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Notes

Biodegradable Poly(ester-anhydride) for New Antifouling Coating

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Introduction

To prevent the development of marine biofilm (settlement and growth of living organisms) on immersed surfaces (ship's hulls, pipeline, and fish cages), it is necessary to develop prevention systems. Tributyltin self-polishing copolymer paints (TBT paints) have been the most successful in combating biofouling on ships.[1] Unfortunately, the TBT systems adversely affect the environment.[2] As an example, it has been shown that extremely low concentrations of TBT cause defective shell growth in the oyster *Crassostrea gigas* (20 ng/L).

Actually, the substitution of TBT paints is realized by the blending of poly(methylmethacrylate-*co*-butylmethacrylate) resins (PMMA−PBMA) with two types of biocides (bioactive molecules). The first corresponds to organic biocides used in agriculture (herbicides and pesticides), and the second corresponds to mineral biocide such as cuprous oxide. Two essential properties have been clearly identified as discriminating factors of antifouling efficiency: erosion (the surface degradation of the film) and presence of biocides at the coating surface during immersion.[3] However, due to severe environmental degradations, the use of toxic molecules and nondegradable polymers is questioned. These concerns have created a considerable interest in producing a new generation of protective systems based on biodegradable polymers. Among these polymers, polyesters (poly(ϵ-caprolactone) and poly(lactic acid)) could be revealed as interesting solutions. Nevertheless, their use is not conceivable due to their low solubility in the solvents used in formulation such as xylene.[4] Polyanhydrides, which combine surface erosion and biodegradability, are also potential matrixes. Polyanhydrides have been used in a number of applications including biomaterials, drug carriers, and tissue engineering.[5−8] They have been extensively investigated as matrixes in the controlled delivery of a number of drugs including antibiotics, anticancer molecules, local anesthetics, proteins, and peptides in the past 20 years.[9] However, polyanhydrides possess limited applications due to the fast erosion rates and lower solubility in common organic solvents except dichloromethane or chloroform.

To improve the properties of these interesting biodegradable polymers, several techniques have been investigated. A variety of poly(ester-anhydride)s have been synthetized, based on adipic acid,[10] ricinoleic acid,[11] salicylic acid,[12,13] cycloaliphatic acid,[14] lithocholic acid,[15] and lactic acid.[16] Blending and copolymerization techniques are also extremely promising approaches.[17,18]

The synthesis of triblock poly(ester-anhydride) based on lactic acid and sebacic acid has been previously proposed by Slivniak and Domb.[16] In the present work and in the same way, we propose to use biodegradable block copolymers composed of poly(ϵ-caprolactone) (PCL) and poly(sebacic acid) (PSA). ϵ-Caprolactone (CL) is a good candidate for the preparation of biodegradable copolymers with polyanhydride. Because of its nontoxicity for living organisms, PCL has been proposed for applications as a biodegradable poly(ester-anhydride).[19−21] PCL could allow decreasing the rate of degradation of polyanhydride by copolymerization. The use of block copolymers could offer the possibility to obtain surface erosion and the control of biocides release. The objective of controlled release is to maximize the preventing effect while minimizing adverse effects on the environment. This study evaluates coating formulation composed of poly(ester-anhydride), organic biocides, and additives by investing the release of the active molecules from the paint with powerful methods such as mass spectrometry (MS), microscopies (scanning electronic microscopy (SEM) and confocal laser scanning microscopy (CLSM)), and microanalysis X (EDX).

Experimental Section

Materials. Monomers of sebacic acid and ϵ-caprolactone were obtained from Acros. The monomers were used without purification. Acetic anhydride, petroleum ether, methanol, and tetrahydrofurane (THF) were purchased from Fisher. Fluorescein was purchased from Aldrich.

Polymers Synthesis. PCL-COOH oligomers were prepared by bulk polymerization of ϵ-caprolactone in the presence of caproic acid. Polymerizations were carried out at 240 °C under a nitrogen atmosphere, in a salt bath (53% KNO_3, 7% $NaNO_3$, 40% $NaNO_2$) for 8 h. The reaction was stopped by dipping the flask in ice. The obtained oligomers were purified by three successive precipitations using THF as solvent and methanol as nonsolvent.

The prepolymers of PCL-$COOCOCH_3$ were prepared from the purified PCL-COOH oligomers by refluxing in excess (1:10 w:v) of acetic anhydride for 30 min with constant stirring. After reaction, the excess of acetic anhydride was removed under reduced pressure at 65 °C. The viscous residue was mixed with dichloromethane and precipitated in ether/petroleum ether (1:1 v/v). The yellow precipitate was collected by filtration and dried in vacuum at room temperature.

PSA prepolymer was prepared by a procedure previously reported by Domb and Langer.[22]

The prepolymers (60:40 wt %, SA:CL) were added to a glass tube with a side arm equipped with a capillary nitrogen inlet. The tube was immersed in an oil bath at 180 °C. After the prepolymers were melted, high vacuum was applied for 1 h. The polymers were precipitated from chloroform solution to petroleum ether.

Preparation of Specimens. The in vitro hydrolysis was evaluated by casting of polymer as films. Copolymer was solubilized in an equal

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Table 1. Composition of Paint (wt %)

composition	amount (g)	composition	amount (g)
polymer	16.3	Tolyfluanid	4.2
solvent	40	additives	28.4
Diuron	5.3		

weight of xylene. Paint was formulated with the copolymer and fillers (additives and bioactives molecules) (Table 1). All the ingredients were dispersed under vigorous agitation (2000 rpm) for 1 h. Then the formulation was filtered through a sifter (100 μm). A layer of coating was deposited with an Automatic Film Applicator (ASTM D823 Sheen Instrument) on a polycarbonate support to give 50 μm thick films. The copolymer and paint were dried at 20 °C until they achieved constant weight.

