Stereoregular Polymers. VII.[1] *Infrared Spectra of Isotactic Polystyrene, Isotactic Poly-α, β, β-trideuterostyrene and Isotactic Poly-p-deuterostyrene*[*1]

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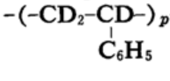
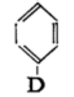
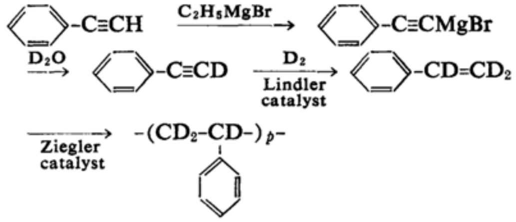
Isotactic polystyrene is a very interesting polymer from the point of view of fine structure and fine texture. Its crystallinity can be varied over wide range, from amorphous to highly crystalline state by heat-treatments, and also a highly oriented sample can be made by hot stretching. We are now studying this substance by use of the X-ray, infrared and density measurements. In this paper we wish to present a report on the results obtained from the changes of infrared spectra with crystallization and the infrared dichroism of isotactic polystyrene (IPS), isotactic poly-α, β, β-trideuterostyrene (IPTDS),  $-(-CD_2-\underset{C_6H_5}{\underset{|}{C}}D-)_p-$ and isotactic poly-*p*-deuterostyrene (IPPDS),  $-(CH_2-CH-)_p-$.

Natta[2] measured the infrared spectra of IPS both at solid and molten states. He showed that the spectrum of IPS at the molten state is similar to that of atactic polystyrene (APS), but did not discuss it further in detail. Liang and Krimm[3] reported the detailed analysis of the infrared spectrum of polystyrene. Their analysis was, however, based only on the commercial ASP, and they have not yet examined the dicroism and the deuteration of this polymer. Deuteropolystyrenes (probably atactic) were prepared by Beachell and Nemphos[4], but the infrared spectra of their products seem not to be published yet.

Samples. — The samples used in this work are IPS, IPTDS and IPPDS polymerized with Ziegler catalyst. The deuterated polymers were prepared according to the following schemes:



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[1] Part I of this series, S. Murahashi, S. Nozakura, M. Sumi and K. Hatada, This Bulletin, 32, 1094 (1959).

[*1] Presented at the Annual Meeting of the Society of High Polymer Science in Tokyo, June, 1958, and at the Symposium on High Polymers in Osaka, October, 1958.

[*2] Present Address: Tôhô Rayon Co., Ltd., Research Institute, Tokushima.

[2] G. Natta, *Makromol. Chem.*, **16**, 213 (1955).

[3] C. Y. Liang and S. Krimm, *J. Polymer Sci.*, **27**, 241 (1958).

[4] H. C. Beachell and S. P. Nemphos, ibid., **25**, 173 (1957).

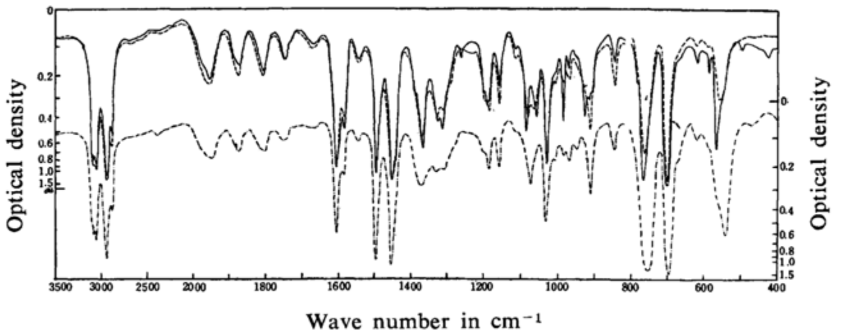


Fig. 1a. Infrared spectra of isotactic polystyrene (—— sample subjected to heat-treatment; - - - - quenched sample) and atactic polystyrene (-·-·-).

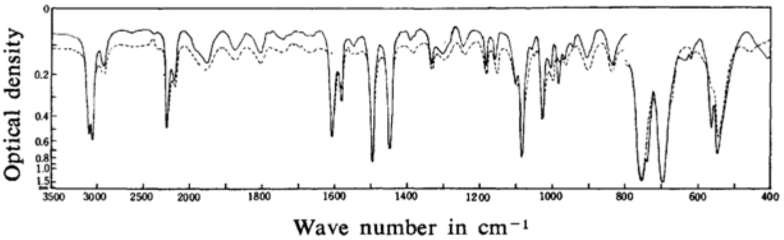


Fig. 1b. Infrared spectra of isotactic poly-α, β, β-trideuterostyrene (—— sample subjected to heat-treatment; - - - - quenched sample).

