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The Vibrational Spectra and Vibrational Assignments of Isotactic Polybutene-1

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The polarized infrared spectra of isotactic polybutene-1 in a hexagonal form will be measured in the region from 4000 to 700 cm^{-1}. The normal vibrations of this polymer, which takes a three-fold helical conformation, will be calculated by the use of the ***GF***-matrix method, with the modified Urey-Bradley force field. It will be found that the parallel and perpendicular bands correspond reasonably well to the calculated frequaencies of the A and E($2\pi/3$) symmetry species respectively. In accordance with these correspondences, the assignments of these bands will be made and their vibrational modes discussed.

In recent years, it has been reported that isotactic polybutene-1 exhibits three polymorphs, namely, a stable hexagonal form,[1-5,8] a stable orthorhombic form,[4,5,7-9] and an unstable tetragonal form,[2,4-9] and that these three crystalline forms exhibit significantly different infrared spectra in the region from 2000 to 400 cm^{-1}.[10-12] The spectral difference may depend upon the molecular conformations of the polymer, but the vibrational analysis of the correlation between the spectral difference and molecular conformations has not yet been dealt with.

On the other hand, the polarized infrared spectra of isotactic vinyl polymers, including the isotactic polybutene-1, were measured by Tadokoro et al.[13] in order to examine whether or not the bands associated with helical structures appear; the 1217 cm^{-1} band of isotactic polybutene-1 in the hexagonal form was proposed as the band to be associated with the helical conformation. Thereafter, the correlations of the infrared spectra with the crystallinity and the stereoregularity of the polybutene-1 samples were studied by Nishioka and Yanagisawa.[14] These studies showed that the absorption band at 1221, 1208, 1098, 1059, 1029, 922, 849, and 816 cm^{-1} in the hexagonal crystals are related to the crystallinity, while the absorption bands at 1220, 972, and 917 cm^{-1} in a carbon disulfide solution of the polymer are directly related to the stereoregularity. However, these bands have scarcely been assigned at all because of the complexity of this molecule.

Thus, in order to obtain some information about these problems, the normal vibrations for the isotactic polybutene-1 molecule of a three-fold helical conformation (hexagonal form) were calculated, using the force constants transferred from simple aliphatic hydrocarbons. The calculated frequencies will be compared with the observed frequencies, and the assignments of bands based on the calculated potential energy distributions will be given for the fundamental bands observed from 4000 to 700 cm^{-1}. The vibrational modes of the absorption bands characteristic of the three-fold helical conformation and other bands will also be discussed.

Experimental

A sample of isotactic polybutene-1 was prepared, with titanium-mercaptide as the catalyst, in the laboratory of the Toyo Soda Industrial Company. The sample was extracted with ethyl ether, and the insoluble part (ca. 75%) was used in this work. The film specimens for the measurement of the infrared spectra were obtained at about 40°C by casting a one percent solution in carbon tetrachloride on glass plates. The oriented film specimens were prepared by annealing the film at 90°C and by then elongating the film at 60°C. The polarized infrared spectra in the regions from 4000 to 2700 cm^{-1} and from 2700 to 700 cm^{-1} were taken

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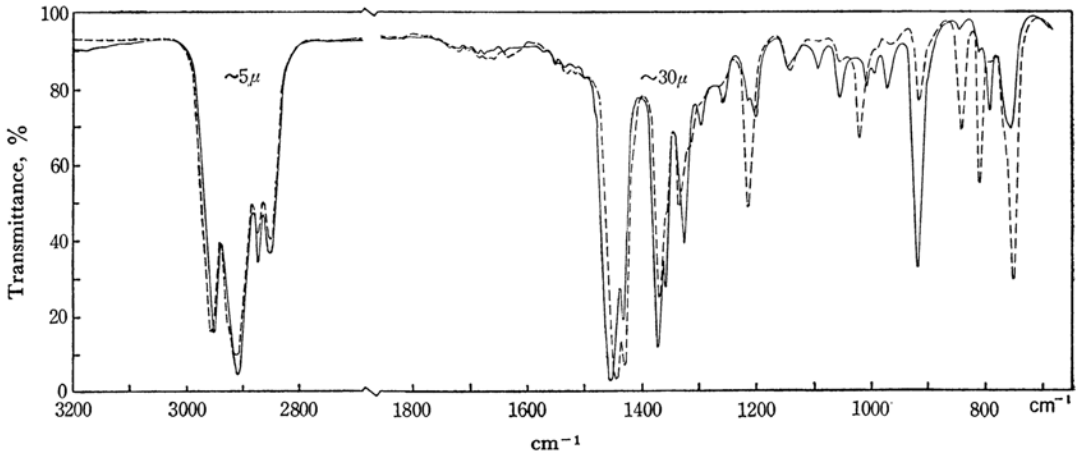


Fig. 1. Polarized infrared spectra of crystalline isotactic polybutene-1 (hexagonal form).
Solid curve: electric vector perpendicular to the direction of stretch
Broken curve: electric vector parallel to this direction.

