Effect of Pressure on the Room-Temperature Transition of Polytetrafluoroethylene and Its Heat of Transition

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INTRODUCTION

In polytetrafluoroethylene there are two closely spaced first-order transitions occurring at room temperature; these are lower by 300° than another first-order transition temperature, which is referred to as the melting point. One of the room-temperature transitions occurs at about 20°C., as discovered by Rigby and Bunn,[1] and the other at about 30°C., as discovered by Quinn, Roberts, and Work.[2] These transitions have been studied by use of the thermal expansion method,[1-3] the calorimetric method,[4-8] x-ray diffraction,[9-12] infrared absorption,[13] and the rheological method.[14]

It is well known that melting points of polymers increase generally with external pressure, and that hence the Clapeyron equation is applicable.[15] It has been reported that the room-temperature transition of polytetrafluoroethylene also increases when the external pressure is elevated,[16] as has been observed for the crystalline melting point of PTFE as well.[17]

This report deals with the effect of external pressure on the room-temperature transition and on some thermodynamic properties of polytetra-fluoroethylene. Some authors have estimated the heat of room-temperature transition of this polymer by using dilatometric data and the Clapeyron equation,[5,16] without confirming experimentally the applicability of the Clapeyron equation. The present authors observed the dependence of the room-temperature transition upon the external pressure for various specimens of polytetrafluoroethylene on the basis of a dilatometric method. From the data the heats of transition of the specimens at atmospheric pressure were calculated by applying the Clapeyron equation. In addition, we measured the heats of transition for the same specimens by means of a calorimeter. The values obtained by these two different methods were in notably good agreement for each specimen.

SAMPLES AND EXPERIMENTAL PROCEDURE

The eleven samples of PTFE powder used in this study (Table I) were of four types: Teflon (Du Pont), Fluon (Imperial Chemical Industries), Polyflon (Osaka Kinzoku Kogyo), and Tetraflon (Nitto Chemical Industry). Irradiated Teflon 1 powder (2) was prepared by Co^{60} γ-irradiation

TABLE I
Dimensions of Specimens

| Specimen	Diameter, mm.	Length, mm.	Weight, g.	Specific gravity, (25°C./25°C.)
(1) Teflon 1 (molding)	10.03	20.08	3.3768	2.162
(2) Teflon 1 (molding) irradiated with 3.3 × 10⁵ r	10.08	20.06	3.4144	2.179
(3) Teflon 6 (extrusion)	10.03	20.05	3.4724	2.205
(4) Teflon 7 (molding)	10.04	20.09	3.4341	2.178
(5) Fluon G1 (molding)	10.04	20.08	3.4317	2.180
(6) Fluon CD1 (extrusion)	10.05	20.12	3.5302	2.230
(7) Polyflon (molding)	10.03	20.09	3.4120	2.178
(8) Polyflon (molding)	10.06	20.04	3.4401	2.179
(9) Tetraflon (molding)	10.04	20.09	3.4765	2.192
(10) Tetraflon (extrusion)	10.07	20.06	3.5083	2.218
(11) Tetraflon (extrusion)	10.04	20.13	3.5069	2.225
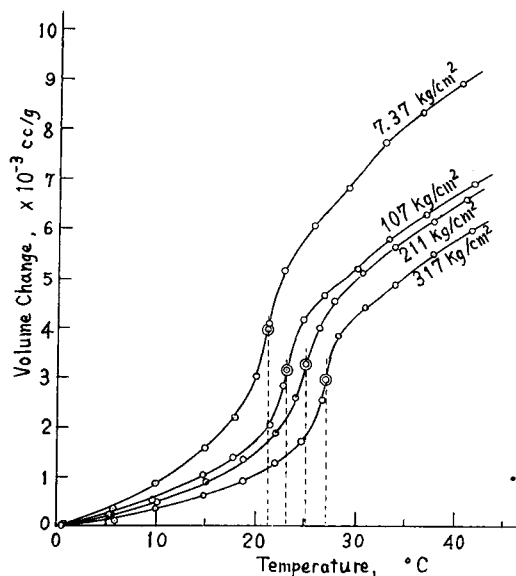
Fig. 1. Thermal expansion of PTFE (Polyflon) under various pressures.

(3.3 × 10⁵ r) of Teflon 1 (1), in order to obtain a sample of lower molecular weight.

