8262 *Macromolecules* **1997,** *30,* 8262−8269

Synthesis and Radical Polymerization of Methacrylate Monomers Containing Cyclotriphosphazene. Thin-Layer Grafts of Their Polymers on a Poly(vinyl alcohol) Surface

Isabelle Dez and Roger De Jaeger*

Laboratoire de Spectrochimie Infrarouge et Raman, CNRS UPR 2631L, Bât. C5,
Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France

Received May 20, 1997; Revised Manuscript Received October 15, 1997[⊗]

ABSTRACT: The reaction between the monohydroxylated cyclotriphosphazene (4-hydroxyphenoxy)pentaphenoxycyclotriphosphazene, **3**—obtained by the reaction of the (4-methoxyphenoxy)pentaphenoxycyclotriphosphazene **2** with BBr_3/H_2O—and methacryloyl chloride, led to a new methacrylate-substituted cyclotriphosphazene, **4**. Radical polymerization of **4** led to the hybrid inorganic−organic poly(cyclophosphazene−methacrylate) **5**. The structures of both classes of compounds were investigated by ^{31}P, ^{13}C, and ^{1}H NMR, infrared spectroscopy, mass spectrometry, size exclusion chromatography, and elemental analysis. The thermal behavior of the new polymer **5** was investigated and compared to the one of poly(phenyl methacrylate) **6**. It was demonstrated that the incorporation of cyclophosphazene as pendant group increases the thermal stability of the corresponding organic polymer. The free-radical promoted grafting of **5** onto poly(vinyl alcohol)surface has been described. The resultant surfaces were studied by ATR-IR, XPS, and contact angle techniques. It was demonstrated that the presence of ethyl functions in **5** increases the grafting yield.

Introduction

Superficial chemical and physical modifications of organic polymers without affecting bulk properties is a challenge which if successful, has far-reaching implications in fields such as adhesion, protective coatings, biomaterials, and so on. For example these modifications can transform an inexpensive material with excellent bulk properties into valuable products for the plastics industry.

These improvements in superficial properties can be obtained by grafting unusual polymers to the surface of conventional polymers.[1,2]

In this area the synthesis of organic carbon-backbone polymers containing pendant side cyclophosphazene moieties is of great interest. Indeed, the extreme reactivity of chlorine atoms in chlorocyclophosphazene precursors toward nucleophiles (e.g. alcohols or amines)[3,4] can be used to introduce a number of functional groups in these polymers.

They are generally obtained from cyclophosphazenes containing a polymerizable group (e.g. vinyl, acrylic, or methacrylic) linked to phosphorus by P−O[5−12] or P−C[13−19] bonds.

Examples are found with homopolymerization, or copolymerization with methylmethacrylate, of (methacryloylethenedioxy)pentachlorocyclotriphosphazene[10] or *gem*-methyl(vinylbenzyl)tetrachlorocyclotriphosphazene.[18]

In a second approach, the cyclophosphazene group can be introduced in the organic polymer, by reaction between two bifunctional molecules. An example is given with the synthesis of cyclophosphazene-substituted polyurethanes from a dihydroxylated cyclotriphosphazene and a diisocyanate.[20]

In this article, we describe the synthesis and the characterization of the interesting monomer mono(4-methacryloyloxyphenoxy)pentakis(4-ethylphenoxy) cyclotriphosphazene, its radical polymerization, and the thermal properties of the corresponding polymer. Furthermore, the grafting of the new cyclophosphazene substituted polymethacrylate onto the surface of poly(vinyl alcohol) (PVA) films is studied.

Results and Discussion

Synthesis and Characterization of the Methacrylate-Substituted Cyclotriphosphazene. The synthetic route to the new methacrylate monomer, mono(4-(methacryloyloxy)phenoxy) penta(4-ethylphenoxy)cyclotriphosphazene, **4**, used as precursor for polymers was shown in Scheme 1.

Cyclotriphosphazenes **1**−**4** were synthesized according to the following method.

The chloropentakis(4-ethylphenoxy) derivative, **1**, was obtained by the interaction of hexachlorocyclotriphosphazene with 4-ethylphenol (5 equiv) in the presence of NaH in tetrahydrofuran according to the procedure described by Spizo et al. for $N_3P_3(OC_6H_5)_5Cl$.[21]

For the synthesis of the (4-methoxyphenoxy)pentakis(4-ethylphenoxy) derivative **2**, the procedure was similar but involved the treatment of **1** with 1 equiv of 4-methoxyphenol. In **2,** the hydroxyl function is blocked by the methyl residue. This group was then removed according to Gleria et al.,[22] by a deprotecting reaction with an excess of boron tribromide followed by the hydrolysis of the complex formed between BBr_3 and the oxygen of the methoxy group [23] to yield **3**.

Finally, the introduction in **3** of the methacrylate moiety was performed by esterification of the hydroxyl function with methacryloyl chloride giving **4**.[24]

Compounds **1**−**4** were characterized by NMR (^{31}P, ^{1}H, ^{13}C), infrared spectroscopy, mass spectrometry, and elemental analysis. The corresponding data are reported in Table 1.

The formation of **2** from **1** was confirmed in ^{31}P NMR by the complete disappearance of signals at $\delta = 7.3$ ppm (d) and $\delta = 22.47$ (t) representative in **1** of the $P(OAr)_2$ and PCl(OAr) groups, respectively, and the appearance of a singlet at $\delta = 9.49$ ppm attributable to the $P(OAr)_2$

