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Research Article

Ring-Opening Polymerisation of *rac*-Lactide Using a Calix[4]arene-Based Titanium (IV) Complex

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cone-25,27-Dipropoxy-26,28-dioxo-calix[4]arene titanium (IV) dichloride (**1**) has been assessed in the ring-opening polymerisation of *rac*-lactide (*L,D*-LA). The polymers formed (PLDA) turned out to display an isotactic stereoblock microstructure (determined by NMR) despite the fact that the catalyst has C_{2v} symmetry. Two techniques were applied for initiating the polymerisation reaction, microwave irradiation, and conventional thermal treatment. The polymers obtained were all characterised by NMR, IR, HPLC-SEC, DSC, and MALDI-TOF analysis. The use of microwave irradiation, applied for the first time to calixarene-based catalysts in the presence of the *rac*-lactide monomer, increased the polymerisation rate compared with that obtained by the other method. On the other hand, standard thermal treatment enabled a slightly better control than microwave irradiation over the molecular weight and molecular weight distribution of the polylactides formed.

1. Introduction

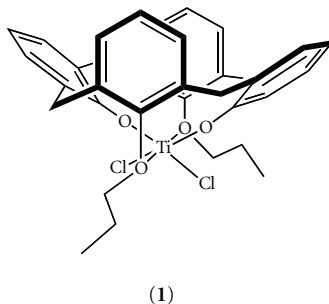
Poly(lactic acids) (PLAs) are biocompatible and biodegradable materials with potential applications in medicine and agriculture, as well as packaging materials. The most efficient method for the synthesis of PLAs is the ring opening polymerisation (ROP) of lactide (LA), which possesses two chiral centers [1–4]. The stereochemistry of the polymer formed determines its physical and mechanical properties, as well as its rate of degradation, and it is therefore important to ensure stereocontrol of the polymerisation process [5–8].

Among the most used catalysts for the ring opening polymerisation of LA, notably in industry, are organotin compounds, for example, $\text{Sn}(\text{Oct})_2$ [9–12]. A major drawback to the use of these tin derivatives is their high toxicity. In this context, the development of new, performing catalysts

based on non toxic metals (e.g., group IV transition metals) remains an important challenge [13–20].

Calix[4]arenes are macrocyclic molecules made of four phenol units linked via methylene bridges connected to the ortho positions of the phenol rings. The presence of four oxygen atoms at the lower rim of these conical molecules provides a valuable platform for the synthesis of poly(phenoxy) metal complexes. Recently, we have reported on a calix[4]arene titanium complex that was found to be active in the ROP of *L*-LA [21]. Here, the calixarene moiety behaves as a small oxo surface protecting one face of the complex, thereby conferring high thermal stability to it [22–25].

In the present work, we describe the use of *cone*-25,27-dipropoxy-26,28-dioxo-calix[4]arene titanium (IV) dichloride (**1**) in the ROP of *rac*-lactide (*L,D*-LA) under thermal activation. The polymerisation was also carried out



SCHEME 1: Structure of *cone*-25,27-dipropoxy-26,28-dioxo-calix[4]arene titanium (IV) dichloride.

under *microwave* irradiation, which is an emerging field of research in polymer chemistry [26–35] (see Scheme 1).

2. Experimental

2.1. General. The manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere using either standard Schlenk techniques or a MBraun glove box. *rac*-Lactide (*L,D*-LA) was obtained from Aldrich (>98%) and purified. The *cone*-25,27-dipropoxy-26,28-dioxo-calix[4]arene titanium (IV) dichloride (**1**) was prepared using a method reported in the literature [36].

2.2. Polymerisation Experiments. *L,D*-LA polymerisation was carried out by charging the desired amount of monomer and the appropriate amount of complex (**1**) into a vial. The vial was either immersed into an oil bath at 130°C or introduced automatically into a microwave oven (Discover S-Class System, CEM). A maximal power of 200 W was applied for the specified time while the temperature was monitored by an IR sensor positioned below the vial.

2.3. Polymer Characterisation. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury 400 apparatus using CDCl₃ as the solvent (solution 0.2 w/w). Melting temperatures (*T_m*) of the polymers were determined by differential scanning calorimetry (DSC) with a Mettler-Toledo DSC 821e instrument equipped with an intracooler. The temperature scale was calibrated with an indium reference sample (melting transition of indium 156.1°C). Aluminum pans were filled with 0.010 g of the polymer sample. The thermal history of the polymers was eliminated by heating the specimen at a rate of 20°C·min⁻¹ to 200°C and by keeping the sample at this temperature for one minute, then by cooling it at 20°C·min⁻¹ to 0°C. The second and third scans were then recorded from 0°C to 200°C. The weight average molecular weight (*M_w*) and molecular weight distribution (*M_w*/*M_n*) of the polymers were evaluated by size exclusion chromatography (HPLC-SEC) using a Perkin-Elmer type Series 2000 apparatus equipped with a Rheodyne 7010 injector (injection loop 200 μL, refraction index detector type LC-30 with two PL GEL columns (length: 30 cm; diameter: 5 μm; Polymer Labs)). The analyses were performed at 30°C using chloroform as solvent, with a flow

