Chemical Modification of Hydroxyl Functions: Introduction of Hydrolyzable Ester Function and Bactericidal Quaternary Ammonium Groups

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ABSTRACT: Polymers carrying a hydrolyzable ester function and bactericidal quaternary ammonium salts were successfully synthesized in 2 steps. The first one was the modification of hydroxyl functions of poly(vinyl alcohol) by chloroacetic anhydride. The structure of synthesized polymers was confirmed by infrared (IR), ¹H-, and ¹³C- nuclear magnetic resonance (NMR). The kinetic results were consistent with a 1-order reaction, and the activation energy in the case of total modification was found to be 16.8 kJ mol⁻¹. The second step was the quaternization of the pendant chlorine atom with a long alkyl chain or aromatic tertiary amines. The percentage of grafting was almost total, except with 3-diethylaminophenol, probably due to steric hindrance. The thermal degradation of polymers was studied. Side chains carrying quaternary ammonium salts begin to degrade at 168°C with the emission of chloride and amine compounds. At about 250°C, acetic and chloroacetic acid are evolved due to acetate and chloroacetate side chains. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2657–2666, 1998

Key words: chemical modification; poly(vinyl alcohol); esterification; quaternary ammonium salts

INTRODUCTION

Coatings showing bactericidal properties are useful in many domains such, as in food manufacturing, hospitals, or antifouling paints.¹⁻⁴

Until now, biocides such as triorganotin compounds were used in antifouling paints.⁵ But harmful effects of tributyltin have been proved on oysters.^{6–8} Its high toxicity towards the environment has lead to the ban on triorganotin antifouling paints in several countries for boats less than 25 meters.⁹ Current alternatives are the addition of biocides, such as weed killers, insecticides, metallic carbamates, or highly halogen compounds, but some products are still very toxic.¹⁰ It is necessary to find a paint that is respectful to the environment, efficient over the long term, economic, and compatible with existing products, and that has a wide activity spectrum. Researchers are leaning towards¹¹ nonwetting coatings that prevent physic adhesion of marine organisms,^{12,13} coatings based on silicon,¹⁴ and prevention of adhesion of marine organisms by inhibition of their secondary metabolites.^{15,16}

We used a new concept, in which the biocide acts by contact and without diffusion in the environment, or with release of a rapidly biodegrad-able molecule.^{17,18}

Our approach appeals to quaternary ammonium salts with long alkyl chains. Their bactericidal activity is already known and used in many domains, such as in pharmaceuticals, desinfectants, shampoos, laundry, and wastewater.^{19–21} They are active on bacteria, and they cause the

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deaths of the cells by destroying cytoplasmic membranes. $^{22-24}$

In our case, quaternary ammonium salts are grafted on the polymer. Until now, quaternary ammonium groups were binded to the polymer with a covalent bond, but the efficiency reached, at maximum, 2 years for an antifouling paint. A self-polishing paint containing a polymer with a hydrolyzable bond will give an efficiency of 5 years.

Our goal is to obtain a polymer with 2 characteristic properties, as follows: a bactericidal activity to prevent development of fouling on coatings, and a hydrolyzable property to obtain a more important durability.

Bactericidal activity is given by quaternary ammonium salts with long alkyl chains grafted on the polymer, and the hydrolyzability is obtained by introduction of hydrolyzable functions, such as ester functions.

To obtain a polymer with these 2 characteristic properties, we have modified poly(vinyl alcohol). This polymer has good film properties and is used in many paint formulations.^{25–27} However, it is soluble in water, and to have good mechanical properties, it is necessary to make it insoluble. Hydroxyl functions are very reactive and permit grafting of different compounds.^{28–30} Eventually, hydroxyl functions can be crosslinked.³¹

The aim of this work is the study of chemical modification of poly(vinyl alcohol) in 2 steps, as follows: the esterification of hydroxyl functions is carried with an acyl chloride or an anhydride chloride, and the quaternization on the chlorine is carried with several tertiary amines to obtain quaternary ammonium groups.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) is a commercial product from Prolabo (Rhodoviol 4/125). The measured percentage of acetate functions is 12%. The viscosity at 4% in water at 20°C is comprised between 3.5 and 5 mPa s. Consequently, the molecular weight is about 20,000 (17,000–22,000). 3-chloropropionic acid, chloroacetyl chloride, chloroacetic anhydride (purity = 90%), dimethyloctylamine, dimethyldodecylamine, dimethylbenzylamine, and 3-diethylaminophenol are commercial products from Aldrich. All reactants were used without purification.