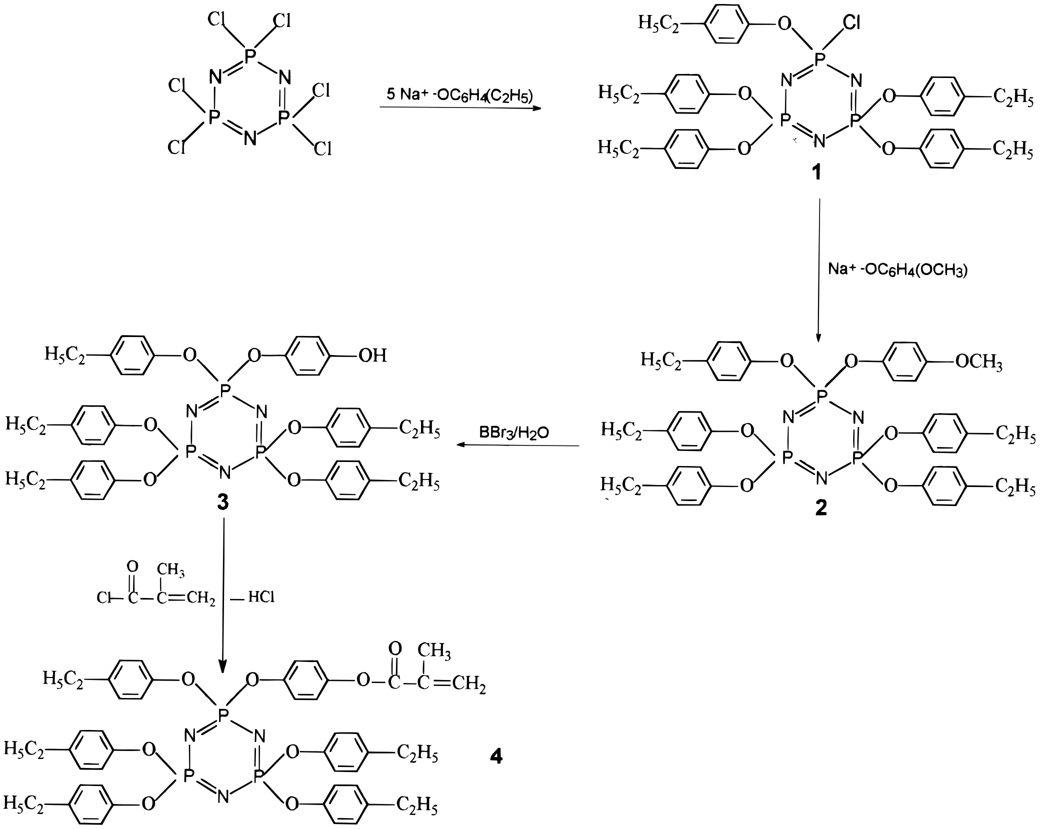
---

* Author to whom all correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1997.

S0024-9297(97)00704-3 CCC: $14.00

Scheme 1. Synthesis of the Methacrylate Precursor 4



groups in **2**. This result is in accordance with a complete substitution of the residual chlorine in **1**. The ^{31}P NMR spectra of **2**, **3** and **4** were similar.

^{1}H NMR spectra of **1**–**4** are represented in Figure 1. The conversion **1** → **4** was characterized by - the appearance of a signal at $\delta = 3.8$ ppm (s, $OC\mathbf{H}_3$) for **2**, its disappearance for the benefit of a signal at $\delta = 4.76$ ppm (s, O**H**) in **3**, and finally the appearance of the signals at $\delta = 2.01$ ppm (s, $H_2C{=}C(C\mathbf{H}_3)-$), $\delta = 5.75$ ppm (s, $(\mathbf{H}_a, H_b)C{=}C(CH_3)-$), and $\delta = 6.33$ ppm (s, $(H_a, \mathbf{H}_b)C{=}C(CH_3)-$) for **4**.

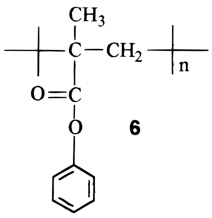
The relative intensities of these signals are in accordance with the molecular structures of **2**–**4**.

The IR spectrum of **3** (Figure 2) showed the broad band characteristic of the OH stretching vibration near $\nu = 3250$ cm^{-1}, which disappeared in the conversion of **3** → **4**. The presence of the methacrylic group in **4** was characterized by the absorption band at $\nu = 1738$ cm^{-1} representative of the carbonyl stretching vibration.

In these reactions, the phosphazene ring was preserved as demonstrated by the presence in the infrared spectra of the bands located around $\nu = 1260$ cm^{-1} ascribed to the ring vibration, at 1180 and 950 cm^{-1} representative of the C–O– and P–O– stretching vibrations in the P–O–C aromatic bonds, respectively.[25]

Polymerization of the Methacrylate Derivative 4: Characterization of the Corresponding Polymer. The second part of the work is related to the synthesis of the new polymethacrylate **5** containing cyclophosphazene as pendant group. It was obtained by radical polymerization of **4** in THF with the use of azobis(isobutyronitrile), AIBN, as initiator according to the procedure described by Inoue et al. [24] (Scheme 2).

5 was characterized by ^{31}P and ^{1}H NMR and IR spectroscopy. The spectral data were compared with those obtained for poly(phenyl methacrylate), **6**, synthesized from the radical polymerization of phenyl methacrylate (Table 2).



6

Just like for **4**, polymer **5** showed in ^{31}P NMR a single signal at $\delta = 9.30$ ppm indicating the equivalence of the phosphorus atoms and consequently the preservation of the phosphazene ring.

^{1}H NMR spectra confirmed the conversion **4** → **5.** Indeed they were characterized—first by the disappearence of the two signals corresponding to the ethylenic protons and second by the substitution of the signals representative in **4** of the methyl and methylene protons in methacrylic and ethyl groups, respectively, by two multiplets centered about $\delta = 1.1$ ppm ($C\mathbf{H}_3$) and $\delta = 2.5$ ppm ($C\mathbf{H}_2$) with relative intensities in a ratio 18:12.

The infrared spectrum of **5** differed from that of **6** principally by the presence of the band at $\nu = 952$ cm^{-1} characteristic of the P–O– stretching vibration of the P–O–C (aromatic) bond. The carbonyl stretching vibration was noted at $\nu = 1751$ cm^{-1} in **5** and **6** against $\nu = 1738$ cm^{-1} for the precursor **4** (Figure 2).

The molecular weights of polymers **5** and **6** determined by size exclusion chromatography (SEC) were $\bar{M}_w = 31\,000$ with a molecular weight distribution $\bar{M}_w/\bar{M}_n = 2$ for **5** and $\bar{M}_w = 159\,000$ with $\bar{M}_w/\bar{M}_n = 7.5$ for **6**.

The thermal stability and degradation behavior of **5-6** were investigated by thermogravimetric analysis in air.

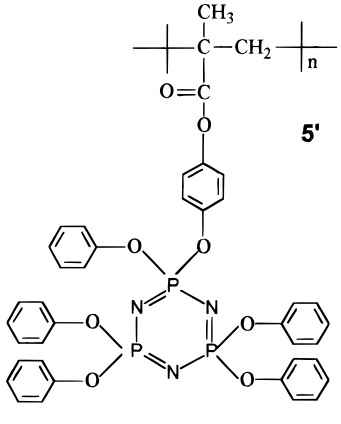
Table 1. Spectroscopic Data for Compounds 1–4 and 4′

