

## Controlled Polymer Grafting on Single Clay Nanoplatelets

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**Abstract:** We report on the controlled chemical grafting of well-defined polymer chains onto individual montmorillonite-type clay nanoplatelets and the direct visualization of the formed hybrid material at the nanoscale level. Our approach is based on the use of a surfactant mixture that contains varying proportions of hydroxyl-substituted alkylammonium and unsubstituted alkylammonium cations to exchange the initial Na<sup>+</sup> counterions of the natural montmorillonite. This allows for the exchange of Na<sup>+</sup> by a tunable amount of hydroxyl functions at the surface of the clays. Those functions are then derivatized into aluminum alkoxides in order to initiate the ring-opening polymerization of  $\epsilon$ -caprolactone directly from the clay surface that was swollen in an organic solvent. Atomic force microscopy measurements on the resulting polymer-grafted nanoplatelets demonstrate the strong dependence of the coating of the individual clay particles with the composition of the surfactant mixture used for the cationic exchange. This allows for the generation of a range of morphologies varying from polymer islands distributed over the clay surface to homogeneous polymer layers thoroughly coating the platelets. Finally, the control that is achievable over the synthesis of this new family of organic–inorganic nanohybrid materials has been extended to the surface grafting of semicrystalline poly( $\epsilon$ -caprolactone)–poly(lactic acid) diblock copolymers with defined compositions.

### 1. Introduction

A very promising alternative to conventional filled polymers consists of the preparation of polymer-layered silicate nanocomposites. The dispersion of nanometer-size silicate nanoplatelets within a polymer matrix leads to nanocomposites exhibiting markedly improved physicochemical properties, such as higher Young's modulus and storage modulus, higher thermal stability and flame retardancy, and more efficient gas barrier properties, compared to pure polymers or conventional microcomposites.<sup>1–10</sup> Because of environmental concerns, this approach, applied to biodegradable and biocompatible synthetic aliphatic polyesters such as poly( $\epsilon$ -caprolactone) (PCL) or poly(lactic acid) (PLA), has been receiving growing attention.<sup>11,12</sup> Indeed, the performance of these polymers can be strongly

enhanced, which could make them good competitors for commodity materials such as polyolefins, while being completely biodegradable.

It is well documented that the efficiency of the clay as a reinforcing agent is strongly determined by its degree of dispersion in the polymer matrix. Two main approaches can be used to prepare polymer/clay nanocomposites: either melt intercalation, for which the clay is mixed with the preformed polymer in the molten state, or in situ intercalative polymerization, where the clay is dispersed in the monomer, which is then polymerized. Depending on the nature of the clay and the preparation conditions, these two methods can lead either to intercalated or exfoliated morphologies or to a coexistence of the two morphologies.

Recently, we reported the synthesis of PCL/montmorillonite nanocomposites (PCL/MMT) by those two approaches (melt intercalation<sup>13,14</sup> and in situ polymerization<sup>15–17</sup>). Those studies have highlighted the key role of (i) the synthetic path used, (ii) the nature of the organic modifier, and (iii) the clay content on

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- (1) *Polymer-clay nanocomposites*; Pinnavaia, T. J., Beall, G. W., Eds.; Wiley Series in Polymer Science; Wiley: New York, 2000.
- (2) Alexandre, M.; Dubois, P. *Mater. Sci. Eng.* **2000**, *R28*, 1.
- (3) Biswas, M.; Ray, S. S. *Adv. Polym. Sci.* **2000**, *155*, 167.
- (4) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.
- (5) Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 983.
- (6) Gilman, J. W. *Appl. Clay Sci.* **1999**, *15*, 31.
- (7) Strawhecker, K. E.; Manias, E. *Chem. Mater.* **2000**, *12*, 2943.
- (8) Krishnamoorti, R.; Vaia, R. A.; Giannelis, E. P. *Chem. Mater.* **1996**, *8*, 1728.
- (9) Messersmith, P. B.; Giannelis, E. P. *Chem. Mater.* **1993**, *5*, 1064.
- (10) Sinha Ray, S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539.
- (11) Sinha Ray, S.; Yamada, K.; Okamoto, M.; Fujimoto, Y.; Ogami, A.; Ueda, K. *Polymer* **2003**, *44*, 6633.
- (12) Chang, J.-H.; An, Y. U.; Sur, G. S. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 94.

