Chemical Modification of Molten Polypropylene by Thermolysis of Peroxidic Compounds

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ABSTRACT: The modification recently developed for polyethylene, based on the thermolysis of peroxyketals and peroxy esters in the molten polymer, was applied to atactic and isotactic polypropylene. The grafting of an ester function onto the backbone of these polyolefins was much less efficient in this case than for the former. The thermal decomposition of such peroxides in polyethylene and isotactic and atactic polypropylenes was analyzed by DSC. These studies showed that the physical state of the polyolefin cannot account for the difference encountered in the functionalization yields. The analysis of the reaction products, generated in the thermolysis of a cyclic peroxy ketal, was realized on the extracts by GC and on the bulk by ^{1}H NMR and DOSY spectroscopies. This led one to conclude that the difference in efficiencies in the chemical modification of the various polyolefins is related to the chemical reactivity of the hydrogens toward 1,1-dimethylethyloxy radicals. Surprisingly, it was found that hydrogen abstraction hardly occurs with polypropylene (either isotactic or atactic) despite the presence of thermodynamically more labile tertiary hydrogen atoms than the ones present in polyethylene. This was attributed to the steric hindrance of the methyl present on the backbone of this polyolefin.

Introduction

Polyolefins are valuable materials according to their price and their high tonnage availability. The pronounced hydrophobic character of such polymers prevents their use in a wide range of applications, despite them offering good mechanical properties.[1,2] A lot of work was then done to make polyolefins more versatile and extend their area of application.[1,2] To achieve this, the main approach consists of randomly introducing polar functions along the backbone of those polymers. Regarding the low reactivity of the C−C and C−H toward nucleophiles and electrophiles, researchers preferred using a free radical process to perform the chemical functionalization of polyolefins. Various systems (UV, plasma, corona discharge, electron beam, etc.) allow initiating such reactions by creating radicals along the backbone of the polymers, but the more convenient route for a “one-pot” modification reaction realized in an extruder is to use free radical initiators such as peroxides.[1,2] Once the active species generated onto the polyolefins, they react with functional alkenes (i.e., monomers) by adding onto their double bond. Depending on the nature of the monomers introduced in the reactional medium, different kinds of functions could then be grafted along the backbone of the materials.[1,2]

In 1996, a discussion with Akzo Nobel led us to envisage the modification of polyolefins by using a slightly different approach. The idea was to employ peroxidic compounds, in the absence of any other additives (i.e., monomers), as their thermal decomposition should provide on their own both the initiating and the functionalizing agents. A deep study was then conducted by our group to investigate the feasibility of such a process to chemically modify polyolefins. Here, it is worth noting that at the time we started there was no claim on such a way to graft functions onto these materials. We realized first the hydroxylation and “ketonization” of polyethylene[3] (PE) via the thermal decomposition of a hydroperoxide in the melted polymer. More recently, various peresters[4,5] and peroxy ketals[4,6] were used in similar conditions in order to graft ester functions onto PE. By this way, polar entities were efficiently introduced onto this polymer. Moreover, the extent of cross-linking material recovered after reaction was relatively low (<10%). This was attributed to the fact that the decomposition of the peroxy derivatives liberated two species with distinct behavior. Indeed, it was shown that the “primary” tBuO radicals generated during the reaction were aggressive enough to abstract a hydrogen from the PE backbone, whereas in the meantime, the alkoxy or acyloxy counterradicals underwent a fast intramolecular rearrangement, the species thus obtained coupling with the formed macroradicals as represented in Scheme 1 for a peroxy ketal.

During the course of our study, Moore et al.[7] presented their work based on the exhaustive use of peroxidic compounds to perform the functionalization of polyolefins. In their case, they realized the thermal decomposition of peroxy esters in melted polypropylene (PP) and grafted acid and ester functions onto the backbone of this polymer. The lower yields encountered by Moore et al.[7] than the ones we obtained after decomposing various peresters in PE prompted us to extend our chemistry to PP functionalization. Hence, the thermolysis of 1-ethoxy-1-(1,1-dimethylethyl)peroxycyclohexane (**1**), 1,1-dimethylethyl 3-ethoxycarbonylperpropionate (**2**), and 1,1-dimethylethyl 6-ethoxycarbonylperhexanoate (**3**) was realized in this latter polymer. It is worth noting that, conversely to the PE case, PP units own an asymmetric carbon atom. A stereoregular

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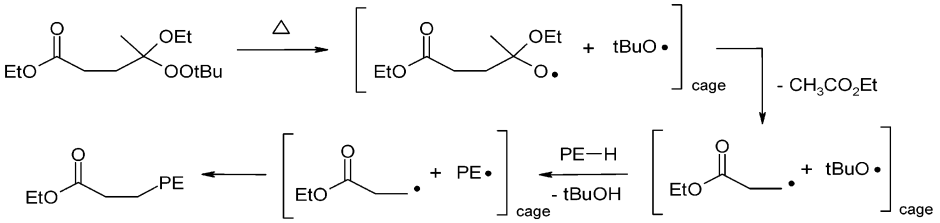
Scheme 1. Example of PE Functionalization by Thermal Decomposition of a Peroxy ketal



arrangement of the latter leads to the production of syndiotactic (alternative relative configuration of the units) or isotactic (identical relative configuration of the units) polymers, the term atactic meaning that the CH_3 pendant side groups are randomly placed all along the backbone. On our side, we thus chose to study the functionalization of PP by working with both the isotactic and atactic polymers in order to get rid of the influence of the tacticity, if any. Moreover, these two polyolefins get distinct average molecular masses and polydispersities. Those were advantageous characteristics that we took profit of for other investigations that will be published.

