

# Crosslinking of High-Density Polyethylene in the Presence of Organic Peroxides

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**ABSTRACT:** The crosslinking efficiency of various commercially available organic peroxides (dicumyl peroxide, *O,O*-*t*-butyl *O*-2-ethylhexylperoxycarbonate, *t*-butyl peroxybenzoate, *t*-butyl 3,5,5-trimethylperoxyhexanoate, and *t*-butyl 2-ethylperoxyhexanoate) was tested on high-density polyethylene (HDPE) in its molten state. The variations of the concentrations of the peroxides versus the crosslinking extent were plotted for these peroxides, and the values were

compared. Dicumyl peroxide was found to be the best crosslinking agent for HDPE. The efficiency of the HDPE crosslinking with each peroxy derivative was analyzed on the basis of the behavior of the radicals generated from it. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 75–81, 2004

**Key words:** polyethylene (PE); crosslinking; peroxides

## INTRODUCTION

Polyethylene (PE) is one of the most versatile thermoplastics and is used in a variety of applications, such as wire and cable insulation. However, its uses are restricted by its low melting point, its solubility in hydrocarbons, and its tendency to crack when stressed. To solve these problems, researchers have crosslinked PE with a high-energy irradiation technique,<sup>1</sup> a moisture crosslinking method,<sup>2</sup> and thermochemical reactions. Among the last, thermochemical crosslinking involving organic peroxides is widely used because of its controlled decomposition rate, minimal side products, and economical process.<sup>3–6</sup> Kharasch and Ford<sup>7</sup> and others<sup>8,9</sup> have studied the crosslinking of PE with dicumyl peroxide (**1**). PE has also been crosslinked with various commercially available di-*t*-alkyl peroxides<sup>10–12</sup> and benzoyl peroxide.<sup>13,14</sup> Recently, Zhou and Zhu<sup>15</sup> reported an electron spin resonance (ESR) study of the thermolysis of several peroxy derivatives (di-*t*-alkyl peroxides, benzoyl peroxide, and *t*-butyl perbenzoate) in high-density polyethylene (HDPE), showing the formation of alkyl and allylic macroradicals, which, by their combination, were responsible for crosslinking.

Recently, our group studied the thermolysis of peroxy derivatives with the aim of performing chemical modifications of PE through the chemical grafting of functions onto its backbone. A preliminary study<sup>16</sup>

showed that, depending on the type and structure of the peroxy derivative, function grafting or crosslinking of the polymer mainly took place. The decomposition of peroxyketals<sup>17</sup> and *t*-butyl peroxyalcanoates<sup>18</sup> allowed the grafting of ester functions; meanwhile, the use of hydroperoxides<sup>19</sup> induced the formation of carbonyl and hydroxyl on the macromolecule. The crosslinking and functional grafting involved the combination of a radical produced by hydrogen abstraction onto PE, with another macroradical for the former or a small radical arising from the peroxide for the latter. In the case of symmetrical peroxides, crosslinking was the main process, and for *t*-alkyl peresters, both processes were competitive.<sup>16</sup> These results prompted us to study the crosslinking of HDPE with commercially available peroxy derivatives and to compare their efficiencies with **1**, which was considered the standard.

## EXPERIMENTAL

### Materials

HDPE (10 g; Acros, Geel, Belgium; ref. 17851) with a molecular weight of 125,000 g/mol was dissolved in 400 mL of 1,2-dichlorobenzene (DCB; Acros, ref. 11318) at 145°C. After the complete dissolution of HDPE in DCB, the solution was added to 1 L of acetone (Xilab Chemicals, Floirac, France) to precipitate the polyolefin, which was filtered and then washed for 24 h in a Soxhlet apparatus with dichloromethane (DCM; Xilab Chemicals). The PE thus obtained was dried *in vacuo* at 60°C until there was no change in the mass.

