Chain branching in high pressure polymerized polyethylene: 2.

J. Vile, P. J. Hendra and H. A. Willis
Department of Chemistry, The University, Southampton, SO9 5NH, UK

and M. E. A. Cudby* and A. Bunn
ICI Petrochemical and Plastics Division, Wilton, TS6 8JE, UK
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In a paper 6 years ago, we reported on the detailed molecular structure of lamellar crystalline high pressure polymerized polyethylenes rich in branching. We showed that the crystalline cores contained few ethyl and butyl side-branches but did contain long side chains. In this paper, we exploit recent developments in technique to refine our observations, improve their rigour and extend them to commercially significant high-pressure polymerized polyethylenes of modest side-branch content. We also study and report on some common ethylene olefin copolymers. We conclude that our earlier conclusions are correct, that the side-branches are bunched rather than being randomly situated along the backbones and that most of the branches, and in particular the branched branches, become concentrated in the inter-core regions on melt crystallization.

(Keywords: branched polyethylene; ^{13}C nuclear magnetic resonance; side branches; transition zone; branch content; nitric acid oxidation)

INTRODUCTION

Until relatively recently, it was not possible to define with any precision, the structure of the chains in high pressure polymerized polyethylene (for convenience referred to in this paper as 'branched polyethylene'). The situation in 1977 was reviewed extensively in the first paper of this series[1] where it was explained that all of the classical methods (infra-red studies, degradation, analyses, etc.) had been rendered obsolete by the then recently developed ^{13}C n.m.r. spectroscopy. This technique enabled one to 'acquire some feel' for the length of the side chains in branched polyethylene and their distribution. We were, and still are, primarily interested in the way the branches controlled the melt crystallization process, and hence the morphology of the solid polymer. To this end, we oxidized (under controlled conditions) solid specimens of branched polyethylenes with nitric acid and then investigated the n.m.r., infra-red, X-ray diffraction and other properties of the oxidized fragments. The oxidation technique is known from experience with linear polyethylene, to strip away the inter-core zones of the stacked lamellae leaving the cores relatively intact[2]. Although the method is fraught with considerable experimental difficulty and some doubt regarding its precise procedure at molecular level, nevertheless, we were able to demonstrate with some conviction that the lamellar cores contained long side chains co-crystallized with the polymethylenic backbones whilst the shorter side chains were to be found in the inter core amorphous layers.

The work we reported was carried out on samples of branched polyethylene especially selected to have very high branch contents. This was necessary if detectable quantities of the branches were to be available for measurement in the oxidized fragments. In this paper, we exploit experimental improvements which have resulted in an increase in the sensitivity of ^{13}C n.m.r. measurements and hence examine commercial grades of branched polyethylene with modest branch concentrations. The analysis of ^{13}C n.m.r. spectra in this type of paraffinic system has also improved in detail and rigour over the last few years†. This too is exploited here. Finally, we have attempted to compare the behaviour of branched polyethylene as it melt crystallizes with that of some random ethylene–propylene, ethylene–butene, ethylene–hexene and ethylene–octene copolymers with particular reference to the role of the branches in influencing the crystallization processes and hence the morphology of the solids.

EXPERIMENTAL

Three specimens of branched polyethylene labelled A, B and C were selected from those available, all of which satisfied the following criteria:

(a) The branch concentration varied between samples but are high enough so that after oxidation sufficient branches to be detectable by ^{13}C n.m.r.

(b) The distribution of side branches should vary between samples.

The specimens selected were deliberately different from those examined and reported in ref. 1 in that the ethyl content was much smaller. If we add our new samples to those reported earlier, we have a wide range of specimens, and therefore for convenience repeat in this paper the relevant data from ref. 1. Samples A, B and C were carefully examined by ^{13}C n.m.r. and the number of

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* New address: School of Chemical Studies, University of East Anglia, Norwich, UK

† It is now possible to distinguish features in the NMR spectrum ascribable to ethyl, butyl, amyl and hexyl plus longer side chains[3].

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branches of each type were estimated. The total of side chains were then normalized against infra-red absorption measurements[4] (see *Table 1*). For reference purposes, 4 copolymers of ethylene were examined. Their composition will also be found listed in *Table 1*.

