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Degradation and Controlled Release Behavior of ϵ-Caprolactone Copolymers in Biodegradable Antifouling Coatings

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Copolymers of caprolactone with δ-valerolactone and L-lactide were synthesized by ring-opening polymerization in the presence of tetrabutoxytitane in order to decrease the crystallinity of polycaprolactone (PCL) and to enlarge its potential applications. The kinetics of degradation and controlled release of bioactive molecules were investigated in aqueous medium at room temperature for 9 months. The influence of the comonomer structures, their molar ratio, and the presence of fillers on these kinetics were examined. Complementary analytical methods were used (i) to quantify the degradation of the copolymers by titration of products of degradation (lactic acid, hydroxycaproic acid, and hydroxypentanoic acid) and (ii) to reveal the degradation processes by determination of molecular weights and thermal characteristics. After aging, films were observed by scanning electronic microscopy and EDX microanalysis to check their capabilities for the release of bioactive agent. The results showed that the incorporation of a comonomer such as L-lactide or δ-valerolactone led to a faster degradation than that of PCL homopolymer. The release of biocides could be correlated with the degradation of copolymer but depended on the structure of the leached molecule.

Introduction

Biodegradable polyesters, such as poly(ϵ-caprolactone) (PCL), poly(L-lactide) (PLLA), and poly(hydroxybutyrate) have been intensively investigated as alternatives to more conventional nonbiodegradable or slowly biodegrading synthetic polymers in order to reduce their impact on the environment.[1−8] Among the family of biodegradable aliphatic polyesters, rubberry PCL and ϵ-caprolactone (CL) copolymers have been attracting much attention, because they can be used as matrixes for drug delivery because of their high permeability to various molecules[9,27] and as additives for the improvement of mechanical properties of other brittle biodegradable polymers. Because of its slower degradation (explained by its hydrophobicity and crystallinity),[10,11] PCL may also constitute an interesting polymer for environmental products such as antifouling paints (coatings used to prevent the growth of marine organisms on ships' hulls) or in fertilizer−herbicide encapsulation for which moderate degradation is required. PCL derivatives are biodegradable and assimilated without any harmful effects on the environment.[12,13]

The in vivo and in vitro degradation of aliphatic polyesters has been extensively investigated. The geometry of the devices seems to be essential because of the internal autocatalysis of carboxyl endgroups formed by chain cleavage.[14] In the case of semicrystalline polymers, amorphous regions are preferentially degraded, since water cannot penetrate crystalline zones.[15,16,23,28,29] With respect to in vitro hydrolysis of PCL, there has been a great deal of investigation into the effects of comonomers. It was found that the hydrolysis of PCL was accelerated by the presence of a second monomer.[19,20] The most commonly invoked influencing factors are the copolymer composition, the molecular weight and molecular weight distribution, and the sequence structure of the copolymer.[17,18,26,30,31] More particularly, in the case of lactide, its incorporation enhances hydrolysis of CL copolymers, regardless of monomer unit distribution (random or blocky).[21−23]

The present study reports the effects of the chemical structure, the amount of comonomers, and the presence of fillers on the hydrolysis and controlled release of bioactive molecules of copolymers obtained by ring-opening polymerization of ϵ-caprolactone and L-lactide or δ-valerolactone using tetrabutoxytitane $Ti(OBu)_4$ as initiator. The aims of this work were (i) to check the potential use of the caprolactone copolymers as binders for antifouling paints and (ii) to study their degradation and release kinetics versus many parameters.

Complementary analytical methods were used to monitor the degradation in order to get data about the involved process. In vitro degradation is commonly characterized by techniques including nuclear magnetic resonance (^{1}H NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). To complete the investigation, we developed analytical tools based on mass spectrometry (ESI-MS) and on energy-dispersive X-ray analysis (EDX). The aim was to get data about the degradation process that occurs during immersion.

Experimental Section

Synthesis. Copolymers were synthesized by bulk ring-opening polymerization of ϵ-caprolactone and δ-valerolactone (δ-VL) or L-lactide (L-LA) in different proportions. Tetrabutoxytitane was used as a catalyst and initiator for the copolymerization. Predetermined amounts of monomers were introduced into a round-bottomed flask. After degassing at 240 °C, the initiator was introduced into the flask. Mechanical stirring was performed for 30 min to homogenize the

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Table 1. Composition of Varnishes and Paints (wt %)

composition	varnishes	paints
polymer	50	16.3
solvent	50	40
Fillers		
Diuron B1		5.3
Cuprous oxide B2		10
Tolylfluanid		4.2
additives[a]		24.2

[a] Titanium oxide, zinc oxide.

mixture. Polymers were recovered by the dissolution/precipitation method with dichloromethane as the solvent and heptane for δ-VL and cool methanol for L-LA as the nonsolvent.

