

# Thermal and Morphological Studies of Chemically Prepared Emeraldine-Base-Form Polyaniline Powder

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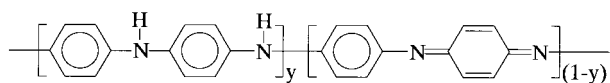
**ABSTRACT:** In this study, emeraldine base (EB)-form polyaniline (PANI) powder was chemically prepared in 1M HNO<sub>3</sub> aqueous solution. The thermal characteristics and chemical structures of this powder were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). A polarizing optical microscope was also used to examine the crystalline morphology of this sample. The results indicated that the EB-form PANI powder had a discernible moisture content. Moreover, in the first run of DSC thermal analysis, the exothermic peak at 170–340°C was due to the crosslinking reaction occurring among the EB-form PANI molecular chains. FTIR and XRD examinations further confirmed the chemical crosslinking reaction during thermal treatment. TGA results illustrated that there were two major stages for weight loss of the

EB-form PANI powder sample. The first weight loss, at the lower temperature, resulted from the evaporation of moisture. The second weight loss, at the higher temperature, was due to the chemical structure degradation of the sample. The degradation temperature of the EB-form PANI powder was around 420–450°C. The degradation temperature of emeraldine salt (ES)-form PANI powder was lower (around 360–410°C) than that of the EB form (around 420–450°C). From the TGA results, I roughly estimated that 2.74 aniline repeat units, on average, were doped with 1 HNO<sub>3</sub> molecule in the ES-form PANI. I found a single crystalline morphology of EB-form PANI, mostly like a conifer leaf. More complex, multilayered dendritic structures were also found. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2142–2148, 2003

**Key words:** thermal properties; FT-IR; X-ray; morphology

## INTRODUCTION

Polyaniline (PANI) is an important member in the family of intrinsically conducting polymers (ICPs). MacDiarmid et al.<sup>1</sup> illustrated that the chemical structure of PANI could be schematically represented by the following formula:



where the value  $1 - y$  represents the oxidation state of PANI. The value of  $y$  can be varied from  $y = 1$  (leucoemeraldine base) to  $y = 0$  (pernigraniline base). If  $y = 0.5$ , the PANI is referred to as emeraldine base (EB)-form PANI. This EB-form PANI cannot be dissolved in common organic solvents. However, it can be dissolved in 1-methyl-2-pyrrolidinone (NMP). Then, freestanding EB-form PANI films can be cast from the NMP solution.<sup>2,3</sup> Moreover, EB-form PANI can be doped in a protonic acid, such as HCl or H<sub>2</sub>SO<sub>4</sub>, and transferred to emeraldine salt (ES)-form PANI,

with a moderately high conductivity up to 10–100 S/cm.

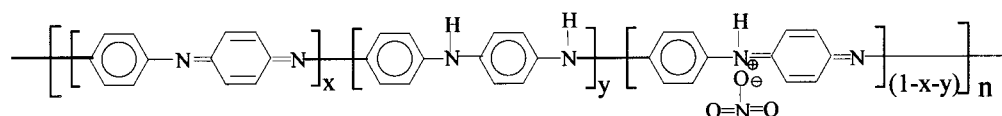
Generally speaking, chemical oxidization and electrochemical synthesis are the two major routes for the preparation of PANI.<sup>4,5</sup> The chemical oxidation polymerization process is particularly important because this synthesis is the most feasible method for producing PANI powder on a large scale. Because PANI has an excellent environmental stability and unique electrochemical properties, many applications of PANI have been studied and developed, such as secondary batteries,<sup>6,7</sup> biosensors,<sup>8,9</sup> corrosion protections,<sup>10,11</sup> and antistatic packaging materials.<sup>12</sup> However, due to its poor thermal processing properties the commercial applications of PANI have been restricted.<sup>4</sup> There have been several reports focusing on the thermal and mechanical properties of PANI. Wei et al.<sup>3</sup> investigated the thermal transitions and mechanical properties of films of chemically prepared PANI. They also studied the thermal characteristics of chemical oxidative synthesized PANI doped with various dopants.<sup>13</sup> Chen et al.<sup>5</sup> studied the thermal analysis, structure, and doping behavior of chemically prepared PANI plasticized with NMP. Stevenson et al.<sup>14</sup> investigated the thermal degradation of HCl-doped EB-form PANI. Gregory et al.<sup>15</sup> studied the thermal characteristics of chemically prepared PANI powder. Chandrakanthi and Careem<sup>16</sup> reported a study on the thermal proper-

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ties to examine the thermal stability of this material and to identify the optimum processing and maximum application temperatures.

