Controlled Synthesis and Characterization of Poly[ethylene-*block*-(L,L-lactide)]s by Combining Catalytic Ethylene Oligomerization with "Coordination-Insertion" Ring-Opening Polymerization

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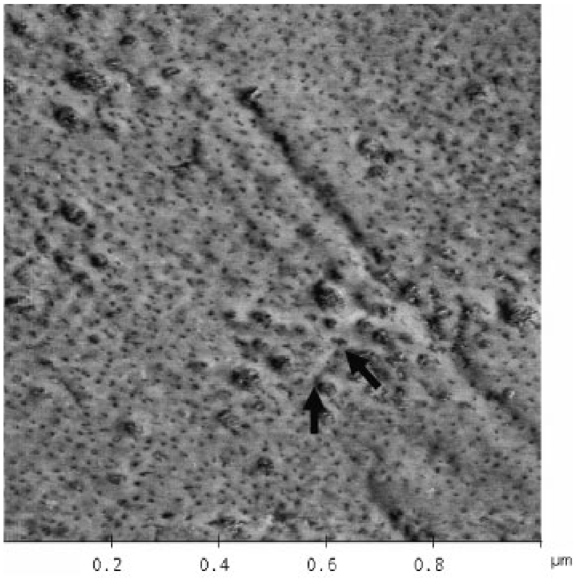
Model poly[ethylene-*block*-(L,L-lactide)] (PE-*block*-PLA) block copolymers were successfully synthesized by combining metallocene catalyzed ethylene oligomerization with ring-opening polymerization (ROP) of L,L-lactide (LA). Hydroxy-terminated polyethylene (PE-OH) macroinitiator was prepared by means of ethylene oligomerization on *rac*-dimethyl-silylen-bis(2-methyl-benz[e]indenyl)-zirconium(IV)-dichloride/methylaluminoxane (*rac*-MBI/MAO) in presence of diethyl zinc as a chain transfer agent, and subsequent in situ oxidation with synthetic air. Poly[ethylene-*block*-(L,L-lactide)] block copolymers were obtained via ring-opening polymerization of LA initiated by PE-OH in toluene at 100 °C mediated by tin octoate. The formation of block copolymers was confirmed by ^{1}H NMR spectroscopy, fractionation experiments, thermal behavior, and morphological characterization using AFM and light microscopy techniques.



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Introduction

The development of new synthetic strategies to incorporate polar segments into polyolefins, such as polyethylene and poly(propylene), in a controlled fashion is one of the most striking challenges in Polymer Chemistry.[1] These new polyolefin architectures with many desirable properties represent an attractive goal both in academia and

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industry.[2] So far, several methods have been reported to incorporate polar monomers directly by transition metal-catalyzed (co)polymerization to yield random polyolefinic copolymers. The synthetic strategy involves increasing both the tolerance of the catalyst towards polar groups and catalyst activity, and enhancing incorporation of polar monomers in polyolefins by coordination polymerization.[2–4] Despite the fact that some authors have already synthesized block copolymers using lanthanide or metallocene catalysts, extensive efforts towards copolymerization of polar monomers with simple olefins, more particularly ethylene, using these catalysts have however yielded minimal success.[5–7] In this respect, combination of coordination polymerization of olefins with different polymerization mechanisms has shown to be another interesting approach to prepare block and graft polyolefinic copolymers based on mono- or multifunctional polyolefin macroinitiators or polyolefin macromonomers in a controlled way.[8–13]

Nevertheless, the preparation of block polyolefinic copolymers is not a straightforward method since this requires high chain-end functionality in the macroinitiators to give well-defined polymers. Matyjaszewski et al. used vinyl-terminated polyolefins as a valuable macroinitiator with sufficiently high chain-end functionality to successfully form block copolymers such as poly[ethylene-*block*-(methyl methacrylate)] and poly(ethylene-*block*-styrene) by means of Atom Transfer Radical Polymerization (ATRP).[9] The vinyl terminated polyethylene was converted to an ATRP macroinitiator by addition of α-bromoisobutyric acid to the vinyl chain extremity. In addition, well-defined poly(ethylene-*block*-lactide) has been prepared by ring-opening polymerization of lactide initiated by a mono-hydroxylated PE[14–16] as synthesized by anionic polymerization of 1,3-butadiene which was end-terminated by ethylene oxide and acidic methanol and hydrogenated to yield the PE-OH macroinitiator.

