

# Synthesis of Polyurethane/Polyethylene Grafted Polymers Using Cyclotriphosphazene as a Coupling Agent

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**ABSTRACT:** The reaction between a dihydroxyphenoxy-cyclotriphosphazene containing allylic functions, **3**, and hexamethylene-1,6-diisocyanate (HDI) leads to a new cyclotriphosphazene-substituted polyurethane **4**. The structures of both classes of compounds involved in that synthesis were investigated by <sup>31</sup>P-, <sup>13</sup>C-, and <sup>1</sup>H-NMR, infrared, and mass spectrometry, size-exclusion chromatography, and elemental analysis. The thermal behavior of **4** was investigated and compared to that of hexaphenoxycyclotriphos-

phazene, N<sub>3</sub>P<sub>3</sub>(OC<sub>6</sub>H<sub>5</sub>)<sub>6</sub>, and of a polyurethane synthesized from 1,3-bis(hydroxy)benzene and HDI. The free-radical-promoted grafting of **4** onto the polyethylene surface is described. The resultant surface was studied by ATR-IR, XPS, and contact-angle techniques. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1925–1934, 2003

**Key words:** polyurethanes; polyethylene (PE); thermal properties; surfaces

## INTRODUCTION

The modification of organic conventional polymers by grafting thin films of other organic or inorganic polymers onto their surface can impart useful properties (hydrophobicity, hydrophilicity, roughness, crystallinity, conductivity, etc.) without modifying the bulk material and so transform inexpensive materials into valuable products. This challenge, if successful, can give rise to materials with very interesting applications in fields such as adhesion, protective coating, and biomaterials.<sup>1,2</sup>

In this area, the synthesis of organic carbon-backed polymers containing pendant side cyclotriphosphazene moieties is of great interest. Indeed, hexachlorocyclotriphosphazene (N=PCl<sub>2</sub>)<sub>3</sub> can be functionalized with a broad range of organic substituents and can transform that inorganic cycle into reactive intermediates useful for the modification of conventional polymeric materials or for the preparation of new monomers for structurally new polymers.<sup>3–6</sup>

There are two possible ways to obtain cyclotriphosphazene-containing polymers. They can be obtained, for example, from cyclophosphazenes containing polymerizable vinyl, acrylic, or methacrylic groups linked to phosphorus by P—O<sup>7–14</sup> or P—C<sup>15–21</sup> bonds. In a second approach, cyclotriphosphazene can be

introduced into an organic polymer by polycondensation of two bifunctional molecules. Examples are given with the synthesis of cyclophosphazene-substituted polyurethanes,<sup>22–5</sup> polyesters,<sup>26</sup> and polyamides<sup>27</sup> and from a bifunctional cyclotriphosphazene.

In the present article, we report the formation of a new allylic-functionalized urethane–phosphazene polymer from hexamethylene-1,6-diisocyanate (HDI) and a cyclotriphosphazene containing allylic functions and two hydroxyl groups. We detail successively the synthesis of the hydroxylated derivative, the characterization of the compounds involved in this process, and the preparation and characterization of the urethane polymer and its thermal properties. Furthermore, the grafting of the new cyclotriphosphazene-substituted polyurethane onto the surface of polyethylene (PE) films was studied.

## EXPERIMENTAL

### Equipment

<sup>31</sup>P-, <sup>1</sup>H-, and <sup>13</sup>C-NMR spectra were recorded in CDCl<sub>3</sub> for compounds **1–3** and in DMSO-*d*<sub>6</sub> for polyurethane **4** using a Bruker WP 300 NMR spectrometer. Chemical shifts (ppm) are positive in the low-field direction and are relative to the external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) or external TMS (<sup>1</sup>H, <sup>13</sup>C). Infrared spectra of the same compounds were obtained as thin films or as KBr pellets using a Bomem MB-100 spectrometer. Molecular weights were obtained using size-exclusion

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chromatography on a Waters Millipore apparatus equipped with Shodex columns using THF as the eluant. The calibration curve was established using polystyrene standards. Mass spectra were recorded with a Nermag R10-10B (fast atom bombardment) spectrometer. Thermogravimetry measurements were performed in air on a Setaram NTB10-8 instrument at a heating rate of 8°C/min. Elemental analyses were carried out at the Service Central d'Analyse CNRS, France.

The ATR-IR spectra were recorded with a Bruker IFS 48 spectrometer using a Graseby Specac continuously variable-angle ATR accessory equipped with a KRS-5 crystal. The XPS analyses were performed in an LHS 10 system (Leybold AG). The X-ray source was operated at 13 kV, 10 mA using Al K $\alpha$  radiation (1486.6 eV). Binding energy calibration was based on Au 4f<sub>7/2</sub> at 84 eV, Ag 3d<sub>5/2</sub> at 368.2 eV, Cu 2p<sub>3/2</sub> at 932.7 eV, and C 1s (—CH<sub>2</sub>— like species) at 285 eV. The analyzer was operated in the fixed retarding ratio (FRR) mode. The vacuum was in the 10<sup>-8</sup> mbar range.

## Materials

PE films were supplied by Goodfellow (Lille, France). The melting point was between 110 and 135°C. They were characterized by infrared spectroscopy (ATR). Absorbance bands (cm<sup>-1</sup>) were as follows: 2916, 2847  $\nu$ (CH<sub>2</sub>); 1472, 1462  $\delta$ (CH<sub>2</sub>); 731, 719  $\Gamma$ (CH<sub>2</sub>). The films of 10  $\mu$ m thickness were cut to 2  $\times$  4.5cm size. Just before use, they were dried at 100°C for 3 h.

Tetrahydrofuran (THF), dichloromethane (DCM), benzene (cancer suspect agent and handling precautions), and dimethyl sulfoxide (DMSO) were obtained from SDS (Solvents Documentation Synthesis, Marseille, France). THF and DCM were purified by distillation and dried over molecular sieves. Sodium hydride (80%), 2-allylphenol, 3,5-dimethoxyphenol, phenol, boron tribromide, and HDI were Aldrich products (Saint Quentin Fallavier, France) and used as received. 4-Dimethylaminopyridine, benzoyl peroxide, and anhydrous sodium sulfate were obtained from Fluka (Saint Quentin Fallavier, France) and used as received. Hexachlorocyclotriphosphazene N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub> (Nippon Soda, Aldrich) was purified by vacuum sublimation. All reactions and manipulations were carried out under an inert atmosphere.