compd	δ ppm			IR frequency (cm^{-1})
	^{31}P NMR	^{1}H NMR	^{13}C NMR	
1	22.47 (t) 7.3 (d) [J = 82.5 Hz]	1.2 (t, 15H, CH_3)) 2.6 (q, 10H, CH_2) 6.8–7.1 (m, 20H, aromatic)	15.6 (s, CH_3) 28.2 (s, CH_2) 121 (m, aromatic) 128.7 (m, aromatic) 141 (m, aromatic) 149 (m, aromatic)	1179 (ν(P–O–Ar)) 951 1268 (ν(P=N))
2	9.49	1.24 (t, 15H, CH_3) 2.67 (q, 10H, CH_2) 3.8 (s, 3H, CH_3) 6.69–7.06 (m, 24H, aromatic)	15.6 (s, CH_3) 28.2 (s, CH_2) 55.5 (s, CH_3) 114.2 (s, aromatic) 120.9 (s, aromatic) 122 (s, aromatic) 128.6 (s, aromatic) 140.5 (s, aromatic) 145 (s, aromatic) 148.7 (m, aromatic) 157 (m, aromatic)	1176 (ν(P–O–Ar)) 951 1264 (ν(P=N)) 2833 (ν(C–H) (OCH_3))
3	9.29	1.20 (t, 15H, CH_3) 2.57 (q, 10H, CH_2) 4.76 (s, 1H, OH) 6.55–6.75 (m, 4H, aromatic) 6.8–7.05 (m, 20H, aromatic)	15.6 (s, CH_3) 28.2 (s, CH_2) 114.1 (m, aromatic) 120.8 (m, aromatic) 122 (m, aromatic) 128.5 (m, aromatic) 140.6 (m, aromatic) 146 (m, aromatic) 148.6 (m, aromatic) 156 (m, aromatic)	1180 (ν(P–O–Ar)) 954 1267 (ν(P=N)) 3238 (ν(O–H))
4	9.33	1.23 (t, 15H, CH_3) 2.01 (s, 3H, CH_3) 2.56 (q, 10H, CH_2) 5.75 (s, 1H, CH_2) 6.33 (s, 1H, CH_2) 6.80–7.05 (m, 24H, aromatic)	15.6 (s, CH_3) 18.4 (s, CH_3) 28.2 (s, CH_2) 100.3 (s, allylic) 114.2 (m, aromatic) 120.9 (m, aromatic) 121.8 (m, aromatic) 122.2 (m, aromatic) 127.2 (m, allylic) 128.6 (m, aromatic) 140.5 (m, aromatic) 148.6 (m, aromatic)	1180 (ν(P–O–Ar)) 953 1267 (ν(P=N)) 1738 (ν(C=O))
4′	8.98	2.1 (s, 3H, CH_3) 5.75 (s, 1H, CH_2) 6.35 (s, 1H, CH_2) 6.85–7.00 (m, 10H, aromatic) 7.1–7.25 (m, 15H, aromatic)	19 (s, CH_3) 103 (s, allylic) 121.1 (s, aromatic) 121.8 (s, aromatic) 122.3 (s, aromatic) 124.9 (s, aromatic) 127 (m, allylic) 129.4 (m, aromatic) 135 (m, aromatic) 152 (s, aromatic)	1175 (ν(P–O–Ar)) 948 1267 (ν(P=N)) 1736 (ν(C=O))

The corresponding TGA curves are reported in Figure 3. In the case of **5**, weight loss mainly occured in the range 360–500 °C, vs 260–430 °C in that of **6**. The temperatures required for 10% weight loss were 270 (**6**) and 395 °C (**5**).

It was also a noteworthy feature that **5** retains 43% of its original weight at 500 °C, contrary to the complete decomposition of **6** at the same temperature. These results clearly show that the incorporation in an organic polymer of the cyclotriphosphazene as pendant group clearly increases its thermal stability reflecting the flame retardant properties of cyclophosphazenes.[13,19,24]

Grafting of 5 onto a Poly(vinyl alcohol) Film Surface—Proposed Mechanism. PVA films were dip-coated with a xylenic solution of **5** containing benzoyl peroxide as a radical initiator. After a few hours, the coated films were heated at 135 °C. The grafted films were then washed with xylene to remove the ungrafted polymer and finally dried. To evaluate the influence of the ethyl functions in the grafting process, polymer **5′** was synthesized according to the procedure described for **5**. The corresponding spectroscopic data as well as those of the intermediate derivative (4-methacryloyloxyphenoxy)pentaphenoxycyclotriphosphazene, **4′**, were reported in Tables 1 and 2.



5'

During the thermal treatment of the PVA/**5**/peroxide system, two processes are supposed to take place: a covalent grafting of **5** onto the PVA film surface and its

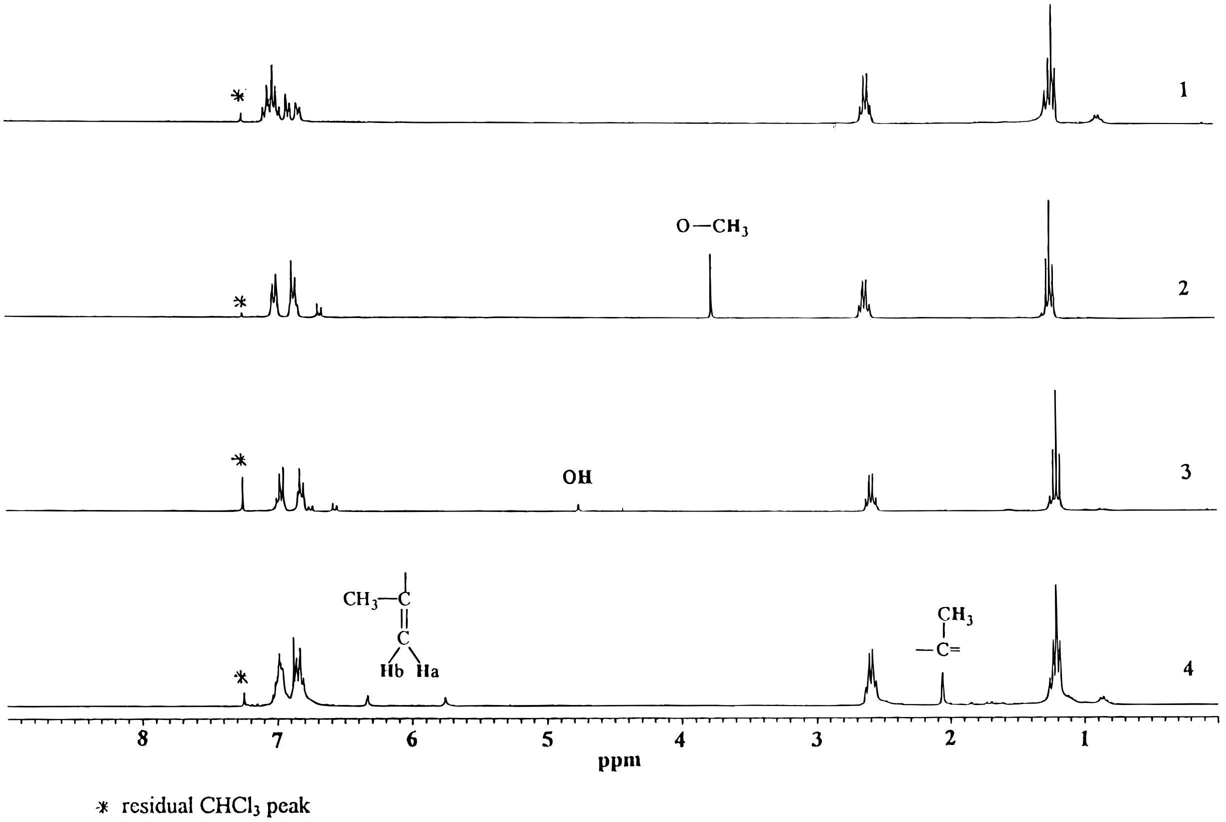


Figure 1. ^{1}H NMR spectra of compounds **1**–**4**.