In the previously mentioned studies, the acidic polymerization media were almost 1M HCl aqueous solution. According to Wang's research,<sup>17</sup> the yield and electrical conductivity of the ES-form PANI prepared

in 1M HNO<sub>3</sub> aqueous solution was higher than in 1M HCl aqueous solution. Therefore, in this study, we used 1M HNO<sub>3</sub> aqueous solution as the acidic polymerization media to prepare EB-form PANI powder. The chemical structure of the ES-form PANI doped by HNO<sub>3</sub> can be schematically represented by the following formula:



The charged NO<sub>3</sub><sup>-</sup> group of HNO<sub>3</sub> associates with the positively charged backbone through Coulomb attractions. The ES-form PANI is not soluble in common organic solvents. In this study, we also tried to estimate how many aniline repeating units, in average, doped with 1 HNO<sub>3</sub> molecule in the ES-form PANI from the results of thermogravimetric analysis (TGA).

Also, the thermal properties of the PANI powder were studied with differential scanning calorimetry (DSC) and TGA. We also studied the crystallinity and chemical structure of thermally untreated and treated EB-form PANIs with X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), respectively. Through these studies, the thermal stability of EB-form PANI powder could be examined in more detail. Moreover, to our knowledge, the crystalline morphology of EB-form PANI crystallized from solution was not revealed. Therefore, in this study, we prepared 0.1 wt % EB-form PANI in an NMP solution and observed the crystalline morphology of EB-form PANI with a polarizing optical microscope.

## EXPERIMENTAL

### Materials

Synthesis-grade aniline, ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), and NMP were purchased from Merck (Germany). Nitric acid (65 wt %) was purchased from Union Chemical Works, Ltd. (Taiwan) All reagents were used as received.

