

Control of Hydration and Degradation Properties of Triblock Copolymers Polycaprolactone-*b*-Polydimethylsiloxane-*b*-Polycaprolactone

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ABSTRACT: The objectives of this study are to observe the effects of the introduction of polydimethylsiloxane (PDMS) on the hydration and degradation of aliphatic polyesters in water, such as poly(ϵ -caprolactone) (PCL). The mechanism of PCL degradation in water is well known, and PDMS is a nonbiodegradable and hydrophobic polymer. The ligation of these two polymers should allow the synthesis of new polymers with hybrid properties in terms of degradation and surface energy. The deterioration in water should be controlled by the ratio of each polymer. The triblock copolymers were synthesized through ring opening polymerization with stannous octanoate as the catalyst. A film of each copolymer was prepared and immersed in distilled water to study their aging. Kinetic results of hydration and degradation show that the addition of PDMS on PCL does not change the profiles of hydration and degradation. But the variation of the structure of the triblock (molecular weight or ratio of each block) allows to increase or decrease the rate of hydration, so as to control its degradation. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40431.

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INTRODUCTION

Biodegradable polymers such as aliphatic polyester have been the subject of intensive researches^{1,2} over the few past decades due to their prospective utilization in environmental and biomedical applications.^{3,4} Poly(ϵ -caprolactone) (PCL) was one of the earliest polymers synthesized by the Carruthers group in the early 1930s⁵ and is one of the most used because of its low price, and its many interesting properties. It is a nontoxic, hydrophobic, and semi-crystalline polymer with a low glass transition that explains its compatibility with a large variety of polymers. PCL can be prepared by ring opening polymerization (ROP).⁶ The biodegradation of aliphatic polyesters in water is well known. The first step is a random hydrolytic ester cleavage autocatalyzed by carbonyl end groups of the polymer chains. The second step depends on the molecular weight and the presence of some microorganisms.^{7–10} Generally, amorphous parts are preferentially degraded because the water can penetrate inside. The water access to the ester bonds is determined by the combined effect of the hydrophobicity, the molecular weight, and the crystallinity.^{11,12} Thus, the degradation of PCL in water is much slower than for other aliphatic polyesters (poly(lactic acid) or poly(glycolic acid)), due to its high hydrophobicity and its high crystallinity. Moreover, Jenkins and Harrison¹³ have shown that the molecular weight of the

PCL chains has an influence on the crystallization kinetic of the polycaprolactone.

Current research has been focused toward modifying existing biodegradable polymers by copolymerizing them with other nontoxic polymers to change their properties and enhance their potential applications.^{14–17}

Organosilicon polymers possess some excellent properties. Polydimethylsiloxane (PDMS), the most important organosilicon in terms of commercial application and the least expensive, has intriguing properties such as high thermal and electric stability, resistance to oxidation and moisture, very low surface energy,^{18–20} and low toxicity.²¹ Nevertheless, the degradation of PDMS occurs under specific conditions (inert atmosphere, under vacuum, high temperature) to form cyclic oligomers.^{22–24} The work of Griessbach and Lehmann²⁵ reports the degradation of PDMS to dimethylsilanediol in many different types of the soils. However, the insolubility of PDMS in water limits its degradation in this medium.²⁶ Thus, PDMS has been used as a modifier for polymers for a variety of applications such as biomedical application or plasticizers.^{27–29}

The synthesis of block copolymers poly(ϵ -caprolactone)-*block*-PDMS-*block*-poly(ϵ -caprolactone) (PCL-*b*-PDMS-*b*-PCL) has been made by Buchholz and Mulhaupt.³⁰ This block copolymer

combines excellent properties of PDMS, as surface modifying, toughening, with the compatibilizing effect of the PCL. Synthesis of these copolymers allows improvement of the properties of degradation and hydration of the PCL and changing their potential applications. It is a good candidate for coating or drug encapsulation.^{31–35} But today the characteristics of hydration and degradation of this copolymer in water remain unknown.

In the present work, linear triblock copolymers PCL-*b*-PDMS-*b*-PCL were synthesized via ROP with different molecular weights and different molar ratios. Then films of these block copolymers were immersed in distilled water. The objectives of this study are to observe the effects of the ligation of PDMS in various ratios on the degradation and hydration of PCL in water. Three main analytical methods are used, the Karl–Fisher coulometer (KF) to check the global hydration of the films, the gel permeation chromatography (GPC) to measure the degradation of polymer chains, and electrospray ionization (ESI) to control the quantity of monomers present in water.

EXPERIMENTAL

Materials

The monomer of ϵ -caprolactone (CL), the PDMS bis(hydroxyalkyl) terminated ($M_n \approx 5500 \text{ g}\cdot\text{mol}^{-1}$), and the catalyst stannous octanoate ($\text{Sn}(\text{Oct})_2$) were purchased from Aldrich Co. The PDMS Tegomer[®] H-Si 2311 ($M_n \approx 2300 \text{ g}\cdot\text{mol}^{-1}$) was kindly supplied by Evonik Industries, Germany. All the products were used as received.

