Infrared Spectra of Poly(acetylene)

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ABSTRACT: The infrared spectra of poly(acetylene), poly(acetylene-d_2), copoly(acetylene+acetylene-d_2), and copoly(acetylene +acetylene-d_1+acetylene-d_2) prepared by the Ti(OC$_4$H$_9$)$_4$—Al(C$_2$H$_5$)$_3$ system over a wide temperature range (*ca.* −100 to 180°C) are reported. A tentative assignment of the observed spectra is made on the basis of model structures in which infinite planar chains of all *trans*, all *trans—cisoid*, and all *cis—transoid* configurations are assumed. The spectral data are best interpreted on the basis of an all *cis-transoid* (or an all *trans-cisoid*) structure for the polymers prepared at temperatures lower than −78°C, and an all *trans* structure for the polymers prepared at temperatures higher than 150°C.

Simplified calculations of the C-H and C-D out-of-plane deformation frequencies are made for various model chains. It has been concluded from a comparison of the observed and calculated frequencies that the *cis*-opening of the triple bond occurs in a polymerization reaction with the Ti(OC$_4$H$_9$)$_4$—Al(C$_2$H$_5$)$_3$ catalyst system at low temperatures.

KEY WORDS   Infrared Spectra/Poly(acetylene)/Deuterated Acetylene/ Ziegler Catalyst/Configuration/*cis*-Opening/Factor Group Analysis/ Normal Vibration/

Structure and properties of poly(acetylene) prepared with Ziegler—Natta catalysts have been investigated by several groups. Natta, *et al.*,[1] presented evidence from chemical properties and X-ray diffraction data, indicating that the poly(acetylene) obtained had linear chains of conjugated double bonds of *trans* configuration along the chains.

A characteristic band at 9.86 μ (1010 cm^{-1})[2,3] in the spectra of poly(acetylene) has been assigned to the out-of-plane deformation vibration of hydrogens attached to *trans* carbon—carbon double bonds. Watson, Jr., *et al.*,[2] observed a band at 14.13—14.9 μ in the spectrum of a polymer prepared from a triisobutylaluminum—titanium tetrachloride system. The band was assigned to the *cis* C-H out-of-plane deformation vibration. From the interpretation of the spectra, they suggested that the polymer obtained from triisobutylaluminum contained both *cis* and *trans* configurations along the polymer chain whereas the polymer prepared with *n*-butyllithium was predominantly *trans*. Recently, Kleist and Byrd,[14] have reported a preparation of *cis* rich poly(acetylene) containing a 60—70% *cis* content obtained by a catalyst system of thermally decomposed iron dimethylglyoximate—2-pyridine and triethylaluminum at 25°C or below.

In this paper, we wish to report the analysis of normal vibrational modes, to make tentative assignments of observed bands in infrared spectra of poly(acetylene), poly(acetylene-d_2), copoly(acetylene+acetylene-d_2), and copoly(acetylene+acetylene-d_1+acetylene-d_2) and to discuss these results in relation to the structures of the polymers.

EXPERIMENTAL

Reagents

Acetylene was purified before use by being passed successively through a sodium hydrogensulfite solution, a Dry Ice—methanol trap, a calcium chloride column, a phosphorus pentoxide column, and finally a tetralin solution of triethylaluminum. Acetylene-d_2 was prepared by adding heavy water (99.75-mol% isotopic purity) to calcium carbide pretreated at 800—900°C under

vacuum for about 3 hr. Mass spectroscopy indicated that the deuterated acetylene contained 99.23 mol% of acetylene-d_2 and 0.77 mol% of acetylene-a_1. A mixture of acetylene-d_0, -d_1, and -d_2 was prepared by using a mixture of light and heavy water. The distribution of deuterium in the mixture was checked by mass spectrum. Titanium tetrabutoxide and triethylaluminum were used as purchased. Solvents were dried and distilled under nitrogen.

Preparation and Measurement

Poly(acetylene), poly(acetylene-d_2), copoly-(acetylene+acetylene-d_2), and copoly(acetylene+acetylene-d_1+acetylene-d_2) were prepared in the form of thin films by introducing acetylene gas to an unstirred concentrated solution of the $Ti(OC_4H_9)_4$—$Al(C_2H_5)_3$ catalyst system or to a reaction vessel in which a concentrated solution of the catalyst was spread over the glass wall to form a polymer film on the surface of the solution. In order to control the thickness of films, the polymerization was interrupted by evacuating the system. Polymerization was carried out at several temperatures over a wide range of *ca.* −100 and 180°C. At polymerization temperatures lower than 80°C toluene was used as solvent, whereas at temperatures higher than 80°C *n*-hexadecane was used. The films obtained were washed repeatedly by toluene, until the solution became colourless. Purification of the films was carried out at the same temperature as the polymerization temperature in order to prevent *cis-trans* isomerization of the polymers. The purified films were spread on a copper mesh

and dried by blowing nitrogen gas on them at room temperature for a few minutes. All the processes were carried out under an atmosphere of nitrogen in order to prevent the oxidation of the polymers. Although the spectra were recorded in the air at room temperature, no spectral change was observed during a few successive scannings.

The infrared spectra were recorded by a Japan Spectroscopic Co. Model IR-G double beam grating spectrophotometer and a Hitachi Model EPI-G3 double beam grating spectrophotometer in the region of 4000—400 cm^{-1}.

ANALYSIS OF NORMAL VIBRATION FOR MODEL STRUCTURES

It has been considered that poly(acetylene) prepared by Ziegler—Natta catalysts is a linear molecule having as many conjugated double bonds as the degree of polymerization. Lennard—Jones studied the linear polyenes of the general formula $C_{2n}H_{2n+2}$ by the LCAO molecular orbital theory and found that as *n* increases, alternate bonds tend to become nearly equal with a length of 1.38Å.[7] This theory has been accepted for a long time. Corradini[4] estimated the length of the C-C bond to be 1.40Å from the calculated resonance energy of poly(acetylene).

Kuhn,[8] however, found that the observed absorption spectra of polyenes 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. Ooshika,[9] using the self-consistent LCAO molecular orbital
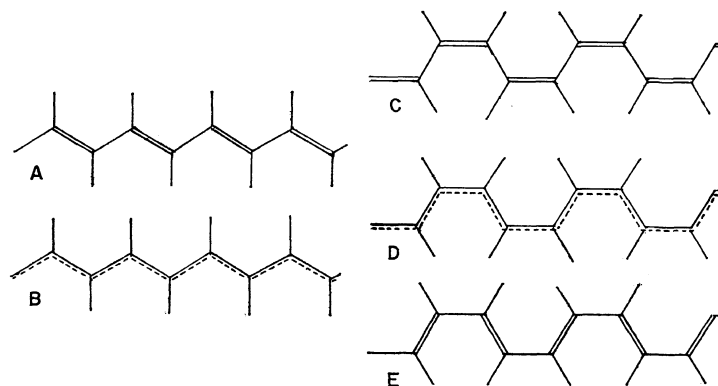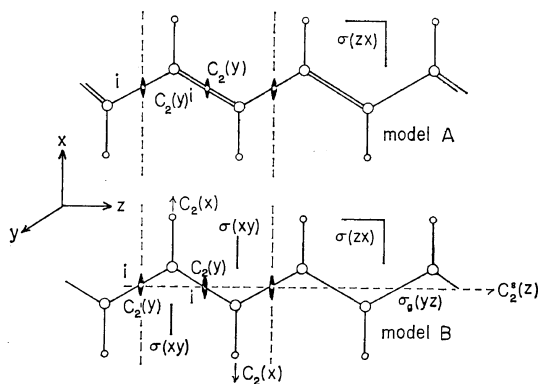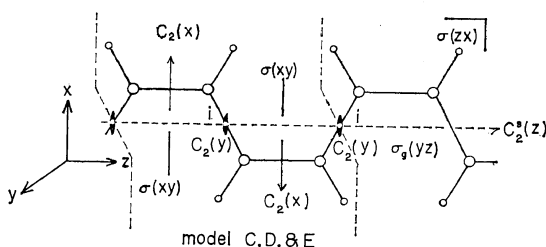

