On the Infrared Spectra of Crystalline Poly-p-fluorostyrene

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During the last few years, many isotactic vinyl polymers have been obtained from various ring-substituted styrene monomers with Ziegler type catalysts[1]. Most of them crystallize with helical molecular conformation similar to that of isotactic polystyrene, but the pitches of the helixes are different from each other depending on the size, the site and the number of substituents. For instances, while poly-*o*-fluorostyrene crystallizes in three-fold helix with the identity period of 6.65 Å, but poly-*p*-fluorostyrene in four-fold helix with the period of approximately 8.3 Å[1]. Further, it has been noticed by Murahashi et al.[2] that the polymers of *p*-methyl, *m*-methyl and *p*-trimethylsilyl styrene prepared with Ziegler catalyst have larger fiber periods of 12.9, 57 and 60.4 Å, respectively.

Recently, from the infrared spectroscopic studies on several isotactic polymers, Tadokoro et al.[3] found that the characteristics of helical structure of the polymers would be indicated in common by the infrared dichroisms of the several absorption bands, especially of the stretching vibrations of the CH_2 groups. Keeping in mind their findings, we measured the infrared spectra of crystalline poly-*p*-fluorostyrene with an aim to find in what respects they would reflect the characteristics of the helical structure of its own.

As a result, it was found that the dichroic ratios of the bands, especially those assigned to the stretching vibrations of CH_2 groups differed from those of polystyrene.

To obtain a theoretical ground for this fact, we calculated the dichroic ratios of the bands associated with CH_2 and CH groups, assuming the polymer chain to have a four-fold helical structure allowed for the observed fiber period.

On the other hand, we analyzed the infrared spectrum of the polymer under the assumption that they, in an approximation, may be divided into two parts, one being associated with the side group and another with the skeletal chain. The molecular vibrations of the former were analyzed in terms of D_{2h} symmetry and those of the latter in terms of $C(\pi/2)$ symmetry.

Experimental

p-Fluorostyrene (4 g.) prepared by an usual method was polymerized in *n*-heptane at 70°C for 10 hr. using triethyl aluminum (0.53 g.) + titanium tetrachloride (0.18 g.) as a catalyst in a sealed tube. The solid product was washed with hot methanol and then boiled in water to change the organometallic compounds contaminated in the polymer into insoluble oxides. The white polymeric substance was dissolved in boiling xylene and the

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[1] G. Natta, F. Danusso and D. Sianesi, *Makromol. Chem.*, **28**, 253 (1958).

[2] S. Murahashi. S. Nozakura, and H. Tadokoro, This Bulletin. **32**, 534 (1959).

[3] H. Tadokoro, S. Nozakura, T. Kitazawa, Y. Yasuhara and S. Murahashi, This Bulletin, **32**, 313 (1959).

solution was filtered. The gelatinous precipitate separated from the filterate kept at room temperature was dried after centrifugation.

To gain a high degree of crystallinity, the polymer film cast from the toluene solution was subjected to heat-treatment at 160°C for 1 hr. in glycerol. It had the density of 1.23 and melting point of 240°C. The oriented film for measurements of the polarized spectrum was made by drawing it to five times the length of the original in boiling water.

The infrared measurements were made in the region of 3500~400 cm^{-1} using Hilger H 800 and Perkin Elmer Model 21 I. R. spectrometers; the former was equipped with the polarizer consisting of a set of six selenium films, each approximetely 5 μ. thick. The amorphous polymer for comparison was prepared with benzoyl peroxide as a catalyst.

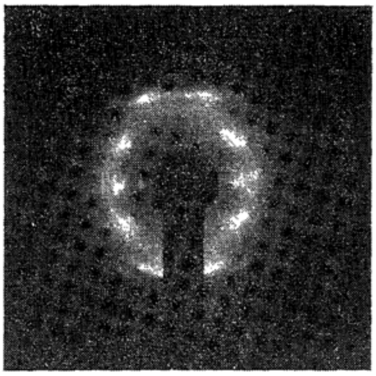

Fig. 1.

