POLYLACTIDES

1. Introduction

Polylactide (PLA) belongs to the family of synthetic aliphatic polyesters and is considered as biodegradable and compostable. It is a thermoplastic, high strength, high modulus polymer that can be made from annually renewable resources. In the past four decades, focus has been on biomedical applications such as drug delivery, resorbable sutures, medical implants, and scaffolds for tissue engineering. More recently, PLA has garnered interest as a new environmentally friendly thermoplastic with wide applicability. As the depletion of petrochemical feed stocks draws near, the production of PLA is increasingly important for a sustainable future. Because of these attractive features and the announcements of large-scale PLA commercialization, research on PLA chemistry, and materials science has been extremely fertile. Since the first paper by Watson (1), PLA has been the topic of several reviews reporting on synthesis and macromolecular design (2,3), synthesis of PLA-based copolymers and their use in medical applications and biodegradation (4–6), hydrolytic degradation in various environments (7), use as biopolymers and biocomposites (8), physicochemical and mechanical properties in relation to composition (9,10), and life cycle assessment applied to high scale production (11).

The aim of this article is to consolidate the information in scientific publications on the synthesis of PLA including recent routes explored to enlarge its properties such as the use of stereoelective (catalytic) initiating systems. From the material science point of view, focus has been on recent technological advances, and more particularly on nanocomposite materials made from PLA.

2. Recent Breakthroughs in Synthesis of PLA

The basic building block for PLA is lactic acid, which was isolated from sour milk by Scheele and first produced commercially in 1881 (12). It is mainly used in food applications as a buffering agent, acidic flavoring agent, and bacterial inhibitor. Lactic acid can be manufactured either by carbohydrate fermentation from, eg, corn, sugar cane, and sugar beet, or by chemical synthesis although the former predominates (13). Lactic acid (2-hydroxypropanoic acid) exists as L(*S*)- and D(*R*)-stereoisomers. L(*S*)-Lactic acid is present in mammals while both stereoisomers are found in bacteria. Fermentation production of lactic acid preferably involves bacteria able to use hexoses as the main nutrient but can also be prepared by other bacteria, fungi, or yeasts. The stereoisomeric ratio of D(*R*)- and L(*S*)-lactic acid is determined by the selectivity of the dehydrogenase involved in the conversion of pyruvate. The as-obtained lactic acid has to be separated from the fermentation broth by successive steps involving (*1*) neutralization with a base, (*2*) first concentration increase, (*3*) conversion into the carboxylic acid form, (*4*) followed by a final and rapid concentration increase to provide valuable aqueous solution grades (14). Liquid–liquid extraction has been described as an alternative recovering route (15), as well as esterification with alcohols followed by distillation and hydrolysis (16).

The conversion of lactic acid into high molecular weight PLA can be carried out following two routes. Lactic acid can be polymerized by either self-condensation or ring-opening polymerization of lactide, its cyclic dimer obtained by depolymerization of low molecular weight polycondensates under reduced pressure and at high temperature (Fig. 1). The polycondensation can be seen as the easiest route, but it is difficult to reach high molecular weights through a solvent-free process. The use of coupling agents, esterification-promoting agents, or multifunctional branching reagents is required, adding cost and complexity (17–25). As an alternative, azeotropic condensation polymerization with high boiling solvents such as diphenyl ether has demonstrated its efficacy though long reaction times are required (26). Some progress has recently been achieved by using tin(II) catalysts activated by various proton acids (27) or by sequential melt/solid polycondensation (28,29).

3. Ring-Opening Polymerization of Lactide

The ring-opening polymerization (ROP) of lactide (LA) was first demonstrated by Carothers in 1932 (30), but high molecular weights were not obtained until improved lactide purification techniques were developed by DuPont in 1954. Polyesters prepared by ROP are the most commonly studied ones as an accurate control over the chemistry allows us to vary the properties of the resulting polymers on purpose, which broadens the PLA application fields. Due to the two stereoisomers of lactic acid the production of lactide results in three potential isomeric forms: D,D(*R,R*)-LA, L,L(*S,S*)-LA, and D,L(*R,S*)-LA or D,L(*meso*)-LA. In addition, a racemic mixture of D,D(*R,R*)- and L,L(*S,S*)-LA [50:50, denoted D,L(*rac*)-LA] characterized by a melting temperature ($T_m = 126°C$) higher than the temperature of the constituting pure stereoisomers is often used as starting monomers.

Early attempts to polymerize LA were based on anionic and cationic processes. In most cases, no control over the polymerization course was reported due to the occurrence of transesterification side reactions: monomolecular (intramolecular) chain transfer with macrocyclics formation (eq. **1a**) and bimolecular (intermolecular) chain transfer, leading to macromolecular chain length redistribution and thus broadening of molecular weight distribution (eq. **1b**).

$$*\!\left(\!-\mathrm{M}-\!\right)_n\!\mathrm{M}^* \underset{k_{p(x)}}{\overset{k_{tr(1)}}{\rightleftharpoons}} *\!\left(\!-\mathrm{M}-\!\right)_{n-x}\!\mathrm{M}^* + \left(\!-\mathrm{M}-\!\right)_x \qquad \text{(1a)}$$

$$*\!\left(\!-\mathrm{M}-\!\right)_n\!\mathrm{M}^* + *\!\left(\!-\mathrm{M}-\!\right)_p\!\mathrm{M}^* \underset{k_{tr(-2)}}{\overset{k_{tr(2)}}{\rightleftharpoons}} *\!\left(\!-\mathrm{M}-\!\right)_{n+q}\!\mathrm{M}^* + *\!\left(\!-\mathrm{M}-\!\right)_{p-q}\!\mathrm{M}^* \qquad \text{(1b)}$$

The extent of these side reactions depends on the monomer conversion and on the structure of the active sites so that species of lower reactivity are more discriminating and characterized by higher selectivity parameters: $\beta = k_p/k_{tr(1)}$

