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THERMAL INVESTIGATION OF THE PHASE COMPOSITION OF POLY(ETHYLENE TEREPHTHALATE). ANALYSIS OF DIFFERENT METHODS OF DETERMINATION OF THE DEGREE OF CRYSTALLINITY OF PARTIALLY CRYSTALLINE SUBSTANCES

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The literature data on the degree of crystallinity of non-deformed poly(ethylene terephthalate) measured at various temperatures have been subjected to comparative analysis. There is no correlation between the results obtained by the different methods. The reason for this is shown to be the imperfections in the methods of determining the degree of crystallinity, which do not provide the true composition of the crystalline phase. Consideration has been paid to the validity of the main principles involved in the thermal method of determining the degree of crystallinity, so as to eliminate the imperfections in the existing methods and to provide the correct value of the mass of the crystalline phase. The phase composition of PET has been analyzed by the thermal method at different temperatures and conditions of crystallization. A marked difference from the literature data is observed in the range of low temperatures.

A number of properties of poly(ethylene terephtalate) (PET) make it a suitable object for investigation of the phase phenomena in the partially crystalline material. PET can be crystallized in a fairly wide temperature range (90–260°); the process of its crystallization can easily be 'frozen' at any stage; the resultant phase structure is stable at room temperature due to the rather high glass transition temperature ($T_g = 70°$). These properties, together with its great industrial significance, account for the large number of investigations of phase composition of PET by different methods.

Nevertheless, there is no unanimity in the literature concerning the data on the degree of crystallinity. The aim of this work is to analyze this fact and to investigate the phase composition of PET by the thermal method [1, 2]. The necessity of consideration of this problem was prompted by the fact that among the investigations on PET there are only few works on the study of its thermal properties; most of them deal with the application of DTA, and in some cases the thermal method of phase analysis seems to be incorrectly used [3].

Experimental

We have studied a semi-industrial sample of PET with molecular mass $\overline{M}_w = 23\,000$ and with a moisture content less than 0.01%. Originally, the polymer represented a crystallized sample of PET in the state of turbid lustreless grains.

Before the experiment the grains had been crushed, placed into calorimeter sample holders and melted in an argon atmosphere during 1 min. The sample mass was 20–100 mg. Measurements were made by methods of dynamic calorimetry. A Perkin-Elmer DSC-2 differential scanning calorimeter and a "thermal bridge" [4] were used in this study. Measurements were made with an accuracy of 1.5%. The density was determined by the method of flotation in a mixture of carbon tetrachloride and hexane.

Analysis of literature data on the phase composition of PET

The data on the phase composition of PET were obtained mainly from density measurements. This is due to the simplicity of the method, its applicability under any laboratory conditions, and the stability of the phase composition of PET at room temperature. Determination of the degree of crystallinity (W) of PET through its density is often used in the literature as a paralell experiment when this value is measured by other methods, and sometimes for calibration as well.

However, the degree of crystallinity determined from the density does not in fact represent the true phase composition, but some "equivalent value" as compared to an ideal crystal. The formula for determining the degree of crystallinity via the density is

$$W = \frac{P_e(P - P_a)}{P(P_c - P_a)} \tag{1}$$

where P_c is the density of the ideal crystal; P_a is the density of the fully amorphous polymer; and P is the density of the polymer sample. This would give the true composition of the crystalline polymer sample consisting of ideal crystals, and the amorphous part were the same as in the fully amorphous state. However, it is well known that polymer crystals are rather imperfect formations, and the state of the amorphous parts in a partially crystalline polymer sample differs greatly from the state of the fully amorphous polymer.

In the literature, the imperfection of determinations of the degree of crystallinity by density measurements has been pointed out more than once. For PET it has been shown particularly in [5–8].

