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Semi-crystalline poly(ε-caprolactone) brushes on gold substrate via "grafting from" method: New insights with AFM characterization

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ABSTRACT

This paper is the first report about the morphology of semi-crystalline poly(ε-caprolactone) (PCL) brushes studied by Atomic Force Microscopy (AFM) in tapping mode. This represents a convenient way to observe how the growth of a polymer proceeds from a thiol monolayer on gold substrate in terms of grafting density and thiol monolayer stability. The synthesis of semi-crystalline PCL brushes was carried out by Ring-Opening Polymerization (ROP) of ε-caprolactone (ε-CL) from hydroxyl end-group of thiol monolayer on gold surface as catalyzed with tin octoate ($Sn(Oct)_2$) at 50 °C. Addition of a sacrificial initiator was also attempted in order to get a finer control over PCL crystals. For a sake of comparison, triazabicyclo[4.4.0]dec-5-ene (TBD) was also investigated as another ROP catalyst active at ambient temperature. The composition and the morphology of resulting semi-crystalline PCL brushes were characterized using X-ray Photoelectron Spectroscopy (XPS) and AFM. In the case of $Sn(Oct)_2$-promoted ROP of CL with or without free (sacrificial) initiator (i.e., benzyl alcohol), different types of morphologies were observed on the gold substrate, due to the thermal instability of thiol-gold bond under the experimental conditions. When TBD was used at ambient temperature, a regular and homogeneous crystalline morphology, i.e., compact PCL crystals, could be observed.

1. Introduction

Tunable surface properties for applications such as wettability [1] and protein adhesion [2] are a major stake of this last decade. Organic [3] and inorganic [4] substrates can be readily coated by synthetic polymers physically- or chemically-adsorbed. However, because of the lack of adhesion between the film and the substrate in physically-absorbed films, covalent bonding represents the more desirable situation. The grafting of polymer brushes from self-assembled monolayer (SAM) [5,6] bearing end-group functions as anchoring sites are often privileged. Usually, SAMs are made from functional thiol molecules covalently bonded on a gold substrate. "grafting from" or "grafting to" methods can be used to produce polymer brushes starting from functional thiol molecules. The "grafting from" approach or Surface Initiated Polymerization (SIP) provides a better control over the types of grafted polymer, the surface-grafting density, and chain-lengths [7]. Many techniques have been used to produce well-defined polymer brushes using controlled polymerizations initiated from such a surface. This can be achieved by ring-opening polymerization [8,9] (ROP), nitroxide mediated polymerization [10] (NMP), reversible addition-fragmentation chain transfer [11] (RAFT) and atom transfer radical polymerization [12] (ATRP).

In this paper, we propose to study the synthesis of poly(ε-caprolactone) (PCL) by ROP of ε-caprolactone

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(ε-CL) from hydroxyl end-group of thiol monolayer on gold surface. This aliphatic polyester is biocompatible, biodegradable, semi-crystalline with a melting point of ca. 60 °C and has a glass transition temperature at about −60 °C. These last features have a great interest in order to shed some light on crystallization process of polymer chains attached to a surface. The aim of this study was to determine the coupling between polymerization conditions and the morphologies of PCL crystals using AFM techniques. We specially focus on the polymerization temperature and on the catalyst for the PCL synthesis (Tin(II) 2-ethylhexanoate vs. triazabicyclo[4.4.0]dec-5-ene). To our best knowledge, such a study was not still carried out. Husemann et al. [13] reported on ROP of CL from gold-surface initiated by aluminium alkoxide and the use of sacrificial initiator in solution to improve the control over the growth of PCL chains. They demonstrated the linear dependence of thickness of PCL film as a function of the degree of polymerization of free polymer derived from the sacrificial initiator. Voccia et al. [14] reported the synthesis of polyester brushes by combining electrografting with grafting of PCL by ROP initiated with aluminium alkoxides at the surface of conducting substrates.

Herein, we prepared semi-crystalline PCL brushes by ROP of CL from hydroxyl end-group of the SAM on gold surface as catalyzed by the commonly used ROP catalyst, i.e., tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) at 50 °C [15]. Addition of a sacrificial initiator was also attempted in order to get a finer control over PCL crystals. After polymerization, the semi-crystalline PCL brushes were characterized by Atomic Force Microscopy in tapping mode (TM-AFM) in order to focus on the morphology of PCL crystals as a very convenient way to study their molecular parameters in terms of grafting density, thiol monolayer stability, and influence of synthesis conditions upon their crystalline morphology and the crystallization of a polymer brush-grafted from a thiol monolayer. To our best knowledge, triazabicyclo[4.4.0]dec-5-ene (TBD) was investigated, for its first time, as an organic catalyst in surface-initiated ROP at ambient temperature. This is to compare the resulting PCL morphologies with those obtained when classical organometallic catalyst, i.e., $Sn(Oct)_2$, is used as ROP catalyst at 50 °C.

