The lamella size distribution in non-isothermally crystallized low density polyethylene

P. J. Mills* and J. N. Hay
The Chemistry Department, The University of Birmingham, Birmingham, B15 2TT, UK

(Received 12 October 1983)

It has been observed that linear and high pressure polymerized low density polyethylenes crystallize with the branches excluded from the crystals, the extent and size of the crystallities which develop being limited by the number and distribution of branches within the molecules. Using a random distribution of branches as a model, the lamellar size distribution has been calculated and compared with those observed experimentally in slow cooled crystallized samples of PE with different degrees of branching. Nitric acid etching of the crystalline regions from the amorphous background followed by g.p.c. analysis of the product, as well as analysis of the melting range have been used to determine crystallite size distribution. Good agreement has been obtained between the observed and calculated values of the most abundant lamellar thicknesses, but problems due to molecular weight fractionation and un-etched amorphous material casts doubt on the experimentally determined size distribution at high and low stem lengths.

(Keywords: linear low density polyethylene; branch distribution; lamellar thickness; melting point; nitric acid etching)

INTRODUCTION

The commercial properties of polyethylene are conventionally categorized in terms of their density. However, for the case of low density polyethylene the arrival of 'linear low' resins has shown dramatically that different types of polyethylene, of equal crystallinity and molecular weight, may show considerable differences in thermal and mechanical properties, many of which can be attributed to differences in the lamella size distribution[1]. Clearly methods to measure lamella size distributions and a model to predict the distribution in terms of molecular parameters would be of great value.

In a recent paper by Pakula[2] concerning the isothermal crystallization of polyethylene, the growth of lamellae was considered to be by segmental nucleation on a crystal side, and consequently there was a critical size of segment between branch points which was required for effective nucleation. The critical size was temperature dependent and the extent of crystallization was determined by the quantity of crystallizable sequences above this critical size.

In this paper we propose an analogous model for non-isothermal crystallization. However additional consideration is given to the commonly observed heterogeneity in the degree of branching with respect to molecular weight for branched polyethylene. The predicted lamella size distributions are then compared with those experimentally measured using nitric acid oxidation and from the melting behaviour using differential scanning calorimetry (d.s.c.).

THEORY

Nitric acid oxidation

Since the discovery by Palmer and Cobold[3] that nitric acid oxidizes amorphous material at a much faster rate than the crystalline regions, nitric acid oxidation has been widely employed by crystallization and morphological studies of polymers in particular polyethylene[4]. The molecular weight distribution as measured by gel permeation chromatography of a sample fully oxidized such that only the crystalline material remains therefore gives a measure of the lamella size distribution in the original material.

Melting behaviour

According to a model proposed by Flory and Vrij[5] and later modified by Hay[6], for the case of n-alkanes with a regular surface layer of end groups, the melting temperature T_m for an alkane of n repeat units is given by

$$T_m = T_m^0[1 - 2RT_m \ln(n)/n\,\Delta h - 2\sigma e'/n\,\Delta h + \Delta Cp\,\Delta T(n-1)/n\,\Delta h] \quad (1)$$

where Δh^0 is the heat of fusion per repeat unit and ΔCp the difference in heat capacity between the crystalline and amorphous phase, both measured at the equilibrium melting point T_m^0. The term $\sigma e'$ arises from the surface free

---

* Present address: Department of Materials Science and Engineering, Bard Hall, Cornell University, Ithaca, New York, 14853, USA.

0032-3861/84/091277-04$03.00

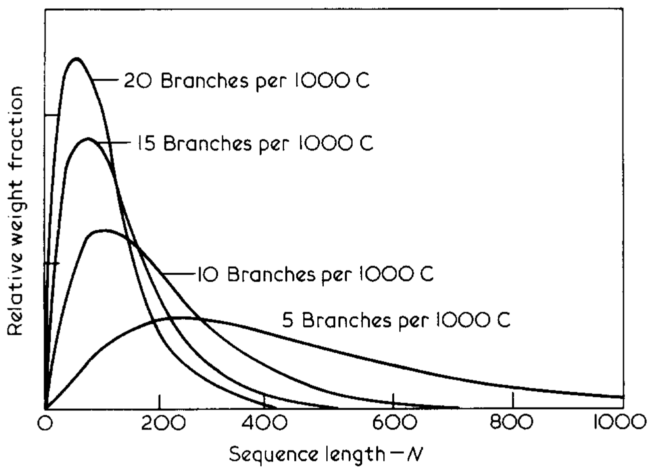

Figure 1 Segment length distribution for randomly distributed branches

energy of the crystal and the $2RT_m\ln(n)$ term from the entropy of mixing of the terminal units with the n units of the alkane chain. This latter term dominates all the others enabling the relationship between T_m and n to be truncated and T_m calculated, with reasonable accuracy by

