Chain branching in high pressure polymerized polyethylene

D. J. Cutler and P. J. Hendra
Chemistry Department, University of Southampton, Southampton SO9 5NH, UK
and M. E. A. Cudby and H. A. Willis
ICI Plastics Division, Welwyn Garden City, Hertfordshire, UK
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We have combined the techniques of ^{13}C nuclear magnetic resonance (n.m.r.) and nitric acid degradation to obtain information on the location of the side chains in branches polyethylene. Surprisingly, we have found that the ethyl and butyl groups are mainly excluded from the crystalline zones. The longer branches can cocrystallize with the main chain. Knowledge of the numbers and types of branch in polymers is of some technological important in polymer science. Short chain branching has a marked effect on the mechanical properties of the polymer, whilst the long chain branching affects the properties of melts.

INTRODUCTION

Chain branching in polyethylene

An early suggestion of chain branching in vinyl polymers came from anomalous osmotic pressure and viscosity data on polystyrene[1,2]. Immediately, uni- and bimolecular branching mechanisms were suggested[3], and Flory developed a model for bimolecular branching[4].

The presence of side chains in polyethylene, prepared by the high pressure polymerization of ethylene, was established in 1940 by Martin and Fox[5]. They found a band near 3000 cm^{-1} in the infra-red spectrum due to a methyl group adjacent to a tertiary carbon atom. Rhodel[6] has proposed that short branches are produced in large numbers by a unimolecular hydrogen transfer reaction (the 'back biting' mechanism), and less frequently long branches by a bimolecular branching reaction[4]. Long chain branching has been proposed in an explanation of anomalous viscosity data. It is further suggested that the number of long branches is molecular weight dependent in that they are concentrated on the longer polyethylene molecules (and are absent when $\bar{M}_w < 5000$[8–11]).

Short chain branching was initially studied using infrared spectroscopy. A band near 1380 cm^{-1} was shown to be due to methyl groups[12,13], and could be used to calculate the concentration of branches. A band claimed to be due to ethyl groups was found near 890 cm^{-1} [14]. In a further infrared study Bryant and Voter[15], have shown that there are no methyl groups pendant from the backbone. Casey, Elston and Phibbs[16] concluded from differential scanning calorimetry (d.s.c.) data that the branches are bunched and/or themselves branched. This possibility had been predicted in 1959 by Willbourn[17]. Tirpak[18], investigating the infra-red dichroism of drawn branched polyethylene, concluded that the ethyl groups were oriented at about 60° to the main chain. Hence, he proposed that they are predominantly on the 1st, 2nd or 3rd carbon of a longer branch, e.g. 2-ethyl hexyl.

The first direct measurement of the distribution of short chain branching in branched polyethylene was made by Kamath and Barlow[19], who exposed samples to γ-rays from ^{60}Co, and analysed the hydrocarbons evolved. Their results, however, do not agree with their infra-red data, or subsequent ^{13}C n.m.r. results. Bovey, Otaka and Dorman[20] studied branched polyethylene with ^{13}C n.m.r., and found resonances due to a variety of branches. Randall[21], also using ^{13}C n.m.r., proposed that the relative proportions of the branches could be calculated from band intensity data e.g. he found 11% C_2, 54% C_4, 17% C_5 and 18% $\geqslant C_6$ in his sample, but could not distinguish between branches of six carbon atoms or more in length. Cudby and Bunn have refined the technique[22], and have shown[23] that the absolute number of each type can be calculated, and further that their estimate of total branches compares well with values from infra-red data.

Thus, it is clear that it is only with the developments of ^{13}C n.m.r. in the last few years that a rigorous analysis of the chemical nature of branched polyethylene has been possible. However, the exact nature of the longer branches is still *sub judice.*

Crystallization of branched polyethylene

Since branched polyethylene is not a 'conventional' block or random homopolymer, properties of the melt crystallized polymer must be influenced by the presence, or otherwise, of the branches in any crystalline or amorphous region.

