

Raman Spectroscopic Study on the Structural Changes of Polyaniline During Heating and Cooling Processes

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ABSTRACT: Polyaniline (PANI) in three ground states—emeraldine base (EB), leucoemeraldine base (LEB), and pernigraniline base (PNB)—were studied by Raman spectroscopy in the temperature scale of -195 to about 375°C . The Raman spectral results demonstrated that a crosslinking reaction occurred on EB chains at high temperatures, whereas the phenyl torsion angles of EB chains decreased during the cooling process. LEB was unstable and was gradually converted to EB during the heating process, although its chain conformation remained stable by cooling. The spec-

tral change tendency of PNB was similar to that of EB during the heating process. Although the torsion angle of PNB also decreased with decreasing temperature, like that of EB, this behavior was hard to observe experimentally because of the relatively “free” rotation of its phenyl rings. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 732–739, 2005

Key words: crosslinking; chain; polyaniline; Raman spectroscopy; torsion angle

INTRODUCTION

Polyaniline (PANI), as a special conducting polymer, has attracted increasing levels of attention over the past 10 years because of its high potential in commercial applications.^{1–3} It differs from other conducting polymers by incorporation of a nitrogen atom between the phenyl rings and, as shown in Scheme 1, pristine PANI can be divided into three classes: leucoemeraldine base (LEB, fully reduced form), emeraldine base (EB, half-oxidized form), and pernigraniline base (PNB, fully oxidized form).⁴

Because the stability of conducting polymers is an essential for their application, some research concerning the thermal stability of PANI has been conducted recently,^{5–7} and most of these works were carried out by using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), or X-ray photoelectron spectroscopy (XPS). However, these techniques can provide only the macroscopic information, such as melting point, phase transition, or decomposition temperature. The structural variations of the polymer chains cannot be determined by these methods.

Raman spectroscopy has proved to be a useful method for studying conducting polymers and can indicate, with a substantial degree of sensitivity, the structural variations of conducting polymers.^{8–10} In this article, we report the Raman spectra of the three different ground states of PANI during the heating and cooling processes; the structural variations of the polymer were also investigated and are discussed herein.

EXPERIMENTAL

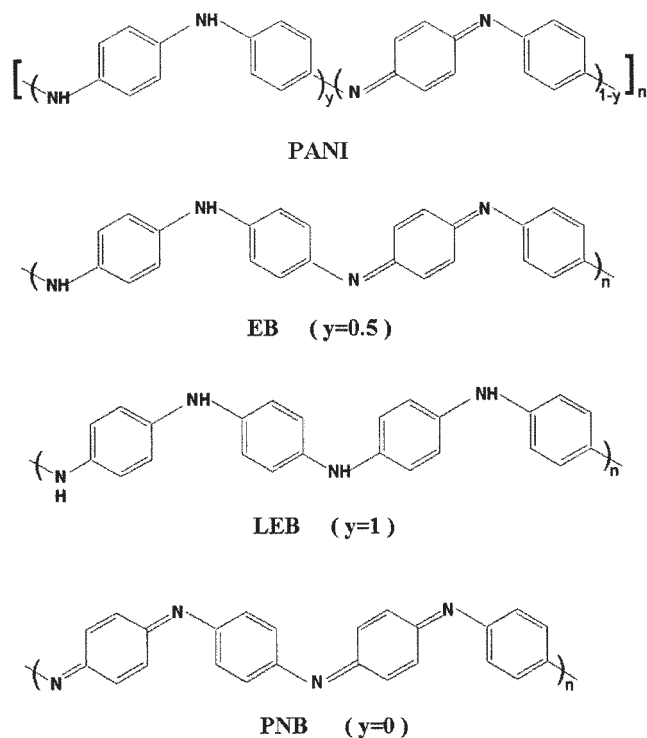
Aniline (Changping Shiyong Chemical Engineering Plant, Beijing China) was refluxed with iron powder for 1 h and then distilled at 182°C . It was further purified by distillation under reduced pressure with nitrogen protection after being dried with sodium hydroxide for 12 h.¹¹ Emeraldine base (EB) was synthesized chemically¹² or electrochemically¹³ in 1M HCl aqueous solution. EB powder was reduced to LEB by treatment with a solution of phenylhydrazine (Xudong Chemical Engineering Plant, Beijing, China).¹⁴ PNB was obtained by oxidation of EB dissolved in *N*-methyl pyrrolidinone (NMP; Chemical Agent Co., Beijing, China) with *m*-chloroperbenzoic acid (Aldrich Chemical Co., Milwaukee, WI) and was precipitated by the addition of triethylamine (The Third Chemical Agent Plant, Tianjin, China).¹⁵

Raman spectra were recorded on an RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, Gloucestershire, UK) using a 514- or 633-nm laser beam and a charge-coupled detector (CCD) at 4 cm^{-1} resolution. The spectra were recorded by using a

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Scheme 1 Molecular structures of the PANI, EB, LEB, and PNB.

