Infrared Spectrum of Some Deuterated Crystalline Polystyrenes.
I. Isotactic Poly-αd_1-styrene

By Masamichi KOBAYASHI

(Received April 14, 1960)

During these a few years many studies have been made on the molecular structure of the stereospecific vinyl polymer, and it has been found that most of isotactic polymers have the helical structure in their crystalline regions mainly because of steric hindrances of side groups.

To make clear the helical structure of the polymer molecule, infrared spectroscopy is one of the most powerful methods as well as X-ray analysis.

Recently, Tadokoro et al[1]. reported the studies on the infrared spectra of isotactic polystyrene and its α, β, β-tri-deuterated derivative and detected that in the spectrum of the polystyrene the absorption bands appearing in region of $1400\sim1180\,\mathrm{cm}^{-1}$, such as the bands at 1364, 1314, 1297 and $1185\,\mathrm{cm}^{-1}$, are characteristic of the three-fold helical structure of the polystyrene molecule and assumed to be associated with the vibrations of CH_2, CH and the carbon skeletal chain.

To make the assignments of these bands more clearly it is desirable to study the spectra of several other deuterated derivatives. For this purpose, isotactic poly-αd_1-styrene was prepared and its infrared spectrum was studied.

Experimental

1. Preparation of αd_1-Styrene.—αd_1-Styrene was prepared by hydrolysis with deuterium oxide of the Grignard reagent of α-bromostyrene. From the massspectroscopic data, it was proved that the monomer prepared contained 99.5% of d_1-styrene. The infrared spectrum of this monomer is shown in Fig. 1 (solid line) in comparison with that of styrene (dotted line). It is justifiable to regard the sample as αd_1-styrene from a few spectroscopic evidences; the appearance of the band at $2230\,\mathrm{cm}^{-1}$ corresponding to the stretching vibration of CD group, the shift of the band corresponding to the C=C stretching from 1628 to $1614\,\mathrm{cm}^{-1}$ on deuteration and appearances of the bands corresponding to the bending vibration (at near $1400\,\mathrm{cm}^{-1}$) and the rocking vibration (at near $1160\,\mathrm{cm}^{-1}$) of CH_2 group in the spectra of both monomers.

To determine more precisely the position of the

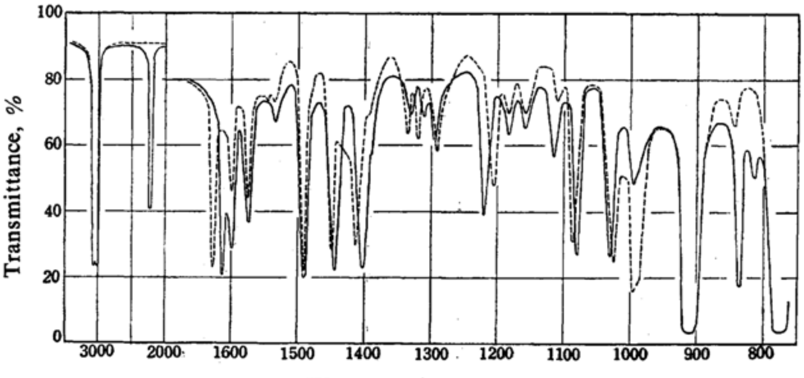

Fig. 1. Infrared spectra of αd_1-styrene (——) and styrene (----).

---

[1] H. Tadokoro, N. Nishiyama, S. Nozakura and S. Murahashi, *J. Polymer Sci.*, **36**, 553 (1959).

deuterium atom in this monomer, the proton magnetic resonance spectrum of this monomer was compared with that of styrene. The spectra were measured using a Nihon Denshi Kogaku N. M. R. spectrometer.

Proton signals of the spectrum of styrene, from lower to higher field, are assigned[2] to H_1, H_2, H_4 and H_3 respectively as shown in Fig. 2. While the signals due to H_3 and H_4 of styrene both split into quartets by spin coupling with H_2 and with each other, the spectrum of the ethylenic protons of the deuterated styrene is doublet with some closely spaced fine structure. If a small coupling constant between H_3 and H_4 is taken into account, this deuterated styrene can be identified as αd_1-styrene.