Figure 1. Possible structures of poly(acetylene).

theory, found that the equilibrium configuration with all bond lengths equal to 1.389Å was less stable in the limit than one in which alternate bonds were of the length of 1.346 and 1.463Å based on the semi-empirical evaluation of several energy integrals. The calculation concerns an infinitely large conjugated cyclic polyene $C_{2n}H_{2n}$,

Figure 2b. Unit cell and symmetry elements of models C, D, and E. Unit cell is shown between thin broken lines.

the result of which is also applicable to an infinitely long linear polyene.

Stability of the polyene molecule depends upon the resonance energy associated with the conjugated double bond system. In order to have the maximum amount of resonance stabilization, the structure of the molecule must be planar.

The possible structures are shown in Figure 1. In these models, A and B have *trans—transoid* skeletons whereas C, D, and E have *cis—transoid* or *trans-cisoid* backbones. In B and D, all C-C bonds are equal in length.

Figure 2a. Unit cells and symmetry elements of models A and B. Unit cell is shown between thin broken lines.

Table I. The character table for the point group C_{2h}, symmetry species, selection rules, and number of normal modes for model A[a]

C_{2h}	E	$C_2(y)$	i	$\sigma(zx)$	Tr	Ro	Activity	N	n
A_g	1	1	1	1			R	4	4
B_g	1	−1	1	−1		R_z	R	2	1
A_u	1	1	−1	−1	T_y		IR	2	1
B_u	1	−1	−1	1	$T_x T_z$		IR	4	2

[a] N and n denote the number of normal modes and of internal vibrations, respectively.

Table II. The character table for the point group D_{2h}, symmetry species, selection rules, and number of normal modes for model B, C, D, and E[a]

| D_{2h}	E	$C_2{}^s(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(zx)$	$\sigma_g(yz)$	Tr	Ro	Activity	for model B		for model C, D, and E	
												N	n	N	n
A_g	1	1	1	1	1	1	1	1			R	2	2	4	4
B_{1g}	1	1	−1	−1	1	1	−1	−1		R_z	R	2	1	2	1
B_{2g}	1	−1	1	−1	1	−1	1	−1			R	2	2	4	4
B_{3g}	1	−1	−1	1	1	−1	−1	1			R	0	0	2	2
A_u	1	1	1	1	−1	−1	−1	−1				0	0	2	2
B_{1u}	1	1	−1	−1	−1	−1	1	1	T_z		IR	2	1	4	3
B_{2u}	1	−1	1	−1	−1	1	−1	1	T_y		IR	2	1	2	1
B_{3u}	1	−1	−1	1	−1	1	1	−1	T_x		IR	2	1	4	3

[a] N and n denote the number of normal modes and of internal vibrations, respectively.

In the model structure A and B one chemical unit of acetylene is contained in the repeating unit, and in the model structure C, D, and E two chemical units of acetylene. The symmetry elements and unit cells of these models are illustrated in Figure 2a and 2b, where the screw axis is denoted by C^s and the glide plane by σ_g.

The normal modes may be treated under the factor groups isomorphous to the point group C_{2h} for model A, and to the point group D_{2h} for models B, C, D, and E. The character tables for the point group C_{2h} and D_{2h} are given in Table I and II, respectively. The number of normal modes (N) and of internal vibrations (n) and selection rules in the infrared (IR) and Raman (R) spectra under each symmetry species derived from the factor group analysis are also shown in Table I for model A and in Table II for models B, C, D, and E.

Notations expressing the bond lengths and the bond angles are given in Figure 3. As internal coordinates we have selected the following: C-H bond stretching (Δs), C-C bond stretching (ΔT and Δt), C-C-C deformation ($\Delta \alpha$, $\Delta \alpha_i = 1/\sqrt{6}\,(2\Delta\phi_{i3}-\Delta\phi_{i1}-\Delta\phi_{i2})$), C-C-H deformation between the C-H bond and the bisector of the C-C-C angle ϕ_{i3} ($\Delta \beta$, $\Delta\beta_i = 1/\sqrt{2}\,(\Delta\phi_{i1}-\Delta\phi_{i2})$), and deformation of the C-H bond out of the plane of the adjacent C-C-C linkage ($\Delta \gamma$). The torsion coordinate around the C-C bond is omitted because the factor group modes do not include any C-C torsional vibrations in the infinite planer molecules. The normalized internal symmetry coordinates for infrared active vibrations are given in Table III. The result of the analysis indicates that the three fundamentals for *trans* models A and B are one C-H stretching, one C-H in-plane deformation, and one C-H out-of-plane deformation and the seven fundamentals for *cis* models including model E are two C-H stretching, two C-H in-plane deformation, one C-C stretching, one C-H out-of-plane deformation, and one C-C-C deformation.
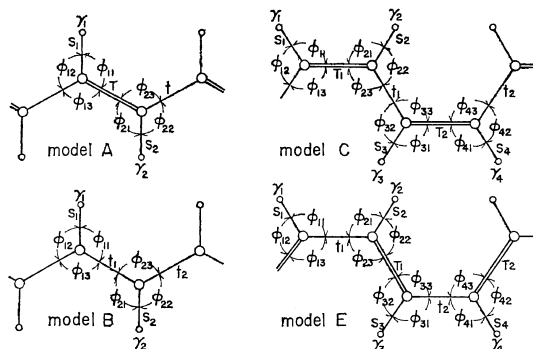
Figure 3. Internal coordinates for model structures. The same sets of coordinates as model C were assumed for model D.