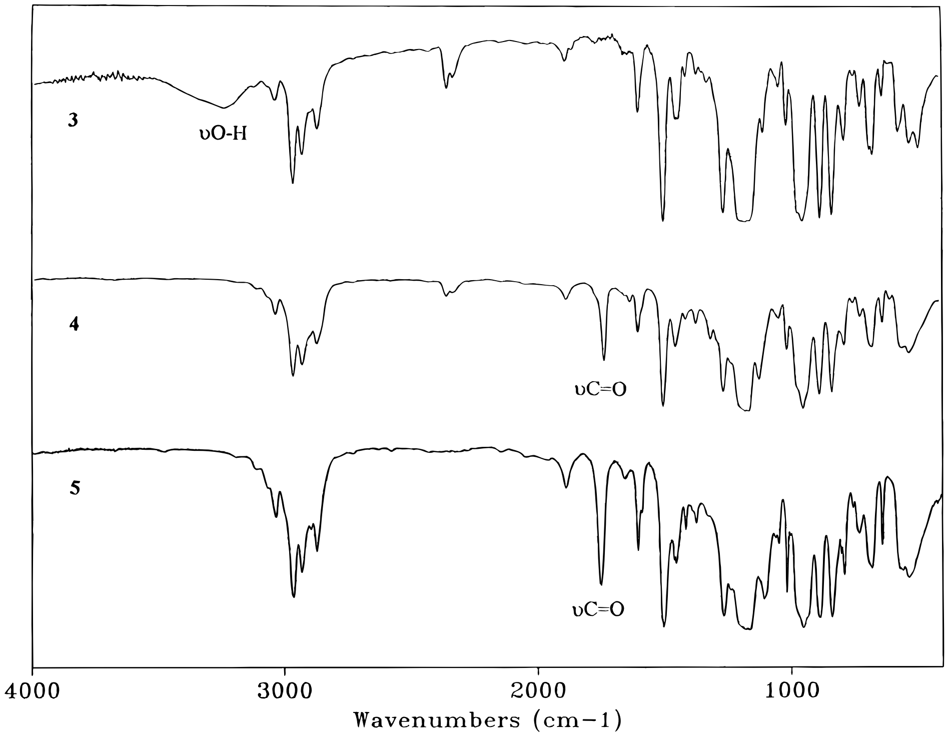


Figure 2. Infrared spectra of **3** and **4** and of polymer **5**.

cross-linking reaction according to the mechanism represented in Scheme 3. The mechanism implies first the thermal cleavage of the peroxide molecules to form free radicals able to abstract hydrogens from **5** and PVA forming the corresponding macroradicals. Then, the subsequent intermolecular combination of **5**/PVA and **5**/**5** radicals can lead to the grafting and to the cross-linking of **5**. According to the works of Schechter et al.[26] and Gleria et al.[27] the grafting site for **5** must be very likely the secondary hydrogen of the ethyl groups in the 4-ethylphenoxy substituants. Thus, the probability for **5** being grafted onto PVA is greater than for a polymer lacking ethyl groups like **5′**.

Surface Characterization of Grafted PVA Films. After treatment, the films were first studied by ATR-IR spectroscopy. The comparison between spectra of the original PVA film and those of films simultaneously treated with **5** and **5′** solutions at the same concentra-

Scheme 2. Synthesis of the Polymethacrylate 5

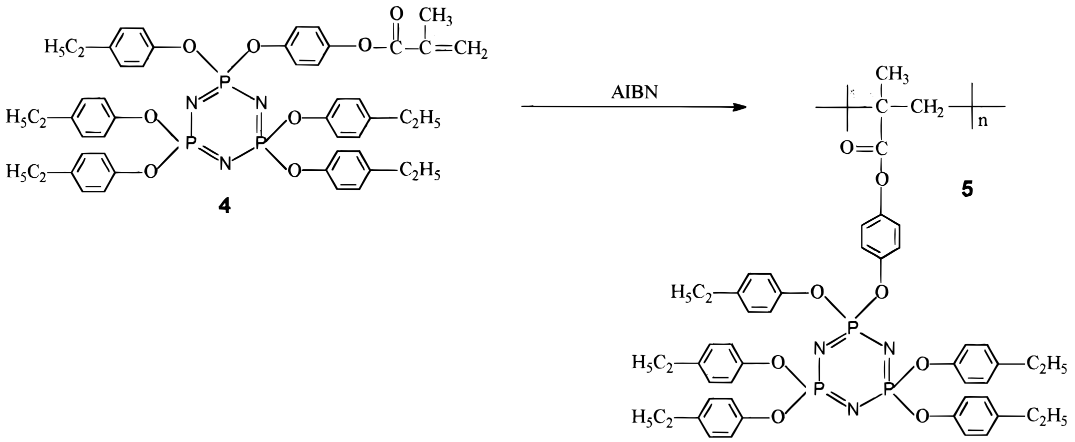


Table 2. Spectroscopic Data for Polymers 5, 6, and 5′

compd	δ ppm ^{31}P NMR	 ^{1}H NMR	IR frequency (cm^{-1})
5	9.30	0.9–1.3 (m, 18H, CH_3) 2.3–2.6 (m, 12H, CH_2) 6.5–7.2 (m, 24H, aromatic)	1180 (ν(P–O–Ar)) 952 1267 (ν(P=N)) 1751 (ν(C=O))
5′	9.00	1.2–1.8 (m, 5H, CH_2–CH_3) 6.6–7.2 (m, 29H, aromatic)	1177 (ν(P–O–Ar)) 950 1266 (ν(P=N)) 1752 (ν(C=O))
6		1.3–1.7 (m, 3H, CH_3) 2.2–2.6 (m, 2H, CH_2) 6.0–7.4 (m, 5H, aromatic)	2870 (ν(C–H) (CH_3)) 2980 2870 (ν(CH) (CH_2)) 2930 1752 (ν(C=O))