$$T_m \simeq T_m^0[1 - 2RT_m\ln(n)/n\,\Delta h] \quad (1a)$$

For the case where the branch units are randomly distributed along the polymer chain and on crystallization are excluded from the lamella regions, the probability of a sequence of n units occuring between consecutive branch points is given by

$$p(n) = (1-p)^2 p^n \quad (2)$$

where $(1-p)$ is the 'branching frequency' namely the ratio of the number of branches to main chain atoms.

As $n \rightarrow \infty$ the number fraction of such sequences $N(n)$ is

$$N(n) = (1-p)^{n-1} \quad (3)$$

Such that the weight fraction of the sequences $W(n)$ is then

$$W(n) = n(1-p)^2 p^{n-1} \quad (4)$$

Figure 1 shows the distribution for several branching frequencies. In order to allow for heterogeneity in the branching frequency in the system examined here further summation is required. The total weight fraction of species of length n, $W_F(n)$, can be calculated as follows

$$W_{F(n)} = \sum_{\min p}^{\max p} W'(p)n(1-p)^2 p^{n-1} \quad (5)$$

where $W'(p)$ is the weight fraction of material of branching frequency $(1-p)$. The weight average sequence length $\bar{n}_w$ is equal to

$$\sum_{n=1}^{n=\infty} W_F(n) \quad (6)$$

and the number average sequence length equals

$$1 \Big/ \sum_{n=1}^{n=\infty} W_F(n)/n \quad (7)$$

MODEL

The model assumes that complete fractionation of segments with respect to their length takes place and that the lemella size distribution is given simply by equation (5). The amorphous material is then considered to be that fraction of material with sequence length lower than the dimensions of the critical size nuclei. Slow stepwise cooling enables each sequence length to crystallize in turn.

Limitations to this model are:

(1) No allowance has been made for the presence of amorphous material. The amorphous material may be considered to arise from two main effects:

(a) The cooling rate being too fast for complete fractionation, this effect being most important for the larger sequences.

(b) The crystallization of segments is hindered by the previous crystallization of other segments along the molecule. As a first approximation the amorphous material is considered to be a certain fraction of the segments independent of their length.

(2) As a result of (1a) as the crystallization develops there is the increased possibility of a number of segments eventually crystallizing at a smaller size nucleus.

The model is however consistent with the observed increased crystallinity of LLDPE samples with decreasing crystallization temperature.

EXPERIMENTAL

Sample characterization

The LLDPE polyethylene Sclair 11B (Dupont) with a molecular weight M_w of 11×10^4 g, M_n 2×10^4 g and a branch structure consisting of 14 ethyl units per 1000 main chain carbon atoms was investigated. Fractionation of the resin with respect to the degree of branching was undertaken using the temperature rising elution method of Desreux and Spiegels[7].

3 g of polymer was dissolved in xylene and deposited on a silica substrate inside a fractionating column two metres in length. Elution of the polymer was by xylene alone. The temperature was increased over the range 50°–120°C by circulating oil from a temperature programmed oil bath through the jacket of the column. The polymer molecules with the highest degree of branching were eluted first the assumption being that the number of branch points per molecule is sufficient to offset the difference in solubility expected for molecules of different molecular weight. Excess acetone was added to the fractions to precipitate the polymer. Values of P, the branching frequency were determined for each fraction by infra-red spectroscopy using a Perkin–Elmer 580B Infra-red Spectrometer.

