Temperature-induced crystallization of oriented polyethylene

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Exotherms of strained polyethylene melts were obtained by means of differential scanning calorimetry. Three peaks occur during crystallization, which are independent of the type of crosslinking. The influence of strain on the areas under the peaks was investigated. With increasing degree of stretching the two higher temperature peaks grow at the expense of the third. The peak at the lowest temperature corresponds to crystallization of the isotropic sample.

(Keywords: crystallization; differential scanning calorimetry; oriented polyethylene)

INTRODUCTION

If one orients chains by deforming a melt, gel or dilute polymer solution, it is known that crystallization occurs in two stages. Owing to the mechanical alignment of the chain molecules needle-shaped crystallites are formed, which in the second crystallization step serve as nuclei on to which further chains grow laterally. The morphology that arises has been well investigated and is represented by the row structure model of Keller and Machin[1]. On the other hand, both the microstructure, i.e. the structure of the extended-chain nuclei and details of the epitaxial overgrowth of the lamellae, and the kinetics of crystallization are largely unknown.

There are several theoretical approaches to describing the crystallization of oriented chains[2-6]. Concerning the possible experimental methods used to investigate the structure of oriented polymers, in the case of calorimetry the melting process has been analysed each time[6-10].

In this work, on the other hand, the crystallization process itself will be directly investigated, to obtain insight into the formation of the morphology.

For the crystallization of oriented polymers, one must distinguish between whether the amorphous polymer is first oriented and then crystallized by temperature change (temperature-induced crystallization) or whether at constant temperature the crystallization is caused by the orientation process (strain-induced crystallization)[11]. The latter temperature may lie above the melting temperature.

EXPERIMENTAL

In order to preserve the orientation of the melt for a sufficient length of time, differently crosslinked polyethylene samples were used for the measurement of the crystallization exotherms. The junction points were either chemical (radiation crosslinked PE (PE GF 4760 G, 5 Mrad)), consisted of entanglements that are stable during the period of the experiment (Hostalen GUR) or were as high-temperature stable crystals (PE 5261 Z and ultra-high modulus PE from Professor I. W. Ward).

The crystallization of these samples was followed directly by differential calorimetry (d.s.c.). For these experiments the material was fixed in the sample holder of the Perkin–Elmer DSC-II calorimeter such that during heating the drawn samples could not shrink[12].

The radiation-crosslinked PE samples were oriented at 152°C and quenched to room temperature. The melting and crystallization curves were then obtained. Each sample was heated to 450 K and cooled again four times. The heating and cooling rate was 5 K min^{-1}. After the first heating and cooling cycle reproducible melting and crystallization curves were obtained.

RESULTS

The occurrence of both strain- and temperature-induced crystallization is not a special property of those polymers described as rubbers, but occurs in each case where the orientation of a strained melt can be maintained sufficiently long. For example, a polyethylene sample that had been radiation-crosslinked in the melt was stretched above the melting temperature, then cooled, and subsequently heated at constant length in the d.s.c. The upper curve in *Figure 1* shows the melting endotherm.

Temperature- and strain-induced crystalline regions are found. Previous experiments had shown that the ratio of strain-induced crystals to the total crystalline fraction remains relatively small for polyethylene. If only the melting curves of the temperature-induced crystals are considered the endotherms are weak or hardly perceptible. On the other hand, if the fixed, oriented melt is cooled in the calorimeter, exotherms for the strain- and temperature-induced crystallization are registered. The temperature-induced fraction generally shows three peaks (*Figure 1*, lower curve).

For measurements on the crystallization exotherms, crosslinked samples were used, in order to preserve the orientation of the melt for the necessary time. The same effect can also be achieved if an oriented sample is not completely melted. If the melting process is terminated

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shortly before the end of melting, as in the example in *Figure 2* at 414 K, and the sample is cooled again, crystallization exotherms are obtained that are very similar to those for crosslinked, oriented samples.

The partially melted, oriented sample shows three exothermic peaks, of which the lowest temperature peak has to be ascribed to isotropic crystallization. From this it is concluded that the partial melt at 414 K was oriented, and that the orientation was preserved by network points formed by the remaining crystallites. The high melting point and electron microscopy[13] indicate that needle-shaped, extended-chain crystals form the junction points.

