Distribution of lamella thicknesses in isothermally crystallized polypropylene and polyethylene by differential scanning calorimetry

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The procedure for obtaining lamellar thickness distribution from differential scanning calorimetry (d.s.c.) curves is presented. The method has been used to study melt-crystallized polypropylene and polyethylene. The melting of the samples as registered by d.s.c. has been analysed and information regarding lamellae thickness is presented. The results obtained were consistent with the thicknesses of lamellar crystallites derived from small-angle X-ray scattering (SAXS) patterns.

(Keywords: lamellar thickness distribution; polypropylene; polyethylene; differential scanning calorimetry; small-angle X-ray scattering)

INTRODUCTION

In contrast to crystalline low-molecular-weight compounds which melt at exactly determined temperatures, high molecular weight polymers are converted to the amorphous state over a range of temperatures. Such behaviour is attributed to the crystallite size distribution which, in turn, depends on the kinetic factors of crystallization. Crystalline lamellae in a given sample of polymer have distinctive melting points, determined by their dimensions in the chain direction. Crystallites with small dimensions melt at lower temperatures (in contrast to those with large dimensions). This can be seen from the well-known Thomson equation[1]:

$$T_m = T_m^\circ\left(1 - \frac{2\sigma_e}{\Delta h_m l}\right) \tag{1}$$

where: T_m is the observed melting point of lamellae of thickness l
T_m° is the equilibrium melting point of an infinite crystal
σ_e is the surface free energy of the basal plane (i.e. fold-containing)
Δh_m is the enthalpy of fusion per unit volume
l is lamellae thickness.

It is assumed[2] that at a given temperature for a sample of molten polymer the rate of heat consumption is proportional to the fraction of lamellae whose thickness is given by the Thomson equation. This enables the distribution of l to be determined. For practical purposes over a limited temperature range the parameters σ_e, Δh_m can be treated as independent of temperature and lamellae thickness.

The purpose of this paper is to propose a new method to determine lamella thickness distribution of samples of polypropylene and polyethylene with a wide variety of crystallite sizes.

EXPERIMENTAL

The films (0.1 mm thick) used in this work were obtained from Hostalen high density polyethylene and F-401 isotactic polypropylene (manufactured by Zakłady Rafineryjne in Płock) on a Brabender laboratory extruder. Both polymers were provided in the form of pellets.

The intrinsic viscosities of PP and PE, determined in decalin at 408 K were found to be 2.72 gl/g and 2.48 dl/g, respectively. Investigations were carried out with the aid of a 990 Du Pont differential scanning calorimeter in a protective atmosphere of nitrogen.

Prior to crystallization each sample (about 8 mg in weight) was heated at 408 K to remove the crystallinity and then quenched to the temperature of interest and isothermally crystallized. The crystallization time was about four times longer than the half-time of polymer crystallization at the given temperature. The melting behaviour of samples prepared in this manner were examined at the heating rate of 10 K/min. It was established that this heating rate value was the most appropriate for our experiments.

The small-angle X-ray scattering (SAXS) intensity distribution of the samples was measured on a conventional Rigaku-Denki 2202 X-ray goniometer with slit collimation system. The intensity was measured by a scintillation counter with a pulse-height analyser. Ni filtered CuK$_\alpha$ radiation was used as an incident X-ray source. A vacuum path between the sample and the counter was used. The weighting functions of the collimating system were obtained by numberical calculations with the equation derived by Hendricks and Schmidt[3]. Correction of experimental scattering curves for collimation errors has been made using the method described by Schmidt[4], as revised by Lin[5].

RESULTS AND DISCUSSION

Determination of the l-distribution is based on a d.s.c.

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curve for a melting polymer. It has been assumed[2] that the flow rate of the heat of fusion (deflection of the d.s.c. trace from the baseline) at a given temperature is directly proportional to the fraction of lamellae with this melting point. Because of the thermal lag, the true peak shape cannot be derived from the observed curve unless this is known or determinable. The limiting thermal resistance between the sample and the sample holder, R_0, can be determined from the slope of the leading edge of the melting peak of a very pure compound. O'Neill[6] has shown that this slope is equal to the ratio of the programmed heating rate (ϕ) to the resistance (R_0). The indicated program temperature (anywhere on the d.s.c. curve) will exceed the true sample temperature by a certain amount. In *Figure 1* it is shown how the true sample temperature was read off the scale by drawing a straight line of slope ϕ/R_0 through the point of interest. This slope was determined by running a d.s.c. curve of the melting of very pure benzoic acid with the same heating rate. The true temperature at the point A (see *Figure 1*) was read off as T, and the deflection AB was measured. The plot of deflection AB against lamella thickness l corresponding to the temperature T as calculated from the Thomson equation, after normalization, yields the distribution curve of lamellae thicknesses.

Table 1 gives the values[2] of σ_e, T_m°, Δh_m taken for the analysis of melting curves from which the l-distributions were derived.

