

SHORT COMMUNICATION

Raman Scattering and Electronic Spectra of Poly(acetylene)

Hideki SHIRAKAWA, Takeo ITO, and Sakuji IKEDA

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
12-1, 2-Chome, Ookayama, Meguro-ku, Tokyo 152, Japan.

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The normal vibrations of infinite linear *trans* and *cis* (*cis-transoid* or *trans-cisoid*)-poly(acetylene) can be treated under a factor group which is isomorphous to the point group D_{2h} .¹ When the *trans* molecule has bond alternation and carbon-carbon bonds being unequal in length, symmetry of the molecule belongs to a factor group which is isomorphous to the point group C_{2h} . Since both C_{2h} and D_{2h} symmetries have a center of inversion, a vibrational mode may be active in the infrared but not in the Raman and *vice versa*.

Raman scattering supplies new vibrational informations which can not be obtained by infrared measurements. Thus, symmetric carbon-carbon stretching vibrations which are active in Raman may give more informations about the configuration of main chain and alternation of the carbon-carbon bonds in the poly(acetylene) or linear polyene chain.

Laser-Raman spectra in the region of 2000-500 cm^{-1} were recorded on the Japan Electron Optics Laboratory Model JRS-C1 laser-excited spectrometer. Raman spectra of poly(acetylene) films were obtained by the front surface reflection method in which the sample was mounted at 45° inclination to the incident beam. The 632.8 nm line of a He-Ne laser, having an output power of ca. 30 mW, was used as the Raman source. An argon ion laser at either 488.0 or 514.5 nm was also used occasionally. In this case, the output power was attenuated as weak as possible in order to prevent the isomerization reaction of the *cis*-poly(acetylene) to *trans* form from a heating effect due to the laser radiation.

The Raman scattering spectrum of all *trans*

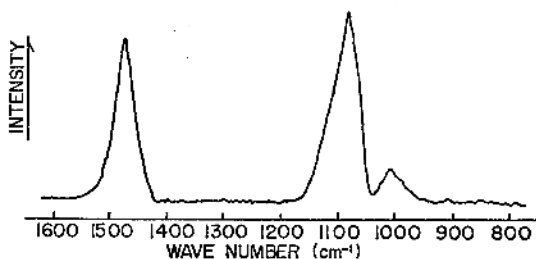


Figure 1. Raman spectrum of *trans*-poly(acetylene); excitation, at 632.8 nm; slit width, 8 cm^{-1} ; scan speed, 25 $\text{cm}^{-1}/\text{min}$.

poly(acetylene) is shown in Figure 1. Two strong bands at 1474 and 1080 cm^{-1} and a weak band at 1016 cm^{-1} were observed. Figure 2 shows the Raman scattering of all *cis*-poly(acetylene) prepared at -78°C. Although the infrared spectrum of the *cis* polymer shows a very weak band at 1015 cm^{-1} which is assigned to *trans* C-H out-of-plane deformation vibration, *trans* bands at about 1500, 1100, and 1016 cm^{-1} besides *cis* bands at 1552, 1262, and 920 cm^{-1} , are observed distinctly in the Raman spectrum. It is considered that a heating effect due to the laser radiation causes irreversible *cis-trans* isomerization to yield the *trans* configuration during the measurements. High frequency shifts of the *trans* bands in the *cis*-poly(acetylene) may be due to the short sequences formed by partial *cis-trans* isomerization. When a strong argon ion laser at 488.0 nm was used as Raman source, the heating effect was too strong to observe the *cis* bands (Figure 2, curve 3).

The *trans*-poly(acetylene) film is an intense black material with a metallic luster, whereas the *cis*-

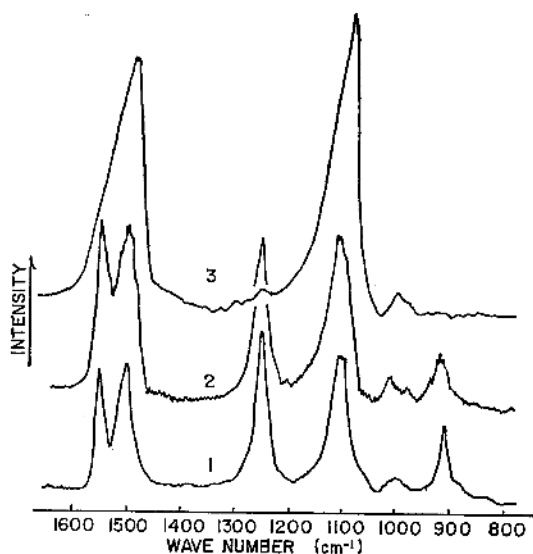


Figure 2. Raman spectra of *cis*-poly(acetylene): (1) excitation at 632.8 nm; slit width, 8 cm⁻¹; scan speed, 25 cm⁻¹/min; (2) excitation at 514.5 nm; slit width, 12 cm⁻¹; scan speed, 25 cm⁻¹/min; (3) excitation at 488.0 nm; slit width, 14 cm⁻¹; scan speed, 25 cm⁻¹/min.