### Synthesis of chloro(2-allylphenoxy)phenoxy cyclotriphosphazene (1)

In a typical reaction, a solution of 2-allylphenol (2.31g, 17.3 mmol) and phenol (14.61 g, 155.2 mmol) in THF was added dropwise into a three-necked round-bottom flask cooled at -10°C containing N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub> (11.97 g, 34.5 mmol) and NaH in excess (6.24 g, 207.9 mmol) in THF. After completion of the addition, the mixture

was stirred at room temperature for 20 h. A <sup>31</sup>P-NMR spectrum of the solution at this stage generally showed the existence of two side products: tetra- and hexasubstituted cyclotriphosphazenes. The first was eliminated by repeating the reaction after addition of a calculated amount (from the <sup>31</sup>P-NMR spectrum) of phenol. Then, the mixture was ultracentrifuged (3000 rpm) to separate the solid from the liquid and the THF removed under reduced pressure. The residue was dissolved in DCM, washed three times with water (20 mL), dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. The major part of the hexasubstituted cyclotriphosphazene was separated from **1** by successive recrystallizations from a diethyl ether/petroleum ether solution at 4°C and removed by filtration. The remaining solution was finally evaporated under a vacuum. **1** was obtained as a clear oil. Yield: 11.1 g, 49%. NMR and infrared characterization data are reported in Table I.

ANAL. Found: C, 59.7%; H, 4.2%; N, 6.2%; O, 12.3%; P, 13.5%; Cl, 4.5%.

### Synthesis of (3,5-dimethoxyphenoxy)(2-allylphenoxy)phenoxy cyclotriphosphazene (2)

A solution of an excess of 3,5-dimethoxyphenol (1.8 g, 11.7 mmol) in THF was added dropwise to a solution of **1** (6 g, 9.07 mmol) with an excess of NaH (0.3 g, 12.5 mmol) in THF. The mixture was heated to 70°C for 24 h, then cooled at room temperature and ultracentrifuged (3000 rpm) to separate the solid from the liquid. THF was removed under reduced pressure. The residue was dissolved in DCM, extracted with 10 % aqueous NaOH (twice), washed with water (three times), and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, **2** was obtained as a yellowish oil. Yield: 3.86 g, 55%. NMR and infrared characterization data are reported in Table I.

ANAL. Found: C, 61.65%; H, 4.65%; N, 5.47%; O, 16.18%; P, 11.76%.

### Synthesis of (3,5-dihydroxyphenoxy)(2-allylphenoxy)phenoxy cyclotriphosphazene (3)

A solution of an excess of boron tribromide (1.4 g, 5.6 mmol) in anhydrous DCM (10 mL) was treated dropwise with a solution of **2** (4 g, 5.14 mmol) in anhydrous DCM (20 mL). The reaction mixture was stirred at room temperature for 3 h and then poured into 30 mL of water. The obtained residue was dissolved in DCM, washed with water (three times), and dried over molecular sieves (4 Å). The solvent was finally removed under reduced pressure. **3** was obtained as clear oily solid. Yield: 2.31 g, 60%. NMR and infrared characterization data are reported in Table I.

TABLE I  
Spectroscopic Data for Compounds 1-3 and Polymer 4

Compound	$\delta$ (ppm)			IR frequency (cm <sup>-1</sup> )		
	<sup>31</sup> P-NMR	<sup>1</sup> H-NMR	<sup>13</sup> C-NMR			
1	22.34 (t) 22.21 (t) 7.02 (d) 6.87 (d) <i>J</i> = 82 Hz	3.3 (m, —CH <sub>2</sub> —)	37 (s, —CH <sub>2</sub> —)	1177 ( $\nu$ P—O—Ar)		
		5.0 (m, =CH <sub>2</sub> )	117 (m, —CH=)	952 ( $\nu$ P—O—Ar)		
		5.8 (m, —CH=)	121 (m, aromatic)	1267 ( $\nu$ P=N)		
		7.4–6.8 (m, aromatic)	125 (m, aromatic)			
			128 (m, aromatic)			
			129 (m, aromatic)			
			133 (s, =CH <sub>2</sub> )			
			137 (s, aromatic)			
			150 (m, aromatic)			
			151 (m, aromatic)			
		2	8.74 (m)	3.2 (m, —CH <sub>2</sub> —)	33 (s, —CH <sub>2</sub> —)	1177 ( $\nu$ P—O—Ar)
				3.7 (s, OCH <sub>3</sub> )	55 (s, OCH <sub>3</sub> )	949 ( $\nu$ P—O—Ar)
				5.0 (m, =CH <sub>2</sub> )	98 (m, aromatic)	1263 ( $\nu$ P=N)
5.8 (m, —CH=)	100 (m, aromatic)			1614 ( $\nu$ C=C, —CH=CH <sub>2</sub> )		
6.4–6.2 (m, aromatic)	117 (m, —CH=)			2842 ( $\nu$ C—H, OCH <sub>3</sub> )		
7.2–6.8 (m, aromatic)	121 (m, aromatic)					
	125 (m, aromatic)					
	127 (m, aromatic)					
	129 (m, aromatic)					
	130 (s, =CH <sub>2</sub> )					
	137 (m, aromatic)					
	150 (s, aromatic)					
	153 (m, aromatic)					
	161 (s, aromatic)					
3	8.94 (m)	3.25 (m, —CH <sub>2</sub> —)	32 (s, —CH <sub>2</sub> —)	1177 ( $\nu$ P—O—Ar)		
		4.95 (m, =CH <sub>2</sub> )	98 (s, aromatic)	951 ( $\nu$ P—O—Ar)		
		5.85 (m, —CH=)	101 (s, aromatic)	1267 ( $\nu$ P=N)		
		6.1–6.0 (m, aromatic)	118 (m, —CH=)	3272 ( $\nu$ O—H)		
		7.2–6.8 (m, aromatic)	121.1 (s, aromatic)			
			121.2 (s, aromatic)			
			125.2 (d, aromatic)			
			129.7 (m, aromatic)			
			130.1 (s, =CH <sub>2</sub> )			
			138 (m, aromatic)			
			150 (s, aromatic)			
			153 (m, aromatic)			
			158 (s, aromatic)			
4	9.46 (m)	1.33 (—CH <sub>2</sub> —)		1178 ( $\nu$ P—O—Ar)		
		3.03 (—CH <sub>2</sub> —)		949 ( $\nu$ P—O—Ar)		
		4.90 (m, =CH <sub>2</sub> )		1261 ( $\nu$ P=N)		
		5.80 (m, —CH=)		1738 ( $\nu$ C—O)		
		7.7–6.8 (m, aromatic)		2944, 2859 ( $\nu$ C—H, —CH <sub>2</sub> —)		
		9.97 (s, NH)				