Synthesis

First Step: Modification of Hydroxyl Functions

By a Carboxylic Acid Containing Chlorine. Poly-(vinyl alcohol) and 3-chloropropionic acid were added in stoichiometric proportions. Reaction was carried out in polar solvent (methyl ethyl ketone or methyl isobutyl ketone) under reflux. A catalytic amount of sulphuric acid was added if necessary.

By Chloroacetyl Chloride. Poly(vinyl alcohol) was added to a small excess of chloroacetyl chloride. The chlorhydric acid produced was trapped in a sodium hydroxide solution. The beginning of the reaction was carried out at 60° C, then under stirring at room temperature. It was sometimes necessary to cool the reactor. The polymer was precipitated in excess petroleum ether several times to eliminate the remaining chloroacetyl chloride. After filtration, the polymer was dissolved in acetone and precipitated in basic water to eliminate traces of chlorhydric acid. Finally, the polymer was filtered out, washed with water, and dried under vacuum. The mass yield obtained was about 80-90%.

By Chloroacetic Anhydride. The reaction was carried out at 80°C in large excess of methyl ethyl ketone (MEK) with a stoichiometric ratio of poly-(vinyl alcohol) and chloroacetic anhydride. Poly-(vinyl alcohol) was insoluble in MEK. Consequently, the solution became clear and more viscous as the reaction progressed. At the end of the reaction, the polymer was precipitated 2 times in basic solution of sodium hydrogencarbonat to eliminate the carboxylic acid that was formed and the remaining chloroacetic anhydride. Polymer was obtained after filtration, wringing, and drying under vacuum. The mass yield obtained was 93–94%.

Second Step: Quaternization of Chlorine by Tertiary Amines

The reaction was carried out at reflux in acetone. Tertiary amine was added in a chosen amount according to the desired percentage of quaternization. At the end of the reaction, acetone was evaporated, and the final polymer was dried under vacuum. The yields of quaternization were determined by coulometry.



Scheme 1 Modification of poly(vinyl alcohol)

Measurements

The size exclusion chromatography (SEC) curves of polymers obtained after first step (PVAM1) were recorded on a Waters size exclusion chromatograph (ultrastyragel columns) in tetrahydrofuran at room temperature coupled with a differential refractometer detector and using polystyrene as standard. Infrared (IR) spectra were recorded on a Nicolet Fourier transform infrared (FTIR) 510 spectrometer with a MCT detector. ¹H nuclear magnetic resonance (¹H-NMR) NMR and ¹³C-NMR were performed on a Bruker spectrometer at 400 MHz using CDCl₃ as solvent and TMS as internal reference.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a Setaram 92 thermal analyzer system. TGA measurements were made at a heating rate of 10° C/min under N₂ at a flow rate of 50 mL/min. Coupling of DTA–TGA with IR were made online. Pyrolysis of polymers were performed on a Hewlett-Packard 5890 Series II chromatograph coupled with a mass spectrometer. Glass transition temperatures were determined on a differential scanning calorimetry (DSC) Setaram 92 analyzer at a heating rate of 5°C/min. Coulometric titrations were recorded on a Sefram system at fixed intensity (10 mA).



Figure 1 IR spectra of poly(vinyl alcohol) and PVAM1 on NaCl pellets.



Figure 2 Reaction of poly(vinyl alcohol) (3.28 mol L^{-1}) with chloracetic anhydride (3.35 mol L^{-1}) in MEK at (**■**) 60, (**♦**) 70, and (**●**) 86°C.

RESULTS AND DISCUSSION

The synthesis of polymers by chemical modification of hydroxyl functions in order to graft quaternary ammonium groups in side chains was carried out in 2 steps (Scheme 1).

The first step is an esterification between a secondary alcohol (hydroxyl functions on the starting polymer) and a carboxylic acid, an acyl chloride, or an anhydride, all containing a chlorine.