Preparation of Specimens. To evaluate the capability of the copolymers for hydrolysis, varnishes and paints were formulated with all these polymers. Varnishes contain equal weights of copolymer and diluting agent (xylene). Paint films were formulated by adding fillers (biocides and additives) following the composition detailed in the Table 1. The blend used is based on a simplified commercial formulation of paint. All the ingredients were dispersed under vigorous agitation (2000 rpm) for 1 h. Then, the solutions were filtered through a 100-μm filter. A layer of coating was deposited with an automatic film applicator (ASTM D823 Sheen instrument) on a polycarbonate support. The varnishes and paint films were dried at 20 °C until they achieved constant weight.

Hydrolytical Degradation. For degradation studies, all specimens possess the same dimensions (7 cm × 7 cm × 60 μm). Each specimen was immersed in a vial filled with 250 mL of distilled water. Degradations were studied at 20 °C. At each degradation time, three replicates of each specimen were withdrawn from the degradation medium. The degradation of copolymers was monitored by GPC for all specimens (varnishes and paints with all the compositions). DSC and Karl Fischer titration were used for evaluation of paints with different compositions during immersion. Analysis of the solutions of each specimen (varnishes and paints with all the compositions) were performed using ESI-MS. The immersion times varied from 1 day to 9 months.[24] The study of erosion and biocide release followed by ESI-MS, SEM, and EDX was carried out for two paints formulated with P(CL−VL) 83/17 and P(CL−LA) 83/17 copolymers.

Measurements. The molecular weights of the polymers after different hydrolysis times were determined by gel permeation chromatography with a Merck pump L-7110 and a column PL gel (mixte D, 5 μm) from polymer laboratories and a Sedex DEDL detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min, and the injection volume was 50 μL. A calibration curve was generated with polystyrene standards (580; 1180; 2360; 4490; 9920; 19 700; 46 500; 96 000; 188 700; 377 400 g/mol) purchased from Polysciences. Partially degraded films were air-dried, at room temperature, for 24 h before GPC measurement.

Differential scanning calorimetry (DSC) analyses were performed on a DSC-2010 TA instrument under nitrogen atmosphere. The samples were scanned from −80 to 80 °C with a heating rate of 10 °C/min, then cooled to −80 °C (3 °C/min), and scanned again from −80 to 80 °C with a heating rate of 10 °C/min. The melting temperature (T_m) was taken as the summit of the melting peak and the melting enthalpy (ΔH) was calculated from the area of the endothermic peak after the second run.

To identify and quantify the products resulting from the hydrolysis, an Agilent technologies Series 1100 instrument comprising a vacuum degasser, an Esquire-LC pump, and an autosampler (Hewlett-Packard) was used. Aqueous solution (20 μL) was directly applied in the electrospray ionization ion trap mass spectrometer without a column. The quantification was based on peak area measurement. The $[M - H]^-$ ions were isolated for the MS-MS fragmentation: m/z are 131, 117, 89, and 231, respectively, for hydroxycaproic acid, hydroxypentanoic acid, lactic acid, and Diuron (*N*′-(3,4-dichlorophenyl)-*N*,*N*-dimethylurea). The solvent consists of H_2O/CH_3CN 50/50 (v/v) containing 0.04% of ammoniac. The split ratio was 0.05%.

Paint plates were immersed in water. Pieces of films were cut off in order to quantify the amount of water present in the film by Karl Fischer titration. A coulometer Metrohm KF 737 equipped with an Oven Metrohm KF 707 ($T = 150$ °C) was used under a nitrogen flow of 200 mL/min. The reactant was Hydranal-Coulomat AG.

SEM was carried out on a JEOL 6460LV microscope equipped with an Oxford INCA 300 X-ray microanalyzer. Samples have been incorporated into a low-viscosity epoxy resin blend (Epo-thin resin, Buehler, Germany). They have been polished by a series of grinding (silicon carbide grinding paper P320 to P1200) with water as the lubricant. Then, the polishing was performed with progressively finer abrasives with two grades of diamond polishing grit suspensions (9 μm and then 3 μm), then alumina (0.05 μm).The polished specimens needed to be sputter-coated with a thin film of conductive material (such as carbon).

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 was directly quantified from chlorine.[25]

Results and Discussion

Synthesis and Characterization of Copolymers. The synthesis of copolymers depicted in Figure 1, involved the reaction of L-lactide or δ-valerolactone with ϵ-caprolactone by ring-opening polymerization in bulk with tetrabutoxytitane as the initiator and catalyst. The number average molecular weights (M_n) and polydispersity indices DPI of these copolymers obtained by GPC are given in Table 2. The copolymerizations with different molar ratios were realized, and the data are shown in Table 2. ^{1}H NMR spectroscopy was used to determine the composition of the copolymers by integration of the VL methylene (4 ppm) or LA methane (5, 15 ppm) and CL methylene (1, 3 ppm) peaks. Note that in all these cases the

