The Infrared Spectrum of Polypyrrole–T₂O System

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ABSTRACT: The infrared spectra of polypyrrole contacting with T₂O gas were observed for *ca.* 100 days. After adding T₂O (1.2 Ci; isotopic purity: 15%) the band at 2180 cm⁻¹ was observed, which is assigned to the N–T stretch. Although the bands at 1560 and 1204 cm⁻¹ were initially strong, they became relatively weak by T β -irradiation. On the other hand, the bands at 1655 and 1400 cm⁻¹ as well as 1700 cm⁻¹ became relatively strong by T β -irradiation. These are explained in terms that the quinonoid-type structure with partially the aromatic-type structure decreases and the structure with probably C=N bonds is formed. It was also found that many carbonyl defects are formed in both the atmosphere and T β -radiolysis.

KEY WORDS Polypyrrole / T β -Radiolysis / Infrared Spectrum / Tritium

We have studied T β -radiolysis for such systems as poly(vinyl alcohol) by means of infrared spectroscopy.^{1–4} The method is quite useful for clarifying structural changes and decomposed species which result from T β -radiolysis. In the present study we will report the infrared spectra of polypyrrole (PPy)–T₂O system, drawing the structural change by T β -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^{5–14} 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^{5–11} 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.^{5,7,10,11} It is also reported^{7,10} that carbonyl groups, C=N bonds and *sp*³ 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,^{5,7,8,10,11} as expected from the formation of carbonyl groups and so on, resulting in further complexity in the spectral features. In this respect, we can expect large structural changes by T β -irradiation (average: 5.7 keV) in the presence of T₂O (H₂O), which gives rise to O₂ and H₂ through ionic and radical intermediates. The advantage of using T₂O 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.

EXPERIMENTAL

PPy was prepared by oxidation of pyrrole (0.1 mol l⁻¹) with FeCl₃ (0.5 mol l⁻¹) in the solvent consisted of acetonitrile (85%) and ethanol (15%). The electronic conductivity of PPy was 0.7 S cm⁻¹. The infrared cell used was analogous one used previously.¹ After the infrared cell, where PPy was set as the KCl disk, was evacuated, T₂O gas (1.2 Ci; the

isotopic purity: 15%), which was prepared for experiments of T₂O ice,³ was added. The infrared spectra were observed over *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 $\pm 5 \text{ cm}^{-1}$ (hot runs).

The sample was hard and granulous with less transmission in the infrared spectrum. So, the crushed samples were stirred in 1 mol l^{-1} 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 (1 mol l^{-1}). The infrared spectra of original PPy, HCl treated PPy and NaOH treated PPy are given in Figure 1.

RESULTS AND DISCUSSION

In Figure 1 the infrared spectrum of original PPy coincides almost with that reported by Lei *et al.*,¹⁰ who prepared PPy using FeCl_3 as the oxidizing agent, as used here, except for the band at 1632 cm^{-1} . As reported by Lei *et al.*,¹⁰ the counter anion in the present system may be Cl^- . The electronic conductivity, 0.7 S cm^{-1} , suggests the dopant level of 0.18–0.21 by reference to the XPS study.¹⁰ On the other hand, the band at 1632 cm^{-1} , which has been scarcely observed in many infrared experiments,^{5–11} has been observed in ClO_4^- doped PPy,⁷ where main bands are observed at 1644 and *ca.* 1410 cm^{-1} above 1200 cm^{-1} , although it has been reported that the infrared spectrum of ClO_4^- doped PPy^{5,6} is almost the same as that of ordinary doped PPy. Hence, it is considered that ordinary doped PPy and ClO_4^- doped PPy are mixed with different concentrations in original PPy.

The infrared spectrum of HCl treated PPy changed to some extent as compared with that of original PPy, as shown in Figure 1. First, the shoulder at 1622 cm^{-1} was observed for the medium band at 1632 cm^{-1} in original PPy

Figure 1. Infrared spectra of (a) original PPy, (b) HCl treated PPy, and (c) NaOH treated PPy.

and, second, the strong band at 1204 cm^{-1} for doublet at 1208 and 1182 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 β -radiolysis. The infrared spectrum of NaOH treated PPy is discussed later in relation to the structural change found here.