Experimental Results

X-ray Diagram. — In Fig. 1 is illustrated the X-ray fiber diagram of the stretched film of crystalline poly-*p*-fluorostyrene (abbreviated to PFS). The measured identity period along the fiber axis was 8.31 Å being similar value reported by Natta et al.[1] This value assumes that the polymer chain is of isotactic configuration and takes four-fold helix in the crystalline regions. The calculated angles of internal rotation of the chain about the C-C bonds with which the helix is formed will be presented later.

Infrared Spectra.—In Fig. 2 are shown the spectra infrared in the region of 3500~400 cm^{-1} of atactic and isotactic PFS together with that of the latter measured at molten state.

In Fig. 3 are shown the polarized spectra of isotactic PFS in the region of 3500~650 cm^{-1}.

The wave numbers, the dichroisms and the relative intensities of the absorption bands are given in Table I.

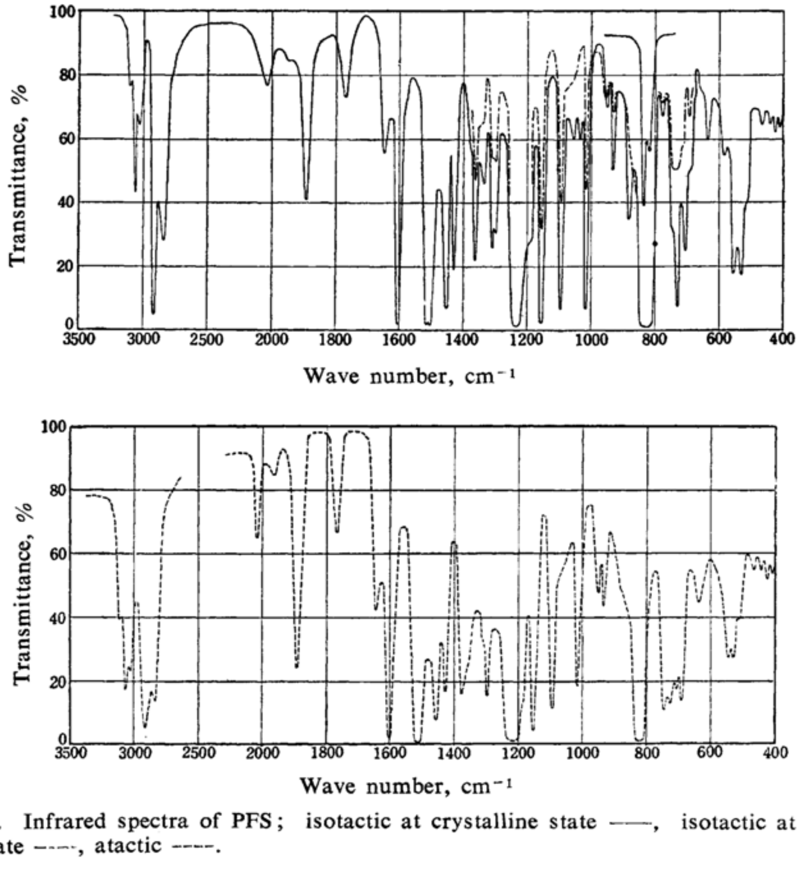

Fig. 2. Infrared spectra of PFS; isotactic at crystalline state ——, isotactic at molten state –·–·–, atactic ----.