and $\gamma = k_p/k_{tr(2)}$, where k_p, $k_{tr(1)}$ and $k_{tr(2)}$ denote the kinetic constants of propagation, monomolecular-, and bimolecular-transfer reactions, respectively (31). The formation of cyclic compounds is thermodynamically inevitable but kinetic conditions can be found to prepare linear macromolecules almost free of ring structures. Due to intermolecular-transfer reactions, the polydispersity index (M_w/M_n) increases more or less rapidly with monomer conversion, eventually reaching the value predicted by the most probable distribution ($M_w/M_n = 2$) in the case of initiators characterized by low selectivity. On the contrary, for highly selective active species, the molecular distribution can be kept narrow until almost complete monomer conversion is achieved and only broadens for a much longer reaction time, well above the monomer-to-polymer conversion. There are a huge number of catalyst–initiator systems that have been shown to be effective in the synthesis of high molecular weight PLA by ROP in solution, in bulk, and even in suspension (32), but control over the lactide ROP usually remains a problem (33–35). From a practical point of view, controlled or living polymerization implies that almost any molar mass (M_n up to 10^6), M_w/M_n (down to predicted by Poisson distribution), required end-groups, and rates of polymerization could be obtained at will. Among others, the ROP of LA has been reported to be promoted by organometallic compounds including tin (36–41), aluminium (42–44), lead and bismuth (45), zinc (46–48), iron (49–51), yttrium (52,53), lanthanum (53,54), and some lower toxicity metals (55–57) reviewed by Okada (58). Although any systematic study on the selectivity of these organometallic compounds has not been performed yet, the selectivity parameter, β, has shown to decrease in the following order for the initiators so far investigated: tin(II) bis(2-ethylhexanoate) [$Sn(Oct)_2$)] $\sim$ $Sn(OBu)_2 > Al(O\textit{i}\text{-}Pr)_3 > Ti(O\textit{i}\text{-}Pr)_3 > Fe(OEt)_3 > La(O\textit{i}\text{-}Pr)_3 > Sm(O\textit{i}\text{-}Pr)_3 > MeO^-K^+$(59). This might at least partially explain the interest in $Sn(Oct)_2$ as the most frequently used activator in ROP of lactides. Besides organometallic derivatives, a purely organic approach to the catalytic ROP of lactides using tertiary amines, phosphines, or carbenes has also been reported (60,61). Finally, note that the solution (62) and bulk polymerization of LA initiated by $Al(O\textit{i}\text{-}Pr)_3$ (63) and $Sn(Oct)_2$ (64,65) occurs with a significantly faster kinetics when these activators are added with an equimolar amount of a Lewis base, 4-picoline and triphenylphosphine, respectively. Such a beneficial coordinative effect not only on the polymerization kinetics but also on the selectivity parameters has not found a clear mechanistic explanation yet. Anyway, such an extraordinary effect of triphenylphosphine on the efficiency of $Sn(Oct)_2$ has opened the way to use the reactive extrusion technology for producing high molecular weight PLA through a continuous single step (66).

Several polymerization mechanisms were proposed: mainly, cationic, activated monomer mechanism, and coordination-insertion mechanism. They have been successively examined and discussed in line with the polymerization of LA promoted by $Sn(Oct)_2$, which finally proved that essentially two mechanisms can be distinguished (39). The first one (activated monomer mechanism) assumes that alcohol or water (ROH) is present, then initiation and propagation steps involve reaction of three simultaneously interacting compounds, eg, in the case of propagation, a PLA chain fitted with a terminal –OH group, LA, and the organometallic derivative (MtX_n) (Fig. 2). In each propagation step, a macromolecule (including one additional lactide monomer unit) with an –OH end-group is regenerated as well as the MtX_n catalyst, either free or aggregated. According to the activated monomer mechanism, MtX_n acts as a catalyst while the true initiator is ROH. The second mechanism that prevails at least when metal alkoxides are used or *in situ* formed (MtX_m–OR), first relies upon the LA complexation onto the MtX_m–OR active species followed by a rearrangement of covalent bonds leading to the cleavage of both the metal–oxygen bond of the initiator and the acyl–oxygen bond of the cyclic monomer (coordination-insertion mechanism, Fig. 3). It results in the formation of PLA chains bearing an alkoxycarbonyl group [RO–C(O)–] with the alkyl radical arising from the initiator at one end and an active metal–oxygen bond at the other chain extremity. The fundamental difference between this mechanism and the activated monomer mechanism is that a covalent organometallic bond is kept active at the end of PLA chains. It comes out that all the alkoxide groups and alcohol molecules are active in the polymerization provided a fast alcohol–alkoxide exchange compared to the initiation and propagation rates. As far as $Sn(Oct)_2$ is concerned, it has been demonstrated that the ROP of LA proceeds through tin(II) alkoxide(s) *in situ* generated by reversible reaction of $Sn(Oct)_2$ with alcohols:

$$\mathrm{Sn(Oct)_2} + n\ \mathrm{R{-}OH} \rightarrow \mathrm{(Oct)_{2\text{-}n}Sn(OR)_n} + n\ \mathrm{OctH}\ (39).$$

High temperatures (170–220°C) permit rapid ROP of LA, but we must remember that the lactide relative concentration in the polymer at thermodynamic equilibrium (principle of chain-growth polymerization reversibility) is important. Devolatilization is thus critical after the bulk polymerization since at least 3–5% lactide remains in the polyester and interferes with resin processing equipment. Figure 4 shows the equilibrium curve of L,L-LA in poly(L,L-LA) considered as amorphous (67). Furthermore, racemization was found to be a significant side reaction in the ROP of L,L-LA promoted by $Sn(Oct)_2$ at high temperature, which increases the relative amount of D,L-(*meso*)-LA in both unreacted monomer and PLA repetitive units (67). Similar to aliphatic polymers that contain heteroatoms in the main chain, PLA is also very sensitive to thermal degradation. In fact, the adverse effect of the melt-processing on PLA was recognized as early as 1967 by Schneider (68) and corroborated by others (69–71). Since the degradation rate under processing conditions strongly depends on the nature and amount of the catalyst–initiator used, a viable industrial strategy consists in the postpolymerization quenching of the metal catalyst–initiator by deactivating agents such as benzoyl peroxides (72), boron compounds, and conventional stabilizers. The efficiency of this method remains, however, limited and cannot prevent some polymer weight loss, yellowing, drop in molar mass, and broadening of the polydispersity index particularly for extended periods of time at high temperature. Interestingly, the use of tiny amounts ($\sim$ 0.2 wt %) of tris(nonylphenyl)phosphite as stabilizer has proven its efficiency to stabilize melt-spun fibers of PLA by decreasing both free radical and hydrolytic degradations (73).

3.1. PLA as Building Blocks For Materials. PLA prepared from D,L(*meso*)- or (*rac*) LA are in general amorphous with a glass transition temperature ranging from 50 to 57°C, which severely limits its use as a bulk material.

Pure poly(D,D-LA) and poly(L,L-LA) have an equilibrium crystalline melting temperature of 207°C (74,75), but typical melting points are in the 170–180°C range. This is due to small and imperfect crystallites, slight racemization, and impurities. It has also been observed that an equimolar mixture of poly(D,D-LA) and poly(L,L-LA) yields an insoluble gel formed by the stereocomplexation (racemic crystallite) of the two enantiopure polymers during crystallization or polymerization. This pure stereocomplex has a melting point of 230°C and mechanical properties greater than enantiopure PLA alone (76–79). The crystal structure of poly(L,L-LA) was reported to be pseudoorthorhombic and to form a left-handed helix conformation, referred as the α-form (80). When drawing fibers of high molar mass at a high drawing ratio, a partial modification of the α-form to a stable β-form was reported (81), and more recently, a γ-form has been obtained by epitaxial crystallization in hexamethylbenzene (82).

Based on the physical properties of enantiopure PLA, eg, poly(L,L-LA), one may conclude that this polyester has significant commercial potential as a textile fiber (83,84). Its mechanical properties are reported to be broadly similar to those of conventional PET although lower melting and softening temperatures are clearly a limitation on its use (85). According to Dorgan and co-workers (86), the mechanical properties of poly(L,L-LA) are comparable to those of polystyrene, and its melt-rheology enables it to be processed rather readily into fibers. As film extrusion has proven to be more difficult (87), brittle poly(L,L-LA) is advantageously plasticized. Among others, two biodegradable, nontoxic plasticizers that have been successfully blended with poly(L,L-LA) are triacetine and tributyl citrate (88,89). A key point for further developments will be to prevent or at least slow down crystallinity changes due to additives (plasticizers), migration upon storage, and to improve weldability of the PLA-based films. PLA is also a promising polymer for various other end-use applications (90). Currently, there is increasing interest in using it for disposable degradable plastic articles (91).

