Studies on the Configuration and Conformation of Polystyrene

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This work was undertaken to investigate the relationship between the chemical configuration of vinyl-type polymer determined by the process of polymerization reaction and the conformation of vinyl-type polymer determined by the physical state of a polymer.

Natta[1] showed that the polystyrene prepared by the Ziegler catalyst contains higher isotactic sequences in its chain configuration and that the crystallizability of this polystyrene is due to the helical conformation[2] of the isotactic chain which makes up the crystalline region of crystallized polystyrene.

Williams et al.[3] also found that the polystyrene prepared by the Alfin catalyst has the same tendency of crystallizability but at a lower degree.

These findings led to two different types of problems. One of them is the existence of configurational isomers, and the concept of isotactic or syndiotactic configurations. The concept of tacticity or stereoregularity is developed in this direction. The distribution of configurational isomers in each sample will be determined by the process of polymerization and solvent extraction.

The other is the existence of conformational isomers for each configurational isomer; and the distribution of conformational isomers for each configuration will be determined by the physical state of the sample and its history such as heat treatment. The dominant existence of the helical conformation of the isotactic chain in the crystalline parts of crystallized polystyrene was the only available information about polystyrene in this direction.

In the present work, the infrared spectra have been measured with four different types of polystyrenes which have been prepared by Ziegler, Natta, Alfin and Radical catalysts and by following extraction processes with cold MEK (methyl ethyl ketone). Measurements of spectra were carried out in various physical states such as quenched solid, crystallized solid, molten state and solution. The differences among spectra of the four polystyrenes in each physical state, and the differences among spectra in the physical state of each polystyrene were interpreted in the terms of configuration and conformation. Crystalline contents of samples were determined by infrared and X-ray methods. The quantitative measure of isotactic configuration has been obtained from the analysis of infrared spectra of sample solutions. The relation between the maximum content of crystallization and the measure of isotactic configuration has been studied.

Experimental

a) **Sample.**—Crystalline polystyrene I (CPS-I) prepared by polymerization with $AlEt_3$-$TiCl_3$ catalyst and crystalline polystyrene II (CPS-II) prepared by polymerization with $AlEt_3$-$TiCl_4$ catalyst and crystalline polystypene III (CPS-III) prepared by polymerization with Alfin Catalyst were used. Each sample of CPS was prepared from the parts insoluble in cold MEK after treating with *n*-heptane. As

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

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

[3] J. L. R. Williams, J. Vandenberche, K. R. Dunham and W. J. Dulmage, *J. Am. Chem. Soc.*, **79**, 1716 (1957).

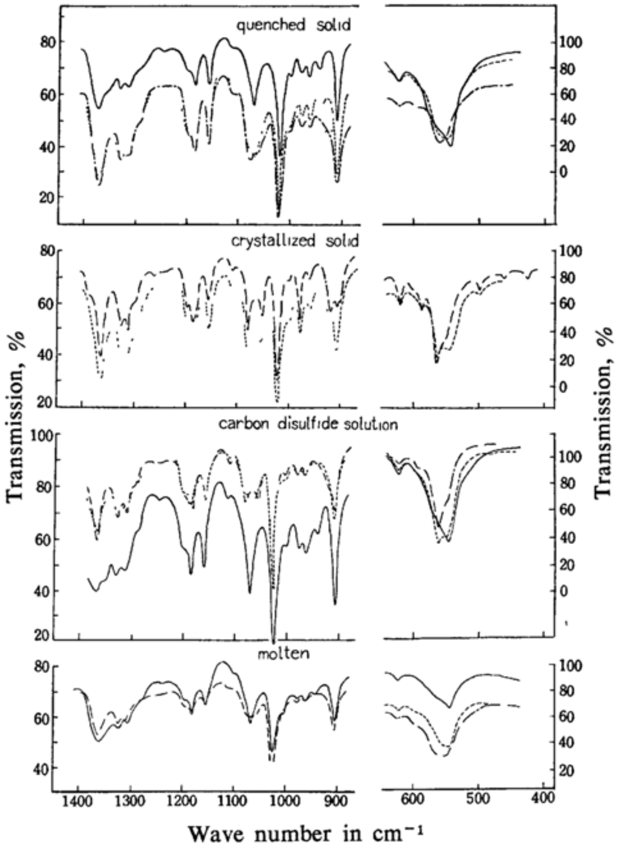

Fig. 1. Spectra of CPS-II, CPS-III and APS in various physical states.

