Functionalization of Polyolefins. Determination of the Structure of Functional Groups Attached to Polyethylene by Free Radical Reactions

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Received June 1, 1989; Revised Manuscript Received October 2, 1989

ABSTRACT: In this paper the unequivocal determination of the structure of the functional groups inserted into polyethylene moieties is described. Detection of the $CH(COOEt)CH_2COOEt$ groups, grafted on the polymer backbone by reaction of molten HDPE with diethyl maleate and with dicumyl peroxide as the radical-generating species, is accomplished by comparative analysis of ^{13}C NMR spectra of the functionalized polymer and two suitably synthesized model compounds: ethyl 3-carbethoxy-4-*n*-propylheptanoate and ethyl 3-carbethoxy-4-*n*-hexyldecanoate.

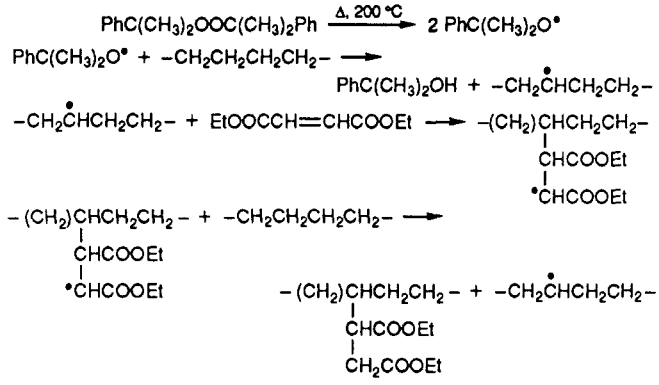
The modification of polyolefins with functional monomers, carried out by free radical reactions, is the most readily available method among those developed in recent years.[1-14] However, the true structure of the inserted functional groups has never been determined in detail, a necessary task in view of the low selectivity of radical reactions. Indeed, free radicals are so reactive that oligomerization of the functional monomer cannot be excluded a priori and the possibility of obtaining functional groups of different length and structure must be taken into account.

Recently we reported the unequivocal determination by ^{13}C NMR spectroscopy of the structure of the functional groups inserted into polyethylene by reaction between the molten polymer and ethyl diazoacetate (EDA) and generation of the functional group by thermal decomposition of the diazo compound.[15] This reaction, which proceeds via a carbene intermediate, allows the clean introduction of *isolated* CH_2COOEt units into the macromolecular backbones, substantially avoiding any side reaction.

An analogous demonstration of functionalization via free radicals has now been obtained by the same NMR method.[15] In the present study we demonstrate that the functional groups introduced into high-density polyethylene (HDPE) by reacting the polymer with diethyl maleate (DEM) at 200 °C in the presence of dicumyl peroxide (DCP) as radical initiator (1.5% by weight in respect to the polymer) are almost exclusively $CH(COOEt)CH_2COOEt$ groups.

A reasonable reaction mechanism involves a radical species, generated by DCP thermal decomposition abstracting a hydrogen atom from the macromolecule. Macroradicals, once formed, immediately attack the unsaturated functional monomer (DEM) and cause its bonding to the macromolecular backbone. Hydrogen transfer between macroradicals and macromolecules allows the completion of this reaction while generation of new macroradicals takes place (Scheme I).

Scheme I



Obviously this cannot be the only operating reaction, because cross-linking or coupling reactions among macroradicals could take place in addition to the irreversible degradation of the polymer. However, our experiments, performed on different polyolefins, such as ethylene–propylene rubber (EPR), atactic and isotactic polypropylene (aPP, iPP), and with a polyolefin/DEM ratio (by weight) equal to 1, show that such side reactions are totally prevented by the presence of DEM. The functionalization of the substrate is the prevailing mechanism.[1,16] Analogous results have also been obtained with HDPE and linear low-density polyethylene (LLDPE). The complete set of results will be discussed in a forthcoming publication.

The present investigation of the structure of functional groups has been performed by synthesizing two model compounds of the functionalized polymer and then comparing their ^{13}C NMR spectra with the analogous spectrum of a sample of functionalized HDPE (FHDPE). Similarities among the spectra were so close that isolated $CH(COOEt)CH_2COOEt$ units along the macromolecular chains (see later) appear to account very well for the functionalities present in polyethylene.

