

Surface Modification of Poly(vinyl alcohol) by Peroxide-Initiated Grafting of a Poly(organophosphazene)

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A poly(organophosphazene) bearing allylic functions (POPZ (1)) has been grafted onto the surface of a poly(vinyl alcohol) (PVA) film with the aid of the benzoyl peroxide initiator. The PVA films were first coated with toluenic solutions of POPZ and peroxide and then heated. After grafting, they were extracted with toluene to remove ungrafted POPZ. The resultant surfaces were characterized by ATR-IR, UV, XPS spectroscopies, X-ray fluorescence spectrometry, and gravimetric and contact angle measurements. The presence of the covalently bonded and cross-linked POPZ on the PVA surface gives it hydrophobic character, which may be helpful in improving the oxygen-barrier properties at high humidity.

Introduction

The modification of organic conventional polymers by grafting thin films of other organic or inorganic polymers onto their surface can impart useful properties without modifying the bulk material. This challenge, if successful, can give rise to materials with very interesting applications.

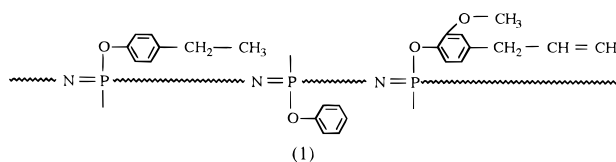
We describe here, a process that involves the radical grafting of a poly(organophosphazene) (POPZ) to the surface of poly(vinyl alcohol) (PVA).

To date, about 400 POPZs have been synthesized, giving a great variety of structures with very diverse physical and chemical properties.¹⁻³ Thus, these polymers can be hydrophilic or hydrophobic, electrical conductors or insulators, photodegradable or photoreistant, flame resistant, and so on.⁴ A part of them are functionalized polymers containing reactive groups such as nitro,⁵ hydroperoxide,⁶ diphenylphosphine,⁷ glucose,⁸ glyceryl,⁹ carboxylic,⁷ or sulfonic acids,^{10,11} with the objective to be bound to other molecules or macromolecules. As examples, we can report the thermally induced grafting reaction of polystyrene onto polyphosphazenes containing 4-isopropylphenoxy substituents by initiating hydroperoxide groups on the tertiary carbon with the use of peroxide initiators,⁶ the attachment of enzymes to polyphosphazenes via a nitrophenoxy group,⁵

and the grafting of poly[bis((methoxyethoxy)ethoxy)-phosphazene] on the surfaces of polypropylene, poly(vinyl chloride), poly(ethylene terephthalate), polycarbonate, and poly(methyl methacrylate).¹²

PVA is one of the largest volume water-soluble resins produced in the world. This production is the result of its chemical and physical properties, particularly the oxygen-barrier performance which, at low humidity, is superior to that of any other polymer. However, this property greatly deteriorates above 60% relative humidity.¹³ Consequently, it is very important to reduce this moisture sensitivity. Thus, the conversion of the hydrophilic surface of PVA films to a hydrophobic one was one of the objectives of this work.

The choice of grafting onto a PVA surface a POPZ (1) containing phenoxy, 4-ethylphenoxy and a few percentage of (2-methoxy-4-allyl)phenoxy substituents was based on the hydrophobicity of corresponding films and on its ease of radical cross-linking due to the presence of allylic functions.⁴



Results and Discussion

Synthesis and Characterization of the Poly(organophosphazene). The POPZ (1) was synthesized by the ATOCHEM Co. at a pilot scale by a two-steps process. First, poly(dichlorophosphazene) (NPCl₂)_n was synthesized by solution polycondensation of *P*-trichloro-*N*-(dichlorophosphoryl)monophosphazene Cl₃P=N-P(O)Cl₂ following a method described previ-

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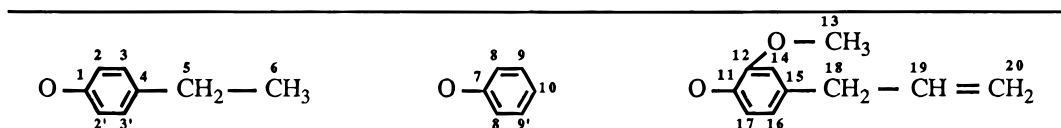
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Table 1. NMR and IR Data of 1