In summary, some properties such as flexural properties, heat distortion temperature, gas barrier properties, impact resistance, and melt viscosity, can still be improved for various end-use applications (92). It will be the topic of the two following sections to survey recent advances in both catalyst design and nanocomposite formulation to better match some of these specific requirements.

3.2. Stereoelective Initiating Systems. Initiators such as aluminum alkoxides (3), tin(II) alkoxides *in situ* generated by reaction between $Sn(Oct)_2$ and alcohols (39), yttrium and lanthanide alkoxides (93), iron alkoxides (94), and calcium-based initiating systems generated *in situ* by exchange of bis(trimethylsilyl)amide ligands with alcohols (95) have been shown to provide a fast and controlled/living polymerization of LA via the previously discussed coordination-insertion mechanism, at least in solution under rather mild conditions. However, all of the above initiators are not bias toward the different lactide isomers, which means that isotactic PLA can only be prepared by ROP of LA stereoisomers, whereas D,L(*rac*)- and D,L(*meso*)-LA will give an amorphous, atactic polyester. Therefore, there is a need for initiators that are not only able to control the ROP but also to discriminate between LA isomers (so-called stereoelectivity). Two different strategies, namely, chain-end control and enantiomorphic site control of the initiator, have been exploited. Figure 5 shows known organic ligands that in combination with an appropriate metal center are capable of inducing stereoelectivity in LA polymerization. Ligands **I**, **II**, and **III** are achiral and probably induce stereoelectivity via a chain-end mechanism. Spassky and co-workers showed that the aluminum alkoxide derived from **I**, eg, by reaction with 1 equiv of $AlEt_3$, followed by the addition of 1 equiv of a primary or secondary alcohol (ROH), (see Fig. 6), imposes a moderate preference for isotactic addition in D,L(*rac*)-LA polymerization (96–100). A higher level of isotacticity was obtained by initiating the D,L(*rac*)-LA ROP by aluminum alkoxide ligated with **II**, particularly when bulky *tert*-butyl substituents were introduced into the aromatic rings (99). Coates and co-workers discovered that β-diimidate (**III**) zinc alkoxide enables the preparation of mostly heterotactic PLA $[-(R-R-S-S)_n-]$ from D,L(*rac*)-LA (100–102). This β-diimidate (**III**) zinc alkoxide was prepared by reaction of $Zn[N(SiMe_3)_2]_2$ with ligand **III**, followed by the addition of a stoichiometric amount of 2-propanol. The result is the formation of dimeric zinc alkoxides and the release of $HN(Si\ Me_3)_2$ (Fig. 7). More recently, a tacticity bias arising from the polymerization of D,L(rac)-LA by using β-diimidate (**III**) tin alkoxide has also been reported though it was less performant than the zinc analogue (103). Finally, let us recall that Kasperczyk and co-workers synthesized heterotactic PLA from D,L(*rac*)-LA by using lithium *tert*-butoxide aggregates (104,105).

Indubitably, the most important breakthrough was Spassky's discovery using stereoelective aluminum complexes of a chiral binaphthyl Schiff's base [(*R*)-**IV**] to initiate D,L(*rac*)-LA polymerization (106). At low conversion, (*R*)-**IV**–AlOMe demonstrated a preference for D,D-LA over L,L-LA to yield mostly optically active poly(D,D-LA) in toluene at 70°C, thanks to an enantiomorphic site control. Furthermore, (*R*)-**IV**–AlO*i*-Pr allows synthesis of semicrystalline, syndiotactic PLA from D,L(*meso*)-LA (107) for the first time. The probability that (*R*)-**IV**–AlO*i*-Pr opens D,L(*meso)*-LA at one of the enantiotopic acyl-oxygen groups, α, has been estimated by ^{13}C nmr spectroscopy to 0.96 reflecting a very high selectivity. Then, it was shown that a racemic mixture of (*R*)- and (*S*)-**IV**–AlO*i*-Pr was able to polymerize D,L(*meso*)-LA forming heterotactic PLA, while in the presence of D,L(*rac*)-LA it yields stereoblock PLA, which easily forms stereocomplexes (108–110). More recently, Feijen and co-workers showed that cyclohexysalen aluminum alkoxide, (*R*,*R*)-**V**–AlO*i*-Pr and *rac*-**V**–AlO*i*-Pr (**V** is referred as the Jacobsen's ligand), provided a high stereoelection and excellent control in both solvent-based and solvent-free LA polymerization (111,112). For example, (*R*,*R*)-**V**–AlO*i*-Pr has a marked preference for the L,L-LA in toluene at 70°C with a selectivity factor, s, of 5.5 up to 50% monomer conversion as calculated from polarimetry measurements. From this value, the difference in activation energies between the transition states for L,L- and D,D-LA enantiomers has been estimated to be 1.16 kcal/mol. Unlike (*R*,*R*)-**V**–AlO*i*-Pr initiated D,L(*rac*)-LA polymerization, the ROP using *rac*-**V**–AlO*i*-Pr affords polymers having microstructures that are conversion-independent. This attests for the absence of significant change in LA enantiomeric composition as the polymerization proceeds and allows accurate determination for a degree of stereoselectivity, Pi (probability of forming a new isotactic dyad), of 0.93 as determined by ^{13}C nmr spectroscopy. The D,L(*rac*)-LA propagation rate with *rac*-**V**–AlO*i*-Pr is lower than with $Al(Oi\text{-}Pr)_3$, achiral **I**-AlOMe or *rac*-**IV**–AlO*i*-Pr in toluene at 70°C, which is most probably due to the rather rigid and bulky nature of the former. Last, but not least, it is worth pointing out that a Pi value of 0.88 was determined for D,L(*rac*)-LA polymerization initiated by *rac*-**V**−AlO*i*-Pr in bulk at 130°C for 2 days (conversion = 95% and $M_w/M_n < 1.4$).

3.3. PLA-Based Nanocomposites. The mechanical properties and crystallization behavior of PLA is very much dependent on the molecular weight and stereochemical configuration of the backbone (9). Thanks to the use of stereoelective catalyst−initiator systems, the stereochemical structure of PLA chains can be enlarged starting from conventionally available LA stereoisomers, D,L(*rac*)- or (*meso*) LA, while the molecular weight can be directly controlled from the initial monomer/initiator molar ratio under adequate conditions (31). The recently developed nanocomposite technology consisting of a polymer and organically modified layered silicate (OMLS, Fig. 8) can be effectively applied (113−117) to improve and vary to a large extent the PLA properties such as thermal stability, mechanical properties, and gas barrier properties. In this context, montmorillonite (MMT) represents the most widely studied layered silicate. MMT is nothing but a layered 2:1 philosilicate characterized by a sandwich-like structure with one octahedral alumina sheet fused in between two tetrahedral silica layers sharing some common oxygen atoms, as schematized in Figure 8. Their layer thickness is of the order of 1nm and they possess a very high aspect ratio (from 100 to 500). Consequently, a small weight percent of OMLS (1−5 wt%) creates much more surface area for polymer−filler interactions than conventional composites when adequately dispersed in the polymer matrix by intercalation, intercalation−floculation, and/or exfoliation. To render the naturally hydrophilic clay filler more compatible with the organic polymer matrix, the hydrated Na^+ or Li^+ cations located in between every aluminosilicate platelets can be replaced by more hydrophobic ammonium (or phosphonium) cations bearing long alkyl chains, functionalized or not. Depending on the nature of the polymer, nanocomposites can be prepared by different methods including solution mixing, melt intercalation (statically or under shear), and *in situ* intercalative polymerization.