Hydrolysis and Biocide Release Study. Each film was cut into 7 cm squares and placed into vials containing 250 mL of distilled water without shaking. The vials were then incubated at 20 °C for 90 days. The degradation media were periodically removed and replaced with fresh water. Analysis of the samples was performed using mass spectrometry equipped with an electrospray source. The dosage of products resulting from degradation and biocides release was isolated from MS fragmentation: sebacic acid (m/z 201), hydroxycaproic acid (m/z 131), and diuron (m/z 231). Samples of films were periodically removed from the aqueous medium and then dried at room temperature. Molecular weights were determined by size exclusion chromatography (SEC). The amount of water present in the film was quantified by Karl Fischer titration. The water localization was observed by confocal laser scanning microscopy (CLSM) by adding fluorescein in water. Scanning electron microscopy (SEM) and microanalysis X (EDX) were used to follow the film morphology and the biocides release during immersion. The biodegradation was evaluated in natural seawater (Atlantic Ocean, France). All experiments were performed in triplicate.

Methods. Infrared spectra were obtained with a Perkin-Elmer Spectrum BX FT-IR system recording to a spectrum v2.00 software. Prepolymer and polymer samples were prepared in dichloromethane and cast onto KBr plates for recording IR spectra.

Thermal analysis was performed by differential scanning calorimetry (DSC) on a Perkin-Elmer. The samples were scanned from −100 to 100 °C with a heating rate of 20 °C/min, then cooling at −100 °C at 3 °C/min, and scanned again from −100 to 100 °C with a heating rate of 20 °C/min. The glass transition temperature (T_g) was taken as the midpoint of the transition, in the first heating run. The melting temperature (T_m) was taken as the summit of the melting peak and ΔH was calculated from the area of the endothermic peak after the second run.

Molecular weights were determined by size exclusion chromatography (SEC) ("mixed C (5 μm)", Polymer Laboratories) using chloroform as eluent at a flow rate of 1 $mL \cdot min^{-1}$. Columns were connected to a DEDL detector. The sample concentration was 10 $mg \cdot mL^{-1}$ and the injection volume was 50 μL. A calibration curve was generated with polystyrene standards of low polymolecularity purchased from Polysciences ($M(g \cdot mol^{-1})$: 2656000; 841700; 320000; 148000; 59500; 28500; 10850; 2930; and 580).

The ^{1}H and ^{13}C NMR spectra of the samples were recorded at room temperature in chloroform ($CDCl_3$) on a Bruker Avance 300 spectrometer.

Electrospray experiments were carried out with a HP-Bruker Esquire-LC Ion-Trap mass spectrometer (Bruker Daltonik GMBH) equipped with an electrospray source ionization (ESI) and a Bruker data analysis software. Twenty microliters of aqueous solution was directly applied in the electrospray interface at a flow rate of 200 μL/min by using a syringe pump (Cole-Parmer Instrument Company). The quantification was based on peak area measurement. Specific $[M - H]^-$ ions of the different products resulting from degradation were isolated for MS−MS fragmentation and unambiguous identification. The solvent is a blend of $H_2O/(CH_3)_2CHOH/ACN$ 10/40/50. The split ratio was 0.05%.

The Karl Fischer titration was performed with a Coulometer Metrohm KF 737 equipped with an Oven Metrohm KF 707 ($T = 150$ °C) under a nitrogen atmosphere (200 mL/min).

The static contact angle of distilled water on the polymer surface was used to evaluate the hydrophobicity by a Digridrop gononiometer. Static contact angles were measured at room temperature. Profiles of sessile drops were characterized using a microscope. Angles were measured with water on various regions of each coating surface.

The SEM was carried out on a JEOL 6460LV microscope equipped with an Oxford INCA 300 X-ray microanalysis. Samples for biocide release were included in a low-viscosity epoxy resin blend (Epo-thin resin, Buehler, Germany). They were polished with a series of grinding (silicon carbide grinding paper P320 to P1200) with water as lubricant. Then the polishing was performed with progressively finer abrasives with two grades of diamond polishing grit suspensions (9 μm and then 3 μm) and then alumina (0.05 μm).The polished specimens needed to be sputter-coated with a thin film of conductive material (such as carbon). Colonized sample was fixed in a glutaraldehyde solution and then washed in a phosphate buffer. Dehydratation was performed in different alcohol/water solutions, and then samples were dried by critical point method. Samples were made metallic with a gold deposit and microscopy pictures were taken with a magnification of 4500 μm under an acceleration voltage of 7 keV. Pictures were taken from secondary electrons.

A cross section of paint films was observed using a Leica DM6000B confocal microscope (Leica Microsystems, Heidelberg, Germany), with the immersion 40× objective. The paint was excited with the 633 nm line of a helium/neon laser, and emission was collected from 650 to 750 nm. Fluorescein was excited with the 488 nm line of argon laser, and emission was collected from 500 to 550 nm. Images were processed using Leica Confocal Software. Paint was observed in green and fluorescein in red.

Analysis of the elements was carried out by EDX analysis using an OXFORD INCA 300 system. To determine their distribution, Smart Map acquisition was used. Smart map performs the simultaneous acquisition of X-ray data from each pixel on the image area. Diuron and tolylfluanid were directly quantified from chlorine and sulfur.[23]

Results and Discussion

Polymer Synthesis and Characterization. The synthesis of copolymer depicted in Figure 1 involved the melt condensation of the PCL and PSA acetate anhydride oligomers. This method was employed by Slivniak to obtain enantiomeric PLA−PSA−PLA triblock copolymers.[16] SEC curves (no shown) prove that product has monomodal molecular weight distribution. The number average molecular weights (M_n), polydispersity indices (DPI), and thermal characteristics of the copolymer are given in Table 2. The values obtained by SEC/polystyrene calibration was in good agreement with the results published by Slivniak for the synthesis of P(LA−SA−LA) copolymers.[16] The polymer composition was determined from the ^{13}C NMR. The ratio of SA to CL in the copolymer is calculated from the ratio of the peak integrations at 36 ppm representing the methylenes next to the anhydride bond for SA monomers (SA_2) and the peak integration at 34 ppm representing the methylene next to the carbonyl for CL monomers (CL_6).