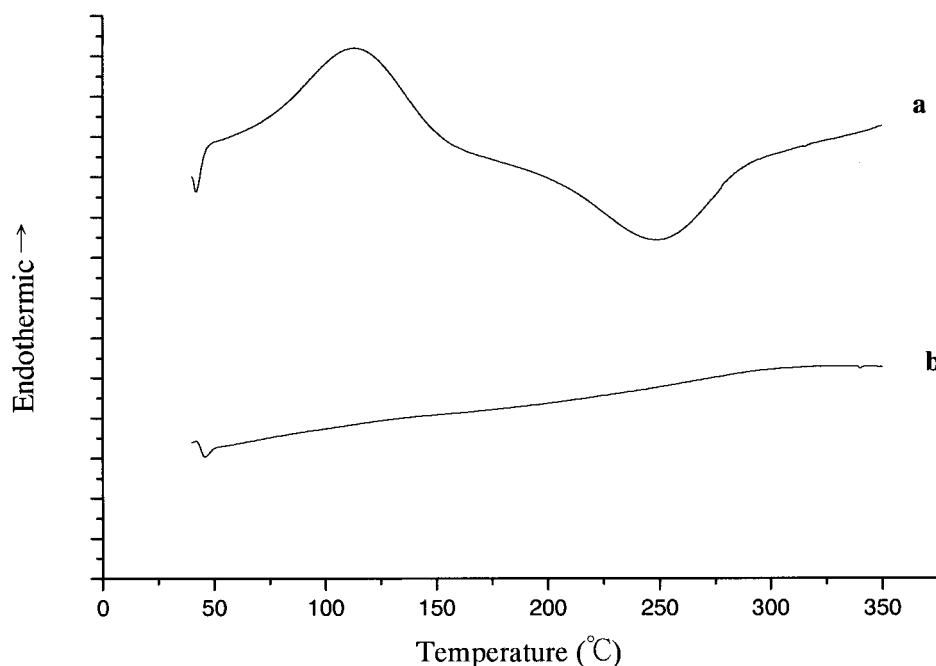
### Preparation of EB-form PANI powder

In this study, EB-form PANI powder was prepared by chemical oxidation with ammonium persulfate on the basis of the procedure described by Cao et al.<sup>2</sup> and Chen et al.<sup>5</sup> Two solutions were prepared previously. Solution A was 200 mL of 1M HNO<sub>3</sub> aqueous solution containing 8 mL of aniline (0.44M). Solution B was 200 mL of 1M HNO<sub>3</sub> aqueous solution containing 20 g of ammonium persulfate (0.44M). The molar ratio of aniline to ammonium persulfate was 1:1. A 1000-mL

four-necked flat-bottomed reactor was used to prepare the PANI powder. A stirrer was put in the reactor to ensure proper mixing. Then, the reactor was kept under vigorous stirring. After that, solution A was poured into this reactor, which was placed into an ice bath, which contained salt and was equipped with a thermometer. After the temperature of solution A was cooled to 0°C, solution B was then slowly added drop by drop into solution A over a period of 150 min. Because the oxidation of aniline is highly exothermic, the addition rate of solution B was properly controlled to prevent any sharp temperature increase because of the polymerization reaction. After 24 h, the precipitated dark green ES-form PANI was recovered from the reaction mixture. Then, this material was filtered and washed with 400 mL of 0.1M HNO<sub>3</sub> solution followed by 400 mL of distilled water until the filtrate was colorless. Furthermore, the precipitate was washed again with methanol until the methanol filtrate was colorless to remove oligomers and other byproducts. Then, the prepared ES-form PANI was converted to EB-form PANI by stirring with 400 mL of 1M NH<sub>4</sub>OH solution at room temperature for another 24 h. At the end of the stirring, the material was filtered and dried under a dynamic vacuum for 48 h. Finally, 6.41 g of the dark blue EB-form PANI powder was obtained (78.1% yield).

### DSC thermal analysis

A differential scanning calorimeter (PerkinElmer model DSC 7, USA) was used to examine the thermal properties of the EB-form PANI powder in a temperature range from room temperature to 350°C at a heating rate of 20°C/min. After the first run finished, the sample pan containing the EB-form PANI powder was cooled to room temperature naturally. Then, this sample pan was reheated from room temperature to 350°C at a heating rate of 20°C/min again. Thermograms for these two conditions were recorded, analyzed, and compared.



**Figure 1** DSC thermal analysis curves of EB-form PANI powder under a  $N_2$  atmosphere: (a) first run and (b) second run (heating rate =  $20^\circ\text{C}/\text{min}$ ).

### FTIR analysis

The chemical structure of the EB-form PANI powder prepared by chemical oxidation was identified by FTIR (Bio-Rad model FTS-155, USA) in the wavenumber range  $400\text{--}4000\text{ cm}^{-1}$  with the number of scans equal to 16. Also, to examine the influence of thermal treatment on the chemical structure of the EB-form PANI, the sample analyzed by DSC was also examined by FTIR. I prepared all of the EB-form PANI specimens for FTIR analysis by grinding powdery samples with KBr powder (weight ratio  $\approx 1:99$ ) and then pressing the mixture into tablets.

### TGA

TGA (PerkinElmer model TGA 7, USA) was conducted to measure the weight loss of the EB-form PANI powder in a temperature range from room temperature to  $700^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$  under a nitrogen stream. The weight loss of ES-form ( $\text{HNO}_3$ -doped) PANI powder in a temperature range from room temperature to  $700^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}/\text{min}$  under a nitrogen stream was also examined.

### XRD analysis

XRD (Rigaku model D-MAX-2B) was used to analyze different EB-form PANI powder samples. One sample was unannealed. The other three samples were annealed at 100, 200, and  $300^\circ\text{C}$  for 1 h, respectively, and were then slowly cooled to room temperature. XRD

results were obtained in a range from  $5$  to  $50^\circ$  ( $2\theta$ ) at a scan rate of  $4^\circ/\text{min}$ .

