMF and pyridine, while the conductivity and yield decreased as the content of cyanoethyl group increased in the system. Moreover, an increase in the feed ratio of *N*- $\beta$ -cyanoethylaniline induced a blue-shift of the absorption bands in the UV-vis and IR region and significant line broadening of ESR

signals together with a reduction in spin density. The XRD patterns of the copolymers lost the characteristic diffraction peaks of emeraldine salt as the ratio of cyanoethyl group increased. The thermal stability of the copolymer was increased with increasing the feed molar ratio of *N*- $\beta$ -cyanoethylaniline. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 140–147, 2007

**Key words:** aniline; *N*- $\beta$ -cyanoethylaniline; conducting polymers; copolymerization

## INTRODUCTION

On account of its peculiar electronic-spatial structure, aniline has a number of valuable physicochemical characteristics. This fact has attracted the more interest for researchers to polymers of aniline and its derivatives, promoting more than 2000 publications on the topic.

Conducting polyaniline (PAN) exhibits extraordinary electronic properties, such as low ionization potential and high electron affinity; as a result, it can be easily reduced or oxidized. PAN has wide variety of applications in batteries, electromagnetic devices, biosensors, gas-separating membranes, electromagnetic shielding, and antistatic materials.<sup>1–5</sup> However, the common usage of this material has been restricted due to its insolubility, infusibility; modest environmental stability and incompatibility with common polymers due to the rigid chain originating from an extended conjugate double bond render it unprocessable.<sup>6</sup> To improve the solubility of PAN, various approaches have been developed. One of these methods is to substitute one or more hydrogen by the electron-donating groups, such as an alkyl, an alkoxy, an aryl hydroxyl, and an amino group,<sup>7–10</sup> or by the electron-withdrawing groups as halogen in an aniline nucleus, like a sulfo group, a carboxyl, an

acyl, and a cyano group.<sup>11–17</sup> Many researches<sup>18–21</sup> have studied different properties of polyaniline and polyacrylonitrile by blending method, while few articles were investigated on the chemical synthesis to prepare acrylonitrile derivatives of polyaniline. Recently, Siddaramaiah<sup>22</sup> has reported a new method to synthesize poly(aniline-co-acrylonitrile) to improve processability of polyaniline, however, they did not mention the solubility of the copolymer in detail.

In this article, a new polymer of poly(aniline-co-*N*- $\beta$ -cyanoethylaniline), which introduced cyano group on the PAN backbone by using *N*- $\beta$ -cyanoethylaniline (CNAn), was prepared by chemical oxidation method and the relationship of electrical conductivity, solubility, and molecular weight with chemical structure was examined systematically. Our present work can provide more useful information on the effect to the physical properties and chemical structures of polyaniline by introduction an electron-withdrawing group on the nitrogen site.

## EXPERIMENTAL

### Materials

Aniline (A.R., Xi'an Chemical Reagent Factory, China) was freshly distilled under reduced pressure before the use in experiments. Acrylonitrile (A.R., Tianjin Reagent Limited Company, China) was distilled before use. Anhydrous aluminum trichloride (A.R., Shanghai Meixing Company, China), hydroquinone (A.R., Tianjin Reagent Limited Company,

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China), and ammonium persulfate (APS) (A.R., Xi'an Chemical Reagent Factory, China) as well as other solvents were used as received without further purification.

### Preparation of *N*-β-cyanoethylaniline

*N*-β-cyanoethylaniline was prepared according to the method reported earlier.<sup>23</sup> The detailed procedures were described: 27.9 g of aniline, 0.2 g of hydroquinone, and 2 g of AlCl<sub>3</sub> with 40 g of distilled water were added into a three-neck flask. Acrylonitrile (19.1 g) was added drop by drop into the mixture below 60°C in an hour. Then the reaction was maintained at 70–80°C for 24 h. After that, the mixture were distilled under reduced pressure to remove excessive acrylonitrile and the crude product attained was washed by 5% (w/w) of aqueous HCl (20–30 mL) and distilled water (40 mL) until the pH value of the filtrate was 6–7, then snow-white powder was attained. The product to be used was dried in vacuum for 48 h.

### Polymerization

Poly(aniline-*co*-CNAn) was chemically synthesized by copolymerization of aniline and CNAn, using APS [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] as an oxidant. The mixture consisting of 1 mL of aniline (0.01M) and 0.73 g of CNAn (0.005M) was dissolved in 15 mL of 1M HCl. The temperature of solution was maintained at 0–5°C and constantly stirred for 4 h under nitrogen gas. To this solution was added drop by drop another solution of 3.45 g ammonium persulfate in 15 mL of 1M HCl. The reaction was continued for 24 h, after which a green precipitate was filtered. The filtrate was washed with 1M HCl until it became colorless, followed by washing with acetone. The precipitate named CP21-HCl was dried in vacuum oven at 60°C overnight. The undoped copolymer, CP21, was obtained by treating the precipitate with excessive NaOH solution and constantly stirring for 24 h. The powder was then collected on a Buchner

