

Chemical Modification of Molten Polyethylene by Thermal Decomposition of Peroxyesters

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ABSTRACT: The functionalization of polyethylene was realized by the thermal decomposition of peroxyesters in molten polymer in the absence of any other additive. Ester and acid functions were introduced onto the polymer operating with various peroxyesters. This grafting resulted from the combination of a polymer radical, generated in the abstraction of a hydrogen from polyethylene by an alkoxy radical, with an acyloxy or carbon-centered radical arising

from the perester. A complete methodology was set up to identify and to titrate the functions present onto the polyethylene and to determine the extent of crosslinked polymer. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 699–707, 2003

Key words: polyethylene; chemical modification; peroxyester; crosslinking; free radicals

INTRODUCTION

Free-radical chemical modifications of polyolefins have been mainly realized by decomposition of a radical initiator in the presence of unsaturated compounds.^{1–11} To our knowledge, only the articles by Moore et al.^{12,13} have described the functionalization of polyolefins, polypropylene in this case, carried out by thermal decomposition of peroxyesters in the absence of any additive. Acid and ester functions were introduced onto polypropylene; one of functionalization mechanisms, invoked in the current study, was the combination of the macroradical, formed in the hydrogen abstraction from the polymer by one of the radicals produced in the decomposition of the perester, with the counter radical of this latter. The grafting yields were not very important (15%).

Since 1996 the functionalization of polyethylene (PE) in the molten state by single thermal decomposition of several peroxyderivatives has been studied by our group. The hydroxylation and “ketonization” of polyethylene were performed via thermal decomposition of a hydroperoxide in molten polymer.¹⁴ In a recent note¹⁵ we reported that various other peroxyderivatives were decomposed in similar conditions and that the grafting of functions onto polyethylene was identified without the observation of an important crosslinking of the polymer for the reactions of the peroxyketals and peresters. Chemical modification

of PE by the thermolysis of 1-(1,1-dimethylethylperoxy)-1-methoxycyclohexane¹⁶ showed the possible grafting of functions on PE. This was realized by the coupling of a radical present on the polyolefin chain, obtained by the abstraction of a hydrogen by the 1,1-dimethylethoxy radical, with the alkyl radical produced in the free-radical rearrangement of the 1-methoxycyclohexyloxy radical. The difficulties identified in the preparation of monoperoxyketals at an industrial level and in their storage prompted us to study more thoroughly the thermal decomposition of peroxyalkanoates in polyethylene. Indeed, such peroxyderivatives, easily prepared and stored, are known to produce simultaneously alkyl and alkoxy radicals, which seem to be required to realize the free radical grafting on PE. This article reports on the study of the chemical modification of this polyolefin in the melt by these peresters.

EXPERIMENTAL

Spectroscopic data

¹H- and ¹³C-NMR spectra were recorded on Bruker AC200 and AC250. IR spectra were recorded on a Perkin-Elmer Paragon 1000, and functionalization yield was determined according to the method developed in the previous work.¹⁶

Materials

1,2-Dichlorobenzene, dichloromethane, pyridine, dimethylformamide, propanoyl chloride, *N,N'*-carbonyldiimidazole, hexanoic acid, dodecanol, 2-(2-ethoxyethoxy)ethanol, 1,2-ethanediol, succinic anhydride, eth-

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anolamine, and tetra-*n*-butylammonium hydroxide were used as received from Acros (France) or Aldrich (France) without any further purification.

The polyethylene used for the functionalization was prepared as previously describes¹⁶: commercially available polyethylene (125,000 g mol⁻¹; ACROS reference 17851) was dissolved at 115°C in 1,2-dichlorobenzene (10 g in 400 mL). After complete dissolution the polymer was precipitated in dichloromethane (1 l) and filtered. It was then washed over 24 h in a soxhlet apparatus with dichloromethane, and the polyethylene powder was dried under vacuum until there was no mass variation.

1,1-Dimethylethylhydroperoxide was obtained after elimination under vacuum (20 mm Hg) at 40°C of the *bis*-(1,1-dimethylethyl)peroxide from the commercial mixture of both compounds (Fluka). 1-Methyl 1-phenylethylhydroperoxide was supplied by Akzo Nobel and used as received.