The polyethylene and copolymer samples were made into sheets ($\approx$0.5 mm thickness), cut into pieces (0.5 cm × 1.0 cm) and digested in hot, highly concentrated nitric acid ($>95\%$ conc.). The details of the procedure and that required to purify the oxidized species will be found in ref. 1.

All ^{13}C n.m.r. spectra were recorded on solutions in *o*-dichlorobenzene using a Varian XL 100-15 pulsed Fourier Transform spectrometer controlled by a Varian 620i computer[5]. Differential scanning calorimetry (d.s.c.) was used to determine the crystallinity and melting point of the oxidized specimens. A Perkin Elmer D.S.C. 2b instrument was used in this work. Some laser Raman measurements are referred to below (obtained on a modified Coderg T800 spectrometer using Ar^+ laser excitation).

RESULTS

In our previous paper on this subject[1], we discussed the optimum conditions for the nitric acid digestion of the polymer and details were given of the weight loss, sample crystallinity (as determined by X-ray diffraction) and the residual branch content, all as a function of time. The data were interpreted assuming a fast initial reaction (in which most of the amorphous material is removed) accompanied by an appreciably slower digestion of the crystalline core. The oxidation results are presented with those transcribed from ref. 1 in *Table 1*. Thus, the consequence of nitric acid oxidation for 6, 12 and 24 h is available. In *Table 1* we also give equivalent data on random copolymers of ethylene with modest amounts of propene, butene, hexene and octene. Several important points arise from consideration of *Table 1*.

(1) The unoxidized branched polyethylenes are similar as far as their butyl and longer side chains are concerned even though the span of methyl contents covers the range 23 to 60 Me for 10^3 C atoms. The primary source of the

Table 1 The results of oxidation on the level of branching in a range of branched polyethylene and ethylene olefine copolymers. For branched polyethylene, samples 1, 2 and 3 refer to an earlier study. Samples A, B and C of lower branch content than the earlier ones are reported for the first time. Three ethylene olefine random copolymers are indicated for comparison

		Side branch content				
Sample	Oxidation[a] time	Ethyl branches/ 1000 C atoms	Butyl branches/ 1000 C atoms	$\geqslant C_5$[b] branches/ 1000 C atoms		Total methyl branches/ 1000 C atoms
1	0 h	11 (100)	14 (100)	12 (100)		37 (100)
	12 h	0 (0)	6 (43)	7 (58)		12 (32)
	24 h	0 (0)	5 (36)	5 (42)		10 (27)
3	0 h	14 (100)	17 (100)	14 (100)		45 (100)
	12 h	4 (29)	6 (35)	9 (64)		19 (42)
	24 h	<1 (<7)	4 (23)	6 (43)		11 (24)
2	0 h	21 (100)	22 (100)	17 (100)		60 (100)
	12 h	3 (14)	5 (23)	11 (65)		19 (32)
	24 h	0 (0)	4 (18)	10 (59)		14 (23)
				Amyl branches/ 1000 C atoms	$\geqslant C_6$[c] branches/ 1000 C atoms	
A	0 h	2.0 (100)	12.5 (100)	3.5 (100)	5.0 (100)	23.0 (100)
	6 h	1.5 (75)	10.0 (90)	3.0 (86)	3.5 (70)	18.0 (78)
	12 h	<1 (<50)	5.0 (40)	~1 (~30)	3.0 (60)	10.0 (43)
	24 h	→				~2 (~9)
B	0 h	3.0 (100)	12.5 (100)	4.0 (100)	8.5 (100)	28.0 (100)
	6 h	~2 (~67)	10.5 (84)	3.0 (75)	6.5 (76)	22.0 (79)
	12 h	~1 (~33)	5.0 (40)	<1 (<25)	4.0 (47)	11.0 (39)
	24 h	→				~2 (~7)
C	0 h	4.5 (100)	17.5 (100)	4.5 (100)	10.5 (100)	37.0 (100)
	6 h	~2 (~44)	9.5 (54)	2.5 (56)	5.0 (48)	19.0 (51)
	12 h	~1 (~22)	6.0 (34)	2.0 (44)	4.5 (43)	13.5 (36)
	Copolymers	Ethylene-[d] butene	Ethylene-[d] hexene		Ethylene-[d] octene	
	0 h	17.5 (100)	12.0 (100)		15.0 (100)	
	6 h	15.0 (85)	9.0 (73)		13.0 (88)	
	12 h	9.0 (49)	4.0 (33)		6.0 (40)	