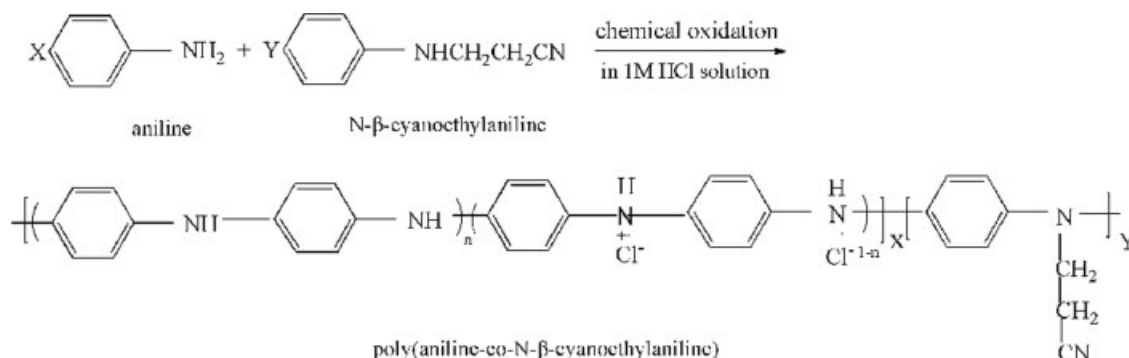
funnel and was washed with distilled water several times. The resulting powder was dried at 60°C for 24 h in a vacuum oven. Similar procedure was followed to synthesize CP11-HCl, CP11, CP12-HCl, CP12, poly(*N*-β-cyanoethylaniline)-HCl (PCNAn-HCl), PCNAn, PAn-HCl, and emeraldine base of PAn (PAn-EB).

The formation of copolymer using aniline and CNAn as comonomers can be described as shown in Scheme 1. There the value (1 - *n*) represents the doped state of PAn. The value of *n* can be varied from *n* = 1 (leucoemeraldine base) to *n* = 0 (pernigraniline salt). If *n* = 0.5 and HCl has been undoped by base, then the PAn is referred to emeraldine base-form PAn. Three feed molar ratio of aniline to CNAn was described by *X* : *Y* as 2 : 1, 1 : 1, and 1 : 2, respectively.

### Measurements

The electrical conductivity of PAn-HCl, PAn-EB, PCNAn-HCl, and PAn-*co*-PCNAn were measured using TH2818 Automatic Component Analyzer (Changzhou Apparatus Factory, China) at ambient temperature employing the two probe method on a pressed pellet according to the formula:  $\sigma$  (electrical conductivity) =  $L/RS$  (*L*, *R*, and *S* referred to the thickness, resistance, and touching area of the sample, respectively.). The pellets were obtained by subjecting the powder sample to a pressure of  $29.4 \times 10^3$  N. The reproducibility of the result was checked by measuring the resistance three times for each pellet. The molecular weights of the polymers were determined by the viscosity method. The intrinsic viscosity ( $[\eta]$ ) values of the polymers were measured for 15 mg/15 mL solutions in *N,N*-dimethylformamide (DMF) at 25°C. An Ubbelohde viscometer was used for the measurements and an average of three readings was taken for the calculation.

Electronic absorption spectra of the undoped polymers were recorded in *N*-methyl-2-pyrrolidone (NMP) solvent in the wavelength range of 280–800 nm at room temperature by using  $\lambda$  35 UV/vis spectrometer (Perkin-Elmer, U.S.A.). The chemical



Scheme 1 Preparation of poly(aniline-*co*-*N*-β-cyanoethylaniline).

**TABLE I**  
Yield, Conductivity, and Intrinsic Viscosity  
of Polyaniline Derivatived with Various  
Degrees of Cyanoethyl Group

Polymer	Yield (%)	Conductivity, $S$ ( $\text{cm}^{-1}$ )	$[\eta]^a$ (dL/g)
PAn-HCl	67.7	$1.40 \times 10^{-1}$	1.72
PAn-EB	—	$1.00 \times 10^{-8}$	—
CP21-HCl	63.2	$2.08 \times 10^{-5}$	0.75
CP11-HCl	60.4	$2.00 \times 10^{-7}$	0.29
CP12-HCl	60.0	$7.00 \times 10^{-8}$	0.23
PCNAn-HCl	38.8	$6.37 \times 10^{-9}$	0.28

<sup>a</sup> Viscosity of the polymer was determined in DMF.

structure of PAn and its copolymers were confirmed by recording infrared spectra using NEXUS 670 (Nicolet, U.S.A.) in the range of 400–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . The KBr pellet technique was adopted to prepare the sample for recording the IR spectra. The ESR spectra were recorded for solid PAn-HCl, PAn-EB, PCNAn-HCl, and PAn-co-PCNAn polymers, using ER200D-SRC spectrometer (Bruker, Switzerland). The sample tube was dried to remove the moisture before recording the spectrum. To obtain the  $g$ -value, ESR spectra of the PAn, PCNAn, and the copolymers were recorded under identical conditions of microwave frequency (9.48 GHz), microwave power (40 dB), modulation frequency (100 KHz), field set (3387 G), scan range (200 G), modulation intensity (2 Gpp), modulation time (200 s), and scan time (200 s). Thermal gravimetric analysis was recorded for homo- and copolymers using ZRY-2P (Shimadzu, Japan) at a heating rate of 10°C/min in nitrogen. The TGA profiles were taken over a temperature range of 25–800°C. X-ray powder diffractometer of XRD-6000 (Shimadzu, Japan) with germanium monochromatic Cu  $K\alpha$  ( $\lambda = 1.5406\text{\AA}$ ) radiation in a transmission mode, using a curved position sensitive detector in the 2 $\theta$  range from 28 to 808 at scan rate of 88/min, was applied to research the crystallinity of the copolymers.