——— APS ········ CPS-III —·—·— CPS-II

the sample of amorphous polystyrene (APS), Styron-666 of Asahi-Dow Company in Japan was used.

Film specimens for the measurement of infrared spectra were prepared by casting from carbon disulfide solution. Solution of polymers were prepared by dissolving the samples in hot carbon disulfide and the undissolved parts of CPS-I and CPS-II were filtered out.

b) Measurement of Spectra.—For measurement of the infrared absorption spectra, a Hitachi EPI-2 infrared spectrophotometer equipped with NaCl and KBr prisms was used. Spectra at the molten state of the samples were observed between 240 and 250°C by using the heating cell. Spectra of carbon disulfide solutions were observed at 2∼5% concentration contained in a cell with 0.5∼1.0 mm. thickness.

c) Density and X-ray Measurements.—A flotation method with NaCl solution was used for the measurement of the density at 30°C. X-ray diffraction diagrams were taken by using a Geigerflex made by Rigaku-Denki Co., Ltd.

Results and Discussion

1. Comparison of Infrared Spectra in Crystallized Solid, Quenched Solid, Solution and Molten State[4]**.**—The infrared spectra of the four different samples have been measured in crystallized solid, quenched solid, solution and molten state. The spectra of these samples in various states are shown in Figs. 1 and 2.

In the molten state, the spectra of the four samples are almost the same. However, there

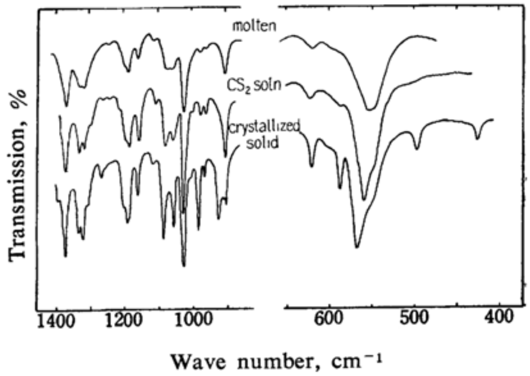

Fig. 2. Spectra of CPS-I in various physical states.

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4) M. Takeda, A. Iimura, A. Yamada and Y. Imamura This Bulletin 32, 1151 (1959).

TABLE I. CLASSIFICATION OF FREQUENCIES

CPS-I			CPS-II			CPS-III			APS	Classification of the band
Cryst. solid	Soln.	Molten	Cryst. solid	Soln.	Molten	Cryst. solid	Soln.	Quenched		
1385	1385		1385							
1364	1364	1364	1364	1364	1370	1365	1367	1367	1370	B
1314	1314	1314	1314	1314	1314	1314	1314	1313	1312	B
1297	1297		1297	1297	1295	1297	1297	1295	1295	B
1258			1258							
1185	1190		1185	1190		1185	1190			B
1085	1080		1085	1080		1080	1080	1079		C_1
		1065 b			1063 b	1065	1068	1068	1070	C_2
1054	1054		1054	1057		1053	1056			C_1
984	978	978 w	984	978 w	978 w	982	978 w	979 w	980 w	A
923			923			921				A
910	908	905	910	908	905	908	908	908	905	
901			901							A
620 s	620 b	620 b	620 s	620 b	620 b	620 s	620 b	620 b	620 b	A
587	588 w, b		587	590 w, b		587	590 w, b	590 w, b		A
568			567			567				C_1
	560			560			560			C_1
		555 b			552 b					C_1
						543	544	546 b	543	C_2
499			499			499				A
			465							A
428			426			426				A

Note. (1) Only the bands which show remarkable change are listed in Table I.
(2) Remarkable change of frequencies of APS is not found with varying state.
(3) w: weak band, b: broad band, s: sharp band.

are definite differences between the band at 555 (symmetrical broad band) of CPS-I and the band at 543 cm^{-1} (asymmetrical broad band) of APS. The band at 546 cm^{-1} (asymmetrical broad band) of CPS-III appeared as the superposition of the above two bands. The rather flat and broad band at 1063 cm^{-1} of CPS-I is different from the sharp band at 1070 cm^{-1} of APS. The spectrum of molten CPS-II is similar to that of molten CPS-I.

The difference of spectra among the samples in quenched solid was very similar to the difference of those in the molten state and became larger in the crystallized solid state.