Synthesis of PCL Standard

PCL was polymerized by ROP of ϵ -CL in the presence of butan-1-ol with $\text{Sn}(\text{Oct})_2$ as catalyst. The polymer molecular weights expected were $3000 \text{ g}\cdot\text{mol}^{-1}$ and $9000 \text{ g}\cdot\text{mol}^{-1}$. For this the ratio of each product was $[\text{Sn}(\text{Oct})_2]/[\text{BuOH}]/[\text{CL}]$ (1 : 1 : 27 n/n) or $[\text{Sn}(\text{Oct})_2]/[\text{BuOH}]/[\text{CL}]$ (1 : 1 : 80 n/n). Typically, ϵ -CL, butan-1-ol, and catalyst were added in a two-neck flask equipped with a magnetic stirrer and were dissolved in small amount of toluene. The flask was immersed in an ice bath and a nitrogen flow was used for 30 minutes to remove air. The system was then heated at 120°C for 11 h in an oil bath. The solution was concentrated and tetrahydrofuran (THF) was added. The polymer was precipitated in a great excess of petroleum ether. The polymers were obtained with a yield greater than 85% and the ^1H NMR and GPC confirmed the structure.

Synthesis of PCL-*b*-PDMS-*b*-PCL

Triblocks were synthesized using ROP of ϵ -CL in the presence of PDMS with $\text{Sn}(\text{Oct})_2$ as catalyst (Figure 1). The copolymer composition was varied by changing the feed ratio of the reactants $[\text{CL}]/[\text{PDMS}]$ (250 : 1; 60 : 1; 30 : 1 n/n with the

Tegomer[®] H-Si 2311 and 148 : 1 n/n with the Aldrich product) to study the properties in function of the size block and the size of the copolymer. Both PDMS have exactly the same structure with two hydroxyls end-group, only the molecular weight changes. The catalyst ratio was always kept the same $[\text{Sn}(\text{Oct})_2]/[\text{PDMS}]$ (2 : 1 n/n). The same procedure as for the synthesis of the PCL standard was used. The only difference was in the reaction time; the system was heated at 120°C for 48 h in an oil bath. Then the solution was concentrated and THF was added. The polymer was precipitated in a large excess of petroleum ether. The copolymers were obtained with a yield of 95%, and these structures were also confirmed using ^1H NMR, FTIR (MIR-ATR), and GPC.

Polymer Characterization

Nuclear Magnetic Resonance of Proton (^1H NMR). ^1H NMR spectra of the copolymers were obtained on a Bruker Avance 500 spectrometer at 500 MHz. The spectrum was taken in deuterated chloroform at 30°C . The composition of copolymers (ratio of the PDMS and PCL blocks) was calculated from the relative intensities of the peak at 0.03–0.09 ppm $[\text{Si}(\text{CH}_3)_2]$ of PDMS and from the peak at 4.04–4.07 ppm $[\text{OCO}(\text{CH}_2)_4\text{CH}_2]$ of PCL. The molecular weight of PDMS is known, so with the ratio PDMS/PCL the molecular weight of the copolymers could be determined.

Differential Scanning Calorimetry. Calorimetric data were obtained using a Mettler-Toledo differential scanning calorimetry (DSC) 822 (Mettler Toledo, Viroflay, France). The calibration was done with indium and zinc. Aluminium pans were used and the sample mass was approximately 10 mg. The samples were first melted to 100°C (first run) at $20^\circ\text{C}/\text{min}$ and kept at this temperature for 2 min, then cooled to -100°C and heated up again to 100°C at $20^\circ\text{C}/\text{min}$ (second run). Temperature and heat of phase transitions were determined from the maxima as well as crystallization areas and melting peaks. The degree of crystallinity was estimated using eq. (1) where ΔH_m is the measured melting enthalpy of the polymeric part of the sample and $\Delta H_{100\%}$ the equilibrium melting enthalpy of 100% crystalline PCL taken equal to $139.3 \text{ J}\cdot\text{g}^{-1}$.³⁶ To obtain the crystallinity of the PCL part, the result was divided by the molar ratio PCL/PDMS of the copolymer.

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \times M_{0\% \text{PCL}} \quad (1)$$

Film Preparation

The block-copolymers PCL-*b*-PDMS-*b*-PCL prepared previously were dissolved in xylene (50 : 50 w/w).³⁷ A layer of coating (200 μm) was applied with an automatic film applicator on a sheet of polycarbonate and was dried at room temperature 48 h before water immersion.