In this work, we report the preparation of poly[ethylene-*block*-(L,L-lactide)] block copolymers by combining metallocene catalyzed ethylene polymerization and "coordination-insertion" ring-opening polymerization (ROP) of L,L-lactide. Key intermediates are hydroxy-terminated oligoethylenes (PE-OH), prepared by means of ethylene polymerization on *rac*-dimethyl-silylen-bis(2-methyl-benz[e]indenyl)- zirconium(IV)- dichloride/methylaluminoxane (*rac*-MBI/MAO) in the presence of diethyl zinc chain transfer agent producing zinc alkyl-terminated oligoethylenes. These oligomers were in situ oxidized with dry air to afford monohydroxylated PE chains. In contrast to the aforementioned methods, this represents a useful way to in situ prepare hydroxylated PE in only one step. For the preparation of block copolymers, the monohydroxylated PE was used as a macroinitiator in the controlled ring-opening polymerization (ROP) of L,L-lactide (LA) as promoted by tin octoate. This type of diblock copolymer synthesis allows the incorporation of "*mechanistically incompatible*" monomers into a single block copolymer, leading to strongly segregated materials that cannot be prepared using the standard sequential addition of monomers technique.[17]

Experimental Part

Materials

All manipulations concerning metallocene-catalyzed olefin polymerization were carried out under dry argon atmosphere using Schlenk tube and glove box techniques. *rac*-Dimethyl-silylen-bis(2-methyl-benz[e]indenyl)-zirconium(IV)-dichloride (*rac*-MBI) was purchased from MCAT GmbH, Konstanz, Germany, Methylaluminoxane (MAO, 10 wt.-% solution in toluene) from Crompton GmbH, Bergkamen. Diethyl zinc (1 M solution in hexane), bromine and 1-methylimidazole were supplied by Fluka and were used without further purification. Toluene (Merck) was distilled over Na prior to use. Ethylene and synthetic air were purchased from Air Liquide. Tetrachloroethane-d_2 was provided by Cambridge Isotope Laboratories. L,L-Lactide (LA) was purchased from Boehringer Ingelheim, and hot-recrystallized three times in dry toluene before use. Tin octoate ($Sn(Oct)_2$) from Sigma-Aldrich was purified by distillation under reduced pressure (10^{-2} mbar) and rapidly dissolved in dry toluene. The accurate concentration of the solution was determined by weighing $Sn(Oct)_2$ recovered after evaporation of toluene.

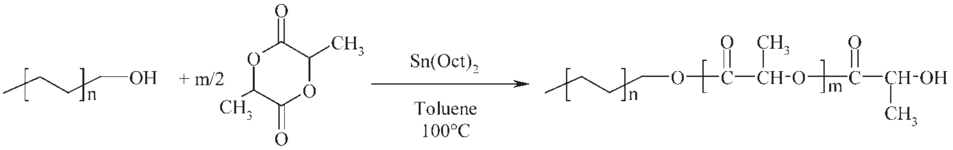
Synthesis of Hydroxyl-Terminated Polyethylene

Polymerizations were carried out at 40 °C in a 200 mL Büchi Miniclave steel reactor previously dried in vacuo and flushed with argon. After injection of toluene, a share of the MAO was added for reactor deactivation. The catalyst was dissolved in toluene and preactivated with the other share of the MAO. The diethyl zinc solution was transferred into the reactor to yield a diethyl zinc concentration of 40 $mmol \cdot L^{-1}$ and the solution was saturated 3 times with 4 bar of ethylene. The catalyst solution was added and ethylene polymerization was conducted at 4 bar for 30 min with a total volume of 100 mL, a catalyst concentration of 3 $\mu mol \cdot L^{-1}$ and a Al:Zr ratio of 5 000:1. The reaction mixture was transferred under argon into a flask equipped with a reflux condenser and a gas injection tube. Synthetic air was bubbled through the suspension at 65 °C for 5 h. The hydroxylated polyethylene (PE-OH) was precipitated in acidic methanol, filtered, washed with methanol and dried at 60 °C in vacuo over night. The number-average molecular weight of PE-OH was of 1 300 $g \cdot mol^{-1}$, while its degree in OH-functionality was of 67% as determined by ^1H NMR.