2. Experimental section

2.1. Materials

Films of gold with thicknesses of 950 Å were deposited onto silicon substrate by using an electron beam evaporator manufactured by Si-Mat (Silicon Materials). A 100 Å thick layer of titanium was used to promote adhesion between silicon and the film of gold. 11-mercapto-1-undecanol was used as received (MUD; 99%; Sigma–Aldrich). The monomer, ε-caprolactone (ε-CL; 99%; Sigma–Aldrich) and benzyl alcohol (B-OH; 99%; Acros organics) were dried 72 h with calcium hydride (CaH_2, Acros organics) and distilled prior to use. Tin(II) ethylhexanoate ($Sn(Oct)_2$; 95%; Sigma–Aldrich) was purified by distillation under high vacuum. Toluene (p.a., Labscan) was refluxed over CaH_2, and was then distilled under reduced pressure. Ethanol (100%) was used as received from Acros organics. Hydrogen peroxide (H_2O_2; 30 wt.% in H_2O; Sigma–Aldrich) was used as received.

2.2. Preparation of initiator monolayer

Gold substrate, with an average grain diameter of 60 nm, was cleaned following different steps. First, the substrate was sonicated in ethanol solution for 2 min and dried with a flow of nitrogen [16]. Then, it was immersed in a solution of hydrogen peroxide for 1 min, washed with large amount of demineralized water and dried by a flow of nitrogen. Finally, the wafer was cleaned with UV/ozone during 30 min [17]. A self-assembled monolayer (SAM) of the thiol initiator, MUD, was obtained by immersion of cleaned gold substrate in a 2 mM ethanolic solution of hydroxylated thiol overnight. After immersion, in the presence of ethanol, the surface was washed, sonicated and rinsed to remove the excess of thiols [18]. Once dried under nitrogen flow, the sample was rapidly transferred into a flask in order to prevent the thiol monolayer from possible oxidization.

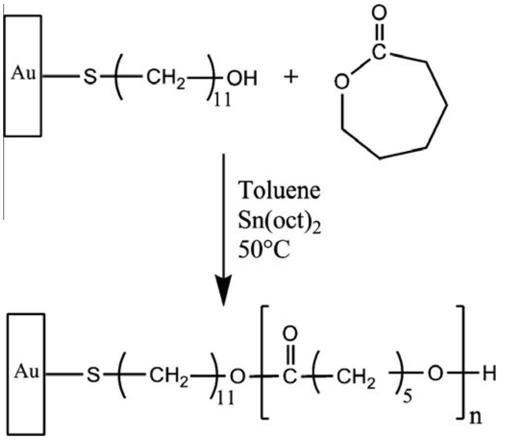
2.3. ε-CL polymerization

Gold surfaces decorated with thiol monolayer are transferred under nitrogen flow in a flame-dried two-neck flask equipped with a three-way stopcock. Toluene (10 mL), $Sn(Oct)_2$ (1 mL of a 0.3 M toluene solution) and ε-caprolactone ($V_{CL} = 16$ mL; $m_{CL} = 16.64$ g; $n_{CL} = 0.015$ mol) were successively added under nitrogen using flame-dried syringes. When a sacrificial initiator was used, benzyl alcohol (0.3 ml; $n_{monomer}/n_{initiator} = 60$), was added to the flask of polymerization. The mixture was then heated at 50 °C over 1 day. The polymerization was then stopped by removing gold substrates rinsed with a large amount of toluene, and dried under nitrogen flow. When sacrificial initiator is added in the medium of polymerization, free PCL was recovered from supernatant by precipitation in heptane, filtration and drying until constant weight at 40 °C under vacuum (yield = 99%). The same synthesis conditions were applied to a bare gold, without hydroxyl thiol SAM, with or without the presence of free initiator in the medium of polymerization.

In the case of TBD-initiated ROP of CL, TBD ($m_{TBD} = 12.74$ mg), chloroform (9 ml) and ε-caprolactone ($V_{CL} = 8$ mL; $n_{CL} = 0.072$ mol) were added to the substrate at ambient temperature. The polymerization was stopped after several hours following the same procedure aforementioned.

2.4. Size exclusion chromatography (SEC) analysis

Size exclusion chromatography (SEC) was performed in THF (sample concentration: 1 wt.%) at 35 °C using a polymer laboratories (PL) liquid chromatograph equipped with a PL-DG802 degazer, an isocratic HPLC pump LC1120 (flow rate: 1 mL/min), a Basic-Marathon Autosampler, a PL-RI refractive index detector and four columns: a guard column PLgel 10 μm (50 × 7.5 mm) and three columns PLgel mixed-B 10 μm (300 × 7.5 mm). Molecular weight and molecular



Scheme 1. ROP of CL from hydroxyl end-group of thiol monolayer.

weight distribution were calculated by reference to a calibration curve built up by using polystyrene standards.

2.5. X-ray Photoelectron Spectroscopy (XPS) analysis

XPS was used to control the elemental composition of the surfaces. All reported spectra were recorded at a 90° take-off angle relative to the substrate with a VG ESCALAB 220iXL spectrometer using the monochromatised Al Kα radiation (1486.6 eV). The core level lines analyzed (C 1s and O 1s) were referenced with respect to the C 1s binding energy conventionally set here at 285.0 eV and characteristic of aliphatic moieties. XPS results were analyzed by curve-fitting of the C 1s signal by using mixed Gaussian–Lorentzian curves after a linear background subtraction.