#### Synthesis of polyurethane (4)

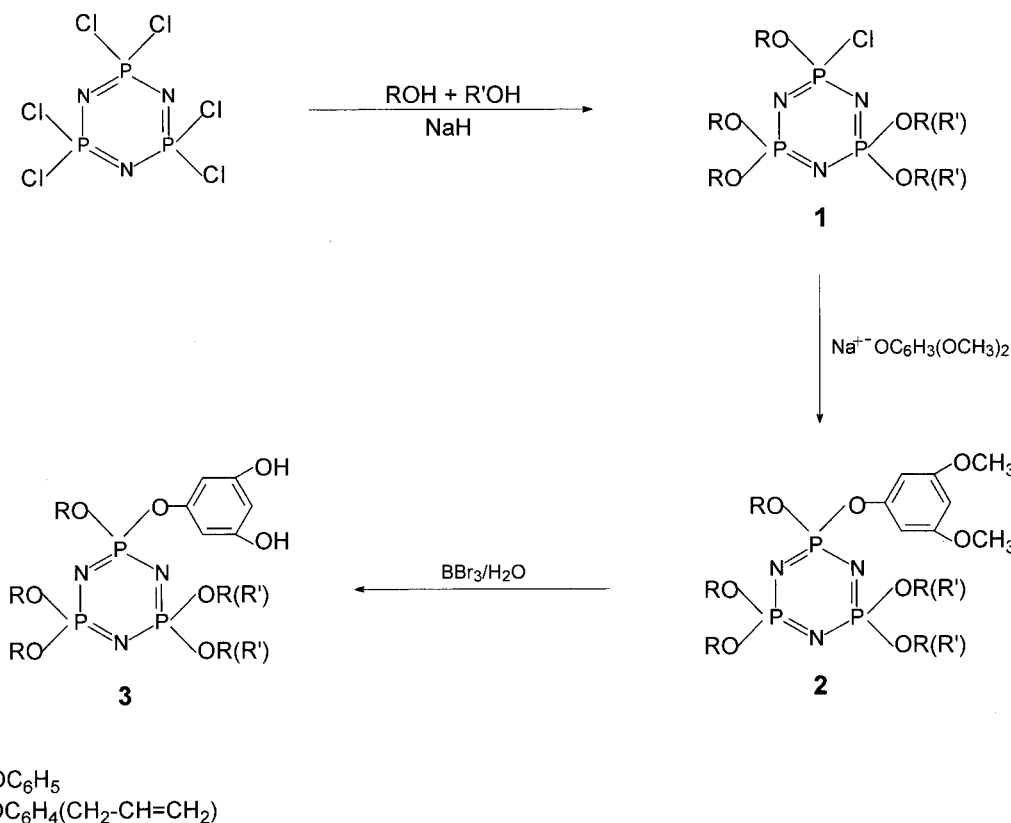
The typical procedure for this preparation was as follows: A solution in benzene containing **3**, HDI (mol ratio, diol/diisocyanate = 1), and 4-(dimethylamino)pyridine (0.005 mol per mol of diol) as the base was refluxed for 24 h. During this period, the precipitation of the polymer occurred. Then, the reaction mixture was cooled at room temperature and ultracentrifuged (3000 rpm) to separate the liquid from the solid. The latter was finally washed with benzene and dried under reduced pressure to give a white solid soluble in DMSO and THF. Spectroscopic data are given in Table I.

#### Synthesis of polyurethane (4')

**4'** was synthesized according to the same procedure described for **4** using (3,5-dihydroxyphenoxy)(penta-phenoxy) cyclotriphosphazene.<sup>23</sup>

#### Grafting procedure

After drying, the film samples were immersed and shaken in solutions of **4** or **4'** in DMSO, with a concentration of 30 g/L in the presence of benzoyl peroxide at room temperature for 3 h. The percentage of benzoyl peroxide used was 3% w/w in comparison with those of **4** or **4'**. The films were treated at 110°C



Scheme 1 Synthesis of the hydroxylated precursor 3.

for 7 h and then soaked and shaken in DMSO for 20 h to remove the excess of the initiator and the ungrafted polymers. Finally, after drying at 110°C for 2 h, film surface analyses were carried out.

## RESULTS AND DISCUSSION

### Synthesis and characterization of the dihydroxylated cyclotriphosphazene

The synthetic route to the new functionalized cyclotriphosphazene containing two free OH groups 3 used as precursor for polyurethanes is outlined in Scheme 1. This synthesis was carried out according to a procedure in three steps already used for the synthesis of (3,5-dihydroxyphenoxy)(pentaphenoxy)cyclotriphosphazene<sup>23</sup>:

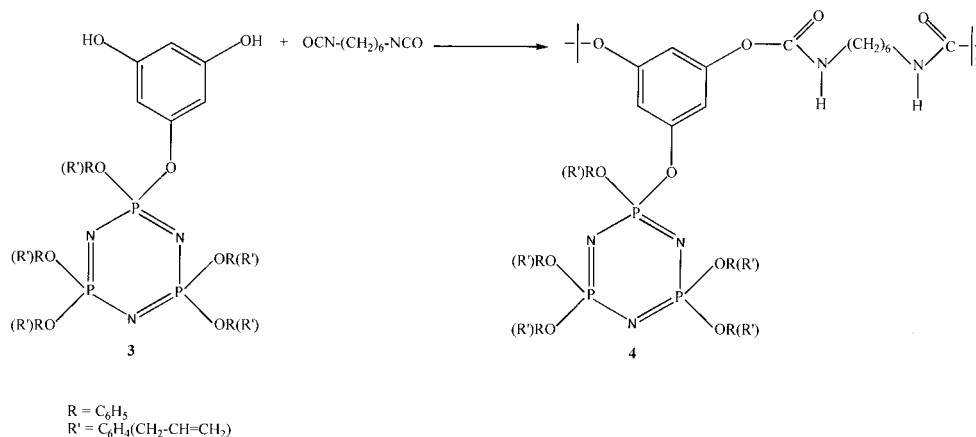
- (i) Treatment of hexachlorocyclotriphosphazene with a mixture of phenol and 2-allylphenol with an experimental ratio of 9/1 in the presence of NaH in tetrahydrofuran, leading to the pentasubstituted derivative 1 according to a procedure previously described for the synthesis of the (pentaphenoxy)(monochloro)cyclotriphosphazene.<sup>28</sup>

- (ii) Reaction of 1 with a difunctional nucleophilic reagent, sodium 3,5-dimethoxyphenolate, to give 2.
- (iii) Reaction of 2 with an excess of boron tribromide, followed by the elimination of CH<sub>3</sub>Br and the hydrolysis of the cyclotriphosphazene boron derivative to give 3. This last procedure was analogous to the one involved in the synthesis of hexakis(4-hydroxyphenoxy)cyclotriphosphazene.<sup>29</sup>

Compounds 1–3 were characterized by NMR (<sup>31</sup>P, <sup>1</sup>H, <sup>13</sup>C), infrared, and mass spectrometries (Table I), and elemental analysis.

The first step of the reaction leads to a mixture of cyclotriphosphazenes with a random distribution of the phenoxides with the allylic groups. It is the reason why the <sup>31</sup>P-NMR spectrum of the corresponding compounds showed two triplets and two doublets centered on  $\delta = 22.3$  ppm and  $\delta = 22.2$  ppm (t) {P[OR(R')]Cl}, and  $\delta = 7.0$  ppm and  $\delta = 6.9$  ppm (d) {P[OR(R')]<sub>2</sub>}, respectively, with the same coupling constant  $J = 82$  Hz, representative of the pentasubstituted cyclotriphosphazene 1.

The multiplicity of the signals, which is due to the coexistence of the phenoxy and allylphenoxy substituents, was found again for two signals at  $\delta = 9.0$  and 8.9



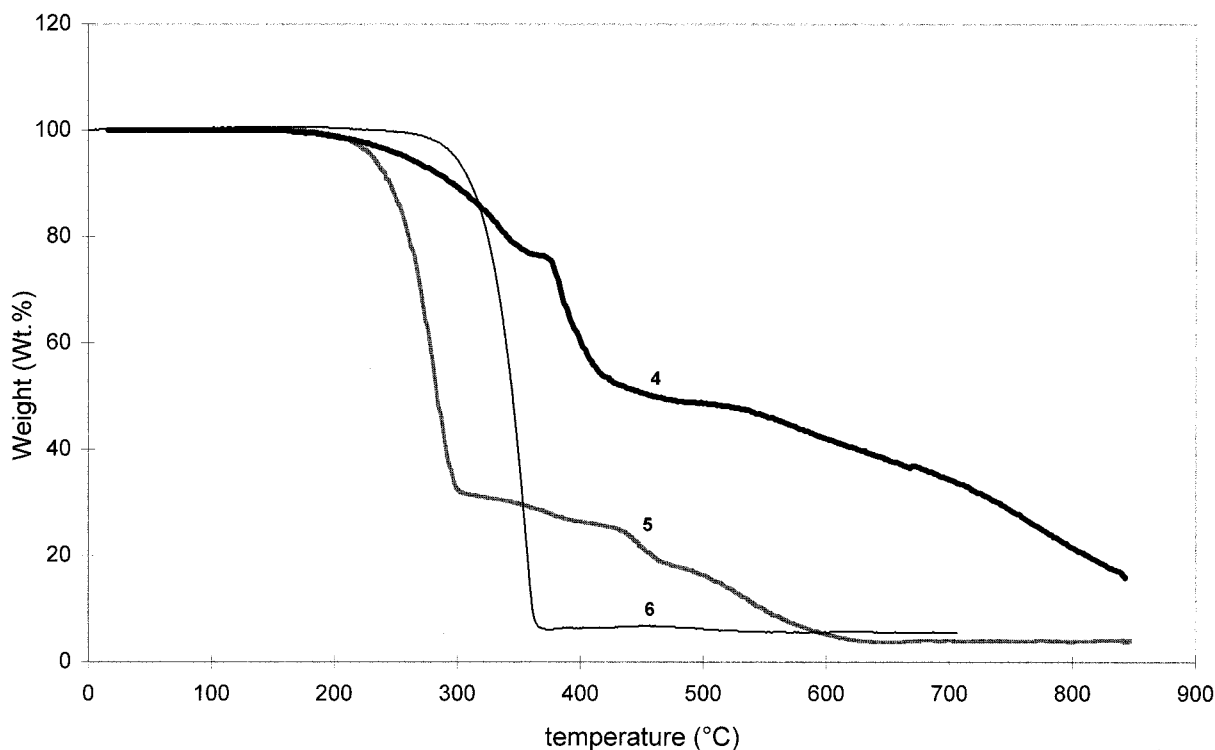
**Scheme 2** Synthesis of the polyurethane 4.

ppm, representative of the  $\{P[OR(R')]_2\}$  groups in the hexasubstituted derivatives. By the quantitative study of the  $^{31}P$ - and  $^1H$ -NMR spectra, it was possible to show that 80% of the pentasubstituted derivatives were obtained and that the phenoxy and allylphenoxy groups were in the ratio of 12/1.

