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Syndioselective Ring-Opening Polymerization and Copolymerization of *Trans*-1,4-Cyclohexadiene Carbonate Mediated by Achiral Metal- and Organo-Catalysts

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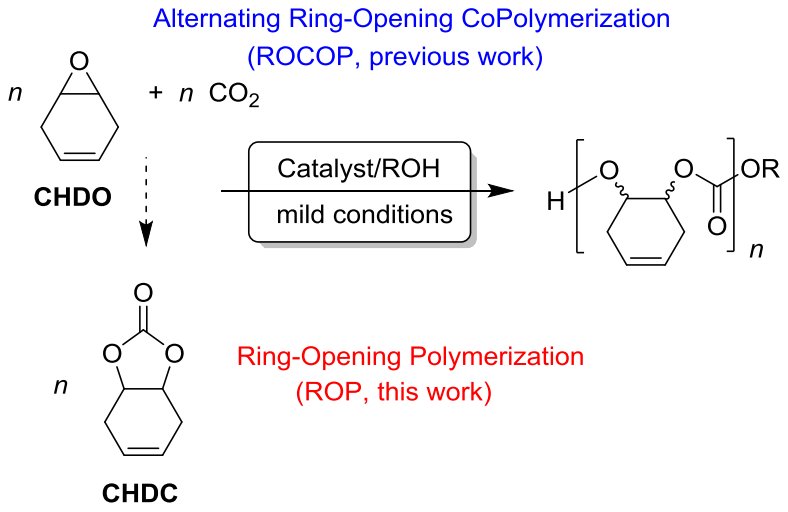
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Abstract: The ring-opening polymerization (ROP) of *trans*-1,4-cyclohexadiene carbonate (CHDC) has been investigated computationally and experimentally. DFT computations indicate that ring-opening of CHDC is thermodynamically possible, yet to a lesser extent than that of *trans*-cyclohexene carbonate (CHC). Effective homopolymerizations of *rac*-CHDC and simultaneous or sequential copolymerizations of *rac*-CHDC with *rac*-CHC and *L*-LA were achieved with a diaminophenolate zinc-based complex ([(NNO)ZnEt]) or a guanidine (TBD) associated with an alcohol. These ROP reactions, which confirmed the lower reactivity of *rac*-CHDC *vs. rac*-CHC, especially in homopolymerization, proceeded without any decarboxylation. Quite uniquely, highly syndiotactic PCHDC was obtained from ROP of *rac*-CHDC with both the zinc- and TBD-based catalysts, as revealed by $^{13}C\{^{1}H\}$ NMR studies. The prepared homopolymers and block or random copolymers were characterized by ^{1}H, $^{13}C\{^{1}H\}$ NMR, MALDI-ToF-MS, SEC and DSC techniques.

Keywords: Cyclic Carbonate, Ring-Opening Polymerization, Stereoselectivity, DFT

Introduction

Aromatic and aliphatic polycarbonates (PCs) are important commodity and engineering materials used in a variety of applications. Classic aromatic PCs derived from bisphenol A (BPA) show valuable thermo-mechanical properties; however, they have raised major concerns related to the toxicity of the latter BPA monomer and of phosgene used as the co-reagent. Although aliphatic PCs do not have properties that match yet those of aromatic PCs derived from BPA, this class of polymers has attracted much interest in recent years. Indeed, depending on the chemical repeat units and the microstructure, some of these polymers show promising thermal properties (*e.g.*, high T_g and T_m).[1] Also, thanks to their functional termini, they can serve as valuable pre-polymers for the production of other important materials (*e.g.*, polyurethanes from dihydroxy-telechelic low molar mass pre-polymers[2]). Moreover, besides the traditional, yet poorly controlled polycondensation reaction between a dialkyl carbonate and an α,ω-diol,[3] aliphatic PCs can be more effectively produced by two alternative routes: a) the metal-catalyzed alternating ring-opening copolymerization (ROCOP) of epoxides/CO_2, and b) the ring-opening polymerization (ROP) of cyclic carbonate monomers (Scheme 1).



Scheme 1. ROCOP and ROP routes toward polycarbonates, illustrated with cyclohexadiene oxide (CHDO) and cyclohexadiene carbonate (CHDC) for the formation of poly(cyclohexadiene carbonate) (PCHDC).

