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FAST DSC APPLIED TO THE CRYSTALLIZATION OF POLYPROPYLENE

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In an effort to find the limit of crystallization of polypropylene, a series of quantitative and semiquantitative DSC experiments at rates up to 10,000 deg/min are described. Even at these fast rates polypropylene crystallized on cooling between 350 ± 15 K and 280 ± 6 K. No "fully amorphous" polypropylene was produced. No initial stage crystallization to the condis state could be proven by quenching after partial crystallization.

The present status of scanning calorimetry permits measurements at heating rates between one and 100 K/min without undue temperature gradient within the sample [1]. Analysis of metastable substances and the study of superheating need, however, faster thermal measurements [2]. It would also be extremely helpful if fast industrial processes such as injection molding, fiber spinning, film blowing and the various conditioning cycles could be duplicated in the scanning calorimeter. Up to the present there have been only the efforts of Hager to develop a fast foil calorimeter [3] and some experiments by us [4] to reach up to and beyond 1000 K/min. In this paper we want to discuss the problem of fast calorimetry, describe several methods for fast measurement and quenching, and apply these to the problem of polypropylene crystallization.

The problem of fast calorimetry

Calorimetric data can be obtained by a simple temperature measurement only as long as the temperature gradient within the sample is experimentally negligible, i.e. is less than perhaps ±0.5 K. With larger temperature gradients, measurements will only yield thermal diffusivity information. The time-dependent heat flux dQ/dt into a disc of thickness L under steady-state conditions, from the underside is given, for example, by

$$dQ/dt = r^2 \pi L \varrho C q \tag{1}$$

or

$$dQ/dt = r^2 \pi \varkappa \, dT/dl \tag{2}$$

where r is the radius of the disc, l the thickness variable (0 at the bottom of the disc, L at the top), ϱ its density, C its heat capacity, q the heating rate and $\varkappa$ the thermal conductivity. In Equations (1) and (2) edge effects are neglected. Equation (1) is a statement of the total heat absorbed by the disc per second, and Eq. (2) is the well-known heat flow equation [5]. In Eq. (2) dQ/dt represents the heat flow normal through the surface $r^2\pi$ at $l=0$ and dT/dl is the temperature gradient. Equating Eqs (1) and (2) and integrating from the bottom surface through which the heat is conducted ($l=0$) to the center plane of the disc ($l = L/2$), one finds that the temperature difference ΔT between these two planes is:

$$\Delta T = \frac{3qL^2}{8k} \tag{3}$$

where k is the thermal diffusivity ($k = \varkappa/\varrho \cdot C$). For typical polymers, and also the common reference substance sapphire (Al_2O_3), the thermal diffusivity is about 10^{-7} m^2/s. One can now easily find the disc thicknesses and heating rates for an arbitrary, convenient ΔT of 0.6 K:

Disc thickness, mm	Heating rate, deg/min	Mass (r = 0.25 cm)
1	10	20 mg
0.1	1000	2 mg
0.01	100,000	200 μg

The mass of the disc is calculated assuming r = 0.25 cm and a density of 1.00 g/cm^3, typical for the standard aluminum pans used for DSC and macromolecular densities.

For a cylinder of radius R with temperature measurement in the center and heat flux across the outer surface Eq. (3) becomes

$$\Delta T = \frac{3 \cdot qR^2}{16\,k} \tag{4}$$

and the limiting dimensions for a ΔT of 0.6 K and for analogous conditions as for the disc are:

Cylinder radius, mm	Heating rate, deg/min	Mass ($l = 5\ R$)
1	20	16 mg
0.1	2000	16 μg
0.01	200,000	16 ng

Again, the lag was calculated midway from the center of the cylinder to the outer surface. For the mass calculation a cylinder length of 5 R was assumed to minimize end effects. The masses decrease more rapidly for the cylinder case since all three dimensions are reduced, in contrast to the disc, where only one dimension was decreased for the three difference cases.

The two sets of computations show that with film thicknesses of about 10 μm or cylindrical samples of perhaps 10 μg mass, heating rates of 10,000 deg/min or more should be possible for calorimetric experiments. The experiments below, as well as the prior efforts [3, 4], support this estimate.

Sample and instrumentation

The polypropylene used in the mesophase study was supplied by Scientific Polymer Products, Inc. and was 97% isotactic. The molecular mass was about 250,000, a range where crystallization is largely molecular mass independent. A standard study of thermal analysis of such polypropylene was carried out several years ago [6].