The process of molding the test pieces from the above-mentioned PTFE powders was as follows. An amount of 280 g. of each resin powder was compressed gradually at room temperature in a cylindrical mold cavity 25 mm. in diameter under a pressure of 200 kg./cm.² After removal from the mold, the resulting preformed specimen was heated slowly in an air oven up to the gel state and sintered at 350°C. for 5 hr., and then the ambient temperature was reduced gradually to room temperature. The cooling rate was about 1.4°C./min. in the temperature range of 350 to 200°C., and was lower below 200°C.

Eleven specimens of cylindrical shape, 10 mm. in diameter and 20 mm. long, were prepared by machining these molded pieces. Their sizes and specific gravities are shown in Table I.

A specimen was set in a bore of a steel cylinder, the diameter of which was nearly equal to that of the specimen at 0°C. The leakproof piston was forced into the bore containing the specimen, which was thus pressed in the direction of the axis. The specimen was maintained at the specified temperature by water circulating around the steel cylinder, and the pressures applied to the specimen during various cycles were 7, 107, 211, and 317 kg./cm.² During each cycle of the experiment the pressure was kept constant while the temperature of the specimen was elevated stepwise from 0 to

50°C., and the change in the length of the specimen with temperature was followed by means of a dial gage attached to the piston. Transition temperatures of each specimen under various pressures were determined from the inflection points of the volume–temperature curves as shown in Figure 1.

A mercury dilatometer was used to obtain accurately the changes in volume of a sample under atmospheric pressure, that is, ΔV_{20} (cc./g.) for the transition at 20°C. and ΔV_{total} (cc./g.) for the combined contribution of the two transitions.

The specific heats and enthalpy changes of the samples were measured by means of an adiabatic calorimeter in vacuo over the temperature range of 0 to 50°C. The apparatus used was similar to that of Hoffman[18] and Kuroda.[6-8] The temperature of the mantle around the sample was automatically maintained the same as that of the sample which was heated electrically with a constant-wattage supply. The rate of temperature increase was about 1°C./5 min. The heats of transition, ΔH_{20} (cal./g.) for the lower transition and ΔH_{total} for the two combined, were obtained from these measurements.

RESULTS AND DISCUSSION

A set of curves of the thermal change of volume for Polyflon (8) under various pressures is shown in Figure 1. Each curve shows two inflections, that is, two transitions—for example, at 21.4 and 31.0°C. under a pressure of 7.37 kg./cm.² As the lower transition predominates strongly over the upper, so here the lower inflection point of the thermal
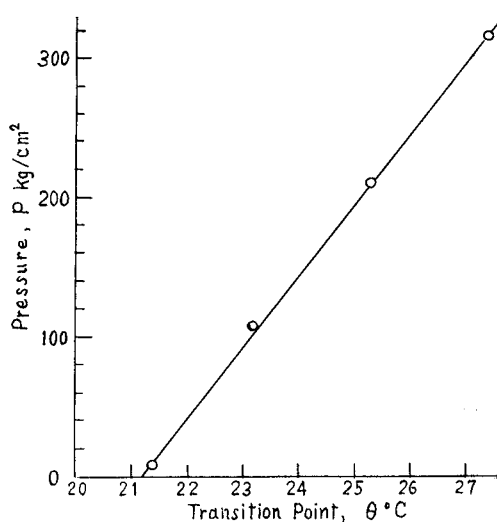

Fig. 2. Dependence of the room-temperature transition of PTFE (Polyflon) upon the external pressure,

expansion curve is referred to as the true room-temperature transition, and the higher one is ignored.

The curve shifts towards higher temperature with increasing external pressure. An example of the relationship between the lower transition temperature and the external pressure is shown in Figure 2 for Polyflon (8). When these transition temperatures are plotted against pressures, a straight line is obtained which can be represented by the equation $P = A(\theta - B)$, where θ is the transition temperature (°C.), P is pressure (kg./cm.^{2}), and A and B are constants characteristic of each sample. The values of A and B, which are shown in Table II, were obtained from the observed values of P and θ by the method of least squares. The constant A represents $dP/d\theta$, the rate of change of external pressure with temperature, and it varied from 49.1 to 67.2 kg./cm.^{2}-°C. for various samples. Weir's experiment[16] shows that $dP/d\theta$ is about 54 atm./°C. for the transition between solid phases of PTFE I and II at pressures below 590 atm. The constant B represents the transition temperature at zero pressure, where the pressure–temperature curve cuts the temperature axis. The values of B varied from 21.23 to 22.52°C. for various samples. These transition temperatures, obtained by extrapolating the P–θ line to zero pressure, are a little higher than the values obtained dilatometrically under atmospheric pressure, as will be discussed later.