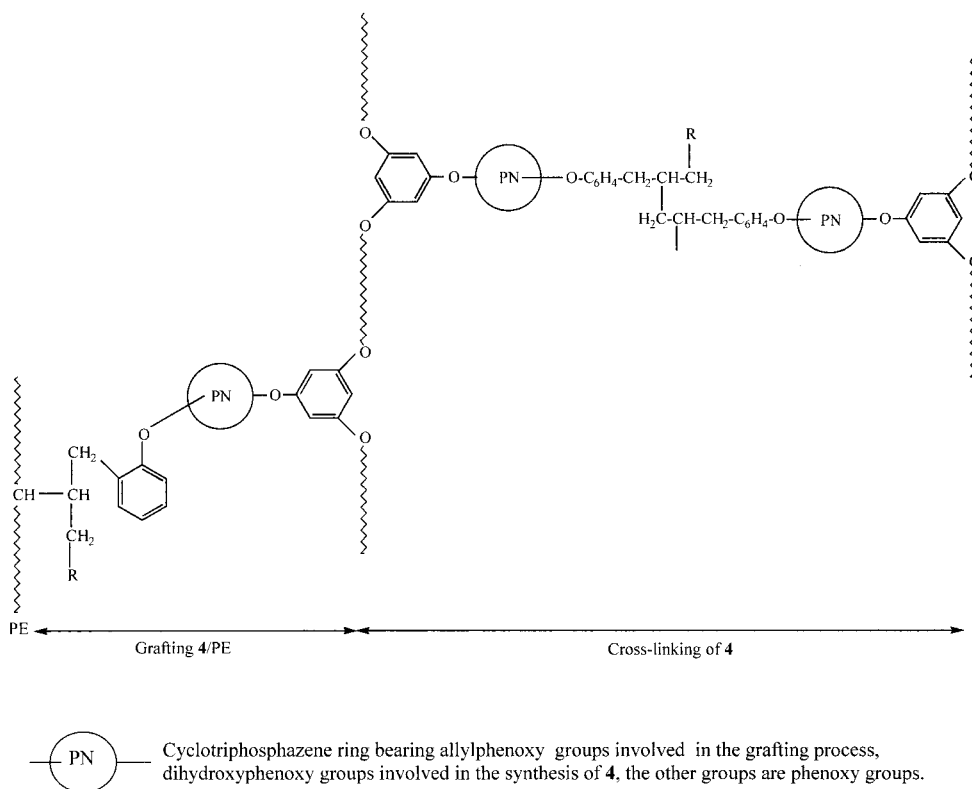
These results were in accordance with the FAB mass spectral data which indicated the molecular ions  $MH^+$  at  $m/e = 636$   $[N_3P_3(OC_6H_5)_5Cl]$ , 676  $[N_3P_3(OC_6H_5)_4(OC_6H_4CH_2-CH=CH_2)Cl]$ , 694  $[N_3P_3(OC_6H_5)_6]$ , 716  $[N_3P_3(OC_6H_5)_3(OC_6H_4CH_2-CH=CH_2)_2Cl]$ , and 734  $[N_3P_3(OC_6H_5)_5(OC_6H_4CH_2-CH=CH_2)]$ . At this stage of the reaction, the elimination of the hexasu-

stituted derivatives was not necessary. In any case, these compounds did not interfere with the next reactions and could be eliminated during the polyurethane synthesis.

The conversion 1 $\rightarrow$ 2 was characterized in the  $^{31}P$ -NMR spectrum by the complete disappearance of the triplets and doublets and the appearance of a multiplet at  $\delta = 8.74$  ppm, indicating a complete substitution of the residual chlorine atoms, and in the  $^1H$ -NMR spectrum by the appearance of a signal at  $\delta = 3.63$  ppm (s,  $OCH_3$ ). The FAB mass spectrum after the second step displayed the following molecular ions  $MH^+$  at  $m/e = 694$ :  $[N_3P_3(OC_6H_5)_6]$ , 734  $[N_3P_3(OC_6H_5)_5(OC_6H_4$



**Figure 1** Thermogravimetry of 4, 5, and hexaphenoxycyclotriphosphazene 6 conducted at a heating rate of 8°C/min in an air atmosphere.



**Scheme 3** Supposed mechanism for the grafting of polymer **4** onto the PE film surface.

CH<sub>2</sub>—CH=CH<sub>2</sub>], 754 {N<sub>3</sub>P<sub>3</sub>[OC<sub>6</sub>H<sub>5</sub>]<sub>5</sub>(OC<sub>6</sub>H<sub>3</sub>(OCH<sub>3</sub>)<sub>2</sub>)}, 792 {N<sub>3</sub>P<sub>3</sub>(OC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>(OC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>—CH=CH<sub>2</sub>)[OC<sub>6</sub>H<sub>3</sub>(OCH<sub>3</sub>)<sub>2</sub>]}, 832 {N<sub>3</sub>P<sub>3</sub>(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(OC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>—CH=CH<sub>2</sub>)<sub>2</sub>[OC<sub>6</sub>H<sub>3</sub>(OCH<sub>3</sub>)<sub>2</sub>]}. After the third step, the presence of the hydroxyl groups in **3** was confirmed by IR spectroscopy by a band at  $\nu = 3272$  cm<sup>-1</sup> (broad) characteristic of the OH stretching vibration, the bands around  $\nu = 1260, 1180,$  and  $950$  cm<sup>-1</sup> being representative of the P=N, C—O—, and P—O— stretching vibrations in the cycle and in the P—O—C— bond, respectively.<sup>30</sup>

