

# EQUILIBRIUM HEAT OF FUSION OF POLYTETRAFLUOROETHYLENE\*

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## ABSTRACT

The reliability of the values of equilibrium heat of fusion,  $\Delta H_m$ , of polytetrafluoroethylene (PTFE), reported in the literature and the inadequacy of the generally accepted value of 13.7 or 14.6 cal/g were discussed. Through extrapolating linear plot of  $\Delta H_m$  vs.  $V_{sp}$  of the thermally aged PTFE virgin as-polymerized samples prepared in accord with ASTM D 1457-81a,  $\Delta H_m^0 = 79.6$  J/g (19.0 cal/g) and  $V_{sp}$  (specific volume of amorphous PTFE at 23°C) = 0.480 cm<sup>3</sup>/g (or  $\rho_a = 2.08$  g/cm<sup>3</sup>) were obtained.

The heats of fusion,  $\Delta H_m$ , of the thermally aged and  $\gamma$ -irradiated samples are different irrespective of the same  $V_{sp}$  value for both samples. A qualitative explanation of this phenomenon was given based on the  $H_v$  patterns of SALS and Kawai's model.

## INTRODUCTION

Since 1950's, different values of the equilibrium heat of fusion,  $\Delta H_m^0$ , of polytetrafluoroethylene (PTFE) have been reported in the literature. In Tab. 1 are listed chronologically the reported values of  $\Delta H_m^0$ . It can be seen that the magnitude of these values is in the range of 12–24 cal/g, i.e. the difference between them is as high as more than twofold. McGeer et al.<sup>[1]</sup> (1952) were the first to measure the  $\Delta H_m^0$  of PTFE at different pressures based on the Clausius-Clapeyron's equation

$$\Delta H_m^0 = T_m \Delta V_m / (dT_m/dP) \quad (1)$$

and the empirical pressure dependence of melting temperature in the form of

$$T_m = A + BP \quad (2)$$

where  $T_m$  is the absolute equilibrium melting temperature,  $\Delta V_m = V_l - V_c$  is the volume change during melting, where  $V_l$  and  $V_c$  are the specific volumes of liquid and crystal at the melting point respectively, and  $P$  is the pressure in atm.,  $A$  and  $B$  being constants. All of these quantities can be derived from PVT experiment. They obtained  $A = 597\text{K}$  and  $B$  (or  $dT_m/dP$ ) = 0.154K/atm. Substituting the corresponding values of  $P$  and  $\Delta V_m$  into the above equations they calculated the values of  $\Delta H_m^0$  of PTFE under different pressures as shown in Tab. 2. It should be pointed out that the value of  $\Delta H_m^0$  under 69 atms. calculated by this method should be 13.7 cal/g but erroneously given as 14.6 cal/g. Sometimes this erroneous value was further mistaken for  $\Delta H_m^0$  under atmospheric pressure and erroneously used to calculate the crystallinity of PTFE samples<sup>[18]</sup>. Because  $\Delta H_m^0$  is an important thermo-

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Table 1 Published values of  $\Delta H_m^0$  of PTFE

| Date | Author                          | Method | $\Delta H_m^0$<br>(J/g) (cal/g) |                                                                                                                           | Ref. |
|------|---------------------------------|--------|---------------------------------|---------------------------------------------------------------------------------------------------------------------------|------|
| 1952 | P. L. McGeer and H. C. Duus     | PVT    | 57.0                            | 13.6                                                                                                                      | [1]  |
| 1957 | G. Gee                          | PVT    | 50.3                            | 12                                                                                                                        | [2]  |
| 1958 | J. M. Lupton                    | PVT    | 57.4                            | 13.7 <sup>1)</sup>                                                                                                        | [2]  |
| 1961 | C. A. Sperati, et al.           | PVT    | 68.4                            | 16.3 <sup>2)</sup>                                                                                                        | [3]  |
| 1972 | R. P. Kusy, et al.              | DSC    | 83.8                            | 20                                                                                                                        | [4]  |
| 1975 | T. Suwa, et al.                 | DSC    | 57.4                            | 13.7                                                                                                                      | [5]  |
| 1979 | H. W. Starkweather, Jr., et al. | DSC    | 75.4 $\pm$ 4                    | 18 $\pm$ 1<br>(virgin powder)<br>33.5 $\pm$ 4 8 $\pm$ 1<br>(melted)<br>79.6 $\pm$ 4 19 $\pm$ 1<br>(coagulated dispersion) | [6]  |
| 1980 | J. J. Weeks, et al.             | DSC    | 72.3                            | 17.3                                                                                                                      | [7]  |
| 1982 | H. W. Starkweather, Jr.         | PVT    | 102.2                           | 24.4<br>(virgin powder)<br>93.0 22.2<br>(melted)                                                                          | [8]  |