The starting polymer was a commercial HDPE containing up to 1% by weight of 1-butene. It was function-

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0024-9297/90/2223-1928$02.50/0

Scheme II

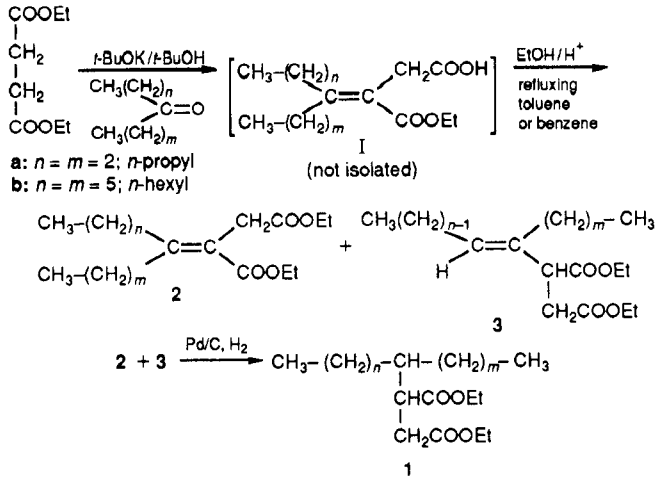


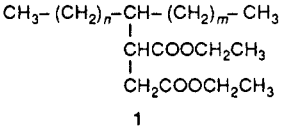
Table I
Chemical Shifts of Carbon Atoms in the Structures of FHDPE, 1a, and 1b[a]

	polymer	1a	1b	1-butene
a	173.50	174.50	174.75	
b	171.74	172.56	172.75	
c, d	60.33	60.86, 60.78	60.94, 60.87	
e, f	14.40	15.00, 14.96	15.01, 14.98	
g	33.0	32.91	33.24	
h	44.6	44.18	44.47	
i	38.5	40.12	40.86	
l, l′		34.73, 34.57	32.63, 32.37	
m, m′		21.43, 21.37	28.41, 28.36	
n, n′			30.56, 30.52	
o, o′			32.85, 32.83	
p, p′			23.70	
z		14.94, 14.89	14.90	
1				11.23
2, β				26.74,[b] 27.32[b]
br				39.69
α				34.06

[a] Chemical shifts are reported in ppm (δ). Internal reference was 1,2-dideuteriotetrachloroethane (74.3 ppm) for the polymer and deuterated benzene (128.7 ppm) for **1a** and **1b**. [b] Literature data do not allow us to assign unambiguously the chemical shifts for 2 and β.

alized by reaction with DEM and DCP following the procedure described in ref 17. Its degree of functionalization was inferred by infrared spectroscopy and calculated to be between 2.5 and 3.0 mol %.[20] The determination of the degree of functionalization has been performed by comparison of the optical density ratio of the carbonyl band (due to the functional groups) in the functionalized polymer and the methylene rocking band due to the ethylene units with the same ratio obtained for mixtures of polyethylene/poly(diethyl fumarate) of known composition. This result has been confirmed in the present study also by quantitative analysis performed by ^{13}C NMR spectroscopy.

According to the proposed mechanism, a suitable "molecular model" must have the following structure:



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with n and m as large as possible. The synthesis of such compounds is not reported in the literature except for short-chain compounds[18,21] ($n = m = 0$) of little practical value for our purpose.

Thus we decided to synthesize these low molecular weight model compounds according to the procedure reported in ref 18 and summarized in Scheme II.

Due to the higher molecular weight of the ketones employed with respect to the reported ones,[18] the condensation reactions were much slower and had to be carried out for prolonged times both for **a** and **b** (up to 67 h for **b**). A mixture of isomers **2** and **3** was obtained in both cases. The composition of these mixtures was quantitatively evaluated by NMR spectroscopy; the mixture of **2a** and **3a** had a 40:60 (in moles) composition, while the corresponding ratio for **2b** and **3b** mixtures was 30:70. The presence of **3** was probably due to the tautomeric rearrangement of the initially formed **2** as a consequence of prolonged heating in the strongly basic medium during the first reaction step.[19]

Moreover, the bulkiness of the intermediate (Ib) first obtained prevented the insertion of salt-forming groups even with strong bases and the separation of the water-soluble Ib sodium salt from the organic-soluble unreacted ketone became impossible; so, purification of the products proved troublesome. Complete purification of the **2b**, **3b** mixture was achieved only by repeated "flash chromatography"[29] on silica gel columns, employing the mixture hexane/ethyl acetate as eluent (see Experimental Part).

The mixtures of **2a** and **3a** and of **2b** and **3b** were then hydrogenated by using palladium as catalyst supported on carbon black. These reactions were rapid and quantitatively converted both **2** and **3** into **1**.

