(Plasticized) Polylactide/(Organo-)Clay Nanocomposites by in situ Intercalative Polymerization

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Introduction

During the last decade, the introduction of nanofillers in biodegradable matrices has allowed to improve the range of properties and possible uses of these environmental-friendly polymers. Amongst nanofillers, layered aluminosilicates such as montmorillonite, have been largely studied. Considering poly(l-lactide) (P(l-lactide)) matrix, direct melt blending the polyester with the clay leads to intercalated or, at best, semi-intercalated/semi-exfoliated nanocomposites, whatever the investigated clay surface cationic organomodifier, even with the use of a compatibilizer as poly(ε-caprolactone) (PCL) or the presence of poly(ethylene glycol) (PEG) as plasticizer. Even if intercalation of polymer chains into the interlayer spacing of layered aluminosilicates brings noticeable improvement in term of mechanical, thermal, and barrier properties compared to unfilled matrix, complete delamination of the clay platelets by polymer chains has proved, for several kinds of polymer, to reinforce to a much larger extent the pre-cited properties.

One of the best methods known to achieve exfoliation consists in promoting the matrix polymerization from initiators located on the clay surface. Such a technique has been successfully applied to the preparation of polyamide...
poly(L-L-lactide) promoted directly from the interlayer space of the organomodified clays.\[10,11\] The "grafting" of PCL chains onto montmorillonite, surface-modified by ammonium cations bearing hydroxyl groups, has also been studied. After activation by tin derivatives, the OH groups proved to be highly efficient for initiating the lactone polymerization and "grafting" the PCL chains onto the layered silicate surface. The density of surface hydroxyl functions has been tuned as a parameter controlling both the molecular weight of the polyester chains and the extent of clay exfoliation.\[12\]

In a very recent communication,\[13\] preliminary experiments on the synthesis of fully exfoliated P(L,L-LA)-based nanocomposites have been reported, as obtained by in situ intercalative coordination-insertion polymerization of L,L-lactide promoted directly from the interlayer space of the organomodified montmorillonite. In line with this first communication, this paper aims at studying the effect of such a polyester chain grafting reaction on the nanocomposite morphology and thermal properties by comparing two different organomodified clays, bearing or not hydroxyl groups, has also been studied. After activation by tin derivatives, the OH groups proved to be highly efficient for initiating the lactone polymerization and "grafting" the PCL chains onto the layered silicate surface. The density of surface hydroxyl functions has been tuned as a parameter controlling both the molecular weight of the polyester chains and the extent of clay exfoliation.\[12\]

Experimental Part

Materials

L,L-lactide was purchased from Boehringer Ingelheim and recrystallized three times in dried toluene (20 wt.-%v) before use. Triethylaluminium (AlEt₃) and tin (ii) octoate (Sn(Oct)₂) solutions, from Fluka and Goldschmidt, respectively, were diluted in dried toluene and stored under nitrogen atmosphere into glass ampoules. PEG (Mₘ = 1 000) (PEG 1000) was supplied by Fluka and recrystallized three times in dried toluene (20 wt.-%v) before use. Three different clays were used and were supplied by Southern Clay Products (Texas, USA). Cloisite® Na⁺ corresponds to the natural unmodified montmorillonite-Na⁺. Cloisite® 25A is a montmorillonite modified with dimethyl 2-ethylhexyl (hydrogenated tallowalkyl) ammonium cations, while Cloisite® 30B is modified with bis-(2-hydroxyethyl) methyl tallowalkyl ammonium cations. The amount of organic materials in the organomodified clays was determined by thermogravimetric analysis as 26.9 wt.-% of organic materials for Cloisite® 25A and 20.1 wt.-% for Cloisite® 30B. Finally, poly(D,L-lactide) (70/30 L/D unity, Mₘ = 85 000, Mₙ/Mₘ = 1.9) was supplied by Cargill-Dow S.A.

Polymerization Process

Before synthesis, the aluminosilicate nanofillers were dried overnight at 70 °C in a ventilated oven, and then at the same temperature under reduced pressure for at least 3.5 h, directly in a flame-dried polymerization vial flask equipped with a three-way stopcock capped by a rubber septum. In parallel, the L,L-lactide monomer (and PEG 1000 when necessary) was purified by three successive crystallizations in dried toluene (20 wt.-%v) in a separated, previously flame-dried, and nitrogen-purged round-bottom flask equipped with a three-way stopcock capped by a rubber septum. The initiator/activator solution, followed by the monomer (and PEG 1000 when needed) in dried THF solution (30 wt.-%v) was then added under nitrogen flow to the reaction vial and the solvent was eliminated under reduced pressure. Polymerizations were conducted in bulk at 120 °C, generally for 48 h. At the end of reaction time, the medium was quenched in liquid nitrogen and recovered by breaking the vial.

Masterbatch Process

In a first step, a highly filled Cloisite® 30B/P(L,L-LA) nanocomposite (53 wt.-% inorganic components) was prepared by in situ polymerization following the previously cited procedure. After the synthesis, a part of such masterbatch was then dispersed into commercial P(D,L-LA) in the molten state using a Brabender counter-rotating internal mixer, in order to reach a global inorganic content of 3 wt.-%. More precisely, the blending step was conducted in the presence of 0.3 wt.-% of Ultranox® 626 stabilizer with a rotation speed of 20 rpm for 4 min and then at 60 rpm for 3 min. The processing temperature was set at 180 °C, but it increased to 190 °C upon mixing. 3-mm thick plates were then shaped by compression moulding at 180 °C. The material was pressed under 150 bar for 120 s, followed by a cycle where the pressure was kept successively at 20, 80, 140 bar for 5 s and then released for 1 s after each pressure moulding increase (in order to get rid of any bubbles), and finally under 30 bar for 240 s. The sample was then cooled down by compressing at 15 °C under 30 bar for 5 min.

Characterization

Thermogravimetric analyses were performed using a Hi-Res TGA 2950 thermogravimetric analyzer from TA instrument...
with a heating ramp of 20 K·min⁻¹ under air flow (74 cm³·min⁻¹) from room temperature to 600°C.

Thermal behavior was measured with a DSC 2920 from TA instruments, with a heating and cooling ramp of 10 K·min⁻¹ from −50°C to 200°C under nitrogen flow and the values were recorded during the second heating scan. The morphological analysis by X-ray diffraction was performed on a Siemens D5000 diffractometer using Cu(Kα) radiation (wavelength: 1.5406 Å) at room temperature in the range of 2θ = 1.5–30° with a scanning rate of 2°·min⁻¹. Molecular weight determination of PLA was carried out after eliminating the clay by cationic exchange reaction with LiCl. First a crude nanocomposite sample was dissolved in chloroform and then treated for 48 h with an equal volume of a 1 wt.-% aqueous LiCl solution. Then centrifuged at 3000 rpm for 30 min in order to separate the polymer solution from the nanofiller. P(t,t-L-LA) chains were recovered by precipitation in a seven-fold volume excess of cold methanol (or heptane) and dried under vacuum at 60°C until constant weight. The Sn-based catalyst residues were removed by liquid-liquid extraction with a 0.1 M HCl aqueous solution and PLA was recovered by precipitation from cold methanol. For eliminating the Al-based catalyst residues, a liquid-liquid extraction was carried out using a 0.5 M aqueous solution of ethylenediaminetetraacetic acid at pH 4.8. Size-exclusion chromatography (SEC) measurements were performed in THF (added with 2 vol.-% of triethylamine) at 35°C using a Polymer Laboratory (PL) liquid chromatograph equipped with a PL-DG802 degazer, an isocratic HPLC pump LC1120 (flow rate: 1 ml·min⁻¹), 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 10 µm mixed-B (300 × 7.5 mm). Molecular weights and molecular distributions were calculated by reference to a universal calibration curve relative to PS standard, and using the Kuhn-Mark-Houwink equation for PLA in THF: \(M_n(PLA) = 0.4055 \times M_n(PS)^{0.58}\). For \(^1H\) NMR analyses, the samples were prepared by introducing 30 mg of polymer chains extracted from the composites in 0.6 ml of deuterated chloroform (added with 0.03% of tetramethylsilane). The used spectrometer was a Bruker AMX-500 working at a frequency of 300 MHz for proton in a magnetic field of 7 T.