The peroxides were commercially available and were used without any further purification: **1** (Aldrich

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TABLE I  
Decomposition of 1 in PE

	1/PE (mmol/g)										
	0.005	0.01	0.02	0.025	0.03	0.035	0.044	0.068	0.117	0.223	0.446
Crosslinking extent (%)	8	9	18	27	45	64	80	87	91	93	98

Chemicals, St. Quentin, France), *O,O*-*t*-butyl *O*-2-ethylhexylperoxy carbonate (2; Akzo Nobel), *t*-butyl peroxybenzoate (3; Aldrich Chemicals), *t*-butyl 3,5,5-trimethylperoxyhexanoate (4; Akzo Nobel, Deventer, The Netherlands), and *t*-butyl 2-ethylperoxyhexanoate (5; Akzo Nobel).

### Thermolysis reaction

HDPE (1 g) was added to a solution of the required quantity of peroxide in 6 mL of DCM/cyclohexane (9/1 v/v). The contents were mixed for 2.5 h at room temperature. Then, the solvents were removed under reduced pressure, in a rotavapor, until a constant mass was obtained.

The polymer/peroxide mixture thus obtained was placed in a Buchiglasuster BMC 100 minireactor (Flawil, Switzerland). The reactor was closed and degassed through the injection of argon for 30 min. The reactor was heated in an oil bath at 160°C for 2.5 h without any stirring.

Differential scanning calorimetry (DSC) studies of the decomposition of peroxy derivatives 1–5 in octadecane and of the melting of PE were performed with a PerkinElmer DSC7 (Courtaboeuf, France) (at 2.5°C min<sup>-1</sup>).

### Isolation and determination of the extent of crosslinked HDPE

After the thermolysis reaction, the polymer, which contained both crosslinked and noncrosslinked parts, was removed from the reactor and cut into small pieces. These pieces were divided into three approximately equal parts placed in three steel bags (100-mesh porosity, 5 cm × 2.5 cm, weight  $W_1$ ; Société Gantois, St. Dié, France). The steel bags containing the polymer pieces (weight  $W_2$ ) were then placed in 125 mL of DCB for 16 h at 145°C with stirring. During this extraction period, all the soluble polymer was dissolved in the medium and thus came out of the steel bags. Remaining inside the steel bags was the crosslinked polymer. Then, the steel bags were isolated from the medium and extracted with 150 mL of DCM for 2 h. After extraction with DCM, the steel bags were dried at 60°C *in vacuo* until a constant mass ( $W_3$ ) was obtained. The crosslinking extent was calculated with the following formula:

$$\text{Crosslinking (\%)} = 100 \times (W_3 - W_1)/(W_2 - W_1) \quad (1)$$

The soluble polymer present in the DCB solution was precipitated by the addition of 400 mL of DCM, filtered, and dried (at 60°C *in vacuo*) to a constant weight ( $W_4$ ). The weights of the crosslinked and soluble polymers indicated a good balance with respect to the starting PE.

### Spectroscopic analysis of the soluble polymer (noncrosslinked)

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the HDPE samples before and after peroxide treatment were recorded with a PerkinElmer Paragon 1000 instrument. The IR films of the noncrosslinked PE (prepared under 9 tons of pressure *in vacuo* with ca. 7 mg of the neat modified polymer) were compared with those of the initial unmodified polymer.

<sup>1</sup>H-NMR spectroscopy

<sup>1</sup>H-NMR spectra were recorded for the HDPE samples before and after peroxide treatment (noncrosslinked part) at 130°C with a Bruker DPX 400 instrument (Wissembourg, France) from a solution in deuterotetrachloroethane.