Distribution curves obtained from samples of PP and PE crystallized at different temperatures are presented in *Figures 2* and *3*. As can be seen isothermal crystallization of the polymers leads to a broad thickness distribution of metastable lamellae. The values of l are scattered in a greater extent for PE than for PP (*Figures 2* and *3*).

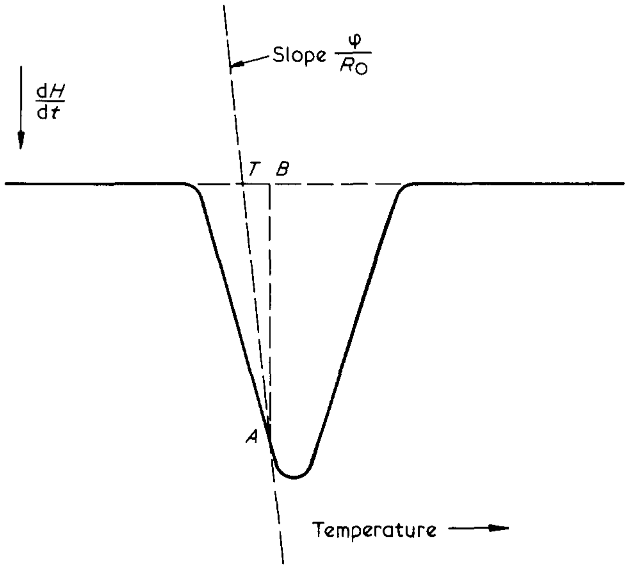

Figure 1 Assessment of the effect of thermal lag on shape of the melting curve. The slope ϕ/R_0 is equal to the slope of initial part of melting endotherm of very pure benzoic acid. The temperature of point A is found from the dashed line at point T

Table 1 Values of T_m^0, σ_e and Δh_m for polypropylene and polyethylene[2]

Parameter	Polypropylene	Polyethylene
T_m^0 [K]	457	415
σ_e (J m^{-2})	49.6 x 10^{-3}	60.9 x 10^{-3}
Δh_m (J m^{-3})	1.34 x 10^8	2.88 x 10^8

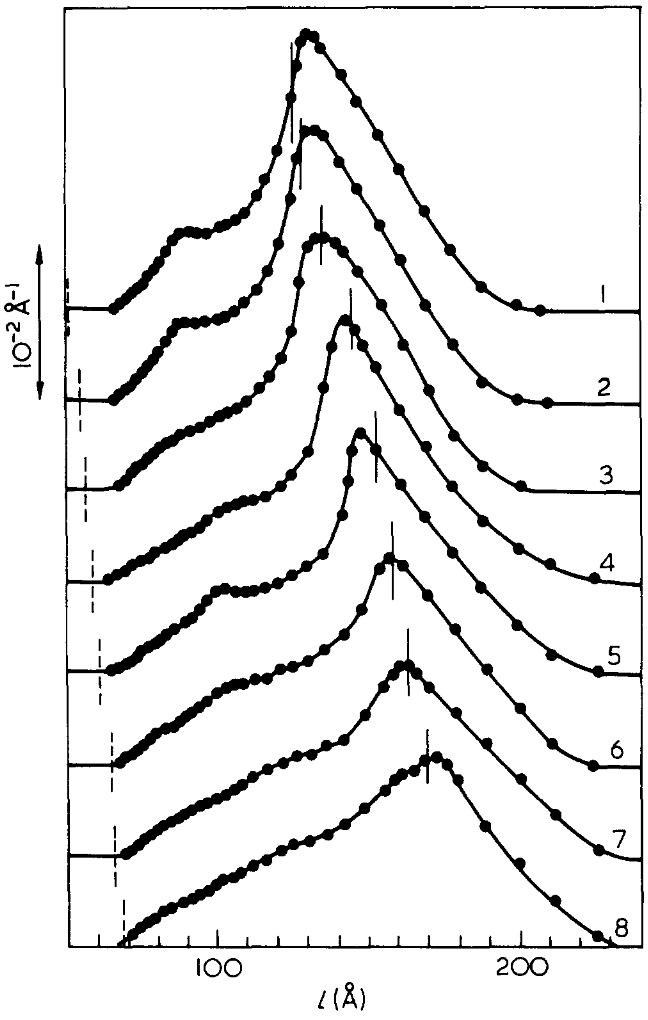

Figure 2 Distributions of lamella thicknesses in polypropylene isothermally crystallized at temperatures: (1) 390 K, (2) 393 K, (3) 395 K, (4) 398 K, (5) 400 K, (6) 403 K, (7) 405 K, (8) 408 K. Vertical continuous lines represent SAXS results whereas vertical dashed lines show critical values l^*

The large differences in fold length of PE lamellae can be due to an appreciable number of macromolecular chains passing through two or several lamellae and or to a formation of extended-chain crystallites.

