# Study of the Change of Crystallinity of Polyethylene on Oxidation by Inverse Phase Gas Chromatography

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## Synopsis

Inverse-phase gas chromatography has been used for monitoring the oxidative degradation of low density polyethylene, which has great industrial importance. Polyethylene was oxidized in a gas chromatographic column at 145°C with an oxygen flow of 10 mL/min for different periods. After oxidation for a specified period, the crystallinity and solvent interaction parameters were monitored. For crystallinity studies, the solvent probe was *n*-decane, and for solvent interaction these were *n*-decane, *o*-xylene, *n*-butanol, and *n*-butyl acetate. With oxidation there was a gradual fall in crystallinity, and after 15 h the crystallinity was practically nil. Total loss of crystallinity also occurred at 175°C with 1 h passage of oxygen. This has also been confirmed by differential scanning calorimetry. The specific retention volumes of polar solvents showed a sharp increase with oxidation. The results, which are different from that reported in the literature, have been explained.

## INTRODUCTION

Various experimental techniques such as oxygen uptake, thermogravimetry, differential thermal analysis, and differential scanning calorimetry are available for the study of thermal and oxidative degradation of polymers. Information leading to physical and chemical changes subsequent to degradation, identification, and quantification of products of degradation and rate expression of the degradative processes can be obtained from these methods. Davis and Peterson,[1] in a bid to develop an accelerated test method for asphalt degradation, carried out its oxidation in a gas chromatograph followed by analysis by inverse-phase GC and determined "interaction coefficient." The advantages of carrying out direct oxidation in a GC column are (i) thin uniform and reproducible film thickness, (ii) easy and precise control of temperature and flow rate of oxygen, (iii) no unnecessary handling of materials between stages, and (iv) uniform oxidation throughout the bulk of material. Evans and Newton[2] have used similar techniques with squalene (model compound for *cis*-polyisoprene) and determined the "retention index" as a measure of oxidation. However, both the interaction parameter and retention index are empirical in nature.

Oxidative degradation of polyethylene, being of great industrial importance, has been studied in detail by many authors. Oxidation of polyethylene causes a change in crystallinity, besides the creation of polar groups and chain scission, and the progress of oxidation can be monitored by the change in crystallinity.[3] There is, however, conflicting evidence in the literature regard-

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ing the trend of change of crystallinity with the progress of oxidation. Winslow and co-workers[4] have observed that the density of linear and branched polyethylene increased with oxidation. The increased density was attributed to oxidative crystallization arising from scission of the constrained chains in the disordered region. Neiman et al.[5] from his NMR studies on the oxidation of polypropylene concluded that the attack of oxygen occurred primarily within the amorphous regions of the polymer and also an increase in amorphous character occurred during oxidation. Hawkins et al.[6] have reported that the rate of oxygen uptake in solid polyethylene during oxidation is inversely proportional to the percent of crystallinity in the polymer, suggesting that amorphous regions in semicrystalline polyethylene were susceptible to oxygen attack. Similar results have also been obtained for polypropylene.[6]

It was, therefore, proposed to measure the change in crystallinity, of polyethylene, with oxidation by carrying out the oxidation in gas chromatograph and measuring crystallinity using inverse GC. The use of inverse GC for measuring crystallinity has already been established.[7-9] The method is much more convenient than other conventional methods such as X-ray and calorimetry since it does not require the knowledge of the properties of 100% crystalline polymer. Besides, various thermodynamic properties of polymer solvent interaction, transition temperatures, and surface properties can be studied by this method.[10,11] In the present work, oxidation of LDPE has been carried out by passing oxygen over LDPE, coated onto chromosorb contained in a GC column, and measuring its crystallinity with progress of oxidation. Retention parameters have been measured using solvents of different polarities.