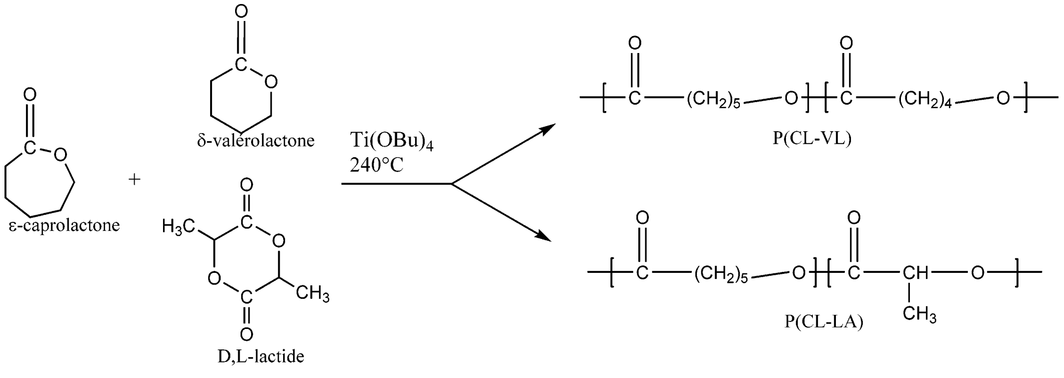


Figure 1. Synthesis of copolymers poly(ϵ-caprolactone−δ-valerolactone) and poly(ϵ-caprolactone−L-lactide).

Table 2. Characterization of Copolymers

	composition (CL, mol %)			
polymers	feed	copolymer	M_n[a]	DPI
P(CL−VL)	85/15	87/13	23 800	1.6
	80/20	83/17	21 700	1.7
	70/30	73/27	22 800	1.9
P(CL−LA)	90/10	88/12	23 300	2.0
	85/15	83/17	25 000	2.1

[a] Determined by GPC, calibration with PS standards.

Table 3. Thermal Characteristics of Polymers and Paints

	polymers			paints		
	T_g[a] (°C)	T_m (°C)	ΔH (g/J)	T_g (°C)	T_m (°C)	ΔH (g/J)
			P(CL-VL)			
87−13	−60	45	55	−46	34	25
83−17	−60	47	40	−42	37	10
73−27	−60	28	65	−51	17	17
			P(CL-LA)			
88−12	−53	36	38	−49	27	9
83−17	−56	30	34	−54	18	10

[a] Glass transition temperature of homopolymers: $T_{gPCL} = -60$ °C; $T_{gPVL} = -62$ °C; $T_{gPLA} = 45$ °C.

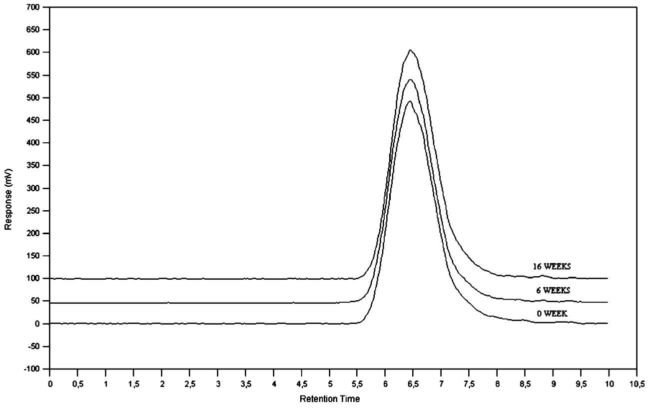


Figure 2. Chromatograms obtained by GPC in THF (flow rate 1 mL/min) for a P(CL−VL) 83/17 copolymer paint before and after its immersion during 6 and 16 weeks.

final ratio is near the initial ratio. All of the copolymers are semicrystalline, exhibiting both glass transition temperature (T_g) and melting temperature (T_m) lower than those of the PCL homopolymer ($T_{mPCL} = 60$ °C; $\Delta H = 60$ J/mol) (Table 3). By adding VL or LA units, the crystallinity of the copolyesters is reduced. For example, T_m is equal to 47 and 30 °C and the melting enthalpy to 40 and 34 J/mol for P(CL−VL) and P(CL−LA) 83/17, respectively. The presence of comonomer perturbs the organization of PCL chains as was expected. In all the cases, T_g increased after preparation of the paint.

Chain structures of the copolymers have been investigated by using ^{13}C NMR spectra (not shown). Poly(ϵ-caprolactone-*co*-L-lactide) has a more alternating structure than poly(ϵ-caprolactone-*co*-δ-valerolactone), which is blocky.

Molecular Weight Changes. As shown by Figure 2, the chromatograms obtained by GPC before and after immersion during 6 and 16 weeks do not reveal any significant changes in the molecular weight of the studied copolymer based on P(CL−VL). Both copolymers P(CL−VL) and P(CL−LA) formulated in varnishes or paint films lead to similar results: The macromolecular chains seem not to be affected by hydrolysis. Their length and distribution are quite stable during the aging.