In the spectra of crystallized CPS-I and CPS-II, a new sharp band appeared at 567 cm^{-1} and the form became an asymmetric one. The broad band at 1063 cm^{-1} of molten CPS-I and CPS-II became a sharp doublet with the maxima at 1085 and 1054 cm^{-1}. In the spectrum of crystallized CPS-III, the intensity of the band increased with maximum at 567 cm^{-1}. The band around 1070 cm^{-1} of CPS-III has shown a very complicated form and probably it has three maxima at 1080, 1065 and 1053 cm^{-1}. It is also recognized that the intensity of the band at 1365, 1314, 1297 and 1185 cm^{-1} increased more in the spectra of crystallized CPS-I, CPS-II and CPS-III than in the spectra of the quenched solids as found by Tadokoro et al.5) They suggested that these bands may be assigned to CH or CH_2 deformation vibrations and are closely related to the intramolecular interactions in the helical chain having the three fold screw axis (alternate sequences of *trans* and *gauche* conformation along the C-C chain). Other new bands with maxima at 984, 923, 901, 620, 587, 499, 465 and 426 cm^{-1} appeared in the crystallized CPS-I and CPS-II, and also the bands with maxima at 982, 921, 620, 587, 499 and 426 cm^{-1} appeared in the crystallized CPS-III. These bands are probably ascribable to the usual crystalline bands. Several heat treatments for crystallization gave no remarkable change in the spectra of APS. This fact suggests that APS does not crystallize appreciably.

The difference of spectrum became very simple in carbon disulfide solution compared to that of the crystallized solid. The bands at 1085, 1054 and 567 cm^{-1} of the crystallized CPS-I, CPS-II and CPS-III still persist in the spectra of the solution, even though slight shifts of absorbance maximum are observed. The bands at 1070 and 543 cm^{-1} of APS remain in the spectra of the solution

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

with no change from those of the solid. The bands at 1364, 1314, 1297 and 1185 cm^{-1} of CPS-I and CPS-II also persist in the spectra of the solution, but a slight decrease of their intensity is noted. Other bands ascribable to the crystalline band disappear or are very much weakened in the spectra of the solutions.

According to the above mentioned observation, it is possible to classify the spectra which differ from sample to sample, into three groups, A, B and C as shown in Table I.

The A group bands are characteristic in the crystallized solid and dissappear instantly or are very much weakened when the crystallized solid is dissolved in solution or is melted. These bands, which are not observed in the spectra of APS, may be assigned to the crystalline bands caused by the perturbation due to rather long range intra- and intermolecular interaction in the microcrystals of polystyrene. The assignment of A group bands to the crystalline bands makes it possible to use them for the quantitative estimation of crystalline contents of the crystallized polystyrene. The maximum crystalline content $X_{\max}$ in polystyrene might be associated with the contents of isotactic configuration in polystyrene, since only the polystyrene which has isotactic configuration can form crystalline regions with its helical conformation. This problem is studied in the 2nd part of this paper.

The B group bands are stronger in the crystallized polystyrene than in the quenched solid or the molten state, and they persist in the spectra of CPS-I, CPS-II and CPS-III even in their solutions, and are not found in that of APS. Our observations are consistent with the assignment⁵⁾ of these bands to the CH or CH_2 deformation vibration which are due to the intramolecular interaction in the helical chain conformation having a three-fold screw axis.

The C_1 and C_2 groups have shown different spectra among four samples in all physical states such as crstallized solid, quenched solid, solution and molten states. The band with maximum at 543 cm^{-1} of APS has been assigned to $\nu_4(B_2)$ vibration mode of mono-substituted benzene by Liang and Krimm⁶⁾. According to this assignment, it can be assumed that the origin of the absorption bands which belong to the C group is the phenyl group vibration which is sensitive to the short range intramolecular interaction along the C-C main chain conformation. It is possible to subclassify the C group bands into C_1 and C_2 based on the differences of samples as shown in Table I. The C_1 group bands then become the characteristic vibrations of the C-C chain, which has the helical conformation or *trans-gauche* alternate conformation along the C-C chain from isotactic configuration. The C_2 group bands may be due to the characteristic vibration of the C-C chain which has mainly *trans* confomation along the C-C chain from syndiotactic configuration. Morton and Taylor⁷⁾ have used the new IR rating method of isotacticity based on the absorption in the 1070 cm^{-1} region of KBr disk samples. The pattern of their spectra in this region is very similar to the pettern of our spectra in the same region which are observed using the sample of crystallized film and solution.

On the basis of the above empirical classification of the characteristic bands of polystyrenes and a possible interpretation of the origin of these absorption bands, the following conclusions are tentatively drawn.