## EXPERIMENTAL

Aimil Nucon 5700 (Nucon Engineers, India) dual column GC with thermal conductivity detector was used for the study. LDPE used was manufactured by Union Carbide (India), having a viscosity-average molecular weight of $\approx$ 33,000. All solvents used were of A.R. grade. Temperatures were measured using standard thermometer to accuracy of 0.5°C. For the purpose of coating polyethylene on inert substrate, accurately weighed LDPE granules were dissolved in warm $p$-xylene, to which was added a known quantity of chromosorb WAW, untreated or DMCS-treated. Glass beads were also tried as substrate. The coating was effected by removing the solvent in a rotary vacuum evaporator. The material was then further dried in a vacuum oven, sieved, and packed in a 1/8 in. stainless steel column of 2-m length. The column was conditioned at 80°C by passage of a carrier gas for about 4 h.

The inlet column pressure was measured by a mercury manometer just near the inlet. The column outlet pressure was taken as atmospheric. Ultrapure hydrogen was used as the carrier gas. The flow of the carrier gas used was 6.5 to 7.5 s/mL. The quantity of solvent (probe) injected varied from 0.01 to 0.1 $\mu$L. The LDPE loading was about 10% of the substrate. $n$-Decane was used as solvent for the purpose of determining crystallinity. The temperature range studied was 76–136°C with 4°C intervals. For the purpose of retention parameters, other solvents, e.g., $o$-xylene, $n$-butyl acetate, $n$-butanol, besides $n$-decane were used. Retention parameters have been determined at arbi-

trarily selected temperatures. Normally 0.6 $\mu$L air was injected along with the liquid sample as an inert marker.

The polyethylene coated in the column was analyzed for crystallinity and solvent polymer interaction. Thereafter the carrier gas was stopped, and oxygen passed through the column for a specified period. Initially air was also used for oxidation purposes. The flow of oxygen was maintained at 10 mL/min. After the *in situ* oxidation, the column was reconditioned for 4 h at 80°C by passing of the carrier gas. The oxidized column was then analyzed for crystallinity and solvent interaction. Thus the experimental process consisted of an analysis mode followed by oxidation mode. In this study, the same column was oxidized at a fixed temperature and oxygen flow rate for different periods, and cumulative effects were studied after each oxidation.

## RESULTS AND DISCUSSIONS

Use of glass beads as substrate did not give uniform coating of LDPE. With untreated chromosorb W, the peaks were nonsymmetrical. However, using DMCS-treated chromosorb WAW, a uniform coating was obtained, and the column gave symmetrical peaks with different solvents. Retention time recorded for different solvents did not show any dependence on the flow rate and sample size within the experimental range of study.

The specific retention volume $V_g$ was calculated using the method of Newman and Prausnitz.[12] The crystallinity has been determined from the plot of $\log V_g$ vs. $1/T$. (Typical plots are given in Fig. 1.) The plots show an inflection at the melt transition $T_m$. A least-square analysis of the different plots of $\log V_g$ vs. $1/T$ above $T_m$, i.e., when the polymer is totally amorphous, showed that this part of the curve was invariably a straight line with correlation over 0.999. Assuming that the solvent probe is absorbed only by the amorphous region, extrapolating these lines to any temperature below $T_m$ gives the specific retention volume $V_g'$ of a totally amorphous polymer at that temperature. The percent crystallinity is then given by the expression $(1 - V_g/V_g') \times 100$, $V_g$ being the experimental specific retention volume at that temperature.

The values of $V_g$ obtained for *n*-decane and LDPE at 76°C using DMCS-treated chromosorb was observed to be much higher ($\approx 1100$ cc/g) as compared to that obtained by using untreated chromosorb ($\approx 680$ cc/g). This difference is attributed to deposition of polydimethyl siloxane (PDMS) on chromosorb during treatment with DMCS. The values of the retention volume $V_R$ were also obtained using blank DMCS-treated chromosorb column (without LDPE). The $V_g$ could not be calculated in this case since it was not possible to find out the exact quantity of PDMS present on chromosorb, either by calcination or by extraction. The calculated values of $V_g$ for *n*-decane and LDPE using DMCS-treated chromosorb, after accounting for the blank $V_R$ (obtained on blank DMCS-treated chromosorb column), tallied closely with the values of $V_g$ for untreated chromosorb, the values being 677 and 672 cc/g, respectively (Table I). Similar observations have also been made by Card and co-workers.[13]