## RESULTS AND DISCUSSION

### Physical properties and conductivity measurements

The intrinsic viscosity values that were measured for the polymers in DMF at 25°C lie in the range of

0.75–0.23 dL/g as shown in Table I. The data showed that the intrinsic viscosity of PAn-co-PCNAn dissolved in DMF decreased drastically with the increase in fraction of cyanoethyl group. The conductivity of the copolymer changed from  $10^{-5}$  to  $10^{-8}$   $S\text{ cm}^{-1}$  gradually with increase in cyanoethyl group. Compared with PAn-HCl, the conductivity of CP12-HCl was decreased by seven orders. The extended conjugation of  $\pi$  orbitals, believed to be responsible for conductivity in polymers, required coplanarity of the atoms involved in the  $\pi$ -cloud delocalization for maximum resonance interaction. The steric effect of the cyanoethyl group in the polymeric chain caused perturbation of the coplanarity of the  $\pi$  system, hence lowering the degree of conjugation as well as hindering charge transfer between chains, and also the effect of electron-withdrawing caused by cyano group led to decrease in electronic density of polyaniline backbone. The band gap increased, which would lead to the observed decrease in conductivity, in accordance with what reported for sulfonic ring-substituted polyaniline.<sup>24–26</sup> The yield of the polymers was determined by the formula:

$$\% \text{ Yield} = W_2/W_1 \times 100\%$$

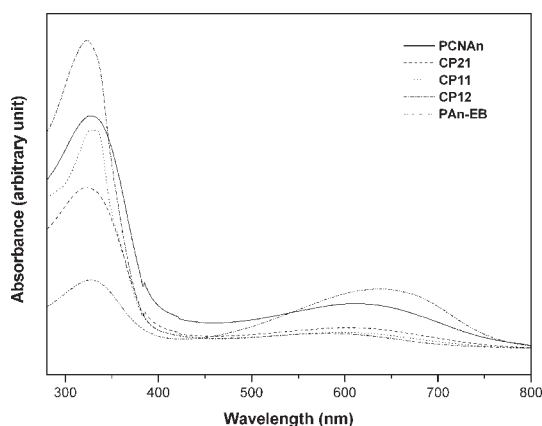
where  $W_1$  was the initial weight of the monomers and  $W_2$  was the weight of the resultant polymer. From Table I, it is demonstrated that the yield decreased drastically from 63.2 to 38.8% with increase in CNAn ratio from 33 to 100%. It can be concluded that the steric effect of cyanoethyl group on —NH— affects the structure of the chain and the molecular weight growth.

With the polarity of solvent increased, the solubility of the polymers increased obviously as shown in Table II. The same phenomenon was also observed with the increase in the content of cyanoethyl group from PAn-HCl to PCNAn-HCl, especially in the solvent of NMP. Compared with the PAn-HCl, all the copolymers had excellent solubility in pyridine. It agreed with the concept that the solid chains acted as “bound solvents” in the class of rigid polymers with flexible side chains.<sup>27</sup> In addition, the increase of solubility may be because of a lowering of the stiffness of polymeric chains. As a consequence of

**TABLE II**  
Solubility of PAn and PCNAn in Various Solvents

Polymer	$\text{H}_2\text{SO}_4(\text{conc.})$	DMF	NMP	Pyridine	THF	$\text{CHCl}_3$	Hexane
PAn-HCl	+	+	+	—	—	—	—
PAn-EB	++	++	++	++	+	—	—
CP21-HCl	++	++	+	++	—	—	—
CP11-HCl	++	++	+	++	—	—	—
CP12-HCl	++	++	++	++	—	—	—
PCNAn-HCl	++	++	++	++	—	—	—

++, well soluble; +, partially soluble; —, slightly soluble or insoluble.



**Figure 1** UV-vis spectra of PAN-EB, PCNAn, and the copolymers that were measured in NMP solution at room temperature.

the cyanoethyl group, these substituted polyaniline had some of the functional polar group that could participate in hydrogen bonds and solvation, thereby increasing their solubility in the strong polar solvents. The results were identical with the conclusion that the electrical conductivity decreased, while the solubility increased as substituted group increased in the copolymers.

### Spectra studies

#### UV-vis spectra analysis

The absorption spectra of PAN-EB, PCNAn, CP21, CP11, and CP12 were compared in Figure 1 with absorption ( $\lambda_{\text{peak}}$  values) values tabulated in Table III. It can be seen from Figure 1 that the spectra consist of two major absorption bands. The first one at 323–328 nm was assigned to the  $\pi$ - $\pi^*$  transition on the basis of earlier studies on PAN<sup>24</sup> and was related to the extent of conjugation between adjacent phenyl rings in the polymer chain. It exhibited a blue-shift from 328 to 323 nm as the proportion of the cyanoethyl group increased in the copolymer. The second absorption band that also showed a blue-shift from 636 nm in PAN-EB to 578 nm in PCNAn was assigned to the “exciton” transition caused by inter-chain or intrachain charge transfer.<sup>25</sup> This band has been found to be dependent on the overall oxidation state of the polymer.<sup>26,28</sup> These blue shifts of the benzenoid absorption peaks indicated the nonplanar conformation of the polymer backbone, since a more-distorted ring conformation was indicative of the reduction of conjugation length or the blue-shift of the absorption peak. Leclerc et al.<sup>29</sup> and Bredas et al.<sup>30</sup> also have reported that certain substituents can induce some nonplanar conformations that decrease the conjugation length (viz., decrease the absorption maximum) along the polymer backbone and thus give higher redox potentials.