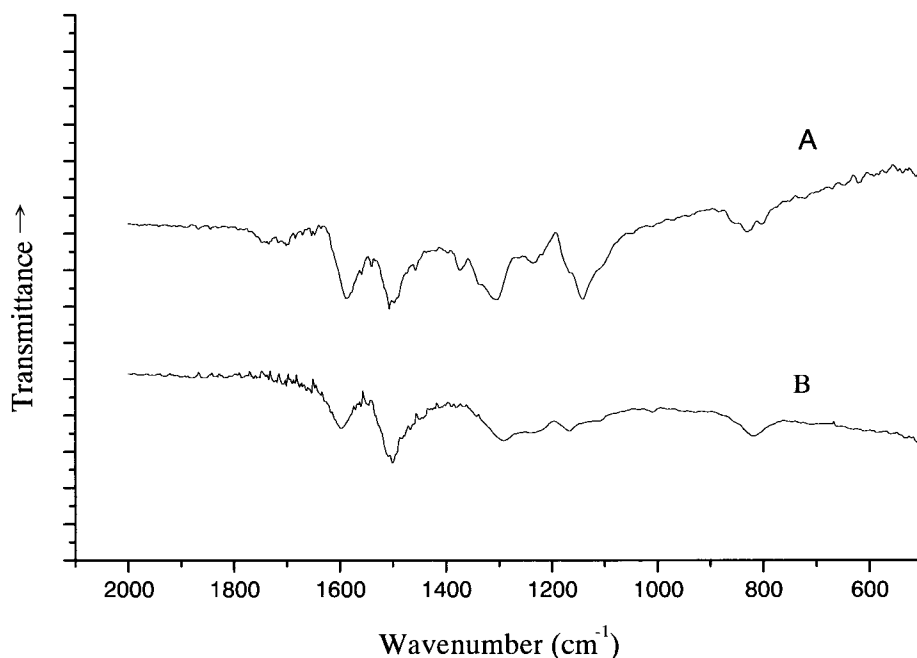
### Morphological examination

EB-form PANI powder (0.01 g) was dissolved in 10 mL of NMP to form a dark blue solution. For polarizing optical examination, a drop of NMP solution containing the EB-form PANI was placed onto a slide. Then, this slide was dried under a dynamic vacuum at  $60^\circ\text{C}$  for 48 h. After that, a polarizing optical microscope (model Olympus BH2-UMA, Japan) was used to examine the crystalline morphology of the EB-form PANI.

## RESULTS AND DISCUSSION

### DSC thermal analysis

Two DSC thermal analysis curves are shown in Figure 1. Figure 1(a) is the DSC thermogram of the EB-form PANI powder in the first run. There were two peaks in Figure 1(a), an endothermic peak at  $50\text{--}160^\circ\text{C}$  and an exothermic peak at  $180\text{--}340^\circ\text{C}$ . According to studies reported previously<sup>1-3</sup>, the EB PANI powder had a discernible moisture content. Therefore, the endothermic peak was most likely due to the vaporization of water. This was in agreement with the TGA results. The chemical process related to the exothermic peak was due to a crosslinking reaction. This crosslinking reaction resulted from a coupling of two neighboring  $\text{—N=Q=N—}$  groups (where Q represents the qui-



**Figure 2** FTIR spectra of EB-form PANI powder: (A) unanalyzed and (B) analyzed by DSC (first run).

noid ring) to give two  $\text{—NH—B—NH—}$  groups (where B represents the benzenoid ring) through a link of the N with its neighboring quinoid ring, as suggested by Scherr et al.<sup>18</sup> Figure 1(b) shows the DSC thermogram of the EB-form PANI powder in the second run. There were almost no significant endothermic or exothermic peaks, as shown in Figure 1(b), because no apparent moisture existed in the sample. Moreover, a crosslinking reaction occurred during the first-run DSC thermal treatment and resulted in a three-dimensional (3-D) chemical structure of EB-form PANI. Therefore, no apparent exothermic peak was observed.