Based on the behaviors of the C class bands, the conformation of the C-C chain of a few monomer units seems to differ among the samples even in their molten states. The intensity of bands in the C_1 group will be related with the content of helical conformation of polystyrene, because its intensity becomes strong in the crystallized state. In the solution, the helical conformation of crystallizable polystyrene is partly preserved, because the persistence of the C_1 and B class bands in the spectra of CPS-I, CPS-II and CPS-III is well recognized and their intensities are stronger than these in the quenched solids. It may be suggested that the intensity ratio D560 to D543 (D560/D543) in the spectra of the solution can be used to measure the content of isotactic configuration of the same polystyrene, as well as the band around 1070 cm^{-1}. In that case the equilibrium content of helical conformation of polystyrene is determined only by its isotactic content of chain configuration, and not by its previous history like heat treatment in the solid state. The observed values of D560/D543 in solution are shown in Table II.

2. Behavior of the Crystalline Bands and the Estimation of Crystalline Content.—Based on the conclusions in part 1, among several crystalline bands of the A group, the intensity of the bands at 984 and 587 cm^{-1} have been used to measure the crystalline content in various polystyrene samples. The possibility of measuring the crystalline content using the intensity of the band at 984 cm^{-1} has also been pointed out by Braun et al.⁸⁾ from their investigation on the temperature dependence of the band.

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

7) A. A. Morton and L. D. Taylor, ibid., **38**, 7 (1959).

8) D. Braun, W. Betz and W. Kern, *Naturwissenschaften*, **46**, 344 (1959).

For avoiding the difficulty of measurement of film thickness, the band at 1030 cm^{-1} has been used as a reference, since the optical densities of this band had a linear relationship with thickness for each sample and were independent of the crystal content of samples as shown in Fig. 3.

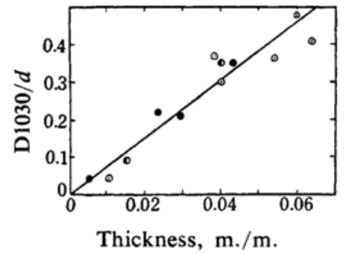

Fig. 3. Linear relation between optical density of 1030 cm^{-1} and thickness.

○ : CPS-I ⊙ : CPS-III
● : CPS-II ◐ : APS

The measured values of D984/D1030 and D587/D1030 are listed in Table II. The linearity between both values suggests that the origin of these bands is the same crystalline band as shown in Fig. 4. The specific volumes of samples were calculated from the measured densities, and are also listed in Table II. From the specific volume, the crystalline content of polystyrene X_{sv} can be calculated by the following equation:

$$X_{sv}=(V_a-V)/(V_a-V_c) \qquad (1)$$

where, V_a is the specific volume of the amorphous part and V_c is the specific volume of the crystalline part.

If the intensities of D587 and D984 are proportional to the crystalline content, the following equation can be proved:

TABLE II. NUMERICAL DATA FOR EACH SAMPLE

Sample	Density (30°C)	Specific volume	D587/D1030	D984/D1030	Crystalline content (%)				D560/D543 in CS_2 soln.
					X_i (587)	X_i (984)	X_{sv}	X_x	
(CPS-I)									
Q-2	1.0529	0.950	0.042	0.082	8	5	0	11.5	
Q-2	1.0582	0.945	0.023	0.067	4	2	8	9.5	
Q-2	1.0582	0.945	0.026	0.060	5	0	8		
Q-2	1.0650	0.939	0.122	0.178	23	23	18		
Q-1	1.0652	0.939	0.122	0.172	23	22	18		
Q-1	1.0683	0.936	0.157	0.201	29	28	23		2.85
Q-1	1.0692	0.935	0.186	0.232	34	34	24	26.6	
Q-190-10	1.0742	0.931	0.204	0.248	38	37	31		
Q-205∼175-310	1.0815	0.925	0.271	0.310	50	49	40		
A-220∼170-480	1.0873	0.920	0.313	0.353	58	58	48		
A-220∼160-480	1.0898	0.918	0.292	0.329	54	53	52		
A-220∼160-750	1.0915	0.916	0.336	0.393	62	66	55	73.3*	
(CPS-II)									
Q-160-30	1.085	0.922	0.167	0.189	31	26	45	24.6	
Q-180-120	1.088	0.919	0.210	0.244	39	36	50		2.26
A-205-60	1.089	0.918	0.236	0.277	44	43	52	51.4*	
(CPS-III)									
Q-1	1.056	0.947	0.012	0.059	2	0	5		
Q-160-30	1.062	0.942	0·022	0.085	4	6	13		1.10
Q-185-120	1.068	0.936	0.078	0.132	14	14	23	16.4	
A-205-60	1.065	0.939	0.087	0.168	16	22	18	17.1*	
(APS)									
Q-1	1.052	0.951	0	0.066	0	2	—	0*	
Q-160-30	1.054	0.949	0	0.057	0	—	2		0.54
A-180-120	1.055	0.948	0	0.060	0	0	3		