- (13) Pantoustier, N.; Alexandre, M.; Degée, P.; Calberg, C.; Jérôme, R.; Henrist, C.; Cloots, R.; Rulmont, A.; Dubois, P. *e-Polym.* **2001**, 009.
- (14) Lepoittevin, B.; Devalckenaere, M.; Pantoustier, N.; Alexandre, M.; Kubies, D.; Calberg, C.; Jérôme, R.; Dubois, P. *Polymer* **2002**, *43*, 4017.
- (15) Lepoittevin, B.; Devalckenaere, M.; Alexandre, M.; Pantoustier, N.; Calberg, C.; Jérôme, R.; Dubois, P. *Macromolecules* **2002**, *35*, 8385.
- (16) Lepoittevin, B.; Pantoustier, N.; Alexandre, M.; Calberg, C.; Jérôme, R.; Dubois, P. *J. Mater. Chem.* **2002**, *12*, 3528.
- (17) Pollet, E.; Paul, M. A.; Dubois, P. New aliphatic polyester layered-silicate nanocomposites. In *Biodegradable Polymers and Plastics*; Chiellini, E., Solaro, R., Eds.; Kluwer Academic/Plenum Publishers: New York, 2003.

the morphological, mechanical, rheological, and thermal properties of the materials. In situ intercalative polymerization was shown to be the most efficient synthetic path since it allows the generation of completely exfoliated morphologies, leading to PCL/MMT nanocomposites with much-improved properties. Such a situation is typically obtained when hydroxyl-substituted alkylammonium cations are used to exchange the initial  $\text{Na}^+$  counterions of the natural clay. By adequate activation of the hydroxyl groups into metal (Sn or Al) alkoxides, the hydroxyl-substituted organo-modified clays (MMT–OH) can then play the role of co-activators for the bulk (i.e., in the absence of any solvent) polymerization of  $\epsilon$ -caprolactone, eventually leading to PCL chain grafting onto the clay surface. Therefore, it appears that one key parameter yielding fully exfoliated nanocomposites with much-enhanced material performances is the covalent bonding between the in situ-grown polyester chains and the ammonium cations covering the clay surface.<sup>15–18</sup>

In that context, it is of particular interest to get better spatial control over the polymer grafting reaction, the growth of polymer material on the silicate layer surface, and the resulting clay delamination. For that purpose, an original synthetic strategy has been designed which consists of (i) controlling the density of the hydroxyl functions covering the surface of the organo-clay, (ii) activating them into aluminum alkoxides, known for their high and selective activity in controlled lactone polymerization, (iii) swelling the so-organo-modified clay in an organic solvent like toluene, and (iv) promoting  $\epsilon$ -caprolactone (CL) polymerization in toluene, as initiated from the clay in suspension.

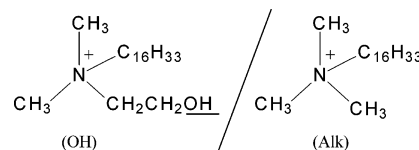
The first step is achieved in the following way: instead of using a surfactant containing 100% OH-functionalized groups, we use different ratios of hydroxyl-terminated alkylammonium (OH) and unsubstituted alkylammonium (Alk) surfactants to exchange the interlayer sodium cations of the natural clay. This particular cationic exchange is expected to disperse a controlled amount of hydroxyl functions at the surface of the clays prior to polymerization. As a consequence, the polymerization of CL and the subsequent PCL chain growth are confined to the OH-bearing sites at the surface of the clay, which can significantly lower the grafting density, compared to an exchange for which the clay is modified by a 100% OH surfactant. Atomic force microscopy (AFM) is then used for direct visualization of the polymer grafted at the surface of single clay platelets. This allows us to follow the gradual coating of individual clay platelets by grafted PCL as the (OH)/(Alk) ratio is gradually increased.

The controlled polymerization/grafting process is then extended to the synthesis of semicrystalline P[CL-*b*-LA] (LA = L,L-lactide) diblock copolyesters, again surface-anchored on the organo-clay. Beyond the aim of understanding the interfacial aspects in exfoliated nanocomposites, this work thus paves the way to a new family of organic–inorganic nanohybrid materials.

## 2. Experimental Section

**2.1. Materials.**  $\epsilon$ -Caprolactone (Fluka) was dried over  $\text{CaH}_2$  and distilled under reduced pressure prior to use. LA was purchased from Boehringer Ingelheim and recrystallized three times in dried toluene (20 wt %/vol) before use. Triethylaluminum ( $\text{AlEt}_3$ ) was purchased

**Scheme 1.** Chemical Structure of the Ammonium Cations Used to Organo-Modify the Natural Sodium Montmorillonite Cloisite–Na (MMT–Na)



from Fluka and diluted with dried toluene.  $\text{AlEt}_3$  solutions were stored in glass ampules under a nitrogen atmosphere. The handling of  $\text{AlEt}_3$  required the work to be performed in an inert atmosphere, free of oxygen and water.

The unmodified montmorillonite–Na (Cloisite–Na, MMT–Na), characterized by a cation-exchange capacity (CEC) of 92 mequiv/100 g, was supplied by Southern Clay Products (Gonzales, TX). 1-Iodo-hexadecane (95%), *N,N*-dimethylethanolamine (99%), and trimethylamine (33 wt % solution in ethanol) were purchased from Aldrich and used without any further purification.