Although the values of $V_g$ obtained from treated and untreated columns were widely different, the values of crystallinity at 76°C obtained from either of them gave practically the same values, i.e., 47.64 and 48.5%, respectively.
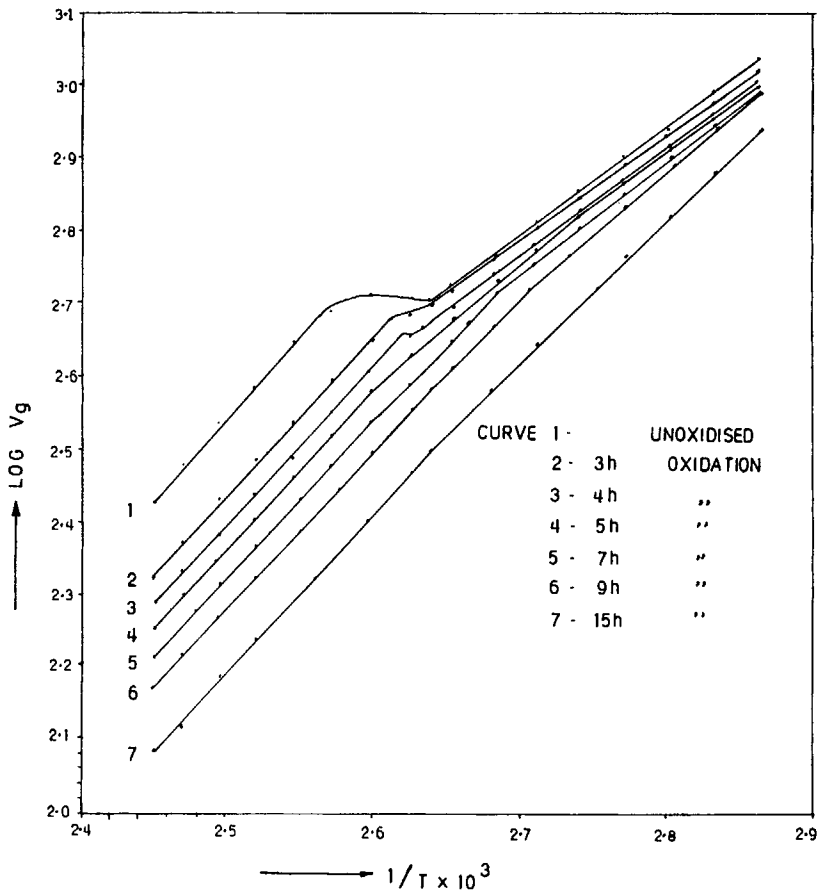
Fig. 1.   Plot of log $V_g$ vs. $1/T$ for various degrees of oxidation (h): (1) unoxidized; (2) 3; (3) 4; (4) 5; (5) 7; (6) 9; (7) 15.

TABLE I
Crystallinity and Specific Retention Volume ($V_g$)

| | Crystallinity percent (76°C) | $V_g$ at 76°C | | | |
|---|---|---|---|---|---|
| | | $n$-Decane | $o$-Xylene | $n$-Butanol | $n$-Butyl acetate |
| Fresh column LDPE on DMCS-treated chromosorb | 47.64 | 677.4 1103.7[a] | 360.9 | 7 | 40.2 |
| Oxidized at 135°C 10 h oxygen | 46.63 | 693.6 | 363.3 | 5.7 | 37.5 |
| Heated at 175°C 7 h without oxygen | 48.50 | 680.1 | — | — | — |
| Oxidized at 175°C 1 h oxygen | Nil | 5.5 | 570.6 | 704.7 | 350.2 |
| LDPE on chromosorb, untreated | 48.5 | 672.0 | — | — | — |

[a]Uncorrected value—see text.

