Die Makromolekulare Chemie **177**, *549–566 (1976)*

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Melting and Degradation Behaviour of Needle-like Poly(oxymethylene) Crystals

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(Date of receipt: April 29, 1975*)

SUMMARY:

DSC/TG (differential scanning calorimetry/thermal gravimetry) simultaneous measurements have been carried out for needle-like and other poly(oxymethylene) crystals and the occurrence of degradation, overlapping the melting, has been confirmed for needle-like and fibrous extended-chain crystals. A theory to analyze the DSC curves with reference to the corresponding TG has been formulated and the contributions from the melt and the degradation have been resolved by means of computer curve-fitting. For needle-like crystals, the heat of fusion, 2260 cal/mol (9450 J/mol) and the melting point, 183–184 °C (as well as the heat of degradation, 13,1$_7$ kcal/mol [55,0$_5$ kJ/mol]) have been obtained and discussed with reference to the data from other samples. Systematic experiments for the effect of running conditions on the shape of DSC curves have been made and described in the Appendix.

ZUSAMMENFASSUNG:

Simultane DSC/TG Messungen wurden für nadelförmige und andere Poly(oxymethylen)-Kristalle durchgeführt. Dabei wurde für die nadelförmigen und faserförmigen Kristalle aus gestreckten Ketten gefunden, daß das Schmelzen von Kettenabbau überlagert ist. Weiterhin wurde eine Theorie zur Analyse der DSC-Kurven in Bezug auf die entsprechenden TG-Kurven abgeleitet. Damit konnten mit Hilfe einer computerberechneten Kurvenanpassung die Anteile, die vom Schmelz- und Abbauprozeß herrühren, bestimmt werden. Für nadelförmige Poly(oxymethylen)-Kristalle wurden folgende Werte erhalten: Schmelzwärme, 2260 cal/mol (9450 J/mol); Schmelzpunkt, 183–184 °C (und Abbauwärme, 13,1$_7$ kcal/mol [55,0$_5$ kJ/mol]). Diese Ergebnisse wurden mit den Werten anderer Proben verglichen. Im Anhang werden systematische Experimente beschrieben, die den Einfluß der Untersuchungsbedingungen auf die Form der DSC-Kurven untersuchen.

1. *Introduction*

The melting behaviour of poly(oxymethylene) has been extensively studied with crystalline specimens from various sources. As typical crystalline polymer,

*) Revised manuscript of June 20, 1975.

poly(oxymethylene) gives well defined folded-chain, lamellar structures both from the melt and solutions. Fibrous extended-chain crystals have also been made available for this particular polymer by the solid-state polymerization of cyclic oligomers. (Previous works relevant to the present study will be cited elsewhere below.)

The needle-like, extended-chain single-crystals of poly(oxymethylene), developed in this laboratory[1,2] in a cationic polymerization system of 1,3,5-trioxane (in the following called: trioxane) in cyclohexane, provided a unique specimen. Electron-microscopy[3] revealed a hexagonal pencil-like habit, and X-ray study[4] confirmed its perfection within the limit of sensitivity. Preliminary thermal analysis[1,2,5] showed a sharp melting maximum at around 190 °C, this melting temperature being higher than those of fibrous extended-chain crystals. This strongly supported the notion that the needle-like crystals consist of extended-chain molecules. The baseline of the thermal analysis curve was stable at least until the melting region was reached. It was recognized, however, that the size of the peaks was clearly too large compared with those from reference specimens, even when the difference in crystallinity was taken into account. In addition, to draw a smooth baseline underneath the peak was difficult. The situation was the same for fibrous poly(oxymethylene) crystals prepared by the cationic solid-state polymerization of trioxane. Degradation effects, to which unstabilized poly(oxymethylene) is generally liable, were suspected and strongly confirmed by simultaneous DSC/TG (differential scanning calorimetry/thermal gravimetry) measurements[6], once the material had started to melt.

In this study, the DSC/TG measurements were renewed, under more controlled conditions, for needle-like crystals and various other specimens. A theory to analyze the DSC curves with reference to the corresponding TG traces was formulated; the DSC curves were separated into the contributions from the melting and the degradation by means of computer curve fitting, and the heat of fusion, as well as the heat of decomposition, was evaluated. The results are discussed in the light of previous work.

Systematic experiments for the effect of measuring conditions on the shape of DSC curves are reported in the Appendix.

2. *Experimental Part*

2.1 Samples

Needle-like crystals were grown as described previously[3,5] and subjected to BF_3 etching[5,7] in order to disrupt the original radial construction and facilitate packing. Two lots of samples were used for the measurements. Needle I was prepared by applying 0,5 cm^3 gaseous BF_3 to 100 mg needle-like crystals (residual weight; 67 mg (67%), length: 15–30 μm). Needle II was prepared from needles obtained from a different batch with 400 cm^3 BF_3 for 17,0 g polymer (residual weight: 10,7 g (63%), length: 30–80 μm).

Fibrillar crystals were prepared by the cationic solid-state polymerization method[8] of trioxane. 2,0 g trioxane were dissolved in 20 ml cyclohexane in a test tube at 50 °C. Soon after 1 cm^3 BF_3 had been added, the tube was quenched in ice water to crystallize the monomer, and then the polymerization was conducted at 40 °C for 1 h (yield: 33%). After washing and drying, the material was heated at 130 °C i. vac. for 1 h to exclude volatile fractions (recovery: 70%).

