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Modulated temperature DSC studies on the phase transitions of poly(ethylene oxide). Effect of temperature step

RAPID COMMUNICATION

Summary — Phase behaviour of poly(ethylene oxide) (PEOX) was investigated by modulated temperature differential scanning calorimetry (DSC) — step scan alternating DSC at different temperature steps. Additional features of reversible and non-reversible components during phase transitions can be found. By increasing the temperature step between subsequent isothermal segments the reversible component of the melting process was decreasing. This effect is due to a shift of the equilibrium state of melting—recrystallization reversible processes towards higher degree of conversion that hinders molecular nucleation and recrystallization. Analysis of the non-reversible component during crystallization showed that an increase in the step caused a very distinct increase in the non-reversible component signal due to enhanced crystallization of the less-defected structures which was facilitated by larger temperature gradient.

Key words: poly(ethylene oxide), modulated temperature differential scanning calorimetry, effect of temperature step, phase transitions, reversible and non-reversible components.

Poly(ethylene oxide) (PEOX), an important semicrystalline thermoplastic polymer, belongs to the group of macromolecular materials that are used in water paints, paper coatings, textile fibres, as components of packaging materials, solid electrolytes and as solubilizing agents for drugs [1—3]. A relatively new application, that is considered as a very promising one, concerns PEOX as a thermal energy storage material since it has large heat of fusion and a congruent melting behaviour [4]. Most of these applications require stable and repeatable phase behaviour under changing temperature conditions. Hence, melting and crystallization of PEOX were the subjects of numerous studies [5—6]. Despite of this research effort there are still uncertainties concerning the nature of phase transitions of PEOX. A new insight may be reached if a new technique — modulated temperature differential scanning calorimetry (MT-DSC) [7] in the step scan alternating (SSA-DSC) mode is applied. In this method, the total heat flow is treated as being the average of the heat flow response to the heat-hold temperature program. The total heat flow can be separated into the reversible and non-reversible components. An additional feature of SSA-DSC technique is that there is no necessity to use Fourier transformation for deconvolution. In this method the response of non-reversible component is calculated directly from the calorimetric data (isothermal segments) and phase lag using is not needed [8].

The aim of this work is to investigate the phase behaviour of poly(ethylene oxide) under modulated temperature conditions of changing temperature step.

EXPERIMENTAL

Material

Poly(ethylene oxide) (PEOX) (molecular weight 3400) was produced by Polysciences Co., Warrington, PA, USA.

Methods

Thermal investigations were performed using a power-compensated Perkin-Elmer „Pyris Diamond DSC". First, sample was heated above its melting temperature at a heating rate of 10 K/min, hold isothermally for 3 min and then cooled to 30°C at a cooling rate of 10 K/min SSA-DSC measurements (t_{iso} = 48 s, b = 2 K/min, different step) were done in closed aluminum pans with sample mass of 8 mg under argon flow of 20 cm^3/min. Prior to use the calorimeter was calibrated with indium standard.

RESULTS AND DISCUSSION

Results of heat flow measurements *vs.* temperature at different steps are presented in Fig. 1.

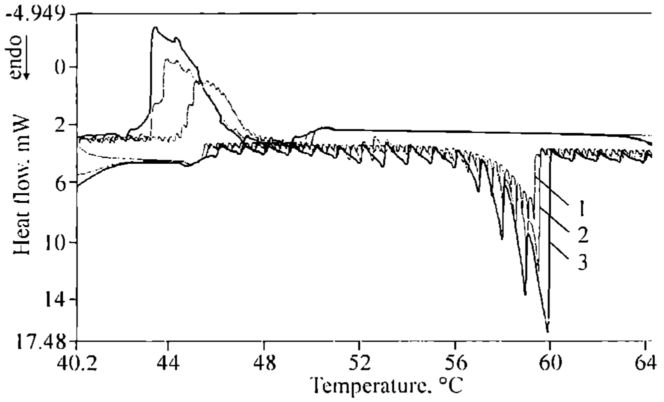

Fig. 1. SSA-DSC profiles of phase transitions of PEOX at different steps: 1 — 0.25 deg, 2 — 0.5 deg, 3 — 1 deg

More information can be obtained if separation of reversible and non-reversible components is applied by *e.g.* oscillating profile superimposed to the normal linear temperature slope during a DSC experiment.

By increasing the temperature step between subsequent isothermal segments, the reversible component of the melting process is decreasing — this effect is due to a shift of the equilibrium state of melting—recrystallization reversible processes towards higher degree of conversion that hinders molecular nucleation and recrystallization (Fig. 2).

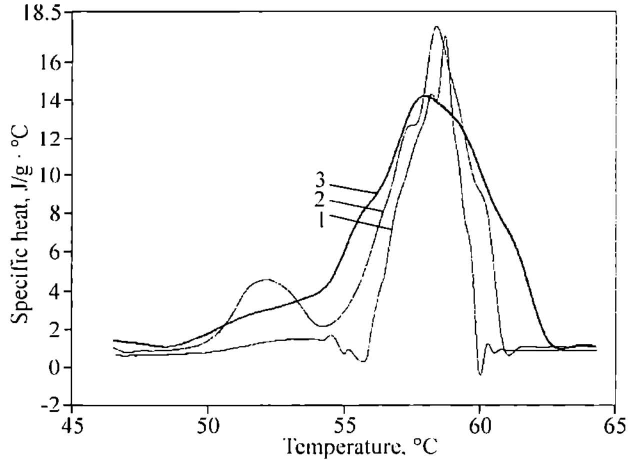

Fig. 2. SSA-DSC profiles of reversible component of the PEOX melting at different steps (numbers of curves as in Fig. 1)

An opposite effect can be observed for non-reversible component during melting (Fig. 3).