Nitric acid oxidation

5 g of finely cut material crystallized from the melt, cooling at 0.03 degrees/min was placed in contact with fuming nitric acid at 60°C in a sealed container, the sample being kept below the surface by glass-fibre paper. The oxidation was allowed to proceed until the weight of sample which remained was equivalent to the crystalline weight as determined from the density of the original material. The g.p.c. of the nitrated product was run at 130°C as a 0.5% w/v solution in *o*-dichlorobenzene using a Waters Gel Permeation Chromatograph, Type 150-C. Calibration of molecular weight with respect to elution

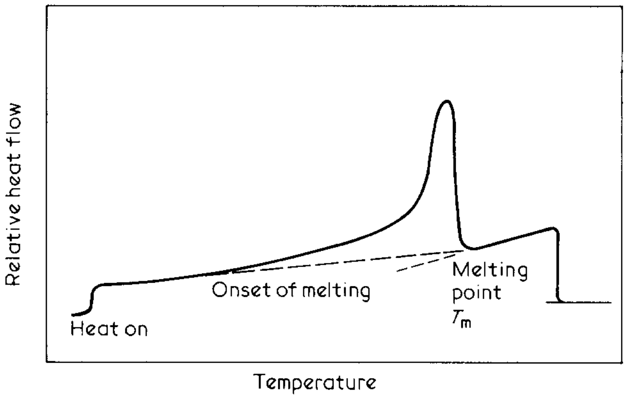

Figure 2 Typical d.s.c. thermogram

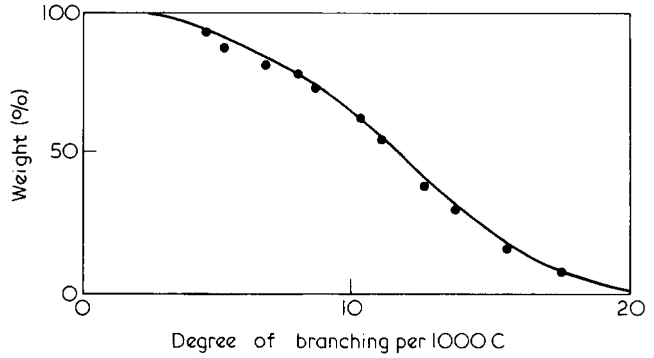

Figure 3 Cumulative weight distribution in the degree of branching for sample 11B

volume for the instrument was undertaken using the polyethylene standard SRM 1475[8], and the number and weight average lamella size was also determined.

Melting behaviour

The melting of the sample was examined using a Perkin-Elmer Differential Scanning Calorimeter, model II linked to a Perkin-Elmer Scanning Autozero, a chart recorder, a Perkin-Elmer Calculator Interface/Digital Read-Out and a Tektronix 31 Programmable Calculator. Approximately 10 mg of the sample was used, the thermogram being corrected for thermal lag by recording measurements at various heating rates (> 10°C/min) in order to prevent annealing effects) and then extrapolating to zero heating rate. The calculator system enabled fast and accurate processing of the thermogram. A typical thermogram is shown in *Figure 2.*

The onset of melting was taken as the point at which the trace deviated from linearity by a pre-set value just above the anticipated experimental scatter. Whilst the end of melting was taken as the point at which the linear region resumed. The base line was assumed to be a straight line connecting these two temperatures. The thermogram was then divided into 2°C wide strips and the value for Δh for each temperature range was calculated from the equations of Broadhurst[10]. The weight fraction of material and the corresponding value of the lamella thickness could also then be determined. At high temperatures where the strip width encompassed several values of n the weight of material melting was equally divided between these values. The weight average and number average lamella size was also calculated.

RESULTS AND DISCUSSION

Figure 3 shows the distribution in the degree of branching present in the sample. The dispersity is of great importance when determining the melting and crystallization behaviour of the bulk polymer as will be reported in a future publication[1]. Recognition of the occurrence of this dispersity goes a long way towards explaining the superior thermal properties of the linear low resins compared with the conventional low-density polyethylenes.

Whilst the weight average and number average lamella sizes determined by d.s.c. and g.p.c. analysis of the products of nitration are in reasonable agreement, (*Table 1*), *Figure 4* shows significant differences in the calculated lamella distributions.

The values of both the maximum and most abundant lamella size present are reasonably consistent, however the Nitration method shows a considerable low molecular weight tail. This may in part be as a result of incomplete oxidation of some of the amorphous material, but of greater significance is the apparent insensitivity of d.s.c. to detect the melting of low concentrations of small lamellae and this has far reaching implications in the use of the technique for measurements of heats of fusion and heat capacities.

Figure 5 enables a comparison of the experimental distributions with those predicted by the models. Before comparison is made it should be noted that no effects, due to the finite length of the molecule, are anticipated, this size being much greater than the maximum lamella size detected.