TABLE I. BAND ASSIGNMENTS OF THE SPECTRA OF ISOTACTIC AND ATACTIC PFS

Isotactic cryst.			Isotactic molt.		Atactic		Assignment
Freq. (cm^{-1})	Dichr.	R. I.	Freq. (cm^{-1})	R. I.	Freq. (cm^{-1})	R. I.	
3112	σ	vw	3112	vw	3112	vw	A_g+B_{2g}
3060	σ	m	3060	m	3060	m	B_{3u}
3026	σ	w	3026	w	3026	w	B_{1u}
2924	σ	s	2924	s	2924	s	ν_{asym} (CH_2)
2849	π	m	2849	m	2849	m	ν_{sym} (CH_2)
2047	σ	w	2047	w	2047	w	530+1515=2045
1891	σ	m	1891	m	1891	m	819+1096=1915
1770	σ	w	1770	w	1770	w	
1647	σ	w	1647	w	1647	w	B_{3u}
1603	—	s	1603	s	1603	s	A_g
1515	σ	s	1515	s	1515	s	B_{1u}
1503	—	s					
1454	(σ)	s	1454	s	1457	s	δ (CH_2)
1448	(π)	s	1448	s	1448	s	
1428	σ	ms	1428	ms	1428	ms	
1377	—	sh	1377	sh	1377	m	
1361	σ	m	1361	m			δ (CH)E
1336	π	w	1336	sh			
1309	σ	m	1309	m	1309	sh	
1300	π	m	1300	m	1300	m	w (CH_2)A
1234	—	vs	1234	vs	1234	vs	ν $(CF)A_g$
1191	π	sh	1191	sh			ν (CC)A
1154	σ	s	1154	s	1154	s	ν $(CF)B_{1u}$
1096	σ	s	1096	s	1096	s	B_{3u}
1056	σ	w	1056	sh	1056	sh	B_{3u}
1035	σ	w					
1015	σ	s	1015	s	1015	s	B_{1u}
950	—	w	950	w	950	w	A_u
932	—	m	932	w	932	w	B_{3g}
881	σ	m	881	sh	881	sh	
832	—	vs	832	vs	832	vs	B_{2u}
819	π	vs	819	vs	819	vs	A_g
738	—	sh	738	sh	748	s	
730	—	s	725	s	725	ms	B_{1u}
708	σ	m	708	sh	708	mw	r (CH_2)E ?
694	σ	s	694	w	694	m	
634		w	634	w	634	w	δ $(CF)B_{2g}$
583		msh	583	msh			
555		s	553	s	545	s	
530		s	530	s	530	s	δ $(CF)B_{2u}$
515		wsh	515	sh	515	sh	
464		vw	464	vw	464	vw	A_g
444		vw	444	vw	444	vw	
425		vw	425	vw	425	vw	δ $(CF)B_{3u}$
410		vw	410	vw	410	vw	

Discussions

In this paper the molecular vibractions of the polymer molecule with four-fold helical structure are analyzed following the same way as described in the previous paper⁽⁴⁾ on isotactic poly-αd_1-styrene; the vibrations of the side group and the skeletal chain are considered separately.

Vibrational Modes of the Side Group. — The molecular vibrations of the side group of PFS correspond to those of *p*-disubstituted benzene. The data useful for our study have

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4) M. Kobayashi, to be published in this Bulletin.

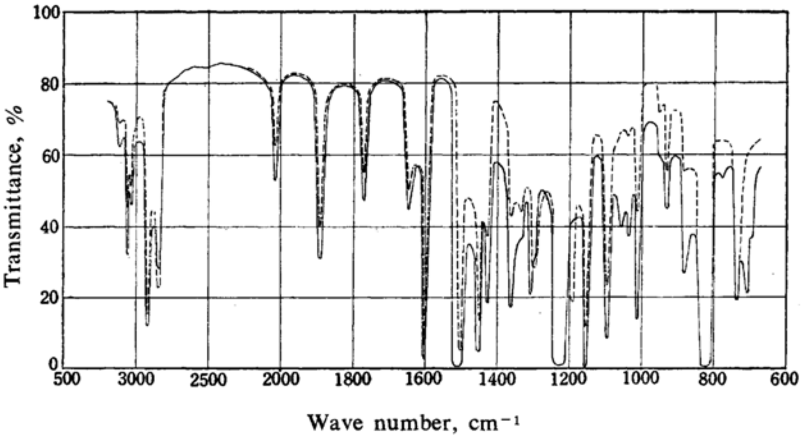

Fig. 3. Infrared dichroism of isotactic PFS. —— Electric vector perpendicular to elongation. ---- Electric vector parallel to elongation.