The second step is the quaternization of the pendant chlorine atom by several tertiary amines containing a long aliphatic chain or an aromatic chain.

Esterification of Hydroxyl Functions by a Carboxylic Acid

It is a Fischer esterification, catalyzed by a mineral acid. But it can be accomplished only if a means is available to drive the equilibrium to the right. There are many ways of doing this, among which are as follows:

- 1. addition of an excess of 1 of the reactants, usually the alcohol;
- 2. removal of the ester or the water by distillation;
- 3. removal of water by azeotropic distillation; and
- 4. removal of water by use of a dehydrating agent or a molecular sieve.

Since the reaction is reversible and limited in aqueous medium, we had to use an organic solvent and work in a heterogeneous medium. The modification of poly(vinyl alcohol) would mean the solubilization of the polymer in the solvent. There was no modification of poly(vinyl alcohol) at 80°C in MEK and at 110°C in methyl isobutyl ketone, with or without acid catalyst.

Esterification of Hydroxyl Functions by an Acid Chloride

The reaction between an alcohol and an acid chloride is, in general, the best method to get an ester. A base is often added to neutralize the formed acid. In our case, chlorhydric acid was trapped by a sodium hydroxide solution. But the treatment of the polymer after reaction was difficult; several washing steps were necessary to eliminate completely chlorhydric acid. That's why the synthesis of the final polymer for later application is better from the anhydrid.

Esterification of Hydroxyl Functions by an Anhydride

The reaction was carried out in MEK at 80-85°C. The reactional medium became homogeneous as the reaction progresses. To neutralize the chloroacetic acid that is formed, the precipitation in a sodium hydrogencarbonat solution must be lead very slowly and under vigorous stirring. The best purification was obtained after 2 precipitations. The white polymer (PVAM1) was dried on fluidized bed under air. Mass yields were about 93– 94%.

Characterizations of PVAM1

The IR spectra of the polymer show the characteristic bands of the chemical modification (Fig. 1). Thus, the wide band at 3343 cm^{-1} , which is characteristic for alcoholic groups, has greatly de-

Table I	Variation	of the	Rate	Constant k
with Ter	nperature			

Temperature (°C)	$\frac{10^2 \text{ k}}{(\text{min}^{-1})}$
60	1.53
70	2.80
86	5.60

	T_d (°C)	$\begin{array}{c} T_1 \ (^\circ\mathrm{C}) \\ (\mathrm{Loss}\ \%) \end{array}$	$\begin{array}{c} T_2 \; (^{\circ}\mathrm{C}) \\ (\mathrm{Loss} \; \%) \end{array}$	$T_3 \;(^{\circ}\mathrm{C}) \\ (\mathrm{Loss} \; \%)$	$\begin{array}{c} T_4 \ (^\circ \mathrm{C}) \\ (\mathrm{Loss} \ \%) \end{array}$	$\begin{array}{c} T_5 \ (^{\circ}\mathrm{C}) \\ (\mathrm{Loss} \ \%) \end{array}$	Total Loss (%)
PVA	275	275 (67)	400 (22)	_	_	_	89
PVAM1	256	256(70)	430 (12)	_	_	_	82
PVAM2	168	60 (10)	168 (21)	235(20)	280 (24)	363 (14)	89

Table IIThermal Degradation

 T_d is the decomposition temperature.

creased. At 1734 cm⁻¹, a broad band is observed, which has been attributed to the ester group absorption. The relative intensity of this band appears to depend on the modification extent in the polymer. It is accompanied by a band at 1180 cm⁻¹ representing ν C—O and by a small band at 790 cm⁻¹ for ν C—Cl. The ester function of the acetate present in the starting poly(vinyl alcohol) is observed by a shoulder at 1750 and at 1248 cm⁻¹ for ν C—O. The bands at 2930, 2950, and 1410 cm⁻¹ are characteristic of CH₂ and CH₃ groups. A double band at 1311 and 1286 cm⁻¹ is characteristic of the stretching CH₂—O. Otherwise ν CH₃—O is represented by a small band at 1375 cm⁻¹.