The values of fold length l were calculated from SAXS patterns by means of the equation[7]:

$$l = s \cdot L \tag{2}$$

and marked on the curves characterizing lamella thickness distribution (*Figures 2* and *3*). Here L is the long spacing and x is the degree of crystallinity determined from the area of d.s.c. melting endotherms. These data agree with the most probable values of l maxima of distribution curves determined by the d.s.c. (*Table 2*). Furthermore, critical values of fold length (l^*) for secondary surface nucleation, resulting from the Lauritzen–Hoffman kinetic theory[8] were indicated (dashed lines in *Figures 2* and *3*).

The proposed method is restricted by several factors. The shape of the d.s.c. curve is determined in general by three competing processes, melting of the sample according to size and perfection of the crystallites, recrystallization, and reorganization of the sample as it is heated up in the scan.

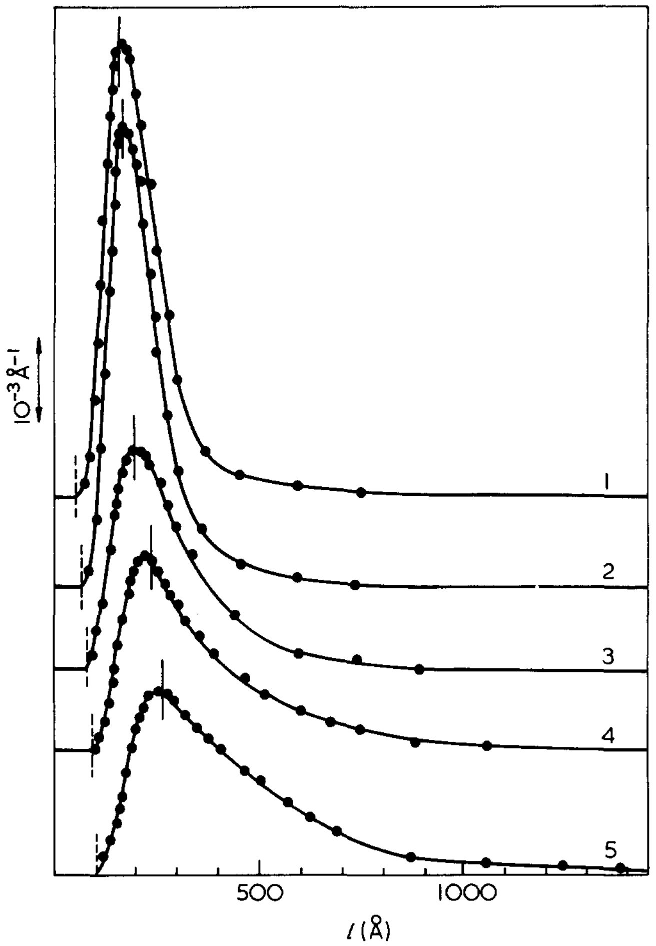

Figure 3 Distribution of lamella thicknesses in polyethylene crystallized at temperatures: (1) 383 K, (2) 388 K, (3) 393 K, (4) 396 K, (5) 398 K

Table 2 Average lamella thicknesses in isothermally crystallized polypropylene and polyethylene determined by d.s.c. and *SAXS*

Polyethylene			Polypropylene		
Crystallization temperature [K]	$l_{\text{d.s.c.}}$ [Å]	$l_{\text{X-ray}}$ [Å]	Crystallization temperature [K]	$l_{\text{d.s.c.}}$ [Å]	$l_{\text{X-ray}}$ [Å]
373	146	136	390	130	123
378	146	139	393	133	126
383	147	143	395	135	133
388	164	156	398	142	143
390	172	167	400	147	151
393	193	193	403	156	156
395	209	218	405	163	166
396	225	228	408	172	171
397	237	239	–	–	–
398	251	264	–	–	–

During the heating in the d.s.c., small molten lamellae can recrystallize into the form of larger lamellae with larger melting points. Refolding in the solid state (without melting) is also possible which results in increased lamella thicknesses. The relative importance of these phenomena will depend on the recrystallization and reorganization rates in relation to the d.s.c. scan rate.

High heating rates should suppress these processes affecting the shape of the d.s.c. thermograms and distorting the obtained distribution curve. From our investigations of effect of heating rate on character of d.s.c. curve it follows that the optimum heating rate is in the range 10–20 K/min.

CONCLUSIONS

The method presented here of interpreting the d.s.c. curves offers many advantages when compared with the usual methods applied for determination of lamella thickness. The major advantages are its simplicity, rapidity, the use of small sample and the fact that distribution of thicknesses is obtained.

On the other hand, care must be taken in interpreting d.s.c. curves since the shape and character of d.s.c. traces are affected by recrystallization and reorganization. Relatively high heating rates should be employed in order to eliminate these processes. Isothermal crystallization of PP and PE results in broad distributions of lamella thickness. In the case of PE the great scatter of lamella thickness can be associated with a considerable number of chains passing through several lamellae and with forming of extended-chain crystals.

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