

MEMORY EFFECT OF LOW-DENSITY POLYETHYLENE CRYSTALLIZED IN A STEPWISE MANNER

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Stepwise crystallization and successive melting of Tipolen low density polyethylene was studied by DSC. As a result of the stepwise crystallization of the polyethylene, there were as many peaks on the melting curve as the number of steps used for the crystallization of the sample. Similar results were obtained on Tipolen low-density polyethylene fractionated by gel permeation chromatography, and on Celene low-density polyethylene, too.

Crystallization and melting processes of polymers show many features different from those of materials of low molecular weight [1, 2]. It is well known that the crystallinity of polymers depends on the temperature, and their melting processes take place in wide temperature intervals. Experimentally determined melting processes and melting point of polymers depend on conditions of previous crystallization. These features are attributed to the macro- and polymolecular nature of they polymers, to the significant role of kinetic factors in their crystallization process, as well as to morphological characteristics of the polymer crystals [3].

It is assumed that a great number of crystallites with different melting points are formed during the crystallization process. Richardson et al. [4] studied in detail melting characteristics of polymethylene copolymers containing short branches. The samples in their investigation were made by stepwise crystallization. In order to be able to reach thermodynamic equilibrium conditions, the samples were held at each temperature for a long time (some days). Mentioned authors have established that the melting point is decreased and the melting interval is increased as a consequence of introducing comonomer units.

This paper deals with the influence of the crystallization conditions and thermal prehistory of polymers on their melting. It is experimentally proved that the separation of crystals with different melting points is possible in their melting processes.

Experimental

In most of our experiments non-fractionated Tipolen FA 2210 low density polyethylene (produced by Chemical Works of Leninváros, Hungary) was used (*m. p.* 388 K; $\text{CH}_3/1000 \text{ C} = 15.3$; $\bar{M}_w = 148\ 000$). Some experiments were made using fractions of Tipolen PE produced by gel permeation chromatography

m. p.: 387 and 392 K, $\bar{M}_w = 76\,000$ and 515 000, respectively, and Celene DFD 6005 low-density PE (produced by Union Carbide, *m. p.*: 389 K).

Perkin–Elmer differential scanning calorimeter Model DSC-2 was used, suitably calibrated at different points of temperature.

Before the stepwise crystallization the samples were melted and held at 423 K until no change resulted in their C_p values.

Results and discussion

The isothermal crystallization of non-fractionated PE was studied. In our experiments the crystallization curves shown in Fig. 1 were obtained. It can be seen that low-density PE can slightly be supercooled, and therefore the induction time of crystallization at temperatures below 383 K is very short. As a consequence, before finishing of the ordinate displacement of the recording pen (due to the transition to isothermal condition) the crystallization process begins, and the initial period of crystallization can not be recorded by DSC. As this period is rather short, the initial part of crystallization curves was determined by

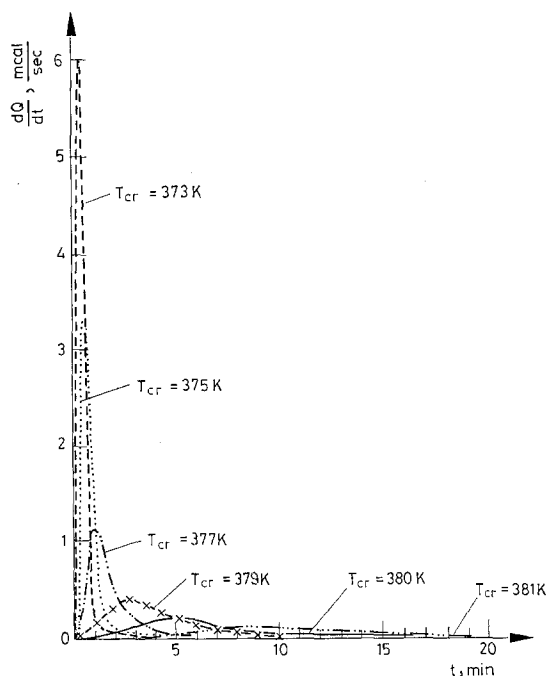


Fig. 1. Superimposed isothermal crystallization curves of Tipolen low-density PE at different temperatures

extrapolation to the isothermal baseline. Results of isothermal crystallization will be published elsewhere [6].