The solubility of the reaction products in chlorinated solvent and not in acetone indicates a uniform product where PCL is incorporated within PSA.[16] PCL alone has good solubility in acetone and chloroform, while PSA as polyanhydrides have a very low solubility in most common organic solvents, except chlorinated solvents.[22] Moreover, the block copolymer can be dissolved in THF, toluene, and xylene. The solubilities of blends of PCL with PSA based on the same ratio used for copolymers were studied. The experimental results indicate that blends of PSA and PCL are only partially soluble in the same solvents.

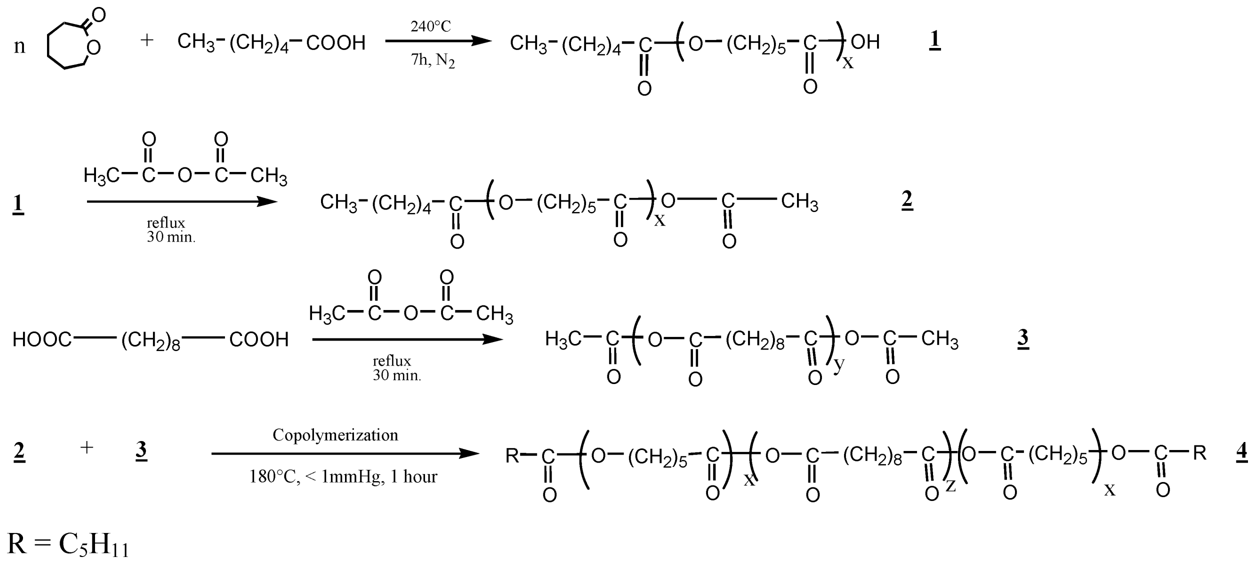

Figure 1. Synthesis of block copolymer.

Table 2. Characteristics of Products

	composition (mol %)	M_n[a] (g/mol)	Ip[a]	yield (%)	T_m[b] (°C)	H_m[b] (J·g^{-1})	IR (cm^{-1})
P(SA−CL)	62−38	9000	1.5	81	49 (PCL) 73 (PSA)	37 (PCL) 36 (PSA)	1725 1748 1810

[a] Determined by SEC in $CHCl_3$, polystyrene calibration. [b] Determined by DSC.

This fact demonstrates that the solubility and film-forming properties of PSA can be improved by the introduction of PCL into the polymer chains.

Blocky structure was confirmed. ^{13}C NMR spectroscopy (Figure 2) confirms that the crude polymer product is a block and not a random copolymer. The possible side reaction of transesterification should result in the formation of mixed sequences and so could be identified by an additional resonance between the PCL and PSA homodiad peaks in the carbonyl region. ^{13}C NMR confirms the absence of any intermediate peaks in this region. Only two peaks are observed at the chemical shifts characteristic of each homopolymer (169 ppm for PSA and 173.5 ppm for PCL). These results are confirmed by DSC analysis. The DSC thermograms (data not shown) show two melting transitions corresponding to a melting transition of each homopolymer. The immiscibility of the two components reflects the blocky character of the copolymer: T_f(PCL) = 49 °C (ΔH_f = 37 J·g^{-1}), T_f(PSA) = 73 °C (ΔH_f = 36 J·g^{-1}) (Table 2).

Hydrophobicity. To evaluate the ability of block copolymer as a binder in antifouling coating, hydrophobicity of polymer was tested. Contact angle measurements were used as simple, sensitive technique for quantifying the hydrophilic/hydrophobic property of a surface. Static contact angle measurements were made between the polymer films and distilled water (Table 3). It can be seen that the static contact angle of poly(ester-anhydride) is intermediate between those of poly(sebacic acid) and poly(ϵ-caprolactone). All were hydrophobic between 74 and 84°, indicating the high hydrophobicity of the studied polymers. This indicates that the hydrophobic segments made from sebacic units and caproyl units are oriented toward the surface to minimize the surface energy and stabilize the polymer−air interface. This result indicates that the block copolymer possesses a higher hydrophobicity than polyandrides based on SA which gave 60−64°.[24]

Capability of Block Copolymer as Binder in Antifouling Paint. The block copolymer is interesting for two reasons: (i) the macromolecular structure is biodegradable, (ii) the respect to solubility in xylene increases the potential use as binder in antifouling paint. To study the use of biodegradable block copolymer, it was blended with biocides and fillers as summarized in Table 1. The result indicates that the copolymer was compatible with paint formulation. The mixing of fillers, additives, and active molecule with the polymer may modify its properties. For example, in the presence of fillers, contact angle with water increases (Table 3). This means that the hydrophobicity of paint coating is reinforced.