#### Synthesis and characterization of the polyurethane **4**

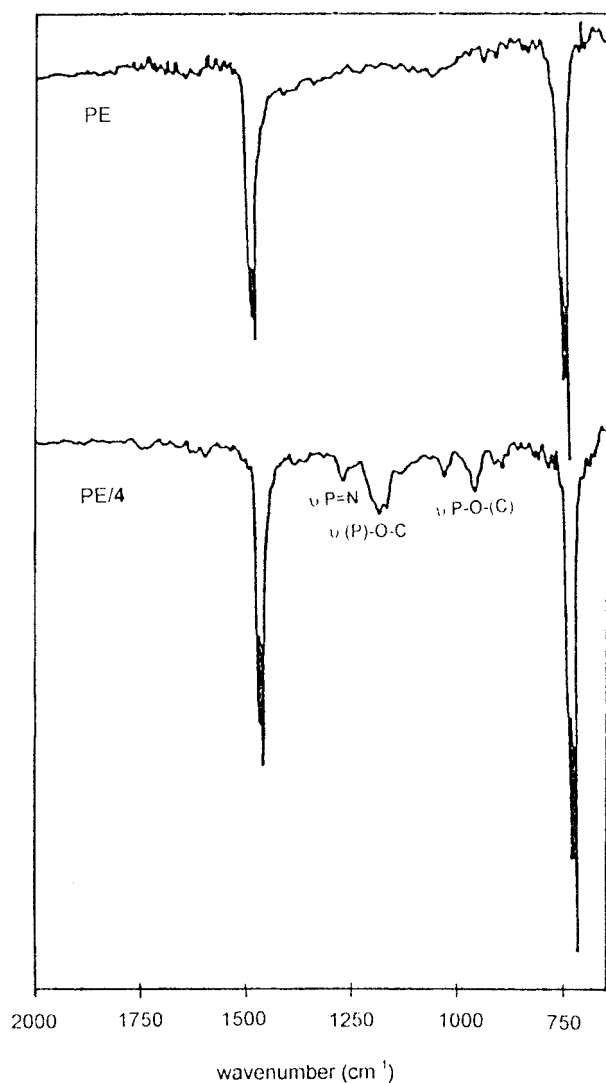
The second part of this work consisted of the synthesis of the new polyurethane **4** containing cyclophosphazene as a pendant group. It was obtained by a reaction between HDI and the hydroxylated derivative **3** (Scheme 2). This reaction was carried out in benzene, using a mol ratio of **3**/diisocyanate = 1, in the presence of the base, 2,4-bis(dimethylamino)pyridine.<sup>21</sup> The obtained polyurethane was a white solid, soluble in DMSO, DMF, and THF. The spectroscopic characterization data are reported in Table I.

Polymer **4** was characterized in the <sup>31</sup>P-NMR spectrum by a singlet at  $\delta = 9.46$  ppm, indicating the equivalence of the phosphorus atoms and, consequently, the preservation of the phosphazene ring. The <sup>1</sup>H-NMR and IR spectra confirmed the formation

of polyurethane **4** (Table I). A singlet representative of the NH protons was observed at  $\delta = 9.97$  ppm. Broad signals corresponding to the methylene —(CH<sub>2</sub>)— and —NHCH<sub>2</sub>— protons were seen at  $\delta = 1.33$  ppm and  $\delta = 3.03$  ppm, respectively.

Finally, **4** was characterized by IR spectroscopy by two absorption bands at  $\nu = 3338$  cm<sup>-1</sup> and  $\nu = 1738$  cm<sup>-1</sup>, attributed to the NH and carbonyl stretching vibrations, respectively. In fact, the NH band presented a double peak. The first around  $\nu = 3315$  cm<sup>-1</sup> is broad and can be attributed to NH groups involved in intermolecular hydrogen bonding (N—H—O=C); the second, narrower, at  $\nu = 3402$  cm<sup>-1</sup>, is characteristic of free NH groups. The molecular weight of **4** determined by steric exclusion chromatography was  $M_w = 22,000$  with a polydispersity index of 2.

One of the features of the cyclotriphosphazene-containing polyurethane **4** is its thermal stability, which was investigated by thermogravimetric analysis in air. The corresponding thermogram is represented in Figure 1. The temperature corresponding to a 10% weight loss ( $T_{10}$ ) was 300°C, and 50% of the original weight was retained at 500°C. This high char yield, which reflects the flame-retardancy properties, is characteristic of cyclotriphosphazene-containing polymers.<sup>23–25</sup> Interestingly, at 600°C, **4** retained approximately 43% of its original weight, whereas polyurethane (**5**) synthesized from the 1,3-bis(hydroxy)benzene/HDI reac-



**Figure 2** ATR-IR spectra of original PE film and film treated with 4.

tion and hexaphenoxycyclotriphosphazene (**6**) were completely degraded at the same temperature.<sup>23</sup>

#### Grafting of 4 onto PE films-surface: proposed mechanism

PE films were dip-coated with DMSO solutions of 4 containing benzoyl peroxide as a radical initiator. Af-

ter a few hours, the coated films were heated at 110°C for 3 h, washed with DMSO to remove the ungrafted polymer, and finally dried.

During the thermal treatment of the PE/4/peroxide system, two processes were supposed to take place: a covalent grafting of 4 onto the PE film surface and its crosslinking reaction according to the mechanism represented in Scheme 3. This mechanism implies, first, the thermal cleavage of the peroxide molecules to form free radicals able to open the double bond of the allylic group in 4 and to abstract hydrogen from PE, forming the corresponding macroradicals.<sup>31</sup> Then, the subsequent intermolecular combination of 4/PE and 4/4 radicals can lead to the grafting and to the crosslinking of 4. The grafting process was confirmed by ATR-IR spectroscopy, contact-angle measurements, and XPS measurements.

#### Surface characterization of grafted PE films

After treatment, the films were first studied by ATR-IR spectroscopy. The comparison between the spectrum of the original PE film and the one of a film treated with 4 showed in the latter weak bands at  $\nu = 1260, 1180, \text{ and } 950 \text{ cm}^{-1}$ , attributed to the stretching vibrations  $\nu \text{P}=\text{N}$ ,  $\nu (\text{P})-\text{O}-\text{C}$ , and  $\nu \text{P}-\text{O}-(\text{C})$ , respectively, characteristic of the substituted phosphazene ring (Fig. 2). This confirmed the occurrence of the grafting process.

The grafted PE films were also studied by contact-angle measurements with water. The results were  $\theta = 97^\circ$  for the uncoated and dried PE film and  $\theta = 102^\circ$  for the film treated with 4. For the uncoated PE film, already being hydrophobic, this change was not significant. The contact-angle values for films treated with 4 were around  $\pm 4^\circ$  across the PE film surface, suggesting a uniform grafting.

