Chemical modification of molten polyethylene by thermolysis of peroxyketals

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Abstract

A new approach in the modification of polyethylene involving the thermolysis of peroxyketals in the molten polymer is presented. Three cyclic and one acyclic peroxyketals were decomposed in polyethylene. The grafting of an ester function by coupling of an alkyl radical bearing such a function, arising from the peroxyketals, and a polymer radical, generated from the polyethylene, was identified. The efficiency of this reaction was measured by infrared spectroscopic determination of the carbonyl of the ester and by saponification of this function. The influence of the concentration of peroxyketal in the polyethylene, of the temperature of reaction, and of the nature of the radical coupling with the one arising from the polymer was investigated. Besides the yields of the functionalization, the extent of "crosslinking" of the polyolefin was determined. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Over the past decades, the free radical chemical modifications of polyethylene, based on the thermal decomposition of radical initiators in the presence of unsaturated compounds, have been intensively studied [1–4]. These reactions were performed directly, in the molten polymer or in a solution of the polymer, in the presence of maleic anhydride [5–9], glycidyl-2-methylpropenoate [10–11] and 2-dimethylaminoethyl-2-methylpropenoate [12]. In 1996, we started a program on the free radical functionalization of polyolefins using the single thermal decomposition of initiators in the molten polymer. The induced decomposition of 1,1-dimethylethyl hydroperoxide [13] was used to perform the hydroxylation of polyethylene. In a recent publication [14], we reported that the chemical modification of polyethylene can be realized via the thermal decomposition of a peroxyderivative in the molten polymer. The decomposition of the peroxidic compound generates two radicals: one of them abstracts an hydrogen from the polyethylene and the second one — or a radical arising from it — combines with the macroradical so formed. Different peroxyderivatives were checked and, among them, peroxyesters and peroxyketals gave the best results [14]. During the course of this work, Moore et al. [15] presented the study

of the decomposition of peroxyesters in the molten polypropylene. The yields of grafting, relative to the peroxyester, were not very important (less than 15%). Among the possible reactions involved in this process, the coupling of a polymeric radical with a radical produced from the initiator was mentioned.
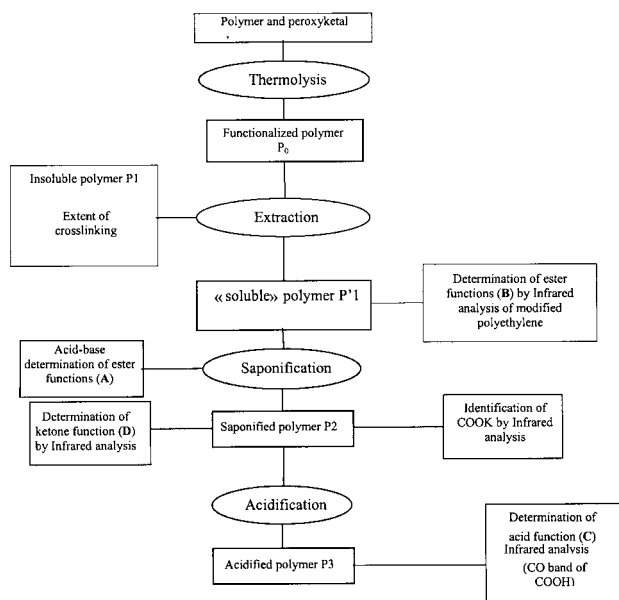
The identification of chemical modification of polyethylene in the molten state [14] by the thermal decomposition of peroxyketals prompted us to investigate such a reaction more deeply. As a first step, to select conditions for this reaction, the influence on the functionalization and the crosslinking of the reaction temperature and of the amounts of peroxyketal were studied. As a second one, the thermolysis of several peroxyketals in polyethylene was performed to identify the general features of the structure of the peroxyketal upon the reaction.

2. Experimental

2.1. Materials

Solvents such as 1,2-dichlorobenzene and dichloromethane were received from Acros and used without any further purification. Octanoic acid, 6-undecanone, 1-dodecene, ethyl hexanoate, ethyl heptanoate, ethyl-6-ethoxycarbonyl hexanoate, 2-methylcyclohexanone supplied from Aldrich and diethyl succinate, ethyl butanoate cyclohexanone,

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Scheme 1. Methodology used for the study of the chemical modification of polyethylene.

ethyl-4-oxo-pentanoate received from Acros and 2-ethoxy-carbonylcyclohexanone purchased from Fluka were used without any purification.

