

## Transitions of Polytetrafluoroethylene at About 90 and 130°C. Studied by X-Ray Diffraction and Infrared Spectra

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### Synopsis

By means of x-ray diffraction, the lattice spacing of the (100) plane for molded polytetrafluoroethylene was measured at different temperatures from 25 to 190°C. In the crystalline region, the linear expansion coefficient, in the direction perpendicular to the molecular chain axis, was obtained as  $1.1 \times 10^{-4} \text{°C.}^{-1}$  below 60°C., as  $1.2 \times 10^{-4} \text{°C.}^{-1}$  above 90°C., and as a minimum value of some  $0.2 \times 10^{-4} \text{°C.}^{-1}$  at about 80°C. As the linear expansion coefficient of the crystalline region in bulk was observed as some  $0.6 \times 10^{-4} \text{°C.}^{-1}$ , the expansion coefficient in the direction of molecular chain axis must be negative except in the transition region near 80°C. The variation of molecular chain axis separation with temperature showed an irregularity at about 80°C. but none near 130°C. in the crystalline region. Infrared absorbance of film samples of PTFE was measured at different temperatures of 25 to 150°C. range for 518, 627, and 639  $\text{cm.}^{-1}$  bands. On absorbance-temperature curves for those bands, irregularities were observed near 30, 50, 90, and 130°C. Particularly with 518  $\text{cm.}^{-1}$  band, a more crystalline sample gave more distinct irregularities near 50 and 90°C. than a less crystalline sample. The change at about 90°C. in infrared spectra may correspond to that obtained by x-ray measurements near 80°C., which was thought to occur in the crystalline region. The results obtained by x-ray and infrared measurements support the previous results by thermal, rheological, and dielectric methods: there exist first-order transitions in the crystalline region at about 90°C. and second-order transitions in the amorphous region at about 130°C.

### INTRODUCTION

It has been found that polytetrafluoroethylene (PTFE) shows several kinds of transitions at various temperatures. They are three first-order transitions occurring in the crystalline region at about 330°C. (melting point),<sup>1-3</sup> 90°C.,<sup>4,5</sup> and 20°C. (room-temperature transition),<sup>2,3,6-19</sup> and three second-order transitions occurring in the amorphous region at about 130°C.,<sup>4,5,20-31</sup> -30°C.,<sup>25,29,30,32</sup> and -90°C.<sup>21-27,29,33,34</sup>

In the previous papers it was pointed out that (1) first-order transitions appeared in the crystalline region in doublets at about 80 and 100°C.,<sup>4,5</sup> (2) the transition at about 130°C. consisted of doublets at about 120 and 140°C. in the amorphous region,<sup>4,5</sup> (3) the Clapeyron equation was applicable to room-temperature transitions at 20 and 30°C.,<sup>19</sup> (4) the transition at about -30°C. occurred in the amorphous region in doublets at about -40 and -15°C.,<sup>32</sup> and (5) the three second-order transitions at about 130,

-30, and -90°C. appeared at two-thirds the absolute temperatures of the three first-order transitions at about 330, 90, and 20°C., respectively; i.e., the so-called 2/3 rule<sup>35-37</sup> apparently seemed to hold. These results were obtained by thermal, rheological, and dielectric methods.

This paper deals with results of measurements for transitions of PTFE at about 90 and 130°C. made by x-ray diffraction and infrared absorption methods.

## X-RAY DIFFRACTION

### Experimental Procedure

X-ray diffraction measurements were made by a Geigerflex D-3F diffractometer (Rigaku-Denki Co., Ltd.) at various temperatures from 25 to 190°C. for molded plate samples of PTFE (Polyflon M-12) which contained 10% quartz powder as an inner standard.

Plate samples, 3 mm. in thickness, were prepared as follows: Polyflon M-12 powder and quartz powder were mixed at a ratio of 10:1 by weight, preformed at room temperature under a pressure of 300 kg./cm.<sup>2</sup>, and the preform was sintered at 370°C. for 3 hr.

A sample was set on the sample holder. The sample and the holder were covered by a cylindrical case of nickel foil. The sample was kept at a constant temperature during each measurement.