In this work, the objectives were to study four known discriminating parameters factors of antifouling efficiency:[3] hydration, hydrolytic degradation, erosion, and biocide release. To evaluate the influence of the formulation, hydration and hydrolytic degradation were studied by comparing the pure polymer (as film) and the corresponding paint. Erosion of paint and biocides release were evaluated only for antifouling coating.

(a) Hydration. Hydration could be considered as the first step of the hydrolysis. The amount of water taken up by the polymer needed to be determined. It was done by two complementary methods (Karl Fisher titration and confocal laser scanning microscopy).

To study hydration, the reference method consists of coulometric Karl Fischer titration by using an oven.[3] The water uptake increased during the first week of immersion to reach a steady state: 2.69 and 4.84% w/w respectively for the pure polymer and the paint film (Table 4). The amount of water in the matrix remained low due to the high hydrophobicity of the copolymer (Table 3). The formulation modified the porosity of the film. The paint is more accessible to water and hydrolytic degradation.

Simultaneously, confocal laser scanning microscopy was performed. It enables visualization of the water uptake in the

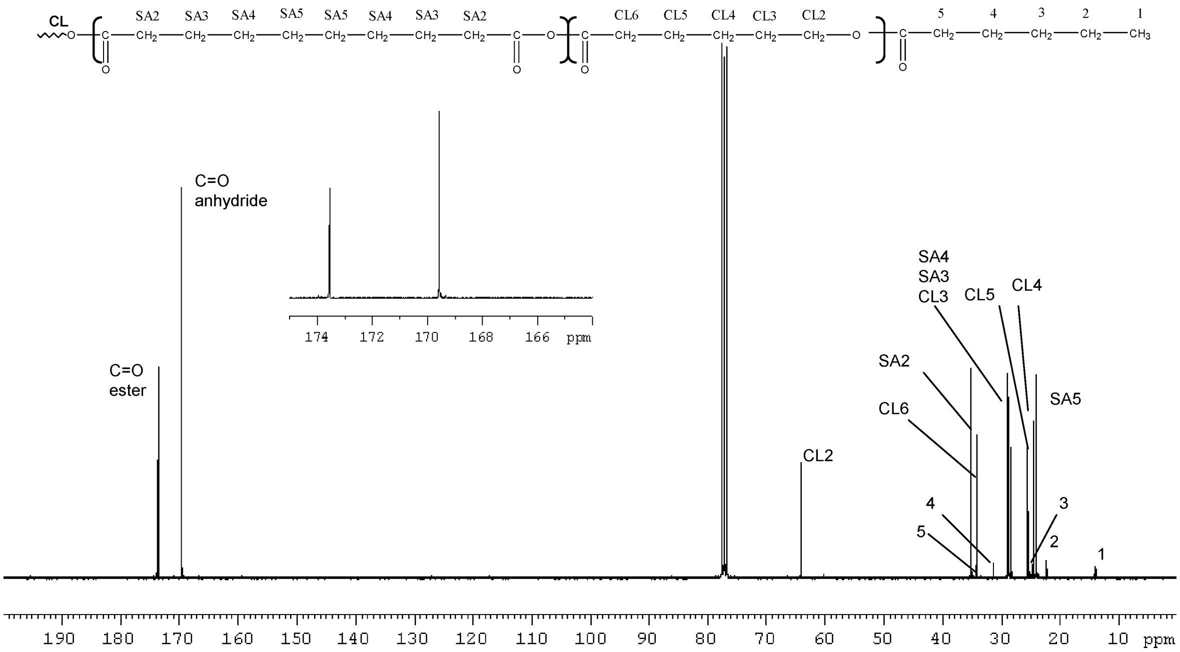

Figure 2. 75 MHz ^{13}C NMR spectrum of the block copolymer.