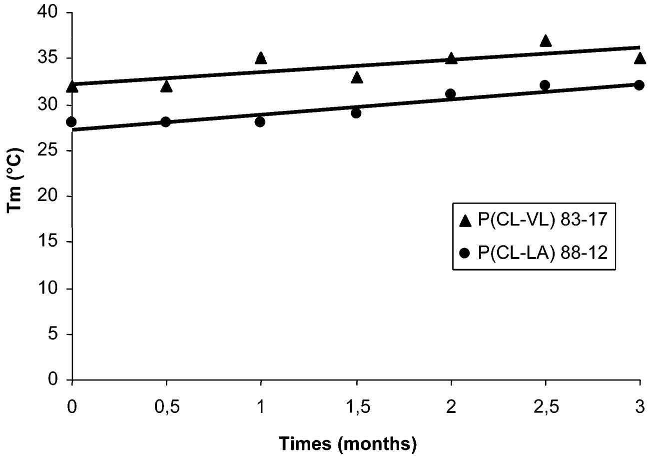


Figure 3. Variations of the melting temperatures of copolymers formulated as paints vs different times of degradation. T_m values were obtained by DSC measurements.

Table 4. Water Uptake of Paints during Immersion[a]

	3 days	1 month	3 months	5 months
		P(CL−VL)		
87/13	4.45 (0.67)	4.69 (0.95)	5.4 (0.70)	5.7 (0.40)
83/17	4.16 (0.65)	4.13 (0.09)	4.65 (0.05)	5.12 (0.32)
73/27	6.39 (0.36)	6.29 (0.12)	7.3 (0.36)	8.7 (0.01)
		P(CL−LA)		
88/12	3.71 (0.41)	4.2 (0.95)	4.8 (0.23)	5.18 (0.13)
83/17	3.56 (0.42)	3.76 (0.03)	5.3 (0.51)	7.4 (0.25)

[a] The hydration levels were determined by Karl Fischer titration. The standard deviation is in brackets.

Thermal Properties. The determination of the glass transition temperature of paints was quite difficult because of the presence of fillers and biocides in large amounts in the formulation that hid this transition. Nevertheless, the melting point was still visible, so this thermal characteristic was checked in order to point out a potential macromolecular reorganization during immersion of the binders. Figure 3 shows the melting temperature of two copolymers formulated as paints before and after 3 months of immersion. In the two cases, the experimental data indicate a slight shift to a higher temperature with degradation time. This result may be explained by the growth of crystalline regions by hydration which increases the available space between chains for movement. Nevertheless, because of the precision of the measurement ($T \pm 3$ °C), these results need to be confirmed over a longer period of immersion, especially as the melting enthalpy values keep being constant and for example are equal to 40 J/mol for P(CL−VL) 83/17.

Water Absorption. Water uptake is the first phenomenon that occurs when polymeric materials are placed in an aqueous medium. Generally, it reflects its bulk hydrophobicity. In this study, water uptake of paint films was determined by Karl Fischer titration. The main experimental results are presented in Table 4.

Both polymers P(CL−VL) and P(CL−LA) exhibited a real hydrophobicity: Their water uptake remained less than 10% after 5 months of immersion, respectively, 8.7% and 7.4% for P(CL−VL) 73/27 and P(CL−LA) 83/17. The incorporation of increasing comonomer amounts favored the water penetration: After 5 months, the water amount was 5.7% for P(CL−VL) 87/13, whereas it reached 8.7% for P(CL−VL) 73/27. Similar results were obtained in the case of P(CL−LA). Both polymers exhibited similar hydration kinetics: The main water uptake takes place during the first 3 days of immersion. After this

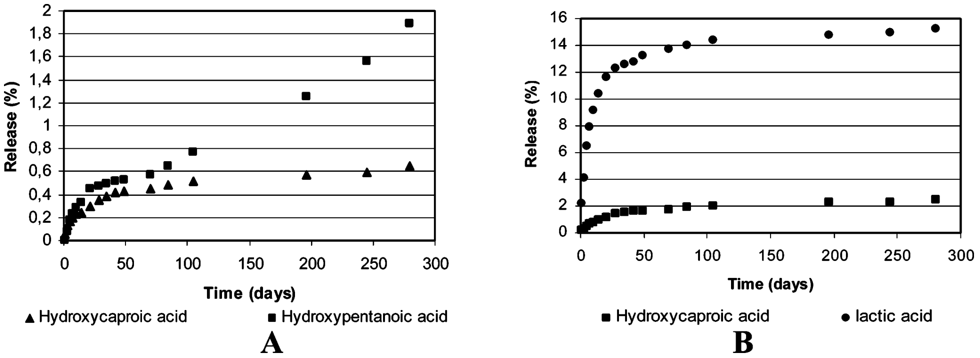


Figure 4. Release kinetics of hydroxycaproic, hydroxypentanoic, and lactic acids determined by ESI-MS analysis: (A) P(CL−VL) 83/17, (B) P(CL−LA) 83/17 in varnishes.

period, the hydration increases regularly to reach a constant value after 6 months of aging.

The effect of the fillers was not significant in the case of the two studied copolymers: Paints and varnishes possess similar hydration kinetics.

