PAPER

Tuning the thermal properties of L-lactide/ε-caprolactone chain shuttled copolymers *via* catalyst selection†

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Chain shuttling copolymerisation (CSP) is a synthetic strategy allowing the one-pot, one-step formation of block copolymers. Initially developed in the frame of coordinative polymerisation of olefins and conjugated dienes, it was recently transferred to the ring-opening polymerisation of cyclic esters. In this contribution, we report six new catalytic systems able to perform the chain shuttling copolymerisation of L-lactide (L-LA) with ε-caprolactone (ε-CL) and to tune the thermal properties of the resulting copolymers. They are based on amino(bis)phenolate supported aluminium complexes bearing different pendant donor arms ((Al(O₂N^L)OBn), L = NEt₂ (**2a**), NBn₂ (**2b**), Py (**2c**), Mor (**2d**)). A Mannich reaction allowed the ligands synthesis. The two new alkoxide complexes **2a** and **2b** were obtained by reaction of the protonated ligands with trimethylaluminium followed by benzyl alcohol in reasonable yield, as well as two already described compounds **2c** and **2d**. Initially assessed as catalysts for L-LA and ε-CL homopolymerisations and statistical copolymerisation, the aluminium compound bearing pyridine as a donor arm (**2c**) resulted in a high selectivity toward lactide. **2c** together with yttrium and aluminium alkoxides, also known for their selectivity for lactide, were successfully assessed for the chain shuttling copolymerisation of L-LA with ε-CL in combination with the three other amino(bis)phenolate supported aluminium complexes that showed a higher selectivity toward ε-CL. Chain shuttling copolymerization *via* transalkoxylation between two different metals, Y and Al, is achieved for the first time, therefore extending the range and scope of cyclic esters CSP. Such an alteration of the nature of the catalysts allowed fine tuning of the thermal properties of the chain shuttled copolymer, as shown by a variation of the glass transition temperature (T_g) of the soft block over *ca.* 25 °C without changing the catalysts ratio and feed of the reaction.

1. Introduction

Global warming has become a growing concern in recent years. Using biomass as a raw material rather than oil may seem appropriate in this context. In the field of plastic/polymer materials, the use of bio-sourced poly(lactic acid) also called polylactide (PLA) emerges as a promising solution. PLA is a biodegradable, compostable and biocompatible aliphatic polyester, with mechanical properties close to those of some oil-based plastics. It allows its use in a wide range of applications such as food packaging, biomedicine or 3D printing, among others.[1–4] The presence of two stereocentres in the lactide monomer, commonly used for the production of PLA, allows the possibility to control the tacticity of the final material depending on the initiator and/or the stereoisomer selected. Poly(L-lactide) (PLLA), a semi-crystalline material, is of high interest as it shares similar properties with polyethylene terephthalate (PET) and polystyrene (PS). However, its inherent brittleness, with low elongation at break and impact resistance limits its applications.[5] To overcome these limitations, PLLA is often used in the form of blend with other polymers and in particular poly(ε-caprolactone) (PCL)[6–8] which displays a much higher elongation at break of up to 300%. Copolymerisation of L-lactide (L-LA) with other monomers can also be explored for this purpose, notably statistical. Random

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copolymer of L-LA and ε-caprolactone (ε-CL) can be synthesised *via* ring-opening copolymerisation using metal-based catalysts,[9] organocatalysts[10] or enzymes.[11]

Chain-shuttling copolymerisation (CSP) has emerged as an interesting strategy to produce block copolymers in a one-pot, one-step process.[12–18] CSP is based on the simultaneous use of two metal-based catalysts able to work in tandem *via* the use of a chain transfer agent allowing the shuttling of the polymer chain between the two active sites (Fig. 1). The two initiators have to be able to copolymerise the co-monomers in the same experimental conditions with a different reactivity ratio, resulting in blocks with different compositions arranged in an alternating fashion. We extended this concept, initially developed based on coordinative copolymerisation of ethylene with α-olefins,[12] to the ring opening polymerisation of cyclic esters.[15] This led to the formation of block copolymers composed of PLLA rich semi-crystalline hard blocks and amorphous poly(L-lactide-*co*-ε-caprolactone) soft blocks. The catalytic system involved commercial Al(OiPr)$_3$ that barely inserts ε-CL[19] combined to an amino(bis)phenolate-supported aluminium complex (see Scheme 1 for the general structure of amino(bis)phenolate ligands) able to insert significant amount of the lactone without significant occurrence of transesterification. The glass transition temperatures (T_g) of the soft block ranged from −8 to +16 °C. For some applications, it can be interesting to reach lower T_g, which can be achieved by producing soft blocks with a higher content of ε-CL. We therefore planned to design catalysts able to statistically copolymerise LA and ε-CL with a higher insertion of ε-CL.