Figure 3 shows an example of the thermal expansion of PTFE (Polyflon no. 8) in a mercury dilatometer under atmospheric pressure. The
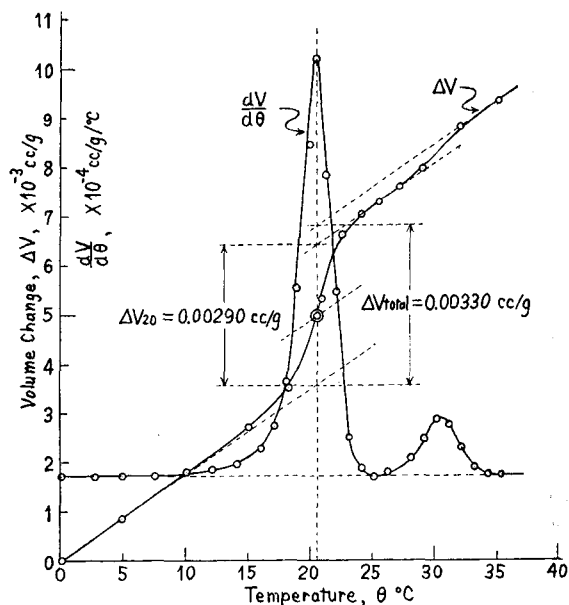

Fig. 3. Thermal expansion of PTFE (Polyflon) under atmospheric pressure.

volume–temperature curve in Figure 3 is similar to those in Figure 1 and has two inflection points, at about 20 and 30°C. Above 35°C., the curve is almost a straight line, and the transition is considered to be accomplished. Running parallel with this straight-line portion are the extrapolated portions of the curve below 20°C. and between 20 and 30°C., as shown in Figure 3. The amount of upward shift between these parallel lines may be taken to represent the volume change due to the transition in the corresponding temperature region. By this method, ΔV_{20} and ΔV_{total} were obtained for the lower transition and for the two transitions combined, respectively, and they are shown in Table III. The ratio of ΔV_{20} to ΔV_{total} varies from 0.83 to 0.88 in the specimens studied, which agrees well with the value of 0.85 estimated by Quinn, Roberts, and Work[2] from their dilatometric studies.

The heats of transition under atmospheric pressure ascribed to the lower transition and to the two transitions combined, ΔH_{20} and ΔH_{total}, were computed for each specimen by the Clapeyron equation, by use of the observed values of $dP/d\theta$, the transition temperatures θ, and the volume changes ΔV_{20} and ΔV_{total} measured by means of mercury dilatometry. The values of ΔH_{20} and ΔH_{total} from the Clapeyron equation are shown in Table III. In the specimens studied, ΔH_{20} varies from 1.03 to 1.68 cal./g., ΔH_{total} from 1.17 to 2.02 cal./g. The ratio of ΔH_{20} to ΔH_{total} ranges from 0.84 to 0.88, which agrees quite well with an estimate of 0.83

TABLE II
Constants of Relationship Between Pressure and
Room-Temperature Transition Points of Various
Polytetrafluoroethylenes
$P = A(\theta - B)$

Specimen	A, kg./cm.^{2} °C.	B, °C.
(1) Teflon 1 (molding)	65.7	21.90
(2) Teflon 1 (molding) irradiated with 3.3 × 10^5 r	56.2	22.45
(3) Teflon 6 (extrusion)	67.2	22.20
(4) Teflon 7 (molding)	61.6	21.44
(5) Fluon G1 (molding)	57.9	21.68
(6) Fluon CD1 (extrusion)	50.9	21.65
(7) Polyflon (molding)	58.4	21.28
(8) Polyflon (molding)	51.3	21.23
(9) Tetraflon (molding)	54.0	21.59
(10) Tetraflon (extrusion)	63.5	22.52
(11) Tetraflon (extrusion)	49.1	21.79

TABLE III
Volume Change and Heat of Transition for Various Polytetrafluoroethylenes in Room-Temperature Transition under Atmospheric Pressure

