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Structure, Conductivity, and Thermopower of Crystalline Polyaniline Synthesized by the Ultrasonic Irradiation Polymerization Method

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ABSTRACT: Polyaniline (PANI) samples were synthesized by an ultrasonic irradiation synthesis method and by a magnetic stirring process. The structure of the polyanilines was investigated by using infrared and UV−vis−NIR spectral analysis, X-ray diffraction, transmission electron microscopy, electron diffraction, and elemental analysis. The results clearly show that the crystallinity of polyaniline synthesized by using the ultrasonic synthesis method is much higher than that synthesized by the stirring synthesis method under similar conditions. Transmission electron microscope observation shows that the polyaniline powder synthesized by using the ultrasonic method consists mainly of hexagonal plates. Electron diffraction results show that the plates are small single crystals with well-developed hexagonal morphology. The lattice parameter of the crystal is $a = b = 4.56$ Å. A network structure model of crystalline polyaniline is proposed. The results of elemental analysis and the solubilities of the two types of PANI support this model. The conductivity and thermopower of polyaniline synthesized by the ultrasonic method are lower than the same properties exhibited by samples synthesized by the conventional method. The results indicate that polyaniline with higher crystallinity does not possess higher conductivity.

Introduction

Polyaniline (PANI) has received much attention because of its electronic, thermoelectric, and optical properties as well as its good environmental stability.[1−5] Polyaniline is conventionally synthesized chemically or electrochemically. In past years, results on the effects of dopants and oxidants on the crystallinity of polyaniline samples have been published.[6−9] Recently, some researchers have studied the relationship between the crystallinity of PANI and its physical properties and have found that the conductivity of PANI samples strongly depends on the degree of crystallinity.[1,10] Mazerolles and co-workers found that there is a well-crystallized region at the center of polyaniline particles prepared by dissolution−solvent evaporation in *N*-methylpyrrolidone (NMP) and then in tetrahydrofuran.[11] To obtain polyaniline materials with special structures and properties, a plasma polymerization technique has been used to prepare polyaniline films and powder.[12,13] Since the 1980s, ultrasonic irradiation, in the frequency range from 20 kHz to 1 MHz, has been widely used in chemical synthesis because it leads to an increase in the rate of many chemical reactions: organic, inorganic, polymerization, etc.[14,15] The value of ultrasonic irradiation to organic chemists lies not only in its ability to accelerate known reactions, particularly those that are heterogeneous in the solvent systems of interest, but also in its ability to generate new chemistry that is not available using existing methodologies because an ultrasonic wave can generate a very extreme reaction environment[16,17] as it passes through a liquid. Low's group has even demonstrated that ultrasonic sonochemical reaction conditions are fully compatible with synthesis of biologically active compounds.[18] Most recently, many research groups have used ultrasound in the synthesis of polymers and composites and have obtained striking results.[19−22] In the present work, we report on the structure and electrical properties of polyaniline synthesized by the ultrasonic irradiation polymerization method. Using a transmission electron microscope (TEM) and electron diffraction (ED), we observed that polyaniline powder synthesized by ultrasonic synthesis consists mainly of small single crystals with well-developed hexagonal morphology. The conductivity and thermopower of the PANIs synthesized using the stirring method and the ultrasonic irradiation method were measured and compared.

Experimental Section

Synthesis by Ultrasonic Irradiation-Induced Polymerization. A quantity of 2.113 g of *p*-toluenensulfonic acid was dissolved in 200 mL of water, and the solution was precooled to 0 °C. 4 g of aniline was added to the solution and dispersed by an ultrasonic disperser (SK2200H, Shanghai Kudos Ultrasonic Instrument Co. Ltd., 59 kHz, 90 W) to form an emulsion. As a catalyzer, 16.9 g of $(NH_4)_2S_2O_8$ was dissolved in 50 mL of water and slowly dropped into the emulsion for over an hour. The reaction continued in the ultrasonic disperser at 0 °C for 20 h. Residue was collected in a Buchner funnel and washed with 200 mL of *p*-toluenensulfonic acid solution (pH < 3). The precipitate cake was dispersed in distilled water and filtered more than six times until the filtrate had a pH of 7 when tested using wet pH paper. The washed product was dried at 40 °C for 8 h in a vacuum dryer. To compare the structure and properties of PANI synthesized by the above process, another kind of PANI was synthesized by using a conventional magnetic stirring method (JJ-79-1, Zhejiang Jintan Scientific Apparatus Co. with stirring rate of 800−1200 rpm) under similar reaction conditions.