TEM observations were performed on two distinct equipments. The first was a Philips CM100 apparatus using an acceleration voltage of 100 kV. Ultrathin section of nanocomposite (ca. 80 nm) were prepared by ultramicrotomy at −130°C (Reichert-Jung Ultracut 3E, FC4E ultra-cryotome equipped with a diamond knife). The second one was a Philips CM200 apparatus using also an acceleration voltage of 100 kV. Before analyses, the samples were cut in sections between 75 and 90 nm of thickness using an ultra-cryotome Leica UCT at −130°C.

### Results and Discussion

Poly(t,t-L-lactide) (P(t,t-LA)) layered silicate (nano)compositions were prepared in bulk (i.e., in the absence of solvent) by intercalative in situ polymerization of t,t-L-lactide directly in the presence of montmorillonite, organo-modified or not. Three different layered clays were used, the unmodified natural montmorillonite Cloisite\(^\text{®}\)Na\(^+\) and two unmodified organoclays, referred as Cloisite\(^\text{®}\)25A and Cloisite\(^\text{®}\)30B. Their characteristics in term of alkylammonium cation nature, relative content, as well as interlayer distance as determined by XRD are presented in Table 1.

#### Influence of the Alkylammonium Cation

**Molecular Parameters and Polymerization Mechanism**

In the first approach, in situ polymerization of t,t-lactide has been conducted in bulk in the presence of a fixed amount of (organo-)clays (3 wt.-% in inorganics), in order to understand the influence of the alkylammonium cation on the resulting composite morphology.

Practically, aluminium triisopropoxide (Al(O\(^i\)Pr\(^3\)) was used as initiator. Indeed, this aluminium alkoxide derivative is known to promote the polymerization of lactide, proceeding via a controlled "coordination-insertion" mechanism. More precisely, the experiments were carried out starting with an initial monomer-to-Al(O\(^i\)Pr\(^3\)) molar ratio equal to 300. The synthetic approach involved the dispersion of the layered silicates in the molten monomer, followed by the addition of the initiator. All the considered polymerizations were conducted at 120°C for 48 h. It has to be noted that, contrary to Cloisite\(^\text{®}\)Na\(^+\) or Cloisite\(^\text{®}\)25A, for which the initiation step is selectively promoted by the alkoxide groups of Al(O\(^i\)Pr\(^3\)), the case of Cloisite\(^\text{®}\)30B, the hydroxyl groups of the alkylammonium cations substituting the filler can also participate in the initiation step, through an exchange reaction between alcohol functions of the ammonium and alkoxide groups of Al(O\(^i\)Pr\(^3\)).

Table 1. Characteristics of used montmorillonites.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Exchanging cation</th>
<th>Organic fraction</th>
<th>Interlayer distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite(^\text{®})Na(^+)</td>
<td>Na(^+)</td>
<td>–</td>
<td>12.1</td>
</tr>
<tr>
<td>Cloisite(^\text{®})30B</td>
<td>(C(<em>{18})H(</em>{33}))N(^+)((\text{C}_2\text{H}_5\text{OH})_2)C(_3)H(_2)</td>
<td>20.1</td>
<td>18.4</td>
</tr>
<tr>
<td>Cloisite(^\text{®})25A</td>
<td>(C(<em>{18})H(</em>{33}))N(^+)((\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5))\text{C}_3\text{H}_2)(\text{CH}_3)_2</td>
<td>26.9</td>
<td>20.4</td>
</tr>
</tbody>
</table>
After extraction of both clays and aluminium residues (see Experimental Part) the recovered P(L,L-LA) chains have been characterized by SEC. As shown in Table 2, the experimental $\bar{M}_n$ are in agreement with the theoretical values. It seems therefore that the polymerization proceeds again through a controlled mechanism. Moreover, the polydispersity indices remain relatively narrow for such polymerization reactions conducted under heterogeneous conditions, i.e., in presence of (organo-)clay.

The possibility to directly graft the PLA chains on the surface of the organoclay through activation of hydroxyl groups bore by the ammonium cation of Cloisite<sup>®</sup> 30B has prompted us to study the influence of the $n_{\text{OH}}/n_{\text{Al}}$ initial molar ratio on its ability to promote the controlled polymerization.<sup>15</sup> Accordingly, the relative content in Al(O’Pr<sub>3</sub>) has been reduced while keeping the L,L-LA/clay ratio (3 wt.-%) constant. The results are gathered and shown in Table 3.

Clearly, a $n_{\text{OH}}/n_{\text{Al}}$ molar ratio as high as 20 is responsible for some loss of control, as evidenced by the difference between theoretical and experimental $\bar{M}_n$ and broadening of the molecular weight distribution. It must be noted that most of the initiating species are actually issued from the organoclay itself, i.e., the filler (hydroxyl groups from Cloisite<sup>®</sup> 30B). A possible explanation to this lack of polymerization control could stand in the partial deactivation of the aluminium alkoxides by protic impurities associated to Cloisite<sup>®</sup> 30B, actually in relatively larger quantity with regard to Al(O’Pr<sub>3</sub>).

In order to know if the control in the polymerization process is function of the initiator nature, experiments have been performed considering only Cloisite<sup>®</sup> 30B and two different activators, namely AlEt<sub>3</sub> and stannous (II) octoate (Sn(Oct)<sub>2</sub>) for various molar ratios compared to the hydroxyl functions of the nanofiller (Table 4). Therefore, the initiation reaction will occur exclusively from the hydroxyl groups of the layered silicates, after their activation in alkoxide species by reaction with AlEt<sub>3</sub> or Sn(Oct)<sub>2</sub>.<sup>16</sup> The polymerization mechanism implies the coordination of the cyclic ester to the metallic atom, followed by the monomer insertion within the metal (Al or Sn) alkoxide bond by cleavage of endocyclic acyl-oxygen bond, in such way that the growing PLA chains remain attached to the metallic atom through an alkoxide bond.

Considering AlEt<sub>3</sub> as initiator precursor (first two entries in Table 4), the $n_{\text{OH}}/n_{\text{Al}}$ molar ratio has been fixed firstly to 1 in order to form diethyl aluminium monoalkoxides by in situ reaction with the hydroxyl groups of the ammonium cations (Figure 1). By increasing the relative amount of AlEt<sub>3</sub>, a $n_{\text{OH}}/n_{\text{Al}}$ molar ratio of 3 has been then envisaged in order to form ideally aluminium trialkoxides as the initiating species at least.

Table 2. Al(O’Pr<sub>3</sub>) promoted polymerization of l,l,l-lactide in presence of 3 wt.-% of (organo-) clay (in bulk, 120 °C, 48 h).

