

# Thermodynamic Properties of Oxidized Polyethylene Crystals

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*Polyethylene crystals grown from dilute solution have been oxidized with hot concentrated nitric acid so that all re-entrant chains are severed. The enthalpy of fusion,  $\Delta H$ , of the product, shown by infra-red analysis to be a mixed acid/ester, is considerably below the figure anticipated for the corresponding n-alkane. There is only a slight increase in  $\Delta H$  on hydrolysis to the dibasic acid.*

SELECTIVE oxidation by hot concentrated nitric acid<sup>1</sup> has proved a powerful tool for the investigation of structures in semi-crystalline polymers. Considerable attention has been focused on polyethylene and the effects of time and temperature are now clearly defined. Both solution- and melt-crystallized<sup>2,3</sup> material have been examined.

The present paper reports the thermodynamic properties of nitric acid-etched polyethylene single crystals: it is part of an extensive investigation of the behaviour of linear polyethylene. The X-ray long spacings of identical samples, similarly treated, have recently been given<sup>2</sup>.

## EXPERIMENTAL

Polyethylene crystals which had been grown at 70°C from 0.1% solution in xylene<sup>4</sup> were treated with 98% nitric acid at 70°C for 48 h and washed as in Reference 1. The work was carried out at I.C.I. Plastics Division through the courtesy of R. P. Palmer.

The oxidation product was hydrolyzed by heating under reflux with potassium hydroxide in tetrahydrofuran or ethyl alcohol for several hours. The resulting potassium salt was filtered and treated with an excess of warm dilute hydrochloric acid to give the long chain dicarboxylic acid (see below); this was washed several times with warm water before drying.

Infra-red spectra were recorded on a Perkin Elmer 457 spectrometer using the potassium bromide disc technique.

Enthalpy changes in the range 20–180°C were determined by adiabatic calorimetry as previously described<sup>4</sup>.

Heats of fusion,  $\Delta H$ , were also determined in a Perkin-Elmer differential scanning calorimeter (DSC) as described by Wunderlich and Cormier<sup>5</sup>.

## RESULTS

### *Analysis and structure*

The original flaky crystal aggregates (density 0.9725 g cm<sup>-3</sup>) disintegrated to give a fine powder (density 1.0135 g cm<sup>-3</sup>) with an overall weight loss of 8%.

Elemental analysis of polymer, oxidized for 48 h at 70°C, agreed with that reported by Keller *et al*<sup>6</sup>: C, 81.1; H, 13.6; N, 0.3; O, 4.8%. After hydrolysis the composition was: C, 80.8; H, 13.4; N, 0.5; O, 5.0%. On

completion of the adiabatic calorimetry (see below) the initially white sample found to be slightly grey; analysis: C, 81.7; H, 13.6; N, 0.3; O, 4.1%. Required values for a dibasic acid  $\text{HOOC}(\text{CH}_2)_n\text{COOH}$  with  $n=75$  or 90 (values in brackets) are C, 81.0 (81.7); H, 13.4 (13.6); O, 5.6 (4.8)%.