ASSIGNMENTS AND DISCUSSION

Infrared spectra of poly(acetylene) and poly-(acetylene-d_2) are shown in Figures 4 and 5, respectively. From the spectra, it can be seen that relative intensities of almost all bands observed vary with the polymerization temperature. Thus, relative intensities of 3013, 1292, and 1015 cm^{-1} bands increase with increasing the polymerization temperature. Intensity of the 1292 cm^{-1} band, however, was very weak in the polymer prepared at 150°C. Corresponding bands in the spectrum of poly(acetylene-d_2) are found at 2231, 916, and 752 cm^{-1}, respectively. Fre-

Table III. The normalized internal symmetry coordinates for infrared active vibration[a]

Model A	Model B			Model C and D	Model E
B_u	B_{1u}	$1/\sqrt{2}\,(\Delta\beta_1-\Delta\beta_2)$	B_{1u}	$1/2(\Delta\beta_1-\Delta\beta_2+\Delta\beta_3-\Delta\beta_4)$	$1/2(\Delta\beta_1-\Delta\beta_2+\Delta\beta_3-\Delta\beta_4)$
				$1/2(\Delta\alpha_1-\Delta\alpha_2+\Delta\alpha_3-\Delta\alpha_4)$	$1/2(\Delta\alpha_1-\Delta\alpha_2+\Delta\alpha_3-\Delta\alpha_4)$
				$1/2(\Delta s_1-\Delta s_2+\Delta s_3-\Delta s_4)$	$1/2(\Delta s_1-\Delta s_2+\Delta s_3-\Delta s_4)$
A_u	B_{2u}	$1/\sqrt{2}\,(\Delta\gamma_1+\Delta\gamma_2)$	B_{2u}	$1/2(\Delta\gamma_1+\Delta\gamma_2+\Delta\gamma_3+\Delta\gamma_4)$	$1/2(\Delta\gamma_1+\Delta\gamma_2+\Delta\gamma_3+\Delta\gamma_4)$
B_u	B_{3u}	$1/\sqrt{2}\,(\Delta s_1-\Delta s_2)$	B_{3u}	$1/2(\Delta s_1+\Delta s_2-\Delta s_3-\Delta s_4)$	$1/2(\Delta s_1+\Delta s_2-\Delta s_3-\Delta s_4)$
				$1/\sqrt{2}\,(\Delta T_1-\Delta T_2)$	$1/\sqrt{2}\,(\Delta t_1-\Delta t_2)$
				$1/2(\Delta\beta_1+\Delta\beta_2-\Delta\beta_3-\Delta\beta_4)$	$1/2(\Delta\beta_1+\Delta\beta_2-\Delta\beta_3-\Delta\beta_4)$

[a] Here $\alpha_i = 1/\sqrt{6}\,(2\Delta\phi_{i3}-\Delta\phi_{i1}-\Delta\phi_{i2})$ and $\beta_i = 1/\sqrt{2}\,(\Delta\phi_{i1}-\Delta\phi_{i2})$.
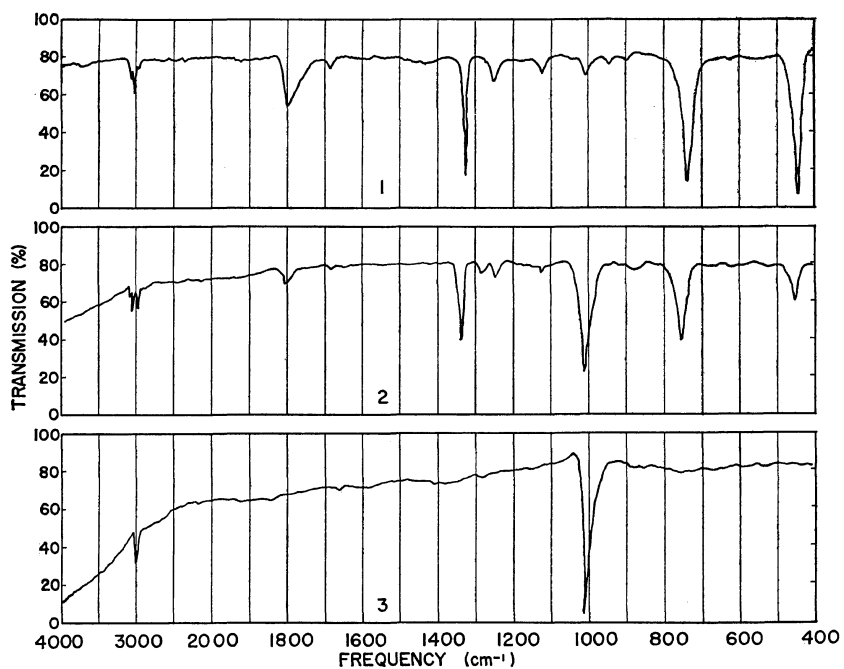
Figure 4. Infrared spectra of poly(acetylene) prepared at (1) −78°C, (2) 20°C, and (3) 150°C.
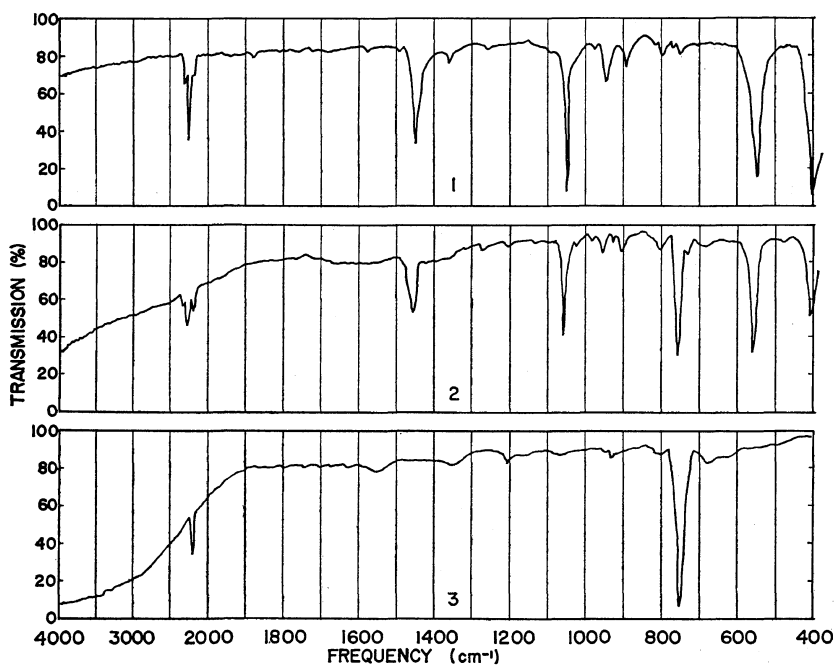
Figure 5. Infrared spectra of poly(acetylene-d_2) prepared at (1) −78°C, (2) 24°C, and (3) 150°C.

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quency ratios of these bands (ν_H/ν_D) are 1.35, 1.41, and 1.35, respectively, which are nearly the same as the factor $\sqrt{13/7}=1.363$ calculated from the relative masses of thehy drogen, deuterium, and carbon atoms. This indicates that these bands may be assigned to C-H stretching or C-H deformation modes.

The out-of-plane deformation vibrations of hydrogen attached to *trans* C-C double bonds in various ethylenic compounds are usually observed in the vicinity of 980—960 cm^{-1}. Conjugation of *tsans* double bonds increases the band frequency. Lunde, *et al.*,[5] have shown that the C-H out-of-plane deformation bands appear at 960 cm^{-1} in *trans*-stilbene, 985 cm^{-1} in *trans*, *trans*-1,4-diphenylbutadiene-1,3, 994 cm^{-1} in all-*trans*-1,6-diphenylhexatriene-1,3,5, and 1010 cm^{-1} in all-*trans*-1,8-diphenyloctateraene-1,3,5,7. On this basis, the 1015 cm^{-1} band is reasonably assigned to the *trans* out-of-plane hydrogen deformation in *trans* configuration along the chains. According to Bellamy,[6] the *trans* C-H in-plane deformation should occur between 1310—1295 cm^{-1}. Therefore, the band at 1292 cm^{-1} is assigned to the *trans* C-H in-plane deformation. The band at 3013 cm^{-1} should be assigned to C-H stretching in *trans* configuration. These assignments are consistent with the result expected from the consideration of both *trans* models (A and B).

