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Chemical Modification of Polypropylene by Decomposition of Unsaturated Peroxides

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ABSTRACT: Chemical modifications of polypropylene were studied via the decomposition of β,γ-unsaturated peroxides. Six peroxy derivatives were used to test the influence of the more important structural parameters (type of peroxide, nature of the unsaturation, and substituents in the allylic position) of such compounds on the efficiency of the grafting of a function and on the degradation of the polymer. Grafting of ester and epoxide functions on the chains of the polyolefin occurred with a slight degradation of these last ones with the use of acrylic peroxides. The decomposition of a styrenic peroxide allowed the grafting of phenyl entities on the backbone and induced structural modifications of the chains (branching). However, no epoxidic groups were detected in this case. Allylic peroxide did not permit any functionalization of the polyolefin but provoked some changes in the structure of the polymer. Mechanisms for the grafting and the degradation of the polypropylene were proposed.

Introduction

Because of its mechanical properties, its chemical stability, and its low cost of production, polypropylene is widely used in textile and nonwoven applications or serves as a raw material for car industry. However, its hydrophobic character makes it incompatible toward small structures as organic molecules or bigger assemblies as polymers.[1,2] Chemical modification of this polyolefin is an easy way to get a more versatile material able to give stable mixtures and hence to enlarge its application fields. Among all approaches investigated, free radical processes are the most used.[1,2] The grafting of functional entities relies on the addition of a macroradical onto the double bond of various monomers such as maleic and acrylic derivatives, sometimes in conjunction with styrene.[3,4] The initiation of this kind of reactions is usually ensured by the thermal decomposition of peroxides in the molten polymer. In 1995, we started to work in this field to develop the exclusive use of peroxy derivatives to perform the functionalization of various polyolefins. Before the publication of our work, Moore et al.[5] communicated results they obtained by decomposing several peresters in polypropylene in order to introduce functional moieties onto this polymer. They attributed the grafting of esters to the reaction of the PP macroradicals with an acrylic derivative generated in situ from the decomposition of the perester (Scheme 1, process A). The coupling of radical species accounted for explaining the introduction of such functions when the reactions were carried out with saturated peroxy derivatives (Scheme 1, process B). Meanwhile, we set up an innovative approach based on the decomposition of unsymmetrical peroxy derivatives[6,7] to chemically modify polyethylene with a low level of cross-linking. The grafting was essentially due to the coupling of a polymer radical, arising from the polyolefin, with a radical coming from the peroxide. An attempt to extend this reaction to polypropylene failed.[8]

Unsaturated peroxides showed their efficiency in functionalizing hydrogen donor solvents via an addition−elimination process[9−12] (Scheme 2). Furthermore, methacrylic double bonds are well-known to trap alkyl radicals. Those two facts prompted us to envisage the decomposition of ethyl 2-(1,1-dimethylethylperoxymethyl)propenoate (**1**) in polypropylene as a way to modify this polyolefin. Encouraging results were obtained in the decomposition of **1** in atactic polypropylene,[13] indicating that the grafting of functional moieties did occur through the addition of the macroradicals onto the double bond of this “acrylic” peroxide (Scheme 2, R = R′ = H, Y = CO_2Et, X = Me, ZH = polypropylene).

In this paper, we describe the study conducted with several unsaturated peroxy derivatives to functionalize polypropylene by means of an induced decomposition in the molten polymer. However, according to the decomposition of the peroxide before the melting temperature of PP, during the heating of the mixture peroxide/PP, reactions were both performed with an atactic and an isotactic polypropylene in order to determine the influence of crystalline zones on the efficiency of the process. The extent of degradation of the polyolefin after reaction was pointed out from the functionalizations involving exclusively the isotactic polymer.

Based on previous results, the selection of the peroxy derivatives involved in this study was done according to the following structural parameters: (i) the presence of substituents in the allylic position, (ii) its chemical nature (peroxide or peroxyketal), and (iii) the reactivity of the double bond (acrylic, styrenic, and vinylic). This led us to design and then synthesize the peroxides shown in Scheme 3.

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). The pellets received were reduced into powder using the procedure previously described.[8] The different peroxy derivatives used in this study were synthesized according to procedures previously described: ethyl