All the <sup>1</sup>H-NMR spectra of the HDPE samples showed the characteristic peak corresponding to methylene protons in the PE chain at 1.2 ppm. Minor broad signals between 5 and 6 ppm and between 3.2 and 4 ppm were attributed to ethylene protons and protons, respectively, on carbon linked to oxygen, resulting from the oxidation of the polyolefin. If the signal observed at 2.4 ppm for the starting polyolefin was due to protons of the remaining acetone, it could not have the same origin for noncrosslinked PE, obtained after treatment with the peroxy derivatives, because DCM was always used, instead of acetone, to precipitate it. Thus, this signal was certainly due to an acetyl group of the polymer that was present in the starting PE. Besides these signals attributed to protons of the macromolecules, some others were systematically observed at 6 (nondeuterated solvent) and 7.5 ppm (residual DCB).

TABLE II  
Decomposition of 2 in PE

	2/PE (mmol/g)						
	0.02	0.04	0.06	0.08	0.1	0.3	0.5
Crosslinking extent (%)	13	40	80	85	89	95	97

## RESULTS AND DISCUSSION

The decomposition of 1–5 in PE was performed in an autoclave at 160°C. Tables I–V summarize the crosslinking extent for different amounts of each peroxide. The crosslinking extent, above a certain peroxide concentration, increased rapidly with a small variation in the peroxide concentration for 1–4 (1, 0.01–0.04 mmol/g of PE; 2, 0.02–0.06 mmol/g of PE; 3, 0.02–0.08 mmol/g of PE; 4, 0.04–0.1 mmol/g of PE), as shown in Figure 1. For 5, the increase was much slower, and it appeared very difficult to reach a crosslinking extent of greater than 70%, even when it was used in a high concentration. In light of the different stabilities of the various peroxy derivatives, the decomposition of 5, which was less stable according to its structure,<sup>20</sup> might have occurred before PE melted, unlike the other ones. Indeed, the polymer sample in the autoclave, placed in a preheated bath at 160°C, did not immediately reach this temperature (ca. 50 min was necessary). To check the behavior of the peroxy derivatives and PE during this heating period, we scanned the heat released during the temperature increase (at 2.5°C min<sup>-1</sup>) from 50 to 160°C for the same amounts of PE and a 0.2M solution of the peroxide compound in octadecane placed in the cell of a DSC apparatus. Similar thermograms were obtained for the decomposition of the various peroxides in octadecane (0.2M). A comparison of the thermograms showed that the decomposition of compounds 1–4 occurred mainly at a slightly higher temperature than the melting of PE. In the case of 5, the decomposition of this perester and the melting of PE occurred essentially in the same range of temperatures. Thus, the decomposition of the perester, during the functionalization of PE, certainly took place partially in the presence of solid and molten polymer. However, for a higher concentration of this perester, it seems that a significant amount of the perester would have remained after the

TABLE III  
Decomposition of 3 in PE

	3/PE (mmol/g)						
	0.02	0.04	0.06	0.08	0.1	0.2	0.4
Crosslinking extent (%)	4	16	46	80	90	96	97

TABLE IV  
Decomposition of 4 in PE

	4/PE (mmol/g)						
	0.02	0.04	0.06	0.08	0.1	0.2	0.4
Crosslinking extent (%)	4	6	7	61	78	95	99

melting of the polymer. This rules out the proposed explanation for the decomposition of the various peroxy derivatives under different conditions (solid or molten polymer). Thus, if the different results obtained with peroxy derivatives do not have a physical origin, a chemical one must be invoked.

As shown in Table VI, for a crosslinking extent of 50%, very different amounts of each peroxide were needed. This shows an important difference in the capacity of each peroxide to crosslink the polyolefin. The lack of crossing of the curves presented in Figure 1 in their pseudolinear medium part confirms the order of the efficiency in the crosslinking of the various different compounds: 1 > 2 > 3 > 4 > 5. Thus, according to the crosslinking of PE based on the coupling of macroradicals, whatever peroxide was used, either some of the peresters were consumed by a reaction other than the homolysis of the O—O bond, or the free radicals produced did not lead, directly or indirectly, to radicals on the backbone of PE. Whatever peroxide compound was involved, its homolytic decomposition generated, in the first step, oxygen-centered radicals. However, they could be of the same type (alkoxy from 1) or different ones (alkoxy and carboxyl for peresters 2–5). If all of them could react by hydrogen abstraction from the polyolefin, they could suffer fragmentation reactions occurring at very different rates, depending on the type of oxygen-centered radical, generating various radicals. Thus, we have to consider successively the radicals produced from peroxy derivatives 1–5 and their reactions in the molten polyolefin.