At present ^{13}C n.m.r. cannot distinguish branches in an amorphous environment from those in a crystalline region. However, X-ray data on melt crystallized α-olefin copolymers[24–26] show that there is an *a*-axis expansion, and a decrease in the crystallite size with an increase in the number of branches. This was taken to mean that the branches are included as 'faults' within the crystalline zones.

On the other hand, Bunn[27] has suggested that this inclusion does not cause *a*-axis expansion, but rather that strain external to the crystalline zones causes the effect and is due to the branches being located at the crystallite surfaces. Also, in his theory of copolymer melting, Flory[28] assumes that the branches cannot cocrystallize with the main chain. Dilatometric studies on melt crystallized copolymers[29] suggest that only methyl groups are accommodated within the

Table 1 The ^{13}C n.m.r. determined side chain distributions of the branched polyethylenes used in this study. Number of branches per 10^3 C atoms. (The error in the branch concentrations is estimated to be ±1 methyl per 10^3 C atoms)

Sample	Branch concentration ethyl	 butyl	 longer
A	11	14	12
B	21	22	17
C	14	17	14

lattice, the longer side chains being excluded. Carbonyl groups have also been shown to enter the crystalline core[30,31]. Although, like the alkyl groups, they cause *a*-axis expansion, they do not lower the melting point or the crystallinity of the solid material. Mandelkern[32], using thermal data, also contends that only methyl groups enter the lattice.

Some relevant data is available from work done on solution grown single crystal material. In 1959 Geil[33] grew crystals of branched polyethylene from solution. If the branches are randomly spaced along the main chain, then some of them must be included within the crystalline zones. More recently[34] ethylene–propylene and ethylene–butene copolymers with up to 30 methyl groups per 10^3 C atoms have been grown chain folded from solution. Martuscelli[35] has shown that the methyl groups can enter the crystalline core more easily than ethyl groups. Keller[36] has confirmed this, and has shown that the ethyl groups are mainly located outside the crystalline core. Those that are included in the crystalline core do so near to the edge where they disrupt the structure.

Thus, a structural model typical of either melt or solution crystallized branched polyethylene has not been established.

RESULTS AND DISCUSSION

In this paper we have studied the crystallization of branched polyethylene from the melt. The approach adopted was as follows: a number of branched polyethylene samples were characterized by ^{13}C n.m.r. They were then melted, quench cooled and etched with fuming nitric acid. After degradation, the relative proportions of ethyl and other side chains were again measured and compared with those obtained prior to etching. The principle behind the method adopted, is that in the reaction between linear polyethylene and fuming nitric acid, the amorphous material is quickly removed to leave a crystalline core which is only slowly attacked[36–41]. Assuming that branched polyethylene behaves in a similar way, any branches left in the material after etching must have been in the crystalline core. In this way one can, in principle, obtain information on the location of the different types of branch within the overall structure. We give experimental details of the investigation below.

Characterization of specimens

Nuclear magnetic resonance spectra were obtained using a Varian pulsed Fourier transform model XL-100-15 NMR spectrometer on very concentrated solutions in dichlorobenzene at 415K.

The total methyl content was determined using a computer deconvolution routine on the band arising from the infrared* active methyl symmetric deformation mode ($\sim 1380\ cm^{-1}$). Unfortunately, nitro groups (which are introduced during etching) absorb strongly in this region and obscure the methyl absorption. To overcome this problem, the nitro groups were reduced to amines by reaction with tin (II) chloride in hydrochloric acid at 333K for one day. Alternatively, the total methyl content was determined by ^{13}C n.m.r.[23]. The error in this value is estimated to be $< \pm 1$ methyl/10^3 C atoms.

The branched polyethylene samples used in this research were then characterized as described in ref 22 and the chain distributions are given in *Table 1*.