The peroxyesters were synthesized according to known procedures²¹⁻²⁷ and were titrated by the method described by Swern²⁸ (purity > 95%). The procedures described below were used:

—For **PE**₁²¹⁻²² and **PE**₂^{21,23}:

0.1 mol of hydroperoxide (1,1-dimethylethylhydroperoxide for **PE**₁ and 1-phenyl-1-methylethylhydroperoxide for **PE**₂) and 0.1 mol of pyridine in solution of pentane (20 mL) at 0°C were placed in a three-necked round-bottom flask equipped with a reflux condenser, a dropping funnel, and a thermometer. Propanoyl chloride (0.1 mol) was then slowly added. The reaction mixture was stirred at 0°C for 1.5 h after the end of the addition and 16 h at room temperature. Then 50 mL of cold water was added, and the organic layer was separated. The aqueous phase was then extracted with 20 mL of petroleum spirit. The organic layers were washed with a saturated solution of Na₂CO₃, then water until neutrality. The crude material, after drying over MgSO₄, was filtered; the solvents were removed by distillation under reduced pressure. The peresters were purified by a silica gel chromatography column (petroleum spirit/ether 98:2). The peroxyester was obtained (yields: **PE**₁ 77%; **PE**₂ 75%).

PE₁: ¹H-NMR (CDCl₃)—δ ppm: 1.90 (q, 2H, CH₂CO); 0.9 [s, 9H, OOC(CH₃)₃]; 0.85 (t, 3H, CH₃).

¹³C-NMR (CDCl₃): δ ppm: 171.6 (C=O); 83.0 (C(CH₃)₃); 25.9 (C(CH₃)₃); 24.5 (CH₂); 9.0 (CH₃).

PE₂: ¹H-NMR (CDCl₃)—δ ppm: 7.6–7.2 (m, 5H, aromatic); 2.20 (q, 2H, CH₂CO); 1.65 [s, 6H, OOC(CH₃)₂]; 1.09 (t, 3H, CH₃).

¹³C-NMR (CDCl₃)—δ ppm: 171.3 (C=O); 144.1 (aromatic Cq); 128.3, 127.5, 125.4 (aromatic); 85.8 [C(CH₃)₃]; 26.5 [C(CH₃)₃]; 24.6 (CH₂); 9.1 (CH₃).

—For **PE**₃,²⁴ **PE**₄,²⁵ **PE**₆,²⁶ **PE**₇,²⁶ and **PE**₈.²⁶

N,N'-carbonyldiimidazole (0.1 mol) in a solution of freshly distilled THF (20 mL) was placed in a three-necked round-bottom flask equipped with a reflux condenser, a dropping funnel, and a thermometer. Hexanoic acid (0.1 mol) for the synthesis of **PE**₃, or **PE**₅ for the other syntheses (0.1 mol), was slowly added. The reaction mixture was then stirred for 1 h. The temperature of the reaction mixture was decreased to 0°C and 1,1-dimethylethylhydroperoxide (0.1 mol) for the synthesis of **PE**₃, or the corresponding alcohol for the synthesis of the others peroxyesters (**PE**₄: ethanol, **PE**₆: dodecanol, **PE**₇: 2-(2-ethoxyethoxy)ethanol; **PE**₈: 1,2-ethanediol) was then slowly added. The reaction mixture was stirred an additional hour at 0°C and 16 h at room temperature. The solvent was removed, and petroleum spirit (20 mL) was added to the organic layer. This was washed twice with cold water (20 mL). The organic layer, dried over MgSO₄, was filtered; the solvent was removed by distillation under reduced pressure. The peroxyester was obtained (yields—**PE**₃: 70%, **PE**₄: 86%, **PE**₆: 53%, **PE**₇: 72%, **PE**₈: 68%). The peresters were purified by a silica gel chromatography column (petroleum spirit/ether).

PE₃: ¹H-NMR (CDCl₃)—δ ppm: 2.26 (t, 2H, CH₂CO); 1.70–1.50 (m, 2H, CH₂CH₂CO); 1.40–1.19 (m, 4H, other CH₂); 1.28 [s, 9H, OOC(CH₃)₃]; 0.86 (m, 3H, CH₃).

¹³C-NMR (CDCl₃)—δ ppm: 171.1 (C=O); 83.1 [C(CH₃)₃]; 31.2, 31.1, 24.6, 22.2 (CH₂); 25.7 [C(CH₃)₃]; 13.8 (CH₃).

PE₄: ¹H-NMR (CDCl₃)—δ ppm: 4.10 (m, 2H, CH₂O); 2.60 (m, 4H, other CH₂); 1.3 [s, 9H, OOC(CH₃)₃]; 1.2 (t, 3H, CH₃).

