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# Vibration and X-ray photoelectron spectroscopies of $FeCl_3$-doped poly(*p*-diethynylbenzene)

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## Abstract

The doping mechanism of poly(*p*-diethynylbenzene), chemically doped with $FeCl_3$, was investigated. Absorption, infrared, far infrared, Raman, X-ray photoelectron spectroscopies were used to determine the nature of the dopant in doped polymer. The experimental results suggest that the charge transfer reaction between the polymer chain and the dopant results in the formation of $FeCl_4^-$ species, the π electron charge delocalization along the polymeric chain and the reduction of $\pi$–$\pi^*$ transition energy.

*Keywords:* Poly(*p*-diethynylbenzene); Doping; Conductivity; Spectroscopy

## 1. Introduction

Conducting polymers have attracted intensive attention in the past 20 years on account of their unique electrical and optical properties [1]. One of the significant aspects of the research in conducting polymer science is the doping process, which is usually achieved chemically or electrochemically. The electrical properties and conduction mechanisms of $I_2$, $FeCl_3$ and $AsF_5$-doped polyacetylenes have been extensively investigated [2,3]. Important for understanding of the conduction mechanism is the role of the dopants in doped conductors. Most models of conduction are based on carrier propagation through chains with disordered and localized charges [4]. Mössbauer, far infrared (FIR), Raman, X-ray photoelectron and electron spin resonance spectroscopies were used to determine the nature of the dopant in doped polymer [5,6].

Poly(*p*-diethynylbenzene) (PDEB) is one member of the polyacetylene family. In our group, soluble PDEB with fairly high molecular weight has been prepared by using nickel and palladium acetylides as catalysts and FT-IR, Raman, UV, $^1H$ NMR and $^{13}C$ NMR spectra suggest a configuration of the polyene chains with branched structure [7–9]. Recently, we found that soluble PDEB shows photoluminescence, electroluminescence, third-order nonlinear optical property and humidity sensitivity [10–15]. Moreover, we reported electrical properties and spectroscopic study of $HClO_4$-doped PDEB [16,17]. Although some papers presented the spectroscopic characterization of various $FeCl_3$-doped conductors [18–20], to our knowledge, there has been no report on $FeCl_3$-doped PDEB.

In this paper, we discuss the results of vibrational and photoelectron spectroscopies in determining the nature of the iron moiety in the $FeCl_3$-doped conductor PDEB.

## 2. Experimental

### 2.1. Materials

PDEB was prepared from polymerization of *p*-diethynylbenzene in 1,4-dioxane-toluene mixed solvent using $Ni(PPh_3)_2(C{\equiv}CC_6H_4C{\equiv}CH)_2$ as catalyst at room

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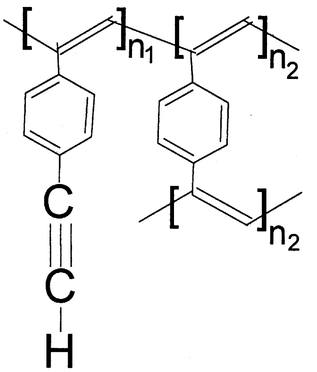


Fig. 1. Chemical structure of PDEB.

temperature, as previously reported [9]. PDEB is orange-yellow powder with a weight average molecular weight of >10000. The chemical structure of PDEB, confirmed by FT-IR, Raman, UV, $^1$H NMR and $^{13}$C NMR spectra [8,9], is shown in Fig. 1.

### 2.2. Doping

A typical chemical doping procedure is as follows: The polymer PDEB (1.28 mmol, 161 mg) was dissolved in $CHCl_3$ (5 ml), and was mixed with a solution of $FeCl_3$ (1.0 mmol, 162 mg) in $CHCl_3$ (5 ml). The mixed solutions were aged at room temperature for 24 h, and then the solvent was removed under vacuum and slightly heat until very dried solids were obtained. The doping level was determined to be 50.1%, and the polymer/dopant mole ratio was 1.28. Other doping procedures with different doping levels and polymer/dopant ratios were carried out analogously.