ε-CL homopolymerisation is generally known to be more efficient than the L-LA one, which may notably be attributed to the increased steric hindrance of lactide due to the methyl groups. However, this trend reverses in copolymerisation, which is usually ascribed to the fact that lactide is more coordinating to oxophilic metals,[20,21] leading to gradient or even block copolymers starting from an equimolar mixture of the monomers with certain systems.[22] Possible strategies to modify the reactivity ratio consist in varying steric hindrance around the active centre of the complex and/or altering the
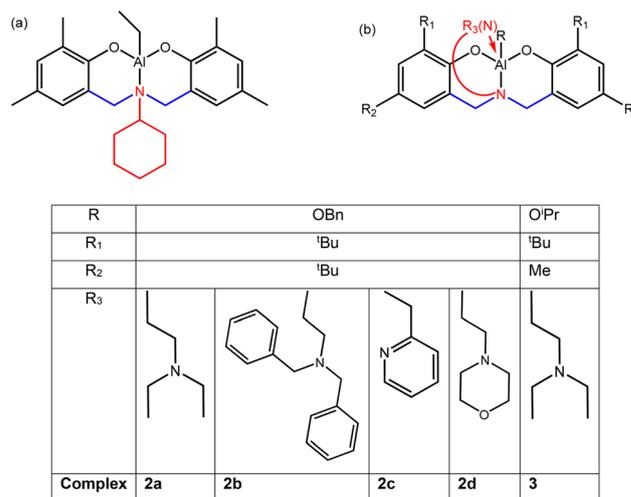
Scheme 1 Aluminium supported amino(bis)phenolate complexes used in our preliminary work (a) and bearing a pendant donor arm considered in the present work for chain shuttling copolymerization (**2a**, **2b**, **2c** and **2d**) and in the literature for homo- and statistical copolymerizations (**3** after ref. 25 and 27) (b).

ligand electron density. In general, increasing the hindrance around the initiator active site tends to promote a higher ε-CL insertion.[20]

Amino(bis)phenolate ligands are particularly interesting for this purpose, as their structure (see Scheme 1) and synthetic route allow a wide variability of the ligand framework. They have been used with aluminium metals to design active catalysts for the ROP of cyclic esters,[23,24] and later, for LA/ε-CL statistical copolymerisation, with the potential to control the selectivity. In addition to the R$_1$ and R$_2$ substituents, the nature of the amino side arms plays a crucial role. For instance, it has been reported that using pyridine as a side arm results in very low ε-CL insertion in the course of a LA/ε-CL statistical copolymerization, whereas employing amino(bis)phenolate Al complexes bearing a tertiary amine leads to significantly higher lactone insertions, with R$_1$ = *t*Bu, R$_2$ = Me
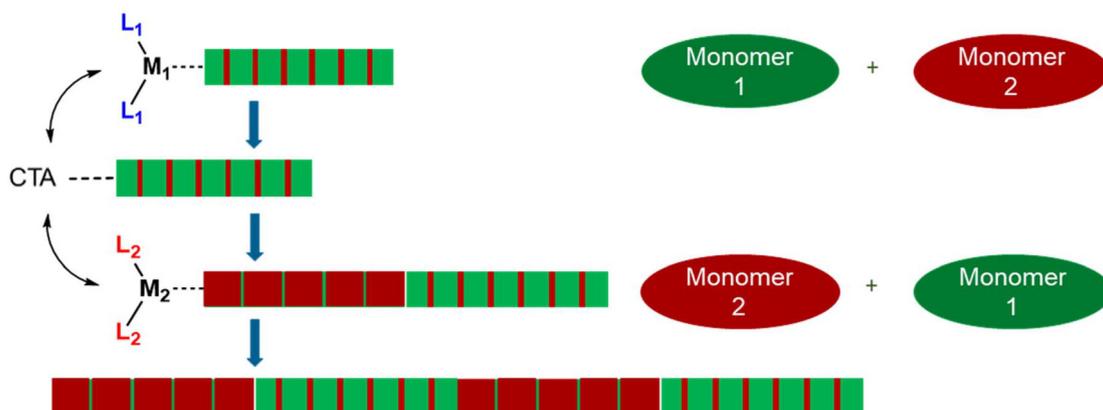

Fig. 1 Chain Shuttling Copolymerisation (CSP). Where M is the catalyst metal, L the ligands and CTA the chain transfer agent.

and R = OiPr (complex **3**).[25] This was rationalized by DFT calculations, which revealed a difference of activation energy for the insertion of the co-monomers into Al-caprolactoyl/Al-lactyl bonds.[26] In addition, regarding our purpose, amino(bis) phenolate supported aluminium complexes have been previously reported to achieve chain shuttling copolymerisation with an aluminium trisalkoxide.[15]

In the present study, we have assessed a variety of amino (bis)phenolate supported aluminium systems for the CSP of L-LA and ε-CL. The ligands were designed based on the following assumptions. We selected structures (shown in Scheme 1) bearing:

- −*t*Bu as R_1 and R_2 substituents as a literature survey tends to show that steric hindrance might increase the insertion of ε-CL in the course of metal catalysed L-LA/ε-CL statistical copolymerisation.

- Amino side-arms with a group allowing a coordination to the aluminium centre. Indeed, such complexes with *e.g.* tertiary alkylamine allows an insertion of ε-CL higher[25] than that afforded by the cyclohexyl substituted complex used in our preliminary work (Scheme 1a).[15]

This includes complexes already described in the literature (**2c** and **2d** see ref. 24) but not assessed for the L-LA/ε-CL statistical copolymerisation to our knowledge, as well as new complexes (**2a** and **2b**). They are first assessed in a comparative way for the homopolymerisation of both monomers, followed by statistical copolymerisation attempts. By combining those amino-(bis)phenolate-supported aluminium complexes, either among themselves or with aluminium and yttrium alkoxides, we report in this contribution six new catalytic systems able to perform the L-LA/ε-CL chain shuttling copolymerisation, leading to various T_g for the soft blocks. As such, the thermal properties of the copolymers can be tuned by selecting the proper CSP catalytic combination.

