

Relationship Between the Chain Fold Period in Poly(ethylene Terephthalate) and the Crystallization Temperature

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Synopsis

The dependence of the fold period in poly(ethylene terephthalate) (PET) crystals on overcooling was investigated by the small-angle x-ray diffraction method, for samples crystallized at 150° to 260°C. The equilibrium melting point T_m , determined simultaneously, was $278^\circ \pm 2^\circ\text{C}$. Using these results, the surface free energy σ_e was calculated.

INTRODUCTION

The folding of macromolecules¹ is one of the basic phenomena in the process of crystallization of polymers. It has been shown that it occurs also in the single crystals of poly(ethylene terephthalate) (PET) crystallized from dilute solution.² In spite of numerous investigations of the process of crystallization of PET from melt, the folding of macromolecules in this polymer crystallized in a block is still little known. Determination of surface free energy σ_e of the crystallographic planes containing the folds^{3,4} is essential in the investigation of the mechanisms of crystal growth. The present work describes the current results obtained during such investigation of folding of macromolecules of PET crystallized from melt.

EXPERIMENTAL

Samples of PET in the form of granules, made by ICI, were degassed under pressure of 10^{-4} mm Hg for 15 hr and then covered with silicon oil and melted at 280°C in 15 min. After being melted, the samples were put into a thermostat the temperature of which was kept to within $\pm 0.1^\circ\text{C}$. The crystallization continued at this temperature for 5 hr within the range of 150° to 260°C.

The following parameters were determined: density, melting point, crystallinity, crystallite size perpendicular to the (010) plane, and chain

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fold length. The measurements of density were carried out on a gradient column containing KI solutions in distilled water. The column was calibrated with an accuracy of $\pm 0.002 \text{ g/cm}^3$. The melting point measurements were made using a standard method⁵ on an optical microscope with a hot stage. The melting point of a single sample was measured with an accuracy of $\pm 0.1^\circ\text{C}$. For five samples crystallized at the same temperature, the crystallization temperature showed a spread of 1° to 2°C . Using the data found, the equilibrium melting point T_m was determined by the graphic method of Hoffman⁶ to be $279^\circ \pm 2^\circ\text{C}$. It seems that the value is somewhat too low. This is probably due to the fact that during melting it was impossible to eliminate the recrystallization in samples crystallized at the lowest temperatures. The crystallinity measurements were made by the x-ray method as modified by Statton,⁷ using a sample rapidly frozen to the temperature of liquid nitrogen as an amorphous standard. A DRON-1 diffractometer, made in the Soviet Union, was used, together with a scintillation counter as recorder.

The crystallite size perpendicular to the (010) plane was measured by the Ruscher and Kochendörfer method.⁸ The fold length can be determined either by the electron microscope¹ or by small-angle x-ray diffraction. The latter technique was used because of its higher accuracy.

The value of the long period was determined by the Bragg equation. X-Ray measurements were made on a Geigerflex diffractometer (Rigaku Denki) with ionizing recording, using a standard goniometer with a slit, and a collimator according to Kratky. The width of the beam after collimation was 0.25° .

The wide-angle and small-angle measurements were carried out with CuK_α irradiation, filtered with Ni.

RESULTS AND DISCUSSION

The results, given in Table I, show that:

1. The density of samples crystallized within the range of 150° to 260°C increases, reaching a maximum value at 240°C .
2. The melting point of samples crystallized below 200°C is on the average 258°C ; that of samples crystallized above 200°C exceeds 260°C .
3. The crystallinity determined by x-ray measurements increases from 47% for samples crystallized at 150°C to 62% for samples crystallized at 240°C .
4. The crystallite size perpendicular to the (010) plane increases from 44 \AA to 68 \AA .
5. The fold period length increases with increase in the temperature of crystallization.

