Resonance Raman and ^{129}I Mössbauer Spectroscopic Study of Iodine Doped in Poly(thienylene)s

Hiroshi Sakai,* Manabu Mizota, Yutaka Maeda, Takakazu Yamamoto,† and Akio Yamamoto†
Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka 590-04
†Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227

(Received August 31, 1984)

Resonance Raman and ^{129}I Mössbauer spectroscopy have been used in a study of iodine doped poly(thienylene)s, which are chemically synthesized by the polymerization of dibromothiophenes. It is shown that the iodine species in the polymers are present predominantly in the form of a polyiodide which consists of unsymmetrical I_3^- and I_2 units. That is, the iodine molecule doped is reduced by taking electrons from the polymer in a similar manner to iodine doped in polyacetylene. This result is consistent with the fact that poly(thienylene)s undergo an increase in electrical conductivity upon doping with iodine.

Extensive studies have been made of electrically conducting organic polymers doped with either strong electron acceptors or donors. Polyacetylene especially, the simplest linear conjugated polymer, has attracted attention because the electrical conductivity can be varied over 12 orders of magnitude from insulator to semiconductor and metal by doping with arsenic pentafluoride (AsF_5) or iodine (I_2).[1] Polymers containing a phenylene ring in the polymer chain, poly(*p*-phenyline),[2,3] poly(phenylene vinylene),[4] and poly(phenylene sulfide),[5–7] also undergo a large increase in electrical conductivity upon doping with AsF_5. This behavior is similar to that of polyacetylene. However, when these polymers are exposed to iodine vapor, a relatively weak electron acceptor, the conductivities do not increase as is observed for polyacetylene. ^{129}I Mössbauer studies have revealed that iodine doped in poly(*p*-phenylene) exists as an almost free iodine molecule, whereas iodine doped in poly(phenylene sulfide) interacts weakly with the sulfur atoms of the polymer chain.[8,9]

Recently poly(thienylene), which consists of a linear sequence of thiophene rings, as shown in Fig. 1, has been found to exhibit a high conductivity ($\approx 10^{-1}$ S/cm) upon exposure of I_2 vapor at room temperature.[10] This is the second polymer which exhibits a high conductivity with the iodine doping. It is important for the understanding of the conduction mechanism to determine the chemical form and the electronic structure of the iodine species present in the polymer. Resonance Raman and ^{129}I Mössbauer spectroscopy are useful methods for investigating the chemical and electronic structures of iodine, and have been successfully applied for iodine-doped polyacetylenes.[11–14] In the present work we report on resonance Raman and ^{129}I Mössbauer spectroscopic studies of the iodine species in poly(2,5-thienylene) and in poly(3-methyl-2,5-thienylene).

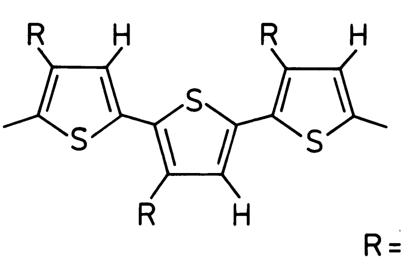

Fig. 1. Idealized chemical structure of poly(2,5-thienylene) or poly(3-methyl-2,5-thienylene).

Experimental

Poly(2,5-thienylene) and poly(3-methyl-2,5-thienylene) were synthesized by the polymerization of 2,5-dibromothiophene and 3-methyl-2,5-dibromothiophene, according to the method described previously.[10] Both powdery polymers used in this work were $CHCl_3$-insolvable fractions. The iodine-doping was carried out by immersing the polymer in a CCl_4 solution of iodine at room temperature for 1 d. The iodine content of the specimen used for the resonance Raman measurement was determined to be 43 wt-% for poly(2,5-thienylene) and 52 wt-% for poly(3-methyl-2,5-thienylene) by gravimetric analysis. Radioactive $^{129}I_2$ ($t_{1/2}=1.7\times10^7$ y), which was prepared by oxidizing Na ^{129}I in Na_2SO_3 solution with 6 M-H_2SO_4 (1 M=1 mol dm^{-3}) and 10%-H_2O_2 and extracting with CCl_4, was used for the Mössbauer sample. The iodine content was found to be 24 wt-% for poly(2,5-thienylene) and 12 wt-% for poly(3-methyl-2,5-thienylene). The sample thickness for the Mössbauer measurement was about 20 mg ^{129}I/cm^2.