1) 685 cal/g of  $\text{CF}_2$  in the original literature.2) 3.42 kJ/mole of  $\text{CF}_2$  in the original literature.Table 2 McGeer's  $\Delta H_m^0$  under different pressures

| Pressure, $P$<br>(atm.) | Melting point, $T_m$<br>(K) | Volume change<br>$\Delta V_m$ (cm <sup>3</sup> /g) | Heat of fusion<br>$\Delta H_m^0$ (cal/g) |
|-------------------------|-----------------------------|----------------------------------------------------|------------------------------------------|
| 1                       | 597                         | 0.145                                              | 13.6                                     |
| 69                      | 508                         | 0.143                                              | 14.6 <sup>1)</sup>                       |
| 207                     | 629                         | 0.085                                              | 8.4                                      |

1) This value is in error and should be 13.7—the author.

dynamic parameter characterizing the intermolecular action and has practical use in the fabrication and application of PTFE, it is not surprising that during the past 30 years, a good deal of effort was made to improve the reliability of this value in order to obtain an accurate  $\Delta H_m^0$  value for PTFE.

Later, Gee and Lupton<sup>[2]</sup> also reported somewhat similar values by the same method. Recently, using an improved PVT apparatus, Starkweather<sup>[8]</sup> published the values of  $\Delta H_m^0$

for both virgin as-polymerized powder and melt processed PTFE samples as 24.4 and 22.2 cal/g respectively, which are almost twice as high as all the previously published values. Starkweather noticed that in McGeer's experiment the pressure produced in their piston type apparatus was non-hydrostatic and that the midpoint of the melting range was taken for the melting point and thus the coefficient  $B$  was as high as 0.154 K/atm. and thought that these were responsible for this discrepancy<sup>1)</sup>. In contrast, Starkweather used a hydraulic equipment and took the end point as  $T_m$  and the corresponding  $dT_m/dP$  was equal to 0.098 K/atm. Besides, considering that the virgin as-polymerized sample was susceptible to superheating, Starkweather recommended 22.2 rather than 24.4 cal/g as the  $\Delta H_m^0$  value for PTFE.

In principle, the method based on Clausius-Clapeyron's equation is a classical way to indirectly determine  $\Delta H_m^0$  of a crystalline substance. However, the macromolecular nature of PTFE such as the broadening of the melting range, the superheating of the extended chain molecule, etc., would introduce uncertainty into the derived result. Therefore, resort had been made to measure  $\Delta H_m^0$  directly by calorimetric method. Although differential scanning calorimeter (DSC) is commercially available and provides a convenient way to measure precisely the heat of fusion of samples, the absence of 100% crystalline sample renders the determination of  $\Delta H_m^0$  difficult. In the past, the heat of fusion of virgin PTFE sample directly measured by DSC was granted to be equal to  $\Delta H_m^0$ , without consideration of its incompletely crystalline nature (Tab. 1). However, the newly developed method to extrapolate the linear relationship between  $\Delta H_m$  and the specific volume,  $V_{sp}$ , of samples with different degree of crystallinity to 100% crystalline condition has been proved to be successful in the determination of  $\Delta H_m^0$  for many linear semicrystalline polymers such as polyethylene, polypropylene and polyoxymethylene etc.<sup>[9]</sup>. In the present work, PTFE samples of different degree of crystallinity prepared either by high temperature aging or  $\gamma$ -irradiation were used to determine  $\Delta H_m^0$  calorimetrically. At the same time the different relationship between  $\Delta H_m$  and  $V_{sp}$  shown by aged and irradiated samples were discussed.