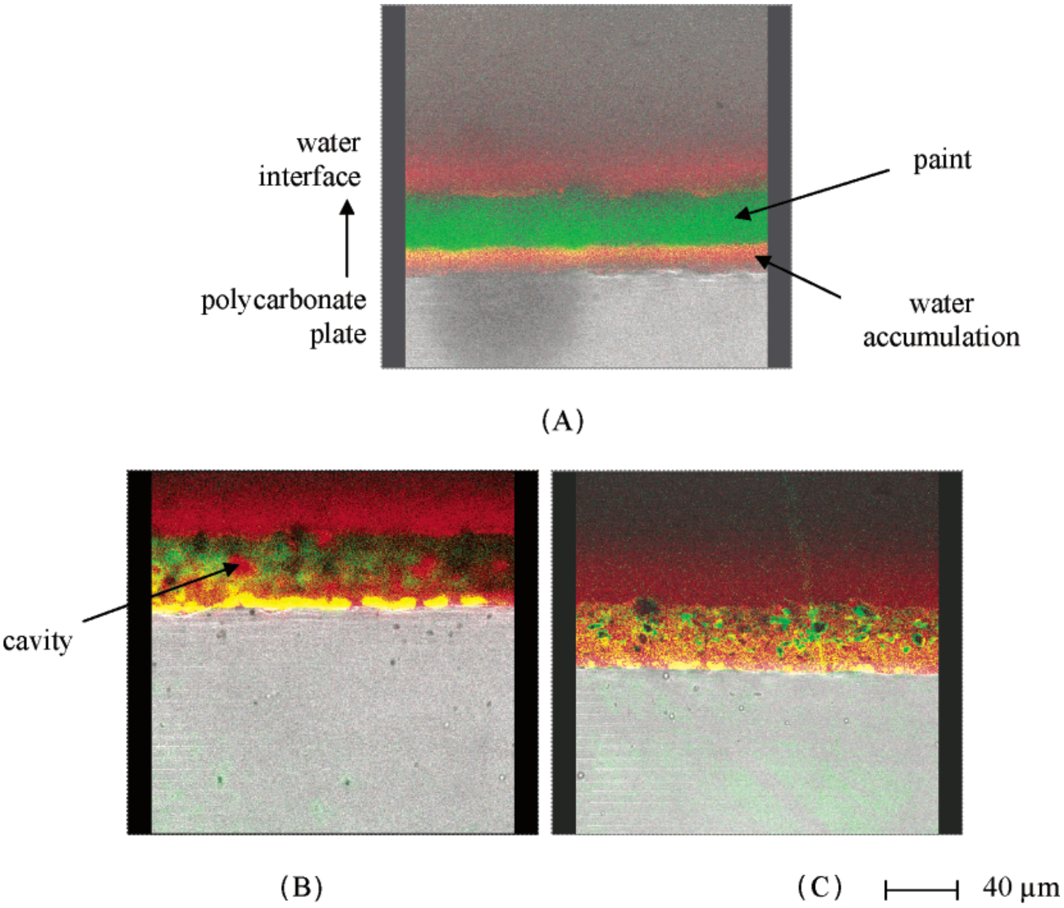

Figure 3. CLSM micrographs of the cross section of paint after 1 week (A), 1 month (B), and 2 months (C) of immersion in demineralized water.

film. The cross section of the film was imaged. Fluorescein was added to water to observe the water absorption in paint. The two components (fluorescein and film) possess different excitation−emission properties. The fluorescence emission can be separated into different channels.

The evolution of cross section during immersion of loaded polymer (in green) was performed (Figure 3A−C). The different photographs revealed an important increase of water (in red) in the thickness of film. In a first time, the water molecules diffuse near the polycarbonate plate: an accumulation is observed after 1 week of immersion (Figure 3A). After this period, many cavities of water are formed (Figure 3C). This can be explained by a hydration−degradation mechanism. The hydration is homogeneous after 2 months.

Table 3. Contact Angle to Water; Standard Deviations Are in Parentheses

polymer	PCL	PSA	block copolymer	paint
water (°C)	84(2)	74(1)	77(2)	112(4)

Table 4. Hydration of Block Copolymer Determined by Karl Fisher Titration; Standard Deviations Are in Parentheses

	water absorption (%)			
	1 week	3 weeks	6 weeks	11 weeks
polymer	2.69 (0.27)	2.65 (0.32)	2.80 (0.35)	2.70 (0.10)
paint	4.84 (0.68)	4.42 (0.88)	4.50 (0.12)	4.80 (0.30)

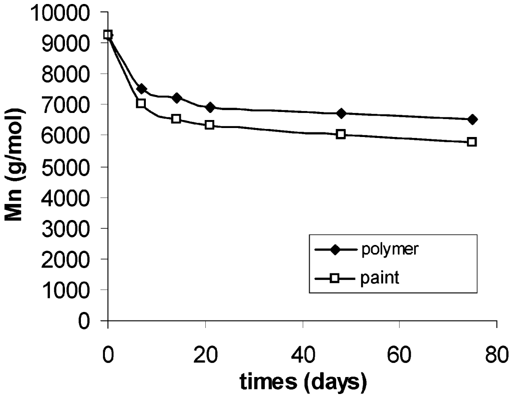

Figure 4. Hydrolysis of copolymer in water at 20 °C monitored by molecular weight decrease (determined by SEC).

(b) Hydrolytic Degradation. The objective was to study the hydrolytic degradation of the poly(ester-anhydride) and to observe the effect of the formulation (presence of bioactive molecules and additives).

The hydrolysis studies were carried out in distilled water at 20 °C. The degradation was monitored by (a) the changes in molecular weight of the polymer by size exclusion chromatography (SEC) and (b) titration of the products resulting from the hydrolysis by ESI-MS. Degradation involves hydrolytic cleavage of anhydride and ester bonds by water. The influence of the formulation was shown by comparing the becoming of the "pure" polymer with the paint.

Figure 4 describes the degradation of both polymer and paint. By comparing the evolution of molecular weight, it can be shown that the loaded copolymer underwent the same degradation as the pure copolymer which kept a M_n of about 6000 g/mol. The presence of fillers (biocides and additives) cannot prevent the hydrolysis of macromolecular chains. Both films (pure polymer and paint) have a two-stage degradation profile: a very rapid hydrolysis of anhydride linkage within the first two weeks, followed by a slower hydrolysis of the remaining poly(ϵ-caprolactone).[25] Results of hydrolysis seem to indicate that the copolymer should indeed be a diblock copolymer because fast hydrolysis of PSA blocks leads to a moderate decrease of M_n. If PSA block was between two PCL blocks, breaking of a bond within the PSA block should at once reduce the molecular weight by a factor of 2.

The titration of the products resulting from the polymer hydrolysis was carried out by ESI-MS spectrometry. At each sampling date, water was collected, analyzed, and replaced to prevent the risk of medium saturation. Figure 5 shows the release profiles of sebacic acid and hydroxycaproic acid through their detection by mass spectrometry in the degradation medium. According to the analysis of the surrounding water, the hydroxycaproic acid is not released (only 0.1% after 80 days of immersion). Nevertheless, the release of sebacic acid was greater but remained weak, about 7%. The different kinetics may be explained by the nature of hydrolyzed functions: ester or anhydride respectively for hydroxycaproic acid and sebacic acid. The anhydride functions are more sensitive to hydrolysis degradation than esters. This suggested that during the first time sebacic acid, a relatively water-soluble component, was released from the matrix, followed by the hydrophobic components of hydroxycaproic acid.

