Synthesis of Semi-Aromatic Di-Block Polyesters by Terpolymerization of Macrolactones, Epoxides, and Anhydrides

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In this contribution, the catalytic behavior of a phenoxy-imine aluminum catalyst and of a bimetallic salen aluminum complex in ring-opening polymerization (ROP) of macrolactones such as ω-pentadecalactone (PDL), ω-6-hexadecenlactone (6HDL) and ethylene brassylate (EB), and in the ring-opening copolymerization (ROCOP) of cyclohexene oxide (CHO) and phthalic anhydride (PA) is described. A significant difference in terms of activity emerged between the two catalysts in the ROP of the macrolactones, while similar behaviors were observed in the ROCOP process. The synthesis of diblock polyesters, by combination of two distinct processes, was performed in a one-pot procedure. The semi-aromatic polyester block was formed first, followed by the polyethylene-like portion produced by ROP of macrolactones.

Introduction

In the last years, the environmental concerns derived from oil-based plastics pollution have turned both the academic and industrial research toward the development of more sustainable materials such as degradable and/or bioderived polymers.[3] Among these, aliphatic polyesters represent the most noteworthy class.[2] Synthetically, polyesters are commonly obtained by either polycondensation of dicarboxylic acids and diols or by ring opening polymerization (ROP) of cyclic esters. While the polycondensation suffers from several drawbacks and it is scarcely controlled, the ROP promoted by metal-based systems, organic catalysts or enzymes is the most efficient route to prepare high molecular weight polyesters in a controlled fashion.[2] Ingeniously designed ROP initiators revealed to be able to promote highly stereo-selective and living processes for the production of polymers with sophisticated structures and architectures.[3]

Polymacrolactones are an interesting class of aliphatic polyesters having a long alkyl chain. They combine properties similar to those of polyethylene (PE) with degradability, although they show slower degradation rates compared to conventional aliphatic polyesters.[4] Polymacrolactones can be obtained by ROP of macrolactones, i.e. lactones at 12 and more carbon atoms.[5,6,7] The interest in macrolactones stems also by their renewable origin: most of them, i.e. pentadecalactone (PDL), ambrettolide, ω-6-hexadecenlactone (6HDL) or ethylene brassylate (EB),[6] can be isolated from plant oil, and they are used in the fragrance industries.[6b] the macrolactones can be also obtained from the full fatty acid chain. The high versatility of the ROP approaches, moreover, allowed the production of various block and random macrolactone-based copolymers with diverse cyclic esters.[5a,9]

While the ROP of aliphatic cyclic esters (lactones, macrolactones and lactides) has been largely studied, the examples of the ROP of cyclic esters having aromatic moieties in the main chain are scanty. The reason is the scarcity of commercially available monomers. Recently, ROP of cyclic butylene terephthalate (cBT) was achieved in solution using an aluminum–salen catalyst. The bulk copolymerization of cBT with PDL was also investigated to elucidate dependence of the copolymer properties from the composition. Block copolymers could not be obtained even by exploiting a sequential monomer feed synthetic strategy.[10]

As anticipated, the paucity of monomers containing aromatic groups is limiting the production of aromatic or semiaromatic polyesters by ROP. In contrast, the alternating ring-opening co-polymerization (ROCOP) of cyclic anhydrides with epoxides recently emerged as a powerful catalytic method for the preparation of structurally diverse polyesters.[11] An important advantage of ROCOP is indeed the availability of large libraries of epoxide and anhydride comonomers as useful building blocks to achieve polymeric materials with structures and functionalities inaccessible by ROP. The presence of aromatic moieties could i.e. impart a hard character to the polymeric macromolecular chains, which may result in diverse...
thermal, mechanical and degradation properties, thus opening the scenario to different applications of the final materials.\textsuperscript{[12]}

Quite recently, the possibility to combine the ROP and ROCOP processes into the same approach has allowed to further enlarge the possible combination of monomers and the accessible polymeric structures. Noteworthy, Williams et al. in 2014 described a novel “switchable” catalysis between ROP and ROCOP achieved by a chemoselective control, in which the depletion of a specific monomer changed the chemistry of the metal–polymer chain end group and resulted in a switch of the polymerization mechanism.\textsuperscript{[13]} This elegant approach has been developed, still now, only with few catalytic systems.\textsuperscript{[14]} Notably, among these, also organocatalysts\textsuperscript{[15]} and multinuclear organometallic catalysts\textsuperscript{[14b,16]} have been described.

