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Two-dimensional Raman spectroscopic study on the structural changes of a poly(3-chlorothiophene) film during the heating process

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Abstract

Two-dimensional Raman spectroscopy has been applied to provide the information on charge carriers and thermal stability of a doped poly(3-chlorothiophene) (PCTh) film. The strong spectral intensity at 1420 cm^{-1} shows that positive polarons are the major charge carriers in doped PCTh. On the other hand, peaks in the 2D contour maps separate the overlapped bands around 1386 cm^{-1}, confirming the existence of positive bipolarons in PCTh. The positive asynchronous cross peak located at 1420/1386 cm^{-1} further indicates that bipolarons have a higher thermal stability compared with polarons in the doped PCTh. The increase of the spectral intensity at 1454 cm^{-1} and the decrease of the spectral intensity at 1420 cm^{-1} indicate that during the heating process, a structural change occurs in the PCTh film.

Keywords: Two-dimensional Raman spectroscopy; Poly(3-chlorothiophene); Oxidized species

1. Introduction

Doped conducting polymers have attracted much attention in the last decades for their high electrical conductivities [1–11]. Due to their potential applications in a wide range of technical devices, including light-emitting diodes [12,13], nonlinear optics [14], fuel cells [15], and so on, thermal stability becomes a significant parameter for the evaluation of the performance of electronic devices based on conducting polymeric materials. However, a satisfactory understanding of the thermal stability of doped conducting polymers has not been arrived yet. Garreau et al. [16] reported the planar-to-nonplanar conformational transitions in polythiophene derivatives, but the materials they studied were in undoped states, which have less applications in the technical devices.

In the present work, we apply two-dimensional (2D) Raman correlation spectroscopy to study the thermal stability of a doped polythiophene derivative, poly(3-chlorothiophene) (PCTh). It is well known that Raman spectroscopy is a powerful tool for investigating the electronic and molecular structures of doped conducting polymers [4–6]. The high resolution of 2D correlation spectroscopy which was proposed by Noda [17–19] allows one to highlight the information which cannot be easily extracted from ordinary one-dimensional (1D) spectra [20]. By tracing and analyzing the spectral changes of PCTh, we can get the corresponding information of the structural changes occurring in the PCTh film under the thermal perturbation. As will be discussed later, our study has led us to the conclusion that with the increase of temperature, an obvious structural change occurs in the PCTh film, which probably influences its conductivity.

Another contribution of this work is that we further provide the information on the charge carriers in the doped PCTh using 2D Raman correlation spectroscopy. An in-depth understanding of the electrical properties of the doped conducting polymers is essential from the views of theoretical study and applications. In recent decades, several theoretical approaches [3,7,8,11], as well as electronic absorption [2], vibrational

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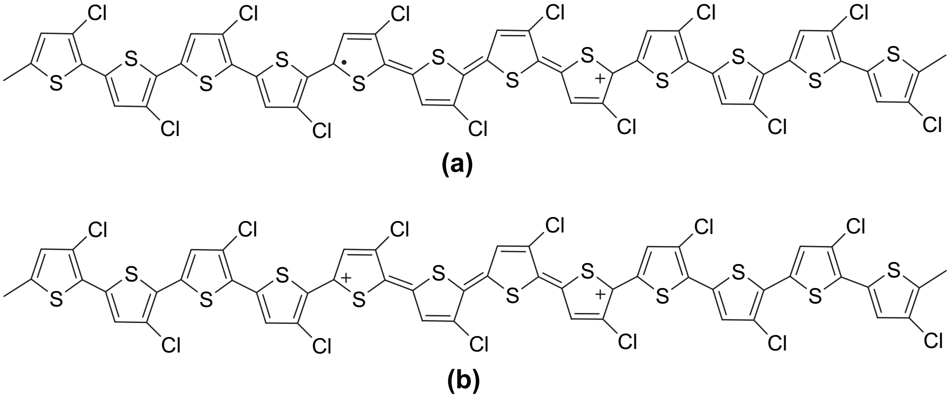

Scheme 1. The quinoid structures in (a) positive polarons and (b) positive bipolarons of PCTh.