Relative intensities of 3057, 3044, 1329, 1249, 740, and 446 cm^{-1} bands in poly(acetylene) and corresponding bands at 2275, 2255, 1050, 947, 548, and 402 cm^{-1} in poly(acetylene-d_2) increase by decreasing the polymerization temperature. Respective frequency ratios of poly(acetylene) to poly(acetylene-d_2) are 1.34, 1.35, 1.27, 1.32, 1.35, and 1.11. From the ratio of 1.11, the 446 cm^{-1} band is clearly such a vibration as no hydrogen atoms are concerned. It is, therefore, concluded that the band is assigned to the B_{1u} C-C-C deformation in *cis* configuration. In the C-H deformation frequency region, Lunde, *et al.*,[5] have shown that the spectrum of *cis* isomer of various diphenylpolyenes contain two bands absent from all *trans* spectra. One is the weak to moderate band assigned to in-plane vibrations of hydrogen attached to *cis* C-C double bonds located at roughly the same wave number, 1430 —1410 cm^{-1}, but in the spectrum of *cis*, *cis*-1,4-

diphenylbutadiene-1,3 the band is shifted to 1368 cm^{-1}. The other band is assigned to out-of-plane vibrations of hydrogen attached to *cis* C-C double bonds which appear at 779—772 cm^{-1}. Hwa, *et al.*,[11] have shown that the *cis* out-of-plane deformation band of *cis*-hexatriene-1,3,5 appears at 818 cm^{-1} by comparison with the spectrum of the *trans* isomer. The two bands at 1329 and 1249 cm^{-1}, on this basis, may be assigned to *cis* C-H in-plane deformation of B_{1u} and B_{3u} modes predicted from the analysis of *cis*—*transoid* (or *trans*-*cisoid*) skeleton models. The band at 740 cm^{-1} is assigned to *cis* C-H out-of-plane deformation. The bands at 3057 and 3044 cm^{-1} are assigned to the B_{1u} and B_{3u} C-H stretching vibrations which are also predicted from the analysis.

It was not possible to identify which band is the B_{1u} or B_{3u} mode in the two C-H stretching bands as well as in the two C-H in-plane deformation bands, because well stretched film to obtain the polarized spectra could not be prepared. The 3057 and 1329 cm^{-1} bands, however, are tentatively assigned to the B_{1u} mode and 3044 and 1249 cm^{-1} bands to the B_{3u} mode, the observed ratio of product rule for B_{1u} is 1.89 being nearly the same as the calculated ratio $2\sqrt{13/14}=1.927$. For the B_{3u} mode the observed ratio of product rule could not be obtained, because there is no unambiguous band of carbon —carbon stretching mode in the spectra of poly-(acetylene) and poly(acetylene-d_2).

Bellamy[6] lists the range of 1680—1620 cm^{-1} for the C-C double bond stretching vibration with a conjugated system, the frequency being lowered toward 1600 cm^{-1}. The C-C single bond stretching occurs between 1200—1000 cm^{-1}. Conjugation increases the single bond frequency. Analysis of the normal vibrational modes in the *cis*—*transoid* (or *trans*—*cisoid* structure indicates that stretching of the C-C double bond or shorter bond should be infrared active mode in *cis*-*transoid* structure (Figure 1C), whereas the C-C single bond or longer bond stretching vibration should be active in the *trans*—*cisoid* structure (Figure 1E). Thus it is expected that a band will appear in the vicinity of 1600 cm^{-1} in the case of *cis*—*transoid* structure and in the range of 1200—1000 cm^{-1} in *trans*—*cisoid* structure. In the case of D structure in which all carbon—carbon bonds

are equal in length and may have intermediate character between single and double bonds, the stretching vibration of the C-C bonds should appear in the vicinity of $1400\,\mathrm{cm}^{-1}$.

As shown in Figure 4, there is no such band either in the vicinity of $1600\,\mathrm{cm}^{-1}$ or $1400\,\mathrm{cm}^{-1}$. A band at $1118\,\mathrm{cm}^{-1}$ in the spectra of poly(acetylene) prepared at low temperature decreases its relative intensity with increasing the polymerization temperature, and is concerned with *cis—transoid* (or *trans—cisoid*) structures. On this basis, the band may be assigned to the carbon—carbon stretching vibration of *trans—cisoid* structure. In the spectra of poly(acetylene-d_2), however, corresponding bands could not be found in the region of $1000-1100\,\mathrm{cm}^{-1}$ expected from small isotope shift.

On standing in air at room temperature, poly(acetylene) prepared by the $\mathrm{Ti(OC_4H_9)}$—$\mathrm{Al(C_2H_5)_3}$ system reacts slowly with oxygen to give an oxygenated material which is characterized in the infrared spectrum by the presence of a strong band at $1670\,\mathrm{cm}^{-1}$ and a medium band at $1720\,\mathrm{cm}^{-1}$ due to the stretching vibrations of carbonyl groups. Higashiura, *et al.*,[17] have tentatively assigned the bands at 1680 and $1720\,\mathrm{cm}^{-1}$ in the oxygenated poly(acetylene) to the stretching vibrations of carbonyl groups of α,β-unsaturated ketone and α-diketone, respectively. We have also observed a relatively strong band at 1800 cm^{-1} in fresh polymers. The band may be due to the *cis* configuration since its intensity increases by decreasing the polymerization temperature.

Bellamy[6] describes overtones of $\mathrm{CH_2}$ wagging which appear in the range of $1750-1800$ and of $1800-1850\,\mathrm{cm}^{-1}$ in the compounds of the type $\mathrm{RR'C=CH_2}$ and $\mathrm{RCH=CH_2}$, respectively. A band in the vicinity of $1800\,\mathrm{cm}^{-1}$ has also been reported in 1,3,5-hexatriene,[10a,11] 1,3,5,7-octatetraene,[10b,18] 1,3,5,7,9-decapentaene,[19,20] 1,3,5,7,9,11-dodecahexaene,[19] and 1,3,5,7,9,11,13,15-hexadecaoctaene.[19] Lippincott, *et al.*, have assigned a strong band at $1810\,\mathrm{cm}^{-1}$ and a medium band at $1750\,\mathrm{cm}^{-1}$ in *trans*-1,3,5-hexatriene[10a] and three bands at 1889 (w), 1802 (s), and $1764\,\mathrm{cm}^{-1}$ (w) in *trans, trans*-1,3,5,7-octatetraene[10b] to combination bands. These observations suggest that

Table IV. Assignments of the infrared spectra of poly(acetylene) and poly(acetylene-d_2)