^1H NMR (500 MHz, $C_2D_2Cl_4$, 120 °C): $\delta = 0.91$ (t, 3H), 1.10–1.70 (m, 2H), and 3.62 (t, 2H).

Synthesis of Poly[ethylene-*block*-(L,L-lactide)]

In a flame-dried round-bottom flask, 0.58 g of PE-OH (4.5×10^{-4} mol) as previously dried by three successive azeotropic



Scheme 2. Sequential ROP of LA initiated by PE-OH/Sn(Oct)$_2$.

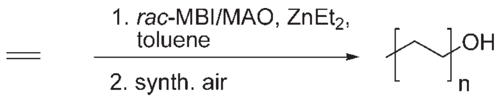
distillations in dry toluene were dissolved in 66 mL of dry toluene at 100 °C. The resulting solution was transferred under nitrogen flow into another flame-dried round-bottom flask, containing 9.96 g of LA (6.89×10^{-2} mol) in order to reach an initial $[LA]_0/[OH]$ molar ratio of 231 ($[LA]_0 = 1$ mol · L^{-1}), while taking into account the degree of hydroxyl functionality for PE-OH (67%). The polymerization of LA initiated by PE-OH was then carried out at 100 °C after adding Sn(Oct)$_2$ as co-initiator in order to reach an initial [Sn]/[OH] molar ratio of 1. At predetermined intervals of time, samples were picked out from the reaction medium, and poured into 7 volumes of heptane. Block copolymers were recovered by filtration and drying under reduced pressure at 60 °C until reaching a constant weight.

Characterization

^{1}H NMR measurements were conducted using a Bruker AMX-300 at 120 °C. Spectra were recorded in $C_2D_2Cl_4$ with 32 scans at 200 MHz. DSC measurements were carried out with a 2920 CE modulated DSC from TA instruments (heating rate: 10 °C · min^{-1}) under nitrogen flow. Atomic force microscopy (AFM) experiments were performed with a Nanoscope III scanning probe microscope. The height and phase images were obtained simultaneously while operating the instrument in the tapping mode under ambient conditions. Images were taken at the fundamental resonance frequency of the Si cantilevers which was typically around 180 kHz. Typical scan speeds during recording were 0.3–1 line · s^{-1} using scan heads with a maximum range of 16 × 16 μm. The flat surfaces of the blend samples which were examined were obtained by cutting with a Diatome diamond knife at −120 °C using a Leica ULTRACUT UCT ultramicrotome equipped with the cryo-chamber Leica EM FCS Light microscopy. Light microscopic images were taken with a Zeiss Axioplan 2 microscope equipped with a digital camera.

Results and Discussion

In Scheme 1, the preparation of the hydroxylated polyethylene is depicted. Ethylene was polymerized on *rac*-MBI activated with MAO. The presence of diethyl zinc as chain transfer agent has a strong impact on the molar mass of the polyethylene which is lowered to 1 300 g · mol^{-1} at the given reaction conditions. The resulting zinc-terminated polyethylene was then treated with synthetic air in situ to obtain a terminally hydroxylated polyethylene with a degree of functionalization of 67%. Accordingly, Shiono et al. prepared hydroxylated isotactic poly(propylene) (PP) with conventional $TiCl_3/AlEt_2Cl$ system in presence of diethyl zinc as transfer agent, and oxygen as quenching reagents.[18] Addition of diethyl zinc enabled to significantly reduce the molecular weight of poly(propylene) by forming Zn-polymer bonds in high concentration (98%). In the presence of oxygen as a quenching reagent, approximately 70% of Zn-carbon bonds could be transferred into hydroxyl group with the formation of ethanol as a by-product. Interestingly, neither the molecular weight of the resulting hydroxylated PP nor its polymer yield was reduced after quenching by oxygen.