TABLE I. SYMMETRY SPECIES, NUMBERS OF NORMAL MODES, SELECTION RULES, AND DICHROISM FOR ISOTACTIC POLYBUTENE-1 MOLECULE UNDER THE GROUP $C(2\pi/3)$*1

	E	C_3^1	C_3^2	Numbers*2	Infrared*3	Raman*4
A	1	1	1	36-2 ($T_\parallel$, $R_\parallel$)	A($\parallel$)	A(p)
E	1	ε^1	ε^2	36-1 ($T_\perp$)	A($\perp$)	A(dp)
	1	ε^{-1}	ε^{-2}	36-1 ($T_\perp$)		

*1 $\varepsilon = \exp(2\pi i/3)$.
*2 $T_\parallel$ and $T_\perp$, pure translations; $R_\parallel$, pure rotation.
*3 A, active; $\parallel$ or $\perp$ indicates that the dipole moment is parallel or perpendicular to the helical axis.
*4 p, polarized; dp, depolarized.

TABLE II. INTERNAL COORDINATES

Bond length	Bond angle	Bond angle	Bond length	Bond angle	Bond angle
$R_1 = C_1\text{-}C_2$	$\Theta_1 = \angle C_2''\text{-}C_1\text{-}C_2$	$\varphi_3 = \angle H_1\text{-}C_1\text{-}C_2$	$r_3 = C_2\text{-}H_3$	$\theta_2 = \angle H_4\text{-}C_3\text{-}H_5$	$\varphi_9 = \angle C_2\text{-}C_3\text{-}H_5$
$R_2 = C_2\text{-}C_1'$	$\Theta_2 = \angle C_1\text{-}C_2\text{-}C_1'$	$\varphi_4 = \angle H_2\text{-}C_1\text{-}C_2$	$r_4 = C_3\text{-}H_4$	$\theta_3 = \angle H_6\text{-}C_4\text{-}H_7$	$\varphi_{10} = \angle H_4\text{-}C_3\text{-}C_4$
$R_3 = C_2\text{-}C_3$	$\Phi_1 = \angle C_1\text{-}C_2\text{-}C_3$	$\varphi_5 = \angle C_1\text{-}C_2\text{-}H_3$	$r_5 = C_3\text{-}H_5$	$\theta_4 = \angle H_6\text{-}C_4\text{-}H_8$	$\varphi_{11} = \angle H_5\text{-}C_3\text{-}C_4$
$R_4 = C_3\text{-}C_4$	$\Phi_2 = \angle C_3\text{-}C_2\text{-}C_1'$	$\varphi_6 = \angle H_3\text{-}C_2\text{-}C_1'$	$r_6 = C_4\text{-}H_6$	$\theta_5 = \angle H_7\text{-}C_4\text{-}H_8$	$\varphi_{12} = \angle C_3\text{-}C_4\text{-}H_6$
$r_1 = C_1\text{-}H_1$	$\Phi_3 = \angle C_2\text{-}C_3\text{-}C_4$	$\varphi_7 = \angle H_3\text{-}C_2\text{-}C_3$	$r_7 = C_4\text{-}H_7$	$\varphi_1 = \angle C_2''\text{-}C_1\text{-}H_1$	$\varphi_{13} = \angle C_3\text{-}C_4\text{-}H_7$
$r_2 = C_1\text{-}H_2$	$\theta_1 = \angle H_1\text{-}C_1\text{-}H_2$	$\varphi_8 = \angle C_2\text{-}C_3\text{-}H_4$	$r_8 = C_4\text{-}H_8$	$\varphi_2 = \angle C_2''\text{-}C_1\text{-}H_2$	$\varphi_{14} = \angle C_3\text{-}C_4\text{-}H_8$