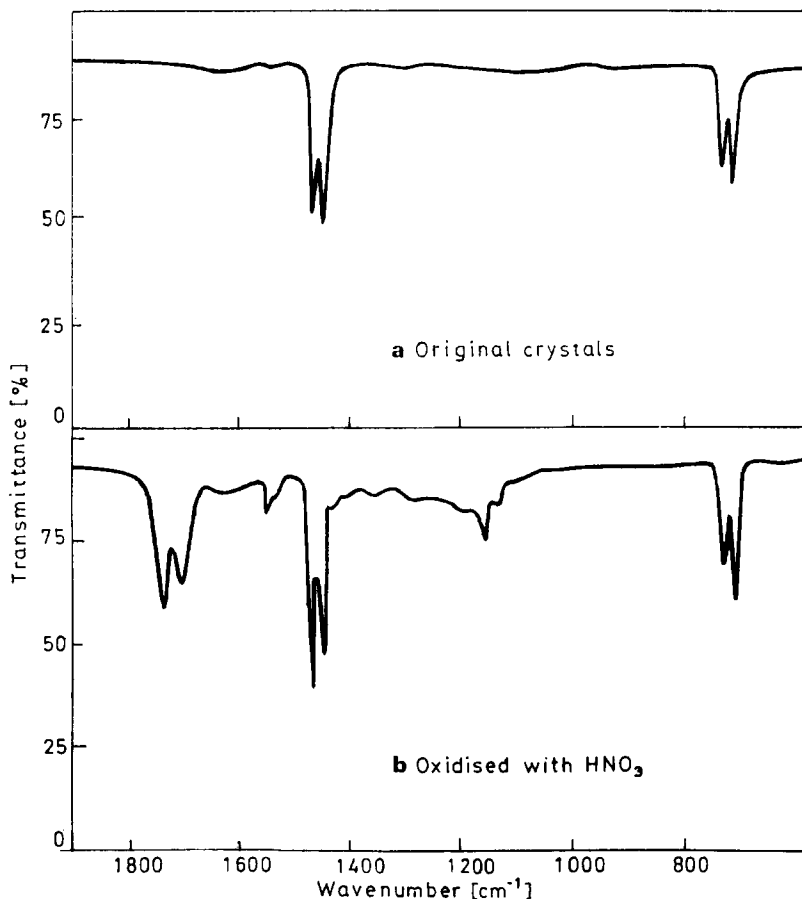


Figure 1a and 1b—Infra-red spectra of oxidized polyethylene crystals

Oxidized polymer showed additional infra-red absorption at 1165, 1550, 1715 and 1745  $\text{cm}^{-1}$  (Figure 1b). Changes on hydrolysis are shown in Figure 1c and 1d. After adiabatic calorimetry no trace remained of the 1550  $\text{cm}^{-1}$  band, but otherwise the spectrum was identical with that in Figure 1b.

#### Melting points and differential calorimetry

The apparent melting point of the original, unoxidized, polymer crystals was about 132°C. The true value for unannealed crystals is probably several degrees lower<sup>6</sup>, but it was not possible to suppress annealing processes even with very high heating rates. By contrast, the melting point of