The high density polyethylene (125 000 g mol^{-1}; Acros ref. 17851) was dissolved in 1,2-dichlorobenzene (10 g in 400 ml) at 115°C. After complete dissolution, the polymer was precipitated in dichloromethane (1 l), filtered and then washed during 24 h in a soxhlet apparatus with dichloromethane. The polyethylene powder was then dried under vacuum until there was no mass variation.

The peroxyketals used were: 1-ethoxy-1-(1,1-dimethyl-ethylperoxy)cyclohexane (**PK$_1$**); 1-ethoxy-2-methyl-1-(1,1-dimethylethylperoxy)cyclohexane (**PK$_2$**); 1-ethoxy-2-ethoxycarbonyl-1-(1,1-dimethylethylperoxy)cyclohexane (**PK$_3$**); and ethyl 4-ethoxy-4-(1,1-dimethylethylperoxy)pentanoate (**PK$_4$**). All of them were synthesized according to reported procedures [16,17] (yields relative to the starting commercial ketone: **PK$_1$** 50%, **PK$_2$** 30%, **PK$_3$** 10%, **PK$_4$** 58%).

PK$_1$. NMR ^{1}H (250 MHz, CDCl$_3$, δ ppm): 3.54–3.46 q, 2H [CH$_2$O]; 1.72–1.21 m, 10H [others protons of the cycle]; 1.17 s, 9H [(CH$_3$)$_3$]; 1.15–1.10 t, 3H ^3J = 7.1 Hz [CH$_3$].

NMR ^{13}C (62.9 MHz, CDCl$_3$, δ ppm): 103.2 [C(OEt)(OOtBu)]; 78.6 [OOC(CH$_3$)$_3$]; 55.6 [OCH_2CH$_3$]; 32.3 and 22.8 [–(CH_2CH_2)$_2$C(OOtBu)(OEt)]; 26.6 [OOC(CH$_3$)$_3$]; 25.7 [CH_2]; 15.6 [OCH$_2CH_3$].

PK$_2$. NMR ^{1}H (250 MHz, CDCl$_3$, δ ppm): 3.75–3.45 m, 2H [CH$_2$O]; 2.4–0.9 m, 15H [others protons of the cycle]; 0.85 s, 9H [OOC(CH$_3$)$_3$]. NMR ^{13}C (62.9 MHz, CDCl$_3$, δ ppm): 105.1 [C(OEt)(OOtBu)]; 78.5 [OOC(CH$_3$)$_3$]; 55.4 [OCH_2CH$_3$]; 33.6 [CHCH$_3$]; 30.0, 28.1, 22.7, 20.8 [$CH_2CH_2CH_2CH_2$]; 26.5 [OOC(CH$_3$)$_3$]; 15.3 and 14.2 [CH_3].

PK$_3$. NMR ^{1}H (250 MHz, CDCl$_3$, δ ppm): 4.20–3.90 m, 2H [CH$_2$OCO]; 3.60–3.40 m, 2H [CH$_2$O]; 2.3–1.3 m, 9H [others protons of the cycle]; 1.25–1.00 m, 6H [CH$_3$]; 0.85 s, 9H [OOC(CH$_3$)$_3$]. NMR ^{13}C (62.9 MHz, CDCl$_3$, δ ppm): 172.7 and 172.0 [CO_2]; 102.9 and 102.8 [C(OEt)(OOtBu)]; 79.0 [OOC(CH$_3$)$_3$]; 59.9, 59.8 and 56.1 [OCH_2]; 45.6 and 45.2 [CCO$_2$Et]; 29.0, 28.5, 26.1, 22.4, 21.9, 20.9 [$CH_2CH_2CH_2CH_2$]; 26.6 [OOC(CH$_3$)$_3$]; 15.4 and 14.3 [CH_3].