TABLE III. THE LOCAL SYMMETRY COORDINATES

S_1	$2^{-1/2}\Delta(r_1+r_2)$	$\nu_s(CH_2)_m$
S_2	$2^{-1/2}\Delta(r_1-r_2)$	$\nu_a(CH_2)_m$
S_3	Δr_3	$\nu(CH)$
S_4	$2^{-1/2}\Delta(r_4+r_5)$	$\nu_s(CH_2)_s$
S_5	$2^{-1/2}\Delta(r_4-r_5)$	$\nu_a(CH_2)_s$
S_6	$3^{-1/2}\Delta(r_6+r_7+r_8)$	$\nu_s(CH_3)$
S_7	$6^{-1/2}\Delta(2r_6-r_7-r_8)$	$\nu_a(CH_3)$
S_8	$2^{-1/2}\Delta(r_7-r_8)$	$\nu_a'(CH_3)$
S_9	$2^{-1/2}\Delta(R_1+R_2)$	$\nu_s(CC)_m$
S_{10}	$2^{-1/2}\Delta(R_1-R_2)$	$\nu_a(CC)_m$
S_{11}	$2^{-1/2}\Delta(R_3+R_4)$	$\nu_s(CC)_s$
S_{12}	$2^{-1/2}\Delta(R_3-R_4)$	$\nu_a(CC)_s$
S_{13}	$2^{-1}\Delta(\varphi_1-\varphi_2+\varphi_3-\varphi_4)$	$r(CH_2)_m$
S_{14}	$2^{-1}\Delta(\varphi_1+\varphi_2-\varphi_3-\varphi_4)$	$w(CH_2)_m$
S_{15}	$2^{-1}\Delta(\varphi_1-\varphi_2-\varphi_3+\varphi_4)$	$t(CH_2)_m$
S_{16}	$20^{-1/2}\Delta(4\theta_1-\varphi_1-\varphi_2-\varphi_3-\varphi_4)$	$\delta(CH_2)_m$
S_{17}	$30^{-1/2}\Delta(5\Theta_1-\varphi_1-\varphi_2-\varphi_3-\varphi_4-\theta_1)$	$\delta(CC)_m$
S_{18}	$6^{-1/2}\Delta(2\varphi_7-\varphi_5-\varphi_6)$	$\delta(CH)$
S_{19}	$2^{-1/2}\Delta(\varphi_5-\varphi_6)$	$w(CH)$
S_{20}	$6^{-1/2}(\varphi_5+\varphi_6+\varphi_7-\Phi_1-\Phi_2-\Theta_2)$	$\delta_s(CC)$
S_{21}	$6^{-1/2}(2\Theta_2-\Phi_1-\Phi_2)$	$\delta'(CC)_m$
S_{22}	$2^{-1/2}(\Phi_1-\Phi_2)$	$\delta(CC)_s$
S_{23}	$2^{-1}(\varphi_8-\varphi_9+\varphi_{10}-\varphi_{11})$	$r(CH_2)_s$
S_{24}	$2^{-1}(\varphi_8+\varphi_9-\varphi_{10}-\varphi_{11})$	$w(CH_2)_s$
S_{25}	$2^{-1}(\varphi_8-\varphi_9-\varphi_{10}+\varphi_{11})$	$t(CH_2)_s$
S_{26}	$20^{-1/2}(4\theta_2-\varphi_8-\varphi_9-\varphi_{10}-\varphi_{11})$	$\delta(CH_2)_s$
S_{27}	$30^{-1/2}(5\Phi_3-\varphi_8-\varphi_9-\varphi_{10}-\varphi_{11}-\theta_2)$	$\delta'(CC)_s$
S_{28}	$6^{-1/2}(2\varphi_{12}-\varphi_{13}-\varphi_{14})$	$r_a(CH_3)$
S_{29}	$2^{-1/2}(\varphi_{13}-\varphi_{14})$	$r_a'(CH_3)$
S_{30}	$6^{-1/2}(\varphi_{12}+\varphi_{13}+\varphi_{14}-\theta_3-\theta_4-\theta_5)$	$\delta_s(CH_3)$
S_{31}	$6^{-1/2}(2\theta_5-\theta_3-\theta_4)$	$\delta_a(CH_3)$
S_{32}	$2^{-1/2}(\theta_3-\theta_4)$	$\delta_a'(CH_3)$
S_{33}	$6^{-1/2}(\varphi_1+\varphi_2+\varphi_3+\varphi_4+\theta_1+\Theta_1)$	redundant coordinates
S_{34}	$6^{-1/2}(\varphi_5+\varphi_6+\varphi_7+\Phi_1+\Phi_2+\Theta_2)$	
S_{35}	$6^{-1/2}(\varphi_8+\varphi_9+\varphi_{10}+\varphi_{11}+\theta_2+\Phi_3)$	
S_{36}	$6^{-1/2}(\varphi_{12}+\varphi_{13}+\varphi_{14}+\theta_3+\theta_4+\theta_5)$	

TABLE IV. FORCE CONSTANTS OF ISOTACTIC POLYBUTENE-1*1

$K(CH)(CH_3)$	4.350 mdyn./Å.	$F(HC)$	0.540*2 mdyn./Å
$K(CH)(CH_2)$	4.050*2	$F(CC)$	0.335*2
$K(CH)(CH)$	3.900*2	$\kappa(CH_3)$	0.008*2 mdyn.·Å
$K(CC)$	2.000	$\kappa(CH_2)$	0.033*2
$H(HCH)$	0.431*2	$\kappa(CH)$	0.063*2
$H(HCC)$	0.186*2	T	0.118*2
$H(CCC)$	0.275*2	G	−0.030
$F(HH)$	0.080*2	F'	−0.1 F

*1 K, stretching; H, bending: F, repulsion; T, trans coupling; G, gauche coupling; κ, intramolecular tension.
*2 Transferred from Ref. 16.

TABLE V. THE C-H STRETCHING VIBRATIONS (IN cm^{-1}) OF ISOTACTIC POLYBUTENE-1

Obsd.*1	Calcd.		Assignment
2961 (∥, vs)	2949 (A)	ν_1	CH_3 asym. stretching, $\nu_a(CH_3)$
	2948 (E)		
2958 (⊥, vs)	2947 (E)	ν_2	CH_3 asym. stretching, $\nu_a'(CH_3)$
	2947 (A)		
2914 (⊥, vs)	2920 (E)	ν_3	CH stretching, $\nu(CH)$
	2919 (A)		
	2909 (E)	ν_4	CH_2 antisym. stretching, $\nu_a(CH_2)_m$
	2910 (A)		
	2908 (E)	ν_5	CH_2 antisym. stretching, $\nu_a(CH_2)_s$
	2907 (A)		
2874 (⊥, s)	2897 (E)	ν_6	CH_3 sym. stretching, $\nu_s(CH_3)$
	2899 (A)		
2851 (⊥, s)	2878 (E)	ν_7	CH_2 sym. stretching, $\nu_s(CH_2)_m$
	2875 (A)		
	2869 (E)	ν_8	CH_2 sym. stretching, $\nu_s(CH_2)_s$
	2867 (A)		

*1 vs, very strong; s, strong

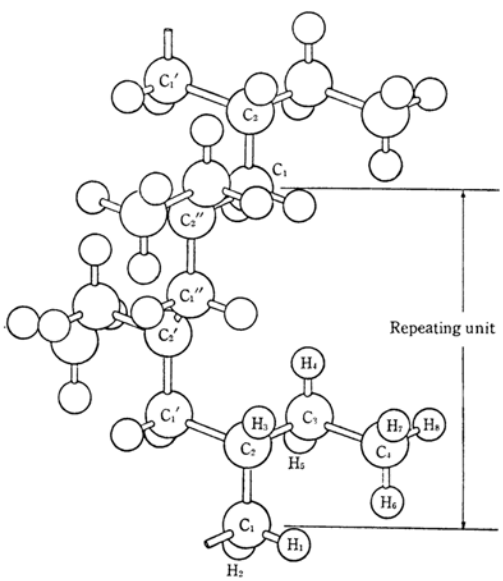


Fig. 2. Unit cell for three-fold helical structure of isotactic polybutene-1.

by using a Perkin-Elmer, model 221, grating spectrophotometer and a Hitachi Ltd., model EPI-S2, spectrophotometer respectively. The polarization measurements were carried out with a silver chloride polarizer. The observed spectra are shown in Fig. 1.