2. Results and discussion

2.1 L-Lactide and ε-CL polymerisation

Prior to statistical and chain shuttling copolymerisation, the **2a–d** complexes were tested for the polymerisation of the monomers. Experiments representative of the ROP of L-LA in toluene at 100 °C in the presence of the different initiators are presented in Table 1. All initiators were found to be active with significant conversions. Complex **2c** led to full conversion in less than 1 h (entry 3) while 53–66% conversions were obtained for **2a**, **2b** and **2d** in 24 h. **2b** shows the lowest conversion with 53%, while **2a** and **2d** have relatively similar conversions around 65%. The activity ranking was found as follow: **2c** (Py) ≫ **2a** (NEt₂) ≅ **2d** (Mor) > **2b** (NBn₂). The higher activity of complex **2c** with a pyridine donor arm agrees with previous studies of the literature, and was attributed to the lower steric hindrance on the pyridine side arm.[28] The lower activity of **2b** observed in this study aligns with this trend. **2d** was reported to be less active than **2c** in bulk at 120 °C,[24] although to a lesser extent. In addition, amino(bis) phenolate Al isopropoxyde bearing a dialkyl amine pendant arm with methyl and *tert*-butyl substituted phenol in the *para* and *ortho* positions respectively (shown as **3** in Scheme 1) were found to be inactive at 70 °C *vs.* the active pyridine substituted analogue.[27]

The activity of the **2a**, **2b** and **2d** amino(bis)phenolate aluminum complexes for the polymerization of lactide in solution is rather modest compared to conventional initiators. For example, the polymerization of lactide by salen aluminum complexes leads to 62% conversion in toluene at 70 °C after 22 h for M/I = 75, 0.6 M.[29] Regarding another conventional catalyst, yet more used in the bulk, the polymerization of lactide mediated by Sn(Oct)₂ leads to 95% yield in toluene at 115 °C after 24 h for M/I = 1000, 1 M.[30] **2c** leads in turn to more significant conversion.

According to SEC data, M_n ranging from 2400 to 7100 g mol⁻¹ were obtained. The experimental M_n were found to be close to the calculated ones. The polymerisations were found to be well-controlled with dispersities in the range 1.06 to 1.12. Based on the MALDI mass spectra, a good control over the mass parameters, in agreement with NMR and SEC results, and end-groups fidelity can be confirmed. Indeed, the main distribution is characterised by polylactide initiated by benzyl alcohol. Moreover, most of the mass spectra shows mass difference of 144 Da between signals of the main distribution, confirming a low amount of transesterification reaction (see

Table 1 L-LA and ε-CL polymerisation with **2a–d** as the initiators

Entry[a]	Complex	Monomer	M/I[b]	t[c]	T (°C)	Conv.[d] (%)	$M_{n\ calcd}$[e] (g mol⁻¹)	$M_{n\ exp}$[f] (g mol⁻¹)	Đ[f]
1	**2a**	L-LA	50	24 h	100	66	4700	4800	1.07
2	**2b**	L-LA	50	24 h	100	53	3800	2400	1.12
3	**2c**	L-LA	50	1 h	100	100	7200	7100	1.06
4	**2d**	L-LA	50	24 h	100	62	4500	4200	1.08
5	**2a**	ε-CL	500	10 min	50	91	51 900	48 700	1.11
6	**2b**	ε-CL	1000	5 min	30	66	75 300	50 600	1.12
7	**2c**	ε-CL	500	10 min	50	1	600	n.d	n.d
8	**2d**	ε-CL	1000	5 min	30	85	97 000	63 200	1.29

[a] Polymerisations conducted in toluene at 1 M (mol L⁻¹). [b] Monomer/initiator molar ratio. [c] Time. [d] Conversion determined by ¹H NMR in CDCl₃. [e] $M_{n\ calcd}$ = (50 × 144 × conversion)/100 for PLA and ([ε-CL]/[Al] × 114 × conversion)/100. [f] Number-average molecular weight determined by size exclusion chromatography in THF with 0.58 as correction factor for PLA,[32] 0.56 as correction coefficient factor for PCL[33] and dispersity.

Fig. SI1–4†). It is worth to note that mass spectra seem to present a huge amount of low mass ions but those distributions are significantly overestimated compare to the main one.[31]

The polymerisation of ε-CL conducted with **2a–d** as the initiators was then investigated in toluene at 30 or 50 °C (Table 1). Entries 5 and 7 were performed at 50 °C in 10 min for monomer/initiator ratio of 500 while entries 6 and 8 were conducted at 30 °C in 5 min for a monomer/initiator ratio of 1000 due to the difference of reactivity of the complexes for the polymerisation of ε-CL. Narrow molar mass distributions with dispersities around 1.1 to 1.3 were obtained. The activity of the initiators could be rated as follow: **2d** (Mor) > **2b** (NBn₂) ≫ **2a** (NEt₂) ≫ **2c** (Pyr). The inactivity of complex **2c** aligns with previous studies of the literature, while **2d** was reported as significantly active in toluene at 25 °C for ε-caprolactone.[24] Similarly, amino(bis)phenolate Al isopropoxyde bearing a dialkyl amine pendant arm with methyl and *tert*-butyl substituted phenol in the *para* and *ortho* positions respectively (shown as **3** in Scheme 1) was found much more active than the pyridine-substituted analogue at 70 °C in toluene.[27] Generally, the results suggest that the polymerisation of ε-CL is more influenced by the nature of the initiator pendant donor arm than for L-LA.