### Dicumyl peroxide (1)

Scheme 1 summarizes the free-radical reactions that we have to consider for the decomposition of this peroxide in PE. Alkoxy radicals are more prone to abstract a hydrogen atom (way a) than to couple with

TABLE V  
Decomposition of 5 in PE

	5/PE (mmol/g)							
	0.02	0.05	0.08	0.1	0.15	0.2	0.3	0.4
Crosslinking extent (%)	0	5	16	35	50	57	61	69

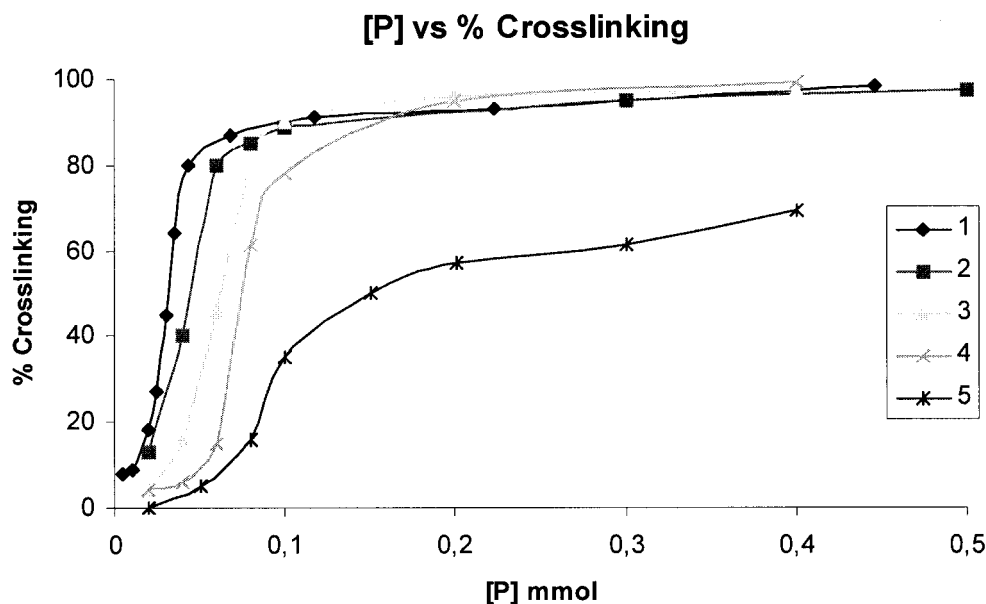


Figure 1 Influence of the concentration of peroxides 1–5 on the crosslinking extent of PE.

an alkyl radical (way b) but may disproportionate with an alkyl macroradical (way c). Then, their main reaction in the polyolefin would be to generate a carbon-centered macroradical by hydrogen abstraction from it. Nevertheless, the temperature of the medium is such that we also need to consider that they may fragment. However, this fragmentation generates a methyl radical (way d), which is known as an aggressive abstractor even toward a hydrogen of an inactivated methylene (way e), to produce a secondary pure alkyl radical of a higher stability than the methyl one. The methyl radical may combine with a macroradical (way f). The combination of two macroradicals (way g) is responsible for the crosslinking of PE.

