ATR-Infrared Spectroscopic Study of n-Doped Polyacetylene Films

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Abstract: The attenuated total reflection infrared (ATR-IR) spectra of *trans*-polyacetylene (*trans*-PA) film doped with sodium (n-doping) were observed in the range of 1900 to 700 cm^{-1}. The observed IR bands were attributed to negatively charged domains created by n-doping electrons. The doping-induced IR bands showed considerable difference from its pristine film. After doping, the out-of-plane CH deformation band of the strong 1010 cm^{-1} region in the pristine film disappeared while several new bands were observed at 1600 (due to C=C stretching), 1400 (due to in-plane CH bending), 1290 and 1174 (due to CH stretching), and 880 cm^{-1} (due to CC stretching) regions for Na-doped PA. In particular, a weak band of C=C stretching at 1600 cm^{-1} was newly obtained for the first time in the present study. The electro conductivity of the doped *trans*-PA film was 10^{2} S/cm and the origins of doping-induced IR bands are discussed in terms of solitons and polarons.

Keywords: polyacetylene, infrared spectroscopy, conducting polymer.

Introduction

Trans-polyacetylene (*trans*-PA; *trans*-(CH)$_n$) is a conjugated polymer which shows metallic electrical conductivity upon doping.[1] Electrical conductivity of PA increase with increasing dopant concentration.[2,3] The pauli spin susceptibility indicative of a metallic density of states appears suddenly at a dopant concentration of about 6 mol%/CH unit (critical value),[3,4] and doped PA can thus be regarded as a metal. When the dopant concentration is below the critical value, charged solitons that have charges but no spin have been proposed as spinless charge carriers.[5] However, the origin of the metalic state is not fully understood. The vibrational spectroscopic studies have been performed to elucidate the structural characteristics of this polymer, and structural information is also useful for understanding the electrical properties of conducting polymers.

Infrared (IR) spectroscopy is increasingly being used as a powerful tool for studying conducting polymers, because it gives us knowledge on molecular structures of transient states as well as their dynamic properties. Various studies have been performed with the vibrational modes around a doping state in *trans*-PA, since three characteristic IR absorption peaks of doped-PA were observed at 1397, 1288, and 888 cm^{-1}.[6] These peaks have been explained to be caused by localized vibrational modes around a charged domains created from doping. According to the Ikeda *et al.*,[6] as for the IR spectrum of doped PA, the peak 888 cm^{-1} has been assigned to the C-C stretching, the peak 1397 cm^{-1} to the C-H bending, and the peak of 1288 cm^{-1} to the C-C width stretching. Mele and Vardeny *et al.*[7,8] have applied the formalism to describe the IR peaks in the vibrational spectra of doped PA. Thus, the wide of the 888 cm^{-1} IR peak has been explained by the distribution of the impurity pinning parameter. On the other hand, Brivio and Mulazzi have insisted that the width of the IR peak is related to the distribution of the finite conjugation length.[9] Calculations for charged PA using the force constant matrix with 3N degrees of freedom have been carried out by some workers.[10-13] Zannoni and Zerbi[10] have calculated the densities of the vibrational states of doped-PA using the force constant method, and Peluso *et al.*[11] have obtained the force constants using the cluster model by the MNDO method. Previous studies[12] showed that static charges and charge fluxes were the main factors to interpret the spectroscopic data of frequencies and intensities, and the calculations of inter-atomic distances and bond energies; they are also useful for the determination of intra-molecular[13] and inter-molecular[14,15] interactions. Mori *et al.*[16] suggested based on the MNDO method that the trends in wavenumbers are similar for positively and negatively charged solitons, and one of the wavenumbers is particularly sensitive to conjugation length. MO calculations by *ab initio* method (6-31G)

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also indicate the dispersion of wavenumbers with conjugation lengthes.[17] By recent dynamical studies using nano or pico-second spectroscopy, the information about the production of charged soliton pairs after photoexcitation and their relaxation by recombination or into polaron *etc.*, has been provided. Charged solitons appear in samples which have been doped or photo-excited. For such samples electronic transition to the soliton level and transitions due to vibrations around a soliton are observed in the IR spectrum.

Nonetheless, the structural analysis about charged species or doamins in *trans*-PA created by doping has not fully been understood by IR spectroscopic method yet. Especially, the IR vibrational band of C=C stretching in the doped *trans*-PA have not been reported at the experimental points of view.

In this paper, we present the attenuated total reflection infrared (ATR-IR) spectra of *trans*-PA films doped with sodium (n-doping) in the range of 1900 and 700 cm^{-1}. We obtained the some new information for the structural analysis about charged species or domains in *trans*-PA created by doping.