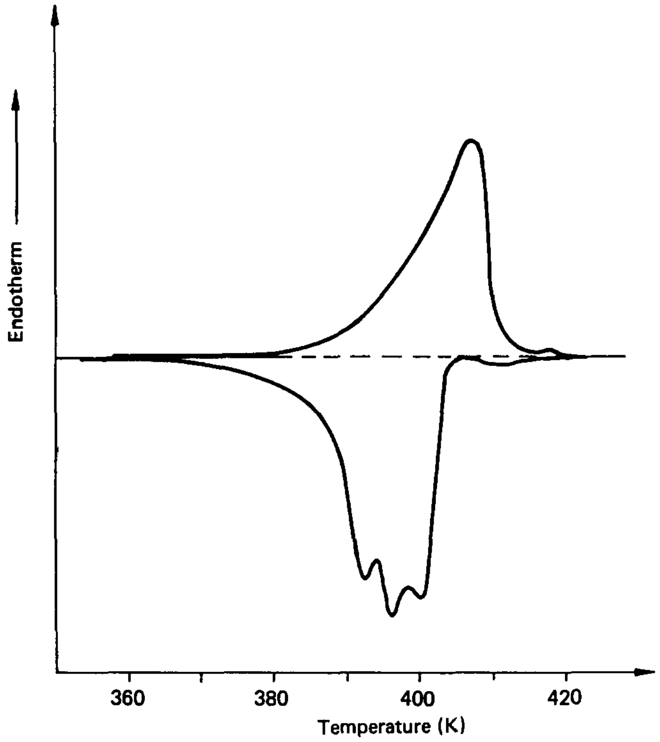

Figure 1 Melting curve (endotherm) and crystallization curve (exotherm) for radiation-crosslinked polyethylene sample stretched to $\lambda = 3.6$ at 152°C. The measurement was carried out with fixed sample ends

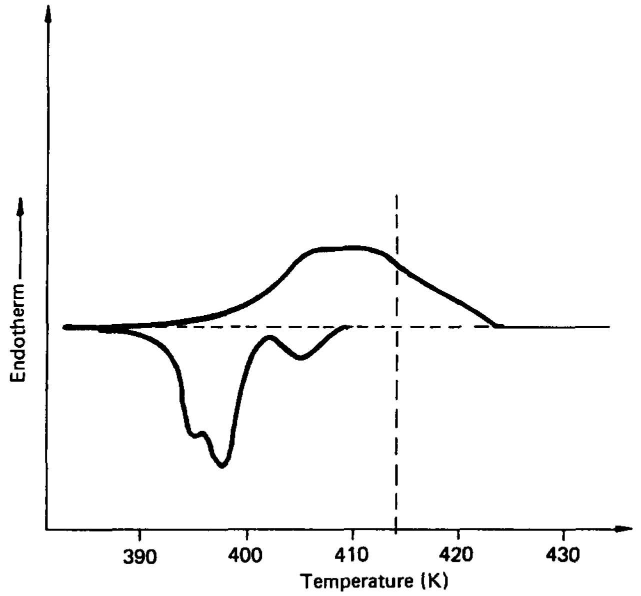

Figure 2 Melting and crystallization curves for oriented polyethylene. Crystallization curve obtained by interrupting the melting process at T_A and then cooling the specimen

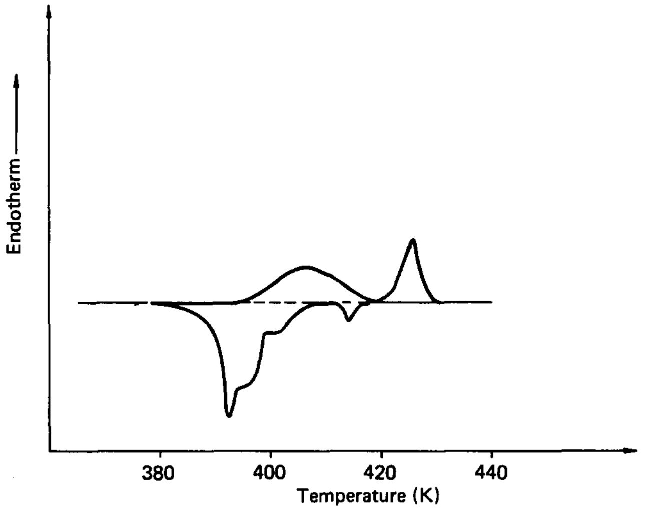

Figure 3 Melting and crystallization curves for drawn, high molecular weight polyethylene with fixed ends