[1,4–6,9,10] and electron-spin-resonance spectroscopies [2], were pursued for the purpose of investigating the central question: which is the major charge carrier in nondegenerate conjugated polymers, polaron or bipolaron? However, due to the internal complexity of doped conducting polymers, most of the literatures just come to a conclusion that the main process of chemical doping is a multistage oxidation (or reduction) reaction of conjugated polymer chains [2].

Polaron and bipolaron correspond to the radical cations and dications, respectively, in traditional chemical terminology. Therefore, by tracing the information of radical cations and dications of PCTh shown in the Raman spectra, polarons and bipolarons can be identified. In this work, the existence of bipolarons in PCTh has been confirmed by 2D Raman spectroscopy. Two kinds of typically oxidized species (quinoid structure) including positive polarons and positive bipolarons in the PCTh polymer chain are depicted in Scheme 1. It is of particular note that the material studied is not a regioregular PCTh, so Scheme 1 is an approximate representation of the true conformation.

2. Experimental section

Poly(3-chlorothiophene) (PCTh) film was electrochemically synthesized using the procedure described in detail in Refs. [21,22]. In this work, the doping level of the PCTh film was approximately 20%.

Raman spectra were obtained by using an RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC., England) employing a 785 nm laser beam and a CCD detector with 4 cm^{-1} resolution. The spectra were recorded by using a 50× objective and accumulated for three times and 30 s each. The temperature range is from 298 K to 448 K and the spectra were obtained in the intervals of 25 K. The power was always kept very low (~0.1 mW) to avoid destruction of the samples. All original spectra were baseline corrected using the Omnic 5.1 software. The software used for the two-dimensional correlation analysis was "2D pocha", composed by Daisuke Adachi (Kwansei Gakuin University, Japan). The 1D spectra shown on the left side and on top of the 2D correlation maps are the average spectra of all the spectra measured over the complete temperature interval and are applied as a reference spectra. In the 2D correlation maps, unshaded regions are defined as the positive correlation intensities, whereas shaded regions are defined as negative ones.

3. Result and discussion

The UV–vis experiment [21] shows that the undoped PCTh films have a very strong visible absorption band, the maximum of which was found to be located at ca. 550 nm. On the other hand, doped species only show a very weak absorption band in this region and have a broad electronic absorption band with a maximum at ca. 850 nm. Accordingly, the 785 nm excitation laser beam was employed to avoid special resonance of the neutral or oxidized species and to get the structural information of both species simultaneously.

A series of 785 nm excited Raman spectra of PCTh obtained in the temperature range from 298 K to 448 K in the intervals of 25 K are shown in Fig. 1. It is of particular note that with the increase of temperature, the spectral intensity at 1420 cm^{-1} decreases fast, whereas the intensity at 1454 cm^{-1} increases continuously and finally becomes the

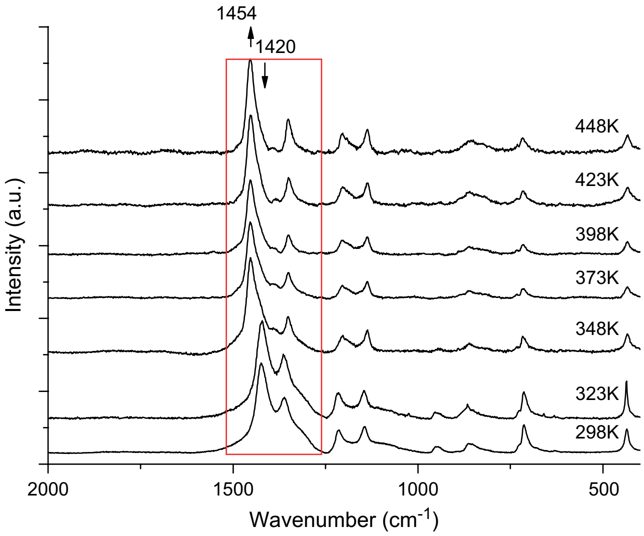

Fig. 1. Raman spectra of PCTh film in the temperature range 298 K–448 K.