Experimental

The *cis*-rich PA films prepared according to shirakawa's method[18] at -78 °C were thermally isomerized to *trans*-PA films at 180 °C for 60 min. The *trans*-PA films were doped with sodium by treating them with a THF solution of sodium naphthalide in a completely sealed ampoule.[19] Although the sodium concentration is not precisely determined in this present study, in our previous paper,[20] we reported the Raman spectra of *trans*-PA doped with Na at various concentrations. From those results, the doping level of samples (b) and (c) can be considered as below 7 mol% "lightly doped" and sample (d) is above 8 mol% "heavily doped", respectively. The conductivity of the doped PA film was measured by the d.c. four probe technique. The absorption spectra can not measured because the sample of *trans*-PA films is very thick (about 1 μm) and an opaque color.

ATR Infrared absorption spectra were measured by a SensIR spectrophotometer with a MCT detector under the ambient conditions. The diamond element as a contact IR objective was used to measure samples using attenuated total reflectance spectroscopy. The diamond is a precision optic that transmits the IR and visible light and the diamond surface is spherical to ensure good contact. In the case of the contact IR, IR light is internally reflected at the sample interface, allowing the measurement of ATR data.

Results and Discussion

Unstretched film of *trans*-PA (about 50 μm thick) was prepared according to the shirakawa method.[18] The *trans*-PA films were doped with sodium at both sides of a film
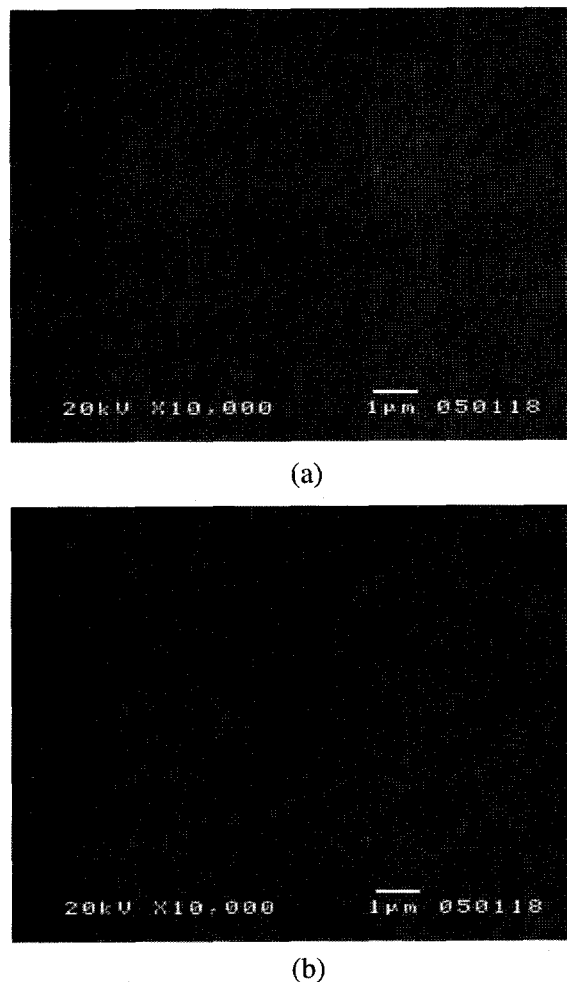

(a)

(b)

Figure 1. SEM micrograph of the surface image of *trans*-PA film. (a) shiny black side and (b) dull side.

according to the dipping in sodium naphthalide solution, and, in the case of fully doped sample, its electrical conductivity was 10[2] S/cm at the shiny side. The Na-doped *trans*-PA film used has different reflections and colors on its two sides, i.e., one shiny black side and other dull side. Here, the shiny black side is contacted surface with acetylene gas and the dull side is contacted surface with glass reactor surface when PA films synthesized according to Shirakawa's method.[18] The observed electrical conductivities and spectroscopic characterizations at the both side of films shown closely resemble each other. The structural characterization of *trans*-PA films was carried out by scanning electron microscopy (SEM). Figure 1 shows the SEM micrograph of the surface image of *trans*-PA film.