Method of degradation of polyethylene

Although the reaction between linear polyethylene and fuming nitric acid has been extensively studied, this is not true for other polymers. To study how branched polyethylene behaves in this reaction, we followed the weight loss, melting point, crystallinity and branch concentrations as a function of the sample thickness, the reaction temperature and time. Another, and important, parameter to follow would have been the molecular weight. Unfortunately it was not possible for us to do so, but we feel that this failing does not detract from the main point of this paper.

Samples for etching were melt pressed into films, quenched into ice/water, and cut up into plaques 1 by 0.5 cm. The degradation was carried out in a vented tube suspended in a thermostatically controlled waterbath. To prevent any differential degradation of the plaques, they were kept below the surface of the acid with a plug of glass wool. The degraded plaques were washed with water and allowed to stand in concentrated ammonium hydroxide to terminate the reaction. The samples were then again washed with water, methanol, and vacuum dried to less than 0.04 mmHg.

The effect of sample thickness was investigated because it was felt that there might be a penetration effect which could affect the validity of our results. Samples of thickness 0.5 and 1.1 mm were prepared in the normal way, whilst specimens only 0.1 mm thick were microtomed off the edge of a quenched film 1.0 mm thick to produce a sample in which we would expect to observe a maximum surface effect.

The results of the degradation at 333K are shown in *Table 2*. Clearly there is a significant different in weight loss between the 1.1 mm and the 0.5 mm thick samples. However, reducing the thickness to 0.1 mm does not appreicably affect the weight loss. Thus, 0.5 mm was chosen for the optimum thickness for all further samples.

Turning now to the effect of temperature on the degradation reactions; the most widely used temperature for the etching of linear polyethylene is 333K. It was therefore decided to use this temperature here. However, the γ-transition of branched polyethylene occurs close to 330K, and as this might be associated with a structural change capable of influencing the reaction, two other convenient temperatures, well removed from this, were selected *viz:* 318 and 348K.

Table 2 The effect of sample thickness on the weight loss of sample A etched at 333K

Oxidation time (h)	Weight loss for different thicknesses (%) 0.1 mm	 0.5 mm	 1.1 mm
6	9	9	3
13	45	40	27
19	50	48	44

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* Infra-red spectra were obtained using a Grubb Parsons Spectromaster mk II infra-red spectrometer on melt pressed films.

Table 3 The effect of reaction temperature on the degradation of sample *A* by fuming nitric acid. The sample was 0.5 mm thick and had been quenched from the melt into ice/water

Oxidation time (h)	Weight loss at different temperatures (%)			Crystallinity* at different temperatures (%)			Side chain loss† at different temperatures (%)		
	318K	333K	348K	318K	333K	348K	318K	333K	348K
0	0	0	0	61	61	61	0	0	0
0.5	–ve	–ve	–ve	61	63	66	3	9	–
1.5	–ve	–ve	–ve	68	68	69	7	15	20
4.5	3	10	24	69	71	81	15	27	61
18.5	4	41	46	75	81	87	24	73	85
40.5	49	58	64	80	86	91	61	–	–

* The X-ray crystallinities were calculated by the straight ratio method using diffraction patterns recorded on a Philips wide angle diffractometer with nickel filtered CuKα radiation (λ = 0.154 nm) as a source;
† infra-red result; — —, not determined

From *Table 3*, we note that any differences between the reactions at 333 and 348K are minor, and may be easily explained in terms of the larger rate constant at the latter temperature. The weight loss for the reaction at 318K appears to be constant for the first 15 h, and then to increase dramatically. This, and the weight gains early in the reaction, are felt to be due to retention of the reaction products. Samples etched at 348K tend to disintegrate, and as the reaction at 318K proceeds at such a slow rate, it was decided to use 333K for further reactions.