Laser Raman spectra were measured with Ar$^+$ (514.5 nm) excitation by using a JEOL-JRS-400T triple monochromator. The data were obtained with compressed pellets of the powdery samples by the front surface reflection method using 60 mW of laser power and a spinning cell, in order to prevent decomposition of the iodine species. No decomposition was observed within this laser power, though the scans were made repeatedly for each iodine-doped sample.

^{129}I Mössbauer effect measurements were performed in a transmission geometry by cooling the source and the absorber sample at 16 K with a closed cycle helium refrigerator "Cryodyne 1020." The Mössbauer source, ^{66}Zn^{129}Te ($t_{1/2}$=70 min) was prepared by neutron irradiation of a 140 mg $^{66}Zn^{128}Te$ compound at flux of 2×10^{13} neutrons/cm^2·s for 1 h in the Kyoto University Reactor (KUR). The source was used repeatedly. The constant acceleration drive was calibrated with an Fe foil.

Results and Discussion

A. Resonance Raman Spectroscopic Study. In Fig. 2 are presented resonance Raman spectra of iodine-doped poly(2,5-thienylene) (iodine content 43 wt-%) and iodine-doped poly(3-methyl-2,5-thienylene) (52 wt-%) excited by the Ar$^+$ 514.5 nm line. Both spectra (170 s, 145 w, 108 m, 63 w, cm^{-1}) are very similar to each other, indicating that the iodine species in both polymers has a similar chemical form. The possibility for the presence of free iodine molecules is clearly ruled out by finding no Raman band around 210 cm^{-1}. It is of interest to compare these spectra with those of iodine-doped polyacetylene. The Raman band at 108 cm^{-1}, also observed for iodine-doped polyacetylene at 105—107 cm^{-1},[11,12] can be assigned to the symmetric stretching vibration of a linear triiodide anion (I_3^-). Isolated and symmetrical I_3^- ions in methanol[15] and $(C_6H_5)_4As^+I_3^-$[16] show the Raman bands at 112 and 113 cm^{-1}, respectively, while the bands for unsymmetrical I_3^- ions and I_3^- units in polyiodides are observed in the 100 to 120 cm^{-1} region.[16,17] The latter distorted I_3^- ions give rise to a second weak band around 150 cm^{-1}, assigned to the antisymmetric stretching vibration. Therefore, the relatively weak band at 145 cm^{-1} observed in iodine-doped poly(thienylene)s is assigned to the antisymmetric vibration band of the distorted I_3^- ion.

On the other hand, the strong Raman band at 170 cm^{-1} seems to be due to an iodine molecule coordinated to the I_3^- ion. It is well known that molecular I_2 acts as a Lewis acid and coordinates to Lewis bases such as I^- and I_3^-. The coordination weakens the I-I bonding and shifts the I-I stretching band to lower frequency. Actually a few polyiodides which consist of I_3^- and I_2 units show the strong Raman bands for the I-I stretching vibration; 172 cm^{-1} for Cs_2I_8[16] and 173 cm^{-1} for $(\alpha\text{-CD})_2Li^+I_5^-8H_2O$.[17] The bands for I_3^- unit in these polyiodides are observed in the 105—110 cm^{-1} region as described previously. Notably the resonance Raman spectra of iodine-doped poly(thienylene)s are similar to the spectrum observed for the $(\alpha\text{-CD})_2Li^+I_3^-I_2 8H_2O$ inclusion compound, in which the iodine chain, constructed of alternate I_3^- and I_2 units, is slightly zigzagged and is included in the cavity of the α-cyclodextrin dimer.[18] Another example of the polyiodide is found in the perylene-iodine complex, which exhibits a high electrical conductivity (≈10^{-1} S/cm) at room temperature. This complex shows resonance Raman bands at 115 m and 145 w cm^{-1} assigned to the unsymmetrical I_3^- unit and at 175 s cm^{-1} to the weakly coordinated I_2 unit.[16] The agreement between the Raman spectra of this complex and of iodine-doped poly(thienylene)s is extremely close.