Experimental Part

Materials. Solvents such as 1,2-dichlorobenzene and dichloromethane were received from Acros and used without any purification. Isotactic and atactic polypropylene were commercial products purchased from Aldrich (respectively ref.42,-789-6 and ref.42,817-5). For a better handling, the pellets received were reduced into powder. For this, 10 g of polyolefin were dissolved in 300 mL of 1,2-dichlorobenzene at 130 °C and then precipitated in acetone (1 L). After filtration, the polymers were washed with refluxing dichloromethane for 48 h in a Soxhlet apparatus. The polypropylene powders were then dried under vacuum until a constant weight was reached. The different peroxy derivatives [1-ethoxy-1-(1,1-dimethylethyl)-peroxycyclohexane (**1**), 1,1-dimethylethyl 3-ethoxycarbonylperpropionate (**2**), and 1,1-dimethylethyl 6-ethoxycarbonylperhexanoate (**3**)] used in this study were synthesized according to procedures previously described[4–6] and stored in a refrigerator. The thermal decompositions of these peroxy derivatives in octadecane were performed in a DSC apparatus to determine the rate constants. This allowed us calculating at 160 °C the times required to decompose 99% of these peroxides. The obtained values are respectively about 4, 16, and 16 min for **1**, **2**, and **3**.

Functionalization and Analysis of the Modified Atactic and Isotactic Polypropylenes. In a 50 mL flask, 0.595 mmol of peroxy derivative dissolved in a 10 mL of cyclohexane/dichloromethane mixture (1/9) were added onto 1 g of powdered polypropylene. The solvents were then slowly removed at room temperature under reduced pressure with a rotavapor until a constant weight (corresponding to the masses of polypropylene and peroxy derivative used for the reaction) was obtained. The polymer/peroxy derivative mixture thus obtained was placed in a reactor (Büchiglasuster BMC 100). Once closed, it was degassed by two freeze/pump/thaw cycles. The atmospheric pressure was recovered by injecting argon in the reactional medium. The reactor was then placed in an oil bath preheated and stabilized at 180 °C (i.e., $T_{\text{reaction}} \approx 160/165$ °C) and let at this temperature for 2.5 h without any stirring. After opening the reactor, the crude polypropylene samples were washed with dichloromethane. The organic phase thus obtained was concentrated under reduced pressure and analyzed by gas chromatography. The polymer was dissolved in 50 mL of 1,2-dichlorobenzene at 130 °C and precipitated in an excess of acetone. After filtration, the powder collected was dried under vacuum at 50 °C until a constant weight was reached.

Analytical Techniques. 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 DB5 column (5% Ph, 30 m length, 0.25 mm inside diameter, 0.25 μm internal phase thickness, pressure 15 psi of 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 peroxy derivatives (1-dodecene as internal standard). The thermal analyses of the polyolefin/peroxy derivative mixtures were performed on a DSC 7 Perkin-Elmer apparatus directed by Perkin-Elmer software. The experiments were run from 50 to 250 °C with a ramp of 2.5 °C/min. Infrared spectroscopy was used to characterize the polypropylene samples. The spectra were recorded on a Perkin-Elmer Paragon 1000. Films of about 7 mg of polypropylene were prepared by 9 ton pressure under vacuum. The modified polymers were compared with films of the initial nonmodified polypropylene. The quantification of the grafting was based on a study presented by Fodor.[8] It was realized by the determination of the relative intensities (RI) of the carbonyl bands (area of the carbonyl band of an ester function vs the area of the CH band of polypropylene at 1450 cm^{-1}) using the internal software of the infrared spectrograph. First, RI of the infrared spectra given by known mixtures of polypropylene/organic compounds bearing an ester function were calculated. The calibration curve obtained by plotting those RI vs the concentrations of the ester function used in a known mass of polypropylene (moles of organic function per 1 g of polymer). These mixtures were prepared as described previously (see functionalization and analysis of the samples section) using diethyl succinate. For each mixture, three spectra were recorded from three different samples, and the average value of RI was used for the plot. The grafting yield (GY) of functionalization reactions, relative to the peroxy derivative involved, can then easily be calculated from the following formula:

$$\mathrm{GY} = \frac{\mathrm{RI} \times m}{n_0 \times 1.66} \times 100$$

where m is the mass of modified polypropylene (g), 1.66 the proportionality coefficient obtained from the calibration curve, and n_0 the number of moles of peroxy derivative used in the reaction. The ^{1}H and DOSY NMR spectra were run at 60 °C with tetrachloroethane-d_2 as solvent. They were recorded on a 400 MHz Varian Unity Inova apparatus fitted with a VT pulsed field gradient multinuclear probe and a Performa II (z gradient).