Ogata and co-workers first prepared blends of P(L,L-LA) and distearyldimethylammonium-modified MMT by the solution casting method in chloroform, but they found only tactoids that are essentially constituted of less than four stacked silicate layers (118). The tactoids form a superstructure in the thickness direction of the film increasing the PLA crystallinity and the storage modulus by a factor of 2 for clay content as tiny as 5 wt%. Partial intercalation of starch-blended PLA (43% of starch and amorphous PLA from Kolon Co.) into clay galleries was achieved also by solution casting in dimethylacetamide by using pristine sodium-MMT, hexadecylamine- or dodecyltrimethylammonium-modified MMT (119). Optimal organoclay content close to 4 wt% has proven to provide the highest improvements in terms of mechanical performances, whereas the oxygen permeabilitiy decreased linearly with loading up to 10 wt%. This last behavior was attributed to an increase in the length of the tortuous paths followed by the gas molecules to cross the nanocomposite film and to specific interactions between molecular oxygen and an alkyl moiety in the organoclays. By comparing nanocomposites prepared from hexadecylamine-modified MMT and mica, the same authors recently showed that partial intercalation occurred with better ultimate mechanical properties for organomodified mica hybrids than MMT (120) ones. It was suggested that hexadecylamine-modified mica in nanocomposites not only induced a stronger interfacial interaction but also imparted a higher rigidity due to the higher clay length.

Bandyopadhyay and co-workers first reported the preparation of intercalated P(L,L-LA)/OMLS nanocomposites by melt mixing in an extruder (121). As evidenced by X-ray diffraction, P(L,L-LA) chains crawled inside the gallery of dioctadecyl trimethyl ammonium-modified MMT or fluorohectorite, but the extent of miscibility was different in the two silicates. The presence of silicate layers impeded the translational and rotational motion of PLA so that the T_g increased from 42 to 57°C, while the crystallization inside the gallery was limited, especially for modified MMT compared to modified fluorohectorite. As a result, PLA/organomodified MMT nanocomposites showed an elastic modulus that is higher than unfilled PLA in the glassy state but is much lower above the T_g due to the increase in the amorphous fraction. Whatever the OMLS were used, the TGA traces under nitrogen attested that the silicate layers act as a barrier for both the incoming gas and also for the gaseous by-products from degradation. In agreement with these observations, melt blending PLA from Cargill-Dow (4.1 mol% D,D-LA) with 3 wt% dimethyl 2-ethylhexyl (hydrogenated tallowalkyl) ammonium-modified MMT at 180–195°C in an internal mixing chamber led to the formation of an intercalated microstructure with a reduced crystallization ability, a slightly higher T_g and significant increase in thermal stability under thermooxidative conditions (122). It is also worth mentioning that a charring behavior was clearly observed when nanocomposites were burned in air without producing burning droplets. Very recently, Okamoto and co-workers reviewed the work they carried out to produce PLA nanocomposites with improved mechanical and various other properties such as biodegradability, crystallization kinetics, rheological behavior, and foaming ability (123). Five OMLS were used throughout their studies and extruded with PLA from Cargill containing from 1.1 to 1.7% D-lactic acid (Table 1). On the basis of WAXD analyses and TEM observations (Figs. 9 and 10), the authors concluded that four different types of nanocomposites were formed. Ordered intercalated-and-flocculated nanocomposites were obtained when C_{18}-MMT and $q C_{18}{}^{2}$-MMT were used as OMLS, mainly due to hydroxylated edge–edge interaction of the silicate layers (124). A more delaminated and intercalated structure was observed in the case of PLA/$q C_{18}$-MMT. PLA/$q C_{16}$-SAP was disordered intercalated due to strong interactions between phosphonium and PLA, while coexisting stacked intercalated and exfoliated nanocomposites structures were formed in PLA/$q C_{13}$(OH)-mica as a result of the chemical and size inhomogeneities of the OMLS. A significant enhancement of the storage modulus has been observed from DMA experiments in the tension-torsion mode. Above T_g, the reinforcement effect of the silicate particles becomes prominent due to the restricted mobility of the intercalated polymer chains. A substantial increase in the flexural modulus of nanocomposites compared to unfilled PLA has also been noted, as well as a higher heat distortion temperature (HDT). As far as the oxygen gas permeability is concerned, PLA/$q C_{16}$-SAP showed the best barrier properties although all the OMLS led to a decrease of the permeability compared to unfilled PLA.

The poly(L,L-LA) matrix leads to highly stiff materials preventing their use in applications such as flexible food packaging. Accordingly, 20 wt% of poly(ethylene glycol) with a molar mass of 1000 (PEG) was systematically incorporated as a biodegradable plasticizer (125) by melt mixing in an internal chamber, together with different layered aluminosilicates (126). X-Ray diffraction analyses showed that all of the studied MMT led to the formation of intercalated nanocomposites, even for the unmodified Na^+−MMT. In the latter case, it was demonstrated that PEG selectively intercalated the interlayer spacing of the clay, however, without promoting any fire retardant properties. The best thermal stability improvements were obtained by using up to 5 wt% bis(2-hydroxyethyl)methyl (hydrogenated tallowalkyl) ammonium-modified MMT in the so-plasticized PLA.

One of the most effective methods of achieveing exfoliation consists of promoting the matrix polymerization from initiators located/anchored on the clay surface. Recently this technique has been approached in the case of the ring-opening polymerization of lactones for the preparation of poly(ϵ-caprolactone)/OMLS nanocomposites (127–129). Similarly, PLA/MMT nanocomposites has been produced by *in situ* intercalative ROP of L,L-LA in the presence of 3 wt% of two different organomodified MMT, ie, Cloisite 25A and Cloisite 30B with dimethyl-2-ethylhexyl (hydrogenated tallowalkyl) ammonium and bis(2-hydroxyethyl)-methyl tallowalkyl ammonium as organic cations, respectively (130). The ROP was carried out in bulk at 120°C for 48 h by using either $Sn(Oct)_2$ or triethylaluminium as activators. Compared to the intercalative structure of PLA/Cloisite 25A nanocomposites, grafting of the growing PLA chains from the hydroxyl groups covering Cloisite 30B allows total exfoliation and delamination of the platelets in the nanocomposites. Exfoliation of the clay platelets is responsible for the improved thermal stability compared to unfilled PLA and even intercalated counterparts.

Finally, it is worth pointing out that high strength PLA fibers with diameters from 100 to 500 nm were successfully electrospun from solutions of PLA/Cloisite 30B nanocomposites (with Cargill PLA containing from 1.1 to 1.7% D-lactic acid) in chloroform. Whether PLA was compounded with OMLS by using an extruder or by simple solution mixing, the microstructure of the nanocomposites fibers was intercalated or rather exfoliated. Whatever the compounding method, the presence of clay enhances the formation of the β-crystalline structure (fibril morphology) to the detriment of the conventional α structure corresponding to lamellar folded-chain morphology (131).