Characteristic bands of anhydride function appear in IR at 1834 and 1768 cm⁻¹; however, the carbonyl band of ester appears at 1733 cm⁻¹. As the reaction progresses, the band at 1834 cm⁻¹ disappears, and the band at 1733 cm⁻¹ increases. Analysis of the reactional medium in IR permits one to follow the advancement of the reaction versus time. The ratio of relative intensities of bands at 1834 and 1733 cm⁻¹ in absorbance give the percentage of disappearance of anhydride. Figure 2 shows the evolution of concentration in anhydride versus time and at several temperatures.

Experiments were carried out with the same concentrations of all reactants and to obtain a total modification of hydroxyl functions. The reaction seems to be a 1-order reaction. It would depend only on the anhydride concentration. At the beginning, poly(vinyl alcohol) is indeed insoluble in reaction medium, like the reaction that occurs in heterogeneous medium. Modification would depend on mole quantity of anhydride that could react on hydroxyl functions.

The rate constants calculated for each temperature are shown in Table I. The activation energy of this process calculated by the Arrhenius plot is 16.8 kJ mol^{-1} .

The ¹H-NMR spectrum shows a signal at 4.1 ppm, which can be assigned to the methylene

protons of chloroacetate groups. The signal at 4.9 ppm belongs to the resonance of the methine protons in the main chain. Signals at δ equal to 1.6–2.0 ppm are due to the methylene protons in the main chain and to the methyl group of acetate groups. A very small signal at 3.8 ppm can be assigned to the proton of hydroxyl group.

The ¹³C-NMR spectra exhibit characteristic chemical shifts at δ equal to 167.3 170.6 ppm, which correspond to the carbonyl carbon atoms of chloroacetate and acetate groups, respectively. The signals at 41.0 and 21.2 ppm correspond to the chloromethyl and methyl carbon atoms of chloroacetate and acetate groups. The carbon atoms of chloroacetate and acetate groups. The carbon atoms in the main chain are represented by signals at δ equal to 70.0–69.0 ppm for the CH and at δ equal to 39.0 ppm for the CH₂.³²

Molecular weights were determined by SEC in tetrahydrofuran. For a total modification of hydroxyl functions, we obtain 1 large peak that corresponds at M_w equals 53,000. By deduction, the molecular weight of poly(vinyl alcohol) is, consequently, about 22,000, which corresponds to the value indicated by the manufacturer (17,000–22,000).

The glass transition temperatures (T_g) of polymers were determined by DSC. All polymers show a T_g at the range of 18–45°C. Poly(vinyl alcohol) has a T_g of 58°C. The more important the modification of PVA, the weaker the glass transition until it reaches, at maximum, 18–23°C. The modification of polymer leads indeed to an extension of side chains, which favors the movements of macromolecules between them. The increase of these movements leads to a decrease of glass transition temperature in comparison with poly-(vinyl alcohol).

Thermal Analysis

We have studied the thermal degradation mechanism of the synthesized polymers. We have noted indeed that all the polymers carrying quaternary ammonium groups began to degrade at 160-200°C, whereas the ungrafted polymers had higher degradation temperatures.



Figure 3 Coupling of DTA–GTA with FTIR: the amount of gases emitted versus time: (a) poly(vinyl alcohol); (b) PVAM1; (c) PVAM2.

To understand the influence of the modification of hydroxyl functions and the role of quaternary ammonium groups, we used differential and gravimetric thermal analysis under gas. A sample of polymer introduced in a alumina crucible was heated with a precise temperature programmation. Following mass losses, endothermic and exothermic effects were simultaneously registered. With coupling between DTA–TGA and FTIR, we have analyzed the gas evolved during the degradation of polymer.

Thermal analysis were carried out between 30 and 600°C at 10°C/min under nitrogen at a flow rate of 50 mL/min. The emitted gas were heated at 149°C.

Initial decomposition temperatures (T_d) and the different phases of decomposition with mass losses for poly(vinyl alcohol) and the 2 modified polymers are resumed in Table II.