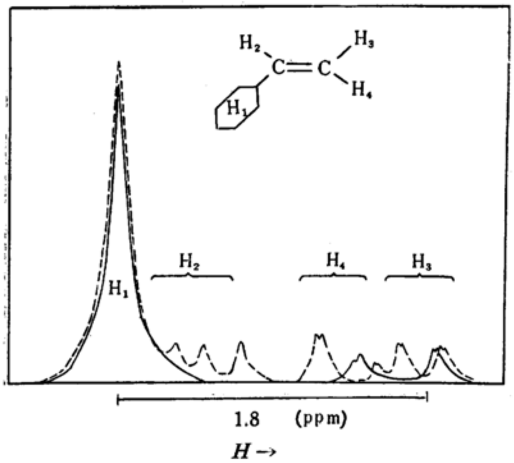

Fig. 2. Proton magnetic resonance spectra of αd_1-styrene (——) and styrene (----) at 40 Mc/sec.

2. Polymerization and Preparation of the Samples for I. R. Measurements.—The monomer was polymerized with Ziegler catalyst ($AlEt_3+TiCl_4$) in *n*-heptane and the polymer prepared was purified by the usual method. The films cast from the toluene solution were oriented by drawing them to about five times their original lengths in boiling water and were crystallized by heating at 60°C for 10 minutes in glycerol.

The I. R. spectra were measured in the region of 3500∼400 cm^{-1} using a Hilger H800 I. R. spectrometer and the polarized spectra were measured in the region of 3500∼650 cm^{-1} using a selenium polarizer.

Experimental Results

In Fig. 3a and 3b are shown the polarized spectra of isotactic poly-αd_1-styrene in the region of 3500∼2000 cm^{-1} and 1600∼650 cm^{-1} respectively. The wave numbers, the dichroisms and the relative intensities of the absorption bands are given in Table I in comparison with those of isotactic polystyrene.

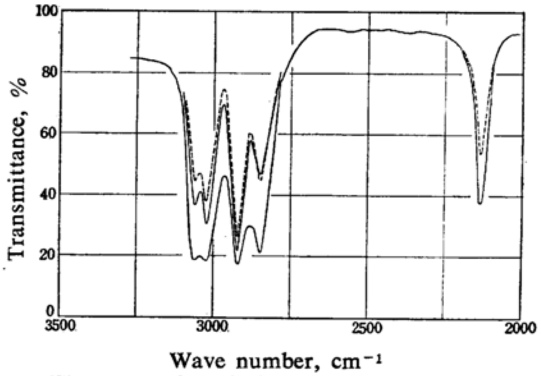

Fig. 3a. Infrared dichroisms of isotactic poly-αd_1-styrene.
—— electric vector perpendicular to elongation
---- electric vector parallel to elongation

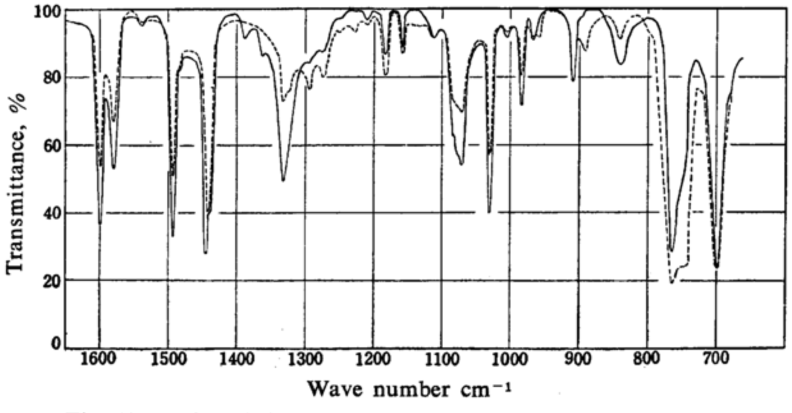

Fig. 3b. Infrared dichroisms isotactic poly-αd_1-styrene.
—— electric vector perpendicular to elongation
---- electric vector parallel to elongation

---

[2] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill Book Company, Inc., New York (1959), p. 238.

