Degradation of nitric acid-treated bulk polyethylene*)

III. Melting behaviour

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Abstract: LDPE samples with differing branching content were treated with fuming nitric acid for times up to 180 h at 60°C. The samples were examined by differential scanning calorimetry and small angle X-ray diffraction. While the crystal thickness derived from the X-ray long period remains practically constant throughout treatment time t, a conspicuous sharpening and shifting of the melting curves to higher temperatures with t is observed. It is suggested that the shift in melting peak is caused by the contribution of the dicarboxylic groups attached to the crystal surface after treatment. It is further shown that the shift depends inversely on the crystal thickness. The comparison of melting points for long time nitric acid treated PE samples with data from dicarboxylic acids has permitted the derivation of an expression for the melting temperature of longer molecular diacids.

Key words: Low-density polyethylene, differential scanning-calorimetry, long period, fuming nitric acid, dicarboxylic acids.

Introduction

In a series of preceding papers, new aspects concerning the detailed degradation of Polyethylene (PE) with fuming nitric acid (FNA) have been reported [1-4]. These studies included the critical influence of the reaction conditions on the amount and nature of oxidized groups as revealed by IR analysis [1] and diamagnetic susceptibility [3], and the selective removal of chain defects by the nitric acid with reference to the problem of the distribution of defects between crystalline and amorphous regions. The acid removes, in fact, the non-crystalline (surface layer) and less perfect regions containing the majority of defects rapidly (30–50 h), leaving the more perfect crystalline lamellae, with a minimum of defects, more difficult to oxidize, as a residue. An interesting feature of the remaining defects is that a fraction of these branches which do not expand the lattice, but are detected by IR analysis, are presumably occluded as “amorphous” and/or cooperative defects within the crystals [4].

The object of the present study is to supplement the above studies on acid treated PE by calorimetric measurements. For this purpose the melting behaviour for three PE samples crystallized from the melt with different levels of chain defects has been investigated. Of special interest was the relating of the variation of the melting range and the shift of the melting peaks to higher temperatures after degradation, to the morphological and structural details of the polymer (lamellar thickness, etc.). Finally the melting temperatures of selectively degraded PE have been compared to the data for dicarboxylic acids. Our results indicate a clear dependence of the chain length on the melting point, thus contributing to fill the lack of data for long (32–100 carbon atoms) chain dicarboxylic acids.

Experimental

The measurements were made with three PE samples supplied by Farbwerke Hoechst, BASF and Eastman (see table 1) with different chain defect concentration e. The original flakes were pressed between two glass plates at 150°C to form a sheet 1 mm thick and then cooled at room temperature. The melt crystallized samples were treated in fuming nitric acid (> 95% HNO₃) at Tₑ = 60°C in open tubes. The reaction time varied between 5 and 180 hours. A detailed description of this process is given elsewhere [1].
Table 1. Weight average molecular weight, defect concentration given as sum of branches plus unsaturations, heat of fusion of FNA treated material and crystallinity prior to the treatment for the investigated samples

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Sample</th>
<th>$M_w \times 10^{-3}$</th>
<th>$\varepsilon$%</th>
<th>$\Delta H$(cal/g)</th>
<th>$\alpha$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hoechst PA-130</td>
<td>1</td>
<td>12.0</td>
<td>1.81</td>
<td>51.6</td>
<td>0.71</td>
</tr>
<tr>
<td>BASF a Wachs</td>
<td>2</td>
<td>9.5</td>
<td>3.49</td>
<td>45.6</td>
<td>0.67</td>
</tr>
<tr>
<td>Epolene C-12</td>
<td>3</td>
<td>11.0</td>
<td>6.90</td>
<td>43.7</td>
<td>0.38</td>
</tr>
</tbody>
</table>

*) Data taken from reference 4.