Observed frequency (cm⁻¹) and intensity						Assignment		
poly(acetylene)			poly(acetylene-d_2)					
3057	vw[a]	vw[b]	—[d]	2275	vw[a]	vw[c]	—[d]	$\mathrm{B_{1u}}$	C–H stretching in *cis*
3044	w	w	—	2255	m	w	—	$\mathrm{B_{3u}}$	C–H stretching in *cis*
3013	vvw	w	m	2231	w	w	m	$\mathrm{B_{3u}}$	C–H stretching in *trans*
1800	m	w	—						$1329+446=1785$?
				1448	s	m	—		$1050+402=1452$?
1690	vw	vvw	—						$1249+446=1695$?
				1360	vw	—	—		$947+402=1349$?
1329	s	m	—	1050	s	m	—	$\mathrm{B_{1u}}$	C–H in-plane deformation in *cis*
				975	vvw	vvw	—		
1292	—	vw	vvw	916	—	vvw	vw	$\mathrm{B_{1u}}$	C–H in-plane deformation in *trans*
1249	w	vw	—	947	w	vw	—	$\mathrm{B_{3u}}$	C–H in-plane deformation in *cis*
				892	w	vw	—		
1118	vw	vvw	—					$\mathrm{B_{3u}}$	C–C stretching in *cis*?
				800	vw	vw	—		
1015	vw	s	vs	752	vvw	s	vs	$\mathrm{B_{2u}}$	C–H out-of-plane deformation in *trans*
980	vvw	—	—	735	vvw	vvw	—		in -(*trans* $\mathrm{CH=CH}$)$_2$- between -(*cis* $\mathrm{CH=CH}$)$_n$-
940	vw	—	—	720	vvw	—	—		in -(*trans* $\mathrm{CH=CH}$)$_1$- between -(*cis* $\mathrm{CH=CH}$)$_n$-
740	vs	s	—	548	vs	s	—	$\mathrm{B_{2h}}$	C–H out-of-plane deformation in *cis*
446	vs	m	—	402	vs	s	—	$\mathrm{B_{1u}}$	C–C–C deformation in *cis*

[a] Intensity in the polymer prepared at $-78°C$, [b] $20°C$, [c] $24°C$, and [d] $150°C$.

the band at about 1800 cm⁻¹ may be characteristic of vinyl groups or conjugated polyenes. Although such bands have been observed in all *trans* or *trans* rich polyenes except *cis*-1,3,5-hexatrene,[11] we could find no such bands in *trans* poly(acetylene. We have tentatively assigned the band at 1800 cm⁻¹ to combinations of C-C-C deformation and C-H in-plane vibrations. Corresponding bands in poly(acetylene-d_2) are observed at 1448 and 1360 cm⁻¹. The intensities of these "combination" bands are considerably greater than would be expected. Their origin is therefore not entirely clear. These assignments are summarized in Table IV.

The spectral data are best interpreted on the basis of all *trans* configuration for the polymers prepared at temperatures higher than 150°C, and all *cis—transoid* (or all *trans—cisoid*) configura-

tions for the polymers prepared at temperatures lower than −78°C. The polymers obtained at the temperature range of −78—150°C, contain both *cis—transoid* (or *trans—cisoid*) and *trans* configurations. The ratio of *cis—transoid* (or *trans—cisoid*) to *trans* configuration depends strongly upon the polymerization temperature. Whether carbon—carbon bonds of poly(acetylene) are equal in length or alternately long or short and whether configuration of poly(acetylene) is *cis—transoid* or *trans—cisoid* could not be made clear at the present time, because of ambiguous assignment of the C-C stretching vibration.

According to factor group analysis, the C-H out-of-plane vibrations in both *cis—transoid* (or *trans—cisoid*) and *trans* skeleton models belong to the B_{2u} or A_u mode in which only one fundamental is contained in either C_{2h} and D_{2h} sym-
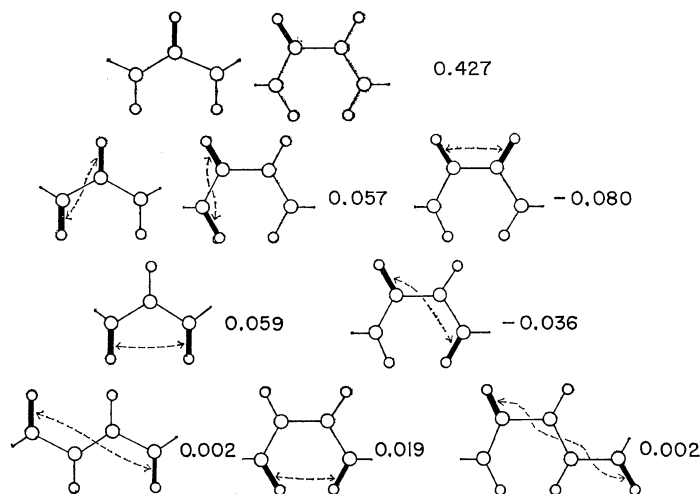

Figure 6. Values of force constants for C-H out-of-plane deformation (in md Å). Interaction constants are shown by two coordinates connected with a broken line.

Table V. Calculated C-H and C-D out-of-plane deformation frequencies

	Frequency, cm⁻¹	
	Obsd	Calcd
trans C-H	1015	1014.8
cis C-H	740	740.5
trans C-D	752	745.2
cis C-D	548	543.7

metry of model structures. If a suitable set of force constants for the C-H out-of-plane deformation mode is available, these frequencies can be easily calculated.

The calculations were carried out for B and D models in which all C-H and C-C bonds and all C-C-H and C-C-C angles were assumed to have common lengths (1.08 and 1.40Å) and a common angle (120°), respectively. Some force constants were estimated from C-H out-of-plane frequencies

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in various α,ω-diphenylpolyenes under the same assumptions as those of poly(acetylene) models. A value of 0.427 mdÅ was obtained for C-H out-of-plane deformation vibrations in both *cis* and *trans* configurations. Several interaction constants are schematically shown in Figure 6. Calculated and observed out-of-plane frequencies are listed in Table V.

In the region of C-H stretching, four very weak bands were observed at 2962, 2931, 2875, and 2853 cm^{-1}. These bands may be assigned to CH$_3$ asymmetric, CH$_2$ asymmetric, CH$_3$ symmetric, and CH$_2$ symmetric stretching, respectively, thus indicating the presence of the ethyl groups from the catalyst in the polymer chains. At the initiation step, acetylene molecules may be inserted between the metal—ethyl bond giving rise to incorporation of the ethyl group at the end of the growing chain.

In previous publications[15,16] we have reported that benzoic acid was identified from the permanganate oxidation products of poly(acetylene) prepared with the systems of TiCl$_4$—Al(C$_2$H$_5$)$_3$ and Ti(OC$_4$H$_9$)$_4$—Al(C$_2$H$_5$)$_3$, and that the formation of benzoic acid is attributed to phenyl groups formed by terminal cyclization of growing chains. No evidence of phenyl groups, however, was obtained from infrared spectra.