Results and Discussion

Thermolysis of Peroxy Derivatives in Isotactic and Atactic Polypropylene. Following our procedure, a mixture of peroxy derivative and polypropylene (either isotactic or atactic), with a relative ratio of peroxide to propylene unit 1/80, was heated for 2.5 h at about 160 °C. The polymers were then analyzed, after reaction, by FTIR which permitted one to observe the presence of an absorption band at 1736 cm^{-1} characteristic of an ester function (Figure 1). Assuming that the modification process occurred according to a free radical coupling, we decided to estimate the grafting yields (GY) of the functionalization reactions (Table 1). One could

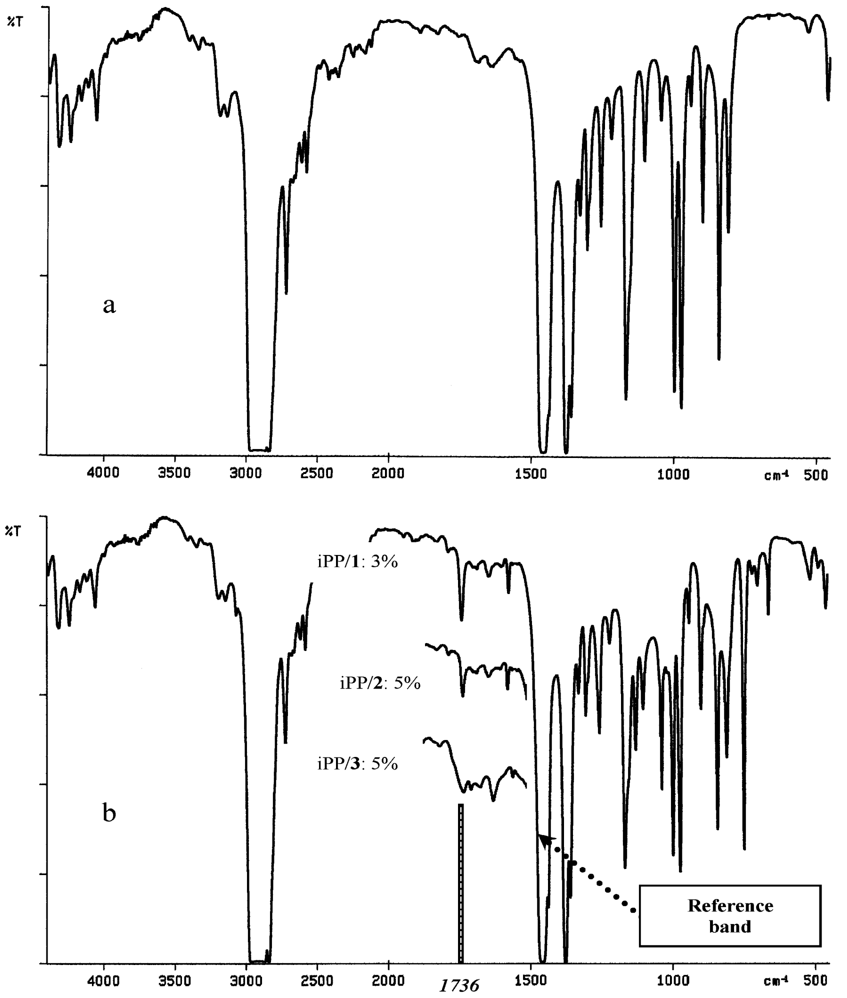


Figure 1. FTIR spectra of isotactic polypropylene (a) and reacted iPP (b).

Table 1. Ester Grafting on Polyolefins by Thermal Decomposition of 1, 2, and 3

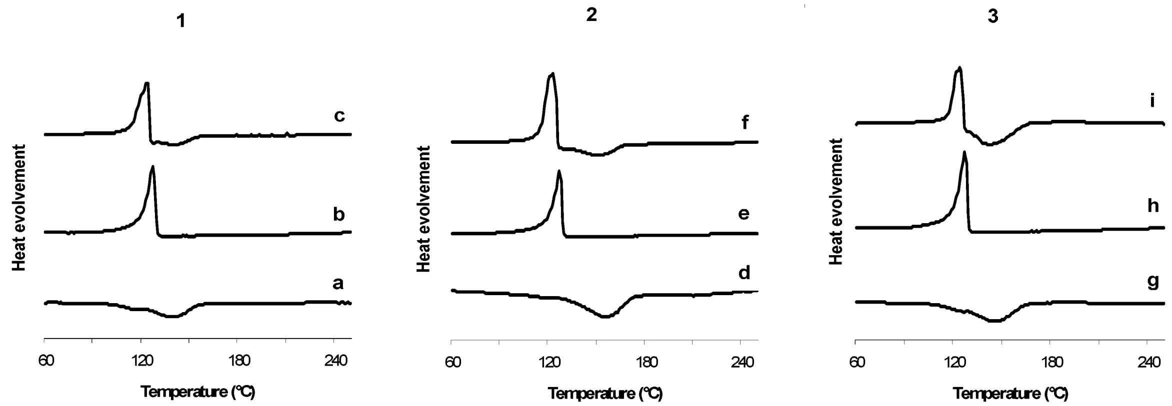
peroxy derivatives	grafting yield (GY),[a,b] %		
	iPP	aPP	PE
1	3	4	30[c]
2	5	9	60[d]
3	5	9	20[d]

[a] Relative to the amount of peroxy derivative. [b] FTIR titration. [c] References 4 and 6. [d] Reference 4.

notice a big difference in the efficiency of **1** in modifying PE (GY close to 30%) and PP, either atactic or isotactic (GY < 10%). The same observation could be done with peresters **2** and **3**. Nevertheless, in these two cases one should be careful in interpreting the grafting yields. Indeed, it is of importance to point out that the ester functions could be introduced according to several mechanisms[5] that make an accurate estimation of the functionalization efficiency tricky. All these elements converged to show that the coupling of the macroradicals with the radicals arising from the decomposition of the peroxy ketal **1** (Scheme 2) or from the decomposition of the peresters **2** and **3** (Scheme 3), according to the mechanism proposed for PE,[4-6] would occur but to a much lower extent in the case of PP.