4. Future of PLA-Based Materials: An Environmental View Point

Compared to most fossil resource-based polymer such as, eg, commodity polyolefins, which have reached maturity over the years, PLA clearly offers the best compromise for continued improvement against current performance characteristics. As aforementioned, PLA is a versatile compostable polymer that is made from 100% renewable resources like corn, sugar beets, or rice. All free energy consumed by biological systems arises from solar energy that is trapped by the process of photosynthesis. In other words, all the carbon, hydrogen, and oxygen in the (poly)saccharide molecules as well as in the final PLA molecule have their origin in water and carbon dioxide. Next to this unique nonfossil origin, it is worth recalling the wide range of packaging, film, and fiber applications that PLA can fill in, leading to products that can ultimately biodegrade into water, carbon dioxide, and in some cases, into biomass. Therefore, PLA can be viewed as a sustainable, renewably sourced plastic and it is interesting to cite here the quite ambitious statement of business philosophy adopted by Cargill Dow (11): “Cargill Dow is a leader in producing plastics from renewable resources, and is dedicated to meeting the world’s needs today without compromising the earth’s ability to meet the needs tomorrow”.

The ideal environmentally sustainable product provides an equivalent function to the products it replaces and is available at competitive costs. For example, Cargill Dow has accordingly applied the life cycle assessment (LCA) tools to their NatureWork PLA. They first reviewed the contributions to the gross fossil energy requirement for PLA (54 MJ/kg for PLA1, see Fig. 11) compared to conventional plastics. Additionally, they proposed some ways and strategies for reducing the energy use by $>90\%$ compared to any of the petroleum-based polymers being replaced. The key improvements associated with the biomass feedstock technology stemmed from the use of the lignin fraction of the raw material to displace fossil-fuel based energy requirements, and the resulting improved economic opportunity to rely on renewable energy (wind) for the balance of facility power need (7 MJ/kg for PLA Bio/WP in Fig. 11).

Interestingly, PLA also has been compared with petrochemical-based polymers taking into account the global warming and water use as impact indicators (Figs. 12 and 13). For example, Cargill Dow’s objective is to decrease the greenhouse gasses from $+1.8$ down to -1.7 kg CO_2 equiv/kg PLA, which can be compared to $\sim +6$ kg CO_2 equiv/kg nylon.

In conclusion, over the long term, LCA demonstrates that PLA production processes can become both fossil-energy free and a source of carbon credits, paving the way to many new or already existing fields of application.

5. Conclusions

Beyond a state of the art on the controlled synthesis of PLA by ring-opening polymerization of LA initiated by various catalyst–initiator systems, this article has tentatively addressed recent technological advances enabling us to strengthen the role of PLA as a substitute to petrochemical-based commodity and engineering plastics and to enlarge its field of applications. On one hand, already developed stereoelective initiators actually offer a great potential in preparing new distinct PLA from readily available LA isomers. It is believed that even more efficient initiating systems with better stereoelectivity and higher thermal stability could be produced through rational initiator design especially assisted by, eg, molecular modeling and combinatorial methods. On the other hand, an insight into the versatility of nanocomposite technology has shown the added value of dispersing high aspect ratio layered fillers within a PLA matrix. Whatever the method used to prepare PLA/OMLS nanocomposites, significant improvements in mechanical and many other materials key-performances have been pointed out. These improvements include mechanical and flexural properties, heat distortion temperature, oxygen gas permeability barrier, thermal stability, and rate of crystallization, ie, several of the known weak points of PLA as compared to conventional petrochemical resins.

6. Acknowledgments

This work was supported by both the *Région Wallonne* and *Fonds Social Européen* in the frame of *Objectif 1-Hainaut: Materia Nova* program. LPCM thanks the “Service Féderaux des Affaires Scientifiques, Techniques et Culturelles” for general support in the frame of the PAI-5/03.

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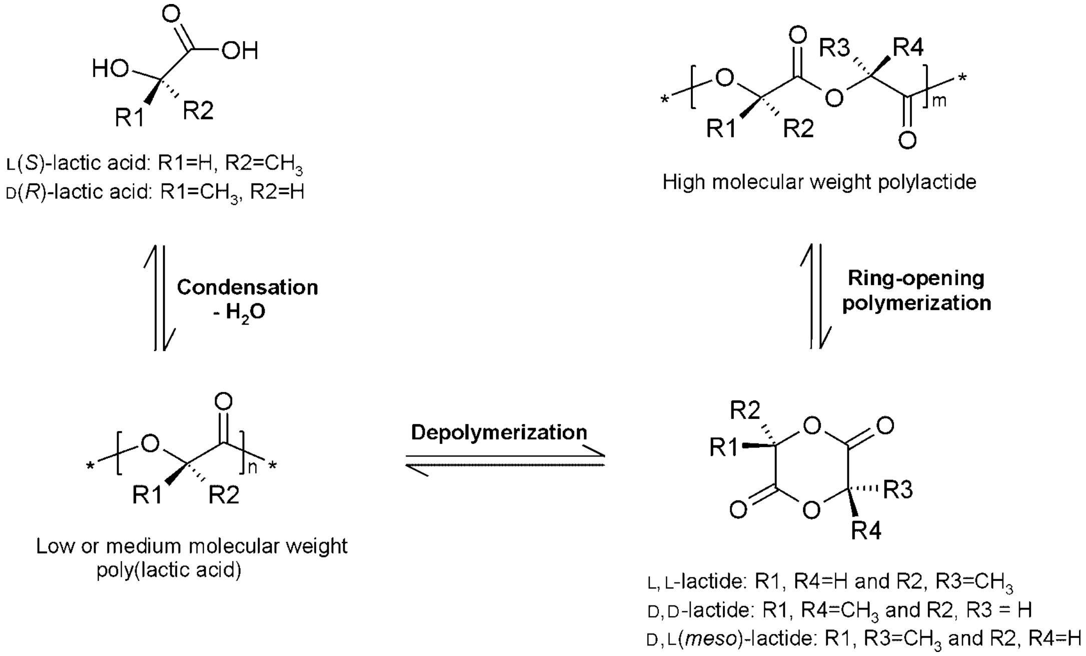


Fig. 1. Synthesis methods for the preparation of lactic acid based polymers.

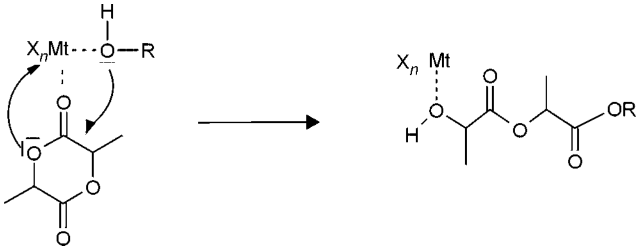


Fig. 2. Activated monomer mechanism.