The versatility of the method has been applied to a large variety of epoxides, anhydrides and cyclic esters, thus producing unprecedented polymeric structures.\textsuperscript{[12,13b,17]} In particular conventional lactones and lactates have been largely used. However, to the best of our knowledge, the combined ROP/ROCOP method has not been applied yet to the ter-polymerization of epoxides, anhydrides and macrolactones. The ROP of macrolactones, indeed, present some peculiar features with respect to the ROP of conventional ring size lactones and lactates. For small ring-size lactones the polymerization is driven by the enthalpy, i.e. by the release of the ring-strain, for lactones having ring dimension higher than 12 atoms, due to the lack of ring strain, it is the entropy to drive the ROP, by the increase of the conformational freedom.\textsuperscript{[18]}

In the ambit of our interest in the combined ROP and ROCOP method, we focused our attention on two aluminum complexes bearing phenoxy-imine moieties, a mono and bimetallic one, as promising catalysts (Scheme 1).\textsuperscript{[18]} Notably, bimetallic and multi-metallic complexes are emerging as efficient catalysts for the polymerization of cyclic esters due to the metals cooperativity.\textsuperscript{[18a,19]} Here we wish to present the results of the study of the polymerization activity of the mono- and the bimetallic complexes in the ROP of diverse macrolactones (PDL, HDL and EB) and in the ROCOP of phthalic anhydride (PA) with cyclohexene oxide (CHO). Finally, the combined ROP/ROCOP ter-polymerization of PA, CHO and a macrolactone is also presented and discussed.

Results and Discussion

Two catalysts were selected (see scheme 1). Complex 1 is a simple phenoxy-imine aluminum bearing a methoxy group on the phenoxy moiety. Previous studies conducted in our group showed that the presence of an electron-donating substituent increased catalytic activity of phenoxy-imine complexes and complex 1 revealed the highest activity among its analogs in the ROCOP of succinic anhydride (SA) and cyclohexene oxide (CHO), overcoming the performance of traditional salen aluminum complexes.\textsuperscript{[14e]}

Complex 2 is a bimetallic species in which each aluminum atom is coordinated to a phenoxy-imine moiety; however, the presence of a backbone of opportune length allows cooperation phenomena between the aluminum reactive centers. This complex revealed high activity in the polymerization of several cyclic esters and in the copolymerization CHO/SA.\textsuperscript{[14b,19a,20]}

Both aluminum complexes were obtained by the reaction between the corresponding proligand and the opportune equivalents of AlMe\textsubscript{3} and proceeded through the elimination of methane to produce the desired complexes in quantitative yields.\textsuperscript{[14b,15,16]} The identity of the complexes was established by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy.

Homopolymerization of Macrolactones

Initially, both catalysts were tested for the homopolymerizations of three macro lactones, \(\omega\)-pentadecalactone (PDL), ethylene brassilate (EB) and \(\omega\)-hexadecen lactone (HDL) (Scheme 2). The interest in PDL stems from its homopolymer, the PPDL, which has been imagined as the sustainable alternative to linear low density polyethylene.\textsuperscript{[19]} HDL is an unsaturated version of the macrolides, and its use offers the opportunity to further functionalize the obtained materials, by i.e. thiol-ene reactions.\textsuperscript{[18c,18d]} The EB or ethylene tridecanedioate, is a macro cyclic diester, which homopolymer shows mechanical properties similar to poly(caprolactone), but has a higher melting temperature, \(~70\ C\), and good thermal stability.\textsuperscript{[21]} One drawback of this monomer is in the difficulties to achieve high molecular masses by conventional ROP catalysis.\textsuperscript{[22]}

Polymerization data are summarized in Table 1. The polymers produced were all characterized by \textsuperscript{1}H NMR, GPC and MALDI-ToF-MS analyses. DSC characterization was conducted on some representative samples.