The long periods $L$ were measured at room temperature by a Rigaku point collimation small angle X-ray camera and calculated according to Bragg's equation. The measurements of the heat content and the melting temperature were performed by a Perkin Elmer (DSC IB) differential scanning calorimeter. In this instrument the temperature of the sample, weighing 2-6 mg, sealed into an aluminium pan, is raised together with an empty reference pan at a constant rate and the differential power input is recorded as a function of temperature. The heating rate used was 8°C/min. The temperature at the maxima of the thermograms was chosen as melting point of the sample. Its precision was found to be better than ± 0.5°C.

Results

Figure 1 shows some typical thermograms of the PE's investigated with differing defect content, in the vicinity of the melting peak. The melting range is, indeed, very broad for all samples but it becomes gradually better defined for lower $\varepsilon$ values. The melting range, measured at half intensity, narrows considerably (from 33° to 10°C for sample 3) and the maxima shift to higher temperature after a sufficiently long etching treatment ($t = 100$ h) (fig. top 1). Two melting peaks are observed for samples 1 and 2, the high temperature peak becoming sharper with $t$. Figure 2 depicts the gradual increase of the high temperature peak as a function of $t$ showing a leveling off after 30-50 h of nitric acid treatment. The limiting $T_m$ value decreases with increasing number of defects. The enthalpy, $\Delta H$ increases during the first treatment hours but for $t > 50$ it also levels off. The final $\Delta H$ values are given in table 1.

The SAXD pattern shows for sample 1 two distinct diffraction rings, for sample 2 one single broader diffraction ring and for sample 3 a rather diffuse halo. This halo becomes very well defined after a few hours of degradation. The variation of the long period as a function of treatment time is given in figure 3. For samples 1 and 2, $L$ clearly diminishes from 170/116 Å down to 152/107 Å respectively. The second maximum for sample 1 at $L \sim 80$ Å remains unaltered with $t$. For sample 3, $L_1$ increases slightly in the first treatment hours and after 20 h it finally decreases. After 30 h the diffraction maxima and the continuous scattering vanish completely in all the samples. The crystal thickness values, $l$, derived from $l \sim L \alpha$, where
\( \alpha \) is the X-ray crystallinity, are also shown in figure 3. In this calculation it is assumed that the chains are normal to the lamellar surface.

**Discussion**

In melt crystallized PE one currently assumes that the melting curve is mainly due to a broad distribution of crystal thicknesses [5]. Although the melting temperature can be lowered at higher heating rates (>10°C/min), for melt crystallized PE this effect is very small [6]. Thinner crystals are the first ones to melt because the surface energy \( \sigma \) depresses the melting point, \( T_m \), linearly with \( 1/l \) according to the Thomson-Gibbs equation:

\[
T_m = T_m^\circ(1 - 2\sigma/l\Delta H_f)
\]

where \( T_m^\circ \) and \( \Delta H_f \) are the melting point and heat of fusion of an infinitely thick crystal respectively. The broad thermograms of figure 1 represent the curves of fractional melting. With increasing number of chain defects: a) the average lamellar thickness becomes thinner (\( T_m \) diminishes). This effect has been previously shown to be due to a preferential exclusion of chain sequences containing defects from the crystals [7, 8] and b) the distribution of crystal thicknesses becomes considerably wider.