#### XPS characterizations

We successively studied the XPS spectra of the PE film, the polyurethane 4 obtained from an infinite overlayer cast from a solution of 30 g/L of 4 in DMSO, and the PE-grafted film. Moreover, to evaluate the

**TABLE II**  
XPS Data for Polymer 4

Element	Peak [binding energy ( $\pm 0.2 \text{ eV}$ )]	Ratio	Surface atomic stoichiometry of 4	Bulk atomic stoichiometry of 4
C(1s)	285.1	nO/nC	$27 \times 10^{-2}$	$21 \times 10^{-2}$
O(1s)	533.7	nN/nC	$11 \times 10^{-2}$	$12 \times 10^{-2}$
	532	nP/nC	$6.5 \times 10^{-2}$	$5.9 \times 10^{-2}$
N(1s)	401.6	nP/nN	0.59	0.47
	399.8			
	398.1			
P(2p)	134.4			

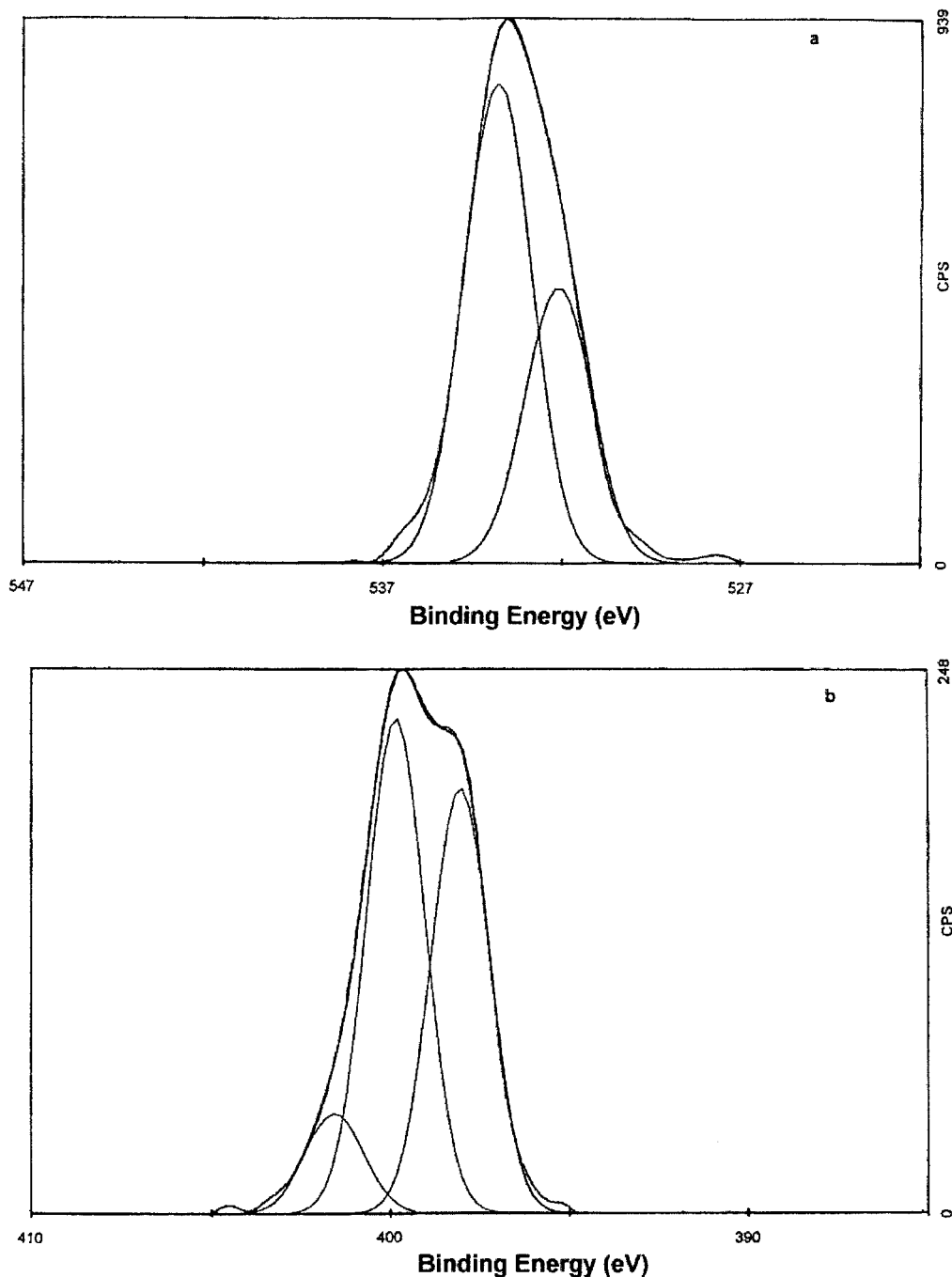


Figure 3 (a) O(1s) and (b) N(1s) XPS spectra of polymer 4.

influence of the allylic functions in the grafting process, the polymer 4' was synthesized according to the same procedure as described for 4.<sup>23</sup> The spectroscopic data for 4' were previously reported.<sup>23</sup> Its SEC molecular weight was  $\bar{M}_w = 21,400$  with a polydispersity index of 4.3.

#### PE and polyurethane 4 films

For the starting PE film, the spectrum contained the C(1s) photopeak at 285 eV.<sup>32</sup> The XPS data for 4 are

reported in Table II. The O(1s) photopeak [Fig. 3(a)] revealed two components: (1) 533.7 eV due to the C—O—P species and (2) 532 eV due to oxygen atoms in the carbonyl groups.<sup>3</sup> The N(1s) profile [Fig. 3(b)] presented three components: (1) 398.1 eV attributed to the —N=P—N= species in cyclotriphosphazene; (2) 399.8 eV due to the urethane groups; and (3) 401.6 eV due to the partially protonated nitrogen atoms.<sup>34,35</sup> The binding energy of the P(2p) level in the —P=N— species in cyclotriphosphazene was 134.4 eV.<sup>36</sup>



TABLE III  
XPS Data for Grafted PE Film

Element	Peak [binding energy ( $\pm 0.2$ eV)]	Ratio	Surface atomic stoichiometry of PE/4
C(1s)	285.4	nO/nC	$17.5 \times 10^{-2}$
O(1s)	532.8	nN/nC	$5 \times 10^{-2}$
N(1s)	401.7	nP/nC	$2 \times 10^{-2}$
	399.9	nP/nN	0.37
	398.3		
P(2p)	134.1		

The O and N surface atomic stoichiometries were close to the bulk atomic ones. Only a slight increase of P was observed in the superficial layers of **4**, leading to a ratio nP/nN which was slightly higher than that for the bulk one (Table II).