A reprecipitate from needle-poly(oxymethylene) was obtained by dissolving 1,0 g needle-like crystals in 10 ml hexafluoroacetone sesquihydrate, buffered by triethylamine, and pouring the solution into a large amount of acetone. The solvent was replaced by benzene and the precipitate was freeze-dried.

Delrin 150X [poly(oxymethylene) diacetate*), from E. I. du Pont de Nemours & Co.] was also used after recrystallisation from the melt at a cooling rate of 10 °C/min (using Perkin-Elmer's DSC-II apparatus). The polymer was also used after crystallizing in a 0,5 wt.-% bromobenzene solution at 130 °C.

2.2 Simultaneous DSC/TG measurements

The 'TG-DSC Standard-type' apparatus of Rigaku-Denki Co. was used. About 1,5 mg samples (measured with an accuracy of ±0,002 mg) were placed and packed carefully at the bottom of the open-type sample pan (5 mm diameter and 2,5 mm tall) in the form of a thin disc. The operational conditions were fixed as follows: DSC sensitivity: 4 mcal/s**), DSC recorder range; 1 mV full scale, TG range; 2 mg full scale, heating-rate: 10 °C/min. The temperature calibration (±0,5 °C) was checked by the melting point of indium, 429,8 K. The flow of nitrogen was adjusted to 85 cm^3/min.

2.3 Calibration of DSC area

The calibration was carried out using the transitions of three substances; potassium nitrate (crystalline transition at 402 K, 12,8 mcal/mg), indium (melting at 429,8 K, 6,97 mcal/mg), and benzoic acid (melting at 395,5 K, 33,8 mcal/mg). A good linearity was established as shown in Fig. 1, from which the conversion factor, $1\,mV \times K = 43{,}9_9$ mcal, was obtained by the least square fitting. The method of analyzing DSC curves is described in the text. The HITAC 8400 computer of this institute was employed for the calculation with FORTRAN programmes.

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*) Systematic IUPAC nomenclature: α-acetyl-ω-acetoxypoly(oxymethylene).

**) In SI-units: 1 cal = 4,1867 J.

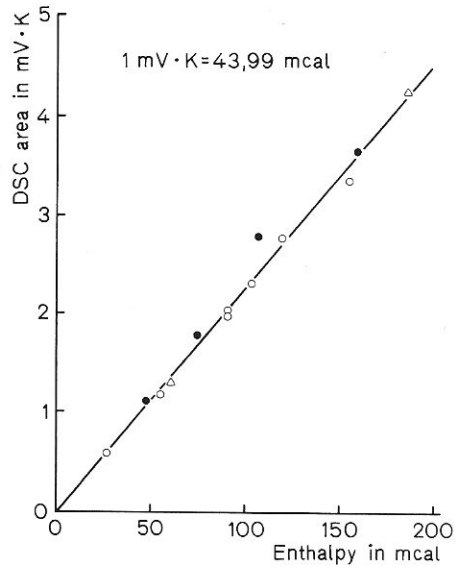

Fig. 1. Area-to-calorie calibration for DSC under conditions described in the Exptl. Part, section 2.3, with standard substances, potassium nitrate (○), indium (●), and benzoic acid (△). The unit of area was taken by [mV × K]. (In SI units: 1 cal = 4,1867 J)

3. *Results and Discussion*

3.1 *DSC/TG (simultaneous measurement of differential scanning calorimetry and weight loss)*

Several runs were made for each sample and satisfactory reproducibility was obtained. Fig. 2 demonstrates a set of differential scanning calorimetry/thermal gravimetry (DSC/TG) curves, covering a wide temperature range right up to the end of decomposition. The features of DSC traces until the end of apparent melting are basically the same as observed[1,2,5] by conventional DSC instruments. Needle-like crystals showed a sharp endotherm peak, having a maximum at ca. 190 °C, although small differences were seen between samples (i.e., Needle I and II, s. Exptl. Part, section 2.1) in the narrowness and the position of the maximum. The trace from the fibrillar crystals, prepared by cationic solid-state polymerization of trioxane, showed a maximum at 188 °C, bearing a characteristic shoulder at ca. 183 °C. That the products of γ-ray polymerization of trioxane show a very similar trace was communicated by *Odajima*[9]. The results from other reference samples were not quite new. (For general reference, a comprehensive paper by *Jaffe* and *Wunderlich*[10] is useful.) For the melt-recrystallized Delrin and the reprecipitate of needle-poly(oxymethylene), single peaks were observed at moderate temperatures,