### 2.3. Conductivity measurements

The samples were ground in a mortar and pressed into pellets under 600 kg/cm$^2$. Conductivity was measured on pressed pellets with the use of an Advantest R6142 programmable d.c. voltage/current generator, a Keithley 196 system DMM and a two-point probe method.

### 2.4. Spectroscopic measurements

UV–Vis spectra in $CHCl_3$ solution were recorded on a General TU-1201 UV–Vis recording spectrophotometer. FT-IR spectra were taken on a Perkin–Elmer System 2000 FT-IR spectrometer with KBr pellets. The FIR spectra were obtained on a Bio-rad FTS6000 spectrometer with Nujol mulls. FT Raman spectra were acquired on a Bio-rad FTS6000 spectrometer fitted with quartz beam splitter and equipped with Raman III accessory with a liquid nitrogen-cooled germanium detector. The defocused 1064 nm line of an air-cooled Nd:YAG near IR laser (coherent) was used to excite spectrum. The sample was excited in 180° arrangement with the laser power of 130 mW. X-ray photoelectron spectroscopy (XPS) spectra were obtained at room temperature on an ESCA 300 spectrometer employing Mg $K\alpha_{1,2}$ radiation ($h\nu = 1253.6$ eV). The typical X-ray power was 15 kV × 10 mA. All the spectra were energy-referenced to the C(1s) photoionization peak, to which was assigned a binding energy of 285.0 eV.

## 3. Results and discussion

Table 1 shows the dependence of conductivity on the doping concentration. The conductivity of original PDEB at room temperature is about $10^{-14}$ S/cm. Upon doping with 22.6–50.1 wt.% $FeCl_3$, the conductivity gradually increases and reaches a maximum value of $4.0 \times 10^{-5}$ S/cm, and then drops off slightly with further increasing the doping concentration. This result is similar to that obtained for $FeCl_3$-doped polyacetylene [21,22]. Shirakawa et al. ascribed this to the chlorination of the double bonds in polyacetylene, which could not contribute to the conduction process [22]. However, the decrease of conductivity in $FeCl_3$-doped PDEB at high doping concentration is not caused by chlorination of the double bonds because chlorination was not observed, which is confirmed by XPS and FT-IR spectroscopies, but probably due to decrease of charge carrier concentration.

The absorption spectrum of $FeCl_3$-doped PDEB is shown in Fig. 2, together with those of the undoped polymer and $FeCl_3$. The maximum absorption of undoped PDEB is at ≈300 nm, the absorption bands of $FeCl_3$ are 327 and 356 nm, while the absorption bands of $FeCl_3$-doped PDEB are at ≈295 and 390 nm. Moreover, the color of the polymer markedly changes from orange-yellow to black upon doping. The color changing and the enhancement of the absorption band at 390 nm agree with the enhanced π electron charge delocal-

Table 1
Dependence of conductivity on doping concentration in $FeCl_3$-doped PDEB

| Doping concentration (wt.%) | PDEB/$FeCl_3$ mole ratio | Conductivity (S/cm) |
|---|---|---|
| 0 | | $5.5 \times 10^{-14}$ |
| 22.6 | 4.40 | $1.7 \times 10^{-12}$ |
| 31.4 | 2.81 | $8.0 \times 10^{-8}$ |
| 41.2 | 1.83 | $3.4 \times 10^{-6}$ |
| 50.1 | 1.28 | $4.0 \times 10^{-5}$ |
| 60.3 | 0.85 | $3.8 \times 10^{-5}$ |
| 71.0 | 0.53 | $3.3 \times 10^{-5}$ |
| 85.0 | 0.23 | $6.5 \times 10^{-6}$ |