The ROP reactions were performed at 110 °C, in toluene solution in the presence of benzyl alcohol (BzOH) as activator. The role of alcohol is that to convert the methyl groups in the more nucleophilic alkoxide groups.\textsuperscript{[23,24]}

The phenoxy-imine aluminum complex 1, in the presence of one equivalent of BzOH, showed moderate activity in the

\begin{scheme}
\includegraphics[width=\textwidth]{scheme1.png}
\caption{Structures of mono and bimetallic aluminum complexes (1, 2).}
\end{scheme}

\begin{scheme}
\includegraphics[width=\textwidth]{scheme2.png}
\caption{Macrolactones investigated in this work.}
\end{scheme}
polymerization of PDL, allowing the conversion of 130 equivalents of monomer after 15 h (run 1, Table 1). With a double amount of BzOH the activity was doubled (compare run 2 with run 3, Table 1). The same beneficial effect was observed in the polymerization of a less reactive monomer as EB (runs 4 and 5, Table 1). Due to the above observation, the polymerization reaction of HDL was performed using two equivalents of BzOH, sufficient to promote the exhaustive alcoholysis of the methyl groups bound to aluminum.

As a general trend, by using catalyst 1, a higher activity was observed in the ROP of HDL (run 6, Table 1). In contrast the EB monomer resulted less prone to ROP than other macrolides. This behavior is not surprising, and it was reported in the literature.\(^{[22]}\) With catalyst 1, the observed trend of reactivity was the following: HDL $>$ PDL $>$ EB.

The same experiments were subsequently performed using the analogous bimetallic complex 2, by using 2 and 4 eq of alcohol. When using a double amount of BzOH respect to the aluminum centers, the TOF increased (cfr run 7 vs 9 for PDL; cfr run 14 vs 15 for HDL, Table 1).

To test the productivity of catalyst 2, a polymerization test with 1000 equivalents of monomer and an excess of BzOH (20 eq) was performed (run 16, Table 1). Under these conditions, a significant increase in the catalyst activity was observed and the molecular masses of the obtained polymers agreed with the amount of alcohol used, suggesting an immortal behavior of the catalyst. For the bimetallic catalyst 2 the same trend of reactivity toward monomers was observed: HDL $>$ PDL $>$ EB.

Interestingly, the reactivity of the bimetallic catalyst 2 was higher than that of the monometallic one 1, when comparing polymerization tests for the same monomers and conducted in analogous conditions. As an example, while in the ROP of HDL with catalyst 1 and 2 eq of BzOH (run 6, Table 1), 20 eq of monomer are consumed in 30 min, the bimetallic catalyst 2 with 4 eq of alcohol (run 12, Table 1) in the same time allowed a conversion of 118 eq of monomer, with a turnover frequency (TOF) of 236 h$^{-1}$. This result compares well with the behavior of the most efficient initiators for the ROP of macrolactones reported so far,\(^{[25]}\) and suggests a beneficial effect of the metallic cooperativity in bimetallic systems.

Analogously, in the ROP of $\omega$-PDL the complex 2 showed an activity much higher than the simple phenoxime-imine complex 1 (compare run 9 with run 3 and run 7 with run 2 8 and 9 with run 2, Table 1), allowing the conversion of 180 equivalents of monomer in 2 hours and showing a turnover frequency (TOF) of 90 h$^{-1}$.

A different result was recently reported in the literature, where a bimetallic species was less active than the corresponding tentacoordinate aluminum complex. The reason for these diverse behaviors can be ascribed to the different steric encumbrance of the two bimetallic complexes.\(^{[26]}\)

A first glance on the molecular weights of the samples obtained with catalyst 1 respect those obtained using 2 suggests that on the bimetallic catalyst two polymeric chains (one for metal center) are growing; although conversion factors and $\beta$ values were determined by GPC analysis in THF using polystyrene standards, while for PDL (d) in CHCl$_3$ using polystyrene standards.\(^{[25]}\) Calculated $M_\text{n}$ (KDa) $= \frac{\text{MM}[\text{eq}]}{2}$× conversion of Mon. [f] Determined by DSC. [g] 0.01 mol of monomer