Scheme 1. Synthesis of hydroxylated polyethylene. [Zr] = 3 μmol · L^{-1}, Al:Zr = 5 000, [ZnEt$_2$] = 40 mmol · L^{-1}, t_p = 30 min, T_p = 40 °C.

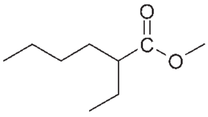
With the hydroxylated PE aforementioned, the preparation of poly[ethylene-*block*-(L,L-lactide)]has been carried out by adding an equimolar amount of Sn(Oct)$_2$ with respect to the initial PE-OH molar concentration as illustrated in Scheme 2.

Under these conditions, Sn(Oct)$_2$ is able to in situ form tin(II) mono- or dialkoxide with hydroxyl compounds, which have shown to be efficient (macro)initiators for the ROP of cyclic esters such as LA (Scheme 3). The ROP of (di)lactones initiated by tin(II) mono or dialkoxide has proven to proceed through a two-step "coordination-insertion" mechanism, which consists of the (di)lactone coordination onto the growing metal alkoxide, followed by a rearrangement of the covalent bonds leading to the insertion of the monomer into the Sn-oxygen bond of the propagating species.[19–21]

It is worth pointing out that first polymerizations of LA mediated by PE-OH/Sn(Oct)$_2$ had been attempted in bulk (absence of solvent) at 175 °C. As a result of the difference in polarity, both PE-OH and LA were immiscible by forming two distinct liquid phases in the reaction medium. However, when Sn(Oct)$_2$ was added as co-initiating species, the reaction medium turned slowly into a single

$$Sn(Oct)_2 + ROH \xleftarrow{\rightarrow} OctSnOR + OctH$$
$$OctSnOR + ROH \xleftarrow{\rightarrow} Sn(OR)_2 + OctH$$

Where Oct =



Scheme 3. In situ formation of tin(II) mono- or dialkoxide where ROH is a hydroxyl compound.

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Table 1. Time-dependence of LA conversion, $\overline{M}_{nPLA}(th)$ and $\overline{M}_{nPLA}(exp)$ of poly(ethylene-*block*-lactide) block copolymers as recovered in toluene at 100 °C by a PE-OH/Sn(Oct)$_2$ macroinitiator ($\overline{M}_{nPEOH} = 1300$ g · mol^{-1}, [Sn]/[OH] = 1, and $[LA]_0 = 1$ mol · L^{-1}).

Entry	**Time**	**LA conversion**[a]	$\overline{M}_{nPLA}(th)$	$\overline{M}_{nPLA}(exp)$[b]
	h	**%**	**g · mol^{-1}**	**g · mol^{-1}**
1	1	34	11 350	10 600
2	2	52	17 450	18 000
3	5.67	87	28 050	27 900

[a] As determined by weighing block copolymers recovered by precipitation in 7 volumes of heptane, filtration, and drying under reduced pressure at 60 °C until reaching a constant weight; [b] As determined by high temperature ^{1}H NMR based on the relative intensity of the repetitive units of the PLA block (–C(O)—C**H**(CH$_3$)–O–) at 5.23 ppm and the PE block (–C**H**$_2$–) at 1.31 ppm taking into account the number-average molecular weight of PE macroinitiator ($\overline{M}_{nPE}$).

phase, attesting for the PE-OH capability of initiating the ROP of LA.