Diffraction intensity was detected by a Geiger counter in the angular range of  $2\theta$  diffraction between 15° and 32°. The wavelength of x-rays used was 1.5405 Å. of  $\text{CuK}\alpha_1$  and the radiation was filtered by a nickel foil.

A series of measurements were made at various temperatures from 25 to 190°C. in ascending order for the same sample.

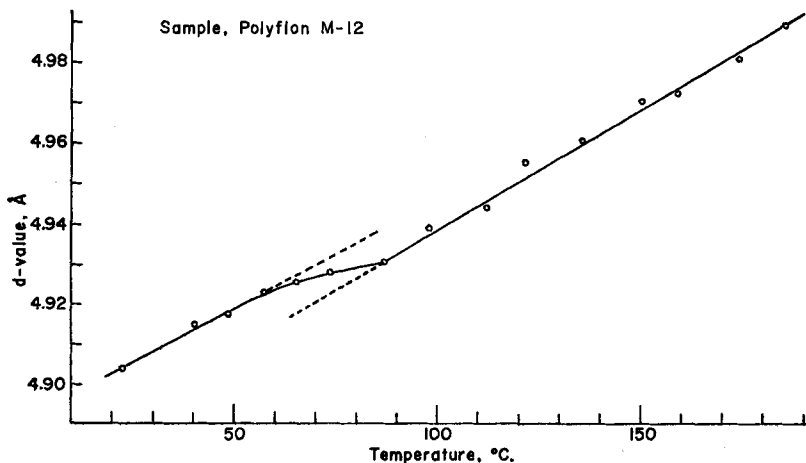


Fig. 1. Variation of  $d$ -value with temperature for the (100) plane of polytetrafluoroethylene.

### Results and Discussion

In each chart of  $2\theta$ -intensity, there appeared a strong diffraction peak near  $18^\circ$ , a weak peak near  $21^\circ$ , a sharp peak between  $26^\circ$  and  $27^\circ$ , and a weak and broad peak between  $31^\circ$  and  $32^\circ$ . Two peaks at about  $18^\circ$  and  $31^\circ$  are due to the (100) and (200) planes of PTFE, respectively.<sup>28,38,39</sup> Peaks at about  $21^\circ$  and  $26^\circ$  are attributed to quartz. The peaks of PTFE shifted toward a smaller angle as the measuring temperature was elevated. In other words the (100) plane spacing became larger owing to thermal ex-