TABLE II. CHARACTER TABLE, NUMBER OF NORMAL MODES AND SELECTION RULES FOR POINT GROUP D_{2h}

	E	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	i	$C_2(z)$	$C_2(y)$	$C_2(x)$	Zero fr.	n	Selec. rule
A_g	+1	+1	+1	+1	+1	+1	+1	+1		6	R.
A_u	+1	−1	−1	−1	−1	+1	+1	+1		2	—
B_{1g}	+1	+1	−1	−1	+1	+1	−1	−1	R_z	1	R.
B_{1u}	+1	−1	+1	+1	−1	+1	−1	−1	T_z	5	I.R.
B_{2g}	+1	−1	+1	−1	+1	−1	+1	−1	R_y	5	R.
B_{2u}	+1	+1	−1	+1	−1	−1	+1	−1	T_y	3	I.R.
B_{3g}	+1	−1	−1	+1	+1	−1	−1	+1	R_x	3	R.
B_{3u}	+1	+1	+1	−1	−1	−1	−1	+1	T_x	5	I.R.

already been published. Freguson et al.5) and Tobin6) have made assignments of the absorption bands of *p*-fluorotoluene and *p*-dichlorobenzene respectively. In applying their results to our aim, it is assumed that the analysis using a point group of D_{2h} woluld be preferable, if it is taken into account that fluorine atom and CH group attached to the para position of benzene nucleus are similar in mass.

Symmetry species, irreducible representations, numbers of normal modes and selection rules for the point group D_{2h} are given in Table II. The selection rules can not be applied rigorously in our case, since the two substituents at the para positions will not suffer the same transition moment. As a result, the fundamentals under all species would become Raman active and those except A_u and B_{1g} infrared active. Referring to the assignments of the bands of *p*-fluorotoluene given by Freguson, we selected out from the spectrum of PFS the bands which might be assigned to the vibrational modes of the side group. They are given in Table III.

It is, of course, anticipated that they will be more or less under the influences of the crystalline field. In fact, considerable differences are observed in some of the bands before and after crystallization or on melting. For example, the band at 1056 cm^{-1} assigned to CH in-plane deformation (B_{3u}) becomes sharper and the intensity of the band at 932 cm^{-1} assigned to CH out-of-plane deformation (B_{3g}) increases on crystallization.

Vibrations of the Skeletal Chain. — Since the molecule of isotactic PFS has four-fold helical structure in the crystalline region, the molecular vibrations of the skeletal chain may be accounted for by using the factor group $C(\pi/2)$7). From the result of the factor group analysis, the normal modes are divided into three symmetry species; A (non-degenerate), B (non-degenerate) and E (doubly degenerate) species. Symmetry species, irreducible representations, selection rules and numbers of the normal modes are given in Table IV. In the calculation of the numbers of the normal modes, the side group attached to the skeletal chain is taken as a mass point. The modes under A and E are infrared active and ones under B are inactive. The fundamentals under

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5) E. E. Freguson, R. L. Hudson, J. Rud Nielsen and D. C. Smith, *J. Chem. Phys.*, **21**, 1736 (1953).

6) M. C. Tobin, *J. Phys. Chem.*, **61**, 1392 (1957).

7) C. Y. Liang and S. Krimm. *J. Chem. Phys.*, **25**, 563 (1956).