As a first hypothesis we assumed that the bad grafting yields obtained in this case raised from the fact that the process took place in the solid state whereas the reactions actually occurred in molten PE. Clearly, we observed that ≈1 h was necessary to reach the expected temperature (160/165 °C) in the bulk. The peroxy derivatives might thus had enough time to be fully decomposed before the crystalline zones of PP were melted ($T_m \approx 160$ °C) whereas this step happened in molten PE ($T_m \approx 110$ °C). Even if this attractive assumption could explain the discrepancies observed between polyethylene and isotactic polypropylene (iPP) (see Figures 2 and 3), it cannot account for the results obtained with the atactic polypropylene (see Figure 4). Indeed, it can be assumed that in the case of aPP the decomposition of the peroxy derivatives mainly occurred in the molten polymer. Therefore, the presence of remaining crystallites cannot explain the lower grafting yields obtained with polypropylene (iPP and aPP). As the physical state of the reactional medium had no effect at all, the difference in efficiencies of the peroxy derivatives **1**, **2**, and **3** in modifying polypropylene must therefore arise from a "chemical" effect.

Analysis of the Low Molecular Weight Compounds Produced in the Decomposition of 1, 2, and 3 in Polypropylene. Products arising from the decomposition of the peroxy derivatives **1**–**3** in polypropylene were collected by washing the crude polymer with dichloromethane. The extracts thus obtained were concentrated under vacuum and analyzed by GC. No unreacted peroxide was identified, proving its total consumption. In the case of the functionalization of polypropylene by **2**, GC analysis of the extracts did not allow to identify any compound in the dichloromethane solution. This was certainly due to the high volatility

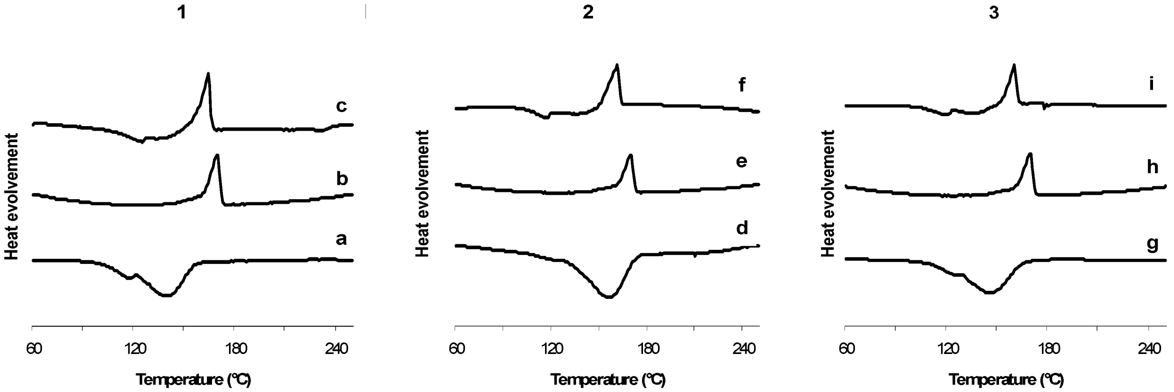


a- Decomposition of **1** in octadécane
b- PE
c- Decomposition of **1** in PE

d- Decomposition of **2** in octadécane
e- PE
f- Decomposition of **2** in PE

g- Decomposition of **3** in octadécane
h- PE
i- Decomposition of **3** in PE

Figure 2. DSC curves related to the decomposition of **1**, **2**, and **3** in polyethylene.



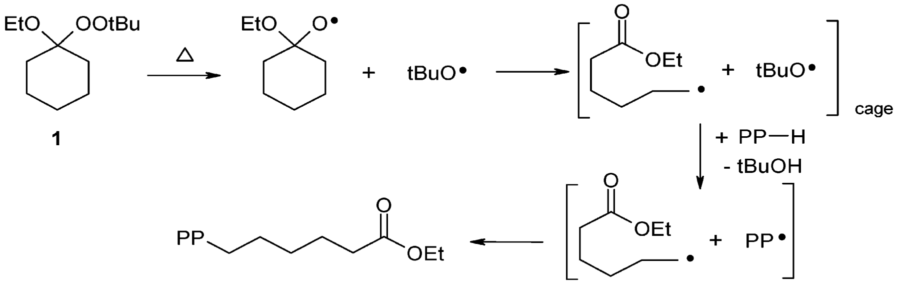
a- Decomposition of **1** in octadécane
b- iPP
c- Decomposition of **1** in iPP