Note. Q-1: Quenched in ice water after keeping the sample at 245∼248°C.
Q-2: Quenched at −70°C after keeping the samples at 270°C.
Q-160-30: Means that the quenched solid was kept at 160°C during 30 minutes and after that, the temperature was lowered slowly.
A-205-60: Means that annealing was made, keeping the sample at 205°C for 60 minutes.
* These values are chosen as the maximum crystalline content X_{max}.

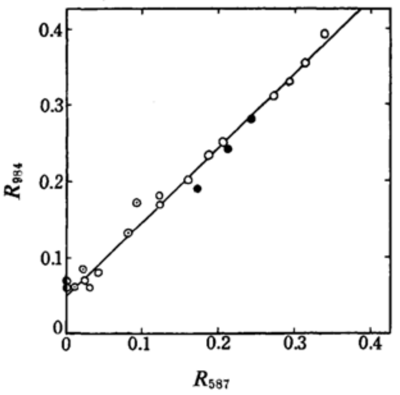

Fig. 4. Linear relation between R_{984} and R_{587}.

○ : CPS-I ⊙ : CPS-III
● : CPS-II ◐ : APS

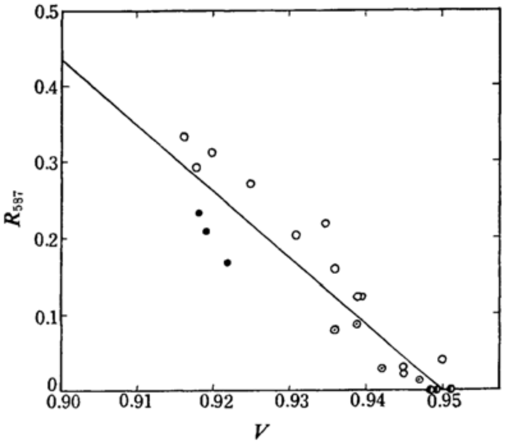

Fig. 5. Relation between R_{587} and specific volume.

○ : CPS-I ⊙ : CPS-III
● : CPS-II ◐ : APS

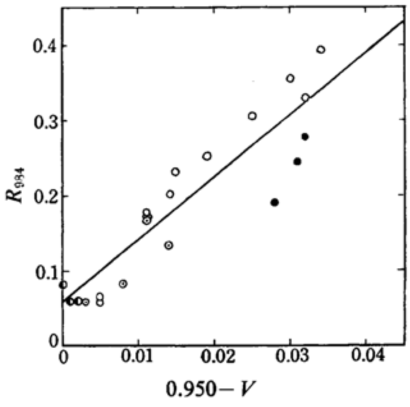

Fig. 6. Relation between R_{984} and $(V_a - V)$.

○ : CPS-I ⊙ : CPS-III
● : CPS-II ◐ : APS

$$R_{587} = \mathrm{D587/D1030} = K_1(V_a - V) \tag{2}$$

$$R_{984} = \mathrm{D984/D1030} = K_2(V_a - V) + A \tag{3}$$

where, K_1 and K_2 are constant, and A is added because the band at 984 cm^{-1} has some intensity even in the amorphous state. From the linear relation between R_{587} and V, and R_{984} and $(V_a - V)$, as shown in Figs. 5 and 6, K_1, K_2 and A were determined experimentally as follows.

$$K_1 = 8.729,\ K_2 = 8.242 \text{ and } A = 0.058.$$

The value of V_a is determined, from Fig. 5, as 0.950 from the value of V at $R_{587} = 0$. The value of V_c is estimated as 0.888 from the results of Natta's X-ray analysis⁹⁾.