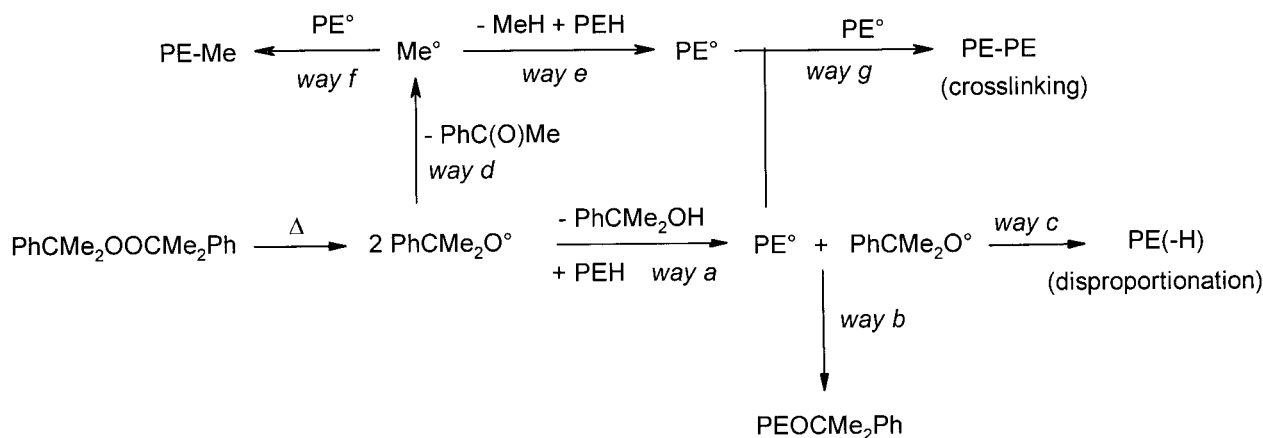
The observation of an allylic radical by ESR<sup>9,15</sup> during the thermolysis of **1** in PE indicates that ethylene bonds may be produced on the backbone of the polymer in the course of the reaction by the disproportionation of an alkyl macroradical with another radical, certainly an alkoxy one (way c). Indeed, if such an unsaturation is initially present in the medium, this stabilized radical will be observed at the beginning of the experiment. The <sup>1</sup>H-NMR spectrum of the starting PE showed the pres-

ence of about  $1-5 \times 10^{-4}$  units of  $\text{CH}_2=\text{CH}$  per methylene after the reaction with **1** (0.06 mmol/g of PE). Similar amounts were identified in the soluble polymer, but no other types of ethylene protons were identified. This indicates that none or very few of the hydrogens in the allylic position of this unsaturation suffered an attack by the methyl or cumyloxy radicals. This is not very surprising because of the relative amounts of both types of hydrogens, even if we assume a much higher reactivity for the allylic one. Also, there was no significant formation of any symmetrically substituted double bond by radical disproportionation on the macromolecule. Because the competition between methylene and allylic hydrogen abstraction in a homogeneous medium is related to their relative concentrations, this rules out the production of allylic radicals under such conditions, although they were identified by ESR. Thus, we have to admit that they are produced in zones with a high local concentration of radicals, favoring efficient disproportionation followed by allylic hydrogen abstraction. The increasing viscosity of the medium with an increasing degree of crosslinking, with a possible exclusion of the peroxide molecules from the network of the polymer, would provoke local phase separations and might be responsible for the late observation of the allylic radicals during the course of the ESR experiment. Similar results were obtained from the <sup>1</sup>H-NMR study of homologous polyolefin samples arising from the decomposition of peresters 2–5.

The crosslinking efficiency of this peroxide (way g) can easily be understood on the basis of the abstraction reactions (ways a and e) produced by the radicals arising in one or two steps from the decomposition of **1**.