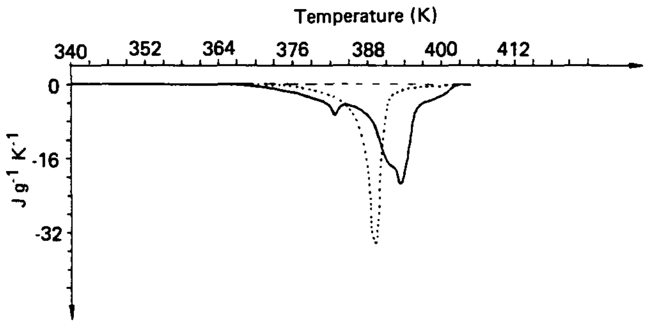

Figure 4 ———, Crystallization curve (exotherm) for radiation-crosslinked PE stretched to $\lambda = 3.2$ at 152°C. ·····, crystallization curve of the isotropic sample ($\lambda = 1$)

There is a third possibility of preserving the orientation of the melt when a very high molecular weight polyethylene (Hostalen GUR) is used. If such a sample is drawn and heated in the calorimeter at constant length until all the crystals have been completely melted, two well separated melting regions are found (*Figure 3*, upper curve). The high temperature position of the second peak indicates the existence of needle crystals.

Surprisingly, two melting regions are still found on heating a second time, although the proportion of needle crystals has become smaller. Owing to the high molecular weight and consequently to a high density of physical crosslinks, the orientation of the chains appears only to be reduced by relaxation processes in the time scale of the experiment, but not removed altogether. Correspondingly, in a cooling run crystallization exotherms for oriented melts (*Figure 3*, lower curve) are registered, the temperature-induced portion of which also show three crystallization phases.

DISCUSSION

The causes for the structure of the exotherms were investigated further. For this purpose, PE (PE GF 4760 G, 5 Mrad) was radiation-crosslinked in the melt and brought at 152°C to the required extension ratio. At room temperature the specimens were then fixed in the sample pans and heated to 450 K in the d.s.c. apparatus. Subsequently, samples were cooled at constant strain and crystallization exotherms registered, as shown in *Figure 4*.

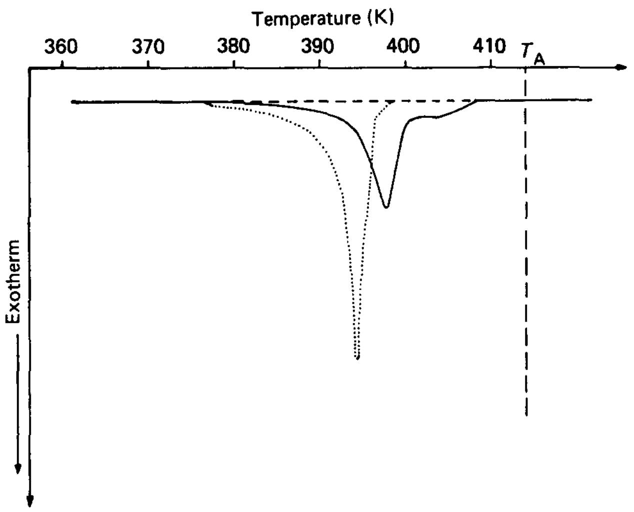

Figure 5 ———, Crystallization curve (exotherm) for ultra-high modulus PE ($\lambda = 20$). Crystallization curve obtained by interrupting the melting process at T_A and then cooling the sample. ·····, Crystallization curve of the isotropic sample ($\lambda = 1$)