#### FTIR spectra analysis

The IR data of PAN-HCl were illustrated as follows: bands at 1555 and 1476  $\text{cm}^{-1}$  were blue-shifted to 1589 and 1495  $\text{cm}^{-1}$  (appeared in PAN-EB), respectively. The presence of absorption peak at 1235  $\text{cm}^{-1}$  is attributed to the aromatic carbon-nitrogen stretching mode.<sup>31</sup> The aromatic C—H in-plane bending modes at 1009  $\text{cm}^{-1}$  were usually observed. The absorption band around 860  $\text{cm}^{-1}$  was characteristic of 1,4-substituted phenyl rings.<sup>22</sup> The FTIR data of PAN-EB were in good agreement with the previously reported results.<sup>31–35</sup> The main peaks at 1589 and 1495  $\text{cm}^{-1}$  corresponded to the quinone and benzene stretching ring deformation. The 1298  $\text{cm}^{-1}$  band was assigned to the C—N stretch of secondary aromatic amine. The 1163  $\text{cm}^{-1}$  peak was assigned to a characteristic vibration mode of the quinone ring. The out-of-plane deformation of C—H on 1,4-disubstituted ring was observed at 826  $\text{cm}^{-1}$ .

According to the ref.<sup>23</sup>, CNAn was obtained and the data of IR spectrum were discussed in the following. The main absorption bands at 3357, 2962, 2914, 2845, 2253, 1600, 1267, 1238, 1213, 751, and 693  $\text{cm}^{-1}$  were reasonably explained on the basis of the normal modes of CNAn. The intense sharp band at 3357  $\text{cm}^{-1}$  may be assigned to the N—H stretching mode. The absorption peaks at 2962, 2914, and 2845  $\text{cm}^{-1}$  can be attributed to the saturate C—H stretching mode. A peak at 2253  $\text{cm}^{-1}$  was due to —C $\equiv$ N group of CNAn. The strong sharp peak at 1600  $\text{cm}^{-1}$  was due to backbone vibration of phenyl ring. The absorption bands around 1267, 1238, and 1213  $\text{cm}^{-1}$  were characteristic of C—N stretching absorption. The peaks at 751 and 693  $\text{cm}^{-1}$  were typical single substituted phenyl rings.

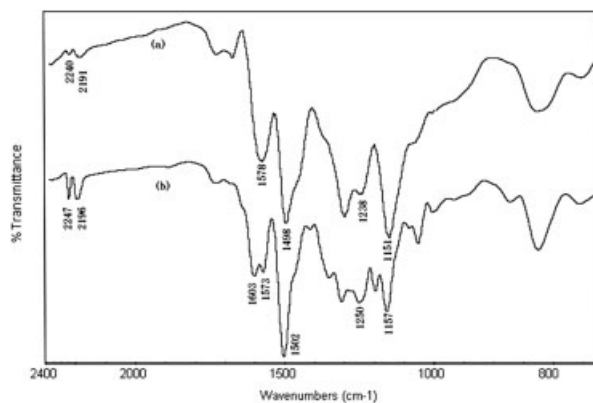
The IR spectrum of CP21-HCl and PCNAn-HCl was shown in Figure 2(a,b), respectively. With the exception of the —C $\equiv$ N absorption band at about 2200 and 2240  $\text{cm}^{-1}$ , the IR spectra of them showed the same characteristic absorption as that of PAN-HCl. The relative intensity of the —C $\equiv$ N stretching band increased as expected with increase in the loading of cyanoethyl group. Compared with that of PAN-HCl, the absorption bands at both spectra had blue shifts obviously. An increase in the feed ratio of

**TABLE III**  
Absorption Maxima of PAN-EB and Copolymers

Polymer	$\lambda^a$ (nm)	
PAN-EB	328	636
CP21	326	611
CP11	324	602
CP12	328	596
PCNAn	323	578

<sup>a</sup> Absorption of the polymers were tested in NMP solution.