2.6. Atomic Force Microscopy (AFM) analysis

AFM measurements were performed in "tapping-mode" (TM-AFM). In this mode, the cantilever holding the probe tip oscillates close to the resonance frequency (ca. 300 kHz) above the sample surface so that the tip is in intermittent contact with the surface at the lower end of the oscillation. The phase of the oscillating tip is very sensitive to the nature of the interaction with the surface. It is well-know that the phase lag is related to the mechanical response of the material when the amplitude is only slightly damped upon contact with the surface [19]. Therefore, simultaneous recording of the phase and the height images provides a map of the local mechanical response. All AFM images were recorded with a Nanoscope IIIa microscope operated at room temperature in air using commercial cantilevers made of silicon with a spring constant of 30 N/m (Veeco). The images were digitally sampled at the maximum number of pixels (512) in each direction, and the Nanoscope image processing software was used for image analysis. Unless otherwise stated, image treatment was limited to a "flattening" operation, whereby a first-order surface representing height variations related to a possible tilt of the sample is subtracted from the original image. Averages of all the values for the height of crystals are taken.

3. Results and discussion

As outlined in the synthetic pathway for the preparation of PCL brushes (Scheme 1), ROP of CL was initiated starting from a hydroxylated thiol monolayer as prepared by immersion of gold surface in a 2 mM ethanolic solution of hydroxylated thiol overnight. AFM in tapping mode (TMAFM) were realized on bare gold and on hydroxyl-terminated thiol monolayer to know the initial morphology of the substrates (see Supporting Figs. S1 and S2). XPS analysis reveals the immobilization of thiol molecules on the gold substrate before polymerization. The S 2p spectrum (Fig. 1) confirms the presence of a gold–sulfur bond with the presence of the S $2p_{1/2}$ level at 163 eV and the S $2p_{3/2}$ level at 161.8 eV. No free thiol group (higher binding ener-

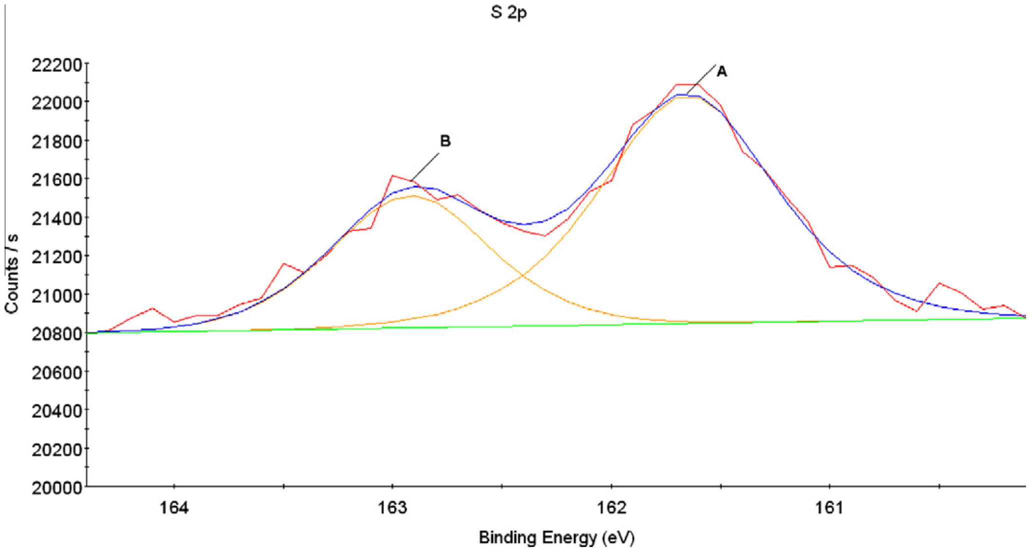


Fig. 1. XPS spectrum (Signal of S_{2p}) of thiol monolayer adsorbed on gold surface. A = S $2p_{1/2}$ and B = S $2p_{3/2}$.

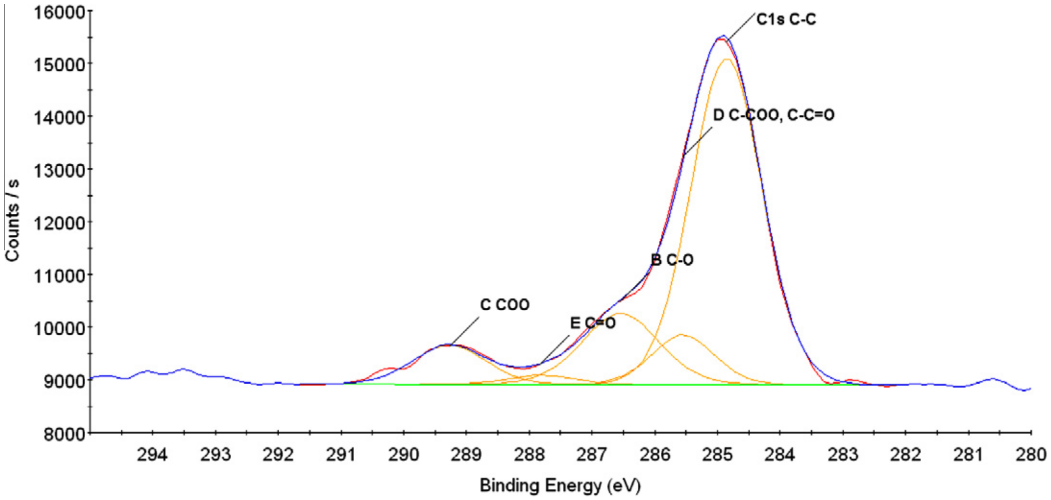


Fig. 2. XPS spectrum (Signal of C_{1s}) of PCL brushes grown by surface-initiated ROP from hydroxyl end-group of thiol monolayer.