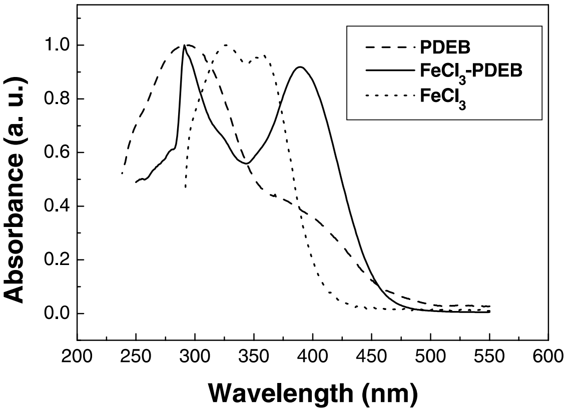


Fig. 2. Absorption spectra of PDEB, $FeCl_3$ and $FeCl_3$-doped PDEB in $CHCl_3$ solution. Doping level: 50 wt.%.

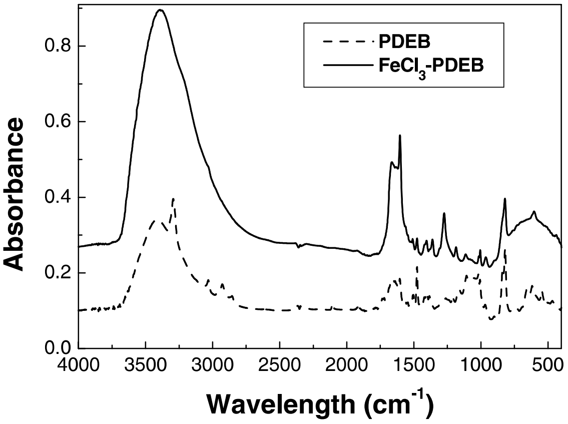


Fig. 3. FT-IR spectra of undoped and $FeCl_3$-doped PDEB (KBr pellets). Doping level: 50 wt.%.

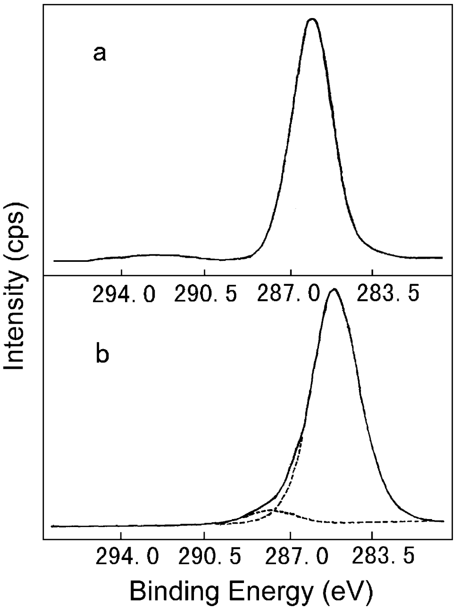


Fig. 4. C(1s) core level XPS spectra for undoped (a) and $FeCl_3$-doped (b) PDEB. Doping level: 50 wt.%.

ization and the reduction of the $\pi \rightarrow \pi^*$ transition energy.

The FT-IR spectrum of $FeCl_3$-doped PDEB shows a new band at 1274 $cm^{-1}$ in comparison with that of undoped PDEB (Fig. 3). The new band may be correlated likewise to defects induced by the charge transfer reaction between the polymer chain and the dopant [23]. The strong band at 3400 $cm^{-1}$ may be due to the interaction of the system with water. No new bands are present in the range 850–650 $cm^{-1}$ attributed to C–Cl stretching vibration [24] which lead us to believe that no chlorination of the main chain occurs.

In the C(1s) spectrum for the undoped PDEB (Fig. 4a), the main line centered at 286.1 eV is rather symmetric and narrow with a full width at half maximum (FWHM) of 2.04 eV, which can be attributed to only one kind of carbon atom [20]. The C(1s) line is associated with a small peak at 292.8 eV, about 6.7 eV from the main line on the high binding energy side of the spectrum. This peak is known to be due to a $\pi \rightarrow \pi^*$ shake-up satellite characteristic for the presence of localized $\pi$ electrons along the chain of the polymer [20].

