Infrared Spectra of Crystalline and Amorphous Polystyrene

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It has been reported¹⁾ that crystalline polystyrene (CPS) prepared by Ziegler type catalyst shows a quite different infrared spectrum from that of amorphous polystyrene (APS) prepared by radical catalyst. It has been also suggested²⁾ that some bands in the spectrum of CPS could be associated with the three fold herical structure³⁾ of isotactic polystyrene.

We have studied the infrared spectrum of CPS-I* in the solid state, in the solution of carbon disulfide***, and in the molten state, and have compared them with the corresponding spectra of APS**. Another

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1) G. Natta, *Makromol. Chem.*, **16**, 213 (1955).

2) H. Tadokoro et al., This Bulletin, **32**, 313 (1959).

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

* Prepared by Ziegler catalyst and separated from insoluble parts with cold methyl ethyl ketone after treating with *n*-heptane.

** Commercial polystyrene, "Styron-666".

*** The solution was prepared by extraction of CPS-I at the boiling point of carbon disulfide.

crystalline polystyrene, CPS-II****, prepared by Alfin catalyst has been studied in the solid state.

The spectra of these samples in various states are shown in Fig. 1. The most remarkable differences between CPS-I and APS in solid are found in the bands at 1085, 1054 and 567 cm^{-1}. These absorption bands of CPS-I in solution are very similar to those of solid CPS-I, but some of the other bands observed in the solid state disappear.

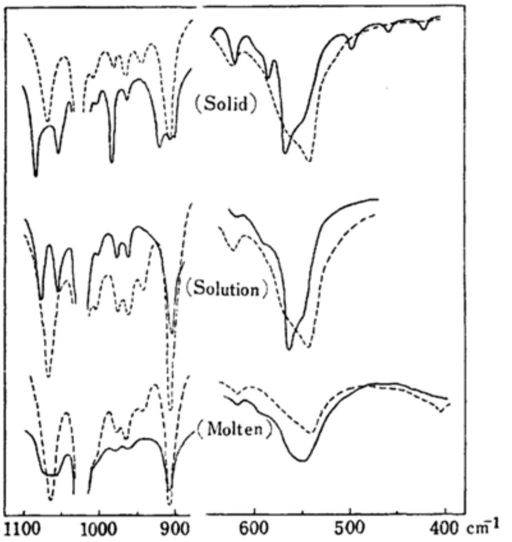

Fig. 1. Infrared spectra of CPS-I and APS in various states.
—— CPS-I ---- APS

In the molten state, the spectrum of CPS-I is almost similar to the spectrum of APS, except for the following points: the doublet at 1085 and 1054 cm^{-1} of solid CPS-I changes into a single and broad band with the maximum at 1070 cm^{-1} with melting, whereas molten APS shows a rather sharp absorption at 1070 cm^{-1}.

The asymmetric band with the maximum at 567 cm^{-1} of solid CPS-I becomes a symmetric and broad band with the maximum at 552 cm^{-1}, while the absorption maximum of molten APS at 543 cm^{-1} remains unchanged.

The observed absorption frequencies are shown in Table I. Complete assignment of the bands at 1085, 1054 and 567 cm^{-1} in both polystyrenes in various states are not yet obtained.

TABLE I. FREQUENCIES IN VARIOUS STATES OF CPS AND APS

CPS-I			APS	Classification
solid	soln.	molten	solid, soln., molten	of the band
1364	1364	1370 w	1370	B
1314	1314	1314 w	1312	B
1297	1297	1295 w	1295	B
1185	1190	1185 w	1182	B
1085	1080			C
		1063 b	1070 s	C
1054	1057			C
984	978 w	978 w	980	A
965	963	963	965	
			945	
923				A
910	908	905	905	
901				A
620 s	620 b	620 b	620 b	A
587				A
567	560			C
		552 b		C
			543	C
499				A
465				A
426				A

s: sharp
b: broad
w: weak in solution and in molten state

However, the differences between the spectra of CPS-I in various states can be used to classify the observed bands in three groups.