2.2   L-LA/ε-CL statistical copolymerisation

Entries representative of the statistical ring-opening copolymerisation of ε-CL and L-LA in toluene at 100 °C mediated by the different initiators are given in Table 2. All complexes were found to be active. A very high selectivity for L-LA was observed for **2c**, while **2a**, **2b** and **2d** were found to insert more ε-CL than L-LA starting from an equimolar mixture of the co-monomers, with similar conversions. This is noteworthy regarding targeted chain shuttled materials. Indeed, the amino(bis) phenolate aluminium complex bearing a cyclohexyl moieties reported in our preliminary work did insert less ε-CL than L-LA, with ca. 80/60 conversions for L-LA and ε-CL respectively at 70 °C in toluene.[15] The higher selectivity for L-LA obtained using **2c** *vs.* **2a** is in line with the literature, as amino(bis) phenolate Al isopropoxyde bearing a dialkyl amine pendant arm with methyl and *tert*-butyl substituted phenol in the *para*

and *ortho* position respectively (shown as **3** in Scheme 1) was found to convert much more ε-CL than the pyridine-substituted analogue at 100 °C in toluene.[25] M_n ranging from 7500 to 8800 g mol⁻¹ were obtained along with narrow molar mass distributions (dispersities Đ in the range 1.05 to 1.17). It is difficult to rationalize the structure/activity/selectivity relationships. However, steric hindrance seems to be an influential factor. Indeed, **2c** is less sterically hindered than **2a**, **2b** and **2d** and leads to the highest activity for the polymerization of lactide, and to the lowest activity for the polymerization of ε-CL. In statistical copolymerization, it leads to the lowest insertion of ε-CL.

NMR is a powerful tool for the structural analysis of poly(L-lactide-*co*-ε-caprolactone) copolymers. In particular, ¹³C NMR provides some information regarding the sequences. L is defined as the lactyl unit and LL as the lactidyl unit. From the MALDI of the L-LA homopolymerisation, we have seen that transesterification does not occur significantly, with mainly multiple of 144 Da, *i.e.* mostly LL sequences. For the statistical copolymerisation, if transesterification inside a lactidyl LL sequence occurs, one may see CLC sequences at 170.8 ppm,[35] which is not the case here as shown in Fig. SI5–7 provided in the ESI section.† Thus, we can reasonably assume that only LL lactidyl sequences are present in our copolymers.

In addition, ¹H NMR allows to determine the composition and the percentage of lactidyl units neighbouring a caprolactoyl unit and *vice versa*. The distribution of the dyads provided in Table 3 is derived from Fig. 2. Signal representative of the caprolactoyl units at 4–4.2 ppm (2H, –CH₂O) can be used to quantitatively determine the percentage of C–C *vs.* C–LL. Then, given that there are as many LL–C dyads in the 5.05–5.25 ppm zone corresponding to 1H PLA as C–LL dyads, one can deduce the amount of LL–LL dyads. From that, we can now determine the lactidyl and caprolactoyl number-average sequence length from the work of Herbert:[36]

$$L_{LL} = (2LL\text{–}LL + LL\text{–}C)/LL\text{–}C \tag{1}$$

$$L_C = (2C\text{–}C + LL\text{–}C)/LL\text{–}C \tag{2}$$

The randomness coefficient η can further be calculated from eqn (3).[36]

$$\eta = (LL\text{–}C)/(2 \times L\text{-}LA \times CL)/100 \tag{3}$$

The values are provided in Table 3.

Complex **2a** leads to a lactidyl number-average sequence length of 3.3, which is higher than the values of 1.6–1.8 found for **2b** and **2d**. The latter also have a randomness coefficient around 0.57–0.59 *vs.* 0.44 for the former. If the order of magnitude of 0.5 indicates a moderately blocky character,‡ a difference of microstructure can be observed between these two groups, with a higher random character for **2b** and **2d**. They also exhibit higher ε-CL insertions.

Table 2 L-LA/ε-CL statistical copolymerisation with **2a–2d** as the initiators

Entry[a]	Complex[a]	L-LA/ε-CL Conv.[b] (%)	t (h)	$M_{n\,calc}$[c] (g mol⁻¹)	M_n[d] (g mol⁻¹)	Đ[d]
9	**2a**	64/80	24	9200	7500	1.10
10	**2b**	58/78	24	8800	8800	1.15
11	**2c**	99/3	4	7400	7600	1.05
12	**2d**	63/81	24	9200	7700	1.17

[a] Copolymerisations conducted at 100 °C in toluene at 1 M (mol L⁻¹) with ([L-LA] + [ε-CL])/[Al] = 100 with [L-LA] = [ε-CL]. [b] Determined by ¹H NMR in CDCl₃. [c] $M_{n\,calc}$ = (50 × 144 × L-LA conversion)/100 + (50 × 114 × ε-CL conversion)/100. [d] Number-average molecular weight determined by size exclusion chromatography in THF corrected as M_n = (M_n raw × 0.56 × ε-CL conversion)/100 + (M_n raw × 0.58 × L-LA conversion)/100.[34]

‡A value of 0 indicates a diblock character, while a value of 1 indicates a fully random copolymer.

