Infrared Spectra of Some Deuterated Crystalline Polystyrenes. II. Isotactic Poly-βd_1-, Poly-α, βd_2- and Poly-β, βd_2-styrene

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In the previous paper¹⁾ were made the assignments of some absorption bands which have been regarded as characteristic of the helical conformation of the isotactic polystyrene (IPS) molecule, and it was concluded that the 1364 cm^{-1} band (σ) was assumed to be due mainly to the CH deformation, the 1297 cm^{-1} band (π) to the CH_2 wagging, the 1195 cm^{-1} band (π) to the CH wagging, and 1185 cm^{-1} band (π) to the stretching of the carbon skeletal chain. But some other bands which are also characteristic of the isotactic polymer remained as unassigned (E. X. the bands at near 1070 cm^{-1} and 900 cm^{-1}).

In order to gain more information for the assignments of the bands, in this paper some deuterated derivatives of IPS were synthesized, in which some of the hydrogen atoms attached to the skeletal chain were substituted with deuterium, such as poly-βd_1-styrene (Iβd_1), poly-α, βd_2-styrene (Iα, βd_2) and poly-β, βd_2-styrene (Iβ, βd_2), and their infrared spectra were investigated.

The characteristic bands showed considerable changes depending on the site and the number of the deuterium atoms in the molecule. On the basis of the results, the discussions were made on the assignments of these bands. But, for some of them, the dependences on deuteration were too complicated to assign them to

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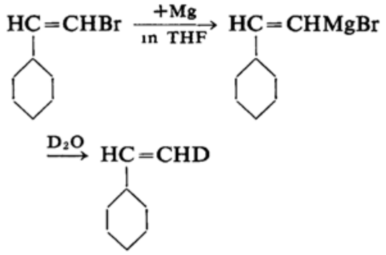
1) M. Kobayashi, This Bulletin, 33, 1416 (1960).

the simple vibrational modes of the molecucle.

The molecule of $I\beta d_1$ or $I\alpha, \beta d_2$ contains two assymmetric carbon atoms in one repeating unit, and the stereoregular polymer of this type has been termed recently "diisotactic polymer" by Natta[2]. Since the monomers used in this research were mixtures of the two geometrical isomers, although detailed discussions on the structure of the polymers of the new type could not be made, a few spectroscopic evidences were gained reflecting the differences in structure between so called threo and erythro diisotactic structures.

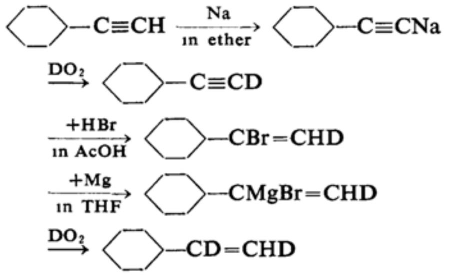
Experimental

Preparations of the Monomers. — βd_1-Styrene was synthesized by hydrolysis with deuterium oxide of the Grignard-reagent of β-bromostyrene;



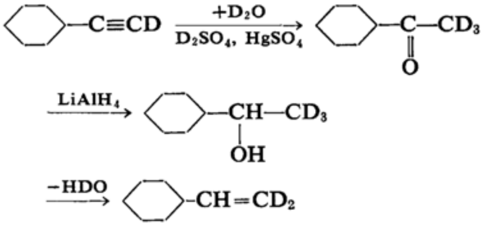
For this deuterated monomer, two geometrical isomers, cis and trans, are considered. Although it has been known that *trans*-β-bromostyrene can be prepared from cinnamic acid dibromide by Nef's method[3], according to which our sample was synthesized, the product usually contains a considerable amount of the cis-isomer. Moreover, it has still been uncertain whether the deuterium atom is substituted at the same position as the bromine by the reactions described above. Therefore, our deuterated monomer may be a mixture of cis- and trans-isomers. The NMR spectroscopic data of the sample showed that the latter was the predominant component (see Fig. 1).

$\alpha, \beta d_2$-Styrene was prepared by the following scheme;



Since the hydrogen atom is assumed to be added to cis and trans position with the same probability in the addition reaction of hydrogen bromide to the deuterated phenylacetylene, the product may be a 1 : 1 mixture of two geometrical isomers. This was confirmed by the NMR measurement as shown in Fig. 1.