Also the plot of $\log V_R$ and $1/T$ for blank DMCS-treated chromosorb did not show any transition within the experimental range of temperature and was straight line. The values of $V_R$ and nature of straight line did not show any change whatsoever, even after oxidation at 145°C for 4 h (conditions being the same as used for oxidation of LDPE). The correlation, slope, and intercept of the two lines, as calculated by least square analysis, are as follows:

|                  | Correlation | Slope  | Intercept |
|------------------|-------------|--------|-----------|
| Before oxidation | 0.9993      | 2.1489 | − 4.4540  |
| After oxidation  | 0.9994      | 2.1450 | − 4.4535  |

From the foregoing it appears that PDMS becomes part of the inert support. Braun and Guillet[10] have shown that the presence of amorphous phase in case of copolymers or the change in inert support does not alter the crystallinity results. As such, no correction in $V_g$ for PDMS have been made for the purpose of calculation of crystallinity. However, retention data have been corrected for the same to bring them on a comparative scale.

Oxidation of LDPE in the column was tried with air and oxygen at different temperatures. Passage of air or oxygen through the column at a temperature of 135°C for 10 h did not show any change in crystallinity or $V_g$ of different solvents as evident from Table I, indicating that the oxidation of polyethylene did not take place. However, passage of oxygen for 1 h at 175°C resulted in sharp drop of $V_g$ for $n$-decane and a sharp rise of $V_g$ for other solvents. The $\log V_g$ vs. $1/T$ plot ($n$-decane) did not show any transition and was a straight line (correlation 0.9995). It is therefore concluded that total loss of crystallinity has occurred under the conditions of oxidation. This change was due to oxidation and not thermal since the percent crystallinity and $V_g$ for decane at 76°C of LDPE heated on a similar column without passage of oxygen at 175°C for 7 h did not show any change from that of fresh LDPE.

The sharp rise of $V_g$ for $n$-butanol, $n$-butyl acetate, and $o$-xylene can be explained on the basis of the well-known mechanism of oxidation of LDPE. The oxidation of LDPE is via free radical mechanism, the primary product being hydroperoxides, which decompose to free radical to initiate a chain reaction. The hydroperoxide then decomposes to alcohols, ketones, and acids. There is a chain scission, resulting in decrease of molecular weight and also evolution of gaseous products like CO, $CO_2$, and $H_2O$. The sharp rise of $V_g$ is therefore due to formation of polar functional groups during oxidation. Since the compounds formed during oxidation are well known, no efforts to identify the same were done in these studies.

In an effort to generate stepwise oxidation data for LDPE, the oxidation was carried out at 145°C in the column for varying periods, the cumulative periods being 3, 4, 5, 7, 9, and 15 h. Figure 1 gives the plots of $\log V_g$ vs. $1/T$ for various stages of oxidation. It is seen that in the original curve (before oxidation), there is only one inflection which is due to melt transition. This inflection which is sharpest in fresh column gradually diminishes as the oxidation progresses. The plot of $\log V_g$ vs. $1/T$ after 15 h oxidation shows a marginal inflection and is practically a straight line similar to one obtained after oxidation for 1 h at 175°C. These results clearly indicate that the whole LDPE has become amorphous with practically total loss of crystallinity due to oxidation.
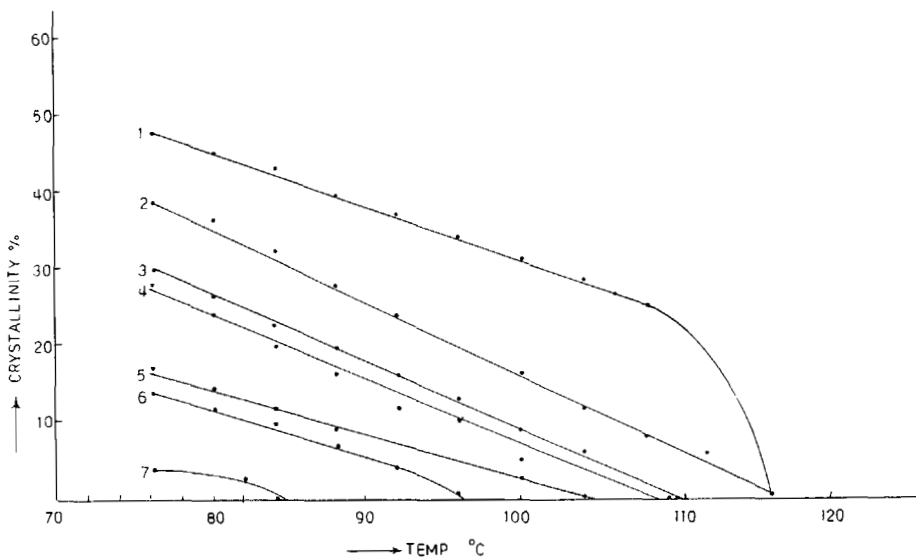
Fig. 2.   Melt curve of LDPE at various stages of oxidation (h): (1) unoxidized; (2) 3; (3) 4; (4) 5; (5) 7; (6) 9; (7) 15.