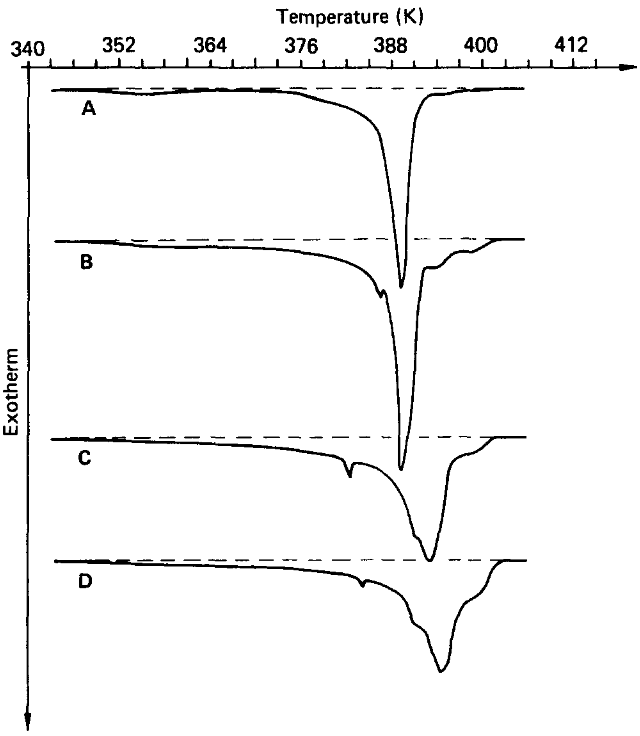

Figure 6 Crystallization curve (exotherm) of radiation-crosslinked PE for various degrees of stretching. Drawing temperature 152°C. (A) $\lambda = 1$; (B) $\lambda = 2.5$; (C) $\lambda = 3.2$; (D) $\lambda = 3.9$

In addition, for the chosen crystallization conditions a fourth peak was registered at lower temperatures. A fourth peak was also registered for Hostalen GUR. However, it appeared on cooling in the temperature region between 60°C and 90°C. It is well known[15] that a monoclinic modification is obtained on crystallizing oriented polyethylene. This is transformed into the orthorhombic modification depending on time and temperature. Since the transformation from a monoclinic structure into an orthorhombic one always occurs exothermically, we may assume that this extra peak, which shows no systematic behaviour with respect to the degree of stretching, can be attributed to such a transformation. For this reason, this peak will not be discussed further.

The three-peak structure is now considered. The lowest temperature peak, which for this material lies at about 390 K, relates to crystallization of the isotropic material. With increased orientation this peak is reduced in size correspondingly. For sufficiently high orientation this peak will presumably vanish completely. This is shown by *Figure 5*. Whereas in *Figure 4* the material still shows a triple peak, in *Figure 5* there are only two peaks. This means that the material is already so highly oriented ($\lambda = 20$) that an isotropic fraction is no longer present. If in an additional experiment the sample is heated to a temperature above the highest melting peak (T_A) and allowed to shrink freely, an isotropic melt is obtained. The crystallization exotherm of this melt is represented by the dotted curve in *Figure 5*. Comparison with the oriented exotherms shows that at the crystallization temperature of the isotropic sample for the case of the highly oriented sample in *Figure 5* a corresponding peak no longer appears.

Both of the high temperature peaks react to the degree of orientation. *Figure 6* gives the dependence on draw ratio.

The area of the high temperature peaks appears to be a measure of the draw ratio. The higher the orientation, the larger is the contribution of this peak to the crystallization enthalpy.

The splitting of the crystallization exotherms into three regions can be related to the concept of inhomogeneous deformation. Assume that in the isotropic sample there already exist regions with differing strength; then on deforming the material neighbouring regions will be oriented to different degrees. The remainder may be oriented such that it corresponds to the macroscopic strain. The drawn sample therefore contains isotropic, affinely deformed and more than averagely oriented regions. The more the material is stretched, the more the highly oriented regions increase at the expense of the isotropic ones.

As a result of the mechanical alignment of the chain molecules, needle-shaped crystals form at each crystallization temperature[14], which in the further crystallization process serve as nuclei on to which chains grow laterally (epitaxially). The lower the crystallization temperature, the greater is the proportion of chains which can grow laterally[14].

SUMMARY

In order to be able to investigate the crystallization of an oriented melt, crosslinked samples must be used. The junction points can be of chemical nature, consist of entanglements which are stable in the time scale of the experiment, or be formed by high temperature resistant crystallites. The crystallization of the oriented melts was investigated directly in the calorimeter. In the crystallization exotherms structures are found that, independently of the type of crosslinking, appear to be characteristic for the crystallization of an oriented melt. The crystallization of oriented polyethylene occurs in various phases. The crystallization exotherms show in each case a triple peak structure. The low temperature peak is related to crystallization of the isotropic material. Whereas the contribution of this peak is reduced by an increasing degree of orientation, the high temperature peak is increased in size correspondingly.

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