¹³C-NMR (CDCl₃)—δ ppm: 171.6 (C=O); 170.0 (CO₂); 83.5 [C(CH₃)₃]; 60.7 (CH₂O); 28.8 and 26.2 (CH₂CH₂); 25.9 (C(CH₃)₃); 14.0 (CH₃).

PE₆: ¹H-NMR (CDCl₃)—δ ppm: 4.0 (t, 2H, CH₂O); 2.70–2.50 (m, 4H, COCH₂CH₂CO); 1.65–1.10 (m, 20H, other CH₂); 1.05 (s, 9H, OOC(CH₃)₃); 0.8 (t, 3H, CH₃).

¹³C-NMR (CDCl₃)—δ ppm: 171.6 (CO₂); 170.0 (CO₃); 83.5 [C(CH₃)₃]; 64.9 (CH₂O); 31.8, 29.6, 29.5, 29.4, 29.3, 29.2, 28.8, 28.5, 26.2, 25.8, 22.6 (CH₂); 26.0 [C(CH₃)₃]; 14.0 (CH₃).

PE₇: ¹H-NMR (CDCl₃)—δ ppm: 4.0–3.90 (m, 2H, CH₂OCO); 3.45–3.15 (m, 8H, CH₂OCH₂CH₂OCH₂); 2.45–2.30 (m, 4H, other CH₂); 1.04 [s, 9H, OOC(CH₃)₃]; 0.91 (t, 3H, CH₃).

¹³C-NMR (CDCl₃)—δ ppm: 171.3 (CO₂); 169.6 (CO₃); 83.1 [C(CH₃)₃]; 70.3, 69.5, 68.6, 66.2, 63.6 (CH₂O); 28.4, and 25.8 (CH₂CH₂); 20.9 [C(CH₃)₃]; 14.9 (CH₃).

PE₈: ¹H-NMR (CDCl₃)— δ ppm: 4.14–4.10 (m, 2H, CH₂OCO); 3.71–3.65 (m, 2H, CH₂OH); 2.65–2.53 (m, 4H, other CH₂); 1.21 (s, 9H, OOC(CH₃)₃).

¹³C-NMR (CDCl₃)— δ ppm: 172.0 (CO₂); 170.1 (CO₃); 83.8 [C(CH₃)₃]; 66.4 and 65.0 (OCH₂CH₂O); 28.7 and 28.2 (CH₂CH₂); 25.9 [C(CH₃)₃].

—For PE₅²⁷:

In a three-necked round-bottom flask equipped with a reflux condenser, a dropping funnel, and a thermometer, succinic anhydride (0.04 mol) was heated at 45°C–55°C. 1,1-Dimethylethylhydroperoxide (0.044 mol) was slowly added. Then pyridine (0.02 mol) was slowly added. The reaction mixture was kept under the same conditions an additional 15 min and then cooled to room temperature. Then 15 mL of chloroform was added, and the reaction mixture was washed with a diluted hydrochloric acid solution (10%). The organic layer was washed with water; after drying, the solvent was removed, and the peroxyester was obtained (yield: 50%).

PE₅: ¹H-NMR (CDCl₃)— δ ppm: 11.3 (s, 1H, OH); 2.63–2.50 (m, 4H, CH₂); 1.21 [s, 9H, OOC(CH₃)₃].

¹³C-NMR (CDCl₃): δ ppm: 177.5 (CO₂); 170.1 (CO₃); 83.8 [C(CH₃)₃]; 28.6 and 25.7 (CH₂CH₂); 25.9 [C(CH₃)₃].

Functionalization of polyethylene and analyses of the polymer after reaction

The complete experimental procedures used to separate and analyze the polymer fractions were similar to ones presented previously.¹⁶ The methodology used to characterize the different organic functions grafted is summarized in Figure 1.

Preparation of the sample

In a 50-mL flask 1 g of powdered polyethylene and 0.45 mmol of the peroxyester in a solution of 6 mL of dichloromethane/cyclohexane (9:1) were mixed during 2.5 h at room temperature. The solvents were removed at room temperature under reduced pressure with a rotavapor until a constant mass (corresponding to the polyethylene and the peroxyketal used for the reaction) was obtained.

Thermolysis of the peroxyester in molten polyethylene

The polymer/peroxyderivative mixture obtained was then placed in a reactor (Büchiglasuster BMC 100). The reactor was closed and degassed twice by the freezing/unfreezing method. The atmospheric pressure was recovered by injection of argon gas. The reactor was heated at 160°C for 2.5 h without any stirring.

