Crystallinity Studies of Polychlorotrifluoroethylene by Infrared Method. I. Measurement of the Degree of Crystallinity

By Hiroshi MATSUO

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Introduction

The measurement of the degree of crystallinity is becoming of increasing importance in the study of polymer properties. Therefore many methods for its estimation have been devised. The crystallinity of polychlorotrifluoroethylene (PCTFE) was studied by Price[1] by volume method, and by Hoffman[2] by specific heat method. It appears of interest to investigate the subject further by infrared method, which is also available for reliable estimation of crystallinity for a number of common polymers[3].

In the course of examination of infrared spectra of PCTFE, the author believed that they yield some bits information about the crystallinity and the state of the orientation. A survey of the spectrum revealed that some of the bands behaved as if they were given by the crystalline parts of the polymer, while others appeared to be produced by the amorphous parts. These discoveries were utilized in the present study of crystallinity of PCTFE, and the degree of crystallinity was estimated independent of other methods.

Effect of Crystallization on the Infrared Bands

PCTFE is an extremely intractable material, because there is no proper solvent at room temperature, and furthermore the spectrum of PCTFE shows such strong absorptions at about 1300–900 cm.$^{-1}$ region that thin films of 0.01–0.03 mm. thickness are necessary for infrared method. Thin films were prepared by extruding Daiflon[4] (NST 270) at above its melting point. The orientation of crystallites in the extruded film was estimated from the intensity distribution around the X-ray diffraction ring. It was examined further with a beam of polarized infrared radiation using a polarizer of silverchloride plates placed immediately in front of the entrance slit of the infrared spectrometer. A comparison of the spectra obtained when the electric vector was vibrating parallel and perpendicular to the extruded direction

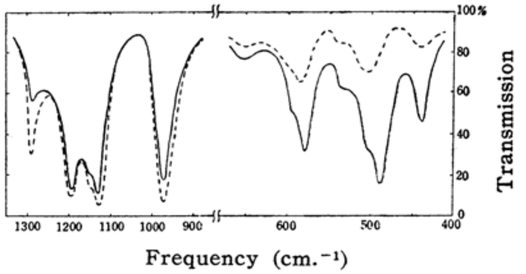

Fig. 1. Infrared spectrum of oriented polychlorotrifluoroethylene, obtained by polarized radiation.
——: electric vector parallel to the extruded direction.
----: electric vector perpendicular to the extruded direction.

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1) F. P. Price, *J. Chem. Phys.*, **19**, 973 (1951).
2) J. D. Hoffman, *J. Am. Chem. Soc.*, **74**, 1696 (1952).
3) J. B. Nichols, *J. Appl. Phys.*, **25**, 840 (1954).

4) Trade name of high molecular weight PCTFE produced by Osaka Kinzoku Kogyo Co.

shows significant dichroism on the majority of absorption bands. This is shown in Fig. 1. These absorption bands indicated not only significant dichroism but also intensity changes as the crystallization proceeded⁵⁾. The latter was examined comparing the spectra of annealed, quenched, and molten samples. In order to eliminate the effect of orientation, these samples were heated at above the melting point beforehand and then annealed or quenched to room temperature. Their spectra are shown in Fig. 2. To obtain the infrared spectrum of molten polymer, a film of the polymer was sealed together with a thermocouple between potassium bromide plates. This was then placed in a heating cell⁶⁾ mounted on the spectrometer.

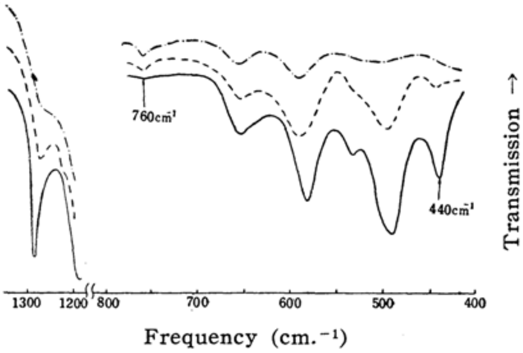

Fig. 2. Infrared spectra of polychlorotrifluoroethylene.
——: annealed sample,
----: quenched sample,
-·-·-: molten sample at 230°C.