These results suggest strongly that iodine doped in poly(thienylene)s exists predominantly as a polyiodide

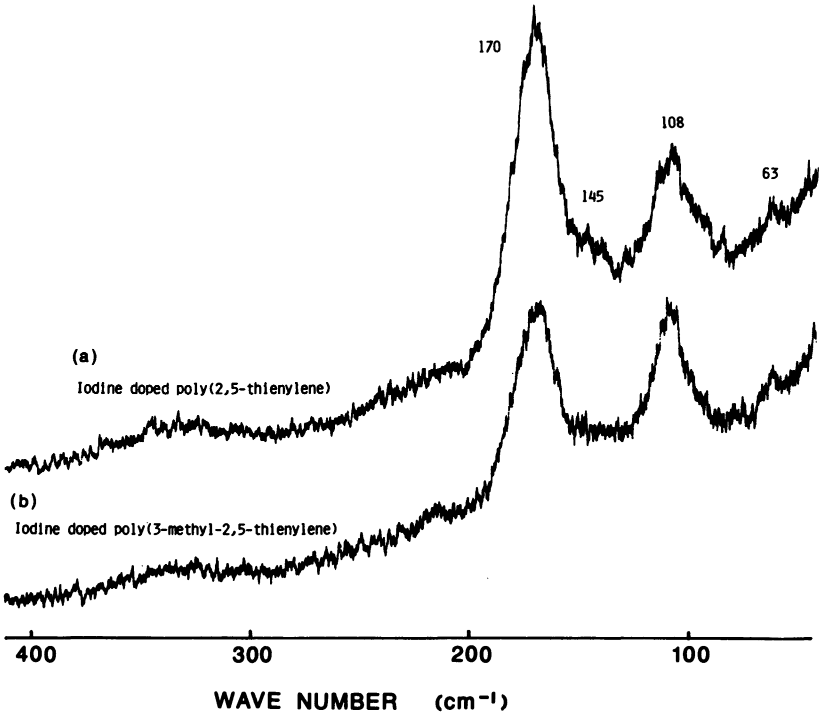

Fig. 2. Resonance Raman spectra of (a) iodine-doped poly(2,5-thienylene) and (b) iodine-doped poly(3-methyl-2,5-thienylene), observed with the 514.5 nm excitation.

made up of alternate I_3^- and I_2 units. In polyacetylene heavily doped with iodine, the strong Raman band is not observed at 170 cm^{-1} but another band appears at 150—160 cm^{-1}.[11,12] The intensity of this band is relatively weak compared to the intensity of the 105—107 cm^{-1} band and depends on the sample treatment. This band, different obviously from the 170 cm^{-1} band observed in iodine-doped poly(thienylene)s, is assigned to the linear I_5^- ion, because of the similarity of the Raman frequency (162 cm^{-1}) of (trimesic acid $H_2O)_{10}$ $H^+I_5^-$, which contains the linear and symmetrical I_5^- chain.[19] That is, the iodine species are present in polyacetylene heavily doped with iodine as the I_3^- chain and the linear I_5^- chain. Both iodine molecules doped in poly(thienylene)s and in polyacetylene act as electron acceptors and form polyiodides, though the chemical forms of these polyiodides differ slightly from each other.

Resonance Raman spectroscopy is obviously useful for the identification of the chemical form of the iodine species in the polymers, but there is a limitation with regard to the quantification of the relative amount of each iodine species, because the relative intensites of the resonance Raman bands are strongly dependent on the excitation wavelength. Furthermore, information about the electronic structure such as the charge distribution and the charge density can not be obtained in this method. ^{129}I Mössbauer spectroscopy can compensate for such disadvantages and has been actually applied to the iodine species in polyacetylene,[13,14] poly(*p*-phenylene),[8] or poly(phenylene sulfide).[9]

B. Mössbauer Spectroscopic Study. ^{129}I Mössbauer spectra of iodine doped in poly(2,5-thienylene) (iodine content 24 wt-%) and in poly(3-methyl-2,5-thienylene) (12 wt-%) are presented in Figs. 3 and 4, respectively. In spite of the different iodine contents, both spectra are similar to each other, which agrees with the result of the resonance Raman spectra. The Mössbauer spectra clearly rule out the presence of the isolated I^- ion, which is inactive and undetectable by Raman spectroscopy. The presence of the I^- ion, observed in polyacetylene extremely lightly doped with iodine,[13] would show the single absorption peak at −0.5 mm/s in the spectrum. Since the spectra are complicated, the presence of the free iodine molecule is not clear. However, the resonance Raman spectra of more heavily doped samples do not indicate the presence of any free iodine molecules.