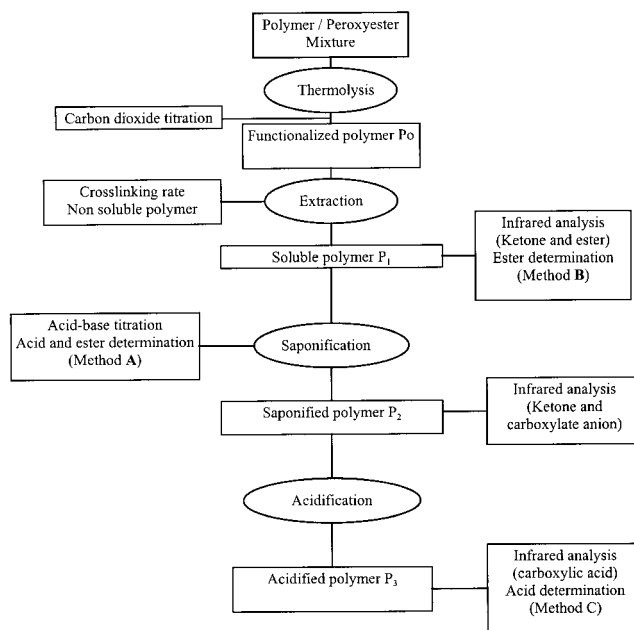


Figure 1 Methodology used for the study of the functionalization of polyethylene

Titration of carbon dioxide produced by thermolysis of the peroxyester

This was performed after the decomposition of the peroxyester, once the reactor was cold and before opening it. The flushing of argon allowed to remove the produced carbon dioxide from the reactor. The evolved gas passed in a solution of DMF/ethanolamine (75/1 v/v) to trap carbon dioxide. The titration of carbon dioxide was then realized with a solution of tetra-*n*-butylammonium hydroxide using phenolphthalein as indicator.

Extraction of the low boiling products issued from the thermal decomposition

After opening the reactor, the cold polyethylene was washed with 10 mL of dichloromethane. The polymer was then cut with scissors, dissolved in 20 mL of 1,2-dichlorobenzene at 125°C, precipitated in 60 mL of dichloromethane, and, finally, the polymer was filtered and dried under vacuum at 60°C.

Extraction of “noncrosslinked” polymer

The dried polymer was placed in porous steel bags (porosity of 140 μ m, Society Gantois, France) and dissolved in 150 mL of 1,2-dichlorobenzene (for 1 g of polymer) at 145°C during 16 h. The “crosslinked” polyethylene was determined after reaction by weighing the dried insoluble part of the polymer (remaining in the steel bag) after drying overnight under vacuum at 60°C.¹⁴ The crosslinking rate (mass of insoluble polymer/mass of starting polyethylene) was calcu-

lated from it. The soluble polymer ("noncrosslinked") was recovered from the 1,2-dichlorobenzene solution after precipitation in dichloromethane, followed by a drying under vacuum at 60°C.

Alkaline treatment

In a flask was placed 0.5 g of "noncrosslinked" polyethylene, which was dissolved in 125 mL of toluene at 110°C. Then 25 mL of a potassium ethanolic solution (0.05 mol l⁻¹) was added. The mixture was heated at 90°C for 2 h. At that time the titration of the remaining base was done using a solution of hydrochloric acid in isopropanol (0.1M) in the presence of phenolphthalein. From this the number of ester functions grafted on the polymer was calculated (Method A). The flask was cooled down and the polymer was recovered after filtration and washed with water (30 mL), ethanol/water (50:50; 20 mL), and acetone (30 mL). The polymer was dried under vacuum at 50°C.

Acid treatment

Dried saponified polymer (0.25 g) was dissolved in a flask with 100 mL of toluene at 110°C. Once the polymer was totally dissolved, 5 mL of concentrated hydrochloric acid (35% in water) was added. After 5 min the temperature was decreased and the polymer precipitated. After filtration the polymer was washed with water (30 mL), ethanol/water (50:50; 20 mL), and acetone (30 mL). The polyolefin was then dried overnight under vacuum at 50°C.

RESULTS AND DISCUSSION

In the preliminary work¹⁵ the qualitative study of the decomposition of peresters in polyethylene showed the potential of such a reaction to graft an ester function onto the polymer (perester/ethylene units = 1/40). These promising results prompted us to study more deeply these reactions, focusing particularly on the nature of the grafted function and its quantification. In several cases a high degree of crosslinking of the polyolefin was observed, which appeared to be a drawback. Thus, to decrease this crosslinking, the reaction was performed in this study with a lower ratio of perester relative to polyethylene, similarly to the peroxyketals¹⁶ (1 mol of perester for 80 ethylene units of polyethylene).