In this respect, the polymerization of LA mediated by PE-OH/Sn(Oct)$_2$ was carried out in toluene at 100°C in order to reach an initial $[LA]_0/[OH]$ molar ratio of 231, while taking into account the degree of hydroxyl functionality for PE-OH (67%). Table 1 shows the time dependence of the LA conversion and number-average molecular weight of the PLA block of the as-obtained copolymer samples. Experimental number-average molecular weight in PLA ($\overline{M}_{nPLA}(exp)$) was determined by high temperature ^{1}H NMR measurements as illustrated in Figure 1 for one of these copolymer samples (entry 1, Table 1).

From Figure 1, the repetitive proton signals of both PLA and PE blocks can be easily observed as well as the protons H$_a$ and H$_b$ assigned to the α-hydroxy methine protons of the PLA end-group and the ester methylene protons at the extremity of the PE block, respectively. No α-hydroxy methylene protons from the PE-OH macroinitiator can be detected (appearing at 3.62 ppm). Such observations clearly indicate that the polymerization of PLA proceeded selectively and quantitatively through the expected coordination-insertion mechanism with an endocyclic O-acyl rupture of the monomer as initiated from the primary hydroxy end-group of the polyolefinic chain.

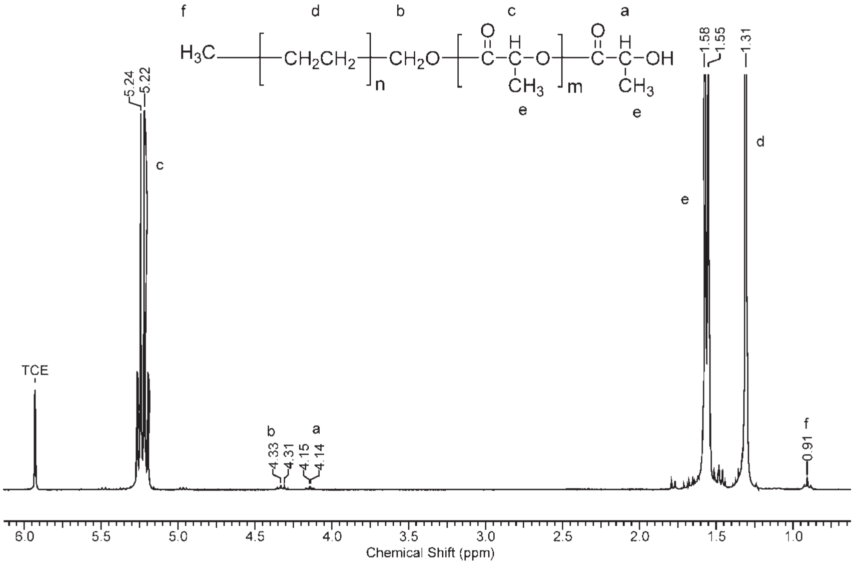

Figure 1. ^{1}H NMR spectrum of poly[ethylene-*block*-(L,L-lactide)] block copolymer as obtained after 1 h (entry 1, Table 1; solvent = C$_2$D$_2$Cl$_4$ at 120 °C).

Assuming that all PE-OH chains have promoted the ROP of LA, $\overline{M}_{nPLA}(exp)$ was determined from $\overline{M}_{nPE}$ of the PE macroinitiator based on the relative intensity of the repetitive methyne protons H$_c$ of the PLA at 5.23 ppm ((–C(O)–C**H**(CH$_3$)–O–) and the repetitive methylene protons H$_d$ of the PE at 1.31 ppm (–C**H**$_2$–) (see Table 1). It is stressed out that the low relative intensity of both H$_a$ and H$_b$ protons does not enable us to calculate the length of PLA blocks from these signals (particularly for the other copolymers recovered at higher LA conversion). The experimental values of $\overline{M}_{nPLA}$ in Table 1 are worth further explanation. When simply calculating $\overline{M}_{nPLA}$ from signals H$_c$ and H$_d$, a too small value for the chain length of the PLA block is obtained. This is due to the fact that at 120 °C in tetrachloroethane-d_2 both the PE chain attached to the PLA block and the unfunctionalized PE chains still remaining in the sample are visible in the spectrum and therefore contribute to signal H$_d$. Thus, the relative intensity of the H$_d$ signal has to be multiplied by the degree of functionalization (0.67) to get rid of the contribution of the homo-PE. The values obtained are shown in Table 1