TABLE VI  
Concentrations of the Various Peroxides Necessary to Crosslink PE to 50%

	Peroxide				
	1	2	3	4	5
Concentration (mmol/g PE)	0.031	0.045	0.062	0.076	0.15



Scheme 1

### O,O-*t*-butyl O-2-ethylhexylperoxycarbonate (2)

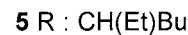
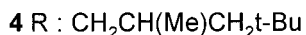
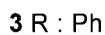
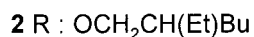
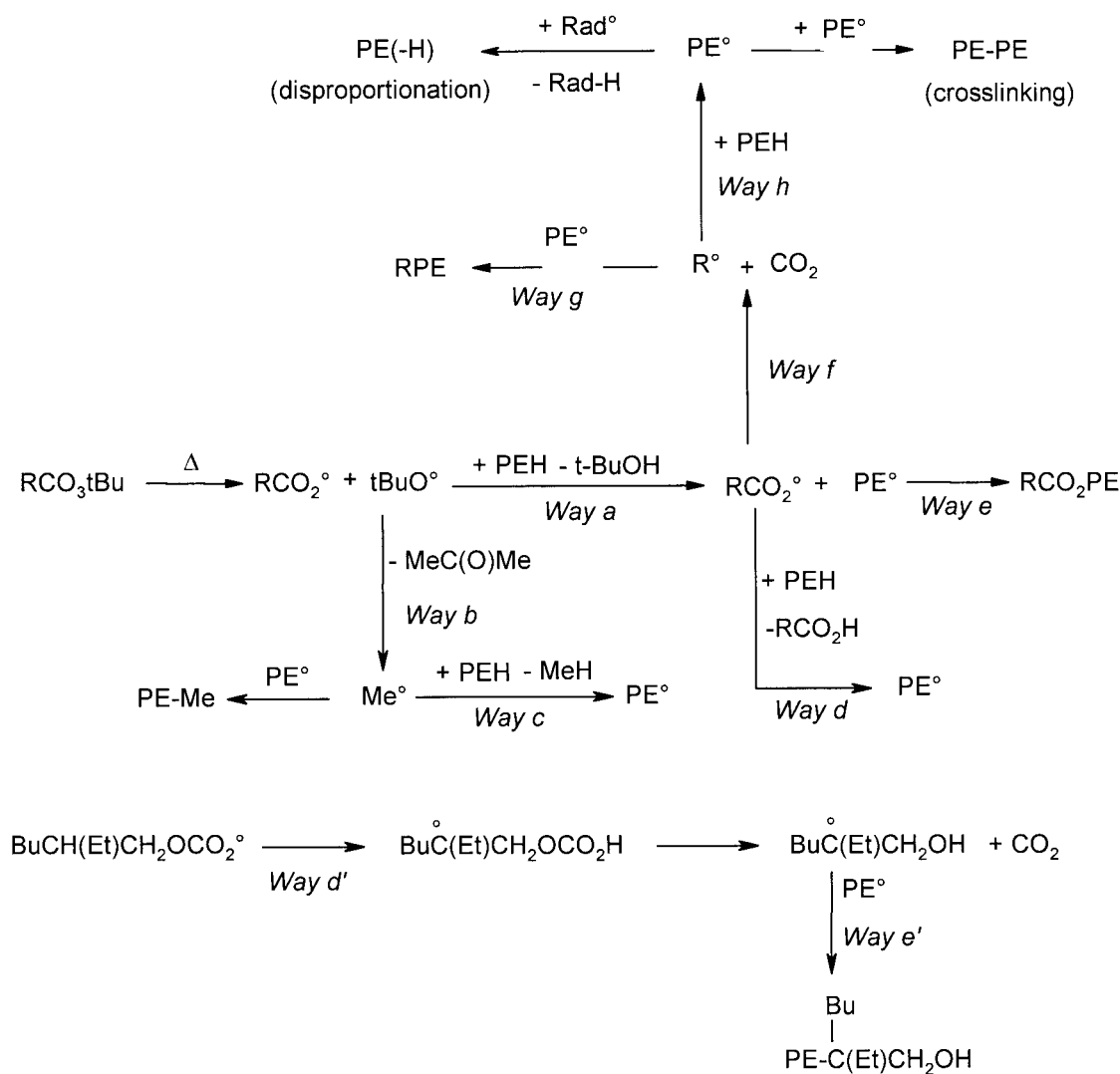
Scheme 2 [R = OCH<sub>2</sub>CH(Et)Bu] describes the free-radical reactions that may occur during the decomposition of percarbonate **2** in PE. The homolysis of the O—O bond generates *t*-butoxy and alkoxy-carboxy radicals. The *t*-butoxy radical readily abstracts a hydrogen from PE (way a) or fragments to generate a methyl radical (way b), as in the case of a cumyloxy radical, with a faster fragmentation for the latter.<sup>21</sup> Then, in a first and reasonable approximation, we can assume that it has a global reactivity in PE similar to that of a cumyloxy radical. Thus, the difference in the crosslinking efficiency between **1** and **2** is certainly not due to the behavior of the alkoxy radical arising from both of them. Taking this into account, we have to consider the counter radicals produced from both peroxy compounds: an alkoxy in the case of **1** and an alkoxy-carboxy in the case of **2**. If fragmentation for the first one (Scheme 1, way d) is a possible competitive process, in the case of the second one, decarboxylation (Scheme 2, way f) is very slow,<sup>22</sup> being less effective than hydrogen abstraction. This one can occur intermolecularly by a reaction on PE (way d) but also by an intramolecular reaction (way d'), a significantly faster process, to generate a tertiary alkyl radical. This radical is certainly not aggressive enough to abstract a hydrogen atom from PE as a methyl radical does, certainly preferring to couple with any carbon-centered radical or disproportionate with an alkoxy one. The absence of a signal in <sup>1</sup>H-NMR arising from CH<sub>2</sub>OH or CH<sub>2</sub>OCO<sub>2</sub> in the soluble (noncrosslinked) polyolefin indicates that the coupling of a macroradical with this tertiary radical (way e') or an alkoxy-carboxyl one (way e) does not occur significantly. The existence of this intramolecular byreaction, producing inactive radicals toward PE, may explain the slight difference in the PE crosslinking efficiency between **1** and **2**.