Fig. 2 shows that the absorption bands at 1290, 580, 506, 490 and 440 cm.⁻¹ increase markedly in intensity and present small shifts as the crystallization proceeds. This increase in intensity indicates that randomly oriented crystallites have been produced in the polymer by the heat treatment and it agrees with the results obtained by X-ray diffraction. These absorption bands whose intensities increase as the crystallization proceeds can be, therefore, regarded as crystalline bands. On the other hand, the intensity of the absorption band at 760 cm.⁻¹ decreases as crystallization proceeds, so that this band can be regarded as an amorphous band⁷⁾. These crystalline and amorphous bands are summarized in Table I, where π means that the absorption in the case of the electric vector parallel to the extruded direction is greater than in the case of the perpendicular electric vector, and σ the reverse case.

TABLE I

INTERPRETATION OF THE INFRARED SPECTRUM OF EXTRUDED PCTFE

Freq. cm.⁻¹	Relative Intensity	Dichroic ratio^a)	Character of band^b)	Probable assignment^c)
438	s	3.7	π c	CClF wagging
490	s	5.6	π c	CF_2 rocking
506	s		σ ? c	CF_2 bending
(535)			c	
580	s	2.2	π c	CF_2 wagging
658	m		π a ?	
723	w		π	
755	w		σ ? a	
972	vs		σ	CCl stretching
1130	vs		σ	CF_2 stretching
(1147)			σ	
1194	vs		σ	CF_2 stretching
1285	s	0.3	σ c	CF stretching

a) dichroic ratio $=\log(I_0/I)_\pi/\log(I_0/I)_\sigma$.
b) c=crystalline, a=amorphous.
c) These assignments are due to C. Y. Liang and S. Krimm, *J. Chem. Phys.*, **25**, 563 (1956).

Degree of Crystallinity

The degree of crystallinity was measured by the use of the crystalline band at 440 cm.⁻¹ and the amorphous band at 760 cm.⁻¹.

The experiments were carried out with a Perkin-Elmer Model 112 Spectrometer equipped with potassium bromide prism. The slit was driven connecting with wavelength drive cam, so as to obtain flat background trace. The resolving powers at 440 cm.⁻¹ and 760 cm.⁻¹ were approximately 3 cm.⁻¹ and 2.5 cm.⁻¹, respectively. Stray radiation at 440 cm.⁻¹ was less than one percent. of the detected radiation. The starting material was a sheet of melt-extruded, quenched film of 0.03 mm. nominal thickness. Samples with various degrees of crystallinity were obtained from it by quenching to room temperature from 230°C or annealing to various crystallization temperatures between 200° and 130°C. Specific volumes were obtained within the accuracy of ±0.0007 from densities measured by the flotation method at 25°C using a solution of bromoform and xylene. In

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5) H. Matsuo, *J. Polymer Sci.*, **21**, 331 (1956).
6) R. E. Richards and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 183 (1945).
7) R. G. J. Miller and H. A. Willis, *J. Polymer Sci.*, **19**, 485 (1956).

this case the optical density D was defined as follows,

$$D=(1/td)\log(I_0/I)$$

where t and d are the thickness and the specific gravity of the sample, I_0 is the height of the background trace obtained by the base-line method at the peak of the band, and I the height of the band peak. As the thickness of the sample had to be accurately measured for the optical density measurements, the following method was used. The portion irradiated by the infrared beam was cut out from the film, and weighed by a microbalance. The area of the surface of the film was determined by direct measurement. Density being known, the effective thickness could be calculated. The accuracy was estimated to be ±0.002 mm.

Since specific volume changes have been used to measure crystallinity, the changes in optical densities at 440 cm.$^{-1}$ and 760 cm.$^{-1}$ were correlated with change in specific volume. Specific volumes were plotted against optical densities for a number of samples. All points lie on a straight line within the accuracy of the experiment, and therefore the following equations were assumed.

$$D_1=K_1{}^cX+K_1{}^a(1-X)$$
$$D_2=K_2{}^a(1-X)$$

and consequently,

$$D_1=K_1{}^c-[(K_1{}^c-K_1{}^a)/K_2{}^a]D_2 \qquad (1)$$
$$R=D_1/D_2=[X/(1-X)](K_1{}^c/K_2{}^a)+(K_1{}^a/K_2{}^a) \qquad (2)$$

where X is the degree of crystallinity; D_1 and D_2 are optical densities at 440 cm.$^{-1}$ and 760 cm.$^{-1}$, respectively; $K_1{}^c$ and $K_1{}^a$ are extinction coefficients of crystalline and amorphous parts at 440 cm.$^{-1}$, respectively, and $K_2{}^a$ is that of the amorphous part at 760 cm.$^{-1}$ R is the ratio of the observed absorbance at 440 cm.$^{-1}$ to that at 760 cm.$^{-1}$, and is independent of the thickness of the sample since the absorbances are determined for two bands in the same sample.