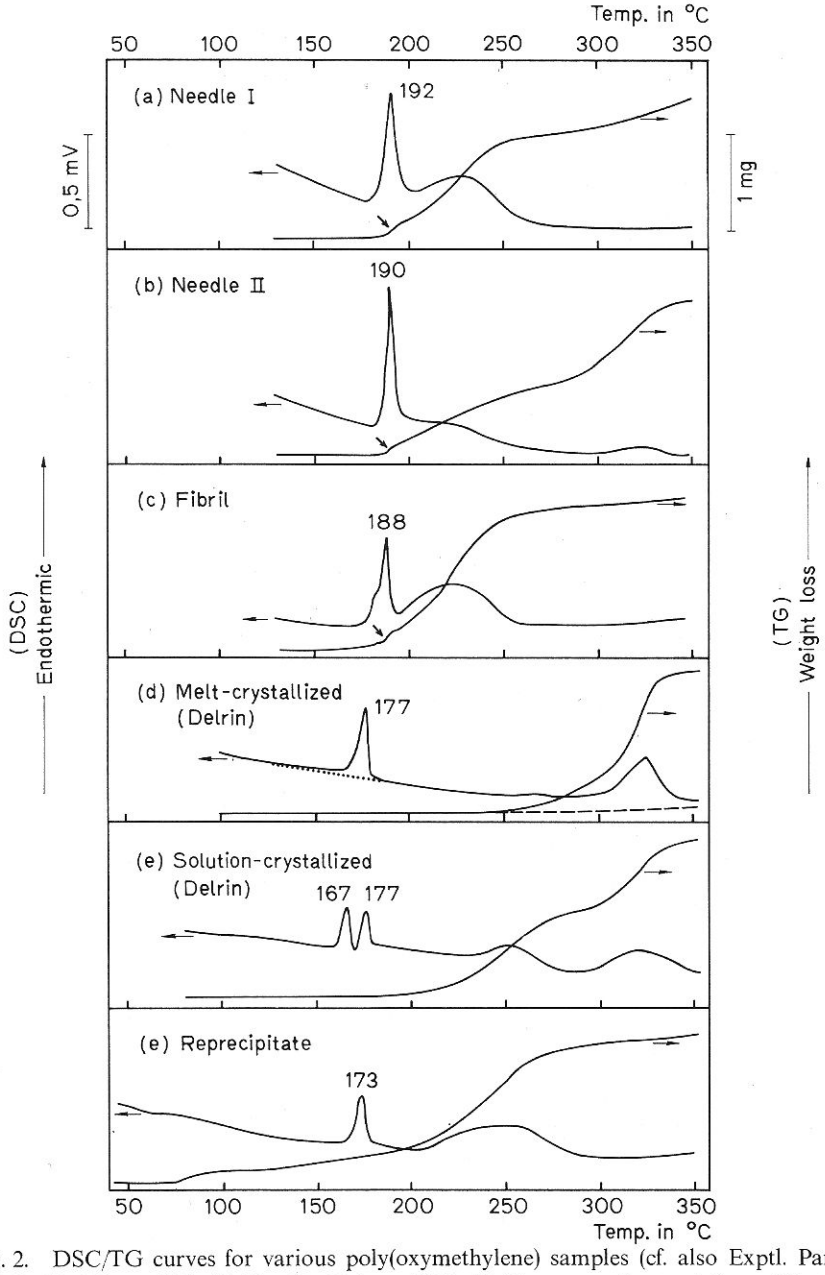

Fig. 2. DSC/TG curves for various poly(oxymethylene) samples (cf. also Exptl. Part). (a) Needle I (run: 103), (b) Needle II (run: 201), (c) fibrous products of the solid-state polymerization (run: 402), (d) melt-recrystallized Delrin (run: 505), (e) solution-crystallized Delrin (run: 701), and (f) reprecipitate of needle-poly(oxymethylene) (run: 604)

177 and 173 °C, respectively. That lamellar crystals grown from dilute solutions show two peaks, involving exotherms by in situ recrystallization, was pointed out formerly by *Carter* and *Baer*[11]. The effect of recrystallization was also discernible for the reprecipitated sample.

Before the melting region was reached, the weight loss by TG was very small for all samples but the reprecipitate. In particular, the excellent stability of needle-like crystals, despite having unblocked chain ends, was confirmed. This is considered to reflect that the crystals consist of molecules of very high molecular weight, the chain ends being small in number and arranged on the surface of the crystals. (Long ago, it was pointed out by *Jaacks*[12] that poly(oxymethylene) prepared cationically in a cyclohexane solution of trioxane had very good thermal stability and postulated a macrocyclic structure for the molecule (without study of the morphology). It could be possible that the polymer had some particular structure similar to the needle-like crystals or others (e.g., feather-shaped crystals[4,13]). The fibrillar crystals showed a slight weight loss before the DSC peak appeared.

In the melting region, a characteristic feature was observed on TG for the needle-like and the fibrillar samples; the curve showed a small but rather abrupt weight loss just around the DSC maximum. This implies that the peaks on DSC can no longer be interpreted as the result of mere phase transition, since a contribution from degradation must have been superimposed. Above this temperature region, unstabilized polymers degraded heavily, between ca. 210 and 250 °C, as is shown by the sharp increase in TG curves and also by the broad maximum on DSC traces. Around 300 °C, another sharp upward inflexion appeared on TG traces, but no corresponding effect was seen on DSC.

The thermal decomposition of poly(oxymethylene) in the absence of oxygen is considered to occur primarily by a simple mechanism[14], the successive depolymerization from chain ends generating formaldehyde. This mechanism may apply to the degradation in the lower temperature region (say up to 250 °C), observed by thermometry. Processes at higher temperatures, involving chain scission[14], seem to be complicated. A brown residue was found, when the runs were interrupted at ca. 300 °C.

