

THE MELTING OF HIGH-PRESSURE POLYETHYLENE SUBJECTED TO STEPWISE HEAT TREATMENT

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By means of stepwise crystallization or heat treatment of high-pressure polyethylene samples with several melting peaks can be produced. The melting curves truly reflect the thermal pre-history of the sample, and during melting a distinct "thermal memory effect" can be observed. The stepwise heat treatment produces individually and independently melting crystallites. The thermal and mechanical stability of crystallites formed by stepwise heat treatment has been studied. The crystallites are stable below the temperature of heat treatment, and also possess a remarkable mechanical stability, retaining the original thermal properties even under very high specific elongation. The change in the character of melting curves as a function of elongation is in unanimous correlation with the structural changes taking place under stretching. The memory effect, strongly expressed in the case of high-pressure polyethylene, can be traced back to the irregular, branched chain structure.

The structures and properties of polymers are greatly influenced by the conditions of crystallization and the thermal and mechanical pre-history of the polymers [1]. Their thermal properties and melting characteristics are also affected by the above factors.

Polymer samples prepared under certain conditions have frequently been observed to give melting curves containing several peaks [2–7]. Thus, the stepwise heat treatment of polyethylene crystallized from melts [2], or polypropylene [3], or rolled and stretched polyethylene foils [4, 5] may produce samples the melting curves of which have several peaks. However, different opinions exist as regards the origin of the melting peaks of heat-treated high-pressure polyethylene [2, 4, 5].

As reported in our previous papers [6, 7], an arbitrary number of melting peaks can be caused to appear in the melting curve of high-pressure polyethylene by applying the method of stepwise isothermal crystallization. We have found that the peaks of the melting curves are due to melting and recrystallization processes [7], and that the melting of high-pressure polyethylene faithfully reflects the thermal history of the sample. This phenomenon was given the name "thermal memory effect".

This paper deals with the characteristic features of the melting of high-pressure polyethylene subjected to stepwise heat treatment, and with the interpretation of the peaks of the melting curves.

We also discuss the thermal and mechanical stability of the structural elements produced by the stepwise thermal treatment (i.e. the carriers of "thermal memory"). Finally, we describe a simplified thermal treatment method developed for the production of polyethylene with many melting peaks.

Experimental

The measurements were performed on foils 200 μm in thickness, made of high-pressure polyethylene, Tipolen FA 2210, produced by the Tiszai Vegyi Kombinát. The polymer has the following characteristics: $T_m = 388$ K, melt flow index (MFI) = 0.2, $\bar{M}_w = 148,000$, number of CH_3 groups/1000 carbon atoms = 15.3. As reference, foils based on Hostalen GF 4760 (Farbwerke Hoechst A.G.) low-pressure polyethylene, and on an ethylene-vinyl acetate copolymer (Miravithen D-2-3 EA) were also studied.

The thermal measurements were run on a Perkin Elmer DSC-2 calorimeter. Heating and cooling rates were uniformly 5 K/min. The approximate weight of specimens was 5 mg.

The mechanical properties of samples were determined with a thread-tearing instrument of Chevenard MI-44 type. The heat-treated samples were stretched in the same instrument.

The foils were treated in a silicone bath.

Results and discussion

Preparation of samples with several melting peaks

High-pressure polyethylene samples with several melting peaks can be prepared by stepwise heat treatment (annealing) or crystallization. The heating programs of these processes are shown in Fig. 1.

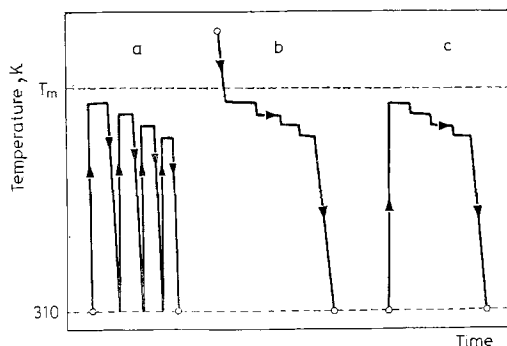


Fig. 1. The programs of stepwise heat treatments; *a* — stepwise annealing, *b* — stepwise isothermal crystallization, *c* — combined method