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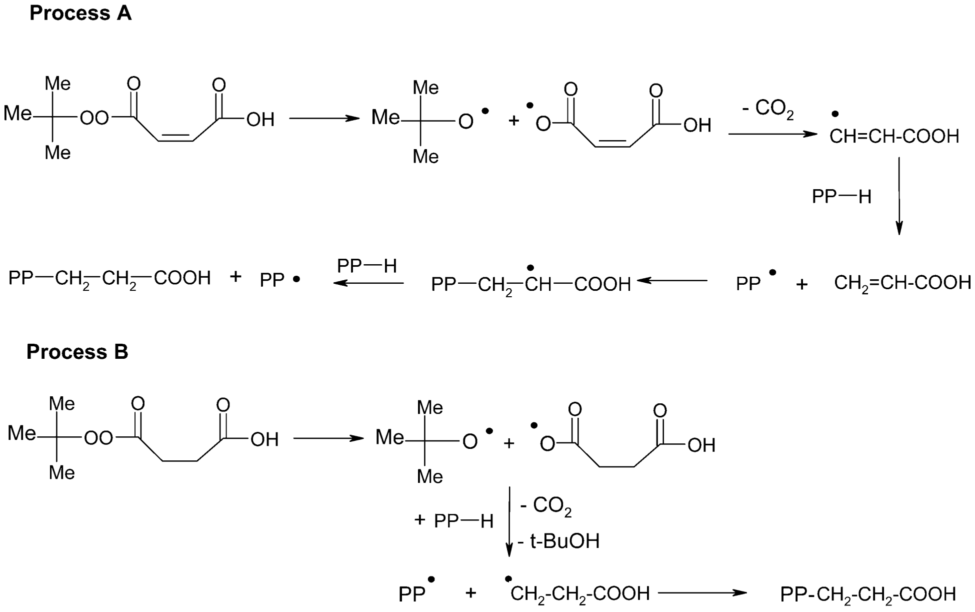
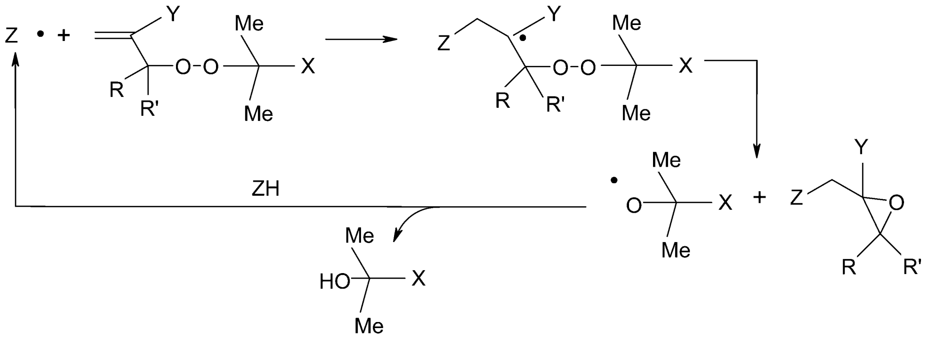
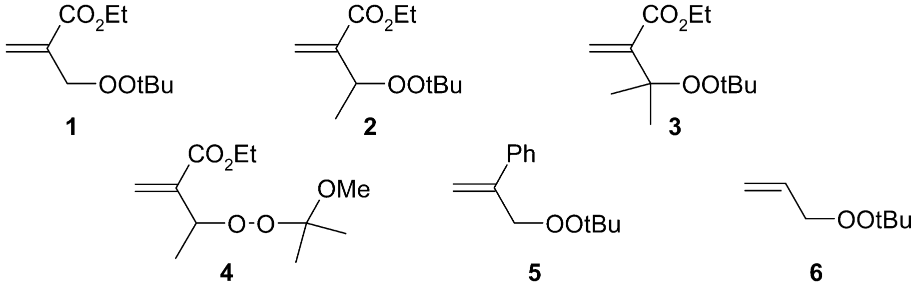
Scheme 1. Functionalization of PP by Peresters[5]



Scheme 2. Induced Decomposition of Acrylic Peroxides



Scheme 3. Unsaturated Peroxides Used for the Chemical Modification of PP



2-(1,1-dimethylethylperoxymethyl)propenoate (**1**),[10] ethyl 2-[1-(1,1-dimethylethylperoxy)ethyl]propenoate (**2**),[10] ethyl 2-[1-(1,1-dimethylethylperoxy)-1-methylethyl]propenoate (**3**),[10] ethyl 2-(1-methoxy-1-methylethylperoxyethyl)propenoate (**4**),[11] 3-(1,1-dimethylethylperoxy)-2-phenylpropene (**5**),[12] and 3-(1,1-dimethylethylperoxy)propene (**6**).[9]

Functionalization and Analysis of the Modified Atactic and Isotactic Polypropylenes. The thermal decompositions of these peroxy derivatives in a mixture of diphenylmethane and triphenylmethane performed in a DSC apparatus[14] showed similar rate constants for the spontaneous decomposition of peroxides, unsaturated or not. This led us to estimate the times required to decompose 99% of these peroxides at 160 °C, in the absence of any induced decomposition. Taking into account the obtained value (about 1.3 h), a total decomposition for all these peroxides after a heating at 160 °C can be assumed.

The procedure used for the functionalization and the analyses of the modified polypropylene were the ones previously described by us[8] and summarized: In a 50 mL flask, 0.595 mmol of peroxyderivative dissolved in a 10 mL of cyclohexane/dichloromethane mixture (1/9) was added onto 1 g of powdered polypropylene. After removing of the solvents at room temperature under reduced pressure with a rotavapor, the polymer/peroxyderivative mixture thus obtained was placed in a reactor (Büchiglasuster BMC 100). Once closed, it was degassed by a flow of argon. The reactor was then placed in an oil bath preheated and stabilized at 180 °C (i.e., $T_{\mathrm{reaction}} \approx$ 160/165 °C) and let at this temperature for 2.5 h without any stirring.

Extraction and Analysis of the Low Boiling Compounds Produced in the Reaction. The reaction bulk was dissolved, directly in the autoclave, in a minimum of toluene. Polypropylene was then precipitated by acetone addition and filtered. The organic phase was then concentrated by careful elimination of the maximum of acetone. The remaining solution was then analyzed by GC to detect the presence of ethyl acrylate.