3.2 Theoretical expression of DSC curves

It was first assumed that DSC curves in the relatively low temperature region (up to ca. 250 °C) involve the heats of three steps; the melting of

crystals (Eq. (i)), the depolymerization from chain-ends liberating formaldehyde (Eq. (ii)), and the evaporation of formaldehyde (Eq. (iii)).

$$\frac{1}{n}\ldots(-CH_2O)_n-\ldots \text{ (solid)} \longrightarrow \frac{1}{n}\ldots(-CH_2O)_n-\ldots \text{ (amorphous)} \quad \text{(i)}$$

$$\ldots-OCH_2OCH_2OH \longrightarrow \ldots-OCH_2OH + CH_2O \text{ (liquid)} \quad \text{(ii)}$$

$$CH_2O \text{ (sorbed)} \longrightarrow CH_2O \text{ (gas)} \quad \text{(iii)}$$

Thus, a DSC curve, $Y(T)$, (as a function of temperature, T) may be described by Eq. (1):

$$Y(T)=dH_f(T)/dT+dH_d(T)/dT+dH_v(T)/dT+B(T) \quad (1)$$

where the three differential terms relate to the endotherms due to the fusion, the depolymerization, and the vaporization of formaldehyde, resp. $B(T)$ is the background. Expression by Eq. (1) without reference to time is possible as the DSC/TG runs were conducted at a constant heating rate.

Since the two steps, the depolymerization and the evaporation of formaldehyde, are assumed to take place with negligible loss of time, the combined heat will be proportional to the slope of the weight decrease curve, $W(T)$ measured by TG:

$$dW(T)/dT=[dH_d(T)/dT+dH_v(T)/dT]/C_3 \quad (2)$$

where C_3 is the sum of ΔH_d and ΔH_v, the heats of depolymerization and vaporization per unit weight, resp.

Blank tests of DSC/TG revealed a smooth instrumental curve for DSC, which varied between runs, but was approximated by the quadratic equation:

$$B(T)=C_1\cdot T^2+C_2\cdot T+C_4 \quad (3)$$

where C_1, C_2, and C_4 are arbitrary parameters. The effect from the change of heat capacity estimated was small and was included in the expression of Eq. (3) (The TG trace itself of blank runs showed a slight upward drift with temperature as indicated by the dotted line in Fig. 2(d). The magnitude was negligible, however, at least below ca. 250 °C).

By substituting the relations of Eqs. (2) and (3) into Eq. (1) one obtains:

$$Y(T)=dH_f(T)/dT+C_3\cdot dW(T)/dT+C_1\cdot T^2+C_2\cdot T+C_4 \quad (4)$$

If a standard temperature, T_0, is chosen at a point far below the start of decomposition and melting (where $W(T_0)=0$, $dW(T_0)/dT=0$, and $dH_f(T_0)/dT=0$) and $Y(T_0)$ is set equal to zero, one of the unknown parameters, C_4, is saved:

$$Y(T)=dH_f(T)/dT+C_1\cdot(T^2-T_0^2)+C_2\cdot(T-T_0)+C_3\cdot dW(T)/dT \tag{5}$$

Of course, the degradation curve, $Y_d(T)$, and the melting curve, $Y_m(T)$, are given by the fractions of Eq. (5):

$$Y_d(T)=C_3\cdot dW(T)/dT+C_1\cdot(T^2-T_0^2)+C_2\cdot(T-T_0) \tag{6}$$

and

$$\begin{aligned} Y_m(T)&=dH_f(T)/dT+C_1\cdot(T^2-T_0^2)+C_2\cdot(T-T_0)\\ &=Y(T)-Y_d(T)+C_1\cdot(T^2-T_0^2)+C_2\cdot(T-T_0) \end{aligned} \tag{7}$$

C_1, C_2, and C_3 may be determined from Eq. (6) by curve fitting using the data at temperatures well below (T_1 to T_2) and well above (T_3 to T_4) the melting region, where $Y_d(T)\equiv Y(T)$ holds.

The heat of fusion per unit weight is calculated by Eq. (8):

$$\Delta H_f=\frac{1}{W_0}\cdot\int_{T_i}^{T_{ii}}(dH_f(T)/dT)dT \tag{8}$$

where T_i and T_{ii} are the lower and the upper limits of melting region, respectively. W_0 is the weight of the specimen.

3.3 Computer analysis of melting and degradation

In-put data for the computer were read from DSC/TG charts by 5-kelvin intervals between 140 and 270 °C and 1-kelvin intervals around peaks. An example of the set of data from Needle I is tabulated in Tab. 1, where the values of setting temperatures, T_0, T_1, T_2, T_i, T_{ii}, T_3, and T_4 chosen are indicated.

The computer calculation was organized as follows. The TG data, $W'(T)$, were corrected for the zero level by:

$$W(T)=W'(T)-W'(T_0) \tag{9}$$

Tab. 1. An example of DSC/TG data-set in-put for computer for poly(oxymethylene) run 103 (Needle I); initial sample weight W_0: 1,550 mg (s. text)