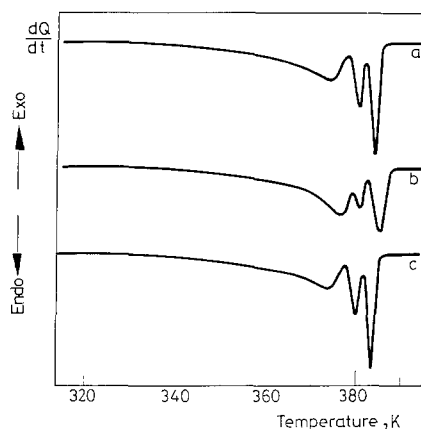


Fig. 2. The melting curves of samples heat treated with methods *a*, *b* and *c* in two temperature steps ($T_1 = 382$ K, $T_2 = 379$ K). Durations of heat treatments: $t_1 = 15$ min, $t_2 = 15$ min for methods *a* and *c*, $t_1 = 210$ min, $t_2 = 15$ min for method *b*

Curve *a* of Fig. 1 shows the heating program of stepwise annealing developed by Gray and Casey [2], and curve *b* the program of stepwise crystallization [6]. However, the preparation of larger specimens, which permit various physical and mechanical properties to be studied, is quite complicated by means of these methods.

In the case of stepwise annealing, problems are caused by the fast cycles of temperature changes. With stepwise crystallization, the time required by the first temperature step may cause problems, and the preparation of specimens with pre-determined size is complicated.

Investigating the effects of the cooling rate and the temperature of re-cooling on the character of the melting curve obtained by stepwise annealing (Fig. 1, curve *a*), we have found that the heating program shown in curve *c* of Fig. 1 produces samples with nearly the same melting curves. This new method is essentially a combination of the above procedures, consisting of a high-temperature annealing step (in which the sample undergoes partial melting) and subsequent isothermal crystallization steps.

The time required by the combined method is shorter, and the method can also be applied to the preparation of large samples with high heat capacity and pre-determined size.

The melting curves of samples heat-treated in micro dimensions (in the specimen holder of the DSC instrument) by the above three methods, with the application of two temperature steps, are shown in Fig. 2. As can be seen, all three methods produce samples with the required number of melting peaks. Methods *a* and *c* lead essentially to the same melting curve, whereas the higher melting peak of the sample prepared by method *b* is less developed even after longer crystallization. In the simplest cases of stepwise annealing or stepwise crystalliza-

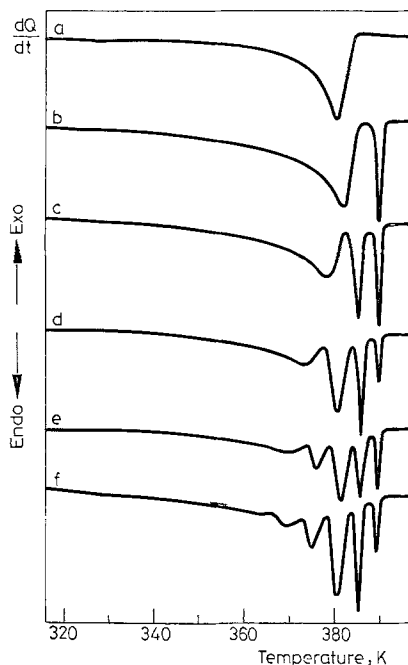


Fig. 3. The melting curves of samples treated with the combined method. Temperatures and durations of heat treatments: *a* — untreated; *b* — 386 K/1.5 hours; *c* — 386 degree/1.5 hours, 381 degree/1.5 hours; *d* — 386 degree/1.5 hours, 381 degree/1.5 hours, 376 degree/1.5 hours; *e* — 386 degree/1.5 hours, 381 degree/1.5 hours, 376 degree/1.5 hours, 371 degree/1.0 hour; *f* — 386 degree/1.5 hours, 381 degree/1.5 hours, 376 degree/1.5 hours, 371 degree/1.0 hour, 366 degree/1.0 hour

tion, the melting curves have $n + 1$ peaks, where n is the number of temperature steps. The peaks can be assigned to the melting of crystallites formed in the various temperature steps and in the cooling step in which the sample is re-cooled from the last temperature step to room temperature.

Illustrating the above, Fig. 3 shows the melting curves of polyethylene foils treated by the combined method, various numbers of temperature steps being applied. (More complicated cases of stepwise crystallization and heat treatment are discussed in other papers of our research group [7, 8].

The thermal stability of the structure produced by heat treatment

The character of the melting curve is determined by the nature of the structural elements formed under the heat treatment, i.e. of the carriers of "thermal memory". In the lack of unanimous information on the nature of these structural elements, we may assume that they are lamellar crystallites of various size or perfection [5], the melting point of which is a function of thickness [9].