**Figure 2** FTIR absorption spectra of (a) CP21-HCl and (b) PCNAn-HCl.

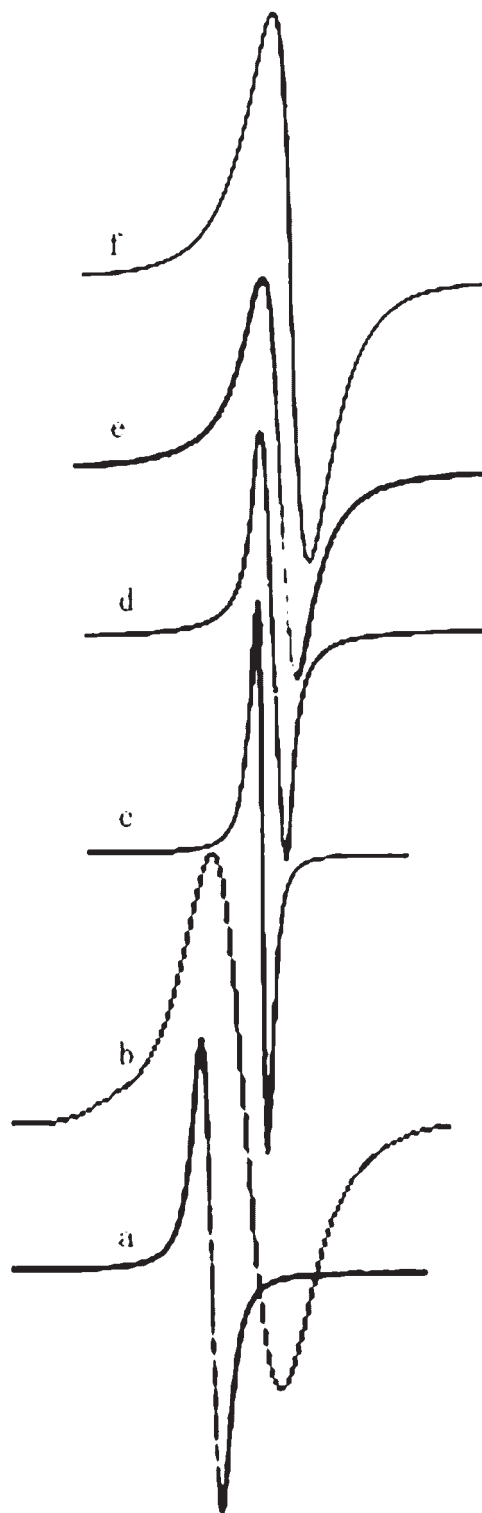
CNAn in the copolymer induced a blue-shift of the absorptions, for example, peak at 1578, 1498, 1238, and 1151  $\text{cm}^{-1}$  in Figure 2(a) was shifted to 1603, 1502, 1250, and 1157  $\text{cm}^{-1}$  in Figure 2(b), respectively. According to the two reasons, one was the steric effect of the cyanoethyl group in the polymer chain caused perturbation of the coplanarity of the  $\pi$  system, the other was the electron-withdrawing effect caused by cyanoethyl group which led to induction effect, then made bond force constant increased and absorption energy increased.

#### ESR spectra

The ambient temperature ESR spectra of PAN-HCl, PCNAn-HCl, and the copolymers were recorded in Figure 3. In Figure 3(a), the spectrum showed a single signal without any hyperfine splitting, which was the same for all copolymers with different compositions of CNAn. The intensity of the ESR signal, which was due to unpaired electrons, was decreased with increasing content of cyanoethyl group [shown in Fig. 3(c–f) and Table IV].

The data obtained from ESR spectra were recorded in Table IV. The  $g$ -value varied from 2.0051 to 2.0047, which were typical of the free radical in nitrogen atom of the polymers. The linewidth of ESR signal broadened from 2.8 to 3.6 G with increase in cyanoethyl group ratio in the copolymer. This broadened line was attributed to the intermolecular steric effect of the substituents, which confined the electron and reduced spin diffusion, and to the spin-density reduction, which corresponded to the poor polaron formation. Compared with the linewidth of PAN-HCl and CP21-HCl, the ESR spectrum of CP21-HCl was slightly narrower than that of PAN-HCl. It was expected that macromolecules with rigid structure showed shorter spin-lattice relaxation time,  $T_1$ , than those with flexible structure.<sup>36–38</sup> On the basis of

above concept, polyaniline had a shorter  $T_1$  and rigid structure compared to copolymer CP21-HCl, which had a longer  $T_1$  and flexible structure. The flexibility of CP21-HCl was due to the existence of cyanoethyl



**Figure 3** ESR spectra of (a) PAN-HCl, (b) PAN-EB, and the copolymers (c) CP21-HCl, (d) CP11-HCl, (e) CP12-HCl, and (f) PCNAn-HCl.

**TABLE IV**  
The *g*-Value, Linewidth and Gain-Value of PAN and its Copolymers

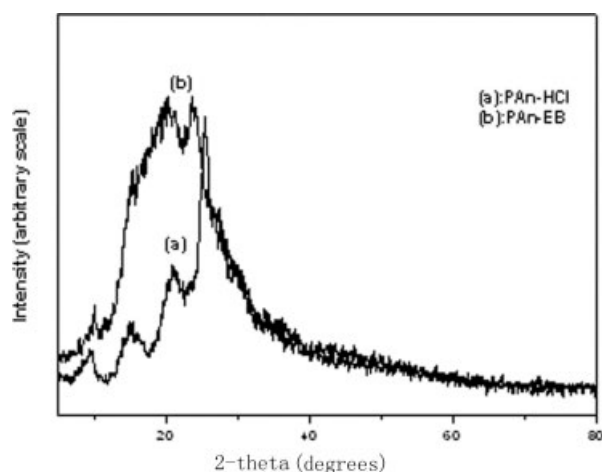
Polymer	<i>g</i> -Value	Linewidth, <i>G</i>	Gain-value <sup>a</sup>
PAn-HCl	2.0019	3.16	$1 \times 10^4$
PAn-EB	2.0048	12.12	$4 \times 10^4$
CP21-HCl	2.0051	2.90	$2 \times 10^2$
CP11-HCl	2.0049	3.16	$2 \times 10^2$
CP12-HCl	2.0047	3.69	$2 \times 10^2$
PCNAn-HCl	2.0051	9.22	$2 \times 10^3$

<sup>a</sup> The gain-value is a parameter which can be modified by the operator of ESR. It is valid to compare the intensity of ESR signal of the copolymers under the same gain-value.