Normal Coordinate Treatment

The molecule of isotactic polybutene-1 in the hexagonal crystals contains three chemical unit, $-CH_2-CH(-CH_2-CH_3)-$, in one turn of the fiber identity period of 6.50 Å.[1-3] The unit cell for this structure is shown in Fig. 2. This model corresponds to the right-handed helix. This infinitely-extended helical structure belongs to the factor group, $C(2\pi/3)$, isomorphous with the point group, C_3; therefore, the molecular vibrations can be treated under the factor group $C(2\pi/3)$. The results of this treatment are given in Table I. Thirty-four of the modes listed in Table I belong to A species and are totally symmetric to the three-fold helical axis. Accordingly, the dipole-moment change for an A mode is parallel to the helical axis. On the other hand, the thirty-five degenerate modes belong to the E species, and the phase difference between adjacent chemical units is $2\pi/3$. The resultant dipole-moment change for an E mode is perpendicular to the helical axis.

TABLE VI. THE OBSERVED AND CALCULATED FREQUENCIES OF ISOTACTIC POLYBUTENE-1 IN THE REGION FROM 1500 TO 700 cm^{-1}

Obsd.*1	Calcd.		Potential energy distributions (%)*2
1463 (⊥, s)	1478 (E)	ν_9	$\delta_a'(CH_3)$ (66), $\delta_a(CH_3)$ (24)
	1478 (A)		$\delta_a'(CH_3)$ (67) − $\delta_a(CH_3)$ (23)
1458 (∥, s)	1476 (A)	ν_{10}	$\delta_a(CH_3)$ (68) + $\delta_a'(CH_3)$ (23)
	1476 (E)		$\delta_a(CH_3)$ (66), $\delta_a'(CH_3)$ (24)
1441 (∥, s)	1475 (A)	ν_{11}	$\delta(CH_2)_m$ (64) − $\delta(CH_2)_s$ (31)
	1475 (E)		$\delta(CH_2)_m$ (90)
1439 (⊥, s)	1473 (E)	ν_{12}	$\delta(CH_2)_s$ (93)
	1473 (A)		$\delta(CH_2)_s$ (65) + $\delta(CH_2)_m$ (31)
1380 (⊥, s)	1407 (E)	ν_{13}	$\delta_s(CH_3)$ (91)
	1407 (A)		$\delta_s(CH_3)$ (92)
1366 (⊥, s)	1378 (E)	ν_{14}	$w(CH_2)_s$ (23), w(CH) (21), δ(CH) (13), $w(CH_2)_m$ (11)
	1372 (A)		$w(CH_2)_s$ (41) + w(CH) (23) + δ(CH) (11)
1342 (∥, m)	1380 (A)	ν_{15}	$w(CH_2)_m$ (36) − δ(CH) (23) + w(CH) (15)
1331 (⊥, m)	1368 (E)		δ(CH) (31), $w(CH_2)_m$ (18), w(CH) (18)
	1341 (E)	ν_{16}	$w(CH_2)_s$ (47), $w(CH_2)_m$ (16)
1321 (∥, w)	1331 (A)		$w(CH_2)_s$ (42) − w(CH) (30) − δ(CH) (11)
1302 (⊥, w)	1312 (E)	ν_{17}	$w(CH_2)_m$ (46), w(CH) (13), δ(CH) (11)
	1299 (A)		$w(CH_2)_m$ (61) + δ(CH) (13)
1263 (⊥, w)	1262 (E)	ν_{18}	$t(CH_2)_s$ (50), $r_a(CH_3)$ (16)
	1280 (A)		$t(CH_2)_s$ (49) + $t(CH_2)_m$ (30)
1222 (∥, m)	1235 (A)	ν_{19}	$t(CH_2)_m$ (30) − δ(CH) (15) + $r(CH_2)_s$ (15) + $r_a'(CH_3)$ (10)
1207 (⊥, w)	1180 (E)		$t(CH_2)_m$ (33), w(CH) (13)
1150 (⊥, w)	1140 (E)	ν_{20}	ν(CC) (36)
	1124 (A)		ν(CC) (43) − $r_a(CH_3)$ (11)
1096 (⊥, w)	1090 (E)	ν_{21}	ν(CC) (32), $r_a(CH_3)$ (13)
1062 (⊥, w)	1027 (E)	ν_{22}	ν(CC) (39), $t(CH_2)_m$ (14)
	1048 (A)	ν_{21}	$r_a'(CH_3)$ (25) + $\nu(CC)_s$ (23)
1028 (∥, w)	1015 (A)	ν_{22}	$\nu_a(CC)_s$ (43) + $\nu_a(CC)_m$ (10)
1015 (⊥, w)	993 (E)	ν_{23}	$\nu_a(CC)_s$ (37), $\nu_s(CC)_s$ (21), $\nu_a(CC)_m$ (17)
	998 (A)		$\nu_a(CC)_m$ (36) − $\nu_a(CC)_s$ (23)
977 (⊥, w)	961 (E)	ν_{24}	$r_a(CH_3)$ (21), $\nu_a(CC)_m$ (19), $\nu_s(CC)_m$ (18)
	966 (A)		$\nu_s(CC)_m$ (25) + $r_a(CH_3)$ (20) − $\nu_s(CC)_s$ (12)
924 (⊥, s)	918 (E)	ν_{25}	$r_a'(CH_3)$ (23), $r(CH_2)_m$ (20), $\nu_s(CC)_m$ (13), $\nu_s(CC)_s$ (10)
848 (∥, w)	874 (A)		$r_a'(CH_3)$ (25) − $\nu_s(CC)_s$ (16) − $\nu_s(CC)_s$ (16) − $\nu_s(CC)_m$ (10)
816 (∥, m)	796 (A)	ν_{26}	$r(CH_2)_m$ (65) − $\nu_s(CC)_s$ (11)
798 (⊥, w)	796 (E)		$r(CH_2)_m$ (30), $\nu_s(CC)_s$ (17), $\nu_s(CC)_m$ (17)
764 (⊥, w)	742 (E)	ν_{27}	$r(CH_2)_s$ (51), $r_a(CH_3)$ (21)
758 (∥, s)	738 (A)		$r(CH_2)_s$ (55) − $r_a(CH_3)$ (24)