No matter which peroxyester decomposed in the polyethylene, the presence of a ketone function onto the polymer was always observed by infrared spectroscopy. This function was titrated by IR, and the values obtained were in the range of 20–110 molar equivalent per 100 moles of peroxyester. As pointed out in previous articles,^{15,16} this functionalization was not directly dependent on the peroxyderivative used

for the chemical modification. The free-radical reaction of oxygen with the polymer radicals and/or the presence of hydroperoxide functions on the polyethylene must be invoked to account for the formation of a ketone on the backbone of the polyolefin.^{17,18}

Functionalization by thermal decomposition of peroxyalkanoates

Thermolyses of PE₁, PE₂, and PE₃ were performed in polyethylene, and the results obtained are presented Table I.

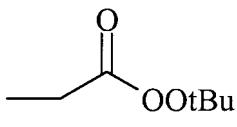
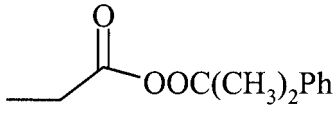
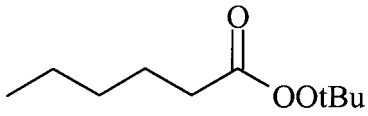
The values showing the extent of crosslinking (Table I) were relatively low no matter which peralkanoate was used. A comparison of the results for PE₁ with the preliminary results¹⁵ showed that the decreasing concentration of perester drastically influenced the formation of nets in the polymer. This observation means the chemical modification of polyethylene on industrial bases by thermolysis of a judiciously chosen peroxyester is promising because a very low ratio of the latter will be employed.

The quantity of ester functions grafted onto the polymer was determined chemically (saponification) and spectroscopically (IR). The results for PE₁ and PE₂, taking into account the errors in both methods, could be considered to be in good agreement. For PE₃, despite several trials, the spectroscopic measurements showed a value higher than 100%. In this case, the presence of a high quantity of ketone could be responsible for this.

The decarboxylation of acyloxy generally occurs in the cage of a solvent.¹⁹ Because in our study 50–60% of carbon dioxide, relative to the perester, was produced, we have to consider the possibility that acyloxy radicals were consumed in the cage by a faster reaction, which could be the coupling represented in Scheme 1. This agrees with the IR identification of an ester function (1738 cm⁻¹) grafted on the polymer after reaction. The IR analysis of the polymer after basic treatment (P₂ in Fig. 1) showed the presence of the OH of an alcohol (3480 cm⁻¹) and of a carboxylate anion (1573 cm⁻¹). The IR identification of carbonyls, after treatment of the "saponified" polyethylenes by thionyl chloride, because of the acyl chloride at 1802 cm⁻¹ and the ester at 1738 cm⁻¹ as well as the formation of an important quantity of "crosslinked" polymer (nonsoluble polymer in 1,2-dichlorobenzene), confirmed the presence of both functions on the backbone of the polymer.

The observation of a carboxylate anion after saponification suggests that acyloxy radicals provided carbon-centered radicals bearing ester or acid functions. A direct titration of acid by potassium hydroxide performed on the soluble polymer (P₁ in Fig. 1) arising from the decomposition of PE₁ in polyethylene showed that the carboxylate, identified above, was

TABLE I
Decomposition of PE₁, PE₂ and PE₃ in Polyethylene

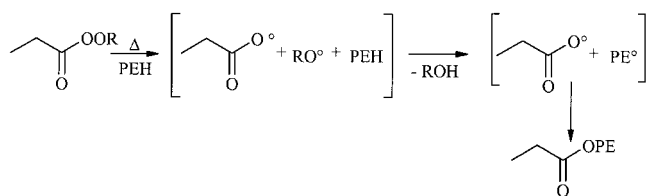
Peroxyesters	Crosslinking extent (%)	Carbon dioxide determined (%)	Ester grafted ^a A ^b	Ester grafted ^a B ^b	Acid ^a C ^b
 PE₁	4	57	44	42	12
 PE₂	3	48	30	38	11
 PE₃	12	50	64	-	38

^a Number of moles of ester or acid functions in the polymer or carbon dioxide per 100 moles of starting peroxyester.

^b See Figure 1.