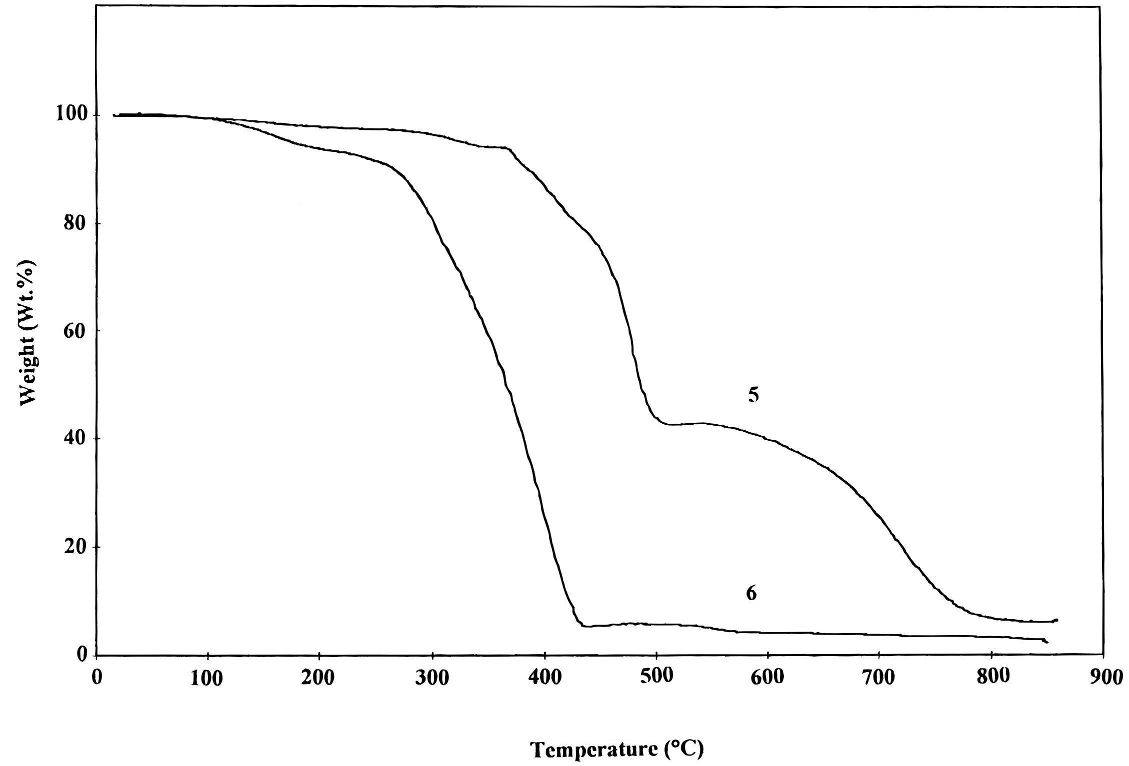


Figure 3. Thermogravimetry of **5** and **6** conducted at a heating rate of 8 °C/min in an air atmosphere.

tion are given in Figure 4. Two factors were revealed: first, the spectra of **5′** coated and thermally treated films were similar to those of the starting PVA. That suggests that only very little grafting or adsorption of **5′** on PVA surface occurs. Second, the bands characteristic of the substituted phosphazene ring appeared in the spectrum of a film treated with **5**. That confirms in this case the occurrence of the grafting process. The grafting was also proved by the result obtained by weighing the films before and after treatment: The grafting yield, nonmeasurable in the case of **5′**, was 7.4% in the case of **5**.

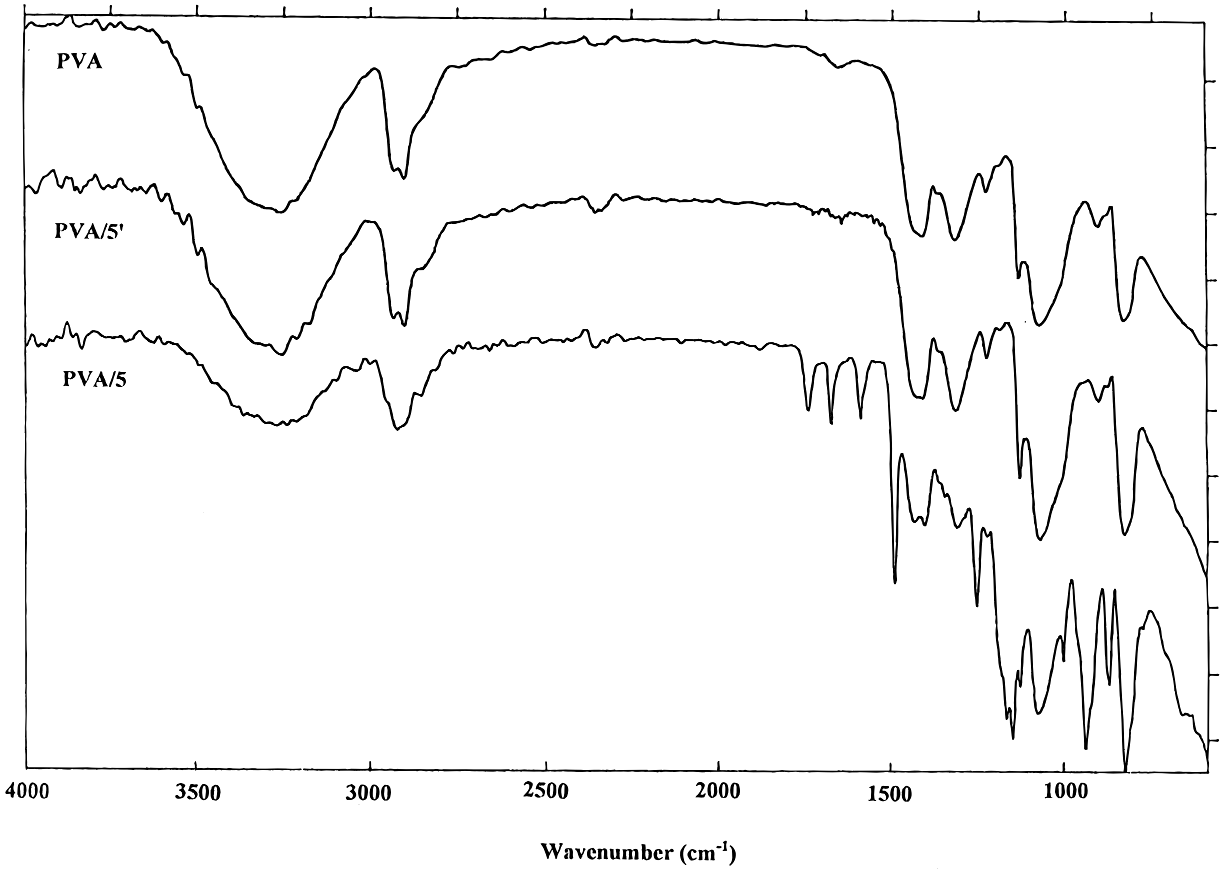
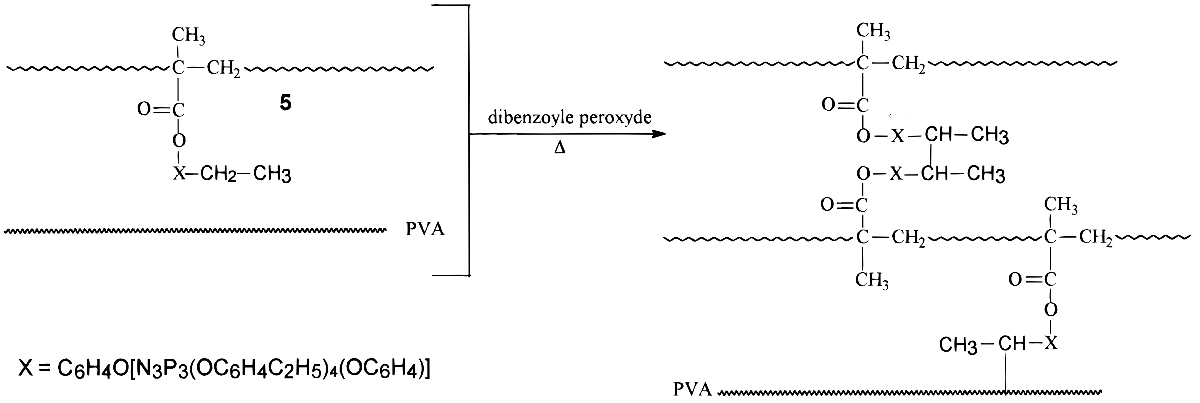


Figure 4. ATR-IR spectra of original PVA film and films treated with **5** and **5′**.