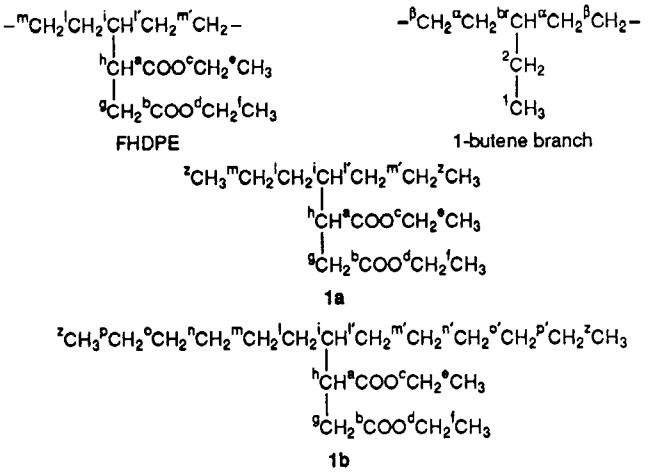
1a and **1b** were characterized by elemental analysis, ^1H NMR, and ^{13}C NMR spectroscopy.

The chemical shifts of the FHDPE, **1a**, and **1b** are compared in Table I. Analogous carbon atoms in the three structures are indicated with identical letters in order to avoid any misleading interpretation. Letters have been assigned according to Scheme III.

The spectrum of FHDPE (Figure 1) and the enlarged zone between 65 and 5 ppm (Figure 2) are reported.

Due to the very good resolution, full assignment of the spectrum was possible. n-Heptane impurities, deriving from the solvent employed to perform extractions, have been detected and marked with an asterisk.

Scheme III
Schematic Representation of the Formulas of FHDPE (Only Functionalized Unit), the 1-Butene Unit Linked to Poly(ethylene), and 1a and 1b[a]



[a] Equal letters refer to equal carbon atoms in the three structures.

