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Polyester layered silicate nanohybrids by controlled grafting polymerization

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Poly(ε-caprolactone) (PCL) layered silicate nanohybrids were synthesized by ring opening polymerization of ε-caprolactone according to a well-controlled coordination–insertion mechanism. Montmorillonites were surface-modified by non functional (trimethylhexadecylammonium) and hydroxy functional alkylammonium cations, *i.e.*, (2-hydroxyethyl)dimethylhexadecylammonium. The hydroxy functions available at the clay surface were activated into tin(II or IV) or Al(III) alkoxide initiators for lactone polymerization, thus yielding surface-grafted PCL chains. The surface-grafted PCL chains were recovered by an ionic exchange reaction with lithium chloride and they were analyzed by size exclusion chromatography. The PCL molar mass was measured as a function of the hydroxy content of the clay that was modulated by exchanging the Na cations with mixtures of non-functional and hydroxy functional ammonium cations of different compositions. Nanohybrids were also characterized by small-angle X-ray diffraction, transmission electron microscopy and thermogravimetry. The PCL molar mass and the nanocomposite morphology (*i.e.*, exfoliation and/or intercalation) were readily tuned by the content of the hydroxy groups available at the clay surface. Surface-grafted aluminium trialkoxide species proved highly efficient in initiating polymerization that leads to PCL chains of controlled molar mass and narrow molecular weight distribution with polydispersity indices as low as 1.2.

Introduction

Polymer/clay nanocomposites represent a new class of materials that display improved mechanical (tensile modulus and strength) and rheological properties, thermal stability, flame retardancy and barrier resistance, even at low clay content (3 wt%), compared to conventional polymer microcomposites filled with more than 20 wt% particles.[1,2] Smectite clays, such as montmorillonite, are extensively used for this purpose, because of high aspect ratios and large surface areas. Na^+–montmorillonite is a crystalline 2 : 1 layered mineral with a central alumina octahedral sheet sandwiched between two silica tetrahedral sheets. Thickness of the constitutive lamellae is *ca.* 1 nm. Because of high hydrophilicity, native montmorillonite is hardly dispersed into traditional hydrophobic polymers. Substitution of hydrophobic onium ions, such as ammoniums with at least one long alkyl group, for the Na^+ (or Ca^{2+}) cations is beneficial to the formation of nanocomposites. A variety of polymer matrices, including *e.g.* nylon-6,[3] polyimide,[4] epoxy,[5] poly(propylene),[6] ethylene–vinyl acetate copolymers[7,8] and poly(ethylene oxide),[9] have been filled by such organo-clays.

Melt intercalation[10] and *in situ* polymerization are the most common techniques for the preparation of polymer/clay nanocomposites.[11] Melt intercalation consists of mixing clay with molten polymer. In *in situ* polymerization, the monomer is firstly intercalated within the clay galleries and then polymerized. Two extreme structures are known for nanocomposites, *i.e.* the intercalated structure in which a single polymer monolayer is sandwiched between the clay layers, whose spacing is increased by a few nanometers, and the exfoliated structure, which results from the complete delamination of the constitutive sheets and dispersion within the polymer matrix. This fine dispersion usually provides the nanocomposite with the best properties. The anchoring of an initiator to the interlayer organic cation is ideal in *in situ* polymerization to form tethered polymer chains and to exfoliate the clay layers. Huang and Brittain[12] prepared nanocomposites by *in situ* radical suspension and emulsion polymerization of methyl methacrylate (MMA). Clay modified by organic ammoniums bearing either an azo or an acrylate group was used to tether the polymer chains. Zeng and Lee[13] used a similar technique to prepare nanocomposites by *in situ* bulk polymerization of MMA and styrene, in the presence of a cationic surfactant containing a polymerizable group. Sogah *et al.*[14] reported on the *in situ* controlled radical polymerization of styrene using a silicate-anchored alkoxyamine as a regulator. In all cases, exfoliated nanocomposites were collected.