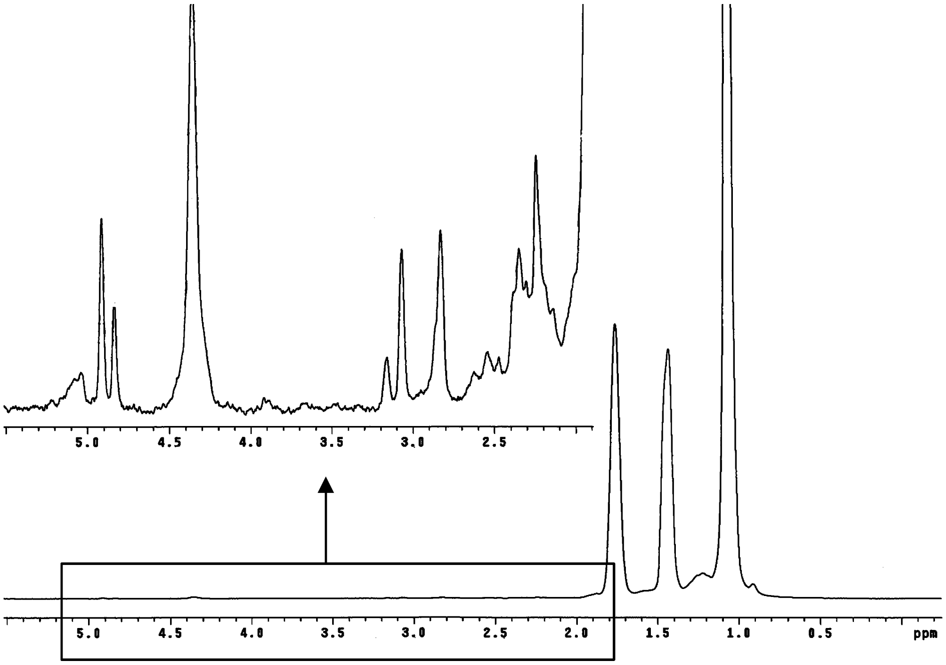


Figure 1. ^{1}H NMR spectrum of sample 1C.

Analytical Techniques. A Varian 3400 with a FID detector fitted with a computer using the Star Chromatography software, equipped with a DB5 column (5% Ph, 30 m length, 0.25 mm inside diameter, 0.25 μm internal phase thickness, pressure 15 psi nitrogen gas carrier), was used to identify ethyl acrylate. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 from films of about 7 mg of polypropylene prepared by a 9 ton pressure under vacuum. The grafting yields were determined using the procedure previously described.[8] The ^{1}H 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) in Akzo Nobel Deventer (Nederland). HT-SEC analyses of modified polypropylenes were performed in Akzo Nobel Arnhem (Nederland) on a Millipore 150 C ALC/GPC from Waters, fitted with a double detector (refractometer/viscosimeter 220R) from Viscotek at 150 °C in 1,2,4-trichlorobenzene (0.1 mL/min).

Results and Discussion

Thermolysis of the Acrylic Peroxide 1 in Isotactic and Atactic Polypropylene. The 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 IR spectra of the samples arising from the decomposition of **1** in atactic and isotactic polypropylene displayed a band at 1736 cm^{-1} characteristic of a carbonyl of an ester. ^{1}H NMR analyses of these samples confirmed the graft of ester groups as a multiplet ($CO_2\mathit{CH_2}CH_3$) visible at 4.2 ppm. The amount of ester functions introduced onto the polymer backbone was determined using both spectroscopic techniques (Table 1). Values found were taken to determine the yields of the functionalization reactions.[8] One can see that the two methods led to results close to one another, regardless of the tacticity of PP (yield = 30−40%). This good agreement between all values indicated that the process by which the functions were grafted occurred in a similar way whether the polymer was atactic or isotactic. So, the higher crystalline character of this latter did not seem to have any influence on the reaction, indicating that the reaction of functionalization occurred certainly in the amorphous part of the polymer or after melting.

Table 1. Yields of Ester or Phenyl Grafting on Atactic and Isotactic Polypropylene by Decomposition of β,γ-Unsaturated Peroxy Derivatives 1−5 at 160 °C (Ratio of Propylene Unit/Peroxide = 80)

			yield of grafting^{a,b} (%)		
polypropylene	peroxide	essay	IR		^{1}H NMR
atactic	**1**	1A	25	28	40
		1B	30		
	2	2A	30	38	40
		2B	45		
	3	3A	45	40	30
		3B	35		
	4	4A	40	30	45
		4B	20		
	5	5A			40
		5B			
isotactic	**1**	1C	25	33	30
		1D	40		
	2	2C	30	30	25
		2D	30		
	3	3C	30	40	30
		3D	50		
	4	4C	20	20	15
		4D	20		
	5	5C			30
		5D			

[a] Based on the peroxide used in the reaction. [b] Ester grafting for **1**−**4** and phenyl grafting for **5**.

The ^{1}H NMR analysis of samples 1A−1D showed also the presence of signals between 2.6 and 3.1 ppm (Figure 1) which were not present in the starting material (Figure 2). Considering the NMR spectrum of the heterocycle produced by the decomposition of **1** in cyclohexane,[10] these peaks were attributed to an epoxide grafted on the backbone of the polymer. Treatment of the solution by sulfuric acid confirmed this attribution.[13]

As an ester and an epoxide functions were both introduced onto the polymer backbone, one could reasonably think the grafting raised from the homolytic decomposition of **1** induced by the addition of the