[a] In the table we report side branch content of untreated and treated specimens oxidised with nitric acid for times of 6, 12 and 24 hours. Side branch contents derived from ^{13}C n.m.r. investigation are then tabulated. Bracketed figures represent the percentage of remaining side branches before and after oxidation

[b] $\geqslant C_5$ is the content of side branches of length $-C_5H_{11}$ and longer totalled together

[c] $\geqslant C_6$ is the content of side branches of length $-C_6H_{13}$ and longer totalled together

[d] Mole % 98.2% ethylene – 1.8% proplyene; 96.2% ethylene – 3.8% butene; 96.7% ethylene – 3.3% octene; 97.4% ethylene – 2.6% hexene

Table 2 Crystallinity measurements

Sample	Density[a] (%)	X-ray[b] diffraction (%)	D.s.c.[c] (%)	Raman[d] spec (%)	D.s.c. normalized Cryst (%)	D.s.c. normalized ΔHf (cal/g)
A	46.5	51.4	33.2	52.0	50.0	43.8
B	42.6	47.9	32.3	45.0	45.0	47.3
C	43.5	43.8	30.9	43.5	43.5	46.8
Ethylene–propylene	–	53.4	48.8	56.5	–	–
Ethylene–butene	–	43.2	37.8	50.0	–	–
Ethylene–hexene	–	49.0	40.6	54.3	–	–
Ethylene–octene	–	43.3	35.3	47.8	–	–

[a] Assumes two components with ρ_{cryst} = 1.013 g/cm[14], $\rho_{noncryst}$ = 0.855 g/cm[17]

[b] Based on the assumption that the X-ray peaks due to a crystalline phase can be separated from the amorphous background[18]

[c] Assumes that the non crystalline material does not contribute to the melting endotherm ΔHf_{cryst} = 65.9 cal/g[19]

[d] Based on the presumption that Raman modes due to a crystalline phase can be separated from those arising from a disordered phase[20]

Table 3 Melting temperature (°C)

Sample	Untreated	6 h	12 h	24 h
A	109	108	111	117
B	109	107	112	114
C	104	106	111	–
ethylene–propylene	121	119	122	–
ethylene–butene	117	120	120	–
ethylene–hexene	125	124	125	–
ethylene–octene	128	125	125	–

differences between the specimens lies in their ethyl contents. As a comparison, the included ethylene butene copolymer has a very high concentration of ethyl group (in this case definitely isolated).

(2) On oxidation for 12 h, several trends of significance appear. Butyl groups are reduced to about forty per cent of their original concentration unless the initial concentration is exceptionally high. This comment appears to apply to the ethylene–hexene copolymer. The ethyl groups seem to behave differently. In the branched polyethylenes the ethyl content is drastically reduced but *not* in the case of the ethylene butene copolymer where 12 h oxidation seems to have a quite modest effect. Longer side chains appear to suffer slow oxidations of 6 and 12 h.

Some years ago, Marsden[6] examined the effect of nitric acid degradation on linear polyethylene and concluded somewhat surprisingly, that oxidation did not significantly alter the melting temperature of polyethylenes. We therefore checked the melting ranges of our oxidized branched polyethylene specimens. The results are presented in *Table 3*. Clearly, oxidation alters this characteristic in copolymers very little, whereas in the polyethylene the melting points invariably rise with oxidation. It is also known that heavily oxidized branched polyethylenes have relatively high degrees of crystallinity as determined by X-ray techniques[6].

DISCUSSION

Before attempting an interpretation of the experimental results described above it is worthwhile to review the present state of knowledge and debate over the nature of the side branches in polyethylenes produced by high pressure polymerization.

In 1953 Roedel[7] proposed a reaction mechanism to explain the formation of the known existence of short chain branches. His mechanism involves intramolecular hydrogen transfer (the so-called 'back biting' mechanism), leading to the formation of butyl side branches resulting from 6 (and 7) membered transition states.

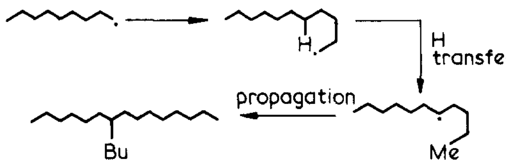

Figure 1 Roedel's mechanism for the production of butyl branches

This mechanism, as it stands, provides no explanation for the known presence of ethyl side groups. However, if after the addition of another molecule of the ethylene to the radical, a further intramolecular hydrogen transfer step occurs—then ethyl groups can indeed be formed[8]. The second hydrogen transfer step produces two adjacent ethyl groups or a 2-ethyl hexyl branch. The process is illustrated below.