In order to check the precision of extrapolation, the sample crystallized isothermally was melted and the enthalpy values (which are proportional to the crystallinity) have been tried to determine from the melting curves. In this case the same methodical problem was found. When the recording pen finishes its shift due to the transition to non-isothermal condition (the shift of the pen is proportional to the sample weight and heat capacity, the sensitivity of the instrument, as

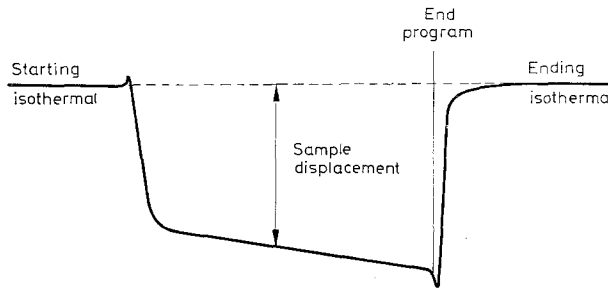


Fig. 2. Shift of the recording pen on the instrument DSC-2

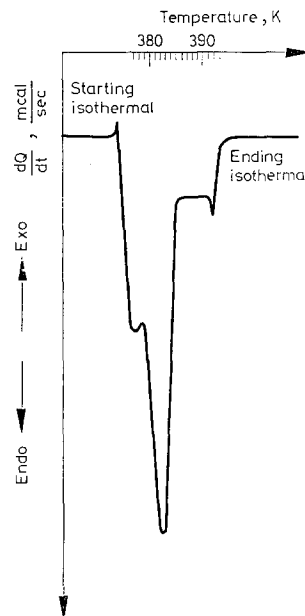


Fig. 3. Melting curve of low-density PE crystallized isothermally

well as to the heating rate, see Fig. 2), a part of the sample has already been melted (Fig. 3). We wanted to avoid this methodical difficulty by freezing the state of the material by rapid cooling ($320^{\circ} \cdot \text{min}^{-1}$). In this case, the heating was started from a lower temperature, and the melting curves of the samples were recorded. As seen from Fig. 4 three peaks can be observed in the melting curves of these

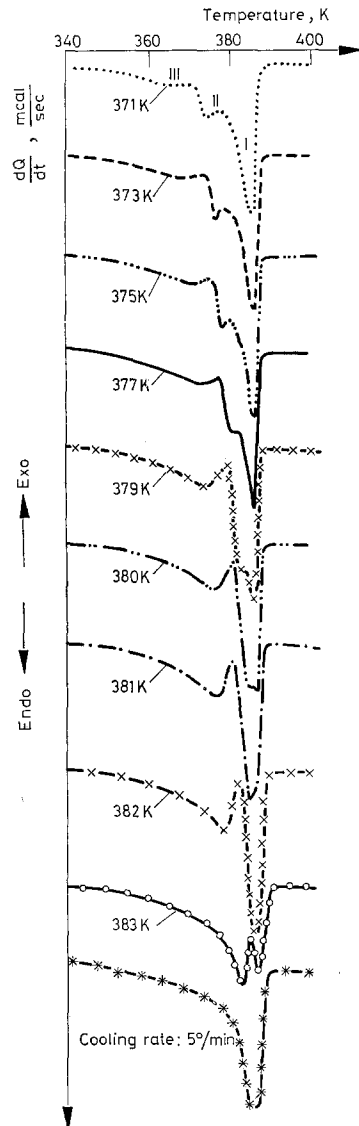


Fig. 4. Melting curves of isothermally-crystallized and then rapidly-cooled PE samples

samples at lower temperatures a wide, blurred peak (on Fig. 4 denoted by III), and a sharp double peak at higher temperature region (denoted by II and I). It has been established that the position of the peak at the highest temperature (I) does not depend upon the isothermal crystallization temperature, and its amplitude related to the amplitude of peak II decreases when the temperature of isothermal crystallization is raised. On low temperature isothermal crystallization the height of peak II is rather small, and this peak is sharply separated from peak I.