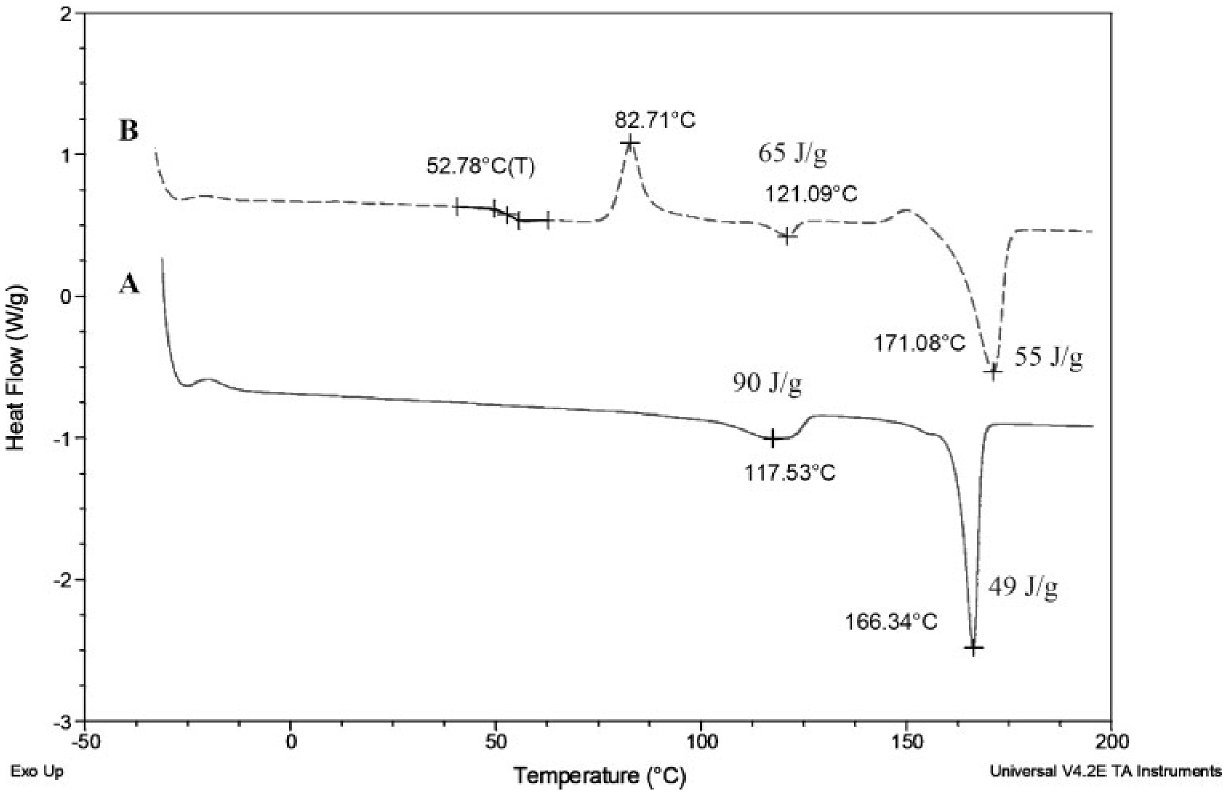

Figure 2. DSC thermograms of poly[ethylene-*block*-(L,L-lactide)] block copolymers obtained after a polymerization time of 1 h (A) and 5.67 h (B) (see Table 1; heating rate: 10 °C · min^{-1} under N_2 flow, 2nd scan).

and are in very good agreement with the theoretical ones. Hence, one can reasonably assume that the polymerization of LA initiated by PE-OH/Sn(Oct)$_2$ has proceeded in a controlled fashion in terms of $\overline{M}_{nPLA}$.

