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Fourier transform infrared spectra of transition metal ion-containing polyanilines synthesized in different reaction conditions

Chunming Yang [*], Chunyan Chen, Yue Zeng

College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, PR China

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Abstract

Fourier transform infrared spectroscopy has been employed to investigate the detailed chain structure changes during the chemical oxidative polymerisation of aniline in different reaction conditions including different polarity reaction medium, reaction temperature, reactants molar ratio and in the presence of different transition metal ions such as Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}. The results show that stronger polarity reaction medium and lower reaction temperature were beneficial to obtain 1,4-*para*-disubstituted linear chain structure polyaniline with higher electrical conductivity. The higher oxidation degree polyaniline contained more linear chain structure than that in lower oxidation degree. Polyanilines containing Fe^{2+} and Cu^{2+} had more linear chain structure than that containing Co^{2+} and Ni^{2+}. These observations were in accordance with experimental measurements of electrical conductivity.

Keywords: Polyaniline; Transition metal ions; FT-IR spectroscopy; Characterization

1. Introduction

Among all the promising electrical conducting polymers, polyaniline exhibits unique advantage both for research and application due to its easy preparation, high conductivity and good environmental stability [1–5]. Since 1970s, a great number of efforts have been devoted to its structure nature, doping and conductivity mechanism, physico-chemical and electrochemical properties associated with its application in electroactive materials [6], sensor components [7,8], anti-corrosion paintings [9,10], secondary battery electrode materials [11] and many other related fields [12,13]. Polyanilines containing some transition metal ions can be used as novel synthetic metal catalyst in some oxidation systems [14,15]. In our previous paper [16], we reported the synthesis of polyanilines containing Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} by oxidizing the complex of aniline with corresponding metal chloride salt in solution. And the preliminary results were given by FT-IR spectroscopy to determine the molecular structure of resulting polyanilines. Here, we mainly employ FT-IR spectra data to elucidate the detailed chain structure changes of the polyanilines synthesized under different reaction conditions such as reaction medium, the molar ratio of reactants, reaction temperature and time, and try to correlate these observations with corresponding electrical conductivity measurements. The aim is to provide some useful information to obtain novel polyanilines containing some transition metal ions with electrical conductivity.

2. Experimental

2.1. Reagents and materials

Aniline was vacuum distilled twice in the presence of zinc powder prior to use. $(NH_4)_2S_2O_8\cdot 2H_2O$, $CuCl_2\cdot 2H_2O$, $FeCl_2\cdot 4H_2O$, $CoCl_2\cdot 2H_2O$, $NiCl_2\cdot 2H_2O$, hydrochloric acid (36%), ammonia (28%), ethanol and acetone were analytical reagents and were used as received.

2.2. Synthesis of polyanilines

Polyaniline hydrochloric acid salt (PAn–HCl) and its emeraldine base (EB) were prepared according to the literature procedure [17]. Polyanilines containing transition metal ions were synthesized as follows: 5 ml distilled aniline was added into

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[*] Corresponding author. Tel.: +86 731 8872285; fax: +86 731 8872531.
E-mail address: chunming@hunnu.edu.cn (C. Yang).

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200 ml solution containing a quantitative amount of transition metal chloride. The solution was stirred for 2 h. Then, a certain amount of oxidant $(NH_4)_2S_2O_8$ was dissolved in 40 ml of the same solvent and added dropwise into the above solution in 30 min. The reaction was carried out with constant stirring for 24 h and the precipitate was filtered and washed thoroughly with 95% ethanol and acetone. The resulting polyaniline product was vacuum dried at 60 °C for 24 h.

2.3. Characterization of polyanilines

The FT-IR spectra for all samples were obtained on a 510P Nicolet FT-IR spectrophotometer in KBr pellets in the range of 4000–400 cm^{-1} with a resolution of 1 cm^{-1}. The electrical conductivities of polyaniline samples were measured at room temperature with dry pressed pellets (Ø12.7 mm × 2 mm, 1 MPa) by the standard four-point probe method.

3. Results and discussion

3.1. FT-IR spectra of polyanilines synthesized in different media

As shown in Fig. 1A, spectrum (a) corresponds to the emeraldine base synthesized according to the standard literature method [17]. Spectra (b–e) correspond to the polyanilines synthesized in 1:9, 3:7, 6:4 and 9:1 (v/v) $EtOH/H_2O$ reaction medium, respectively.