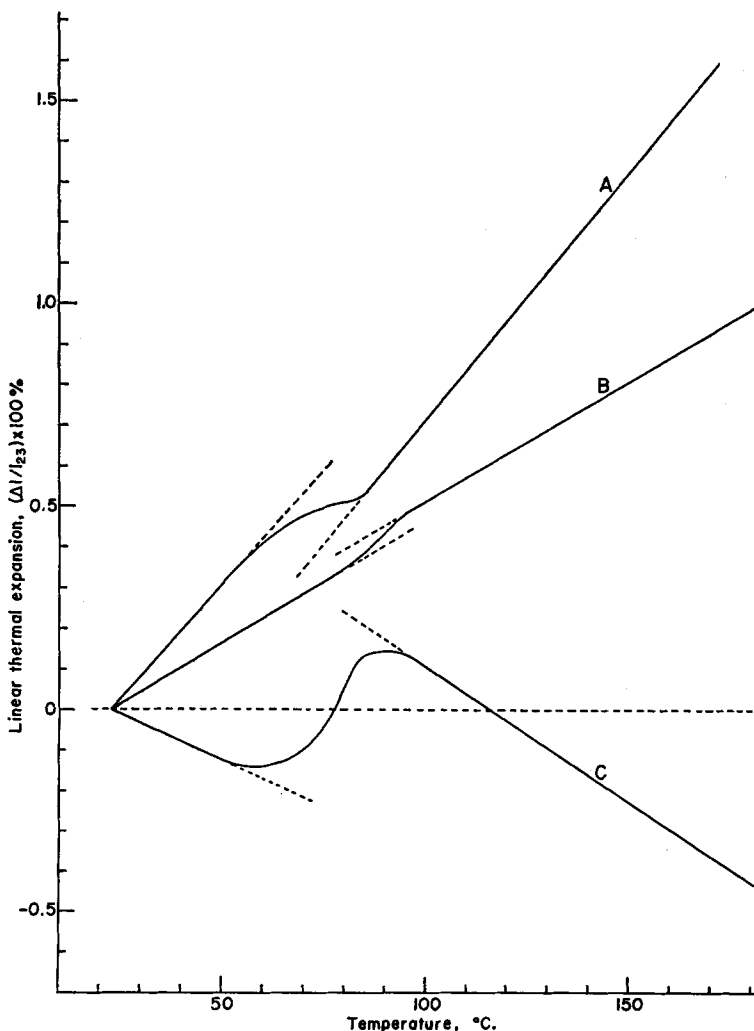


Fig. 2. Anisotropy in linear thermal expansion for the crystal of polytetrafluoroethylene: (A) in the direction perpendicular to the molecular chain; (B) in bulk; (C) in the direction parallel with the molecular chain, calculated from the values on the curves A and B.

pansion. The  $d$ -value of quartz should be constant, 3.343 Å., in the temperature range from 25 to 190°C., but the observed values sometimes deviate from the constant owing to experimental error, possibly owing to thermal deformation of the sample surface. If the observed  $d$ -values of quartz are not constant, observed  $d$ -values of (100) for PTFE must be corrected so as that the  $d$ -value of quartz for the maximum peak at about 26° is to be 3.343 Å.

An example of the relation between  $d$ -value of the (100) plane for PTFE and temperature is shown in Figure 1. Since the  $d$ -value of quartz was confirmed to be almost constant, 3.342–3.345 Å. in this example, corrections for that of PTFE were unnecessary over the temperature range. In this figure the slope of the curve gives a thermal expansion coefficient in the direction perpendicular to the (100) plane, i.e., parallel with the axis of the molecular chain in the crystalline region. As the crystal lattice is hexagonal above the room-temperature transition,<sup>13</sup> the thermal expansion coefficient must be isotropic in the plane perpendicular to the molecular chain axis. The thermal expansion coefficient is obtained from Figure 1 as  $1.1 \times 10^{-4} \text{C.}^{-1}$  below 60°C. and  $1.2 \times 10^{-4} \text{C.}^{-1}$  above 90°C., and as a minimum value of some  $0.2 \times 10^{-4} \text{C.}^{-1}$  at about 80°C. On the curve in Figure 1 it is difficult to find any irregular change at about 130°C. where distinct transitions should occur.<sup>4,5</sup> In a previous paper,<sup>5</sup> the thermal expansion coefficient of the crystalline region in bulk was  $0.6 \times 10^{-4} \text{C.}^{-1}$ , which was obtained by extrapolation to 100% crystallinity. Therefore the ex-

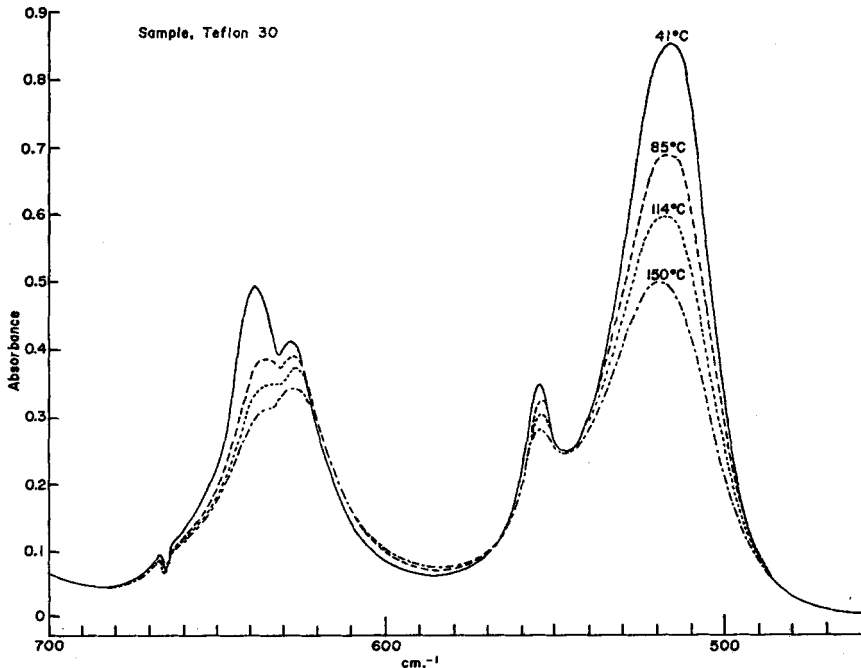


Fig. 3. Infrared absorption spectra of polytetrafluoroethylene at various temperatures.