For the present thermal analyses either a DuPont 900 or 990 thermal analyzer were used to record temperature T and ΔT or time t and ΔT. The temperature signals were taken either from the 910 DSC-cell or external thermocouples. Temperature calibrations were carried out with the usual standard melting substances [7]. Amplitude calibrations were based on heats of fusion, and the areas of the recording evaluated by planimetry. The use of a modified DTA cell in conjunction with the DuPont 900 thermal analyzer for heating rates up to 400 K/min by installation of a more powerful heater was described earlier [8, 9].

The temperature range of interest was from about 200 K to 500 K. Experimentation involved either time and temperature controlled crystallization, interrupted by quenching in various constant temperature baths, followed by standard (slow) DSC analysis of the quenched samples, or by quenching or heating under fast measuring conditions.

For isothermal crystallization the sample of polypropylene was held for about 10 minutes in an external constant temperature bath at 473 K, well above the equilibrium melting temperature of 460.7 K [6]. This time and temperature were found sufficient to destroy all nuclei. The open DSC-cell was kept in the isothermal mode at the desired crystallization temperature under time-base conditions. At an arbitrarily chosen time zero, the sample pan was transferred and the DSC-cell closed. Figure 1, curve I gives a typical run. After the initial, irregular signal due to closure of the cell and temperature equilibration, the crystallization exotherm is clearly observable. Curves J–N indicate the interrupted crystallizations for which the samples were removed at the indicated times from the DSC-cell and quenched in liquid nitrogen and stored for later, standard analyses.

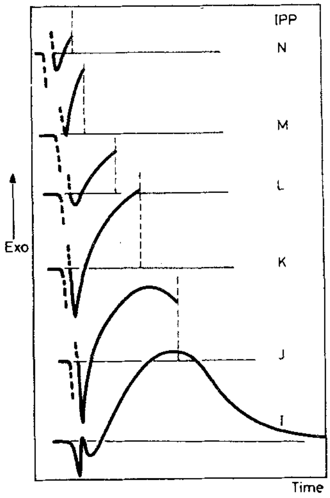

Fig. 1 Isothermal crystallization traces of isotactic polypropylene, interrupted at the indicated times for quenching in liquid N_2

For the fast measuring experiments various configurations of sample and thermocouple were immersed in different high and low temperature baths. A collection of common low temperature bath liquids are listed in Table 1. High temperature baths are usually electrically controlled and contain for temperature above about 350 K suitable grades of silicone oil. It is also possible to use a (high or low) temperature controlled Al-block and insert sample and reference into loosely packed small diameter glass beads (about 10 μm).

The samples of about 1 mg size or less were attached directly to the standard DuPont DTA thermocouples and either immersed directly into the heating or cooling bath if mechanical and chemical stability permitted, or they were protected by a drawn-out capillary (standard 1.6 to 1.8 mm diameter capillaries). Some typical heating rates for the glass capillary protected thermocouples are listed below for the insertion into the glass-bead filled Al block.

Fixed heating bath temperature, K	Range of measurement, K	Heating rate, deg/min
523	130–420	4000
573	130–420	4500
623	130–470	5000
673	130–520	5500
773	130–520	9000

Without glass capillary protection 10,000 K/min heating rate was accomplished over the 130–400 K measuring range by insertion in the 520 K bath. Also, using silicon oil instead of glass beads for heat transfer increases the heating rate, but complicates the sample handling. The values listed above are thus lower limits, some average cooling rates estimated by timing ΔT are:

Cooling bath type and temperature, K	Range of measurement, K	Cooling rates with and without glass capillary, K/min	
Boiling liq. N_2	520–250 K	4,000	6,000
Glass bead fill Al-block Cooled by boiling liq. N_2	520–250 K	6,000	8,000
Freezing *n*-pentane	520–250 K	10,000	> 10,000

Typical baselines from the over 100 taken are shown in Figures 2 and 3. It is easily seen that 100 to 200 K wide temperature ranges with practically linear baselines can be obtained and increasing the heating rates improves the flatness of the baseline.

