# *Infrared Spectra of Isotactic Poly-α-olefins*[*]

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In the previous paper[1], we have reported that the infrared absorption bands at 1364, 1314, 1297 and 1185 $\mathrm{cm}^{-1}$ of isotactic polystyrene (IPS) and its derivatives are considered to be closely associated with the helical structure of the isotactic polymers (mainly due to the $CH_2$, CH and C–C vibrations of the main chain having the alternate sequence of gauche and trans conformations) and that these bands may be used as the criterion for the isotactic structure. Furthermore, it has been confirmed from the infrared spectra of the mixture of IPS and isotactic poly-$\alpha, \beta, \beta$-trideuterostyrene (IPTDS) that these bands are originated from the intramolecular interactions in the helical chain[2]. In this communication we wish to report the results obtained

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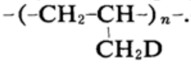
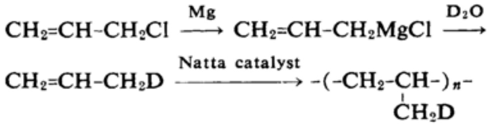
[1] H. Tadokoro, S. Nozakura, T. Kitazawa, Y. Yasuhara and S. Murahashi, This Bulletin, 32, 313 (1959).

[2] H. Tadokoro, T. Kitazawa, S. Nozakura and S. Murahashi, *Chem. High Polymers* (*Kôbunshi Kagaku*), 17, 231 (1960).

from the infrared spectra measured on the following polymers in order to examine whether similar bands appear or not.

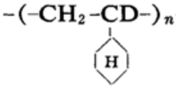
*Polypropylene.*—We have used the ethyl ether extract of Moplen MS as the atactic sample (APP), and its *n*-heptane residue as the isotactic sample (IPP).

*Isotactic and Atactic Poly-3-deuteropropene-1 (IPP-3D and APP-3D)*  $-(-CH_2-\underset{CH_2D}{CH}-)_n-$.—Prepared according to the following scheme, and separated by the same procedure as in the case of polypropylene:



$$CH_2{=}CH{-}CH_2Cl \xrightarrow{Mg} CH_2{=}CH{-}CH_2MgCl \xrightarrow{D_2O}$$
$$CH_2{=}CH{-}CH_2D \xrightarrow{\text{Natta catalyst}} -(-CH_2-\underset{CH_2D}{CH}-)_n-$$

*Polybutene-1.*—Polymerized with Ziegler catalyst. We used the ethyl ether extract as the atactic sample (APB), and its residue as the isotactic sample (IPB).

*Isotactic Polyvinylcyclohexane (IPVCH) and Poly-α-deuterovinylcyclohexane (IPDVCH)* —  $-(-CH_2-CD-)_n-$.—(kindly given by Professor C. G. Overberger of the Polytechnic Institute of Brooklyn).

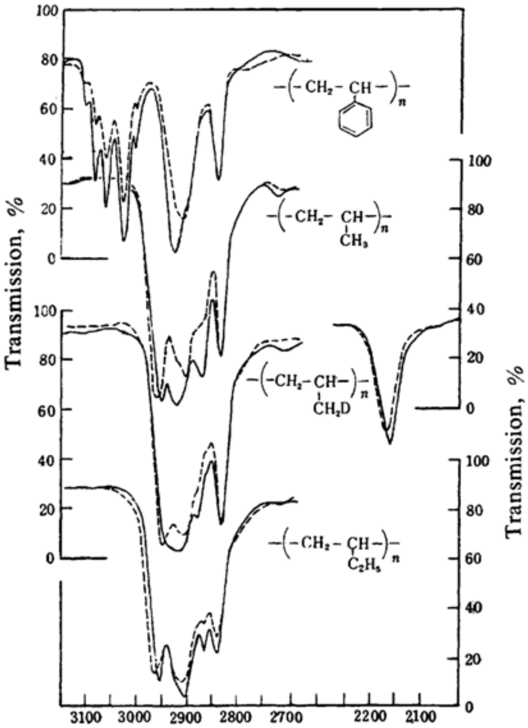


Fig. 1. Infrared dichroism of isotactic polystyrene, polypropylene, poly-3-deuteropropene-1 and polybutene-1 (LiF optics).

—— Electric vector perpendicular to elongation

---- Electric vector parallel to elongation

Figure 1 shows the infrared dichroism (LiF optics) of IPP, IPP-3D and IPB as well as IPS for reference. The bands in the 3$\mu$ region appear at nearly the same frequencies as the characteristic values of the $CH_2$ and $CH_3$ stretching modes of *n*-paraffins (2960(∥) 2953 (⊥): $\nu_a$ ($CH_3$), 2920(⊥) : $\nu_a$ ($CH_2$) (*E*), 2905 (∥): $\nu_a$ ($CH_2$) (*A*), 2876(⊥) : $\nu_s$ ($CH_3$) (*E*), 2844(no): $\nu_s$ ($CH_2$) (*A* and *E*) for IPP). As we have already reported, no (or weak) dichroism of the 2849 cm$^{-1}$ $\nu_s$ ($CH_2$) band and the distinguished perpendicular dichroism of the 2924 cm$^{-1}$ $\nu_a$ ($CH_2$) band of IPS may be interpreted by the inclination of the $CH_2$ group. This dichroic feature may be expected to be found in the spectra of all kinds of helical isotactic polymers[3]. In fact, this feature has been