pansion coefficient in the direction of molecular chain is estimated to be about  $-0.5 \times 10^{-4} \text{C.}^{-1}$  below  $60^\circ\text{C.}$  and  $-0.7 \times 10^{-4} \text{C.}^{-1}$  above  $90^\circ\text{C.}$ , and gives a positive maximum value at about  $80^\circ\text{C.}$

Such an anisotropy as this in linear thermal expansion for the crystal of PTFE is illustrated in Figure 2. The curves *A*, *B*, and *C* in Figure 2 show plots of the values in the direction perpendicular to the molecular chain, those in bulk, and those in the direction parallel with the molecular chain, respectively. Curve *A* is rewritten from the values in Figure 1. Curve *B* is drawn so that the linear expansion coefficient is  $0.6 \times 10^{-4} \text{C.}^{-1}$  below  $80^\circ\text{C.}$  and above  $100^\circ\text{C.}$ , and gives a small change at about  $90^\circ\text{C.}$ <sup>5</sup> Curve *C* is drawn such that three times the value on curve *B* minus two times of value on Curve *A* is to be equal to the value on curve *C* at each temperature.

These facts suggest that some change in crystalline structure occurs at about  $80^\circ\text{C.}$  while no change takes place at about  $130^\circ\text{C.}$  This supports the previous results<sup>4,5</sup> that there appeared first-order transitions in crystalline region at about  $90^\circ\text{C.}$  and second-order transitions in amorphous region at about  $130^\circ\text{C.}$

## INFRARED SPECTRA

### Experimental Procedure

The infrared spectra were obtained for film samples of PTFE by a Perkin-Elmer Model 521 spectrometer in the  $450\text{--}800 \text{ cm.}^{-1}$  region at different temperatures from  $30$  to  $150^\circ\text{C.}$

Films of PTFE were prepared by a casting method from commercial Teflon 30 aqueous dispersion. The PTFE dispersion was sprayed uniformly on a polished chromium-plated ferrotype plate. The plate covered with sprayed PTFE was dried, and heated in an oven at  $360^\circ\text{C.}$  for about half an hour, and then cooled in the oven slowly or quenched in ice-water. The sintered PTFE film was removed from the plate carefully. The thickness of the films was about  $4 \mu$ , and their crystallinity varied with the cooling rate. The crystallinities of the film samples were measured by the infrared absorption method.<sup>17</sup>

The film sample was set in a cell with KBr windows, the air in which was kept at various measuring temperatures within  $\pm 0.1^\circ\text{C.}$  A series of measurements were made at different temperatures from  $30$  to  $150^\circ\text{C.}$  in ascending order.

### Results and Discussion

Absorbance at several absorption bands in the  $450\text{--}800 \text{ cm.}^{-1}$  region changed with temperature, as is illustrated in Figure 3. The band at  $518 \text{ cm.}^{-1}$  is assigned to  $\text{CF}_2$  rocking, and those at  $627$  and  $639 \text{ cm.}^{-1}$  to  $\text{CF}_2$  wagging.<sup>17</sup>

Absorbances at  $518$ ,  $627$ , and  $639 \text{ cm.}^{-1}$  are plotted against temperature in Figure 4 for samples with  $46$  and  $78\%$  crystallinities. On these

curves in Figure 4, slightly irregular changes are perceptible at about 30, 50, 90, and 130°C. Particularly on the curve for 518  $\text{cm}^{-1}$ , changes in absorbance at about 50 and 90°C. are more pronounced for the sample with a higher crystallinity, 78%, than those for a lower crystallinity, 46%. The