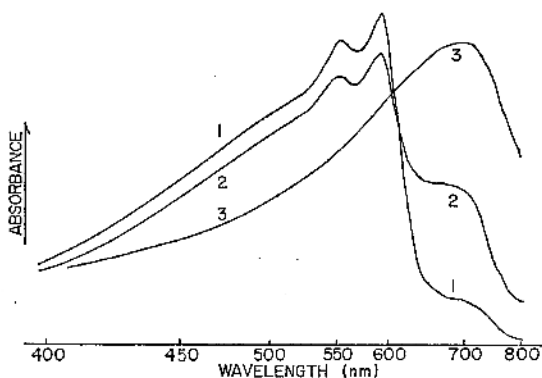


Figure 3. Electronic spectra of poly(acetylene): (1) *cis*-poly(acetylene) prepared at -78°C; (2) *cis*-poly(acetylene) partly isomerized at 110°C for 3 min; (3) completely isomerized to *trans*-poly(acetylene) at 180°C for 2 min.

polyacetylene film has a copper-like luster. Very thin films of *trans* and *cis* polymers show deep blue and clear red colours, respectively. Figure 3 shows the electronic spectra of poly(acetylene) in which the *cis* and *trans* contents are varied. The spectra were obtained for an extremely thin film which was polymerized at -78°C on the

inside wall of 1-cm quartz cell and isomerized *in situ* by heating with an oil bath. Strong absorptions due to the lowest $\pi \rightarrow \pi^*$ transition were observed in the visible region with maximum at 594 nm for an all *cis* polymer and at 700 nm for an all *trans* polymer.

As expected from a great number of electronic spectra of conjugated linear polyenes which are shown by general formula such as $H(CH=CH)_nH$ ($n=3, 5, 6, 8$, and 10),⁴ $CH_3(CH=CH)_nCH_3$ ($n=3-9$),⁵ $C_6H_5(CH=CH)_nC_6H_5$ ($n=1-7$),⁶ and carotenoides,⁷ the wavelength of absorption becomes progressively longer as the length of the conjugated chain is extended. The longest linear polyene having known structure is dodecaprenol- β -carotene⁷ which has nineteen conjugated double bonds and exhibits an absorption maximum at 531 nm in petroleum ether.

According to the simple free-electron model¹³ or LCAO molecular orbital theory,¹⁴ the transition energy between the highest occupied and the lowest vacant level tends to zero for an infinitely long polyene which has no bond alternation, thus the wavelength should become infinite. H. Kuhn,⁸ however, found that the observed wavelength could only be interpreted by the free-electron theory if the bond length were supposed to alternate throughout the chain, even in very long chains. Kuhn,⁸ Dewar,⁹ and Streitwieser¹⁰ presented values of 622, 536, and 583 nm, respectively, as the convergent values for the infinitely long polyene in which the bond alternation was assumed. Although a large number of linear conjugated polyenes have been discussed by many investigators, synthetic and isolated natural polyenes as well as those subjected to the theoretical studies are usually in the all *trans* form, and there are few reports on the all *cis* long polyenes. However, as shown for the all *trans* polyenes, the tendency for the wavelength to approach a finite value with increasing chain length may also be expected for the all *cis* polyenes. The convergent wavelength may be shorter than the corresponding value of the all *trans* polyene, because the degree of the π -electron localization or bond alternation in the all *cis* form is stronger than in the all *trans* form due to the twisting around the single bond caused by the steric repulsion between the two hydrogen atoms located in every other double

bond along the all *cis* sequence. The degree of polymerization or the number of conjugation of poly(acetylene), however, is not known at the present time; the polymers prepared under different conditions give the maximum at the same wavelength. The wavelength at 594 and 700 nm for *cis* and *trans*-poly(acetylene), respectively, may be the convergent values for the lowest $\pi \rightarrow \pi^*$ transition of linear conjugated *cis* and *trans*-polyenes.