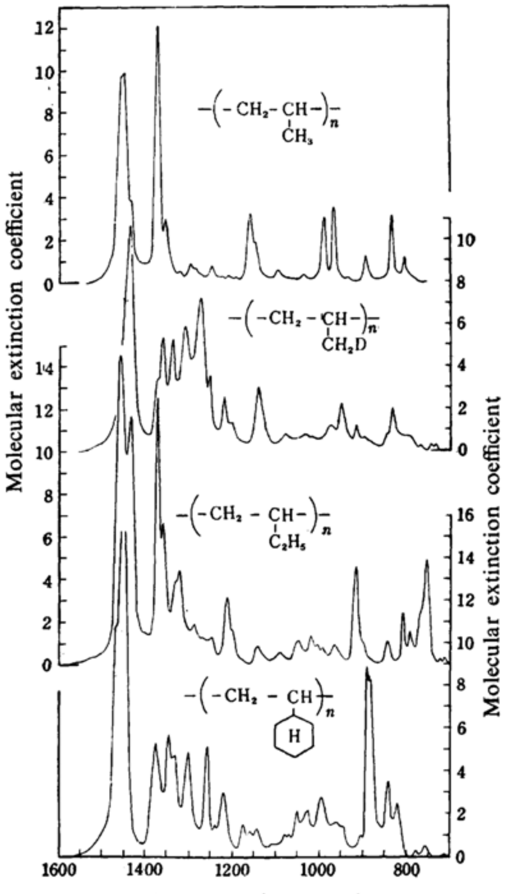


Fig. 2. Infrared spectra of isotactic poly-$\alpha$-olefins.

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

observed in the spectra of IPP and IPP-3D. Although IPP-3D has another $CH_2$ group in the side chain besides the $CH_2$ group in the main chain, it will be clear from a simple consideration that the dichroism of the $\nu_s$ ($CH_2$) band may be absent, if the $CH_2$ group assumes the three stable positions about the C-$CH_2D$ axis with equal probability. This dichroic feature is obscured in the cases of IPB, IPVCH and IPDVCH, because of the complexity due to the existence of $CH_2$ groups in the side chain. In the spectra of IPS and IPP, there are appreciable shifts between perpendicular and parallel components of the $\nu_a$ ($CH_2$) band, and furthermore the perpendicular component occurs at higher frequencies and parallel ones at lower in both spectra. The splitting of the perpendicular and parallel components are also observed in the $\nu_a$ ($CH_3$) bands in the spectra of IPP and IPB, but in these cases the perpendicular ones occur at lower frequencies. The splitting of the $\nu_a$ ($CH_2$) bands may be explained from the factor group consideration reported already in the case of IPS⁽⁴⁾. The band splitting of the $\nu_a$ ($CH_3$) modes involves an interesting problem in relation to the perturbation of the environment to the local degeneracy of the $CH_3$ group.

Figure 2 is the infrared spectra (1600~700 $cm^{-1}$) of isotactic poly-$\alpha$-olefins rewritten on the scale of molecular extinction coefficient. In Fig. 3, the spectra of the isotactic and atactic samples of poly-$\alpha$-olefins at room temperature were compared with those of the molten states of the isotactic samples. Figure 4 shows the infrared dichroism (NaCl region) of isotactic poly-$\alpha$-olefins. We have found that several bands at 1400~1100 $cm^{-1}$ region of the spectra of isotactic poly-$\alpha$-olefins show behavior similar to that of the bands of IPS and its derivatives mentioned at the beginning of this article. The bands observed at 1364

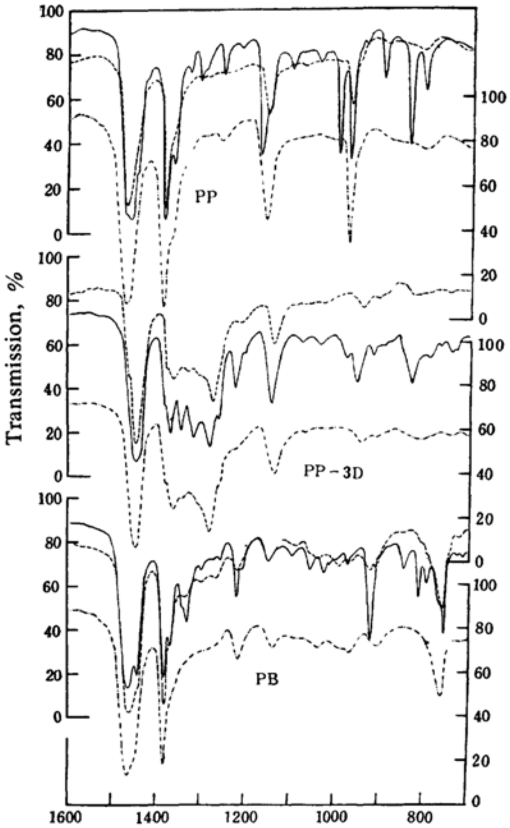

Fig. 3. Infrared spectra in various states of poly-$\alpha$-olefins.
—— Isotactic samples
---- Atactic samples
-·-·- Molten states of isotactic samples