The changes in the structural parameters given above are generally in good agreement with the data in the literature.⁹⁻¹¹ It was observed that the fold length increases with the crystallization temperature. The increase may be interpreted as an increase in the lamellar thickness, which is in agreement with the finding of Geil.¹

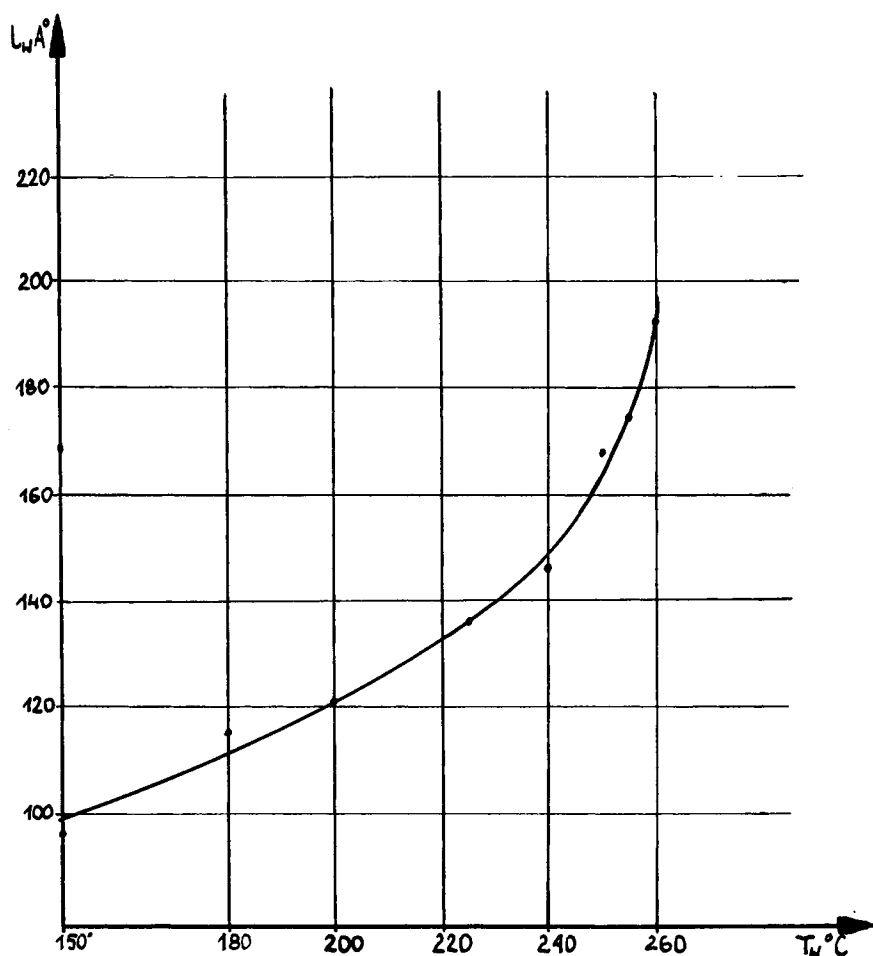


Fig. 1. Dependence of fold period in PET on crystallization temperature.

The dependence of the fold length l (also called fold period) on the crystallization temperature is shown in Figure 1. The curve is similar to that found earlier for polyethylene.¹

Assuming that the results obtained in the present work can be described by the equations verified for polyethylene, describing the relationship between the melting point of a lamellar crystal and its thickness (dimension in the direction of the chain axis), the following equation has been used^{3,4}:

$$T_l(l) = T_m \left[1 - \frac{2 \cdot \sigma_e}{(\Delta H_f) \cdot l} \right] \quad (1)$$

where l is the lamellar thickness in the direction of the chain axis (the fold period); T_m is the equilibrium melting point of PET crystals; ΔH_f is the latent heat of fusion per unit of crystal volume at temperature T_m ; and σ_e is the surface free energy of the crystal face containing folds.

On the other hand, according to the kinetic theory of chain folding,⁴ the relation between the fold length l and the crystallization temperature is as follows:

$$l = \frac{(2\sigma_e + 2\epsilon/l_0)T_m}{\Delta H_f \cdot (\Delta T)} + \frac{kT}{l_0 \cdot \sigma_s} \quad (2)$$

where $\Delta T = T_m - T$; T is the crystallization temperature; σ_s is the surface free energy of the crystal face without folds; l_0 is the fold height in the direction b of an elementary net in the two-dimensional nucleus on the crystal wall; k is the Boltzmann constant; and ϵ is the edge free energy.