^1H NMR (ppm)	^{13}C NMR (ppm)	^{31}P NMR (ppm)	IR (cm^{-1})
1.04 (t, $\text{CH}_3(6)$)	151.8 (s, aromatic(7))	-19.2 (s)	3050 w $\nu(\text{C-H})$ aromatic
2.36 (q, $\text{CH}_2(5)$)	150 (s, aromatic(1))		2964 m, 2871 $\nu(\text{C-H})$ aliphatic
3.28 (s, $\text{CH}_3(13)$)	139 (s, aromatic(4))		1594 m, 1507 F $\nu(\text{C-C})$ aromatic
3.09 (s, $\text{CH}_2(18)$)	128.7 (s, aromatic(9,9'))		1455 w $\delta(\text{C-H})$ aliphatic
4.92 (s, $\text{CH}_2(20)$)	127.9 (s, aromatic(3,3'))		1209 vs(br) $\nu_{\text{as}}(\text{P=N})$
5.72 (s, $\text{CH}(19)$)	123.2 (s, aromatic(10))		1022 w $\delta(\text{C-H})$ aromatic
6.55 (m, aromatic)	121.3 (s, aromatic(8,8'))		947 vs(br) $\nu(\text{P-O-Ph})$, $\nu(\text{P-N})$
6.75 (m, aromatic)	121 (s, aromatic(2,2'))		837 s $\delta(\text{C-H})$ aromatic
	28 (s, $\text{CH}_2(5)$)		770 m $\delta(\text{C-H})$ aromatic
	15.5 (s, $\text{CH}_3(6)$)		689 m $\delta(\text{C-C})$ aromatic
			537 s(br) $\delta(\text{PNP})$, $\delta(\text{NPN})$

ously.¹⁴ Second, the chlorine atoms in $(\text{NPCL}_2)_n$ were replaced by reaction with the sodium salts of phenol, 4-ethylphenol, and (2-methoxy-4-allyl)phenol in chlorobenzene solution.¹⁵

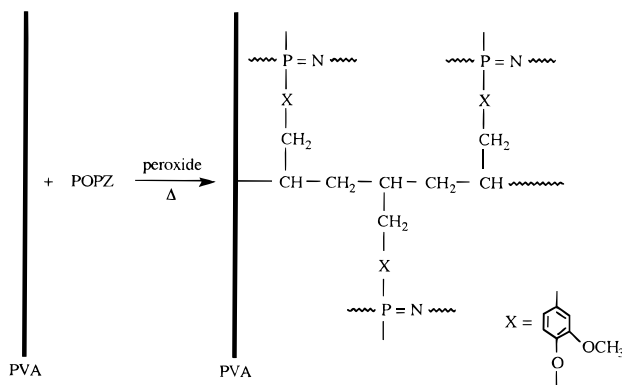
Polymer **1** was characterized by ^{31}P , ^1H , and ^{13}C NMR spectroscopy, infrared spectroscopy, and elemental analysis (see Table 1 and Experimental Section). ^1H NMR spectroscopy was used to estimate the percentage of the different side groups: phenoxy, 38.5%; 4-ethylphenoxy, 60%; (2-methoxy-4-allyl)phenoxy, 1.5%. These data formed the basis of the calculated elemental microanalysis values. The glass transition temperature was $T_g = -21.6^\circ\text{C}$ and the intrinsic viscosity $[\eta] = 99\text{ mL/g}$. The molecular weight, determined by light scattering, was 1.24×10^6 , and the polydispersity index, determined by gel permeation chromatography, was $M_w/M_n = 14$.

Grafting Process. The film samples were dip-coated with toluenic POPZ solutions containing benzoyl peroxide as a radical initiator. After a few hours, the coated films were heated at 80 or 110 $^\circ\text{C}$. The grafted films were then washed with toluene to remove ungrafted polymer and, finally, dried. A control film was also prepared, using the same procedure but without peroxide.