**2.2. Synthesis of Ammonium Cations.** 2-Hydroxyethyl(hexadecyl)-dimethylammonium iodide  $(\text{CH}_3)_2(\text{C}_{16}\text{H}_{33})\text{N}^+(\text{CH}_2\text{CH}_2\text{OH})$  was prepared by a quaternization reaction as follows. 1-Iodo-hexadecane (7.75 g, 0.022 mol) was dissolved in ethanol (200 mL) and reacted with *N,N*-dimethylethanolamine (2.0 mL, 0.020 mol) at 70 °C for 20 h. After solvent evaporation, the reaction product was precipitated in diethyl ether, purified by recrystallization in acetone, and recovered as a white powder that was dried under vacuum at ambient temperature for 24 h. Melting point, 86 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.9 ppm,  $\text{CH}_3$ ; 1.2–1.4 ppm,  $(\text{CH}_2)_{13}$ ; 1.8 ppm,  $\text{N}-\text{CH}_2-\text{CH}_2$ ; 3.4 ppm,  $(\text{CH}_3)_2\text{N}$ ; 3.6 ppm,  $\text{N}-\text{CH}_2$ ; 3.8 ppm,  $\text{N}-\text{CH}_2\text{CH}_2\text{OH}$ ; 4.15 ppm,  $\text{CH}_2\text{OH}$ .

Hexadecyltrimethylammonium  $(\text{CH}_3)_3\text{N}^+(\text{C}_{16}\text{H}_{33})$  iodide was similarly prepared by reaction of 1-iodohexadecane (9.86 g, 0.028 mol) with trimethylamine (6.0 mL, 0.025 mol) in 200 mL of ethanol. The product was purified by recrystallization in ethanol to yield a white powder. Melting point, 118 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 0.9 ppm,  $\text{CH}_3$ ; 1.2–1.4 ppm,  $(\text{CH}_2)_{12}$ ; 1.8 ppm,  $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2$ ; 2.35 ppm,  $\text{N}-\text{CH}_2\text{CH}_2$ ; 3.4 ppm,  $(\text{CH}_3)_2\text{N}$ ; 3.55 ppm,  $\text{N}-\text{CH}_2$ .

**2.3. Preparation of Organophilic Clays.** The different organo-modified montmorillonites used in this work were obtained by exchanging the natural Cloisite–Na with varying ratios of two different surfactants, 2-hydroxyethyl(hexadecyl)dimethylammonium and hexadecyltrimethylammonium cations, referred to here as (OH) and (Alk), respectively (Scheme 1), in different molar ratios. The resulting exchanged montmorillonites (called MMT–(Alk/OH) hereafter) thus contain varying proportions of (OH) groups.

The mixtures used for the co-exchange reaction contained 10, 25, 50, or 75% OH-substituted cations. The exchange reaction was performed in water at 85 °C for 24 h and led to organo-clays coined MMT *x*% (OH), with *x* = 10, 25, 50, and 75. The modified clays were extensively washed with hot water and collected by freeze-drying. The intercalated ammonium compositions were determined from  $^1\text{H}$  NMR analysis of the aqueous solution left after clay intercalation. The results show that the two ammonium species intercalate according to their relative concentration in the starting solution (within a relative error of  $\pm 4\%$ ). Intercalated clays were analyzed by X-ray diffraction (XRD), with the basal spacing increasing from 1.21 nm for MMT–Na to ca. 1.90 nm for the organo-clays, independent of the composition of the mixture of intercalated ammonium cations. The organic content of all the organo-modified montmorillonites was in the 18–24 wt % range, as determined by thermogravimetric analysis (TGA). This is consistent with the complete exchange of the  $\text{Na}^+$  cations on the basis of the MMT–Na CEC value of 92 mequiv/100 g.

**2.4. Polymerization/Grafting onto Organo-Clays.** **2.4.1. PCL Surface Grafting.** Before polymerization, the organo-modified MMT–(Alk/(OH)) clays were dried in a ventilated oven at 70 °C for one night. A desired amount of organo-clay was further dried in a round-bottom

(18) Viville, P.; Lazzaroni, R.; Pollet, E.; Alexandre, M.; Dubois, P.; Borcia, G.; Pireaux, J.-J. *Langmuir* **2003**, *19*, 9425.