INFRARED SPECTRA OF COPOLY(ACE-TYLENE+ACETYLENE-d_2) AND COPOLY(ACETYLENE+ ACETYLENE-d_1+ACETYLENE-d_2)

The infrared spectra of copoly(acetylene+acetylene-d_2) and copoly(acetylene+acetylene-d_1+ acetylene-d_2) show differences from superimposed spectra of poly(acetylene) and poly(acetylene-d_2) especially in the region of C-H and C-D out-of-plane deformation vibrations. The C-H and C-D out-of-plane deformation bands shift to lower frequency in *trans* configuration whereas to higher frequency in *cis—transoid* or *trans—cisoid* configuration and split into several bands. Thus, the *trans* C-H deformation vibrations appear between 1015—930 cm^{-1}, the *trans* C-D bands 745—715 cm^{-1}, the *cis* C-H bands 810—743 cm^{-1}, and the *cis* C-D bands 663—552 cm^{-1} in the case of copoly(acetylene+acetylene-d_2). Figures 7 and 8 show the spectra of all *trans* copolymers pre-

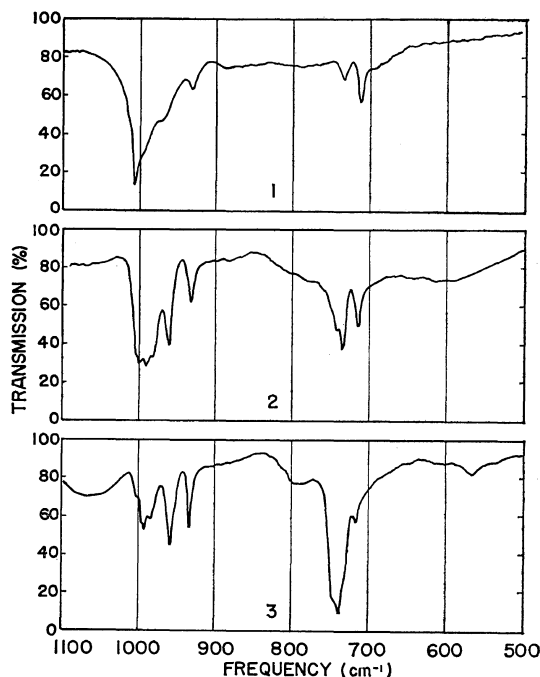**Figure 7.** Infrared spectra of copoly(acetylene+ acetylene-d_2) prepared at 150°C: 1, feed monomer ratio, C$_2$H$_2$/C$_2$D$_2$=80/20; 2, 50/50; 3, 20/80.
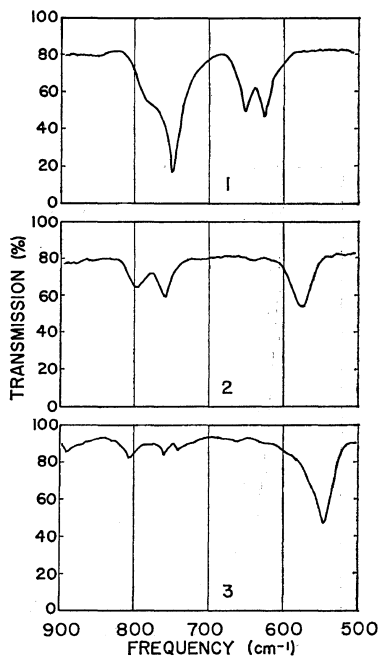
Figure 8. Infrared spectra of copoly(acetylene+ acetylene-d_2) prepared at −78°C: 1, feed monomer ratio, C$_2$H$_2$/C$_2$D$_2$=80/20; 2, 50/50; 3, 20/80.

pared at 150°C and of all *cis—transoid* (or all *trans—cisoid*) copolymers obtained at −78°C, respectively, in the region of C-H and C-D out-of-plane deformation frequencies. As shown in the Figures, these shifts and splittings vary with the monomer ratio in the copolymers. Interaction between C-H and C-D out-of-plane vibrations may give rise to the shifts and splittings in the copolymers.

Simplified calculations of C-H and C-D out-of-plane deformation frequencies were made for various model chains having repeating units of $-(C_2D_2)_m-(C_2H_2)_n-$ in which both n and m were based on the in-phase mode of $-(C_2D_2)_m-$ and $-(C_2H_2)_n-$ using a set of force constants given in Figure 6, and carried out for three models: (1) all trans skeleton, (2) all *cis—transoid* (or all *trans—cisoid*) skeleton in which two adjacent hydrogen or deuterium atoms originated from an acetylene molecule are arranged in *cis* configuration (*cis* I), and (3) in *trans* configuration (*cis* II). Examples for each model in the case of $m=1$ and $n=1$ are illustrated in Figure 9, where only skeletons are shown. The calculated results are shown in Figure 10 for the *trans* model, in Figure 11 for the *cis* I model, and in Figure 12 for the *cis* II model.

In a comparison of the calculated result of the *trans* model with spectra of the copoly(acetylene

$+$acetylene-d_2) prepared at 150°C, the bands at 932, 964, 983, and 990 cm^{-1} may be assigned to the *trans* C-H out-of-plane deformations in $-(CH{=}CH)_n-$ between $-(CD{=}CD)_m-$ $m{\geq}1$, where $n{=}1,2,3$, and 4, respectively, and the bands at 715 and 735 cm^{-1} to the C-D out-of-plane deformations in $-(CD{=}CD)_1-$ between $-(CH{=}CH)_{1-2}-$ and $-(CD{=}CD)_2-$ between $-(CH{=}CH)_{1-3}-$, respectively. Comparison of the calculated result based upon the *cis* models with observed spectra in the copolymer prepared at
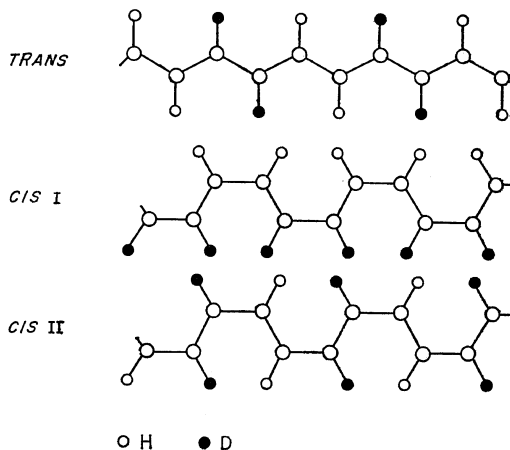