PE films treated with **4** and **4'**

The XPS data for the **4** grafted film (PE/4) from a solution 4-DMSO 30 g/L are given in Table III. The spectrum showed the P(2p) and N(1s) photopeaks, indicating the occurrence of the grafting process. Nevertheless, the surface atomic ratios nO/nC, nN/nC, nP/nC, and nP/nN of PE/4 were lower than were the same bulk atomic ratios of the polyurethane film **4**, suggesting a deposited layer thickness lower to the depth analyzed by XPS ( $\leq 100$  Å). The XPS spectra of PE films treated with **4'** in the same conditions were similar to those of the starting PE; they showed only the C(1s) photopeak at 285 eV and no P(2p) and N(1s) photopeaks were detected. These results clearly demonstrated that the grafting reaction was dependent on the allylic functions introduced in the cyclotriphosphazene.

## CONCLUSIONS

A new cyclotriphosphazene-containing polyurethane, carrying in its structure a few percentage of reactive allylic double bonds, was synthesized. The thermal behavior of this new hybrid organic-inorganic polymer was compared with the one of a similar free cyclotriphosphazene polymer synthesized from 1,3-bis(hydroxy)benzene and 1,6-hexamethylene diisocyanate. It was showed that the incorporation of the phosphazene cycle as pendant group increased the thermal properties of the polymer. The presence of the *o*-allylphenoxy groups and the use of benzoyl peroxyde as an initiator allowed this hybrid polymer to be grafted onto a PE film surface. Therefore, the functionalized cyclotriphosphazene acted as a coupling agent for the association PE-polyurethane. Given the large diversity of possible phosphorus-bonded substituents in cyclotriphosphazenes, this method should allow one to confer

very diverse properties (e.g., electrical conductivity, resistance to solvents and chemicals, and photoresistance) to the surface of many carbon-backed polymers.

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## References

- Swift, G.; Carraher, C. E.; Bowman, Jr., C. N. *Polymer Modification*; Plenum: New York, London, 1997.
- Chan, C. M. *Polymer Surface Modification and Characterization*; Carl Hanser Verlag: Munich, Vienna, New York, 1994.
- Allcock, H. R. *Phosphorus-Nitrogen Compounds. Cyclic Linear and High Polymers Systems*; Academic: New York, London, 1972.
- Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice-Hall: Englewood Cliffs, NJ, 1992.
- Allen, C. W. *Trends Polym Sci* 1992, 2, 342.
- De Jaeger, R.; Gleria, M. *Prog Polym Sci* 1998, 23, 179.
- Allen, C. W.; Ramachandran, K.; Brown, D. E. *Inorg Synth* 1989, 25, 74.
- Inoue, K.; Takagi, M.; Nakano, M.; Nakamura, H.; Tanigaki, T. *Makromol Chem-Rapid* 1988, 9, 345.
- Inoue, K.; Nakano, M.; Takagi, M.; Tanigaki, T. *Macromolecules* 1989, 22, 1530.
- Inoue, K.; Nakahara, H.; Tanigaki, T. *J Polym Sci Pol Chem* 1993, 31, 61.
- Inoue, K.; Nitta, H.; Tanigaki, T. *Makromol Chem-Rapid* 1990, 11, 467.
- Brown, D. E.; Allen, C. W. *J Inorg Organomet P* 1991, 1, 189.
- van de Grampel, J. C.; Alberda Van Ekenstein, G. O. R.; Bass, J.; Buwalda, P. L.; Jekel, A. P.; Oosting, G. E. *Phosph Sulfur Silicon* 1992, 64, 91.
- Allen, C. W.; Shaw, J. C.; Brown, D. E. *Macromolecules* 1988, 21, 2653.
- Dupont, J. G.; Allen, C. W. *Macromolecules* 1979, 12, 169.
- Allen, C. W.; Bright, R. P. *Macromolecules* 1986, 19, 571.
- Allen, C. W.; Shaw, J. C.; Brown, D. E. *Macromolecules* 1988, 21, 2653.
- Bosscher, G.; Meetsma, A.; van de Grampel, J. C. *J Chem Soc Dalton Trans* 1997, 1667.
- Bosscher, G.; Hagen, H.; Meetsma, A.; Jekel, A. P.; van de Grampel, J. C. *Phosphorus Sulfur* 1996, 67, 109.
- Bosscher, G.; van de Grampel, J. C. *J Inorg Organomet P* 1995, 5, 209.
- Bosscher, G.; Wieringa, R. H.; Jekel, A. P.; van de Grampel, J. C. *J Inorg Organomet P* 1996, 6, 255.

22. Kajiwara, M.; Saito, H. *J Macromol Sci Chem A* 1981, 16, 873.
23. Dez, I.; De Jaeger, R. *J Inorg Organomet P* 1996, 6, 111.
24. Dez, I.; De Jaeger, R. *Phosphorus Sulfur* 1997, 130, 1.
25. Dez, I.; Levallois-Mitjaville, J.; Grutzmacher, H.; Gramlich, V.; De Jaeger, R. *Eur J Inorg Chem* 1999, 1673.
26. Miyata, K.; Muraoka, K.; Itaya, T.; Tanigaki, T.; Inoue, K. *Eur Polym J* 1996, 32, 1257.
27. Chen-Yang, Y. M.; Chuang, Y. H. *Phosphorus Sulfur* 1993, 76, 261.
28. Spizzo, F. Thesis, University of Padova, Padova, 1992.
29. Medici, A.; Fantin, G.; Pedrini, P.; Gleria, M.; Minto, F. *Macromolecules* 1992, 25, 2569.
30. Thomas, L. C. *Interpretation of the Infrared Spectra of Organophosphorus Compounds*; Heyden: London, 1974.
31. Doyer, V. Thesis, Université des Sciences et Technologies de Lille, 1995.
32. Beamson, G.; Clark, D. T.; Kendrick, J.; Briggs, D. *J Electron Spectrosc* 1991, 57, 79.
33. Pemberton, L. Thesis, Université des Sciences et Technologies de Lille, 1996.
34. Dillingham, R. G.; Boerio, F. J. *J Adhesion* 1987, 24, 315.
35. Pemberton, L.; De Jaeger, R.; Gengembre, L. *Polymer* 1998, 39, 1299.
36. Fewell, L. L. *J Appl Polym Sci* 1990, 41, 391.