Proposed Mechanism. The proposed mechanism for the graft and cross-linking of **1** onto the surface of PVA films is represented in Scheme 1. In the presence of a peroxide, the free radicals generated by its decomposition, may extract hydrogen atoms of the substrate and add to the double bond of the allylic groups, to give PVA and POPZ macroradicals. Subsequent intermolecular combination of PVA-POPZ and POPZ-POPZ radicals can lead to the grafting and to the cross-linking of POPZ. Since the interaction between the solvent and the PVA film is very weak (the swelling degree with toluene is less than 1% after 48 h), this grafting will only occur on the film's surface.¹⁶

Surface Characterization of Grafted PVA Films.
Effect of POPZ Concentration. After treatment, the films were studied by ATR-IR spectroscopy and X-ray fluorescence spectrometry. The comparison between the

Scheme 1



ATR-IR spectra of original PVA film and those of POPZ treated films with and without peroxide is given in Figure 1. Two factors are revealed. First, the spectra of coated and thermally treated films without peroxide (Figure 1b) are similar to those of the starting PVA (Figure 1a). This result suggests that only very little adsorption of POPZ on PVA surface occurs, due to the low degree of swelling of PVA in toluene. Second, new absorbance bands appear in the spectra of films treated with POPZ/peroxide solutions, principally at $\nu = 1593$, 1507, 1196, and 947 cm^{-1} . These bands, which are respectively attributed to the C-C(aromatic), $-\text{P=N}-$, and P-O-C stretching vibrations in POPZ,¹⁷ confirm the occurrence of the grafting process. Their intensities increase with the POPZ concentration (spectra c-e). When this last is 70 g/L, the spectrum is nearly identical with that of POPZ, with the progressive disappearance of the broad band absorption at $\nu = 3292\text{ cm}^{-1}$ representative of the O-H stretching vibration.

From a quantitative study of these spectra, it is possible to follow the evolution of the grafting reaction. This can be done by measuring the intensity ratios of the bands at $\nu = 1593\text{ cm}^{-1}$ characteristic of the $\nu(\text{C-C})$ aromatic in POPZ and $\nu = 837\text{ cm}^{-1}$, representative at once of the $\delta(\text{C-H})$ aromatic in POPZ and $\nu(\text{C-C})$ in PVA. The increase of this ratio as a function of the POPZ concentration (25–85 g/L) is shown in Figure 2. For each concentration, two films were simultaneously treated.

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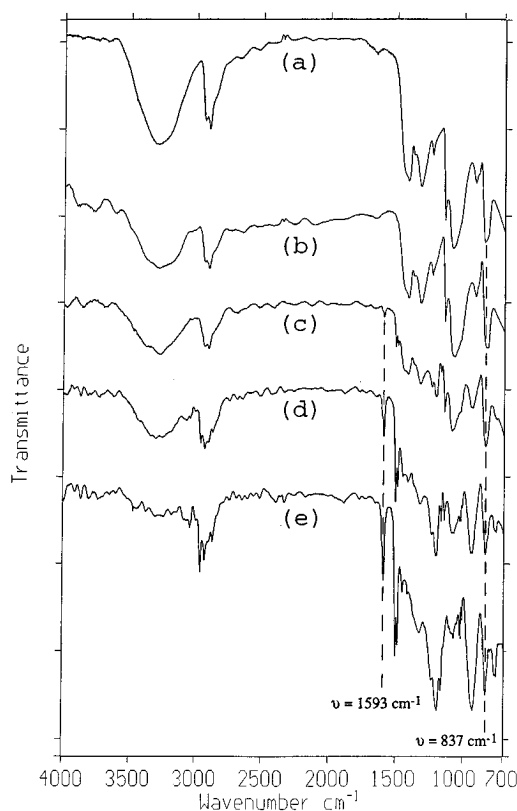


Figure 1. ATR-IR spectra of grafted PVA films as a function of POPZ concentration. (a) Virgin PVA. (b) PVA + POPZ 25 g/L without peroxide. (c)–(e) PVA + POPZ + peroxide ((c) POPZ 25 g/L, (d) POPZ 55 g/L, (e) POPZ 70 g/L).