XPS spectrum (Fig. 4b) shows quite remarkable changes on the C(1s) signal of PDEB upon doping with $FeCl_3$ (50 wt.%) in $CHCl_3$ solution. First of all, the core level is shifted towards lower binding energy by 1.1 eV. This energy shift is clearly related to a charge transfer reaction between the carbon atoms in the polymeric chain and the dopant species. Jugnet et al. [25] proposed the following interpretation. Upon doping, electrons are extracted from the $\pi$ extended states of the polymeric chain. Since the density of these states is rather low and flat in the vicinity of the Fermi energy ($E_F$), there results a large shift of $E_F$ into the valence band, and the core level moves towards lower binding energy following the $E_F$ shift. The second evident change is the complete disappearance of the localized shakeup satellite signal at 292.8 eV, probably because of enhancement of $\pi \rightarrow \pi^*$ shakeup satellite from the modification of the electronic structure of PDEB by doping and the enhanced $\pi$ electron charge delocalization along the polymeric chain. The third remarkable change is the broadening of the signal at the high binding energy side. The C(1s) spectrum is decomposed into two components at 285.0 and 287.9 eV with respective intensity ratios of 1.00 and 0.13. The appearance of the peak at 287.9 eV can be interpreted in terms of enhancement of $\pi \rightarrow \pi^*$ shakeup satellite [16,20].

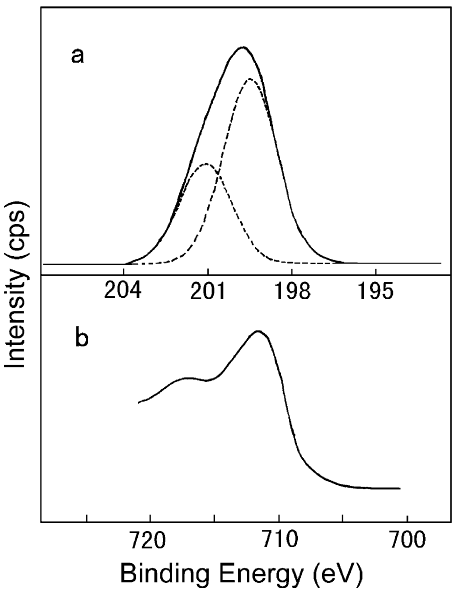


Fig. 5. Cl($2p_{3/2,1/2}$) (a) and Fe($2p_{3/2}$) (b) core level XPS spectra for $FeCl_3$-doped PDEB. Doping level: 50 wt.%.

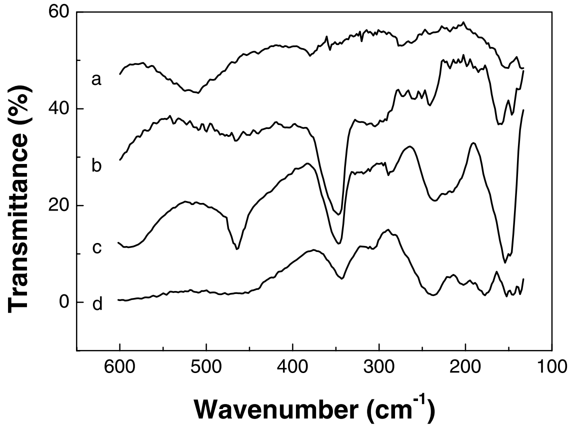


Fig. 6. FIR spectra of PDEB (a), $FeCl_3$-doped PDEB (b), $FeCl_3 \cdot 6H_2O$ (c) and $FeCl_2 \cdot 4H_2O$ (d). Doping level: 50 wt.%.