We attempted first to analyze the spectra in terms of three different iodine sites, *i.e.*, the superposition of three quadrupole octet patterns, assuming those asymmetry parameters to be zero. In the case of the spectrum of iodine-doped poly(3-methyl-2,5-thienylene) (Fig. 4), the fitting analysis indicated acceptable agreement between observed and calculated spectra, though the line-width of the intermediate quadrupole split pattern was broadened considerably. This broadening is presumed to be due to an overlap of the spectra originated from two iodine sites which have slightly different values of the quadrupole coupling constant (e^2Qq) and the isomer shift (δ). The best fitted subspectra of each component and their peak positions for the three unequivalent iodine sites are represented

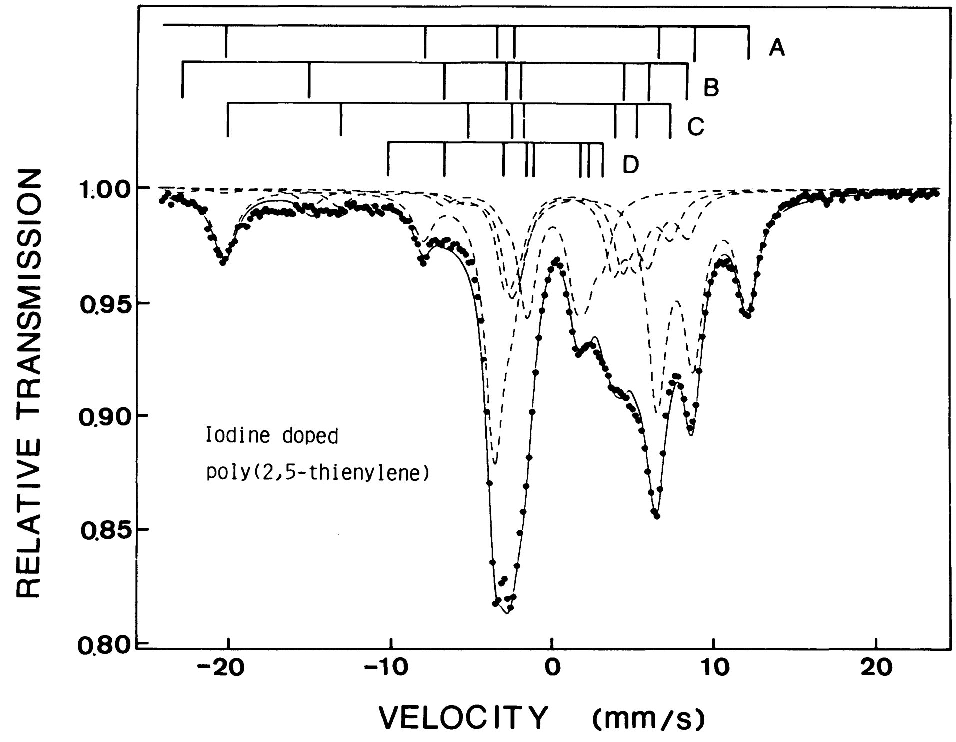

Fig. 3. ^{129}I Mössbauer spectrum of iodine doped in poly(2,5-thienylene) at 16 K.