TABLE III. ASSIGNMENTS OF THE BANDS DUE TO THE SIDE GROUP

p-FT	PFS		*p*-FT	PFS	
ν (CH)			δ (C-C-C)$_{\text{in}}$		
3071	3112	A_g	1099	1096	B_{3u}
3071	3112	B_{2g}	728	730	B_{1u}
3069	3060	B_{3u}	455	464	A_g
3043	3026	B_{1u}	313		B_{2g}
δ (CH)			ring		
1222	(1211)	B_{2g}	842		A_g
1044	1056	B_{3u}			
1017	1015	B_{1u}	δ (C-C-C)$_{\text{out}}$		
825	819	A_g	695	694	B_{3g}
			390		A_u
γ (CH)			152		B_{2u}
956	950	A_u			
929	932	B_{3g}	ν (CF)		
817	832	B_{2u}	1214	1234	A_g
(810)		B_{1g}	1157	1154	B_{1u}
ν (CC)			δ (CF)		
1614	1647	B_{3u}	638	634	B_{2g}
1602	1603	A_g	503	530	B_{2u}
1512	1515	B_{1u}	422	425	B_{3u}
1299	(1300)*	B_{2g}	341		B_{3g}

ν (CH); CH stretching, δ (CH); CH in-plane deformation, γ (CH); CH out-of-plane deformation, ν(CC); CC stretching, δ (C-C-C)$_{\text{in}}$; CC in-plane deformation, δ (C-C-C)$_{\text{out}}$; CC out-of-plane deformation, ν (CF); CF stretching, δ (CF); CF deformation.

* The 1300 cm^{-1} band observed may be due mainly to w (CH_2).

A and E should exhibit parallel (π) and perpendicular (σ) dichroisms respectively. Physically, the symmetry species A, E and B mean that the neighboring monomer units constituting the helix vibrate with a definite phase difference of 0, $\pm\pi/2$ and π, respectively.

Infrared Dichroism. — Bearing in mind the fact noted in the introduction that infrared dichroisms of several bands, especially of those due to the CH_2 stretching vibrations, have been detected as reflecting helical structures of the isotactic polymers, the infrared dichroisms of the stretched film of isotactic PFS were measured (see Fig. 3). It was demonstrated that the 2849 cm^{-1} band assigned to the CH_2 symmetric stretching exhibited a considerable π nature and the 2924 cm^{-1} band assignable to the CH_2 antisymmetric stretching showed a slight σ nature. These facts do not coincide with Tadokoro et al.'s results on isotactic polystyrene and others; the former band shows almost no dichroism and the latter a considerable σ nature.

This discrepancy may be attributed to the reason that the plane of the methylene group in the helix of PFS is inclined to the fiber axis in a different way from that of isotactic polystyrene. In other words, this is attributed to the difference in conformation of the skeletal carbon chain between them.

To gain a concrete ground for this, we calculated the theoretical dichroic ratios ($A_{\parallel}/A_{\perp}$) of the absorption bands. In doing this, however, precise knowledge about the conformation of the molecule of PFS is needed. For this purpose, the data available at present is the observed fiber period of the polymer. A helical structure of an isotactic polymer which gives a definite identity period is determined by the angles of internal rotation of the chain elements about the C–C bonds, provided that the length of C–C bond and the bond angle are kept at constant.

From the mathematical calculations presented in the appendix, we can search for the angles of internal rotation which will fulfill the conditions that the helix of PFS has the observed identity period of 8.31 Å and contains four monomer units in one pitch. In Table V is given the relation between the angles of internal rotation (θ_1 and θ_2) and the calculated identity period, R. In this table ν_x, ν_y and ν_z are the components of the unit vector of the fiber axis in an internal Cartesian coordinate. Using them, calculation of the dichroic ratio may be made.

θ_1 (or θ_2) is the angle with which a given bond is rotated from the trans position with the clockwise direction taken as plus when seen from the lower indexed carbon atom (see Fig. 4). If $\theta_1=0°$ and $\theta_2=120°$, R will give an identity period 6.65 Å of the three-fold helix (isotactic polystyrene).