$\beta, \beta d_2$-Styrene was prepared as following;



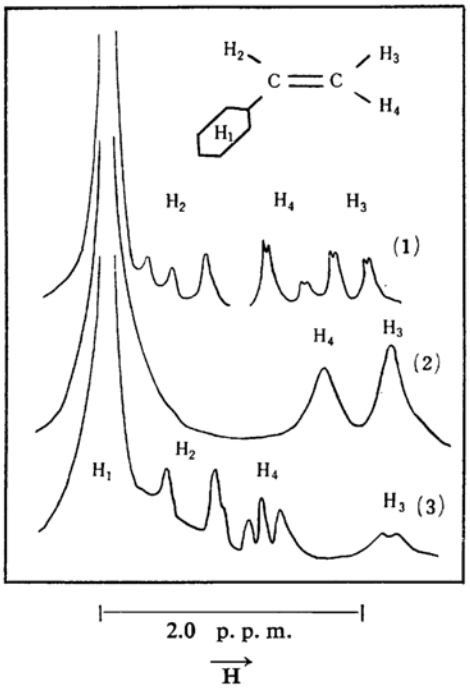


Fig. 1. Proton magnetic resonance spectra of styrene and its deuterated derivatives.

(1) Styrene (2) $\alpha, \beta d_2$-Styrene
(3) βd_1-Styrene

Polymerization. — The monomers were polymerized with Ziegler type catalyst and the samples of the crystalline polymers for infrared measurements were prepared according to the same method as that described in the previous paper.

Infrared Spectra Measurements. — The infrared spectra of each sample was measured using a Hilger H800 infrared spectrometer and the polarized spectra were measured with a selenium polarizer.

Experimental Results

The polarized spectra in the regions of 3500~1600 cm^{-1} and 1600~650 cm^{-1} of the oriented samples are shown in Fig. 2 and Figs. 3a—3c respectively.

Depending on the site and the number of the deuterium atoms substituted in the polymer molecule, some remarkable differences in

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[2] G. Natta, *Makromol. Chem.*, 35, 94 (1960).

[3] J. V. Nef, *Ann.*, 308, 267 (1899).

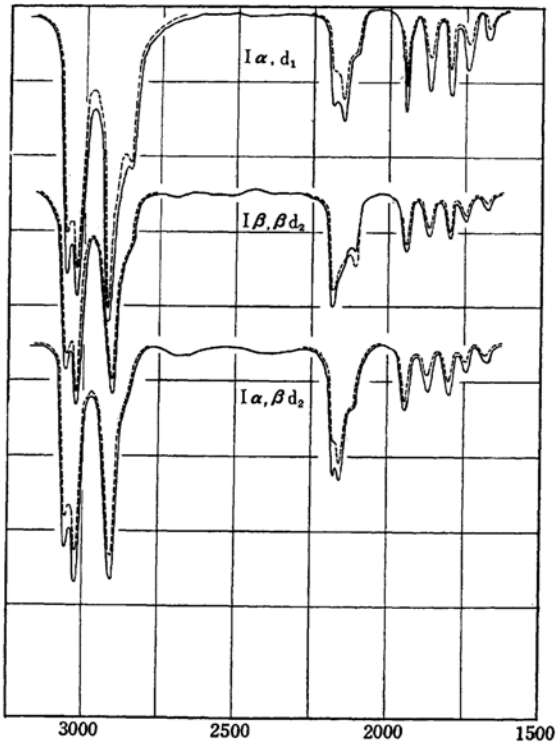

Fig. 2. Infrared dichroisms of the deuterated derivatives of isotactic polystyrene.
—— Electric vector perpendicular to elongation
---- Electric vector parallel to elongation

spectrum among the samples were observed, mainly in the regions of 2500~2000 cm^{-1} (associated with the stretching vibrations of the CD and the CD_2 groups), 1450~1180 cm^{-1} (the deformational vibrations of the CH and the CH_2 groups), 1100~1040 cm^{-1} and 920~890 cm^{-1}. In Table I the main bands of the samples in these regions are compared with each other. The data of IPS and Iαd_1 are cited for comparison.