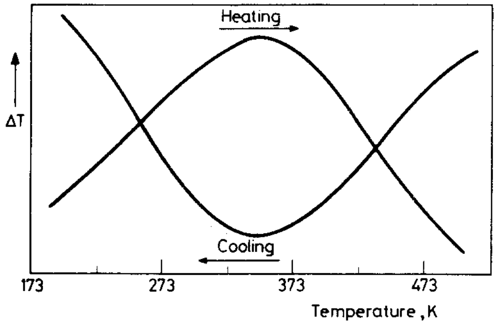

Fig. 2 Heating and cooling baselines at about 4000 deg/min in the range of measurement (see text). Sample and reference thermocouples were immersed in glass beads contained in a to constant temperature cooled or heated Al-block

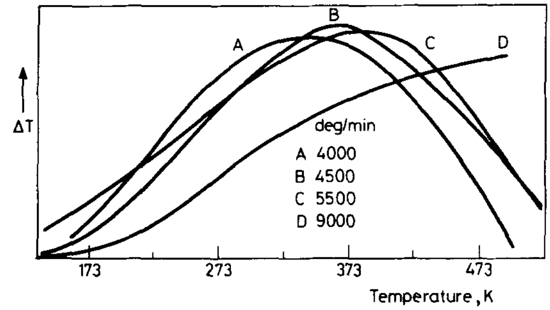

Fig. 3 Change of baselines on heating at different rates (for conditions see text)

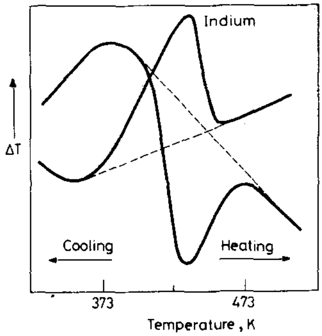

Fig. 4 Heating and cooling curves of about 1–3 mg indium at rate of 4000 deg/min

Typical calibration runs with Indium are shown in Fig. 4. The averages from 16 experiments yielded peak temperatures on heating at 442 ± 5 K and on cooling at 429 ± 2 K. The beginning of melting occurred at 431 ± 8 K, in agreement with the melting temperature of Indium (429.3 K). Considerable lags in temperature measurement are also in evidence. Estimates of the areas corresponding to the heats of crystallization were reproducible to about ± 12%. Improvements which are being attempted are to go to lower-mass thermocouples by using vapor deposition techniques and to make the sample handling more reproducible. For the present purpose this first attempt at fast DSC indicates that rates of 10,000 deg/min are realistic goals.

Fast crystallization of polypropylene

1. Summary of literature and formulation of the problem

It is well established that linear macromolecules crystallize first as lower melting, unstable or metastable crystals that improve as crystallization time increases [10]. For polypropylene it was shown, in addition, that on quenching from the melt a glass of a conformationally disordered crystal, a condis crystal, results [6]. This condis crystal structure was first described by Natta et al. [11], and called initially a smectic, liquid-crystalline phase. A rather large number of parallel studies of crystallization of polypropylene were published in 1984 [6, 12–20]. For earlier references see also references 17 and 10. It was suggested that in the melt short-segment helices [13] are already preformed (quasi-crystalline structure of the liquid, see Ref. 21). Crystallization occurs then at low temperature by formation of the metastable glass [6, 12, 18] that already has a crystallinity close to that of the ultimate (monoclinic) crystal (typically 40–60%). The major transition to the monoclinic crystal occurs on long term annealing or heating only above 330 K with an exotherm of about −600 J/mol (recalculated to 100% crystallinity; compare to the heat of fusion of 6900 J/mol). On heating at 50 deg/min, the exotherm peak-temperature is at about 380 K [6]. The goal of this research was to get information on the sequence of polypropylene crystallization under different crystallization conditions.

2. Experimental results

First, a series of quench experiments followed by analysis were performed in constant temperature baths (see Table 1) at 77.3 K, 195.2 K, 273.2 K, 298 K, 333 K, 343 K, 353 K, 358 K, and 368 K. Up to 298 K quench temperature there was no major change in the exotherm of the condis to monoclinic transition at about 371.2 ± 12 K (9 measurements at 20 deg/min). The 333 K quench revealed still a small exotherm and was similar in character to the 329 K annealed trace of a liquid nitrogen quenched polypropylene, analyzed earlier [6]. At higher quench temperatures no exotherm was found. A small annealing endotherm about 25 K above the quench temperature indicated in these samples the thermal history. For all quench experiments the ultimate, monoclinic melting-peak temperature was 437.1 ± 2.1 K (18 measurements at 20 deg/min) and the crystallinity, as estimated from the monoclinic crystal fusions, was 47 ± 6%.

The results from the interrupted crystallizations, as illustrated in Fig. 1, are shown in Fig. 5. The initial crystallinity is the percentage of the ultimately found crystallization as measured on fusion. For the 15 experiments the ultimate crystallinity was 42.9 ± 6.0%, with little difference for the different crystallization temperatures.