By plotting D_1 against D_2, a straight line was observed. Equation (1) means that the value of the inclination of the line corresponds to $(K_1{}^c-K_1{}^a)/K_2{}^a$ and the value of its intersection with the ordinate axis corresponds to $K_1{}^c$. Furtheremore, Equation (2) indicates that the value of R of the completely amorphous state correspond to $(K_1{}^a/K_2{}^a)$. However, since the completly amorphous material could not be obtained by quenching the polymer from the molten state, the value of R of the completely amorphous state was determined by the following method. Daifoil[8] No. 50, which was a product of pyrolysed PCTFE and was a viscous liquid at room temperature, was used as an amorphous standard for the high molecular weight PCTFE. Its spectrum was very similar to that of the molten high molecular weight PCTFE, except for the existence of the absorption band at 1340 cm.$^{-1}$, which would be due to $=CF_2$ group[9]. Thus $R=2.05$ was obtained for completely amorphous polymer at room temperature. The same value of R was measured in the molten state which was obtained by heating Daiflon film to 240°C in the heating cell; it appears, therefore, that little change in the intensity of the absorption bands at elevated temperatures would be expected. Thus $K_1{}^c=9.02$, $K_1{}^a=2.12$, and $K_2{}^a=1.03$ were obtained, and the degree of crystallinity could be calculated from Equation (2):

$$X=(R-2.05)/(R+6.67) \qquad (3)$$

The degree of crystallinity of PCTFE as a function of temperature was calculated from the measurement of R at various temperatures by the use of Equation (3). A film of 0.03 mm. thickness of the polymer which was quenched from above its melting point to room temperature, was inserted into the heating cell and degrees of crystallinity at various temperatures were measured. They are shown in Fig. 3. The sample was heated slowly to 100° then

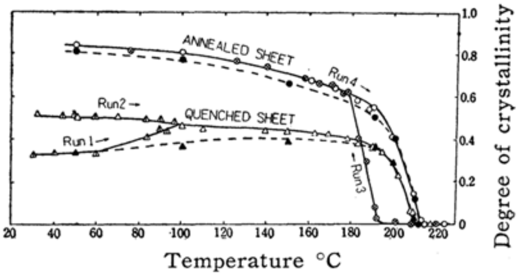

Fig. 3. Degree of crystallinity of polychlorotrifluoroethylene as a function of temperature.
(△) Run 1, (△) Run 2 with quenched sample,
(⊗) Run 3, (○) Run 4 with annealed sample;
(▲, ●) obtained by Hoffman by specific heat method with quenched and annealed samples, respectively.

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[8] Trade name of low molecular weight PCTFE produced by Osaka Kinzoku Kogyo Co.

[9] R. B. Barnes and R. C. Gore, *Anal. Chem.*, **20**, 402 (1948).

cooled down to room temperature (Run 1), and was heated again to 225° (Run 2). These data were listed in Fig. 3 as "quenched". The material was then cooled at a rate of 0.3°C/min. from 225° to room temperature (Run 3), and another run made to 225° (Run 4). These data were listed as "annealed". The degree of crystallinity of the quenched and the annealed sample obtained by the present method and that by Hoffman[2] by specific heat method agree with each other within ca. ±5%; this may be regarded satisfactory. Run 1 shows a definite increase in crystallinity of the quenched sample in the range of 80 to 100° as it is heated. This was confirmed further by the fact that the sample showed higher crystallinity than the original one when it was cooled from 100° to room temperature again. This definite increase must be due to super-cooled amorphous forming crystallites as the viscosity decreases sufficiently to permit recrystallization. On the other hand, the annealed sample apparently contains a few small crystallites which melt as low as 100°, and on further heating, the crystallinity steeply drops from about 196° and reaches zero at 212°. Between 180° and 212°, Run 3 and Run 4 do not coincide, and it may partly owe to non-attainment of equilibrium. The hysteresis shown by the non-coincidence of melting point (212°) and freezing point (195°) in this Figure was also observed in the measurements of specific volume, and dielectric constant and loss of PCTFE[10].