Table 1
The assignments of the bands of PCTh in the spectral range 1600−1250 cm^{-1}

Assignments	Frequencies (cm^{-1})		Symbols
	Neutral species	Oxidized species	
C_α=C_β ring stretching (*anti*)	1495	1495	ν_1
C_α=C_β ring stretching	1455		ν_2
Quinoid (radical cations)		1420	Q_1
Quinoid (dications)		1390	Q_2
C_β−$C_{\beta'}$ ring stretching	1355	1367	ν_3

For reference, see Refs. [1,2,5,6,9].

dominating band in the spectral range 1600−1250 cm^{-1}. Table 1 summarizes the assignments of the bands that occurred in this range according to the literatures [1,2,5,6,9]. One sees that the bands at 1454 and 1420 cm^{-1} are, respectively, the characteristic bands of the neutral and the oxidized species. Thus, the intensity changes of these two bands indicate that the content of oxidized species of PCTh is decreasing, whereas the content of neutral species is increasing during the observed interval of the heating process.

As mentioned above, the oxidized states of the doped conjugated polymers are more complex compared to their corresponding neutral states. In the present work, the strong band at 1420 cm^{-1} confirms the existence of positive polarons in doped PCTh. On the other hand, it seems that 1D spectra lack the information about positive bipolarons. However, we cannot exclude the probability of the existence of positive bipolarons by taking into account the strong overlapping between the bands. In order to separate the overlapped bands, the 2D correlation analysis of PCTh is performed as shown in Fig. 2.

The occurrence of the autopeak ($\nu_1 = \nu_2$) around 1386 cm^{-1} located at the diagonal line in the 2D synchronous contour map (Fig. 2a) clearly confirms the existence of positive bipolarons, even if the signal is very weak compared to the other autopeaks around 1454, 1420 and 1365 cm^{-1}. According to the rules of Noda [17], the autopeaks indicate that the intensities of these four bands change to a great extent under the thermal perturbation.

Except for the autopeaks, two negative cross peaks Φ(1454/1420 cm^{-1}), Φ(1454/1365 cm^{-1}) and one positive cross peak Φ(1420/1365 cm^{-1}) are also found in Fig. 2a. The cross peak $\Phi(\nu_1/\nu_2)$ in the synchronous map represents the simultaneous or coincidental changes of spectral intensity variations measured at ν_1 and ν_2. A synchronous cross peak becomes positive if the spectral intensities at ν_1 and ν_2 are either increasing or decreasing together under the external variable during the observation interval. On the other hand, a negative cross peak indicates that one of the spectral intensities is increasing while the other is decreasing [20]. Therefore, the cross peaks Φ(1454/1420 cm^{-1}), Φ(1454/1365 cm^{-1}) and Φ(1420/1365 cm^{-1}) illustrate that the band at 1365 cm^{-1} should be assigned to the C_β−$C_{\beta'}$ ring stretching mode in the oxidized species of PCTh.

The asynchronous cross peaks in Fig. 2b provide much more interesting information about the sequential order of the aforementioned bands. If $\Phi(\nu_1, \nu_2) > 0$, a positive asynchronous cross peak $\Psi(\nu_1, \nu_2)$ represents that the intensity change at ν_1 occurs predominantly before ν_2, and a negative one means an opposite behavior. However, if $\Phi(\nu_1, \nu_2) < 0$, this rule is reversed [20]. On the basis of the above set of rules, the same sign of the synchronous and asynchronous cross peaks located at 1454/1420 cm^{-1} indicates that the spectral intensity at 1454 cm^{-1} changes at a lower temperature than the spectral intensity at 1420 cm^{-1}. Since these two bands are attributed to the different species of PCTh, this cross peak illustrates that during the heating process, the response of the neutral species (benzenoid structure) to the thermal perturbation occurs earlier than that of the oxidized species (quinoid structure). In Fig. 2b, the bands at 1386 and 1365 cm^{-1} are also found to share the negative asynchronous cross peak with the band at 1454 cm^{-1}, which gives a strong support to the aforementioned result. A more interesting cross peak located at 1420/1386 cm^{-1} attracts our attention because we confirm again the existence of the positive bipolarons from