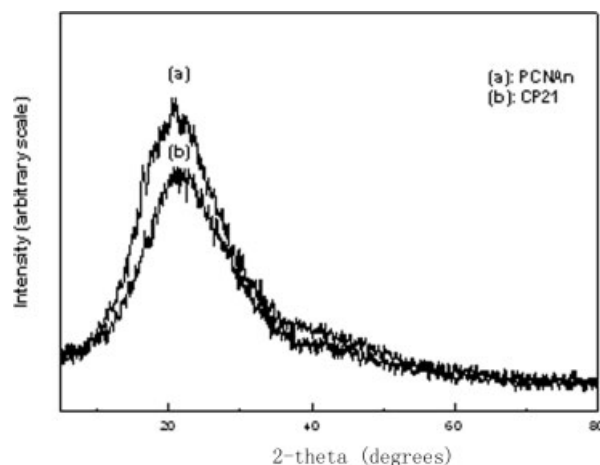
group in the polymer backbone, whereas polyaniline had a rather planar structure and conjugated electronic state. The linewidth of the ESR spectrum also showed a correlation with the conductivity, that is, the conductivity was decreased with an increase of the linewidth.

#### X-ray diffraction analysis

Wide angle X-ray diffractogram of the PAn-HCl, PAn-EB, PCNAn-HCl, and CP21-HCl was shown in Figures 4(a,b) and 5(a,b), respectively. It can be noticed from Figure 4 that four peaks at  $25.45^\circ$ ,  $21.04^\circ$ ,  $14.90^\circ$ , and  $9.44^\circ$  ( $2\theta$ ) for PAn-HCl, and at  $23.95^\circ$  and  $20.28^\circ$  ( $2\theta$ ) for PAn-EB were observed, respectively. The peak at  $25.45^\circ$  was due to the crystalline nature of PAn-HCl<sup>38</sup> and usually PAn-EB exhibited only a broad amorphous reflection at  $2\theta = 19^\circ$ .<sup>39</sup> From Figure 5, it demonstrated the crystallinity of PCNAn-HCl and CP21-HCl showed amorphous at about  $23^\circ$ , which were similar to that of PAn-EB. It illustrated if 33% (molar ratio) of CNAn was introduced in this copolymer, the crystalline



**Figure 4** X-ray diffraction patterns of (a) PAn-HCl and (b) PAn-EB.

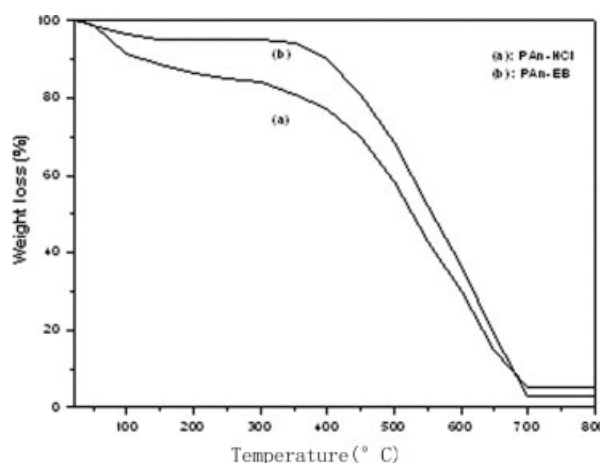


**Figure 5** X-ray diffraction patterns of (a) PCNAn-HCl and (b) CP21-HCl.

structure of PAn-HCl could be destroyed. This suggested that the polyaniline backbone alignment should be hindered by the side chains, which strongly supported again the concept of the intermolecular steric effect of the substituted cyanoethyl group.

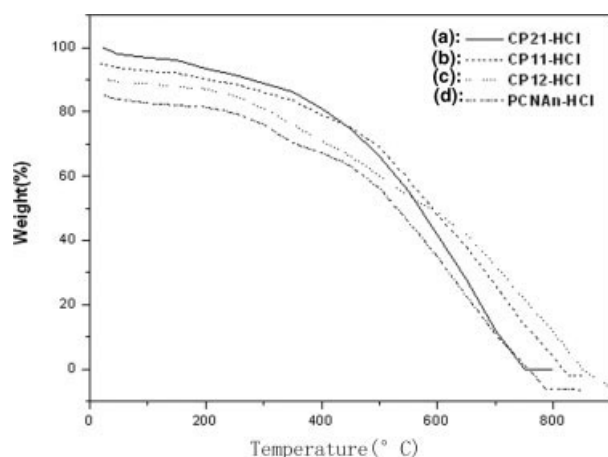
#### Thermal analysis

TGA thermogram for PAn-HCl and PAn-EB was shown in Figure 6(a,b), respectively. The TGA thermogram of CP21-HCl, CP11-HCl, CP12-HCl, and PCNAn-HCl was shown in Figure 7(a-d), respectively. From Figure 6(a,b), it can be seen that the typical PAn-HCl undergoes three-step thermal degradation processes, whereas PAn-EB shows only two-step thermal degradation behavior. In case of PAn-HCl,