Specimen	Transition temp., °C.	$dP/d\theta$, kg./cm.²-°C.	Volume change, cc./g.		Heat of transition from Clapeyron equation,[a] cal./g.		Heat of transition from calorimetry, cal./g.	
			ΔV_{20}	ΔV_{total}	ΔH_{20}	ΔH_{total}	ΔH_{20}	ΔH_{total}
(1) Teflon 1	21.0	65.7	0.00260	0.00305	1.18	1.39	1.00	1.18
(2) Teflon 1 (irradiated)	20.0	56.2	0.00395	0.00475	1.53	1.83	1.85	2.25
(3) Teflon 6	21.6	67.2	0.00360	0.00420	1.67	1.95	1.42	1.60
(4) Teflon 7	20.3	61.6	0.00295	0.00345	1.25	1.46	1.50	1.80
(5) Fluon G1	20.4	57.9	0.00310	0.00360	1.24	1.43	1.32	1.60
(6) Fluon CD1	21.0	50.9	0.00480	0.00575	1.68	2.02	1.85	2.25
(7) Polyflon	19.8	58.4	0.00285	0.00335	1.14	1.34	0.96	1.20
(8) Polyflon	21.0	51.3	0.00290	0.00330	1.03	1.17	1.35	1.75
(9) Tetraflon	21.0	54.0	0.00332	0.00392	1.24	1.46	1.50	1.85
(10) Tetraflon	21.4	63.5	0.00320	0.00370	1.40	1.62	1.60	2.02
(11) Tetraflon	21.2	49.1	0.00395	0.00465	1.34	1.58	1.45	1.84

[a] $dP/dT = \Delta S/\Delta V = \Delta H/T\Delta V$ (Clapeyron equation), whence

$$\Delta H \text{ (cal./g.)} = 0.02344(273.15 + \theta°C.) \frac{dP \text{ (kg./cm.}^2)}{d\theta \text{ (°C.)}} \Delta V \text{ (cc./g.)}$$

obtained by Marx and Dole[5] from their calorimetric study.

As an example, the result of calorimetric measurements for molded Polyflon (8) is shown in Figure 4. The shapes of the enthalpy–temperature curve and the specific heat–temperature curve in Figure 4 are similar to those of volume–temperature curve and
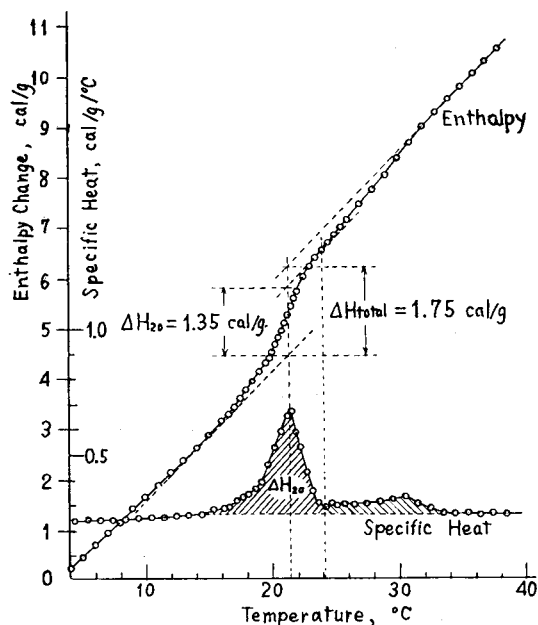

Fig. 4. Enthalpy and specific heat of PTFE (Polyflon) vs. temperature.

the $(dV/d\theta)$–temperature curve in Figure 3, respectively. The enthalpy changes corresponding to the area under the two peaks on the specific heat–temperature curve in Figure 4 must be equal to the corresponding transition heats. The values of transition heats, ΔH_{20} and ΔH_{total}, obtained calorimetrically for the same molded samples as were used in the above-mentioned dilatometric methods, are listed in Table III. The values for ΔH_{20} vary from 0.96 to 1.85 cal./g., and those for ΔH_{total} from 1.18 to 2.25 cal./g. The ratios of ΔH_{20} to ΔH_{total} from calorimetric measurements of eleven samples are in the range of 0.77 to 0.89, which is somewhat wider than the range of values calculated from the Clapeyron equation. The values of ΔH_{20} or ΔH_{total} obtained by the two different methods, i.e., the Clapeyron equation and calorimetry, are in reasonably good agreement, as seen in Table III. This fact shows that the Clapeyron equation is applicable to the room-temperature transition of PTFE, as it is to melting points of other polymers.