(A) Under the first group come the bands at 984, 923, 901, 620, 587, 499, 465 and 426 cm^{-1}. They disappear instantly or are very much weakened when CPS-I dissolves in solution or melts. These bands, which are not observed in the spectrum of APS, may be assigned to the vibrational bands caused by the perturbation by rather long range intra- and intermolecular interactions in the CPS-I crystal. The band at 984 cm^{-1} is considered as a typical crystalline band by Tadokoro et al[4].

(B) Under the second group come the bands at 1365, 1314, 1297 and 1185 cm^{-1}. They are stronger in crystallized CPS-I than in quenched one, and persist in the spectrum of the solution. These bands have been assigned[2] to the CH or CH$_2$ deformation vibrations, which are closely associated with the intramolecular interaction in the herical chain having a three-fold screw axis.

(C) The doublet at 1085~1054 cm^{-1} and

**** Separated from insoluble parts in cold methyl ethyl ketone after treating with n-heptane.

4) H. Tadokoro et al., Symposium of High Polymer, Osaka, Oct., 1958.

the asymmetric bands at 567 cm^{-1} in solid CPS-I and at 543 cm^{-1} in APS could form the third group, because they appear differently in the spectra of molten CPS-I and APS.

The band at 567 cm^{-1} is tentatively assigned by the following reason: The Raman band at 558 cm^{-1} of APS has been assigned to the ν_{6A} mode, an in-plane vibration of benzene nuclei of A_1 mode, by Liang and Krimm[5], which derives from a Raman active and infrared inactive mode of benzene. If all the phenyl radicals in the herical conformation of a polystyrene molecule vibrate in the same phase in the ν_{6A} mode, the dipole moment of the molecule changes along the screw axis of the conformation. It is possible in this case that the ν_{6A} mode is infrared active and shows parallel dichroism which is actually found in our experimental data shown in Fig. 2. Thus we may expect that the band at 567 cm^{-1} is an *X*-sensitive vibration of monosubstituted benzene[6], and sensitive to the short range interaction between the phenyl group and the herical C-C main chain which has alternate *trans* and *gauche* conformations[7].

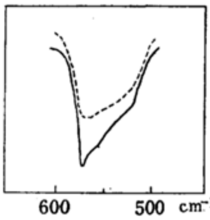

Fig. 2. Dichroism of the 567 cm^{-1} band in solid CPS-I.
—— Electric vector parallel to elongation
---- Electric vector perpendicular to elongation

The band at 543 cm^{-1} of APS is assigned to an *X*-sensitive vibration which is affected by another short range interaction between the phenyl group and the C–C main chain of APS which may have mainly *trans-trans* conformation sequence in their syndiotactic parts.

The doublet at 1085$\sim$1054 cm^{-1} of CPS-I and singlet at 1070 cm^{-1} of APS are probably assigned also to the same type of vibration.

On the basis of the above empirical classification of characteristic bands of CPS-I and APS, as a possible interpretation of the origin of these absorption bands, the following tentative conclusions are drawn.

Based on the behavior of C class band, the conformation of CPS-I along the C-C main of a few monomer units seems to differ from that of APS in their molten states. This may lead us to expect that the change of the bands at 1085, 1054 and 567 cm^{-1} must be connected with the content of the isotactic configuration of CPS-I. If this is assumed, it should be suggested that the isotactic contents in the chain configuration of CPS-II is smaller than that of CPS-I, since the C band of CPS-II in the solid state is quite similar to that of molten CPS-I as is shown in Fig. 3.

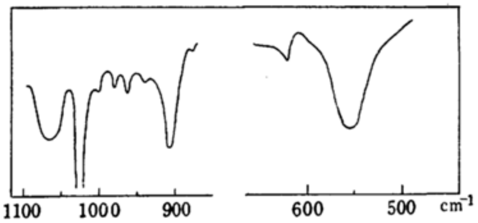

Fig. 3. Infrared spectrum of solid CPS-II.

In solution, it is interesting to note that the herical conformation of isotactic polystyrene is partly reserved, because the persistence of the bands at 567, 1085, 1054 and also 1364, 1314, 1297, 1185 cm^{-1} of crystallized CPS are well recognized.

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

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

[7] W. R. Krigbaum, D. K. Carpenter and S. Newman, *J. Phys. Chem.*, **62**, 1586 (1958).