gies) is observed [18]. First attempts were carried out by ROP of CL initiated with commonly used ROP catalyst, i.e., $Sn(Oct)_2$ at 50 °C (in toluene) in the absence of a free (sacrificial) initiator with hydroxyl-terminated thiol monolayer as initiating sites. It is worth noting that $Sn(Oct)_2$ is active as a ROP catalyst from 40 °C [20]. The mechanism for ROP of this cyclic ester initiated by $Sn(Oct)_2$ and OH-group is largely reported in the literature [15]. Accordingly, the polymerization reaction takes place through a coordination–insertion mechanism, involving the *O*-acyl cleavage of the cyclic monomer. After one polymerization day, the ε-CL polymerization was stopped and several washings were realized with a good solvent of PCL chains (toluene). The resulting substrates were analyzed by XPS to attest the presence of a polyester film. The XPS survey spectrum reveals the presence of carbon (C_{1s} centered at 285 eV), oxygen (O_{1s} centered at 532.5 eV), sulfur (S_{2p} centered at 163 eV), gold (Au_{4d5} centered at 335.5 eV) and also some tin residues (Sn_{3d} centered at 487.5 eV). The peak quantitative analysis gives intensities of ~40% in carbon, ~33% in oxygen, ~6% in tin, ~19% in gold and ~0.46% in sulfur. Fig. 2 shows the carbon XPS spectrum of the polyester film grafted on gold surface, the C_{1s} spectrum being fitted into different components (C–C, C–O, COO, *C*–COO and C=O). The XPS measurements thus confirm the formation of a PCL thin film. We also noted the presence of a small quantity of tin atom that is trapped inside the film.

The resulting surfaces have been imaged by TMAFM in order to observe the crystals vs. disordered organization on the PCL on gold surface. Samples were analyzed in different areas and the images are representative of the material and reproducible at different magnifications. Fig. 3

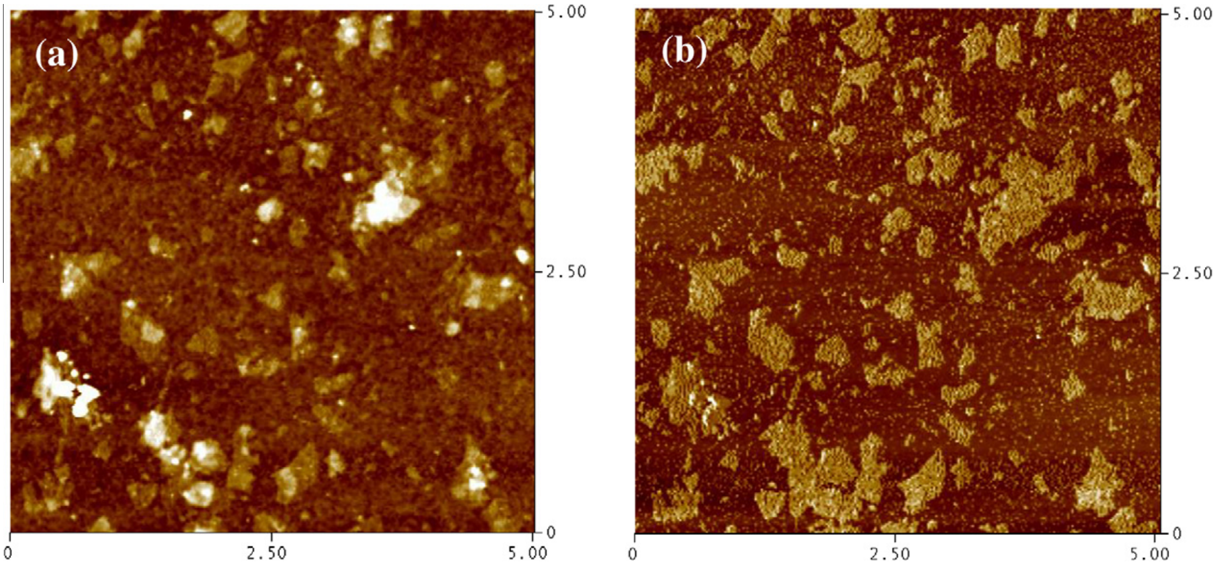


Fig. 3. TMAFM height (a) and phase (b) images (5 x 5 μm^2) of PCL brushes obtained by grafting from on gold surface with $Sn(Oct)_2$ at 50 °C without free initiator. Z scale for height and phase images is, respectively, 20 nm and 90°.