X-ray diffraction experiments were carried out on a D max-γA model (Japan Rigaku) X-ray diffractometer with Cu Kα radiation. The PANI powder was mixed with KBr (1:50) and pressed into pellets to obtain the infrared (IR) spectrum on a Nicolet 20SX FT-IR and the ultraviolet−visible (UV/vis)

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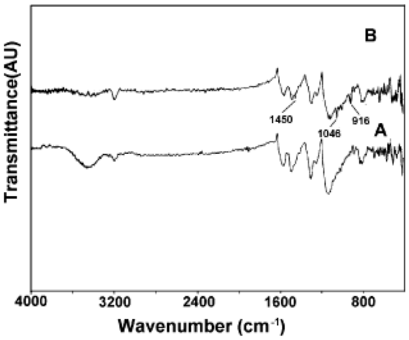


Figure 1. IR spectrum of polyaniline synthesized by ultrasonic irradiation and by electromagnetic stirring: (A) polymerized by electromagnetic stirring; (B) polymerized by ultrasonic irradiation.

spectrum on a Hitachi 340 UV−vis. The absorbance of KBr was subtracted at the time the data were collected. The transmission electron microscope (TEM) observations and the electron diffraction (ED) measurements were carried out on a Hitachi model H-800 TEM. Elemental analysis of C, H, and N was performed on a PE2400 elemental analyzer, and the elemental analysis of S was carried out by using an ARL9400-XRF X-ray fluorescence analyzer. The powder product was pressed (800 MPa) into rods of 0.6 mm diameter and 10 mm length for measurements of the conductivity and thermopower in the temperature range from room temperature to 200° C.

Results and Discussion

Figure 1 shows the IR spectra of PANI synthesized by ultrasonic irradiation and PANI synthesized by the stirring method. Both of the IR spectra are in good agreement with previously reported results.[10,23,24] The appearance of the 1562 and 1486 cm^{-1} modes in both spectra is consistent with quinoid and benzenoid ring deformations, respectively. The 1295 and 792 cm^{-1} bands can be assigned to C−N stretching of the secondary aromatic amine and an aromatic C−H out-of-plane bending vibration, respectively. We can see that the aromatic C−H in-plane bending mode in PANI synthesized by ultrasonic irradiation (1114 cm^{-1}) splits into two small peaks at the top. This indicates that there are two kinds of carbon−hydrogen stretching modes in PANI synthesized by ultrasonic irradiation. In this spectrum we find two absorption bands at 1450 and 916 cm^{-1}, which correspond to a 1,3,5-trisubstituted ring. This result indicates that the structure of PANI synthesized by ultrasonic irradiation is different than PANI synthesized by the stirring method. In addition, we find a higher peak at 3321 cm^{-1}, which results from cross-linking moieties.[25] As suggested by other authors, the absorption band at 3436 cm^{-1} may be attributed to the N−H stretching vibration.[26,27] This feature of the spectrum of PANI synthesized by ultrasonic irradiation becomes quite small and nearly disappears. This is possibly caused by a decrease in the number of hydrogen atoms connected to nitrogen atoms in the polymer resulting from the special structure of PANI synthesized by ultrasonic irradiation. A band corresponding to the conducting protonated form is observed at 1238 and 1246 cm^{-1} in the spectra of PANIs synthesized by both methods. The 1245 cm^{-1} band, corresponding to the stretching mode of S=O in the $-SO_3$ group, was found in both spectra, indicating that $-SO_3$ groups exist in both forms.

The UV−vis spectra of PANI synthesized by ultrasonic irradiation and PANI synthesized by the stirring method are shown in Figure 2. The spectrum of PANI synthesized by stirring exhibits two peaks: an absorption peak at 422 nm corresponding to the $\pi-\pi^*$ transition of the benzenoid ring[28] and an absorption peak at about 739 nm, which can be assigned to polaron band transitions.[29−31] In the spectrum of the PANI synthesized by ultrasonic irradiation, the $\pi-\pi^*$ transition peak shifts to 451 nm, and the peak at 739 nm becomes very weak, which indicates that the environments of the quinoid and benzenoid rings are apparently changed, and the polarons are more localized than in the other form.