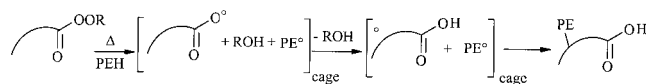
initially grafted as an acid. Therefore, the single ester grafted onto the polyolefin was propanoate by C—O bond creation. Several mechanisms could explain the grafting of this acid function onto polyethylene in the decomposition of a *t*-alkyl peralkanoate:

- an intramolecular rearrangement of the acyloxy radical via a hydrogen transfer to produce a carbon-centered radical and its coupling with a macroradical (Scheme 2).
- two consecutive intermolecular hydrogen transfers in the cage to generate the carbon-centered radical, which would couple with the macroradical (Scheme 3).
- the trapping of carbon dioxide, arising from the decarboxylation of the acyloxy radical, by the macroradical, followed by a hydrogen transfer (Scheme 4).

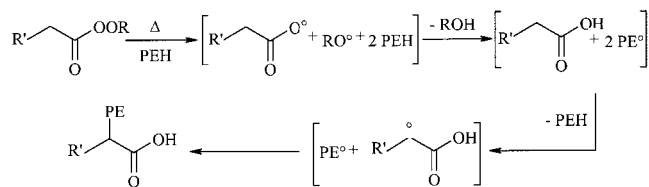


Scheme 1

A comparison of values **A**, **B**, and **C** for the three peresters used (Table I) indicates a difference in the chemical modification of polyethylene via the coupling of the macroradical with an alkyl radical and an oxy radical: about 30% could be attributed to the reaction of the carbon-centered radical bearing the carboxylic function for **PE₁** and **PE₂** and 60% for **PE₃**. This supports the involvement of an intramolecular rearrangement of the produced acyloxy radical, even if, to our knowledge, no intramolecular hydrogen transfer has been identified for acyloxy radicals, which is not surprising according to the fast rate of its decarboxylation.¹⁹ Hydrogen transfers generally occur when the transition state is not tight, which is the case for 1,5- and 1,6-reactions, whatever the attacking radical.²⁰ The production of a lower ratio of ester/acid (comparison of **B** and **C**) for **PE₃** than for **PE₁** and **PE₂** agreed with the involvement of such intramolecular 1,5- and/or 1,6-transfers of hydrogen (Scheme 5). However, this cannot be considered an argument for or against the existence of similar 1,3- and/or 1,4-transfers in the case of **PE₁** and **PE₂**.



Scheme 2



Scheme 3

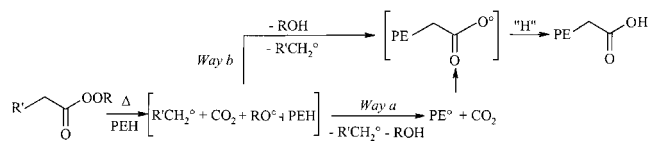
Even if the reaction of carboxylation of an alkyl radical is unknown in solution, we decided to test if it would occur in the molten PE. Then, *bis*-(1,1-dimethyl)peroxide was decomposed at 160°C in polyethylene under an atmosphere of carbon dioxide or argon. The formation of similar amounts of acid in both cases ruled out the carboxylation of a free alkyl radical in molten polyethylene (Scheme 4, *way a*). However, these experiments did not exclude the possibility of such a reaction in the cage of solvent (Scheme 4, *way b*).

The difficulty, if not impossibility, of finding experiments to prove or invalidate the third hypothesis about the mechanism, depicted in Scheme 3, did not allow us to go further. However, identification of the acyloxy radical of a faster coupling with a macroradical than its decarboxylation can be considered support for the possible existence of a reaction of abstraction of a hydrogen to the polymer by an acyloxy radical. Then, if the "acid" grafting for PE₃ could be essentially attributed to an intramolecular hydrogen transfer, it is very difficult to discriminate among the two proposals, described in Schemes 2 and 3, for PE₁ and PE₂.

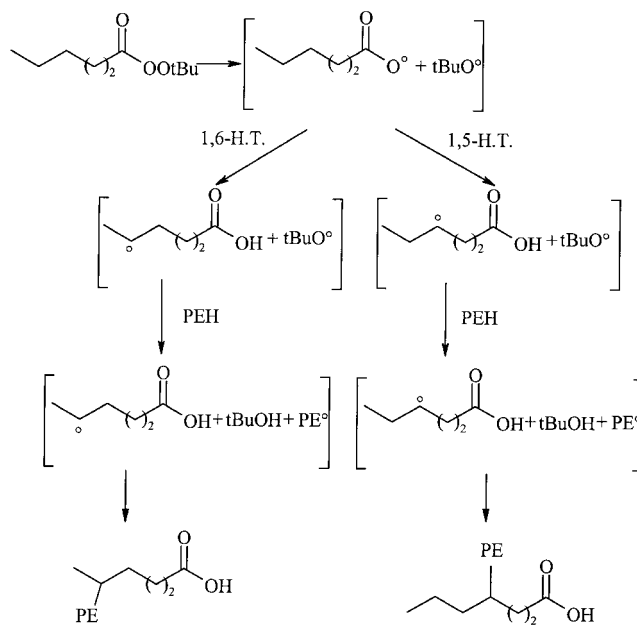
The results obtained with PE₁ and PE₂ are not significantly different, indicating that the influence of the alkylperoxy part is negligible. This is not surprising, given that the alkoxy radical arising from it can either abstract a hydrogen from the polyethylene or generate by β scission a methyl radical that would react similarly. This observation is in agreement with those of Moore,^{12,13} who identified the influence of the alkylperoxy moiety only when the alkyl radical, liberated in the β -scission of the *t*-alkoxy radical, was an ethyl radical.