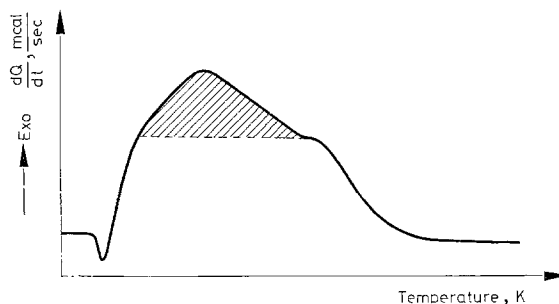


Fig. 5. Post-crystallization of isothermally-crystallized PE on rapid cooling to room temperature

By increasing the isothermal crystallization temperature peak II shifts in the direction of peak I, and at very high isothermal crystallization temperatures the two peaks merge. It may be suggested that peak II corresponds to that part of the sample crystallized on isothermal conditions whereas peak I comes from the melting of that part of the sample crystallized during the cooling process to the isothermal crystallization temperature.

To check whether the state of the material crystallized isothermally could be frozen or not the thermal behaviour of PE during rapid cooling was registered. In Fig. 5 can clearly be seen that post-crystallization occurs. We suggest that peak III appearing at lower temperature region corresponds to the melting of regions crystallized during the rapid cooling process from the isothermal crystallization temperature. From curves in Fig. 4 it can be concluded that in the case of low-density PE a separate melting peak corresponds to the sample part crystallized under different conditions.

In order to check this conclusion stepwise crystallization was carried out as follows: the PE melt was held at 423 K, then the temperature was lowered to 381 K. At this temperature the sample was crystallized isothermally and the temperature was lowered further in a stepwise manner by steps of 20, 10, 5 and 3° down to room temperature. At each temperature the completion of the crystallization was waited for. Melting curves of samples crystallized in such a manner are demonstrated on Fig. 6. It was established that a separate peak in the

melting curve corresponds to each step in the crystallization, except for the low temperature steps (in Fig. 6 a melting curve of gradually cooled PE is shown as well).

A similar stepwise crystallization was performed without the melting of all of the material: here the first step was a 2 hours annealing process at 385 K. After the annealing the temperature was lowered in the stepwise manner described above. The melting curve is similar to those shown in Fig. 6. The only difference is that the peaks are separated more sharply in the case of "stepwise annealing".

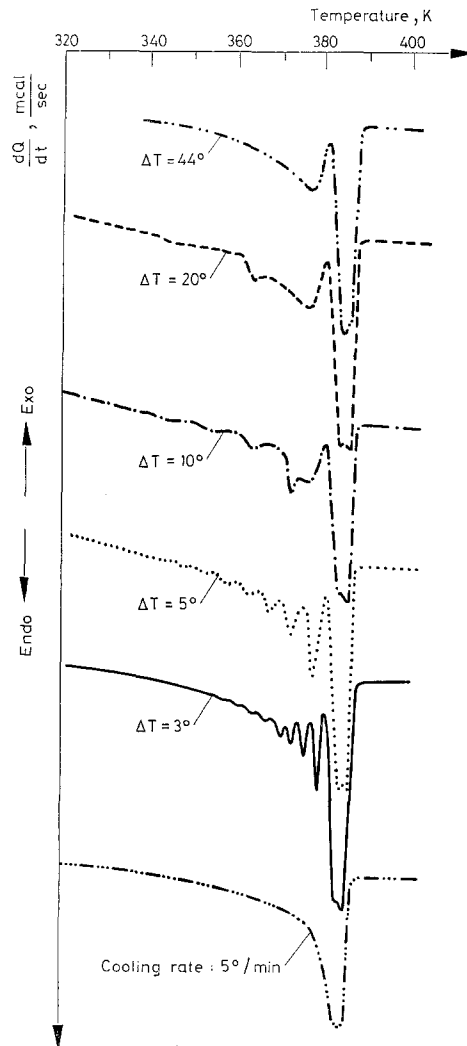


Fig. 6. Melting curves of low-density PE samples crystallized in a stepwise manner