The most reasonable values of θ_1 and θ_2 for PFS will be present between $-10°$ and $-12°$ and between 94° and 95° respectively, provided

TABLE IV. SYMMETRY SPECIES, IRREDUCIBLE REPRESENTATIONS, NUMBER OF NORMAL MODES AND SELECTION RULES FOR POINT GROUP C($\pi/2$)

	E	C^1	C^2	C^3	N	Zero fr.	n	I.R.	R.
A	+1	+1	+1	+1	18	T_π, R_π	16	A	A
B	+1	−1	+1	−1	18		18	F	A
E	+1	+i	−1	−i	18	(T_σ, R_σ)	(16)	A	A
	+1	−i	−1	+i	18			A	A

TABLE V. ANGLES OF INTERNAL ROTATION AND FIBER PERIOD FOR FOUR-FOLD HELIX

θ_1	θ_2	ν_x	ν_y	ν_z	R*,**
0	90	0.438	0.899	0	8.86 Å
−10	94	0.368	0.926	−0.081	8.39
−12	95	0.354	0.930	−0.098	8.29

* Assuming C–C bond length of 1.54 Å and C–C–C bond angle of 116°.

** The observed fiber period of PFS is 8.31 Å.

that the C–C–C bond angle takes the same value as that of polystyrene, 116°.

Dichroic ratio is expressed for a uniaxial orientation as follows;

$$A_{\parallel}/A_{\perp}=2\cot^2\varphi$$

where φ is the angle between the transition moment and the fiber axis. If a unit vector $\boldsymbol{m}$ of a transition moment accompanied with a vibrational mode of the CH_2 group is defined by the components m_x, m_y and m_z in the Cartesian system (x_i, y_i, z_i), it follows that

$$\cos\varphi=\boldsymbol{\nu}^{\top}\cdot\boldsymbol{m}=\nu_x m_x+\nu_y m_y+\nu_z m_z$$

On the other hand, if a unit vector $\boldsymbol{m}'$ of a transition moment accompanied with a vibrational mode of the CH or the phenyl group is defined by the components m'_x, m'_y and m'_z in the Cartesian coordinate (x_{i+1}, y_{i+1}, z_{i+1}), the corresponding expression is

$$\begin{aligned}\cos\varphi&=\boldsymbol{\nu}^{\top}\cdot\boldsymbol{A}_1\boldsymbol{m}'\\&=\nu_x(m'_x\cos\omega+m'_y\sin\omega)\\&\quad+\nu_y(m'_x\sin\omega\cos\theta_1\\&\quad-m'_y\cos\omega\cos\theta_1+m'_z\sin\theta_1)\\&\quad+\nu_z(m'_x\sin\omega\sin\theta_1\\&\quad-m'_y\cos\omega\sin\theta_1+m'_z\cos\theta_1)\end{aligned}$$

where $\boldsymbol{A}_1$ is the matrix of the orthogonal transformation defined in the appendix.

Using the values of ν_x, ν_y and ν_z, the dichroic ratios of the absorption bands due to the vibrational modes of the CH_2 and CH groups were calculated. The results are given in Table VI.

It is shown as expected that they depend on the angles of internal rotation, θ_1 and θ_2. The changes in dichroic ratio of the bands due to the CH_2 stretching vibrations are of importance by reason of that described above. The dichroic ratios of the ν_{sym} (CH_2) band and the ν_{asym} (CH_2) band increase with θ_2.

TABLE VI. THE CALCULATED DICHROIC RATIOS FOR FOUR-FOLD HELICAL POLYMER

Vibrational mode	$\theta_1=0°$	$\theta_1=-10°$	$\theta_1=-12°$
ν_{sym} (CH_2), δ (CH_2)	0.781	1.073	1.132
ν_{asym} (CH_2), r (CH_2)	0	0.013	0.019
w (CH_2)	5.122	3.626	3.422
δ (CH)	0	0.013	0.019
w (CH)	5.122	3.626	3.422

Since when $\theta_1=0$, the calculated values do not depend on the number of monomer unit in one pitch provided that the bond angle is kept at constant ($\theta_2=120°$ for three-fold helix, $\theta_2=90°$ for four-fold helix), the values for $\theta_1=0°$ may be regarded as those of isotactic polystyrene. Therefore, the results well explain the differences between PFS and polystyrene in polarization property of the bands due to the CH_2 stretching vibrations.