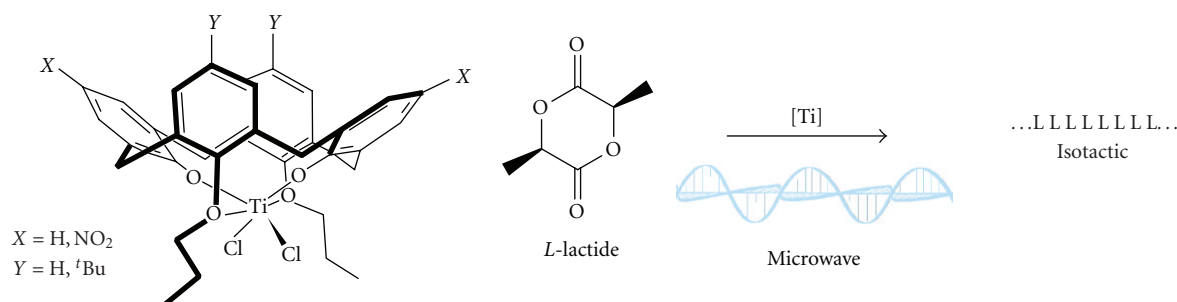
rate of 1.0 mL·min⁻¹ using polymethylmetacrylate (PMMA) standard to calibrate the system [37]. The samples were prepared by dissolving 0.005–0.006 g of polymer in 2 mL of chloroform (corresponding to ca. 3 g·L⁻¹). The WAXD analyses were done using a D8 Advance (Bruker) with a Solx solid state detector, using a Bragg-Brentano Geometry. All the samples were preventively heated at 120–130° for three days before analysis. The samples were exposed to a Cu Kα X-ray source with a wave length (λ) of 1.541 Å. The angle of incidence was varied from 4° to 50° by steps of 0.02 θ for a period of 1.5 seconds. The periodical distances (*d*) of the main peaks were calculated according to Bragg's equation ($\lambda = 2d \sin \theta$). MALDI-TOF analyses were carried out on a Ultraflex MALDI TOF/TOF from Bruker, with the following instrumental settings. In linear mode IS1 was set to 25 kV, IS2 to 23.70 kV, with a delay time of 80 nano seconds. In reflectron mode IS1 was set to 25 kV, IS2 to 21.50, with a delay time of 20 nano seconds.

3. Results and Discussion

As reported recently, the polymerisation of *L*-lactide with **1** under microwave conditions leads to isotactic PLLA (see Scheme 2).

In the present work the catalytic runs were carried out under solvent-free conditions, using either conventional heating or microwave irradiation. All analytical investigations (HPLC-SEC [36], DSC [37], NMR [38–41], MALDI-TOF [42, 43], and WAXD [44]) were consistent with the formation of PLLA polymers. The MALDI-TOF spectra unambiguously revealed that transesterification reactions had occurred during polymerisation.

We first investigated the influence of the monomer/catalyst ratio ($[L,D-LA]/[Ti]$) (Table 1). Applying a $[L,D-LA]/[Ti]$ ratio of 200 led to a conversion of 96%, which corresponds to an activity of 9.2 kg(PLDA)·mol⁻¹(Ti)·h⁻¹ (Table 1, entry 1). Increasing the $[L,D-LA]/[Ti]$ ratio to 1994 increased the catalyst activity, the latter reaching a value of 65.3 kg(PLDA)·mol⁻¹(Ti)·h⁻¹ (Table 1, entries 1-4). Within the 200–1500 range of $[L,D-LA]/[Ti]$, a roughly linear dependence of the activity on the $[L,D-LA]/[Ti]$ molar ratio was observed (Figure 1). It is noteworthy that the activity of the catalyst was slightly higher in the case of *L,D*-LA than when using *L*-LA [28].

SCHEME 2: Ring opening polymerisation of *L*-lactide under microwave irradiations.TABLE 1: Thermally induced polymerisation of *L,D*-LA using complex (1)^(a).