TABLE I. INFRARED SPECTRA OF ISOTACTIC POLYSTYRENE AND ISOTACTIC POLY-αd_1-STYRENE AND VIBRATIONAL ASSIGNMENTS

Polystyrene			Poly-α d_1-styrene			Assignments
Freq. (cm^{-1})	Dichr.	R. I.	Freq. (cm^{-1})	Dichr.	R. I.	
3082	σ	mw	3082	σ	mw	ν(CH) phenyl
3060	σ	s	3060	σ	s	
3025	σ	s	3025	σ	s	
2923	σ	vs	2923	σ	vs	$\nu(CH_2)$ asym
2849	—	s	2849	—	s	$\nu(CH_2)$ sym.
			2134	σ	m	ν(CD)
1602	σ	s	1600	σ	s	k* mode A_1
1580	σ	ms	1580	σ	ms	l* mode B_1
1493	σ	s	1495	σ	s	m* mode A_1
1452	σ	vs	1447	σ	vs	n* mode B_1
1444	—	ssh	1440	—	ssh	$\delta(CH_2)$ A+E
1389	σ	vw	1388	σ	vw	
1364	σ	ms				δ(CH)E
			1334	σ	ms	δ(CD)E ?
1314	σ	m				
1297	π	mw	1295	π	mw	$w(CH_2)$A
			1275	π	w	δ(CD)
1261	σ	w				
			1227	π	vw	
			1210	σ	vw	
1195	π	mw				w(CH)A
1185	π	mw	1183	π	mw	ν(CC)A
1180	?	mw	(1180)**			δ(CH) phenyl
1154	—	mw	1158	—	mw	c* mode B_1
1110	σ	w	1115	σ	w	
1080	σ	m	1084	σ	m	CH (or CD), CH_2+ phenyl
			1072	σ	msh	
1048	σ	m				
1028	σ	ms	1031	σ	ms	b* mode A_1
1005	σ	w	1005	σ	w	p* mode A_1
985	σ	m	985	σ	m	cryst. sensitive
964	—	w	968	—	w	h* mode A_2
			960	π	w	w(CD)A
920	σ	m				
906	π	m	910	—	m	i* mode B_2
898	π	mw	891	π	mw	
842	σ	mw	842	σ	w	g* mode A_2
783	π	ssh				
755	π	vs	765	π	vs	f* mode B_2
			748	π	ssh	
			705	π	vs	
700	π	vs	700	π	vs	
615		w	615		w	s* mode B_1
579		mw	570		mwsh	skeletal
557		s	557		s	v* mode+skeletal
489		vw	489		vw	skeletal

* Assignments of the normal mode of monosubstituted benzene according to Whiffen's notation.

** This band is assumed to overlap the band at 1183 cm^{-1}.

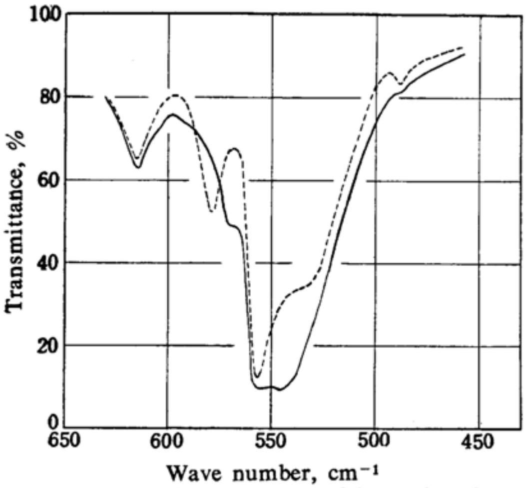

Fig. 3c. Infrared spectra of isotactic poly-αd_1-styrene (——) and isotactic polystyrene (----).

Discussions

1. General Discussions.—In the crystalline region, the molecule of isotactic polymer consists of a sequence of repeating units with a regular spatial arrangement. Strictly speaking, therefore, the molecular vibrations of the whole polymer molecule should be considered for the analysis of the absorption bands. Nevertheless, the normal modes of the phenyl group and the skeletal chain may be analyzed separately for the sake of simplicity. Comparing the spectrum of the isotactic polystyrene with that of the atactic one, most of the absorption bands associated with the phenyl group differ from each other by a small amount and, hence, this approximation seems reasonable for our case.

Since the molecular vibrations of the phenyl groups of polystyrene and its deuterated derivatives in which the deuterium is substituted in the skeletal chain may be regarded as those of monosubstituted benzene having a point symmetry C_{2v}³⁾, the assignments of some bands of these polymers immediately can be made from the well-known results on the molecular vibrations of monosubstituted benzene. In our case, the assignments are made according to Whiffen's notaion⁴⁾. The results are given in the last column of Table I. These bands are common to polystrene and the deutero-derivatives in wave number and dichroism. The bands assignable to the modes belonging to A_1 species, e. g., 1600, 1495, 1031 cm^{-1} bands, and B_1 species, e. g., 1580, 1462 cm^{-1} bands have σ nature, and, on the other hand, B_2 species, e. g., 765 cm^{-1} band, have π nature. These polarization properties may be interpreted by the molecular structure determined by Natta and Corradini⁵⁾.

