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R. A. BALTENAS, L. A. IGONIN

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Abstract

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R. A. BALTENAS, L. A. IGONIN

THERMOGRAPHIC STUDY OF THE MELTING OF POLYETHYLENE

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In a previous work ([1]), autohesion processes in polyethylene under high pressure were investigated. It was established that autohesion is clearly observed already below the melting temperature, which is especially characteristic of branched polyethylene. We associated this phenomenon with recrystallization processes occurring at the interface.

In the present work, the features of the melting of polyethylene under pressure and the influence of various factors on the kinetics of the melting process were studied by the method of thermographic analysis.

Three types of polyethylene having different degrees of order were investigated: high-pressure polyethylene with a degree of branching of 3.3 CH_3/100 CH_2 and a crystallinity of 60% (PE-1), low-pressure polyethylene with a degree of branching of 1.06 and a crystallinity of 79% (PE-2), and polyethylene obtained on oxide catalysts with a degree of branching of 0.4 and a crystallinity of 89% (PE-3).

The method of thermographic analysis has found wide application in the study of polymers ([2–6]). We developed a method of thermographic analysis that makes it possible to obtain melting thermograms both under normal conditions and at high pressure (up to 3000 kg/cm^2). The sample weight was 0.8 g, the chamber diameter 8 mm, and aluminum oxide served as the standard. The heating temperature was measured in the body of the instrument. The heating rate was 2 deg/min.

The thermograms were recorded on a highly sensitive compensation potentiometer.

The thermograms presented in Fig. 1 show the course and thermodynamic quantities of the melting of polyethylene with different degrees of order at different pressures. From these curves it is seen that the final melting temperature (determined from the position of the peak) increases with increasing pressure (Fig. 2), and the character of this increase is almost the same for all polyethylenes (Fig. 3), except for the region of low pressures (up to 1000 kg/cm^2), where the dependence of the melting temperature on pressure for branched polyethylene differs noticeably from that for more ordered polyethylene. At the same

Fig. 1

Figure 1: Fig. 1

time, the melting interval broadens with increasing pressure; this is especially noticeable for the less ordered polyethylene. The heats of melting (determined from the peak area) increase slightly with increasing pressure. The kinetics of the melting process as a function of pressure for these samples does not differ appreciably.

The data obtained indicate that pressure has a stronger effect on the melting process of branched, least ordered polyethylene.

Figure 4a presents melting thermograms of PE-1 as a function of the cooling rate. A decrease in the crystallization rate causes a noticeable broadening of the melting interval, while a polymer obtained by rapid cooling (at a rate of 70°/sec) melts in a narrow temperature interval.

The broadening of the melting interval with increasing pressure and decreasing crystallization rate apparently has the same origin. It is known that,

that the crystallization rate of polyethylene strongly affects the crystallinity of the polymer, but is little reflected in the final melting temperature. Ordering under favorable thermal conditions increases owing to an increase in the long period ([7,8]). It may be assumed that an increase–

Fig. 1. Thermograms of the melting of polyethylene under pressure: *a*–PE-3; –PE-2; –PE-1

Fig. 2 Fig. 3

Fig. 2. Melting temperatures of polyethylene as a function of pressure: 1–PE-3; 2–PE-2; 3–PE-1

Fig. 3. Change in dT/dP as a function of pressure: 1–PE-3 and PE-2; 2–PE-1

–of the long period during slow cooling increases the local internal stresses at defective sites and, as a consequence, zones of a less thermally stable crystalline lattice are created near the defects. These zones begin to break down at lower temperatures, causing broadening of the melting interval.

Compression of polyethylene by the application of external pressure has a greater effect–

corresponds to defective sites [9], and this, apparently, is the cause of the appearance of local internal stresses. This assumption is confirmed by the data presented in Fig. 4b and c. A comparison of the effect of pressure on the melting interval of rapidly and slowly cooled samples shows that, in the presence of a large amount of unrecrystallized polymer (a quenched sample), the applied pressure causes a noticeable broadening of the melting interval. At the same time,

in a crystalline lattice well formed during slow cooling, the applied pressure changes the melting interval only slightly.

During isothermal crystallization, well-formed supramolecular structures are produced in polyethylene; they have a perfect crystalline lattice, which affects the character of melting of these crystalline formations, expressed by a sharp peak analogous to that of linear polyethylene, the width of which depends little on pressure (Fig. 4c). The second small peak is apparently associated with internal stresses that were created during slow cooling after isothermal crystallization.

A considerable broadening of the melting interval under pressure for cold-drawn polyethylene ("necks") (Fig. 4d) is caused by substantial disorientation of the structures.

The data presented above show that the broadening of the melting interval of a crystalline polymer containing a significant number of defects is associated with local internal stresses arising at defective sites, which lower the thermal stability of the crystalline lattice and cause a shift of the temperature of the onset of melting to lower temperatures.

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Institute of Chemistry and Chemical Technology
Academy of Sciences of the Lithuanian SSR

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Fig. 4. Thermograms of melting of PE-1: **a** –as a function of the cooling rate at cooling rates of 70 (1), 3 (2), and 0.27 deg/min (3); **b** –quenched sample (cooling rate 70 deg/sec); **c** –slowly cooled sample (0.27 deg/min); **d** –sample crystallized isothermally (at 100°); **e** –melting of "necks." **b, c, d, e** –under pressure: 1 –0, 2 –3000 kg/cm^2.

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