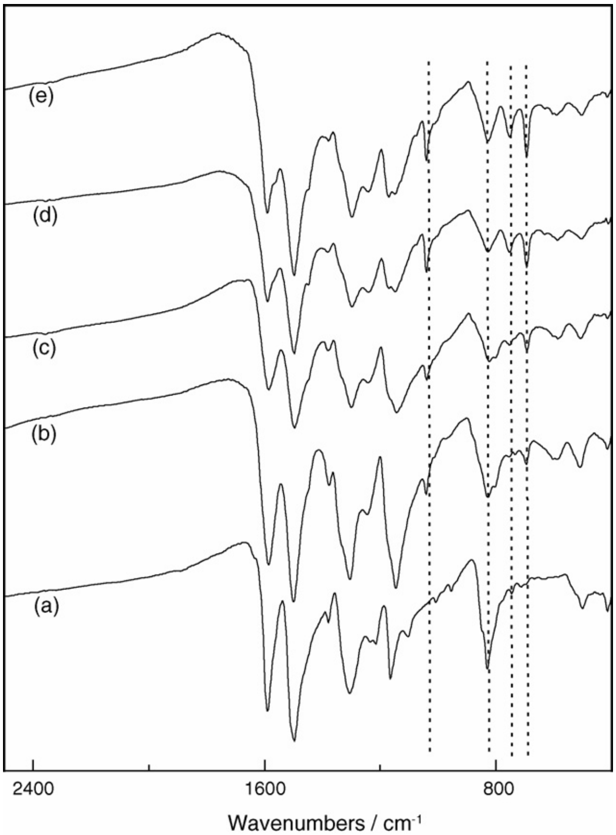

Fig. 1. (A) FT-IR spectra of EB (a) and polyanilines synthesized in different media: (b) in 1:9 $EtOH/H_2O$; (c) in 3:7 $EtOH/H_2O$; (d) in 6:4 $EtOH/H_2O$; (e) in 9:1 $EtOH/H_2O$. (B) FT-IR spectra in the range of 1000–1200 cm^{-1}. (C) FT-IR spectra in the range of 600–900 cm^{-1}.

It can be found that emeraldine base shows five main characteristic absorption peaks at 1592, 1497, 1302, 1165 and 828 cm^{-1}, attributed to the $\nu_{N=Q=N}$, ν_{N-B-N}, ν_{C-N}, the characteristic mode of N=Q=N (where Q and B stand for the quinonoid and benzenoid unit, respectively) and C–H out-of-plane bending on 1,4-*para*-disubstituted benzene ring, respectively [18].

It is worth to notice that the FT-IR spectrum of polyaniline obtained in the different polarity reaction medium is greatly different: (i) the absorption peak at 1165 cm^{-1}, which was referred to by Chiang and MacDiarmid [19] as a measure of the degree of electron delocalization on polyaniline molecular chain, changes tremendously with the increase of the polarity of reaction medium; (ii) the absorption bands corresponding to different substitution mode on benzene ring change very quickly with the change of polarity of the reaction medium.

As shown in Fig. 1B, it is very clear that the peak at 1165 cm^{-1} gradually decreased with the increase of polarity of reaction medium from 9:1 to 6:4 (v/v) $EtOH/H_2O$, while the peak at 1145 cm^{-1} gradually increased concomitantly. When the polarity of solution was increased to 1:9 (v/v) $EtOH/H_2O$, the peak at 1165 cm^{-1} disappeared completely while the peak at 1145 cm^{-1} becomes the strongest. Therefore, we can conclude that the electrical conductivity for these samples should increase from (e) to (b) according to the electron delocalization degree on their molecular chains [19]. As a matter of fact, the conductivities for these samples were measured to be 8.0×10^{-5}, 1.0×10^{-4}, 1.65×10^{-3} and 3.36×10^{-3} S cm^{-1}, respectively. It clearly indicates that stronger polar reaction medium is beneficial to obtain higher conductivity polyaniline.

On the other hand, substitution mode on the benzene ring of polyaniline also changes accordingly with the change of reaction medium polarity as shown in Fig. 1C. When the polarity of medium is very weak (in 9:1, v/v, $EtOH/H_2O$), three absorption peaks appear at 827, 752 and 694 cm^{-1} in spectrum (e), another middle strong absorption peak can be observed at 1040 cm^{-1} [20] at the same time as shown in Fig. 1B. It indicates that 1,2-*ortho*-disubstituted and/or 1,2,4-trisubstituted modes on the benzene ring of polyaniline may dominate in the weaker polarity reaction medium. With the increase of medium polarity from (e) to (b), the absorption peak at 694 cm^{-1} was found to become smaller gradually and the peak at 752 cm^{-1} also decrease and almost disappear at spectrum (b). Meanwhile, the peak corresponding to 1040 cm^{-1} also decreased accordingly. However, the peak at 827 cm^{-1} becomes stronger gradually. These observations suggest that 1,4-*para*-disubstitution mode on benzene ring of polyaniline dominate with the increase of polarity of reaction medium. It means that the linear chain structure is overwhelming over the branch chain structure in polyaniline molecule chains. This conclusion also greatly supports that the linear chain structure is more beneficial to electrical conductivity of polyaniline than other branch chain structures.