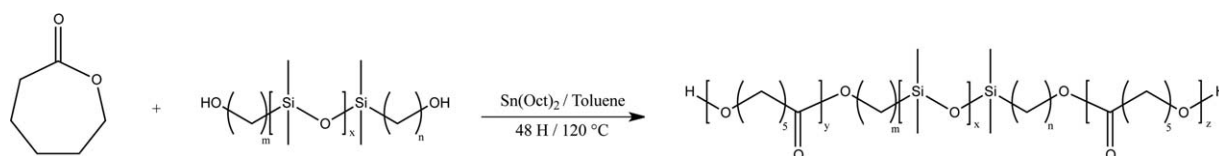


Figure 1. Synthesis of PCL-*b*-PDMS-*b*-PCL by ring opening polymerization.

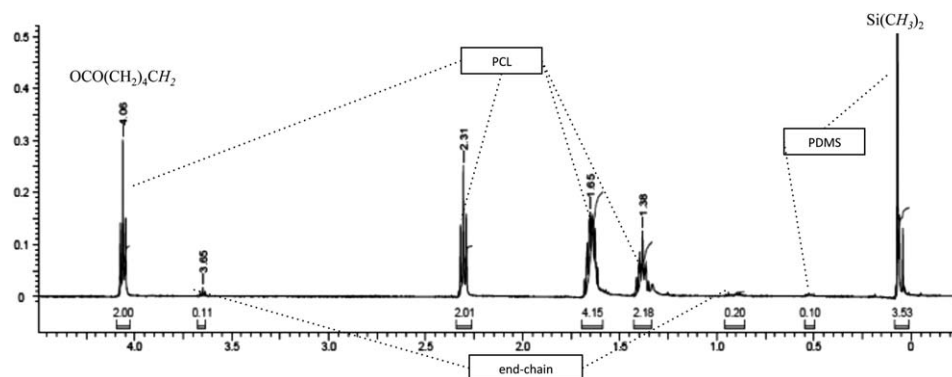


Figure 2. ^1H NMR spectrum of PCL-*b*-PDMS-*b*-PCL.

Measurement

KF Coulometer. The quantity of water in the triblock copolymer during the immersion were determined using a Metrohm KF 737 equipped with a Metrohm Oven KF 707 ($T = 150^\circ\text{C}$), which was used under a nitrogen flow of $200\text{ mL}\cdot\text{min}^{-1}$. The reactant was Hydranal-Coulomat AG. To measure only the water in the film, the samples were wiped before inserted in the coulometer.

Gel Permeation Chromatography. Gel permeation chromatography (GPC) spectra were measured using a Merck pump L-7110, two columns PLgel (Mixed-E, $3\ \mu\text{m}$ and Mixed-D, $5\ \mu\text{m}$) from polymer laboratories, and a Sedex DEDL detector. THF was used as an eluent at a flow rate of $1\text{ mL}\cdot\text{min}^{-1}$, and the injection volume was $20\ \mu\text{L}$. The calibration was done with polystyrene standards (Easical PS-2) from Agilent Technologies. Before the dilution in THF, the films of block copolymer were dried in a oven at 40°C during 4 days to eliminate water.

Electrospray Ionization. A mass detector Bruker Esquire-LC preceded by a HPLC Agilent 1100 performed the quantity of monomer release in the water. About $20\ \mu\text{L}$ of a solution (50 : 50 v/v) of filtered water sample and acetonitrile-ammoniac 0.04% was injected. The eluent was a mixture of water and acetonitrile (50 : 50 v/v) with 0.02% of ammoniac and the flow

rate was $0.05\text{ mL}\cdot\text{min}^{-1}$. To determine the concentration of the samples, standards solution of 6-hydroxyl hexanoic acid were prepared ($200, 500, 1000, \text{ and } 2000\ \mu\text{g}\cdot\text{L}^{-1}$) in the same mixture than the eluent. Negative ion mode was used for ESI measurement to detect the ion $131\ ([\text{M}-\text{H}]^-)$ of 6-hydroxy hexanoic acid).

RESULTS AND DISCUSSION

Synthesis of PCL-*b*-PDMS-*b*-PCL and PCL

In the present work, the ROP of CL was carried out with two different PDMS (Tegomer[®] and Aldrich) as the initiator. They have the same molecular structure but the molecular weight changes (2300 and $5500\text{ g}\cdot\text{mol}^{-1}$), and $\text{Sn}(\text{Oct})_2$ was used as catalyst. These syntheses were carried out at 120°C for 48 h to obtain a complete conversion of the monomer. The structure of the copolymers synthesized was determined using ATR-FTIR, GPC, and ^1H NMR. The FTIR (cm^{-1}): 2943 (C-H, methylene of PCL), 1725 ($>\text{C}=\text{O}$, ester of PCL); 800 (Si-C, methyl of PDMS), 1097 (Si-O, main chain of PDMS), and ^1H NMR spectra (Figure 2) exhibited all the relevant peaks of the two components allow to confirm the structural features of both polymers. Then the presence of a monomodal peak on the GPC (not shown) proved the bond between the PCL and PDMS. The molecular weight of each triblock copolymers were determined