20 \times objective lens and the laser power was always kept very low (<0.5 mW) to avoid destruction of the samples. Some complex Raman peaks were divided into component Gaussian or Lorentz peaks with proper background subtraction using an "automatic fitting" program provided with the Raman spectrometer. A special cell set (Linkam Scientific Instrument Ltd., Tadworth, UK) was used to control the temperature of the samples. The sample was cooled with liquid nitrogen and the rate of temperature change was controlled to be 1 $^\circ\text{C min}^{-1}$. At a given temperature, the sample was kept for 3 min to obtain the spectrum.

RESULTS AND DISCUSSION

It has been reported that the Raman spectroscopic features of PANI depend strongly on the wavelength of the excitation laser beam, and the enhancement of Raman modes is directly correlated to the UV-vis/near-infrared (NIR) absorption.¹⁶ Emeraldine base has two absorption peaks at about 325 and 630 nm. The former peak is assigned to the π to π^* transition of phenyl units, and the latter peak is attributed to the excitation of quinoid units.¹⁶ Thus, the wavelength of the Raman excitation source, which is close to these two bands, will lead to special enhancement of the bands related to phenyl or quinoid units, respectively. The wavelength of the 514-nm laser beam lies between

325 and 630 nm, so neither the bands related to phenyl units nor the bands associated with quinoid units will be enhanced specifically. Therefore, the 514-nm laser excited Raman spectra can reflect the structural variations of both quinoid and phenyl units of PANI. In this work, the Raman spectra of PANI were recorded using a 514- or a 633-nm beam to observe the vibration modes of phenyl and quinoid units simultaneously or to observe the bands related to the quinoid units individually. The assignments of the Raman bands of PANI are listed in Table I,^{17,18} and "B" and "Q" indicate the bands associated with the phenyl and quinoid units, respectively.

The 633-nm excited Raman spectra of emeraldine base during the heating process are illustrated in Figure 1. EB has a relatively good thermal stability in the temperature scale of 25 to 100 $^\circ\text{C}$. However, with increasing temperature the features of the Raman spectra change dramatically. First, a new band at about 1648 cm^{-1} was found, and its intensity was enhanced with increasing temperature. This band can be attributed to the crosslinked structures of EB, as reported in the literature.^{5,6,19} Second, the band at about 1615 cm^{-1} increased, whereas the bands at about 1585 and 1485 cm^{-1} decreased with increasing temperature. The first band is assigned to the C—C stretching of phenyl units and the latter two bands are attributed to the C=C and C=N stretching of quinoid units, respectively. Thus, these spectral variations are explained primarily by the crosslinking of PANI chains, resulting in the conformational transition from a quinoid state to a phenyl state. The spectral changes of these Raman bands also concomitantly confirmed the crosslinking reaction on PANI chains. However, the spectral phenomena described above cannot be observed clearly in the 514-nm excited Raman spectra (Fig. 2). This can be explained by the fact that the 514-nm laser cannot resonate with the vibration modes of quinoid units of PANI. As shown in Figure 2, the Raman bands around 1220 and 1485 cm^{-1} decrease slightly with increasing temperature in the

TABLE I
Assignments of the Raman Bands of PANI

Wavenumber (cm^{-1})		Assignment
1615–1610	B	C—C stretching
1585–1595	Q	C=C stretching
1560–1550	B	C—C stretching
1486–1495	Q	C=N stretching
1415–1425	Q	C—C stretching
1213–1225	B	C—N stretching
1180–1185	B	C—H bending
1160–1165	Q	In-plane C—H bending
~ 840	B	Amine deformation
~ 780	Q	Ring deformation
~ 750	Q	Imine deformation

