Infrared Absorption Bands Possibly Associated with the Helical Structure of Polystyrene, Poly-p-methylstyrene and Poly-m-methylstyrene Prepared with Ziegler Catalyst

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In a previous paper[1] we have briefly suggested the possibility that the several bands of the spectrum of isotactic polystyrene might be associated with the threefold screw-axis of this polymer. On carrying out further studies in relation to this problem, we have found some experimental facts which supports this possibility as well as the inference that poly-*p*-methylstyrene and poly-*m*-methylstyrene prepared with Ziegler catalyst might have the isotactic structure, although they did not show distinct crystallinity.

Fig. 1 partly reproduces the spectra of of the films of crystallized and quenched

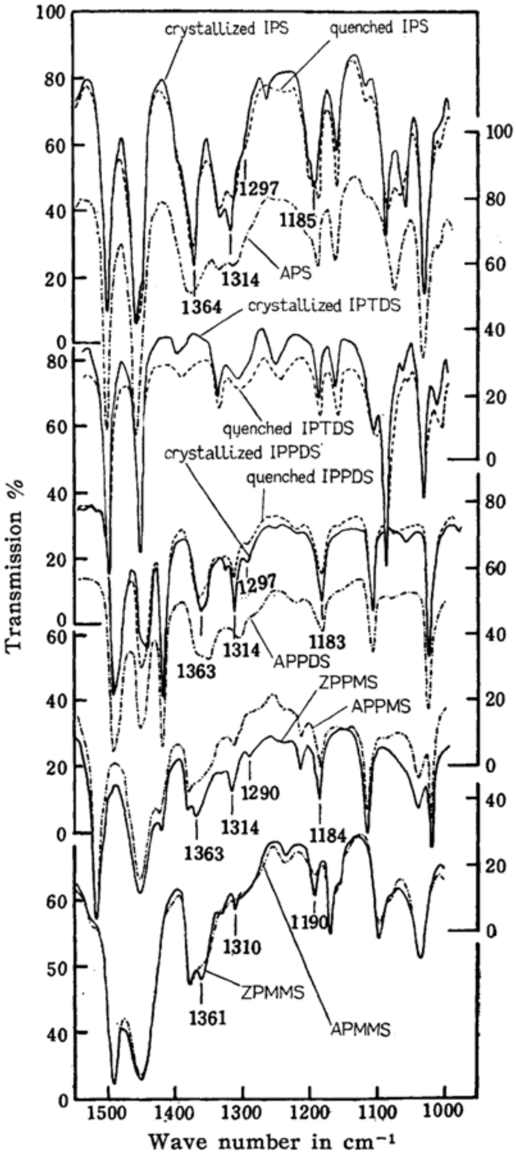

Fig. 1. Infrared spectra of crystallized and quenched IPS, APS, crystallized and quenched IPTDS, crystallized and quenched IPPDS, APPDS, ZPPMS, APPMS, ZPMMS and APMMS.

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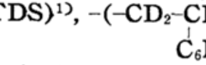
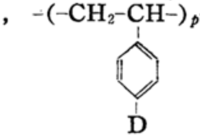
[1] H. Tadokoro, N. Nishiyama, S. Nozakura and S. Murahashi, *J. Polymer Sci.*, to be published.

isotactic polystyrene (IPS)[2,3] atactic polystyrene (APS), crystallized' and quenched isotactic poly-α,β,β-trideuterostyrene (IPTDS)[1], 
$-(-CD_2-\underset{C_6H_5}{\underset{|}{CD}}-)_p-$, crystallized and quenched isotactic poly-*p*-deuterostyrene (IPPDS),  atactic poly-*p*-deuterostyrene (APPDS), poly-*p*-methylstyrene prepared with Ziegler catalyst (ZPPMS), atactic poly-*p*-methylstyrene (APPMS), poly-*m*-methylstyrene prepared with Ziegler catalyst (ZPMMS) and atactic poly-*m*-methylstyrene (APMMS). Fig. 2 shows the polarized spectra of the oriented-and-crystallized IPS, IPTDS and IPPDS samples. The spectra of IPS and IPPDS exhibit several bands showing the same dichroism and the similar behavior on crystallization at nearly the same wave numbers; 1364 ($\perp$), 1314 ($\perp$), 1297 ($\parallel$) and 1185 cm^{-1} ($\parallel$). These four bands appear in weak intensity even in the spectra of quenched samples of IPS and IPPDS which give amorphous X-ray patterns, while they do not appear in the spectra of APS and APPDS. As these four bands are absent in the spectrum of IPTDS, these bands are considered to be not directly associated with the vibrations of the phenyl group, but with that of main chain. The first three bands at 1364, 1314 and 1297 cm^{-1} may be in the region assignable to CH_2 and CH wagging and CH_2 twisting, and the fourth at 1185 cm^{-1} in the region of CH_2 twisting and C–C stretching[4]. Hence the bands in these regions may be expected to be easily affected by the changes of the skeletal configurations. We could therefore consider that those bands are closely associated with the intramolecular interactions in the helical chain having the three-fold screw-axis (alternate sequence of *gauche* and *trans* conformation)[2,5]. The occurrence of these bands in the spectra of the quenched samples of IPS and IPPDS may be interpreted as indicating the existence of the locally remained helical structure in the amorphous region.