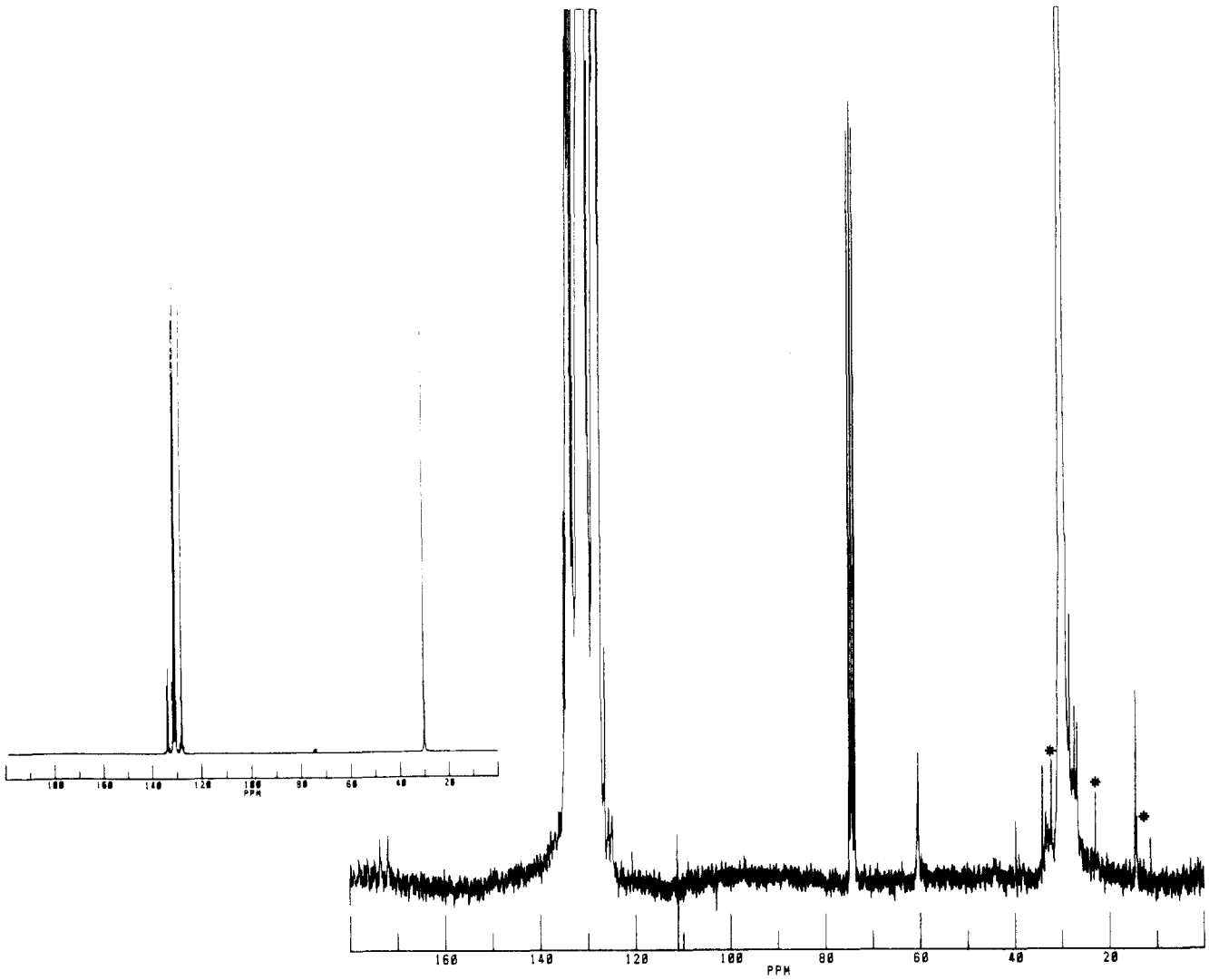


Figure 1. ^{13}C NMR spectrum of FHDPE (signals due to *n*-heptane impurity are marked with an asterisk). The inset shows the same spectrum reduced 128 times.

In the FHDPE spectrum two signals at 174 and 172 ppm unequivocally belong to the magnetically different carbons of the ester groups; the absence of oligomers of the functional monomer possibly bonded to the hydrocarbon skeleton is evidenced by the lack of any other signal in this spectral region. Signals due to the methine carbons are scarcely visible, but by comparison of the h and i bands of **1a** and **1b** with the polymer spectrum two weak and broad signals become observable between 35 and 45 ppm. Together with the polymer carbonyl signals, they are reported in Figure 3 marked with asterisks. These two weak bands represent the methine carbon atoms or the "junction point" between the polymer and the functional monomer constituting a true "fingerprint" of the modified polymer.

The chemical shifts for h carbons are practically identical (Table I). A little difference is detectable for the i carbons, but in this case the structural differences in the aliphatic chains between FHDPE and **1a** and **1b** may play a foundamental role in generating the observed discrepancy, as a consequence of the lower mobility of the macromolecule and its different entanglement around the i carbon.

The polymer spectrum does not show any other signals due to the paraffinic chain, probably because they are buried under the largest one of the methylene groups. This finding confirms the similarities between FHDPE and **1b**; in fact all **1b** signals from l to o lie in the range 28–33 ppm, which is the same range covered by the majority of FHDPE carbon atoms.

Actually the ^{13}C NMR spectrum of the polymer shows some additional signals; these are due to the ethylene as a EBE triad, without the presence of BBE or BBB triads.[22,23] From these data with 1% butene units allowed for, the degree of functionalization, as measured by ^{13}C NMR, is between 2.5 and 3.0%, with the hypothesis of equal NOE for all methyls, due both to 1-butene and to succinate units. In addition the influence that the chiral center h exerts on the chemical shifts of the carbon atoms that are up to five bonds away is clearly detectable. Table I shows that, owing to the small differences introduced in the chemical environment of apparently identical carbon atoms by a chiral center, all the bands from l to o are split into doublets and the amount of their separation regularly diminishes on passing from l–l′ (0.3 ppm in **1b**) to o–o′ (0.02 ppm in **1b**).

From all these considerations it is evident that the observed similarities between the ^{13}C NMR spectra of FHDPE, **1a**, and **1b** strongly support the idea of the presence of single $CH(COOEt)CH_2COOEt$ units along the macromolecular chains, as expected from the reaction mechanism (Scheme I); moreover, it has been demonstrated that this reaction allows one to perform a clean chemical modification of a paraffinic structure by introducing