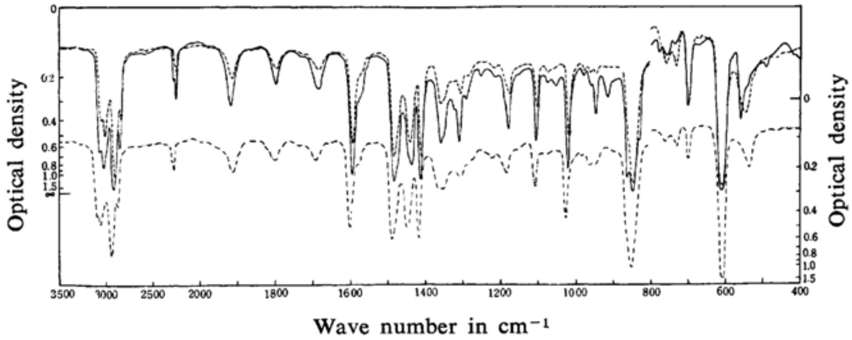
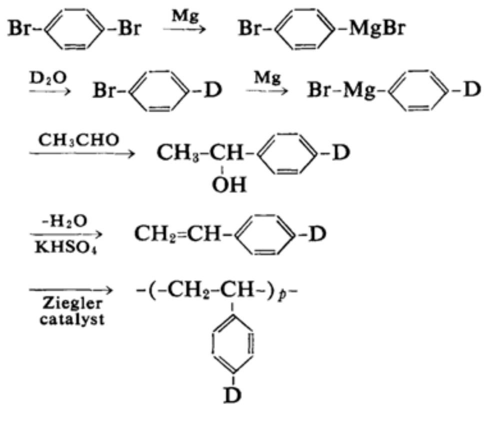


Fig. 1c. Infrared spectra of isotactic poly-*p*-deuterostyrene (—— sample subjected to heat-treatment; - - - - quenched sample) and atactic poly-*p*-deuterostyrene (-·-·-).



The films for the infrared measurements were cast on a metal plate[*3] from toluene solution, and were subjected to one of the following treatments: 1) quenching, 2) heat-treatment after quenching, and 3) elongation and subsequent heat-treatment. The quenched sample was prepared by heating in Wood's alloy at about 240°C[*4] for $15\sim30$ sec., and subsequent quenching in cold water. The oriented sample was prepared by stretching very slowly in boiling water, until it could be stretched no more (about 5 times of the original length). Heat-treatment was taken in Wood's alloy at about 180°C for 30 min. The crystallization and the

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[*3] A glass plate and the surface of water were also used for casting the film.

[*4] The melting point of IPS is reported to be 230°C[2].

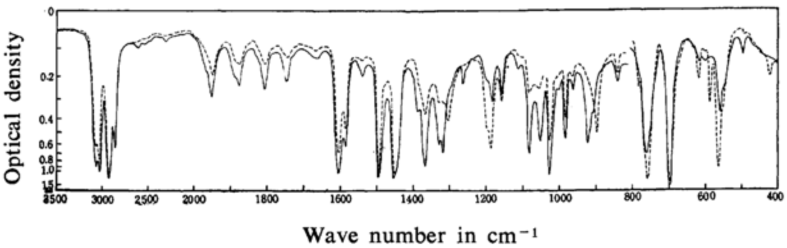


Fig. 2a. Infrared dichroism of isotactic polystyrene: —— electric vector perpendicular to elongation, - - - - electric vector parallel to elongation.

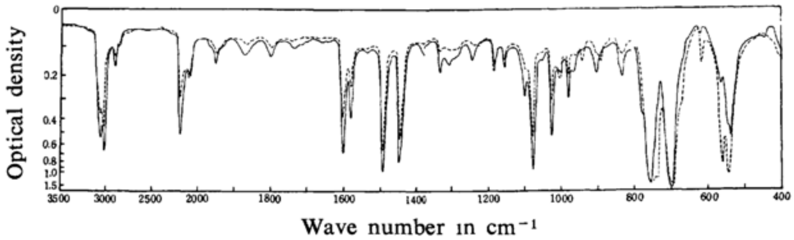


Fig. 2b. Infrared dichroism of isotactic poly-α, β, β-trideuterostyrene: —— electric vector perpendicular to elongation, - - - - electric vector parallel to elongation.

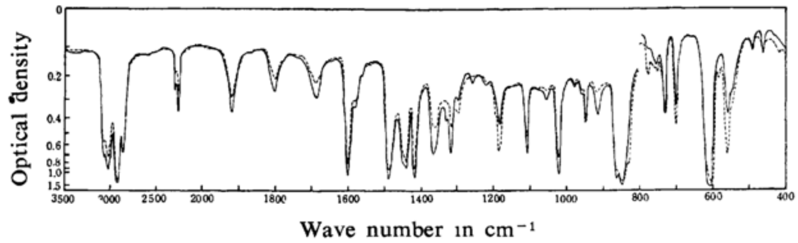


Fig. 2c. Infrared dichroism of isotactic poly-*p*-deuterostyrene: —— electric vector perpendicular to elongation, - - - - electric vector parallel to elongation.

orientation of the samples were confirmed by the X-ray photographs.

Infrared spectra were measured by using a Hitachi Model EPI-2 recording infrared spectrophotometer with sodium chloride and potassium bromide prisms and silver chloride polarizers.