The values of both P_a and P_c as used by the different authors for the calculation of W differ, so it appears reasonable to compare the results of different works on the basis of the experimental values of P. Figure 1a shows density values taken at different temperatures of crystallization, including the main literature data on non-deformed PET. The lines in Fig. 1 refer to the averaged values for the different conditions of crystallization (taking into account density changes depending in the temperature of crystallization (T_c) for each literature source). Point scattering for the same conditions and temperatures of crystallization, which comprises up to 30% of the difference $P_c - P_a$ (Fig. 1a), may be brought about both by the development of heterogenous formations (bubbles, holes) during the thermal processing of

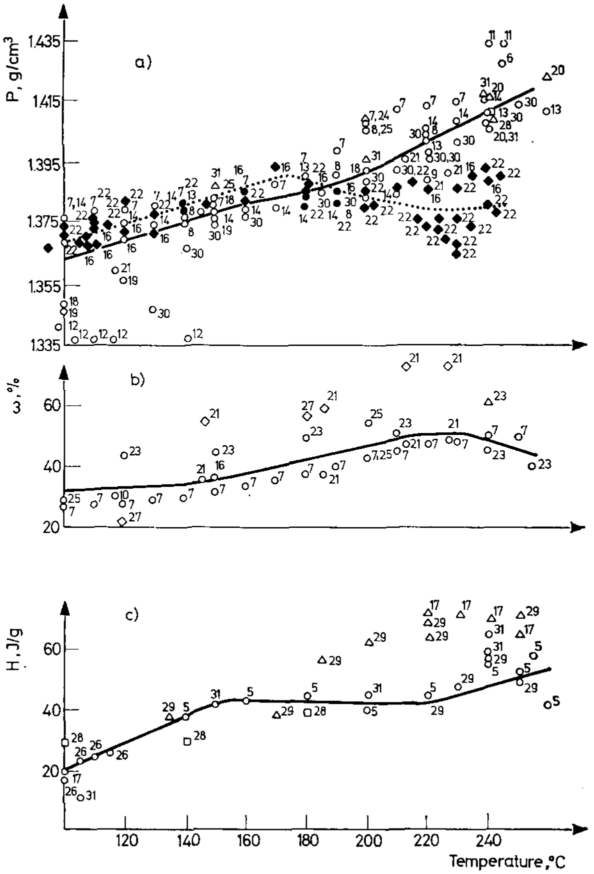

Fig. 1. Literature data on density (a), degree of crystallinity according to X-ray analysis (b), and heats of fusion (c) of non-deformed PET at different temperatures and conditions of crystallization; ○ — crystallization from the amorphous state; ♦ — crystallization from the melt; △ — data for the sample of maximum crystallinity obtained by prolonged annealing; □ — thermal effect of crystallization; ◇ — degree of crystallinity according to infrared spectroscopy. The numbers at the points correspond to the references

PET and by insufficient consideration of the influence of the sample history upon the phase composition. The calculation of W from the averaged density lines with $P_a = 1.336$ and $P_c = 1.457$ [9] is illustrated in Fig. 2.

The degree of crystallinity determined by X-ray analysis, using the direct correlation of the dispersion intensities of the crystalline and amorphous ranges, corresponds to the true phase composition. However, the practical difficulties due to the scattering of these dispersions, which greatly overlap, often result in errors in the determination of W. Further, in the case of defective crystals a proportion of the dispersions of the crystalline regions is lost, and as a rule partially crystalline

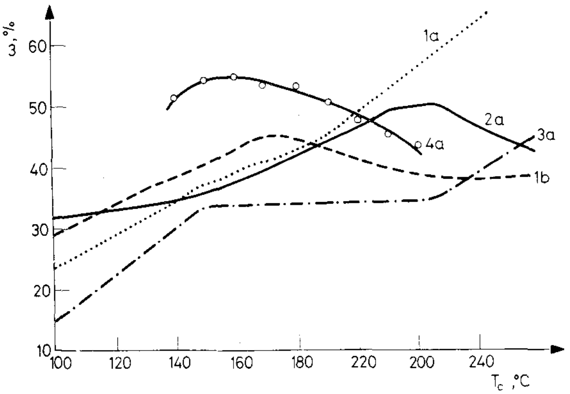

Fig. 2. Averaged values of the literature *W* data, determined from density measurements (1), X-ray analysis (2) and heats of fusion (3) for non-deformed PET crystallized under isothermal conditions from the amorphous state (a) and from the melt (b); (4) values of *W* determined by DSC [1, 2]