PK$_4$. NMR ^{1}H (200 MHz, CDCl$_3$, δ ppm): 3.80–3.60 q, 2H [CH$_3$CH_2OCO]; 3.30–3.00 q, 2H [CH$_3$CH_2O]; 2.00–1.80 m, 2H [CH$_2$CH_2COO]; 1.60–1.45 m, 2H [CH_2CH$_2$COO]; 1.02 s, 9H [OOC(CH$_3$)$_3$]; 1.00–0.65 m, 9H [CH$_3$]. NMR ^{13}C (50.3 MHz, CDCl$_3$, δ ppm): 173.3 [CO]; 103.9 [COOtBu]; 78.8 [OOC(CH$_3$)$_3$]; 60.3 [CH$_3$CH_2OCO]; 56.5 [OCH_2CH$_3$]; 31.3 [OCOCH_2]; 29.6 [OCOCH$_2CH_2$]; 26.3 [OOC(CH$_3$)$_3$]; 20.2 [CCH$_3$]; 15.2 and 14.0 [OCH$_2CH_3$ and OCH$_2CH_3$].

2.2. Functionalization and analysis of the modified polyethylene

The methodology used to study and characterize the different organic functions (e.g. the chemical modification of polyethylene) grafted is presented in Scheme 1. With that process it was possible to estimate the quantity of ester, acid and ketone functions present on the modified polyethylene.

2.2.1. Preparation of the sample

In a 50 ml flask, 1 g of powdered polyethylene and the corresponding amount of the peroxyderivative (see Tables 1–3; for 10 equivalents, 3.57 mmol; for 20 equivalents, 1.79 mmol; for 40 equivalents, 0.89 mmol; for 80 equivalents, 0.45 mmol and for 100 equivalents, 0.36 mmol) in a solution of 6 ml of dichloromethane/cyclohexane (9:1),

Table 1

Influence of the temperature of reaction on the modification of polyethylene by decomposition of **PK$_1$** (20 ethylene units per mole of peroxyketal)

Temperature (in °C)	Extent of crosslinking (%)			Ethyl hexanoate (yield %)[a]			Ethyl-6-(1,1-dimethylethoxy) hexanoate (yield %)[a]			Relative intensity of the carbonyl band versus the CH band (RI)		
140	2	0	1	2	1	1	9	5	2	4.9	3.9	4.1
150	7	10	9	6	5	8	30	29	37	12.1	16.4	17.6
160	13	20	13	7	9	3	22	26	16	15.6	16.0	15.1

[a] Relative to the initial number of moles of **PK$_1$**.

Table 2
Influence of the relative amounts of PK_1 and polyethylene in the modification of that polyolefin

Entry	Ethylene units per mole of PK_1	Extent of crosslinking (%)		Relative intensity corrected (RIC)	
a	10	18	29	2.7	2.9
b	20	13	13	3.1	3.1
c	40	8	8	4.7	5.5
d	80	8	5	5.1	4.9
e	100	7	6	6.8	5.9

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 masses of polyethylene and peroxyketal used for the reaction) was obtained.

2.2.2. Reaction of functionalization

The polymer/peroxyderivative mixture obtained was then placed in a reactor (Büchiglasuster BMC 100). The reactor was closed and degassed twice by the freeze/pump/thaw method. The atmospheric pressure was recovered by injection of argon. The reactor was heated at the chosen temperature (140, 150 or 160°C) for 2.5 h, without any stirring.

2.2.3. Extraction and analysis of the products arising 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. The dichloromethane and dichloromethane/1,2-dichlorobenzene solutions were mixed. The dichloromethane was removed using a rotavapor and the

products arising from the peroxyketal were identified by NMR and/or mass spectroscopy. They were separated by a silica gel column chromatography. Reaction products were identified by gas chromatography via the comparison to commercial sample (ethyl butanoate, ethyl hexanoate, ethyl heptanoate, ethyl-6-ethoxycarbonyl hexanoate). Ethyl-6-(1,1-dimethylethoxy)hexanoate was identified by NMR and, ethyl 2-(1,1-dimethylethoxy)-6-ethoxycarbonyl hexanoate and ethyl-6-(1,1-dimethylethoxy)heptanoate by mass spectroscopy:

