CHEMISTRY LETTERS, pp. 1411-1414, 1978. Published by the Chemical Society of Japan

RAMAN SPECTRA OF POLYACETYLENE AND HIGHLY CONDUCTING IODINE-DOPED POLYACETYLENE

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The Raman spectra of conductive polyacetylene-iodine complexes and their parent polymers have been studied. The *trans*-rich polyacetylene film contains *trans* segments of various lengths while the *cis*-rich polyacetylene film is composed of relatively long *cis* sequences. The doped iodine takes either the form of $(I_3^-)_x$ or I_5^-.

Recently polyacetylene-halogen complexes were found to have high electrical conductivities.[1,2] Structural information on these materials is needed in order to understand the mechanism of such high conductivities. However, it is difficult to obtain a clear-cut conclusion concerning their structure since these materials as well as their parent polymers are essentially mixtures of components. Resonance Raman spectroscopy is suited to the problems of this kind in that it is able to afford selective information on a component provided that the light source is properly chosen. We have studied the Raman spectra of *cis*-rich polyacetylene (Sample A), *trans*-rich polyacetylene (Sample B), and the complexes with iodine of controlled amounts using ten laser lines in the region of 325.0∿752.5 nm as the light source.

Figure 1 shows the electronic absorption spectra of the films of polyacetylenes and polyacetylene-iodine complexes measured prior to the Raman studies. For the iodine complexes new absorptions appear in the near-infrared region which may be assigned to the CT band. The resonance Raman effect observed in this study is primarily concerned with the absorptions from the ultraviolet to visible region. Typical Raman spectra of the films are shown in Figure 2. It should be noticed that, since the isomerization of the *cis* linkage to the *trans* occurs during the Raman measurements, the Raman spectrum of 'purely *cis*' polyacetylene could not be obtained. Rather, the Raman lines due to the *trans* sequences were observed from Sample A with considerable intensities as shown in Figure 2a. The C=C($\nu_{C=C}$) and C-C(ν_{C-C}) stretching vibrations, especially the former, are known to be sensitive to the number of conjugated bonds $N_{C=C}$.[3,4] The I-I stretching vibrations of various iodine-containing compounds have been shown to be sensitive to the state of iodine.[5] Accordingly, these vibrations are useful markers for studying the chain-length and the state of iodine.

The separation of the three peaks in the electronic absorption spectrum of the film of Sample A (Figure 1a) is 1340 and 1260 cm^{-1}. These peaks are reasonably assigned to the vibrational structure mainly due to the $\nu_{C=C}$ vibration in the excited

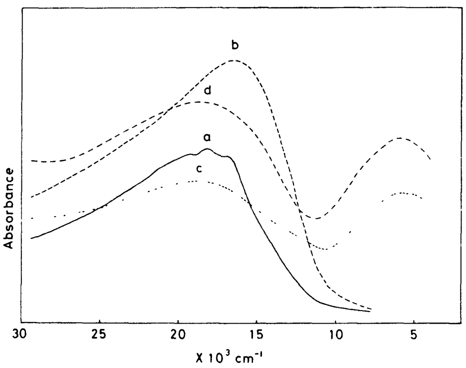

Figure 1(top). Absorption spectra of polyacetylenes and polyacetylene-iodine complexes. (a),Sample A (*cis*-rich); (b),Sample B (*trans*-rich); (c),Sample A plus iodine [$(CHI_{0.205})_x$]; (d),Sample B plus iodine [$(CHI_{0.12})_x$].

