A study of linear low-density polyethylenes: branch content, branch distribution and crystallinity

C. France, P. J. Hendra, W. F. Maddams and H. A. Willis
Department of Chemistry, The University of Southampton, Southampton SO9 5NH, UK
(Received 23 June 1986; accepted 13 October 1986)

Three linear low-density polyethylenes (LLDPE's), have been studied using nitric acid oxidation and solvent extraction techniques. These methods are well established in the morphological analysis of low density polyethylenes and related materials. Coupled with familiar spectroscopic and calorimetric methods, this publication highlights the comparability and significant differences between the morphology of the LLDPE's and that of high pressure polymerized ethylene homopolymers. The most significant conclusion is that the branches are unevenly distributed along the chains. The extractable fraction of the samples contains more branching than the residue. The branched material is concentrated in the intercore zones of the lamellar stacks, i.e. the cores are predominantly pure polymethylene. This comment applies both to rapidly cooled and annealed specimens alike.

(Keywords: linear low-density polyethylene; chain branching; nitric acid oxidation; solvent extraction)

INTRODUCTION

Linear low-density polyethylene (LLDPE), a collective term used to describe copolymers of ethylene with a small concentration of an α-olefin[1], has increased markedly in commercial importance in recent years, for two reasons. The first is a development of a new generation of more versatile catalysts, making it possible to copolymerize higher α-olefins with ethylene in a low pressure gas or liquid phase process. Secondly, the different properties exhibited by the LLDPE's render this class of materials more suitable in some applications than conventional high or low pressure polyethylenes. It is claimed that LLDPE has greater tensile strength, tear strength, and a higher environmental stress crack resistance than the former and better flexibility than the latter. Neither are the LLDPE's equivalent to a blend of conventional high and low pressure polyethylenes, since the latter has been shown to consist of a heterogeneous mixture of two crystalline phases, each phase peculiar to the material used in the blend[2,3].

A large proportion of the range of LLDPE's now commercially available are ethylene/1-butene copolymers, and so contain ethyl branches. Hexyl branched material, as well as a limited number of methyl, butyl and isobutyl branched copolymers have also been produced.

Branching typically occurs in fifteen to twenty carbon atoms per thousand along the main chain. These materials provide the polymer spectroscopist with a series of polyethylenes containing a high level of a particular type of branch, and are therefore valuable both for fundamental studies and for analytical characterizational work. In the former context, and in the light of earlier work from this laboratory on the morphology of a series of LDPE samples[4], it is clearly of interest to examine a representative range of LLDPE materials. This paper presents the results of such a study.

A morphological understanding of the branch sitings is relevant to the composition of the disordered zones, on which the physical performance of the material depends.

EXPERIMENTAL

Samples

Three samples were chosen as being representative of the rather wide range of LLDPE materials now available, both with respect to branch type and concentration. They were:

(i) A BP Chemie ethylene/1-butene copolymer, containing 18.5 ethyl branches per thousand carbon atoms.
(ii) Unifos 8141, ethylene/1-hexene, 8.1 butyl branches per thousand carbon atoms.
(iii) Dowlex 2045, ethylene/1-octene, 11.5 hexyl branches per thousand carbon atoms.

The branching levels in the above materials were determined by ^{13}C n.m.r. spectroscopy.

Techniques

The melting points of the samples were determined by applying standard techniques to the relevant thermogram obtained from a Perkin–Elmer DSC-2 calorimeter. The instrument was calibrated by comparing the polymer thermogram with that obtained from a known weight of indium. The melting point is defined as the temperature at which the leading edge of the indium endotherm intersects with the baseline of the polymer thermogram, arranged so that the leading edge passes through the thermogram peak. This method was recommended by the instrument manufacturer[5] and has proved satisfactory in previous work in this laboratory.

0032-3861/87/050710-03$03.00

Three independent methods were used for monitoring crystallinity: density, differential scanning calorimetry and Raman spectroscopy.

Density values were obtained from a density gradient column; crystallinities being calculated on the basis that

$$\rho \text{ crystalline}:\rho \text{ amorphous} = 1.00:0.85 \text{ g cm}^{-3}$$

It is necessary to adopt a value of ΔH_{fusion} for the crystalline material in calculating crystallinity from d.s.c. measurements. The value of 66.2 cal g^{-1} suggested by Aggarwal[6] was used.