<table>
<thead>
<tr>
<th>Code</th>
<th>Clay</th>
<th>$n_{\text{L-LA}}/n_{\text{Al}}$</th>
<th>$n_{\text{OH}}/n_{\text{Al}}$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Conv.&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$DP_{\text{th}}$</th>
<th>$\bar{M}_n$ th&lt;sup&gt;c&lt;/sup&gt;</th>
<th>$\bar{M}_n$ exp&lt;sup&gt;f&lt;/sup&gt;</th>
<th>$\bar{M}_n$/conv&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN3Na</td>
<td>Cloisite® Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>300</td>
<td>–</td>
<td>100</td>
<td>100&lt;sup&gt;)&lt;/sup&gt;</td>
<td>14 400</td>
<td>16 500</td>
<td>1.5</td>
</tr>
<tr>
<td>SN3A25</td>
<td>Cloisite® 25A</td>
<td>300</td>
<td>1.8</td>
<td>100</td>
<td>35&lt;sup&gt;)&lt;/sup&gt;</td>
<td>5 040</td>
<td>5 400</td>
<td>1.2</td>
</tr>
<tr>
<td>SN3B30</td>
<td>Cloisite® 30B</td>
<td>300</td>
<td>1.8</td>
<td>100</td>
<td>35&lt;sup&gt;)&lt;/sup&gt;</td>
<td>5 040</td>
<td>5 400</td>
<td>1.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> $n_{\text{OH}} = m_{\text{clay}} \times$ organic content (in %) $\times$ 2/MW (ammonium cations).

<sup>b</sup> As determined by gravimetry after extraction of clay and catalytic residues.

<sup>c</sup> $DP_{\text{th}} = [\text{L,L-LA}]_0/[[\text{Al}] \times 3]$ $\times$ conv.

<sup>d</sup> $\bar{M}_n$ th = $DP_{\text{th}} \times 144$.

<sup>e</sup> As determined by size-exclusion chromatography (SEC).

Table 3. Influence of the $n_{\text{OH}}/n_{\text{Al}}$ initial molar ratio on the in situ polymerization of L,L-Lactide promoted by Al(O’Pr<sub>3</sub>) in presence of 3 wt.-% of Cloisite® 30B (in bulk, 120 °C, 48 h).

<table>
<thead>
<tr>
<th>Code</th>
<th>$n_{\text{L-LA}}/n_{\text{Al}}$</th>
<th>$n_{\text{OH}}/n_{\text{Al}}$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Conv.&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$DP_{\text{th}}$</th>
<th>$\bar{M}_n$ th&lt;sup&gt;c&lt;/sup&gt;</th>
<th>$\bar{M}_n$ exp&lt;sup&gt;f&lt;/sup&gt;</th>
<th>$\bar{M}_n$/conv&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN3B30(I)</td>
<td>300</td>
<td>1.8</td>
<td>100</td>
<td>35</td>
<td>5 040</td>
<td>5 400</td>
<td>1.2</td>
</tr>
<tr>
<td>SN3B30(II)</td>
<td>3 640</td>
<td>20</td>
<td>100</td>
<td>58</td>
<td>8 350</td>
<td>6 600</td>
<td>1.6</td>
</tr>
</tbody>
</table>

<sup>a</sup> $n_{\text{OH}} = m_{\text{clay}} \times$ organic content (in %) $\times$ 2/MW (ammonium cations).

<sup>b</sup> As determined by gravimetry after extraction of clay and catalytic residues.

<sup>c</sup> $DP_{\text{th}} = [\text{L,L-LA}]_0/[[\text{Al}] \times 3 + \text{[OH]}_0]$ $\times$ conv.

<sup>d</sup> $\bar{M}_n$ th = $DP_{\text{th}} \times 144$.

<sup>e</sup> As determined by SEC.
From the conversion, it can be deduced that the polymerization rate is function of the aluminium alkoxide nature that initiates the reaction. Indeed, the polymerization kinetics is much more rapid, when aluminium monoalkoxides are concerned, in comparison to trialkoxides. This behavior is in opposition to results obtained for the polymerization in solution or in homogeneous conditions (in bulk) of L,L-lactide. Indeed, Barakat et al. have shown that aluminium trialkoxides were able to promote L,L-LA polymerization in a controlled way with a much higher rate than diethyl aluminium monoalkoxide species. Such a discrepancy can be explained by the difficulty to form aluminium trialkoxide species by reacting AlEt₃ with the dihydroxylated ammonium species, actually ionically anchored on the clay surface of Cloisite³⁰B. Indeed, owing to the specific structure of Cloisite³⁰B interlayer spacing, the probability to form a large amount of trialkoxide species is rather low (Figure 2). Most probably, a mixture of aluminium mono-, di-, and tri-alkoxides is formed, which is responsible for the low monomer conversion, the loss of polymerization control and the bimodality of the molecular weight distribution. The experimental $M_n$ greatly diverge

![Silicate layer](image1.png)

![Silicate layer](image2.png)

![Silicate layer](image3.png)

Figure 1. Schematic representation of the L,L-lactide polymerization performed in situ from Cloisite³⁰B using triethylaluminium (AlEt₃) as initiator (R stands for tallow alkyl chain).

<table>
<thead>
<tr>
<th>Code</th>
<th>Activator</th>
<th>$n_{OH}/n_{Met}$</th>
<th>Conv. (%)</th>
<th>$DP_{th}$</th>
<th>$M_n$ th</th>
<th>$M_n$ exp</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3B30A11</td>
<td>AlEt₃</td>
<td>1</td>
<td>85</td>
<td>142</td>
<td>20 500</td>
<td>10 300</td>
<td>1.7</td>
</tr>
<tr>
<td>N3B30A13</td>
<td>AlEt₃</td>
<td>3</td>
<td>23</td>
<td>41</td>
<td>6 000</td>
<td>Bimodal</td>
<td>Bimodal</td>
</tr>
<tr>
<td>N3B30Sn1</td>
<td>Sn(Oct)₂</td>
<td>1</td>
<td>71</td>
<td>120</td>
<td>17 280</td>
<td>14 100</td>
<td>2.4</td>
</tr>
<tr>
<td>N3B30Sn2</td>
<td>Sn(Oct)₂</td>
<td>2</td>
<td>94</td>
<td>160</td>
<td>23 000</td>
<td>11 600</td>
<td>2.4</td>
</tr>
</tbody>
</table>

$\text{a) } n_{OH} = m_{\text{clay}} \times \text{organic content (in %)} \times 2/MW$ (ammonium cations).

$\text{b) As determined by gravimetry after extraction of clay and catalytic residues.}$

$\text{c) } DP_{th} = [\text{L,L-LA}]_0/[\text{OH}]_0 \times \text{conv.}$

$\text{d) } M_n \text{ th} = DP_{th} \times 144.$

$\text{e) As determined by SEC.}$

$\text{f) Bimodal distribution.}$
from the theoretical values, whatever the initial \( n_{\text{OH}}/n_{\text{Al}} \) molar ratio (Table 4).

In parallel, \( \text{Sn(Oct)}_2 \) has been approached, as well the \( n_{\text{OH}}/n_{\text{Sn}} \) molar ratio has been fixed from 1 to 2 (Table 4), while keeping the organomodified clay-to-monomer ratio constant. The in situ formation of tin alkoxide active species through the following equilibrium (Equation (1)) has been proposed for taking into account the polymerization activity of \( \text{Sn(Oct)}_2 \) in the presence of alcohol (\( n_{\text{OH}} \))[11]

\[
\text{Sn(Oct)}_2 + n_{\text{OH}} \rightleftharpoons \text{Sn(Oct)}_{2-n}(\text{OR})_n + n \text{OctH}
\]

(1)

Even though the polymerization occurs smoothly with a lactide conversion higher than 90\% after 24 h at 120 °C (for \( n_{\text{OH}}/n_{\text{Sn}} = 2 \)), it appears that no control over the polymerization could be reached. In conclusion, these results therefore bring the evidence that the results obtained for the polymerization of a lactone in some defined conditions cannot be directly extended to another lactone. Indeed, while \( \varepsilon \)-caprolactone can be polymerized in a perfectly controlled way in presence of clay and using different activators like tin octoate or \( \text{AlEt}_3 \) it is not the case for \( l,l \)-lactide, at least within the investigated experimental conditions.[12,18]