Scheme 3. Supposed Mechanism for the Grafting of Polymer 5 onto the PVA Film Surface



X = $C_6H_4O[N_3P_3(OC_6H_4C_2H_5)_4(OC_6H_4)]$

Contact Angle Measurements. The previous films were also studied by water contact angle measurements. The results showed a noticeable increase of the contact angle from $\theta = 44°$ for the uncoated and dried PVA film, to $\theta = 96°$ for the film treated with **5**. That increase was less important in the case of films treated with **5′** (from $\theta = 44°$ to $\theta = 79°$). In the two cases, the contact angles were around ±3° across the PVA film surface, suggesting an uniform grafting of **5** and **5′**.

As mentioned previously, IR spectroscopy did not allow the grafting of **5′** to be detected. This observation is apparently in accordance with the lack of ethyl functions in the polymers **5′**. However the contact angle variation proved a PVA surface modification. The heteroatoms N and P were usable as probes to check the effectiveness of the coating; therefore, PVA films treated with **5** and **5′** solutions at the same concentration (50 g/L) were studied by XPS analysis.

X-ray Photoelectron Spectroscopy. The XPS data for the PVA polymer before grafting and after treatment with **5** and **5′** are reported in Table 3.

For the starting PVA film, the relative intensities of the two photopeaks C(1s) at 285 eV ($-CH_2-$) and 286.5 eV ($-CHOH-$) and the nO/nC surface atomic ratio are close to the theoretical values for the (CH_2-CHOH) unit.[28,29] The spectra of samples of PVA coated and thermally treated contained new P(2p) and N(1s) photopeaks at 134.3 and 398.2 eV, respectively, which were not present in the spectrum of the starting polymer. The spectrum of a film treated with **5** is reported in Figure 5. These new P(2p) and N(1s) peaks correspond to the phosphazene ring in **5** and **5′**. Indeed, the nP/nC and nN/nC surface atomic ratios are, respectively, 6.6×10^{-2} and 6.1×10^{-2} for **5** and 7.2×10^{-2} and 6.7×10^{-2} for **5′** and lead to $nP/nN = 1.08$ and 1.07, which are slightly higher values than the bulk ones.

Table 3. XPS Data for Ungrafted and Grafted PVA Films

	peak				surface atomic stoichiometry			bulk atomic stoichiometry	
	PVA BE (±0.2 eV)	PVA/5 BE (±0.2 eV)	PVA/5′ BE (±0.2 eV)		PVA	PVA/5	PVA/5′	5	5′
C(1s)	285 286.5	285	285	nO/nC	49×10^{-2}	18.6×10^{-2}	22.9×10^{-2}	16.4×10^{-2}	19.4×10^{-2}
O(1s)	532.8	533.6	533.6	nN/nC		6.1×10^{-2}	6.7×10^{-2}	6.0×10^{-2}	7.2×10^{-2}
N(1s)		398.2	398.3	nP/nC		6.6×10^{-2}	7.2×10^{-2}	5.96×10^{-2}	7.15×10^{-2}
P(2p)		134.3	134.2	nP/nN		1.08	1.07	0.99	0.99

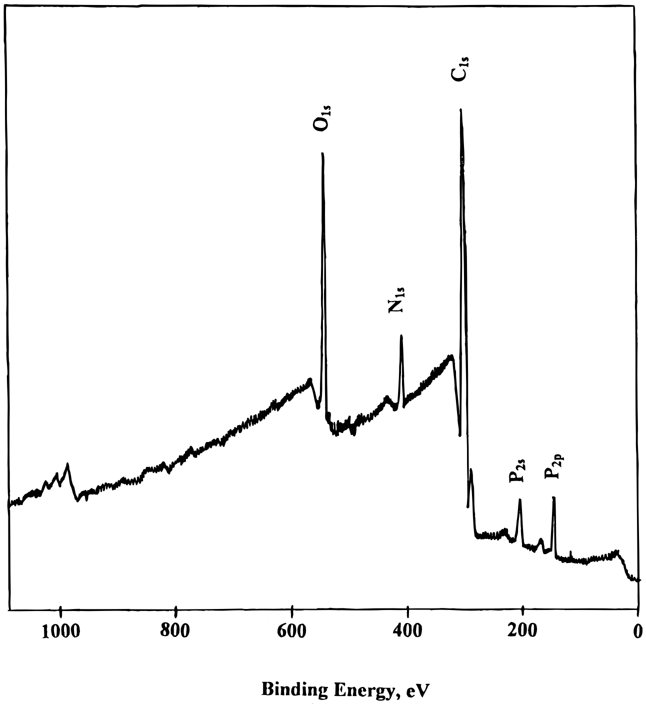


Figure 5. XPS spectrum of PVA film treated with **5**.

In the two cases, also, the surface and bulk atomic ratio are quite similar, suggesting even for **5′** a deposited layer thickness at least equal to the depth analyzed by XPS.

Nevertheless, the results obtained in IR spectrometry and contact angle measurements were in accordance with the greater probability for polymer **5,** which has more methylene groups, to be grafted and cross-linked than polymer **5′**.

Experimental Section

Equipment. ^{31}P, ^{1}H, and ^{13}C NMR spectra were recorded in $CDCl_3$ for compounds **1**−**6** and **4′** and **5′** using a Bruker WP 300 NMR spectrometer. Chemical shifts (ppm) are positive in the low-field direction and are relative to external 85% H_3PO_4 (^{31}P) or external TMS (^{1}H, ^{13}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 by means of size exclusion chromatography on a Waters Millipore apparatus equipped with Shodex columns using THF as eluant. The calibration curve was established using polystyrene standards. Mass spectra were recorded with a vision 2000 MALDI-TOF apparatus Finnigan Mat (Bremen, Germany), in reflection mode, with an N_2 laser, 337 nm, and matrix 2.5 DHB (dihydroxybenzoic acid), 10 mg/mL (MeOH/H_2O). Thermogravimetry measurements were performed in air on a Setaram NTB10-8 instrument at a heating rate of 8 °C/min. Elemental analysis were carried out at the Service Central d'Analyse CNRS, Vernaison, France.

Contact angle measurements were made using a Kruss contact-angle goniometer at ambient humidity and temperature. All reported values were the average of at least 10 measurements taken at different locations on the films surface.