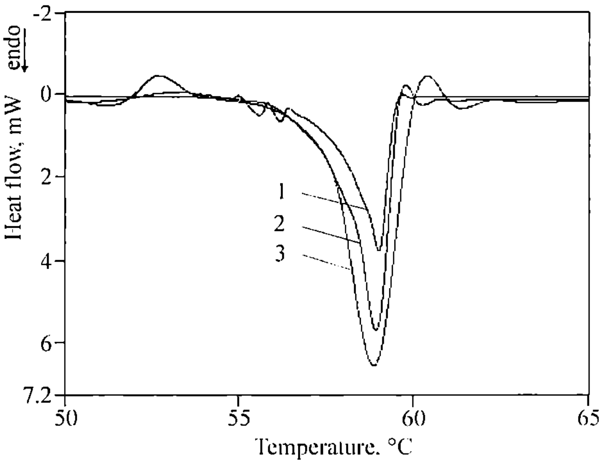

Fig. 3. SSA-DSC profiles of non-reversible component of the PEOX melting at different steps (numbers of curves as in Fig. 1)

If temperature step is increasing, the number of kinetically driven processes that are non-reversible, is also increasing. Non-reversible component of the PEOX melting process describes complete phase transition of lamellae that are arranged in spherical structures — spherulites. In the lamellae, polymer chains are either fully extended or folded, a small number times.

The crystallization behaviour of PEOX was investigated by applying both Avrami and Lauritzen—Hoffman theories. There is some uncertainty of the crystallization regime since a change in morphology (crystallographic orientation of the growth front) may overlap with a regime II—III transition [9]. SSA-DSC results of the course of reversible and non-reversible components of PEOX crystallization are presented in Fig. 4 and 5.

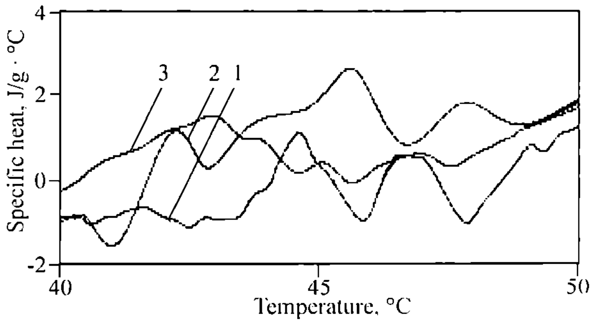

Fig. 4. SSA-DSC profiles of reversible component of the PEOX crystallization at different steps (numbers of curves as in Fig. 1)

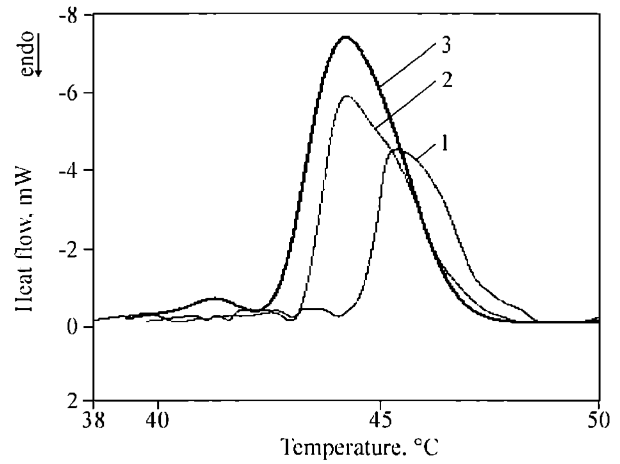

Fig. 5. SSA-DSC profiles of non-reversible component of the PEOX crystallization at different steps (numbers of curves as in Fig. 1)

The reversible component signal shows a perturbed character, which was also found for other polymers [10]. More information can be found if analysis of the non-reversible component is performed. An increase in the step causes a very distinct increase in the non-reversible component signal. One can explain preliminarily this effect by the influence of lamellae alignment in spherulites at non-uniform temperature field — it has already been found by atomic force microscopy (AFM) and SEM investigations for isotactic polypropylene that the change of the lamellae alignment in spherulites was the result of the competition of lamellae to fill the space during growth at the temperature gradient [11].

CONCLUSIONS

Modulated temperature DSC yields additional information (in comparison with classical DSC) about the phase behaviour of poly(ethylene oxide) as allows to separate the reversible and non-reversible components of the (total) heat flow. On the basis of performed measurements, described by different modulated temperature program we can draw the following conclusions:

— By increasing the temperature step between subsequent isothermal segments, the reversible component of the melting process was decreasing.

— This effect is due to a shift of the equilibrium state of melting—recrystallization reversible processes towards higher degree of conversion that hinders molecular nucleation and recrystallization.

— Analysis of the non-reversible component during crystallization showed that an increase in the step caused a very distinct increase in the non-reversible component signal due to enhanced crystallization of the less-defected structures which was facilitated by larger temperature gradient.

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