#### FTIR analysis

To investigate whether the crosslinking reaction really occurred, the FTIR examination was conducted at room temperature. Two EB-form PANI powder samples were examined (untreated and treated by DSC thermal analysis). The results are illustrated in Figure 2. Figure 2(A) shows the FTIR results of the EB-form PANI powder without DSC thermal analysis. Figure 2(B) shows the FTIR results of the EB-form PANI powder treated by DSC thermal analysis (first run). The intensity ratios of the FTIR absorption of the  $\text{C=C}$  stretching vibration of quinoid rings ( $1592\text{ cm}^{-1}$ ) to that of benzenoid rings ( $1508\text{ cm}^{-1}$ ) and the electronic-like absorption peak of  $\text{—N=Q=N—}$  ( $1150\text{ cm}^{-1}$ ) both decreased when the EB-form PANI powder was treated by DSC thermal analysis. These results proved the occurrence of the crosslinking reaction from quinoid rings to benzenoid rings. Figure 3 illustrates the thermal crosslinking reaction among EB-form PANI

molecular chains.<sup>18</sup> Similar results were obtained by Chen et al.<sup>5</sup> and Gregory et al.<sup>15</sup>

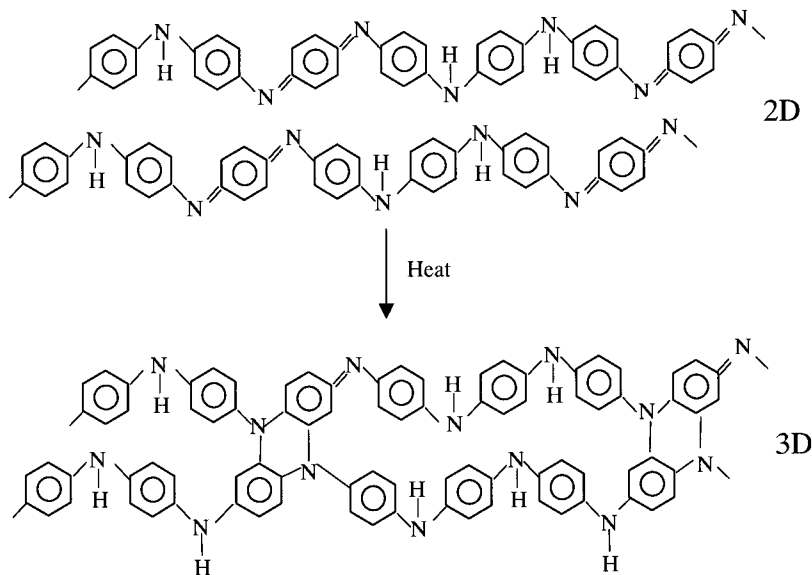
#### TGA

Figure 4 shows that the moisture and  $\text{HNO}_3$  contents of the ES-form PANI were around 10% ( $\Delta Y_1$ ) and 18% ( $\Delta Y_2$ ), respectively. Therefore, the weight percentage of PANI should have been around 72%. To estimate how many aniline repeating units doped with 1 molecule in PANI, I set up eq. (1):

$$\frac{100 - \Delta Y_1 - \Delta Y_2}{\Delta Y_2} = \frac{M_1 \times X}{M_2 \times 1} \quad (1)$$

where  $\Delta Y_1$  and  $\Delta Y_2$  are the weight losses of moisture and  $\text{HNO}_3$ , respectively;  $M_1$  and  $M_2$  are the molecular weights of aniline and  $\text{HNO}_3$ , respectively; and  $X$  is the number of aniline repeating units. Therefore, according to eq. (1), I substituted  $\Delta Y_1$ ,  $\Delta Y_2$ ,  $M_1$ , and  $M_2$  with 10, 18, 92, and 63, respectively. Then, I obtained the value of  $X$  at around 2.74. This implied that there were roughly 2.74 aniline repeat units, on average, doped with 1  $\text{HNO}_3$  molecule in the ES-form PANI.