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 a LHS 10 system (Leybold AG). The X-ray source was operated at 13 kV, 10 mA using Al Kα radiation (1486.6 eV). Binding energy calibration was based on Au $4f_{7/2}$ at 84 eV, Ag $3d_{5/2}$ at 368.2 eV, Cu $2p_{3/2}$ at 932.7 eV, and C1s ($-CH_2$-like species) at 285 eV. The analyzer was operated in the FRR mode (fixed retarding ratio). The vacuum was in the 10^{-8} mbar range.

Materials. Poly(vinyl alcohol) (PVA) films manufactured by Nippon Gohsei Film Co. Limited (Japan) under the trademark Bovlon were supplied by the Castel Fils Society (France). The melting point was 227 °C and the heat resistance 220 °C. They were characterized by infrared spectroscopy (ATR). Absorbance bands (cm^{-1}) are as follows: 3292, ν(O−H); 2938, 2905, ν(C−H); 1450, δ(C−H + O−H); 1419, $\delta(CH_2)$; 1373, $\gamma_\omega(CH_2)$; 1321, δ(C−H + O−H); 1235, γ_ω(C−H); 1142, ν(C−O + C−C); 1085, ν(C−OH) + δ(O−H); 913, $\gamma_r(CH_2)$; 844, ν(C−C). The films of 14 mm thickness were cut to 2 × 4.5 cm size. Just before use, they were dried at 100 °C for 3 h.

Tetrahydrofuran (THF), dichloromethane (DCM), and xylene obtained from SDS (Solvants Documentation Synthesis, France), were purified by distillation and dried over molecular sieves. Sodium hydride (80%), 4-ethylphenol, 4-methoxyphenol, phenol, boron tribromide, methacryloyl chloride, and triethylamine were Aldrich products and used as received except for the triethylamine, which was distilled from KOH. Azobis(isobutyronitrile) (AIBN), benzoyl peroxyde, and anhydrous sodium sulfate were obtained from Fluka and used as received. Hexachlorocyclotriphosphazene $N_3P_3Cl_6$ (Nippon Soda) was purified by vacuum sublimation. All reactions and manipulations were carried out under inert atmosphere.

Synthesis of Chloropenta(4-ethylphenoxy)cyclotriphosphazene (1). In a typical reaction, a solution of 4-ethylphenol (18.60g, 152.3mmol) in THF was added dropwise into a three-necked round-bottom flask cooled at −10 °C containing $N_3P_3Cl_6$ (10.6 g, 30.46 mmol) and NaH in excess (4.53 g, 188.8 mmol) in THF. After completion of the addition, the mixture was stirred at room temperature for 20 h. A ^{31}P NMR spectrum of the solution at this stage generally shows the existence of two side products: the dichlorotetrakis(4-ethylphenoxy)- and hexakis(4-ethylphenoxy)cyclotriphosphazenes. The first was eliminated by repeating the reaction after addition of a calculated amount (from the ^{31}P NMR spectrum) of 4-ethylphenol. 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. Hexakis(4-ethylphenoxy)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 vacuum. **1** was obtained as a clear oily solid. Yield: 70% (16.53g). NMR and infrared characterization data are reported in Table 1. Anal. Calcd for $C_{40}H_{45}N_3O_5P_3Cl$ (**1**): C, 61.89; H, 5.80; N, 5.41; O, 10.31; P, 11.99; Cl, 4.58. Found: C, 62.03; H, 5.94; N, 5.35; O, 10.41; P, 11.82; Cl, 4.35. Mass spectrum: calcd, $m/e = 775$; found, $m/e = 776$ (MH^+).

Synthesis of (4-Methoxyphenoxy)pentakis(4-ethylphenoxy)cyclotriphosphazene (2). A solution of 4-methoxyphenol (1.54 g, 12.5 mmol) in THF was added dropwise to a solution of **1** (9.67 g, 12.5 mmol) with an excess of NaH (14 mmol, 0.34 g) in THF. The mixture was heated to 70 °C for

24 h and then cooled at room temperature and ultracentrifuged (3000 rpm) to separate the solid from the liquid. The THF was removed under reduced pressure. The residue was dissolved in DCM, extracted with 10% aqueous NaOH (two times), washed with water (three times), and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, we obtained **2** as a yellowish oil. Yield: 72% (7.75 g). NMR and infrared characterization data are reported in Table 1. Anal. Calcd for $C_{47}H_{52}N_3O_7P_3$ (**2**): C, 65.3; H, 6.0; N, 4.9; O, 13.0; P, 10.8. Found: C, 65.6; H, 6.2; N, 4.8; O, 12.5; P, 10.6. Mass spectrum: calcd, $m/e = 863$; found, $m/e = 864$ (MH^+).

Synthesis of (4-Hydroxyphenoxy)pentakis(4-ethylphenoxy)cyclotriphosphazene (3). A solution of 7.8 g (9.0 mmol) of boron tribromide in anhydrous DCM (30 mL) was treated dropwise with a solution of 7.75 g (9.0 mmol) of **2** in anhydrous DCM (50 mL). The reaction mixture was stirred at room temperature for 3 h and then poured into 50 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: 70% (5.3 g). NMR and infrared characterization data are reported in Table 1. Anal. Calcd for $C_{46}H_{50}N_3O_7P_3$ (**3**): C, 65.0; H, 5.9; N, 4.9; O, 13.2; P, 10.9. Found: C, 64.4; H, 6.0; N, 4.7; O, 12.7; P, 10.2. Mass spectrum: calcd, $m/e = 849$; found, $m/e = 850$ (MH^+).

Synthesis of (4-(Methacryloyloxy)phenoxy)pentakis(4-ethylphenoxy)cyclotriphosphazene (4). A solution of methacryloyl chloride (0.65 g, 6.3 mmol) in THF was added dropwise to a solution of **3** (5.3 g, 6.3 mmol) and triethylamine (0.63 g, 6.3 mmol) in THF. After the reaction was stirred for 5 h, the resulting amine hydrochloride was removed by filtration, and the solvent was removed under reduced pressure. The residue was dissolved in DCM, washed with water (three times), and dried over molecular sieves (4 Å). After removal of the solvent under reduced pressure, **4** was obtained as a brown viscous oil. Yield: 95% (5.48 g). NMR and infrared characterization data are reported in Table 1. Anal. Calcd for $C_{50}H_{54}N_3O_8P_3$ (**4**): C, 65.5; H, 5.9; N, 4.6; O, 14.0; P, 10.1. Found: C, 65.9; H, 6.5; N, 4.5; O, 13.0; P, 9.7. Mass spectrum: calcd, $m/e = 917$; found, $m/e = 918$ (MH^+).

Synthesis of (4-(Methacryloyloxy)phenoxy)pentakis(phenoxy)cyclotriphosphazene (4′). **4′** was synthesized according to the procedure described for **4**. The starting product in this case was chloropentakis(phenoxy)cyclotriphosphazene. NMR and infrared characterization data are reported in Table 1. Anal. Calcd for $C_{40}H_{34}N_3O_8P_3$ (**4′**): C, 61.8; H, 4.4; N, 5.4; O, 16.5; P, 12.0. Found: C, 61.0; H, 4.4; N, 5.0; O, 16.0; P, 11.1. Mass spectrum: calcd, $m/e = 777$; found, $m/e = 778$ (MH^+).