substances are defective. A systematic error also arises because the X-ray instruments record only crystallites with dimensions not less than a definite value. In particular, in [10, 11] it has been found that for PET such a value is 15 – 30 nm. Hence, the higher the concentration of defects and the smaller the crystallites in a polymer, the more the value of *W* as determined by X-ray analysis differs from the true value of the degree of crystallinity of the polymer. Literature data on non-deformed PET, determined by X-ray analysis, are presented in Fig. 1b.

Enthalpy values for determination of the phase composition of PET were applied in a few works. In these works the method of comparison of the thermal melting effects of the sample (ΔH_m) and an ideal crystal (100%) (ΔH_0) was used to determine the degree of crystallinity:

$$W = \frac{\Delta H_m}{\Delta H_0}. \tag{2}$$

Earlier [2] we criticized this method. Neither *W* determined from Eq. (2) nor that determined from the density represents the true composition of the crystalline phase, but rather some value equivalent with respect to an ideal crystal. Moreover, the information obtained from Eq. (2) may be more misleading as regards the phase composition of the polymer than *W* determined from the density, for while P_c is determined precisely enough by X-ray analysis, ΔH_0 is evaluated via indirect assumptions, i. e. extrapolation. Further, the phase composition of a polymer at the melting point does not correspond to that in the crystalline state, because partial melting and recrystallization take place in the intermediate thermal interval.

The values of ΔH_0 used by the different authors differ by up to 15%. The values of the thermal effects of melting were therefore taken to compare the literature data (Fig. 1c). Figure 1c also shows the values of the thermal effects of crystallization

(ΔH_c). However, these data are very few and no systematic investigations were performed.

Averaged data obtained by X-ray analysis and calculated from the averaged values of the density and the heats of fusion (Eq. (2)) (ΔH_0 is assumed to be 127 J/g [9]) are compared in Fig. 2. It is clear that there is no correlation between the W values obtained by the different methods, the difference between the data obtained by the different methods being as much as 25 – 50%. From the above-mention imperfections in the methods of determining W it is clear that the errors characteristic of each method result in an apparent decrease in the true degree of crystallinity of the polymer.

Analysis of phase composition of PET by DSC

We earlier proposed a method of determining W [1] based on the simultaneous measurement of two thermal values referring to different phases (the increase of the heat capacity at the glass transition and the thermal effects of the phase transition) for several states of the sample, which differ in the degree of crystallinity but have the same structure. In [2] it has been shown that this method has none of the imperfections characteristic of the existing methods of determining W and permits establishment of the true composition of the crystalline phase.

In the literature on polymers the degree of crystallinity is sometimes considered to be a value devoid of strict physical sense. This does not prove to be correct from either the theoretical or the practical points of view. The concentration of the crystalline phase of the polymer affects all of its physicochemical and operating properties, and is thus a most important parameter. As mentioned above, because of the imperfections in the method of determining W, this was neglected, for it does not lead to the true value of the degree of crystallinity, but provides a useless "equivalent value".