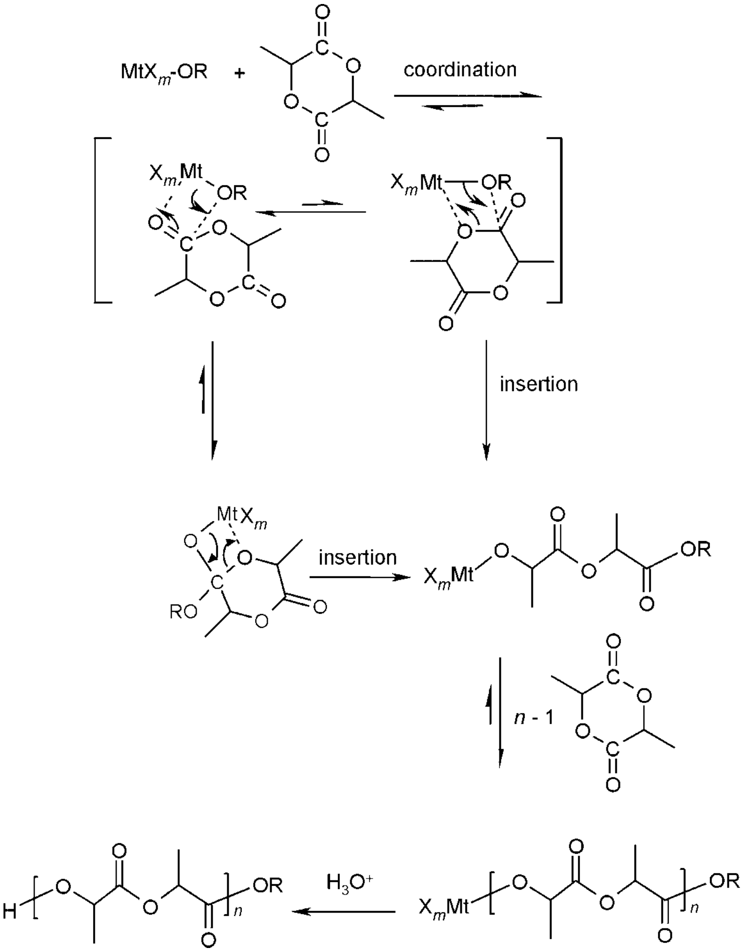


Fig. 3. Coordination-insertion mechanism.

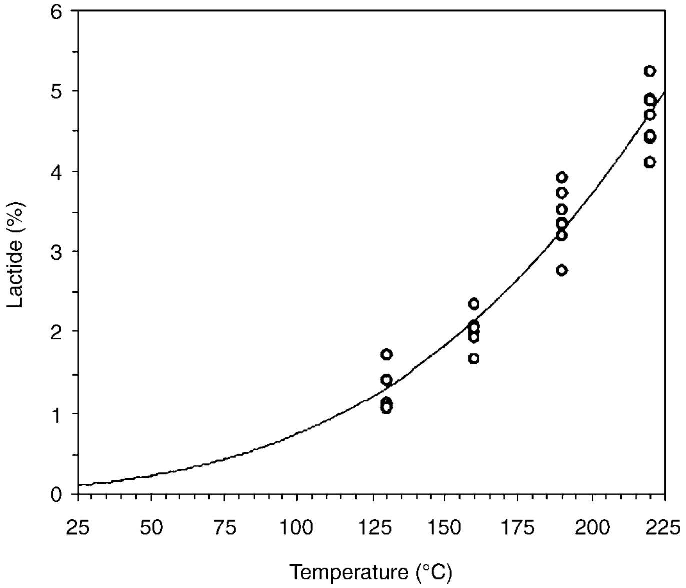


Fig. 4. Monomer equilibrium curve for L,L-LA polymerization (amorphous phase). The solid line is the equilibrium model fitting with $\Delta H_p = -23.3$ kJ/mol, $\Delta S_p = -22.0$ J/mol/K (67).

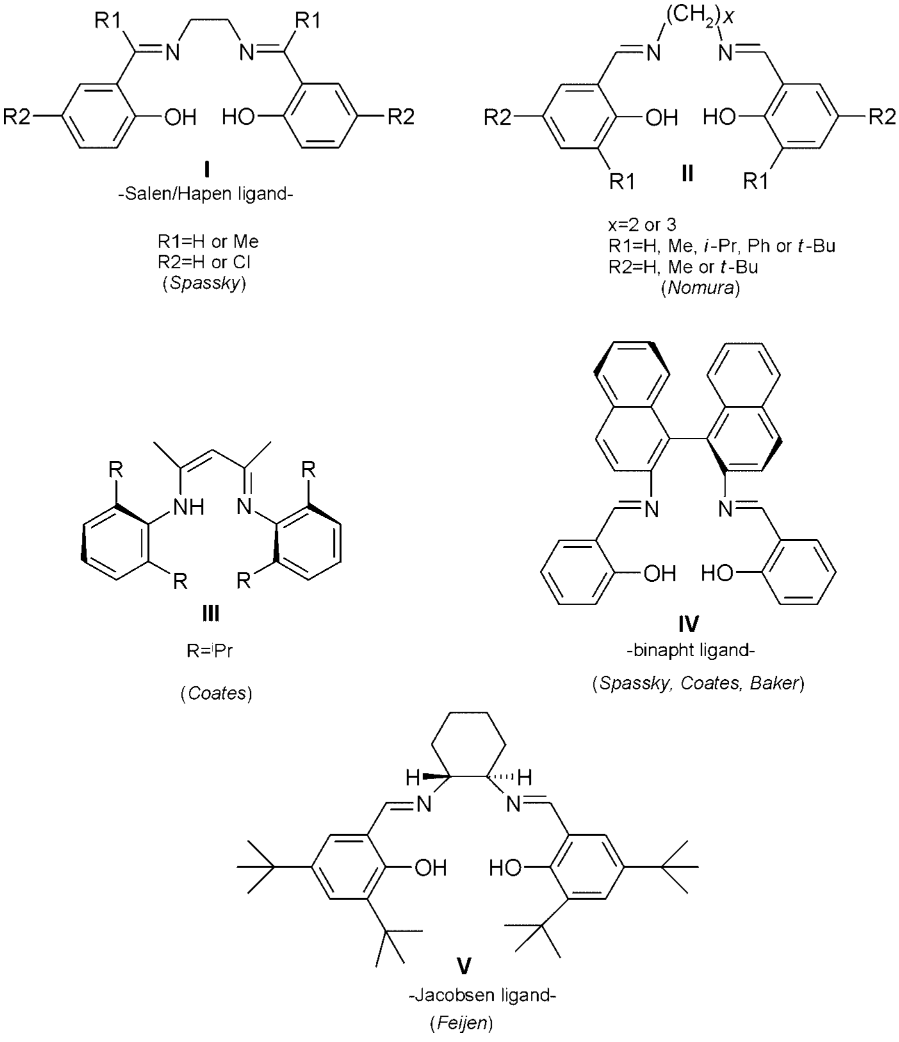


Fig. 5. Ligands explored in the synthesis of stereoelective initiators for the ROP of LA.

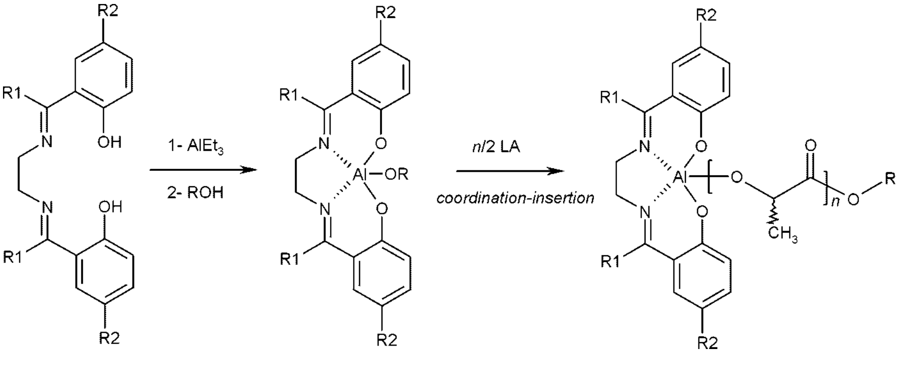


Fig. 6. Sketch for the preparation of stereoelective aluminum alkoxides active in ROP of LA. Actual structures of “ligands” are shown as derivatives **I**, **II**, **IV**, and **V** in Figure 5.