Synthesis of Polymer 5. Weighed amounts of **4**, AIBN, and THF were charged into polymerization tubes and the tubes were degazed and sealed. The polymerization was carried out by shaking the tube in a thermostat maintained at 70 °C. After 3 h, the tube was opened and the reaction mixture was poured into hexane. The polymer was purified by repeated precipitation from THF into hexane, ultracentrifuged (3000 rpm) and dried in vacuo at 60 °C (yield: 55%). NMR and infrared characterization data are reported in Table 2. Anal. Calcd for $[C_{50}H_{54}N_3O_8P_3]_n$ (**5**): C, 65.5; H, 5.9; N, 4.6; O, 14.0; P, 10.1. Found: C, 65.5; H, 6.1; N, 4.5; O, 14.2; P, 9.8. Molecular weight (GPC): $\bar{M}_w = 3.1 \times 10^4$; $\bar{M}_w/\bar{M}_n = 2$.

Synthesis of Polymer 6. The procedure followed was the same as for **5** using phenyl methacrylate (obtained from phenol and methacryloyl chloride) instead of **4**. NMR and infrared characterization data are reported in Table 2. Anal. Calcd for $[C_{10}H_{10}O_2]_n$ (**6**): C, 72.3; H, 6.2; O, 19.8. Found: C, 72.1; H, 6.3; O, 19.5. Molecular weight (GPC): $\bar{M}_w = 15.9 \times 10^4$; $\bar{M}_w/\bar{M}_n = 7.5$.

Synthesis of Polymer 5′. The procedure was the same as that for **5**, using **4′** instead of **4**. Anal. Calcd for $[C_{40}H_{34}N_3O_8P_3]_n$ (**5′**): C, 61.8; H, 4.4; N, 5.4; O, 16.5; P, 12.0. Found: C, 61.8; H, 4.4; N, 5.2; O, 16.0; P, 11.4. Molecular weight (GPC): $\bar{M}_w = 8.4 \times 10^4$; $\bar{M}_w/\bar{M}_n = 8$.

Grafting Procedure. After being dried, the film samples were immersed and shaken in xylenic **5** or **5′** solutions, with a concentration of 50 g/L in the presence of benzoyle peroxide at room temperature for 15 h. The percentage of benzoyle peroxide used was 3% w/w in comparison with that of **5** or **5′**. The films were treated at 135 °C for 7 h. and then soaked and shaken in xylene for 20h to remove excess of initiator and ungrafted polymers. Finally, after the films were dried at 110 °C for 2 h, film surfaces analyses were carried out. The grafting yield was given by:

$$G\% = ((W(\text{grafted film}) - W(\text{initial film}))/W(\text{initial film})) \times 100$$

Acknowledgment. We thank Dr. L. Gengembre (Laboratoire de catalyse hétérogène et homogène, CNRS URA 402, Université des Sciences et Technologies de Lille Bât. C3, 59655 Villeneuve d'Ascq, France) for helpful discussions and his assistance in performing the XPS experiments.

References and Notes

(1) Pemberton, L.; De Jaeger, R. *Chem. Mater.* **1996**, *8*, 1391.
(2) Allcock, H. R.; Fitzpatrick, R. J.; Visscher, K. *Chem. Mater.* **1992**, *4*, 776.
(3) Allen, C. W. *The Chemistry of Inorganic Homo and Heterocycles;* Haiduc, I., Sowerby, D. B., Eds; Academic Press: New York, 1987, Vol. 2, p 501.
(4) Allen, C. W. *Chem. Rev.* **1991**, *91*, 119.
(5) Allen, C. W.; Ramachandran, K.; Brown D. E. *Inorg. Synth* **1989**, *25*, 74.
(6) Inoue, K.; Takagi, M.; Nakano, M.; Nakamura, H.; Tanigaki, T. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 345.
(7) Inoue, K.; Nakano, M.; Takagi, M.; Tanigaki, T. *Macromolecules* **1989**, *22*, 1530.
(8) Inoue, K.; Nakahara, H.; Tanigaki, T. *J. Polym Sci., Part A: Polym. Chem.* **1993**, *31*, 61.
(9) Inoue, K.; Nitta, H.; Tanigaki, T. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 467.
(10) Brown, D. E.; Allen, C. W. *J. Inorg. Organomet. Polym.* **1991**, *1*, 189.
(11) van de Grampel, J. C.; Alberda Van Ekenstein, G. O. R.; Bass, J.; Buwalda, P. L.; Jekel, A. P.; Oosting, G. E. *Phosphorus, Sulfur Silicon* **1992**, *64*, 91.
(12) Allen, C. W.; Shaw, J. C.; Brown, D. E. *Macromolecules* **1988**, *21*, 2653.
(13) Dupont, J. G.; Allen, C. W. *Macromolecules* **1979**, *12*, 169.
(14) Allen, C. W.; Bright, R. P. *Macromolecules* **1986**, *19*, 571.
(15) Allen, C. W.; Shaw, J. C.; Brown, D. E. *Macromolecules* **1988**, *21*, 2653.
(16) Bosscher, G.; Meetsma, A.; van de Grampel, J. C. *J. Chem. Soc., Dalton Trans* **1997**, 1667.
(17) Bosscher, G.; Hagen, H.; Meetsma, A.; Jekel, A. P.; van de Grampel, J. C. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1996**, *67*, 109.
(18) Bosscher, G.; van de Grampel, J. C. *J. Inorg. Organomet. Polym.* **1995**, *5*, 209.
(19) Bosscher, G.; Wieringa, R. H.; Jekel, A. P.; van de Grampel, J. C. *J. Inorg. Organomet. Polym.* **1996**, *6*, 255.
(20) Dez, I.; De Jaeger, R. *J. Inorg. Organomet. Polym.* **1996**, *6*, 111.
(21) Spizzo, F. Thesis**,** University of Padova, Padova, Italy, 1992.
(22) Medici, A.; Fantin, G.; Pedrini, P.; Gleria, M.; Minto, F. *Macromolecules* **1992**, *25*, 2569.
(23) McOmie, J. F. W.; Watts, M. L.; West, D. E. *Tetrahedron* **1968**, *24*, 2289.
(24) Inoue, K.; Kaneyuki, S.; Tanigaki, T. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 149.
(25) Thomas, L. C. *Interpretation of the Infrared Spectra of Organophosphorus Compounds*; Heyden: London, 1974.
(26) Schechter, H.; Barker, H. C. *J. Org. Chem.* **1956**, *21*, 1473.
(27) Gleria, M.; Minto, F.; Fontana, G.; Bertani, R.; Facchin, G. *Macromolecules* **1995**, *28*, 4399.
(28) Lopez, G. P.; Castner, D. G.; Ratner, B. D. *Surf. Interface Anal.* **1991**, *17*, 267.
(29) Boulanger, P.; Magermans, C.; Verbist, J. J.; Delhalle, J.; Urch, D. S. *Macromolecules* **1991**, *24*, 2757.

MA9707042