Temp. in °C	TG $\frac{W'(T)\cdot 50}{mg}$	DSC $\frac{Y'(T)\cdot 100}{mV}$	Temp. in °C	TG $\frac{W'(T)\cdot 50}{mg}$	DSC $\frac{Y'(T)\cdot 100}{mV}$
140	5,2	38,5	196	13,0	41,0
145	5,2	36,6	197	13,65	35,7
150→T_0	5,2	34,8	198	14,15	33,4
155	5,2	33,0	199	14,6	31,6
160→T_1	5,2	31,4	200	15,0	30,6
165	5,2	29,2	201	15,4	30,0
170→T_2	5,2	27,5	202	15,8	29,6
175	5,25	26,1	203	16,35	29,6
178	5,3	25,3	204	16,9	29,75
179	5,3	25,0	205→T_{ii}	17,55	30,0
180→T_i	5,35	25,0	206	18,2	30,4
181	5,4	25,1	207	18,8	30,8
182	5,5	25,9	210→T_3	21,3	32,2
183	5,6	27,1	215	25,3	33,8
184	5,7	29,0	220	30,0	35,4
185	5,8	31,2	225	34,4	36,7
186	5,9	34,0	230	40,6	37,5
187	6,05	39,2	235	45,6	36,8
188	6,35	49,0	240	50,6	33,2
189	6,7	58,0	245→T_4	54,4	27,8
190	7,25	68,5	250	57,8	22,1
191	8,05	76,2	255	58,1	18,3
192	8,95	81,0	260	58,9	16,0
193	10,1	65,3	265	59,5	14,5
194	11,2	57,1	270	60,2	13,4
195	12,2	49,6			

and $dW(T)/dT$ was calculated by the five-point Stirling equation. The DSC data, originally in the unit mV, were corrected and converted into the unit mcal/K by:

$$Y(T)=[Y'(T)-Y'(T_0)]\cdot\alpha \tag{10}$$

where α (=43,99 mcal/(mV·K)) is the conversion factor determined with standard substances (s. Exptl. Part and Fig. 1).

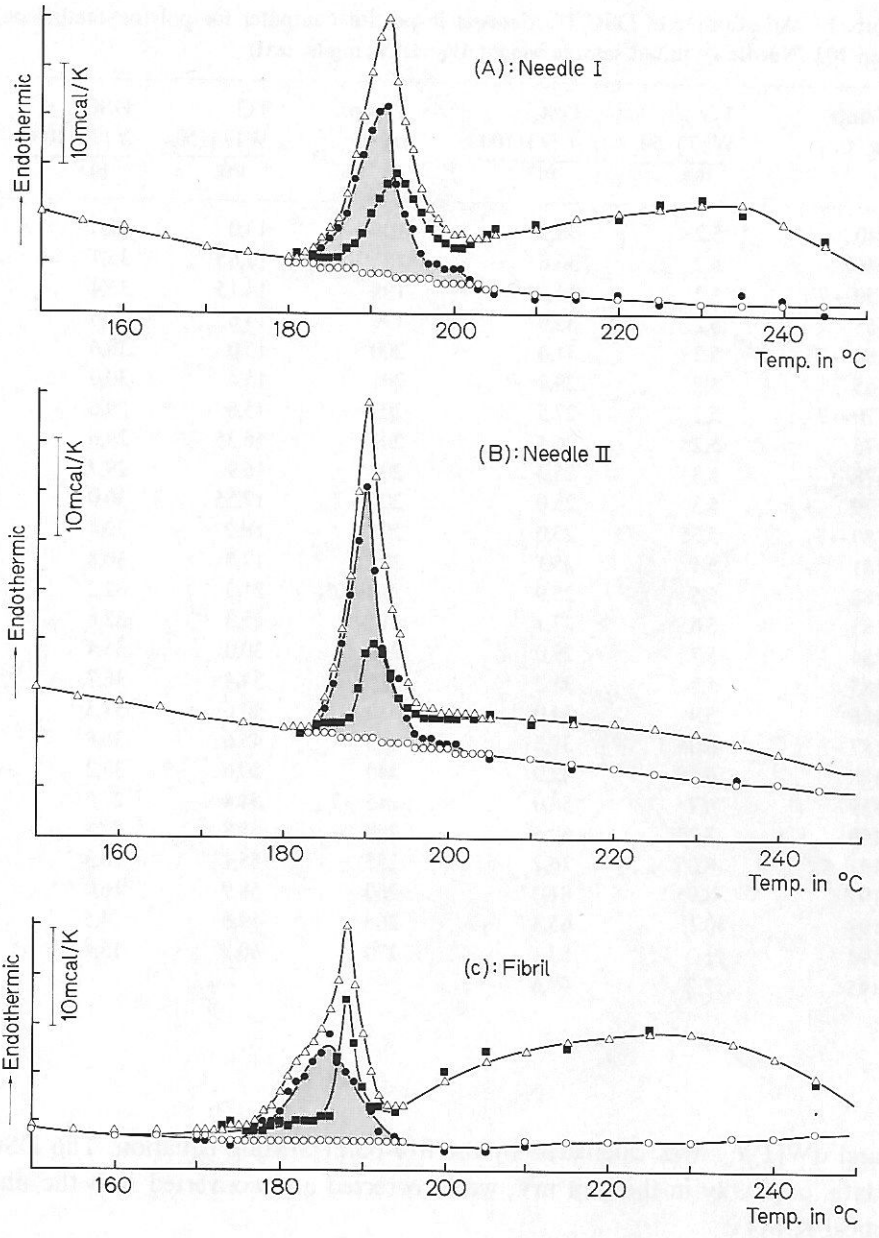

Fig. 3. Results of computer analysis of DSC curves for various poly(oxymethylene) samples (cf. Exptl. Part): Needle I (run: 103) (A), Needle II (run: 201) (B), and the fibrous crystals (run: 402) (C). Plots drawn by the computer to the accuracy of $\pm 0{,}25$ mcal/K; (△): total DSC curve, (■): degradation, (●): melting, (○): background

The data between T_1 and T_2 and between T_3 and T_4 were applied to Eq. (6) and C_1, C_2, and C_3 were determined by the least-square method. For each run, the degree of fitting, σ in mcal K^{-1} mg^{-1} was evaluated by:

$$\sigma=\{\Sigma[Y(T)-Y_d(T)]^2/(N-1)\}^{1/2}/W_0 \tag{11}$$

where N is the number of fitting points in the above temperature regions. W_0 was represented by the original weight of the specimens, although minor fractions had been lost before melting.

