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Functionalization of Polyolefins. Structure of Functional Groups in Polyethylene Reacted with Ethyl Diazoacetate

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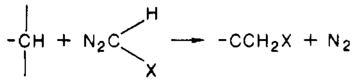
The introduction of polar groups in polyolefins is usually performed by a free-radical mechanism using peroxides and various unsaturated polar molecules.[1] The structure of functional groups introduced by this method is difficult to predict and has not been clarified up to now.

On the other hand, the reaction of paraffins with carbene derivatives produced in situ by decomposition of diazo compounds has been shown[2] to proceed by insertion into the carbon–hydrogen bond as shown in the scheme

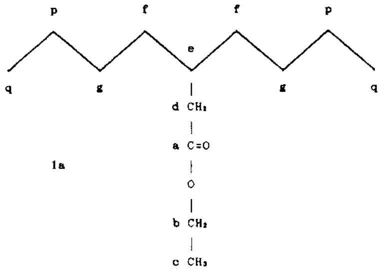


$$-\overset{|}{\underset{|}{C}}H + N_2C\begin{matrix}H\\X\end{matrix} \rightarrow -CCH_2X + N_2$$

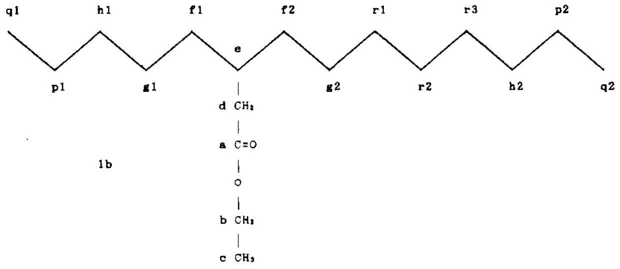
This last approach has been used to introduce well-defined groups into polyolefins such as polyethylene and polypropylene, using either methyl diazoacetate with rhodium carboxylates as catalysts[3] or thermal decomposition of ethyl diazoacetate (EDA).[4]

In this note the unequivocal determination of the structure of the functional groups introduced into high-density polyethylene (HDPE) by reaction with EDA is described on the basis of NMR analysis of the polymer compared to low molecular weight structural models.

Ethyl (3-butyl)heptanoate (**1a**) and ethyl (3-pentyl)undecanoate (**1b**) have been chosen as structural model compounds.



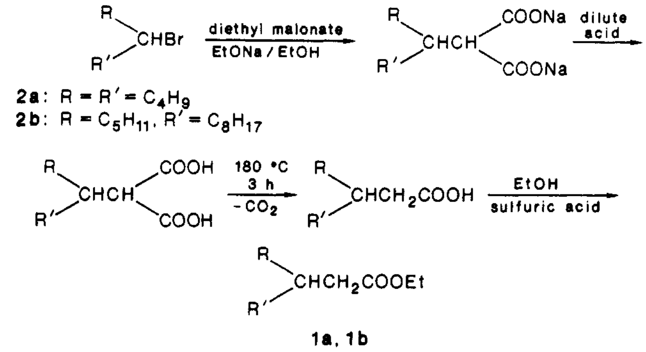
1a



1b

1a and **1b** differ in their symmetry, and the comparison of the ^{13}C NMR spectra allows a determination of the influence of the shortening of the methylene chains on the chemical shifts of the carbon atoms at a fixed distance from the functional groups and verification of structural similarities among the spectra of polymer and model compounds.

Scheme I



1a, 1b

Table I
Chemical Shifts of Functionalized PE and Low Molecular Weight Models[a]

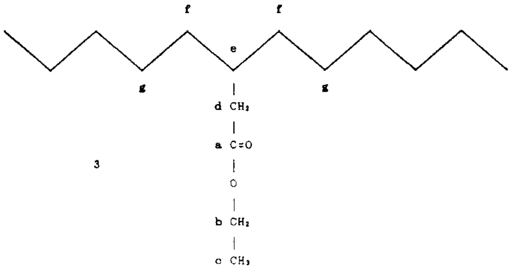
	polymer 3	model 1a	model 1b
a	173.40	173.52	173.55
b	59.95	59.99	60.00
c	14.41	14.29	14.32
d	39.68	39.33	39.36
e	35.45	35.04	35.14
f	34.42	33.67	34.03 (f1), 33.97 (f2)
g	26.81	28.82	26.64 (g1), 26.30 (g2)
r1			30.01
r2			29.70
r3			29.44
h			32.21 (h1), 32.02 (h2)
p		22.99	22.78 (p1), 22.72 (p2)
q		14.06	14.06 (q1), 14.00 (q2)

[a] Letters refer to C atoms as in structures **1a**, **1b**, and **3**.