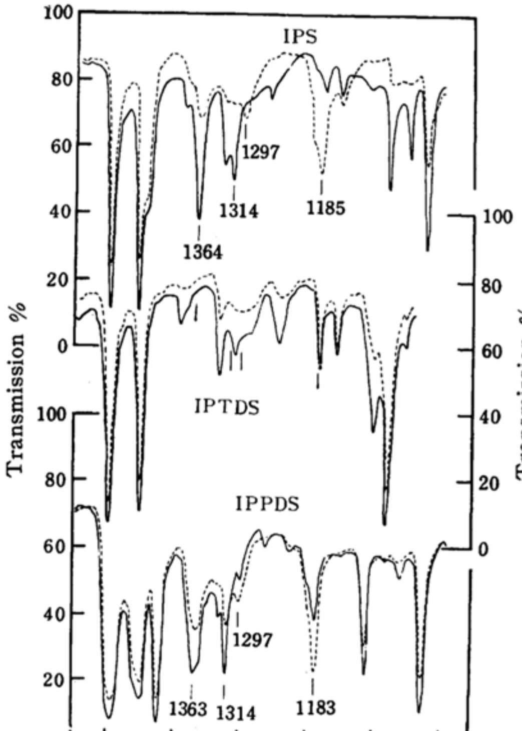


Fig. 2. Polarized infrared spectra of IPS, IPTDS and IPPDS.
—— electric vector perpendicular to elongation
------ electric vector parallel to elongation

It is interesting to note that the difference between the spectra of ZPPMS and APPMS as well as that between those of ZPMMS and APMMS are closely analogous to that between the spectra of quenched IPS and APS. Similar bands appear also at nearly the same positions in the spectra of ZPPMS (1363, 1314 and 1290 cm^{-1}) and ZPMMS (1361, 1310 and 1190 cm^{-1}) prepared with Ziegler catalyst, although these polymers are not appreciably crystalline. On the other hand, these bands are absent in the spectra of ordinary APPMS and APMMS. In view of the similarity pointed above, it can be inferred that ZPPMS and ZPMMS may have also isotactic and local helical structure just as quenched IPS has. Now the tentative explanation for the reason why these polymers are difficult to be crystallized in spite of their possible isotactic structure, would be that the packing of the neighboring molecular

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[2] G. Natta and P. Corradini, *Makromol. Chem.*, **16**, 77 (1955).

[3] S. Murahashi, S. Nozakura, M. Sumi and K. Hatada, This Bulletin, to be published.

[4] For example, Fig. 4 of the paper by Nielsen et al. J. R. Nielsen and A. H. Woollett, *J. Chem. Phys.*, **26**, 1391 (1957).

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

chains in hypothetical crystalline lattices of these polymers may be considered to be not so close on account of the existence of the *p*- or the *m*-substituent methyl groups.

The inference of the existence of local helical structure is strongly supported by the experimental results that the densities of several samples of ZPPMS ($1.015_2 \pm 0.0008$ g./cc.) were always higher than those of APPMS ($1.011_0 \pm 0.0008$ g./cc.). These density values were measured by the flotation method using aqueous sodium chloride solution at 25°C.

Thus, it may be considered that ZPPMS and ZPMMS might be crystallized if some adequate conditions of orientation and thermal treatments were found. In this standpoint of view, we are now going to study the crystallization of these polymers by use of X-ray-, infrared- and density measurements.

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