We first investigated the stability of structural units carrying the thermal memory, i.e. the problems of erasing the thermal memory.

It was found that the melting characteristics of heat-treated samples do not change appreciably upon extensive storing (over one year), indicating that the structural elements formed under heat treatment are quite stable, and detectable post- or re-crystallization does not take place at room temperature.

The thermal stability of these structural elements was investigated on samples characterized by the melting curve shown in curve *f* of Fig. 3. The samples were heated up to temperatures corresponding to the foot-ends of melting peaks (T_h), then cooled to 310 K, and the melting curves were measured. It should be noted that the temperatures corresponding to the foot-ends of melting peaks were practically identical to the temperatures applied in the stepwise heat treatment (T_a), i.e. $T_h \cong T_a$. The thermal effects occurring in the partial heating steps and in the cooling step were also recorded.

Figure 4 shows the results of a series of measurements. Curve *a* corresponds to the partial and stepwise melting which takes place upon heating. Curve *b* proves unanimously that the molten part is crystallized in the cooling step. The melting curve of the partially heated and then re-cooled sample (curve *c*, Fig. 4) indicates that all the peaks located below the temperature of heating disappear, being replaced by a broad peak which arises from the melting of crystals produced by re-cooling. It is also evident from the curves that the melting peaks beyond T_h remain unchanged. The above results are shown in Fig. 5, which contains the melting curves of specimens heated to different temperatures and then cooled back to 310 K. It follows unambiguously from the experimental data that the peaks of the melting curves are really melting and not recrystallization peaks. In the case of recrystallization the melting curve would also change beyond T_h , and the area under the section of the curve above T_h would increase in proportion

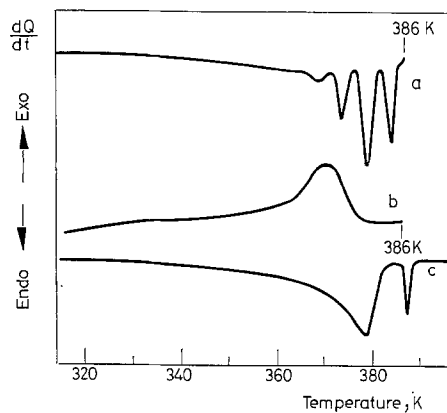


Fig. 4. The effect of partial melting on the melting curve; *a* — partial melting on heating to 386 K, *b* — crystallization on cooling, *c* — melting curve of partially melted and re-cooled sample

to the fraction of recrystallized substance. An increase in heating rate does not influence the relative intensities and positions of the peaks in the melting curve, supporting the above conclusion.

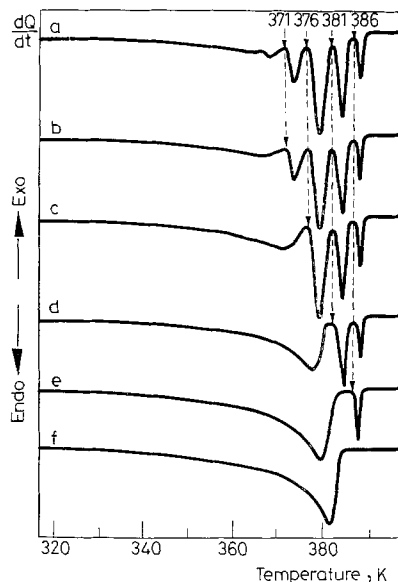


Fig. 5. Melting curves of samples partially melted and recooled to 310 K; *a* — original sample subjected to stepwise heat treatment, *b* — *f*: partially melted samples. *b* — 371 K, *c* — 376 K, *d* — 381 K, *e* — 386 K, *f* — 423 K

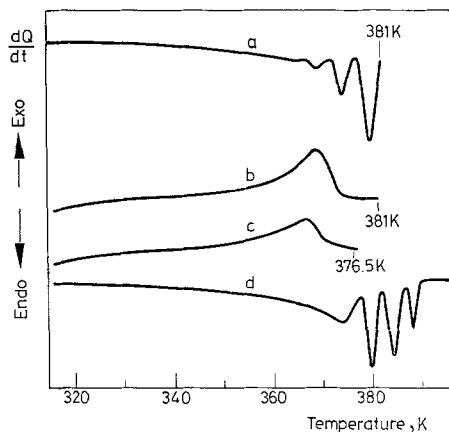


Fig. 6. Partial erasing of thermal memory by heating to 381 K and restoring of the third melting peak by heat treatment ($T = 376$ K, $t = 90$ min); *a* — melting on heating to 381 K, *b* — crystallization on recoiling from 381 K to 310 K, *c* — crystallization on recoiling after heat treatment at 376 K, *d* — final melting curve after the cycle *a* — *c*