**Table 1.** (Co)Polymerization Time for Synthesizing the PCL (and PCL-*b*-PLA)-Grafted Clay Nanohybrids with Defined Inorganic Content

MMT x% (OH)	polymerization time (hours)	clay content <sup>a</sup> (wt % in inorganic)
10	168	58
25	72	52
50	24	50
75	24	57
100	1/168 <sup>b</sup>	3

<sup>a</sup> Determined by thermogravimetric analysis (TGA). <sup>b</sup> Block copolymerization between CL and LA: values for PCL and PLA blocks, respectively (noted PCL/PLA).

flask in a vacuum at 70 °C for 3 h. The dried clay was then allowed to swell in 100 mL of dry toluene for 1 h at 70 °C under a nitrogen atmosphere. The intercalated hydroxylated ammonium cations were then derivatized into aluminum-alkoxide-active species by reaction with triethylaluminum, AlEt<sub>3</sub>, ([OH]/[Al] = 3) for an additional hour at 70 °C. A given amount of  $\epsilon$ -caprolactone (CL) was then added under nitrogen, and the reaction was allowed to proceed at 70 °C for 1–7 days, depending on the type of organo-clay. The polymerization reaction was stopped by the addition of diluted HCl, and the resulting PCL-grafted nanohybrids were recovered after solvent and residual monomer removal, performed by drying the mixture at 85 °C under reduced pressure for 24 h.

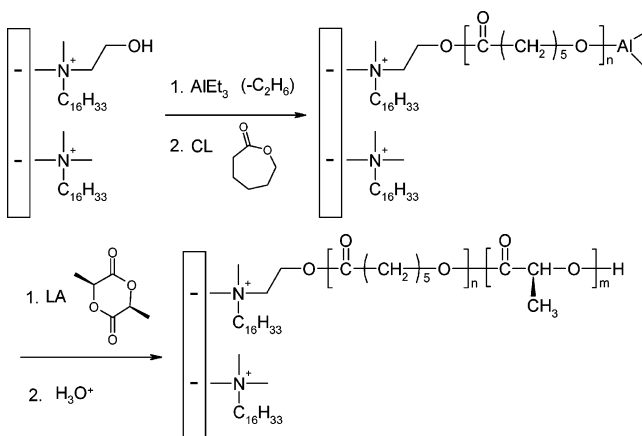
**2.4.2. P[CL-*b*-LA] Diblock Copolymer Surface Grafting.** Poly-[CL-*b*-LA] diblock copolymers were synthesized via sequential copolymerization of CL and LA monomers, conducted in solution (dry toluene). The drying, swelling, and derivatization processes of the organo-clay were performed as described above. A given amount of CL was then added under nitrogen, and the reaction was carried out at 40 °C for 1 h. Then, part of the reaction medium was set aside for further characterization. A desired amount of LA, previously dissolved in hot, dry toluene, was then added to the reaction medium, and the polymerization was allowed to proceed at 70 °C for 7 days. The polymerization reaction was stopped by the addition of diluted HCl, and the resulting copolymer-grafted nanohybrids were immediately recovered by precipitation in cold methanol, filtration, and drying in a vacuum until the weight remained constant.

**2.5. Nanocomposite Characterization.** TGA was performed under an air flow (75 cm<sup>3</sup>/min) at a heating rate of 20 K/min from room temperature to 600 °C with a Hi-Res TGA 2950 from TA Instruments. The clay content of each composite was assessed by TGA as the residue left at 600 °C. A previous comparative TGA study was carried out in triplicate on a separate sample, attesting to the excellent reproducibility in terms of temperature ( $\pm 2$  °C) and weight loss ( $\pm 1$  wt %). The inorganic content of the obtained nanocomposites is reported in Table 1. Nanohybrids containing between 50 and 60 wt % of inorganic matter were prepared by the aforementioned method. This composition range was selected in order to favor the AFM visualization of a large number of individual clay platelets.

The thermal behavior was analyzed by differential scanning calorimetry (DSC), using a DSC 2920 from TA Instrument at a heating rate of 10 K/min from –100 to 200 °C under a flow of nitrogen. The reported values were recorded during the second heating scan.

The morphological analyses by XRD were performed on a Siemens D 5000 powder diffractometer using the Cu K $\alpha$  radiation (wavelength = 1.5406 Å) at room temperature in the range of  $2\theta = 1.5$ –30° with a scanning rate of 2°/min.

For AFM imaging, the as-synthesized nanohybrids were dissolved in toluene to reach a final concentration of 0.1 wt %, and the solutions were deposited by casting on mica substrates. The images were recorded in tapping mode (TM) in ambient atmosphere at room temperature with a Nanoscope IIIa microscope (Veeco Inst., Santa Barbara, CA). The probes were commercially available silicon tips, with a spring constant

**Scheme 2.** Synthetic Pathway to the Synthesis of Clay-Surface-Grafted (Co)Polyesters

of 24–52 N/m, a resonance frequency in the 264–339 kHz range, and a typical radius of curvature in the 10–15 nm range. Unfiltered TM topography images were recorded with the highest sampling resolution available, i.e., 512 × 512 data points.