Release of Monomers. *(A) Effects of the Comonomer Structure and Distribution on Hydrolysis.* Hydrolysis of binders was studied by the titration of released molecules resulting from degradation in the surrounding water. For the two studied polymers, the molecules of interest are hydroxycaproic acid, hydroxypentanoic acid, and lactic acid. Figure 4 presents the amount of degradation products in water at 20 °C versus the immersion time. The developed analytical method based on ESI-MS was confirmed to produce reproducible data: Its standard deviation was <5%. In the case of P(CL−VL), whatever the composition, the degradation is very low: Only 0.6% and 0.5% of hydroxypentanoic acid and hydroxycaproic acid, respectively, was hydrolyzed after 3 months of immersion. The amount of VL detected (2%) was slightly higher than the amount of CL. This result may be explained both by the structure of the copolymer and by the distribution of comonomer in the macromolecular chains. Furthermore, the P(CL−VL) possesses a blocky structure. The data enable us to hypothesize that the PVL blocks are preferentially degraded and lead to a larger amount of VL in the surrounding water. These data correlated with those obtained in a previous study:[34] The number of carbon atoms in the side chain of the lactone monomers determined the hydrophobicity of the polymers, which was not favorable for water penetration causing degradation. Nevertheless, the degradation is limited by the remaining crystallinity of the copolymer.

In the case of P(CL−LA), the degradation happens more rapidly: 14% of the lactic acid is hydrolyzed after 3 months. PLA is well-known for its rapid degradation.[8,14] As shown in Figure 4, lactic acid is released more rapidly than hydroxypentanoic acid: The data may be explained by the higher hydrolyzability of lactic acid unit sequences and the higher solubility in water of lactic acid. The degradation is driven by the number of lactic acid units in the copolymer, with hydroxycaproic acid units being the more hydrophobic part. Thus, the rate of hydrolysis and release of lactic acid molecules in the aqueous phase can be modulated by variation of the molar ratio of hydrophobic monomer units. ^{13}C NMR spectra have shown that the distribution is random. By comparing GPC, DSC analysis, and ESI-MS titration, it is possible to hypothesize that the degradation occurs preferentially at the chain ends. The hydrolysis of P(CL−LA) 83/17 copolymers (14% of lactic acid units after 3 months) does not lead to a change of the molecular weight of macromolecular chain and thermal properties (T_m and mean molecular weights keep being constant).

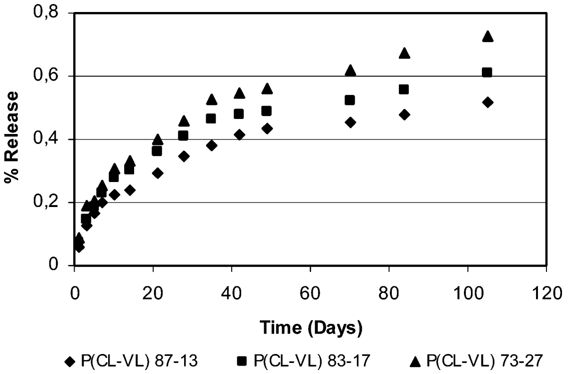


Figure 5. Release kinetics of hydroxycaproic acid for various compositions of the P(CL−VL) copolymer varnishes determined by ESI-MS analysis.

(B) Effect of the Composition on Hydrolysis. Three copolymers having caprolactone/valerolactone molar ratios of 87/13, 83/27, and 73/27 with the same molecular weight (20 000 g/mol determined by GPC with a polystyrene calibration) have been examined. The release of hydroxycaproic acid at 20 °C is detailed in Figure 5. The degradation of the copolymer with the highest amount of valerolactone (P(CL−VL) 73/27) was the fastest. These results were in good agreement with the previously published results concerning P(CL−VL) degradation.[34] In the case of P(CL−LA) copolymers, similar results were obtained with 1.2% and 2.4% of hydroxycaproic release for P(CL−LA) 88/12 and 83/17, respectively.

The incorporation of increasing amount of comonomer (VL or LA) in PCL leads to the reduction of crystallinity and enhances the degradation process.

(C) Effect of the Fillers on Hydrolysis. The impact of fillers on hydrolysis rate was studied by quantifying the degradation products released from paints during immersion. Figure 6 compares the experimental data obtained for the copolymers formulated as varnishes and paints. The presence of fillers in the formulation (biocides, cuprous oxide, titanium oxide, zinc oxide) prevents the release of degradation products in the surrounding water: For example, for P(CL−LA) 83/17 copolymer, after 250 days of immersion, 15% and 10% of lactic units are hydrolyzed, respectively, in varnish and in paint. The data may be explained by (i) a reduced degradation resulting from a reduced accessibility of ester linkages due to interactions with fillers or (ii) a reduced release of the degradation products which are imprisoned in the film by interactions with fillers. At the moment, the obtained data do not enable us to choose one explanation or another. From the point of view of the coating, this result is particularly interesting. It underlines the possibility of modulating the film dissolution by modifying its composition.