Using the experimentally determined values of fold periods of the macromolecules and the melting temperature, $T_m(l)$, together with the equilibrium melting temperature T_m and the latent heat of fusion of ideal crystals of PET in eqs. (1) and (2), it is possible to determine the surface free energy σ_e . Accurate values of both the latter quantities are not known up to date. Thus, in the present calculations, the highest value of ΔH_f available in the literature, namely, 127×10^7 erg/cm³, and $T_m = 278^\circ\text{C}$ given by Roberts¹² and Taylor¹³ were accepted. Interpretation of experimental data for $1 \rightarrow \infty$ given in Figure 2 gives T_m close to 280°C . The values of σ_e calculated with the aid of eqs. (1) and (2) are presented in Table I. Equation (1) gives value of σ_e within the limits 23–33 erg/cm², depending on the conditions of supercooling. The value of σ_e determined

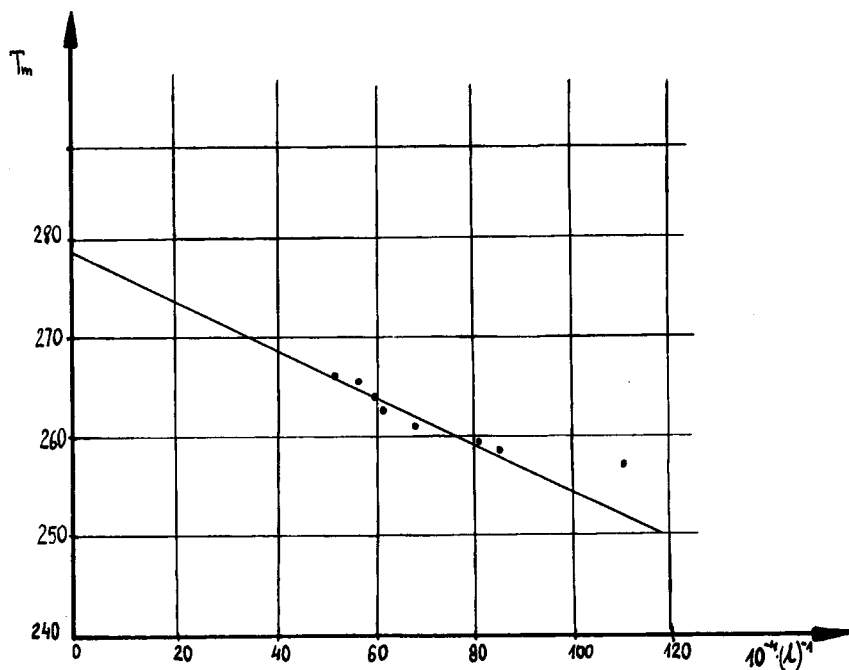


Fig. 2. Dependence of $T_m(l)$ on l^{-1} from eq. (2).

from Figure 2 is 29 erg/cm². In order to determine the value of σ_e from eq. (2) more accurately, it is necessary to know the edge free energy ϵ and σ_s . As a point of approximation, it was accepted that $\epsilon = 0$, and the term including σ_s was omitted. The last column of Table I presents the values of σ_e obtained by this simplified formula. Because of this simplification, the above values of σ_e are too high.

The value of σ_e determined from Figure 3 (23.5 erg/cm²) is in close agreement with that obtained from eq. (1). It seems, however, that more accurate values of σ_e are those obtained from eq. (1), because they are less sensitive to variation in T_m . The values of σ_e obtained from eqs. (1) and (2) are generally in good agreement with the existing theories of folding of macromolecules.

SUMMARY

Measurements made by the small-angle x-ray diffraction method confirmed that the chain fold period of PET crystals is inversely proportional to the cooling rate. A similar relationship was previously found for poly-