TRANS

CIS I

CIS II

○ H   ● D

Figurre 9. Arrangement of H and D atoms along model chains in the case of $m{=}1$ and $n{=}1$.
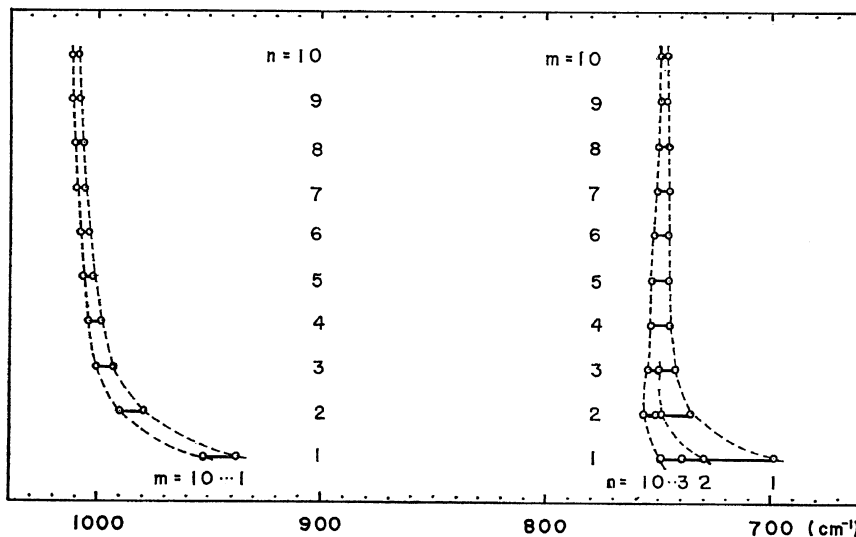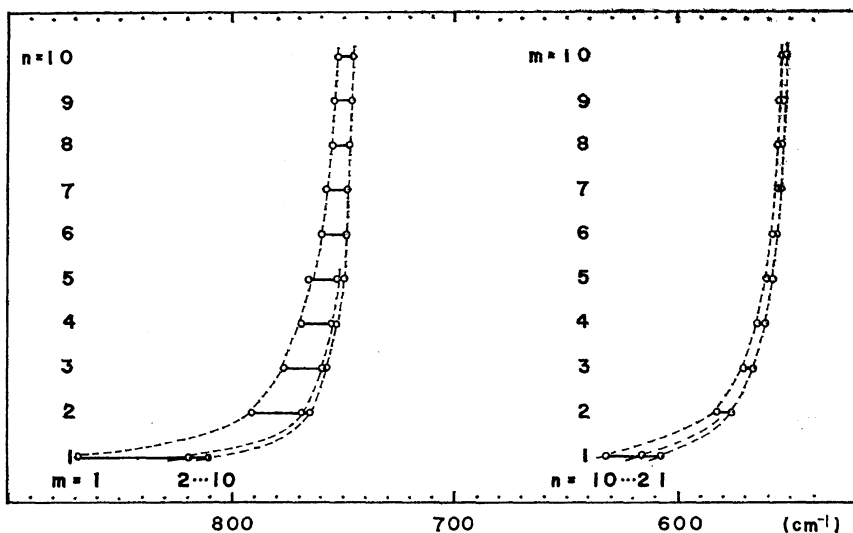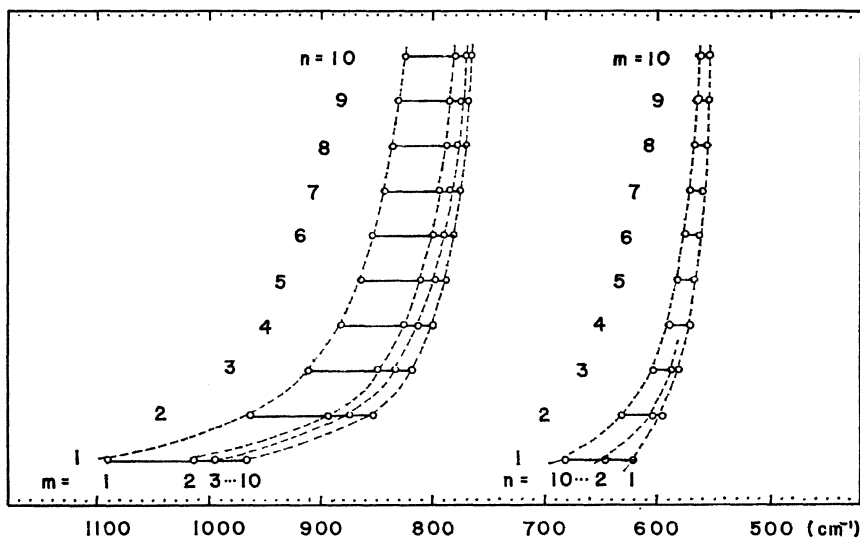

Figure 10. Locations of the calculated frequencies of C-H and C-D out-of-plane deformation modes in all *trans* model copolymers. Repeating unit is $-(C_2D_2)_m-(C_2H_2)_n-$.

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Figure 11. Locations of the calculated frequencies of C-H and C-D out-of-plane deformation modes in *cis* I type model copolymers. Repeating unit is $-(C_2D_2)_m-(C_2H_2)_n-$.


Figure 12. Locations of the calculated frequencies of C-H and C-D out-of-plane de formation modes in *cis* II type model copolymers. Repeating unit is $-(C_2D_2)_m-(C_2H_2)_n-$.

$-78°C$ leads to the result that arrangement of hydrogen and deuterium atoms in the copolymer seems likely to have the same arrangement as in the *cis* I model. Thus, the bands at 810, 800, and 760 cm^{-1} may be assigned to the *cis* C-H out-of-plane deformations in $-(CH=CH)_n-$, between $-(CD=CD)_m-$ $m \geq 1$, where $n=1$, 2, and 3—5, respectively. In these sequences two hy-

drogen atoms as well as two deuterium atoms in a chemical unit of acetylene are in *cis* configuration. Corresponding frequencies calculated on the basis of the *cis* II model are about 1000, 880, and 820 cm^{-1}, respectively, which are too high to be assigned to the observed *cis* C-H out-of-plane frequencies. The assignments are collected in Table VI. The copoly(acetylene+

Table VI. Assignments of C-H and C-D out-of-plane deformation
vibrations in copoly(acetylene+acetylene-d_2)

Frequency, cm^{-1}		Assignment	
trans C-H out-of-plane deformation			
1000	$-(CH=CH)_n- \quad n \geqq 5$	between $-(CD=CD)_m-$	$m \geqq 1$
990	$-(CH=CH)_4-$	between $-(CD=CD)_m-$	$m \geqq 1$
983	$-(CH=CH)_3-$	between $-(CD=CD)_m-$	$m \geqq 1$
964	$-(CH=CH)_2-$	between $-(CD=CD)_m-$	$m \geqq 1$
932	$-(CH=CH)_1-$	between $-(CD=CD)_m-$	$m \geqq 1$
trans C-D out-of-plane deformation			
742	$-(CD=CD)_m- \quad m \geqq 3$	between $-(CH=CH)_n-$	$n \geqq 1$
735	$-(CD=CD)_2-$	between $-(CH=CH)_{1-3}-$	
715	$-(CD=CD)_1-$	between $-(CH=CH)_{1-2}-$	
cis C-H out-of-plane deformation			
810	$-(CH=CH)_1-$	between $-(CD=CD)_m-$	$m \geqq 1$
800	$-(CH=CH)_2-$	between $-(CD=CD)_m-$	$m \geqq 1$
760	$-(CH=CH)_{3-5}-$	between $-(CD=CD)_m-$	$m \geqq 1$
748	$-(CH=CH)_n- \quad n \geqq 6$	between $-(CD=CD)_m-$	$m \geqq 1$
cis C-D out-of-plane deformation			
653	$-(CD=CD)_1-$	between $-(CH=CH)_n-$	$n \geqq 2$
626	$-(CD=CD)_1-$	between $-(CH=CH)_1-$	
600	$-(CD=CD)_2-$	between $-(CH=CH)_n-$	$n \geqq 1$
580	$-(CD=CD)_3-$	between $-(CH=CH)_n-$	$n \geqq 1$
562	$-(CD=CD)_4-$	between $-(CH=CH)_n-$	$n \geqq 1$
551	$-(CD=CD)_5-$	between $-(CH=CH)_n-$	$n \geqq 1$
546	$-(CD=CD)_m- \quad m \geqq 6$	between $-(CH=CH)_n-$	$n \geqq 1$
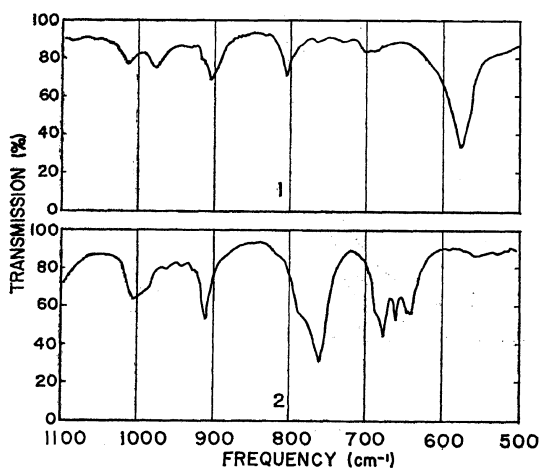
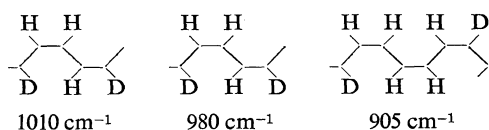**Figure 13.** Infrared spectra of copoly(acetylene+ acetylene-d_1+acetylene-d_2) prepared at $-78°C$: 1, feed monomer ratio, $C_2H_2 : C_2HD : C_2D_2 = 15 : 47 : 38$; 2, $67 : 29 : 4$.
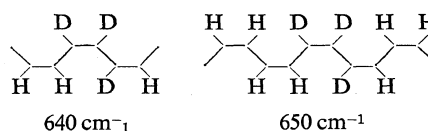
than those in the *cis* I model but smaller than those in the *cis* II model, as may be expected from the calculated results of the *cis* I and *cis* II models. Spectra of the terpolymer prepared from different deuterated monomer compositions at $-78°C$ are shown in Figure 13. In fact, larger shifts than those in the copoly(acetylene+acetylene-d_2) are observed in the terpolymers. Several bands are tentatively assigned to the sequences which occur with high probabilties estimated from monomer compositions.