Poly(ε-caprolactone) (PCL) layered silicate nanocomposites have the advantage adding biocompatibility and biodegradability to the traditional properties of nanocomposites. They can be prepared by *in situ* ring-opening polymerization of ε-caprolactone in the presence of an organophilic clay, such as organo-modified montmorillonite. Messersmith and Giannelis[15] used montmorillonite exchanged with protonated 12-aminododecanoic acid and Cr^{3+}-exchanged fluorohectorite, a synthetic mica type of silicate.[16] Recently, a Sn-based catalyst such as tin(II) octoate[17] and dibutyltin(IV) dimethoxide[18] have been reported to efficiently promote the polymerization of ε-caprolactone in the presence of organo-modified clays.

In this study, we aim at investigating further such catalysts for grafting the PCL chains onto clay modified by onium salts bearing hydroxy groups with the purpose of preparing perfectly

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well tailored PCL/clay nanocomposites. The effect of experimental parameters, such as the hydroxy functionality of the clay surface or the nature of the catalyst, on PCL molar mass and polydispersity, and on the exfoliation degree has been highlighted. Based on this study, we propose herewith conditions that allow control of all the molecular parameters of the grafted polyester chains, *i.e.*, control over the grafting efficiency (quantitative grafting), grafting density (number of grafted chains per surface unit), length of the grafted polyester chains (predetermined by the initial monomer-to-clay surface hydroxy functions molar ratio), molecular weight distribution (with a polydispersity index as narrow as 1.2) and the extent of clay exfoliation/delamination.

Experimental

Materials

ε-Caprolactone (Fluka) was dried over CaH_2 and distilled under reduced pressure prior to use. Triethylaluminium ($AlEt_3$), bis(2-ethylhexanoic acid) tin(II) salt (tin(octoate), $Sn(Oct_2)$) and dibutyltin dimethoxide ($Bu_2Sn(OMe)_2$) were purchased from Fluka, Goldschmidt, and Aldrich, respectively, and diluted with dried toluene. $AlEt_3$, $Sn(Oct)_2$ and $Bu_2Sn(OMe)_2$ solutions were stored in glass ampoules under nitrogen atmosphere. The cation exchange capacity (CEC) of the natural sodium montmorillonite (Cloisite® Na, Southern Clay products, Texas, USA) was 92 meq per 100 g. The silicate layers were 0.96 nm thick and 250 to 500 nm wide with an interlayer distance of 0.25 nm. 1-Iodohexadecane (95%), *N*,*N*-dimethylethanolamine (99%) and trimethylamine (33 wt% solution in ethanol) were purchased from Aldrich and used without purification.

Synthesis of ammonium cations

2-Hydroxyethyl(hexadecyl)dimethylammonium iodide $(CH_3)_2(C_{16}H_{33})N^+(CH_2CH_2OH)$ was prepared by a quaternization reaction as follows. 1-Iodohexadecane (3.87 g, 0.011 mol) was dissolved in ethanol (100 mL) and reacted with *N*,*N*-dimethylethanolamine (1.0 mL, 0.010 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}H-NMR ($CDCl_3$): 0.9 ppm, CH_3; 1.2 to 1.4 ppm, $(CH_2)_{13}$; 1.8 ppm, $N\text{-}CH_2\text{-}C\mathit{H}_2$; 3.4 ppm, $(CH_3)_2N$; 3.6 ppm, $N\text{-}CH_2$; 3.8 ppm, $N\text{-}C\mathit{H}_2CH_2OH$; 4.15 ppm, CH_2OH.

Hexadecyltrimethylammonium $(CH_3)_3N^+(C_{16}H_{33})$ iodide was similarly prepared by reaction of 1-iodohexadecane (3.87 g, 0.011 mol) with trimethylamine (2.94 mL, 0.010 mol) in 100 ml ethanol. It was purified by recrystallization in ethanol (white powder). Melting point: 118 °C. ^{1}H-NMR ($CDCl_3$): 0.9 ppm, CH_3; 1.2 to 1.4 ppm, $(CH_2)_{12}$; 1.8 ppm, $N\text{-}CH_2\text{-}CH_2\text{-}C\mathit{H}_2$; 2.35 ppm, $N\text{-}CH_2C\mathit{H}_2$; 3.4 ppm, $(CH_3)_2N$; 3.55 ppm, $N\text{-}CH_2$.