Figure 5 shows the TGA results of the EB-form and ES-form PANI powders under a  $\text{N}_2$  atmosphere. For the EB-form, there were two major stages for the weight loss of the PANI powder sample. The first weight loss, at around  $100^\circ\text{C}$ , resulted from the evaporation of moisture, which was consistent with the DSC results.<sup>15</sup> The second weight loss, at the higher temperature, indicated chemical structure degrada-



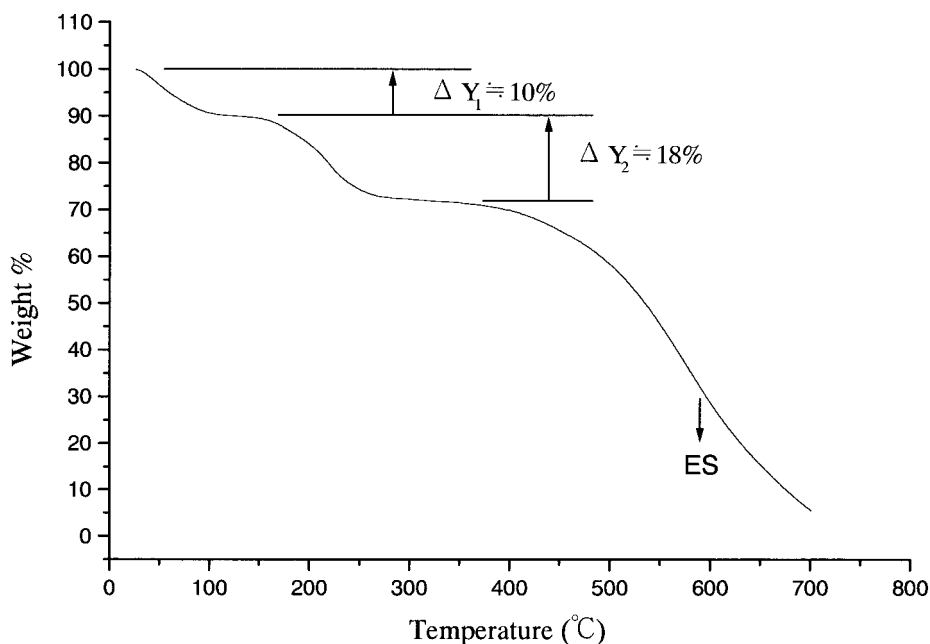
**Figure 3** Thermal crosslinking reaction among EB-form PANI molecular chains.

tion of the PANI molecule; the degradation temperature was around 420–450°C. For the ES-form PANI powder, there were three major stages for weight loss, around 100, 200, and 360–410°C, which were assigned to the removal of moisture, HNO<sub>3</sub>, and the degradation of the PANI molecule, respectively. This apparently indicated that the degradation temperature of the EB-form PANI powder was higher than that of the ES form. This may have been caused from the HNO<sub>3</sub> gas formed during the heating process; this strong acid vapor accelerated the degradation of the ES-form PANI powder. Also, this showed that the moisture content of the ES-form PANI powder was higher than

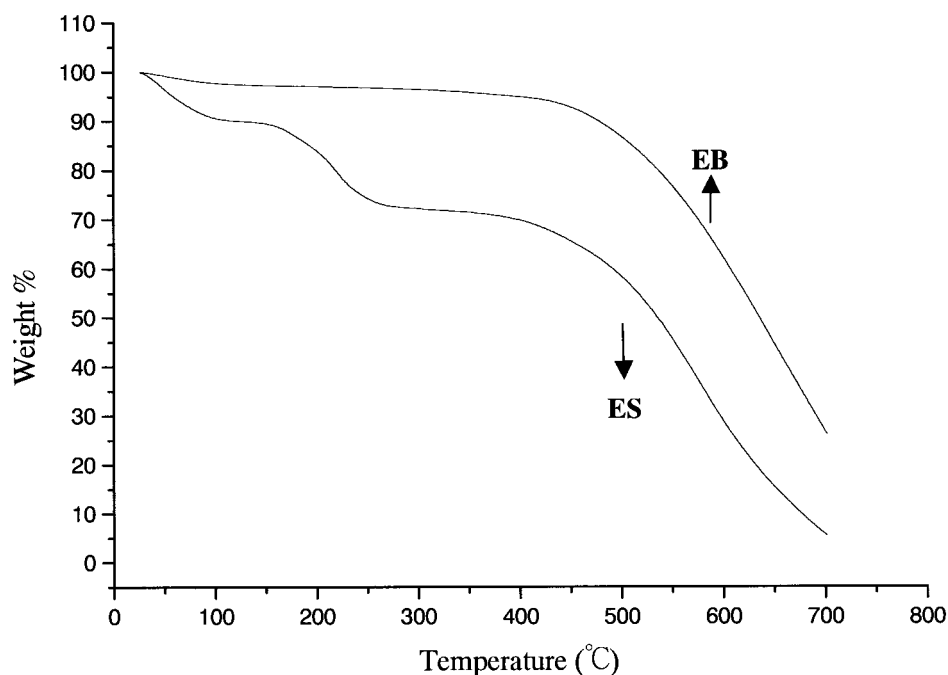
that of the EB form, as shown in Figure 5. This result was similar to that of the HCl-doped ES-form PANI powder reported by Wei et al.<sup>3</sup>