Through the parameters, C_1, C_2, and C_3, curves for the background, the degradation and the melting were calculated from $B(T)-B(T_0)$, Eq. (6) and Eq. (7), resp.

ΔH_f was then calculated by the integration of Eq. (8), using the trapezoidal method.

At the second stage, the curve fitting and the calculations were repeated by fixing the parameter C_3.

The results of DSC/TG measurements from the two lots of needle-like and fibrillar crystals, five from each sample, were subjected to the computer analysis. Examples of DSC curves are displaced by the computer plots in Fig. 3, in which fractions from the melting and the degradation, as well as the background, have been separated. It is remarkable that the endothermal maxima involved both, heats of melting and degradation, the magnitude of the latter being far from negligible.

For the two lots of needle-like crystals, Needle I and Needle II, both degradation and melting maxima appeared to occur around the apparent peaks; the degradation maxima were found at 193 and 191 °C, i.e. ca. 1 degree above those of melting, 192 and 190 °C, respectively. In the case of the fibrillar crystals, the apparent peak at 188 °C was proved to indicate decomposition, whereas the true melting peak was found at 186 °C, as was implied by the characteristic shoulder of the DSC trace.

The melting of folded-chain type poly(oxymethylene) crystals has been widely studied in the light of theories[15] with respect to the crystallization condition and the thermodynamic melting point was estimated at around 200 °C. E.g., 200, 202, and 206 °C were reported by *Wissbrun*[16], *Carter* and *Baer*[11], and *Majer*[17], respectively. Carter and Baer also determined 210 °C from the lamellar thickness and the melting temperature of crystals. On the other hand, the melting temperatures measured for as-polymerized, extended-chain crystals and regarded directly as the equilibrium melting points

are rather low: e.g., 182,5, 186–187, 187, and 191,5 °C have been reported by *Jaffe* and *Wunderlich*[10], *Baccaredda* et al.[18], *Korenaga* et al.[19], and *Munoz-Escalona* et al.[20]. Although the occurrence of degradation as well as the imperfection of specimens were implicitly ignored in these measurements, these values are not much different from those seen in this study after the resolution.

In most previous works cited above (as for polymers in general), peak temperatures of thermal analysis curves were evaluated, because melting started rather gradually. Theoretically it is more reasonable to adopt the initiation of melting or the lower foot of peaks (as discussed in the Appendix). In fact, temperature calibration of the apparatus is normally made in this way using transitions of metals or simple substances. In the present cases, the lower foot was definable (as in Fig. 3) within the accuracy of ± 1 °C; i.e., 183, 184, and 175 °C for Needle I, Needle II, and the fibrillar crystals, respectively. These values are several degrees lower than the peak temperatures. The difference will be greater for melt-recrystallized samples (because melting tends to occur in broader ranges), although the foot of a peak is generally blurred and not easily definable. This may be the reason for the large difference between the values of melting point evaluated by the indirect and the direct method, i.e., from folded-chain and fibrous specimens, respectively, mentioned above.

The foot temperature from needle-like crystals, 183–184 °C is apparently similar to 182,5 °C (extrapolated to zero-heating-rate) determined with fibrous specimens by *Jaffe* and *Wunderlich*[10].

There has been no firm explanation for the occurrence of the degradation maximum in the melting region. First, a chemical effect, associated with the catalytic species left unremoved, was suspected and the measurement was repeated after refluxing the needles in a dilute solution of triethylamine (5 wt.-% in ethanol/water, 50/50 v/v mixture) and washing thoroughly. No significant difference was observed on the DSC/TG traces, however. A possible mechanism would be as follows: It is reasonable to assume that the degradation is accelerated when the melting starts and the chain ends become mobilized. The elimination of formaldehyde would be retarded, however, as the phase changes from the loose mass to the molten state and decomposition turns to a reaction producing formaldehyde dissolved in the molten polymer.

The determined heats of degradation, C_3 ($=\Delta H_d + \Delta H_v$), and melting, ΔH_f, are summarized in Tab. 2. These quantities were to some extent affected by the choice of setting temperatures, namely by T_4, the upper limit of

Tab. 2. Summary of the computer analysis for various poly(oxymethylene) samples (SI-units: 1 cal=4,1867 J).