Thus, to consider W as a parameter of a polymer it is necessary to provide tis correct determination. In addition the parameter itself must be exactly defined. Quantitative distinction between the different parts of a partially-crystalline polymer gave the opportunity to consider it as a multiphase system. This approach introduces uncertainty into the concept of the degree of crystallinity not only when different polymers are correlated, but within different states of the same sample, too. One must distinguish between the phases according to those properties which have a qualitative difference. In a two-phase system each of the phases is characterized by its own parameter, and the sum of the parameters corresponds to the total mass of the polymer. In [1, 2] it is illustrated that a crystalline polymer satisfies these requirements. The jump in heat capacity at the glass transition, ΔC_p and the thermal effect of transition, ΔH, correspond to the total mass of the polymer. In fact, all particles contribute to one of these values. For example, the defects in the crystalline structure, no matter whether inside or outside the crystallites, affect the values of the heats of phase transitions. Similarly, separate parts of chains unable to undergo conformational transitions (for example tight passages or sections at the border of amorphous regions) do not cause an increase in the heat capacity itself, but affect its value by diminishing the conformational possibilities of the neighbouring chains.

On the other hand, it is impossible to determine W merely by correlating the parameters of the sample and a sample of known crystallinity, as the values of the parameters of the polymer are functions not only of the mass but also of the phase structure. In particular, the enthalpy of the phase transition cannot be used to correlate an ideal crystal (Eq. 2.), because the enthalpy of the phase transition of real polymer crystals differs greatly from this value. Thus, the problem of measuring the degree of crystallinity according to the value of the thermal effect of the phase transitions is reduced to determining the enthalpy of crystallization (melting) of the polymer sample. The solution of this problem is given in [1, 2]. The correlation between the parameters of the crystalline and amorphous parts of the polymer for several states differing in crystallinity but having the same structure must be expressed by a linear function. This follows from the mass additivity. The value of the enthalpy of the phase transition for the given state of the sample is included in the constant of the linear equation, and hence may easily be calculated.

The identity of the structure of the states of sample is checked via the linearity of the experimental points of the plot $\Delta C_p = f(\Delta H)$. The degree of deviation from linearity is characteristic of the experimental error, as the accuracy of measurments of heat capacity and thermal effects in calorimetric experiments is usually higher. The plot may be used to determine the enthalpy of the phase transition. The straight line $\Delta C_p = f(\Delta H)$ extrapolated to $\Delta C_p = 0$ gives the value of the enthalpy of the crystalline phase formation for the state of the sample, ΔH_0^i. From the relation of the thermal effects of the phase transition (ΔH_i) to this value, we can obtain the real value of the degree of crystallinity (W_r):

$$W_r = \frac{\Delta H_i}{\Delta H_0^i}\,. \tag{3}$$

Equations (2) and (3) differ in their sense. As ΔH_0 is the enthalpy of the phase transition of an ideal crystal, we can obtain from Eq. (2) only an equivalent value of W, which has no real sense. In Eq. (3) ΔH_0^i is the enthalpy of the phase transition of a crystal in the same state in which the thermal effect is measured, so that the correlation between them provides the true composition of the crystalline phase.

It should be pointed out that the suggested method is of a general character and can be used in the other methods for any parameter of a crystalline polymer, for all parameters dependent on mass depend on the structure as well. The state of the latter is changeable, depending on the environment, the history, the way it was obtained, and other factors. It is impossible to determine properly the phase composition of a polymer state without taking these features into consideration.

Figure 3 presents experimental data on the increase of the heat capacity at the glass transition and the thermal effect of PET crystallization, characteristic of the correlation of these parameters at different temperatures of crystallization from the amorphous state ("cool crystallization"). The experiment was performed ac-