Table 3 Poly(ʟ-lactide-*co*-ε-caprolactone) statistical polymers microstructure

Entry	Initiators	ʟ-LA[a] mol%	(LL–LL)[b] mol%	(LL–C)[b] mol%	(C–C)[b] mol%	L_{LL}[c]	L_C[d]	η[e]
9	**2a**	47.5	25.2	22.2	30.4	3.3	3.7	0.44
10	**2b**	35.5	8.3	27.2	37.3	1.6	3.7	0.59
12	**2d**	37.1	10.5	26.5	36.4	1.8	3.7	0.57

[a] Composition determined by ^{1}H NMR in CDCl$_3$. [b] Dyad distribution (see text). [c] Lactidyl number-average sequence length determined using eqn (1). [d] Caprolactoyl number-average sequence length determined using eqn (2). [e] Randomness coefficient determined using eqn (3).
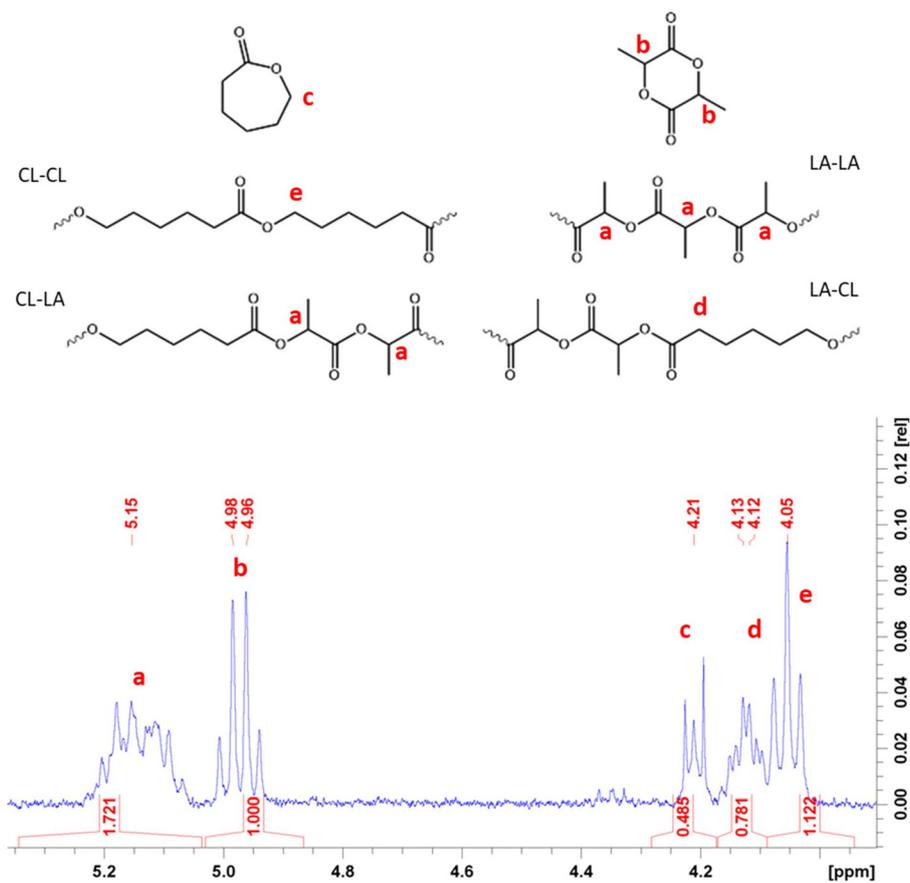

Fig. 2 ^{1}H NMR spectrum in CDCl$_3$ of poly(ʟ-LA-*co*-ε-CL) synthetized using **2a** (entry 9 -crude product) in the 4–5.5 ppm region.

2.3 ʟ-LA/ε-CL chain shuttling copolymerisation

Regarding chain shuttling copolymerisation, the combination of two catalysts exhibiting different selectivities towards the co-monomers were targeted. From the previous section, it can be seen that **2c** has a very high selectivity for lactide, making it a suitable catalyst to produce the hard block. **2a**, **2b** and **2d** insert much more ε-CL, which is desirable to produce soft blocks. Therefore, three experiments were conducted where **2c** was combined to the three other complexes, under similar experimental conditions for comparison (entries 13–17 in Table 4). The higher activity of **2c** prompted us to put the soft block catalysts in excess. A chain shuttling agent was not introduced at this step, as we highlighted in our previous study[15]

that the shuttling can operate without. Introducing it would result in a reduction in molar mass of the final materials. It should also be noted that average number-average molecular weights (from *ca.* 6000 to 13 000 g mol^{-1}) were targeted at this step to be able to perform DOSY (Diffusion Order NMR Spectroscopy) analyses, which is crucial to prove the occurrence of chain shuttling copolymerisation (see here after).

All three combinations lead to significant conversion. Considering that **2c** is highly selective for ʟ-LA and that the soft block initiator polymerises both ʟ-LA and ε-CL, it was anticipated that the conversion for ʟ-LA would exceed that of ε-CL when both initiators are involved, which indeed was the case. Regarding the activity, the following ranking could be established from entries 13, 14 and 16: **2a** (NEt$_2$) > **2b** (NBn$_2$) >