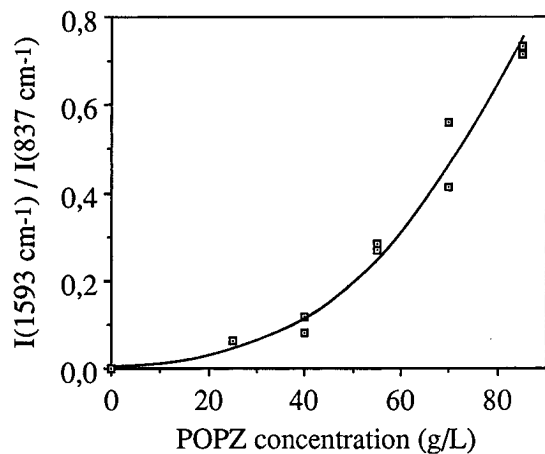


Figure 2. Variations of the intensity ratio of IR bands at $\nu = 1593 \text{ cm}^{-1}$ and $\nu = 837 \text{ cm}^{-1}$ versus POPZ concentration.

X-ray emission provides also a convenient and sensitive means for the identification and measurement of phosphorus present on the surface of the films. Therefore, a range of grafted samples having the same surface were studied by X-ray fluorescence and the emitted P K α radiation analyzed. The data in Figure 3, which show the increase in intensity of this radiation versus POPZ concentration (25–100 g/L), confirm the results of the IR(ATR) study.

These results (IR and X-ray fluorescence) are also in accordance with those obtained by weighing the films, before and after treatment, although this technique is unsuited for the low concentrations. In Figure 4, the grafting yield ($G\%$) is plotted as a function of POPZ concentration (10–60 g/L). Its continuous increase and

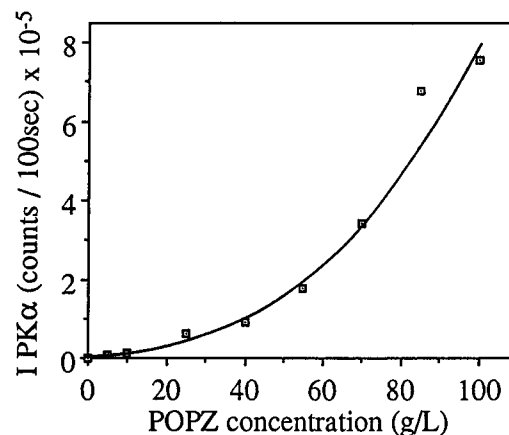


Figure 3. X-ray fluorescence: variations of the intensity of the P K α radiation versus POPZ concentration.

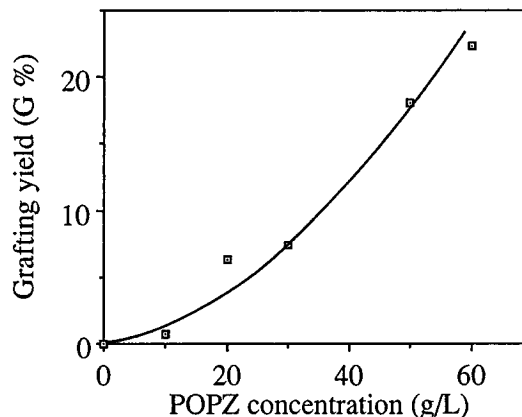


Figure 4. Variations of the grafting yield as a function of POPZ concentration.

its value, unequivocally support the intervention of a cross-linking reaction. Assuming the covering of the PVA surface by a homogeneous film of POPZ, its thickness can be evaluated from the knowledge of the POPZ density, of the films' surface, and of the grafting yields. The results were 0.5 and 1.5 μm for respectively 20 and 60 g/L POPZ concentration.