### Table 1. Polymerizations of macrolactones promoted by 1 and 2.

| Run\(^{[h]}\) | Cat | Mon | BzOH [eq] | Time [h] | Conv.\(^{[i]}\) [%] | TOF \([h^{-1}]\) | $M_n$ [KDa] | $M_n$[\text{calc}] [KDa] | $\beta$ | $\Delta$ °C |
|------------|-----|-----|-----------|---------|----------------|----------------|-----------|--------------------------|------|----------|
| 1          | 1   | PDL | 1         | 15      | 67             | 9              | 68.0\(^{[i]}\) | 32.2                      | 1.86 | 91.8     |
| 2          | 1   | PDL | 1         | 12      | 12             | 6.7\(^{[i]}\)   | 5.8        | 1.36                     |      |          |
| 3          | 1   | PDL | 2         | 21      | 21             | 19.6\(^{[i]}\)  | 10.1       | 1.38                     |      |          |
| 4          | 1   | EB  | 1         | 9       | 0.8            | 5.2\(^{[i]}\)   | 4.8        | 1.42                     | 65.09|          |
| 5          | 1   | EB  | 2         | 19      | 1.6            | 13.9\(^{[i]}\)  | 10.3       | 1.38                     |      |          |
| 6          | 1   | HDL | 2         | 10      | 40             | 14.1\(^{[i]}\)  | 5.0        | 1.40                     | 60.03|          |
| 7          | 2   | PDL | 2         | 69      | 69             | 31.4\(^{[i]}\)  | 16.6       | 1.54                     |      |          |
| 8          | 2   | PDL | 4         | > 99    | 67             | 21.6\(^{[i]}\)  | 23.8       | 1.52                     |      |          |
| 9          | 2   | PDL | 4         | 90      | 22.3\(^{[i]}\)  | 21.6         | 1.57       |                          |      |          |
| 10         | 2   | PDL | 4         | 33      | 132            | 15.8\(^{[i]}\)  | 8.0        | 1.44                     |      |          |
| 11         | 2   | EB  | 4         | 80      | 1.7            | 30.1\(^{[i]}\)  | 21.6       | 1.43                     |      |          |
| 12         | 2   | HDL | 4         | 59      | 236            | 29.8\(^{[i]}\)  | 14.9       | 1.68                     |      |          |
| 13         | 2   | HDL | 4         | 1       | 168            | 32.4\(^{[i]}\)  | 21.2       | 1.61                     |      |          |
| 14         | 2   | HDL | 4         | > 99    | 133            | 33.0\(^{[i]}\)  | 24.9       | 1.54                     |      |          |
| 15         | 2   | HDL | 2         | 66      | 66             | 26.3\(^{[i]}\)  | 16.9       | 1.55                     |      |          |
| 16\(^{[i]}\) | 2   | HDL | 20        | 2       | 67             | 70            | 10.8\(^{[i]}\) | 8.3          | 1.53                     |      |          |

\(\text{Conv.}\) = \frac{\text{Conv.\([\%]\) ≈ } \frac{\text{Conv.\([\%]\) \times 100}}{\text{Conv.\([\%]\)}}\times 100}

\(\text{TOF} = \frac{\text{Conv.\([\%]\)}}{\text{Time\([h]\)}}\)

[a] All reactions were carried out at 110 °C with cat = 10 μmol and 2 mmol of monomer in toluene (0.5 mL). [b] Determined by $^1$H NMR. [c] Experimental $M_n$ and $\beta$ values were determined by GPC analysis in THF using polystyrene standards, while for PDL (d) in CHCl$_3$ using polystyrene standards. [e] Calculated $M_n$ (KDa) $= \frac{\text{MM}[\text{eq}]}{2}$× conversion of Mon. [f] Determined by DSC. [g] 0.01 mol of monomer

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range of the observed masses (3000–6000 m/z) no cyclic polymers were detected in the spectrum.

Kinetic studies conducted with complex 2 showed that the polymerization of PDL obeyed first-order kinetics in monomer with instantaneous initiation and with a $K_{\text{app}} = 0.0212 \text{ min}^{-1}$ (Figure 2).

Finally, the bimetallic complex 2 was tested in the copolymerization of equimolar amounts of PDL and HDL (100 equivalents). The reaction was performed under the same reaction conditions used for the related homopolymerizations and, after 4 hours, a complete conversion of both monomers was achieved. The obtained copolymer, analyzed by $^1$H NMR, revealed a composition coherent with the monomer feed (50:50). The molecular masses (32.5 KDa) were in agreement with the theoretical values and showed a monomodal distribution ($\bar{D} = 1.8$).

The thermal analyses of the obtained polymers showed sharp endotherms for both the homopolymers of HDL and PDL (Tm = 60.03 and 91.80 °C, respectively). For the copolymer, a single melting peak was observed (Tm = 73.7 °C), with a value intermediate between those of the homopolymers.

ROCOP of Cyclohexene Oxide (CHO) and Phthalic Anhydride (PA)

Subsequently, the cyclohexene oxide (CHO) and phthalic anhydride (PA) copolymerization was studied (Scheme 3) with both the catalysts. Both PA and CHO are commercial chemicals used at scale in the polymer industry. Currently, they are manufactured from petroleum, however, routes to CHO from 1,4-cyclohexadiene, a waste product of plant oil self-metathesis, and to PA from corn stover are reported.