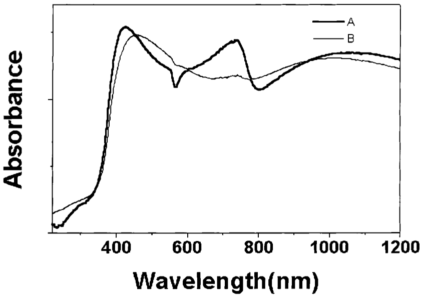


Figure 2. UV−vis spectra of PANI synthesized by magnetic stirring and PANI synthesized by ultrasonic irradiation: (A) polymerized by magnetic stirring; (B) polymerized by ultrasonic irradiation.

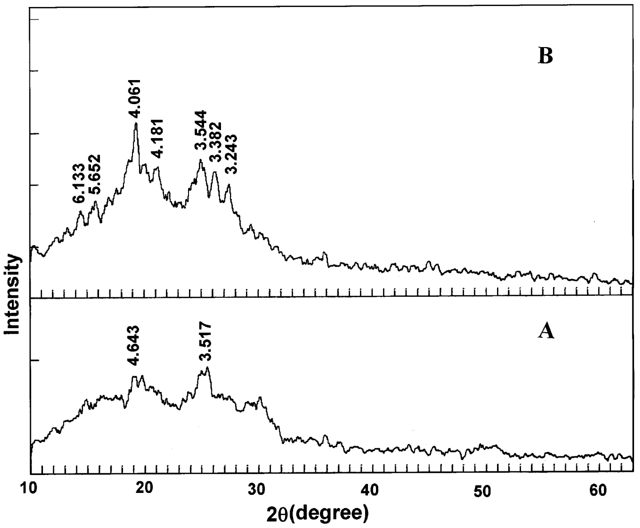


Figure 3. X-ray diffraction patterns of the PANI samples: (A) polymerized by magnetic stirring; (B) polymerized by ultrasonic irradiation.

Figure 3 shows the X-ray diffraction patterns of the samples. In the pattern of PANI synthesized by the stirring method, there are three main peaks at about 15°, 20°, and 26° (2θ), consistent with the third, fourth, and fifth peak in the XRD patterns of polyanilines observed by other groups.[1,10] However, in the XRD pattern of PANI synthesized by ultrasonic irradiation, there are seven sharp peaks in the range 10°−30°. These data indicate that PANI synthesized by ultrasonic irradiation is a well-crystallized polymer. In both XRD patterns, no peaks of low-molecular-weight crystalline compounds that would potentially be present in PANI (*p*-toluenesulfonic acid, ammonium peroxydisulfate, and its decomposition product ammonium sulfate) were found.

Figure 4 shows the TEM images and ED patterns of the two PANI powders. One can see that most of the