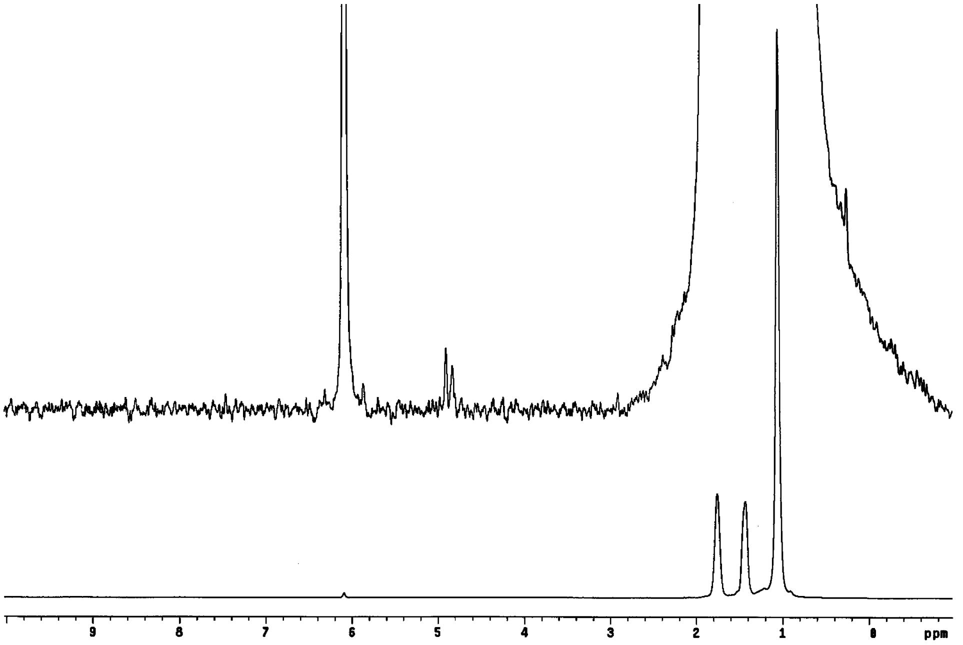
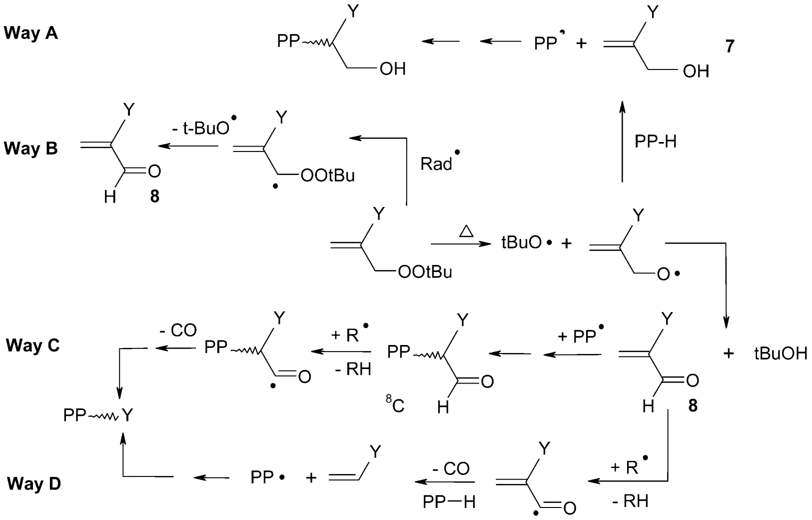


Figure 2. ^{1}H NMR spectrum of isotactic polypropylene.

Scheme 4. PP Functionalization by Thermolysis of Unsaturated Peroxides



macroradicals onto its double bond (Scheme 2, R = R′ = H, X = Me, Y = CO_2Et, Z = PP). Considering relative integrations of the peaks corresponding to the epoxidic protons (AB system at 2.6−3.1 ppm) and of the ones of the backbone (0.9−1.9 ppm), the yield in which this entity was grafted onto PP could be determined in regards to the amount of peroxide initially used for the reaction. A lower value than the one found for the grafting of ester functions was obtained (18% vs 30%). This indicated that beside the homolytic-induced decomposition of the acrylic peroxide **1**, another mechanism contributed to the grafting of ester functions onto PP. According to the rate constant of the spontaneous decomposition of the peroxide at 160 °C,[14] one could admit that a great part of the peroxide disappeared by such a process. The alkoxy radicals hence generated could diffuse in the medium and abstract a hydrogen from the polyolefin, this leading to the formation of the hydroxyacrylic ester **7** (Scheme 4, Y = CO_2Et, way A). Addition of a PP macroradical onto the double bond of this derivative may be a way of introducing ester functions onto the backbone of the polymer. However, one could notice the absence of protons corresponding to the C*H*$_2$OH moiety onto the ^{1}H NMR of the sample. In a previous study dealing with the thermolysis of various peroxy derivatives in polypropylene, we showed that the radicals arising from the homolysis of the O−O bond can readily react in the cage.[8] In the present work, one could observe that radical entity had a very reactive allylic hydrogen in α of the oxy radical. This would then favor the disproportionation of the species to produce aldehyde **8** (Scheme 4, Y = CO_2Et, way C). Such a compound might also be produced via the induced decomposition of **1** arising from an allylic hydrogen abstraction as we pointed out earlier (Scheme 4, Y = CO_2Et, way B).[15] The trapping of a polymer radical by this unsaturated molecule might also explain the introduction of ester functions onto the backbone of the polyolefin (Scheme 4, Y = CO_2Et, way C). The presence of aldehydic protons on the ^{1}H NMR spectra of the modified polymers could have been a valuable proof of this mechanism. However, if signals at 9.9 ppm were actually observable, their relative integrations were not sufficient to account for the grafting of ester functions

Table 2. Analyses for the Isotactic Polypropylene Degradation after the Decomposition of β,γ-Unsaturated Peroxy Derivatives 1−6 at 160 °C (Ratio of Propylene Unit/Peroxide = 80)

essay	$\bar{t}^a$ (s)	$\overline{M}_n$ (g/mol)	$\overline{M}_w$ (g/mol)	$\overline{M}_z$ (g/mol)	I_p
starting material	75.7	53 000	191 000	437 000	3.6
1C	37.4	30 000	88 000	178 000	3.0
1D	37.7				
2C	40.4	28 000	85 000	180 000	3.1
2D	39.2				
3C	33.3	24 000	59 000	107 000	2.5
3D	31.2				
4C	37.7	34 000	90 000	175 000	2.7
4D	38.7				
5C	50.2	42 000	187 000	573 000	4.5
5D	40.6				
6C	45.4	34 000	126 000	266 000	3.7
6D	45.6				