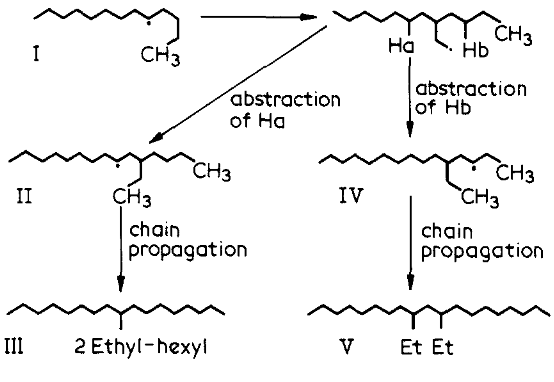

Figure 2 Willbourn's mechanism for the production of branched and bunched branches

Clearly, this process may be continued to give groups 3, 4, 5 or more, short branches.

Mandelkern and coworkers[9], on investigating the shorter branches in branched polyethylene, observed resonances in the ^{13}C n.m.r. spectrum ascribable to branched and 1,3 paired ethyl branches. They therefore suggest the Roedel's backbiting mechanism, which would produce only isolated ethyl groups, needs to be modified. Willbourn's suggested mechanism is not completely satisfactory, either in that although it predicts the presence of branched branches and paired ethyl groups, it requires that the concentration of ethyl groups is greater than that of butyl groups. However, Mandelkern's observation is that n-butyl branches are invariably present in the highest concentration and the data in *Table 1* confirms this. It is therefore clear that a more detailed and systematic study of polymerization mechanism needs to be undertaken.

Stoiljkovich and Jovanovich[10] recently proposed that the number and type of branches present in branched polyethylene depend on the degree of order of the compressed ethylene molecules during the polymerization reaction. They suggest that the mechanism for short chain branching is based on the organization of supermolecular species in compressed ethylene, and hence support the mechanisms put forward earlier by Van der Molen[11] and Machi[12]. Van der Molen[11] suggested as an alternative to Roedel's back biting mechanism, that β migration of the primary free radical occurs (1:3 hydrogen transfer). Machi *et al.*[12] went on to propose that bimolecular complexes of ethylene react together for chain propagation to occur and that these activated complexes can produce chain branching on occasion.

Turning now to the formation of branched branches: evidence for their presence was first formulated by Tirpak[13] who concluded from detailed infra-red dichroic studies of oriented polymers that ethyl groups are present and tend to be oriented approximately 60° from the chain axes. This observation leads to the proposal that they are predominantly on the 1st, 2nd or 3rd carbon atom of a single branch, e.g. a 2-ethyl hexyl unit. Carey, Elston and Phibs[14] concluded on the basis of d.s.c. data that some 60% of the short chain branches are themselves branched or tightly bunched along the backbone. Axelson *et al.*[9] observed in n.m.r. studies resonance at 37.6 ppm in the ^{13}C spectrum of branched polyethylene and identified this with a methine carbon atom in a 1,3 diethyl branch. Thus we may confidently assume that these complex branches do in fact occur in this type of polyethylene.

Structural model for branched polyethylene

It is clear from our nitric acid degradation results that the ethyl groups when present are largely excluded from the crystalline cores and are hence accessible. The more bulky butyl groups appear to be more widely distributed throughout the structure. Considering now the ethylene butene and ethylene hexene copolymers it is clear that these behave differently to the branched polyethylenes. Since the copolymers are random with side chains situated some 100 Å apart or so on average this observation is expected. Clearly only some of the side groups will find themselves in the cores. Keller[21-24] has commented in the past on the structure of ethylene butene copolymers and reaches much the same conclusion regarding the situation of the ethyl groups.

One feasible explanation for the marked accessibility of the ethyl group in polyethylenes 1, 2 and 3 is to place them within larger structural units such as 1,3-diethyl branches or 2-ethyl hexyl units both being sufficiently bulky and angular to preclude their pesence within cores. The oxidation data of *Table 1* and that on melting points contained in *Table 3* leads us to the further conclusion that long side chains (and of course butyl ones) must be present in the cores. Thus we have long linear branches within the crystalline cores and branched ones without. Cocrystallization of long linear side branches is not a novel proposal[15].