1a and **1b** were obtained by the procedure shown in Scheme I.

The ^{13}C NMR spectral data of **1a** and **1b** are reported in Table I.

HDPE was functionalized by reacting the polymer with EDA by the procedure described in ref 4. The mechanism of this reaction allows one to propose structure **3** for a section of functionalized polymer.



3

The ^{13}C NMR spectrum of functionalized HDPE (FHDPE) is reported in Figure 1 and relevant data summarized in Table I.

In the ^{13}C NMR spectrum (Figure 1) of functionalized polyethylene (FHDPE) one may assign the peaks to carbon atoms a to g shown in **3** (equal letters identify carbon atoms at the same distance from the functional groups either in the polymer or in the model compounds).

The spectra of the low molecular weight models **1a** and **1b** markedly resemble that of FHDPE. These similarities are more evident in the **1b** spectrum, where the influence of methyl groups on the f and g peaks is attenuated by the greater number of methylene groups on both sides (2 and

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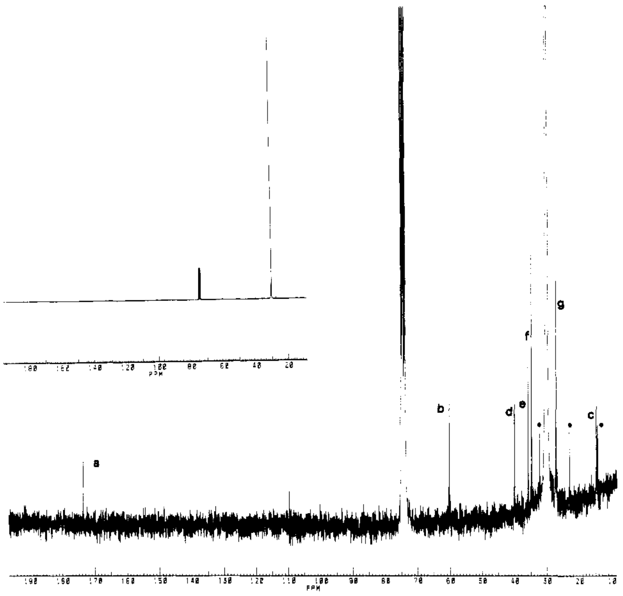

Figure 1. ^{13}C NMR spectrum of high-density polyethylene functionalized with ethyl diazoacetate. The insert shows the same spectrum reduced 256 times. Letters are referred in Table I; asterisks show heptane impurity.

5 by each side) inserted between them and the g carbons.

Indeed the asymmetric model **1b** shows chemical shifts of d–g closer to those of the corresponding C atoms in the polymer than **1a**; similarities are enhanced by considering, successively, the d–g carbon atoms.

The chemical shifts of the d atom in **1a** and **1b** are similar, with that of **1b** slightly closer to the FHDPE chemical shift. Differences between the **1a** and **1b** spectra become more consistent when considering the e–g peaks; in particular, the last two assignments approximate very well the f and g FHDPE chemical shifts.

In the FHDPE spectrum (Figure 1) peaks are also observed (marked with an asterisk) attributable to *n*-heptane used for performing extractions of the functionalized polymer; the evaluated concentration of *n*-heptane in FHDPE is <0.1% w/w, showing the dramatic potentialities of ^{13}C NMR spectroscopy to detect impurities at very low concentrations.

The observed similarities among the spectra of FHDPE and of the low molecular weight models **1a** and **1b** strongly support the idea that the functional groups attached to the HDPE chain by thermal decomposition of EDA are in fact $-CH_2COOEt$ groups, as expected from the carbene mechanism shown in Scheme I.

In this sense, ^{13}C NMR spectroscopy has been shown to be a very powerful tool, allowing us to detect carbonyl groups, which are really "dispersed" to very low concentration (approximately 0.3–0.4% w/w with respect to the polymer) in the aliphatic moiety. The most important conclusion from the present work, however, is the demonstration of the possibility of performing a clean chemical modification on a paraffinic macromolecule.

It is worth mentioning that structure **3** corresponds to that of a linear copolymer of ethylene with ethyl 1-butenoate, which up to now has not even been prepared by direct copolymerization.