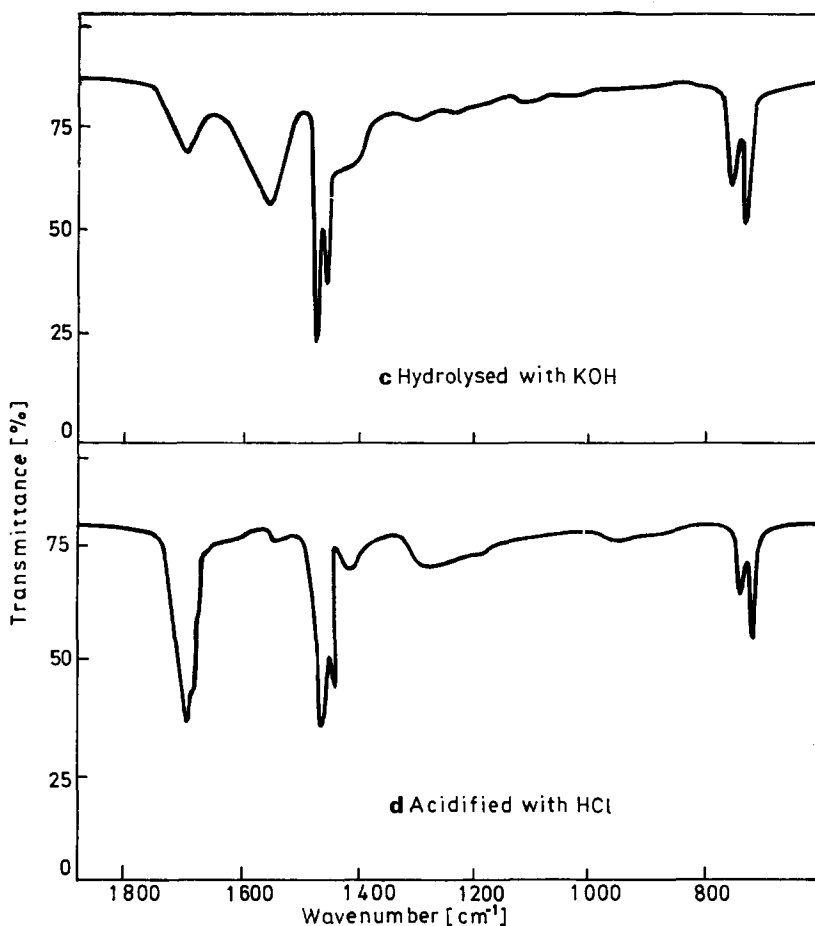


Figure 1c and 1d—Infra-red spectra of oxidized polyethylene crystals

oxidized crystals ( $114 \pm 1^\circ\text{C}$ ) was found to be independent of heating rate in the range  $0.1\text{--}32^\circ\text{C min}^{-1}$ ; the extreme heating rates in adiabatic and differential calorimetry respectively. (Most DSC measurements used a rate of  $8^\circ\text{C min}^{-1}$ .) In both cases (inset, Figure 2) a small fraction remained unmelted until  $122^\circ\text{C}$ —the apparent melting point by polarizing microscopy.

Hydrolyzed material, the true dibasic acid, had a single melting peak at  $122^\circ\text{C}$ .  $\Delta H$  (DSC) increased from 215 to  $225\text{ J g}^{-1}$  on oxidation and to  $230\text{ J g}^{-1}$  on hydrolysis.

Results were independent of sample treatment; as-prepared, solution-grown and melt-grown material being identical.

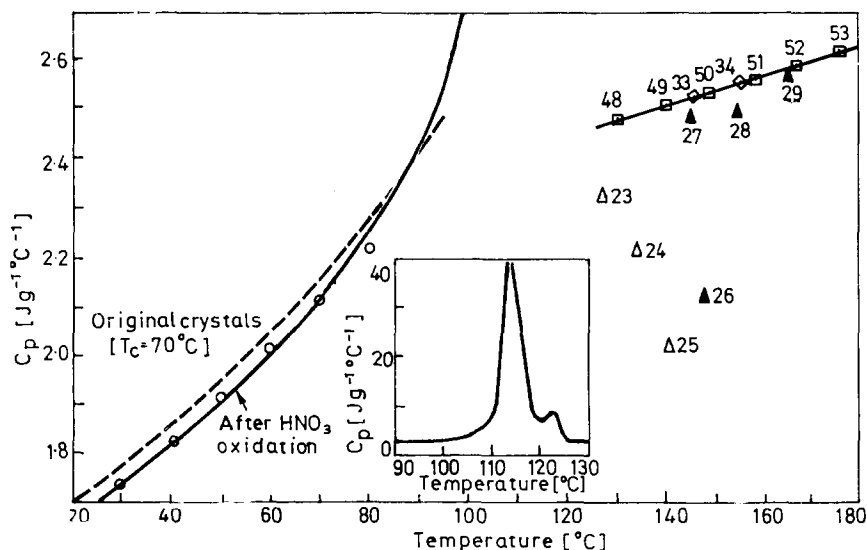
#### Adiabatic Calorimetry

Specific heats of polyethylene single crystals after oxidation by nitric acid are shown in Figure 2. For comparison, results are also given for

some untreated crystals<sup>6</sup>. The liquidus for oxidized crystals was given by

$$C_p = 2.075 + 3.06 \times 10^{-3} (T) \quad \text{J g}^{-1} \text{ } ^\circ\text{C}^{-1} \quad (1)$$

Above 80°C heat was evolved in the calorimeter and the temperature continued to rise slowly, even after cessation of energy input. A similar effect is well known for semi-crystalline polymers below their melting points<sup>4, 7</sup>, and is attributed to annealing. The present case was unique, however, since the 'steady state' temperature continued to rise even when all polymer was molten. This suggests a chemical, rather than physical, origin. Both processes may occur simultaneously below the melting point. At higher temperatures the chemical effect alone is operative and the magnitude may be estimated either from the rate of increase of the calorimeter temperature at the end of a run, or from the apparent specific heat. In the latter case, heat of reaction leads to an anomalously large temperature rise for a given energy input. Specific heats (triangles, *Figure 2*) appear lower than given



*Figure 2*—Specific heat of original<sup>6</sup> (broken line) and oxidized (full line) crystals. (Melting behaviour inset)

Run numbers and symbols show approach to equilibrium in melt; circles show calculated values for  $C_{75}$  *n*-alkane<sup>15</sup>

in equation (1) and the difference gives an average figure for the rate of heat evolution over the period of energy input (rates also shown in *Table 1*). All rates are derived from one experiment and a rate process plot is only valid for early stages of the reaction. The rate increases with temperature (open triangles, *Figure 2*) but at about 150°C the reaction is well advanced and the rate falls off rapidly (closed triangles, *Figure 2*).