The polymerization reactions were initially performed at 110 °C and in the presence of a single equivalent of the onium salt (PPNCl) as co-catalyst (run 1, Table 2). A significant increase in activity was observed with catalyst 1 when the polymerization was performed in the presence of two equivalents of PPNCl (cf runs 1 and 2, Table 2). As a result, all the polymerization runs were conducted with 2 eq of PPNCl.

In the ROCOP of CHO/PA, no significant differences in terms of activities were observed, both complexes 1 and 2 could promote the quantitative conversion of the monomers within 2 hours (runs 2 and 3, Table 2). In fact, as previously discussed for copolymerization of similar substrates (cyclohexene oxide and succinic anhydride) with these bimetallic aluminum complexes, no cooperative phenomena are evident. This could be a consequence of a dissociative mechanism favored by the
The copolymer composition was estimated by ¹H NMR analysis performed in CDCl₃ by using a 600 MHz spectrometer, by comparing the integrals of the signals of epoxide/anhydride sequences with those of epoxide homosequences.

The ¹H NMR analysis showed perfectly alternated microstructures; no evidence of the presence of polyether sequences; no evidence of the presence of polyether sequences with those of epoxide homosequences.

The glass transition temperature for sample 3 of Table 2 was 140.7°C, a value similar to that previously reported for poly(pentadecalactone) reaction was performed in the absence of solvent (run 4, Table 2). The number average molecular weight values (Mₙ) achieved only after 32 hours producing a diblock copolymer poly(cyclohexene phthalate)-block-poly(pentadecalactone).

The ¹H NMR spectrum of the crude polymer accounted for a copolymer containing a 1:1:1 ratio of the monomers, coherently with the formation of two blocks (one made by the polypentadecalactone, the other by the alternating copolymer CHO/PA) with the same length and in complete agreement with the initial feed ratio of the monomers and their conversions (Figure 3).

Subsequently, the relative lengths of the two blocks were modulated by varying the amount of PDL or CHO and PA added in the polymerization mixture (see runs 2 and 3, Table 3).

To get further insights into the copolymer microstructure, a sample of poly(cyclohexene phthalate)-block-poly(pentadecalactone) (run 1, Table 3) was analyzed by ¹³C NMR (Figure 4).

### Table 3. Ter-polymerizations of CHO, PA and macrolactones promoted by 1 and 2.

| Run | PDL [eq] | HDL [eq] | CHO [eq] | PA [eq] | Cat  | t [h] | Conv [%) | Mₙ,cat [KDa] | Mₙ,th [KDa] | E [%) | Tₘ [°C] |
|-----|---------|---------|---------|---------|------|------|---------|-------------|-------------|------|---------|
| 1   | 100     | –       | 100     | 80      | 1    | 32   | 83      | 23.5        | 39.6        | 1.63 | 92.19   |
| 2   | 200     | –       | 100     | 80      | 1    | 96   | 61      | 33.9        | 50.4        | 1.70 | 94.01   |
| 3   | 100     | –       | 200     | 150     | 1    | 32   | 66      | 22.1        | 56.3        | 1.46 | 88.19   |
| 4   | 8       | –       | 8       | 6       | 1    | 20   | 19      | 4.4         | –           | –     | –       |
| 5   | 100     | –       | 100     | 80      | 2    | 25   | 99      | 31.2        | 44.7        | 1.77 | 89.11   |
| 6   | –       | 100     | 100     | 80      | 2    | 96   | 45.7    | 15.7        | 41.5        | 1.43 | 52.51   |
| 7   | –       | 200     | 100     | 80      | 2    | 22   | 97      | 20.5        | 43.6        | 1.60 | 85.19   |

[a] All reactions were conducted at 110°C with cat = 10 μmol in toluene (0.5 mL) and PPNCl 20 μmol. [b] Conversions of PDL or HDL were determined by ¹H NMR; for PA conversions were more than 99%. [c] Experimental Mn and Ð values were determined by GPC analysis in CHCl₃ using polystyrene standards.  
[d] Determined by DSC.

At the end, we explored the possibility to promote a combined catalysis ROP/ROCOP with both catalysts (1 and 2). The copolymerizations were performed in the presence of phthalic anhydride (PA), a macrolactone (PDL or HDL), and cyclohexene oxide (CHO) that was in excess respect to anhydride (Scheme 4).