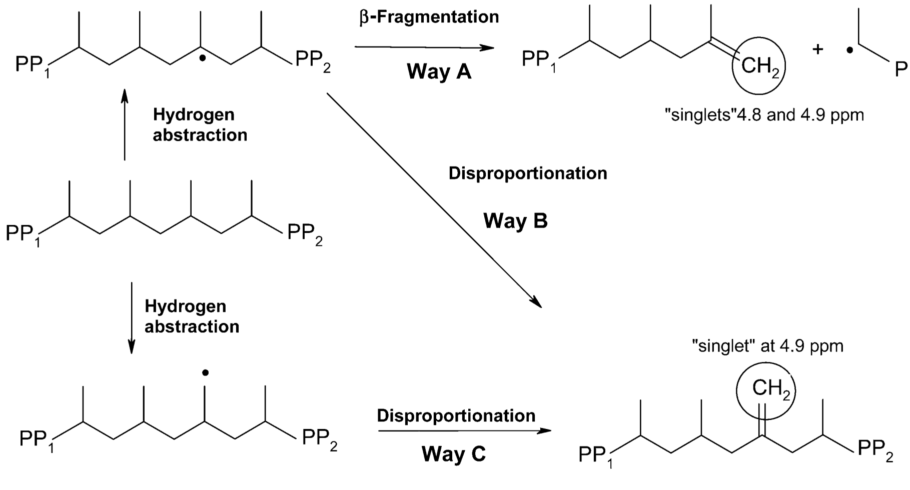
[a] Average value of three consecutive measurements.

by this way. The rapid decarbonylation of aldehydes[16] under radical conditions can be invoked to explain the low amount of aldehydic protons visible on the spectra. It can be noticed that such a rearrangement might also occur either after reaction between the PP macroradicals and compound **8** (Scheme 4, Y = CO_2Et, way C) or directly on aldehydic unsaturated ester **8** (Scheme 4, Y = CO_2Et, way D). Production of ethyl acrylate during the thermolysis of **1** in polypropylene was confirmed as this compound was detected in the extracts collected after reaction. Then, both mechanisms involving compound **8** may contribute to the grafting of ester functions. This can explain their excess regarding the overall yields of the functionalization reactions.

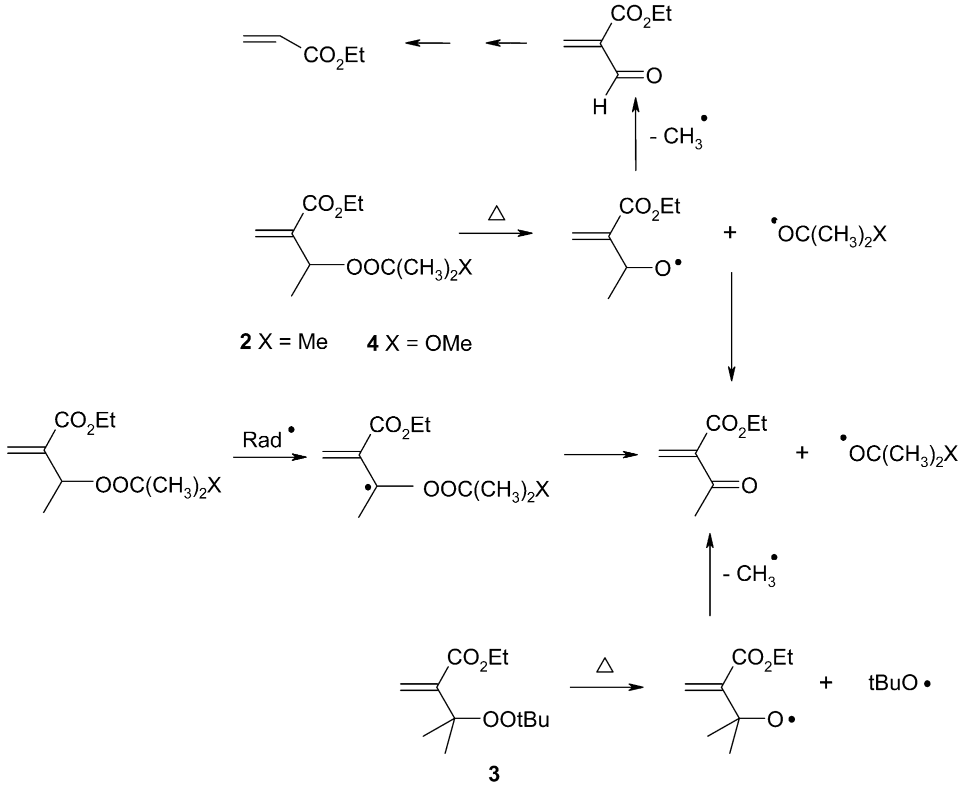
It was also important to point out the extent of degradation the polyolefin underwent during the process. For this purpose, we set up a simple and rapid method applicable in any laboratory.[17] It was based on the measurements of the free fall times of an item placed in solutions made from PP samples and 1,2-dichlorobenzene ($c = 50$ mg/mL) under controlled conditions. Results obtained are reported in Table 2.

Comparison of the fall times obtained in the case of samples 1C and 1D and of the starting polymer indicated that the extent of degradation was similar for the two treated polymer samples. SEC analyses confirmed this finding. In other words, during the thermolysis of **1** in the polymer, the macroradicals generated reacted by β-fragmentation to produce two shorter chains, one bearing a terminal unsaturation and the other the radical entity. It is interesting to underline that the size distribution of the chains of polypropylene was slightly narrower (decrease of the polydispersity). Yamazaki[18] showed by ESR that the hydrogens of methine units were those abstracted first during the process. In a second time, the tertiary carbon centered radicals hence produced fragmented readily. The ^{1}H NMR spectra of samples 1A−1D displayed peaks at 4.8−4.9 ppm. These signals revealed the presence of ethylenic protons onto the backbone of the polymer. Shape and intensity of the peaks indicated that two types of unsaturation existed together. One raised from the fragmentation of the tertiary alkyl macroradicals (Scheme 5, way A) whereas the other may come from the disproportionation of either tertiary or primary macroradicals (Scheme 5, ways B and C). The identification of lower averaged molecular weights for the modified isotactic polypropylenes confirmed the existence of the fragmentation. Considering this fast reaction given by tertiary radicals, it was rather surprising to observe the formation of a terminal double bond via this disproportionation. In an other hand, it is well established that the abstraction of methylenic hydrogens is far easier than methylic ones. Thus, the formation of a terminal double bond might only be explained by a selective disproportionation of the tertiary radicals due to a steric hindrance that prohibited the oxy radicals to easily abstract methylenic hydrogen atoms. This finding was in agreement with the results of Solomon and colleagues,[19] who identified a change in the reactivity of *tert*-butoxy radicals toward hydrogens with an increase of β-substitutions in the case of branched hydrocarbons. This result also might be explained by a selective production of this type of double bond from the disproportionation of the radical arising from the hydrogen abstraction on a methyl of the polyolefin. Indeed, in a previous paper[8] we proposed the initial abstraction of such a hydrogen, leading through a free radical rearrangement to the tertiary alkyl radical identified by ESR. However, at this stage of knowledge it is dangerous to draw any conclusion as the signals corresponding to the ethylenic protons were also present on the spectrum of the starting material. So, complementary experiments would be worthwhile to go further in this way but operating with a polymer free of any kind of unsaturation.