d- Decomposition of **2** in octadécane
e- iPP
f- Decomposition of **2** in iPP

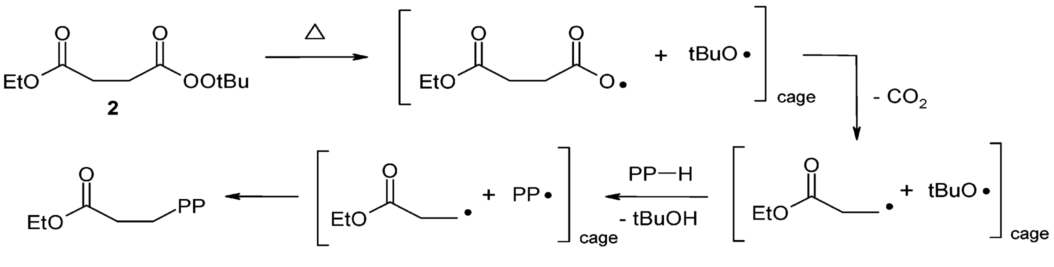
g- Decomposition of **3** in octadécane
h- iPP
i- Decomposition of **3** in iPP

Figure 3. DSC curves related to the decomposition of **1**, **2**, and **3** in isotactic polypropylene.

Scheme 2. Polypropylene Functionalization by Thermal Decomposition of 1



Scheme 3. Polypropylene Functionalization by Thermal Decomposition of a Perester



of the products formed which may have been removed during the concentration of the solution. Thermolysis of **1** and **3** generated two main molecules: ethyl hexanoate (**4**) and ethyl 6-(1,1-dimethylethoxy)hexanoate (**5**). The reaction of formation of **5** (Scheme 4, way A) was in direct competition with the functionalization of PP (Scheme 4, way C). Although free radical termination generally occurs via two competitive processes, coupling and disproportionation, ethyl 5-hexenoate, arising from the latter, could not be identified in the reaction products. This indicates that the radicals only terminated by coupling. **4** was produced in the reaction

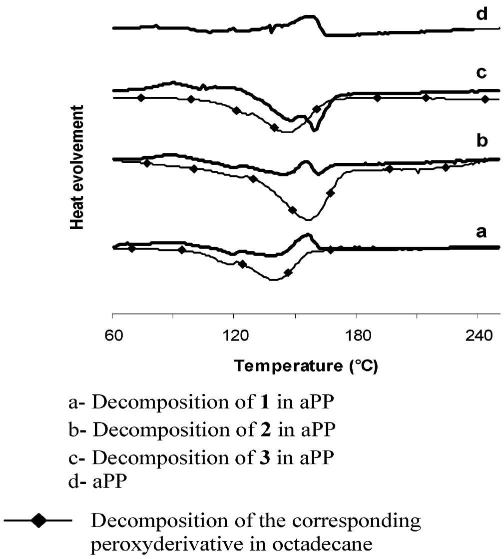


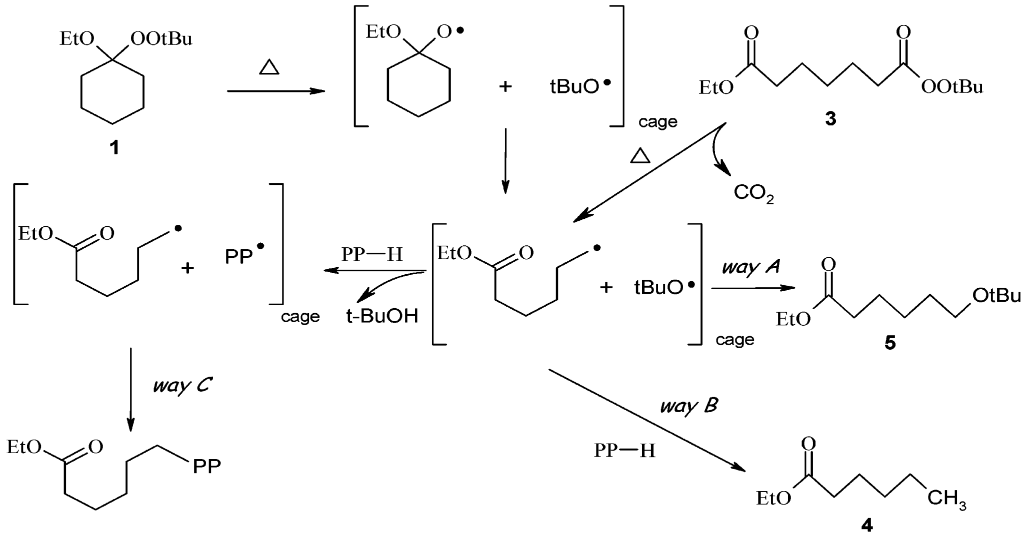
Figure 4. DSC curves related to the decomposition of **1**, **2**, and **3** in atactic polypropylene.