Sample	Run	Sample weight in mg	$\Delta H_d+\Delta H_v$[a] kcal/mol (C_3[d], floated)	ΔH_f[b] cal/mol (C_3[d], floated)	σ[c] mcal K^{-1} mg^{-1} (C_3[d], floated)	ΔH_f[b] cal/mol (C_3[d], fixed)[e]
Needle I	101[f]	1,526	13,76	2073	0,169	2009[g]
	102[f]	1,583	11,46	2258	0,214	2340
	103[f]	1,549	13,38	2224	0,308	2218
	104[f]	1,550	12,45	2146	0,376	2241
	105[f]	1,526	10,89	2060	0,114	2227
		—	—	—	—	(av.: 2256)
Needle II	201[f]	1,665	12,73	2226	0,056	2229
	202[f]	1,537	15,73	2286	0,152	2269
	204[f]	1,517	20,05[g]	1618	0,130	2034[g]
	205[f]	1,544	15,82	2156	0,154	2211
	206[f]	1,582	14,91	2331	0,169	2259
		—	—	—	—	(av.: 2259)
Fibril	401[h]	1,539	12,41	1764	0,119	1895
	402[h]	1,572	12,02	1647	0,092	1812
	404[h]	1,539	11,83	1616	0,158	1766
	405[h]	1,515	12,46	1628	0,131	1763
	406[h]	1,515	14,56	1581	0,181	1452[g]
		—	—	—	—	(av.: 1809)
Average	—	—	13,17	—	0,172	—

[a] ΔH_d: heat of depolymerization; ΔH_v: heat of vaporization of formaldehyde.
[b] ΔH_f: heat of fusion.
[c] σ: degree of fitting (s. Eq. (11)).
[d] C_3: heat of degradation per unit weight $=\Delta H_d+\Delta H_v$.
[e] C_3 fixed at 13,17 kcal/mol.
[f] Setting temps.: $T_0=150$, $T_1=160$, $T_2=170$, $T_i=180$, $T_{ii}=205$, $T_3=210$, $T_4=245\,°C$.
[g] Omitted from average.
[h] Setting temps.: $T_0=140$, $T_1=150$, $T_2=160$, $T_i=170$, $T_{ii}=195$, $T_3=210$, $T_4=245\,°C$.

the fitting range. The setting temperatures (cf. footnotes f), h), Tab. 2) were selected after many trial operations. The values of heat of degradation, using C_3 obtained from different runs, fell in the relatively narrow range, between 11 and 15 kcal/mol. Since it should be theoretically a constant regardless of the kind of samples, the scattering was taken as experimental. The average, 13,1$_7$ kcal/mol was smaller than the corresponding values, 15,3 kcal/mol cited by *Brown*[21] as the result of a thermodynamic calculation for a polymerization system.

The values of the heat of fusion obtained by fixing C_3 at the average value of 13,17 kcal/mol (giving the degree of fitting, $\sigma = 0{,}226$ mcal K^{-1} mg^{-1}) are listed in the last column of Tab. 2, with averages for each sample. (When $C_3 = 15{,}3$ kcal/mol was used, σ changed to 0,312 mcal K^{-1} mg, resulting in larger scattering in the value of the heat of fusion).

The values of the heat of fusion for two lots of needle-like crystals (Needle I and Needle II in Tab. 2) agreed well at ca. 2260 cal/mol. This was larger than those estimated from the data of less perfect specimens by giving a conventional correction for crystallinity. The value obtained for the fibrillar products of the cationic solid-state polymerization, 1810 cal/mol is apparently similar to that reported for the products of γ-ray polymerization, 1890 cal/mol, reported by *Munoz-Escalona* et al.[20]. Direct comparison would not be meaningful, however, because the effect of degradation was not clarified in the former measurement. A correction of the present result for the degree of crystallinity ($\approx 90\%$[5]) leads to the heat of fusion for 100% crystallinity, 2010 cal/mol.

The heat of fusion evaluated for the melt-recrystallized Delrin (by estimating a smooth background as in Fig. 2(d)) averaged at 1470 cal/mol as given in Tab. 3. The degree of crystallinity of this sample, measured by the same method as used previously[5], was 68%. This gives 2170 cal/mol for 100% crystallinity. This is not consistent with those obtained by the similar procedure, 1760 and 1780 cal/mol, reported by *Inoue*[22] and *Starkweather* and *Boyd*[23], respectively; (1796 cal/mol was also obtained by *Korenaga* et al.[19] from a polymer/diluent system).

The needle-like crystals are considered to be the most perfect poly(oxymethylene) crystals ever studied, but how close the present measurement came to the true property of the polymer is not immediately certain. One point concerned is, whether chain scission, assumed to be negligible in the present analysis, did not occur at appreciable rate namely in the process of melting, giving rise to an overestimation for the value of the heat of fusion. In the

Tab. 3. Heat of fusion, ΔH_f, of melt-crystallized Delrin (s. Exptl. Part), (SI-units: 1 cal=4,1867 J)

Run	Sample weight in mg	ΔH_f cal/mol
501	1,483	1491
502	1,639	1463
503	1,607	1408
504	1,564	1474
	—	(av.: 1470)

case of preparing polymer solutions from as-polymerized extended-chain crystals of poly(oxymethylene) in general, occurrence of chain scission during dissolution is highly probable, making the determination of the "original" molecular weight difficult, although solutions once prepared are stable to such a degree that the viscosity measurement can be managed. In our preliminary experiments with needle-like crystals, the measurement of solution viscosity was not reproducible, the data scattering at a low level corresponding to the average molecular weight, below ca. 150 thousands, whereas at least 1,5 millions (equivalent to the molecular length of $\approx 10\,\mu m$) is expected for the single-crystal structure. Molecular weight, measured after melting of the crystals, was also low. Chain scission during the destruction of the original crystalline state could be possible by virtue of localized strains within each crystal, introduced for kinetic reasons, i.e., when heating or solvation occur in off-equilibrium conditions.