Table I. Molecular Weight of the Triblock Copolymers

Block ^a copolymers	Molecular weight of PDMS ($\text{g}\cdot\text{mol}^{-1}$)	Theoretical ratio ^b PCL- <i>b</i> - PDMS- <i>b</i> -PCL (%)	^1H NMR ratio ^c PCL/PDMS (%)	Theoretical mass ^c ($\text{g}\cdot\text{mol}^{-1}$)	^1H NMR mass ($\text{g}\cdot\text{mol}^{-1}$)	GPC ^e mass ($\text{g}\cdot\text{mol}^{-1}$ eq PS)	PDI	Crystallinity ^d (%)
Copol 50s	2300	25- <i>b</i> -50- <i>b</i> -25	49/51	4500	5200	9200	1.22	15.9
Copol 66s	2300	33- <i>b</i> -33- <i>b</i> -33	66/33	9000	8000	12,000	1.28	32.9
Copol 66l	5500	33- <i>b</i> -33- <i>b</i> -33	63/37	22,500	22,500	25,000	1.24	26.2
Copol 90s	2300	45- <i>b</i> -10- <i>b</i> -45	89/11	32,000	31,000	35,200	1.35	42.8
PCL 3000	-	-	-	3000	2900	6500	1.23	54.4
PCL 9000	-	-	-	9000	9100	14,000	1.12	59.5

^as for the copolymers with the PDMS $2300\text{ g}\cdot\text{mol}^{-1}$ and l with the PDMS $5500\text{ g}\cdot\text{mol}^{-1}$.

^bCalculated with the starting molecular ratio of e-CL and PDMS.

^cCalculated with the relative intensities of the peak at 0.03–0.09 ppm and at 4.04–4.07 ppm.

^dCalculated by DSC.

^ein THF as eluent and with polystyrene standard

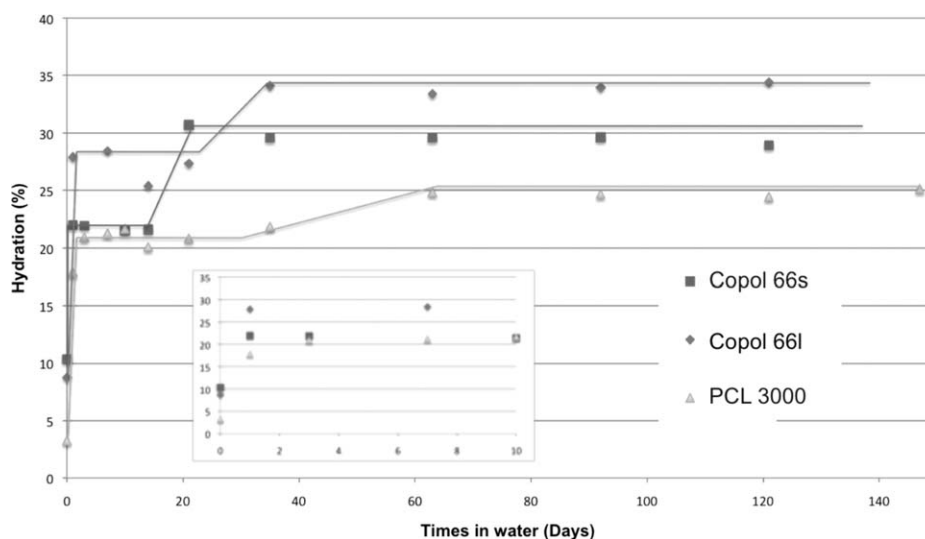


Figure 3. Influence of the molecular weight on the hydration followed by Karl-Fisher titration.

using GPC and ^1H NMR. As shown in Table I, all the copolymers were synthesized with expected molecular weight and ratio. The difference between both molecular weights comes to the use of polystyrene standard for the GPC method.

The polymerization of PCL references at 3000 and 9000 $\text{g}\cdot\text{mol}^{-1}$ were carried out by the same method except that the initiator was replaced by the butan-1-ol. The structure and the molecular weight of the polymers were confirmed using GPC and ^1H NMR (Table I). The aim to polymerize these polymers was to have reference to see the effect of the addition of PDMS. Approximately 3000 $\text{g}\cdot\text{mol}^{-1}$ is the theoretical molecular weight of one block PCL of Copol 66s and 9000 $\text{g}\cdot\text{mol}^{-1}$ is approximately the molecular weight of Copol 66l. The Copol with s was synthesized with the short PDMS ($M_n = 2311 \text{ g}\cdot\text{mol}^{-1}$) and Copol with l was synthesized with the Aldrich PDMS.