### 3. Results and Discussion

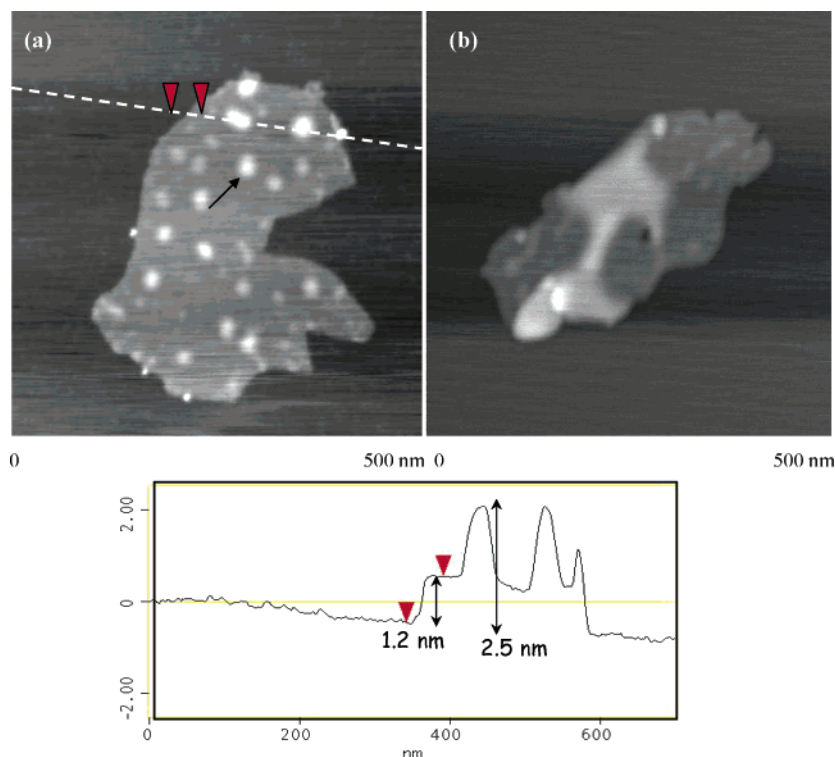
**3.1. Synthesis of Clay-Surface-Grafted (Co)Polyesters.** The grafting of PCL chains onto single clay platelets has been performed according to an original three-step synthetic strategy. The first step relies upon the organo-modification of sodium montmorillonite by a mixture of two alkylammonium cations, one of them being functionalized by a primary hydroxyl group. The cationic exchange reaction was readily carried out in water at ca. 85 °C (see Experimental Section).<sup>15,16</sup> The efficiency of the exchange reaction was evidenced by both XRD and TGA experiments, while the relative composition in alkylammonium cations, OH-functionalized or not, was attested by <sup>1</sup>H NMR and proved to strictly fit the impregnation bath composition at the start. The second and third steps consist of selectively activating the OH functions into aluminum alkoxides and initiating the polymerization/grafting of CL from the activated clay surface, respectively. This synthetic strategy is represented in Scheme 2.

Aluminum alkoxides are well known for their high efficiency to promote the controlled ring-opening polymerization of CL under very mild conditions.<sup>19</sup> Accordingly, triethylaluminum has been reacted with the surface OH functions of the organo-clay swollen in toluene. The evolution of ethane as a volatile byproduct attests that the aluminum-alkoxide-active species is indeed formed. CL polymerization has then been carried out by adding the desired amount of lactone monomer. As reported in the Experimental Section, several organo-clays have been tested with relative OH function concentration ranging from 10 to 100%. In all cases, polymerization occurred smoothly and reached a PCL-to-clay composition close to 50 wt %, i.e., an ideal composition for allowing the visualization of numerous individual clay nanoplatelets and the polymer grafting onto their surface.

It is worth pointing out that the PCL grafting onto the organo-modified montmorillonite is demonstrated by the impossibility

(19) Mecerreyes, D.; Jérôme, R.; Dubois, P. Novel Macromolecular Architectures Based on Aliphatic Polyesters: Relevance of the “Coordination-Insertion” Ring-Opening Polymerization. In *Advances in Polymer Science*; Hilborn, J. G., Ed.; Springer: New York, 1999; Vol. 147, p 1 and references therein.