### $\Delta H_m$ OF VIRGIN AS-POLYMERIZED POLYMER

A Perkin-Elmer DSC-2C differential scanning calorimeter was used to measure the heat of fusion of PTFE samples. A scanning rate of 10°C/min was used. The instrument was calibrated with high purity indium and the baseline in the temperature range of interest was flattened according to standard procedures<sup>[19]</sup>. The endothermic area was defined by connecting the pre- and postmelting baselines. By careful measuring the area with a planimeter, it was estimated that the precision of the calorimetric measurements was better than  $\pm 1.5\%$ . X-ray crystallinity was determined by a Rigaku X-ray diffractometer (Model 2028). The results obtained for 7 virgin PTFE samples are shown in Tab. 3. Since the determination of crystallinity of PTFE was based on the relative intensities of peak (100) and the nearby amorphous peak just at somewhat higher  $2\theta$ <sup>[20]</sup>, the high intensity of peak (100) for virgin PTFE powder obscured the presence of amorphous peak and thus resulted in a higher value of X-ray crystallinity. The DSC measured  $\Delta H_m$  values of virgin as-polymerized PTFE powder

1) Starkweather pointed out that had McGeer et al. used the end point of the transition as melting point, a much lower value of  $B$  would have been obtained.

Table 3 Heat of fusions of virgin PTFE samples

|                         | 1    | 2    | 3    | 4    | 5    | 6    | 7    |
|-------------------------|------|------|------|------|------|------|------|
| $\Delta H_m$ (J/g)      | 67.9 | 67.9 | 67.0 | 67.9 | 71.6 | 67.4 | 68.3 |
| X-ray crystallinity (%) | 98.9 | —    | —    | 99.4 | 99.3 | 98.6 | 99.0 |

samples supplied by Chinese or foreign company are shown in Tab. 3. The values are in the range of 67–71 J/g (16–17 cal/g). The magnitude of these values is undoubtedly less than the equilibrium heat of fusion,  $\Delta H_m^0$ , for all samples were not 100% crystalline. Since the  $\Delta H_m^0$  value for PTFE quoted in literature including some books<sup>[10,11]</sup> is 13.7 cal/g, it is of significance to evaluate correctly the value of  $\Delta H_m^0$  of PTFE.

### $\Delta H_m^0$ OF VIRGIN PTFE

In order to construct a plot of  $\Delta H_m$  vs.  $V_{sp}$ , one must at first prepare PTFE samples with different degree of crystallinity. Two methods of preparing samples were used: one was  $\gamma$ -irradiation, and the other, thermal aging. It is well-known that the crystallinity of PTFE increases with the increase of radiation dose or time of thermal aging.

In a preliminary experiment, PTFE sheets supplied by "The 9th Plastic Works, Tianjin"  $1 \times 12 \times 30$  mm in size and with similar original density were irradiated in a  $^{60}\text{Co}$  radiation source. The density, crystallinity and  $\Delta H_m$  of irradiated samples were measured and given in Tab. 4. From Tab. 4 it can be seen that the crystallinity increases with the increase of dose. According to the relation  $X_c = \Delta H_m / \Delta H_m^0$ , the enthalpy of fusion of PTFE can be estimated and was in the range of 67–105 J/g (16–25 cal/g). The commercial PTFE sheets may contain some voids and the crystallinity determined by X-ray method may be overestimated, therefore it is reasonable to assume that the correct  $\Delta H_m^0$  value should be higher than 67 and lower

Table 4 Crystallinity and  $\Delta H_m$  of commercial PTFE sheet after  $\gamma$ -irradiation

| No.            | Dose (röntgen)    | Density (g/cm <sup>3</sup> ) <sup>1</sup> | Crystallinity (%)           |                        |              | $\Delta H_m$ (J/g) | Estimated range of $\Delta H_m^0$ (J/g) |
|----------------|-------------------|-------------------------------------------|-----------------------------|------------------------|--------------|--------------------|-----------------------------------------|
|                |                   |                                           | Density method <sup>2</sup> | IR method <sup>3</sup> | X-ray method |                    |                                         |
| A <sub>0</sub> | 0                 | 2.167                                     | 41                          | 72                     | 73           | 33.1               | 45.2–80.4                               |
| A <sub>2</sub> | 1.10 <sup>4</sup> | 2.171                                     | 43                          | 74                     | 78           | 34.3               | 44.0–80.0                               |
| A <sub>4</sub> | 5.10 <sup>5</sup> | 2.187                                     | 50                          | 79                     | 83           | 52.8               | 63.3–105.6                              |
| A <sub>7</sub> | 5.10 <sup>6</sup> | 2.206                                     | 59                          | 85                     | 87           | 61.6               | 70.4–104.3                              |
| A <sub>9</sub> | 5.10 <sup>7</sup> | 2.247                                     | 77                          | 89                     | 98           | 66.2               | 67.4–85.9                               |