The results of DSC confirm the decrease of the crystallinity caused by the PDMS block (Table I). The Copol 66s has a lower crystallinity (32.9%) than PCL 3000 (54.4%), which represent one of this PCL block, and PCL 9000 (59.5%), approximately the same molecular weight. Furthermore, the more the ratio of PDMS is important, the lower the crystallinity is. Hence, the addition of PDMS breaks the high crystallinity of PCL.

Hydration of PCL-*b*-PDMS-*b*-PCL Films

The water absorption is the first thing that occurs when the polymer matrices are immersed in water. Before immersion, all the polymer films on the polycarbonate were homogenous and transparent with a thickness of 80 μm . But over time, it can be visually seen that the polymer matrices become more opaque

with hydration, so the water has diffused in the polymer matrix.

Effect of the Addition of PDMS and Molecular Weight

As shown in Figure 3, Copol 66s, Copol 66l, and standard (PCL 3000) have the same outline of hydration, a first hydration in the first days, and a second hydration after approximately 20–30 days. The homopolymer of PCL, with a molecular weight of 3000 $\text{g}\cdot\text{mol}^{-1}$, hence the same theoretical size as a PCL block of Copol 66s is used as standard. PCL has a low hydration during the first three days compared with the Copol 66s. To quantify the first step of hydration, the diffusion coefficients were calculated experimentally from the percentages of hydration of the films ($H\%$), time (t), and thickness of the film (l) as shown in eq. (2) (Table II),^{38,39} it is the average value between $t = 0$ and $t = t$. Fick's law can be used considering that during the first days the polymers were not degraded. Thereafter, PCL 3000 has a slower hydration in the second step. After 65 days, the hydration of PCL was complete and was of 25% of the polymer weight, whereas the Copol 66s contained 30% of water at the end. The difference could be explained by the lower crystallinity of the Copol 66s, so the water can penetrate easily in the polymer matrix. The percentage of hydration of the triblock copolymers proved that the addition of PDMS changes the hydration properties of the PCL without changing the profile of hydration; the hydration still proceeds in two steps.

$$D = \frac{\pi}{16} \left[\frac{d \left(\frac{H\%_t}{H\%_\infty} \right)}{d \left(\frac{\sqrt{t}}{t} \right)} \right] \quad (2)$$

Moreover, the molecular weight of the copolymers has a great importance on the kinetic of first step of hydration. The results

Table II. Diffusion Coefficient and the Crystallinity of the Copolymers

	Copol 66s	Copol 66l	PCL 3000	Copol 90s	Copol 50s
$D \text{ (cm}^2\cdot\text{s}^{-1}\text{)}$	3.06E-12	8.34E-12	2.47E-12	2.87E-13	2.49E-12
Crystallinity (%)	32.9	26.2	54.4	42.8	15.9

of the hydration of Copol 66s and Copol 66l show an increase of the percentage of water in the copolymers (30% and 33%, respectively, after 40 days), but this difference is insignificant due to the standard deviation of the KF (1%). Hence, the molecular weight of PDMS blocks has no influence on the hydration rate. Nevertheless, the principal variation was on the kinetic of hydration. In the first days, the diffusion coefficients calculated experimentally show that the copolymer with the lowest crystallinity (Copol 66l) has a higher diffusion of water. But after 3 weeks Copol 66s has a complete hydration, whereas Copol 66l needs to wait 1 week more. Hence, the high molecular weights have a quicker hydration, after one day of immersion Copol 66l has a hydration of 28% and 21% for Copol 66s. It is likely that the first plate is due to the polymer reorganization, hence the matrix polymer reorganization takes more times with high molecular weight.

Effect of the Ratio Variation

The objective of second experiment (Figure 4) was to change the ratio PCL/PDMS to study its influence on the copolymer hydration. Varying molecular ratio enables to enhance alternatively the low surface energy of the PDMS or the crystallinity of the PCL. When the PCL blocks were longer than the PDMS blocks (Copol 90s, composed of 90% of PCL), the hydration was low (16% after 40 days). For Copol 50s (50% of PCL), it was 25% after 40 days. In both the cases, the percentage of water in the matrix was lower than for the copolymer with each block of the same size (Copol 66s). The coefficients of diffusion were determined during the first phase of hydration (3 days) (Table II). The variation of crystallinity due to ratio PCL/PDMS seems to have an influence on the kinetic of hydration during this step. The copolymer with the highest crystallinity has the lowest diffusion coefficient.

Hence, the results show that the addition of the PDMS on PCL allows breaking the high crystallinity of the PCL when it is added with a ratio 33/66 due to the higher percentage of water in the copolymer film Copol 66s and Copol 66l than in the reference (Figure 3). But when one of the polymer blocks was in

large majority, the percentages of water in the films were lower than the PCL reference. Thus, it appears possible to control the hydration of the PCL-*b*-PDMS-*b*-PCL with the ratio of each block.