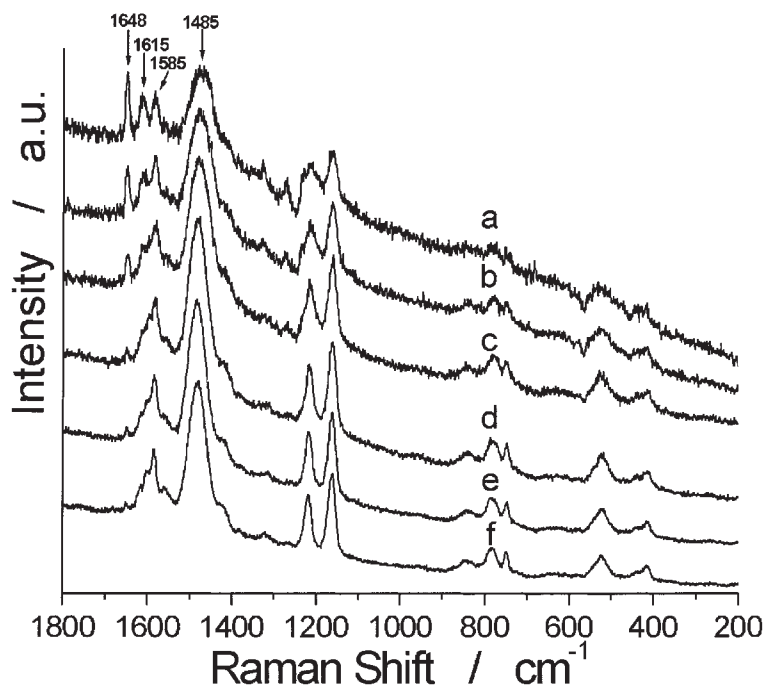


Figure 1 Excited Raman spectra (633 nm) of EB recorded during the heating process: (a) 300°C; (b) 275°C; (c) 250°C; (d) 175°C; (e) 100°C; (f) 25°C.

range of 25 to 250°C. These two bands are attributed to C—N and C=N stretching of PANI chains, respectively, which implies that the thermal stability of the C—N and C=N bonds is poorer than that of the C—C bond. When the temperature exceeded 250°C, the widths of the Raman bands increased and their inten-

sities decreased with increasing temperature. Finally, the spectrum loses its fine structures and only a broad band appears, indicating an extensive decomposition of PANI.

The 514-nm excited Raman spectra of emeraldine base, recorded during the cooling process, are shown

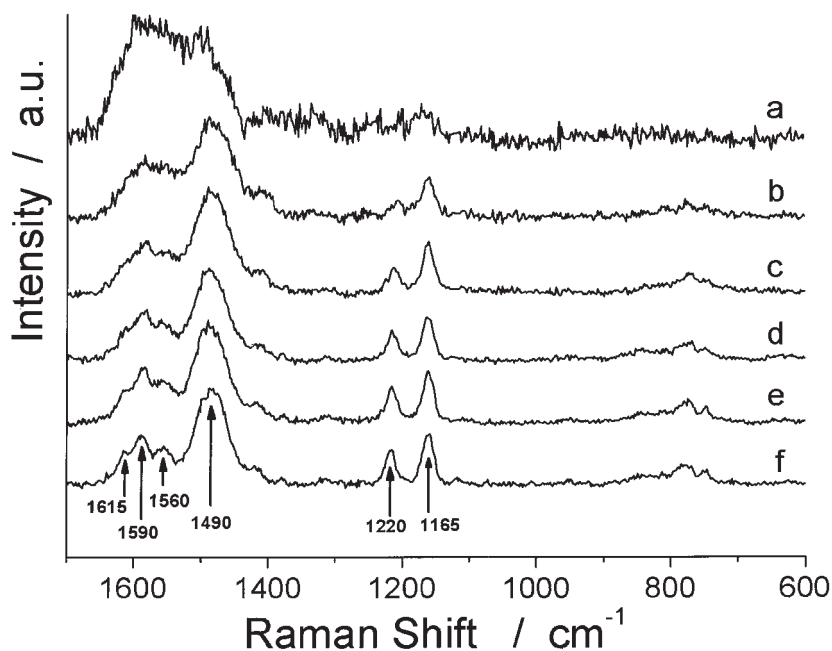


Figure 2 Excited Raman spectra (514 nm) of EB recorded during the heating process: (a) 375°C; (b) 325°C; (c) 250°C; (d) 175°C; (e) 100°C; (f) 25°C.