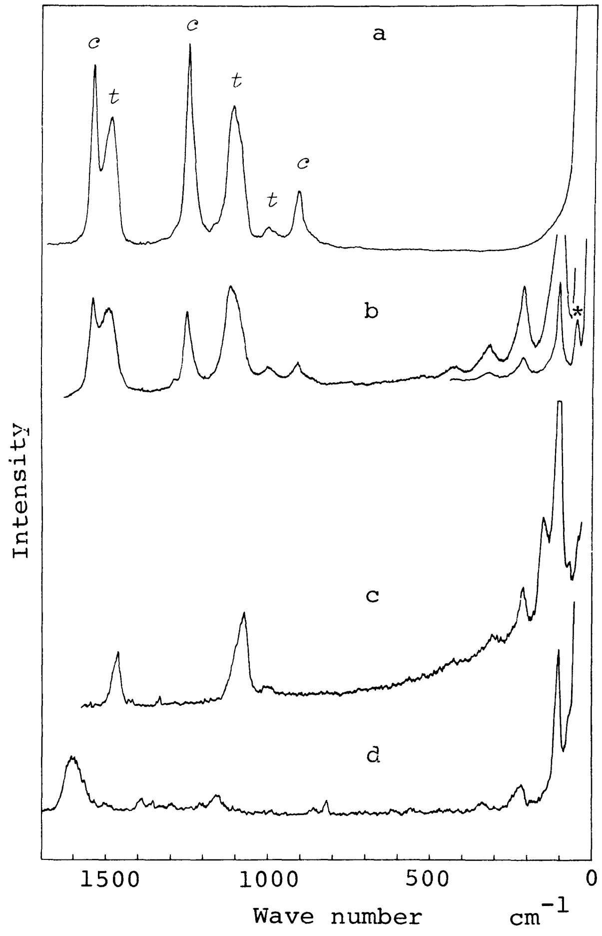

Figure 2(middle). Raman spectra of polyacetylenes and polyacetylene-iodine complexes. (a),Sample A(*cis*-rich) with 514.5-nm line, *c* and *t* indicating the bands due to the *cis* and *trans* sequences, respectively; (b), Sample A plus iodine [$(CHI_{0.205})_x$] with 514.5-nm line (*,possibly a grating ghost); (c),Sample B (*trans*-rich) plus iodine [$(CHI_{0.12})_x$] with 676.4-nm line; (d),Sample B plus iodine [$(CHI_{0.12})_x$] with 325.0-nm line.

electronic state. The appearance of vibrational structure indicates that practically all the *cis* sequences in Sample A are long enough to give a spectrum of an infinitely long *cis* polymer chain. In other words, Sample A originally consists of polymer chains with fairly long *cis* sequences from the viewpoint of absorption spectrum. The Raman $\nu_{C=C}$ frequency of the *cis* sequences in Sample A was almost independent on the excitation wavelength (Table 1) in contrast to what was observed for the $\nu_{C=C}$ frequency of the *trans* sequences (see below).

The Raman $\nu_{C=C}$ frequency due to the *trans* sequences was found to depend markedly on the wavelength of excitation as given in Table 1. In the broad absorption of Sample B (Figure 1b), many absorptions arising from each *trans* segment are overlapped. Therefore, the Raman intensity of $\nu_{C=C}$ of a certain segment is enhanced when an excitation wavelength is in resonance with the absorption of this segment. The third column of Table 1 gives the corresponding $N_{C=C}$ estimated from the $\nu_{C=C}$-$N_{C=C}$ relationship for *trans* polyene homologs of known chain lengths (Figure 3). As Gill *et al.*[4] first pointed out, the length dependence of $\nu_{C=C}$ is appreciable only in relatively short polyenes. However, rough estimation of chain length from the $\nu_{C=C}$ frequency is possible up to $N_{C=C}$=50 or so. Apparently, various *trans* segments of $N_{C=C}$=4 to ca. 100 exist in the film of Sample B, though it is not easy to know quantitatively the relative abundance of each segment. Sample B was obtained through thermal treatment of Sample A. Therefore, it is reasonable to think that the *trans* segments of various lengths were produced in the thermal isomerization process starting from the long *cis* sequences. Individual *trans* segments may be connected by some structural defects like a *cis* linkage.

Table 1. Dependence of $\nu_{C=C}$ (cm^{-1}) on wavelength of excitation and estimated chain length[a]

λ (nm)	*trans* (CH)$_x$ $\nu_{C=C}$	$N_{C=C}$	(CHI$_{0.01}$)$_x$ $\nu_{C=C}$	$N_{C=C}$	(CHI$_{0.12}$)$_x$ $\nu_{C=C}$	$N_{C=C}$
676.4	1466	≥100	1467	≥100	1465	≥100
647.1	1469		1470		1472	
568.2	1474	∿50	1472	∿50	1484	∿25
530.9	1477	∿30	1476	∿30	1493	17∿20
514.5	1485	∿25				
488.0	1496	17∿20				
441.6	1522	9∿10	1533	8∿9	1539	7∿8
350.7	1583	5	1590	4∿5	1603	4
325.0	1596	4	1598	4	1607	4

[a] $\nu_{C=C}$(λ) of *cis* polymer: 1543(514.5), 1546 (488.0), and 1550(441.6) for (CH)$_x$; 1545 (514.5) and 1542(488.0) for (CHI$_{0.057}$)$_x$; 1544(514.5) and 1541(488.0) for (CHI$_{0.205}$)$_x$.