It seems that the following hydrophobic properties of the copolymer come to the major polymers:

- the high crystallinity of the PCL long chains for Copol 90s
- the low energy surface of the PDMS for Copol 50s

Study of the Degradation of PCL-*b*-PDMS-*b*-PCL Films by GPC

The degradation of polyesters is a cleavage of the ester moieties in the amorphous parts, because the water can penetrate these areas. Hence, the degradation has to be relative to the hydration shown previously. The results of the degradation presented in Figure 5 give the effect of the molecular weight (Copol 66s/66l) and the effect of the addition of PDMS on the degradation (Copol 66s/PCL 3000). The addition of PDMS increases the degradation compared with the PCL reference, because the addition of PDMS breaks the crystallinity of the PCL (>50% for the PCL alone and <35% for the Copol 66). These results are in agreement with the fact that the amorphous parts were preferably degraded. Furthermore, the degradation was faster for the copolymer with the highest molecular weight, but after 200 days both copolymers lost the same mass. Then after 270 days in water the degradation was stopped approximately at 45% for Copol 66s and 55% for Copol 66l. The copolymer with the lowest crystallinity is the most degraded. Otherwise, the low mass losses between each measurement show that only the PCL blocks were degraded and more precisely that only the end of the chains was degraded. PDMS block being located in the middle, its cleavage would have led to more important mass losses.

The effects of the size of PCL blocks on the degradation are presented in Figure 6. The kinetics of degradation by GPC of the three copolymers confirm that the hydration and degradation are linked, because the Copol 66s is the most degraded and

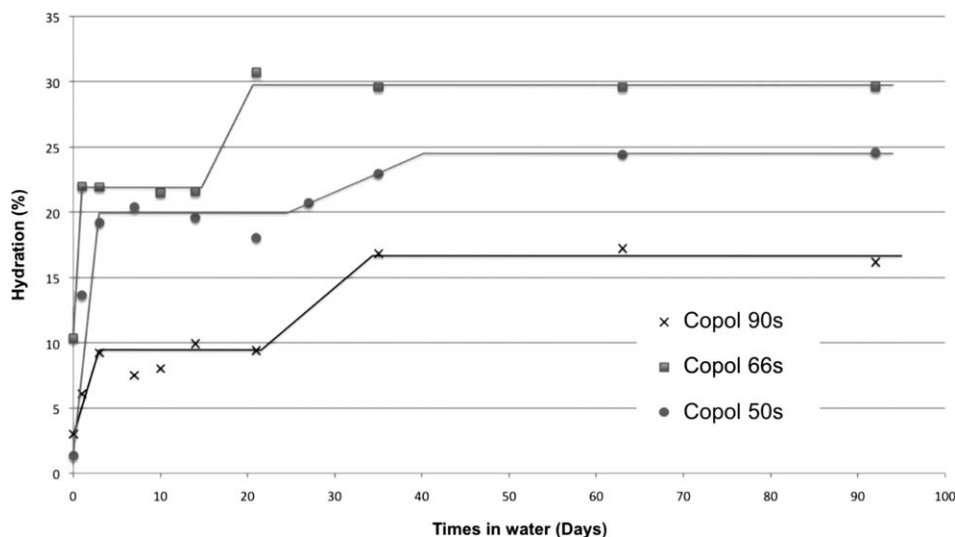


Figure 4. Influence of the ratio PCL/PDMS on the hydration followed by Karl-Fisher titration.

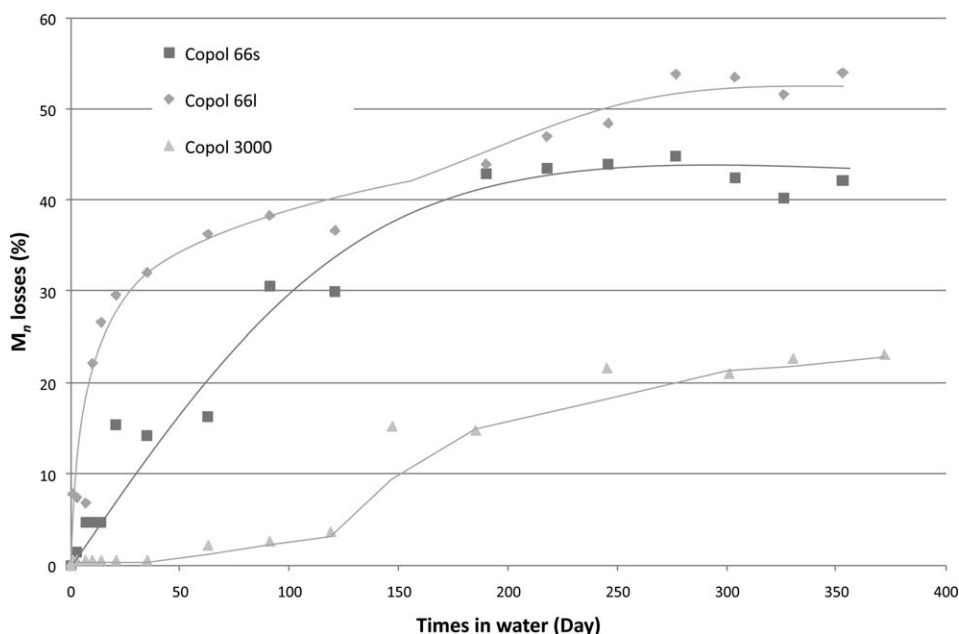


Figure 5. Influence of the molecular weight on the degradation followed by GPC.