**Figure 1.** Top: Topographic ( $500 \times 500 \text{ nm}^2$ ) TMAFM images showing the surface morphology of an individual clay platelet for a PCL–MMT nanohybrid in which MMT is exchanged by 10% (OH)-containing surfactant (a) and by 25% (OH)-containing surfactant (b). The vertical grayscale is 5 nm. Bottom: Cross-sectional analysis of image (a).

to separate the polyester chains from the clay by tentative solubilization in good solvents, such as toluene, THF, or chloroform. Even in the presence of an excess of lithium chloride salt, known to cationically exchange with the intercalated ammonium cations,<sup>15–17</sup> recovery of the PCL chains (covalently attached to these ammonium cations through an ester bond) proved to be extremely difficult, which most often prevented the molecular characterization by size exclusion chromatography (SEC). Interestingly, one SEC analysis could be performed on the extracted PCL chains that were polymerized from the clay surface modified with the lowest content in OH functions, i.e., 10%. A number average molecular weight ( $M_n$ ) of 2900 g/mol has been determined; such a value is in very good agreement with the molecular weight expected on the basis of the monomer-to-hydroxyl molar ratio and the CL monomer conversion ( $M_{n,\text{theor}} = 3000 \text{ g/mol}$ ).

Another piece of evidence for the control achievable over the polymerization/grafting reaction is the sequential block copolymerization of CL and LA monomers. As expected for a controlled process, P[CL-*b*-LA] diblock copolymers were generated and surface-grafted onto the organo-clay (see Table 1). Their relative comonomer composition agrees with the starting composition, and each polyester block is shown to crystallize, with melting temperatures at 53 and 150 °C for PCL and PLA blocks, respectively. It has also been possible to readily tune up the crystallinity of each polyester block by controlling the surface-grafted copolyester composition and molecular weight, as evidenced by DSC characterization. Clearly, the possibility to graft such diblock copolyesters onto organo-clays is a strong indication that the (co)polymerization grafting reaction is indeed controlled. The complete characterization of

these surface-grafted diblock copolyesters is beyond the scope of this paper and will be the topic of a forthcoming communication.

**3.2. Visualization of PCL Chain Grafting onto Single Clay Nanoplatelets.** In this section, we present the tapping mode atomic force microscopy (TMAFM) results for thin deposits of the different nanohybrids as the proportion of (OH) functions in the clay is gradually increased. As a reference system, the organo-modified clays, prior to polymerization, were first investigated (results not shown here). In this case, we observe smooth and featureless individual clay platelets that show a constant height profile of  $1.2 \pm 0.2 \text{ nm}$ , independent of the relative amounts of the two ammonium ions. We never observe the presence of impurities that has been recently reported in the atomic force microscopy (AFM) imaging of layered clay materials,<sup>20</sup> most probably because our clay is from a different origin. The height of the platelets observed in this case corresponds to the value expected for uncoated clay platelets (i.e., clay + alkylammonium surfactant without PCL).

The results for nanohybrids in which MMT is modified by a surfactant mixture containing 10 and 25% (OH) groups are shown in Figure 1. The TMAFM topographic images of these two nanohybrids reveal isolated clay platelets lying flat on the substrate surface, with their geometrical contours being well contrasted with respect to the substrate surface. In contrast to the featureless platelets observed before polymerization, they are now partially coated either by round-shaped particles (left image, for 10% (OH)) or by more spread out domains (right image, for 25% (OH)).

(20) Piner, R. D.; Terry, T. X.; Fisher, F. T.; Qiao, Y.; Ruoff, R. S. *Langmuir* **2003**, *19*, 7995.

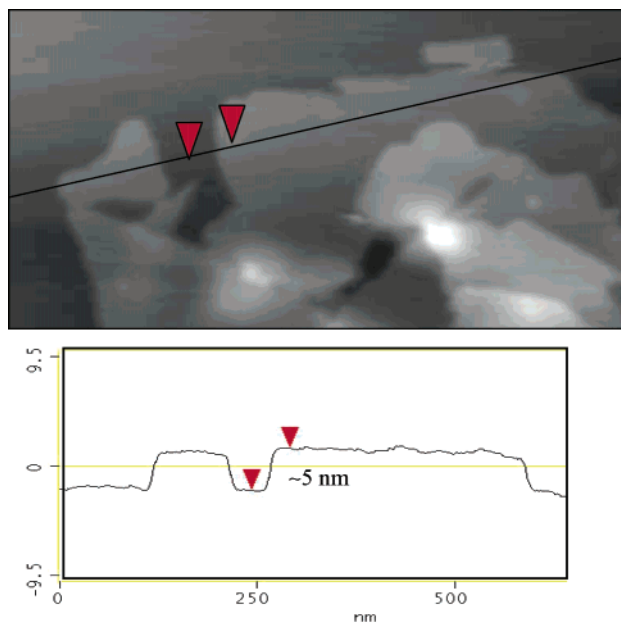
The profile analysis performed on those layers indicates that the brighter domains on top of the platelets are 2.5 nm high with respect to the substrate surface, while the flat, uncovered areas of the platelets are about 1.4 nm high. TMAFM imaging under much higher loading force conditions was carried out to test the mobility of those domains. Typically, this was realized by modifying the ratio ( $R$ ) between the setpoint amplitude ( $A_{sp}$ ) and the amplitude of the free-oscillating cantilever ( $A_0$ ):  $R = A_{sp}/A_0$ . The reduction of this ratio leads to the increase of the loading force on the sample. A semiquantitative description of the loading force relies on the typical instrument settings used; the amplitude of the oscillation was lowered as much as possible (down to  $R = 0.5$ ), meaning high loading forces. Under these conditions, for which the imaging conditions were still correct, it was found that the position of the grafted domains did not change.