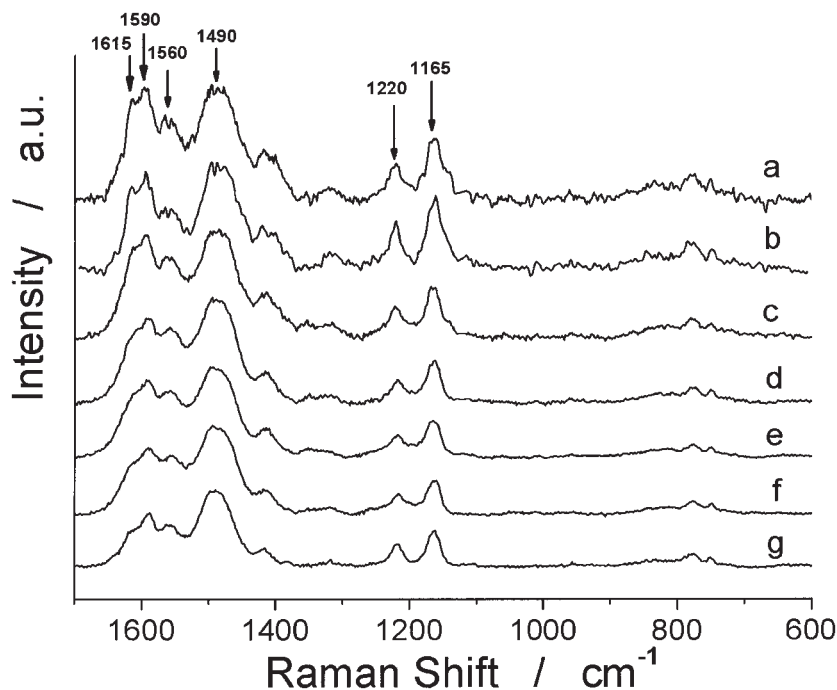


Figure 3 Excited Raman spectra (514 nm) of EB during the cooling process: (a) -190°C ; (b) -150°C ; (c) -130°C ; (d) -110°C ; (e) -70°C ; (f) -40°C ; (g) -10°C .

in Figure 3. It is clear from this figure that the Raman spectra change dramatically. First, the most intense peak of the spectrum recorded at room temperature appeared at about 1490 cm^{-1} . However, the peak at about 1590 cm^{-1} increases gradually with decreasing temperature. At -190°C , the intensity of this band is almost identical to that of the 1490 cm^{-1} band. To investigate the variation of Raman bands, some complex Raman peaks are divided into component Gaussian or Lorentz peaks. A typical sketch map of band division is displayed in Figure 4 and the intensity ratio of these two bands (I_{1590}/I_{1490}) versus temperature is plotted in Figure 5. Second, the Raman signal at about 1615 cm^{-1} , which is attributed to C—C stretching of phenyl units in PANI, is very weak at room temperature, whereas this peak becomes relatively strong and distinct at low temperatures. Figure 4 also displays the temperature dependency of intensity ratio of the bands at 1615 and 1590 cm^{-1} (I_{1615}/I_{1590}).

It is known that PANI differs from other conducting polymers, such as polythiophene, because the backbone of PANI is not planar and has a helical conformation resulting from a ring torsion (so-called conformons, or conformational defects, in some reports).²⁰ The equilibrium chain conformation is determined by the competition between the π -electron delocalization or "resonance" energy, and the inter-ring steric repulsion. The former factor favors all phenyl rings and nitrogen atoms in a plane, whereas the latter forces the rings out of that plane.²¹ In addition to the dihedral angles between phenyl rings, attributed to the sp^2

and/or sp^3 type of the nitrogen atoms that are located between the rings of the backbone, PANI may have a wide variety of forms, resulting in the geometrical disorder of PANI.²² From the vibrational perspective, the disorder is the result of an irregular arrangement of chemical bonds (mainly C—N bonds) as well as of the presence of electrical defects (dihedral angles between phenyl rings). The former leads to the orientational disorder, and the latter leads to electrical disorder. In crude approximation, the Raman stretching modes are sensitive to electrical disorder, whereas orientational disorder of polymeric backbone would essentially affect the bending and external modes.²² Therefore, the relative intensity changes of the peaks at about 1490 and 1590 cm^{-1} may reflect the electrical variation of the PANI backbone. Because the average ring torsion angle depends on the temperature, a larger ring torsion angle at a higher temperature is expected.^{21,23} It is reasonable to deduce that the ring torsion angle decreases with decreasing temperature. Thus, the electron cloud, which is primarily "bounded" within quinoid units (the rigid quinoid unit displays coplanar structure) at high temperature, may be somewhat delocalized and shifted to phenyl units as the temperature decreases. This leads to the decrease of the C=N stretching band. However, it affects the intensity of C=C stretching peak less than that of C=N stretching peak, because the more rigid structure of quinoid ring was influenced a little by the change of the torsion angle. Thus, (I_{1590}/I_{1490}) increases with the temperature decrease. On the other