Scheme 5. Free Radical Generation of Unsaturations on Polypropylene Backbone



Scheme 6. Spontaneous and Induced Decompositions of Peroxides 2−4



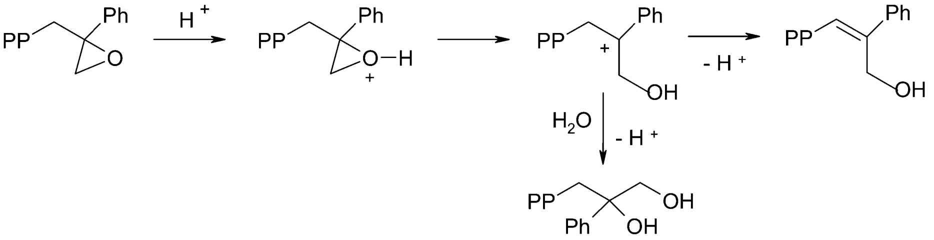
The chemical modification of the polyolefin was performed through the addition of the macroradicals onto acrylic compounds (peroxide **1** or products arising from its decomposition). The Mark−Houwink plots permitted to point out that none of our samples were branched (see Figure 3 in Supporting Information). Taking this into account, we may assume that the free radical centers obtained after the macroradical was trapped by non-peroxidic acrylic derivatives reacted by hydrogen transfer or disproportionation, but not by coupling with a macroradical.

Thermolysis of the Acrylic Peroxides 2 and 3, Substituted in Allylic Position in Isotactic and Atactic Polypropylene. The identification of ester grafting due to the formation of acrylic compounds arising from the reactivity of allylic hydrogens present in **1** (induced decomposition of **1** by allylic hydrogen abstraction and/or disproportionation of oxy radicals generated in the homolysis of the peroxidic bond) prompted us to synthesize peroxides **2** and **3**, corresponding to the formal substitution of one or both allylic hydrogens in **1**.

The samples of polypropylene chemically modified by the decomposition of these peroxides were analyzed by IR and ^{1}H NMR. Ester grafting was then proven, and yields of functionalization were calculated from these spectra (Table 1). The first remark to do was the observation of similar values than the ones obtained for **1** (Table 1), whatever was the tacticity of the polyolefin involved in the reaction. So, substitution of the allylic hydrogen atoms by one or two methyls did not seem to influence the yields of ester grafting. ^{1}H NMR characterization of polypropylene samples 2A−2D showed the presence of signals at 2.6−3.1 ppm, which were attributed to the proton of the epoxide grafted on the polyolefin backbone via the homolytic induced decomposition of the peroxide by macroradical (Scheme 2, R = H, R′ = Me, X = Me, Y = CO_2Et, Z = PP). It was unfortunately impossible to determine the yield of epoxide grafting because of the presence of numerous signals, several of them being very weak ("diastereoisomeric structures" due to the existence of two asymmetric carbons on each heterocycle). In the case of peroxide **3**, ^{1}H NMR did not allow to have more information on epoxide grafting arising from the absence of proton on the grafted heterocycle. Then, it was not possible to determine whether free radical additions to non-peroxidic acrylic derivatives might be involved in the functionalizations. Indeed, these monomers might have been produced, in a similar fashion than with **1**, from the reactions described Scheme 6.

The degradation of the polyolefin caused by the decomposition of peroxides **2** and **3** was approached by the determination of the fall times on the various samples and later by HT-SEC (Table 2). One can see from the results described in this table that the substitution of one allylic hydrogen by a methyl of peroxide **1** did not seem to influence the degradation of the isotactic polypropylene. Conversely, the substitution of the second appeared to have an effect, with the production of macromolecules of smaller averaged molar masses. Analysis of the Mark−Houwink plots (Figure 4 in Supporting Information) indicated a similar structure of the various chains with no branching. Considering that about 60−70% of the peroxide used in the reaction did not participate to the grafting, in all cases it was difficult to explain the difference of degradation of the polymer in connexion with the allylic hydrogen substitution. The single difference that we could notice between peroxides **1**−**3** was the production during decomposition of peroxide **3** of two tertiary alkyloxy radicals unable to disproportionate. Then, one could imagine a higher escape of the oxy radical from the cage. However, this could not explain the results since, as

Scheme 7. Acidic Hydrolysis of Epoxide Resulting from the Thermolysis of Peroxide 5 in Polypropylene



earlier pointed out, the decrease of the length of the polyolefin chains was higher when the polymer was treated by peroxide at low concentration.[20]

Thermolysis of the Acrylic Peroxyketal 4 in Isotactic and Atactic Polypropylene. As peroxyketals are less stable than dialkyl peroxides, it appeared interesting to use an acrylic peroxyketal for the chemical modification of polypropylene and to compare the results with the ones given by peroxide **2**. ^{1}H NMR spectra of the samples of polypropylene modified by **4** showed the presence of CH_2O protons of the ester entity and of the epoxidic one. As in the case of peroxide **2**, the difficulty to estimate the epoxide grafting did not allow to know precisely the way they were introduced onto the polyolefin backbone. Indeed, two processes may be responsible of the grafting as shown in Schemes 2 and 6.