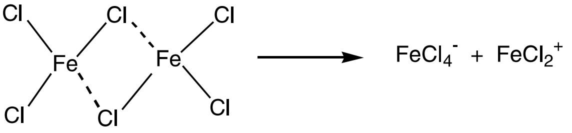
From the Cl(2p) core level spectrum (Fig. 5a), we can observe that chlorine shows two unresolved spin–orbit doublet. The Cl(2p) spectrum can be decomposed into two components at 199.4 and 201.0 eV with FWHM of 2.24 eV and respective intensity ratios of 1.0 and 0.5, which are assigned to Cl($2p_{3/2}$) and Cl($2p_{1/2}$). The narrow peak of the Cl($2p_{3/2}$) suggests that only one species of chlorine exists and chlorine is bonded to iron, thus precluding any chlorination of the double bond of PDEB, consistent with the FT-IR spectrum. The Fe($2p_{3/2}$) core level spectrum for the $FeCl_3$-doped PDEB is shown in Fig. 5b. The main line centered at 711.3 eV and the satellite at about 5.6 eV from the main line on the high binding energy side of the spectrum were observed. The XPS data indicate that $FeCl_4^-$ species is probably present in $FeCl_3$-doped PDEB [18].

To further ascertain the nature of the dopant in the doped polymer we have resorted to combining FIR and Raman spectra. Fig. 6 gives the FIR spectrum of $FeCl_3$-doped PDEB together with those of PDEB, $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$. The present results show that $FeCl_3$-doped PDEB, $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ have some overlapping bands. However, the band at 347 $cm^{-1}$ in $FeCl_3$-doped PDEB is intense compared to the band at the same frequency of the spectrum of $FeCl_2 \cdot 4H_2O$. The FIR spectrum of $FeCl_3$-doped PDEB shows a weak band at 146 $cm^{-1}$. These two bands correspond to the infrared-active $\nu_3$ and $\nu_4$ vibrations in $FeCl_4^-$ moiety [26,27]. The strong band at 465 $cm^{-1}$ in $FeCl_3 \cdot 6H_2O$ is absent in doped PDEB. Thus, FIR spectroscopies indicate that both $FeCl_2$ hydrate and $FeCl_4^-$ are probably present in the $FeCl_3$-doped PDEB.

We cannot obtain Raman spectrum of $FeCl_3$-doped PDEB because the doped sample is black and absorption of the laser and effect of heat occur.

No one method of characterization is entirely conclusive, but a combination of various techniques has been proven to be useful to probe the doping mechanism. On the basis of absorption, infrared, far infrared and X-ray photoelectron spectroscopies, we propose that both $FeCl_4^-$ and $FeCl_2 \cdot nH_2O$ exist in $FeCl_3$-doped PDEB. The good stability of $FeCl_3$-doped PDEB to air indicates that the $FeCl_2$ moiety is imbedded in the polymer because $FeCl_2$ is unstable to air. It should be emphasized that XPS, basically a surface technique, is able to identify the Fe(II) species.

Anhydrous $FeCl_3$ is known to be a dimer and undergoes dissociation in solution as follows:



The $FeCl_4^-$ is coordinately saturated and stable, while $FeCl_2^+$ is unstable. $FeCl_2^+$ is an oxidizing agent and can react easily with the polymer chain, which has rich π electrons, to induce a possible charge transfer according to the following pathway:

$$FeCl_2^+ + PDEB + nH_2O \rightarrow PDEB^+ + FeCl_2 \cdot nH_2O$$

## 4. Conclusions

Upon doping with $FeCl_3$, conductivity of PDEB increases 9 orders of magnitude, and reaches $10^{-5}$ S/cm showing the semiconductor characteristics. The conductivity gradually increases and then drops off slightly with increasing the doping concentration, and the decrease of conductivity at high doping concentration is not due to chlorination of the double bonds but probably due to decrease of charge carrier concentration. UV–Vis, FT-IR, FIR and XPS spectroscopies suggest that the charge transfer reaction between the polymer chain and the dopant results in the formation of $FeCl_4^-$ species and the electron charge delocalization along the polymeric chain.

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