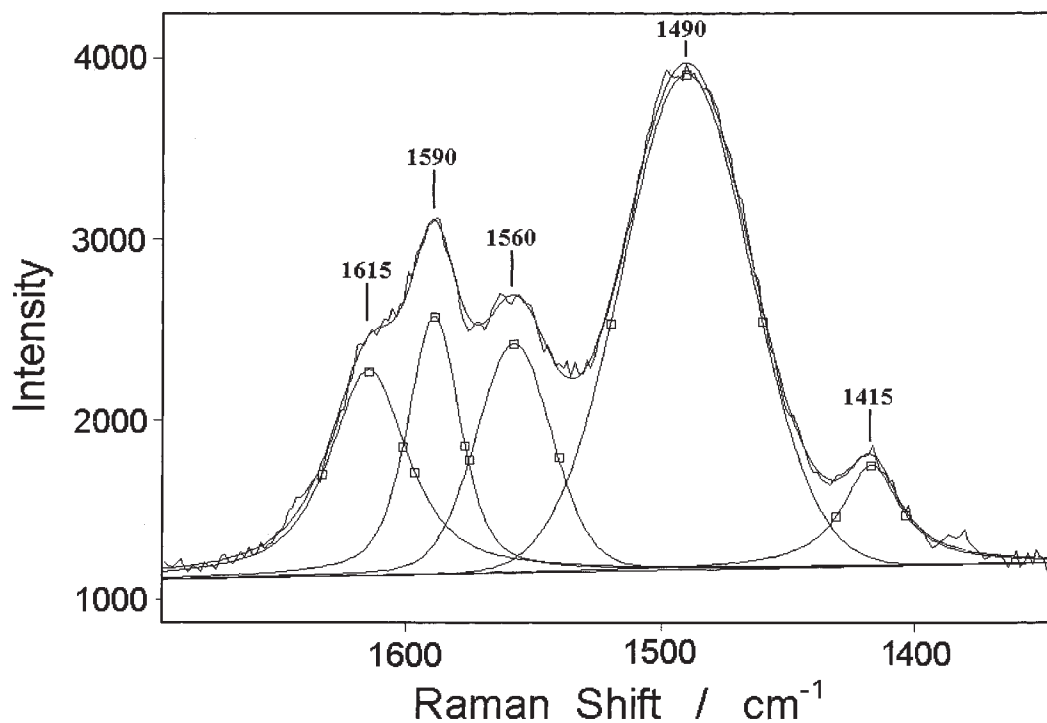


Figure 4 A typical sketch map of Raman band separation.

hand, the delocalization of the electron cloud, from quinoid units to phenyl units, leads to the relative increase of the electron cloud intensity of phenyl units when the temperature decreases. Therefore, (I_{1615}/I_{1590}) also increases with decreasing temperature. This

coincides with the change of the intensity ratio of band at about 1590 to about 1490 cm^{-1} . However, these variations were unobvious in the 633-nm excited Raman spectra because the 633-nm laser has selective enhancement to the bands related to quinoid units.