A larger amount of epoxide is necessary for allowing the insertion of the macrolactone on the alkoxylate–aluminum bond of the growing chain because the carboxylate intermediate is unable to initiate the ROP of the cyclic lactone.

The first set of experiments was performed in the presence of the monometallic catalyst 1 (runs 1–4, Table 3). The comonomers, PDL or HDL, CHO and PA were added simultaneously in the polymerization medium and the reaction was monitored by ¹H NMR analysis of minimal amounts of the polymerization mixture (run 1, Table 3). After 5 hours the phthalic anhydride was completely consumed, while no conversion of PDL was detected (run 1, Table 3).

Almost complete conversion of the macrolactone was achieved only after 32 hours producing a diblock copolymer poly(cyclohexene phthalate)-block-poly(pentadecalactone).

The ¹H NMR spectrum of the crude polymer accounted for a copolymer containing a 1:1:1 ratio of the monomers, coherently with the formation of two blocks (one made by the polypentadecalactone, the other by the alternating copolymer CHO/PA) with the same length and in complete agreement with the initial feed ratio of the monomers and their conversions (Figure 3).

The combined ROP/ROCOP catalysis: The Combined ROP/ROCOP Catalysis

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Subsequently, the relative lengths of the two blocks were modulated by varying the amount of PDL or CHO and PA added in the polymerization mixture (see runs 2 and 3, Table 3).

To get further insights into the copolymer microstructure, a sample of poly(cyclohexene phthalate)-block-poly(pentadecalactone) (run 1, Table 3) was analyzed by ¹³C NMR (Figure 4).
The recorded spectrum nicely showed the presence of the signals of the two distinct blocks. The carbonyl region is usually diagnostic of the kind of copolymer obtained. Interestingly only two carbonyl signals were detected, one at 174.17 ppm, relative to the PDL homo-sequences, the other at 166.82 ppm, relative to the semiaromatic cyclohexene phthalate sequences. Additional carbonyl atoms were not detected, thus indicating the absence of transesterification reactions.

To definitively confirm the blocky structure of the copolymers, different experiments were performed. A DOSY NMR spectrum (see Figure 5) of the copolymer obtained in run 1, Table 3, showed that the signals of the polymer sequences had the same diffusion coefficient, and therefore belonged to the same structure.

Subsequently, a low molecular weight sample was prepared with catalyst 1 (run 4, Table 3) to analyze its structure by MALDI-ToF MS. For this sample two major distributions were observed attributable to di-block structures in which perfectly alternated fragments of CHO-PA units were joined to short sequences of PDL by isolated cyclohexene oxide units (Figure 6).

The chain end-groups for the first distribution were calculated to correspond to water initiation that may be present as impurity in the polymerization medium. The other family of signals, of comparable intensity, corresponded to polymer chains having as chain end groups the chlorine atoms of the iminium salt used as cocatalyst.

The terpolymerization reaction of PDL, PA and CHO was also attempted in the presence of catalyst 2 (run 5, Table 3). After 25 hours, NMR analysis of an aliquot of the reaction mixture demonstrated the quantitative conversion of phthalic anhydride and PDL, thus confirming a better performance of the bimetallic catalyst in comparison to the monometallic one. The DOSY NMR analysis confirmed the formation of a di-block copolymer.

The same results were obtained in terpolymerization of PA and CHO with the unsaturated macrolactone HDL. Runs 6 and 7 of Table 3 summarise these polymerization studies in the presence of catalyst 2. The block structure of poly[(cyclohexene phthalate)-block-poly(ω-6-hexadecenlactone)] was corroborated by DOSY NMR spectroscopy which showed a single diffusion coefficient (Figure 7).

Thermal analyses were carried out by DSC on the terpolymer samples of run 5 and 6, prepared in similar conditions but...
Moisture and air-sensitive materials were manipulated under nitrogen. The analyses revealed the Tm of 92.19 °C for the terpolymer prepared with PDL, and of 52.51 °C for the terpolymer prepared with HDL, which were attributed to the melting peaks of the polymacrolactone blocks. On the contrary, the Tg of the poly(cyclohexene phthalate) block, was not detected.