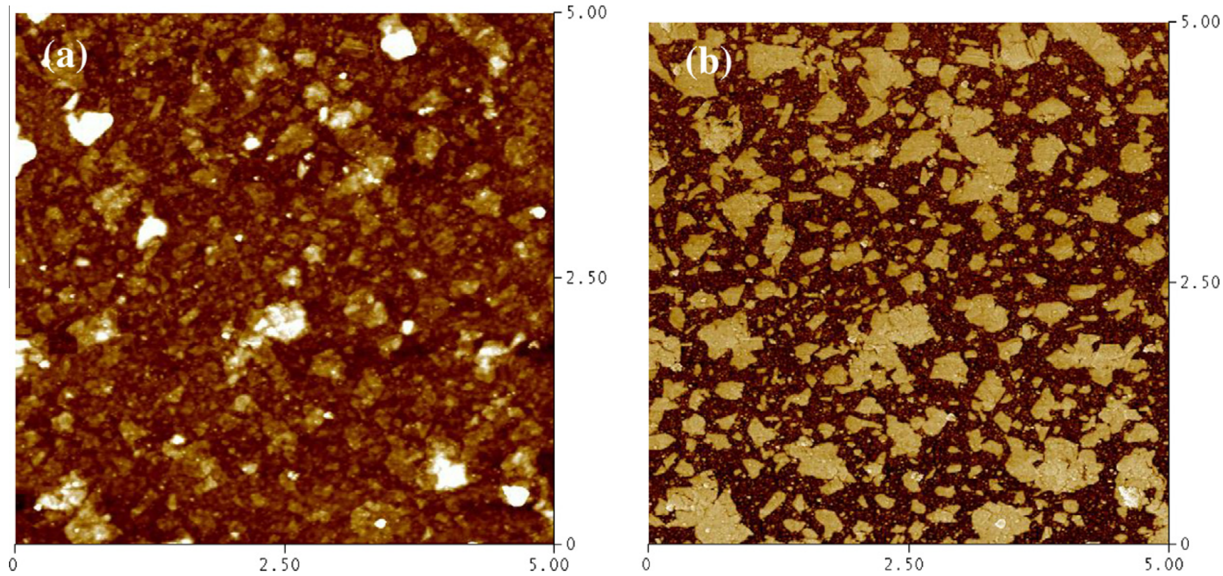


Fig. 4. TMAFM height (a) and phase (b) images (5 x 5 μm^2) of PCL brushes obtained by grafting from on gold surface with $Sn(Oct)_2$ at 50 °C with free initiator. Z scale for height and phase images is, respectively, 20 nm and 90°.

shows that some PCL crystals are disparately observed on the entire surface. The density of resulting PCL crystals is quite low, indicating the lack of control over growing PCL chains. Generally, like physically-adsorbed PCL film, the crystal morphology evolutes and depends on the molar mass of the polymer chains and of the film thickness. Different morphologies like butterfly [21], dendrite [22,23] or spherulite [24] can be observed in the case of physically-adsorbed PCL thin film. However, in our cases, longer polymerization times did not improve a lot the density and the thickness of PCL crystals grafting from gold surface, leading again to the same morphology.

On surface, controlling the polymerization degree (DP = ratio between monomer and initiator) and then, the molecular weight of the PCL chains is difficult because the number of initiating groups on monolayer of gold substrate is unreliable. In this respect, some authors have tried to add a free initiator for a better control over the number of initiating groups. The influence of a free initiator (benzyl alcohol), called sacrificial initiator, has been investigated over the molecular control of polymer growth from the surface during the polymerizations of CL. The addition of a free initiator have a real impact on the polymerization of PCL and then, on the growth of crystals. As explained by Husemann et al. [13], the sacrificial initiators allow a dynamic exchange between the free and the anchored initiators. The density of PCL crystals on gold surface is drastically increases (Fig. 4). Some studies have shown that the molecular-weight of the free polymer derived from the free initiator could be the same as on surface. According to these studies, the free initiator could control the density and the thickness of PCL brushes. Accordingly the synthesis of PCL has been carried out under the same conditions, i.e., with (Fig. 4) and without (Fig. 3) the presence of a sacrificial initiator (benzyl alcohol). In the presence of the sacrificial initiator, free PCL chains were analyzed by SEC in order to compare the molecular weight of free PCL with the thickness of PCL brushes. A number-average molecular weight ($\overline{M_n}$) of ~5000 g/mol in good correlation with the theoretical one was determined, together with a very low index of polydispersity (~1.1). ^{1}H NMR analysis confirmed that the polymerization started effectively from the hydroxyl group of the benzyl alcohol. All these features attest that ROP of CL was well controlled in the presence of a sacrificial initiator like benzyl alcohol. PCL crystals almost cover the entire surface with an average height of 11 nm (see *Supporting* information for section analysis, Fig. S3). One major advantage of semi-crystalline polymer brushes is the observation, directly on AFM pictures, of how the growth proceeds. Interestingly, the molecular weight of PCL can be roughly estimated from the thickness and the crystallographic unit cell via the simple relation:

The degree of polymerization (DP) = 2 h/c *where* h and c are the crystal thickness (nm) and the axe c of crystallographic unit cell (nm) respectively.

The values of crystallographic axes are well-known for PCL crystals ($a = 0.75$ nm, $b = 0.5$ nm, $c = 1.73$ nm [25]. Accordingly, $\overline{M_n}$ of PCL crystal grafted on surface is estimated around 1300 g/mol for a height of 11 nm. It should be noted that the determination of the molecular weight on a precise area of a few tens nm cannot be achieved by conventional analytical methods such as SEC or NMR. However, since $\overline{M_n}$ of free PCL chains has been evaluated at around 5000 g/mol, all PCL crystals on surface theoretically would have had an average height of ~50 nm. The polymerizations from the surface therefore seem to be more heterogeneous then when performed in solution. Even if we cannot absolutely exclude chain folding, it should be very difficult for densely grafted chains to fold (steric hindrance). In addition, a recent paper shows that chain-folding does not occur during the crystallization of PCL in a brush-like morphology [26]. As concerns the tilt angle of PCL chains in the crystals, the ratio between free and grafted chains molecular weight is very large (by a factor of 5) and cannot thus be accounted for.