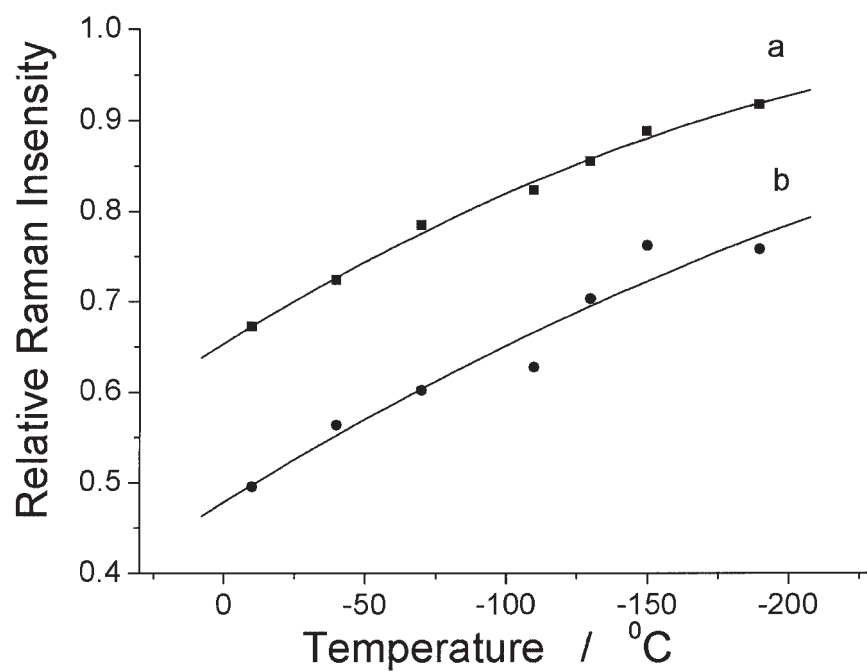


Figure 5 Plots of Raman band intensity ratios versus temperature: (a) I_{1615}/I_{1590} ; (b) I_{1590}/I_{1490} .

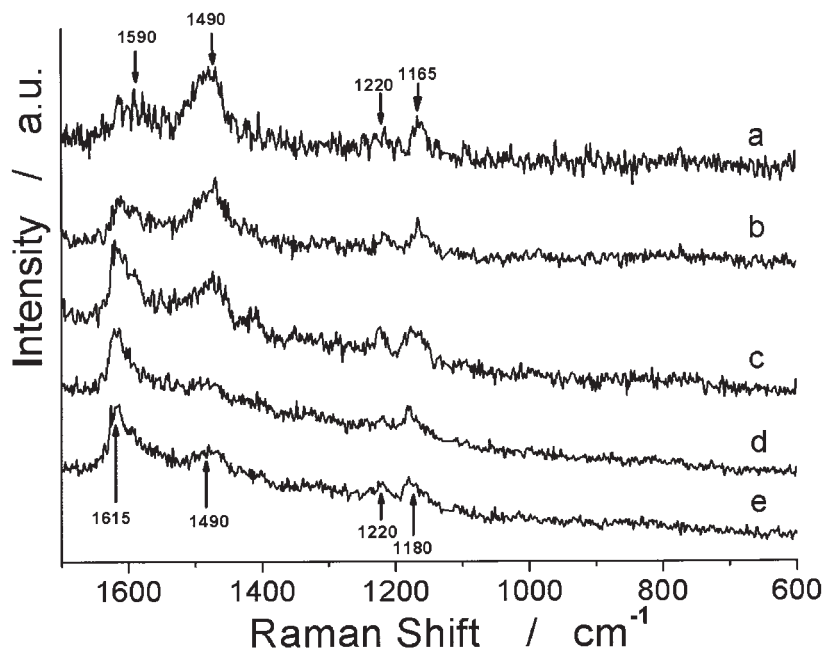


Figure 6 Raman spectra of LEB recorded during the heating process: (a) 180°C; (b) 140°C; (c) 100°C; (d) 60°C; (e) 20°C.

In further study of LEB and PNB, we found that stable spectra could not be obtained by our Raman spectrometer using the 633-nm laser beam, whose power was relatively high. However, the power of the 514-nm laser beam could be adjusted to cover a large scale. Thus, only 514-nm excited Raman spectra of LEB and PNB were recorded. The 514-nm excited Raman spectra of fully reduced PANI, leucoemeraldine base (LEB), during the heating process are presented in Figure 6. The S/N ratios of the spectra were poor because the poor thermal stability of LEB prevents applying strong excitation power for Raman detections. In the course of the experiments, we found that LEB was so sensitive to the power of the laser that even a low power of the laser (~ 0.4 mW) with a focused beam (diameter of the laser beam: $1 \mu\text{m}$) may cause dramatic Raman changes with time. To obtain a stable spectrum of LEB, the power of the excitation laser was limited to about 0.2 mW, and the incident beam was defocused (diameter of the laser beam: $100 \mu\text{m}$). As shown in this figure, the most intense band of the spectrum obtained by excitation at 514 nm appeared at about 1615 cm^{-1} at room temperature. With increasing temperature, the peak at 1615 cm^{-1} decreased and shifted to 1590 cm^{-1} , whereas the band at 1490 cm^{-1} increased and became the most intense peak of the spectra. Moreover, the spectrum recorded at 140°C was very similar to that of EB, which indicated that LEB was unstable and converted to the most stable form of PANI, EB, during the heating. Figure 7 shows the cooling process Raman spectra of leucoemeraldine base. As the figure shows, the LEB remained

stable when the temperature decreased and its Raman spectra were invariable.