it was the most hydrated. But for the Copol 90s and Copol 50s, the first was the most degraded. It could be explained by the short chains of PCL in the Copol 50s and the nondegradation of the PDMS. But it seems that the PCL units close to the PDMS block were difficult or impossible to degrade. It seems that the water present in the film are not be able to initiate the hydrolytic ester cleavage due to the PDMS hydrophobic properties. For the Copol 90s, the degradation in the water was very slow during 90 days due surely to the high crystallinity of the PCL chains. Approximately 5% of the molecular weight was lost (<10 units of PCL by chains). Then the degradation increased and was stopped after 200 days.

Hence, the hydration and the degradation of the PCL-*b*-PDMS-*b*-PCL films are linked, most the film was hydrated. But the PCL blocks were not fully degraded, the random hydrolytic ester cleavage was stopped. And in water any degradation of the PDMS block was observed, the GPC spectrum of the degradation of Copol 66l shows monomodal peaks (Figure 7). Hence, the PDMS being the medium block, if it was degraded there should be a second peak or an important difference on the retention time.

Study of the Degradation of PCL-*b*-PDMS-*b*-PCL Films by ESI

The quantity of 6-hydroxyl hexanoic acid (monomer of the PCL) in the wastewater allows us to confirm the hypothesis

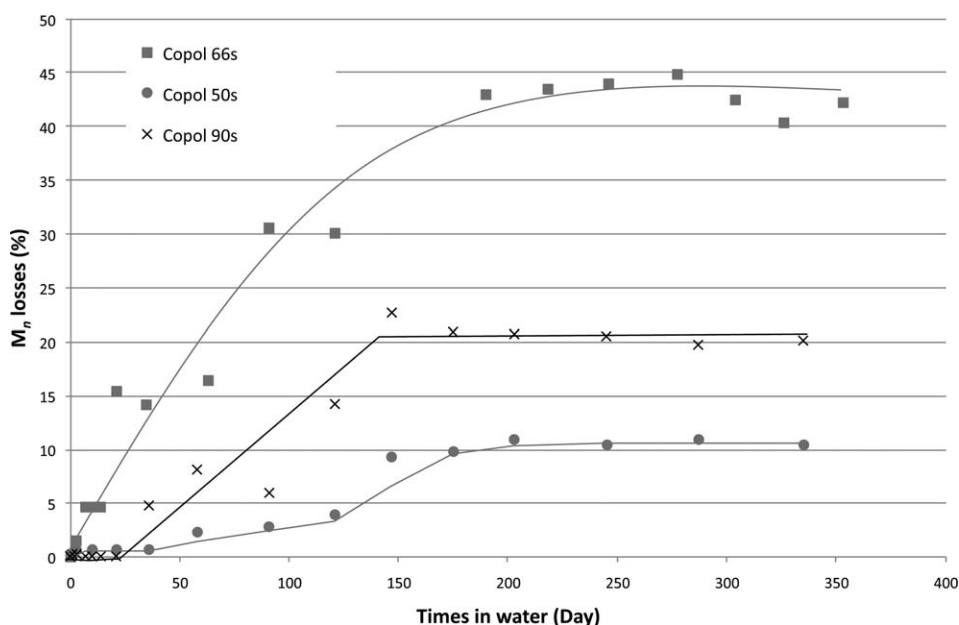


Figure 6. Influence of the ratio PCL/PDMS on the degradation followed by GPC.