The phase image of surface after ROP of CL (Fig. 4b) shows an assembly of bright objects dispersed in a dark area. As in Dynamic Mechanical Analysis (DMA) experiments, the AFM phase signal is obviously determined by the elasticity vs. viscous behaviour of the film. With respect to this, we expect that SAMs on gold characterized by a quasi-pure elastic behaviour appears in black (i.e., phase shift near zero). In contrast, the polymer crystals probably involve a non-negligible inelastic component (i.e., the phase shift should be different than zero). This is in agreement with the comparison between phase and topography images of Fig. 4, higher objects corresponding to polymer crystals exhibit the largest phase shifts. A careful focus of the sample reveals another morphology (Fig. 5b) with an intermediate contrast (see *Supporting information for section analysis, Fig. S4*). We observe three zones: compact PCL crystal, disordered PCL and the monolayer of thiol. The height difference between β zone and χ zone is very low but the height section is slightly different. On the other side, the section analysis of phase image reveals a large difference of contrast between the three zones. The presence of disordered PCL surface tethered polymers could be explained by an insufficient grafting density and thus, a decrease of the anchored functional thiol on the gold surface [27]. This is corroborated by the low height of these polymeric chains.

Crystallization appears as a very convenient tool to study the morphology of a polymer brush in terms of grafting density. Moreover, crystallization allows observing the heterogeneous character of the surface tethered polymers on the surfaces that cannot be deduced from conventional techniques like ellipsometry measurement. Finally, we observe two types of morphologies of PCL crystals as well shown in another scanned area (Fig. 6). Although the 'classical' morphology of crystal is compact (see Figs. 3 and 4), ordered structures with very irregular shape, similar to a dendrite usually observed for diffusion-controlled growth, have been noticed. This dendritic growth requires chain motion, and is usually observed in physically-adsorbed polymer film [22,23]. It is worth noting that without the added sacrificial initiator, the presence or not of polymer chains was checked in the medium of polymerization by precipitation of the corresponding supernatant in heptane. We observed the absence of precipitation or a small fraction of PCL in the solution that is not detected under this condition. This indicates that no polymerization had taken place in solution. Furthermore, polymerizations promoted with or without sacrificial initiator on bare gold surfaces were carried out. As expected, in both cases, we did not observe the adsorption of PCL chains on bare gold surfaces after ROP of CL.

These observations support the idea that the dendritic growth of PCL observed for Tin octoate catalyst is directly related to the desorption of the thiol initiators (Scheme 2). Although $Sn(Oct)_2$-promoted ROP of CL was carried out at 50 °C, i.e., at a lower temperature for the initial cleavage of the bond between gold and sulfur (above 60 °C), thiol-based molecules can be readily desorbed into the medium of polymerization. Initiated from either the hydroxyl extremity or the thiol extremity of thiol-based molecules released during ROP of CL, the resulting PCL chains physically adsorb on the substrate. The adsorption of these crystals for the surface is important because the sample have undergone several washings with good solvent of PCL, i.e., toluene. However, the dendrite-like crystal can be readily removed out by the utilization of ultrasound bath in a toluene solution, giving an additional support to