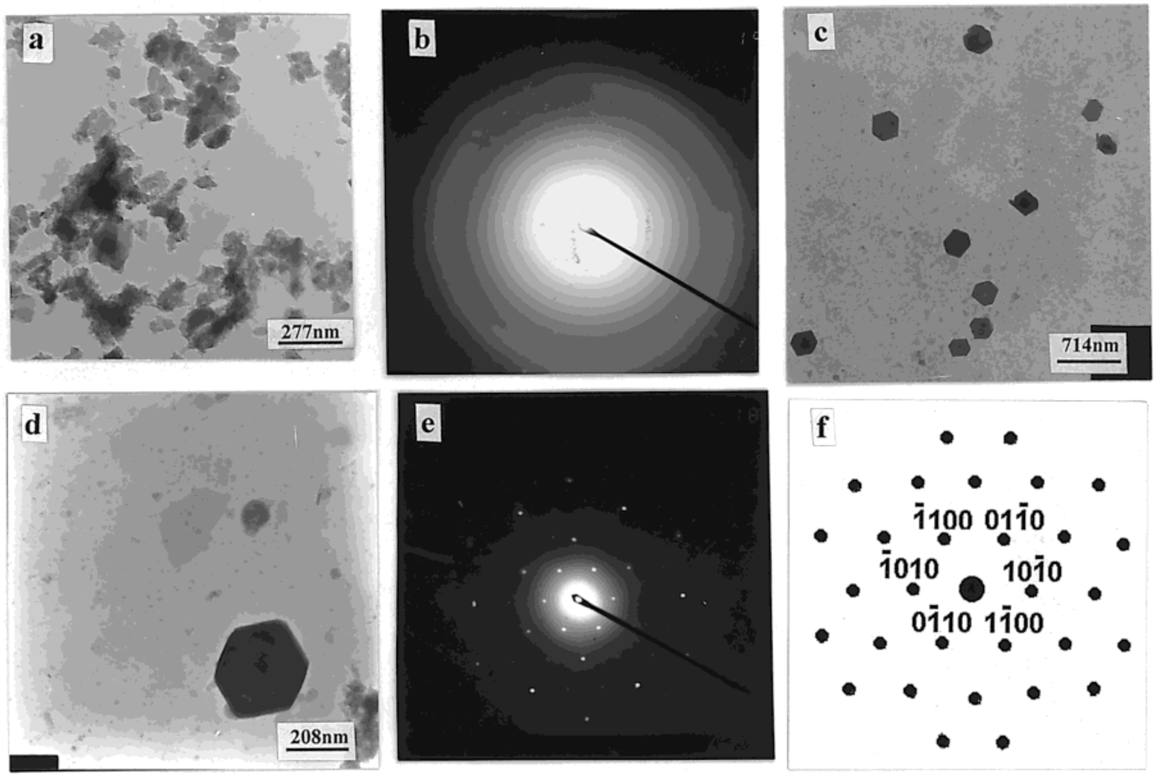


Figure 4. TEM images and ED patterns of PANI synthesized by different synthesis methods: (A) TEM image of the PANI powder synthesized by magnetic stirring; (B) ED pattern of a PANI plate synthesized by magnetic stirring; (C, D) TEM image of the PANI powder synthesized by ultrasonic irradiation; (E) ED pattern of a PANI hexagonal plate synthesized by ultrasonic irradiation; (F) indexed ED pattern of the single crystalline PANI.

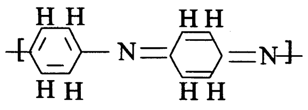
Table 1. Elemental Analysis of PANIs Synthesized by Stirring and Ultrasonic Irradiation

	elemental analysis				chemical composition			
	C	H	N	S	C	H	N	S
PANI synthesized by ultrasonic irradiation	64.05	4.04	11.13	8.66	6.00	4.545	0.907	0.304
PANI synthesized by stirring method	61.92	4.66	9.63	8.60	6.00	5.423	0.799	0.278

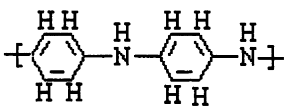
particles in PANI synthesized by stirring are thin plates (Figure 4a). The diffraction circles in the ED pattern of one of the plates (Figure 4b) shows that PANI synthesized by stirring is a typical noncrystalline polymer. Figure 4c,d shows the TEM images of a powder sample of PANI synthesized by ultrasonic irradiation. We observed that most particles are thin hexagonal plates of diameter between 250 and 300 nm in this case. Figure 4e shows the ED pattern of the hexagonal plates. From the ED pattern, we can deduce that the plate is a single crystal with hexagonal structure. The indexed pattern is illustrated in Figure 4f. One of the cell parameters of the crystal calculated from the pattern is $a = b = 4.56$ Å. The other cell parameter c cannot be calculated from this pattern. Cell parameter a is slightly larger than the sum of the lengths of the diagonal of one benzene ring and the C−N bond distance, indicating that a structure unit in the polyaniline crystal consists of one phenyl ring and a bridge nitrogen atom. As mentioned in the section on XRD, no low-molecular-weight crystalline compounds that would potentially be present in PANI exist in the product because of careful washing. The tiny crystals in the product powder of PANI synthesized by the ultrasonic method are crystalline PANI.