1) By buoyancy method, at 23°C.

2) In the calculation of crystallinity,  $\rho_a$  was taken as 2.083 (based on the result of the present work).  $\rho_c$ , 2.302 (taken from ref. [12]).

3) Film sample, thickness, 20  $\mu$ .

than 105 J/g (or higher than 16 and lower than 25 cal/g).

In order to minimize the uncertainty resulting from the presence of voids in the commercial PTFE sheet samples, more compact or void-free standard sheet samples were prepared according to ASTM D 1457-81a in later experiments. The samples were uniform and the density deviation was within  $\pm 0.0002$ . For preparing thermally aged samples, standard sheet samples were subjected to thermal aging at  $380 \pm 2^\circ\text{C}$  for 2 to 600 hours. Density and  $\Delta H_m$  increased with the lengthening of aging time, because the longer the aging time, the lower the  $MW$  of PTFE, and thus the larger the crystallinity<sup>[17]</sup>. In Fig. 1 there does exist a linear relationship

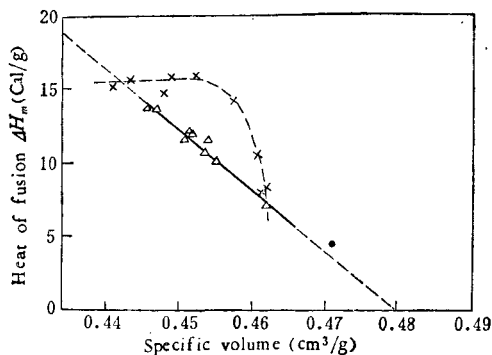


Fig. 1  $\Delta H_m$  vs.  $V_{sp}$  plot of PTFE standard sheet samples

$\triangle$  thermally aged at  $380^\circ\text{C}$ .

$\times$   $\gamma$ -irradiated at room temperature.

$\bullet$  quenched sample.

between  $\Delta H_m$  and  $V_{sp}$ . Through linear regression, an expression in the form

$$\Delta H_m = 837.0 - 1743.5V_{sp} \quad (\text{J/g}) \quad (3)$$

was given with a correlation coefficient 0.97. Equation (3) is useful for the determination of  $\Delta H_m^0$ , the equilibrium heat of fusion and  $V_{sp}^a$ , the specific volume of completely amorphous PTFE at  $23^\circ\text{C}$ , if the boundary conditions are substituted to it. That is, if  $V_{sp}^c$  (specific volume of 100% crystalline PTFE, equals to 0.4344 ( $1/2.302$ ) as calculated based on the crystallographic parameters of PTFE) is substituted for  $V_{sp}$ ,  $\Delta H_m^0 = 79.6 \text{ J/g}$  is derived; if  $\Delta H_m$  is put into zero, the  $V_{sp}^a$  obtained is equal to 0.4800 or  $\rho_a = 2.083 \text{ g/cm}^3$ , which is presumed to be reasonable and is a little higher than that of the generally accepted value  $2.0 \text{ g/cm}^3$ , measured indirectly on the basis of low molecular weight liquid perfluoroalkane<sup>[13]</sup>. This value is in fair conformity with the recently published value of Starkweather<sup>[14]</sup>, within a deviation of about 1%.