The 514-nm excited Raman spectra of pernigraniline base during the heating process are presented in Figure 8. Like the spectral variation of EB, the band assigned to the C—N bond shows a level of stability inferior to that of other bonds with increasing temperature. Furthermore, when the temperature is $>250^\circ\text{C}$, the Raman bands become broader, whereas their intensities decrease with increasing temperature. Finally, the spectrum loses its fine structures and shows only a broad band, with a maximum at about 1500 cm^{-1} .

Figure 9 shows the Raman spectra of pernigraniline base recorded during the cooling process. In contrast to EB, PNB does not show distinct Raman spectral variation during the cooling process. It has been found that PNB differs from EB and LEB in many aspects, such as thermochromic behavior arising from its special chemical structure.²¹ Moreover, it is reported that PNB differs from EB and LEB in its torsion potential curve shape. In the torsion energy–dihedral angle figures, PNB exhibits a double-well-shaped curve with two minima of almost equivalent torsion energies.²³ Furthermore, the energy barrier existing between the two minima is fairly low. However, the LEB and EB present similar shapes of two continuous steps with much higher energy barriers.²³ This indicates that the rotation of phenyl rings in the PNB is freer than that in LEB or EB. Therefore, we conclude that the invariability of the Raman spectra of PNB is attributed to the rapid rotational movement of phenyl units, and the

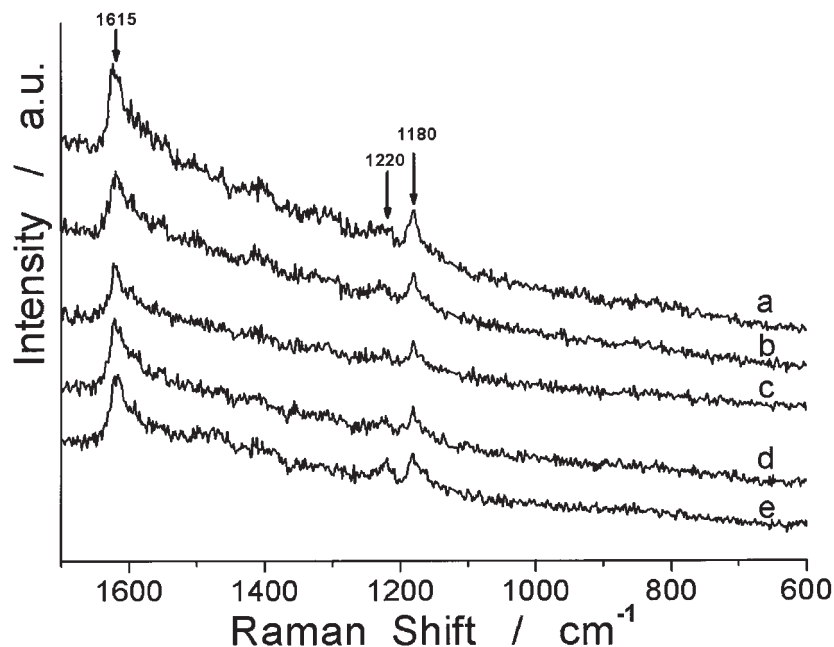


Figure 7 Raman spectra of LEB recorded during the cooling process: (a) -195°C ; (b) -150°C ; (c) -90°C ; (d) -45°C ; (e) 0°C .

decrease in tension angle during the cooling process cannot be monitored by Raman spectra.