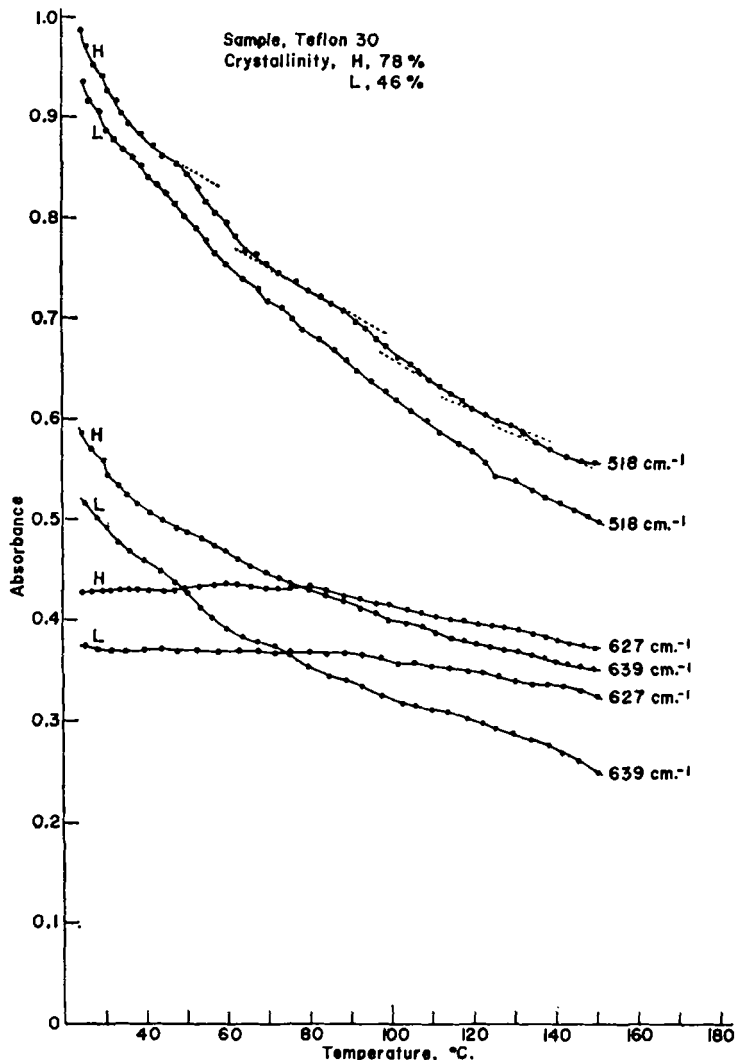


Fig. 4. Variation of infrared absorbance with temperature for film samples of polytetrafluoroethylene.

change at about 90°C. seems to show some change in the crystalline region, which may correspond to the change at about 80°C. measured by x-ray diffraction in the present paper and by other methods in previous papers.<sup>4,5</sup> The interpretation of the change in absorbance at about 50°C., is not yet

established. A little change at about 130°C. on the curves in Figure 4 seems to correspond to second-order transitions in previous results.<sup>4,5</sup>

### CONCLUSION

By x-ray diffraction, an irregularity in thermal expansion in the crystalline region of PTFE was observed at about 80°C., but no noticeable irregularity was found near 130°C. Also in the infrared absorption for film samples of PTFE, slightly irregular changes of absorbance at 518, 627, and 639  $\text{cm.}^{-1}$  bands appeared near 90 and 130°C. Especially at 518  $\text{cm.}^{-1}$  band, a more crystalline sample showed more noticeable irregularity at about 90°C. than a less crystalline sample.

The results obtained by x-rays and infrared absorption in the present work agree fairly well with the previous results<sup>4,5</sup> that first-order transitions occurred at about 90°C. in the crystalline region and second-order transitions at about 130°C. in the amorphous region.