Morphology

WAXS analyses were performed in order to characterize the morphology of the obtained composites prepared by in situ intercalative polymerization of \( l,l \)-lactide initiated by \( \text{Al(O'Pr)}_3 \).
Cloisite® initiated by Al(O\(_2\)) and VI for
prepared by in situ intercalative polymerization of L,L-LA
related nanocomposites (each filled with 3 wt.-%
noted for interlayer distance
Macromol. Chem. Phys. 2005
on 3 wt.-% of natural or organomodified montmorillonites
The thermal degradation behavior of nanocomposites based
Thermal and Crystallization Behavior
Figure 3. WAXS diffractograms of Cloisite\(^{\text{R}}\)Na\(^{+}\) (curve (a)), Cloisite\(^{\text{R}}\)25A (curve (c)), Cloisite\(^{\text{R}}\)30B (curve (e)), and the
related nanocomposites (each filled with 3 wt.-% inorganics)
prepared by in situ intercalative polymerization of L,L-LA
initiated by Al(O\(_2\))Pr\(_3\) (curves (b), (d), and (f), respectively); I is
noted for interlayer distance \(d_{(001)}\) of 12.0 Å, II for \(d_{(001)}\) of 22.9 Å,
III for \(d_{(001)}\) of 20.4 Å, IV for \(d_{(001)}\) of 28.3 Å, V for \(d_{(002)}\) of 14.5 Å,
and VI for \(d_{(001)}\) of 18.4 Å.

As shown in Figure 3, both Cloisite\(^{\text{R}}\)25A and
Cloisite\(^{\text{R}}\)Na\(^{+}\) led to intercalated nanocomposites. As far
as Cloisite\(^{\text{R}}\)Na\(^{+}\) is concerned, in situ polymerization allows
to prepare an intercalated nanocomposite while only micro-
composites could be recovered by direct melt-blending a
preformed PLA matrix with the same pristine (non
modified) clay.[19] An explanation can stand in the swelling
step of the layered silicates in the molten monomer before
performing the initiation, so that the PLA chains can grow
directly in the interlayer space of the clay. Such intercala-
tion of a lactone monomer in the interlayer spacing of a
Na\(^{+}\)-montmorillonite has already been reported both theo-
retically and experimentally for \(\varepsilon\)-caprolactone.[11,20]

When the in situ intercalative polymerization of L,L-
lactide is carried out in presence of Cloisite\(^{\text{R}}\)30B, no
diffraction peak can be detected by WAXS (compare curves
(e) and (f) in Figure 3). Such a result suggests the formation
of an exfoliated structure and was confirmed by TEM as
recently reported in our first communication.[20] In this
case, exfoliation is thus favored by the PLA chains grafting
on the alkylammonium cations of the nanofiller, through
their hydroxyl groups (as sketched in Figure 1).

Thermal and Crystallization Behavior
The thermal degradation behavior of nanocomposites based
on 3 wt.-% of natural or organomodified montmorillonites
prepared by in situ intercalative polymerization of L,L-
lactide initiated by Al(O\(_2\))Pr\(_3\) was studied by thermogravi-
metric analysis. Figure 4 shows the thermograms recorded
under air flow for the nanocomposites based on
Cloisite\(^{\text{R}}\)Na\(^{+}\), Cloisite\(^{\text{R}}\)25A and Cloisite\(^{\text{R}}\)30B (3 wt.-% in
organics) as well as for the P(L,L-LA) matrix extracted
from the Cloisite\(^{\text{R}}\)25A-based nanomaterials (see Experimental Part).
Both intercalated and exfoliated nanocomposites
degraded at higher temperatures compared to the
selectively extracted PLA chains.

The temperature at which 50% weight loss is recorded
increases in the following order: unfilled PLA < inter-
calated PLA/Cloisite\(^{\text{R}}\)Na\(^{+}\) < intercalated PLA/
Cloisite\(^{\text{R}}\)25A < exfoliated PLA/Cloisite\(^{\text{R}}\)30B. When
intercalation of PLA chains takes place between clay plate-
lets, a significant difference in thermal degradation can be
observed between Cloisite\(^{\text{R}}\)Na\(^{+}\) (Figure 4, curve (b)) and
Cloisite\(^{\text{R}}\)25A-based (Figure 4, curve (c)) nanocomposites.
Indeed, the lower delay in degradation is noted for the
natural sodium montmorillonite. This difference may rely
on either a less regular and extended clay platelet inter-
calation for Cloisite\(^{\text{R}}\)Na\(^{+}\) compared to Cloisite\(^{\text{R}}\)25A or an
effect from the absence of organomodifier within
Cloisite\(^{\text{R}}\)Na\(^{+}\) based nanocomposite. Thus, the thermal
degradation for the nanocomposite based on Cloisite\(^{\text{R}}\)30B
arises at a higher temperature (temperature at which 50 wt.-%
loss is recorded: 362 °C compared to 325 °C for unfilled
P(L,L-LA). This increase in thermal stability occurs while
the molecular weight of the P(L,L-LA) chains, surface-
grafted to Cloisite\(^{\text{R}}\)30B, is much lower (\(\overline{M}_n = 5,400\)) than
those measured for the P(L,L-LA) matrix formed in presence of
Cloisite\(^{\text{R}}\)Na\(^{+}\) or 25A (\(\overline{M}_n \sim 15,000\), see Table 2).

![WAXS diffractograms](image)

**Figure 3.** WAXS diffractograms of Cloisite\(^{\text{R}}\)Na\(^{+}\) (curve (a)), Cloisite\(^{\text{R}}\)25A (curve (c)), Cloisite\(^{\text{R}}\)30B (curve (e)), and the related nanocomposites (each filled with 3 wt.-% inorganics) prepared by in situ intercalative polymerization of L,L-LA initiated by Al(O\(_2\))Pr\(_3\) (curves (b), (d), and (f), respectively); I is noted for interlayer distance \(d_{(001)}\) of 12.0 Å, II for \(d_{(001)}\) of 22.9 Å, III for \(d_{(001)}\) of 20.4 Å, IV for \(d_{(001)}\) of 28.3 Å, V for \(d_{(002)}\) of 14.5 Å, and VI for \(d_{(001)}\) of 18.4 Å.

![Thermal dependence of weight loss](image)

**Figure 4.** Temperature dependence of weight loss for nanocomposites containing 3 wt.-% (relative to inorganics) of (b) Cloisite\(^{\text{R}}\)Na\(^{+}\), (c) Cloisite\(^{\text{R}}\)25A, and (d) Cloisite\(^{\text{R}}\)30B, directly compared to the PLA matrix (a) as recovered after extraction from the nanocomposite (c) (heating rate of 20 °C·min\(^{-1}\), under air flow).
behavior has to be assigned both to clay layer delamination and P(L,L-LA) chain grafting onto the clay surface.\(^{[13]}\)

Finally, DSC analysis reveals, as was already observed for nanocomposites prepared by direct melt blending,\(^{[19]}\) that the nature of the clay organomodification does not affect neither \(T_g\) nor \(T_m\) values of the PLA chains, standing around 62 and 170 °C, respectively. As far the melting enthalpy is concerned, a value of ca. 55 J · g\(^{-1}\) was found, whatever the nature of the filler.