Consequently, during the stepwise heat treatment, well-defined crystallites with independent melting peaks are formed in the individual treatment steps, and these peaks are separated from those of crystallites formed in other heat treatment steps. The crystallites are stable below the given annealing temperatures T_a (i.e. they do not melt or recrystallize), and thus the thermal memory produced can be thermally erased only by melting the crystallites. Since a heat treatment below T_a does not affect the melting curve beyond this temperature, the thermal memory erased by partial melting (and the structure corresponding to it) can be restored, or replaced by a new arbitrary memory by means of a new heat treatment. This possibility is shown in Fig. 6.

The mechanical stability of structural elements formed by heat treatment

Upon the effect of mechanical stresses, crystalline polymers may undergo recrystallization processes which involve various structural changes [10]. The structural changes are particularly important in the neck formation stage of stretching. Such structural changes may also be reflected in the characteristics of melting. It is therefore worth studying the melting properties of heat-treated samples as a function of elongation, and simultaneously determining the stability of structural elements with independent melting peaks with respect to mechanical stresses.

The samples heat-treated with the combined method have a stress *vs.* elongation diagram characteristic of crystalline polymers, and show a distinct neck formation period during stretching. Depending on the conditions of thermal treatment, the stress corresponding to neck formation is around 10^7 N/m², and the relative deformation is in the range of 15–20%, close to that of untreated samples. The melting curves of specimens stretched to different extents have shown that, in the deformation stage preceding neck formation, stretching does not influence the properties of melting curves. The melting curves of specimens taken from the necked portions of samples stretched to various extents in the neck formation stage can be seen in Fig. 7. It is apparent from the curves that, upon increase of the percentage elongation, the original melting peaks gradually disappear, being replaced by a broad melting peak. With increasing percentage elongation the overlap of the melting peaks becomes more expressed, starting at low-temperature peaks, and gradually involving peaks at higher temperatures. It can also be seen that some traces of the peak at the highest temperature still remain at very high specific elongations. It is very interesting that at relatively high elongations (e.g. 161%), far beyond the neck formation stage (15–20%), the melting curve is practically unchanged. This proves that the structural elements formed by heat treatment have remarkable mechanical stability (they do not melt or recrystallize); the structure remains intact in the necked part, and disintegrates only at very high elongations.

According to generally accepted opinions on the stretching of crystalline polymers [10], the spherulitic structure is gradually transformed into a fibrillar one.

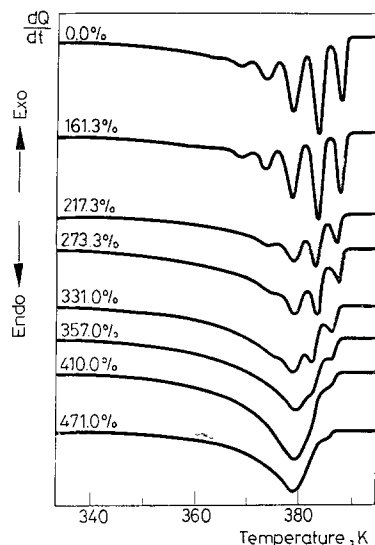


Fig. 7. The melting curves of samples stretched to various degrees (see the labels on the curves)

During this process, the originally lamellar crystals disintegrate into smaller blocks, which, by becoming ordered along the direction of stress but retaining chain folding, produce the fibrillar structure. With further increasing elongation, the fibrils containing microblocks with folded chains may be transformed into crystallites with expanded chains by sliding of the polymer chains on one another.

The results of thermal measurements can be brought into full agreement with the changes occurring upon stretching, if the melting peaks are assigned to lamellar crystallites of various thicknesses formed during heat treatment, or to crystallite fractions disintegrated into microblocks, and if the elimination of melting peaks is regarded as the disintegration of crystallites with folded chains.

The above results, supporting the model which interprets the changes in structure by thermal measurements [10], provide a more accurate picture of the processes taking place during neck formation. Comparing our results on the thermal stability of structural units formed by thermal treatment with the data of Fig. 7, it can be ruled out that neck formation and subsequent deformation (to elongations of ca. 160–200%) may involve the melting of lamellar crystallites. The thermal investigations also indicate that in the stepwise rearrangement of the original structure, the smaller or less perfect crystallites (with lower melting points) are completely destroyed at lower specific elongations.