Ethyl-6-(1,1-dimethylethoxy)hexanoate. NMR [1]H (250 MHz, $CDCl_3$, δ ppm): 4.20–4.00 q, 2H [CH_3CH_2O]; 3.30–3.20 m, 2H [CH_2OtBu]; 2.30–2.15 m, 2H [CH_2CO]; 1.70–1.25 m, 6H [others CH_2]; 1.20 t, 3H [CH_3]; 1.10 s, 9H [$OC(CH_3)_3$]. NMR [13]C (62.9 MHz, $CDCl_3$, δ ppm): 170.0 [CO_2]; 73.5 [$(CH_3)_3CO$]; 61.3 and 60.2 [CH_2CH_2O and CH_3CH_2O]; 34.3 [CH_2CO_2]; 30.3, 25.8 and 24.9 [others CH_2]; 27.5 [$(CH_3)_3CO$]; 14.3 [OCH_2CH_3].
Ethyl-6-(1,1-dimethylethoxy)heptanoate. m/z: 157.1; 130.1; 101; 57.1; 28.
Ethyl 2-(1,1-dimethylethoxy)-6-ethoxycarbonyl hexanoate. m/z = 187.1; 159.1 (MacLafferty); 57.1; 29.

2.2.4. Extraction of the "non-crosslinked" polymer

The dried polymer was placed in porous steel bags (porosity 140 μm, 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 — [13]. The extent of crosslinking (mass of insoluble polymer/mass of starting polyethylene) was calculated from it. The soluble polymer ("non-crosslinked") was recovered from the 1,2-dichlorobenzene

Table 3
Thermolysis of peroxyketals PK_1–PK_4 in molten polyethylene at 160°C (80 ethylene units per mole of peroxyketal)

Peroxide	Extent of crosslinking (%)	Typical IR bands	Grafting yields (%)[a]				
			Ester grafted method **A**	Ester grafted method **B**	Acid grafted method **C**	Ester grafted average **(A + B + C)/(3)**	Ketone grafted method **D**
PK_1	9	1737; 1719 1176	32	50	48	43	69
PK_2	18	1738; 1719 1175	30	30	38	33	52
PK_3	5	1738; 1719 1177	35	40	52	43	52
PK_4	8	1738; 1719 1176	51	67	51	56	80

[a] Relative to the initial number of moles of peroxyketal.

solution after precipitation in dichloromethane followed by a drying under vacuum at 60°C. The infrared analysis was then carried out.

2.2.5. Alkaline treatment

0.5 g of "non-crosslinked" polyethylene was placed in a flask and dissolved in 125 ml of toluene at 110°C. Then, 25 ml of an ethanolic solution of KOH (0.05 mol l^{-1}) were 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 (0.1 M) in presence of phenolphthalein. From it, 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 and IR spectrum was recorded.

2.2.6. Acid treatment

0.25 g of the dried saponified polymer 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; it was then analyzed by IR.

2.3. Gas chromatography

Gas chromatography was performed on a VARIAN 3400 with a FID detector fitted with a computer using the STAR CHROMATOGRAPHY software. The apparatus was equipped with a column DB5 (5% Ph, 30 m length, 0.25 mm inside diameter, 0.25 μm internal phase thickness, pressure 10 psi nitrogen gas carrier). It was used to identify (by comparison with standards) and to determine the amounts of products arising from the thermal decomposition of the peroxyketals (1-dodecene as internal standard).

2.4. Infrared spectroscopy

The infrared spectra were recorded on a Perkin–Elmer Paragon 1000. Films of about 7 mg of polyethylene were prepared by a 9 tons pressure under vacuum. The modified polymer was compared with films of the initial non-modified polymer.

The quantification of the grafting was based on a study presented by Fodor [18]. It was realized by the determination of the relative intensities (RI) of the carbonyl bands (area of the carbonyl band versus the area of the CH$_2$ band at 720 cm^{-1}) using the internal software of the infrared spectrograph. RI of the infrared spectra given by known mixtures polyethylene/organic compounds bearing ester or acid or ketone function were calculated. Calibration curves

were obtained by plotting those RI versus the concentrations of the organic function used in a known mass of polyethylene (moles of organic function per 1 g of polymer). These mixtures were prepared as described previously (Section 2.2.1) using diethyl succinate for the ester, octanoic acid for the acid and 6-undecanone for the ketone. For each mixture, three spectra were recorded from three different samples and the average value of RI was used for the plot.