### *t*-butyl perbenzoate (3)

The decomposition of *t*-butyl perbenzoate generates *t*-butoxy and benzoyloxy radicals (Scheme 2; R = Ph). This last one decarboxylates (way f) more readily than the alkoxy-carboxy radical.<sup>22,23</sup> Assuming a similar behavior for the *t*-butoxy radicals and cumyloxy radicals and considering that the generated phenyl radical can be considered as aggressive as the methyl radical toward hydrogen atoms,<sup>24</sup> we find that **3** should be as effective as **1** in PE crosslinking, but this is not the case. Indeed, the coupling of the PE macroradical with the phenyl and benzoyloxy radicals (ways g and e) can be ruled out because of the absence of aromatic hydrogens of the phenyl ring in the <sup>1</sup>H-NMR spectrum of the soluble (noncrosslinked) polymer. However, because peresters are more sensitive to homolytically induced decomposition or polar rearrangements<sup>25</sup> than dialkyl peroxides are, we can find in the existence of such reactions an explanation for the differences in the PE crosslinking efficiency of **1**–**3**.

### *t*-butyl 3,5,5-trimethylperoxyhexanoate (4)

In Scheme 2 [R = CH<sub>2</sub>CH(Me)CH<sub>2</sub>t-Bu], the possible radical reactions occurring during the thermolysis of **4** in PE are presented. Unlike the previous carboxy radicals mentioned in this article, aryloxy and alkoxy-carboxy, acyloxy radicals are prone to fast decarboxylation,<sup>26</sup> generating alkyl radicals (way f). Nevertheless, their coupling reactions with PE macroradicals in the cage (way e), advanced to explain the grafting of ester functions during the decomposition of peralkanoates in PE,<sup>18</sup> show that decarboxylation is not a single reaction produced by these radicals in a viscous medium, isomerization and coupling with a macroradical being mentioned. The <sup>1</sup>H-NMR study of the soluble (noncrosslinked) polymer did not allow the identification of larger amounts of protons borne by