Although the coincidence between the observed property and the predicted value of dichroism of the ν_{asym} (CH_2) is yet qualitative, it would be accepted as correct if we take into account of the contribution from the chain segments randomly oriented in the amorphous regions.

Absorption Bands Characteristic to the Helical Structure of PFS.—As in the cases of polystyrene and its several derivatives, the bands characteristic of the helical structure (alternate sequence of trans and gauche conformations) of the polymer molecule are observed in the spectrum of isotactic PFS. They do not disappear even at molten state and are assumed to be associated mainly with the deformational vibrations of the CH_2 or CH group or the skeletal modes.

The band at near 1450 cm^{-1} may be ascribed to the CH_2 bending ($\delta(CH_2)$). Using the differential method it was made clear that this band consisted of two bands at 1454 and 1448 cm^{-1}, having σ and π nature respectively, and the former might be assigned to $\delta(CH_2)E$ and the latter to $\delta(CH_2)A$.

The five bands at 1361 (σ), 1336 (π), 1309 (σ), 1300 (π) and 1191 (π)cm^{-1} of isotactic PFS may correspond to the bands which have been detected by Tadokoro et al. as characteristic of the helical structure of isotactic polystyrene and others. Measurements of the dependence of the spectrum on temperature showed that with increasing temperature the band at 1336 cm^{-1} decreased its relative intensity and disappeared at molten state, on the other hand, the other four bands were hardly affected by temperature change. Then, the four bands may be considered as indicating rather the characteristics of the polymer molecule itself than the interactions of neighboring molecules in the crystalline lattice.

On the basis of the results on the assignments of the bands characteristic of isotactic polystyrene[4], the assignments of these bands may be made as follows; the 1361 cm^{-1} band is assigned to the CH deformation under the E species (δ (CH)E), the 1300 cm^{-1} band to the CH_2 wagging under the A species (w

(CH_2)A), the 1191 cm^{-1} band to the CC stretching under the A species (ν (CC)A). The 1309 cm^{-1} band is still unassigned.

The difference between isotactic PFS and atactic one in spectrum are observed also in the region of 690∼750 cm^{-1}. The band at 738 cm^{-1} of isotactic PFS has smaller intensity than the corresponding band at 748 cm^{-1} of atactic one. This fact remains even at molten state. The σ band at 708 cm^{-1} of isotactic PFS decreases its intensity with increasing temperature, on the other hand, the band at 694 cm^{-1} shows the reverse change. Although the CH_2 rocking mode is anticipated to be ovserved in this region and, from polarization property, the 708 cm^{-1} bond is assumed to be assigned to it, the precise assignment to date is open to question.

The results of the discussions on the assignments of the absorption bands are given in the last column of Table I.

Appendix

The Geometrical Structures of Polymers with Helical Structure. — Spatial configuration of a vinyl polymer is determined primarily by angles of internal rotation of C–C bonds. If the spatial position of each monomer unit in the helix is equivalent, the conformation of the polymer chain is defined by two angles of internal rotation as described below. The internal Cartesian coordinates are defined as shown in Fig. 4. The matrix which transforms the coordinate from $(x_{i+1}, y_{i+1}, z_{i+1})$ to (x_i, y_i, z_i) system, or from $(x_{i+2}, y_{i+2}, z_{i+2})$ to $(x_{i+1}, y_{i+1}, z_{i+1})$ system is represented by $\boldsymbol{A}_1$ (or $\boldsymbol{A}_2$);

$$\boldsymbol{A}=\begin{pmatrix} \cos\omega & \sin\omega & 0 \\ \sin\omega\cos\theta & -\cos\omega\cos\theta & \sin\theta \\ \sin\omega\sin\theta & -\cos\omega\sin\theta & -\cos\theta \end{pmatrix}$$

where $\theta=\theta_1(\boldsymbol{A}_1)$ or $\theta=\theta_2(\boldsymbol{A}_2)$, and ω is the supplement angle of C–C–C and angle.