Table 1 Suitable liquids for low temperature bath[a]

	MP, K	BP, K
Nitrogen	63.1	77.3
Isopentane (2-methyl butane)	113.3	301.0
Methylcyclopentane	130.8	345.0
n-Pentane	143.5	309.3
Allyl alcohol	144.2	370.2
Ethyl alcohol	155.9	351.7
Isobutyl alcohol	165.2	381.3
Acetone	177.8	329.4
Toluene	178.2	383.8
Ethylacetate	189.2	350.2
Dry ice and acetone	195.2	—
Water	273.2	373.2

[a] Note that the boiling point (BP) is not very suitable for quick cooling because of the insulating effect of the vapor produced on insertion of a hot sample. Also observe that all compounds but nitrogen, dry ice, and water are combustable and their vapors form explosive mixtures with air.

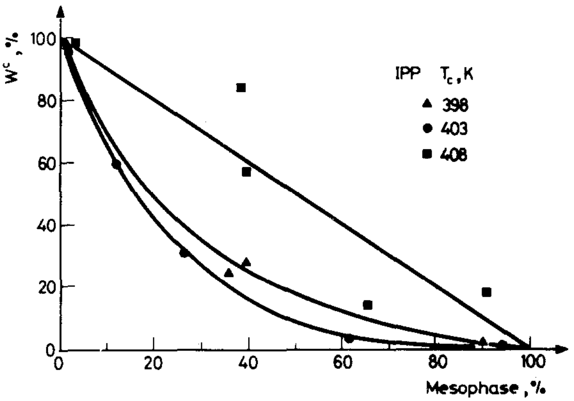

Fig. 5 Results of interrupted isothermal crystallization of polypropylene at the indicated temperatures. Initial crystallization indicates the percentage relative to the ultimate heat of fusion. The mesophase percentage is relative to the area for full mesophase crystallization as found in the direct quench experiments

The fast cooling and heating experiments are illustrated in Fig. 6. About 100 experiments were completed at rates of about 4000 deg/min. In all of these crystallization began at 350 ± 15 K and was completed at about 280 ± 6 K.

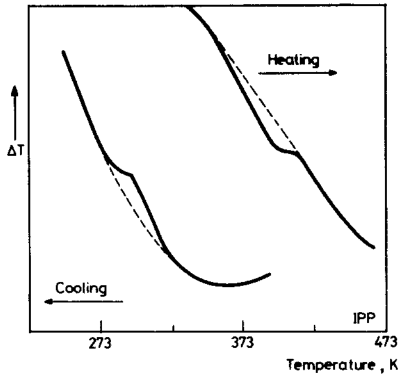

Fig. 6 Heating and cooling curves of isotactic polypropylene at rate of 4000 deg/min

3. *Discussion*

The quenching experiments of Fig. 6 show that the initial crystallization to the mesophase stops before the glass transition of the amorphous (atactic) polymer (260 K) is reached. Crystallization begins, on the other hand, only close to the temperature where the condis crystals are already metastable against long-time annealing (glassy ≈330 K). Since it was shown before [6] that crystallization to condis as well as monoclinic crystals increases the glass transition, one must conclude that the observed crystallization is terminated by the increase in glass transition caused by the crystallization.

The interrupted crystallization experiments show, in turn, that in the chosen crystallization range (398–408 K) the condis to monoclinic transition, if it occurs at all, is faster than the melt to condis transformation. If this were not so, the amount of condis crystal measured by the exotherm on heating at about 380 K should be consistently above the diagonal of Fig. 5. The preponderance of data-points below the diagonal seems to indicate that in the presence of monoclinic crystals the condis to monoclinic transition is enhanced.

One must thus conclude that the ordering of the preformed, imperfect helices [13] to the condis glass is a process which requires even faster thermal analysis than is at present available.

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Zusammenfassung — Eine Reihe von quantitativen und semiquentitativen DSC-Versuchen mit Aufheizgeschwindigkeiten bis 10 000 K/min wurden ausgeführt, um die Grenze der Kristallisation von Polypropylen festzustellen. Sogar bei diesen schnellen Aufheizgeschwindigkeiten kristallisiert Polypropylen beim Abkühlen zwischen 350 ± 15 K und 280 ± 6 K. Kein „völlig amorphes" Polypropylen wurde erhalten.

Резюме — С целью обнаружения температурного предела кристаллизации полипропилена, проведен ряд количественных и полуколичественных ДСК измерений при скоростях нагрева до 10 000 К/мин. Даже при таких скоростях полипропилен при охлаждении кристаллизуется между 350 ± 15 К и 280 ± 6 К. Не было получено «полностью аморфного» полипропилена. Начальная стадия кристаллизации в конденсированное состояние не была подтверждена путем быстрого охлаждения частично закристаллизованного продукта.