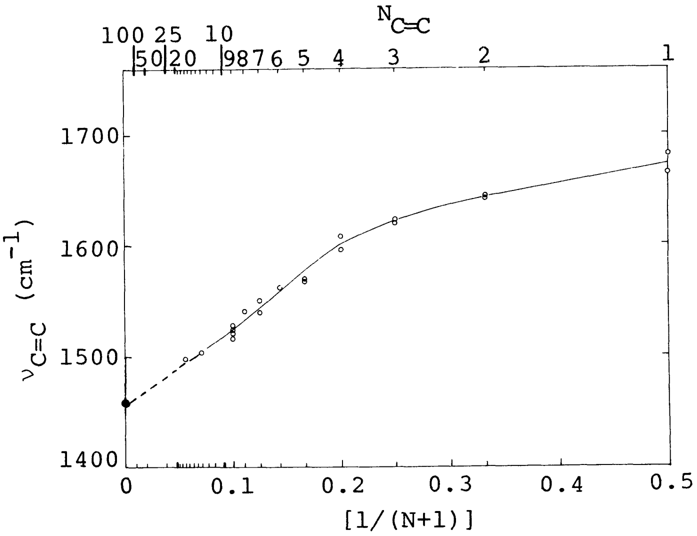

Figure 3. The $\nu_{C=C}$-$N_{C=C}$ relationship *trans* polyenes. ○, Observed values taken from Refs. 3,4,6-8; ●, The limiting value estimated in this work.

As described above, the *cis* Raman frequency showed little dependence on the excitation wavelength. At present this may be interpreted in either of the following two ways. (1) The Raman spectrum (Figure 2a) was obtained from a circle area (in the rotating film of Sample A) irradiated with an exciting laser beam. In that circle area original long *cis* sequences coexisted with shorter *trans* segments produced by the laser irradiation. The long *cis* sequences gave the Raman $\nu_{C=C}$ at about 1546 cm^{-1}, which must be close to the limiting value for an infinitely long *cis* sequence. Shorter *cis* segments might also be present between the *trans* segments, but those were not observed in the resonance Raman spectrum possibly because of lower concentrations or for some other reasons. (2) For any *cis* sequence the Raman $\nu_{C=C}$ frequency remains almost constant. So far, nothing is known about the $\nu_{C=C}$-$N_{C=C}$ relationship for the *cis* sequence. This point should be studied in future using *cis* polyene compounds.

As iodine was absorbed in Sample B, an upward shift of the Raman $\nu_{C=C}$ frequency was observed for each excitation wavelength shorter than 650 nm (Table 1). The shift value may be used as a measure of iodine concentration. By contrast, the *cis* $\nu_{C=C}$ frequency was not affected by the intake of iodine. Such findings may provide a key for elucidating the nature of interactions between polyacetylene and iodine. Although more studies are needed to understand these findings thoroughly, our tentative interpretation is as follows. The charge transfer from the polyene chain to iodine would cause a red shift of the absorption of each *trans* segment, though this point is not clear in Figure 2d because of severe overlapping of another absorption due to I_3^- and/or I_5^- (see below). As a result, for the iodine complex of Sample B a given excitation wavelength comes into resonance with the absorption of a shorter *trans* segment than for Sample B itself. If the $\nu_{C=C}$-$N_{C=C}$ relationship of Figure 3 holds also for the iodine complex, the $N_{C=C}$ value of the *trans* segment in resonance with each excitation wavelength is calculated as listed in Table 1. Little shift of the *cis* $\nu_{C=C}$ frequency with the intake of iodine seems to support the above-mentioned view that it is close to the limiting frequency of an infinitely long *cis* sequence.

The bands in the low frequency region are due to the I-I stretching vibrations. The band at 103±6 cm^{-1} and its overtones were observed irrespective of the excitation wavelength. The band at 147±1 cm^{-1} was distinctly observed only with a red light (752.5 and 676.4 nm). It has recently been shown that the linear I_3^- polymer in the crystal of (benzamide)$_2H^+I_3^-$ gives I-I stretching band at 108 cm^{-1} and its overtones by 514.5-nm excitation.$^{5)}$ We have studied this compound using 676.4∿441.6-nm lasers. A weak shoulder band around 150 cm^{-1} (possibly the I_3^- antisymmetric stretching) was observed with 514.5 and 441.6 nm but not with a red light. Accordingly, the 103-cm^{-1} band and its overtones are assigned to $(I_3^-)_x$ and the distinct band at 147 cm^{-1} is definitely due to other species. It is likely that this band is due to I_5^- ion perturbed by the interaction with polyacetylene. Among several compounds containing various modifications of iodine, (trimesic acid·$H_2O)_{10}H^+I_5^-$ has a band (162 cm^{-1}) closest to this frequency.$^{5)}$ As mentioned above, $(I_3^-)_x$ bands were observed with any wavelength of excitation between 752.5 and 325.0 nm. This is reasonably understood since (benzamide)$_2H^+I_3^-$ has a broad absorption of $(I_3^-)_x$ in the 300∿700-nm region and $(I_3^-)_x$ in polyacetylene may well have a similar spectrum. It is interesting to note that the 223-cm^{-1} band was stronger than the 109-cm^{-1} band with 350.7-nm excitation. We tentatively assign this band as the overlap of $2\nu(I_3^-)$ and fundamental band of I_2 of trace amount.

Hsu *et al.*$^{9)}$ studied the Raman spectra of polyacetylene-iodine complexes and reached the same conclusion as ours concerning the state of iodine on a different basis.

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(Received October 18, 1978)