Table 4 L-LA and ε-CL chain shuttling copolymerisation

Entry[a]	Hard block Initiator (HBI)	Soft block Initiator (SBI)	HBI/SBI/LA/ε-CL Mol. ratio[b]	L-LA/ε-CL Conv.[c] (%)	t (h)	$M_{n\ calc}$[d] (g mol⁻¹)	M_n[e] (g mol⁻¹)	$Đ$[e]	(LL-LL)[f] mol%	(LL-C)[f] mol%	(C-C)[f] mol%	L_{LL}[g]	L_C[h]	η[i]
13	2c	2a	1/5/500/500	79/48	16	14 000	12 200	1.08	69.0	9.8	11.4	15.1	3.3	0.29
14		2b	1/5/500/500	33/35	16	7300	3900	1.12	47.2	16.3	20.3	6.8	3.5	0.35
15				51/61	30	11 800	7000	1.08	46.7	16.8	24.8	6.3	3.2	0.34
16		2d	1/5/500/500	46/39	16	9200	6800	1.10	54.6	15.1	15.3	8.2	3.0	0.36
17				64/45	24	12 000	9600	1.11	58.2	14.9	12.8	7.9	2.9	0.32
18	Al(OiPr)₃	2a	1/5/250/250	92/51	6	5900	6300	1.13	70.2	9.6	10.5	15.6	3.2	0.30
19	OY₅(OCH(CH₃)₂)₂)₁₃	2a	1/5/250/250	94/59	6	6700	6500	1.17	70.1	6.4	17.1	22.8	6.3	0.18
20		2d	1/5/250/250	46/30	6	3300	2600	1.48	59.7	12.3	15.4	19.4	5.8	0.21
21			1/5/500/500	93/67	16	13 800	13 700	1.23	65.4	6.8	20.9	20.2	7.1	0.17

[a] Copolymerisations conducted at 100 °C in toluene at 1 M (mol L⁻¹). [b] Corresponding to the metal ratio: [Y] or [Al] HBI/[Al] SBI/LA/CL. [c] Determined by ¹H NMR in CDCl₃. [d] For entries 13–17 $M_{n\ calc}$ = ((500 × 144 × L-LA conversion)/100 + (500 × 114 × -CL conversion)/100)/6; for entry 18 $M_{n\ calc}$ = ((250 × 144 × L-LA conversion)/100+ (250 × 114 × -CL conversion)/100)/8; for entries 19–21 $M_{n\ calc}$ = ((HBI/SBI/LA/CL mol. ratio × L-LA conversion)/100 + (HBI/SBI/LA/CL Mol. ratio × 114 × -CL conversion)/100)/7.6 (the 7.6 denominator corresponds to the number of initiating alkoxide moieties: 5 for the 5 equiv. of soft initiator, plus 2.6 for the yttrium hard block initiator. Indeed, the latter is a cluster with 13 alkoxides moieties for 5 yttrium moieties, which makes an average of 2.6 per Y). [e] Number-average molecular weight determined by size exclusion chromatography in THF corrected as M_n = (M_n raw × 0.56 × ε-CL conversion) + (M_n raw × 0.58 × L-LA) and dispersity. [f] Dyad distribution (see text). [g] Lactidyl number-average sequence length determined using eqn (1). [h] Caprolactoyl number-average sequence length determined using eqn (3). [i] Randomness coefficient determined using eqn (2).

2d (Mor). Narrow molar mass distributions were obtained in all cases, with dispersities close to 1.1. The molar mass distributions are monomodal (see Fig. SI8–10 in the ESI section†), which agrees with the occurrence of chain shuttling.

DOSY analyses of the copolymers were then performed. The measurement of the diffusion coefficient allows to confirm whether lactyl and caprolactoyl units are within the same macromolecule or if it is a mixture of two different (co-)polymers that would have been produced independently by the two different initiators. In the former case, lactyl and ε-caprolactoyl units will share the same diffusion coefficient, while in the latter case, two different coefficients will be detected. A typical DOSY analysis presented in Fig. 3 shows a single diffusion coefficient, consistent with the occurrence of transalcoxylation in the course of the polymerisation. This is the case for all three systems (see Fig. SI14 and 15 in the ESI section† for the two other DOSY analyses). Moreover, as observed before in the course of the statistical copolymerisation, ¹³C NMR analysis indicated the absence of LCL enchainments indicating the absence of significant transesterification reactions.

In order to potentially extend the scope of L-LA/ε-CL chain shuttling copolymerisation, we further assessed Al(OiPr)₃ as hard block catalyst, as it successfully performed the CSP reaction with the amino(bis)phenolate-supported aluminium complex bearing the cyclohexyl pendant arm in our previous work (see Scheme 1 and ref. 15). Entry 18 and related DOSY experiment represented Fig. SI16† shows that the Al(OiPr)₃/**2a** combination is also efficient for L-LA/ε-CL CSP. We finally assessed if amino(bis)phenolate aluminium complexes could be associated to other metal centres to conduct CSP. In that frame, yttrium alkoxides were selected due to their established efficacy as catalysts for the ROP of cyclic esters with a high selectivity towards lactide in the course of the L-LA/ε-CL statistical copolymerisation.[37,38] Representative experiments are shown as entries 19–21 in Table 4 with **2a** and **2d** as soft block initiators. As observed using **2c** as the hard block initiator, the activity in the presence of **2d** was found to be lower. Higher molar mass can be obtained by increasing the monomers over
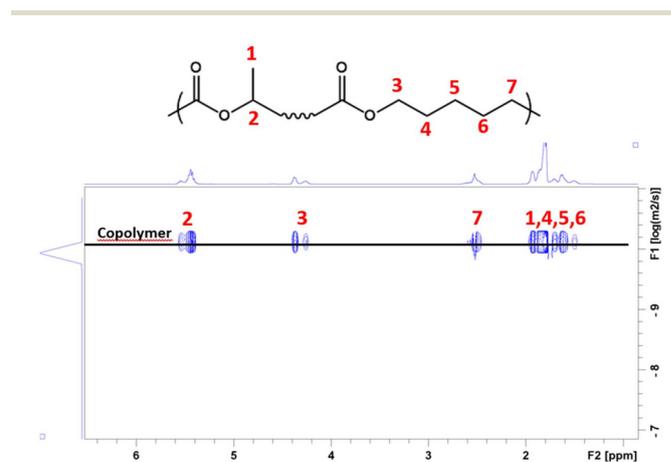