of 5-ethoxycarbonylpentyl radicals with polypropylene (Scheme 4, way B). Both esters **4** and **5** were also identified in the decomposition of **1** in polyethylene.[6] The difference of yields observed between the polypropylene and polyethylene functionalizations should lie in the relative efficiencies of the competitive processes (Scheme 4). The balance between these reactions is controlled by the diffusion of the radicals initially formed by the scission of the O—O bond. To try to answer to this question, the decomposition of **1** was studied in octadecane and compared with the ones in PP and PE. When the decomposition was run in aPP, the titration of the extracts by GC permitted one to point out that **5** was produced with a yield of 30%, relative to **1**; meanwhile, **4** was present only as traces. A slightly lower yield of formation of **5** (21%) and a higher one (7%) for **4** were observed in the decomposition of the peroxy ketal in polyethylene, the reaction being conducted under similar conditions. The identification of similar amounts of **4** and **5**, for the reaction performed in octadecane, is in favor of the main generation of **4** by hydrogen abstraction after escape of the cage and **5** by radical coupling in the cage for the reactions performed into polymers. However, it is important to note that the incomplete balance of the "1-ethoxycyclohexyloxy" entity of the peroxy ketal **1**, present in the reaction products (close to 35% for aPP and 60% for PE) encountered after titration, shows the limits of this method. This inaccuracy may certainly be caused by the numerous operations necessary to reach the various results. It must be emphasized that the way PP was collected may be responsible for this inaccuracy. Indeed, by precipitating the polyolefins after reaction, small chains might be lost, as pointed out by Moore.[7] If such fragmented polymers bore functional entities, the yields determined above would be in this case underestimated. Therefore, a technique allowing to directly perform the titrations in the bulk would be more efficient.

The NMR technique called DOSY (diffusion ordered spectroscopy) can allow, in certain conditions, a virtual "separation" of the low and high molecular weight products.[9] This methodology was applied on the whole sample. Indeed, the experiments were carried out in sealed tubes, and after reaction the NMR solvent was directly added into them for analysis. A cartography of the different compounds present in the same mixture can then be deduced from the NMR analysis by plotting the diffusion coefficients—or equivalent parameters—versus the chemical shifts. Thermolysis of **1** in atactic polypropylene was then performed in a sealed tube according to our standard conditions. After cooling, this tube was opened and tetrachloroethane-d_2 was directly introduced, the medium being homogenized by a slight heating. The whole solution was then transferred in a NMR tube, heated again, and analyzed at 60 °C (^{1}H NMR and DOSY). The spectra obtained are represented in Figures 5 and 6. To facilitate the understanding of the DOSY cartography, the analysis will be presented by horizontal sections (A, B, and C) from the bottom to the top on the way of decreasing diffusion coefficients:

(i) In zone A, five signals are present at 2.05, 5.20, 5.90, 7.10, and 7.35 ppm. These signals could be attributed to protons of acetone, tetrachloroethane, dichloromethane, and 1,2-dichlorobenzene. The presence of these last two compounds is due to an incomplete elimination of these solvents used in the preparation of the polypropylene. Acetone was produced by β-scission of 1,1-dimethylethoxy radicals generated in the homolysis of the peroxidic bond. It must be noted that

Scheme 4. Production of Low Molecular Products in the Decomposition of 1 and 3



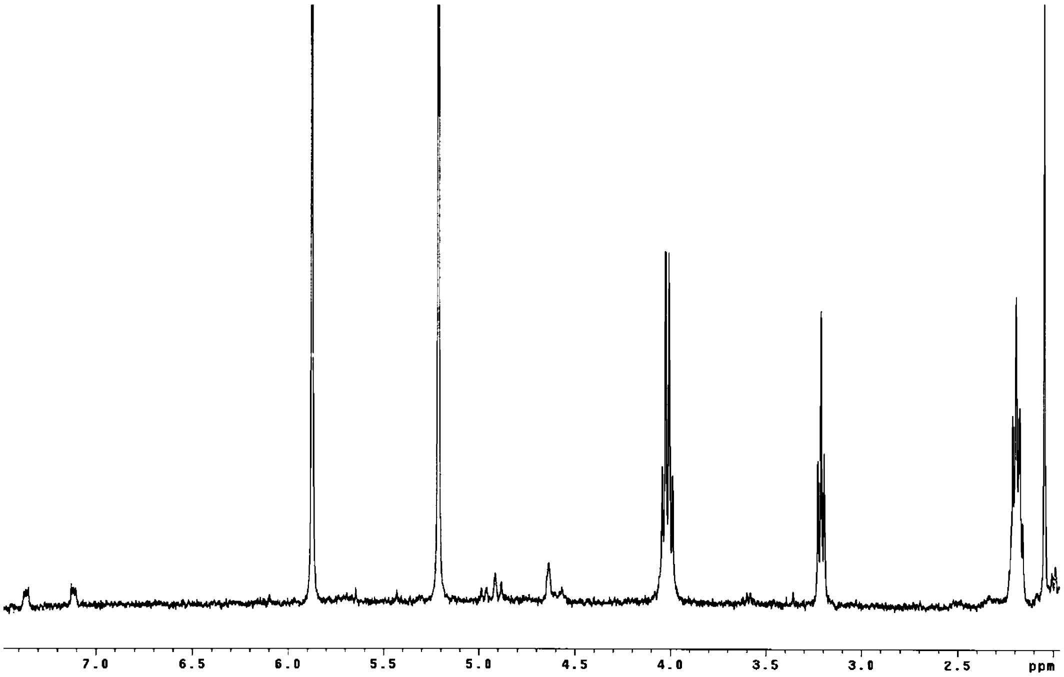


Figure 5. ^1H NMR spectrum (400 MHz, $C_2D_2Cl_4$) of the bulk arising from the decomposition of **1** in amorphous polypropylene.