2.4.1. Qualitative analysis

In the case of Table 1 the RI presented were the ratios of the areas of the carbonyl bands (including ester and ketone) versus the area of the methylene band at 720 cm^{-1}. In the particular case of Table 2, to compare the different concentrations, RI were corrected to take into account the fact that the initial quantity of peroxyketal was changing. The RI obtained in each attempt was brought back to a standard (1 mol of peroxyketal for 10 ethylene units) to give the value of the relative intensity corrected (RIC). Therefore, RI obtained for y ethylene units were corrected using the formula:

$$RIC = RI \times \frac{y}{10}$$

2.4.2. Quantitative results

To estimate the number of ester functions grafted onto the polyolefin only the soluble polymer was considered. The results reported in Table 3 were obtained assuming a similar RI for the ketone functions before and after saponification. RI$_{ester}$ was calculated from the values measured on the IR spectra of the modified polyethylenes by the following equation:

$$RI_{ester} = RI_{carb} - RI_{ketone}$$

where RI$_{carb}$ is the relative intensity of the carbonyl band of the modified polyethylene spectrum before saponification; RI$_{ketone}$ the relative intensity of the carbonyl band of the modified polyethylene spectrum after saponification; and RI$_{ester}$ the relative intensity due to the ester band of the modified polyethylene spectrum before saponification

The yield of functionalization of the polyethylene (EG), relative to the peroxyketal involved in the reaction, can easily be calculated from the following formula:

$$EG = \frac{RI_{ester} \times S}{n_0 \times 1.52} \times 100$$

where S is the mass of non-crosslinked polymer (g); 1.52 the proportionality coefficient obtained with the calibration; and n_0 the number of moles of peroxyketal used in the reaction.

The estimation of the yield of functionalization (AG) of the polyethylene by the thermolysis of the peroxyketal, based on the measurement of the acid function present on the polymer after saponification and acidification, was similarly obtained:

$$RI_{acid} = RI_{carbsa} - RI_{ketone}$$

where RI_{carbsa} is the relative intensity of the carbonyl band of the modified polyethylene spectrum after saponification and acidification; and RI_{acid} the relative intensity due to the carboxylic acid band of the modified polyethylene spectrum after saponification and acidification.

$$AG = \frac{RI_{acid} \times S}{n_0 \times 1.40} \times 100$$

where 1.40 is the proportionality coefficient obtained with the calibration

The estimated yield of production of ketone functions on the polyethylene KG can be calculated in the same way, assuming that a ketone function is generated by the decomposition of 1 mol of peroxyketal:

$$KG = \frac{RI_{ketone} \times S}{n_0 \times 0.68} \times 100$$

where 0.68 is the proportionality coefficient obtained with the calibration.

3. Results and discussion

3.1. Conditions of thermolysis of peroxyketals in molten polyethylene

A preliminary study of the functionalization of polyethylene by peroxyketal PK_1 was performed to select the reaction temperature and the relative amounts of the reactants. The selection was realized on the basis of a good functionalization yield of the polymer for a low extent of crosslinking.

Three different temperatures of reaction — higher than the melting temperature of the polyethylene — were chosen for a total decomposition of the peroxyketal occurring in less than 2.5 h. The ratio of the reactants was 20 ethylene units per mole of peroxyketal. Three different experiments were performed for each temperature (Table 1).

A partition of the modified polymer was also realized by a treatment with hot 1,2-dichlorobenzene. This gave rise to an approach for estimating the efficiency for macroradicals to combine (see Table 1; extent of crosslinking).

Two compounds arising from the decomposition of PK_1 were identified: ethyl hexanoate and ethyl-6-(1,1-dimethylethoxy)hexanoate. The alkyl radical, generated in the rearrangement of the radical 1-ethoxycyclohexyloxyl [17], abstracted a hydrogen atom from the medium to produce the former compound or combined with the 1,1-dimethylethoxyl radical to give the second one (Scheme 2).