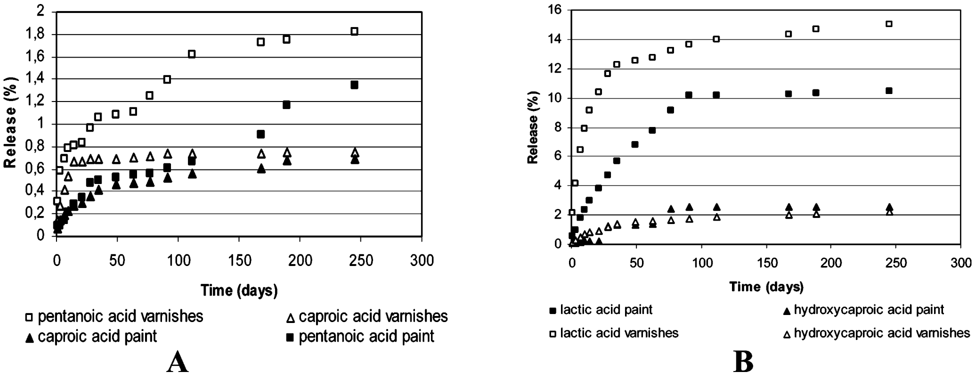


Figure 6. Effect of the fillers on the hydrolysis: (A) P(CL−VL) 83/17, (B) P(CL−LA) 83/17 in varnishes and paints.

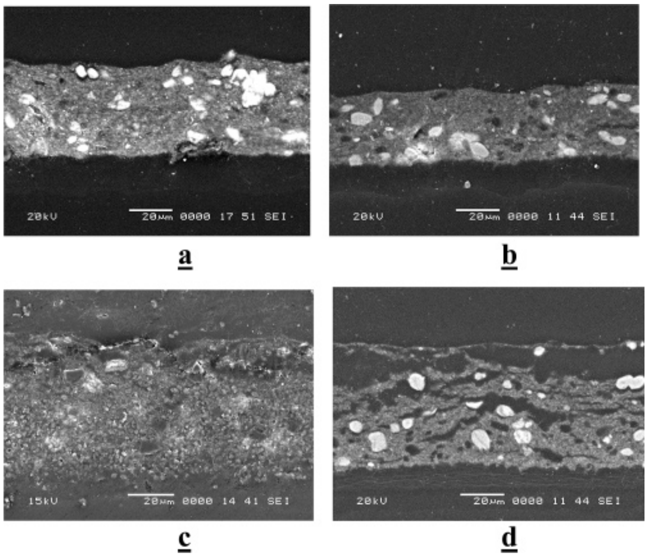


Figure 7. SEM micrographs of paint film cross-sections of P(CL−VL) 83/17 (a) before immersion, (b) after 5 months of immersion; P(CL−LA) 83/17 (c) before immersion, (d) after 5 months of immersion.

Scanning Electron Microscopic Observation. 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 active molecules from degradable polymer matrixes. Erosion designates the sum of all processes that can lead to the loss of mass from the matrix, including a deletion of the coating. A series of SEM micrographs were recorded during immersion. It enables us to study the effect of erosion type (surface versus bulk degradation). In Figure 7a−d, the cross-sections of paint films from P(CL−VL) 83/17 and P(CL−LA) 83/17 copolymers can be visualized. They were found to be relatively heterogeneous with numerous micro-domains of biocides whose sizes can reach about 10 μm. During the first 5 months of contact with aqueous media, significant changes in the film aspect can be observed. The decrease of paint thickness indicates the erosion of binder, which is more important in the case of P(CL−LA). These polyester copolymers are known to follow a bulk degradation mechanism.[8−14] The micrographs enable us to visualize the impact of hydration and hydrolysis and confirm previous results: Many cavities are formed in the entire cross-section of the films for both copolymers, including at the surface of the polycarbonate plate. The degradation of P(CL−LA) is more important than that of P(CL−VL).

In Vitro Release of Bioactive Compound. The evolution of toxicant distribution during immersion was performed using two complementary methods. To study the compositional changes, the reference method used consists of the spectrometric analysis (ESI-MS) or inductively coupled plasma (ICP) analysis of the surrounding water to quantify the amount of released molecules. Simultaneously, EDX analysis was performed. It enables us to quantify the active molecules retained in the film. It presents many other advantages: no limit on the aging conditions (for example salts amounts) and the visualization of the biocide distribution.