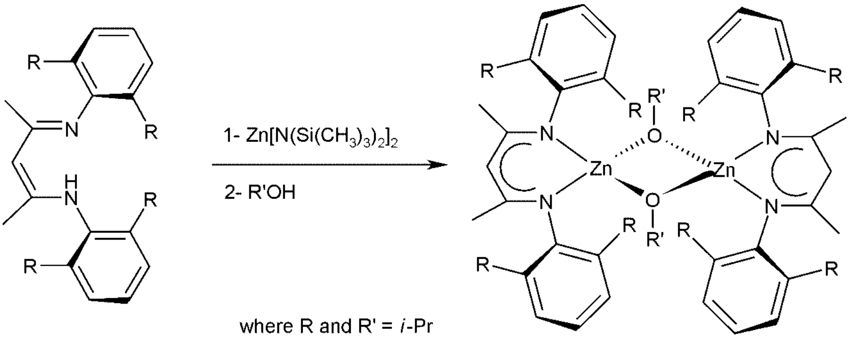


Fig. 7. Synthesis of the β-diimidate (**III**) zinc alkoxide.

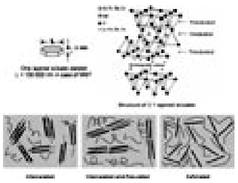


Fig. 8. Schematic illustrations of the three extreme classes of thermodynamically achievable polymer/layered silicate nanocomposites.

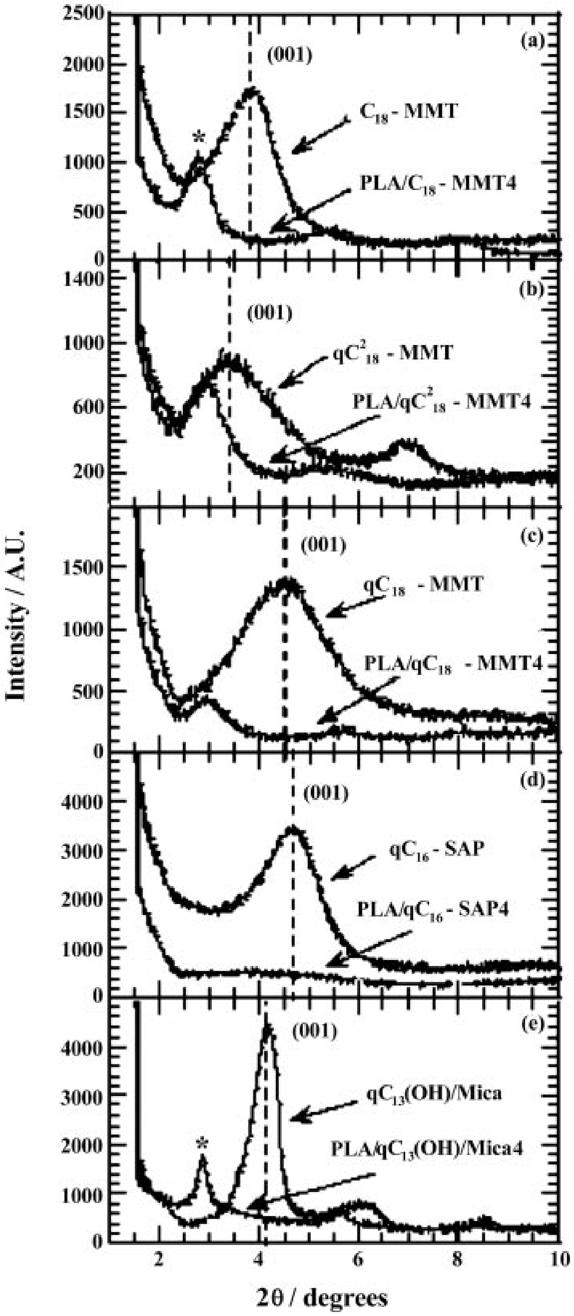
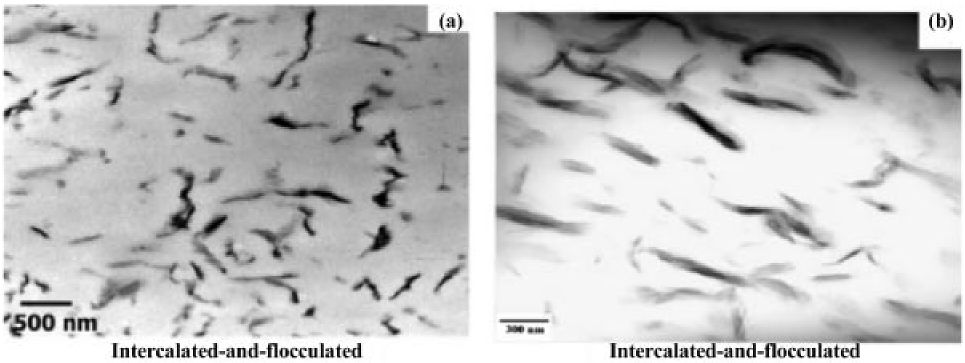
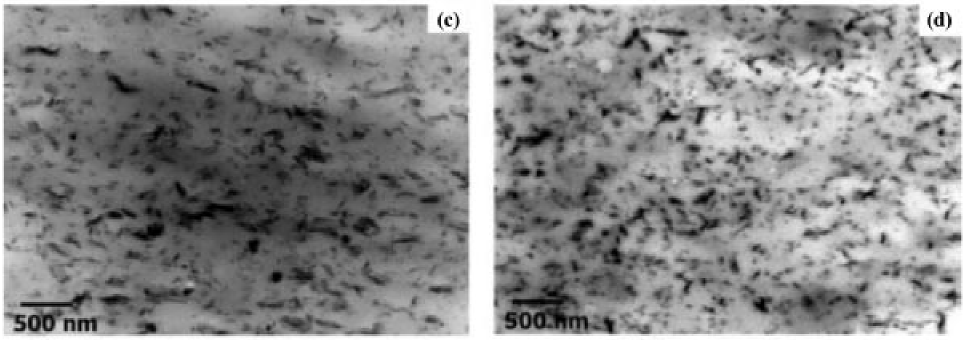


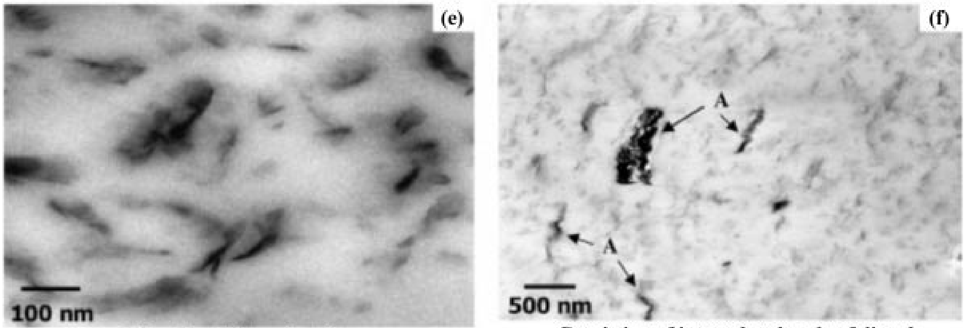
Fig. 9. WAXD patterns of pure OMLS powders and corresponding nanocomposites sheets: (**a**) PLA/C_{18}-MMT; (**b**) PLA/qC^2_{18}-MMT; (**c**) PLA/qC_{18}-MMT; (**d**), (**e**) PLA/qC_{16}-SAP; (**f**) PLA/qC_{13}(OH)-mica (117).