Results and Discussion

Features of the Spectra. — Fig. 1 shows the spectra of IPS (a), IPTDS (b) and IPPDS (c), together with those of atactic samples (lower curve in Figs. 1a and 1c) for reference. In the figures the solid lines are for the samples subjected to heat-treatment and broken lines for the quenched samples. In Fig. 2, polarized infrared spectra of the oriented samples of IPS (a), IPTDS (b) and IPPDS (c) were shown. The solid lines represent transmission with the electric vector perpendicular to the stretching direction, and the broken lines that with the electric vector parallel to the stretching direction. In Figs. 1 and 2, the films used for the absorption measurements with sodium chloride prism are not all the same as those for the measurements with potassium bromide prism. The spectral data and the tentative assignments were also shown in Tables I—III.

As shown in Fig. 1, the spectra exhibit considerable changes with crystallization. The bands at 1364, 1314, 1297 and 1185 cm^{-1} in the spectrum of IPS are very sensitive to crystallization, and have strong dichroic nature. These four bands appear in weak intensity even in the spectrum of quenched samples of IPS, while do not appear in the spectrum of APS. On the other hand, the spectra of IPTDS do not show any bands at these four positions. The band at 1070 cm^{-1} of APS which splits slightly into two bands in the spectrum of the quenched IPS, undergoes large splitting with increase in intensity and sharpness in the spectrum of the crystallized IPS. The resulting two bands are at 1080 and 1048 cm^{-1}, showing strong perpendicular dichroism. The spectrum of the quenched IPS is similar

TABLE Ia. SPECTRAL DATA AND TENTATIVE ASSIGNMENT OF IPS (CRYSTALLIZED)

Frequency in cm^{-1}	Intensity[a]	Dichroism	Tentative assignment[b)]
3103	w	⊥	$\nu(CH)_{ph}$
3082	m	⊥	
3060	s	⊥	
3026	s	⊥	
3002	w	⊥	
2924	vs	⊥	$\nu_a(CH_2)$
2849	m		$\nu_s(CH_2)$
1946	w	⊥	combination of $\gamma(CH)_{ph}$
1872	w	⊥	
1801	w	⊥	
1748	w	⊥	
1675	w	⊥	
1602	s	⊥	$\nu(CC)_{ph}$, k (A_1)
1583	m	⊥	$\nu(CC)_{ph}$, l (B_1)
1542	w		
1493	s	⊥	$\nu(CC)_{ph}$, m (A_1)
1452	vs	⊥	$\nu(CC)_{ph}$, n (B_1)
1444	sh		$\delta(CH_2)$
1387	sh	⊥	
1364	s	⊥	associated with helical configuration
1324	m	⊥	
1314	m	⊥	associated with helical configuration
1297	m	∥	associated with helical configuration
1260	w		
1197	sh		
1185	m	∥	associated with helical configuration
1181	w	∥	$\beta(CH)_{ph}$, a (A_1)
1154	w	∥	$\beta(CH)_{ph}$, c (B_1)
1111	w	⊥	$\beta(CH)_{ph}$, d (B_1)
1080	m	⊥	
1048	m	⊥	
1028	s	⊥	$\beta(CH)_{ph}$, b (A_1)
1004	vw	∥	
985	m	⊥	$\gamma(CH)_{ph}$, j (B_2)
965	w		$\gamma(CH)_{ph}$, h (A_2)
920	m	⊥	$\gamma(CH)_{ph}$, i (B_2)
906	w		
898	m	∥	
842	w		$\gamma(CH)_{ph}$, g (A_2)
775	sh	∥	
755	vs	∥	$\gamma(CH_{ph})$, f (B_2)
697	vs		
620	w	∥	
586	m	∥	
566	s	∥	
550	sh		
499	w	⊥	
429	w	∥	

a) vs: very strong, s: strong, m: medium, w: weak, vw: very weak.

b) Whiffen's notations for the vibrational modes of the monosubstituted benzenes were used in this table.
$\nu(CH)_{ph}$: phenyl CH stretching, $\nu(CC)_{ph}$: phenyl CC stretching, $\beta(CH)_{ph}$: phenyl CH in-plane deformation, $\gamma(CH)_{ph}$: phenyl CH out-of-plane deformation, $\nu_a(CH_2)$: CH_2 asymmetric stretching, $\nu_s(CH_2)$: CH_2 symmetric stretching, $\delta(CH_2)$: CH_2 bending.