Preparation of organophilic clays

Cloisite® Na was intercalated by mixtures of monohydroxy ammonium cation, $(CH_3)_2(C_{16}H_{33})N^+(CH_2CH_2OH)$ and non-functional ammonium cations, $(CH_3)_3N^+(C_{16}H_{33})$, of various compositions. This co-intercalation by 0, 25, 50, 75 and 100% of a monohydroxy containing ammonium iodide salt was performed in water at 85 °C and led to organo-clays coined montmorillonite (MMT)–$(CH_2CH_2OH)_x$, with x = 0, 25, 50, 75 and 100. The modified clays were extensively washed with hot water and collected by freeze-drying. The intercalated ammonium compositions were determined from ^{1}H-NMR analysis of the aqueous solution left after clay intercalation. Intercalated clays were analyzed by XRD, with the basal spacing increasing from 1.21 nm for Cloisite® Na to *ca.* 1.90 nm for the organo-clays. The organic content of all the organo-modified montmorillonites was in the range of 18–24 wt% as determined by thermogravimetric analysis (TGA, see Table 1).

Table 1 Modification of montmorillonite by mixtures of alkylammonium and monohydroxylated ammonium: XRD and TGA analyses

MMT-$(CH_2CH_2OH)_x$ (OH content, x%)	Diffraction peak^a/Å	Organic content (wt%)^b
100	19.0	21.2
75	19.0	24.7
50	19.1	21.7
25	18.8	18.9
0	19.3	19.6

^{a}Main peak in the small angle region (native montmorillonite (Cloisite® Na): 12.1 Å). ^{b}TGA between 200 and 450 °C (under helium flow; heating rate: 10 °C min^{-1}.)

Polymerization procedure and PCL extraction

Nanocomposite preparation by *in situ* intercalative preparation of ε-caprolactone and consecutive PCL extraction for characterization have been described elsewhere.[18] Polymerization reactions with $AlEt_3$ and $Bu_2Sn(OMe)_2$ were allowed to proceed for 24 h at room temperature and with $Sn(Oct)_2$ for 24 h at 100 °C. All the samples were characterized by a filler content expressed as the amount of inorganic fraction (montmorillonite layers) in the obtained nanocomposite (x wt% inorganics).

Characterization

Size exclusion chromatography (SEC) was carried out in THF at 35 °C with a Polymer Laboratory (PL) liquid chromatograph equipped with a refractive index detector and a set of three columns (a guard column, PLgel 10 μm (50 × 7.5 mm) and two columns, PLgel mixed-B 10 μm (300 × 7.5 mm)) calibrated by PS standards. Absolute molar masses were calculated by using the Mark–Houwink relationships $[\eta] = KM^a$ for PS and PCL ($K_{PS} = 1.25 \times 10^{-4}$ dL g^{-1}, $a_{PS} = 0.707$, $K_{PCL} = 1.09 \times 10^{-3}$ dL g^{-1}, $a_{PCL} = 0.600$). X-Ray diffraction (XRD) patterns were recorded with a Siemens D500 diffractometer on sheet-like samples hot pressed at 100 °C. XRD data were collected by X-ray generator equipment (Cu-Kα, λ = 0.15406 nm) between 1.5 and 25° of steps of 0.04°. TEM observations were performed with a Philips CM100 apparatus using an acceleration voltage of 100 kV. Ultrathin sections (*ca.* 80 nm) were cut at −130 °C from 3 mm thick hot-pressed plates with a Reichert–Jung Ultracut 3E, FC4E ultra-cryomicrotome. ^{1}H-NMR spectra were recorded for solutions in $CDCl_3$ (30 mg per 0.6 mL) with a Bruker AMX-300 apparatus.

Results and discussion

Preparation of organoclays with a controlled content in hydroxy functions

As aforementioned, ε-caprolactone can be readily polymerized by tin(II and IV)-based catalysts in the presence of organo-modified clays.[17,18] Interestingly, it has been observed that, when hydroxy groups are made available on the clay surface, the growing PCL chains remain grafted onto the clay.