The melt curves for the original LDPE and oxidized LDPE at various stages of oxidation have also been given in Figure 2. It is quite apparent from the curves that with the progress of oxidation, there is lowering of melt transition and also the nature of melt curve changes to practically linear after oxidation. The lowering of melt transition is presumably due to lowering of molecular weight of LDPE during oxidation.

Figure 3 shows the variation of crystallinity with oxidation at temperatures 76, 84, and 92°C. Apparently the decrease in crystallinity is regular and falls
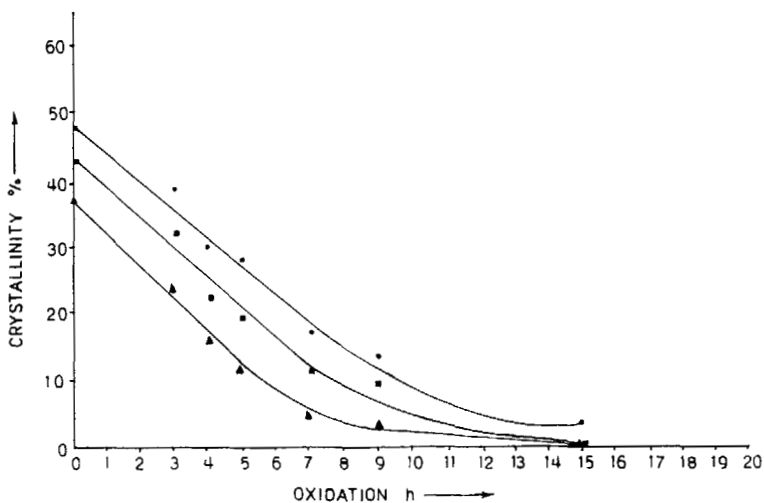


Fig. 3.   Variation of crystallinity with oxidation calculated at different temperatures (°C): (●) 76; (■) 84; (▲) 92.

on a smooth curve. It is pertinent to mention that crystallinity at temperatures below 76°C has not been calculated as it would require extrapolation of the curve for $V_g$, thereby introducing inaccuracies.

The material removed from the column after 15 h oxidation was found to be deep yellow-colored, indicating oxidative degradation of LDPE.

Winslow and co-workers[4] have, on the contrary, reported an increase in crystallinity of LDPE during oxidation on the basis of increased density and observed the appearance of additional crystalline sites of slightly different density by X-ray diffraction. This increase in crystallinity has been explained by a more orderly structure caused by chain scission in the disordered region.