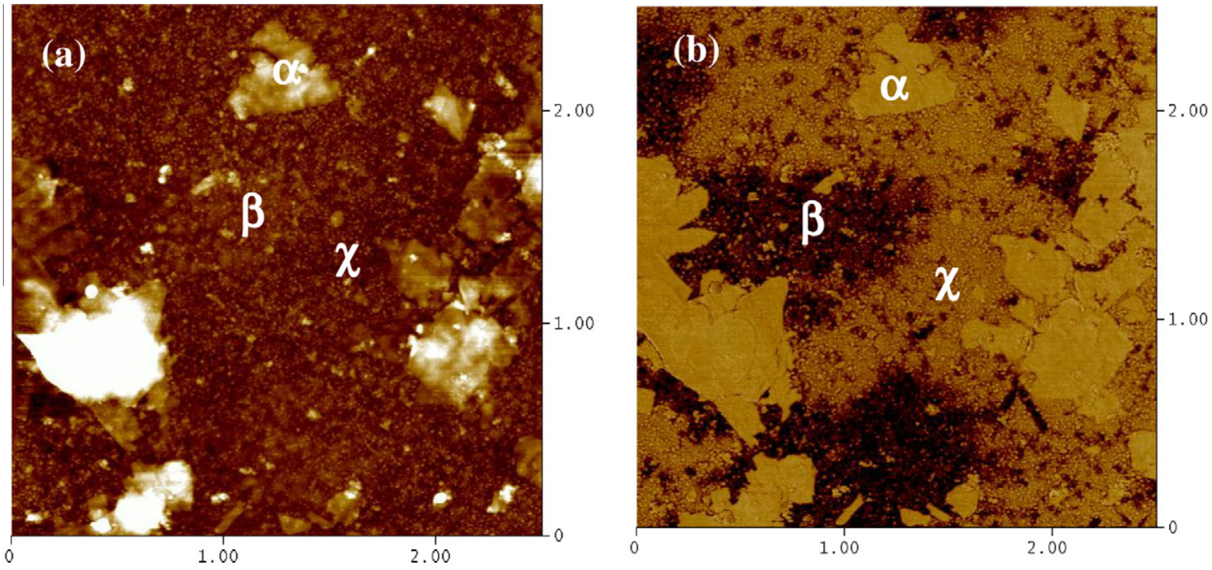


Fig. 5. TMAFM height (a) and phase (b) images (2.5 x 2.5 μm^2) of PCL brushes obtained by grafting from on gold surface with $Sn(Oct)_2$ at 50 °C with free initiator. Three different zones are highlighted: compact crystal (α), the monolayer of thiol (β) and disordered PCL chains (χ). Z scale for height and phase images is, respectively, 20 nm and 90°.

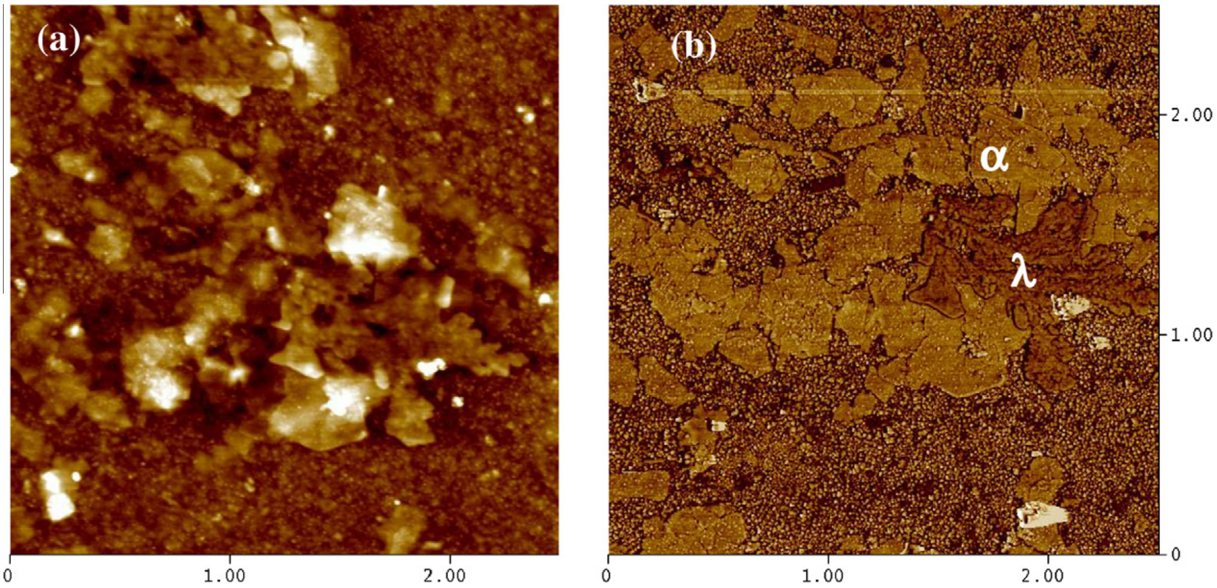
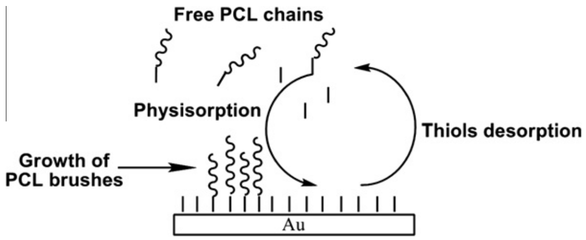


Fig. 6. TMAFM height (a) and phase (b) images (2.5 x 2.5 μm^2) of PCL brushes obtained by grafting from on gold surface with $Sn(Oct)_2$ at 50 °C with free initiator. Two different morphologies are observed: crystal compact (α) and crystalline dendrite (λ). Z scale for height and phase images is, respectively, 20 nm and 80°.



Scheme 2. Explanation of the presence of dendrite crystal of PCL on surface.

the physical adsorption of free PCL on surface. It seems that the presence of specific functional groups on the surface favouring adsorption of PCL chains (e.g., hydroxyl).

To support our theory, we have polymerized another substrate of thiol-monolayer at ambient temperature in order to avoid this desorption of Au–S bonds as observed with the formation of dendrites during surface-initiated ROP of CL. Since, $Sn(Oct)_2$ requires being activated at least at 40 °C, we used 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as organocatalyst for the ROP of CL at ambient temperature for its first time in surface-initiated ROP of CL. TBD has shown to be efficient in the polymerization of cyclic esters in a fast and controlled manner [28]. After 6 h of polymerization from the hydroxyl group, TM-AFM showed compact PCL crystal on the entire surface of the sample (Fig. 7). The average height of the PCL crystal is 13 nm. No dendrite crystals are observed on all the entire surface of the corresponding substrate. It is worth noting that the density of PCL was high enough, not requiring the use of a free initiator for better density of PCL crystals. Furthermore, the evolution of the average thickness of PCL chains in function of the polymerization times was investigated with TBD catalyst (Fig. 8). The PCL chains grow linearly during the first time of polymerization. After 6 h, the thickness of the PCL brush reaches a plateau value. This saturation of the thickness can be related to the steric hindrance exerted by neighbouring chains. This interpretation is further supported by the discrepancy between Mw of free and grafted chains.