As an extension of these preliminary results, it was worth investigating whether tin(II), tin(IV) or aluminium alkoxides allow the control of both the molecular parameters of the grafted PCL (molar masses, polydispersity) and the structure of the resulting hybrids (degree of exfoliation, density of grafting, *etc.*). For this purpose, sodium montmorillonite has been co-intercalated by mixtures of alkylammonium cations and monohydroxylated ammonium cations of different compositions, *i.e.*, the hexadecyltrimethylammonium cation $(CH_3)_3N^+(C_{16}H_{33})$

and (2-hydroxyethyl)hexadecyldimethylammonium cation $(CH_3)_2(C_{16}H_{33})N^+(CH_2CH_2OH)$. These cations have been synthesized by quaternization of the parent tertiary amines by 1-iodohexadecane in ethanol (see Experimental section). A similar strategy was recently reported by Sogah *et al.*,[14] who prepared PS/clay nanocomposites with a constant silicate content and PS chains of various length. Layered silicates were accordingly intercalated by benzyltrimethylammonium cations, part of them bearing an alkoxyamine function, *i.e.*, a regulator for the styrene radical polymerization.

The molar compositions of the cation mixtures have been fixed at 0, 25, 50, 75 and 100% of the monohydroxylated ammonium and designated as MMT–$(CH_2CH_2OH)_x$, with x representing the OH content. The ^{1}H-NMR analysis of the aqueous solution of the ammonium cations before and after the clay intercalation allows us to check that the actual composition of the co-intercalated ammonium cations corresponds to the initial composition. Clay intercalation has been confirmed by XRD analysis, which shows that the interlayer space increases from 1.21 nm (for Cloisite® Na) to *ca.* 1.90 nm for the organo-modified clay, whose organic content (TGA) is close to 21 wt%. The main characteristic features of the five organo-modified clays are listed in Table 1.

Preparation of poly(ε-caprolactone)/clay nanocomposites: effect of the intercalated ammonium cations on the extent of clay exfoliation

The clays organo-modified with a controlled amount of hydroxy functions were first used to test if the molar mass of the clay surface-grafted PCL chains can be predetermined whilst keeping the clay content constant (*e.g.* 3 wt%).

In a first series of experiments, tin(II) octoate was selected as the polymerization activator. The organo-modified clays were dispersed in liquid ε-caprolactone (3 wt% inorganics) and then $Sn(Oct)_2$ ([monomer]/[Sn] = 300) was added. After polymerization, the molar mass of PCL was found to decrease with increasing content of the hydroxy groups available at the clay surface (Table 2). Indeed, the molar mass is 56 000; 47 000 and 28 000 for OH-deprived organo-modified clay and clay containing 50 and 100% monohydroxylated ammonium cations, respectively.

This observation suggests, at least qualitatively, that polymerization is initiated by the surface-anchored hydroxy groups activated in Sn(II) alkoxides by reaction with $Sn(Oct)_2$.[19] In the absence of monohydroxylated ammonium cations, polymerization is initiated by residual protic impurities (water, silanol, *etc.*). Polymerization initiation on the clay surface and the PCL growth in a "grafting-from" manner have a strong effect on the morphology of the PCL/layered silicate nanocomposites. Fig. 1 shows the XRD patterns for PCL filled with MMT–$(CH_2CH_2OH)_x$ (3 wt% inorganics). PCL is still able to crystallize in these compositions, as demonstrated by the presence of diffraction peaks at $2\theta = 21.4$, 22.0 and 23.8°, which are characteristic of the (110), (111) and (200) reflection planes of the orthorhombic crystal structure of PCL, respectively.[20] The diffraction peak at low 2θ angles, typical of intercalated clay structures, disappears as the hydroxy content of the layered silicates and thus the PCL grafting density are increased (see insert in Fig. 1), which is expected for a transition from an intercalated structure to an exfoliated one. Extensive exfoliation only occurs when the silicate sheets are surface-modified by more than 25 wt% monohydroxylated ammonium. Below this value, partially intercalated/partially exfoliated structures coexist, as assessed by a broad diffraction centered at *ca.* 30 Å ($2\theta = 3°$), instead of *ca.* 19 Å for the ammonium-intercalated clay. These observations are also supported by TEM. Fig. 2 shows TEM micrographs for nanocomposites containing 3 wt% of inorganics, *i.e.* MMT–$(CH_2CH_2OH)_x$ with x = 100, 50 and 0%. Individual clay platelets are randomly distributed within PCL when the hydroxy content is 50% and higher. No aggregate is observed, in line with the extensive exfoliation suggested by XRD. In the case of non-functionalized ammonium ($x = 0$; hexadecyltrimethylammonium), clay aggregates are visible in the polymer matrix (Fig. 2c). Only intercalation is observed by XRD analysis in agreement with the broad peak in the small angle region (*ca.* 30 Å).