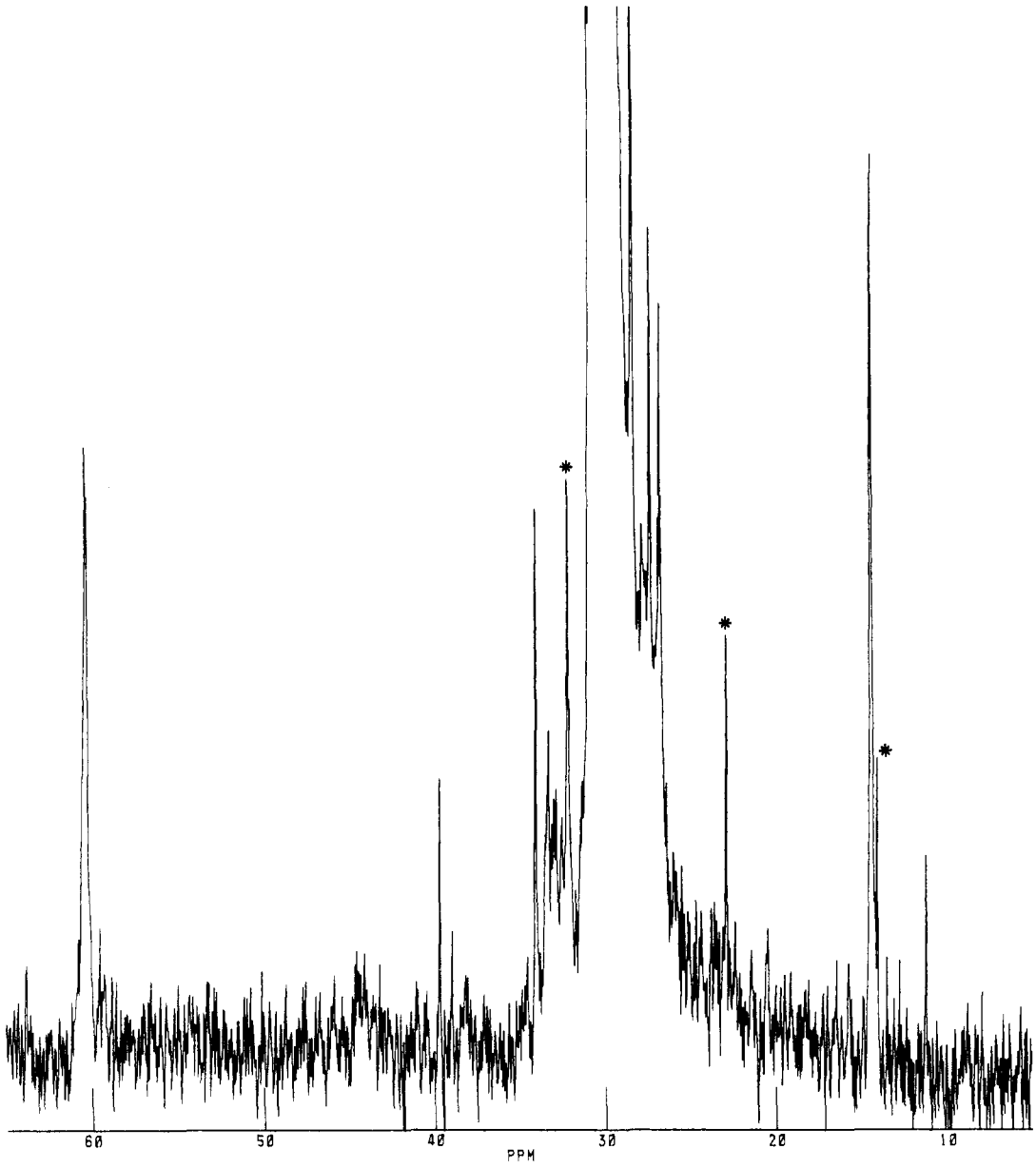


Figure 2. ^{13}C NMR enlarged spectrum of FHDPE between 65 and 5 ppm. All signals reported in Table I are visible.

groups whose structures are in good agreement with that predicted on the basis of known mechanisms.

Experimental Part

^{13}C NMR spectra of FHDPE have been run at 50.33 MHz on a Bruker AC 200 spectrometer at 120 °C in 1,2,4-trichlorobenzene containing 20% 1,2-dideuteriotetrachloroethane. About 60K scans with a small pulse angle (45°) and a delay of 1 s in order to avoid saturation of the carbonyls,[24] 64K memory, and an acquisition time of ≈3 s were used. ^{13}C NMR spectra of model compounds have been run in the neat, adding deuterated benzene for lock and referencing. The following experiments were performed: ^{13}C (WALTZ decoupled);[25] DEPT editing,[26] which together with additivity rules[27] and some literature comparisons[28] allows the full assignment of the spectra.

In the ^1H NMR spectra assignments of 1, 2, and 3, the following symbols have been used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dt = double triplet, dq = double quartet, m = multiplet, bs = broad signal. Signals are given as chemical shifts (δ, ppm), multiplicity, peak area, attribution, coupling constant.

