

## 論文

### ポリピロール-T<sub>2</sub>O系の赤外スペクトル

金坂 績・織田 和宏

富山大学理学部  
〒930 富山市五福3190

### The Infrared Spectrum of Polypyrrole-T<sub>2</sub>O System

Isao KANESAKA and Kazuhiro ODA

Faculty of Science, Toyama University,  
Gofuku 3190, Toyama 930, Japan

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#### Abstract

The infrared spectra of polypyrrole contacting with T<sub>2</sub>O gas were observed for *ca.* 100 days. After adding T<sub>2</sub>O (1.2 Ci; isotopic purity: 15%) the band at 2180cm<sup>-1</sup> was observed, which is assigned to the N-T stretch. Although the bands at 1560 and 1204cm<sup>-1</sup> were initially strong, they became relatively weak by Tβ-irradiation. On the other hand, the bands at 1655 and 1400cm<sup>-1</sup>, as well as 1700cm<sup>-1</sup>, became relatively strong by Tβ-irradiation. This is explained in that the quinonoid-type structure with partially aromatic-type structure decreases and a structure with probable C=N bonds is formed. It was also found that many carbonyl defects are formed in both the atmosphere and Tβ-radiolysis.

#### 1. Introduction

We have studied Tβ-radiolysis for such systems as poly(vinyl alcohol) by means of infrared spectroscopy.<sup>1-4)</sup> The method is quite useful for clarifying structural changes and decomposed species which result from Tβ-radiolysis. In the present study we will report the infrared spectra of polypyrrole (PPy)-T<sub>2</sub>O system, drawing the structural change by Tβ-irradiation.

PPy prepared by electrochemical oxidation of pyrrole in the presence of inorganic salts includes counter anions as dopant. This is true for PPy prepared by chemical oxidation. That is, doped PPy has cation defects, so-called polaron and bipolaron, which play important role in electronic conductivity.

The vibrational study of PPy<sup>5-12)</sup> has been widely carried out in relation to the structural change accompanying with electrochemical redox. On the other hand, the infrared spectra of doped PPy<sup>5-9)</sup> reveal quite complex features that they depend on the method of oxidation and the kinds of dopant and their concentrations. The similar feature is also seen in reduced PPy.<sup>5, 8, 9)</sup> It is also reported<sup>5, 8)</sup> that carbonyl groups, C=N bonds and sp<sup>3</sup> C-H bonds are formed.

The complex spectral features result clearly from the fact that PPy is easily oxidized with different amounts of dopant. On the other hand, PPy is chemically active,<sup>5, 6, 8, 9)</sup> as expected from the formation of carbonyl groups and so on, resulting in further complexity in the spectral features. In these respects, we can expect large structural changes by T $\beta$ -irradiation (average: 5.7 keV) in the presence of T<sub>2</sub>O (H<sub>2</sub>O), which gives rise to O<sub>2</sub> and H<sub>2</sub> through ionic and radical intermediates. The advantage of using T<sub>2</sub>O is: (1) T with high density is substituted in N-H groups and (2) no surface effect is expected because the substitution by T takes place in whole PPy.

## 2. Experimental

PPy was prepared by oxidation of pyrrole(0.1mol/l) with FeCl<sub>3</sub>(0.5mol/l) in the solvent consisting of acetonitrile(85%) and ethanol(15%). The electronic conductivity of PPy was 0.7 s/cm. The infrared cell used analogous one used previously.<sup>1)</sup> After the infrared cell, where PPy was set as the KCl disk, was evacuated, T<sub>2</sub>O gas (1.2Ci; the isotopic purity: 15%), which was prepared for experiments of T<sub>2</sub>O ice,<sup>3)</sup> was added. The infrared spectra were observed during *ca.* 100 days. The infrared spectra were recorded on a JASCO FT/IR 8000S or IR 302A spectrometer. The observed wavenumbers were calibrated using those of polystyrene and believed to be accurate within  $\pm 5$  cm<sup>-1</sup> (hot runs).