**Figure 6** TGA thermograms of typical (a) PAn-HCl and (b) PAn-EB.

the first step weight loss occurred in the temperature range of 46.7–170°C with a mass loss of 12%, which was due to expulsion of loosely bounded water molecule and HCl on the surface of the polymer. The second step weight loss occurred in the range of 170–337.3°C with a weight loss of 7%, which can be attributed to the loss of dopant HCl. The third and final step weight loss occurred in the temperature range of 337.3–697.9°C with a mass loss of 79.5%. The weight loss in this step was due to degradation of main PAn-chain.<sup>40–44</sup> The typical thermal decomposition of PAn-EB only showed two-step weight loss between 52.7 and 209°C, and 350 and 702.9°C for first and second step with a mass loss of 4.4 and 91.4%, respectively. The first and second weight loss was attributed to the loss of water bounded to the polymeric chain and structural decomposition of polymer,<sup>45</sup> respectively. The temperature range of decomposition and the percentage weight loss for PAn-HCl, PCNAn-HCl, and their copolymers are given in Table V. It was found that PAn-PCNAn copolymers only showed two-step weight loss except for CP21-HCl. In all of them, the first step weight loss was besides that it was similar to PAn-HCl, which was due to the expulsion of loosely bounded water molecule, also included the loss of dopant and destruction of hydrogen bonds formed between polar group —CN and hydrogen atom on —NH— in polyaniline backbone. From initial temperature to 250°C, the slope of these curves decreased slightly [seen Fig. 7(b) to 7(c) and 7(d)]. It illustrated that the weight loss of the copolymers decreased slightly and also the association between molecules and polymeric chains through the formation of hydrogen bonds was responsible for higher thermal stability, as more energy was required to overcome the hydrogen bonds prior to the decomposition of the polymer



**Figure 7** TGA thermograms of PCNAn-HCl and the copolymers of PAn-*co*-PCNAn.

**TABLE V**  
TGA Results of Polymers

Polymer	Process	$T_i$ (°C)	$T_m$ (°C)	$T_f$ (°C)	Weight loss (%)
PAn-HCl	1	46.7	125	170	12.0
	2	170	—	337.3	7.0
	3	337.3	379.2	697.9	79.5
PAn-EB	1	52.7	—	209	4.4
	2	350	399.1	702.9	91.4
CP21-HCl	1	23	389.6	735.7	99.5
CP11-HCl	1	42	72	135	3.0
	2	135	—	830	96.0
CP12-HCl	1	52.7	—	237.1	3.3
	2	237.1	—	875	96.5
PCNAn-HCl	1	47.6	266.2	345.5	6.5
	2	345.5	499.2	754.9	85.3

$T_i$ , initial degradation temperature;  $T_m$ , maximum degradation temperature; and  $T_f$ , final degradation temperature.

backbone. The thermal stability of the copolymers was improved slightly with increase in the feed molar ratio of CNAn in the course of synthesizing the copolymers.

## CONCLUSIONS

A new kind of copolymer based on *N*-β-cyanoethylaniline and aniline were synthesized successfully by oxidative coupling using ammonium persulfate as the oxidant. The resultant copolymers had better solubility in common organic solvents especially in DMF and pyridine. However, the yield, the conductivity, and the molecular weight decreased with increase in the content of CNAn, which was due to the steric effect and electron-withdrawing effect of cyanoethyl group. Chemical structure of PAn, PCNAn, and the copolymers were confirmed by FTIR spectra. It showed a greater blue-shift if a higher content of CNAn was supplied. The undoped state of poly(aniline-*co*-*N*-β-cyanoethylaniline) in NMP solvent was confirmed by UV-vis spectra and showed an obvious blue-shift owing to the steric effect of the substituted cyanoethyl group. The linewidth in ESR spectra broadened obviously, while the conductivity decreased with increase in the feed ratio of cyanoethyl group. XRD studies revealed that the copolymers were amorphous in nature, as the introduction of cyanoethyl group destroyed the good crystallinity of PAn-HCl. From TGA thermograms, it was noticed that PAn-HCl underwent three-step thermal degradation process, whereas their copolymers underwent two-step weight loss. It revealed that the thermal stability of PAn-PCNAn copolymers was improved with increasing feed molar ratio of CNAn in the polymerization, which may be due to the hydrogen bond interaction between —CN and —NH—.