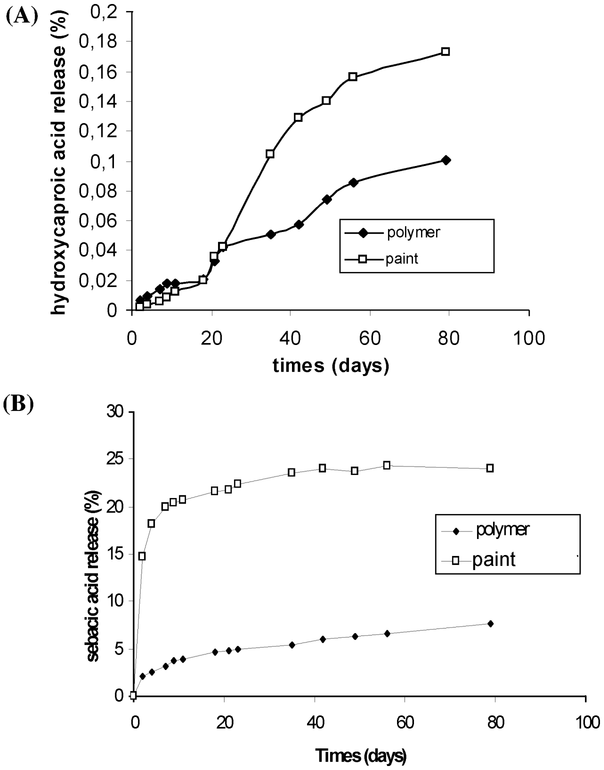

Figure 5. Release of (A) hydroxycaproic acid and (B) sebacic acid from polymer and paint determined by ESI-MS.

The mixing of fillers, additives, and active molecules with the polymer may modify the release profile. It can be seen that the hydrolytic rate of the polymers increases in the presence of fillers. The pure polymer and the paint clearly underwent different aging. Sebacic acid was rapidly released over several days: 20 and 5% of the total content was observed after 10 days for paint and "pure" polymer, respectively. These results confirm that the formulation modified the porosity and permeability of the film: the added molecules increase the water diffusion (Table 4) and the hydrolysis of polymer. Moreover, these results suggest that hydrophobicity is not an essential factor of hydrolytic degradation (Table 3).

(c) Erosion. Scanning electronic microscopy observation (SEM) has been employed for the study of erosion. Erosion is one of the fundamental mechanisms that control the release of actives molecules from antifouling paints. Erosion designates the sum of all processes that can lead to the loss of mass from a matrix including a deletion of the coating. SEM enables determination of the mode of erosion type (surface versus bulk degradation). Morphological changes of copolyanhydrides with different compositions were previously studied by SEM as described by Mathiowitz et al.[26] In the case of surface erosion, the authors characterized two distinct morphologies: the intact (in the core of the cylinder) and eroding zones (cortex). In a previous work, we used SEM to obtain

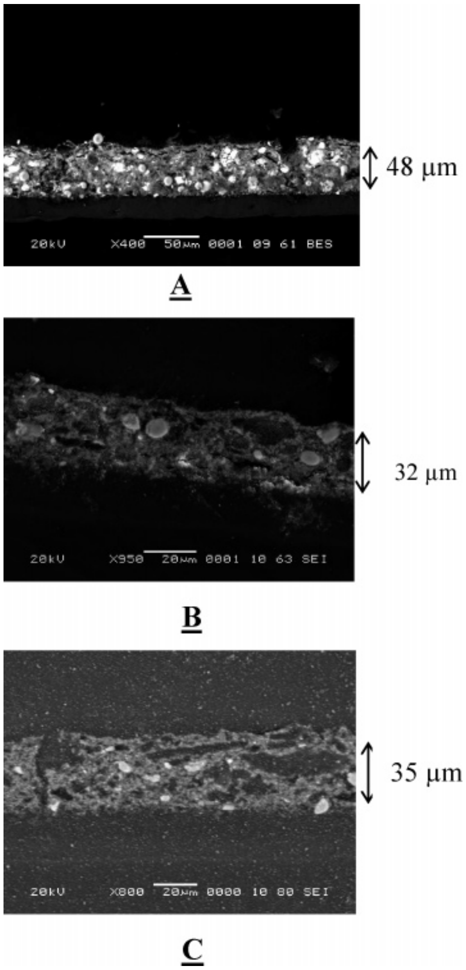

Figure 6. SEM micrographs of the cross section of paint before immersion (A) and after 2 months (B) and 9 months (C) of immersion in demineralized water.

qualitative and quantitative data about erosion of antifouling paint, which was particularly difficult to obtain.[23]

Morphology of the paint cross section was examined by scanning electron microscopy (SEM), which is shown in Figure 6. A series of SEM micrographs were recorded during immersion in demineralized water at room temperature. During the first 2 months of contact with water, changes in the film aspect were not significant. However, an important decrease of thickness film could be observed (40% average after 2 months of immersion) (Figure 6B). After this period, the thickness seemed to be relatively constant (Figure 6C). It is known that matrixes of poly(ester-anhydrides) keep their original shape for a long time even if the erosion front has reached the center of the matrixes.[27] This is due to the crystalline polymer structures such as poly(ϵ-caprolactone) which are resistant to degradation in these degradation conditions.[3] The micrographs enable visualization of the impact of hydrolysis and hydration: many cavities are formed in the entire cross section of the films after several months of immersion (Figure 6C). Previous results were proved that the pores are formed as a result of erosion/degradation and not release of fillers (confirmed by analysis of surrounding water by ESI-MS[4]).