Discussion

The Bands due to the Stretchings of the CD and the CD_2 Groups. — The CD (and CD_2) stretching bands appear in the region of 2200~2100 cm^{-1}. The well-known three-fold helical structure of the molecule of IPS is reflected by the polarization properties of the bands; (1) all bands due to the CD stretching show a remarkable σ nature, and (2) 2186 cm^{-1} band (corresponding to the CD_2 assymmetric stretching) and the 2106 cm^{-1} band (the CD_2 symmetric stretching) of Iβ, βd_2 show σ and π nature respectively.

The frequency of the CD stretching depends on the position of the deuterium in the molecule. While the band of Iαd_1 appears at 2134 cm^{-1}, two σ bands appear at 2183 and 2150 cm^{-1} in Iβd_1.

As described in the introduction, two kinds of isotactic structure can be considered for the molecule of Iβd_1. On the basis of the results of the factor group analysis for the three-fold helical polymer, although two bands due to the CD stretching are expected to be observed in Iβd_1, they should be of opposite dichroism. Therefore, the two σ bands of our sample may predict the presence of the two stereo-isomers in the sample. These bands differ in intensity with each other (the 2150 cm^{-1} band

TABLE I. ABSORPTION BANDS CHARACTERISTIC OF THE HELICAL CONFORMATION OF ISOTACTIC POLYSTYRENE

IPS		Iαd_1		Iβd_1		Iβ, βd_2		Iα, βd_2		Assignment
Freq. cm^{-1}	RI	Freq. cm^{-1}	RI	Freq. cm^{-1}	RI	Freq. cm^{-1}	RI	Freq. cm^{-1}	RI	
				2183 σ	m	2186 σ	ms	2187 σ	ms	ν (CD) or ν (CD_2)
				2150 σ	m	2150 σ	msh	2155 σ	ms	
		2134 σ	m	2102 —	wsh	2106 π	m	2102 —	m	
1444 —	ssh	1440 —	ssh							δ (CH_2) A+E
1364 σ	ms			1363 σ	ms	1356 σ	mw			δ (CH) (mainly)
		1334 σ	ms					1332 σ	ms	
1314 σ	m	1311 σ	m	1311 σ	m	1301 σ	m	1311 σ	m	δ (CH)
1297 π	mw	1295 π	mw	(1297) σ	wsh	(1297) σ	wsh	(1295) σ	mw	w (CH_2) A
1195 π	mw			1195 π	mw	1195 π	vw			w (CH) A
1185 π	mw	1183 π	mw	1185 π	mw	1181 π	mw	1180 π	mw	ν (CC) A
1180 π	mw									
1080 σ	m	1084 σ	m	1084 σ	ms	1080 σ	s	1080 σ	s	skeletal mode + in-plane deformation
		1072 σ	m	1071 σ	msh			1070 σ	msh	
1048 σ	m									
920 σ	m	910 —	m	912 σ	m	908 σ	m	908 σ	m	i-mode + r(CH_2)
906 —	m									
898 π	w	891 π	mw	903 π	m	905 π	m	905 π	m	

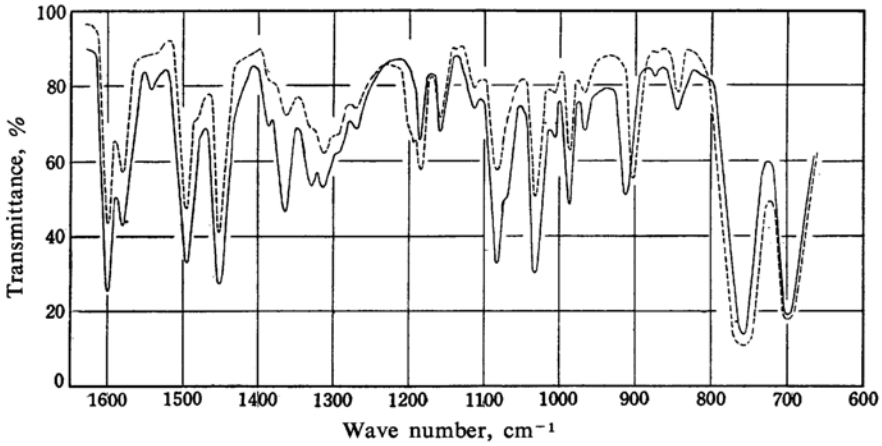

Fig. 3a. Infrared dichroisms of Iβd$_1$.