Fig. 3 DOSY analysis of a chain shuttled copolymer synthetized using **2a** and **2c** (entry 13).

initiators ratio, as shown in entry 21. To our delight, the DOSY experiments (Fig. SI17 and 18 in the ESI section†) show that the transalkoxylation is efficiently occurring between yttrium and amino(bis)phenolate aluminium alkoxides. By comparing entry 21 to entry 16, it can be seen that the activity is significantly higher using the yttrium precursor as the hard block catalyst than **2c**. We also conducted a model ^{1}H NMR study that shows that the amino(bis)phenolate moieties remains on the aluminum center even after heating an equimolar mixture of $OY_5(OCH(CH_3)_2)_{13}$ and **2a** as a case study at 80 °C in deuterated benzene (found in the ESI section as part 7 and Fig. SI19 and SI20†).

Finally, the lactidyl and caprolactoyl number-average sequence lengths were also determined for the chain shuttled copolymers for the sake of comparison. It can be seen that, due to the high selectivity of the hard block catalysts for the lactide comonomer, the lactidyl number-average sequence lengths are significantly higher than those obtained for the

statistical copolymer, in the 6.3–22.8 range *vs.* 1.6–3.3 respectively. The randomness coefficient, as a consequence, is lower for the chain shuttled copolymers (0.17–0.36 *vs.* 0.44–0.59 for the statistical copolymers).

2.4   Thermal properties of chain shuttled copolymers

The thermal properties of some samples were finally characterised, and are given in Table 5, while the DSC thermograms are provided Fig. 4. It should be noted that, due to the low molar mass requirements for DOSY analyses, not all samples from Table 4 could easily be precipitated. From Table 4, it can be seen that in the presence of **2c** as the hard block catalyst, the highest molar masses were obtained in combination with **2a**, which was thus selected to study the thermal properties. The samples obtained from entry 13 show two glass transition temperatures together with a melting point. The lower T_g is at −14 °C starting from an equimolar mixture of the co-monomers. In comparison, $Al(OiPr)_3$ leads to a higher soft block T_g

Table 5   Thermal properties of chain shuttled copolymers

Entry[a]	Hard block initiators	Soft block initiators	Conv.[b] LA/ε-CL (%)	t (h)	$M_{n\ calc}{}^{c}$ (g mol⁻¹)	$M_n{}^{d}$ (g mol⁻¹)	$Đ^c$	$T_{g1}{}^{e}$ (°C)	$T_{g2}{}^{e}$ (°C)	$T_m{}^{e}$ (°C)	ΔH^e (J g⁻¹)
13	**2c**	**2a**	79/48	16	14 000	12 200	1.10	−14	46	74	5.4
21	$Al(OiPr)_3$	**2a**	60/22	6	6500	7000	1.08	2	49	117	17
22	$OY_5(OCH(CH_3)_2)_{13}$	**2a**	92/69	16	13 900	13 600	1.27	−22	44	120	10.5
23		**2d**	93/67	16	13 800	13 700	1.23	−24	44	129	15

[a] Copolymerisations conducted at 100 °C in toluene at 1 M (mol L⁻¹) with metal ratio: [Y] or [Al] HBI/[Al] SBI/LA/CL = 1/5/500/500. [b] Determined by ^{1}H NMR in CDCl₃. [c] For entry 13 $M_{n\ calc}$ = ((500 × 144 × L-LA conversion)/100 + (500 × 114 × -CL conversion)/100)/6; for entry 21 $M_{n\ calc}$ = ((500 × 144 × L-LA conversion)/100 + (500 × 114 × -CL conversion)/100)/8; for entries 22–23 $M_{n\ calc}$ = ((500 × 144 × L-LA conversion)/100 + (500 × 114 × CL conversion)/100)/7.6 (the 7.6 denominator corresponds to the number of initiating alkoxide moieties: 5 for the 5 equiv. of soft initiator, plus 2.6 for the yttrium hard block initiator. Indeed, the latter is a cluster with 13 alkoxides moieties for 5 yttrium atoms, which makes an average of 2.6 per Y). [d] Number-average molecular weight determined by size exclusion chromatography in THF corrected as M_n = (M_n raw × 0.56 × ε-CL conversion) + (M_n raw × 0.58 × L-LA) and dispersity. [e] Glass transition temperatures, melting temperature and melting enthalpy determined by Differential Scanning Calorimetry (DSC).
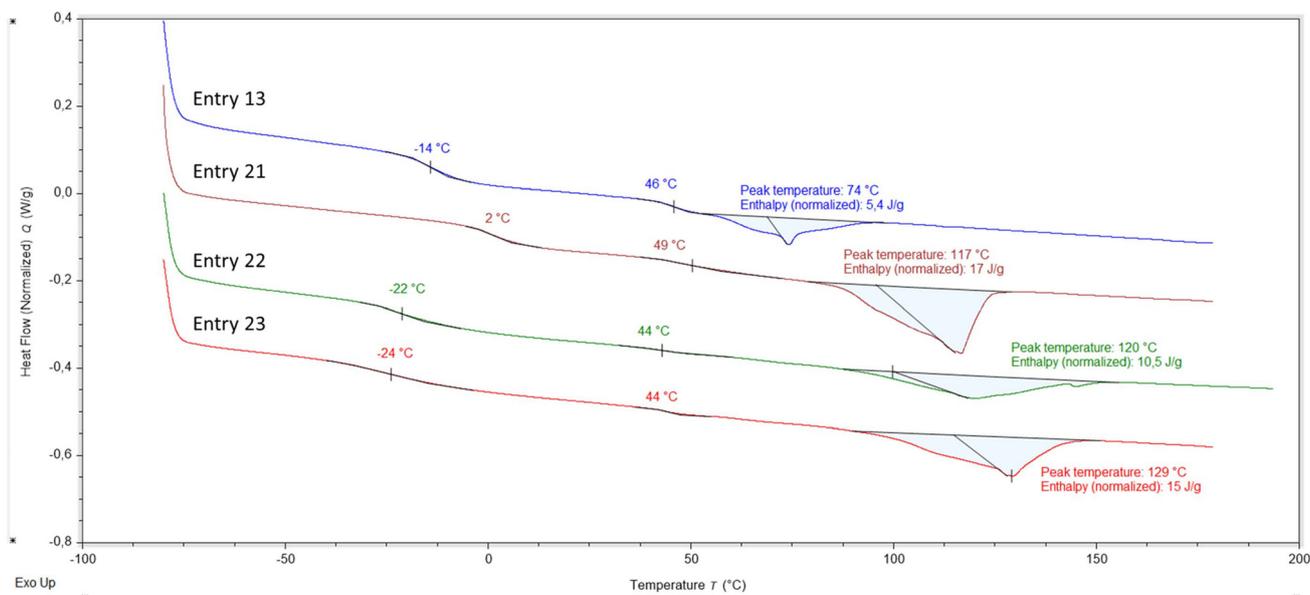