Intercalated-and-flocculated Intercalated-and-flocculated



Intercalated Disordered intercalated



Disordered intercalated Coexisting of intercalated and exfoliated

Fig. 10. TEM images of various nanocomposites: (**a**) PLA/C_{18}-MMT; (**b**) PLA/qC^{2}_{18}-MMT; (**c**) PLA/qC_{18}-MMT; (**d**), (**e**) PLA/qC_{16}-SAP; (**f**) PLA/qC_{13}(OH)-mica (117).

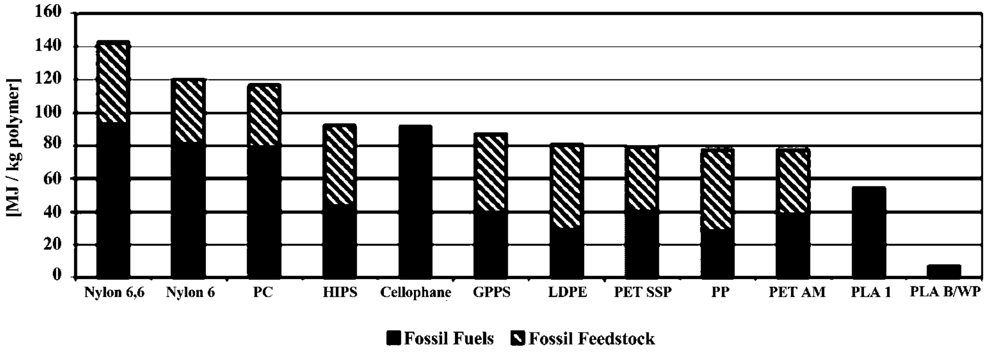


Fig. 11. Fossil energy requirements for some petroleum-based polymers and polylactide. The cross-hashed part of the bars represents the fossil energy used as chemical feedstock (the fossil resource to build the polymer chain). The solid part of each bar represents the gross fossil energy use for the fuels and operations supplies used to drive the production processes. PC = polycarbonate; HIPS = high impact polystyrene; GPPS = general purpose polystyrene; LDPE = low density polyethylene; PET SSP = poly(ethylene terephthalate), solid-state polymerization (bottle grade); PP = polypropylene; PET AM = poly(ethylene terephthalate), amorphous (fibers and film grade); PLA1 = polylactide (first generation); PLA B/WP (polylactide, biomass/wind power scenario) (11).

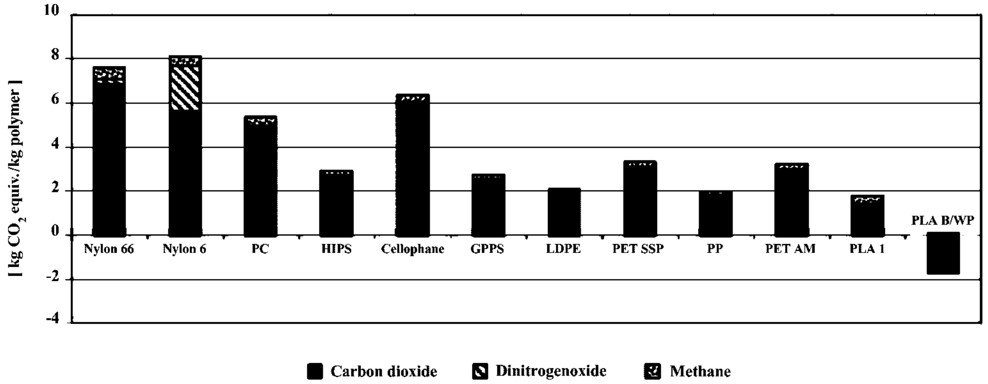


Fig. 12. Contribution to global climate change for some petrochemical polymers and the two polylactide polymers. PC = polycarbonate; HIP-S = high impact polystyrene; GPPS = general purpose polystyrene; LDPE = low density polyethylene; PET SSP = poly(ethylene terephthalate), solid-state polymerization (bottle grade); PP = polypropylypropylene; PET AM = poly(ethylene terephthalate), amorphous (fibers and film grade); PLA1 = polylactide (first generation); PLA B/WP (polylactide, biomass/wind power scenario) (11).

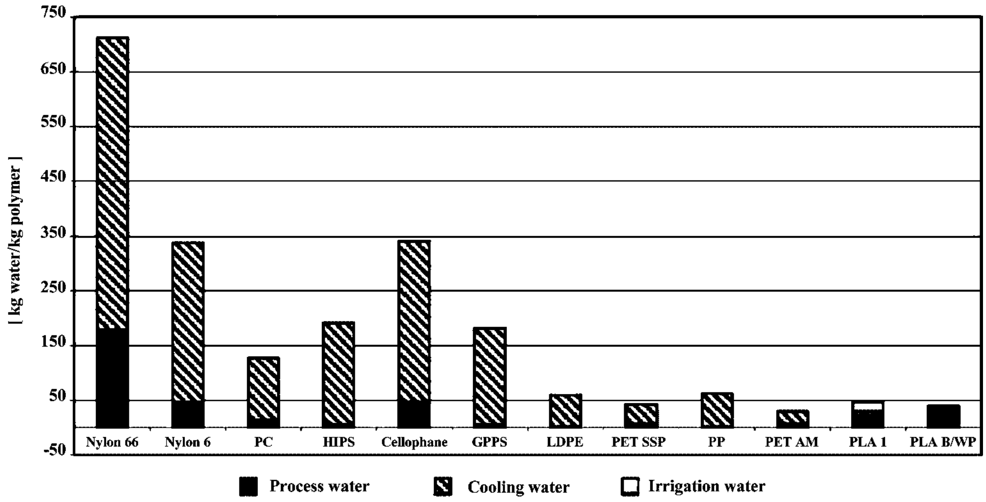


Fig. 13. Gross water use by petrochemical polymers and the two PLA cases (11).

Table 1. **Characteristic Parameters and Designation of the Studied OMLS Melt Blended with PLA**

OMLS Code	Pristine layered silicates	Organomodifiers	Particle length, nm	CEC[a] meq/100g
C_{18}-MMT	MMT	octadecylammonium	~150	110
q$C^{2}{}_{18}$-MMT	MMT	dioctadecyldimethylammonium	~100	90
qC_{18}-MMT	MMT	octadecyltrimethylammonium	~100	90
qC_{16}-SAP	saponite	hexadecyltributylphosphonium	~50	87
qC_{13}(OH)-mica	Fluorine mica	*N*-(cocoalkyl)-*N*,*N*-[bis(2-hydroxyethyl)]-*N*-methyl ammonium	200–300	120

[a] CEC = cation exchange capacity.