## References

1. Gustafsson, G.; Cao, Y.; Treay, G. M.; Klaretter, F.; Colaneri, N.; Hegger, A. J. *Nature* 1992, 357, 477.
2. Bartlett, P. N.; Patricia, B. M. A.; Sin, K. L. C. *Sens Actuators* 1989, 19, 125.
3. Anderson, M. R.; Mattes, B. R.; Reis, H.; Kaner, R. B. *Science* 1991, 252, 1412.
4. Kanatzidis, M. G. *Chem Eng News* 1990, 68, 36.
5. Trivedi, D. C.; Dhawan, S. K. In *Frontiers of Polymer Research*; Prasad, P. N.; Nigam, J. K., Eds.; Plenum: New York, 1992; p 419.
6. MacDiarmid, A. G.; Kaner, R. In *Handbook of Conducting Polymers*; Skotheim, T., Ed.; Marcel Dekker: New York, 1986; p 689.
7. Watanabe, A.; Mori, K.; Iwabuchi, A.; Iwasaki, Y.; Nakamura, Y. *Macromolecules* 1989, 22, 3521.
8. Gupta, M. C.; Umare, S. S. *Macromolecules* 1992, 25, 138.
9. Liao, Y. H.; Angelopoulos, M.; Levon, K. *J Polym Sci Part A: Polym Chem* 1995, 33, 2725.
10. Storrer, G. D.; Colbran, S. B.; Hibbert, D. *Synth Met* 1994, 62, 179.
11. Manohar, S. K.; MacDiarmid, A. G. *Synth Met* 1989, 29, E349.
12. Yue, J.; Epstein, A. J.; MacDiarmid, A. G. *Mol Cryst Liq Cryst* 1990, 189, 255.
13. Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. *J Am Chem Soc* 1991, 113, 2665.
14. Wei, X. L.; Wang, Y. Z.; Long, S. M.; Bobeczko, C.; Epstein, A. J. *J Am Chem Soc* 1996, 118, 2545.
15. Chan, H. S. O.; Ng, S. C.; Sim, W. S.; Tan, K. L.; Tan, B. T. G. *Macromolecules* 1992, 25, 6029.
16. Mikhael, M. G.; Padias, A. B.; Hall, H. K. *J Polym Sci Part A: Polym Chem* 1997, 35, 1673.
17. Sato, M.; Yamanaka, S.; Nkaya, J.; Hyodo, K. *Electrochim Acta* 1994, 39, 2159.
18. Huaiguo Xue.; Zhiquan Shen.; Chunmei Li. *Biosens Bioelectron* 2005, 20, 2330.
19. Park, Y. H.; Park, C. R. *Synth Met* 2001, 118, 187.
20. Talbi, H.; Just, P.; Hyphen, E.; Dao, L. H. *J Appl Electrochem* 2003, 33, 465.
21. Xue, H.; Shen, Z.; Zheng, H. *J Appl Electrochem* 2002, 32, 1265.
22. Jeevananda, T.; Sissaramaiah; Seetharamu, S.; Saravanan, S.; D'Souza, L. *Synth Met* 2004, 140, 247.
23. Liang, G. J.; Juan, L. J.; Zhao, Y.; Zhi, Y. *J Xiangnan Univ* 2004, 25, 55.
24. Euler, W. B. *Solid Commun* 1986, 57, 857.
25. Stafstrom, S.; Bredas, J. L.; Epstein, A. J.; Woo, H. S.; Tanner, D. B.; Huang, W. S.; MacDiarmid, A. G. *Phys Rev Lett* 1987, 59, 1464.
26. Asturias, G. E.; MacDiarmid, A. G.; McCall, R. P.; Epstein, A. J. *Synth Met* 1989, 29, E157.
27. Wen-Yue Zheng.; Kalle Levon.; Jukka Laakso.; Jan-Eric Österholm. *Macromolecules* 1994, 27, 7754.
28. Masters, J. G.; Sun, Y.; MacDiarmid, A. G.; McCall, R. P.; Epstein, A. J. *Synth Met* 1991, 41, 715.
29. Leclerc, M.; Daprano, G.; Zotti, G. *Synth Met* 1993, 55-57, 1527.
30. Bredas, J. L.; Street, G. B.; Themans, B.; Andre, J. M. *J Chem Phys* 1985, 83, 1323.
31. Dong, Q. *Infrared Spectral Method (in Chinese)*; Chemical Industry of Petroleum Press: Peijing, 1977.
32. McCall, R. P.; Roe, M. G.; Ginder, J. M.; Kusunoto, T.; Epstein, A. J. *Synth Met* 1989, 29, E433.
33. MacDiarmid, A. G.; Manohar, S. K.; Masters, J. G.; Sun, Y.; Weiss, H.; Epstein, A. J. *Synth Met* 1991, 41-43, 621.
34. Quillard, S.; Louarn, G.; Buisson, J. P.; Boyer, M.; Lapkowski, M.; Pron, A.; Lefrant, S. *Synth Met* 1997, 84, 805.
35. Zeng, X.-R.; Ko, T.-M. *Polymer* 1998, 39, 1187.
36. Ito, O.; Seki, H.; Iino, M. *Bull Chem Soc Jpn* 1987, 60, 2967.
37. Seki, H.; Ito, O.; Iino, M. *Energy Fuels* 1988, 2, 321.
38. Duber, S.; Wieckowski, A. B. *Fuel* 1982, 61, 433.
39. Pouget, J. P.; Jozefowicz, M. E.; Epstein, A. J.; Tang, X.; MacDiarmid, A. G. *Macromolecules* 1991, 24, 779.
40. Khor, S. H.; Neoh, K. G.; Kang, E. T. *J Appl Polym Sci* 1990, 40, 2015.
41. Yue, J.; Epstein, A. J.; Zhong, Z.; Gallagher, P. K.; MacDiarmid, A. G. *Synth Met* 1991, 41, 765.
42. Wei, Y.; Hsueh, K. F. *J Polym Sci Part A: Polym Chem* 1989, 27, 4351.
43. Zeng Xingrong.; Gong Kecheng. *Synth Mater Aging Appl* 2001, 4, 8.
44. Palaniappan, S.; Narayana, B. H. *J Polym Sci Part A: Polym Chem* 1994, 32, 2431.
45. Chandrakanthi, N.; Careem, M. A. *Polym Bull* 2000, 44, 101.