The interpretation of thermal decomposition of poly(vinyl alcohol) is easy and agrees with literature. The amount of emitted gas versus time shows a broad peak at 33 min (Fig. 3). It corresponds to the first decomposition phase (between 275 and 400°C), followed by a shoulder at 44 min for the second decomposition phase (after 400°C). Infrared spectra of first peak show several products (Table III).

For the second decomposition step, CO_2 , CO, and aromatic compounds are major: they result

	νCOOH	$\nu \mathrm{CH}_2$	νC==0	νC==C	Other Bands
Acetic acid	3590	_	1795		1176
Acetaldehyde	—	2820 - 2732	1758	—	1418 - 1373
Acrolein	_	3022 - 2927	1727	_	989-927
Crotonaldehyde	_	3022 - 2927	1727	1646	964
Formaldehyde	_	2893 - 2748	1782, 1743, 1705	—	—

Table III Products and Their Characteristic Bands



Scheme 2 Thermal decomposition of poly(vinyl alcohol).

from the decomposition of the principal macromo-

lecular chain. Scheme 2 shows the thermal de-

solvent used for the reaction (methyl ethyl ke-

tone) is binded with the macromolecules, in spite

of several precipitations: it is emitted at 28 min.

As hydroxyl functions are present in a weak

quantity, and the presence of aldehydic com-

pounds is hidden by other products. At 32 min, IR spectrum shows the following 2 major com-

pounds: acetic acid and chloroacetic acid. A pyrolysis has confirmed these results. Thus, the prin-

cipal degradation of PVAM1 is resumed in

For the PVAM2, we have studied a polymer

For the polymer modified by chloroacetic anhydrid (PVAM1), the first decomposition corresponds to 2 gas emissions at 28 and 32 min. The

composition of poly(vinyl alcohol).

Scheme 3.

with the following structure:



Scheme 3 Thermal decomposition of PVAM1.

and dimethyloctylamine. At 26 min (between 235 and 280°C), lots of CO_2 and CO are evolved due to the decomposition of chains carrying quaternary ammoniums groups. During the fourth decomposition phase, acetic acid and chloroacetic acid are evolved. From 363°C, aromatic compounds resulting from the decomposition of the principal macromolecular chain are emitted.

Quaternization of Pendant Chlorine by Several Tertiary Amines (PVAM2)

The intermediate polymer is quaternized by the following 4 different amines: dimethyloctylamine, dimethyldodecylamine, dimethylbenzylamine, and 3-diethylaminophenol. For aliphatic amines, the reaction was carried out in acetone at reflux. At reflux and at each time, there was a total quaternization (yield of 100%), although the used solvent had a middle polarity (Fig. 4).

For aromatic amines, the reaction was carried out in a ether–alcohol at 80°C. However, the yield with dimethylbenzylamine was complete, and the yield with 3-diethylaminophenol was limited at



We have also made a pyrolysis that allows one to interpret the IR spectra. Gram–Schmidt shows the emission of 5 major products, each corresponding to a different decomposition phase. Until 168°C, the solvent of the reaction (an ether– alcohol) is emitted because it is difficult to eliminate by drying. At 21 min (between 168 and 235°C), we observe the following chloride and amine compounds: chloromethane, chlorooctane,



Figure 4 Quaternization of PVAM1 by dimethyloctylamine in acetone (\blacksquare) at 60°C and (\blacktriangle) at reflux.



Figure 5 Reaction of quaternization with several tertiary amines: (\blacksquare) dimethyloctylamine; (\blacklozenge) dimethyldodecylamine; (\blacklozenge) dimethylbenzylamine; (\blacktriangle) 3-diethylaminophenol.

10%. Reactivity of nitrogen is, indeed, very weak, probably due to steric hindrance and to the bad accessibility of the amine.

Yields of quaternization were determined by coulometric titration of chloride ions (Fig. 5). Chloride ions vary between 0.39 and 3.35 mol/kg for the quaternization with dimethyloctylamine.

For further applications, the solubility of polymers in water were tested. From 1.03 mol/kg, the polymer becomes soluble in water. It corresponds at 14% of grafted groups with a long carbon chain (8 atoms). Balance between the hydrophilicity of quaternary nitrogen and the hydrophobicity of the long alcanoic chain goes over to the nitrogen.