Reaction between Diethyl Succinate and Heptan-4-one. In a three-necked flask equipped with a magnetic stirrer, a dropping funnel, and a reflux condenser, under nitrogen atmosphere, 200 mL of *tert*-butyl alcohol and 7.9 g of potassium (0.202 mol) are poured. The mixture is then heated until complete dissolution of potassium is achieved; then a mixture of 17.0 g of heptan-4-one (0.149 mol) and 31.6 g of diethyl succinate (0.222 mol) is added in 15 min and the resulting solution heated up to a gentle reflux for 14 h. After the mixture is cooled at room temperature, it is acidified with 10% HCl to slight acidity (pH ≈6), the large excess of *tert*-butyl alcohol is evaporated under reduced pressure, and the resulting viscous solution is diluted with water. The organic phase is separated and the aqueous solution is washed with diethyl ether (2 × 50 mL). The recovered organic phases are collected and then washed with a 10% aqueous solution of K_2CO_3 (2 × 70 mL); the resulting aqueous phase, once separated, is made strongly acid with concentrate HCl. An organic layer promptly develops; it is diluted with diethyl ether and collected. The remaining aqueous phase is washed with diethyl ether (2×50 mL), all ethereal phases are collected together and washed with a 5% sodium bicarbonate solution and then with water. The organic solvent is evaporated under reduced pressure; 34.8 g of a brown residue is recovered and directly poured in a claisen together with 60 mL of absolute ethanol, 85 mL of anhydrous benzene, and 2 mL of concentrated sulfuric acid. The resulting mixture is heated under reflux for 4 h; then a part of the solvents mixture (80 mL) is distilled off and replaced with a mixture of absolute ethanol (30 mL) and anhydrous benzene (46 mL). Reflux is restored

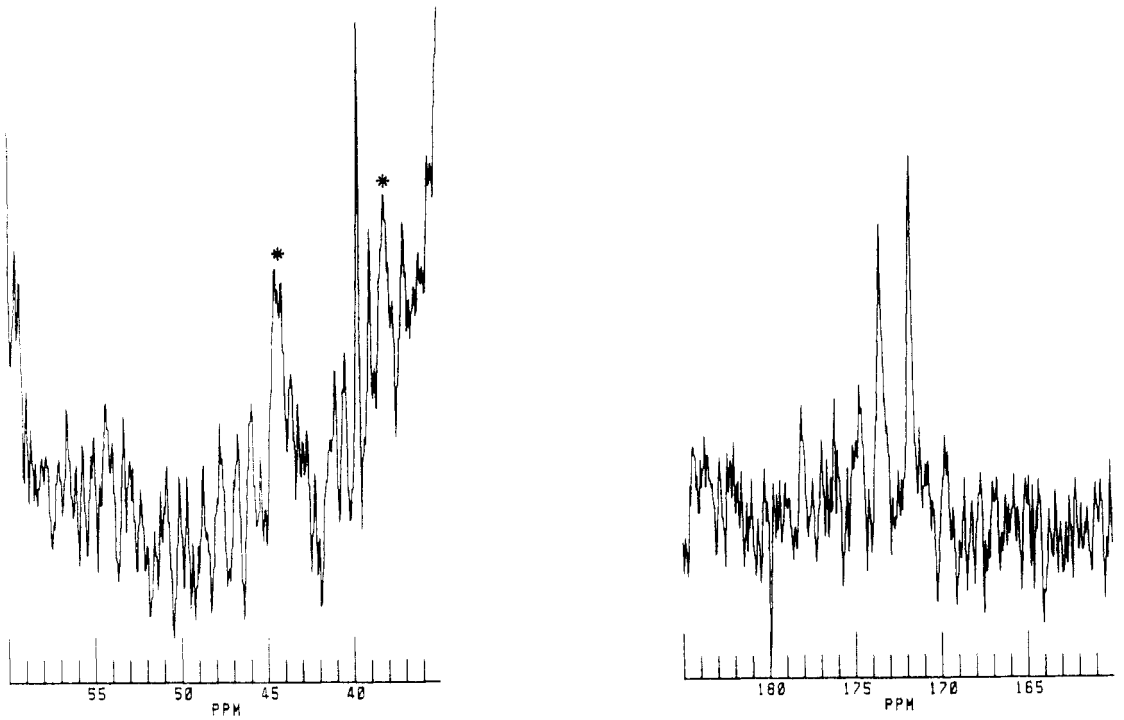


Figure 3. ^{13}C NMR spectrum of FHDPE. In the two spectral zones, the carboxylic and the methinic signals (marked with an asterisk) are shown.

for 3 h and finally the solvents are distilled off. The organic residue is diluted with water and separated, and the aqueous phase is washed with diethyl ether (4 × 50 mL). The organic phases, collected, are washed with 5% aqueous solution of K_2CO_3 and then with water. From the organic phase 30.0 g of a mixture of **2a** and **3a** is recovered by distillation (bp 102–105 °C (0.25 mmHg), yield 75%). It has been characterized by ^1H NMR spectroscopy.