*1 vs, very strong; s, strong; m, medium; w, weak.

*2 δ_a and δ_a', asymmetric deformations; δ_s, symmetric deformation; ν_s, symmetric stretching; ν_a, antisymmetric stretching; δ, bending; w, wagging; t, twisting; r, r_a, and r_a', rockings. The $(CH_2)_m$ and $(CH_2)_s$ represent methylene units of the main chain and the ethyl group, respectively.

The internal coordinates of a unit cell are expressed in vector notations, as in Eq. 1:

$$q = \begin{Vmatrix} q(j) \\ q(j') \\ q(j'') \end{Vmatrix} \quad (1)$$

where $q(j)$, $q(j')$, and $q(j'')$ represent the coordinates of unprimed, single-primed, and double-primed atoms, as is shown in Fig. 2. Table II lists the elements of the internal coordinate $q(j)$. For the present coordinates, the freedom of internal rotation about CC bonds is ignored. These internal coordinates, q, were transformed into the local symmetry coordinates, S, as expressed in Eq. 2:

$$S = \begin{Vmatrix} S(j) \\ S(j') \\ S(j'') \end{Vmatrix} \quad (2)$$

The elements of the local symmetry coordinates, $S(j)$, together with four redundant coordinates, are listed in Table III.

The $\boldsymbol{G}$ or $\boldsymbol{F}$ matrix based on the local symmetry coordinates may be factored into three matrices by the unitary transformation;[15] $\boldsymbol{G}$(A), $\boldsymbol{G}$(E), and

15) H. Tadokoro, *J. Chem. Phys.*, **33**, 1558 (1960); **35**, 1050 (1961).

TABLE VII. THE L MATRIX ELEMENTS OF ISOTACTIC POLYBUTENEPOLYBUTENE-9 (A SPECIES)*1

	1478	1476	1475	1473	1408	1380	1372	1331	1299
$\nu_s(CC)_m$	0	0	0	0	0	0	0	0	0
$\nu_a(CC)_m$	0	0	0	0	0	−1	1	0	0
$\nu_s(CC)_s$	0	0	0	0	0	0	0	0	0
$\nu_a(CC)_s$	0	0	0	0	0	0	1	0	0
$r(CH_2)_m$	0	0	0	0	0	0	2	−2	1
$w(CH_2)_m$	0	0	0	0	0	8	0	0	9
$t(CH_2)_m$	0	0	0	0	0	−3	0	2	3
$\delta(CH_2)_m$	1	−1	−12	8	0	0	0	0	0
$\delta(CH)$	0	0	0	0	1	−6	−4	4	4
$w(CH)$	0	0	0	0	0	5	−6	6	−3
$r(CH_2)_s$	0	0	0	0	0	1	0	0	0
$w(CH_2)_s$	−1	0	0	0	2	0	−8	−7	0
$t(CH_2)_s$	0	0	0	0	0	2	0	0	−3
$\delta(CH_2)_s$	0	1	8	12	0	0	0	0	0
$r_a(CH_3)$	1	3	0	0	0	0	0	1	0
$r_a'(CH_3)$	3	−1	0	0	0	0	1	1	0
$\delta_s(CH_3)$	0	0	0	0	13	0	3	0	0
$\delta_a(CH_3)$	7	12	−1	0	0	0	−1	0	0
$\delta_a'(CH_3)$	−12	7	−1	0	0	0	1	1	0