The crystallites produced by stepwise heat treatment are particularly resistant to compression strains; the character of the melting curves shows no observable changes even after compressions of 400–500%.

Structural interpretation of thermal memory effect

Our investigations indicate that the melting of high-pressure polyethylene very truly reflects the thermal history of the sample (thermal memory effect). Comparisons with other polymers have shown that under a stepwise heat treatment the ethylene-vinyl acetate copolymer of irregular structure behaves similarly to high-pressure polyethylene. In contrast, no thermal memory effect could be observed in the case of low-pressure polyethylene of regular structure subjected to the combined stepwise heat treatment. However, after disruption of the regularity of the low-pressure polyethylene chain by cross-linking (with X-rays), blurred peaks became observable in the melting curve upon the effect of a heat treatment with the combined method. With increasing degree of cross-linking, the phenomenon of thermal memory becomes increasingly more pronounced.

Consequently, the thermal memory effect can be traced back to the irregularity (branching, foreign monomeric units, cross-linking) of the molecular chains. Arising from the irregularities of the chains, polymolecularity according to chemical structure is enhanced, whereby a spectrum of crystallites different in size (lamellar thickness) and perfection is formed. The structural characteristics and hence the melting properties of these crystallite components are effected by the conditions of crystallization and heat treatment.

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RÉSUMÉ — Par cristallisations ou traitements thermiques graduels du polyéthylène haute pression, on parvient à produire des échantillons à plusieurs pics de fusion. Les courbes de fusion reflètent, de façon fidèle, l'histoire thermique de l'échantillon et, lors de la fusion, un "effet de mémoire thermique" distinct peut être observé. Le traitement thermique graduel produit des cristallites qui fondent de façon individuelle et indépendante. On a étudié la stabilité thermique et mécanique des cristallites formés par traitement thermique graduel. Les cristallites sont stables au-dessous de la température du traitement thermique et possèdent aussi une stabilité mécanique remarquable, conservant les propriétés thermiques originales même lors d'une élongation spécifique très forte. La variation du caractère des courbes de fusion en fonction de l'élongation est en corrélation avec les changements structuraux qui ont lieu lors de l'étirage. L'effet de mémoire, fortement exprimé dans le cas du polyéthylène haute pression, peut être rattaché à la structure irrégulière, à chaîne ramifiée.

ZUSAMMENFASSUNG — Durch stufenweise Kristallisation oder Wärmebehandlung von Hochdruck-Polyäthylen können Proben mit mehreren Schmelzpunkten hergestellt werden. Die Schmelzkurven reflektieren deutlich die Wärmevergangenheit der Probe und während des Schmelzens kann ein bestimmter "thermischer Memorieeffekt" beobachtet werden. Die stufenweise Wärmebehandlung erzeugt individuell und von einander unabhängig schmelzende Kristallite. Die thermische und mechanische Stabilität der durch stufenweise Wärmebehandlung gebildeten Kristallite wurde studiert. Die Kristallite sind unterhalb der Temperatur der Wärmebehandlung stabil und besitzen auch eine bemerkenswerte mechanische Stabilität, wodurch die ursprünglichen thermischen Eigenschaften selbst bei sehr hohen spezifischen Elongationen beibehalten werden. Die Änderungen des Charakters der Schmelzkurven als Funktion der Elongation stehen in eindeutiger Korrelation zu den Strukturänderungen, welche während Dehnung stattfinden. Der im Falle von Hochdruck-Polyäthylen stark zum Ausdruck kommende Memorieeffekt kann auf die unregelmäßige Struktur mit verzweigten Ketten zurückgeführt werden.

Резюме — С помощью ступенчатой кристаллизации или тепловой обработки полиэтилена высокого давления, могут быть получены образцы с несколькими циклами плавления. Кривые плавления точно отражают термическую предисторию образца и во время плавления наблюдался отчетливый „термический эффект памяти”. При ступенчатой термообработке образуются кристаллы, плавящиеся индивидуально и независимо друг от друга. Изучена термическая и механическая устойчивость кристаллитов, образующихся при ступенчатой термообработке. Кристаллиты стабильны ниже температуры тепловой обработки и обладают значительной механической устойчивостью, сохраняя первоначальные термические свойства даже при очень высоком специфическом удлинении. Изменение характера кривых плавления, как функция удлинения, хорошо коррелируется со структурными изменениями, имеющими место при вытягивании. Эффект памяти, сильно выраженный в случае полиэтилена высокого давления, может быть восстановлен обратно до нерегулярной структуры с разветвленной цепью.