^1H NMR (internal standard TMS, solvent $CDCl_3$): δ 5.30 (t, 1 H, HC=C in **3**, 7 Hz), 4.14–4.12 (dq, 4 H + 4 H, $COOCH_2$ in **2** and **3**, 7.1 Hz), 3.40 (dd, 1 H, $CHCOOEt$ in **3**, 10.2 Hz, 5.1 Hz), 3.35 (s, 2 H, CH_2COOEt in **2**), 2.90 (dd, 1 H, CH_2COOEt in **3**, 16.6 Hz, 10.2 Hz), 2.45 (dd, 1 H, CH_2COOEt in **3**, 16.6 Hz, 5.1 Hz), 2.20–1.85 (bs, 4 H + 4 H, CH_2C=CCH_2 in **2** and **3**), 1.50–1.30 (bs, 4 H + 2 H, CH_3CH_2 in **2** and **3**), 1.24 (dt, 6 H + 6 H, OCH_2CH_3, 7.0 Hz), 0.95 ppm (m, 6 H + 6 H, CH_3CH_2 in **2** and **3**).

Preparation of Ethyl 3-Carbethoxy-4-*n*-propylheptanoate. In a 100-mL vessel, equipped with a magnetic stirrer, is poured 13.0 g of a mixture of **2a** and **3a** together with 50 mL of 95% ethanol and 0.17 g of charcoal-supported palladium. Hydrogen is allowed to flow in the resulting mixture, and its absorption is controlled by a suitable gas buret. When absorption ceases, the mixture is filtered and the ethanol is evaporated under reduced pressure. The residue is distilled and 11.7 g of **1a** (yield 89%) is collected (bp 106 °C (0.5 mmHg)).

Elemental analysis: C, calcd 66.14, found 67.12; H, calcd 10.36, found 10.63.

^1H NMR (internal standard TMS, solvent $CDCl_3$): δ 4.13 (q, 4 H, $COOCH_2$, 7.1 Hz), 3.00 (m, 1 H, $CHCOOEt$), 2.70 (dd, 1 H, CH_2COOEt, 10.8 Hz, 16.6 Hz), 2.30 (dd, 1 H, CH_2COOEt, 16.6 Hz, 3.8 Hz), 1.85–1.70 (bs, 1 H, $CHCH(COOEt)CH_2$), 1.45–1.10 (*m*, 14 H, aliphatic CH_2 and $COOCH_2CH_3$), 0.90 (m, 6 H, aliphatic CH_3).

^{13}C NMR: see Table I.

Reaction between Diethyl Succinate and Tridecan-4-one. In a three-necked flask equipped with a magnetic stirrer, a dropping funnel, and a reflux condenser, under nitrogen atmosphere, 50 mL of *tert*-butyl alcohol and 1.8 g of potassium (0.045 mol) are poured. The mixture is then heated until complete dissolution of potassium is achieved; then a mixture of 8.2 g of tridecan-4-one (0.041 mol) and 8.5 mL of diethyl succinate (0.051 mol) is added in 15 min and the resulting solution is heated up to a gentle reflux for 67 h. After the mixture is cooled at room temperature it is acidified with 10% HCl to slight acidity (pH ≈6), the large excess of *tert*-butyl alcohol is evaporated under reduced pressure, and the resulting viscous solution is diluted with water. The organic phase is separated and the aqueous solution is washed with diethyl ether (3 × 50 mL).

The organic solvent of the collected organic phases is evaporated under reduced pressure and gentle heating is employed in order to allow complete removal of unreacted *tert*-butyl alcohol; 13.7 g of an oily residue is recovered and directly poured in a claisen together with 40 mL of absolute ethanol, 50 mL of anhydrous toluene, and 1.6 mL of concentrated sulfuric acid. The resulting mixture is heated under reflux for 45 h, and then the solvent mixture is distilled off. The organic residue is diluted with pentane and water and then separated, and the aqueous phase is discarded. By distillation of the organic phase a fraction containing nonreacted ketone is recovered early (bp 95–100 °C (0.4 mmHg)) and then a yellow oily residue is distilled off (bp 185 °C (0.4 mmHg)). It is collected and purified by "flash chromatography",[29] employing silica gel (Merck) and an eluting mixture hexane/ethyl acetate (95:5 v/v). A mixture of **2b** and **3b**, 4.9 g, is recovered (yield 33%). It has been characterized by ^1H NMR spectroscopy.