The ATR-IR spectra at the shiny side of the Na-doped PA film are shown in Figure 2. The IR spectra of PA doped with sodium at the some different doping level were observed as can be seen in Figure 2. The Na doping level increases from spectrum (b) to (d). Pure PA film has a strong band in the
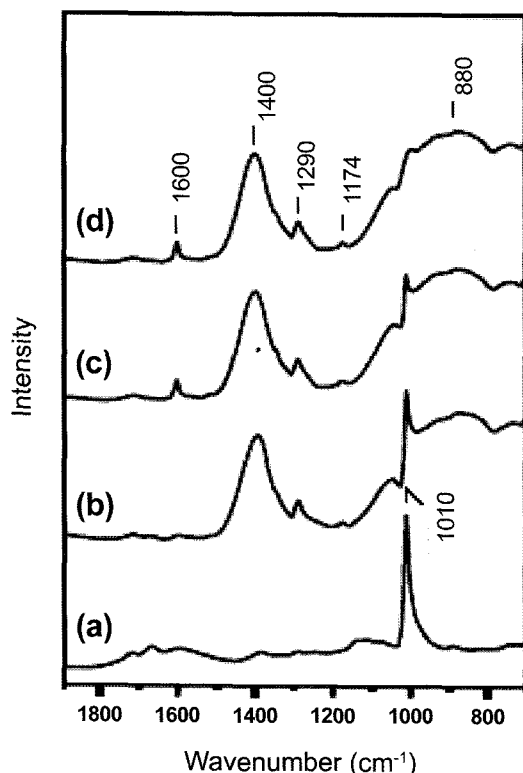
Figure 2. ATR Infrared spectra of *trans*-PA (a) pristine *trans*-PA and (b)-(d) Na-doped *trans*-PA. The Na concentration of the doped samples increases in the order sample (b) to (d).

1010 cm^{-1} (Figure 2(a)) has been assigned to the C-H out-of-plane bending deformation of hydrogens attached to *trans* carbon-carbon double bonds or C=C wagging.[21] This bands in various ethylenic compounds are usually observed in the vicinity of 1005-960 cm^{-1}. In general, the conjugation length of *trans* double bonds increases with the frequency of this band. Lunde *et al.*,[22] have shown that the C-H out-of-plane deformation bands apper at 960 cm^{-1} in *trans*-stilbene, 985 cm^{-1} in *trans, trans*-1,4-diphenylbuta-1,3-diene, 994 cm^{-1} in all-*trans*-1,6-diphenylhexa-1,3,5-triene, and 1010 cm^{-1} in all-*trans*-1,8-diphenylocta-1,3,5,7-tetraene. Ikeda *et al.*,[6] have also reported in the 1015 cm^{-1} for the IR spectrum of *trans*-PA and in the 740 cm^{-1} for the IR spectrum of *cis*-PA, respectively. On this basis, the 1010 cm^{-1} band (in Figure 2(a)) is reasonably assigned to *trans* out-of-plane hydrogen deformation in *trans* configuration along the chains. According to Bellamy,[23] the *trans* C-H in-plane deformation should occur between 1310-1295 cm^{-1} and the C-C double bond stretching vibration with a conjugated system show at the range of 1680-1620 cm^{-1}, the frequency being lowered toward 1600 cm^{-1}. The C-C single bond stretching occurs between 1200-1000 cm^{-1} and conjugation increases the single band frequency. But, the intensity of these bands are very weak. The IR spectra of *trans*-PA doped with sodium are shown in Figures 2(b)-(d). The Na concentration increases from spec-

trum (b) to (d). The doping level of sample (b) and (c) can be considered as "lightly doped" and sample (d) is "heavily doped" in our previous paper.[20] The IR spectra of these doped *trans*-PA samples are quite different with its pure *trans*-PA film. Especially, the 1010 cm^{-1} band in pure *trans*-PA is disappeared with doping, instead of, the new major IR bands which appear on doping are observed at 1600, 1400, 1290, and 880 cm^{-1} for *trans*-(CH)$_n$. The widths of the 1400 and 1290 cm^{-1} bands are comparable with those of the bands of intact *trans*-PA, whereas that of the 880 cm^{-1} band is significantly broader. Previous workers[6-8] had already reported three characteristic IR absorption peaks at the range of 1370-1400 (in-plane CH bending), 1288-1295 (C-C width stretching), and 900-880 cm^{-1} (C-C stretching) with isotope experimentals. Inagaki *et al.*[6] have also calculated the normal modes of *trans*-(CH)$_n$ and *trans*-(CD)$_n$ in the isolated chain approximation.