Rate effects are important because they could lead to errors in the cal-

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culation of  $\Delta H$ . Fortunately, evidence indicates that they are negligible below about 120°C. The anomalous specific heats (open triangles, *Figure 2*) extrapolate to the line of equation (1) at about this temperature.  $\Delta H$

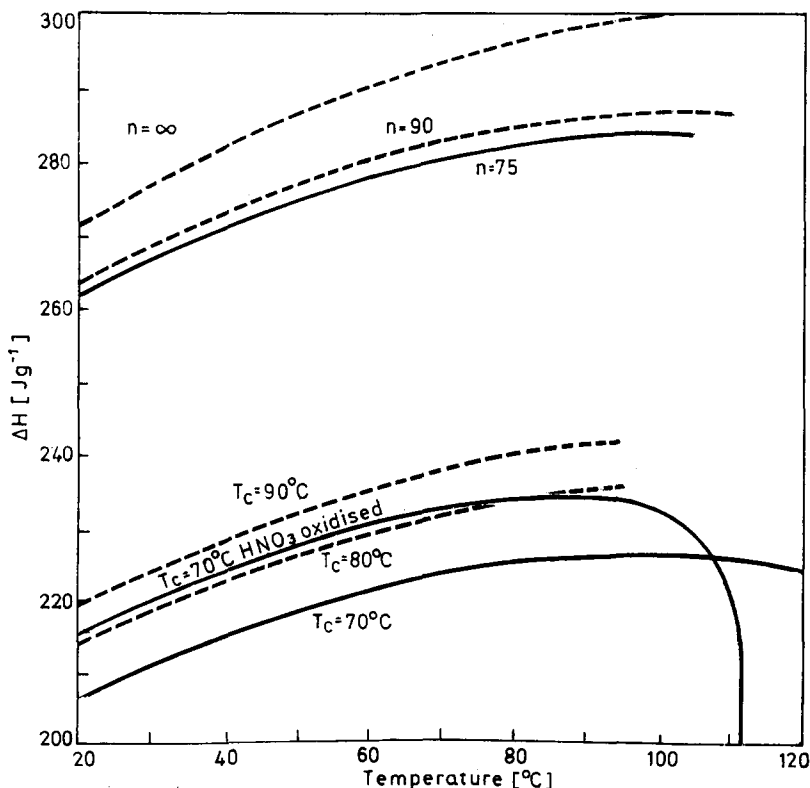
*Table 1.* Rate of heat evolution in molten polymer (arranged in chronological order to show approach to completion at high temperatures)

Temperature (°C)	124.3	128.1*	135.2*	142.3*	146.0	149.3*
Rate, $\text{J g}^{-1}\text{min}^{-1}(\times 10^3)$	13.2	12.6	25.3	41.8	45.1	37.5
Temperature (°C)	153.0	143.5	146.8*	150.0	155.9*	162.0
Rate, $\text{J g}^{-1}\text{min}^{-1}(\times 10^3)$	40.6	5.4	4.4	7.0	7.0	15.0

\*Average temperatures (see text)

was therefore calculated in the normal way<sup>4</sup> using equation (1) and the observed enthalpy increments into the melt. *Figure 3* shows  $\Delta H$  for solution-grown crystals before<sup>6</sup>, and after, treatment with nitric acid.