Table 1 gives the results of elemental analysis of PANI synthesized by both methods. The average number of hydrogen atoms allotted to each aromatic ring in PANI synthesized by ultrasonic irradiation is 1 less than that in PANI synthesized by the stirring method. The number of sulfur atoms for every six carbon atoms is about 0.3, indicating that there are $-SO_3^-$ groups in the polymers.

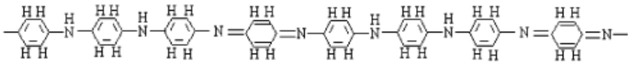
From the above discussion, we can propose structural models of PANI synthesized by the stirring method and by the ultrasonic irradiation method (Figure 5). PANI synthesized by the stirring method consists of oxidized units of the form



and reduced units of the form



A. PANI synthesized by stirring method



B. PANI synthesized by ultrasonic irradiation

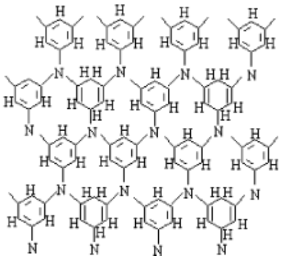


Figure 5. Schematic representative of the twostructural models.

We propose that the number of oxidized units is same as that of the reduced units. The structural model of PANI synthesized by ultrasonic irradiation is shown in Figure 5a. In such a structure, there is one quiniod ring among four aromatics. The average number of hydrogen atoms for every aromatic ring is 4.5. The actual number of hydrogen atoms for every phenyl ring is larger than 4.5, because of the existence of hydrogen atoms absorbed on $-SO_3^-$ and at the top of the polyanine chains. From the above discussion, we know that quinoid rings still exist in PANI synthesized by ultrasonic irradiation. In addition, the crystal structure of PANI synthesized by ultrasonic irradiation should be a network structure consisting of 1,3,5-trisubstituted phenyl rings with hexagonal symmetry. Therefore, we propose a structural model of crystalline PANI synthesized by ultrasonic irradiation as shown in Figure 5b. In this structure, the percentage of quinoid rings in PANI is the same as that in the polyaniline chain in PANI synthesized by the stirring method. Each of the aromatic rings is connected with three other aromatic rings by using nitrogen atoms as bridge atoms. The hexagonal pattern shown in Figure 4e was obtained when directing the incident electron diffraction beam perpendicular to the plane of the network. In such a structure, the theoretical average number of hydrogen atoms in every aromatic ring is 3.5, which is 1 less than that in PANI synthesized by ultrasonic irradiation consistent with the elemental analysis results. The linkage between the network layers is possibly a van der Waals or other weak bond.

The solubility of the two PANIs supports the structural model we have suggested. The PANI synthesized by the stirring method dissolves easily in *N*-methylpyrolidone (NMP) and forms a blue-violet solution even without stirring. However, the PANI synthesized by ultrasonic irradiation hardly dissolves in NMP, even if dispersed by ultrasonic irradiation for 20 min. In the model, every phenyl ring connects to three others and forms 1,3,5-trisubstituted rings, and no N−H bond exists in the network structure. This is the reason why peaks corresponding to the trisubstituted ring can be found, and the peak corresponding to N−H stretching vibration disappears in the IR spectrum of PANI synthesized by ultrasonic irradiation. In the network structure, the proton mobility should be lower than that in linear PANI because of the existence of some nonconjugated units in the network. Thus, the 739 nm band in the UV−vis spectrum of PANI synthesized by ultrasonic irradiation becomes weaker.