The infrared spectra of the PPy-T₂O system are given at various times (*t* in day) in Figure 2. In Figure 2-A the sharp band at 2180 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 cm^{-1} . This indicates that T distributes in whole PPy. On the other hand, the O-T stretch, which is expected at *ca.* 2100 cm^{-1} for the condensed state, was not observed, which indicates a small amount of absorbed water in PPy.

In Figure 2-A the N-H and N-T stretches are observed clearly, as found in moderately reduced PPy.^{7,10,11} However, this is not explained in terms of decrease in dopants, because the absorbance in the PPy-T₂O system increases, as a whole, below 2500 cm^{-1} , which

Figure 2. (A) Infrared spectra of PPy-T₂O system above 2000 cm⁻¹ at various times (*t* in day). The band arrowed is due to CO₂. (B) Infrared spectra of PPy-T₂O system below 2000 cm⁻¹.

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

β -irradiation.

In Figure 2-B a weak band at 1710 cm⁻¹ and the intensity enhancement at 1400 cm⁻¹ are observed at *t* = 0 as compared with that in Figure 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 (Figure 1-b) and at two months (Figure 2-B, *t* = 0) after the HCl treatment, between HCl treated PPys. This probably means that PPy is not stable as it is in the atmosphere.

In Figure 2-B we can see that the strong bands at 1560 and 1204 cm⁻¹ at *t* = 0 become relatively weak at *t* ≥ 31, whereas the bands at 1655 and 1400 cm⁻¹ as well as 1700 cm⁻¹ become relatively strong. Qian and Qin⁷ have reported the infrared band at 1697 cm⁻¹ in oxidized materials of SO₄²⁻ doped PPy applied for 0.8 V vs. SCE for 2 h in a Na₂SO₄ solution and assigned it to the C=O stretch. Hyodo and Macdiarmid⁶ have also assigned the strong band at 1706 cm⁻¹ in SO₄²⁻ doped poly(N-methyl pyrrole) to the C=O stretch. Hence, the band at 1700 cm⁻¹ in Figure 2-B is assigned to the C=O stretch. The carbonyl defects, carbonyl-per-ring, are expected to be *ca.* 0.5 at *t* > 90 by reference to the FT-IR/XPS study.¹⁰ The band at 1710 cm⁻¹ at *t* = 0 is, hence, assigned to the C=O stretch, whose bond may be formed in the atmosphere.

As described above, two main infrared bands at 1644 and *ca.* 1410 cm⁻¹ are observed in ClO₄⁻ doped PPy.⁷ Hence, we can see that the bands enhanced with T β -irradiation correspond well to those in ClO₄⁻ doped PPy.⁷ This means that the structure of PPy changes from that with the strong bands at 1560 and 1204 cm⁻¹ to that with the bands at 1655 and 1400 cm⁻¹. The bands at 1560 and 1204 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.⁸ On the other hand, the structure of ClO₄⁻ doped PPy reported by Qian and Qin⁷ seems to be

different from that of ordinary PPy, which is also supported from complete differences in the infrared spectra of reduced PPy⁷ between Cl⁻ and ClO₄⁻ doped PPys. ClO₄⁻ doped PPy⁷ has probably C=N bonds from the band at 1644 cm⁻¹, although Inoue *et al.*¹²⁾ have suggested the formation of polaron in ClO₄⁻ doped PPy from their Raman study. By intuition we propose that the structure formed by T β -irradiation is such oxidized one losing hydrogen atoms from N-H groups as:

Inganas *et al.*¹⁵ have proposed the formation of the oxidized structure with C=N bonds by treating PPy with alkaline solutions. The infrared spectrum of NaOH treated PPy gives the broad shoulder at 1620 cm⁻¹ and the increase in intensity at *ca.* 1400 cm⁻¹, as shown in Figure 1-c. Hence, these bands are reasonably attributed to the oxidized structure with C=N bonds in consistence with our proposal for the structural change in the PPy-T₂O system, although the wavenumber, 1655 cm⁻¹, is somewhat higher than that in NaOH treated PPy.

Accordingly, it is concluded that the structure with probably C=N bonds is formed by T β -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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