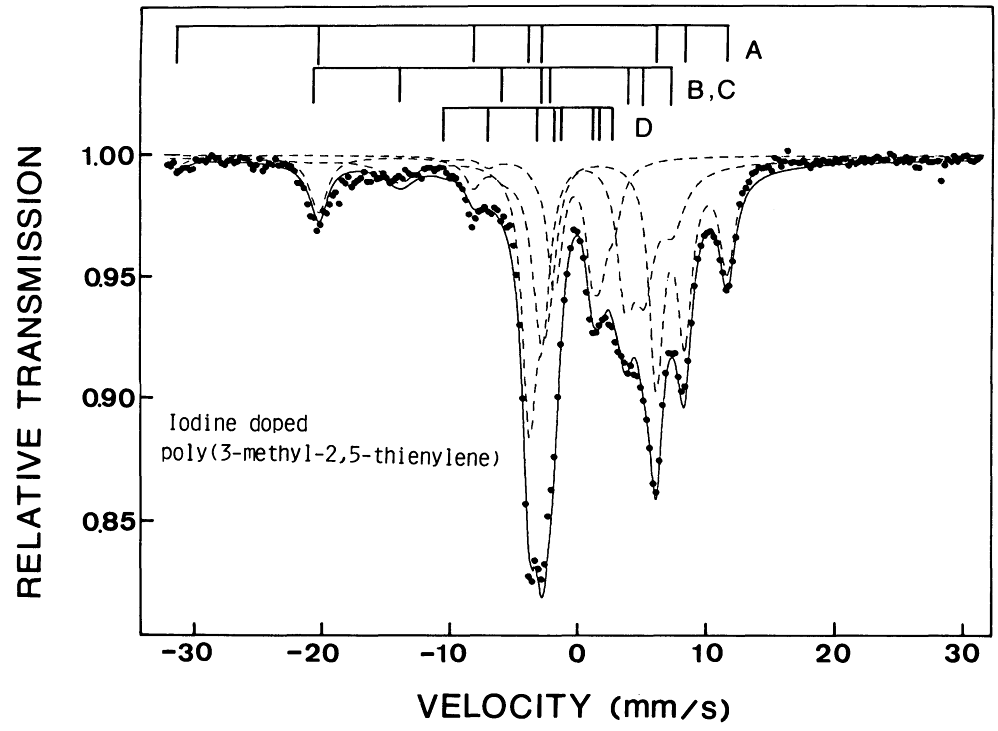

Fig. 4. ^{129}I Mössbauer spectrum of iodine doped in poly(3-methyl-2,5-thienylene) at 16 K.

by dashed curves and stick diagrams, respectively, as shown in Fig. 4. Since the sub-spectrum with the intermediate quadrupole splitting is expected to consist of two slightly different iodine sites, the notations B and C are used for these two iodine sites. On the other hand, for the more expanded spectrum of iodine-doped poly(2,5-thienylene) (Fig. 3), a satisfactory agreement was not obtained by the analysis with three different iodine sites. The analysis of the spectrum with four unequivalent iodine sites gave rise to a reasonable agreement, as shown in Fig. 3. The dashed curves represent the best fitted sub-spectra for each iodine site and the stick diagrams indicate the peak positions of the sub-spectra, where the four iodine sites are symbolized with A, B, C, and D. The obtained Mössbauer parameters, such as the quadrupole coupling constant (e^2Qq), isomer shift (δ), full-width at half-maximum (2Γ), and relative area, are summarized in Table 1.

The e^2Qq and δ values for site A are larger than those for the free iodine molecule in inert matrices ($e^2Qq=-1587$ MHz, $\delta=+0.98$ mm/s for I_2 in hexane[20]), which indicates that the iodine atom of site A has a slightly positive charge density. Such an iodine atom is observed in the central iodine of linear triiodide anions (I_3^-); $e^2Qq=-1750$ MHz, $\delta=+1.40$ mm/s for the central iodine of CsI_3:[21] $e^2Qq=-1725$ MHz, $\delta=+1.48$ mm/s for $[Ru(cp)_2I]I_3$.[22] It is therefore reasonable to assign site A to the central iodine atom in an I_3^- ion. The e^2Qq values for the terminal iodine atoms of the unsymmetrical I_3^- in CsI_3 are found to be -1025 MHz and -580 MHz from the ^{129}I Mössbauer measurement.[21] These values are in good agreement with those obtained from the ^{127}I NQR method;[23] 1007 MHz and 574 MHz at 77 K, converted to ^{129}I using the ratio $^{129}Q/^{127}Q=0.7013$. For the symmetrical I_3^- in $[Ru(cp)_2I]I_3$, the e^2Qq value is -808 MHz for both terminal iodine atoms[22], and indicates the average of two e^2Qq values for the terminal iodines in the unsymmetrical I_3^-. Since each e^2Qq value for site C or D is comparable to that for each terminal iodine of CsI_3, we assign site C and site D to the two terminal iodine atoms in the unsymmetrical I_3^- ion.