TABLE Ib. SPECTRAL CHANGES OF POLYSTYRENE WITH CRYSTALLIZATION

APS	Quenched IPS	Crystallized IPS	Changes with crystallization
1583 (m)	1583 (m)	1583 (m)	increase intensity
—	—	1444 (sh)	appear
—	—	1387 (sh)	〃
1370 (m)	1367 (s)	1365 (s)	
1328 (m)	1324 (m)	1324 (m)	
1306 (m)	1312 (m)	1314 (m)	increase intensity
—	1297 (vw)	1297 (m)	
—	—	1260 (w)	appear
—	—	1185 (m)	
1070 (m)	1075 (m) 1056 (m)	1080 (m) 1048 (m)	
—	—	985 (s)	
980 (w)	980 (w)	—	
943 (w)	—	—	(APS only)
906 (m)	906 (m)	920 (m) 906 (m) 898 (m)	
—	—	775 (sh)	appear
755 (vs)	755 (s)	755 (vs)	increase intensity
620 (w)	620 (w)	620 (w)	〃
—	590 (w)	586 (m)	〃
557 (sh) 542 (s)	557 (m)	566 (s) 550 (sh)	
—	—	499 (w)	appear
—	—	429 (w)	〃

TABLE II. SPECTRAL DATA OF IPTDS

Frequency in cm^{-1} a)	Intensity	Dichroism	Changes with crystallzation
3102	w	⊥	
3083	m	⊥	
3058	s	⊥	
3021	s	⊥	
2997	w	⊥	
2910	w	⊥	
2195	s	⊥	
2095	m	(∥)	
1950	w	⊥	
1875	w	⊥	
1805	w	⊥	
1602	s	⊥	
1581	m	⊥	increase intensity
1537	vw	⊥	
1493	s	⊥	
1447	s	⊥	
1385	w	⊥	increase intensity
1328	w	⊥	
1303	w	⊥	
1292	vw(broad)		
1240	w	⊥	
1179	w	∥	
1154	w	⊥	
1100	m	⊥	increase intensity
1077	s	⊥	
1052	vw	⊥	increase intensity
1025	m	⊥	
1006	w	∥	increase intensity
1000	vw	⊥	

TABLE II (Continued)

980	m	⊥	increase intensity
965	w	⊥	
940	w	∥	appear
903	w	⊥	898 cm^{-1} (quenched IPTDS)
891	w	∥	
840	w	⊥	
834	w	⊥	
774	sh	⊥	appear
754	vs	∥	
740	s	∥	appear
697	vs	⊥	
620	w	∥	
562	m	∥	increase intensity
548	s	∥	545 cm^{-1} (quenched IPTDS)

a) Data on the crystallized IPTDS.

TABLE III. SPECTRAL DATA OF IPPDS

Frequency in cm^{-1} [a]	Intensity[a]	Dichroism	Changes with crystallization
3071	s	⊥	
3024	s	⊥	
2997	sh	⊥	
2925	vs	⊥	
2850	s		
2290	w	⊥	
2264	m	⊥	
1920	m	⊥	
1803	w	⊥	
1689	w	⊥	
1600	s	⊥	
1578	sh	⊥	
1487	s	⊥	
1441	s	⊥	1446 cm^{-1} (quenched IPPDS)
1417	s	⊥	
1363	m	⊥	increase intensity
1355	sh		
1325	vw	⊥	increase intensity
1314	m	⊥	〃
1297	w	∥	〃
1265	w	⊥	appear
1220	w	⊥	
1183	m	∥	increase intensity
1107	m	⊥	
1077			(toluene ?)
1055	w	⊥	appear
1021	s	⊥	
980	w		
960	w		
948	m	∥	increase intensity
915	w	⊥	appear
862	m	⊥	increase intensity
846	vs	⊥	
830	sh	∥	appear
776	w	⊥	
730			(toluene ?)
699	m	∥	
609	vs	⊥	605 cm^{-1} (quenched IPPDS)
560	m	∥	545 cm^{-1} (quenched IPPDS and APPDS)
493	vw	⊥	

a) Data on the crystallized IPPDS.

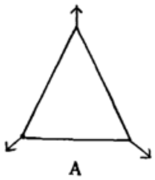
on the whole to that of APS, but is different on the points that 1) the 1070 cm^{-1} band splits in the quenched IPS and 2) the 542 cm^{-1} band in APS shifts to 557 cm^{-1} in the quenched IPS. These cases may be considered to be the examples that the infrared spectrum indicates the existence of localized regularity in some narrow region, which can be hardly observed from the X-ray photographs. The band at 985 cm^{-1} shows marked change of intensity with heat-treatment.*5 It is an interesting fact that a band which shows behavior similar to this band in the spectrum of IPS (crystallization-sensitive and perpendicular natures) appears also at the same wave number (980 cm^{-1}) in the case of IPTDS. This fact suggests that these bands appear from the similar origins and it would be considered that the bands can be used for the determination of the degree of crystallinity. In the spectra of IPPDS (Figs. 1c and 2c), the band at 948 cm^{-1} is also very sensitive to crystallization, but has parallel dichroism, differing from the 985 cm^{-1} band of IPS. The band which appears at about 906 cm^{-1} in the spectrum of APS as well as the quenched IPS splits with crystallization into two bands, i. e. the perpendicular band at 920 cm^{-1} and the parallel one at 898 cm^{-1} (Fig. 2a). The intensity of the 755 cm^{-1} band increases remarkably with crystallization.