Having obtained  $\Delta H_m^0 = 79.6 \text{ J/g}$ , we calculated the crystallinity of virgin powder samples of various origin in Tab. 3 in terms of their respective  $\Delta H_m$ . The crystallinity thus calculated is in the range of 84–90%. The same calculation was also performed for samples listed in Tab. 4. The values obtained are similar to those obtained by the density method, but lower than those obtained by both X-ray and IR methods, since the determination of crystallinity by IR is based on the X-ray method<sup>[12]</sup>. It is well-known that the degree of crystallinity of a polymer, determined from different method may not agree. This is because the mea-

measurements may be sensitive to different definitions of crystalline order. The lower crystallinity value by calorimetric method can be attributed to the smallness of the polymer crystals. The higher surface free energy due to increased surface area results in the decrease of  $\Delta H_m$  during melting<sup>[21]</sup>.

The relationship between  $\Delta H_m$  and  $V_{sp}$  of irradiated sheet samples is also shown in Fig. 1. In this case, the relationship is no longer linear, because under higher dosage, the deterioration effect of  $\gamma$ -irradiation on the crystals leads to the lowering of melting point and the broadening of the melting range, and no further increase of  $\Delta H_m$  can be achieved. Even when the dose was raised to  $10^8$ – $10^9$  rontgen,  $\Delta H_m$  of only about 63J/g was reached which tended to further decrease at further increased dose.

#### $H_v$ SCATTERING PATTERNS OF THERMALLY AGED AND $\gamma$ -IRRADIATED PTFE

As mentioned above, the  $\Delta H_m$  vs.  $V_{sp}$  relationship was linear for thermally aged samples while samples irradiated in air at room temperature showed a different regularity. From Fig. 1, it can also be seen that the two samples one thermally aged and the other  $\gamma$ -irradiated have different  $\Delta H_m$  values although the  $V_{sp}$  of both samples is the same (e.g.,  $\sim 0.452$ ). The difference is as much as 35%. Therefore, a question was raised, i.e. besides possible difference in  $MW$ , why the same material with the same  $V_{sp}$  value could give different enthalpy change during melting. In order to clarify this contradiction, structure studies were carried out by means of X-ray, IR and SALS techniques. No any useful information was obtained from the X-ray diffraction pattern and IR spectrum, but the  $H_v$  patterns of SALS showed a definite discrepancy between the two samples.

Figures 2–5 are the  $H_v$  patterns of commercial films subjected to either thermal aging or  $\gamma$ -irradiation with sample conditions shown in Fig. 1. After thermal aging for 8 hours, the  $\Delta H_m$  for the film sample was 32.3J/g and the corresponding  $H_v$  pattern showed four-leaf clover appearance with azimuthal scattering angle  $90^\circ$  (or  $+$  type, Fig. 2). This is a typical  $H_v$  pattern of PTFE rod crystal. When this aging was followed by  $\gamma$ -irradiation, the original  $90^\circ$   $H_v$  pattern turned to  $45^\circ$  (or  $\times$  type) as shown in Fig. 3. At the same time, the value of  $\Delta H_m$  was raised to 41.1J/g. On the contrary, a film sample which had been  $\gamma$ -irradiated with a dose of  $1.5 \cdot 10^6$  rontgen had a  $\Delta H_m$  of about 57.8J/g and showed a  $45^\circ$   $H_v$  pattern (Fig. 4); if this  $\gamma$ -irradiated sample was followed by high temperature thermal aging, its  $H_v$  pattern tended to turn back to  $90^\circ$  again (see Fig. 5) and  $\Delta H_m$  value lowered to 26.8 J/g. According to the models suggested by Rhodes and Stein<sup>[22]</sup>, and Kawai et al.<sup>[15,23]</sup>, the SALS  $H_v$  scattering pattern may be either  $+$ ,  $\times$  type or even circularly symmetric, depending upon the inclined angle of the optical axis of a random assembly of anisotropic rods with respect to the rod direction and upon the inter-rod interference. Therefore, the super-molecular structure change resulting from the molecular rearrangement at a higher local temperature produced by the interaction of radiation particles with structure<sup>[16]</sup> can be presumed to be responsible for the above mentioned phenomenon.