**Influence of Clay Loading**

By using the in situ polymerization technique, it has been previously shown that intercalation or exfoliation of the clay platelets in the P(L,L-LA) matrix can be achieved in function of the organomodification of the aluminosilicates. In order to study the influence of the clay loading on nanocomposite morphology, we have focused our attention on Cloisite\(^{®}\) 25A, leading to intercalated species, and on Cloisite\(^{®}\) 30B, giving exfoliated nanocomposites, at least at 3 wt.-% in inorganic. Practically, in situ intercalative polymerizations of L,L-lactide were conducted in bulk, using Sn(Oct)\(_2\) (\(n_{\text{L,L-LA}}/n_{\text{Sn}} = 300\)) as activator when Cloisite\(^{®}\) 25A was concerned, and AlEt\(_3\) (\(n_{\text{OH}}/n_{\text{Al}} = 1\)) as aluminium alkoxide precursor for Cloisite\(^{®}\) 30B-based experiments. It must be noted that all the experimental conditions were adapted in function of the filler nature with the aim to reach 100% of conversion while tentatively limiting transesterification reactions. It has been therefore decided to conduct in situ polymerization at 120 °C for 24 h as far as Sn(Oct)\(_2\) was concerned and for 48 h when AlEt\(_3\) was used as activator. Table 5 presents the initial experimental conditions of the considered in situ polymerization and the molecular parameters of the extracted PLA chains.

Concerning the polyester chains issued from the nanocomposites based on Cloisite\(^{®}\) 25A (Table 5), the molecular weights remain relatively constant (around 38 000 as \(M_n\)) whatever the clay content. It can, therefore, be concluded that both the clay and the alkylammonium cation of this filler behave as spectator entities in the initiation and propagation processes.

On the contrary, when the relative content in Cloisite\(^{®}\) 30B is increased, the concentration in hydroxyl functions in the medium is consequently higher, which should lead to P(L,L-LA) grafts characterized by a lower degree of polymerization. Monomer conversion (Table 5) does not seem to be complete, which is actually in discrepancy with TGA results (see hereafter). Indeed, one cannot preclude an under-estimation of the conversion due to some fractionation as the polyester chains were recovered by precipitation from cold methanol, a solvent for the monomer but also for P(L,L-LA) oligomers. When considering polymers chains formed in nanocomposites containing 1 or 3 wt.-% of Cloisite\(^{®}\) 30B, the experimental molecular weight of the extracted PLA obtained by SEC differs significantly from the predicted ones on the basis of the hydroxyl content in the reaction medium. However, when the in situ polymerization of L,L-lactide is conducted in the presence of 5 wt.-% of Cloisite\(^{®}\) 30B, a relatively good agreement between experimental and theoretical PLA molecular weights is found. Such a discrepancy might find some explanation in the investigated PLA extraction process, i.e., an ionic exchange reaction between the ammonium cations bearing the PLA grafts and lithium cations (see Experimental Part). It appears that this technique, thus used for eliminating the silicate layers from the polymer chains, is more adapted to shorter polyester chains. As the chains length increases, the accessibility to cationic sites of the layered silicates is more

### Table 5. Influence of the clay content on monomer conversion and molecular parameters of the P(L,L-LA) chains extracted from nanocomposites based on Cloisite\(^{®}\) 25A and Cloisite\(^{®}\) 30B (in bulk, 120 °C, 48 h) and their thermal transitions and melting temperature.

<table>
<thead>
<tr>
<th>Code</th>
<th>Clay</th>
<th>Conv. a)</th>
<th>(M_n) th b) (g · mol(^{-1}))</th>
<th>(M_n) exp c) (g · mol(^{-1}))</th>
<th>(M_n/\bar{M}_n)</th>
<th>(T_g) f) °C</th>
<th>(T_m) f) °C</th>
<th>(\Delta H_m) f) J · g(^{-1})</th>
</tr>
</thead>
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<tr>
<td>SN1A25</td>
<td>Cloisite(^{®}) 25A d)</td>
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<td>99</td>
<td>–</td>
<td>35 300</td>
<td>&gt;2</td>
<td>55</td>
<td>170</td>
</tr>
<tr>
<td>SN3A25</td>
<td></td>
<td>3</td>
<td>98</td>
<td>–</td>
<td>40 000</td>
<td>&gt;2</td>
<td>62</td>
<td>172</td>
</tr>
<tr>
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<td></td>
<td>5</td>
<td>97</td>
<td>–</td>
<td>39 000</td>
<td>&gt;2</td>
<td>62</td>
<td>170</td>
</tr>
<tr>
<td>SN10A25</td>
<td></td>
<td>10</td>
<td>98</td>
<td>–</td>
<td>36 000</td>
<td>~2</td>
<td>62</td>
<td>171</td>
</tr>
<tr>
<td>SN1B30</td>
<td>Cloisite(^{®}) 30B e)</td>
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<td>81</td>
<td>64 800</td>
<td>17 800</td>
<td>~2</td>
<td>60</td>
<td>180</td>
</tr>
<tr>
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<td></td>
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<td>85</td>
<td>20 500</td>
<td>10 300</td>
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<td>93</td>
<td>6 600</td>
<td>ND</td>
<td>ND</td>
<td>61</td>
<td>170</td>
</tr>
</tbody>
</table>

a) As determined by gravimetry after extraction of clay and catalytic residues.

b) \(M_n\) th = \([\text{L,L-LA}]_0/[\text{OH}]_0\) × conv. × 144.

c) As determined by SEC; polydispersity indices close to 2 in all entries (ND, not determined).

d) Sn(Oct)\(_2\) as promoter: \(n_{\text{L,L-LA}}/n_{\text{Sn}} = 300\) (in bulk, 120 °C, 24 h).

e) AlEt\(_3\) as promoter: \(n_{\text{OH}}/n_{\text{Al}} = 1\) (in bulk, 120 °C, 48 h).

f) By DSC under nitrogen flow from –10 to 200 °C (10 °C · min\(^{-1}\)).
difficult for an alkaline cation such as lithium cation, leading to a less efficient extraction of the longer P(L,L-LA) chains.

In term of morphology, as revealed by WAXS analysis (Figure 5), intercalation of PLA chains into the interlayer spacing of Cloisite<sup>®</sup>25A is highlighted by a shift of d<sub>(001)</sub> peak of the organoclay (noted I in Figure 5) in the nanocomposite towards lower 2θ angles. As an example, considering a nanocomposite prepared from 5 wt.-% of Cloisite<sup>®</sup>25A, the interlayer distance d<sub>(001)</sub> in the nanocomposition (noted V in Figure 5) approaches 33 Å, while it has a value of 20.4 Å in the corresponding organoclay. Moreover, increasing the nanofiller content leads to a more precisely defined and narrow d<sub>(001)</sub> diffraction peak (noted II, III, V, and VII for 1, 3, 5, and 10 wt.-% Cloisite<sup>®</sup>25A, respectively) and better definition of d<sub>(002)</sub> diffraction peak (noted IV, VI, and VIII for 3, 5, and 10 wt.-% Cloisite<sup>®</sup>25A, respectively), as a consequence of more regular platelets stacking at higher clay content, for instance 10 wt.-% in inorganics. As far as Cloisite<sup>®</sup>30B-based nanocomposites are concerned, no trace of diffraction peak showing up at low 2θ angle can be observed on the XRD patterns (from 1 to 10 wt.-% in inorganics, Figure 6 where the dashed line and star show the localization of the diffraction peak for Cloisite<sup>®</sup>30B).