#### XRD analysis

Figure 6 illustrates three XRD spectra of unannealed and annealed (200 and 300°C) EB-form PANI powder samples. For the unannealed EB-form PANI powder sample [Fig. 6(a)], the XRD result indicated a broad amorphous diffraction peak around 20° and two weak crystalline peaks at around 10, 15, and 25°. Because the



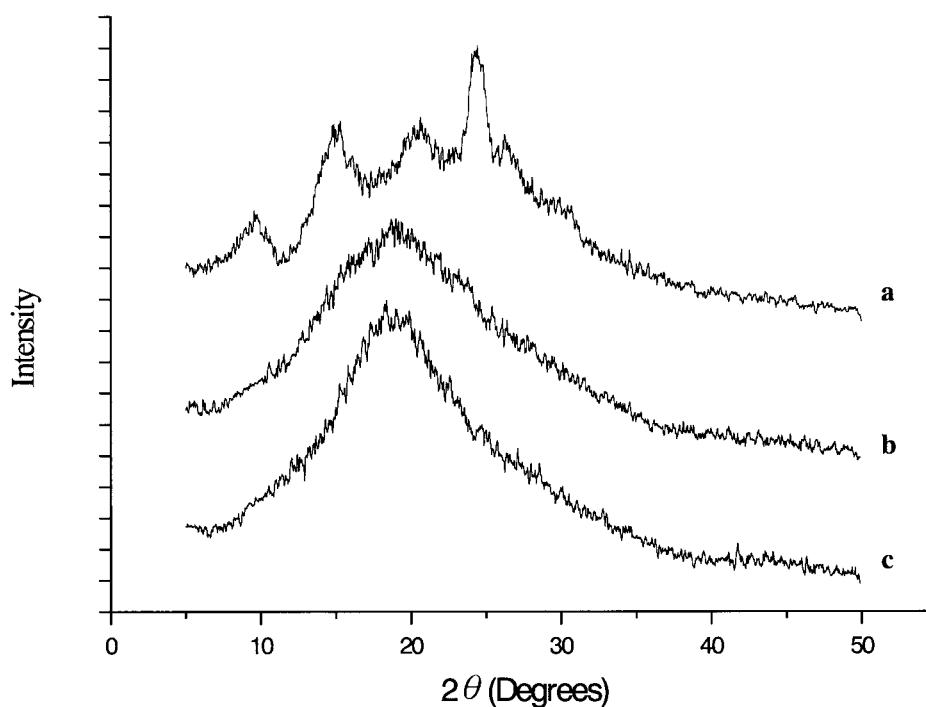
**Figure 4** TGA curve of ES-form PANI powder under a nitrogen stream (heating rate = 20°C/min).