Treatment with Factor Group. — The crystal structure of IPS analyzed by Natta et al.5) and Bunn et al.6) belongs to trigonal symmetry class. The molecular chain in the crystalline state has a structure of three-fold screw axis. An infinitely extended molecule of three-fold screw symmetry may be represented by a one-dimensional space group. When the interchain interaction is negligible, it is adequate to consider its factor group $C(2\pi/3)$ shown in Table IV7). The symmetry operation, C^1, bringing any structural unit into coincidence with an adjacent unit, consists of a rotation of $2\pi/3$ about the screw axis followed by a translation of 1/3 of the identity period of 6.65 Å along the axis. In the case of this group $C(2\pi/3)$, there appear the species A and E. In species A whole structural units vibrate in the same phase, and the direction of the transition moment is parallel with the screw axis. In species E, the phase of the vibration of a structural unit is different from that of the adjacent structural unit by $2\pi/3$, and consequently the direction of the transition moment is perpendicular to the screw axis. In the cases in which the interaction among the structural units is so strong that the frequencies of the A and the E modes clearly split, these bands should show strong dichroism. On the contrary, in the cases in which the interaction among the structural units is not so strong, and the frequencies of the A and the E modes are nearly equal, both bands, i. e. the parallel band of the species A and the perpendicular band of the species E, superpose in the same location of the spectrum. In this case the dichroism of the more intense component will appear. Which dichroism appears may be decided by the angle between the direction of the transition moment in each structural unit and the screw axis. It should be mentioned here that the vibrational modes, in which the interaction between the neighboring helical molecules is strong, can not be interpreted by the aforementioned method of factor group for a single molecular chain.

TABLE IV. SYMMETRY SPECIES, IRREDUCIBLE REPRESENTATIONS, NUMBER OF NORMAL MODES, AND SELECTION RULES FOR ISOTACTIC POLYSTYRENE UNDER THE GROUP $C(2\pi/3)$

	E	C^1	C^2	Null vib.		n	I. R.	Raman
A	1	1	1	$T_{\parallel}$	R	46	active ($\parallel$)	active
E	1	ε	ε^2	$T_{\perp}$		47	active ($\perp$)	active
	1	ε^{-1}	ε^{-2}	$T_{\perp}$		47		

$\varepsilon = \exp i(2\pi/3)$



A

E

Methylene Group Vibrations.—The CH_2 antisymmetric stretching band at 2924 cm^{-1} shows a distinguished perpendicular nature, which is explainable by the fact that the direction of the transition moment of this vibrational mode of each structural unit is nearly perpendicular to the screw axis. On the other hand, the CH_2 symmetric stretching band at 2849 cm^{-1} shows only very weak dichroism. The direction of the transition moment of this vibrational mode is on the bisector of the angle H–C–H of the methylene group. The angle between this direction and the screw axis is considered to be about 58° from the angle 116° of the C–C–C of the main chain of this polymer estimated by Natta et al.8)

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*5 In the spectra of APS and quenched IPS, a weak band is observed at 980 cm^{-1}.

5) G. Natta and P. Corradini, *Makromol. Chem.*, **16**, 77 (1955).

6) C. W. Bunn and E. R. Howells, *J. Polymer Sci.*, **18**, 307 (1955).

7) A detailed description on the factor group analysis of a helical molecule will be found in C. Y. Liang and S. Krimm, *J. Chem. Phys.*, **25**, 563 (1956).

8) G. Natta and P. Corradini, *J. Polymer Sci.*, **20**, 251 (1956).

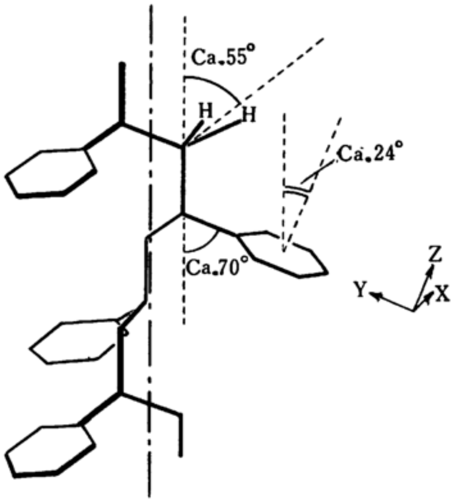

Fig. 3. The molecular structure of isotactic polystyrene in the crystalline state.

(Fig. 3). For perfect uniaxial orientation, the dichroic ratio, R, defined as the ratio of the optical densities with electric vector respectively parallel and perpendicular to the orientation direction, is given by $R=2\cot^2\varphi$, where φ is the angle between the transition moment and the orientation direction. If $\varphi=54°44'$, $R=1$, i. e., the band exhibits no dichroism. The critical angle for $R=1$ is considered to increase only a small amount, when the orientation deviates from the perfect one. For instance, if the transition moments are uniformly distributed in a 20° angular range, the critical angle is 54°54'.[9] Thus the absence of the dichroic nature of the CH_2 symmetric stretching band could be explained, since the aforementioned angle 58° is near this critical angle. These dichroic natures of CH_2 stretching bands are hence considered to be characteristic of the helical structure (alternate sequence of trans and gauche conformations) of isotactic polystyrene. The same feature was found in the case of CD_2 stretching bands of IPTDS (2195 and 2095 cm^{-1}).