The thermal stability of the Cloisite<sup>®</sup>30B-based nanocomposites containing from 1 to 10 wt.-% nanoclay has been analyzed by TGA and compared with P(L,L-LA) extracted from 5 wt.-% Cloisite<sup>®</sup>30B nanocomposite (M<sub>n</sub> ~ 14 000) (Figure 7). Whatever the filler content, these nanocomposites exhibit a better thermal stability than the unfilled matrix. Such a delay in the degradation temperature may be ascribed to a decrease in oxygen and volatile degradation products permeability/diffusivity due to the homogeneous dispersion/delamination of clay sheets, arising from the barrier properties of this high aspect ratio filler. Char formation is also responsible for such an increase in thermal stability.<sup>[5]</sup> While the best thermal properties are observed for nanocomposites filled with 1 and 3 wt.-% of exfoliated Cloisite<sup>®</sup>30B, the temperature shift is less important when filled with 5 and 10 wt.-%. Two interrelated phenomena may be at the origin of this decrease. First, the extent of clay dispersion in PLA matrix decreases with the clay loading, as a result of sterical hindrance around the clay platelets, which are knocking each other at high filler loading. Another explanation relies upon the decrease in molecular weight of the grafted PLA chains, expected from the higher concentration in initiating species at higher Cloisite<sup>®</sup>30B content. Finally, no trace of residual monomer, characterized by a volatilization around 200 °C, can be observed attesting for the quantitative conversion of L,L-LA upon polymerization.
Finally, considering the nanocomposites based on Cloisite® 30B, DSC analyses have shown that a filler content as low as 1 wt.-% does not significantly influence the $T_g$ of the matrix, as the thermal transition is kept closed to 55 °C (Table 5). Indeed, $T_g$ for a commercial P(t,l-LA) characterized by the same molecular mass has been detected around 55 °C, under the same analysis conditions. However, as the filler content increases from 3 to 10 wt.-%, a slight increase in $T_g$ has been evidenced and could be explained by the limitation of the chains relaxation following their intercalation in the interlayer spacing of the clay. The relatively low extent of intercalated polyester chains compared to completely free ones in the nanocomposites based on 1 wt.-% in inorganics is probably the reason why such phenomenon is not observed at such a low loading. In addition, the $T_m$ values of the polyester matrix chains are not influenced by the filler loading. In parallel, the $\Delta H_m$ values have been kept relatively constant with the clay loading, the aluminosilicate platelets cannot be therefore considered as nucleating agents. As far as the Cloisite® 30B based nanocomposites are concerned (Table 5), the decrease of the melting enthalpy at higher filler content could be related to the P(t,l-LA) chains length. Indeed, as the Cloisite® 30B loading in the nanocomposites increases, the concentration of hydroxyl groups initiating the t,l-lactide polymerization increases in the same manner, leading to shorter P(t,l-LA) grafts, which need less thermal energy to melt. On the other hand, all the samples are characterized by a glass transition temperature as high as 61 ± 1 °C, $T_g$ typical for non-plasticized P(t,l-LA) chains. Such a value is consistent, once again, with a quantitative conversion of t,l-LA to P(t,l-LA), as lactide is known to be a good plasticizer for P(t,l-LA).

**Masterbatch Process**

Melt intercalation of preformed polymers and in situ intercalative polymerization are the two techniques most commonly used to prepare polymer/clay nanocomposites. The first method is effective whenever the thermodynamics of the molten polymer/organoclay pair allows the chains to crawl within the clay interlayer spaces, so pushing the individual sheets apart from each other. The second method relies on the swelling of the organoclay by the liquid monomer (or by the molten monomer if solid) followed by the in situ polymerization initiated by a suitable compound. The chains growth in the clay galleries can trigger the clay exfoliation and the nanocomposite formation in case of adequately organomodified clays.

Knowing that the best improvement of the matrix properties is most often achieved by the complete delamination of the aluminosilicate layers, there is therefore a lot of interest to prepare exfoliated nanocomposites at large scale industrial production level. However, the in situ polymerization approach presents the major disadvantage to imply organometallic catalysts, degradation-sensitive monomer, and in some cases solvent(s), which could limit its (industrial) exploitation where the technique of melt intercalation is preferred.

For that purpose, another approach, combining both the in situ intercalative polymerization and the melt intercalation processes, has been envisaged. A highly-filled organomodified clay/PLA masterbatch is first prepared by in situ polymerization of t,l-lactide, followed by melt mixing it with commercially available PLA matrix (plasticized with PEG 1000 or not). The main advantage of this particular technique stands in the possibility to obtain nanocomposite with a high degree of exfoliation, which cannot be achieved by direct melt blending of the polyester with the clay.

This original process has already been used in order to prepare PCL and poly(vinyl chloride) (PVC) layered silicate nanocomposites.[21] Highly-filled PCL masterbatches (with typical content of nanoclay in the range of 25–50 wt.-%) were first prepared by the in situ ε-caprolactone polymerization. The masterbatches were then melt blended with either PCL or PVC (actually known to be miscible to PCL) such that the final clay content was lower than 10 wt.-%. Depending on the alkylammonium cation used to modify the filler surface, exfoliated nanostructures have been evidenced by both WAXS and TEM. In addition, highly-loaded PCL/Cloisite® 30B masterbatches have been recently studied for the preparation of nanocomposites based on poly(propylene), polystyrene, high impact polystyrene, polyethylene, and acrylonitrile-butadiene-styrene terpolymer.[22] The PCL chains grafted on the filler were acting as compatibilizing agent between the filler and the tested matrices.

Based on these encouraging results, the masterbatch technique has been studied to prepare PLA-based nanocom-
posites containing 3 wt.-% of clay, dispersed in commercially available PLA and plasticized PLA. Both nanocomposites have been characterized in terms of morphology as well as thermal and crystallization behaviors.

Synthesis of P(l,l,-LA)/Cloisite\textsuperscript{\textregistered}30B Masterbatch

First of all, a P(l,l,-LA) masterbatch based on high Cloisite\textsuperscript{\textregistered}30B content has been prepared by ring-opening polymerization of L,L-lactide in bulk at 120°C for 16 h, using AlEt\textsubscript{3} as activator (n\textsubscript{OH}/n\textsubscript{Al} = 1). An initial amount of approximately 30 wt.-% inorganic clay with respect to monomer was fixed, in order to ensure a relatively good dispersion of the layered aluminosilicates in the molten l,l,-lactide. In order to recover a P(l,l,-LA) composite highly loaded by Cloisite\textsuperscript{\textregistered}30B, the polymerization time has been adapted to limit the monomer conversion. As L,L-lactide is one of the best known plasticizer for PLA chains, and knowing the brittleness of the PLA matrix in which the masterbatch has to be dispersed in a second step, residual monomer was not totally removed.

TGA analysis has been used to determine the final clay content of the masterbatch, which reached 53 wt.-% in clay. Unfortunately, due to the huge difficulty to quantitatively extract the clay and catalytic residues (by cationic exchange reaction and aqueous washing step) from the “grafted” P(l,l,-LA) chains, it has not been possible to determine the experimental $\bar{M}_n$ of the grafted P(l,l,-LA) chains, neither by SEC nor NMR. However, knowing the clay loading (53 wt.-%) and assuming that all hydroxyl functions of the Cloisite\textsuperscript{\textregistered}30B would have participated in the initiation step of polymerization, one can estimate an $\bar{M}_n$ of ca. 1,400 (per PLA graft).

In contrast to the exfoliated nanocomposites prepared by the same technique, i.e., in situ polymerization, but with a lower filler content (3 wt.-%), a perfectly intercalated structure has been evidenced for this highly-filled masterbatch, as revealed by the WAXS diffractogram compared to more conventional melt blending, both composites have been analyzed by WAXS and TEM in order to characterize the clay dispersion in the matrix as well as its dispersion. Figure 9 presents X-ray diffractograms recorded for the masterbatch (curve (a)) characterized by its high filler level is hindered by the limited volume remaining available for delamination of every silicate layer.\textsuperscript{[11]} Moreover, in order to exfoliate each clay platelet, the P(l,l,-LA) chains, grafted by the in situ polymerization starting from the hydroxyl groups of the Cloisite\textsuperscript{\textregistered}30B ammonium cations, have to be characterized by a molecular weight high enough to peel apart the layers. As the filler content is extremely high in the masterbatch, the quantity of hydroxyl groups able to promote the l,l,-lactide polymerization is also high, leading to P(l,l,-LA) chains with a relatively low degree of polymerization (thus estimated to ca. 10). These chains, while being grafted to the aluminosilicate surface, remain therefore too short to imply a subsequent clay exfoliation.