The σ band which is crystallization-sensitive appears at the same wave number, 985 cm^{-1}, as those of polystyrene and poly-α, β, β d_3-styrene. This may be due to interactions between the phenyl groups of the neighboring molecules in the crystalline lattice.

In Fig. 3c are shown the spectra of isotactic poly-αd_1-styrene (solid line) and isotactic polystyrene (dotted line) in the region of 650～450 cm^{-1}. The band at 557 cm^{-1} which has been detected⁶⁾ as characteristic of the isotactic configuration of the polystyrene molecule also appears in isotactic poly-αd_1-styrene. This band might be assigned to the v-mode coupling with the skeletal vibration.

The molecular vibrations of the skeletal chain (consisting of CH (or CD) and CH_2 groups) of isotactic polystyrene or isotactic poly-αd_1-styrene may be considered as those of a one-dimensional three-fold helical chain having a point symmetry C $(2\pi/3)$⁷⁾. From the factor group analysis it is concluded that the normal vibrations of this chain are divided into two symmetry species; A (non-degenerate) and E (doubly degenerate), and the fundamentals of the former should have π nature and those of the latter σ nature. In physical meanings, the symmetry species correspond to the phase differences between the vibrations of the neighboring monomer units. Therefore, the normal modes of the helix can be considered as ones composed of the basic modes of the monomer units.

As for the stretching vibrations of CH_2 and CH (or CD) groups and the CH_2 bending vibration, the normal modes under the symmetry species A have almost the same frequencies as those under E species. The observed absorption band due to each of such modes, therefore, may be considered as that consisting of two overlapping bands, one being assigned to the mode under A and another to that under E.

The polarization properties of these bands depend on the chain conformation of the polymer molecule. In the spectrum of poly-αd_1-styrene, the band at 2923 cm^{-1} (antisymmetric CH_2 stretching) has σ nature and the band at 2849 cm^{-1} (symmetric CH_2 stretching)

---

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

4) D. C. Whiffen, *J. Chem. Soc.* **1956**, 1350.

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

6) M. Kobayashi, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

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

shows almost no dichroism. These results coincide whih Tadokoro et al.'s results on isotactic polystyrene and its several derivatives[8]. The band at 2134 cm^{-1} (CD stretching) has σ nature, and the band at 1440 cm^{-1} (CH_2 bending) shows almost no dichroism. Dichroic ratio is expressed for a uniaxial orientation as

$$(A_{\parallel}/A_{\perp}) = 2\cot^2\psi$$

where ψ is the angle between the transition moment accompanied with the vibration and the fiber axis.

The dichroic ratios calculated on the basis of the predicted molecular conformation are as follows; zero for $\nu_{\text{asym}}(CH_2)$, 0.78 for $\nu_{\text{sym}}(CH_2)$ and $\delta(CH_2)$, and 0.27 for ν(CD). The results well fit the polarization properties of these bands.

As for the deformation vibrations of CH_2 and CH (or CD) groups except $\delta(CH_2)$, the frequencies of the normal modes under A species, in general, differ from those under E. Since the relative intensity of each fundamental of these modes depends on the chain conformation of the polymer molecule, the assignments of some bands, therefore, may be made from the polarization properties and the relative intensities of the bands. Further, the changes in spectrum on deuteration give us some additional information for this purpose. On the basis of the molecular structure of isotactic polystyrene, it seems reasonable that relatively large intensities are expected for the banbs assignable to the deformation of CH (or CD) under E, δ(CH)E (δ(CD)E), the wagging of CH (or CD) under A, w(CH)A (w(CD)A), the rocking of CH_2 under E, r(CH_2)E, the wagging of CH_2 under A, w(CH_2)A, and the stretching of the skeletal carbon atoms under A, ν(CC)A.

2. Bands in the Region of 1400∼1180 cm^{-1}. —In this region appear the bands which have been considered by Tadokoro et al. as characteristic to the helical structure of polystrene.