In a preliminary publication [14], the mechanism of functionalization of the polyethylene (by the thermolysis of PK_1) was attributed to the combination of two radicals as described in Scheme 3. According to the identification after reaction of different carbonyl functions (ester or ketone) in IR spectroscopy on the polyethylene, the functionalization of the "non-crosslinked" polymer was estimated in that
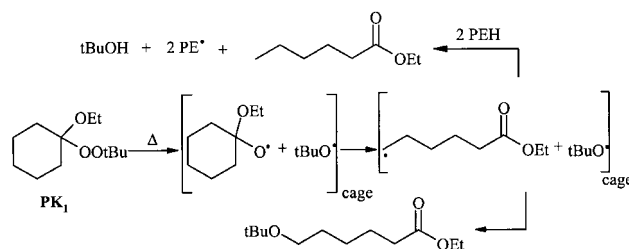
Scheme 2. Mechanism of formation of ethyl (6-(1,1-dimethylethoxy) hexanoate and ethyl hexanoate in the decomposition of PK_1.

study via RI of the large carbonyl band versus the C–H band at 720 cm^{-1} (Table 1).

The analysis of the results given in Table 1 indicates:

- a good homogeneity and reproducibility in the results obtained;
- an increase in the extent of crosslinking of the polyethylene with temperature;
- a higher functionalization yield at 150 and 160°C than at 140°C;
- a more efficient production of ethyl hexanoate and ethyl-6-(2,2-dimethylethyloxy)hexanoate at the higher temperatures.

These remarks are consistent with a partial decomposition of PK_1 at 140°C but no residual peroxyketal could be identified at the end of the reaction. Therefore, the differences observed between 140°C and the other temperatures cannot be explained.

Even if the extent of crosslinking appears slightly higher at 160°C than at 150°C, we selected 160°C as reaction temperature for all the peroxyketals (closer condition of reaction to the one used for the modification of the polyethylene in an extruder).

To choose the best ratio of the reactants in order to settle the best conditions for the modification of polyethylene, two sets of experiments with five different ratios of the polyolefin and PK_1 (10, 20, 40, 80 and 100 ethylene units per mole of peroxyketal) were performed.

As previously described, ethyl hexanoate and ethyl-6-(1,1-dimethylethoxy)hexanoate were identified in the
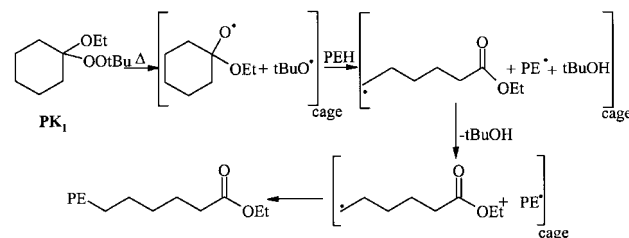
Scheme 3. Mechanism of functionalization of polyethylene by the thermolysis of PK_1.

solvent of extraction of the modified polyethylene (Scheme 1). The quantity of peroxyketal, relative to the polymer used in the reaction, diminished and then the concentrations of these products decreased; their titrations became hazardous and were not presented.
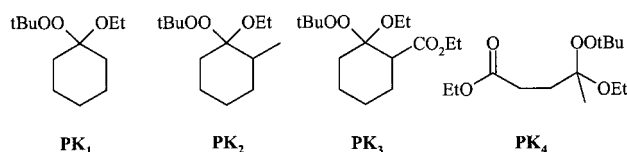
To estimate the efficiency of the functionalization, an easily accessible parameter is necessary and RI of the band of the carbonyl towards the one of C–H was selected. However, in order to have comparable values, this parameter was corrected to account for the use of different amounts of PK_1 for the same quantity of polyethylene. The values dealing with the functionalization yield (RIC) and the extent of crosslinking are mentioned in Table 2 because they represent the parameters permitting the analysis of the efficiency of the free radical modification of the polyethylene.

The extent of crosslinking of the polymer seems similar for the high values of the reactant ratios (100, 80 and 40) but increases with the lower ones (20 and 10). These results are not surprising considering the use of the decomposition of peroxides in polyethylene to bring about its crosslinking [19,20].