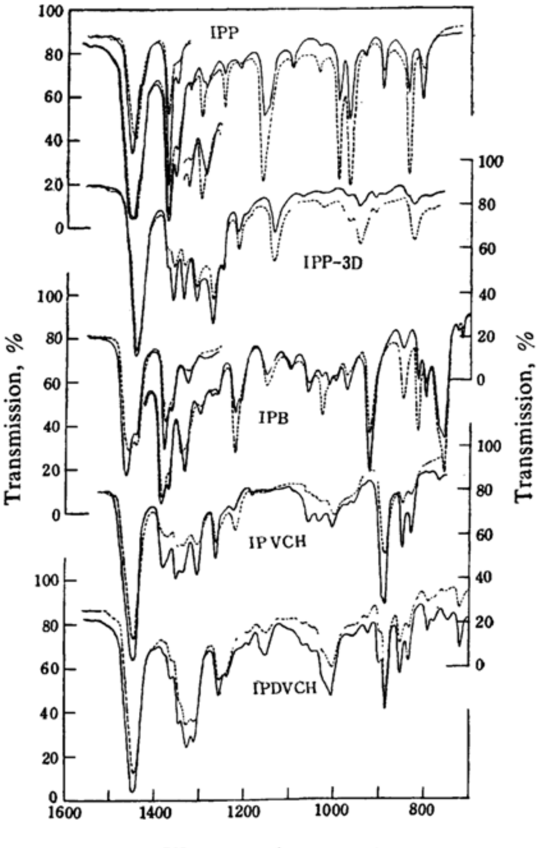

Fig. 4. Infrared dichroism of isotactic poly-$\alpha$-olefins (NaCl optics).
—— Electric vector perpendicular to elongation
---- Electric vector parallel to elongation

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4) H. Tadokoro, N. Nishiyama, S. Nozakura and S. Murahashi, ibid., 34, 381 (1961).

$cm^{-1}$ in the spectra of IPS and its derivatives[1,3,5] appear also in the spectra of IPP, IPP-3D, IPB and IPP-3, 3, $3D_3$[6] at the same frequency, and moreover exhibit the same characteristic behavior: (1) the perpendicular dichroism, (2) similar intensity (2∼5 in molecular extinction coefficient), (3) absence in the cases of the atactic samples and (4) decrease of the intensity with heating and disappearance at molten state. This band is not observed in the spectra of IPTDS, isotactic poly-$\alpha D_1$-styrene[7], IPP-1, $1D_2$[6], IPP-2D[6]. The above mentioned inference for this band may be considered to be supported strongly by these experimental evidences. Especially, the constancy of the frequency (1365∼1360 $cm^{-1}$) extending over the various samples of IPS, its derivatives and isotactic poly-$\alpha$-olefin swill suggest the approximate localization of the vibrations in the skeleton and the attached hydrogen atom, comparing them to the bands described subsequently. Some bands similar to the 1185 $cm^{-1}$ band of IPS (and 1183 $cm^{-1}$ of isotactic poly-*p*-deuterostyrene, 1184 $cm^{-1}$ of isotactic poly-*p*-methylstyrene, 1190 $cm^{-1}$ of isotactic poly-*m*-methylstyrene, 1184 $cm^{-1}$ of isotactic poly-*p*-trimethylsilylstyrene) are observed in the spectra of IPP (1167 $cm^{-1}$), IPP-3D (1216 $cm^{-1}$), IPB (1217 $cm^{-1}$) and IPVCH (1217 $cm^{-1}$) with the same parallel dichroism, the similar intensity (2.5∼4.5 in molecular extinction coefficient) and the similar band shapes. In addition this band is absent in the spectra of atactic samples and IPTDS, IPDVCH, IPP-1, $1D_2$[6], IPP-2D[6] and IPP-3, 3, $3D_3$[6]. Consequently these bands are considered to be due to similar origin. In spite of the approximate constancy of the frequency in the case of IPS and its derivatives, the frequency differs considerably in the spectra of poly-$\alpha$-olefins. This fact suggests that in the mode assignable for this type of band the vibration in the main chain would couple with those of the side chain appreciably in the cases of poly-$\alpha$-olefins, while it would not do so with the phenyl side group.

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[5] M. Kobayashi, K. Nagai and E. Nagai, ibid., **33**, 1421 (1960).

[6] C. Y. Liang, M. R. Lytton and C. J. Boone, *J. Polymer Sci.*, **44**, 549 (1960).

[7] M. Kobayashi, This Bulletin, **33**, 1416 (1960).