Furthermore, a linear relationship between the degree of crystallinity and the specific volume was obtained within the experimental uncertainty (Fig. 4). It leads to extrapolated values of 0.4901±0.001 and 0.4575±0.001 for specific volumes of completely amorphous and crystalline materials, respectively. Generally the degree of crystallinity can be also determined from specific volume method by the equation

$$X=(V_a-V)/(V_a-V_c)$$

However, so far as PCTFE is concerned, the value of specific volume for completely amorphous material (V_a) and that for completely crystalline material (V_c) have not as yet been determined with sufficient accuracy for computing absolute values of X, even by the extrapolation method of specific volume from the molten state[10,11] and by X-ray diffraction method[12]. Using $V_a=0.4901$ and $V_c=0.4575$ obtained by the present method, the degree of crystallinity was determined from the measurement of the specific volume V by the following equation,

$$X=(0.4901-V)/0.0326 \qquad (4)$$

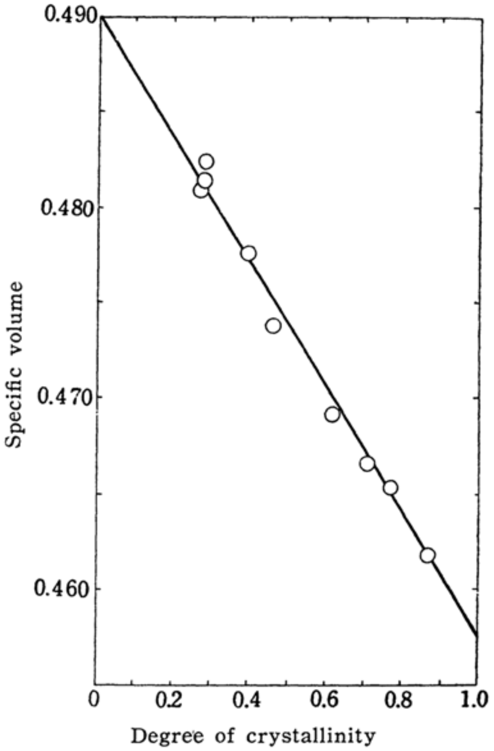

Fig. 4. Correlation of specific volume with degree of crystallinity of polychlorotrifluoroethylene.

In Table II, degrees of crystallinity obtained from infrared method and from specific volume method are shown. From this Table, it is apparent that amorphous material could not be obtained by such a quenching procedure of the molten polymer and the crystallinity of the quenched polymer attains to 27%, and, by annealing at higher crystallization temperature for several hours, the crystallinity of the annealed polymer amounts to 87%.

Summary

The crystalline-amorphous ratio, and consequently the degree of crystallinity of polychlorotrifluoroethylene was measured by use of the ratio of observed absorbance of crystalline band at 440 cm.$^{-1}$ to that of amorphous band at 760 cm.$^{-1}$. The crystallinity as a function of temperature was measured by this method, and it was in

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[10] F. P. Price, *J. Am. Chem. Soc.*, **74**, 317 (1952).
[11] S. Furuya, *J. Polymer Sci.*, **20**, 587 (1956).
[12] H. S. Kaufman, *J. Am. Chem. Soc.*, **75**, 1477 (1953).

TABLE II
PATICULARS OF SAMPLES OF PCTFE

Specific volume	Thickness mm.	$\log(I_0/I)$		$R^{a)}$	Crystallinity, %		Condition of heat treatment
		at 440 cm.$^{-1}$	at 760 cm.$^{-1}$		from I. R.$^{b)}$	from sp. vol.$^{c)}$	
—	—	0.119	0.058	2.0	0	—	measured at 240°
0.4825	—	0.292	0.054	5.4	28	23	quenched from 230° to dry-ice temperature
0.4815	0.029	0.255	0.047	5.4	28	26	quenched from 230° to room temperature
0.4810	0.026	0.196	0.037	5.3	27	28	quenched from 230° to room temperature
0.4775	0.027	0.290	0.037	7.7	39	39	quenched film was heated at 130°
0.4739	0.030	0.310	0.033	9.4	46	50	quenched film was heated at 130°
0.4691	0.024	0.301	0.019	15.8	61	64	annealed from 230° to room temperature
0.4666	0.032	0.522	0.023	22.7	70	72	annealed from 230° to room temperature
0.4654	0.030	0.487	0.016	30.4	76	76	annealed from 230° to room temperature
0.4618	—	0.316	0.005	63.2	87	87	annealed at 190° for 3 hr.

a) $R = \log(I_0/I)\,440\ \text{cm.}^{-1}/\log(I_0/I)\,760\ \text{cm.}^{-1}$.
b) calculated from Equation (3).
c) calculated from Equation (4).

good agreements with that obtained by specific heat methd. Furthermore, a linear relationship between the degree of crystallinity and the specific volume was found, and it leads to extrapolated values of 0.4901 and 0.4575 for the specific volumes of completely amorphous and crystalline materials, respectively.

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Electrical Communication Laboratory
Nippon Telegraph and Telephone
Public Corporation
Musashino-shi, Tokyo