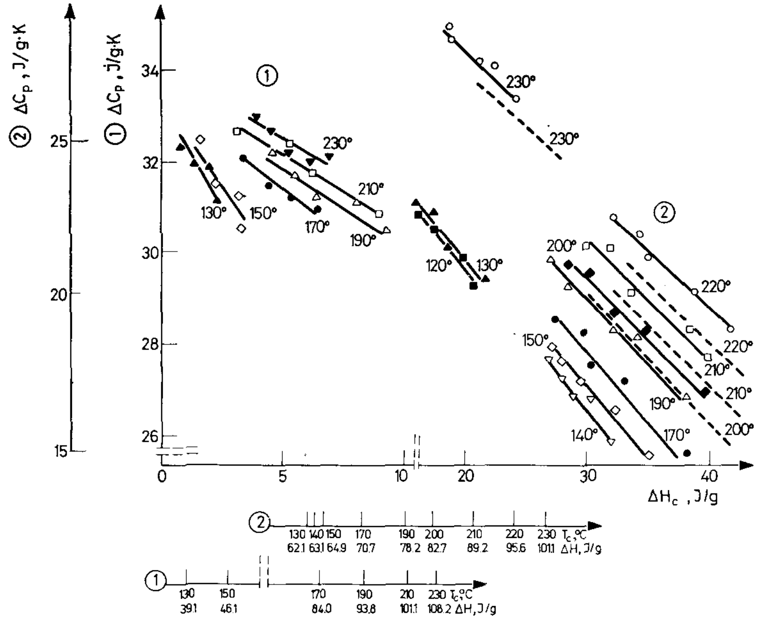

Fig. 3. Dependence of the thermal effect of crystallization on the increase in heat capacity at the glass transition of PET crystallized from the melt (dotted lines) and from the amorphous state (continuous lines). (1) — beginning of crystallization; (2) — end-stage of primary crystallization are shown on the curve. Points of intersection of the line with the abscissa and the corresponding values of ΔH and T_c are given below

cording to the following procedure. To standardize the history of the sample, it was first melted at 285° in an argon atmosphere and then cooled down at a rate of 320°/min to −70°. The resultant amorphous sample was held for 30 min at 85° (with the aim of forming a nucleus) and for 24 hours at room temperature. It was then heated at a rate of 320°/min up to the temperature of crystallization. At some time after the beginning of crystallization the process was interrupted and the resultant sample was quenched by fast cooling to a temperature lower than T_g. Then, during heating at a rate of 20°/min, the increase in heat capacity at the glass transition was recorded. The procedure was repeated several times with various exposure periods at T_c, i. e. with various values of the degree of crystallinity. Values of the thermal effect and the increase in heat capacity were measured from the DSC trace. This method permits the comparison of samples with different degrees of crystallinity but with the same degree of perfection of the crystalline phase. The correspondence of each pair ΔC_p and ΔH_c to the same state was provided by fast cooling at the rate of 320°/min. Isothermal crystallization from the melt was performed by the same method.

In Fig. 3 it is shown that for each T_c the correlation between ΔH_c and ΔC_p is linear (with an error of not more than 3%). This testifies to the same structure of

Table 1

Parameters of crystallization and glass transition

Crystallization from the amorphous state								
T_c	Time of crystallization	Half-time of crystallization	ΔH_c	Temperature range of glass transition			ΔC_p	Density
				Beginning	End			
	(τ_c)	($\tau_{1/2}$)		T_g^b	T_g^e	ΔT_g		P
°C	min	min	J/g	°C	°C	°C	J/g · K	g/cm^3
130	24.0	9.1	21.7	71.0	103.0	32.0	0.205	1.360
140	16.8	4.4	32.2	71.0	103.0	32.0	0.154	1.376
150	11.6	2.9	34.2	71.0	103.0	32.0	0.150	1.381
160	8.5	2.0	35.9	71.0	103.0	32.0	0.149	1.385
170	7.0	1.4	37.6	70.9	102.4	31.5	0.149	1.388
180	6.2	1.1	38.6	70.9	101.5	30.6	0.152	1.390
190	6.3	1.0	38.3	70.7	100.2	29.5	0.166	1.392
200	6.8	1.2	40.6	70.4	98.9	28.5	0.170	1.392
210	9.0	2.0	40.2	70.0	97.5	27.5	0.181	1.390
220	20.6	3.5	42.0	69.2	96.4	27.2	0.191	1.387
230	45.0	12.1	24.3	67.7	95.4	27.7	0.258	1.379

the correlated states of the sample and to the fact that any pair of values ΔH_c and ΔC_p corresponds to the same state of the sample. The change in the slope of the straight lines with the increase in T_c is a result of the difference between the strucures formed. These data refer to the period of peak recording in the DSC curve, i. e. to the period of primary crystallization. Corresponding parameters of the crystallization and the glass transition are given in Table 1.