Entry	[<i>L,D</i> -LA]/[Ti] Ratio	Conversion ^(b) (%)	Activity ^(c)	<i>M_w</i> ^(d) (g·mol ⁻¹)	<i>M_n</i> ^(e) (g·mol ⁻¹)	MWD ^(f)	<i>T_g</i> ^(g)
1	200	96%	9.2	18400	15000	1.2	53.0
2	500	87%	21.0	19100	14900	1.3	52.1
3	1000	88%	42.3	27600	22400	1.2	50.0
4	1994	67%	65.3	43200	36900	1.2	41.7

^(a) *T* = 130°C, time = 3 h; ^(b) determined by ¹H NMR; ^(c) kg(PLDA)·mol(Ti)⁻¹·h⁻¹; ^(d) number average molar mass measured by HPLC-SEC; ^(e) weight average molar mass measured by HPLC-SEC; ^(f) molecular weight distribution; ^(g) glass transition temperature as measured by DSC analysis.

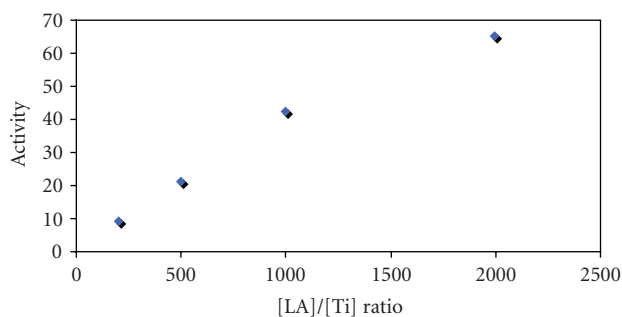
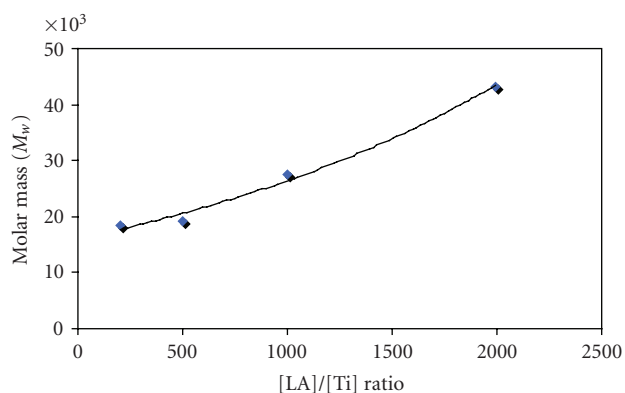


FIGURE 1: Variation of the activity as a function of the monomer/catalyst ratio.

FIGURE 2: Variation of the molecular weight (*M_w*) of PLDA as a function of the monomer/catalyst ratio.

Size exclusion chromatography analysis of the polymers formed revealed that, as expected, the molecular weight (*M_w*) increased with increasing [*L,D*-LA]/[Ti] ratio (Figure 2), the highest *M_w* determined value being 43×10^3 g·mol⁻¹ (Table 1, entry 4). However, the *M_w* values were much lower than expected. As already suggested for PLLA, this may be rationalized in terms of intramolecular transesterification during the propagation process [21, 28]. The occurrence of this phenomenon was confirmed by the presence in the MALDI-TOF spectra of peaks separated by intervals corresponding to half of the molecular weight of the monomer. Despite the observed transesterification process, the polymers obtained displayed molar mass distribution (MWD) indexes in the restricted range of 1.2–1.3, which indicates that the polymerisation process was relatively well controlled.

The DSC thermograms of the PLDA revealed only one glass transition temperature (*T_g*) for each sample. This temperature decreased from 53.0 to 41.7°C when the size of

the polymer chain increased (*M_w* increased) (Table 1, entries 1 to 4).

Furthermore, the ¹H-NMR spectrum of each sample revealed an unexpected microstructure (see an example in Figure 3). The spectrum shows two well-resolved peaks, of equal normalized intensity, at *ca.* 5.21 and 5.22 ppm representing hexad stereosequences of *isisi* and *iiisi*, respectively. According to pairwise Bernoullian statistics, an equal probability for *isisi* and *iiisi* stereosequences implies that the polymerisation process is random [38–41]. Considering that the calixarene complex becomes chiral after insertion of the first incoming lactide (be it *L* or *D*), it may be anticipated that for the following step a preferential insertion of one of the monomers (*L*-LA or *D*-LA) takes place. In fact, careful analysis of the ¹H NMR spectrum revealed a higher intensity for the *iii* sequence (almost 4 times than each other peak). In keeping with the studies of Coates et al. [15,

TABLE 2: Microwave- assisted polymerisation of *L,D*-LA using complex (1)^(a).