This means that the diffusion of the water molecules and degradation products into the matrix is enhanced. It can be concluded that the polymer follows a bulk and not a surface degradation mechanism. This result can be explained by the initial thickness of the film (48 μm): it was thin enough to consider that after 2 months in an aqueous medium the outer zone was totally eroded. After this period of immersion, the matrix underwent principally erosion of polyester. These results confirm previous results. Kricheldorf and Jürgens suggested that the diffusion of water into the sample with a random hydrolysis over the bulk of the material was the major process in the case of poly(ester-anhydride).[28]

(d) Biocide Release. To determine the release characteristics and mechanisms of biocide release from coating, a study was conducted by employing Diuron (herbicide) and Tolylfluanid (pesticide) as reference biocides. They are hydrophobic and largely used in antifouling coatings. Titration was carried out by determining the leached amount in the surrounding medium by ESI-MS and by quantifying the concentration of molecules that remained in the film by EDX.

Cumulative release profiles of Diuron from paint obtained by ESI-MS analysis show that about 58% of the Diuron was released after 2 months of immersion (data not shown). After this period, the release rate was much slower and then became stationary. This release pattern can be explained by the polymer degradation characteristics described earlier which indicate SA release in the first 10 days. During this time, the anhydride bonds are degraded, releasing SA comonomer. In contrast, the hydrophobic component, CL, entraps the drug and the release rate is slow. These data were confirmed by EDX analysis of the film. It enables quantification of the active molecules retained in the film and leads to their spatial distribution.[23] It presents many others advantages: no limit on the aging conditions (salts amounts, for example), the visualization of the biocides, etc. Figure 7 displays the X-ray maps obtained for both biocides before and during immersion. The percent of released molecules obtained by EDX analysis is also indicated. The Diuron distribution in the cross section of the paint was homogeneous as shown in Figure 7(**1**). In contrast, many clusters were observed in the case of Tolylfluanid: the distribution was inhomogeneous (Figure 7(**3**)). The clusters size can reach the 40 μm length. This result revealed a potential interaction between the Tolylfluanid molecules and fillers added in the formulation. The difference of biocides distributions may also be explained by their initial size distribution which is more important in the case of Tolyfluanid.

The two X-ray maps revealed an important decrease of Diuron concentration in the thickness of paint film, during the immersion (Figure 7(**2**)). The percent of released molecules reached 55% after 2 months. The release of the molecule occurs in the bulk of the film thickness: the diffusion seemed to be effective. For Tolyfluanid, the X-ray map proved that the diffusion is prevented. The molecules implicated in clusters migrated with more difficulty than those dispersed (Figure 7(**4**)). These micrographs reveal that different release rates can be observed following the studied biocides. The diffusion involves different variables (temperature, salinity, pH, solubility of active molecules, etc.).[29] In our case, the difference of release can be explained by a difference of solubility in water (Diuron is more soluble than Tolylfluanid). These results were in agreement with the previously published results concerning commercial paints based on PMMA−PBMA resin.[23]

These results showed that poly(ester-anhydrides) can be used as matrix for the controlled release of biocides from coating. The kinetics of leaching may be modulated by choosing the nature of loading compounds used and makes it possible to maintain protection for many months.

Biodegradable Coating Efficiency. The efficiency of biodegradable coating was studied in seawater (Atlantic Ocean, France). To study the colonization after 3 weeks of immersion

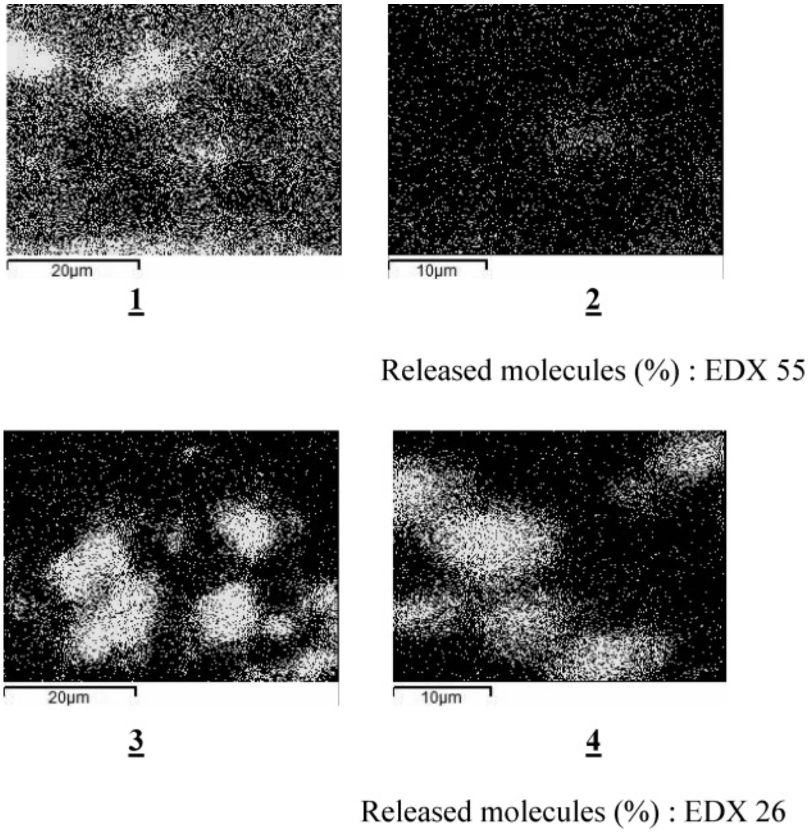

Figure 7. Distribution of booster biocides in the cross section of paints: Diuron before (**1**) and after 2 months (**2**) of immersion; Tolylfluanid before (**3**) and after 2 months (**4**) of immersion.