Scheme 2

carbons linked to an oxygen atom (ester or ether) than in the starting PE. This indicated for **4** a different behavior than that of the peresters previously decomposed in this polymer. Indeed, the thermolyses of various peralkanoates in PE produced very little crosslinking, but efficient functionalization was observed.<sup>18</sup> Even if higher crosslinking extents were observed for *t*-butyl perhexanoate and 3-dodecyloxycarbonyl perpropanoate, it does not appear reasonable to believe that increasing the number of carbon atoms in alkyl group R would be very much responsible for the changing of the reactivity. An explanation must be found in the difference in the behaviors of the various acyloxy radicals and alkyl radicals generated in the thermolyses of the different peresters. Correlating the results and the structures of the various peralkanoates,

we find that the main structural difference is the presence of a methyl on the  $\beta$ -carbon for **4**. Therefore, the different results may be explained by either a disfavored coupling of the acyloxy radical with the macro-radical (way e) or a favored decarboxylation (way f) of the acyloxy radical in the case of **4**. Then, whatever the explanation is, we now have to consider the behavior of alkyl radicals R. The one generated from **4** is primary, like the others produced from the linear peresters.<sup>18</sup> The main difference from the pure alkyl ones arising from *t*-butyl and cumyl perpropanoate or *t*-butyl perhexanoate remains the presence of a methyl substituent on the  $\alpha$ -carbon in the radical center. If we consider that such a radical would disproportionate more readily than a linear primary alkyl one, a possible explanation can be advanced. However, such a

reaction would be more operative for the alkyl radicals arising from the persuccinates<sup>18</sup> because of the formation of a double bond conjugated with an ester. Taking this remark into account and the efficient ester function grafting on PE with a peroxide/acrylate system,<sup>27–30</sup> we can conclude that the functionalization by peroxy succinic derivatives may originate from a mechanism other than the coupling previously advanced.<sup>18</sup> This analysis shows that it is actually very difficult to simply explain the obtained results. A fundamental study of the behavior of alkyl and acyloxy free radicals in a viscous medium is an important goal if we would like to properly use free-radical reactions for the chemical modification of polyolefins.

### *t*-butyl 2-ethylperoxyhexanoate (5)

Although the decomposition of this perester occurs in the same range of temperatures as the melting of PE, we have to consider the free-radical reactions produced by the radicals generated by the decomposition of **5**. Scheme 2 [R = CH(Et)Bu] summarizes the principal free-radical reactions that can occur. The fast decarboxylation of the acyloxy radicals and the low efficiency in hydrogen abstraction to PE by the generated alkyl radical are certainly responsible for the formation of lower crosslinking extents in the polyolefin. Indeed, this secondary alkyl radical has a structure similar to the one produced by hydrogen abstraction from PE. This radical may disappear via coupling with a macroradical or disproportionate with a *t*-butoxy one. Whatever the given reaction is, it consumes two radicals with no production of a link between the two macromolecules.

## CONCLUSIONS

Peresters are less efficient initiators than **1** for the crosslinking of PE. The order of the efficiency of the various peroxy derivatives is as follows: **1** > **2** > **3** > **4** > **5**. The low efficiency of the last one is certainly partly due to decomposition occurring before the total melting of the polyolefin, which favors radical–radical reactions for the radicals arising from perester **5**, and partly due to the low reactivity of the alkyl radical produced by decarboxylation of the acyloxy one. For the other free-radical initiators, the decomposition of which occurs in the molten polymer, the difference in the reactivities of the radicals generated in the homolysis of the O—O bond or arising from the fragmenta-

tion of the oxygen-centered ones is largely responsible for the efficiency of the crosslinking of PE.

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