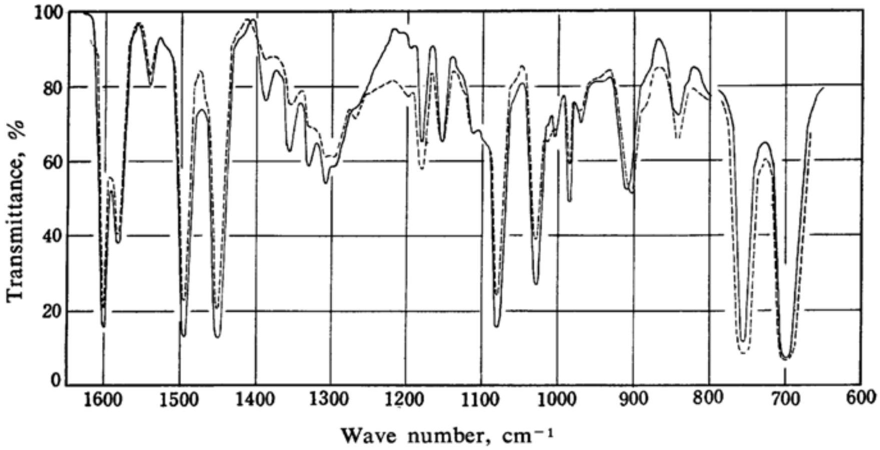

Fig. 3b. Infrared dichroisms of Iβ, β, d$_2$.

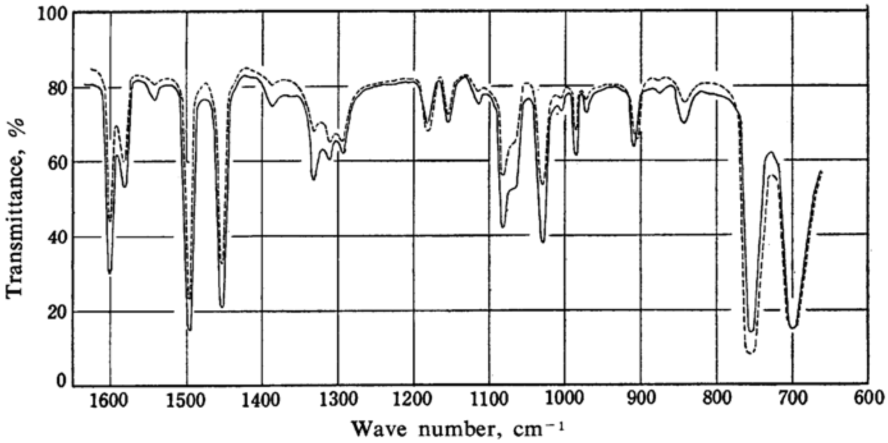

Fig. 3c. Infrared dichroisms of Iα, βd$_2$.

—— Electric vector perpendicular to elongation

- - - - Electric vector parallel to elongation is greater than the 2183 cm^{-1} band) and this fact is assumed to result from the composition of the geometrical isomers of the monomer used.

The same discussions should be undertaken about Iα, βd$_2$, nevertheless, in this case, we could not make a simple assignment because of the complexity resulting from an interaction between the neighboring CD groups.

The Bands in the Region of 1450～1180cm^{-1}.—The spectra of the region are very important since the absorption bands characteristic of the isotactic polymers appear mainly in this region. The strong shoulder at 1440 cm^{-1} appearing in IPS and Iαd$_1$ is not observed in the other deuterated samples. This fact supports the conclusion assigning the band to the CH$_2$ bending. The 1364 cm^{-1} σ band of IPS is affected by deuteration; it appears at slightly lower frequency (1363 cm^{-1}) in Iβd$_1$, appears at 1356 cm^{-1} and decreases its intensity in Iβ, β d$_2$, appears at 1334 cm^{-1} in Iαd$_1$, and at 1332 cm^{-1} in Iα, βd$_2$.