These results show that using ambient temperature with an adequate initiating system like TBD for ROP of CL reduces the desorption phenomenon of Au–S bond as observed at higher temperature, i.e., 50 °C, in the case of $Sn(Oct)_2$-promoted ROP of CL. This leads to semi-crystalline compact PCL crystals with high-density.

4. Conclusions

Semi-crystalline PCL brushes are grafted on gold surface by the polymerization of CL from hydroxyl end-group of thiol monolayer promoted by $Sn(Oct)_2$ at 50 °C and by TBD at ambient temperature. Due to the high degree of crystallinity of PCL, these resulting brushes show a great interest to understand how the growth of polymer proceeds. In the case of $Sn(Oct)_2$-promoted ROP of CL at 50 °C, it was possible to identify the crystal and disordered part of this polymer and to show the morphology of a grafted PCL crystal using AFM technique. Use of free initiator in the medium of polymerization has an impact on the homogeneity of the growth but no parallel between the growths from the anchored or the free initiator can be made. Following to the values of crystallographic axes, the length of PCL chains of each crystal have been determined. With this kind of brushes, we observe a "classical" PCL crystal but also another morphology, a dendrite. This irregular growth is due to the instability of the thiol mono-

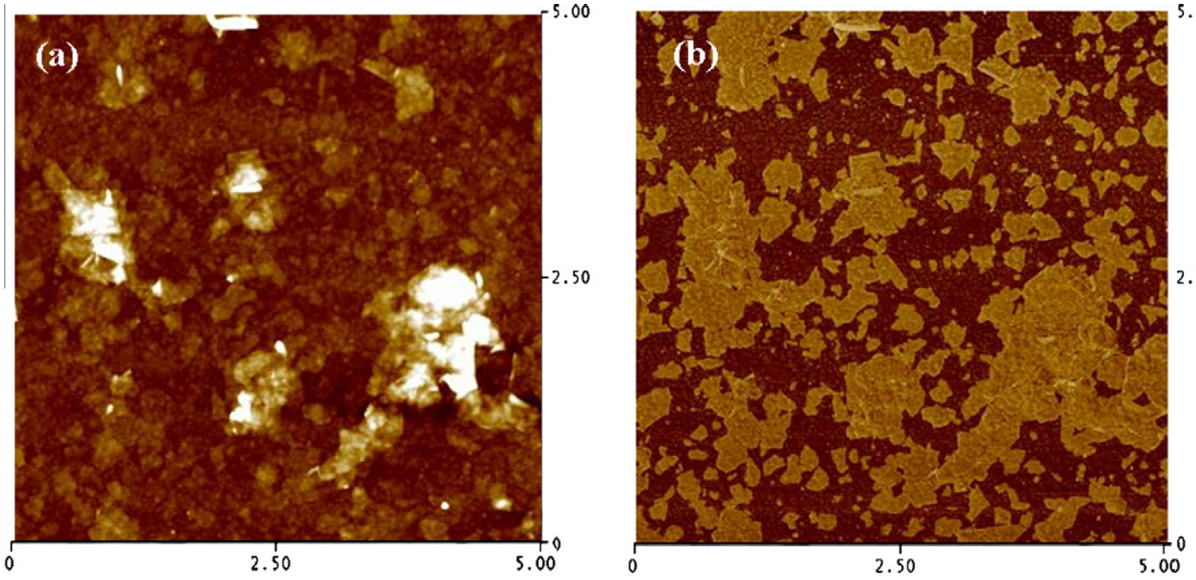


Fig. 7. TMAFM height (a) and phase (b) images (5 x 5 μm^2) of PCL brushes obtained by grafting from on gold surface with TBD at room temperature. Z scale for height and phase images is, respectively, 40 nm and 70°.

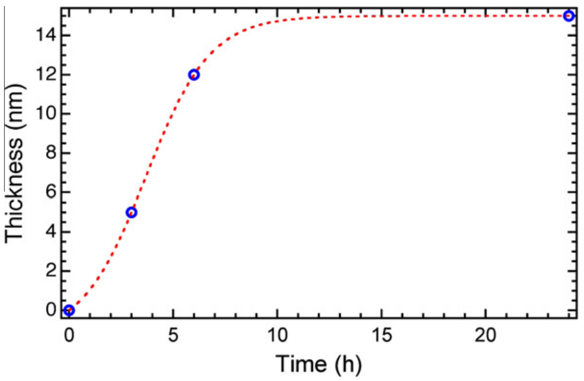


Fig. 8. Evolution of the average thickness of PCL chains in function of the polymerization times with TBD catalyst.

layer when ROP of CL is promoted at 50 °C using $Sn(Oct)_2$ as catalyst. We demonstrate that ROP of CL should be promoted at lower temperature, i.e., at ambient temperature in the presence of TBD as catalyst for the stability of the monolayer.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.eurpolymj.2010.04.022.

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