Combining the equations (1), (2) and (3), the following relationships are obtained:

$$X_{sv} = 16.13(0.950 - V) \tag{4}$$

$$X_i(587) = 1.85(R_{587}) \tag{5}$$

$$X_i(984) = 1.96(R_{984} - 0.058) \tag{6}$$

where $X_i(587)$ and $X_i(984)$ are the crystalline content by the infrared method from the 587 cm^{-1} and 984 cm^{-1} bands, respectively. The determined values of crystalline content for each sample are shown in Table II, and the agreement among X_{sv}, $X_i(587)$ and $X_i(984)$ is satisfactory considering the difference of methods. Another approximate estimation¹⁰⁾

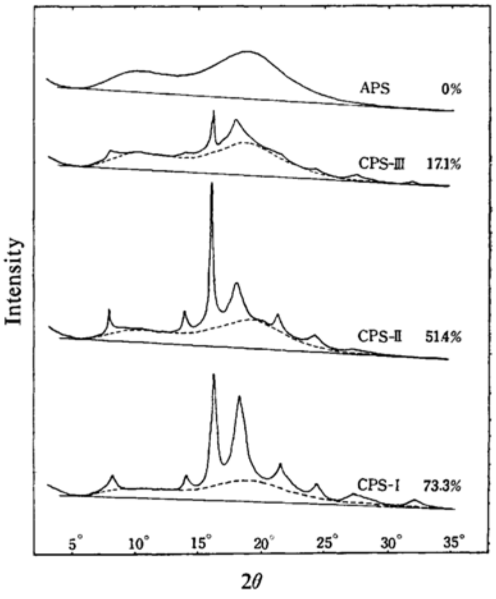

Fig. 7. X-ray diffraction diagrams of each polystyrene at maximum crystallinity and their crystalline contents.

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

10) G. Natta et al., Atti. *accad. nazl. Lincei, Rend., Classe sci. fis., mat. e nat.*, **22**, 11 (1957).

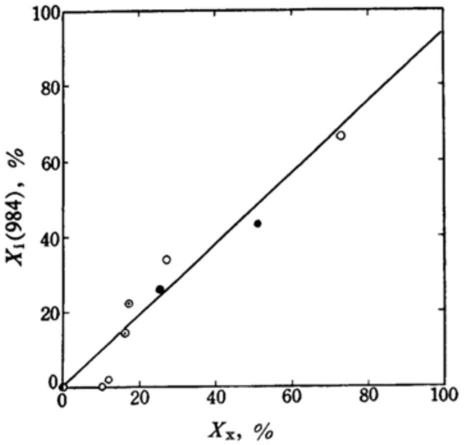

Fig. 8. Linear relation between $X_1(984)$ and X_x.

○ : CPS-I ⊙ : CPS-III
● : CPS-II ◐ : APS

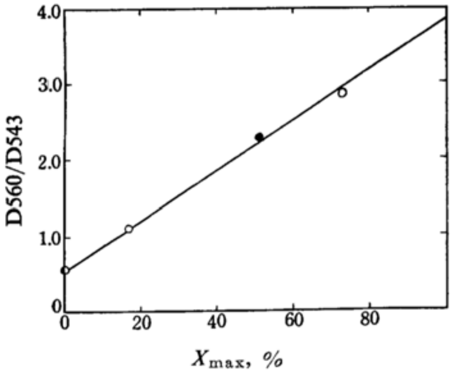

Fig. 9. Linear relation between D560/D543 and maximum crystallinity for each sample.

○ : CPS-I ⊙ : CPS-III
● : CPS-II ◐ : APS

of the crystalline content, X_x, by X-ray diffraction curve has been tried, and the values are also shown in Table II. The diffraction curve of APS in Fig. 7 has been used as the standard curve of amorphous parts. The estimated curve of amorphous parts was drawn through the point ($2\theta=12.5°$) on the experimental curve of the crystallized polystyrene making it similar to the standard curve in the direction of intensity. The intensity at $2\theta=12.5°$ was little influenced from the scattering of the crystalline parts which had the strong peaks at $2\theta=8.1°$ and $2\theta=16.2°$. The ratio of crystalline region to total area is taken as the agreement between X_x and $X_1(984)$ was satisfactory as shown in Fig. 8. The determined values of X_x for the most crystallized state of the four polystyrenes, CPS-I, CPS-II, CPS-III and APS, are taken as the maximum crystalline content, X_{max}, of each polystyrene. A strong correlation was found between X_{max} and the ratio D560/D543 in the solution, as shown in Fig. 9. This will suggest that both the maximum crystalline content, X_{max}, and D560/D543 in the solution can be used to measure the content of isotactic configuration of polystyrene from the quantitative point of view. The same treatment of the band at around 1070 cm^{-1} in the solution may be possible for the determination of the isotactic content of polystyrene, but is not considered in this paper.

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