A fractionation experiment has also been carried out on the block copolymer as recovered after 5.67 h (last entry, Table 1). The block copolymer was accordingly solubilized in hot 1,1,2,2-tetrachloroethane, followed by a cooling step to room temperature, and gentle addition of THF as non-solvent of PE-OH. Before addition of THF, a small amount of a precipitate (less than 2 wt.-% of the entire copolymer) was recovered at r.t. The FT-IR analyses of the precipitate attested for the exclusive presence of PE homopolymer, which can be assigned to the fraction of PE not being hydroxy-terminated. The most striking feature was that adding large amount of THF led to the formation of a colloidal solution with the total absence of any precipitate. These results strongly indicate the formation of a poly(ethylene-*block*-lactide) block copolymer as prepared by ROP of LA initiated with the PE-OH macroinitiator. It is worth noting that due to the colloidal behavior of the block copolymers in THF, i.e. a selective solvent of PLA, no size-exclusion chromatography has been attempted in THF for determination of the molecular weight distribution.

DSC analyses of two poly[ethylene-*block*-(L,L-lactide)] samples recovered after 1 and 5.66 h (entries 1 and 3, Table 1) provided additional evidences regarding the formation of blocky structures (Figure 2). Both blocks are able to crystallize with both melting temperatures of the PLA block (ca. 170 °C) and the short PE block (ca. 120 °C), while the glass transition of PLA block can be detected for the last copolymer (ca. 55 °C). Increasing the relative content of PLA sequence enhanced its melting enthalpy, while the melting enthalpy of PE block is decreasing.

Morphological Characterization

The formation of a blocky structure cannot be reliably proved by NMR and DSC analysis alone. Therefore, the morphology of the poly[ethylene-*block*-(L,L-lactide)] was investigated by atomic force microscopy (AFM) and light microscopy techniques. In Figure 3 AFM images of a PE-*block*-PLA (entry 3) are shown. In the upper picture (scale: 1 000 nm) micro phase separation is clearly visible. The dark phases represent the harder polymer, thus polyethylene, and are shown to be homogeneously distributed. The PLA block did not crystallize because the sample was cooled down very fast and therefore the amorphous PLA

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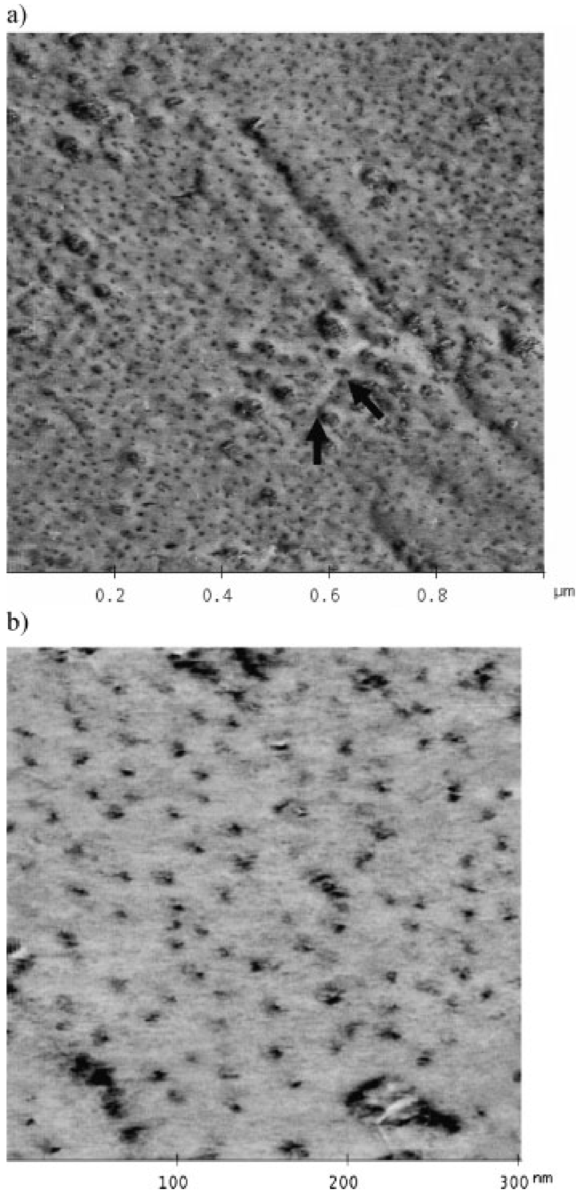