In other words, the super-molecular structure is different for thermally aged and  $\gamma$ -irradiated samples and so is the energy absorbed during melting. As the  $H_v$  pattern of the thermally aged sample is the same as that of the typical rod crystal and satisfactory linear relationship exists between  $\Delta H_m$  and  $V_{sp}$ , the value  $\Delta H_m^0 = 79.6\text{J/g}$  should be reliable. As

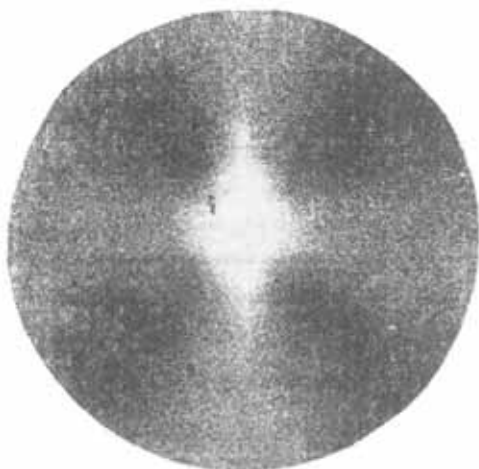


Fig. 2  $H_v$  pattern of PTFE film thermally aged for 8 hours

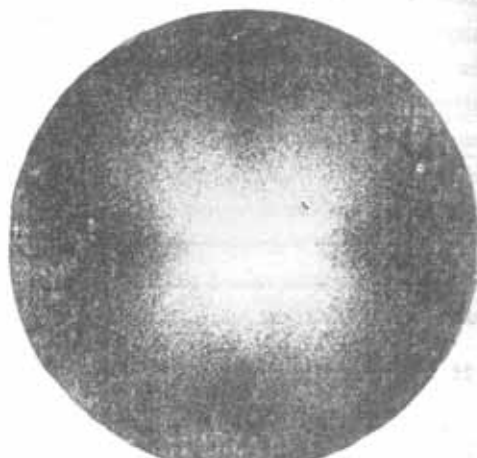


Fig. 3  $H_v$  pattern of PTFE film subjected to  $1.5 \cdot 10^6$  rontgen  $\gamma$ -irradiation after 8 hours thermal aging

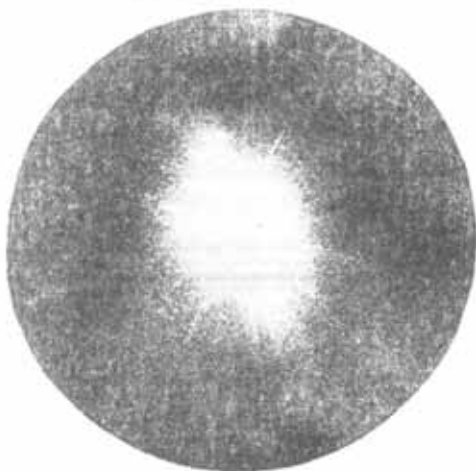


Fig. 4  $H_v$  pattern of PTFE film subjected to  $1.5 \cdot 10^6$  rontgen  $\gamma$ -irradiation

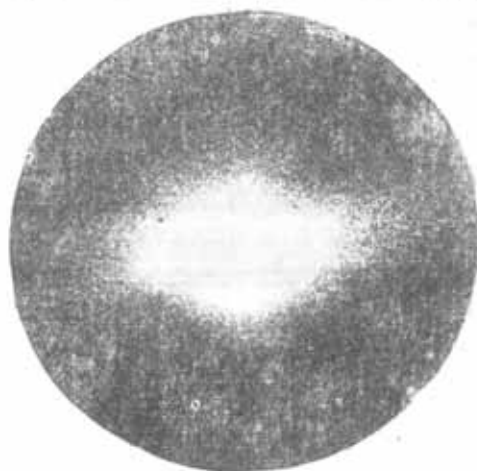


Fig. 5  $H_v$  pattern of PTFE film irradiated as shown in Fig. 4 but further thermally aged for 6 hours

to the  $\gamma$ -irradiated sample, it cannot be used to determine the  $\Delta H_m^0$  not only because of its non-linearity between  $\Delta H_m$  and  $V_{sp}$ , but also its difference in supermolecular structure from the normal PTFE. This fact has been further ascertained in our later study on factors affecting room temperature transition of PTFE. We found that with higher radiation dose, the transition temperature of the irradiated samples shifted to lower temperature and the (108) peak disappeared as evidenced by DSC and WAXD; while for the thermally aged samples, no such changes were found and all the structure characteristics of the original PTFE remained unchanged.

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