During the first hours of acid treatment the chains are selectively broken in the amorphous regions. After treatment the shape and position of the DSC curves is independent of heating rate. The initial increase of \( L \) for sample 3 with the lowest \( T_m \sim 80^\circ \)C is, most probably, due to an overall annealing effect occurring during the first minutes of acid treatment. Indeed for sample 3, \( \Delta T = T_m - T_R \sim 20^\circ \)C value, which yields an instant exaltation of \( L \) at \( T_R \) [9]. After \( \sim 50 \) h of treatment time the chains are reduced to a length close to the thickness of the lamellae. In addition, the narrowing of the melting range of degraded PE towards the low temperature side is a consequence of a narrowing of crystal size distribution due to a preferential acid digestion of the less perfect and thinner crystallites. The presence in the thermograms of two maxima, after degradation, suggests the appearance of two crystal types having different thicknesses and/or different crystalline perfection [10]. The low temperature maximum for sample 1 corresponds to a crystal thickness of \( \sim 65 \) Å, a value which fits with a stack of thin lamellae giving the second SAXD periodicity of \( \sim 80 \) Å. Recent experiments of Gedde [11] on isothermally crystallized and annealed PE suggest that the low temperature peak is due to a molecular fractionation during cooling of the samples. It is noteworthy that the two low temperature maxima for samples 1 and 2 and the only maxima for sample 3 lie nearly at the same \( T_m \). Thus one could expect a similar defective structure for these crystals.

The observed prevalence of a fraction of branches occluded in the lattice, for the long time etched material [4], could be consistent with the view of lamellae both with different thicknesses and differing chain defect content (fig. 4). The decrease of enthalpy (table 1) with increasing \( \varepsilon \) indicates the deterioration of crystalline perfection with increasing level of remnant defects for the treated samples.

The major effect in the thermograms after etching is, however, the remarkable shift of the melting peak to higher temperatures (fig. 2). The magnitude of the shift increases with higher branching content yielding thinner crystals (fig. 3). Earlier data from Illers [12] on melt crystallized PE did not show, except for one
single low density sample, any dependence of the peak position upon treatment time. The shift observed in the melting peak can be a consequence of one or a combination of the following two effects: an increase of the average crystal thickness after the acid attack, or a contribution of the dicarboxylic groups terminating the crystal surface. Both effects could equally contribute to the enhancement of \( T_m \). Since the crystal thickness derived from SAXD does not change with degradation time the first alternative has to be dismissed. We conclude, therefore, that the shift in the melting peak is most probably due to the elevation of the melting temperature caused by the contribution of the dicarboxylic groups. In order to substantiate this viewpoint let us analyse the melting temperatures of PE after acid treatment in the light of the data for dicarboxylic acids [13]. Figure 5 shows the \( T_m \) values as a function of number of carbon atoms, \( n \) within the crystalline stem. The melting temperatures for the PE samples before treatment and the melting curve for paraffins [14] are also given for comparison. Data of Illers [12] and Keller for an etched PE sample (B) are included. The lack of data for longer dicarboxylic acids makes difficult the extrapolation for \( n > 32 \). \( T_m \) data reported by Kilian and coworkers [16] on a series of even dicarboxylic acids with \( n \) ranging from 14 up to 56 exhibit, however, values considerably higher (130–135°C) than those reported for \( n \leq 32 \). These authors attribute this anomaly to the linkage of hydrogen bonds between chain ends forming long chains capable to fold similarly to the chain folding occurring in PE. From figure 5 it is evident the remarkable increase tendency for the \( T_m \) of PE after FNA etching. One observes a decrease in the melting temperature difference between acid treated and untreated samples when \( n \) increases. For degraded samples with \( n > 120 \) this difference is undetectable. Assuming that for very long chain acids one must tend to the equilibrium melting point of PE \( T_m^0 = 414.6 \) K [17] and letting the melting curve to pass through the point \( n = 32 \), \( T_m = 396.2 \) K, a hyperbolic curve

\[
T_m = 414.6 - \frac{n + 85.0}{n + 90.3}
\]

(dotted line) is tentatively proposed.

Since from IR analysis [18] the structure of the treated samples should mainly consist of chains having dicarboxylic acid nature the depression of \( T_m \) data obtained from the dotted curve could be connected to the actual chain length distribution for the treated samples. The presence of shorter chain species could act as impurities in the melting of the samples contributing to the lowering of \( T_m \). In addition, the roughness of the surface layer after treatment and the presence of some remaining chain loops occluded within the crystal core [19] could contribute too to this depression.

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References


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