The sample was hard and granulous with less transmission in the infrared spectrum. So, the crushed samples were stirred in 1mol/l HCl solution for 24 h, washed by water for 24 h at 90°C and dried at 90°C (HCl treated PPy). The similar procedure was also done using NaOH (1mol/l).

## 3. Results and discussion

Figure 1 shows the infrared spectra of original PPy and HCl treated PPy. The infrared spectrum of original PPy coincides almost with that reported by Lei *et al.*,<sup>8)</sup> who prepared PPy using FeCl<sub>3</sub> as the oxidizing agent, as used here, except for the band at 1632 cm<sup>-1</sup>. As reported by Lei *et al.*,<sup>8)</sup> the counter anion in the present sys-

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tem may be Cl<sup>-</sup>. The electronic conductivity, 0.7 s/cm, suggests the dopant level of 0.18-0.21, dopant-per-ring, by reference to the XPS study.<sup>8)</sup> On the other hand, the band at 1632 cm<sup>-1</sup>, which has been scarcely observed in many infrared experiments,<sup>5-9)</sup> has been observed in ClO<sub>4</sub><sup>-</sup> doped PPy,<sup>5)</sup> whose infrared spectrum differs completely from that in Fig. 1, as shown in Fig. 3-b. Hence, it is considered that ordinary doped PPy and ClO<sub>4</sub><sup>-</sup> doped PPy are mixed with different concentrations in original PPy.

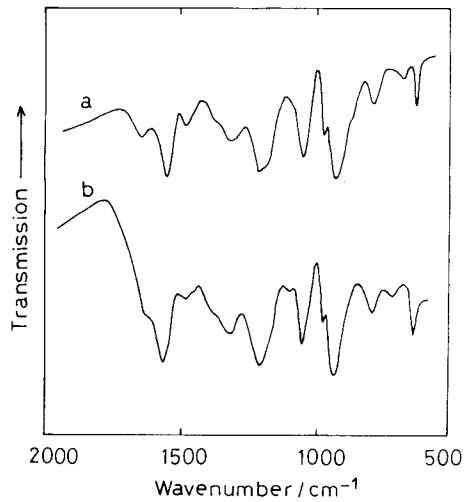


Fig. 1. Infrared spectra of (a) original and (b) HCl treated PPy.