Figure 3. AFM phase images of poly[ethylene-*block*-(L,L-lactide)] block copolymer (Table 1, entry 3). Some PE lamellae are marked by arrows.

forms the softer matrix. From the lower picture (scale: 300 nm) the dimension of the PE phases can be estimated to be very small around 8–11 nm. In addition, crystalline PE lamellae are visible. Some of these crystalline domains are labeled by arrows in Figure 3. These results attest for the formation of a true block copolymer as the presence of homopolymer would lead to phase separation on a micrometer scale.

In addition to AFM, light microscopy images of growing PLA spherulites were taken. In contrast to the AFM images, the PLA is now able to crystallize due to tempering the sample at the adequate temperature. For taking these images, the sample was first molten completely at 200 °C for 3 min, cooled down and tempered at 140 °C. Surprisingly, even at 110 °C only the PLA block crystallized and no spherulites assigned to PE were observed. The absence of such PE spherulites can be described as a confinement effect of PLA block on short length PE.[15] In Figure 4, a growing PLA spherulite of several 100 microns is depicted at 2 different times. The presence of such perfect spherulites is a strong indication for the absence of any homopolymers and corroborates the blocky structure of the obtained material.

Conclusion

Model poly[ethylene-*block*-(L,L-lactide)] (PE-*block*-PLA) was successfully synthesized by combining metallocene catalyzed polymerization of ethylene with ring-opening polymerization (ROP) of L,L-lactide (LA). Terminally hydroxylated polyethylene (PE-OH) macroinitiator was first prepared by means of ethylene polymerization on *rac*-MBI/MAO in the presence of diethyl zinc as a chain transfer agent, and subsequent in situ oxidation with synthetic air. PE-*block*-PLA block copolymers were obtained in toluene at 100 °C from the PE-OH by controlled ring-opening polymerization of LA mediated by tin octoate ($Sn(Oct)_2$). ^1H NMR experiments showed that the polymerization of LA initiated by PE-OH/$Sn(Oct)_2$ proceeded in a controlled fashion in terms of $\overline{M}_{nPLA}$. The resulting PE-

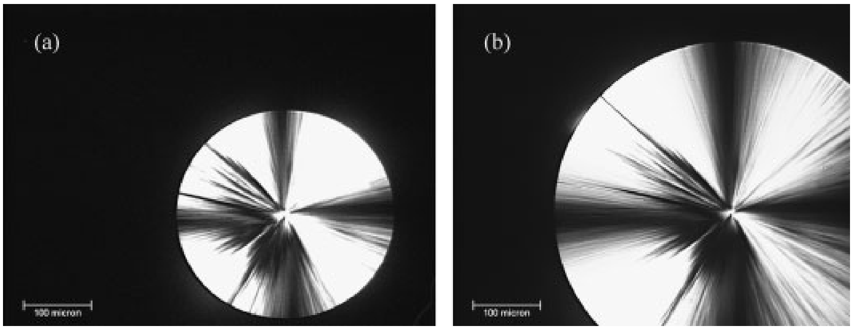

Figure 4. Light microscopy image of a growing PLA spherulite (entry 3) at 140 °C at two different times (20 (a) and 30 sec (b)).

block-PLA exhibited a blocky structure as supported by selective fractionation experiments and DSC measurements. Morphological characterization by AFM and light microscopy also confirmed the presence of a block copolymer as micro phase separation was observed as well as the growth of perfect spherulites.

In conclusion, this simple strategy opens the way to the utilization of poly[ethylene-*block*-(L,L-lactide)] block copolymers as compatibilizer in melt-blends based on PLA and PE, but more preferably as strongly segregated materials in view of their fascinating morphologies and their potential applications as nanotemplates that cannot be prepared using the standard sequential addition of monomers technique.

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