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Some comments on the melting and recrystallization of polyoxymethylene by high-speed and StepScan differential scanning calorimetry

RAPID COMMUNICATION

Summary — Melting process of polyoxymethylene (POM) was studied by both high-speed differential scanning calorimetry (DSC) and StepScan DSC. It has been observed that for high scan rate (hundreds degrees per minute) side effects as *e.g.* recrystallization are eliminated. POM macromolecules do not undergo reorganization and a complete melting occurs. The influence of heating rate on the shape of melting peak has been discussed in context of metastability of polymeric crystal structures. Low heating rate facilitates recrystallization, due to molecular nucleation. Molecular nucleation exists when more defected or composed of shorter chains crystallites melt in the vicinity of high-melting polymer crystals, consisting of longer chains. These crystallites undergo nucleation and recrystallization on the existing unmelted crystals. The recrystallization process can be observed by means of modulated temperature differential scanning calorimetry, as it has been shown in this study.
Key words: high-speed DSC, StepScan DSC, polyoxymethylene, melting, recrystallization.

Polyoxymethylene (POM) is one of the most common thermoplastic polymers and finds a broad use as an engineering material in *e.g.* electrical and computer industry. POM forms two crystal modifications: the stable trigonal form (*t*-POM), consisting of (9/5) helical molecules [1], and metastable orthorhombic form (*o*-POM), consisting of (2/1) helical molecules [2] — that is why the number of symmetry operations which converts the crystal unit cell of POM into itself is one of the highest among polymeric materials. Orthorhombic POM metastable form transforms to the stable trigonal form when the samples are subjected to drawing which is performed due to the reason that the oriented POM shows an ultra high modulus — it is caused by the presence of extended-chain crystals where a part of the polymer could still appears as chain-folded lamellae [3]. Extended chains can be obtained in specific polymerization [4] or during processing [5, 6] when the melting region is approached and acting jointly process throughout the crystals becomes dominating.

Depending on its character, all kinds of reorganization process may play an important role [7, 8], so the metastable system is striving for thermodynamic equilibrium during the heating run. Such reorganization can be partly avoided by high rate heating [9], so the relationship between crystallization, the resulting morphology, and subsequent melting becomes transparent. An excellent tool for this kind of investigations is newly developed technique of high-speed calorimetry (High Performance DSC — HyperDSC™) [10, 11] which makes possible to perform quantitative measurements at very high, controlled (including constant) heating (or cooling) rates of hundreds degrees per minute. In that respect, high-speed DSC lays on the other end of the scale of DSC measurements conditions which ends up with StepScan DSC in "isothermal-heating" mode [12, 13].

In this work both high-speed and StepScan DSC were applied to study the melting and recrystallization behavior of semicrystalline POM to investigate the influence of heating mode on the reorganization effects.

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EXPERIMENTAL

Materials

POM (acetate end-capped) of molecular weight equal 41 000 and crystallinity degree 0.47 was a product of Aldrich, Milwaukee, WI, USA.

Methods

Thermal investigations were performed by using Perkin-Elmer Pyris Diamond DSC. Samples of *ca.* 2 mg weight were placed in sealed aluminum pan and were heated above their melting temperature at heating rate of 10 K/min, held isothermally for 3 min and then cooled to 30 °C at cooling rate of 10 K/min to erase the thermal history. Then the "proper" measurement was performed: high-speed DSC — heating rate = 5, 10, 20, 50, 100, 150 or 200 K/min, and StepScan DSC — t_{iso} = 48 s, b = 2 K/min, step = 1 deg. Prior to use, the calorimeter was calibrated with indium standard at 10 K/min (for the power compensation DSC the heat of fusion is independent on the heat transfer rate, and, consequently, on the scan rate).

Crystallinity degree (X_c) of initial POM was calculated using the equation:

$$X_c = \frac{\Delta H - \Delta H_a}{\Delta H_m^0} = \frac{\Delta H_m}{\Delta H_m^0} \qquad (1)$$

where: ΔH_m^0 — *heat of melting of 100 % crystalline polymer (326.3 Jg⁻¹) [14], ΔH_m — heat of melting of polymer under investigation, determined by DSC.*

RESULTS AND DISCUSSION

It can be seen that peaks obtained under high-speed conditions are more symmetrical (Fig. 1, curves 6 and 7) as compared with those obtained at lower heating rates, *i.e.* 5 or 10 K/min (Fig. 1, curves 1 and 2, respectively). For the latter group of measurements, the slope of onset
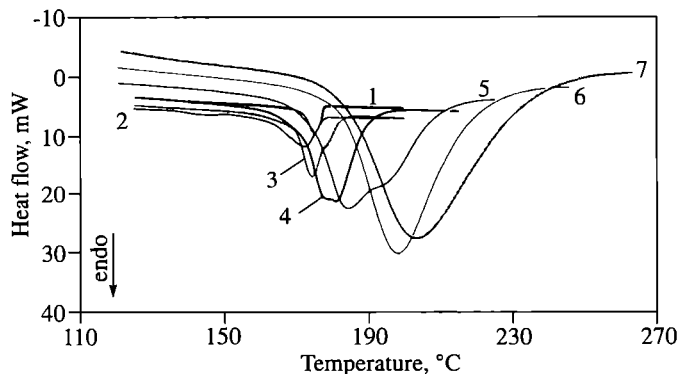

Fig. 1. DSC curves of POM melting at different heating rates (in K/min): 1 — 5, 2 — 10, 3 — 20, 4 — 50, 5 — 100, 6 — 150, 7 — 200

baseline starts at temperatures well below the extrapolated peak onset temperature. This is probably due to the recrystallization phenomenon of the previously melted polymer fractions of lower molecular weights, which contain more defects than their high-molecular weight analogues.