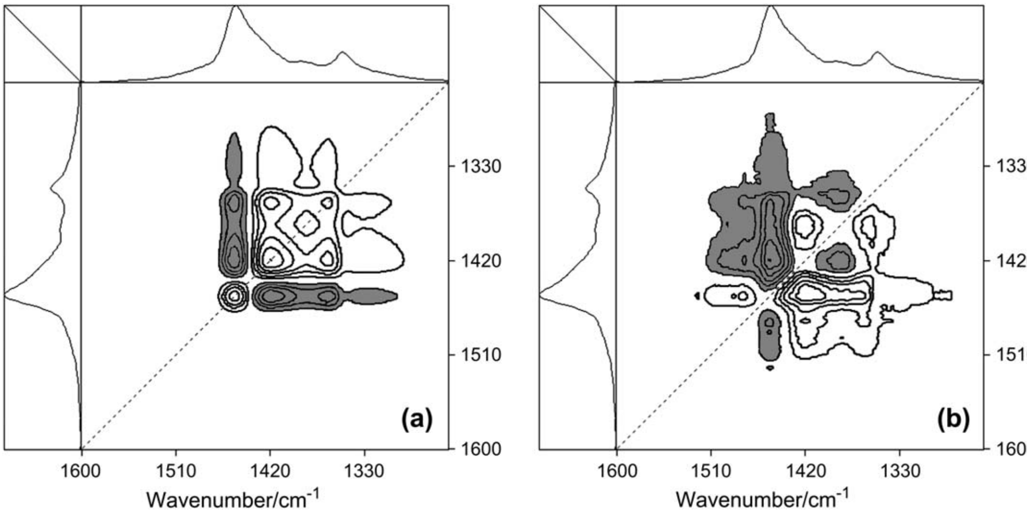

Fig. 2. Two-dimensional (a) synchronous spectrum and (b) asynchronous spectrum of the PCTh film in the range 1600−1250 cm^{-1}.

it. Also, this cross peak indicates that the thermal stability of the positive polarons is lower than that of the positive bipolarons in doped PCTh.

In summary, the oxidized species in PCTh in this work are mainly presented as positive polarons, while the bipolarons account for the minor parts. During the heating process, the content of the oxidized species decreases whereas that of the neutral species is increasing. And the motion sequential order of the different species is given by the following steps: the neutral species → the oxidized species (positive polarons) → the oxidized species (positive bipolarons).

In the neutral species of PCTh, the thiophene rings are connected by single bonds (C–C) (benzenoid structure) at the 2,5-positions as plotted in Scheme 1. On the other hand, the thiophene rings in the oxidized species are connected by double bonds (C=C) (quinoid structure), leading to a relatively high rigid conformation. Thus, it is reasonably imagined that the thiophene rings in the neutral species have larger freedom of motion compared with those in the oxidized species. During the heating process, the conformational change of the neutral species is certain to occur earlier than that of the oxidized species.

According to the literature, positively charged segments in polypyrrole are susceptible to a nucleophilic attack by oxygen or water [23]. Other researchers also find that the conductivity of doped conducting polymers, including PTs, decreases gradually as the samples are stored in air mainly due to the attack of oxygen and moisture [24]. In this work, it seems that the increase of the temperature accelerates the reaction processes, leading to the reduction of the oxidized species and causing the structural change of the oxidized species finally. Thus, the intensities at 1420 and 1386 cm^{-1} decrease fast in the first stage of the heating process, accompanied by the continuous increase of the intensity at 1454 cm^{-1}.

4. Conclusion

In the present work, two-dimensional Raman correlation spectroscopy is applied to the study of poly(3-chlorothiophene) (PCTh) film under thermal perturbation. The autopeak at 1386 cm^{-1} and the positive cross peak $\Psi(1420/1386\ \mathrm{cm}^{-1})$ occur in the 2D synchronous and asynchronous contour maps, respectively, allowing us to trace the minor part of the charged carriers in PCTh (positive bipolarons). $\Psi(1420/1386\ \mathrm{cm}^{-1})$ also indicates that the bipolarons have relatively higher thermal stability than polarons in doped PCTh. The neutral species have a quicker motion under the thermal perturbation due to its larger freedom compared to the oxidized species. On the other hand, the increase of temperature accelerates the attack of oxygen and moisture to the oxidized species and promotes the structural change in the PCTh film.

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