	1280	1235	1124	1048	1015	998	966	874	796	738
$\nu_s(CC)_m$	0	0	−1	0	−1	0	−1	−1	0	0
$\nu_a(CC)_m$	0	0	−2	−1	1	−2	0	0	0	0
$\nu_s(CC)_s$	0	0	1	−1	0	−1	1	−1	1	0
$\nu_a(CC)_s$	0	0	0	−1	2	1	0	0	0	0
$r(CH_2)_m$	0	0	1	−1	0	0	2	−1	−6	0
$w(CH_2)_m$	0	0	0	1	0	0	−1	0	0	0
$t(CH_2)_m$	6	−6	−1	−3	−2	1	0	−1	0	0
$\delta(CH_2)_m$	0	0	0	0	0	0	0	0	0	0
$\delta(CH)$	0	4	2	2	2	−1	0	0	0	0
$w(CH)$	0	0	−1	−1	0	0	1	0	−2	0
$r(CH_2)_s$	0	−4	2	1	1	−1	0	0	0	−5
$w(CH_2)_s$	0	0	0	−2	0	0	−1	1	0	0
$t(CH)_s$	8	2	1	2	2	−3	−2	−2	0	0
$\delta(CH_2)_s$	0	0	0	0	0	0	0	0	0	0
$r_a(CH_3)$	−3	−3	3	0	1	−2	−4	0	0	3
$r_a'(CH_3)$	0	3	2	−5	−2	0	−2	4	0	−1
$\delta_s(CH_3)$	0	0	0	0	0	0	0	0	0	0
$\delta_a(CH_3)$	1	1	−1	0	0	0	1	0	0	0
$\delta_a'(CH_3)$	0	−1	0	−1	0	0	0	1	0	0

*1 The first row represents the calculated frequencies.

$G(E^*)$ or $F(A)$, $F(E)$, and $F(E^*)$. The resultant matrix, $G(A)$ or $F(A)$, is a real symmetric matrix of Order Thirty-two, while $G(E)$ or $F(E)$ is an Hermitian matrix of Order Thirty-two. $G(E^*)$ or $F(E^*)$ is the complex conjugated matrix of $G(E)$ or $F(E)$. Therefore, the symmetry coordinates of this helical structure are expressed as in Eq. 3:

$$\begin{aligned} S(A) &= 3^{-1/2}[S(j)+S(j')+S(j'')] \\ S(E) &= 3^{-1/2}[S(j)+S(j')e^{i\omega}+S(j'')e^{2i\omega}] \\ S(E^*) &= 3^{-1/2}[S(j)+S(j')e^{-i\omega}+S(j'')e^{-2i\omega}] \end{aligned} \quad (3)$$

where $\omega=2\pi/3$.

The force constants used in this work were transferred from the values of ethane, propane, and isobutane;[16] they are shown in Table IV. In the calculations, the bond lengths of R(C–C) and r(C–H) were taken as 1.54 and 1.09 Å respectively, and all the bond angles were assumed to be tetrahedral (109°28′) for the sake of simplicity. As an analytical method of calculating the normal vibrations, the GF-matrix method of Wilson was used.[17] The calculations of normal frequencies, L matrices, potential energy distributions, and phase angles were made with an OKITAC 5090A electronic digital compurter

16) H. Takahashi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **83**, 976, 978, 980 (1962).
17) E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

Table VIII. The L matrix elements of isotactic polybutene-1 (E species)*1

	1478	1476	1475	1473	1407	1378	1368	1341	1312	1262	1180	1140	1090	1027	993	961	918	796	742
$\nu_s(CC)_m$	0	0	0	0	0	0	0	0	0	0	0	1	0	1	0	1	1	1	0
												(64)		(−53)		(−13)	(43)	(22)	
$\nu_a(CC)_m$	0	0	0	0	0	1	1	0	0	0	0	1	2	0	1	1	0	0	0
						(53)	(27)					(−18)	(−8)		(0)	(−34)			
$\nu_s(CC)_s$	0	0	0	0	0	0	0	0	0	0	0	1	1	0	1	0	1	1	0
												(25)	(14)		(2)		(−76)	(12)	
$\nu_a(CC)_s$	0	0	0	0	0	1	0	0	0	0	0	1	0	2	2	0	0	0	0
						(28)						(16)		(−37)	(8)				
$r(CH_2)_m$	0	0	0	0	0	1	1	0	1	1	3	2	0	1	1	0	4	4	1
						(−78)	(16)		(23)	(−44)	(72)	(80)		(76)	(−11)		(−70)	(−22)	(5)
$w(CH_2)_m$	0	0	0	0	0	4	5	5	8	2	2	0	1	1	0	0	0	0	0
						(8)	(82)	(−26)	(−41)	(−12)	(87)		(−10)	(29)					
$t(CH_2)_m$	0	0	0	0	0	3	2	3	3	0	6	3	2	3	1	0	1	0	0
						(1)	(56)	(−61)	(−17)		(−5)	(24)	(81)	(−48)	(5)		(45)		
$\delta(CH_2)_m$	1	2	14	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	(−56)	(6)	(0)	(68)															
$\delta(CH)$	0	0	0	0	1	4	7	3	3	3	1	2	0	2	1	1	1	0	1
					(1)	(19)	(16)	(53)	(−71)	(−5)	(79)	(74)		(61)	(83)	(24)	(−31)		(10)
$w(CH)$	0	0	0	0	1	6	5	3	4	1	4	2	3	2	1	0	1	0	0
					(0)	(41)	(28)	(−28)	(0)	(−80)	(8)	(22)	(−50)	(−8)	(41)		(70)		
$r(CH_2)_s$	0	0	0	0	0	0	1	0	0	2	2	2	2	1	0	0	0	1	5
							(11)			(2)	(−64)	(−48)	(−3)	(64)				(−73)	(−4)
$w(CH_2)_s$	1	0	0	0	2	6	3	8	3	0	0	0	1	1	1	2	1	0	0
	(0)				(0)	(32)	(−74)	(−3)	(−18)				(14)	(13)	(40)	(−52)	(−45)		
$t(CH_2)_s$	0	0	0	0	0	0	4	1	3	8	0	2	1	2	1	3	2	0	1
							(14)	(−77)	(−52)	(5)		(−32)	(−9)	(58)	(−80)	(−9)	(−28)		(−5)
$\delta(CH_2)_s$	0	1	2	14	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		(14)	(−70)	(0)															
$r_a(CH_3)$	1	3	0	0	0	0	0	1	1	4	1	2	3	1	1	4	0	1	3
	(0)	(0)						(−3)	(−29)	(3)	(−41)	(−76)	(4)	(−71)	(−48)	(−29)		(−40)	(−8)
$r_a'(CH_3)$	3	1	0	0	0	0	0	1	0	2	3	2	2	3	1	3	4	1	2
	(0)	(1)						(−5)		(4)	(−80)	(0)	(13)	(33)	(67)	(−73)	(−43)	(35)	(6)
$\delta_s(CH_3)$	0	0	0	0	13	3	0	0	0	0	0	0	0	0	0	0	0	0	0
					(0)	(30)													
$\delta_s(CH_3)$	7	12	2	0	0	0	0	0	0	2	0	0	1	0	0	1	0	0	0
	(0)	(0)	(10)							(3)			(4)			(−29)			
$\delta_a'(CH_3)$	12	7	1	0	0	1	0	1	0	0	1	0	0	0	0	0	1	0	0
	(0)	(1)	(−78)			(31)		(−3)			(−78)						(−43)		