In the melting region of the high-molecular weight poly(ethylene oxide) (PEOX) small endothermic responses to modulation have been found by using temperature modulated DSC (TM-DSC) [15, 16]. They stem from poorer crystallized macromolecules that show higher reversing melting contributions and can be generally described by molecular nucleation concept as the cause of metastable region between melting and crystallization. Under our experimental conditions, at low heating rates, a small number of macromolecules remain partially crystallized, *i.e.* they do not have to undergo renewed molecular nucleation for recrystallization, whereby at (extreme) high heating rates there is no time for reorganization and melting is complete since locally reversing melting usually is perfect in time. Additionally, melting progress to such a high degree, that an insufficient attachment to the crystal exist, overcomes the nucleation barrier (Fig. 2).
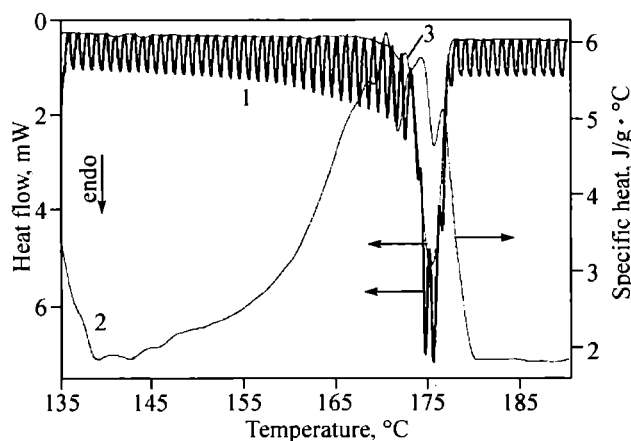

Fig. 2. StepScan DSC curves of POM melting: 1 — underlying heat flow, 2 — reversing heat flow, 3 — non-reversing heat flow

The reversing component of the melting process of POM describes the partial melting of lamellae which are able to recrystallize at isothermal segments in a system that contains the higher molecular weight crystals. Such crystals act as nucleants for molten macromolecular chains as it had also been observed in the case of PEOX [17, 18].

The energy input within a relatively long time for lower heating rates (Table 1) keeps the segmental motions at low level, making thus reorientation of flexible molecules possible.

Time of melting decreases with an increase in heating rate except for the heating rates of 10 and 200 K/min. In the first case this is probably due to the competing role of

T a b l e 1. Characteristics of the melting region of POM at different heating rates

Heating rate K/min	T_{onset} °C	T_{max} °C	T_{end} °C	Heat of melting J/g	Time of melting s
5	171.5	175.1	177.7	159.3	79.4
10	162.9	172.4	177.8	153.9	101.7
20	169.3	174.2	179.9	149.9	36.3
50	170.7	180.9	189.5	156.3	24.2
100	173.3	184.4	209.9	157.4	23.6
150	182.2	198.3	219.2	155.0	15.6
200	182.4	203.2	235.1	158.1	16.9

the melting and reorganization process under these particular thermal conditions, while in the latter one the difference between the time of melting at another extreme heating rate (200 K/min) is within experimental error. It has been observed for POM an PEOX that the morphologies change from the extended-chain crystals to the lamellar crystals. This effect was interpreted as being caused by the in-phase oscillations of parallel transition dipoles within one crystallite [3]. The transition dipolar coupling theory predicts that the magnitude of this effect depends also on the orientation of the molecular chains within the lamella, i.e. it decreases with an increase in the inclination angle of the chain axis measured from the lamella normal.

In the next group of measurements ("medium" speed = 20, 50 and 100 K/min) the shapes of DSC profiles are slightly different from the first group ones and reveals an occurrence of two maxima that originate from two endothermic peaks. The measurements conditions (relatively high heating rate, short melting time) make recrystallization practically impossible, but segmental motions are still not intensive enough to prevent completely local reversible melting of macromolecules. For high-speed measurements (150 and 200 K/min) a rapid and simultaneous melting of all fractions takes place. No recrystallization is observed on the basis of peak symmetry. Polymer crystals usually do not melt by the precise inverse of the crystallization process. If one observes the melting of a spherulite can see that it simply fades away, its radius does not shrink as the opposite of the growth process. The melting is a sort of the process throughout the crystals. The isolated extended molecules are retracting in an already random melt of lower molecular weight material while the single crystals may melt in a co-operative manner [17, 18]. Although the molecules expand rapidly on melting single crystals they take longer to reach an "equilibrium" degree of entanglement.

Reorganization phenomenon that occurs at low heating rates of macromolecular materials can be minimized by either crosslinking [19] or etching away the amorphous phase but both techniques are not straightforward and not always give reproducible results — applying of high heating rates is much more convenient route.

CONCLUSIONS

Applying of high-speed and StepScan differential scanning calorimetry makes it possible to obtain additional information about the course of the melting process of polyoxymethylene. Under modulated temperature conditions the partial melting of lamellae, which are able to recrystallize at isothermal segments in the presence of higher molecular weight crystals, takes place. On the other hand, extremely high heating rates causes the elimination of majority of the reorganization process during polymer melting.

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