Although the greater effect of the substitution of α-hydrogen on the frequency may suggest a validity of assigning the band of IPS mainly to the CH deformation, the changes in frequency and intensity on β-deuteration show that this band should be assigned to a more complicated vibrational mode.

Admitting a few differences in frequency, the 1314 cm^{-1} σ band of IPS observed in each of the deuterated derivatives; 1311 cm^{-1} in Iαd$_1$, Iβd$_1$ and Iα, βd$_2$, and 1301 cm^{-1} in Iβ, βd$_2$. Since the corresponding band does not appear in poly-α, β, βd$_3$-styrene (Iα, β, βd$_3$)[4], this band may be assumed to be associated with a deformational mode of the CH group of the skeletal chain.

From the fact that the 1297 cm^{-1} band of IPS was not observed in the deuterated derivatives except Iαd$_1$ (the σ bands appearing at the same frequency in β-deuterated derivatives should be distinguished from it because of the discrepancy of polarization property), this may be assigned to the CH$_2$ wagging.

The 1195 cm^{-1} π band of IPS is not observed in the α-deuterated derivatives but appears at the same frequency in Iβd$_1$ and Iβ, βd$_2$, in the latter case a moderate decrease in relative intensity being accompanied by it. This fact may support the assumption assigning the band to the CH wagging.

The Bands at near 1070 cm^{-1}.—The 1070 cm^{-1} band of atactic polystyrene (APS) splits into two σ bands (1080 cm^{-1} and 1040 cm^{-1}) in IPS at crystallized state. The similar splitting of of IPS has been observed even in a molten or dissolved sample in these cases the peaks become obtuser and are spaced more closely). Therefore, the band splitting is assumed to arise from an intramolecular interaction between neighboring groups. This assumption seems to be supported by the following experimental facts which have been detected by Tadokoro et al.[5],*; the 1048 cm^{-1} band of IPS appears in a mixed sample of IPS and Iα, β, β d$_3$, while the crystallization sensitive band at 983 cm^{-1} of IPS decreases in intensity in the mixed sample and, therefore, has been concluded to be associated with an intermolecular interaction of the neighboring molecules in the crystalline lattice.

Although it was expected that some information would be gained about this band splitting from the data of various kinds of deuterated derivatives, the changes in the bands on deuteration are so complicated that it seems difficult to make a precise assignment. The 1048 cm^{-1} band of IPS disappears in the skeletal-deuterated samples regardless of the positions of the deuterium atoms in the molecules. The same facts have been observed[6] in the case of poly-*p*-deuterostyrene. The 1080 cm^{-1} band of IPS appears in all of our samples and also in Iα, β, βd$_3$. The relative intensity decreases with the number of the hydrogen atoms of the β-position, while it is hardly affected by whether the α-position is deuterated or not. In the deuterated samples having one or two hydrogen atoms at the β-position, such as Iαd$_1$, Iβd$_1$ and Iα, βd$_2$, the σ band appears at near 1070 cm^{-1}. The corresponding band is not observed in Iβ, βd$_2$ and Iα, β, βd$_3$. These results are shown in Fig. 4.

Although these facts may imply a contribution of the CH and the CH$_2$ groups to the band splitting in IPS, that of the phenyl group must be considered since the bands are also remakably affected by the deuteration of the phenyl nucleus. Referring to the spectroscopic data of many other vinyl polymers, it may be expected that a σ band may be found due to the stretching vibration of the skeletal chain, ν(CC)E, in this region.

These bands may be assumed to be associated with skeletal modes coupled with a CH in-plane-deformation of the phenyl group.

The Bands at near 900 cm^{-1}.—The 906 cm^{-1} band of APS splits into three bands, 920 cm^{-1} (σ), 906 cm^{-1} (no-dichroism) and 898 cm^{-1} (π), in the crystallized sample of IPS. The band

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

[5] H. Tadokoro, T. Kitazawa, S. Nozakura and S. Murahashi, *High Polymer Chem. (Kobunshi Kagaku)*, **17**, 231 (1960).

* The authors did not discuss the 1048 cm^{-1} band in their paper, but in the spectra shown in the Fig. 3 of the paper we can find out the fact pointed out here.