The values reported in Table 2 show a trend for the functionalization of polyethylene: with lower reactant ratios (entries a and b), the functionalization appears less efficient than with higher one (entries c, d and e). However, it must be emphasized that, in these preliminary experiments, the function introduced on the polymer, due to the combination of a polymer radical with the alkyl one (Scheme 3), was assumed to be an ester. The identification of a ketone besides the ester function, on the basis of the IR absorption [14], shows the limit of that approach. However, the qualitative results depicted above allowed us to select conditions of reaction for the study of the thermolysis of peroxyketals in molten polyethylene: a homogeneous mixture of polyethylene and peroxyketal (80 ethylene units per mole of peroxyderivative) heated at 160°C during 2.5 h would allow a good functionalization of the polymer.

3.2. Functionalization of polyethylene by the thermolysis of different peroxyketals

Three peroxyketals (used for the functionalization of polyethylene) deriving from substituted cyclohexanones (Scheme 4) were studied in order to see if the nature of the radical produced by the rearrangement of the alkoxyalkoxyl radical, generated in the thermolysis of the peroxy-

derivative, has an influence on the efficiency of the functionalization as well as on the crosslinking of the polyolefin. Peroxyketal PK_4 was also decomposed in the same conditions in order to analyze the effect of the formation of a neutral molecule (ethyl acetate) close to the radical pair involved in the functionalization. Such a molecule, formed from the alkoxyalkoxyl radical, and a molecule of t-butanol, arising from the hydrogen abstraction to the polymer by the t-butoxyl one, lie around/between the reactive species (polymer radical and "functional" radical). Their presence might then disfavor or prohibit the contact — necessary to generate the carbon–carbon bond permitting the functionalization of the polyolefin — between these radicals, indirectly provoking their diffusion in the medium.

The thermal decomposition of the cyclic peroxyketals produced an alkoxyalkoxyl radical generating by the same mechanism a primary radical (PK_1) or a secondary radical (PK_2 and PK_3). The polarity of the radicals issued from PK_2 and PK_3 were different, nucleophilic (PK_2) and electrophilic or ambiphilic (PK_3).

Molecular compounds were identified after the thermolysis of the peroxyketals:

- for PK_1: ethyl hexanoate and ethyl-6-(1,1-dimethylethoxy)hexanoate;
- for PK_2: ethyl-6-(1,1-dimethylethoxy)heptanoate, ethyl butanoate and ethyl heptanoate;
- for PK_3: ethyl-6-ethoxycarbonylhexanoate and ethyl 2-(1,1-dimethylethoxy)-6-ethoxy carbonyl hexanoate.

In the reaction performed with PK_4, the homologous molecular products were not determined according to their low boiling points (difficulty to separate them from the solvent in the gas chromatography analysis).

If the thermolysis of PK_1 and PK_3 generated the same types of products by hydrogen abstraction and coupling, in the reaction given by PK_2, another compound was identified besides these two. The production of ethyl butanoate (in the thermolysis of PK_2 in polyethylene) could be attributed to a reaction of β-scission (Scheme 5), similar to the one observed in the free radical treatment of polypropylene in close reaction conditions [21,22].

The polyethylenes obtained after modification were treated as mentioned in Scheme 1 in order to determine the extent of crosslinking and the functionalization yield relative to the peroxyketal. These results are given in Table 3.

Scheme 4. Peroxyketals used for the functionalization of polyethylene.
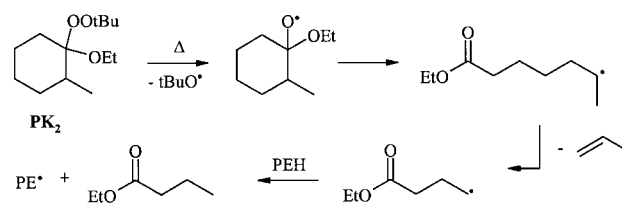
Scheme 5. Formation of ethyl butanoate in the thermolysis of PK_2 in polyethylene.

The analysis of these different values shows:

- a very low extent of crosslinking with peroxyketals **PK**$_1$, **PK**$_3$ and **PK**$_4$ and slightly higher with **PK**$_2$;
- not very different values for the yields of functionalization by radical combination between a macroradical and an alkyl one, determined by methods **A**, **B** and **C** (Scheme 1); the average value obtained from each of them indicates an uncertainty of about 10%;
- a difference in the efficiency for the functionalization with the various peroxyketals;
- an important production of ketone.