Conclusion

The catalytic behavior of monometallic and bimetallic phenoxime aluminum complexes in the ROP of different macrocycles such as pentadecalactone (PDL), ω-6-hexadecenlactone (6HDL) or ethylene brassylate (EB) was analyzed. The same systems were used for the synthesis of semi-aromatic polyesters by ring-opening copolymerization of cyclohexene oxide and phthalic anhydride. Diblock copolymers were also obtained from the combination of two distinct processes using a chemoselective one-pot procedure where the semi-aromatic polyester block was first formed followed by a second chain segment produced by ROP of macrolactones. These copolymers are the first examples described in the literature of di-block copolymers with one polyethylene-like block and a semi-aromatic polyester as a second block. We may envisage that such di-block copolymers would work as good compatibilizers for immiscible blends of polyethylene (PE) and poly(ethylene-terephthalate) PET, two of the most used commodity plastics. Recently the synthesis of multiblock copolymers made of PE and PET was described; the copolymers were tested as compatibilizer additives for melt reprocessed blends of unsorted PE and PET.[30]

The prepared poly(cyclohexene phthalate)-block-(ω-pentadecalactone) and poly(cyclohexenophthalate)-block-polyc(ω-6-hexadecenlactone) copolymers, as semi-aromatic polyesters, may represent the degradable renewable alternatives to the PE/PET block copolymers and may have potential application for the recycling of PET/PE unsorted mixtures.[31]

Experimental Section

Materials and Methods

Moisture and air-sensitive materials were manipulated under nitrogen using Schlenk techniques or an MBraun Labmaster glovebox. Toluene and methanol were refluxed over Na and distilled under nitrogen. Tetrahydrofuran (THF) was refluxed over Na and benzophenone and distilled under nitrogen. Monomers (Sigma-Aldrich) were purified before use: ω-6-hexadecenlactone (6HDL), ω-penta-decalactone, and cyclohexene oxide were distilled under vacuum on CaH₂ and stored over 4 Å molecular sieves. Pthalic anhydride (PA) was crystallized from dry toluene.

CDCl₃ and toluene-d₈ were purchased from Eurisotop and used as received. The aluminum complexes were synthesized according to previously reported procedures.[14,15,16] All other reagents and solvents were purchased from Aldrich and used without further purification.

Instruments and Measurements

NMR spectra of polymers were performed in CDCl₃ at room temperature on Bruker Avance 300, 400 or 600 spectrometers (¹H: 300.13, 400.13, 600.13 MHz; ¹³C: 75.47, 100.62, 150.92 MHz, respectively). The resonances are reported in ppm (δ) and the coupling constants in Hz (J), and are referenced to the residual solvent peak at δ = 7.16 ppm for CDCl₃ and δ = 7.27 ppm for CDCl₄. Spectra recording was performed using Bruker-TopSpin v2.1 software. Data processing was performed using TopSpin v2.1 or MestReNova v6.02 software.

2D DOSY PGSE NMR spectra of the block copolymers were recorded on a Bruker Avance 600 spectrometer: 2 mg of the polymer were dissolved in 0.5 mL of CDCl₃, and the spectra were recorded at room temperature without spinning; the parameters δ and Δ were kept constant during the experiments, whereas G was varied from 2 to 95 % in 25 steps, 64 scans per step.

Molecular weights (Mn, and Mw) and molecular weight dispersions (Đ) were measured by gel permeation chromatography (GPC). The measurements were performed at 30 °C on a Waters 1525 binary system equipped with a Waters 2414 Refractive Index (RI) detector and a Waters 2487 Dual λ Absorption (UV, λabs = 220 nm) detector, using tetrahydrofuran as the eluent (1.0 mL min⁻¹) and employing a system of four Styrage HR columns (7.8 × 300 mm; range 103–106 Å). Narrow polystyrene standards were used as reference and Waters Breeze v3.30 software for data processing. When CHCl₃ was used as solvent Styrage HR3 columns and Styrage HR4 columns were used.

A MALDI-ToF-MS analysis was performed on a Waters Maldi Micro MX equipped with a 337 nm nitrogen laser. An acceleration voltage of 25 kV was applied. The polymer sample was dissolved in THF with Milli-Q water containing 0.1 % formic acid at a concentration of 0.8 mg mL⁻¹. The matrix used was 2,5-dihydroxybenzoic acid (DHBA) (Pierce) and was dissolved in THF at a concentration of 30 mg mL⁻¹. Solutions of the matrix and polymer were mixed in a volume ratio of 1:1. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in reflection mode.