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

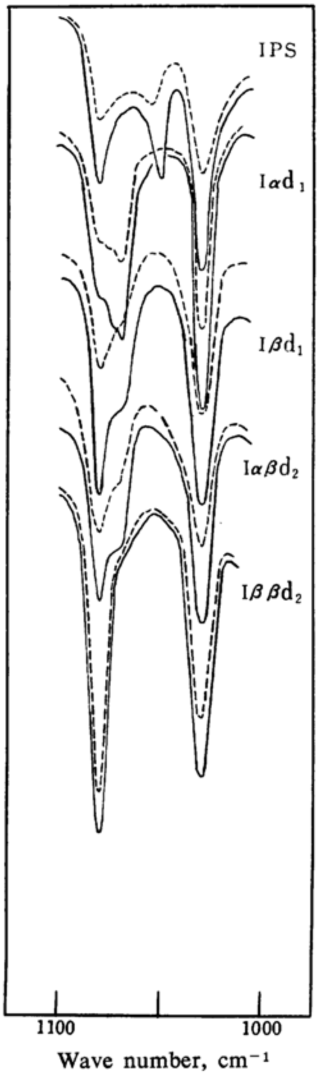

Fig. 4. Absorption bands at near 1070 cm^{-1}.

—— Electric vector perpendicular to elongation
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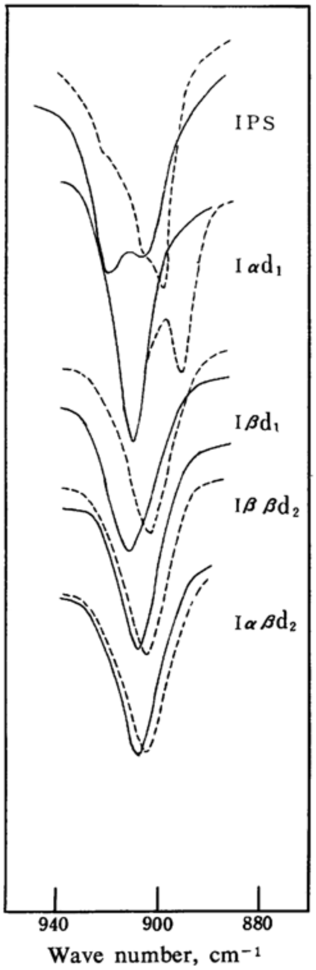

Fig. 5. Absorption bands at near 900 cm^{-1}.

—— Electric vector perpendicular to elongation
---- Electric vector parallel to elongation

splitting is sensitive to the degree of crystallinity of the sample and is not observed in the quenched or molten sample. Although it is expected that at this frequency the π band assignable to Whiffen's i-mode of mono-substituted benzene (out-of-plane CH deformation) may be found, it was detected that the bands were affected by deuteration of the skeletal hydrogen atoms as shown in Fig. 5. In Iβd_1, Iα, βd_2 and Iβ, βd_2, the closer spaced two bands of equal intensity appear at near 900 cm^{-1} (912 cm^{-1} and 903 cm^{-1} in the case of Iβd_1; 908 cm^{-1} and 905 cm^{-1} in Iα, βd_2 and Iβ, βd^2), the higher band showing σ nature and the lower band π nature. Similar bands were observed in Iα, β, βd_3. They may be assigned to i-mode and the difference in polarization property may correspond to the phase difference of the vibration of the neighboring phenyl groups in one molecule. The spectrum in this region of Iαd_1 is different not only from that of IPS but from that of the other deuterated samples; in this case the band exhibiting a remarkable σ nature is not observed and the corresponding 910 cm^{-1} band shows almost no dichroism. Further, the π band of smaller intensity appears at the lower frequency, 891 cm^{-1}. From these facts it may be concluded that the CH_2 rocking vibration has an influence on the spectrum in this region.

Thus the effects of deuteration on the spectrum, especially that in the region of 1500~850 cm^{-1} are very complicated. For the assignments of the bands in this region, one should take into account some couplings of the deformations of the phenyl group with the skeletal modes or with the CH (or CH_2) deformational modes.

From this point of view the studies are in progress on the infrared spectra of some ring-deuterated derivatives of IPS.

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