These assignment are consistent with the resonance Raman spectra (108 cm^{-1} and 145 cm^{-1} bands), indicating the presence of an unsymmetrical I_3^- ion, as previously described. Since the unsymmetrical I_3^- ion consists of three unequivalent iodine sites with relative populations of 1:1:1, the relative absorption areas of the sub-spectra corresponding to sites A, C, and D are expected to be 1:1:1. However, the absorption area obtained for the sub-spectrum of the site A is 2.7 to 2.8 times that of site D, as shown in Table 1. This result predicts the presence of another iodine atom (designated as site A′) with the same charge density as the central iodine atom in the I_3^- ion. The strong Raman band at 170 cm^{-1} suggests that the I_2 unit interacting with the I_3^- unit exists in iodine-doped poly(thienylene)s. Therefore, the iodine atom of site A′ and an iodine atom of site B seem to constitute this I_2 unit. It is appropriate to assign site A′ to the iodine atom coordinating to one (site D) of the unsymmetrical I_3^- ion and site B to the terminal iodine atom of the I_2 unit, because

TABLE 1. ^{129}I MÖSSBAUER PARAMETERS FOR IODINE DOPED IN POLY(2,5-THIENYLENE) AND POLY(3-METHYL-2,5-THIENYLENE)

	Site	e^2Qq / MHz	$\delta^{a)}$ / $mm \cdot s^{-1}$	$2\Gamma^{b)}$ / $mm \cdot s^{-1}$	Relative$^{c)}$ area	$U_p{}^{d)}$	$h_p{}^{e)}$
Iodine-doped poly(2,5-thienylene)	A	-1750 ± 20	1.27 ± 0.04	1.35 ± 0.06	2.8	1.09	1.21
	B	-1262 ± 20	0.63 ± 0.04	1.32 ± 0.06	1.0	0.78	0.78
	C	-1111 ± 20	0.52 ± 0.04	1.32 ± 0.06	1.0	0.69	0.71
	D	-539 ± 20	-0.05 ± 0.04	1.24 ± 0.06	1.0	0.33	0.33
Iodine-doped poly(3-methyl-2,5-thienylene)	A	-1726 ± 20	1.29 ± 0.04	1.38 ± 0.06	2.7	1.07	1.22
	B, C	-1156 ± 20	0.57 ± 0.04	1.75 ± 0.06	1.9	0.72	0.74
	D	-533 ± 20	-0.04 ± 0.04	1.34 ± 0.06	1.0	0.33	0.33

a) Isomer shifts (δ) are relative to the ZnTe source. b) Line-widths (2Γ) are full-width at half-maximum. c) Relative areas are normalized with respect to the D site. d) $U_p = e^2Qq/e^2Qq_{atom}$, $e^2Qq_{atom} = -1608$ MHz. e) $\delta = 1.5\,h_p - 0.54$ (mm/s).

the values of e^2Qq and δ suggest that the former (the bridging iodine atom) is positively charged and the latter is negatively charged.

Consequently the iodine species present in poly(thienylene)s have the following structure:

[I——I——I······I——I]$^-$
site C A D A′ B

Taking into account the above structure of the iodine species, the absorption area for the sites A and A′ is still large compared with those for each site B, C, or D. The enhanced absorption area is explained on the basis of the difference in the recoilless fraction. That is, the recoilless fractions of sites A and A′ are larger than those of sites B, C, and D, because the central and bridging iodine atoms are bound to two neighboring iodine atoms. This effect is often observed for the I_3^- ions in $[Ru(cp)_2I]I_3$[22] and a β-carotene-iodine complex,[24] in which the central atom indicates stronger absorption intensity than each terminal atom. The fit achieved by assuming the asymmetry parameters to be zero gave rise to a satisfactory result. Accordingly even if they would not be zero, they may be small. This suggests that the iodine species made up of the I_3^- and I_2 units possesses a nearly linear arrangement.