More recently, several research groups found that sulfonic-doped polyanilines and their salts have a self-organized structure.[11] Some models for the crystalline structure of PANI and its salts were suggested.[32,33] Mazerolles and co-workers have even investigated the structure of polyaniline-doped sulfuric acid after dissolution−solvent evaporation in *N*-methylpyrolidone (NMP) and then tetrahydrofuran (THF).[11] They found some small but well-organized regions in the noncrystalline polymer powder. High-resolution transmission electron microscope (HRTEM) images showed that crystalline grains (only 20−50 nm) exhibiting well-characterized 0.59 nm interreticular spacing were identified as ES-I emeraldine salt. In our work, the PANI crystals grew well. The structure of crystalline PANI in the present work is different than the structure found in their work, and the size of crystalline PANI particles in this work is much larger. The special structure and the larger size of crystalline PANI obtained in present work are caused by the ultrasound irradiation used in the synthesis process. The effect of ultrasound on chemical reactions has been explained using the “hot spot” theory,[17] the “electrical theory”,[34] and a model based on plasma discharge.[35] Although there are many different explanations of the origin of the chemical effects of ultrasound, there is no doubt that the extreme conditions generated by bubble collapse lead to the formation of free radicals, mechanical shocks, high shear gradients, and very rapid and efficient mixing in multiphase systems.[18] When an ultrasonic wave passes through a liquid medium, a large number of microbubbles form, grow, and collapse in a few microseconds, an effect that is called ultrasonic cavitation. Sonochemical theory calculations and corresponding experiments suggest that ultrasonic cavitation can generate local temperatures as high as 5000 K and local pressures as high as 500 atm, with heating and cooling rates greater than 10^9 K/s, a very extreme environment.[16,17] Between the microbubble and the bulk solution, the interfacial region around the bubble has very large gradients of temperature, pressure, and electric field as well as rapid motion of molecules leading to the production of excited states, bond breakage, formation of free radicals, mechanical shocks, high shear gradients, and very rapid and efficient mixing in multiphase systems. Some investigators have proved that ultrasound can cause chain cleavage,[36,37] ring-opening,[38,39] and radical initiation in polymerization.[40] The network structure of PANI in the present work is different from the results of other groups because of the bond-breakage, ring-opening, and other special characteristic effects of ultrasonic irradiation. Because the rapid motion of molecules leads to very efficient mixing, e.g., emulsification, the extent of catalyzation in a solution under ultrasonic irradiation becomes much greater than under stirring. Therefore, we believe this is the explanation of how the size of PANI crystals can be much larger than that obtained in other work.

Figure 6 shows the dependence of conductivity of the PANIs on the measurement temperature. The temperature dependence exhibits a typical semiconducting behavior and fits Mott’s formula.[18]

$$\sigma(T) = \left[\sigma_0 \exp -\left(\frac{T_0}{T}\right)^{-1/2}\right] \qquad (1)$$

The conductivity of PANIs increases with increase in

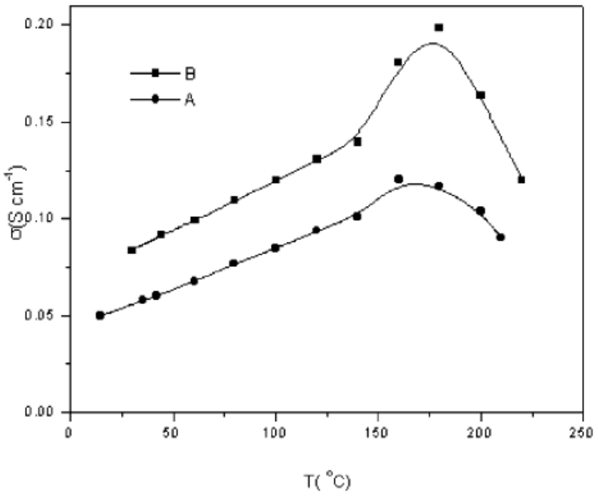


Figure 6. Dependence of conductivity on temperature: (A) PANI synthesized by magnetic stirring; (B) PANI synthesized by ultrasonic irradiation.

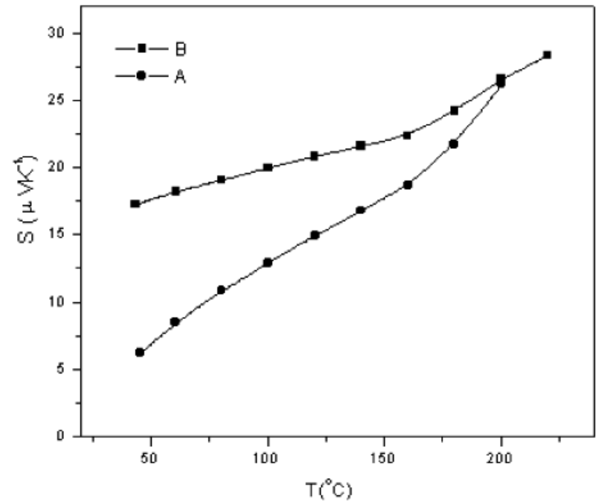


Figure 7. Dependence of thermopower on temperature: (A) PANI synthesized by magnetic stirring; (B) PANI synthesized by ultrasonic irradiation.

temperature below 175 °C. However, for temperatures higher than 175 °C, the conductivity decreases with increasing temperature. The decrease in the conductivity at higher temperatures is caused by the additional scattering that results from the decomposition of the polymers.