Fig. 4   Thermograms of the chain shuttled copolymers.

of 2 °C in similar conditions (entry 21), with higher melting point and melting enthalpy. The lower molar mass obtained for the sample synthesised with Al(OiPr)$_3$ can be ascribed to the presence of three alkoxide initiating groups on the aluminium centre *vs.* one for **2c**. The lowest glass transition temperatures were obtained for the copolymers synthesised with the yttrium alkoxide initiator combined to **2a** or **2d**, around −22 to −24 °C starting from an equimolar mixture of the co-monomers (entries 22 and 23). The glass transition temperature of the soft blocks follow the ε-CL content of the sample: the highest for the former, the lowest the T_g. Regarding the hard block, the T_g are all in the same range. The chain shuttling between aluminum amino(bis)phenolate and yttrium allows to reach microstructures with a lower T_g for the soft block and higher melting points. This can be further linked to longer lactidyl and caprolactoyl number-average sequence lengths, and to an overall lower randomness coefficient. It may also somehow be linked to higher activity and selectivity of the yttrium hard block initiator toward lactide (see Table SI3†). This might further lead to a wider range of mechanical properties. As a matter of fact, tuning of the thermal properties of the chain shuttled copolymer can be realised by changing the type of catalysts, with a variation of the T_g of the soft block over *ca.* 25 °C starting from a similar equimolar mixture of the co-monomers. Fine analyses of the phase segregation states and the mechanical properties of those materials will be reported in a forthcoming paper.

3. Conclusion

We have reported in this contribution six new catalytic systems for the ʟ-LA/ε-CL chain shuttling copolymerisation. They are based on four different amino(bis)phenolate complexes bearing a pendant donor arm in the form of a tertiary alkylamine (**2a**), a tertiary dibenzylamine (**2b**), a pyridine (**2c**) and a morpholine (**2d**) functional group. The corresponding ligands were synthesised by a Mannich condensation procedure. Two new alkoxide complexes and two already reported ones were obtained in reasonable yield through a two-steps treatment with trimethylaluminium followed by benzyl alcohol. They were initially investigated for the polymerisation of ʟ-LA and ε-CL. The polymerisation of the latter was found to be much faster than the former, and barely dependant on the nature of the pendant donor arm. Complex **2c** led to the highest activity regarding the polymerisation of ʟ-LA. Narrow molar mass distributions were obtained in most cases with dispersities around 1.1.

Statistical copolymerisations of ʟ-LA and ε-CL were successfully conducted in the presence of all complexes with dispersities below 1.2. Complex **2c** showed a high selectivity toward lactide, while **2a**, **2b** and **2d** led to ε-CL conversions higher than ʟ-LA. This selectivity differences prompted us to assess the chain shuttling copolymerisation of ʟ-LA and ε-CL using **2a**, **2b** and **2d** in combination with several hard block initiators including **2c**, Al(OiPr)$_3$ and OY$_5$(OCH(CH$_3$)$_2$)$_{13}$. The high selectivity of the two latter complexes for lactide was known

from the literature. All systems were found to able to perform the chain shuttling copolymerisation. To our knowledge, this is the first description of amino(bis)phenolate complexes bearing a pendant arm for CSP. Additionally, we report for the first time the ʟ-LA/ε-CL chain shuttling copolymerisation between two different metals, *i.e.* Al and Y. This allows tuning of the thermal properties of the chain shuttled copolymers, as shown by a variation of the T_g of the soft block over 25 °C by changing the catalytic system without altering the reaction feed. The fine microstructure and properties of the so-formed materials will be discussed in a forthcoming paper.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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