^1H NMR (internal standard TMS, solvent $CDCl_3$): δ 5.30 (t, 1 H, HC=C in **3**, 7 Hz), 4.14–4.12 (dq, 4 H + 4 H, $COOCH_2$ in **2** and **3**, 7.2 Hz), 3.40 (m, 1 H, $CHCOOEt$ in **3**), 3.35 (s, 2 H, CH_2COOEt in **2**), 2.90 (dd, 1 H, CH_2COOEt in **3**, 16.7 Hz, 10.3 Hz), 2.45 (dd, 1 H, CH_2COOEt in **3**, 16.7 Hz, 5.1 Hz), 2.20–1.85 (bs, 4 H + 4 H, CH_2C=CCH_2 in **2** and **3**), 1.40–1.10 (bs, 16 H + 14 H, aliphatic CH_2 in **2** and **3** and 6 H + 6 H, OCH_2CH_3), 0.95 ppm (m, 6 H + 6 H, aliphatic CH_3 in **2** and **3**).

Preparation of Ethyl 3-Carbethoxy-4-*n*-hexyldecanoate. Into a 100-mL vessel, equipped with a magnetic stirrer, is poured 4.1 g of a mixture of **2b** and **3b** together with 50 mL of 95% ethanol and 0.17 g of charcoal-supported palladium. Hydrogen is allowed to flow in the resulting mixture, and its absorption is controlled by a suitable gas buret. When absorption ceases, the mixture is filtered and the ethanol is evaporated under reduced pressure. The residue is tested for purity by TLC. Owing to its good purity it has been directly characterized by elemental analysis and ^1H NMR and ^{13}C NMR spectroscopy. **1b** (3.8 g, yield 93%) has collected. Elemental analysis: C, calcd 70.74, found 71.15; H, calcd 11.31, found 12.19.

^1H NMR (internal standard TMS, solvent $CDCl_3$): δ 4.13 (m, 4 H, $COOCH_2$), 3.00 (m, 1 H, $CHCOOEt$), 2.70 (dd, 1 H, CH_2COOEt, 10.9 Hz, 16.5 Hz), 2.30 (dd, 1 H, CH_2COOEt, 16.5 Hz, 3.7 Hz), 1.73 (bs, 1 H, $CHCH(COOEt)CH_2$, 1.45–1.10 (m,

26 H, aliphatic CH_2 and $COOCH_2CH_3$), 0.90 (m, 6 H, aliphatic CH_3).

^{13}C NMR: see Table I.

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Thermal Degradation of Microbial Copolyesters: Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and Poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate)

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Received June 28, 1989

ABSTRACT: Thermal degradation processes of microbial copolyesters were studied in the temperature range 100–200 °C by monitoring the time-dependent changes in molecular weights of melt samples. Two types of copolyesters, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P(3HB-*co*-3HV); 3HV = 0–71 mol %) and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P(3HB-*co*-4HB); 4HB = 0–82 mol %), were used in this study. All copolyester samples used were thermally unstable at temperatures above 170 °C, and their molecular weights decreased rapidly with time. The time-dependent changes in molecular weights during the thermal degradation followed the kinetic model of random chain scission at ester groups. The rates of random chain scission were independent of the compositions of the copolyesters but dependent strongly on temperature. These copolyester samples were thermally stable at temperatures below 160 °C. It has been suggested that the microbial copolyesters with melting temperatures below 160 °C are applicable to conventional plastics processing methods.

Introduction

A wide variety of micoroorganisms produce an optically active polyester, poly(3-(*R*)-hydroxybutyrate) (P(3HB)) as an intracellular storage polymer.[1] P(3HB) is a thermoplastic degradable in the environment, by either hydrolytic or enzymatic degradation processes.[2–5] Industrial-scale fermentation production of P(3HB) has begun,[6–8] and P(3HB) is attractive as an environmentally degradable material that can be processed like conventional commodity thermoplastics. However, P(3HB) is thermally unstable at temperatures above the melting point (around 180 °C), and a drastic reduction in the molecular weight occurs during processing in the temperature range 180–200 °C.[9–11]

This problem has been resolved by the development of a fermentation process to produce microbial copolyesters with lower melting temperatures.[12,13] Imperial Chemical Industries (ICI) has produced commercially a copolyester of 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV) by the fermentation process in which *Alcaligenes eutrophus* is grown in culture media containning propionic acid and glucose[12] and marketed it as Biopol

0024-9297/90/2223-1933$02.50/0