Effect of Extraction Time. As we mentioned earlier, after the thermal treatment, the grafted films were washed with toluene in order to remove unreacted POPZ. The effect of this extraction was followed by ATR (IR) measurements. For this purpose, a PVA film was first coated with the solution toluene–POPZ (50 g/L)–benzoyl peroxide (3% w/w) POPZ, treated at 110 $^{\circ}\text{C}$, and washed with toluene for 20 h at ambient temperature. Then, the same film was extracted by Soxhlet with toluene for an additional 20 h. The ATR-IR spectra before and after soxhlet extraction were compared, and the preceding intensity ratios determined. The values obtained were 0.11 and 0.10, respectively, that can be considered identical, give a strong indication that POPZ is covalently bonded to the PVA film surface.

Effect of Temperature. The effect of temperature was studied by IR measurements from two PVA films coated with the same solution (POPZ (60 g/L)–benzoyl peroxide (3% w/w POPZ)–toluene) and thermally treated at 80 $^{\circ}\text{C}$ in the first case and 110 $^{\circ}\text{C}$ in the second. The determination of the previous intensity ratios shows an increase in the amount of grafted POPZ with temperature (ratio at 110 $^{\circ}\text{C}$ /ratio at 80 $^{\circ}\text{C}$ = 1.6).

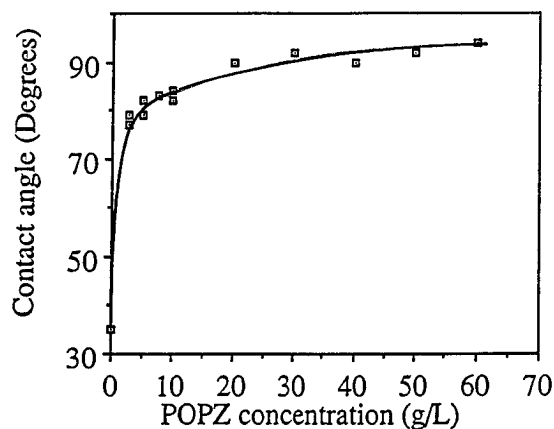


Figure 5. Variations of contact angle measurements versus POPZ concentration.

Contact Angle Measurements. Samples treated with POPZ solutions of various concentrations (2.5–60 g/L) were studied by water contact angle measurements. The variations of these versus concentration are represented in Figure 5. The curve shows a noticeable increase of the contact angle from $\theta = 35^\circ$, for the uncoated control, to $\theta = 92^\circ$ which is a value not significantly different from the one obtained for a POPZ film deposited on a glass plate ($\theta = 99^\circ$). It can be noted that the contact angle increases rapidly and reaches its maximum value for a 20 g/L POPZ concentration, indicating a hydrophobic PVA surface completely covered by grafted POPZ. For each concentration, the contact angle was always $\pm 4^\circ$ across the PVA film surface, suggesting a uniform grafting of POPZ.

Homogeneity of Grafted Surfaces. During the thermal treatment, the coated films are suspended in a drying oven at the desired temperature, and as a result, the coating solution flows down the PVA surface. Thus, the uniformity of the grafted POPZ layer on the film surfaces was examined. Ultraviolet spectra of aryloxy-substituted polyphosphazenes are characteristic of the phosphorus-bonded substituents¹ (in our case the phenoxy groups), so this technique was then a powerful tool for the identification of POPZ on the PVA surface. For this purpose, we have used a double-beam spectrophotometer and studied the films inserted in Teflon frames by transmission with an ungrafted film as reference. Because the surface beam is small (1×0.2 cm) in comparison with that of the films (2×4.5 cm), it was possible to explore successively the top and the bottom of the films. Thus, a series of films treated with solutions of POPZ (the concentration varying from 10 to 100 g/L) was analyzed. The UV spectra as a function of the POPZ concentration are represented in Figure 6. It should be noted that the absorbance is maximum at 267 nm (264 nm for the poly(bisphenoxyphosphazene))¹⁸ and that the POPZ can be only detected for concentrations above 10 g/L. The variations of the absorbance at 267 nm versus POPZ concentration for the top (a) and the bottom (b) of the films are represented in Figure 7. The amount of grafted POPZ is effectively higher for b than for a, the difference increasing with the viscosity of the coating solution.