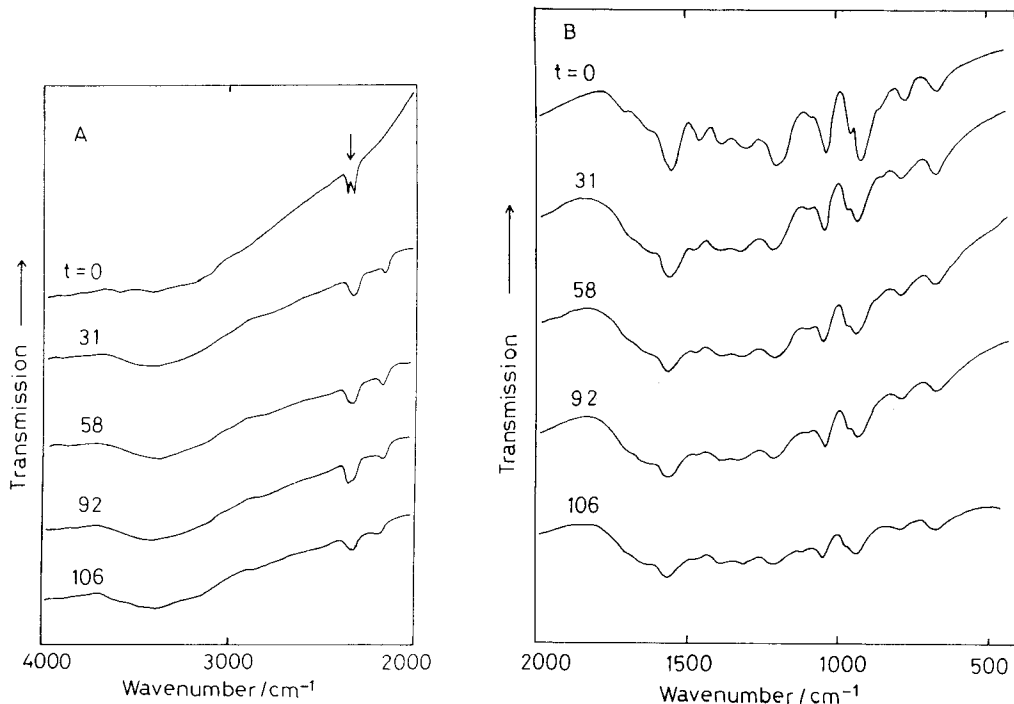


Fig. 2. (A) Infrared spectra of PPy-T<sub>2</sub>O system above 2000 cm<sup>-1</sup> at various times (*t* in day). The band arrowed is due to CO<sub>2</sub>.

(B) Infrared spectra of PPy-T<sub>2</sub>O system below 2000 cm<sup>-1</sup>.

The infrared spectrum of HCl treated PPy changed to some extent as compared with that of original PPy, as shown in Fig. 1. First, the shoulder at  $1622\text{ cm}^{-1}$  was observed for the medium band at  $1632\text{ cm}^{-1}$  in original PPy and, second, the strong band at  $1204\text{ cm}^{-1}$  for doublet at  $1208$  and  $1182\text{ cm}^{-1}$  was observed. The spectral changes may not indicate the significant structural change because of the slight change in the relative intensity of strong bands. On the other hand, the transmission of HCl treated PPy was higher in the infrared spectrum. So, we used HCl treated PPy for T $\beta$ -radiolysis.

The infrared spectra of the PPy-T<sub>2</sub>O system are given at various times ( $t$  in day) in Fig. 2. In Fig. 2-A the sharp band at  $2180\text{ cm}^{-1}$  is observed at  $t \geq 31$ , which is assigned to the N-T stretch, by referring to the N-H stretch at  $3400\text{ cm}^{-1}$ . This indicates that T distributes in whole PPy. On the other hand, the O-T stretch, which is expected at *ca.*  $2100\text{ cm}^{-1}$  for the condensed state, was not observed, which indicates a small amount of absorbed water in PPy.

In Fig. 2-A the N-H and N-T stretches are observed clearly, as found in moderately reduced PPy.<sup>5, 8, 9)</sup> However, this is not explained in terms of decrease in dopants, because the absorbance in the PPy-T<sub>2</sub>O system increases, as a whole, below  $2500\text{ cm}^{-1}$ , which indicates increase in conductivity. The increase in absorbance over the wide region suggests structural changes in conjugated systems, which may be the scission of chains and/or the formation of bonds between chains due to T $\beta$ -irradiation.

In Fig. 2-B a weak band at  $1710\text{ cm}^{-1}$  and the intensity enhancement at  $1400\text{ cm}^{-1}$  are observed at  $t=0$  as compared with that in Fig. 1-b, although HCl treated PPy is used in both spectra. That is, there are somewhat differences in the infrared spectra, which are observed soon (Fig. 1-b) and at two months (Fig. 2-B,  $t=0$ ) after the HCl treatment, between HCl treated PPy's. This probably

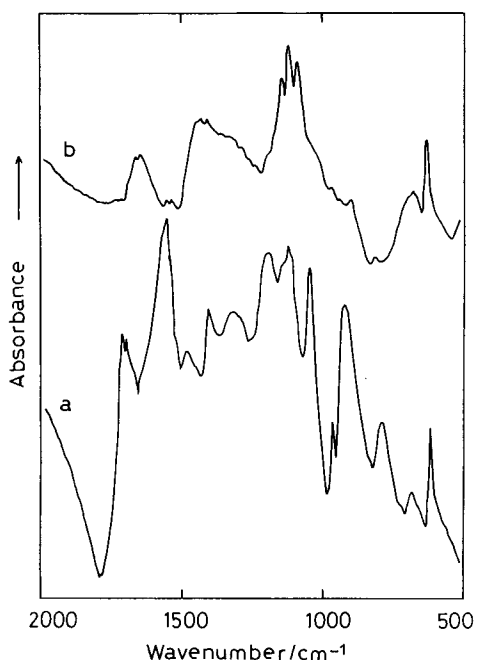
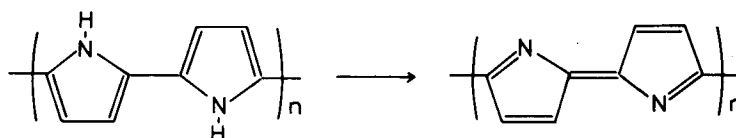