Whilst there is excellent agreement between the experimentally measured value for the most abundant lamella

Table 1 Number average lamellae thickness (as number of $-CH_2$ units)

	D.s.c. determination		Nitration products by g.p.c.	
Sample no.	No. average	Wt. average	No. average	Wt. average
11B	64	80	55	75

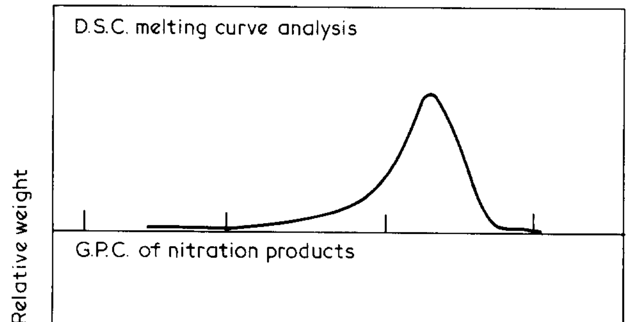

Figure 4 Lamella size distributions: (a) from d.s.c.; (b) from nitration

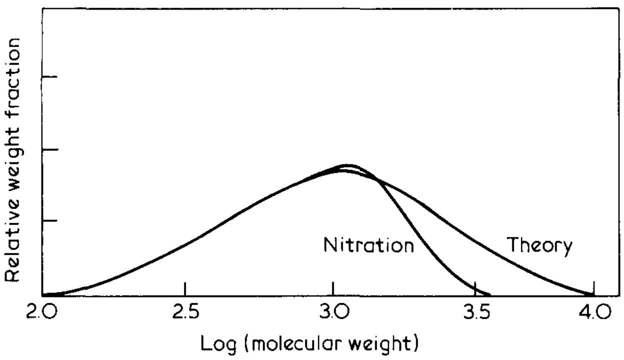

Figure 5 Comparison of experimental lamella size distributions obtained from nitration with the theoretical distributions

size and that predicted by the model, as had been anticipated, complete fractionation of segments with respect to their length is easier for the smaller sequences. As mentioned previously the larger un-crystallized sequence could crystallize as either interconnecting lamella or chain-folded sequences and contribute to the low molecular weight region, neither event is allowed for in the models however the good agreement between model and experiment in this region suggests that this effect is not of great significance.

What at first consideration may appear surprising is the apparent mobility of the shorter chain segments during crystallization when the polymer chain at this stage may interconnect several lamella. However this 'interconnection' is largely surpressed by the heterogeneity present in the degree of branching, therefore as a first approximation the crystallization of each segment can be considered to be independent of previous events.

CONCLUSION

In determining the lamella size distribution of a polyethylene sample measurement of the molecular weight distribution of material produced by selective nitric acid oxidation of the amorphous material offers greater sensitivity than the analysis of the melting behaviour both in the detection of the low molecular weight material and the resolution of the high molecular weight material.

The correlation between the theoretical distribution predicted by the model and that measured, whilst offering considerable evidence for the premis that the distribution is determined by the distribution of inter-branch sizes also reflects the complexity of the non-isothermal crystallization of branched polyethylene.

ACKNOWLEDGEMENTS

We are grateful to the SERC and BP Chemicals Ltd. (Grangemouth) for the joint sponsorship of a CASE award for P.J.M. during the course of this work.

REFERENCES

1 Mills, P. J. *Ph.D. Thesis*, University of Birmingham, 1982
2 Pakula, T. *Polymer* 1982, **23**, 1300
3 Palmer, R. P. and Cobbold, A. J. *Makromol. Chem.* 1964, **74**, 174
4 Keller, A. and Udagawa, Y. *J. Polym. Sci., A-2* 1972, **10**, 221
5 Flory, P. J. and Vrij, A. *J. Am. Chem. Soc.* 1963, **85**, 3548
6 Hay, J. N. and Wiles, M. *Makromol. Chem.* 1977, **178**, 623
7 Desreux, V. and Spiegels, M. C. *Bull. Soc. Chim. Belges.* 1950, **59**, 476
8 *J. Res. Natl. Bur. Stand.* 1972, **76A**, 2
9 Mills, P. J. and Hay, J. N. *Polymer* 1982, **23**, 1380
10 Broadhurst, M. G. *J. Res. Natl. Bur. Stand.* 1963, **67A**, 3