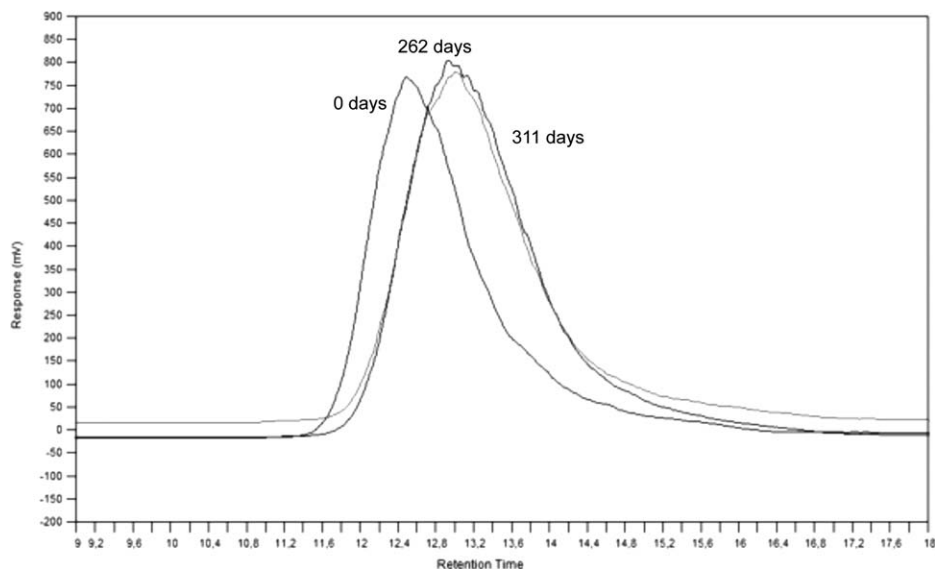


Figure 7. Kinetic degradation of Copol 66l.

how the chains were degraded, in monomers or/and in oligomers. Figure 8 shows that the percentage of 6-hydroxyl hexanoic acid found in the wastewater of Copol 66s increases progressively during 250 days, after which the degradation of the copolymer was completed. But the percentage of hexanoic acid was lower than the percentage of mass losses by the copolymer. After 250 days, the percentage of monomer was 8% and the copolymer had lost 27% of its molecular weight. Hence, the rest of the PCL degraded was surely the oligomers of the PCL, which cannot be detected by the ESI method used. The same results were observed for the other copolymer films. In average, twice the quantity of oligomers were present in wastewater than monomers. Moreover, the same sample was studied directly and after one month to see if a degradation of the oligomers or a polymerization of the hexanoic acid with the oligomers was possible. The same results were obtained for both analyses.

Hence, the majority of the PCL-*b*-PDMS-*b*-PCL films were degraded in small oligomers by the end of the PCL chains.

CONCLUSION

Triblock PCL-*b*-PDMS-*b*-PCL copolymers were prepared by ring opening polymerization. By varying the ratio of PDMS and PCL blocks and the molecular weight of the resultant copolymer, a variation of the hydration, as well as the degradation rate, was observed after immersion in water. The kinetics of hydration depend on the ratio of each block and also the molecular weight. The addition of PDMS on PCL increases the hydration compared with the PCL polymer without changing the profile of hydration. The mass losses of the copolymer films analyzed using GPC were related to the hydration of the copolymer films. Then the degradation of the triblocks was a

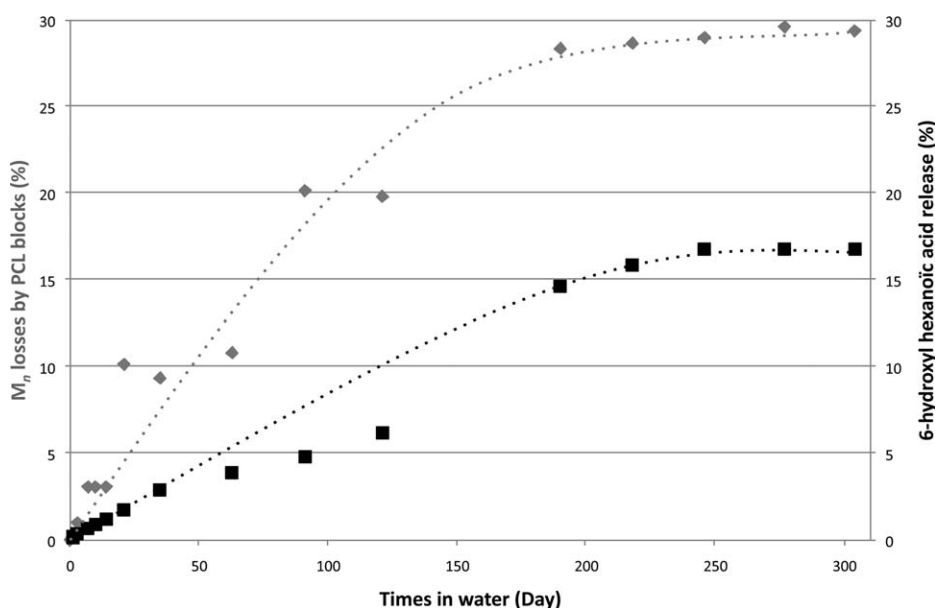


Figure 8. Degradation by GPC \blacklozenge and by ESI \blacksquare of the Copol 66s.

degradation of the PCL end-chains to small oligomers in majority. Hence, the addition of PDMS allows us to change the hydration properties of the PCL. And the kinetics of degradation could be controlled with the ratio of PCL and PDMS in the copolymer. But the addition of PDMS does not change the mechanisms involved during the hydration and degradation.

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