As mentioned earlier, besides chain scission a large number of polar groups are generated on oxidation of polyethylene. These new molecules with polar functional group attached to them would be different species from polyethylene and may have densities different from LDPE. Moreover, the generation of polar groups in the molecules would cause formation of ordered regions due to polar interactions, which in turn could lead to increase in density and formation of additional crystalline phase, as observed by Winslow. Such species possibly do not interfere in the present studies since the plot log $V_g$ vs.
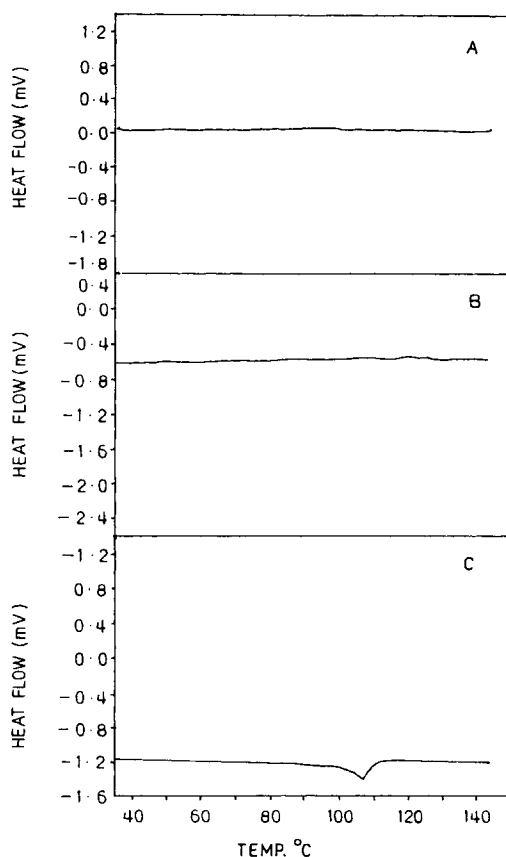


Fig. 4. DSC of LDPE coated chromosorb: (A) after oxidation at 175°C for 1 h; (B) after oxidation at 145°C for 15 h; (C) unoxidized.

TABLE II
Specific Retention Volume ($V_g$) with Progress of Oxidation,
Specific Retention Volume

| Probes \ Period of oxidation | Original | 3 h | 4 h | 5 h | 7 h | 9 h | 15 h |
|---|---|---|---|---|---|---|---|
| Decane | 677.43 | 635.30 | 596.87 | 596.66 | 597.51 | 571.82 | 444.88 |
| o-Xylene | 360.93 | 611.37 | 662.15 | 723.14 | 783.36 | 805.82 | 782.28 |
| Butanol | 7.05 | 286.79 | 347.85 | 397.58 | 493.81 | 496.45 | 524.90 |
| Butyl acetate | 40.22 | 215.08 | 244.72 | 275.43 | 311.03 | 328.48 | 325.90 |

$1/T$ at different stages of oxidation invariably show one transition and no fresh transition is observed. The loss in weight of LDPE during oxidation due to formation of volatile products like CO, $CO_2$, and $H_2O$, etc. does not affect the crystallinity calculations since the ratio of $V_g/V_g'$ is independent of the weight of the polymer. However, the column material after oxidation at 145°C for 15 h and 175°C for 1 h on ignition, showed practically the same weight loss, as in case of fresh LDPE-coated material.

The total loss of crystallinity on oxidation have been confirmed by DSC. The oxidized material did not show any transition, whereas the fresh material showed an endotherm at 106°C (Fig. 4).

Hawkins et al.[6] have reported that the attack of oxygen is more pronounced in the amorphous region than in the crystalline region during oxidation studies at temperatures below $T_m$. In the present study, oxidation has been done at 145°C, i.e., at temperature much higher than $T_m$, where the polyethylene was totally amorphous. Oxidation in these conditions has possibly formed crosslinks, resulting in a drop in crystallinity.

Table II shows the variation of specific retention volume with progress of oxidation. Although there is a systematic and slow decrease of $V_g$ of n-decane with oxidation, the decrease is not significant up to 7 h oxidation. After 15 h the $V_g$ drops from 677.4 to 444.8, showing that even after 15 h the polyethylene retains sufficient nonpolar character. In case of n-butanol, n-butyl acetate, and o-xylene, however, there is a sharp initial rise which then tapers off. The rise is sharpest in case of n-butanol, which has the highest polarity.

## CONCLUSIONS

Inverse phase GC coupled with in situ oxidation in the column can give valuable information regarding the change in the polymer with the extent of oxidation. The results for LDPE gives a clear indication that there is lowering of crystallinity, increased polarity of the material, and lowering of melt transition with oxidation.

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