The method of Strobl and Hagedorn[7], based on a band intensity analysis near 1400 cm^{-1}, was used to determine the crystallinity from Raman data obtained from a Coderg T800 spectrometer.

The Raman longitudinal acoustic mode was used to monitor the lamellar core thickness by the well established method used previously in this laboratory[4,8].

The branch content of the samples was determined by infra-red[9] and ^{13}C n.m.r. spectroscopy. The infra-red method, which uses the molar absorbance of the 1378 cm^{-1} band, yields values which are dependent on branch length[10,11]; it is customary to refer to the values so obtained as 'methyl' contents. The ^{13}C n.m.r. method is specific for individual types of branches, and work involving a comparison of the two methods is currently being undertaken in this laboratory.

Either method is highly reproducible, and satisfactory relative values of branch content may be obtained for any particular experiment. The choice of method used was dependent on the nature and quantity of the sample.

The ^{13}C n.m.r. spectra were run at 67.78 MHz on a JEOL FX270 spectrometer. 10% solutions in a 4:1 mixture of hexachlorobutadiene and 1,2-tetrachloroethane-d_2 were heated at 140°C for several hours to ensure complete dissolution and homogeneity. Spectra were run at this temperature using between two thousand and five thousand accumulations to obtain satisfactory signal to noise ratios.

Two types of information were gained from the spectra: the content of isolated branches of the particular type in question, and the non-random or 'bunching' behaviour of the branches, assessed in terms of the concentration of 1,3- and 1,5-dialkyl groups, based on the assignments of Hsieh and Randall[12,13].

The three samples were subjected to soxhlet extraction with n-heptane for 48 h. This solvent was chosen because it removes a significant proportion of the polymer and should, in principle, give a degree of fractionation with respect to molecular weight and possibly branching. Prior to extraction, the samples were melt crystallized by quenching from 150°C in iced water. They were then cut into pieces approximately 3 × 3 × 5 mm. The residue after extraction was dried to constant weight in a vacuum oven, and the extract was recovered from solution by way of a rotary evaporator.

The melt crystallized polymers, in the form of specimens 10 × 5 × 0.5 mm were digested in fuming nitric acid at 60°C; the conditions were chosen to be comparable with earlier work[4,14,15]. After completion of the reaction, residual nitric acid was removed by successive washing with water, ammonium hydroxide, water and then methanol. The samples were finally dried in a vacuum oven.

RESULTS AND DISCUSSION

Solvent extraction

Previous work[16] has shown the value of solvent extraction in achieving a degree of fractionation with respect to branching and molecular weight. The solvent in fact removes lower melting point material which is composed of the lower molecular weight fraction of the polymer, and also branched material which is unable to form the higher melting point crystals characteristic of more linear chains[17].

The results for the branching levels, determined by infra-red spectroscopy, for the original materials together with the respective extracts and residues, are given in *Table 1*.

The low proportion of extractable material present in the Unifos 8141 suggests that the bulk of this material is of a high molecular weight. Although the extract has a markedly higher level of chain branching than that of the original material, the fact that it comprises a relatively small proportion of the total makes it difficult to draw any firm conclusions.

An appreciable degree of extraction has occurred in both the hexyl and ethyl branched polymers with the extracts showing a substantial increase in branch content and a corresponding decrease in the residues. It is reasonable to surmise that the increased branching is associated with polymer chains of lower molecular weight, although this conclusion must remain tentative until a detailed fractionation is undertaken with the appropriate characterization of the materials so obtained.

An extraction undertaken on a conventional high pressure, low density polyethylene, Alkathene 23, the results from which are included in *Table 1*, show that fractionation with respect to chain branching is clearly poor. The implication here is that branching is uniform with respect to molecular weight, which is not the case with the LLDPE's studied.

Table 2 gives values for the lamellar core thickness and the crystallinity for the original material and the residue from the extractions. Each of the three residues shows an increase in crystallinity and core thickness. Although this may be partly attributable to an annealing effect during the extraction at 98°C, another factor may be the decrease in branch content, since branching may limit the extent of the crystalline phase if branches are rejected from the crystal cores.