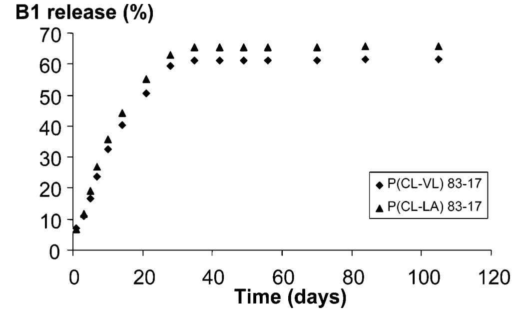


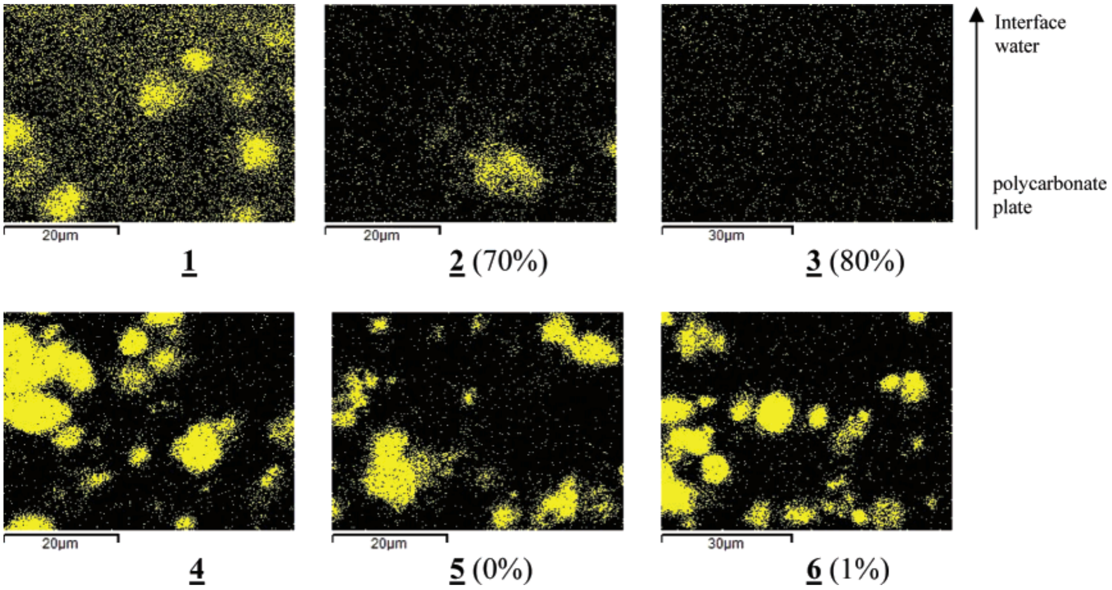
Figure 8. Release of biocide B1 for two copolymers P(CL−VL) 83/17 and P(CL−LA) 83/17 formulated in paint.

(A) ESI-MS and ICP Measurements. Two biocides (dimethylurea B1 and cuprous oxide), which have good antifouling properties, were chosen as model molecules. The release kinetics were similar for both copolymers: About 60% of the biocide B1 was released after 35 days of immersion (the standard deviation was not more then ±5%). This biocide release from the paints followed typical biphasic kinetics, i.e., a fast release at the beginning and then slowing to reach a constant value (Figure 8). Moreover, copolymer composition (relative amounts of comonomers) had no significant effect on biocide release (data not shown).

In the case of the cuprous oxide (data not shown), the experimental curves obtained by ICP for all the binders showed that the release rate could be considered nearly zero. Its release was limited to 1% of the total mixed amount because of its poor solubility in water.

(B) EDX Analysis. We have previously shown that microanalysis is a powerful tool for the study of antifouling paint.[25] In comparison to conventional microanalysis, the EDX analysis can be carried out directly on paint film and determines the amounts of all the elements in a single analysis. It is a powerful tool to study the filler distribution and more precisely the effect of the formulation on this distribution.

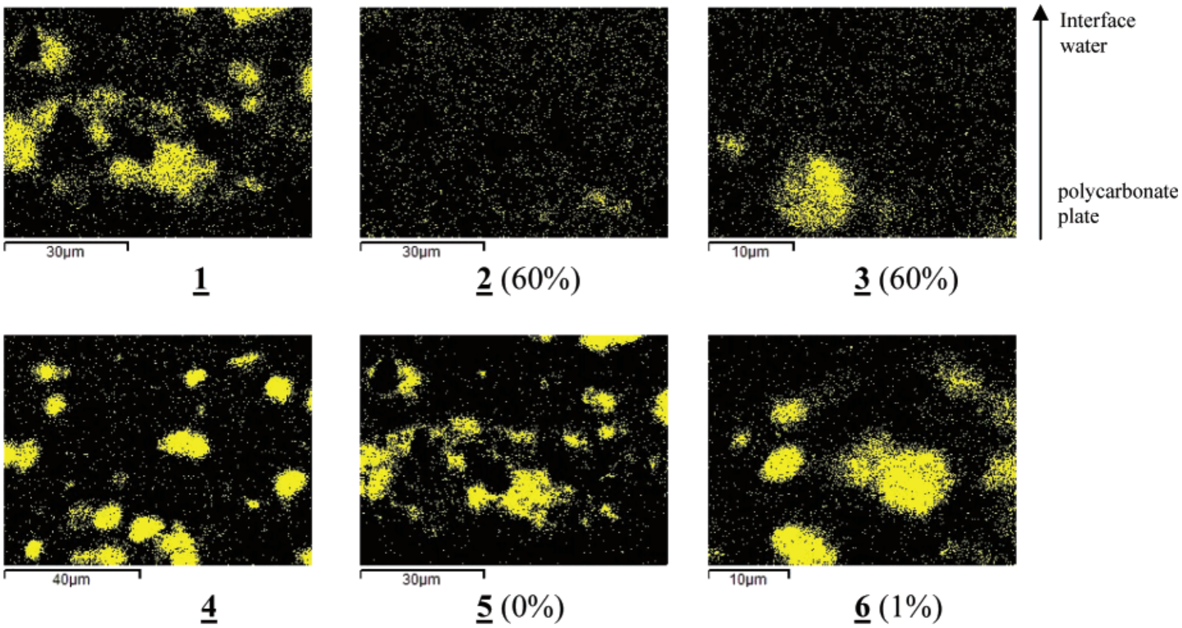
Among the different mixed fillers, biocides are the most interesting because of their contribution to antifouling activity. Copper is widely used for its bactericidal property and its moderating effect on erosion. It is a key product in an antifouling formulation, but its actual function remains unknown.