(Plasticized) Poly(l-Lactide)/Cloisite\textsuperscript{\textregistered}30B

Nanocomposite(s) From Masterbatch Dispersion

Two nanocomposites, based on both pure PLA and PLA plasticized with 20 wt.-% of PEG 1000, have been prepared by melt blending a commercial PLA matrix (L/D 70/30, $\bar{M}_n = 85,000$) with the previously synthesized Cloisite\textsuperscript{\textregistered}30B-based masterbatch (thus filled with 53 wt.-% clay) in order to finally reach an inorganic loading of 3 wt.-%. As the aim of the technique is to improve exfoliation when compared to more conventional melt blending, both composites have been analyzed by WAXS and TEM in order to characterize the clay dispersion in the matrix as well as its dispersion. Figure 9 presents X-ray diffractograms recorded for the masterbatch (curve (a)) characterized by its high filler level is hindered by the limited volume remaining available for delamination of every silicate layer.\textsuperscript{[11]} Moreover, in order to exfoliate each clay platelet, the P(l,l,-LA) chains, grafted by the in situ polymerization starting from the hydroxyl groups of the Cloisite\textsuperscript{\textregistered}30B ammonium cations, have to be characterized by a molecular weight high enough to peel apart the layers. As the filler content is extremely high in the masterbatch, the quantity of hydroxyl groups able to promote the l,l,-lactide polymerization is also high, leading to P(l,l,-LA) chains with a relatively low degree of polymerization (thus estimated to ca. 10). These chains, while being grafted to the aluminosilicate surface, remain therefore too short to imply a subsequent clay exfoliation.

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upon mixing. Indeed, the diffraction peak \( d_{001} \) (noted IV), situated around 2.5° as 2\( \theta \) angle, is relatively well defined and narrow, and stands close to the \( d_{001} \) initially attributed to the masterbatch. However, a TEM picture recorded for this nanocomposite (Figure 10) reveals that the nanofiller platelets are extremely well dispersed and co-exist with a limited amount of intercalated stacks (more likely responsible for the diffraction around 2.5°). Clearly, the proposed masterbatch process allows for reaching high level of exfoliation while starting from a commercially available matrix.

Considering the plasticized P(D,L-LA)-based nanocomposite, a relatively weak and large \( d_{001} \) diffraction peak (noted V) has been detected in the X-ray diffraction pattern (Figure 9, curve (c)), corresponding to an interlayer distance of 43.9 Å. Knowing that the two nanocompositions (based on unplasticized matrix and based on plasticized P(D,L-LA) have been prepared using the same operating conditions, it appears that PEG 1000 seems to act as a second compatibilizer between the aluminosilicate layers and the polyester chains, the first one being the P(L,L-LA) grafts covering the clay surface. Indeed, the significant difference in interlayer spacing (ca. 10 Å) between the two nanocomposites, as well as a more diffuse diffraction curve are indicative for improved clay destructuration.

In addition, it must be reminded that a direct melt blend of P(D,L-LA) with 20 wt.-% of PEG 1000 and 3 wt.-% of Cloisite® 30B gives intercalated structure characterized by an interlayer distance around 37.8 Å.[4] The increase of the interlayer spacing up to 43.9 Å for the nanocomposite obtained by the masterbatch redispersion can therefore be explained by the compatibilizing effect between each blend components due to the grafting of short P(L,L-LA) chains directly on the silicate layers.

In term of crystallization behavior, the dispersion of montmorillonite in a PLA matrix through the masterbatch process does not affect the \( T_g \) of the polyester chains,
Table 6. Influence of masterbatch process on thermal and crystallization parameters of Cloisite\textsuperscript{®} 30B-based PLA nanocomposites.

<table>
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<th>Code</th>
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<th>(\Delta H_c) (J g(^{-1}))</th>
<th>(T_m) (°C)</th>
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<tr>
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<td>26</td>
<td>83</td>
<td>2.4</td>
<td>152</td>
<td>42.9</td>
</tr>
</tbody>
</table>

\(^{a}\) N3B30 stands for the nanocomposite based on 3 wt.-% Cloisite\textsuperscript{®} 30B prepared by melt blending.

\(^{b}\) N3B30m is noted for the nanocomposite prepared from the redispersion of the Cloisite\textsuperscript{®} 30 masterbatch in PLA matrix in order to reach a 3 wt.-% clay loading.

\(^{c}\) pN3B30m is noted for the nanocomposite prepared from the redispersion of the Cloisite\textsuperscript{®} 30 masterbatch in plasticized (with 20 wt.-% PEG 1000) PLA matrix in order to reach a 3 wt.-% clay loading.

In situ Polymerization in Presence of PEG

Due to its relative brittleness, P(\(L,L\)-LA) thus needs to be plasticized in order to fulfill mechanical requirements, which will allow to extend its application domain. For that specific reason, we have been attached in a first approach to prepare nanocomposites by melt blending the P(\(L,L\)-LA) matrix and a selected plasticizer, PEG 1000, together with the nanofiller. However, as for most of the plasticizers, PEG 1000 tends to diffuse out of the material and accumulates at the nanocomposite surface, leading to structural matrix changes upon ageing.\(^{[23,24]}\) One attractive solution relies upon the in situ intercalative polymerization again carried out in bulk and directly in the presence of end-hydroxylated PEG 1000. This should lead to the polymerization of \(L,L\)-lactide as initiated by the hydroxyl end-groups of \(z_{\text{OH}}\)-diOH PEG 1000 plasticizer, thus in presence of the organoclay. The as-synthesized P(\(L,L\)-LA)-b-PEG-b-P(\(L,L\)-LA) triblocks might lead to a better stabilization of the plasticizer within the materials.

Practically, as the best results in term of morphology as well as thermal behavior have been obtained for Cloisite\textsuperscript{®} 30B-based nanocomposites, it has been decided to study this organoclay directly in the presence of \(z_{\text{OH}}\)-diOH PEG 1000. \(Sn(Oc)_2\) has been used as activator and added to the reaction medium in a \(n_{\text{OH}}/n_{Sn}\) molar ratio equal to 2, where \(n_{\text{OH}}\) takes into account hydroxyls groups from both PEG 1000 and Cloisite\textsuperscript{®} 30B. It must be noted that the \(n_{\text{OH}}/n_{Sn}\) molar ratio was fixed to 2 based on the results obtained for the homopolymerization of \(L,L\)-lactide conducted in the presence of 3 wt.-% of Cloisite\textsuperscript{®} 30B, which led to rather acceptable monomer conversion under the studied experimental conditions.

As a matter of fact, two types of hydroxyl groups co-exist in the reaction medium, i.e., those present on the ammonium cation that modifies the clay and the OH-end groups of the PEG chains. Different types of chains can therefore be formed: P(\(L,L\)-LA) homopolymers “grafted” to the silicate layers and P(\(L,L\)-LA-b-EG-b-\(L,L\)-LA) triblock copolymers more likely present as intercalated species within the organoclay galleries. The influence of the \(z_{\text{OH}}\)-diOH PEG 1000 amount for a constant filler content of Cloisite\textsuperscript{®} 30B (3 wt.-%) has been more closely studied. While keeping constant the loading in Cloisite\textsuperscript{®} 30B in the nanocomposite, different relative contents in \(z_{\text{OH}}\)-diOH PEG 1000, varying from ca. 1 to 16 wt.-%, have been added in order to vary the P(\(L,L\)-LA) sequence length in the triblock copolymers as well as for the surface-grafted P(\(L,L\)-LA) chains. In order to avoid any fractionation of the polyester chains upon P(\(L,L\)-LA) precipitation, heptane has been used as non-solvent (rather than methanol—known to precipitate P(\(L,L\)-LA) chains of higher molecular weight only) to recover the polyester chains after clay and metal residues extraction.\(^{[4]}\) H NMR analysis of the extracted polymers has allowed to evaluate the monomer conversion, degree of polymerization, and weight fraction of PEG compared to in situ generated PLA (Table 7).