Glass transition temperatures (Tg), melting points (Tm) and enthalpy of fusion (ΔHm) of the polymer samples were measured by differential scanning calorimetry (DSC) using aluminum pans and a DSC 2920 TA Instruments apparatus, calibrated with indium. Measurements were performed under nitrogen flow with a heating rate of 10 °C min⁻¹ in the range of −80 to +220 °C. DSC data were processed with TA Universal Analysis v2.3 software and are reported for the second heating cycle.

Synthetic Procedures

Synthesis of poly(ω-pentadecalactone). A typical polymerization is described here for the sample of run 8B in Table 1. A Schlenk tube was charged sequentially with the precatalyst (3.94 mg, 10 μmol), the monomer (504 mg, 2.0 mmol), toluene (0.5 mL) and benzyl alcohol (BzOH, 0.40 mL of a 0.1 M toluene solution, 40 μmol). The mixture was readjusted at 110 °C and magnetically stirred for the required time, and then cooled to room temperature. The mixture was dissolved in a minimal amount of CHCl₃, and then added dropwise to methanol under rapid stirring. The precipitated polymer was recovered by filtration, washed with methanol and dried at 30 °C overnight in a vacuum oven. ¹H NMR (400 MHz, CDCl₃, 298 K) δ 3.96 (t, J = 6.5 Hz, 2H, −CH₂O−), 2.20 (t, J = 7.7 Hz, 2H, −CO(O)CH₂−), 1.54–1.49 (m, 4H, −C(O)CH₂−), 1.30–1.11 (m, 18H, CH₃).
Synthesis of Poly(ω-6-hexadecen lactone). A typical polymerization is described here for the sample of run 12 in Table 1. A Schlenk tube was charged sequentially with the precatalyst (3.94 mg, 10 μmol), the monomer (504 mg, 2.0 mmol), toluene (0.5 mL) and BzOH (0.40 mL of a 0.1 M toluene solution, 40 μmol). The mixture was thermostated at 110 °C and magnetically stirred for the required time, and then cooled to room temperature. The mixture was dissolved in a minimal amount of CHCl₃ and then added dropwise to methanol under rapid stirring. The precipitated polymer was recovered by filtration, washed with methanol and dried at 30 °C overnight in a vacuum oven. ¹H NMR (300 MHz, CDCl₃, 298 K) δ 5.37 (bs, 2H; –CH(OH)₂ –), 1.75–1.71 (bs, 4H; –O(CH₂)₂ –), 1.48–1.12 (bs, 14H; CH₂).

Synthesis of Poly(ethylene brassilate). A typical polymerization is described here for the sample of run 11 in Table 1. A Schlenk tube was charged sequentially with the precatalyst (3.94 mg, 10 μmol), the monomer (542 mg, 2.0 mmol), toluene (0.5 mL) and BzOH (0.40 mL of a 0.1 M toluene solution, 40 μmol). The mixture was thermostated at 110 °C and magnetically stirred for the required time, and then cooled to room temperature. The mixture was dissolved in a minimal amount of CHCl₃ and then added dropwise to methanol under rapid stirring. The precipitated polymer was recovered by filtration, washed with methanol and dried at 30 °C overnight in a vacuum oven. ¹H NMR (300 MHz, CDCl₃, 298 K) δ 6.3 Hz, 4H; δ = 7.8 Hz, 4H; –O(CH₂)₂ –), 1.77–1.54 (bs, 4H; –O(CH₂)₂ –), 1.25 (m, 36H; CH₂).

Synthesis of Poly(cyclohexene phthalate). A typical polymerization is described here for the sample of run 1 in Table 2. A Schlenk tube was charged sequentially with phthalic anhydride (222 mg, 1.5 mmol), cyclohexene oxide (196 mg, 2.0 mmol), the precatalyst (3.94 mg, 10 μmol), and PPNCl (11.5 mg, 20 μmol) in 0.5 mL of CHCl₃ and magnetically stirred for the required time, and then cooled to room temperature. The mixture was dissolved in a minimal amount of CHCl₃ and then added dropwise to methanol under rapid stirring. The precipitated polymer was recovered by filtration, washed with methanol and dried at 30 °C overnight in a vacuum oven.

Acknowledgements

The authors thank Dr Patrizia Iannece for Maldi ToF spectra and Dr Patrizia Oliva for NMR assistance.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Block copolymers · Copolymerisation · Ring-opening polymerisation · Schiff bases · Aluminum

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