C-H out-of-plane deformation

1010 cm^{-1} 980 cm^{-1} 905 cm^{-1}

C-D out-of-plane deformation
Isolated C-D between C-H, 670 cm^{-1}

640 cm^{-1} 650 cm^{-1}

acetylene-d_1+acetylene-d_2) may have sequences consisting of odd number of C-H and/or C-D bonds. Frequency shift of C-H and C-D out-of-plane due to such sequences may be larger

The *cis* configuration of the two adjacent hydrogen atoms originated from an acetylene molecule clearly demonstrates that the *cis*-opening of the triple bond occurs in the polymerization reaction with the $Ti(OC_4H_9)_4$—$Al(C_2H_5)_3$ catalyst system at low temperature. Irreversible *cis—trans* isomerization occurs at high polymerization temperature to the form *trans* sequences.

TRANS AND CIS SEQUENCES IN POLY(ACETYLENE)

As discussed in the previous section, the polymers obtained in a temperature range of -78 to $150°C$ contain both *cis* and *trans* configurations. In the spectra of various conjugated polyene, the splitting of the C-H out-of-plane deformation band has been observed in the presence of a conjugated *cis—trans* diene group,[5,12,13] triene, and tetraene.[5] Ludde, *et al.*, have shown that in the series of α,ω-diphenylpolyene of the general formula, C_6H_5-$(CH=CH)_n$-C_6H_5 $n=1$ to 4, all isomers containing both a *trans* and a *cis* double bond(s) display a doublet in contrast to the all-*trans* forms in the region of C-H out-of-plane deformation. They have considered that a *trans* C—C double bond, either isolated or in conjugation with any other bond, gives rise to

a vibrational frequency (986—995 cm^{-1}) of C-H out-of-plane deformation whereas conjugation of a *cis* to a *trans* double bond brings a new vibrational frequency (945—971 cm^{-1}) of C-H (*trans* $C=C$) out-of-plane band.

In the spectra of poly(acetylene), there is neither band shift nor splitting of both *trans* and *cis* C-H out-of-plane bands except in the spectrum of a *cis* polymer which contains a trace amount of *trans* configuration. The spectrum shows three very weak bonds at 1015, 980, and 940 cm^{-1}. To make clear the assignments of these bands and to estimate the sequence length of *cis* and *trans* configurations in the poly(acetylene) chain, simplified calculations have been made for model chains consisting of repeating units of -(*trans* $CH=CH)_m$-(*cis* $CH=CH)_n$- in which m and n were varied both from 1 to 10. The calculations were again based on the in-phase mode of -(*trans* $CH=CH)_m$- and -(*cis* $CH=CH)_n$- using the same set of force constants used in the calculation of C-H out-of-plane bands of the copolymers. The result is shown in Figure 14. Comparison of the result with the observed bands leads to the assignments that 940 cm^{-1} band to -(*trans* $CH=CH)_1$- between -(*cis* $CH=CH)_n$- sequences, 980 cm^{-1} band to -(*trans* $CH=CH)_2$- between -(*cis* $CH=CH)_n$- sequences, and 1015 cm^{-1} band

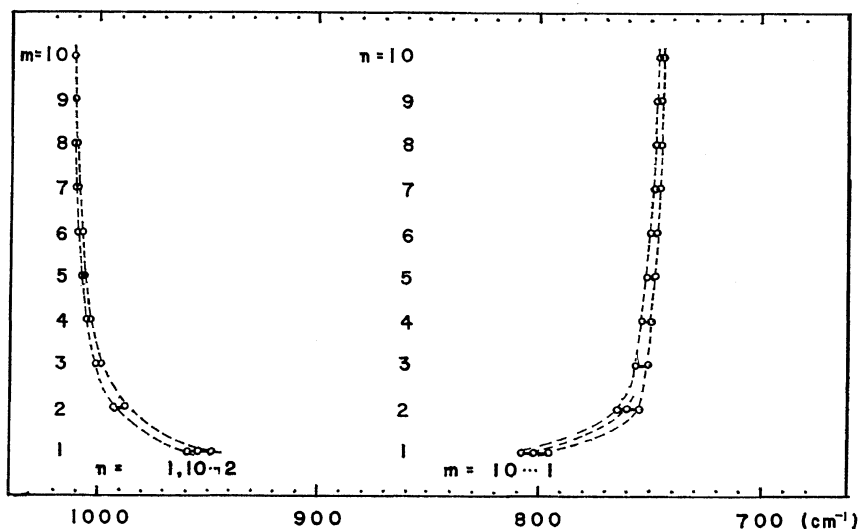Figure 14. Locations of the calculated frequencies of C-H out-of-plane deformation modes in *cis—trans* model copolymers. Repeating unit is -(*trans* $CH=CH)_m$-(*cis* $CH=CH)_n$-.

to $-(trans\ \mathrm{CH}=\mathrm{CH})_m-$ $(m \geq 2$, between $-(cis\ \mathrm{CH}=\mathrm{CH})_n-$ sequences. The result of the calculation indicates that a band is expected in the vicinity of 805 cm^{-1} which should be assigned to the *cis* C-H out-of-plane deformation corresponding to $-(cis\ \mathrm{CH}=\mathrm{CH})_1-$ between $-(trans\ \mathrm{CH}=\mathrm{CH})_n-$ sequences. The band, however, could not be found in the region of 805 cm^{-1}. This suggests that there is no isolated *cis* unit in *trans* sequences.

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