Differences in transition heats or volume changes among various samples may arise entirely from differences in the degrees of crystallinity of the samples, as has been pointed out by other authors.[7,8] With increase in the degree of crystallinity, increases are witnessed in the heat of transition and the volume change. The linear relationship between crystallinity and specific gravity for PTFE has been shown by infrared absorp-

tion,[13,19,20] x-ray diffraction,[12] and calorimetry experiments.[7] If the heat of room-temperature transition is directly proportional to the crystallinity, a linear relationship between the transition heat and the specific gravity should be found, as was done by Kuroda.[7] However, in our experiments, such definite linearity was not obtained, although there was a certain dependence of the transition heat upon crystallinity. It may be that in our preparation of specimens, the preforming pressure of 200 kg./cm.² was not high enough for all the resin powders, and the sintering temperature of 350°C., or the sintering time of 5 hrs., may not have been sufficient to minimize the void content of the molded samples. Therefore, there is a possibility that some voids remained in the samples. Kuroda prepared samples with different specific gravities from one PTFE powder, Teflon, under different cooling conditions, while we prepared them from various PTFE powders (Teflon, Fluon, etc.) under the same molding conditions. The irregularity we found between the transition heat and the specific gravity is assumed have arisen from the variety of samples and also from the void content.

We measured the transition temperature for each sample under atmospheric pressure or *in vacuo* by means of three methods. The first was mercury dilatometry under atmospheric pressure; the results obtained by this method are shown in Table III. The second was pressure dilatometry at zero pressure; the values determined thereby for B in the equation $P = A(\theta - B)$ are shown in Table II. The third was calorimetry *in vacuo*. The effect of the pressure difference of about 1 kg./cm.² among these three methods upon the transition temperature may amount to about 0.02°C./kg./cm.²; it is thus negligibly small. The transition temperatures measured by pressure dilatometry for each sample are a little higher than those found by mercury dilatometry. This may be explained as follows. In pressure dilatometry, the external pressure was not uniform over the sample as it is in the case of compression by a liquid; it was applied by a piston in the direction of the axis of the cylinder. As the diameter of the steel cylinder was maintained almost constant during the experiment, friction forces due to the deformation of the specimen must have arisen not only internally but also between the specimen and the cylinder wall. Accordingly, the real pressure causing an elevation of the room-temperature transition may have been greater than the pressure measured from the compression

force of the piston, and even at apparent zero pressure some pressure may have been added and the transition temperature may have increased. In other words, even at apparent zero pressure in pressure dilatometry, some additional work may have been done against the friction force between the specimen and the wall surface of the steel cylinder and against the internal friction force due to deformation of the specimen, causing an elevation of the temperature.

The transition temperature measured calorimetrically was a little higher than that obtained by mercury dilatometry, probably owing to a delay in heat transfer through the specimen.

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Synopsis

The volume–temperature behavior of various molded specimens of polytetrafluoroethylene was measured under

various external pressures in the range of 0 to 50°C. The lower of the two closely spaced room-temperature transition points, designated θ (°C.), which was obtained from the volume–temperature curves under various pressures, increased linearly with the external pressure P (kg./cm.²). The values of $dP/d\theta$ for the various molded samples studied ranged from 49.1 to 67.2 kg./cm.² °C., and were characteristic of the samples. The heats of transition due to the lower transition and to the two transitions combined, ΔH_{20} and ΔH_{total}, respectively, under atmospheric pressure, were calculated from the Clapeyron equation by use of the observed values of $dP/d\theta$ and the volume changes at the transitions ΔV_{20} and ΔV_{total} (cc./g.). The calculated transition heats ΔH_{20} varied from 1.03 to 1.68 cal./g., and ΔH_{total} varied from 1.17 to 2.02 cal./g.; hence the ratio $(\Delta H_{20}/\Delta H_{total})_{calc}$ ranged from 0.84 to 0.88. In addition, the heats of transition of the same samples were measured by means of an adiabatic calorimeter under atmospheric pressure. The transition heats observed for ΔH_{20} ranged from 0.96 to 1.85 cal./g., and those for ΔH_{total} ranged from 1.18 to 2.25 cal./g., and hence $(\Delta H_{20}/\Delta H_{total})_{obs}$ was between 0.77 and 0.89. The values of heats of room-temperature transition obtained by these two different methods were in fairly good agreement, which shows that the Clapeyron equation is applicable to the room-temperature transition of polytetrafluoroethylene, as it is to melting points of other polymers.