X-ray Photoelectron Spectroscopy. As mentioned previously, two processes are claimed to take place

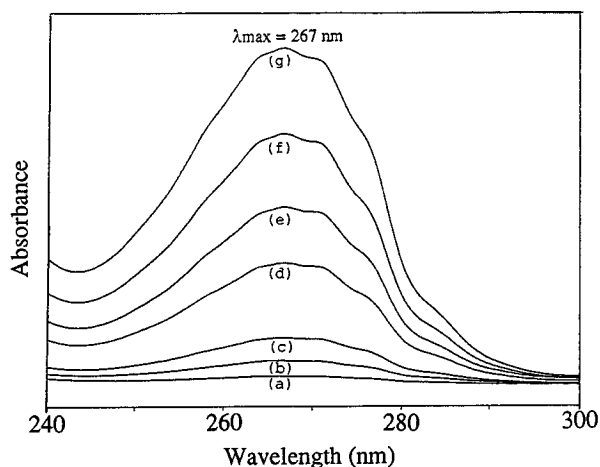


Figure 6. UV spectra of grafted PVA films as a function of POPZ concentration: (a) 10, (b) 25, (c), (d) 55, (e) 70, (f) 85, (g) 100 g/L.

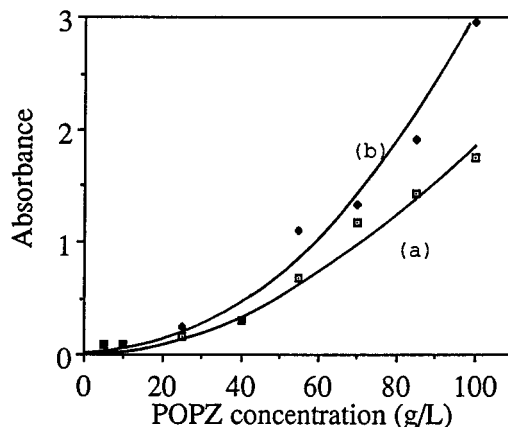


Figure 7. Variations of the 267 nm UV absorbance versus POPZ concentration for the top (a) and the bottom (b) of the films.

during the thermal treatment of the POPZ/PVA/peroxide system, i.e., the covalent grafting of the POPZ onto the PVA film surface and its cross-linking reaction. These two processes result from radical formation and combination at the carbon atoms of the POPZ side groups. Thus POPZ has a greater probability of being grafted onto PVA than onto a polymer surface lacking bonds needed for radical grafting, i.e., poly(tetrafluoroethylene) (PTFE).

Therefore, PVA and PTFE films were simultaneously treated with the same dilute POPZ–peroxide solution ([POPZ] = 0.5 g/L) and studied by XPS analysis. The spectra of the PVA films contained the P(2p) and N(1s) peaks at 134.2 and 397.9 eV, respectively, with a stoichiometric ratio N/P = 1.0 characteristic of POPZ. These peaks were not present in the spectra of the PTFE films. This result provided additional evidence for the covalent grafting of POPZ onto the PVA film surface.

Conclusion

A method to graft poly(organophosphazenes) containing allylic functions onto a poly(vinyl alcohol) film surface using benzoyl peroxide initiators has been studied. That simple technique produced high levels of grafting and conferred the hydrophobic character of the polyphosphazene, to the organic polymer surface (without modifications of its bulk properties). This could

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be important for the preservation of the oxygen-barrier properties of poly(vinyl alcohol) at high humidity and, consequently, of great interest for packaging applications. In addition, the variety of choices of phosphorus-bonded substituents in polyphosphazenes indicates that with this method it should be possible to confer very diverse properties (e.g., electrical conductibility, resistance to solvents and chemicals, photoresistance, etc.) to the surface of many carbon based polymers.