If one compares the results given by **PK**$_1$ and **PK**$_2$, a higher extent of crosslinking and a lower yield of functionalization relative to the peroxyketal are noticed for the second one. The behavior of the alkyl radical in the competitive reactions, hydrogen abstraction, coupling with the macroradical or β-scission, is certainly responsible of the existence of such a result. The comparison of the yields of functionalization of polyethylene by both compounds indicates an easier reaction for the combination of the polymer radical with the primary alkyl radical issued from **PK**$_1$ than with the secondary alkyl, given by **PK**$_2$. The existence of a stronger steric hindrance could explain this result. The comparison of these results with **PK**$_3$ ones would be in favor of such an effect if the existence of polar effect in the coupling of carbon centered radicals is negligible. On the other hand, the identification of ethyl butanoate in the reaction products of the thermolysis of **PK**$_2$ agrees with a fast β-scission in competition with the combination. Then, the differences identified in the functionalization of polyethylene by these two peroxyketals could find their origin in the existence of the β-scission. Indeed, the formation of a molecule of propene may disfavor the interaction between the alkyl radical and the polymer radical. This would favor the escape of the radicals from the "cage" and then a more efficient hydrogen abstraction to the polyethylene, responsible for the higher crosslinking rate. However, the results obtained with the peroxyketal **PK**$_4$ are not confirming such an hypothesis because the β-scission of the alkoxyalkoxyl radical, involved in this process, produces a molecule of ethyl acetate and the functionalization yield is even better than with **PK**$_1$. Nevertheless, such a rather surprising observation can be understood on the basis of the rearrangement of the alkyl radical issued from **PK**$_1$, identified earlier by us [17] (Scheme 6). Indeed, as shown by the low yield of functionalization of polyethy-
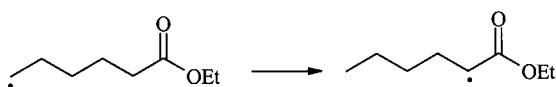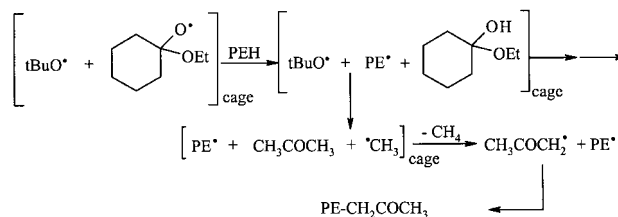
Scheme 7. Mechanism of grafting of a ketone onto polyethylene.

lene by **PK**$_3$, the rearranged radical does not efficiently combine with the polymer radical.

In each experiment, we observed the formation of a ketone with yields in the range of 52–80% relative to the peroxyketal, assuming the formation of one function per mole of peroxyderivative. The single origin found to generate such a function from the peroxyketals involves the 1,1-dimethylethoxyl radical by the mechanism represented in Scheme 7. However, values higher than 100% for the total functionalization yields relative to the peroxyketals, calculated on the bases of ketone and ester formation, show that such a mechanism is unlikely or would be involved to only a very low extent. As pointed out in the preliminary publication [14], the reaction of oxygen with the polymer radicals and/or the presence of hydroperoxide in the polymer must be invoked to account for the formation of ketone on the backbone of the polymer [23,24].

4. Conclusions

This study shows the efficient functionalization of polyethylene by the thermolysis of peroxyketals in the molten polymer. An ester function could be grafted on the polymer with yields in the range of 20–50% relative to the peroxyketal without very much crosslinking of the polymer. The ester function grafted could be generated in the rearrangement of the alkoxyalkoxyl radical produced (cyclic peroxyketals) or directly present on the peroxyketal (**PK**$_3$ and **PK**$_4$). The results obtained with these last two peroxyketals show that functions compatible with the synthesis of peroxyketals and the conditions of reaction could be similarly grafted on polyethylene via the formation of a functionalized alkyl radical, arising from the decomposition of the peroxyketal.

Scheme 6. Rearrangement of the alkyl radical arising from **PK**$_1$ [17].

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