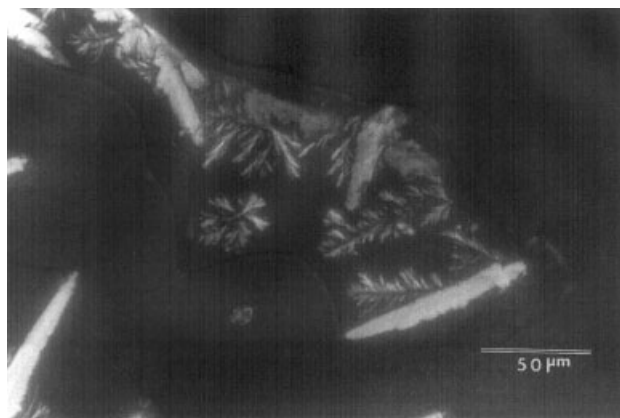
**Figure 5** TGA curves of EB-form and ES-form PANI powder samples under a nitrogen stream (heating rate = 20°C/min).

XRD result of the annealed sample (100°C) was almost same as that of unannealed sample, the XRD curve of the annealed sample (100°C) is not shown in Figure 6. This indicated that the temperature (100°C) was not higher enough to make a chemical crosslinking reaction during the annealing process. For the annealed EB-form PANI powder samples at 200 and 300°C, the

XRD results [Fig. 6(b,c)] indicated that they were completely amorphous. These results confirmed the conclusion that a chemical crosslinking reaction was involved during the annealing process. This chemical crosslinking resulted in forming a 3-D structure and decreasing the crystallinity of EB-form PANI powder apparently.



**Figure 6** XRD spectra of three different EB-form PANI powder samples: (a) unannealed, (b) annealed at 200°C for 1 h, and (c) annealed at 300°C for 1 h.



**Figure 7** Polarizing micrograph of crystalline EB-form PANI under an optical microscope at 530 $\times$  (the specimen was crystallized from an NMP solution containing EB-form PANI).

### Morphological examination

Figure 7 illustrates the polarizing micrograph of crystalline EB-form PANI. I observed a single crystalline morphology of EB-form PANI, mostly like a conifer leaf. As shown in Figure 7, I also found more complex multilayered dendritic structures. Generally, for polymers crystallized from the bulk, the end result is typically the formation of spherulites. For polyethylene, the initial crystalline structure formed is a single crystal with folded-chain lamellae. These quickly lead to the formation of sheaf-like structures called *axialites* or *hedrites*. As growth proceeds, the lamellae develop on either side of a central reference plane. The lamellae continue to fan out, occupying increasing volume sections through the formation of additional lamellae at appropriate branch points.<sup>19</sup> However, from the polarizing micrograph in Figure 7, the crystalline morphology of the EB-form PANI was a little different from that of polyethylene. From the thermal analysis results, I observed the chemical crosslinking reaction occurring among EB-form PANI molecule chains at above 170°C. Therefore, it was difficult to observe the crystalline morphology of the EB-form PANI under hot melt and cooling processes.

### CONCLUSIONS

DSC thermal analysis curves indicated that the EB-form PANI powder had a discernible moisture content. This phenomenon was in agreement with the TGA results. Moreover, in the first run of the DSC thermal analysis, an exothermic peak at 170–340°C was found. This peak was due to the chain crosslinking, resulting from a coupling of two neighboring  $-\text{N}=\text{Q}=\text{N}-$  groups to give two  $-\text{NH}-\text{B}-\text{NH}-$  groups through a link of the N with its neighboring

quinoid ring. The FTIR examinations further confirmed the chemical crosslinking reaction among the EB-form PANI molecular chains. TGA results illustrated that the degradation temperature of the EB-form PANI powder was around 420–450°C. Also, from the TGA curve of the ES-form PANI, I estimated that 2.74 aniline repeating units, on average, doped with 1  $\text{HNO}_3$  molecule. The XRD results showed that the unannealed EB-form PANI powder had a small amount of crystallinity. However, for the annealed EB-form PANI powder sample (at 200°C or 300°C for 1 h), there was only a broad amorphous diffraction peak. This phenomenon again illustrated that if the thermal energy was high enough, the chemical crosslinking reaction occurred among the EB-form PANI molecular chains. The polarizing micrograph of the crystalline EB-form PANI was successfully revealed. I found the single and the more complex multilayered dendritic crystalline morphologies of the EB-form PANI.

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