The charge density localized on each iodine atom is calculated from the values of e^2Qq and δ by the usual procedure;[25,26]

$$e^2Qq = -U_p \cdot e^2Qq_{atom},$$
$$\delta(mm/s) = 1.5\,h_p - 0.54 \text{ (ZnTe source)},$$

where e^2Qq_{atom}, the atomic iodine quadrupole coupling constant, is equal to 1608 MHz for ^{129}I, and U_p, the number of unbalanced *p* electrons, is proportional to the difference of $5p_\sigma$ and $5p_\pi$ electron populations; h_p is the number of p electrons removed from the $5s^25p^6$ (I^-) configuration. Therefore, when the bonding of iodine is formed by only $5p_\sigma$ electrons, one expects the relationship $U_p = h_p = 1 \pm i$ to be valid, where *i* is the ionic character. When $5p_\pi$ electrons take part in bond formation, in addition to $5p_\sigma$ electrons, the relationship that $U_p < h_p$ is generally observed. On the other hand, the contribution of 5s electrons leads to the relationship that $U_p > h_p$ because of the decrease in the *s* electron density at the nucleus. The values of U_p and h_p obtained from the above expressions are given in Table 1. They are in good agreement with each other for the terminal iodine atoms of sites B, C, and D, indicating that the bonding is mainly due to $5p_\sigma$ electrons. The charge densites localized on sites B, C, and D are evaluated to be −0.22, −0.30, and −0.67 respectively, for the iodine species present in poly(2,5-thienylene). For the iodine species in poly(3-methyl-2,5-thienylene), the iodine atoms at sites B and C are negatively charged by about 0.27, and iodine at site D by 0.67.

On the other hand, it is evident that the U_p value is smaller than h_p for the central (site A) and bridging (site A′) iodine atoms. This tendency is generally observed for the central iodine atom in the I_3^- ions[21,22,24] and for the bridging iodine atom in amine-iodine charge transfer complexes.[27,28] In our previous paper[28] it was proposed that the tendency was explained in terms of the contribution of $4d_\sigma$ electrons to the bond formation rather than the participation of the π-bonding. That is, the chemical bond of the I_3^- ion is described by a mixture of a four-electron three-center bond and a covalent bond of the $d_\sigma p_\sigma$ hybrid orbitals. The contribution of the $4d_\sigma$ electrons remarkably increases the isomer shift but hardly increases the quadrupole coupling constant. The charge densities localized on the central and bridging iodine atoms are consequently evaluated to be +0.07 to +0.09 from the U_p values.

The total charge densities are close to unity for the iodine species present in both polymers, as can be seen below.

charge −0.30 +0.09 −0.67 +0.09 −0.22
I——I——I·········I——I
site C A D A′ B
[iodine species in poly(2,5-thienylene)]

charge -0.27 $+0.07$ -0.67 $+0.07$ -0.27
I——I——I ········ I——I
site C A D A′ B
[iodine species in poly(3-methyl-2,5-thienylene)]

The charge densities for sites B and C are not rigorously equal because of the broad line-width of the corresponding sub-spectrum for iodine-doped poly(3-methyl-2,5-thienylene), then the value of -0.27 represents the average value of sites B and C. The iodine species observed in this polymer is essentially identical to that in poly(2,5-thienylene). The charge densities for sites A′ and B of the I_2 unit are close to those for sites A and C in the I_3^- unit, which suggests that the intermolecular $I_D \cdots I_{A'}$ bonding is considerably strong. This result is also supported by the fact that the I_2 unit shows the stretching vibration band at 170 cm^{-1}, largely shifted from 210 cm^{-1} of the isolated I_2 molecule.

In summary, resonance Raman and ^{129}I Mössbauer spectroscopy have revealed the chemical forms and the electronic structures of the iodine species in poly(2,5-thienylene) and in poly(3-methyl-2,5-thienylene). The iodine species are found to be present predominantly in the polymers as polyiodides consisting of unsymmetrical I_3^- and I_2 units. That is, the iodine molecule doped acts as an electron acceptor and produces the positive holes in the polymers, in a similar manner to iodine doped in polyacetylene. This result strongly suggests that poly(thienylene)s undergo an increase in electrical conductivity upon doping with iodine.

We wish to thank Professor Takenobu Higashimura (Research Reactor Institute, Kyoto University) for his encouragement. We are greateful to Professor Masamichi Kobayashi (Department of Polymer Chemistry, Osaka University) for his valuable discussion on the Raman spectra. We are also indebted to Mr. Shuichi Muraishi (JEOL Ltd.) for the measurements of the Raman spectra.