*1 The first row represents the calculated frequencies.

(4000 core locations) using the programs described previously.[18,19] The calculated frequencies are shown in Tables V and VI, where they are compared with the observed frequencies. The vibrational assignments based on the potential energy distributions are shown in the last columns of Tables V and VI. The $\boldsymbol{L}$ matrix elements for the A and E symmetry species are listed in Tables VII and VIII respectively. In Table VII, the phase relations among the symmetry coordinates are represented by the signs plus and minus, which stand for in-phase and out-of-phase respectively. In Table VIII, each element for the E species is expressed by the amplitude, $|L_{jk}|$, and the phase angle (in parentheses), δ_{jk}, in degrees. The phase relations among the symmetry coordinates in a certain normal vibration are represented by the difference in phase angles (see Ref. 18).

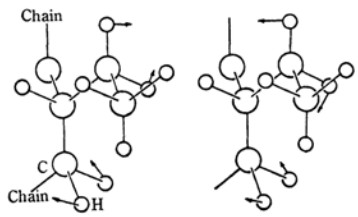
Discussion

The factor group analysis shows that the vibrational modes belonging to the A and E symmetry species have parallel ($\parallel$) and perpendicular ($\perp$) dichroisms respectively when the molecular chain is oriented along the stretching direction of the film specimen. As Tables V and VI show, the observed frequencies of parallel and perpendicular bands correspond reasonably well to the calculated frequencies of the A and E species respectively. The average deviations in this work are 1.29 (A species) and 1.12 (E species) %.

C–H Stretching Vibtations.—In the region from 3000 to 2800 cm^{-1} four perpendicular bands, at 2958, 2914, 2874, and 2851 cm^{-1}, and one parallel band at 2961 cm^{-1}, are observed. The assignments of these bands are given in Table V. All bands in this region are assigned to the overlapped modes of the A and the E species for each C–H stretching vibration. In addition to that, the CH_2 stretching vibrations for the main chain and the ethyl group are assigned to the same bands (see Table V).

CH_2 Bending and CH_3 Deformation Modes.—In the region from 1500 to 1370 cm^{-1}, three perpendicular bands, at 1463, 1439, and 1380 cm^{-1}, and two parallel bands, at 1458 and 1441 cm^{-1}, are observed. The strong bands at 1463 and 1458 cm^{-1} are assigned to the CH_3 asymmetric deformation modes, namely, $\delta'_a(CH_3)$(A, E) and $\delta_a(CH_3)$(A, E). The strong perpendicular band at 1380 cm^{-1} is easily assigned to the CH_3 symmetric deformation mode, $\delta_s(CH_3)$(A, E). The assignments of these bands related to the methyl group are consistent with those of isotactic polypropylene.[18,20-22]

The intense parallel band at 1441 cm^{-1} and the medium intensity band at 1439 cm^{-1} are assigned together to the CH_2 bending modes, but the CH_2 bending modes of the main chain and the ethyl group couple with each other in this polymer. The schematic representations of these CH_2 bending modes are shown in Figs. 3(a) and 3(b). On the basis of these normal modes, it may reasonably be understood that the 1441 cm^{-1} band has an intense parallel dichroism.



(a) (b)

Fig. 3. Vibrational modes for a chemical unit of the parallel band at 1441 cm^{-1} (a) and the 1439 cm^{-1} band (b).

CH_2 Wagging, CH_2 Twisting, CH Bending, and CH Wagging Modes.—In the region from 1370 to 1200 cm^{-1}, five perpendicular bands, at 1366, 1331, 1302, 1263, and 1207 cm^{-1}, and three parallel bands, at 1342, 1321, and 1222 cm^{-1}, are observed. As is shown in Table VI, all the bands observed from 1370 to 1300 cm^{-1} are assigned to the mixed modes of the CH_2 wagging, the CH bending, and the CH wagging. In this region, the medium intensity bands at 1331 and 1342 cm^{-1} appear in the spectra of a hexagonal form and are either extremely weak or do not appear in other crystalline forms.[12] The character of these bands may be due to the coupling of the CH_2 wagging (main chain), the CH bending, and the CH wagging modes (see Table VI).