These nanocomposites have been analyzed by TGA as well.

Table 2 *In situ* polymerization of ε-caprolactone in the presence of MMT–$(CH_2CH_2OH)_x$ (3 wt% of inorganics) and catalyzed by $Sn(Oct)_2$ at 100 °C for 24 h ([OH]/[Sn] = 300). Effect of the relative content of the hydroxy-containing ammonium cations

MMT–$(CH_2CH_2OH)_x$ (OH content, x%)	Conversion (%)	M_n[a]/g mol^{-1}	M_w/M_n
100	93	28 000	1.8
75	96	36 500	1.8
50	97	47 000	1.8
25	98	53 500	1.9
0	98	56 000	2.0

[a] Molar mass in PCL equivalent.

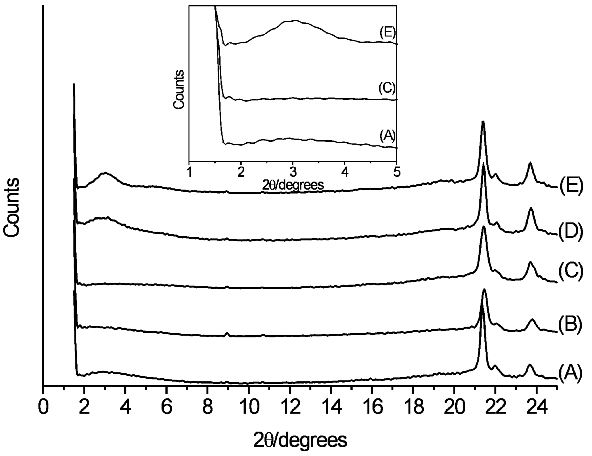

Fig. 1 XRD patterns for PCL/MMT–$(CH_2CH_2OH)_x$ nanocomposites prepared in the presence of $Sn(Oct)_2$. Effect of the content of monohydroxylated ammonium cations used in the Na exchange of native MMT : (A) x = 100%, (B) x = 75%, (C) x = 50%, (D) x = 25%, (E) x = 0%. The insert shows a zoom of the low angle area (1 to 5°) for curves (A), (C) and (E).

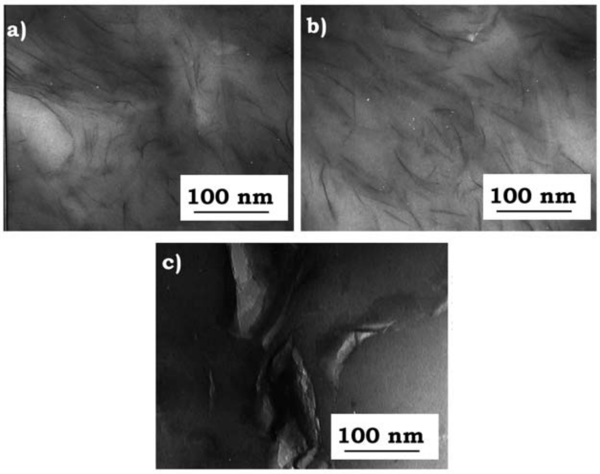

Fig. 2 TEM images for the PCL/MMT–$(CH_2CH_2OH)_x$ nanocomposites prepared in the presence of $Sn(Oct)_2$: a) x = 100%, b) x = 50%, c) x = 0 % (see Table 3).