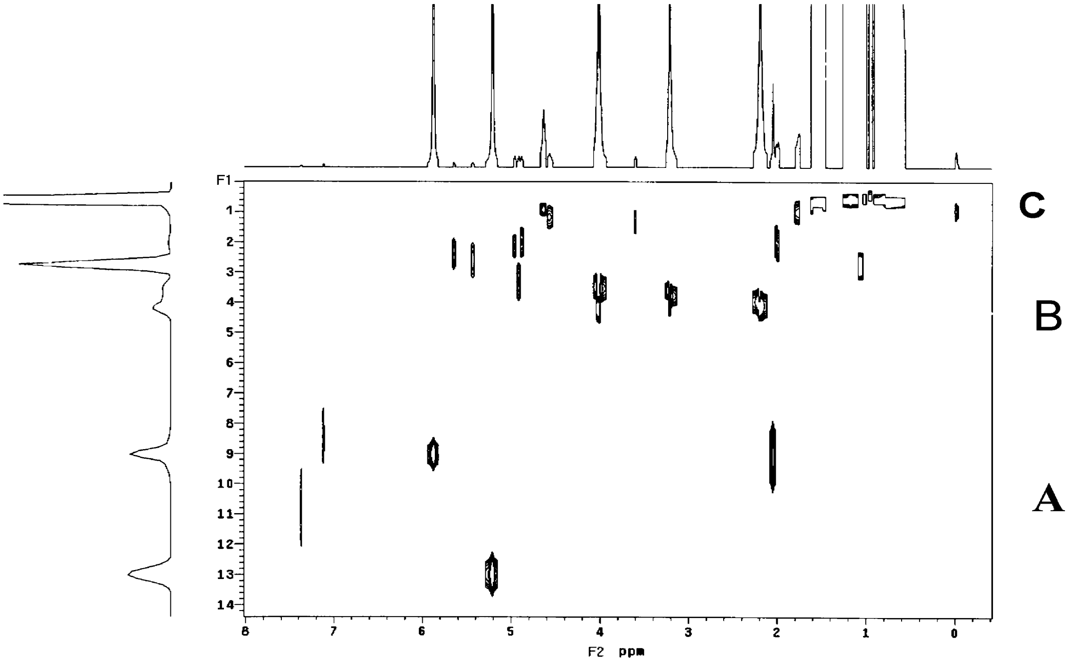
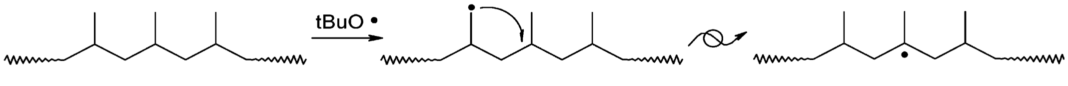


Figure 6. 2D-DOSY (400 MHz, $C_2D_2Cl_4$) of the bulk arising from the decomposition of **1** in atactic polypropylene.

Scheme 5. 1,6-Intramolecular Rearrangement of the Primary Macroradicals



1,1-dimethylethanol could not be identified in the DOSY spectrum. Two different explanations could be given: (i) 1,1-dimethylethoxy radicals fragmented faster than they abstracted a hydrogen to the polyolefin backbone and then no alcohol was produced; (ii) the chemical shift of protons of the "1,1-dimethylethyl" group of the alcohol are too close from the ones of the same entity present in ethyl 6-(1,1-dimethylethoxy)hexanoate, prohibiting the software to differentiate the two signals, and therefore they do appear overlapped on the DOSY cartography. The scanning of the spectrum of both compounds showed that the chemical shifts of the 1,1-dimethylmethyl protons was significantly different for the alcohol and **5** when the analyzed mixture contained these two molecules in similar amounts. Decreasing the ratio of the alcohol in the mixture led to shift the signal toward the one attributed to the protons of **5**, this making impossible to identify in the spectrum the protons of the 1,1-dimethylmethyl group arising from the alcohol. Considering these elements, it can be concluded that, if produced, 1,1-dimethylethanol was present in a very low amount in the solution.

(ii) In zone B, several signals are present. The combination of ^{1}H NMR (Figure 5) and DOSY cartography (Figure 6) led to identify the presence of ester **5** [$CH_2OC(O)$: t, 4 ppm; CH_2O: t, 3.2 ppm; $CH_2C(O)$: t, 2.2 ppm; $C(CH_3)_3$: s, 1 ppm]. If the two signals related to the protons of methylenoxy groups are considered, one can notice an excess for the integration of the two protons of the ethoxy group (at 4 ppm) relative to the ones of the methylene of the ether entity (at 3.2 ppm). This indicates the presence in the medium of other ethyl esters. Indeed, compounds bearing similar protons make the signals indistinguishable, even if they are bore by molecules having different diffusion coefficients. Ethyl hexanoate, identified in the extracts, must surely be one of them as well as the ethyl ester entity grafted on polypropylene. The relative yields of formation of the two esters **5** (75%) and **4** (15%) could be determined through the integration of signals at 3, 2, and 4 ppm, assuming an ester grafting on PP with a yield close to 10% relative to **1** (determined by integration of the $CH_2OC(O)$ signals of the ^{1}H NMR spectrum of the corresponding isolated modified polymer). The ^{1}H NMR spectrum from this sample, using the DOSY technique, confirms the ethyl ester entities were grafted on the macromolecule (signal at 4 ppm in zone C) and did not arise from remaining impurities trapped in the lattices of the polymer (absence of the corresponding signals in zone B of the DOSY cartography).