The grafting yields regarding the amount of ester functions present onto PP after reaction are reported in Table 1. Values found by estimating the extent of degradation using the “fall time” approach are summarized in Table 2. The grafting yields of ester functions were slightly lower when the functionalization reaction was carried out with the isotactic polymer. It was also interesting to note that the peroxyketal **4** appeared to be less efficient than peroxide **2**, but not in the case of the atactic polymer. An explanation may relay on the fact the decomposition of the peroxyketal occurred before the crystalline zones were melted in the case of the isotactic polymer, as shown by a DSC study of the thermolysis of a saturated peroxyketal in PP.

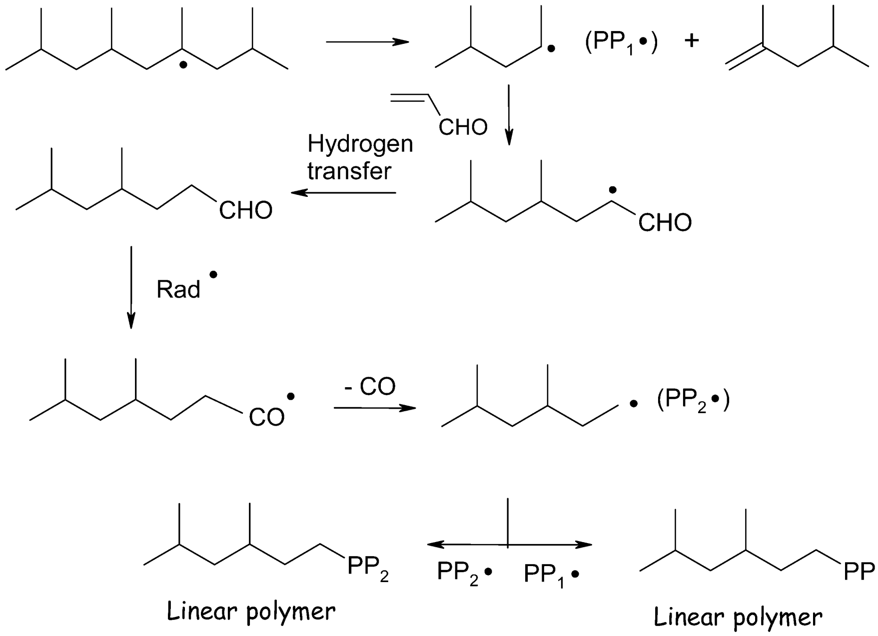
The degradation of the polymer chains appeared to be similar when **2** and **4** were used (see Figures 4 and 5 in the Supporting Information).

Thermolysis of Nonacrylic Unsaturated Peroxides 5 and 6 in Isotactic and Atactic Polypropylene. First, it is important to underline that determination of the kind and the amount of functions introduced onto polypropylene after reaction could only be pointed out by ^{1}H NMR spectroscopy as no carbonyl entity was possibly grafted using peroxides **5** and **6**.

The ^{1}H NMR spectra of the samples resulting from the thermolysis of peroxide **5** in atactic and isotactic polypropylenes displayed signals in the area where aromatic protons are usually observed. Such a finding proved the grafting of phenyl entities onto polymer backbone. The efficiency of the peroxide to chemically modify PP was assessed regarding the level of functions grafted. Values found are summarized in Table 2. These results seemed to indicate that peroxide **5** had the same ability as **1** to functionalize the polyolefin, either atactic or isotactic. However, no epoxidic protons could be identified on the spectra. This led to thinking that either the grafting of phenyl rings did not happen owing to the homolytic-induced decomposition of the peroxy derivative (Scheme 2, R = R′ = H, X = Me, Y = Ph, Z = PP) or the epoxide moiety was not stable in the conditions of the reaction. The presence of a signal at 3.7 ppm, absent in the starting material, indicated the existence of protons attached to a carbon linked to an oxygen. The addition of the polypropylene radical to the unsaturated alcohol derivative arising from the spontaneous decomposition of **5** (Scheme 4, Y = Ph, way A) may explain the presence of such a signal. On the other hand, styrenic epoxide functions are known to be more sensitive toward protic reactants than the acrylic ones.[21] This could explain the occurrence of such a transformation (Scheme 7) not observed when using acrylic peroxides. However, the amount of alcohol functions introduced onto PP was very low. In other words, if the two mechanisms described above contributed to the grafting of phenyl rings, they were minor phenomena. The above studies carried out with acrylic peroxy derivatives showed the likeliness of producing unsaturated compounds either by disproportionation in the cage of the radical species or by allylic attack. Similar reactions might also be evoked in this case to explain the grafting of phenyl rings onto the backbone of the polyolefin (Scheme 4, Y = Ph, ways B−D). As previously found with the acrylic peroxides, even if aldehydic protons were identified on the ^{1}H NMR spectra of samples 5C and 5D, this cannot be an absolute proof of the existence of this mechanism as the level, in which this functionality was present, was very low.