Functionalization by thermal decomposition of 3-(1,1-dimethylethylperoxycarbonyl)-propionic acid derivatives

The use of *t*-alkyl peresters of monoperoxysuccinic acid instead of *t*-alkyl peralkanoates appeared to be an easy way to increase the number of acid and ester



Scheme 4



Scheme 5

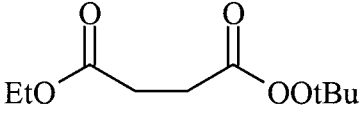
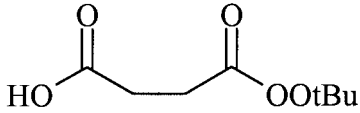
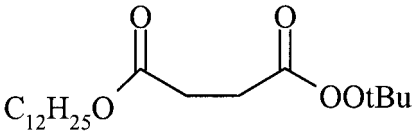
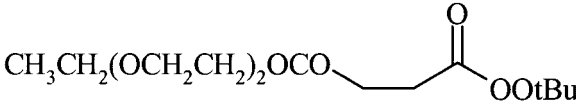
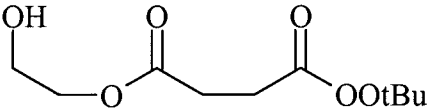
functions grafted onto polyethylene. Indeed, based on the results obtained with the peralkanoates, for each grafting of an acyloxy radical or the corresponding "rearranged" radical, two functions would be grafted per C—C- and C—O-created link. On the other hand, the combination of the polymer radical and the alkyl radical generated in the decarboxylation of the functional acyloxy radical, arising from the derivatives of monoperoxysuccinic acid, would give a second possibility, to graft an ester and/or an acid function onto the polyolefin. This was not the case for peralkanoate because the liberated alkyl radical did not have any function.

A comparison of the results obtained with this family of peresters (Table II) showed:

- a similar production of carbon dioxide in the thermolysis of the different peresters;
- functions bearing carboxyl groups grafted onto the polyolefin;
- the balance of the initial carboxylic entities, based on the presence of ester and acid functions grafted onto the polyethylene and recovered carbon dioxide, to be quite low;
- the extent of polymer crosslinking influenced by the nature of the acyloxy part of the perester.

The balance of the carboxyl entities (CO₂ and ester functions grafted onto polyethylene) shows that 40–50% of the peresters derived from monoperoxysuccinic acid (there are two carboxylic entities per mole of perester) were producing other compounds. This indicates the behavior of the radicals arising from these compounds was different from those given by the

TABLE II
Decomposition of PE₄ to PE₁₀ in Polyethylene

Peroxyesters	Crosslinking extent (%)	Carbon dioxide determined (%) ^a	Ester grafted ^a A ^b	Ester grafted ^a B ^b	Acid ^a C ^b
 <p>PE₄</p>	8	50	62	58	52
 <p>PE₅</p>	3	50	54	35	45
 <p>PE₆</p>	12	45	66	72	38
 <p>PE₇</p>	2	45	61	46	39
 <p>PE₈</p>	2	54	63	46	30

^a "Moles" of ester, acid functions in the polymer or carbon dioxide per 100 moles of starting peroxyester.