The σ band at 1364 cm^{-1} of isotactic polystyrene disappears on deuteration, and the corresponding σ band of similar intensity appears at 1334 cm^{-1} in poly-αd_1-styrene. This fact may support the assumption that the band at 1364 cm^{-1} is mainly due to δ(CH)E. Whether the 1334 cm^{-1} band may be assigned to δ(CD)E is still in question, for there is a possibility of the appearance of the band associated with the phenyl group at this position.

The 1297 cm^{-1} band of isotactic polystyrene appears also in isotactic poly-αd_1-styrene, but not in the trideutero-derivative. Therefore, this band may be assigned to w(CH_2)A.

In the spectrum of isotactic polystyrene, there are three bands, i. e., 1195 (π), 1185 (π) and 1180 cm^{-1} (?) bands in the vicinity of 1180 cm^{-1}. The two π bands disappear in isotactic poly-αd_1-styrene. Since the CC stretching band and the CH wagging band are expected to be observed in this region, it seems reasonable to presume that one of them is due to ν(CC)A and another is to w(CH)A. The following facts may be cited to support the assignments of ν(CC)A to the 1185 cm^{-1} band and w(CH)A to the 1195 cm^{-1} band. (1) The 1195 cm^{-1} band appears in isotactic poly-βd_1-styrene.[9] (2) The 1183 cm^{-1} band of poly-αd_1-styrene shows a remarkable π nature. Although a band assignable to the a-mode (A_1) of the phenyl group is expected to appear in the vicinity of 1180 cm^{-1}, the 1183 cm^{-1} band could not be assigned to this mode because of its polarization property. Therefore, this may be due to the overlapping of the CC stretching mode and the a-mode.

The weak π band appears at 1275 cm^{-1} on deuteration. This may be due to the CD deformation. The weak π band at 960 cm^{-1} which appears on deuteration may be assigned to w(CD)A.

3. Other Bands. — Remarkable changes in the spectrum on deuteration are observed in the regions of 1085∼1040 cm^{-1} and 920∼810 cm^{-1}. While the atactic polystyrene band at 1070 cm^{-1} splits into two σ bands at 1080 and 1048 cm^{-1}, the corresponding bands of isotactic poly-αd_1-styrene appear at 1084 cm^{-1} and 1072 cm^{-1}. It seems reasonable to assume these bands as associated rather with the characteristics of the helical polymer chain themselves than with the interaction between the neighboring molecules in the crystalline lattice, for these bands do not disappear even at molten state. From the fact that the bands corresponding to them do not appear in some ring-substituted derivatives, e. g., poly-*p*-deutero-styrene[8] or poly-*p*-halogeno-styrenes[10], these may be due to the coupling of a vibrational mode of the phenyl group and that of CH_2 or CH (or CD).

Corresponding to the bands of isotactic polystyrene at 920 (σ), 910 (no dichroism) and 898 (π) cm^{-1} which are very sensitive to the crystallization degree of the sample, the π band and the band showing almost no dichroism appear at 891 cm^{-1} and 910 cm^{-1}

---

[8] H. Tadokoro, S. Nozakura, T. Kitazawa, Y. Yasuhara and S. Murahashi, This Bulletin, 32, 313 (1951); S. Murahashi, S. Nozakura and H. Tadokoro, ibid., 32, 534 (1959).

[9] M. Kobayashi, presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

[10] K. Nagai, M. Kobayashi and E. Nagai, presented at the 8th Annual Meeting of the Society of Polymer Science of Japan, Tokyo, May, 1959.

respectively in isotactic poly-αd_1-styrene. The band at near 910 cm^{-1} of both polymers may be assigned to an out-of-plane deformation of CH of the phenyl group (probably i-mode) since the corresponding band appears also in poly-$\alpha, \beta, \beta d_3$-styrene. The assignments of the other two bands are left uncertain for the present.

Summary

In Table I are given the results of discussions described above on the assignments of the absorption bands.

The bands characteristic to the isotactic polymers, i. e. the bands appearing in the region of 1400~1180 cm^{-1} or in the vicinity of 1070 and 900 cm^{-1}, are proved as associated with the CH_2 and CH groups.

To make assignments of the bands more precisely, the studies are in progress on the infrared spectra of the other several deuterated derivatives, such as poly-βd_1-, poly-$\alpha, \beta d_2$ and poly-β, β d_2-styrenes.

The author is indebted to Mr. Seiichi Mima for mass spectroscopic measurements and to Mr. Hiroshi Shima for measurements of proton magnetic resonance spectra.

Osaka Industrial Research Institute
Oyodo-ku, Osaka