Values of the degree of crystallinity calculated from Eq. (3) for different temperatures and crystallization conditions are shown in Fig. 2 (4a). The resultant curve, as shown above, represents the true composition of the polymer crystalline phase. The greatest difference from the data of other methods is observed in the low-temperature range of crystallization. This is to be expected, as with the lowering of T_c the defects in the crystallin formations increase and the number of small crystallites rises. These circumstances result in the increase of the error of determining W by the existing methods, i. e. via the density (because of the increase in the difference between the densities of a real and an ideal crystal); by X-ray structure analysis (because of the loss of dispersion on the defects in the crystals and the increase in the number of small crystals not recorded by the X-ray structure analysis), by NMR (because of the decrease of order in the crystalline phase), and by the thermal method via formula (2) (because of the increase in the difference between the enthalpy of melting of a real and an ideal crystal).

It should be noted that the method described may be used for the express-analysis of W as well. For this purpose, ΔC_p at the glass transition and ΔH_m (considering of PET under different conditions

Crystallization from the melt						
τ_c	$\tau_{1/2}$	ΔH_c	T_g^b	T_g^e	ΔT_g	ΔC_p
min	min	J/g	°C	°C	°C	J/g · K
—	—	—	—	—	—	—
20.0	5.4	28.7	69.8	103.0	33.2	0.158
13.2	3.8	30.9	69.8	102.7	32.9	0.156
9.8	2.5	33.0	69.8	102.0	32.2	0.153
7.9	1.8	35.0	69.8	100.6	30.8	0.156
6.2	1.1	36.8	70.6	99.5	28.9	0.156
6.5	1.4	38.3	70.3	98.2	27.9	0.158
8.5	1.7	41.2	69.9	97.1	27.2	0.155
13.0	2.3	42.2	69.5	96.1	26.6	0.163
27.0	4.7	43.1	68.7	95.4	26.7	0.175
56.0	18.4	27.9	67.4	94.8	27.4	0.246

partial melting) are measured during heating. The jump in heat capacity (ΔC_p^0) of the fully amorphous polymer is then measured. These two points of the curve are connected by a straight line and the value ΔH_0^i is determined according to the intersection of this line with the axis ΔH_m. The resultant value of ΔH_0^i will be somewhat less and that of W somewhat greater than the true values of these parameters. For example, for the initial state of the sample of PET the difference was 7%. To make the slope of the straight line more precise some additional experiments should be made with the initial sample, the process of melting being interrupted at the very beginning, and the values ΔC_p and ΔH_m corresponding to the resultant state being measured.

The curve expressing the dependence of the enthalpy of crystallization on the temperature (Fig. 4), determined according to the data of the curve of Fig. 3, has three distinct ranges. Up to 140° the slope of the curve is insignificant, and the enthalpy of crystallization is low. In the range 140–200° a fast and monotonous increase of the enthalpy is observed, together with the increase of T_c, while the rate increases to a certain extent. With the increase of temperature, the mechanism of improvement of the crystalline structure probably changes slightly.

Careful performance of the experiment allows detection of a slight difference between the slopes of the straight lines approximating the points of the curve $\Delta C_p = f(\Delta H_c)$ which correspond to the beginning and end of crystallization (Fig. 3). The degree of perfection of the crystallites arising at different moments of crystallization is evidently slightly different.