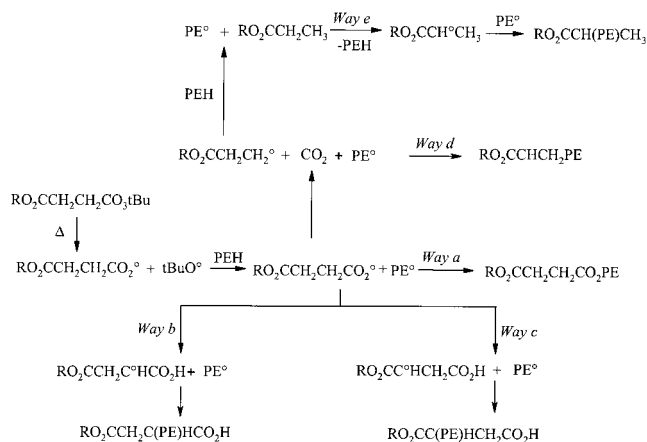
^b See Figure 1.

peralkanoates (a good balance was obtained for them). The observation of a low yield of grafting shows that such radicals were not coupling efficiently with the polymer radical and then would escape from the cage. The identified very low crosslinking extents indicate that they were not able to abstract a hydrogen to the polyolefin. This would result from higher stability than that of the pure secondary alkyl radicals, which would be generated by the abstraction of a hydrogen from polyethylene. These radicals are certainly carbon-centered radicals in α to the carbonyl of an ester or an acid, instead of a pure alkyl one, as for PE₁–PE₃. This may agree with the hypothesis advanced previously to explain the differences in polyethylene functionalization by the decomposition of peroxyketals arising from substituted cyclohexanones.¹⁶ The main

part of these radicals is certainly disappearing via their self coupling.

Taking into account the reactions involved in the free-radical grafting of carboxyl entities proposed in the thermal decomposition peroxyalkanoates in polyethylene, the involvement of the reactions depicted in Scheme 6 can be envisaged.

Among all the proposed mechanisms, *way a* (Scheme 6) is the only one producing a C—O bond. As already presented, different determinations are allowed to approach the quantity of grafting by C—C bond and C—O bond creation. An estimation of the grafting by a C—C bond creation could be done through the acid determination (C). In Table II the important (C) values indicate that this grafting is very efficient. The comparison of A or B to C shows that the



Scheme 6

function grafting by C—O bond formation (Scheme 6, way a) is certainly very low. This result differs drastically from the ones obtained with the peroxyalkanoates (PE_1 , PE_2 , and PE_3). The mechanism analysis (Scheme 6) shows that functionalized acyloxy radicals could either decarboxylate or generate more readily a carbon-centered radical by intra- or intermolecular hydrogen transfer (Scheme 6, way b and c), similar to those described for PE_1 (schemes 3 and 4). The comparison of the carbon dioxide productions reported in Tables I and II proves the similarity of the rate of decarboxylation for the various acyloxy radicals. Then, the difference in the behavior of acyloxy radicals must be attributed to the transfer reactions (Scheme 6, ways b and c) which appear to be faster than the coupling with the polymer radical for the functional acyloxy radicals. The decarboxylation reaction is also responsible for the production of carbon-centered radical bearing esters functions which would combine with the polymer radical (Scheme 6, ways d and e). However, taking into account the previous remarks on the low efficiency of the coupling of a macroradical and a carbon-centered radical bearing an alkoxy carbonyl entity, it can be tempting to attribute the grafting by C—C bond formation mainly to way d.

The results of Table II might indicate that the presence of a long alkyl chain in the perester favors the extent of crosslinking ($PE_6 > PE_4 > PE_5, PE_7, PE_8$), in agreement with a similar high value also obtained with PE_3 . However, as the efficiency of the grafting, because of the coupling of the radicals, apparently is not influenced by this factor, it is difficult to imagine that it could result from faster diffusion of the more lipophilic acyloxy radical.

For the peresters PE_4 – PE_8 , the amount of ester and acid functions grafted (A: 0.54–0.66 per mole of perester) was similar to the one obtained using PE_3 (0.64) but higher than that with PE_1 (0.44). The grafts of acid entities—determined after saponification and acidifi-

cation—in the same range for the peresters PE_3 – PE_8 , were higher than for the t-alkyl perpropanoates. However, the less extensive crosslinking with the succinic derivatives than with PE_3 favors their use. A second advantage of monoperoxysuccinic acid derivatives is having the possibility of using this reaction to graft any function compatible with the synthesis of the perester and the process of chemical modification of polyethylene, as the primary alcohol one from PE_8 .

CONCLUSION

This study showed that it is possible to graft ester and acid functions onto polyolefin by decomposition of peresters in molten polyethylene. This occurred through the creation of a C—C bond or a C—O bond generated by the combination of a polymer radical and the acyloxy radical or an alkyl radical obtained from the latter by decarboxylation or hydrogen transfer. The use of functional alkanic acids as succinic acid derivatives to prepare the perester appears to be promising for the graft of different functions onto polyethylene.

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