Résumé

On mesure la variation de volume de différents échantillons moulés de polytétrafluoroéthylène sous différentes pressions extérieures dans un domaine de température allant de 0° à 50° C. Le point le plus bas des deux points de transition voisins à température normale, θ °C, obtenu par les courbes de volume en fonction de la température sous différentes pressions, augmente linéairement avec la pression extérieure, P kg/cm². Les valeurs de $dP/d\theta$ pour les différents échantillons moulés étudiés sont de l'ordre de 49, à 67,2 kg/cm² °C, et elles sont caractéristiques des échantillons. On étudie les chaleurs de transition de la transition la plus faible et de la transition globale ΔH_{20} et ΔH_{total} respectivement, sous pression atmosphérique, par les équations de Clapeyron, en se servant des valeurs observées de $dP/d\theta$ et du changement de volume à la transition, ΔV_{20} et ΔV_{total} cc/g. Les chaleurs de transition calculées pour ΔH_{20} varient de 1,03 à 1,68 cal/g, et pour ΔH_{total} de 1,17 à 2,02 cal/g et le rapport de ΔH_{20} à ΔH_{total} est de l'ordre de 84 à 88%. De plus, les chaleurs de transition de mêmes échantillons ont été mesurées au moyen d'un calorimètre adiabatique sous pression atmosphérique. Les chaleurs de transition observées pour ΔH_{20} sont de l'ordre de 0,96 à 1,85 cal/g et pour ΔH_{total} de 1,18 à 2,25 cal/g et le rapport de ΔH_{20} à ΔH_{total} est de l'ordre de 77 à 89%. Les valeurs des chaleurs de transition à température normale obtenues à partir de ces deux méthodes différentes sont en très bon accord, ce qui montre que l'équation de Clapeyron est applicable à la transition à température normale du polytétrafluoroéthylène de même que dans le cas des points de fusion des autres polymères.

Zusammenfassung

Die Volumsänderung verschiedener Giessproben von Polytetrafluoräthylen wurde unter variiertem, äusseren Druck im Temperaturbereich von 0° bis 50°C gemessen. Der niedrigere von den beiden nahe beieinander liegenden Umwandlungspunkten bei Raumtemperatur, θ°C, der aus Volums-Temperaturkurven bei variiertem Druck erhalten wurde, nahm mit dem äusseren Druck P kg/cm² linear zu. Die Werte von $dP/d\theta$ lagen für verschiedene Giessproben im Bereich von 49,1 bis 67,2 kg/cm². °C; sie waren für die Proben charakteristisch. Die Unwandlungswärme der niedrigeren sowie de kombinierten totalen Umwandlung, ΔH_{20} bzw. ΔH_{total}, unter Atmosphärendruck wurden nach der Clapeyron-Gleichung unter Benützung der beobachteten $dP/d\theta$-Werte und der Volumsänderung am Umwandlungspunkt, ΔV_{20} und ΔV_{total} cc/g. berechnet. Die berechneten Werte liegen für ΔH_{20} zwischen 1,03 und 1,68 cal/g und für ΔH_{total} zwischen 1,17 und 2,02 cal/g; das Verhältnis von ΔH_{20} zu ΔH_{total} liegt im Bereich von 84 bis 88%. Zusätzlich wurden die Unwandlungswärmen der gleichen Proben in einem adiabatischen Kalorimeter unter Atmosphärendruck gemessen. Die gemessenen Werte liegen für ΔH_{20} im Bereich von 0,96 bis 1,85 cal/g und für ΔH_{total} von 1,18 bis 2,25 cal/g; das Verhältnis von ΔH_{20} zu ΔH_{total} beträgt 77 bis 89%. Die Werte der Umwandlungswärme für die Raumtemperaturumwandlung, die nach diesen beiden Methoden erhalten wurden, stimmten ziemlich gut überein, was beweist, dass die Gleichung von Clapeyron, so wie im Falle der Schmelzpunkte anderer Polymerer, auch auf die Raumtemperaturumwandlung von Polytetrafluoräthylen angewendent werden kann.