(iii) Zone C corresponds to the higher molecular weight molecules present in the medium. This is confirmed by the very intense signals between 0.5 and 1.6 ppm corresponding to the protons of polypropylene. Signals at 4.6 and 4.8−5 ppm could be attributed to the ethylenic protons bore by different double bonds, present in the starting polyolefin as observed on its ^{1}H NMR spectrum.

DOSY experiments on the raw material arising from the decomposition of **1** in polyethylene could, unfortunately, not be performed because of the presence of insoluble cross-linked polymer formed during the functionalization process. In this case, it was thus not possible to obtain a complete balance of the becoming of the radicals formed by the homolysis of the O−O bond of the peroxy ketal.

In the course of the decomposition of **1** in polypropylene, the main reaction of the radicals arising from the homolysis of the peroxidic bond is the combination of 1,1-dimethylethoxy and 5-ethoxycarbonylpentyl (75%). 1,1-Dimethylethoxy radicals, when they are not coupling, fragment to produce acetone and a methyl radical which is able to abstract a hydrogen to polypropylene. 5-Ethoxycarbonylpentyl radicals are either abstracting a hydrogen to polypropylene, after escape of the cage (15%), or combining in the cage with a macroradical to allow the functionalization of the polyolefin (10%).

The different functionalization yields of polyethylene and polypropylene seem to depend on the efficiency of hydrogen abstraction by the 1,1-dimethylethoxy radicals. According to the C−H BDE, one could expect the tertiary hydrogens in PP to be more reactive toward abstraction than the primary and secondary in either PP or PE.[10,11] If we consider the mechanism of functionalization of polyolefins based on the thermolysis of **1**, assuming similar viscosity of the medium, the combination of the alkyl and alkoxy radicals could be taken as a clock reaction to compare the efficiency of hydrogen abstraction from the polyolefin by the alkoxy radical. The identification of higher amounts of **5** for the reaction performed in polypropylene than in polyethylene would indicate that hydrogen abstraction seems to be more difficult from the first polyolefin than from the second one. This can be attributed to a steric hindrance to abstract the tertiary hydrogens as well as the secondary ones of polypropylene backbone, caused by the presence of methyl groups. This is in total agreement with the results of Solomon et al.,[10] who identified recently such an effect in the abstraction of the various hydrogen atoms present in 3-methylpentane and 2,4-dimethylpentane by 1,1-dimethylethoxy radicals. They pointed out a very different reactivity of the methyne and methylene units in both molecules that they attributed to the steric hindrance caused by the presence of a methyl group in their neighborhood in the case of the last alkane. It is worth noting that until now ESR studies permitted to point out only the formation of tertiary macroradicals.[11] This certainly lies in the fact that, after abstraction of the primary hydrogen atoms, the unstable species thus obtained undergo a rapid intramolecular rearrangement (Scheme 5).

Conclusion

Thermolyses of peroxy ketal **1** and peresters **2** and **3**, performed in polypropylene, according to the conditions previously set up to chemically modify polyethylene, appeared to be much less efficient (yield of functionalization relative to the peroxide of about 5−10%). It was shown that the period (i.e., before or after the melting of the crystalline zones) when the decomposition of these peroxides started in polyethylene or in atactic and isotactic polypropylenes cannot account for the difference of the functionalization efficiency. The DOSY technique permitted to show that the 1,1-dimethylethoxy radical prefers to combine with its counter alkyl radical than to abstract a hydrogen to the polymer backbone of PP. A much lower reactivity of 1,1-dimethylethoxy radicals toward polypropylene hydrogens than toward the ones of polyethylene has to be therefore seriously envisaged. This could be attributed to the steric hindrance of the methyl groups present on the backbone of the former, protecting the methyne and the methylene from the radical attack.

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References and Notes

(1) Naqvi, M. K.; Choudhary, M. S. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1996**, *C36*, 601.

(2) Hogt, A. H.; Meijer, J.; Jelenic, J. In *Reactive Modifiers for Polymers*; Al-Malaïka, S., Eds.; Chapman & Hall: London, 1997; p 84 and references therein.

(3) Navarre, S.; Maillard, B. *Eur. Polym. J.* **2000**, *36*, 2531−2539.

(4) Navarre, S.; Maillard, B. *J. Polym. Sci., Part A* **2000**, *38*, 2957−2963.

(5) Navarre, S.; Saule, M.; Maillard, B. *J. Appl. Polym. Sci.* **2003**, *87*, 699−707.

(6) Navarre, S.; Maillard, B. *Polymer* **2001**, *42*, 4509−4516.

(7) Assoun, L.; Manning, S. C.; Moore, R. B. *Polymer* **1998**, *39*, 2571−2577.

(8) Fodor, Z. S.; Irving, M.; Tudos, F.; Kelen, T. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2539−2550.

(9) Jayawickrama, D. A.; Larive, C. K.; McCord, E. F.; Roe, D. C. *Magn. Reson. Chem.* **1998**, *36*, 755−760.
(10) Dokolas, P.; Looney, M. G.; Musgrave, S.; Poon, S.; Solomon, D. H. *Polymer* **2000**, *41*, 3137−3145.
(11) Yamazuki, T.; Seguchi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3383−3389.

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