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### Résumé

Au moyen de la diffraction aux rayons-X, l'espacement du réseau du plan (100) de polytétrafluoroéthylène a été mesuré à différentes températures allant de 25 à 190°C. Dans la région cristalline, le coefficient d'expansion linéaire dans la direction perpendiculaire à l'axe de la chaîne moléculaire était trouvé égal à  $1.1 \times 10^{-4} \text{°C}^{-1}$  au-dessus de 60°C, de  $1.2 \times 10^{-4} \text{°C}^{-1}$  au-dessus de 90°C et une valeur minimum de  $0.2 \times 10^{-4} \text{°C}^{-1}$  à environ 80°C. Comme le coefficient de dilatation linéaire de la région cristalline en bloc était égal à  $0.6 \times 10^{-4} \text{°C}^{-1}$ , le coefficient de dilatation dans la direction de l'axe de la chaîne moléculaire doit être négatif sauf dans la région de transition au voisinage de 80°C. La variation de la séparation des axes des chaînes moléculaires avec la température montrait une irrégularité à environ 80°C, mais pas au voisinage de 130°C dans la région cristalline. L'absorption infrarouge des échantillons de films de PTFE a été mesurée à différentes températures de 25 à 150°C pour les bandes à 518, 627 et 639  $\text{cm}^{-1}$ . Au départ des courbes d'absorption-température pour ces différentes bandes, on a observé des irrégularités au voisinage de 30, 50, 90 et 130°C. Particulièrement, pour la bande à 518  $\text{cm}^{-1}$ , un échantillon plus cristallin fournissait des irrégularités plus distinctes vers les 50 et 90°C, plutôt qu'un échantillon moins cristallin. Le changement à environ 90°C des spectres infrarouges pourrait correspondre à celui obtenu par mesures aux rayons-X aux environs de 80°C qui est attribué à la région cristalline. Les résultats obtenus par rayons-X et par mesures infrarouges confirment les résultats antérieurs des méthodes thermique, rhéologique et diélectrique: des transitions de premier ordre existent dans la région cristalline à environ 90°C et des transitions de second ordre dans la région amorphe à environ 130°C.

### Zusammenfassung

Mittels Röntgenbeugung wurde der Gitterabstand der (100)-Ebene von geformtem Polytetrafluoräthylen bei verschiedenen Temperaturen von 25 bis 190°C gemessen. Im kristallinen Bereich ergab sich der lineare Ausdehnungskoeffizient in der Richtung senkrecht zur Molekülkettenachse unterhalb 60°C. zu  $1.1 \times 10^{-4} \text{grad}^{-1}$ , oberhalb 90°C. zu  $1.2 \times 10^{-4} \text{grad}^{-1}$  und bei etwa 80°C. zu einem Minimum von  $0.2 \times 10^{-4} \text{grad}^{-1}$ . Da der lineare Ausdehnungskoeffizient des kristallinen Bereiches in Masse zu  $0.6 \times 10^{-4} \text{grad}^{-1}$  gemessen wurde, muss der Ausdehnungskoeffizient in der Richtung der Molekülkettenachse, mit Ausnahme des Umwandlungsbereiches um 80°C., negativ sein. Die Abhängigkeit des Abstandes der Molekülkettenachsen von der Temperatur zeigte bei etwa 80°C., nicht aber in der Nähe von 130°C. im kristallinen Bereich eine Unregelmässigkeit. Die Infrarotabsorption von PTFE-Filmproben wurde bei verschiedenen Temperaturen von 25 bis 150°C. für drei Banden bei 518, 627, und 639  $\text{cm}^{-1}$  gemessen. In den Absorptions-Temperaturkurven dieser Banden traten Unregel-



mässigkeiten in der Nähe von 30, 50, 90, und 130°C. auf. Besonders die Bande bei 518  $\text{cm.}^{-1}$  wies bei einer stärker kristallinen Probe deutlichere Unregelmässigkeiten bei 50 und 90°C. auf als bei einer weniger kristallinen. Die im Infrarotspektrum bei etwa 90°C. auftretende Änderung kann der mit Röntgenmessungen bei etwa 80°C. erhaltenen entsprechen, die dem kristallinen Bereich zugeschrieben wurde. Die durch Röntgen- und Infrarotmessungen gewonnenen Ergebnisse bilden eine Stütze für die früheren Ergebnisse thermischer, rheologischer und dielektrischer Methoden, nämlich für das Auftreten von Umwandlungen erster Art im kristallinen Bereich bei etwa 90°C. und Umwandlungen zweiter Art im amorphen Bereich bei etwa 130°C.

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