$\Delta H$  (DSC) and  $\Delta H$  (adiabatic) both increase by about 5%. Quantitative agreement between the two heats of fusion is not expected since  $\Delta H$  (DSC) refers to temperatures near the melting point whereas adiabatic values are more accurate at low temperatures where pre-melting (the rapid decrease



*Figure 3*—Heats of fusion (adiabatic calorimetry) of various polyethylene crystals<sup>6</sup> (adiabatic calorimetry, growth temperature,  $T_c$ , shown) and *n*-alkanes<sup>15</sup>  $\text{C}_n\text{H}_{2n+2}$  (calculated values, *n* shown)

in  $\Delta H$  above 100°C, *Figure 3*) is insignificant. The calculation of  $\Delta H$  (adiabatic) assumes that equation (1) is valid for the original oxidized, but unmelted, material whereas it actually refers to material which has reacted at high temperatures. The only gross change apparent from spectroscopic evidence is the disappearance of the  $-\text{NO}_2$  band<sup>1</sup> at 1550  $\text{cm}^{-1}$ . This is a trivial difference compared with that between either type of oxidized crystal and the *n*-alkanes or polyethylenes—and even for the latter,  $C_p$  is very similar to that of equation (1)<sup>8</sup>. The assumption therefore appears to be valid.

No investigation has been made of the high temperature reaction. It might be due to attack by residual nitric acid which washing has not removed. This is unlikely since all evidence indicates that reaction in the amorphous region has ceased (see below); further oxidation is restricted to the exposed crystalline flanks from which nitric acid should readily be washed. A more likely cause is reaction of the oxidized material itself, either internally, perhaps to form anhydrides, or externally with the calorimeter metal.

#### DISCUSSION

##### *The structure of oxidized polyethylene*

The general features of the oxidative attack of hot nitric acid on polyethylene are clearly established. Less dense regions are preferentially attacked and there is a considerable decrease in molecular weight as chains in the reactive zone are severed. Broken chains are mainly terminated by heavy groups<sup>9</sup> (see below) giving an overall increase in density.

The above conclusions were confirmed by the present work. An unexpected result was the high proportion of esterified acid groups. Bands (*Figure 1b*) at 1165 and 1745  $\text{cm}^{-1}$  are attributable to C—O and C=O stretching vibrations, respectively, in aliphatic esters<sup>9</sup>. They, and the absorption at 1715  $\text{cm}^{-1}$  (characteristic of C=O groups in associated carboxylic acids<sup>9</sup>) vanished on hydrolysis with potassium hydroxide (*Figure 1c*). (Residual absorption at *ca* 1715  $\text{cm}^{-1}$  was probably due to ketonic carbonyl groups since the intensity was unchanged by prolonged hydrolysis). These were replaced by the asymmetrical stretching vibration of the carboxylate ion at 1550  $\text{cm}^{-1}$ . Treatment of the solid salt with dilute hydrochloric acid led to the immediate reappearance of the band at 1715  $\text{cm}^{-1}$  but no absorption at 1745  $\text{cm}^{-1}$  (*Figure 1d*). This eliminates any possibility that the latter is due to unassociated carboxyl groups<sup>10</sup>. Since *solid* polymer was oxidized, total association could have been hindered by the solid matrix. All subsequent reactions were carried at temperatures similar to, or lower than, the original oxidation and therefore subsequent association should not have been favoured. The absence of any absorption at 1745  $\text{cm}^{-1}$  after hydrolysis, confirmed that the original band was due to ester carbonyl groups.

Molar extinction coefficients for C=O groups in long chain dimerized acids (1715  $\text{cm}^{-1}$ ) are some 50% greater than those in esters (1745  $\text{cm}^{-1}$ )<sup>11</sup>. Since the two bands are of comparable intensity (*Figure 1b*) the majority of oxidized chains terminate in ester groups. An 'internal' ester of the

type  $\text{RCOOR}'$ , where both R and R' are incorporated in the crystalline matrix, is unlikely since it has been shown<sup>2</sup> that after 48 h oxidation, the molecular weight corresponds to only a single traverse of the crystal.

Takamatsu and Konaga<sup>12</sup> have demonstrated that there are two alkali-sensitive groups per molecule of oxidized polyethylene. It is assumed that these occur at either end of the alkane-like product and the overall hydrolysis product is a long chain dibasic acid.