These peaks have been explained to be caused by localized vibrational modes around a charged domains created from doping. In the three characteristic bands, only the band of 1290 cm^{-1} has an extremely weak counterpart in the undoped spectrum. In addition, they concluded that the 1370 cm^{-1} peak arises from the so called "phase kink" regions of the polymer. In particular, a weak band at 1600 cm^{-1} range was newly obtained for the first time in the present study. This band can be assignated to the C=C stretching. In our previous paper,[24] the IR absorption spectra of the anion and radical anion of α,ω-diphenylpolyene [Ph(CH)$_n$Ph$^-$ and Ph(CH)$_n$Ph$^{\bullet-}$] had been reported as the model compounds of a negative soliton and polaron in *trans*-PA. This C=C stretching band in model compounds of *trans*-PA shown that the relative intensity decrease regularly with conjugated chain length increases, but the wavenumbers are not changed. According to the ref. 24, these peak positions also are about 45-50 cm^{-1} lower than the corresponding band of its neutral states, but the relative intensity of C=C stretching band in neutral state was very weak as shown in Figure 2(a) of this experiments. Anyway, the IR spectra obtained from the negative soliton and polaron model compounds showed considerable difference from their neutral species [Ph(CH)$_n$Ph], in these charged spaces model compounds, the peaks between 1502 and 1541 cm^{-1} are assigned to the C=C stretching mode, and the relative intensity decrease regularly with chain length (n) increases, but the intensities of CH in-plane bending modes occurred between 1464-1375 cm^{-1} are correspondingly strengthened with the chain length increased. According to the MNDO calculations on the anions of C$_5$H$_7$ to C$_{33}$H$_{35}$ reported by Mori *et al.*,[16] infrared vibration of C=C stretching mode calculated at 1600 cm^{-1} range, and its wavenumbers were not particularly sensitive to the conjugation length, and its relative intensities. In doped PA, the C=C stretching band was not found in the experimental method. The large absorbance at 1400 cm^{-1} is attributed to the CH bending vibrations along the charged (CH)$_n$ backbone, and their relative inten-

sites are drastically enhanced by charge distribution along the chain. According to the calculation results by Mori *et al.*,[16] the CH bending modes for the cations of $C_{13}H_{15}$, $C_{17}H_{19}$, and $C_{33}H_{35}$ as the model compounds of *trans*-PA have been reported at 1397, 1376, and 1358 cm^{-1}, respectively. These bands have reported as the corresponding to the 1397 cm^{-1} band in the lightly iodine doped *trans*-PA.[4,6] Piaggio *et al.*[25] reported that the infrared peak of 1397 cm^{-1} in doped PA shifts appreciably toward higher frequencies as the length of the conjugated sequences is shortened. The broad peak centered at about 880 cm^{-1} is also characteristic of doped PA and has been generally attributed to vibrations about a charged soliton, and has been explained by the distribution of the impurity pinning parameter. It is extremely broad and has no counterpart in the IR spectrum of pristine PA. Since both its intensity and bandwith are similar to the 1400 cm^{-1} band and because it shifts on deteration,[26] it is also believed to originate from a vibronically active Ag mode and not from ionization of dopant states as suggested by others.[27] Since no Raman band appears at this position in either the *cis* or *trans* form of pristine PA, it appears that this band has undergone a frequency shift. It is also possible that several IR activated Ag modes contribute simultaneously to this extremely broad band. Brivio and Mulazzi *et al.*[9] have explained that the width of the 880 cm^{-1} peak is related to the distribution of the finite conjugation length.

As described above, the doping-induced IR bands of *trans*-PA are clearly different from that of pristine *trans*-PA. Tentative assignments for the observed bands have been discussed in the base of results obtained in the previous papers.[6-9,16,20,24]

However, for the more correct discussion about the differentia of structural and vibrational origin between *trans*-PA and doped *trans*-PA, especially 1600 cm^{-1} peak, the IR study of doped *trans*-$(CD)_n$ and *trans*-$(^{13}CH)_n$ with sodium are need, and more extensive studies for soliton and polaron structures are absolutely needed to clearly understand the self-localized charge domains in doped PA because Su[27] and Kivelson[28] have been actually proposed the soliton and polaron lattice structures in doped PA, respectively. IR spectra of the negative soliton and polaron model compounds of *trans*-PA, *trans*-diphenylpolyenyl anions and radical anions of *trans*-diphenylpolyene, have been reported in our previous paper.[25] In particular, the C=C stretching bands of negative soliton and polaron model compounds are measured at 1502 -1541 cm^{-1} range and 1583-1603 cm^{-1} range, respectively. The relative intensity of C=C stretching bands at negative soliton model compounds decrease regularly with chain length increase, but the wavenumbers are not changed. IR spectra of model compounds of negatively polaron in *trans*-PA are some different with those of the soliton models. Especially, the C=C stretching peaks (1583-1603 cm^{-1} range) are weaker than those of the soliton models and are 60-80 cm^{-1} higher frequency regions than corresponding bands of soliton models. These variance of spectrum between soliton and polaron

indicates that the bond orders or bond alternations of soliton models are somewhat different from those of polaron models. From this reason, a weak C=C stretching band of 1600 cm^{-1} newly obtained in the this study can be discussed as the induce from the polarons (self-localized negatively charge domains) in doped *trans*-PA. Actually, to explain the metallic properties of heavily doped *trans*-PA, Kivelson and Heeger[28] have proposed a polaron lattice structure.

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