Considering the extent of degradation pointed out for samples 5C and 5D (Table 2), one could notice an important discrepancy between the two reactions of functionalization. The comparison of the IR spectra showed the presence of an intense carbonyl band at 1710 cm^{-1} for sample 5D. This indicated that an oxidation reaction additionally occurred during the processing of the polymer or even while submitting the polyolefin to the action of the peroxide. For this reason, the sample was discarded from the following discussion. Comparison of the fall times measured for samples 1C, 1D, and 5C seemed to indicate a higher degradation of backbone when it was treated by **1** rather than with **5**. This observation fit well with previous works,[3,4] showing that the adjunction of styrene while using maleic anhydride or glycidyl methacrylate monomers for the modification of PP under radical conditions helped to decrease the degradation of the polymer. The Mark−Houwink plots (see Figure 6 in the Supporting Information) showed that sample 5C had long chain branching. We thus have to consider that conversely to the case of the acrylic peroxides a coupling occurred between two PP macroradicals (fragmented or not), either before or after they added onto a styrenic as shown in Scheme 8. Cartier and Hu[4] previously proposed the existence of such radical couplings to explain the variation of the viscosity during the course of the functionalization of polypropylene. This remark goes well with the production of branched polypropylene when reacted in the presence of 1,3-butadiene.[22] Indeed, in this case, an allylic radical was obtained by addition of the macroradical to buta-

Scheme 8. Free Radical Reactions Resulting of the Decomposition of 6 in Polypropylene



diene, and allylic and benzylic radicals have generally similar behavior due to the stabilization of the unpaired electron by delocalization on several atoms.

The spectroscopic analyses (IR and ^{1}H NMR) of samples 6C and 6D of the polypropylene modified by decomposition of peroxide **6** did not allow identifying the presence of any functionality grafted on the polymer. The absence of epoxide entity could be surprising if we consider that epoxypropanylation of cyclohexane was observed with a yield of about 30%[9] in the thermolysis of **6** in this cycloalkane. During the reaction, the peroxide might disappear by two main competitive processes: the spontaneous decomposition and the homolytic-induced decomposition by the addition elimination process. The first one is less affected by the viscosity of the medium than the second one, which is a chain reaction needing the migration of the species. It is thus not surprising that the chemical modification of PP through the induced decomposition of the peroxy derivative appeared to be less efficient in this case than in cyclohexane. This hypothesis was validated by considering the yields of functionalization of cyclohexane and of polypropylene using the thermolysis of the acrylic peroxide **1**. It is therefore reasonable to envisage that the allylic peroxide **6** disappeared essentially by spontaneous decomposition or eventually by homolytic-induced decomposition resulting from allylic hydrogen abstraction and do not participate to the grafting of epoxide functions on the backbone of the polypropylene. It is interesting to underline that both reactions (Scheme 4, Y = H, ways A and C) consuming peroxide **6** would lead to the formation of acrolein. This compound is reactive toward alkyl radicals and would then allow the grafting of aldehydic entities on the polyolefin. However, ^{1}H NMR analyses of samples 6C and 6D did not allow observing that aldehydic protons were grafted onto the polymer. This showed either that acrolein did not react with the macroradicals or that the aldehyde functions or/and even acrolein itself were degraded during the reaction. To check whether radicals, escaped from the cage, might react onto the polypropylene to provoke degradation of the polyolefin, we submitted these samples to fall time measurements and HT-SEC analysis (Table 2). Lower fall times were obtained for 6C and 6D than for the starting material. This showed that a radical degradation occurred in this case, as suspected. Nonetheless, if HT-SEC of these samples confirmed these first results, it was interesting to note that the polydispersity of the modified polymers had a value very close to the one of the starting material. This was rather surprising if we consider the results described in the literature[23] or found with the acrylic peroxides. Additionally, the Mark−Houwink plots (see Figure 7 in Supporting Information) permitted to point out that no sample was branched although it was the case when using peroxide **5**. This indicated the termination reaction mainly involved macroradicals having the unpaired electron on a terminal carbon. It is worth noting that such radicals arise from fragmentation reactions. Taking into account what we obtained above with the different peroxy derivatives tested, we had to envisage that the acrolein molecules produced in the medium might be responsible for such a termination as they get the ability of trapping readily alkyl radicals. Considering this and the easy free radical decarbonylation of aldehydes,[16] the mechanism described Scheme 8 was found to be a valuable way permitting to explain the polydispersity and the few degradations of the polyolefin when submitted to the action of **6**. The fact that no branching was detected may be relevant of an absence of trapping of the PP internal carbon radicals and also of the inefficiency of the alkyl radical arising from the aldehydic functions grafted onto the backbone to react by coupling.

Conclusion

The decomposition of the acrylic peroxides **1**−**4** in PP allowed introducing ester functions onto its backbone with yields in the range of 30−40%, regarding the initial amount of the peroxide involved in the reactions. A thorough analysis of all samples permitted to attribute the functionalization to (i) a free-radical-induced decomposition of the unsaturated peroxide followed by an addition elimination process involving the macroradicals to produce glycidic esters and (ii) a free radical addition of macroradicals onto acrylic monomers generated in situ from the spontaneous decomposition of the peroxide.

Whatever was the acrylic peroxy derivative involved, no significant effect was pointed out because of the presence of methyl in allylic position. Meanwhile, it seemed that the nature of the peroxidic function had an influence since the functionalization reactions carried out with peroxide **2** gave better results than those involving its homologous peroxyketal **4**. The extent of degradation of the polyolefin occurred similarly whatever peroxide was used.

The study of the modification of polypropylene based on the decomposition of these unsaturated peroxides pointed out the importance of chemical nature of the substituent bore by the double bond onto the mechanism of the reaction. With an acrylic peroxy derivative (peroxide **1**) the grafting occurs owing to an addition−elimination process, whereas with the styrenic (**5**) or allylic (**6**) peroxides, the main way of consumption was due to a spontaneous decomposition generating radicals that further disappeared by disproportionation in the cage. The nature of the substituent played also an important role on the extent and kind of degradation the polypropylene underwent during the process of functionalization. In the case where styrenic compounds where produced, long chain branching of the polymer was observed. For the reaction involving the allyl *tert*-butyl peroxide, termination by coupling of radicals at the end of the chain was the predominant reaction.

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Supporting Information Available: Mark−Houwink plots for isotactic polypropylene and samples 1C−6C. This material is available free of charge via the Internet at http://pubs.acs.org.

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