We thank Dr. *I. Murase*, of Sumitomo Chemical Industry Co., Ltd., Osaka, for his earlier collaboration. We also thank Prof. *M. Gordon*, of Essex University, England, for his valuable criticisms of the original draft and help with the preparation of the masnuscript.

Appendix. Effect of running conditions on the shape of DSC curves

The heating-rate dependence of melting-peak temperatures for polymers, observed by DSC or DTA (differential thermal analysis), has aroused interest. It was claimed that the large heating-rate dependence was characteristic and mandatory for extended-chain crystals and the "super-heating" mechanism was proposed by *Wunderlich* and his group[10,24]. Leaving aside whether one agrees with the proposed mechanism, this gave a general warning for the interpretation of such curves.

In our experience[6,13] with feather-shaped and needle-like crystals of poly(oxymethylene), "super-heating" was not noticed, when small amounts of specimens were packed carefully. In such time-dependent measurements, it is rather natural that the shape of the curves is affected by the running conditions or factors related to the conduction of heat (e.g., the heating-rate, the weight of the sample, the bulkiness of the sample, and the way of packing). The response of the apparatus has to be checked in advance. (Degradation such as observed for the present specimens, if involved, will be another time-dependent process.) Experimental results to test these effects have been reported[25,26]. Here, they were checked with the needle-like crystals for which the starting or the foot temperature of melting are definable more easily.

The DSC-II apparatus of Perkin-Elmer Co. was employed for convenience, realising that samples may not be heated in the same way as in the DSC/TG apparatus. After packing into open-type pans (but with lids) by the standard procedure (i.e., by means of the manufacturer's press equipment), samples were well sandwiched between aluminium plates with flat bottom by pressing with a flat end of a piece of rod.

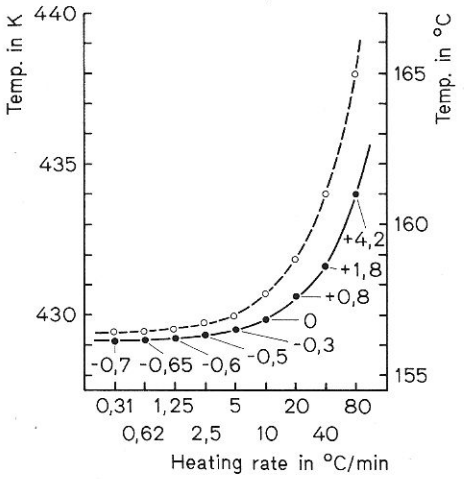

Fig. 4. Peak (○) and foot (●) temps. from the melting of indium (1,22 mg) plotted as a function of logarithmic heating-rate (DSC-II)

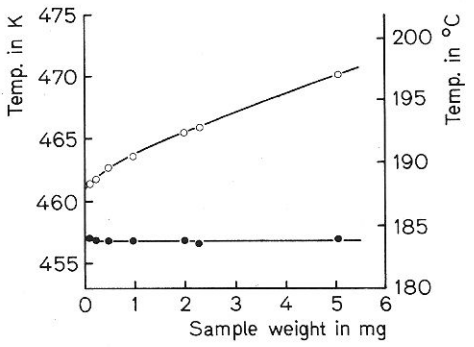

Fig. 5. Plots of DSC peak (○) and foot (●) temps. vs. the weight of sample for Needle II (DSC-II); heating-rate; 10 °C/min, fixed

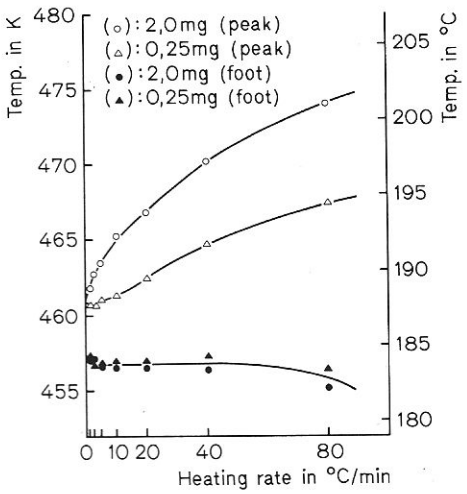

Fig. 6. Plots of DSC peak and foot temps. vs. the heating rate, for Needle II at two different sample weight levels (DSC-II)

First, the result of the calibration runs with indium is shown in Fig. 4, in which the foot and the peak temperatures are plotted as a function of logarithmic heating-rate. The temperature axis was standardized by the foot at 10 °C/min. The foot itself showed a remarkable upward trend with the heating-rate and, assuming this to be instrumental, the difference from the standard level was used for calibration. The peak temperature was found to increase more steeply, widening the gap from the foot, even for this metal specimen.

Fig. 5 shows the effect of sample weight for the needle-like crystals (Needle II) at the constant heating-rate of 10 °C/min. The peak temperature increased with the weight of the sample, while the foot temperature was maintained at a constant level at ca. 184 °C. (The start of the peak was naturally not so sharp as with the metal, but the foot was definable within the accuracy of ± 1 °C, by taking the point where the curves deviate and take off from the baseline.) Fig. 6 shows the effect of the heating-rate on the foot and the peak temperatures. The foot was again kept almost constant (after the calibration mentioned above). The peak temperature calibrated increased with the heating-rate, more largely with larger amount of sample. The tendency is similar to those reported and attributed to "super-heating".

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