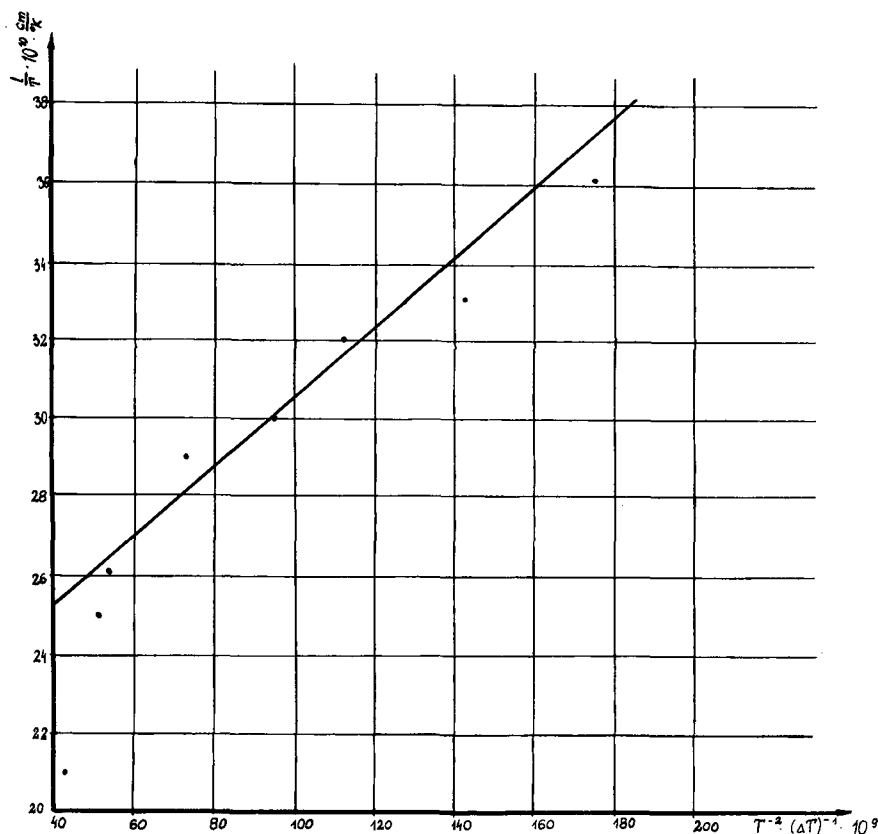


Fig. 3. Dependence of l/T on $T^{-2}(\Delta T)^{-1}$ from eq. (2).

TABLE I
Results of Measurements for PET Crystallized at Different Temperatures

Crystallization temp., °C	Melting point, °C	Density, g/cm ³	Degree of crystallinity, %	Effective crystallite size from (010), Å	Fold period length, Å	σ_e , erg/cm ² , calculated from	
						eq. (1)	eq. (2)
150	256.9	1.374	47	44	87.9	23.3	90.9
180	258.5	1.383	52	48	114.7	27.7	93.6
200	260.0	1.397	56	54	120.5	27.8	91.0
225	259.3	1.401	58	58	147.2	28.6	80.7
240	262.2	1.405	62	64	156.0	29.7	68.3
250	263.5	1.403	60	68	168.0	31.0	54.2
255	265.3	1.401	60	65	174.1	32.3	46.1
260	266.0	1.398	60	63	191.6	33.2	39.6

ethylene. The equilibrium melting point was also found for PET, the value being similar to that anticipated theoretically.¹³ Based on the above results, the free surface energy σ_e of the crystal face containing folds was calculated.

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References

1. P. H. Geil, *Polymer Single Crystals*, Interscience, New York, 1963.
2. N. Yoshida and H. Sato, *Kobunshi Kagaku*, **26**, 644 (1969).
3. J. J. Lauritzen and J. D. Hoffman, *J. Res. Natl. Bur. Stand.*, **64A**, 73 (1960).
4. J. D. Hoffman and J. J. Lauritzen, *J. Res. Natl. Bur. Stand.*, **65A**, 247 (1961).
5. W. C. McCrone, Jr., *Fusion Methods in Chemical Microscopy*, Interscience, New York, 1957.
6. J. D. Hoffman and J. J. Weeks, *J. Res. Natl. Bur. Stand.*, **63A**, 13 (1962).
7. P. D. Dismore and W. O. Statton, *J. Polym. Sci. C*, **13**, 133 (1966).
8. Ch. Ruscher, *Faserforsch. Textiltech.*, **9**, 485 (1958).
9. J. H. Dumbleton, K. P. Bell, and T. Murayama, *J. Polym. Sci.*, **12**, 2491 (1968).
10. M. Mrozowski and W. Lewaszkiewicz, *Polimery*, **15**, 290 (1970).
11. J. H. Dumbleton, *Polymer*, **10**, 539 (1969).
12. D. C. Roberts, IUPAC International Symposium on Macromolecular Chemistry, Leiden, 1970.
13. G. W. Taylor, *Polymer*, **3**, 543 (1962).

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