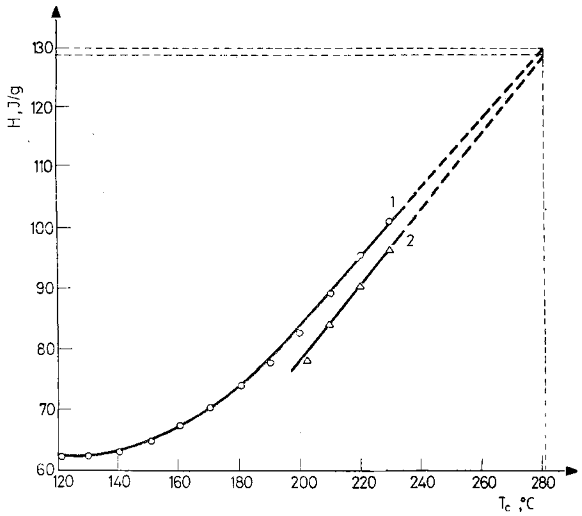

Fig. 4. Dependence of the enthalpy of crystallization of PET on T_c.Conditions of crystallization: (1) — from the amorphous state; (2) — from the melt. Extrapolation of ΔH values to the equilibrum melting temperature, 282°, is shown by dotted lines

The plot $\Delta C_p = f(\Delta H_c)$ permits establishment of the difference in the amorphous structures of the samples crystallized at different T_c values. Extrapolation of the straight lines before crossing the ordinate axis gives the value ΔC_p, which decreases with the decrease of T_c, pointing to a significant conformational restriction of the macromolecules in amorphous regions with crystallites of smaller dimensions. This is confirmed by the T_g data (Table 1): the higher the T_c, the lower the temperature of the glass transition.

The dependence of the enthalpy of crystallization on T_c higher than 200° (Fig. 4) may be approximated by a linear function. Extrapolation of this straight line to the eqilibrum melting temperature $T_m^0 = 282°$ [32] gives the value of the enthalpy of crystallization of an ideal crystal, 129 ± 0.5 J/g, which is somewhat higher than that obtained by Edgar and Hill [32], and generally used now (127 J/g), but less than the value presented by Drescher and Wegner [33] (136 J/g. However, the exactness of this definition depends on the accuracy of the equilibrum temperature of melting, T_m^0, used.

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ZUSAMMENFASSUNG — Eine vergleichende Analyse der Literaturangaben bezüglich des bei verschiedenen Temperaturen gemessenen Kristallisationsgrades von nicht-deformiertem Poly(äthylen-terephthalat) wurde durchgeführt. Zwischen den mit verschiedenen Methoden erhaltenen Ergebnissen besteht keine Korrelation. Es wurde gezeigt, daß der Grund hierfür in der Unvollkommenheit der Methoden zur Bestimmung des Kristallisationsgrades liegt, da diese nicht die wahre Zusammensetzung der Kristallinen Phase angeben. Die Gültigkeit der wichtigsten Prinzipien, welche die thermische Bestimmung des Kristallisationsgrades unter Ausschaltung der Unvollkommenheit der bestehenden Methoden gewährleisten und den richtigen Wert der Masse der kristallinen Phase angeben, wurden in Erwägung gezogen. Die Analyse der Phasenzusammensetzung von PET wurde durch die thermische Methode bei verschiedenen Temperaturen und Kristallisationsbedingungen durchgeführt. Ein deutlicher Unterschied zu den Literaturangaben kann im Bereich der niedrigen Temperaturen beobachtet werden.

Резюме — Проведён сравнительный анализ литературных данных по степени кристалличности при различных температурах недеформированного образца полиэтилентерефталата. Корреляция между результатами, полученными разными методами, отсутствует. Показано, что причина этого обстоятельства заключается в недостатках методов определения степени кристалличности, не позволяющих получить истинное содержание кристаллической фазы. Рассмотрена обоснованность основных положений, на которых базируется тепловой метод определения кристалличности, свободный от недостатка существующих способов и позволяющий получить действительное значение массы кристаллической фазы. Тепловым методом проведп анализ фазового состава полиэтилентерефталата при различных температурах и условиях кристаллизации. Заметное отличие от литературных данных наблюдается в области низких температур.