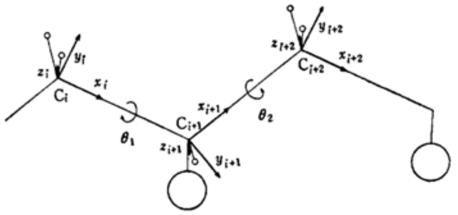

Fig. 4. Internal coordinates for vinyl polymer.

If the unit vector of the fiber axis in (x_i, y_i, z_i) system is defined by $\boldsymbol{\nu}$ $(\nu_x, \nu_y, \nu_z)^{\top}$, the following relation is introduced;

$$\boldsymbol{\nu} = \boldsymbol{A}_1\boldsymbol{A}_2\boldsymbol{\nu}$$

Since $\boldsymbol{A}$'s are matrixes of orthogonal transformation,

$$(\boldsymbol{A}_1{}^{\top}-\boldsymbol{A}_2)\boldsymbol{\nu} = \boldsymbol{0}$$

Then, it follows that

$$(\cos\theta_1-1)\nu_y+(\sin\theta_1)\nu_z = 0 \qquad (1)$$

$$\sin\omega(1-\cos\theta_2)\nu_x+\cos\omega(\cos\theta_2-\cos\theta_1)\nu_y - (\cos\omega\sin\theta_1+\sin\theta_2)\nu_z = 0 \qquad (2)$$

$$-(\sin\omega\sin\theta_2)\nu_x+(\sin\theta_1+\cos\omega\sin\theta_2)\nu_y + (\cos\theta_2-\cos\theta_1)\nu_z = 0 \qquad (3)$$

As $\boldsymbol{\nu}$ is unit vector

$$\nu_x{}^2+\nu_y{}^2+\nu_z{}^2 = 1 \qquad (4)$$

If the fiber period of n-fold helix is R,

$$R/n = \boldsymbol{\nu}^{\top}\cdot(\boldsymbol{b}+\boldsymbol{A}_1\boldsymbol{b})$$

where

$$\boldsymbol{b} = (b,\ 0,\ 0)^{\top}$$

b is the CC bond length. Therefore,

$$R/n = b\{(1+\cos\omega)\nu_x+(\sin\omega\cos\theta_1)\nu_y + (\sin\omega\sin\theta_1)\nu_z\} \qquad (5)$$

To construct n-fold helix, the following condition must be satisfied; the angle between the projection of $\overline{C_iC_{i+1}}$ to the plane perpendicular to the fiber axis and the one of $\overline{C_{i+2}C_{i+3}}$ to the same plane must be $2\pi/n$. Then,

$$(\boldsymbol{A}_1\boldsymbol{A}_2\boldsymbol{1}\times\boldsymbol{\nu})\cdot(\boldsymbol{1}\times\boldsymbol{\nu}) = \cos(\pi-2\pi/n)$$

Then,

$$\cos^2\omega+\sin^2\omega\cos\theta_2 - \{\nu_x{}^2+\nu_x\nu_y\sin\omega\sin\theta_1\sin\theta_2 - \nu_x\nu_z(1+\cos\theta_1)\sin\omega\sin\theta_2\} = \cos(n-2)\pi/n \qquad (6)$$

Provided that fiber period, C–C–C bond angle, C–C bond length and number of monomer units in one pitch of the helix are known, it is possible to calculate the angles of internal rotation, θ_1 and θ_2, using the Eqs. 1—6.

In Table V are given the results of the calculation for four-fold helix. In this calculation, the C–C bond length of 1.54 Å and the C–C–C bond angle of 116° are assumed.

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