From Figure 6, we observe that the value of the conductivity for the PANI synthesized by stirring is smaller than that of the PANI synthesized by ultrasonic irradiation. In our work, *p*-toluenensulfonic acid was used as a doping addition in the synthesis process. Since *p*-toluenensulfonic acid is a strong acid, PANI doped by it is capable of self-protonation.[41] The conductivity of *p*-toluenensulfonic acid doped PANI is independent of external protonation over a broad pH range (5−7.5).[41] In addition, all PANIs synthesized in this work were washed with distilled water until the pH of the filtrate solution rose to 7. Therefore, no other compound should be present to affect the conductivity. Results of elemental analysis show (Table 1) that approximately 30% of the total number of phenyl rings in both kinds of polymers are monosubstituted by $-SO_3^-$ groups. The difference in conductivity between the PANIs caused by the amount of dopant should thus not be very large. From the above discussion, it appears that the difference in conductivity between the two PANIs is caused mainly by the difference in crystal structure. Well-crystallized PANI possesses lower conductivity because of decreased proton mobility caused by the presence of nonconjugated units in the network.

We can therefore conclude that higher crystallinity causes a lower conductivity for PANI under the same conditions as regards the dopant acid and the amount of dopant. From these results, the correlation between crystallinity and electrical conductivity is clear; the greater the degree of crystallinity, the lower the conductivity. In other work on the effect of the crystallinity of PANI on its electrical conductivity, it can be seen that the degree of crystallinity in those studies depends on the dopant species and/or the amount of dopant. Although the degree of crystallinity in the PANIs was different in that work, the difference between the electrical conductivity of PANIs with different crystallinity was probably mainly caused by the dopant species and/or the amount of dopant. In our research, with the same dopant species and the nearly same amount of dopant, the degree of crystallinity of the PANI appears to depend only on the synthesis method. Therefore, we contend that this result should reflect the real correlation between crystallinity and electrical conductivity. In this situation, the PANI with the higher degree of crystallinity possesses lower electrical conductivity. In addition, the structure of PANIs synthesized in other studies is different from that synthesized in present work, which could cause the difference of conductivity between the two different crystalline PANIs synthesized by ultrasonic irradiation and conventional stirring.

Figure 7 shows the dependence of the thermopower of the PANIs on the measurement temperature. The thermopower of PANI synthesized by ultrasonic irradiation is about 5 μV K^{-1} at room temperature, which is slightly higher than that of the PAN investigated by Subramaniam.[42] The thermopower of PANI synthesized by stirring is about 17 μV K^{-1}, which is much higher. The thermopower of conventional PANI is much higher than that of PANI synthesized by ultrasonic irradiation. Our measurements show that the thermopower of the two kinds of PANI increases with increasing temperature. This result is in agreement with that obtained by Subramaniam.[42]

Conclusion

Polyanilines were synthesized by using conventional magnetic stirring and an ultrasonic irradiation method. IR and UV−vis spectra of the PANIs showed the structure of PANI synthesized by ultrasonic irradiation is different from that synthesized by the stirring method. XRD, TEM, and ED prove that polyaniline synthesized by ultrasonic radiation polymerization is a well-crystallized product with a hexagonal structure. A two-dimensional network structural model for PANI synthesized by ultrasonic irradiation has been suggested. Elemental analysis and other characterizations of the two kinds of PANIs support the model. The special crystal structure of PANI synthesized by ultrasonic irradiation exhibits bond-breakage, open-rings, and other special effects of ultrasonic irradiation during the polymerization process. The investigation shows that the PANI with higher crystallinity possesses lower conductivity, which is in contradiction to the results obtained by other research groups. We conclude that the decrease of conductivity of crystalline PANI is caused by the presence of nonconjugated units in the polymer.

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