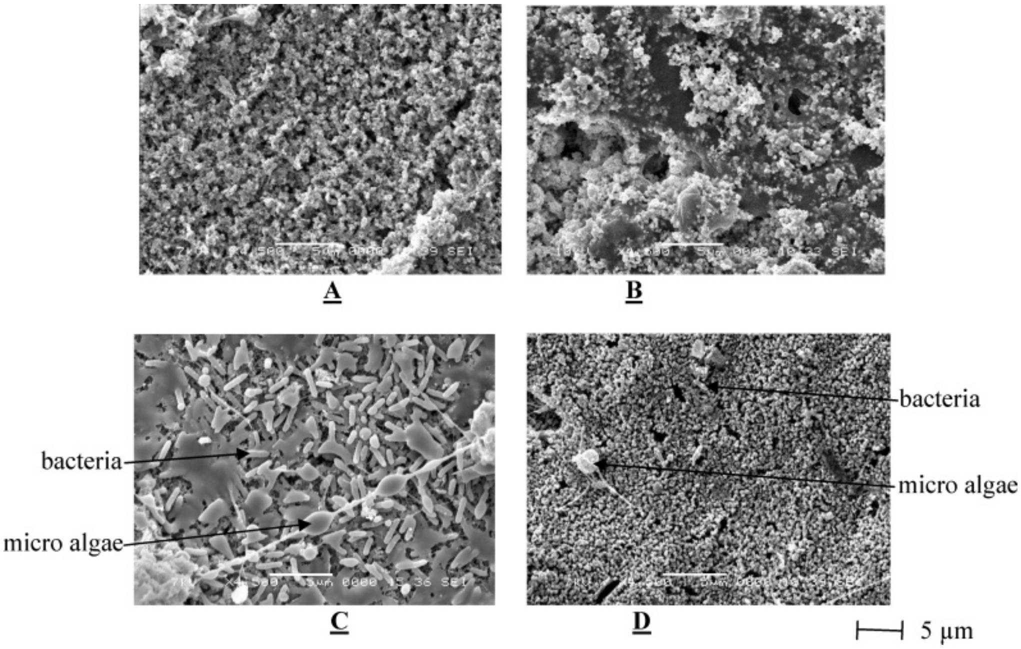

Figure 8. Colonization of coating observed by SEM microscopy after 3 weeks of immersion: (A) PMMA−PBMA paint; (B) TBT paint; (C) paint without antifouling activity; (D) P(SA−CL) paint.

in a natural site, the comparison was made between four paints: two reference commercial paints (PMMA−PBMA paints and TBT paints), a paint without antifouling activity, and a paint based on block copolymer. The reference commercial paints prevented fouling adhesion: the images obtained by SEM after many treatments of dehydration showed a clean surface with few adhered bacteria (Figure 8A,B). The formulation without antifouling properties was rapidly colonized (Figure 8C): bacteria and microalgae were observed. The experimental paint showed good antifouling activity: adhesion of fouling on the coating is limited (Figure 8D).

The biodegradability of these natural coatings was assessed by studying SEM micrographs of the cross section of paint film. Figure 9 shows changes in thickness with time in natural seawater. In the case of block copolymer, the decrease is more significant than for others paints (PMMA−PBMA paints and TBT paints): the sample was completely eroded in 10 weeks. The block copolymer is biodegradable in seawater compared

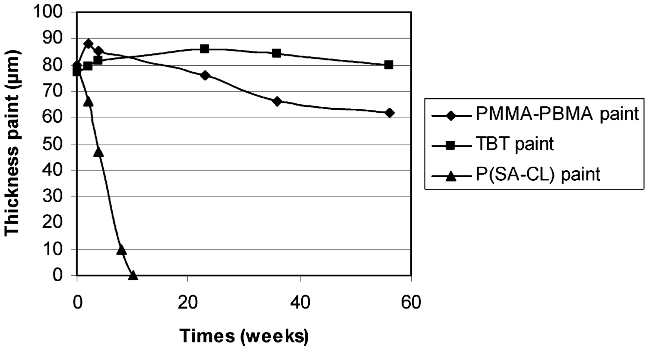

Figure 9. Erosion of paints in natural seawater. The deviation standard is ±3%.

to PMMA−PBMA paints and TBT paints. The extent of erosion can be explained by the influence of enzymatic degradation on block copolymer based on PCL and PSA. Rutkowska et al.[30] and Tjusi and Suzuyoshi[31] had shown that specific conditions of the seawater environment (enzymatic degradation and mechanical stress) are favorable for the degradation of PCL. It is the first time that poly(sebacic acid) was studied in a complex medium such as seawater. Moreover, this result showed that the presence of biocides and fillers cannot perturb the biodegradation of paint in seawater. These results were particularly interesting because the biodegradation in seawater offers a surface ablation of paint.

Conclusion

This work describes the use of block copolymer composed of sebacic and caproyl units as binder in antifouling paints. To achieve controlled release, bioactive molecules and additives were successfully incorporated into copolymer films. Complementary analytical methods (SEC, DSC, SEM, CLSM, EDX, and ESI-MS) were used to discuss the hydration−degradation−erosion process, to quantify the degradation of copolymers, and to estimate the capability of the release of bioactive agent. This polymer has potential use as a binder for antifouling applications. The polymer possesses the essential characteristics for such application: solubility, compatibility with fillers, controlled degradation, and molecules release for several months. The prevention of biofouling settlement and growth was obtained on a natural site. The coating was completely eroded after 10 weeks of immersion, which is too fast. Future works include the development of binders with suitable biodegradation and erosion to maintain efficiency for many months.

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