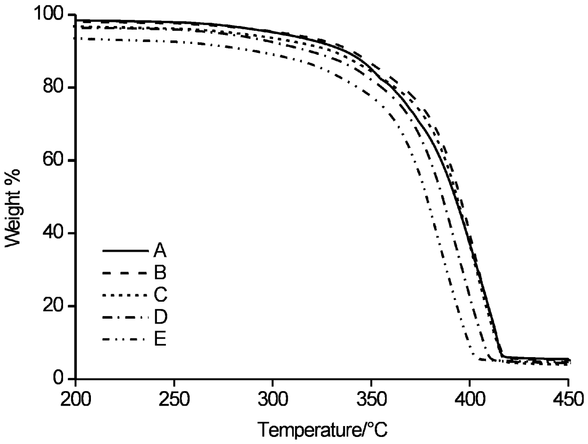

Fig. 3 Temperature dependence of weight loss (under an air flow) for PCL-based nanocomposites filled with 3 wt% (relative of inorganics) of MMT–$(CH_2CH_2OH)_x$: (A) $x = 0\%$, (B) $x = 25\%$, (C) $x = 50\%$, (D) $x = 75\%$, (E) $x = 100\%$ and prepared by *in situ* polymerization catalyzed by $Sn(Oct)_2$.

The thermograms in Fig. 3 show that the temperature at which the degradation occurs decreases when the hydroxy content is increased beyond $x = 50\%$. Decrease of the PCL molar mass (from 47 000 down to 28 000 for $x = 50$ and 100%, respectively) in nanocomposites with an exfoliated morphology can again explain this observation.[21] For the other two samples ($x \leqslant 25$ and 0%), no significant effect on the degradation temperature is observed in spite of a higher molar mass for the grafted PCL chains (Table 2). The intercalated structure of these nanocomposites is responsible for this change in thermal stability. At constant molar mass, exfoliated structures impart higher thermal resistance because of a finer clay dispersion.[1]

In an additional series of experiments, dibutyltin dimethoxide ($Bu_2Sn(OMe)_2$) was substituted for $Sn(Oct)_2$ while using the same organo-modified clays MMT–$(CH_2CH_2OH)_x$ (3wt% of inorganics). Polymerization was carried out in bulk at room temperature, for 24 h, with a [monomer]/[Sn] ratio = 300. SEC analysis data for the PCL chains released by ion exchange are shown in Table 3. The molar masses at different hydroxy contents show a relatively constant value (molar masses range between 16 000 and 18 000 for all investigated samples). This observation may appear *a priori* surprising. Contrary to $Sn(Oct)_2$, dibutyltin dimethoxide is not only a catalyst but it is also an initiator of polymerization through its methoxide functions. Furthermore in the presence of an alcohol, a rapid exchange between tin alkoxide (methoxides) species and alcohol molecules is known to take place.[19] Then, the propagating species (metal alkoxide) is temporarily converted into a dormant site through the reaction with another alcohol molecule. Actually it is important to mention the relatively high content of tin(IV) methoxide functions ([monomer]/[methoxide] = 150) compared to the clay hydroxy groups and the high activity of tin(IV) alkoxides for promoting intermolecular transesterification reactions. Therefore one may expect a relatively limited effect of the hydroxy content on the molecular weight of the PCL chains.

Table 3 *In situ* polymerization of ε-caprolactone initiated by $Bu_2Sn(OMe)_2$ in the presence of MMT–$(CH_2CH_2OH)_x$ (3 wt% of inorganics) at room temperature for 24 h ([OH]/[Sn] = 300). Effect of the hydroxy content of the ammonium cations

MMT–$(CH_2CH_2OH)_x$ (OH content, x%)	Conversion (%)	$M_n{}^a$/g mol^{-1}	M_w/M_n
100	98	15 500	1.8
75	98	16 500	2.0
50	98	18 000	1.9
25	99	16 500	2.2
0	98	18 500	2.0

[a] Molar mass in PCL equivalent.