In opposition with other amines, quaternization with 3-diethylaminophenol has an effect on solubility. The polymer becomes insoluble in water. It can be explained by formation of hydrogen bonds between hydroxyl functions of phenol.

Characterization of PVAM2

Infrared spectra of quaternized polymer show an increase of the band at 2926 cm⁻¹, representative of CH₂, CH₃, and a moving of the ester group at



Figure 6 IR of PVAM2 (12% acetate, 7% hydroxyl, 40% chloroacetate, and 41% quaternary ammonium salts side chain with dimethyloctylamine).

Groups	δ in ppm (¹ H-NMR)	δ in ppm (¹³ C-NMR)
—CO— CH_2 —N ⁺ (CH ₃) ₂ —	3.8	65.5
$-\!\!-\!\!\operatorname{CH}_2\!-\!\!-\!\!\operatorname{N}^+\!(CH_3)_2\!-\!\!-\!\!\operatorname{CH}_2\!-\!\!-$	3.5	50.7
$-N^+(CH_3)_2$ $-CH_2$	3.8	62.7
$- \mathrm{N}^+ (\mathrm{CH}_3)_2 - \overline{\mathrm{CH}_2} - CH_2 - \mathrm{C}_9 \mathrm{H}_{19} -$	2.0	32.0
$\mathrm{CH}_{2}C_{9}H_{19}\mathrm{CH}_{3}$	1.2 - 1.3	29.7; 29.1; 26.5; 22.8
$-C_9H_{19}$ $-CH_3$	0.8	14.2
CH_2 in the main chain	1.7	38.2
CH in the main chain	4.7 - 5.6	—

Table IV NMR of PVAM2 Quaternized by Dimethyldodecylamine

1743 cm⁻¹ (Fig. 6). The more important the quaternization, the greater the intensity of the band at 2926 cm⁻¹ in comparison with the band at 1743 cm⁻¹. A broad band appears at 3267 cm⁻¹, which is characteristic of water absorption by quaternary ammoniums. In a dessicant medium, this band disappears. The stretching N—CH₃ is represented by a small band at 1466 cm⁻¹. The measure of the intensity ratio of bands at 2926 and 1743 cm⁻¹ allows one to measure the percentage of grafting.

The ¹H-NMR and ¹³C-NMR spectra of PVAM2 quaternized by dimethyldodecylamine show the characteristic signals of the pendant quaternary ammonium salts,³³ as can be seen in Table IV.

With a high degree of quaternization of PVAM1, signals representing the chloroacetate, acetate, and hydroxyl groups disappear. Other small signals at δ equal to 2.5–3.0 ppm are due to impurities or remaining solvents. For ¹³C-NMR, the signal at 165.3 ppm belongs to the carbonyl carbon atoms of quaternary ammonium groups. The methine carbon atoms in the main chain are invisible. They must be at δ equal to 60.0–80.0 ppm. On the other hand, acetate groups are represented by 2 small signals at 170.5 ppm for the carbonyl and at 21.4 ppm for the methyl.

Table VGlass Transition Temperaturesof PVAM2

Nature of Pendant Chain	Glass Transition (°C)		
Benzyl	28-85		
Octyl	31–36		
Dodecyl	38–41		

Glass transition temperatures of quaternized polymers change according to the nature of quaternary ammonium grafted (Table V).

For octyl and dodecyl, the glass transition is nearly the same, whatever the percentage of quaternization is. For the benzyl, with a grafting rate of 49%, the glass transition is 85°C, and with a grafting rate of 13%, it is 28°C. The introduction of aromatic rings seems to increase the rigidity of polymer and the glass transition temperature.

CONCLUSION

We have studied the chemical modification of poly(vinyl alcohol) by an anhydride, but it can also be applied to other polymers containing hydroxyl functions, such as poly(vinyl butyral). We have successfully synthesized polymers with an ester function and quaternary ammonium salts. Thermal analysis of products show that they are stable until about 160°C. Grafting of chloroacetate and quaternary ammonium salts modify glass transition temperatures by decreasing them.

The biocidal properties of these polymers are assessed on a melting pot of marine bacteria to determine the most bactericidal structure. The bactericidal polymers are incorporated as binders in antifouling paints.

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