The positional stability of those particles, their absence in the nonpolymerized system, and the evolution of the morphology with the amount of (OH)-containing surfactants (see below) clearly indicate that the particles we observe here correspond to the domains of grafted PCL.

For the 10% (OH) system, most of these PCL-grafted domains are isolated. This allows for estimation of their volume and, consequently, for calculation of the number of PCL chains contained in a single domain. As an example, the area pointed to by the black arrow in Figure 1a is characterized by a shape corresponding to a short cylinder with an apparent volume of about  $1400 \text{ nm}^3$ . Considering the PCL density (1.07) and molar mass (2900 g/mol), we estimate that the number of PCL chains in that domain lies between 150 and 300, depending on the exact size of the tip (AFM imaging of very small features can indeed lead to an overestimation of the lateral size of those features because of the convolution of the topographic profile by the profile of the tip<sup>21,22</sup>).

Considering the size of the PCL chains (approximately 30 units for a 2900 g/mol PCL), and the fact that, in the extreme case where they are fully extended, those PCL chains would be 25 nm long, any polymer domain observed in the AFM images is no farther than 25 nm from hydroxyl-substituted ammonium ions. This means that the polymer domains can be used as markers for the position of OH-substituted ammoniums. On that basis, the “spotty” morphology observed in Figure 1a is an indication of phase separation between OH-substituted and unsubstituted ammonium ions. Each polymer spot lies over an area with a large number of OH-substituted ammonium ions, while the large uncovered areas bear the unsubstituted ammonium ions. Along that line, it is noteworthy that the PCL domains in Figure 1a occupy  $\sim 15\%$  of the nanoplatelet surface, which is in rather good agreement with the 10/90 OH/Alk ratio used to prepare the clay.

The morphology of the system containing 25% (OH)-substituted ammonium ions is illustrated in Figure 1b. In this case, instead of being dispersed into individual domains, the grafted PCL always forms more spread out patches, partly covering the platelets. The height of the PCL-covered areas with respect to the substrate surface lies within the 2.5–3 nm range, as in the case of the 10% (OH) system. This higher coverage clearly originates in the presence of a larger number of grafting



**Figure 2.** Top: Topographic ( $550 \times 225 \text{ nm}^2$ ) TMAFM image showing the surface morphology of individual clay platelets for a PCL–MMT nanohybrid in which MMT is exchanged by 50% (OH)-containing surfactant (the vertical grayscale is 25 nm). Bottom: Cross-sectional analysis.

sites at the surface of the clay. This thus demonstrates that the amount of grafted polymer strongly depends on the proportion of hydroxyl groups present at the surface.

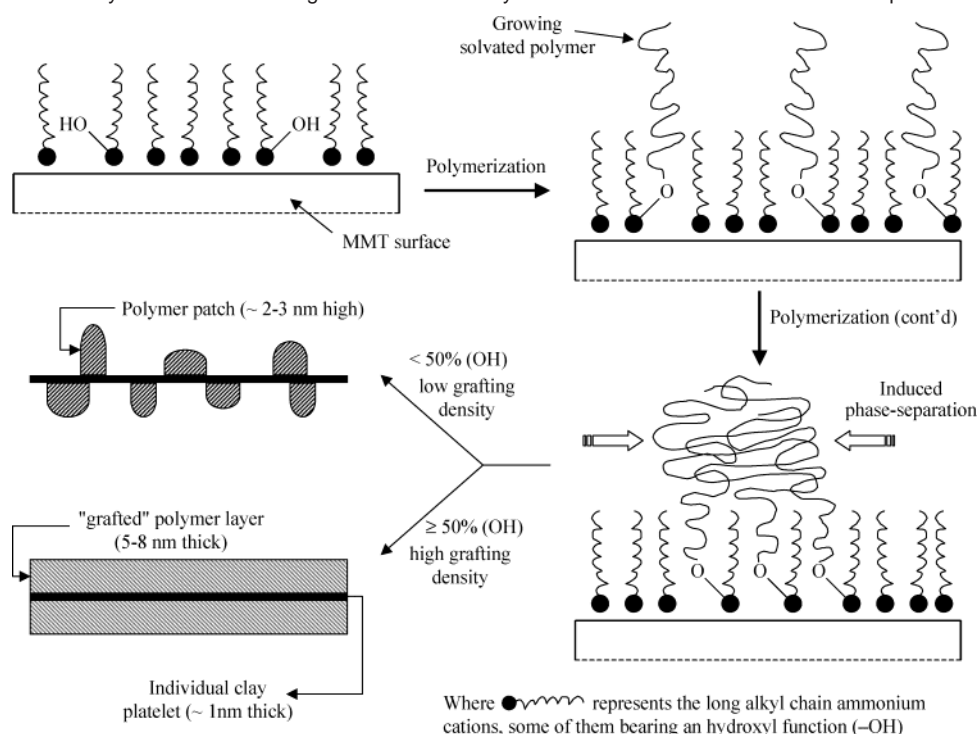
The situation where the clay is exchanged with a surfactant mixture containing higher amounts of (OH) functions, for instance 50%, is illustrated in Figure 2. The surface of single clay platelets appears again to be featureless. However, the section analysis indicates that the platelets are, in this case, significantly thicker than their pristine counterparts:  $5 \pm 1 \text{ nm}$  vs  $1.2 \pm 0.2 \text{ nm}$ . This thickening demonstrates that the platelets are now entirely and homogeneously covered by PCL, consistent with the increase in the grafting density. Consistently, at this point, any further increase of the OH proportion in the surfactant mixture leads to additional thickening of the platelets. For instance, for 75% (OH) content, the height of individual layers with respect to the substrate surface increases into the 6–8 nm range. Clearly, this evolution in the platelet thickness is coherent with the increase in the amount of PCL present on the platelets and with the increase in the number of grafting sites.