CONCLUSIONS

Raman spectroscopy has proved to be a useful method for studying the structural characteristics of conducting polymers. Raman spectral results demonstrated

that a chain crosslinking reaction occurred in EB at high temperatures, which resulted in chain conformational transition from a quinoid form to a phenyl form. The average ring torsion angle of EB decreases with decreasing temperature. This causes an increase in intensity ratios of I_{1590}/I_{1490} and I_{1615}/I_{1590} with decreasing temperature. LEB is unstable and gradually converts to EB during the heating process, although it

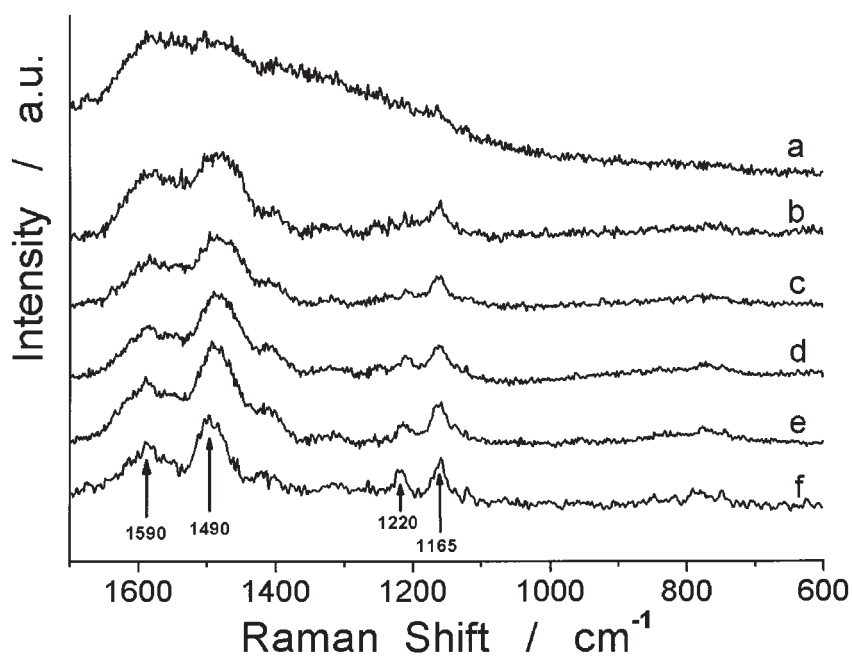


Figure 8 Raman spectra of PNB recorded during the heating process: (a) 275°C ; (b) 250°C ; (c) 225°C ; (d) 175°C ; (e) 100°C ; (f) 25°C .

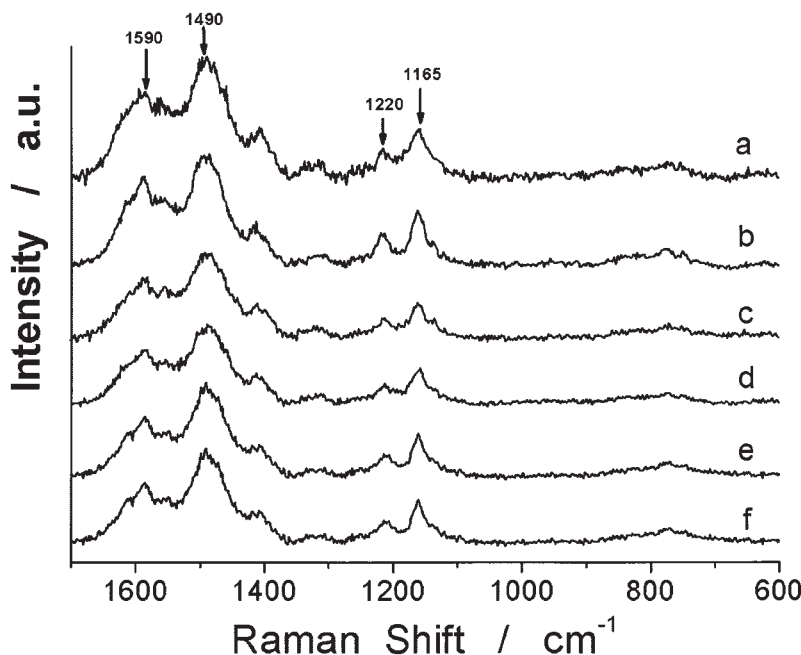


Figure 9 Raman spectra of PNB recorded during the cooling process: (a) -195°C ; (b) -160°C ; (c) -120°C ; (d) -80°C ; (e) -40°C ; (f) 0°C .

remains stable by cooling. PNB shows a change tendency similar to that of EB during the heating process. Although the torsion angle of PNB also decreases with decreasing temperature, like that in EB, it is difficult to observe experimentally because of the relatively "free" rotation of the phenyl ring in PNB.

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