In the region of 1400~1100 cm^{-1} the spectra of IPS and IPPDS change remarkably by heat-treatment (crystallization) and show distinguished dichroism as shown in Figs. 1 and 2. On the other hand, the absorption bands of IPTDS in this region which have comparatively weak dichroism, are not affected appreciably by heat-treatment, and are considerably different from those of IPS and IPPDS. The four bands (1364, 1314, 1297 and 1185 cm^{-1}), appearing in weak intensity in the spectra of quenched IPS and IPPDS, increase their intensity with crystallization, while they do not appear in the spectra of APS and APPDS (atactic poly-*p*-deuterostyrene). As these bands are absent in the spectra of IPTDS, these bands are considered to be not directly associated with the vibrations of the phenyl group, but mainly with that of the main chain. These four bands are also supposed to be closely associated with the helical structure of the IPS molecule in crystalline region, the detailed discussions of which we will report in the subsequent paper. On this problem we have briefly reported already.[10]

Phenyl Group In-plane Vibrations.—Now we wish to discuss the vibrational modes associated with the benzene ring. By calculating from the X-ray data of Natta et al.[5], it is estimated that the y and the z axes of the benzene ring shown in the figure in Table V are at an angle of about 70° and about 24° to the screw axis, respectively, and the x axis at an angle of about 14° from the plane normal to the screw axis as shown in Fig. 3.

The vibrations of monosubstituted benzene which has point symmetry of C_{2v} are useful for a step to the assignments of the bands due to phenyl group of polystyrene as studied by Liang et al.[3] in the case of APS previously. On the spectra and the vibrations of monosubstituted benzenes, a number of works have been done by many workers.[11-17] In Table V, we reproduce the symmetry species, the total number of normal vibrations associated with each species, n, and the infrared and the Raman activity to be expected, from the paper by Liang and Krimm[3]. As shown in this table, the transition moment for A_1 species is in the y direction, that for B_1 in the x direction and that for B_2 in the z direction, which is the out-of-plane vibration. We may presume the dichroism of the bands, placing these phenyl groups on the three-fold screw axis. In the cases of A_1 and B_1 species (of C_{2v}), the component E (of $C(2\pi/3)$) must be more intense than the component A and so the dichroism should be perpendicular. On the contrary in the case of species B_2, the component A must be more intense and thus the parallel nature should appear.

The fact that the bands mainly due to the

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[9] C. Y. Liang and S. Krimm, *J. Chem. Phys.*, **27**, 1437 (1957).

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

[11] C. R. Bailey et al., *J. Chem. Soc.*, **1946**, 299.

[12] E. K. Plyler, *Discussions Faraday Soc.*, No. **9**, 100 (1950).

[13] D. H. Whiffen, *J. Chem. Soc.*, **1956**, 1350.

[14] R. R. Randle and D. H. Whiffen, "Molecular Spectroscopy", Institute of Petroleum, London (1955), p. 111.

[15] Y. Kakiuchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1591 (1956).

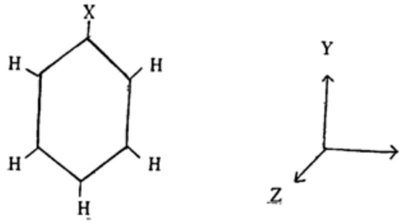
[16] Y. Kakiuchi, ibid., **77**, 1839 (1956).

[17] D. H. Whiffen, *Spectrochim. Acta*, **7**, 253 (1955).

TABLE V. SYMMETRY SPECIES AND NUMBER OF NORMAL MODES FOR MONOSUBSTITUTED BENZENE[3]

C_{2v}	E	$C_2(y)$	$\sigma(xy)$	$\sigma(yz)$	Null vib.	n	IR	R
A_1	1	1	1	1	T_y	12	a	a
A_2	1	1	−1	−1	R_y	4	f	a
B_1	1	−1	1	−1	T_x, R_z	12	a	a
B_2	1	−1	−1	1	T_z, R_x	8	a	a

f=forbidden a=active



z-Axis is normal to the plane of the benzene ring.

CH stretching modes of phenyl group at about 3000 cm^{-1} show perpendicular dichroism, is in good agreement with the presumption described above, because these bands should belong to A_1 or B_1 symmetry species.

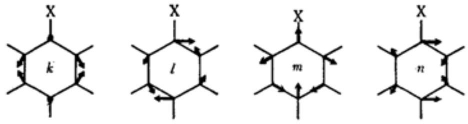
The bands at 1946, 1872, 1801, 1748 and 1675 cm^{-1} (IPS and IPTDS) all show perpendicular dichroism. The similar bands in the spectra of monosubstituted benzenes have been assigned to the binary combinations of the CH out-of-plane deformation vibrations of phenyl group as shown in Table VI by Whiffen[17] and Kakiuchi[16] independently. Liang and Krimm[3] have assigned these bands in the case of polystyrene as shown in the same table. The assignments of these bands to symmetry species A_1 or B_1 by all these authors are in accord with the perpendicular dichroism of the bands. But the assignments of the component fundamental frequencies 906 and 755 cm^{-1} by Liang and Krimm[3] are different from those by Whiffen[17] and Kakiuchi[16]. On this problem more detailed discussion will appear later.