Experimental Section

Ethyl (3-butyl)heptanoate (**1a**) was obtained in 40% yield by reacting 5-bromononane (5.39 g, 2.6×10^{-2} mol; **2a**) with an ethanol solution of sodium diethylmalonate (2.61×10^{-2} mol) according to literature methods,[5] subsequently, the initially formed product was saponified and decarboxylated at 180 °C for 3 h. The crude acid obtained (2.5 g) was esterified with "super dry" ethanol (17 mL) and a catalytic amount of concentrated sulfuric acid (1 mL), by refluxing the mixture over 20 h. The final product **1a** was isolated by distillation under reduced pressure (2.15 g, 1×10^{-2} mol); bp 115–125 °C (23 mmHg), in good agreement with literature data.[6] It was characterized by ^1H NMR and ^{13}C NMR spectroscopy. ^1H NMR (in $CDCl_3$, TMS): δ 4.13 (q, 2 H), $-OCH_2CH_3$), 2.23 (d, 2 H, $-CHCH_2COOEt$), 1.85 (br m, 1 H, $-CHCH_2COOEt$), 1.26 (m, 15 H, aliphatic CH_2 + OCH_2CH_3), 0.89 (t, 6 H, CH_3). ^{13}C NMR: see Table I.

Ethyl (3-pentyl)undecanoate (**1b**) is not described in the literature; it was obtained in 41% yield by the procedure described above for the synthesis of **1a**. **1b** was characterized by elemental analysis (Calcd: C, 75.99; H, 12.75. Found: C, 74.96; H, 12.72) and by ^1H NMR and ^{13}C NMR spectroscopy. ^1H NMR (in $CDCl_3$): δ 4.12 (q, 2 H, $-OCH_2CH_3$), 2.22 (d, 2 H, $-CHCH_2COOEt$), 1.85 (br m, 1 H, $-CHCH_2COOEt$), 1.26 (m, 25 H, aliphatic CH_2 + OCH_2CH_3), 0.89 (t, 6 H, CH_3). ^{13}C NMR: see Table I.

HDPE was functionalized by reacting the polymer with EDA by the procedure described in ref 3. ^{13}C NMR spectra of FHDPE were run in 1,2-dideuteriotetrachloroethane solutions (200 mg/3 mL) at 110 °C, 10-mm NMR tube. A total of 40000 scans, with 45° pulses and a relaxation time of 5 s, was necessary in order to obtain the spectrum shown in Figure 1.

Due to the low content of functionalized units special care was paid to the signal to noise ratio. Thus, the Ernst angle[7] was used with an approximate T_s obtained by considering the NMR experiments on low-density polyethylenes.[8,9]

The quantitative analysis was performed by comparing the intensities of peaks g and f (belonging to the main chain near branches) with the polyethylene peaks, on the reasonable hypothesis of equal NOE's for all the backbone carbon atoms. Assignments, shown in Table I were made by additivity rules.[10] The ^{13}C NMR spectra of model compounds were run in $CDCl_3$ at room temperature in 10% by volume solutions, on a Varian VXR-300 spectrometer operating at 75.4 MHz.

Registry No. **1a**, 80256-56-0; **1b**, 117801-00-0; HDPE, 9002-88-4.

References and Notes

(1) Ruggeri, G.; Aglietto, M.; Petragnani, A.; Ciardelli, F. *Eur. Polym. J.* **1983**, *19*, 863.
(2) Von E. Doering, W.; Knox, L. H. *J. Am. Chem. Soc.* **1956**, *78*, 4947; **1961**, *83*, 1989.
(3) Demonceau, A.; Noels, A. F.; Hubert, A. J.; Teyssié, P. 2nd IUPAC Symposium on Organometallic Chemistry Directed toward Organic Synthesis, Dijon, France, 1983.
(4) Skell, P. S.; Aglietto, M.; Ruggeri, G.; Speranza, S.; Ciardelli, F. Italian Patent 48950A/85, 1985.
(5) *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman: London, 1978.
(6) Malthete, J.; Canceill, J.; Gabard, J.; Jacques, J. *Tetrahedron* **1981**, *37*, 2823.
(7) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of NMR in One and Two Dimensions*; Oxford Science Publications: 1987; p 125.
(8) Axelson, D. E.; Levy, G. C.; Mandelkern, L. *Macromolecules* **1979**, *12*, 41.
(9) Cavagna, F. *Macromolecules* **1981**, *14*, 215.
(10) Stothers, J. B. *Carbon-13 Spectroscopy*; Academic Press: New York, 1972.

Gas Permeability of a Polystyrene/Polybutadiene Block Copolymer Possessing a Misoriented Lamellar Morphology

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Introduction

In an earlier paper,[1] the gas permeability of a polybutadiene/polystyrene block copolymer with highly oriented lamellar domains was investigated. The mor-