References

1) See, for example, Y.-W. Park, A. J. Heeger, M. A. Druy, and A. G. MacDiarmid, *J. Chem. Phys.*, **73**, 946 (1980) and the references cited therein.

2) D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, *J. Chem. Phys.*, **71**, 1506 (1979).

3) L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G. Miller, and R. H. Baughman, *Synthetic Metals*, **1**, 307 (1979).

4) G. E. Wnek, J. C. W. Chien, F. E. Karasz, and C. P. Lillya, *Polymer*, **20**, 1441 (1979).

5) J. F. Rabolt, T. C. Clarke, K. K. Kanazawa, J. R. Reynolds, and G. B. Street, *J. Chem. Soc., Chem. Commun.*, **1980**, 347.

6) R. R. Chance, L. W. Shacklette, G. G. Miller, D. M.Ivory, J. M. Sowa, R. L. Elsenbaumer, and R. H. Baughman, *J. Chem. Soc., Chem. Commum.*, **1980**, 348.

7) L. W. Skacklette, R. L. Elsenbaumer, R. R. Chance, H. Eckhardt, J. E. Frommer, and R. H. Baughman, *J. Chem. Phys.*, **75**, 1919 (1981).

8) H. Sakai, T. Matsuyama, H. Yamaoka, and Y. Maeda, *Bull. Chem. Soc. Jpn.*, **56**, 1016 (1983).

9) H. Sakai, T. Matsuyama, H. Yamaoka, and Y. Maeda, *Chem. Phys. Lett.*, **101**, 490 (1983).

10) T. Yamamoto, K. Sanechika, and A. Yamamoto, *Chem. Lett.*, **1981**, 1079; *Bull. Chem. Soc. Jpn.*, **56**, 1503 (1983).

11) S. L. Hsu, A. J. Signorelli, G. P. Pez, and R. H. Baughman, *J. Chem. Phys.*, **69**, 106 (1978).

12) I. Harada, Y. Furukawa, M. Tasumi, H. Shirakawa, and S. Ikeda, *J. Chem. Phys.*, **73**, 4746 (1980).

13) T. Matsuyama, H. Sakai, H. Yamaoka, Y. Maeda, and H. Shirakawa, *Solid State Commun.*, **40**, 563 (1981); *J. Phys. Soc. Jpn.*, **52**, 2238 (1983).

14) G. Kaindl, G. Wortmann, S. Roth, and K. Menke, *Solid State Commun.*, **41**, 75 (1982).

15) K. Kaya, N. Mikami, Y. Udagawa, and M. Ito, *Chem. Phys. Lett.*, **16**, 151 (1972).

16) R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **101**, 7568 (1979).

17) R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **100**, 3215 (1978); *ibid.*, **102**, 3322 (1980).

18) M. Noltemeyer and W. Saenger, *Nature*, **259**, 629 (1976).

19) F. H. Herbstein and M. Kapon, *Acta Crystallogr., Sect. A*, **28**, 74 (1972).

20) S. Bukshpan, C. Goldstein, and T. Sonnino, *J. Chem. Phys.*, **49**, 5477 (1968).

21) B. S. Erhlich and M. Kaplan, *J. Chem. Phys.*, **51**, 603 (1969).

22) M. J. Potasek, P. G. Debrunner, W. H. Morrison, Jr, and D. N. Hendrickson, *J. Chem. Phys.*, **60**, 2203 (1974).

23) A. Sasane, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, **71**, 3249 (1967).

24) T. Matsuyama, H. Sakai, H. Yamaoka, and Y. Maeda, *J. Chem. Soc., Dalton Trans.*, **1982**, 229.

25) N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy," Chapman and Hall, London (1971).

26) S. L. Ruby and G. K. Shenoy, "Mössbauer Isomer Shifts," ed by G. K. Shenoy and F. E. Wagner, North-Holland, Amsterdam (1978), Chapter 9b.

27) C. H. W. Jones, *J. Chem. Phys.*, **62**, 4343 (1975).

28) H. Sakai, Y. Maeda, S. Ichiba, and H. Negita, *J. Chem. Phys.*, **72**, 6192 (1980).