The described phenomenon (which can be called a “memory effect of stepwise crystallization”) was observed by us first in Tipolen FA 2210 low density PE, but the same experiments were carried out using fractions of this PE obtained by gel permeation chromatography (Fig. 7), and Celene PE, too. In all cases similar melting behaviour was observed. However, using high-density Hostalen PE, the peaks could be separated slightly. It is assumed, that the branching of the PE plays a decisive role in the described memory effect.

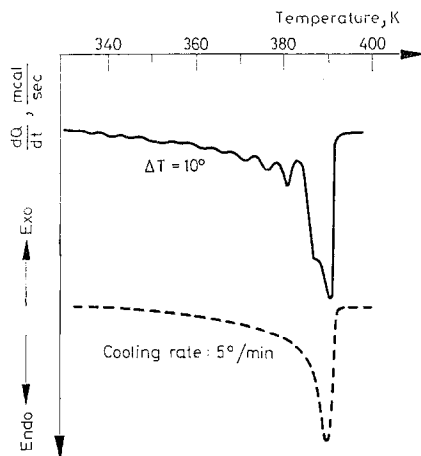


Fig. 7. Melting curves of a fraction of low-density PE crystallized in a stepwise manner and by continuous cooling ($M_w = 515\,000$)

In order to get information as to whether this phenomenon is caused by recrystallization, PE crystallized in the stepwise manner was rapidly heated [5] (the heating rates were 20 and 40° · min⁻¹). In both cases similar melting curves were obtained. Therefore, it is probable that the memory effect is not caused by recrystallization processes.

Comparison of the thermal behaviour of low-density PE with those of high density PE, Moplen polypropylene (for which two peaks are obtained), as well as Miraviten copolymer (ethylene-vinylacetate copolymer) shows that the described memory effect is a consequence of irregularities in the molecular structures of the polymers. It is probable that under different crystallization conditions crystallites of different sizes and different defectivities are obtained, which, of course, melt at different temperatures.

Investigation of the memory effect of stepwise crystallization is in progress in our laboratory. Results obtained by other methods will be published later.

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ZUSAMMENFASSUNG — Die stufenweise Kristallisierung und das graduelle Schmelzen des Polyäthylens geringer Dichte "Tipolen" wurden mittels DSC studiert. Als Ergebnis der stufenweisen Kristallisierung des Polyäthylens befanden sich so viele Peaks in der Schmelzkurve wie die Zahl der zur Kristallisierung der Probe angewandten Stufen. Ähnliche Ergebnisse wurden bei der Fraktionierung des Polyäthylens geringer Dichte "Tipolen" mittels Gel-permeationschromatographie, sowie im Falle des Polyäthylens geringer Dichte "Celene" erhalten.

RÉSUMÉ — On a étudié, par analyse enthalpique différentielle (DSC) la cristallisation graduelle et la fusion successive du polyéthylène à faible densité "Tipolen". La cristallisation graduelle du polyéthylène fournit autant de pics sur la courbe de fusion qu'il n'y en avait d'étapes lors de la cristallisation de l'échantillon. On a obtenu de résultats similaires en effectuant la fractionation, par chromatographie à perméation de gel, du polyéthylène à faible densité Tipolen et aussi en étudiant le polyéthylène Celene, également à faible densité.

Резюме — С помощью дифференциальной сканирующей калориметрии была изучена ступенчатая кристаллизация полиэтилена низкой плотности типа Типолен с последующим его плавлением. Как следствие ступенчатой кристаллизации, на кривой плавления наблюдали столько пиков, сколько ступеней использовали при кристаллизации образца. Подобные результаты были получены на низко-плотном полиэтилене типа Типолен, фракционированного с помощью гель-хроматографии, а также на низко-плотном полиэтилене типа Челен.