Quantitative conversion is assumed since no trace of residual monomer has been evidenced by \(^1\)H NMR. Indeed, \(L,L\)-lactide being insoluble in heptane, the presence of any residual monomer would have been observed by \(^1\)H NMR analysis.

In order to interpret the results, one has to remind previous observations for \(L,L\)-lactide polymerization in the presence of Cloisite\textsuperscript{®} 30B. It has been shown that when high \(DP_{L,L-LA}\) were targeted, a large discrepancy between the theoretical and experimental values was observed, with much lower experimental \(DP_{L,L-LA}\). This difference has been explained by the difficulty to exchange by Li\textsuperscript{+} cations the ammonium salts grafted with longer PLA sequences. As a result, only the shorter PLA chains were extracted and...
therefore analyzed by SEC, which led to an under-estimation of the actual molecular weight of the grafted PLA chains. A similar behavior seems to be observed in Table 7 where a better agreement between the theoretical and experimental $DP_{L,L-LA}$ values is obtained for the lower values of $DP_{th}$ (entries 3 and 4).

As revealed by WAXS analyses (not shown here), the relative content in PEG 1000 does not affect the morphology of the resulting nanocomposites. Again, the complete disappearance of the diffraction peak characteristics of Cloisite®30B attests for the complete loss in the organization of the clay platelets.

TGA thermograms (Figure 11a, b) display two distinct degradation steps. Based on their relative importance, the first step has been assigned to the degradation of $P(L,L-LA)$ sequences, while the second (occurring at higher temperature) can be attributed to more thermally stable PEG blocks. This attribution is fully confirmed by measuring the relative weight loss of the two consecutive degradations, which leads to a PEG content ($PEG_{TGA}$) in good agreement with the initial content in PEG (Table 8).

Finally, DSC analyses have revealed that the plasticizing effect of the PEG sequences in situ polymerized triblock copolymers is only detectable for a PEG content of 8.5 wt.-% as attested by the decrease of the $T_g$ (down to 41 °C). At ca. 16.2 wt.-% in PEG, a much more significant plasticizing effect has been evidenced with a $T_g$ as low as -12 °C, which can be explained by a conjugated effect of high PEG content and the formation of very short $P(L,L-LA)$ sequences ($DP_{L,L-LA} = 14$, entry 4 in Table 7).

**Conclusion**

In contrast to the melt blending technique, for which only intercalated $P(L,L-LA)$/nanocomposites can be recovered, the in situ polymerization of $L,L$-lactide in presence of Cloisite®30B leads to exfoliated morphology. This nanostructure has been explained by the possibility to initiate the polymerization through activation of the hydroxyl groups covering the silicate layer surface. The good distribution/dispersion of the clay platelets, that directly arises from the polyester chains grafting, gives largely improved properties to the materials, such as significantly increased thermal

### Table 7. Influence of the PEG 1000 content on molecular parameters of in situ polymerized $P(L,L-LA)$ in nanocomposites filled with 3 wt.-% Cloisite®30B (in bulk, 120 °C, 48 h, Sn(Oct)$_2$, \(n_{OH}/n_{Sn} = 2\)).

<table>
<thead>
<tr>
<th>Code</th>
<th>PEG content</th>
<th>(n_{OH}(PEG)/n_{OH} \text{ total} )</th>
<th>Conv.</th>
<th>(DP_{th} )</th>
<th>(DP_{exp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC1N3B30</td>
<td>0.8</td>
<td>0.28</td>
<td>100</td>
<td>114</td>
<td>28</td>
</tr>
<tr>
<td>SC5N3B30</td>
<td>4.4</td>
<td>0.69</td>
<td>100</td>
<td>50</td>
<td>23</td>
</tr>
<tr>
<td>SC10N3B30</td>
<td>8.5</td>
<td>0.82</td>
<td>100</td>
<td>29</td>
<td>19</td>
</tr>
<tr>
<td>SC20N3B30</td>
<td>16.2</td>
<td>0.91</td>
<td>100</td>
<td>16</td>
<td>14</td>
</tr>
</tbody>
</table>

$^a$) Determined by $^1$H NMR.

$^b)$ \(DP_{th} = [L,L-LA]/([OH]_{PEG} + [OH]_{clay}) \times \text{ conv.} \)

$^c)$ Determined by $^1$H NMR using the relative intensity of the methine protons from the repetitive unit in the chain (–CH(Me)–O–C(O)–) and the end groups (–CH(Me)–OH); $DP_{exp} = I_{unit}/I_{end \text{ group}} \times 2$.

### Table 8. Relative content in PEG involved the Cloisite®30B based nanocomposites (3 wt.-% in inorganics).

<table>
<thead>
<tr>
<th>Code</th>
<th>PEG content</th>
<th>PEG$^{TGA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt.-%</td>
<td>wt.-%</td>
</tr>
<tr>
<td>SC1N3B30</td>
<td>0.8</td>
<td>ND$^c$</td>
</tr>
<tr>
<td>SC5N3B30</td>
<td>4.4</td>
<td>4.7</td>
</tr>
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<td>8.5</td>
<td>10.7</td>
</tr>
<tr>
<td>SC20N3B30</td>
<td>16.2</td>
<td>16.8</td>
</tr>
</tbody>
</table>

$^a$) PEG content at start (see Table 7).

$^b$) As determined by TGA (from Figure 11a).

$^c$) Too low to be detected.
stability or higher degree of crystallinity compared to intercalated nanostructure at same clay loading. Moreover, intercalated nanocomposites have been successfully prepared starting directly from Cloisite® Na⁺, while melt blending this non-organomodified filler with preformed PLA only yields microcomposites. Interestingly enough, semi-exfoliated/semi-intercalated nanocomposites based on 3 wt.-% of Cloisite® 30B and (plasticized) P(\(\text{D,L-LA}\)) have been successfully prepared by the redispersion in commercially available (plasticized) P(\(\text{D,L-LA}\)) of a highly filled masterbatch, itself prepared by in situ polymerization of \(\text{L,L-lactide}\) in presence of the nanofiller.

Finally, in situ polymerization of \(\text{L,L-lactide}\) conducted in presence of both dihydroxylated PEG 1000 and Cloisite® 30B have been studied. P(\(\text{L,L-LA-b-EG-b-L,L-LA}\)) triblock copolymers have been synthesized in situ directly in presence of the organoclay. Whatever the weight ratio in PEG 1000 initially fixed, intensive clay platelets destruction has been achieved. The plasticizing effect of the PEG sequence, thus entrapped in the triblock copolymers have been highlighted by the significant \(T_g\) decrease of the nanocomposite, e.g., from 60 to 12 °C at 16.2 wt.-% content in PEG. Moreover, the thermal degradation of the resulting nanocomposites was dependent on the relative content in PEG blocks, and the thermal stability decreases as the polyether level increases within the triblock copolymer. In conclusion, this contribution shows the unique possibility to tune up the morphological and thermal properties of P(\(\text{L,L-LA}\)) layered silicate nanocomposites by adequately combining in situ catalytic polymerization “masterbatch” melt blending and matrix plasticization along with nanocomposition preparation.

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