Nitric acid etching

Various workers have shown that the etching of low-density polyethylene by fuming nitric acid results in

Table 1 Infra-red results of branching determinations on four polyethylene samples after solvent extraction

Sample	Extract (wt%)	Branch content per 1000C		
		Original	Extract	Residue
BP Chemie ethyl branched LLDPE	25	24	38	15
Unifos 8141 butyl branched LLDPE	7	11	35	10
Dowlex 2045 hexyl branched LLDPE	29	12	19	8
Alkathene 23 LDPE	36	37	–	33

Table 2 Results of lamellar core thickness determinations on three LLDPE samples before and after solvent extraction

Sample	Original polymer				Residue			
	L.A.M. peak (cm^{-1})	Core thickness (Å)	Crystallinity (%)		L.A.M. peak (cm^{-1})	Core thickness (Å)	Crystallinity (%)	
			d.s.c.	density			d.s.c.	density
BP Chemie ethyl branched	19.0	150	34	42	18.0	159	52	54
Unifos 8141 butyl branched	17.5	163	46	52	16.5	173	52	55
Dowlex 2045 hexyl branched	20.5	139	34	43	18.5	154	55	54

preferential removal of the amorphous inter-lamellar material, leaving the crystalline core largely intact[18,19]. It therefore follows that branching associated with the disordered material will be lost upon nitric acid etching, and a comparison of the branching levels before and after such treatment will provide information on the placement of the branches with respect to the crystalline core. This approach has already proved successful in the case of high pressure low density polyethylene[4,14].

The determination of the branch content in the residue after nitric acid treatment by the conventional infra-red spectroscopy method is fraught with difficulty, as the nitro groups present in this material absorb strongly at 1384 cm^{-1} which obscures the 1378 cm^{-1} band used in the infra-red analysis. The branching level was therefore established by ^{13}C n.m.r. spectroscopy. The results are presented in *Table 3*.

Since up to 90% of the branching has been lost after subjection to fuming nitric acid, it is evident that the majority of branches are excluded from the crystalline core. The values given for the weight loss must represent a minimum in terms of polymeric material, since they take no account of the nitro and carboxyl groups which are introduced during the treatment. With the exception of Unifos 8141, the results indicate that removal of the amorphous and interlamellar zones must be substantially complete.

The presence of regular tight chain folding in polyethylene has been a subject of considerable controversy, and although the consensus opinion now accepts its presence in solution crystallized polymer, there is strong evidence for non-adjacent folding in melt crystallized materials[20]. Indeed it is necessary to accept the presence of a substantial proportion of loose folds in order to account for the predominant exclusion of branches from the crystalline core.

Glotin and Mandelkern[21] have applied the method of Strobl and Hagedorn[7] to determine the proportions of the three phases present in an ethyl branched polyethylene, prepared by hydrogenating a polybutadiene, similar in composition and structure to the BP Chemie material. They found an interfacial content of 15% and this requires the presence of a significant proportion of loose folds which, it is reasonable to surmise, are the sites of the majority of the branches.

CONCLUSION

The distribution of branches on the chain segments present in amorphous and interfacial regions must be markedly greater than those segments which constitute the crystalline core, since there is no evidence to suggest that branches in the crystalline core are removed by nitric acid etching. This conclusion is in line with the results of the solvent extraction experiments reported above, and is not at variance with the n.m.r. evidence, which simply sets a limit on the amount of tight chain bunching.

Given that there is this non-statistical distribution of the branches, it is reasonable to anticipate that crystallization will occur in such a way that the majority of the branches are excluded from the crystalline lattice. The overall morphology is thus envisaged to be of a similar nature to that proposed in ref. 14.

Table 3 ^{13}C n.m.r. results of branching determinations on three LLDPE samples after nitric acid etching

Sample	Original branch content per 1000C	Weight loss (%)	Residual branch content per 1000C
BP Chemie ethyl branched	18.8	34	2.0
Unifos 8141 butyl branched	8.1	26	1.1
Dowlex 2045 hexyl branched	11.5	34	1.3

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