The important result to stress here is that, for OH proportions  $\geq 50\%$ , all the platelets are completely and homogeneously covered. This raises the question of whether the phase separation between OH-containing and unsubstituted ammonium ions mentioned above occurs during the cationic exchange or during the polymerization process. In our opinion, the observation of half-coated platelets in the 50% (OH) system would have suggested that the phase separation takes place during the cationic exchange, with polymer chains growing only over the OH-containing domains. In contrast, the homogeneous coating observed here clearly points to a homogeneous mixing of the two ammoniums at the platelet surface.

Therefore, the coexistence of PCL domains and uncovered areas that is observed in the 10 and 25% OH systems (instead of a thinner homogeneous polymer coating) probably means that the OH-containing ions, which initially were homogeneously dispersed on the platelet surface, gather during the

(21) Keller, D. J. *Surf. Sci.* **1991**, 253, 353.

(22) Bustamante, C.; Keller, D. J. *Phys. Today* **1995**, 48, 32.

**Scheme 3.** Sketch for the Polymer Surface Grafting onto Individual Clay Platelets and Concomitant Phase Separation

polymerization process via lateral mobility (Scheme 3). Most probably, the driving force for such an assembly is the aggregation of the growing PCL chains to form polymer domains. This lateral mobility is made possible because the ammonium ions interact electrostatically with the clay surface; positional interchange of ammonium ions is therefore relatively easy and is promoted by the affinity between neighboring grafted PCL chains, furthermore, solvated by toluene, i.e., the solvent in which the polyester chains are growing during the polymerization.

#### 4. Summary

The chemical grafting of polymer chains onto clay nanoplatelets is obtained by a coordination–insertion polymerization of  $\epsilon$ -caprolactone in toluene with a montmorillonite-type clay that is previously exchanged by varying proportions of hydroxyl-substituted alkylammonium and unsubstituted alkylammonium cations. The resulting hydroxylated clay particles play the role of polymerization initiators, leading to the grafting and growing of PCL chains directly at the surface of the clay platelets. The polymerization is well controlled, as evidenced by the unique possibility to grow semicrystalline diblock copolymers between CL and LA, the composition of which is predictable, from the organo-clay surface.

The direct visualization of the polymer grafted onto the clay platelets brings important new information on the structure of those nanohybrid materials: first, the grafting density drastically increases as the proportion of OH-substituted alkylammonium cations used to organo-modify the clay is increased. Second,

the polymer deposit is not simply a continuous film growing in thickness with increased OH content. Instead, separate polymer islands are formed in the low-OH-content systems, probably as a result of a phase separation between the ammonium ions induced by the polymerization reaction. Homogeneous coverage and subsequent thickening only take place from 50% OH content. When this situation is achieved, adjacent platelets become fully independent of each other (because they are fully covered by the polymer), which greatly favors exfoliation.

This work also highlights the possibility of producing organic–inorganic nanohybrids, where the nanoscale components are linked to each other through electrostatic interactions. We are now investigating how the control achievable over the (co)polymerization, the grafting density, the composition, and the crystalline structure of the grafted (co)polymer chains, as well as over the mobility of the ammonium cations to which the polymer is covalently anchored, can be exploited to tune the properties of those hybrid materials.

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