The observation of intense Raman bands may be attributed to the resonance-enhancement effect which is observed when the exciting frequency approaches or enters the region of electronic absorption of the molecule. Since the electronic absorption in the visible region may be due to $\pi \rightarrow \pi^*$ transition between the highest occupied and the lowest vacant π orbitals in the polymer, enhanced-Raman active modes depend on the contribution of the carbon—carbon single and double bond stretching vibrations. Similarity of the spectral features with those of carotenoide, β -carotene (1527 and 1158 cm^{-1}) and lycopene (1516 and 1156 cm^{-1})² and the electronic spectrum suggest an alternation of double and single bond in the *trans* poly(acetylene). Thus, the 1474 and 1080 cm^{-1} bands are tentatively assigned to carbon—carbon double and single bond stretching vibrations, respectively.

Ivanova, Yanovskaya, and Shorygin¹¹ have reported the Raman spectra of polyenedicarboxylic acid diethyl esters ($\text{C}_2\text{H}_5\text{OOC}(\text{CH}=\text{CH})_n\text{COOC}_2\text{H}_5$, $n=1-8$). They observed two strong bands at about 1600 and about 1140 cm^{-1} . Frequencies of the band in the region of double bond stretching vibration decrease gradually from 1664 cm^{-1} for $n=1$ to 1540 cm^{-1} for $n=8$. The 1140 cm^{-1} band also shows a slight decrease from 1210 cm^{-1} for $n=1$ to 1137 cm^{-1} for $n=8$. The same tendency is observed for diphenylpolyenes¹² (1567 and 1145 cm^{-1} for $n=5$, 1552 and 1142 cm^{-1} for $n=6$) and carotenoides.² Lower frequency shifts in poly(acetylene) indicate that the number of conjugation in poly(acetylene) is longer than that of lycopene ($n=13$).

Factor group modes of *cis* polymer are distributed among the symmetry species as $4\text{Ag} + \text{B}_1\text{g} + 4\text{B}_2\text{g} + 2\text{B}_3\text{g} + 2\text{A}_u + 3\text{B}_1\text{u} + \text{B}_2\text{u} + 3\text{B}_3\text{u}$ in which Raman active species are Ag , $\text{B}_{1\text{g}}$, $\text{B}_{2\text{g}}$, and $\text{B}_{3\text{g}}$. The result of analysis indicates that

there are one Ag carbon—carbon double bond stretching and two carbon—carbon single bond stretching modes, one is Ag and the other $\text{B}_{2\text{g}}$ in *cis-transoid* configuration; whereas polymer of *trans-cisoid* configuration has two carbon—carbon double bond stretching modes, one is Ag and the other $\text{B}_{2\text{g}}$, and one Ag carbon—carbon single bond stretching mode. Since the spectrum of the *cis* polymer indicates one double bond stretching at 1552 cm^{-1} and two single bond stretching vibrations at 1262 and 920 cm^{-1} , it can be concluded that configuration of the *cis* polymer is *cis-transoid*. The result confirms the previous work¹ that the *cis*-opening of triple bond occurs in a polymerization reaction of acetylene with $\text{Ti}(\text{OC}_4\text{H}_9)_4\text{—Al}(\text{C}_2\text{H}_5)_3$ catalyst system at low temperatures.

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REFERENCES

1. H. Shirakawa and S. Ikeda, *Polymer J.*, **2**, 231 (1971).
2. L. Rimai, R. G. Kilponen, and D. Gill, *J. Amer. Chem. Soc.*, **92**, 3824 (1970).
3. D. J. Berets and D. S. Smith, *Trans. Faraday Soc.*, **64**, 823 (1968).
4. F. Sondheimer, D. A. Ben-Efraim, and R. Wolovsky, *J. Amer. Chem. Soc.*, **83**, 1675 (1961).
5. F. Bohlman and H. Manhardt, *Chem. Ber.*, **89**, 1307 (1956).
6. K. H. Hausser, R. Kuhn, and A. Smakula, *Z. Phys. Chem.*, **B29**, 384 (1935).
7. P. Karrer and C. Eugster, *Helv. Chim. Acta*, **34**, 1805 (1951).
8. H. Kuhn, *J. Chem. Phys.*, **17**, 1198 (1949).
9. M. J. S. Dewar, *J. Chem. Soc.*, 3544 (1952).
10. A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N.Y. 1961.
11. T. M. Ivanova, L. A. Yanovskaya, and P. P. Shorygin, *Opt. Spectroscopy*, **18**, 75, (1965).
12. P. P. Shorygin and T. M. Ivanova, *Soviet Phys., Doklady*, **8**, 493 (1963).
13. N. S. Bayliss, *J. Chem. Phys.*, **16**, 287 (1948).
14. J. E. Lennard-Jones, *Proc. Roy. Soc. (London)*, **A158**, 280 (1937).