Fig. 3. Infrared spectra of (a) oxidized materials of  $\text{SO}_4^{2-}$  doped PPy and (b)  $\text{ClO}_4^-$  doped PPy (taken from Ref. 5).

means that HCl treated PPy is not stable as it is in the atmosphere.

In Fig. 2-B we can see that the strong bands at 1560 and 1204  $\text{cm}^{-1}$  at  $t=0$  become relatively weak at  $t \geq 31$ , whereas the bands at 1655 and 1400  $\text{cm}^{-1}$  as well as 1700  $\text{cm}^{-1}$  become relatively strong. Qian and Qin<sup>5)</sup> have reported the infrared spectra of oxidized materials of  $\text{SO}_4^{2-}$  doped PPy applied for 0.8 V *vs.* SCE for 2 h in a  $\text{Na}_2\text{SO}_4$  solution and  $\text{ClO}_4^-$  doped PPy, which are given in Fig. 3-a and -b, respectively. In Fig. 3-a, the band at 1697  $\text{cm}^{-1}$  has been assigned to the C=O stretch. Hence, the band at 1700  $\text{cm}^{-1}$  in Fig. 2-B is assigned to the C=O stretch. The carbonyl defects, carbonyl-per-ring, are expected to be *ca.* 0.5 by reference to the FT-IR/XPS study.<sup>8)</sup> The band at 1710  $\text{cm}^{-1}$  at  $t=0$  is, hence, assigned to the C=O stretch, whose bond may be formed in the atmosphere.

The infrared spectrum of  $\text{ClO}_4^-$  doped PPy<sup>5)</sup> in Fig. 3-b differs completely from that in Fig. 1. There are strong and broad bands at 1644  $\text{cm}^{-1}$  and in the region 1400  $\sim$  1300  $\text{cm}^{-1}$  in Fig. 3-b, where the sharp bands at 1145, 1120 and 670  $\text{cm}^{-1}$  are due to  $\text{ClO}_4^-$  ions. We can see that the bands enhanced with T $\beta$ -irradiation correspond well to those in Fig. 3-b. This means that the structure of PPy changes from that with the strong bands at 1560 and 1204  $\text{cm}^{-1}$  to that with the bands at 1655 and 1400  $\text{cm}^{-1}$ . The bands at 1560 and 1204  $\text{cm}^{-1}$  are attributed mainly to the quinonoid-type structure and partially to the aromatic-type structure by reference to the analysis based on the effective conjugation coordinate.<sup>6)</sup> On the other hand, the structure of  $\text{ClO}_4^-$  doped PPy in Fig. 3-b seems to be different from that of ordinary PPy, which is also supported from complete differences in the infrared spectra of reduced PPy<sup>5)</sup> between  $\text{Cl}^-$  and  $\text{ClO}_4^-$  doped PPys.  $\text{ClO}_4^-$  doped PPy in Fig. 3-b has probably C=N bonds from the band at 1644  $\text{cm}^{-1}$ , although Inoue *et al.*<sup>10)</sup> have suggested the formation of polaron in  $\text{ClO}_4^-$  doped PPy from their Raman study. By intuition we propose that the structure formed by T $\beta$ -irradiation is the oxidized one losing hydrogen atoms from N-H groups, as shown by the structural change:



Accordingly, it is concluded that the structure with probably C=N bonds is formed by T $\beta$ -irradiation and, further, many carbonyl defects are formed. The other structural change, probably scission of chains and/or formation of bonds between chains, is also suggested.

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