Degradation of the amorphous vs. crystalline material

Since the frequency of the Raman† active longitudinal acoustic mode (*LAM*) is inversely proportional to the length of the *trans* CH_2–CH_2 sequence of the crystalline core[42], any change in the core thickness as a consequence of the nitric acid degradation would be reflected in an increase in the frequency of the *LAM*. During the degradation of sample *A* at 333K, no significant change was observed during the first 12 h. There was, however, a 10% reduction in the Raman estimated core thickness during the subsequent 12 h. Thus, removal of the amorphous content of branched polyethylene predominates in degradation carried out at 333K in the first phase of the reaction. After this, it is clear that degradation of the crystalline core is significant.

As annealing is thought to involve structural reorganization of a polymer, its effect on the degradation reaction was studied. Samples were maintained at 370K for 2 h prior to etching. The reaction was carried out on polyethylene *A* for times ranging from 0.5 to 40.5 h. *Table 4* shows a comparison of the data for the annealed sample, with that for a melt quenched specimen. If annealing does produce any structural reorganization, then we would expect the weight and side chain loss for the two samples to be different.

The crystallinity and *LAM* were unchanged after annealing, showing that there was no significant change in the molecular order. This conclusion is supported by the similarity of the data for the quenched and annealed samples in *Table 4*. The difference in weight loss, early in the reaction, may be thought to be due to an increase in density during annealing. This leads to slow diffusion of the reaction products into the surrounding acid which gives rise to an anomalously low observed reaction rate. The problem solves itself when the macrostructure of the polymer breaks down once degradation is extensive.

Table 5 shows the distribution of branches, as determined by ^{13}C n.m.r., for three branch polyethylenes before degradation, after etching for 12 h (when most of the amorphous material has been removed), and after etching for 24 h (when virtually all the amorphous material has been removed, and the core is only slightly degraded). From these data we conclude that the rate of loss of each type of branch is consistent from sample to sample, and furthermore, the loss of ethyl groups is matched by the loss of butyl groups.

The fact that about half of the longer groups remain, even after degradation for 24 h, requires that many reside in a crystalline environment. However, only a small number of butyl groups survive, and almost all of the ethyl groups are removed after 24 h of degradation. Clearly, this means that they must have been excluded from the core during the crystallization process, or that they must be very sensitive to the acid wherever they lie in the system (i.e. accessible through 'Channels' of imperfection[36,43]. We find the latter proposal unacceptable because degradation would require replacement of the ethyl side chains within a crystalline environment by bulky –COOH and –NO_2 groups.

Thus we are faced with a dilemma; it is widely considered that in branched polyethylene the ethyl side groups are normally accommodated within the crystalline cores, but that the butyl groups have difficulty in so doing. On the other hand, the longer branches can co-crystallize easily. Our data cannot be interpreted in this way.

The data reported here, together with some new data and a structural model of branched polyethylene, will be presented and discussed in a subsequent paper.

Table 4 The effect of annealing sample A on the degradation reaction. Q, quenched sample; A, annealed sample

Oxidation time (h)	Weight loss (%)		Side chain loss (%)		Crystallinity (%)	
	Q	A	Q	A	Q	A
0.5	–ve	–ve	9	8	63	64
1.5	–ve	–ve	15	16	68	68
4.5	10	2	27	30	71	72
13.5	41	13	73	67	81	83
40.5	58	51	–	–	86	85

–, not determined; * infra-red result

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† Raman spectra were obtained from a Coderg T800 (triple monochromator) powered by a Spectra Physics model 170 argon ion laser, operating at 514.5 nm.

Table 5 The effect of nitric acid degradation of the number of ethyl (C_2), butyl (C_4) and longer ($\geqslant C_5$) branches per 10^3C atoms for three branched polyethylenes, as determined by ^{13}C n.m.r.

Oxidation time (h)	Sample *A*			Sample *B*			Sample *C*		
	C_2	C_4	$\geqslant C_5$	C_2	C_4	$\geqslant C_5$	C_2	C_4	$\geqslant C_5$
0	11	14	12	21	22	17	14	17	14
12	0	6	5	3	5	11	4	6	9
24	0	5	7	0	4	10	1	4	6

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