The measurement of degree of crystallinity in polymeric species produces a set of conclusions which are phenomenological. With care, however, the comparison of the apparent crystallinity determined by a variety of methods can be useful, since none measure the strictly defined molar proportion of crystalline species but rather estimate against various criteria the state of order of the specimen. Of all the methods available, the most stringent is X-ray diffraction since well developed crystalline order over considerable interatomic distance is required to satisfy the Bragg Equation. However, vibrational spectroscopy can indicate the presence of chemical species regardless of their environments or if appropriate analyses of the spectra are used the technique can indicate the presence or otherwise of bundles of extended regular chains. Thus we could envisage the proportion of a specimen crystalline to infra-red and Raman spectroscopy yet amorphous as far as X-ray diffraction is concerned.

We have measured the crystallinity of several of our specimens by a variety of methods including X-ray diffraction, thermal measurements, density and vibrational spectroscopy. The results and the premise in each case upon which the estimations are based are given in *Table 2*. It is quite clear that branched polyethylenes A, B and C have crystallinity values near 45% for all methods other than d.s.c. The consequently anomalous low value of ΔH_{fus} has previously been noted[16]. In the copolymers, the situation is a little more complicated but again d.s.c. provides rather low estimates. If we arbitrarily equate the crystallinity estimates from each technique the inevitable consequence is that the ΔH_{fus} value for the branched material differs from that of linear polyethylene as follows:

$$\Delta H_{\mathrm{fus}} \text{ branched P.E.} \approx 45 \text{ cals/g}$$

$$\Delta H_{\mathrm{fus}} \text{ linear P.E.} \approx 64.9 \text{ cals/g}$$

This proposition presupposes that any thermal effect near 120°C contributed by the amorphous phases in linear or

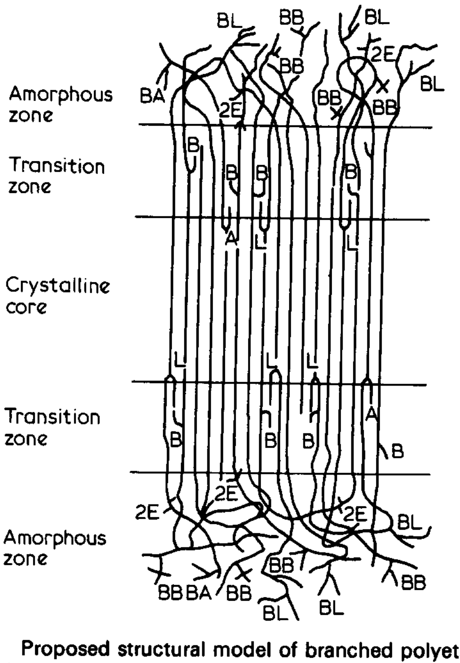

Figure 3 Proposed structural model of branched polyethylenes used in this investigation, where B = butyl branch; A = amyl branch; L = hexyl and longer branches; E = ethyl branch; BB = branched butyl branches; BA = branched amyl branches; BL = branched hexyl and longer branches

branched polyethylenes is either negligible or at least identical in each case; a daunting presumption. If a model in branched polyethylenes containing a three phase system with an essentially crystalline core sandwiched between paracrystalline layers (between amorphous material) is accepted, then the ΔH_{fus} of the core is probably close to 65 cal/g. If we further presume that methods of crystalline estimation other than d.s.c. tend to record crystalline and paracrystalline species as ordered we can estimate the ΔH_{fus} value for the paracrystalline phase at about 25 cal/g. Although far from proved we feel this model cannot be regarded as impossible since it is almost certain that the paracrystalline phase would be sensitive to oxidation after the amorphous phase is removed and its distorted crystalline nature would result from the inclusion of side branches. In conclusion, our suggested structure is shown in *Figure 3* where it can be seen that the crystalline zone is highly ordered, containing only a few isolated amyl and longer branches, the paracrystalline layers contain some isolated butyl branches and the amorphous zone, having a liquid like structure, contains bunched and branched branches. One weakness the authors fully accept is that we have presumed throughout this work a degree of homogeneity that may not be present. It may well be that a higher degree of branching is associated with short chains. This point will be discussed in a future publication.

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