1 **2** (70%) **3** (80%)

4 **5** (0%) **6** (1%)

Figure 9. B1 distribution in the cross-section of P(CL−VL) 83/17 paint after different times of immersion: (1) $t = 0$; (2) $t = 2$ months; (3) $t = 5$ months. B2 distribution in the thickness of P(CL−VL) 83/17 paint after different times of immersion: (4) $t = 0$; (5) $t = 2$ months; (6) $t = 5$ months. The percentage values correspond to the released molecules determined by EDX.



1 **2** (60%) **3** (60%)

4 **5** (0%) **6** (1%)

Figure 10. B1 distribution in the thickness of P(CL−LA) 83/17 paint after different times of immersion: (1) $t = 0$; (2) $t = 2$ months; (3) $t = 5$ months. B2 distribution in the thickness of P(CL−LA) 83/17 paint after different times of immersion: (4) $t = 0$; (5) $t = 2$ months; (6) $t = 5$ months. The percentage values correspond to the released molecules determined by EDX.

Film porosity and texture, which are dependent on the filler loading and also the variation in particle size and shape, are known to be important controlling factors.[32,33] The pigment volume concentration (CPV) of an antifouling paint is often allowed to vary within a certain range. If the critical pigment volume concentration (CPVC) is exceeded, there is insufficient binder to fill out the space among the fillers, leading to a porous film. On the other hand, the CPV must be high enough to ensure that some particles are in contact with other particles. The SEM micrographs of paint surfaces (data not shown) showed that there was enough paint vehicle to fill the interstices between the particles: The CPVC was not reached. Furthermore, the CPV could be considered a constant in the formulations. In such conditions, the sole factor capable of changing the paint texture was the biocide distribution.

The different X-ray maps revealed an important decrease of biocide B1 concentration in the thickness of paint film, during the immersion. The percentage values of released molecules reached 75% and 60% after 5 months, respectively, for P(CL−VL) and P(CL−LA) polymers (Figures 9 and 10). The release of the molecule occurs in the totality of the film thickness: The diffusion seemed to be effective until the period of immersion. No front of release or dissolution can be observed.

These data confirmed the titration realized by the ESI-MS. The calculated percents determined by the two methods were similar: For example, after 2 months of immersion, for P(CL−LA) 83/17, the ratio of released molecules was, respectively, 0.60 and 0.63 by EDX analysis and ESI-MS.

The trends for cuprous oxide release are different: No significant leaching can be observed for both polymers (Figures

9 and 10). The release can be neglected: Less than 1% of released molecules were determined by EDX analysis. This also confirms the data obtained by ICP analysis.

Conclusions

Biodegradable polyesters can be considered as alternatives to more conventional non-biodegradable synthetic polymers in order to prevent major environmental pollution. Among the family of biodegradable aliphatic polyesters, PCL and ϵ-caprolactone (CL) copolymers are particularly attractive because of their numerous potential applications. As an example, PCL may constitute an interesting polymer for the development of environmental products such as antifouling paints.

Copolymers of L-lactide/ϵ-caprolactone and δ-valerolactone/ϵ-caprolactone were synthesized with different compositions using $Ti(OBu)_4$ as initiator. This article described the main characteristics of these copolymers during hydrolytic degradation. Complementary analytical methods (GPC, DSC, SEM, EDX, ESI-MS, ICP) were used to discuss the degradation process, to quantify the degradation of copolymers, and to estimate the capability for release of the bioactive agent. The hydrolytical properties of the copolymers were affected by the incorporation and composition of comonomer. L-Lactide or δ-valerolactone led to a faster degradation than PCL homopolymer. Nevertheless, this hydrolysis depends on the comonomer structure: The lactide copolymer undergoes an important degradation (14% of hydrolyzed groups for 3 months of immersion), whereas the P(CL−VL) degrades weakly (less than 1% of hydrolyzed groups for 3 months of immersion). For both copolymers, the degradation occurs at the end of the macromolecular chains: No variation can be observed in molecular weight and thermal characteristics. The release of biocides can be correlated with the degradation of copolymer but depends on the structure of the leached molecule and more particularly its solubility in water.

The potential use of CL copolymers in antifouling paints was also examined. The selected polymers possess the different essential characteristics for such application: solubility in common aromatic solvents, compatibility with fillers, controlled degradation, and molecule release. Different coatings were formulated and tested on a natural site. The prevention of biofouling settlement and growth was obtained for more than 1 year.

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