Entry	Time (min)	Conversion ^(b) (%)	Activity ^(c)	M_w ^(d) (g·mol ⁻¹)	M_n ^(e) (g·mol ⁻¹)	MWD ^(f)	T_g ^(g)
1	20	3%	2.9	—	—	—	—
2	40	38%	17.1	—	—	—	—
3	60	68%	19.4	22300	17400	1.3	46.0
4	80	88%	18.9	27100	20900	1.3	50.1

^(a) $[L,D\text{-LA}]/[\text{Ti}]$ ca. 200, *L,D*-LA = 1 g, maximal power 200W; ^(b) determined by ¹H NMR; ^(c) kg(PLDA)·mol(Ti)⁻¹·h⁻¹; ^(d) number average molar mass measured by HPLC-SEC; ^(e) weight average molar mass measured by HPLC-SEC; ^(f) molecular weight distribution; ^(g) glass transition temperature as measured by DSC analysis.

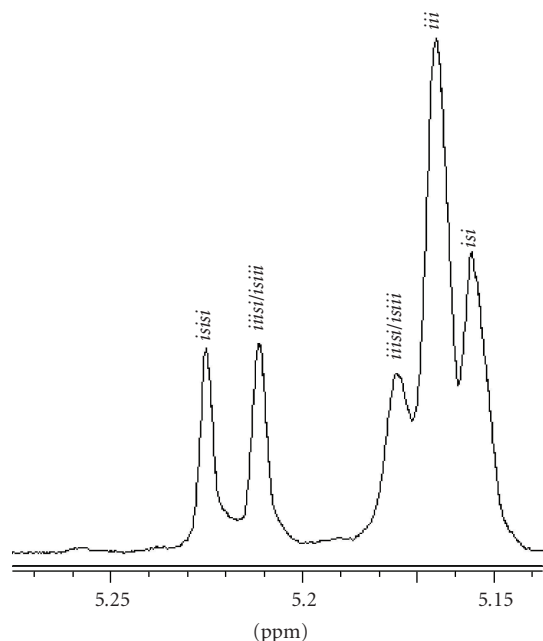


FIGURE 3: Homonuclear decoupled ¹H NMR spectrum of the methine region of PLDA obtained in Table 1, entry 1.

16], this observation may be assigned to a partial isotactic-stereoblock structure. The relatively high proportion of *isii* sequences may be interpreted in terms of a concomitant transesterification process. It is important to note that whatever the $[L,D\text{-LA}]/[\text{Ti}]$ ratio applied, the polymerisation experiments led to PLDAs with similar microstructures, as revealed by the corresponding ¹H NMR spectra. These observations suggest that the stereochemistry of the insertion step is mainly controlled by a chain-end mechanism.

As a next step, the polymerisation reactions were carried out using microwave irradiation (MW). For these runs, summarized in Table 2, a $[L,D\text{-LA}]/[\text{Ti}]$ ratio of 200 was used. As expected, the conversion increased with increasing reaction time, the conversion reaching 88% after 80 minutes (Table 2, entry 4). The maximum activity was obtained after 60 minutes (Table 2, entry 3), longer polymerisation time leading to some polymer decomposition (a brown colour and smell of aldehyde could be noticed). Careful analysis of the conversion versus time diagram (Figure 4) revealed that the polymerisation requires an activation time of about 20 minutes. Interestingly, we observed that in these

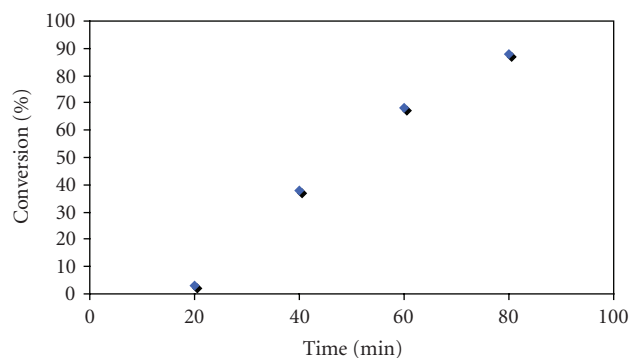


FIGURE 4: Conversion for *L,D*-LA against polymerisation time.

polymerisation reactions carried out under MW conditions, lower M_w and M_n values were obtained than those obtained using the standard heating technique.

4. Conclusions

In conclusion, we have presented for the first time the use of a calixarene complex in the ring-opening polymerisation of *L,D*-LA using thermal or microwave heating. By comparison with experiments carried out with conventional thermal heating, the use of microwaves energy induced an increase of the polymerisation rate, the thermal method leading to a slightly better control of the molecular weight and molecular weight distribution. The most striking feature of the polymers formed is their partial isotactic-stereoblock microstructure, which is likely controlled by a chain end mechanism. Further studies are in progress which will concentrate on modified versions of the titanium complex with the aim of improving the activity as well as the stereochemical control of the polymerisation reaction.

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