TABLE VI. ASSIGNMENTS OF THE MAIN COMBINATION BANDS IN 2000∼1700 cm^{-1} REGION BY LIANG ET AL., WHIFFEN AND KAKIUCHI

Wave number cm^{-1}	Assignments	
	Liang and Krimm[3]	Whiffen[17] and Kakiuchi[16]
1946	$\nu_{17A}(A_2)+\nu_5(B_2)$, B_1	$j(B_2)+h(A_2)$, B_1
1872	$\nu_{17B}(B_2)+\nu_5(B_2)$, A_1	$i(B_2)+h(A_2)$, B_1
1801	$\nu_{10A}(A_2)+\nu_{17A}(A_2)$, A_1	$g(A_2)+h(A_2)$, A_1
1748	$\nu_{10A}(A_2)+\nu_{17B}(B_2)$, B_1	$i(B_2)+g(A_2)$, B_1

Notations of the vibrations in this table are those of Liang et al. and of Whiffen, respectively.

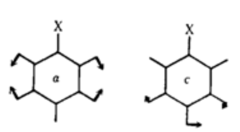
The four bands at 1602, 1583, 1493 and 1452 cm^{-1} (IPS and IPTDS) show perpendicular dichroism, and are not affected appreciably by deuteration. These facts are consistent with the assignments to the in-plane C–C stretching vibrations of phenyl group by Whiffen et al.[13,14] as follows[*6].



	(A_1)	(B_1)	(A_1)	(B_1)
IPS	1602	1583	1493	1452 cm^{-1}

Liang et al.[3] also have assigned these four bands to the C–C stretching model, except the assignments of 1602 and 1583 cm^{-1} bands (to the l and k modes, respectively).

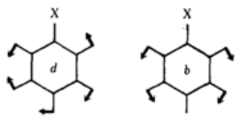
In the region of 1400∼1100 cm^{-1} the hydrogen deformation vibrations (CH_2 wagging and twisting, and CH wagging) of the main chain may couple to some extent with the in-plane vibrations of the benzene ring, showing the complex nature of the spectrum in the case of non-deuterated sample. In the spectrum of IPTDS the bands due to the vibrations of the deuterium of the main chain would shift to lower frequency region, and thus the aforementioned coupling may be removed. Accordingly the bands in this region may be considered to be mainly due to the vibrational modes of the benzene ring in the case of IPTDS. Thus the 1179 and 1154 cm^{-1} bands of IPTDS may be assigned to the a and c modes of monosubstituted benzene according to the Whiffen's notation.[9] It is difficult to settle the assignments of the 1328 and 1240 cm^{-1} bands from the present data.



	(A_1)	(B_1)
IPS	1185	1158 cm^{-1}
IPTDS	1179	1154

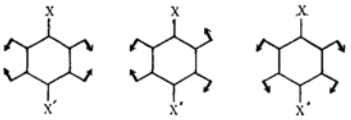
The 1070 cm^{-1} band (APS) may be assigned to the $d(\nu_{18B})(B_1)$ mode. The splitting of this band in the case of IPS may be explained by the intramolecular interaction. The 1028 cm^{-1} band may be assigned to the b $(\nu_{18A})(A_1)$ mode, as Whiffen and Liang et al. assigned.

[*6] In this paper the notation of the vibrational modes of the monosubstituted benzene by Whiffen (shown with h, j.⋯) will be mainly used for convenience, but those by Liang and Krimm (ν_{10A}, ν_{17A},⋯) will also be added if necessary.



	(B_1)	(A_1)
IPS	1080, 1048	1028 cm^{-1}
APS	1070	1028

The 1183, 1107 and 1021 cm^{-1} bands of IPPDS are considered to be the following CH in-plane modes, as Whiffen[14] and Ingold[11] assigned in the cases of *p*-substituted benzenes.



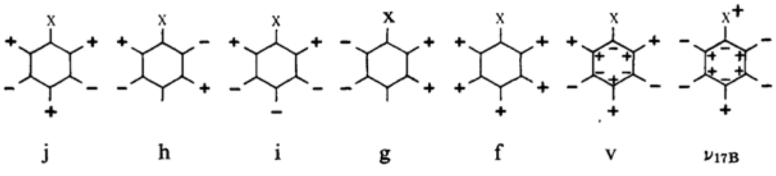
	(A_1)	(B_1)	(A_1)
IPPDS	1183	1107	1021 cm^{-1}
PPMS	1184	1110	1017

Here we have shown the data of poly-*p*-methylstyrene (PPMS) from our paper[10] for reference. The vibrational modes of the 1185 and 1028 cm^{-1} band of IPS are the same with those of the 1183 and 1021 cm^{-1} bands of IPPDS (and of the 1184 and 1017 cm^{-1} band of PPMS) respectively. In the cases of these two vibrational modes the hydrogen atom of the *p*-position does not move significantly. Thus, the experimental fact that the substitution of the *p*-hydrogen atom with deuterium or methyl group does not affect these two bands appreciably may be reasonably explained. The 1106 cm^{-1} band of IPPDS and the 1110 cm^{-1} of PPMS are supposed to be characteristic of the *p*-substituted benzenes. It is natural that the bands which correspond to the c and d modes of IPS do not appear in the spectra of IPPDS and PPMS, since these modes contain the displacement of *p*-hydrogen atom.