The parallel band at 1222 cm^{-1} closely related to stereoregularity and crystallinity is observed in three crystalline forms.[12] This fact indicates that the 1222 cm^{-1} band is not affected by the molecular conformations. Therefore, it may easily be understood that this band is characteristic of stereoregularity. According to the present work, this band corresponds to the ν_{19}(A) vibration of the calculated frequency at 1235 cm^{-1}. The ν_{19}(A) vibration is associated with the CH_2 twisting, the CH bending, and the ethyl rocking modes. For this band, Tadokoro et al.[13] suggested that, in the mode assignable, the vibration

18) H. Tadokoro, M. Kobayashi, M. Ukita, K. Yasufuku, S. Murahashi and T. Torii, *J. Chem. Phys.*, **42**, 1432 (1965).
19) M. Ukita, *Bul. Gov. Ind. Res. Inst., Osaka (Osaka Kogyo Gijitsu Shikensho Kiho)*, **16**, 42 (1965).
20) T. Miyazawa and Y. Ideguchi, This Bulletin, **36**, 1125 (1963); **37**, 1065 (1964).
21) C. Y. Liang, M. R. Litton and C. J. Boone, *J. Polymer Sci.*, **54**, 523 (1961).
22) R. G. Snyder and J. H. Schatschneider, *Spectrochim. Acta*, **20**, 853 (1964).

in the main chain would couple with that of the side group. This suggestion is clearly confirmed by the present work. The 1207 cm^{-1} band related to crystallinity appears only in the hexagonal form.[12] The character of this band may be due to the coupling of the CH_2 twisting (main chain) and the CH wagging modes.

CC Stretching, CH_2 Rocking, and CH_3 Rocking Modes.—In the region from 1200 to 1000 cm^{-1}, four perpendicular bands, at 1150, 1096, 1062, and 1015 cm^{-1}, and one parallel band, at 1028 cm^{-1}, are observed. The weak bands in this region are mainly assigned to the CC stretching modes, except for the 1062 cm^{-1} band, which is assigned to the coupling vibration of the CH_3 rocking and the CC stretching modes of the ethyl group. The CC stretching modes which are not localized in several CC symmetry coordinates are represented by ν(CC) in Table VI.

In the region from 1000 to 700 cm^{-1} five perpendicular bands, at 999,* 977, 924, 798, and 764 cm^{-1}, and three parallel bands, at 848, 816, and 758 cm^{-1}, are observed. The weak band at 977 cm^{-1} is assigned to the overlapped vibration (A and E species) of ν_{23}, which is associated with the coupling of the CC stretching modes of the main chain with the CH_3 rocking mode. The crystalline sensitive band at 924 cm^{-1} corresponds to the ν_{25}(E) vibration, which is associated with the coupling of the CH_2 rocking mode in the main chain with the CH_3 rocking mode. The schematic representation of this mode for a chemical unit is shown in Fig. 4(a). This mode has a transition moment perpendicular to the helical axis; therefore, the E vibration of this mode should have an intense perpendicular dichroism. This calculated result shows a good agreement with the observed result. The crystalline sensitive band at 848 cm^{-1} is assigned to the coupling vibration of the CH_3 rocking and the CC stretching modes. The medium intensity band at 816 cm^{-1} and the weak band at 798 cm^{-1} are assigned to the coupling vibration of the CH_2 rocking (main chain) and the CC stretching modes. Similar bands associated with the CH_2 rocking and the CC stretching modes have been observed at 841 ($\parallel$, medium) and 809 ($\perp$, weak) cm^{-1} in isotactic polypropylene.[18,20,22] It should be noted that similar bands are observed in this region.

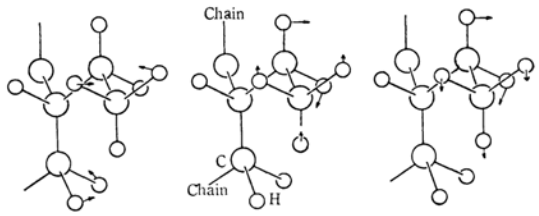


Fig. 4. Vibrational modes for a chemical unit of the perpendicular bands at 924 cm^{-1} (a) and at 764 cm^{-1} (b), and the parallel band at 758 cm^{-1} (c).

With respect to ethyl rocking vibrations, Havey and Ketley[23] observed the infrared spectra for seven polymers with an ethyl group, and found that the ethyl rocking vibrations appear in the region from 785 to 760 cm^{-1}. According to the present work, the perpendicular band at 764 cm^{-1} and the parallel band at 758 cm^{-1} are to be assigned to the ethyl rocking modes, namely, ν_{27}(E) and ν_{27}(A) respectively. Therefore, the assignments by Havey et al. are consistent with the calculated results. The schematic representations of these modes for a chemical unit are shown in Figs. 4(b) and 4(c).

The dichroic properties of the observed bands can reasonably be explained by the normal modes. The molecular vibrations in the far infrared region will be reported on in the near future.

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* The weak perpendicular band at 999 cm^{-1} is observed in the spectra of three crystalline forms, and it is difficult to obtain a reasonable correspondence with a calculated frequency. Therefore, this band may be associated with the vibration of the atactic part or the end group of isotactic polybutene-1.

23) M. C. Havey and A. D. Ketley, *J. Appl. Polym. Sci.*, **5**, 246 (1961).