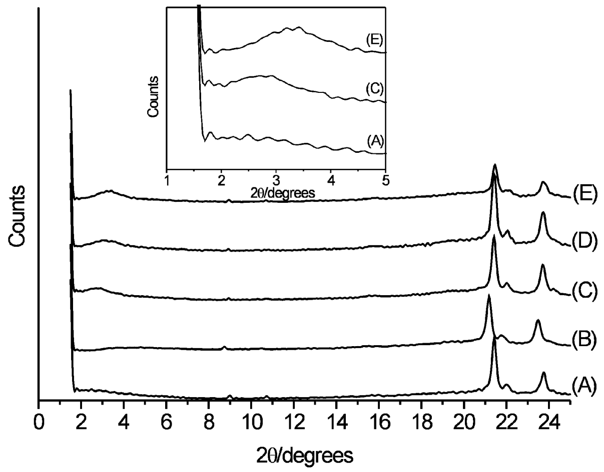

Fig. 4 XRD patterns for the PCL/MMT–$(CH_2CH_2OH)_x$ nanocomposites prepared in the presence of $Bu_2Sn(OMe)_2$. Effect of the content of monohydroxylated ammonium cations used in the Na exchange of native MMT: (A) $x = 100\%$, (B) $x = 75\%$, (C) $x = 50\%$, (D) $x = 25\%$, (E) $x = 0\%$. The insert shows a zoom of the low angle area (1 to 5°) for curves (A), (C) and (E).

Similar to the previous series of nanocomposites, XRD (Fig. 4) and TEM (not reported here) show that the organomodified clay is completely exfoliated when the hydroxy content is high ($x = 75$ and 100 %), whereas intercalation mainly occurs at lower hydroxy contents ($x = 0$ and 25). A difference can however be found for the MMT $(CH_2CH_2OH)_x$ clay with $x = 50\%$. Indeed, an intercalated morphology is observed when the lactone polymerization is initiated by $Bu_2Sn(OMe)_2$ (insert in Fig. 4), in contrast to complete exfoliation when the polymerization is catalyzed by $Sn(Oct)_2$, as observed by TEM (Fig. 2b). At that intermediate chain grafting density, the molar mass of the PCL chains would have a decisive effect, with a sufficiently high chain length being required for exfoliation to occur ($M_n = 47\,000$ *vs.* 18 000; entries 3 in Tables 2and 3, respectively).

Preparation of poly(ε-caprolactone)/clay nanocomposites: control of molar mass and molar mass distribution

Although the experiments reported up to now have shown that the length of the PCL chains could be controlled, the molar mass distribution is rather broad ($M_w/M_n \sim 2$) as a result of side transesterification reactions. This characteristic feature can however be improved further by converting the surface hydroxy groups into aluminium trialkoxides. The completely hydroxylated clay (MMT–$(CH_2CH_2OH)_x$ with $x = 100$ %) was derivatized into the aluminium trialkoxide active species by reaction with $AlEt_3$ ([OH]/[Al] = 3). Polymerization was carried out in bulk at room temperature, with 3 wt% of inorganics for 24 h. The monomer conversion was 52%, and an agreement between the theoretical molar mass ($M_n = 19\,800$) and the experimental value (21 000) is again excellent attesting to the quantitative grafting of all *in situ* formed PCL chains. In addition to this control, it is worthwhile pointing out that the molar mass distribution is symmetrical and narrow with a polydispersity index as low as 1.2. This improved control on the PCL molecular parameters has prompted us to investigate further this polymerization–grafting reaction (for the synthesis of clay surface-grafted diblock copolyesters, for instance) as will be reported elsewhere.

Conclusion

Poly(ε-caprolactone)–grafted layered silicate nanohybrids have been prepared by intercalative polymerization of ε-caprolactone according to a controlled coordination–insertion mechanism. For this purpose, montmorillonite has been modified by exchange of the constitutive Na cations by ammonium cations bearing one hydroxy function, which are the precursors to aluminium or tin(II or IV) alkoxides, all known to initiate the controlled polymerization of ε-CL. The constitutive silicate sheets have been accordingly grafted by a predetermined amount of PCL chains of a predictable molar mass and a narrow molar mass distribution (in the case of the Al trialkoxide species). The surface density of the hydroxy groups has been modulated by exchanging mixtures of non-functional alkylammonium and monohydroxylated ammonium cations of known composition with the Na cations. For a constant content of inorganics (3 wt%), the molar mass of the PCL chains decreases when the actual content of the hydroxy groups is increased. At high hydroxy content, X-ray diffraction and transmission electron microscopy show the complete exfoliation of the silicate sheets in the polyester layered silicate nanohybrids. The thermal stability of these nanocomposites is much higher than unfilled PCL or merely intercalated montmorillonite (no chain grafting).

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