Experimental Section

Materials. Poly(vinyl alcohol) films manufactured by Nippon Gohsei Film Co. Limited (Japan) under the trademark Bovolon 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 are as follows: 3292 ν (O-H); 2938, 2905 ν (C-H); 1450 δ (C-H + O-H); 1419 δ (CH₂); 1373 γ_w (CH₂); 1321 δ (C-H + O-H); 1235 γ_w (C-H); 1142 ν (C-O + C-C); 1085 ν (C-OH) + δ (O-H); 913 γ_r (CH₂); 844 ν (C-C).

The films of 14 μ m thickness were cut to 2 \times 4.5 cm size. Just before use, they were dried at 100 °C for 3 h.

Poly[phenoxy-(4-ethylphenoxy)(2-methoxy-4-allylphenoxy)-phosphazene] (POPZ) supplied by ATOCHEM Co. was synthesized following a method described previously.¹⁵ Elemental anal. calcd from ¹H NMR data: C, 64.24%; H, 5.51%; N, 5.15%; P, 11.41%. Found: C, 65.42%; H, 5.49%; N, 5.09%; P, 10.91%.

Toluene (Aldrich) was used after drying on molecular sieves. Benzoyl peroxide was obtained from Fluka and used as received.

Equipment. ³¹P, ¹H, and ¹³C NMR spectra were recorded in CDCl₃ with a Bruker WP 300 NMR spectrometer. Chemical shifts are given in parts per million from TMS (¹H, ¹³C) or 85% H₃PO₄ (³¹P) as external standard.

Elemental analysis was carried out at the Service central d'analyse CNRS, France.

Contact angle measurements were made using a Face (Kyowa) contact-angle goniometer at ambient humidity and temperature. The volume of the applied drop was 1 μ L. All reported values are the average of at least eight measurements taken at different locations on the film surface.

Infrared spectra were recorded with a Bruker IFS 48 spectrometer. For POPZ polymer, spectra were obtained from films between KBr windows. For PVA films, a Graseby Specac continuously variable angle ATR accessory equipped with a KRS-5 crystal was used to obtain all ATR-IR spectra.

Size-exclusion chromatography was carried out at ATOCHEM Co. on a water 150 ALC/GPC instrument. The columns used were a set of two similar Shodex 80M, with styrene-divinylbenzene organic micropacking as the stationary phase and THF with added LiBr (0.1 mol/L) as the eluent. A chromatix CMX 100 low-angle laser light scattering (LALLS) detector was inserted on line between the outlet of the columns and the inlet of the refractometer.¹⁹

The UV absorption spectra were recorded using a Cary 1 Varian double-beam spectrophotometer. Polymers were analyzed in the form of films using a PVA film as reference. All reported absorbance values are the average of at least four measurements taken at the top or at the bottom of the PVA film.

X-ray fluorescence measurements were performed on grafted PVA films having the same surface with a Philips PW 1400 spectrometer, including an X-ray tube with a chromium anode and a pentaerythritol analyzing cristal. The counting was made on the P K α radiation during 100 s for each sample. The results were corrected from the background which was determined on a virgin PVA film.

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 K α 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 C_{1s} (-CH₂- 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.

Swelling Determination. PVA films were immersed for 48 h in toluene at 25 °C. After this time, they were taken out from the solution, the excess of toluene was removed by a piece of blotting paper, and then they were quickly weighed. The swelling degree was determined according to

$$\text{swelling degree \%} = ((W_s - W_0)/W_0) \times 100$$

where W_0 is the weight of the dry film and W_s the weight of the swollen film.

Grafting Procedure. The film samples were supported in Teflon frames for treatment. After drying, they were immersed and shaken in toluenic phosphazene solutions, with POPZ concentrations varying between 2.5 and 100 g/L, in the presence or not of benzoyl peroxide at room temperature for 15 h. The percentage of benzoyl peroxide used was 3% w/w in comparison with that of POPZ. The films were treated at 80 or 110 °C for 7 h and then soaked and shaken in toluene for 20 h to remove excess initiator and ungrafted POPZ. Finally, after having dried at 110 °C for 2 h, films surfaces analysis were carried out. The grafting yield was given by

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

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