Phenyl Group Out-of-plane Vibrations. — As mentioned in the previous section, the assignments of the two bands at 906 and 755 cm^{-1} by Liang et al. are different from other authors (Whiffen[13] and Kakiuchi[16]), although the assignments of the other three bands (985, 965 and 842 cm^{-1}) in this region by all these authors are the same. They assigned these bands as shown in Table VII. The crystallization-sensitive 985 cm^{-1} band may be assigned to the j mode by considering the position. The 906 cm^{-1} band which splits into two bands of different polarizations with crystallization is assigned to the ν_{17B} vibration by Liang et al., while the band at 908 ± 10 cm^{-1} of monosubstituted benzenes was assigned to the i mode by Whiffen. Kakiuchi has calculated the frequency of this i mode to be 897 cm^{-1} assuming the mass of the substituent atom to be infinite, and has made the similar assignment as Whiffen's. On the other hand, Liang and Krimm have assigned the 755 cm^{-1} band to this i mode. The 755 cm^{-1} band (the 751 ± 15 cm^{-1} band of monosubstituted benzene) was assigned to the f mode known as the "umbrella" vibrational mode by Whiffen. Kakiuchi has calculated the frequency of this mode to be 716 cm^{-1}, and has made similar assignment. To this f vibrational mode, Liang and Krimm have assigned the band at 700 cm^{-1}. Although it is difficult to decide which

TABLE VII. CH OUT-OF-PLANE VIBRATIONS OF IPS

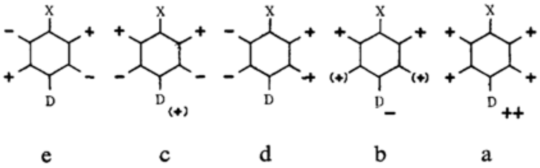
IPS			Monosubstituted benzene				
Frequency in cm^{-1}	Intensity	Dichroism	Average frequency and intensity (Whiffen)		Vibrational mode (sym. species) (Whiffen)	Calculated frequency (Kakiuchi)	Polystyrene (Liang et al.)
985	m	⊥	982 ± 6	vw	$j(B_2)$	1004	$\nu_5 = j$
965	w	⊥	962 ± 6	w	$h(A_2)$	984	$\nu_{17A} \fallingdotseq h$
906 { 920 898	m m	⊥ ∥	908 ± 10	mw	$i(B_2)$	897	ν_{17B}[a)]
842	w	⊥	837 ± 10	w	$g(A_2)$	837	$\nu_{10A} \fallingdotseq g$
760	vs	∥	751 ± 15	vvs	$f(B_2)$	716	$\nu_{10B} \fallingdotseq i$
700	vs	—	697 ± 11	vs	$v(B_2)$	—	$\nu_{11} \fallingdotseq f$



a) No vibrational mode which corresponds to the ν_{17B} of Liang and Krimm's notation is in Whiffen's assignment.

TABLE VIII. CH OUT-OF-PLANE VIBRATIONS OF IPPDS

IPPDS			*p*-Deuterotoluene (Kakiuchi[18])		
Frequency in cm^{-1}	Intensity	Dichroism	Frequency in cm^{-1}		Vibrational mode
			Calculated	Assigned	
960	w	—	984	951	e
948	m	$\parallel$	963	944	c
846	vs	$\perp$	837	840	d
			835	838	b
609	vs	$\perp$	630	607	a



assignment we should accept for polystyrene, it seems to be more favorable to apply Kakiuchi's assignment for this case, because of the agreement of the calculated value with the observed. Here we should mention the unexplainable dichroism of the 985 and 906 cm^{-1} bands, which are expected to have parallel dichroism because of their symmetry species B_2. These complexities of the bands sensitive to crystallization, would have occurred from the interaction between the molecules in the crystalline lattice and could not be explained by the treatment on a single helical chain, which is a first approximation for the interpretation of the spectra of crystalline polystyrene.

The assignment of the CH out-of-plane vibrations of IPPDS can be made as shown in Table VIII on the basis of the work on *p*-deuterotoluene by Kakiuchi. Although the vibrational mode assigned to the 948 cm^{-1} band of IPPDS is similar to that of the 983 cm^{-1} band of IPS, the dichroisms of these two bands are different from each other, as described in the previous section. This difference may be explained by the change of the nature of the interaction between the molecular chains in the crystalline lattice owing to the deuteration of the *p*-position.

For detailed interpretation of the spectrum and the elucidation of the nature of intermolecular interaction in crystalline region, further accumulation of the experimental data is going on.

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[18] Private communication.