#### *Melting points*

The treatment reported here gives material with an X-ray long spacing of about 9.5 nm ( $95\text{\AA}$ )<sup>2</sup>. This approximates to a  $\text{C}_{75}$  *n*-alkane which has a melting point of  $108^\circ\text{C}$ <sup>13</sup>. The mixed acid/ester melts at  $114^\circ\text{C}$  and the hydrolysis product at  $122^\circ\text{C}$ . Thermograms of *partially* oxidized polyethylene crystals usually show two peaks. There is little change in the position of the main peak in the later stages of reactions as the higher melting shoulder is reduced in size<sup>14</sup>. The correct melting point is therefore  $114^\circ\text{C}$ , even if unreacted polymer accounts for the higher endotherm. Reaction conditions in this work were chosen to give *total* interfacial oxidation and the invariance of results with method of sample preparation is indeed good evidence for this. It is probable that the shoulder found here is due to dibasic acid which was present before hydrolysis. This is supported by the similarity of the melting point of hydrolyzed material.

Carboxylic acids are associated even in the molten state<sup>9</sup>; long chain dibasic acids are therefore hydrogen bonded as infinite chains. The number of conformations that an acid can assume is restricted, and is less than that of an alkane of the same chain length. Thus the entropy of fusion of the acid is less, and the melting point is greater than that of the corresponding alkane. This assumes that  $\Delta H$  is similar (no additional energy is required since hydrogen bonds are still present in the melt). Experimental support is provided by the small effect of hydrolysis on  $\Delta H$ . Hydrogen bonding fully explains the increase in melting point in the series alkane < mixed-acid/ester < dibasic acid.

#### *Thermodynamic properties*

Specific heats,  $C_p$ , of long chain compounds are relatively insensitive to end group effects. At room temperature, calculated<sup>15</sup> values of  $C_p$  for alkanes in the range  $\text{C}_{75}$ – $\text{C}_{90}$  (which differ by < 1%) are only 2–3% below results<sup>6</sup> for polyethylene crystals of a comparable thickness. The present results are in agreement with these findings. In the range  $30$ – $80^\circ\text{C}$ ,  $C_p$  decreases by some 2.5% on oxidative scission to a value very close to that of the corresponding alkane (*Figure 2*).

The above differences of 1–2%, although showing the consistency of the measurements, are not sufficient to draw conclusions regarding the surface morphology. A clearer thermodynamic distinction between polymeric and short chain crystals is possible if based on  $\Delta H$  at, say, room temperature. Here the difference is perhaps 25%, *Figure 3*, where it is seen that the oxidized crystals of this work are little changed thermodynamically from the original material containing re-entrant chains. Chemically there is a closer analogy with the *n*-alkanes. These conflicting results may only be

reconciled if oxidized crystals have a high concentration of defects. If these are concentrated at the lamellar surfaces, then oxidized crystals must have a totally disordered region some six carbon atoms deep at either end of each molecule. This figure is only approximate since spatial requirements preclude too abrupt a change of order in the interfacial regions. There will certainly be considerable lattice disorder in this area to accommodate carboxyl and ester groups. The small increase in  $\Delta H$ (DSC) on hydrolysis may reflect the more uniform packing possible if all surface groups are carboxyl; but  $\Delta H$  is still considerably below the value for *n*-alkanes (Figure 3).  $\Delta H$  for a long chain *n*-alkane (C<sub>48</sub>) containing 5% of impurity (C<sub>46</sub>) is about 8% less than calculated at room temperature<sup>15</sup>. The present figures—16% below the anticipated value—are therefore reasonable as the surface morphology will be considerably less perfect than that of the alkane. The latter will be relatively smooth with occasional surface vacancies due to the impurity with a shorter chain length. Oxidized polymer has not only surface carboxyl groups but small concentrations of carbonyl and nitro groups which have been neglected. The role of these is not known but they must be located at the crystalline interfaces, contributing to the general surface imperfection. Heats of fusion are compared well *below* the melting point, because near this temperature quite small traces of impurity can greatly depress  $\Delta H$ .

The increase in  $\Delta H$  on oxidation is about 5%. Other workers have found increases of 12%<sup>14, 16</sup> for crystals grown at higher temperatures. This may reflect true morphological differences in the original crystals. At the same time  $\Delta H$  remains considerably below the figure to be expected for a long chain *n*-alkane; quantitative work assuming equivalent structures must be seriously in error.

*This work forms part of the research programme of the Division of Molecular Science of the National Physical Laboratory. The help of R. P. Palmer and I.C.I. Plastics Division with the nitric acid oxidation is gratefully acknowledged.*

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(Received 25 September 1969)

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