ROCOP's attractive features include the use of carbon dioxide, the possibility to reach high molar mass polymers, and also to access sometimes high stereoselectivities via desymmetrization of achiral *meso* epoxides with chiral catalysts.[4] On the other hand, ROCOP faces the issue of incomplete alternating selectivities, which may result in the formation of ether units along the PC chain, and also the formation, alongside the PC, of the corresponding five-membered ring cyclic carbonate (5CC) monomer. A large number of ROCOP studies involved cyclohexene oxide (CHO) and hence led to the production of poly(cyclohexene carbonate) (PCHC), along with variable amounts of its corresponding 5CC monomer (*i.e.*, cyclohexene carbonate, CHC).[5] Whereas the vast majority of catalysts for CHO/CO_2 ROCOP promote the formation of atactic PCHC, some of them, essentially Zn, Cr or Co complexes based on chiral salen or β-diketiminate derivatives, enable the synthesis of syndiotactic- (up to 81% of *r*-centered tetrads)[6] or isotactic- (up to (*R*,*R*)/(*S*,*S*) = 98:2)[7] enriched PCHCs.

ROP of cyclic carbonates (CCs) is another privileged procedure to access well-defined, high molar mass aliphatic PCs.[8] Given the ready availability of a large number of 5CCs from epoxide carboxylation (*vide supra*) or from biosourced 1,2-diols,[9] the valorization of these monomers into PCs certainly deserves consideration. Yet, whereas six- and, to a lesser extent, seven-membered ring CCs have been quite selectively polymerized by ROP under mild operating conditions, the related 5CCs have hardly been ring-opened (co)polymerized.[10] This is obviously related to their small ring-strain and poor polymerizability,[11] which is intimately associated to their abovementioned easy formation. Hence, although several ROP catalyst systems have been identified for the copolymerization

of ubiquitous 5CCs such as ethylene and propylene carbonates, the reactions proceed only at high temperatures with poor-to-modest 5CC conversion, and they are always accompanied by a partial or total decarboxylation of the latter monomer.[10] On the other hand, there are a few examples of strained 5CCs which can undergo selective ROP. Endo and coworkers first performed the successful ROP of the sugar-derived 5CC, methyl 4,6-*O*-benzylidene-2,3-*O*-carbonyl-*R*-D-glucopyranoside, without decarboxylation using *n*-BuLi, MO*t*Bu (M = Li, Na, K) or DBU as initiators ($M_{n,SEC}$ up to 20 200 g.mol^{-1}, $Đ_M$ = *ca*. 1.8).[12] Also, we have reported recently the easy and efficient ROP of *trans*-cyclohexene carbonate (CHC).[13] PCHCs with controlled molar masses ($M_{n,NMR}$ up to 17 000 g.mol^{-1}, $Đ_M$ = *ca*. 1.2) and a slight isotactic bias (P_m up to 76%) were obtained by ROP of the racemic monomer (*rac*-CHC) catalyzed by zinc diaminophenolate, zinc β-diketiminate, yttrium bis(phenolate) complexes, or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), in combination with an alcohol as a co-initiator. Purely isotactic PCHC was synthesized for the first time via ROP of enantiopure (*R*,*R*)-CHC with a zinc/benzyl alcohol catalyst system. Parallel to the work of Haba *et al.* who used *t*BuOLi to initiate the ROP of CHC,[14] we unveiled the determining impact of the fused *trans*-cyclohexyl ring-strain to enable the ROP of CHC, as opposed to *meso*-CHC which is unreactive.

In this contribution, we now report that the ROP of *trans*-cyclohexadiene carbonate (*trans*-1,2-cyclohex-4-enyl cyclocarbonate, *trans*-CHDC, Scheme 1) can be performed also by various metal-based or organo-catalysts. The corresponding poly(cyclohexadiene carbonate) (PCHDC) has just been recently reported by the ROCOP route from *meso*-CHDO (cyclohexadiene oxide, that is 1,2-epoxy-4-cyclohexene, Scheme 1)[15] and was obtained in a non-stereoselective manner. Quite uniquely, we evidence that the ROP of *rac*-CHDC, despite the use of *non-chiral* catalysts, affords pure syndiotactic PCHDCs; besides; highly isotactic PCHDC has been prepared independently from enantio-enriched *trans*-CHDC. The effective preparation of copolymers of CHDC with CHC and *L*-lactide is presented as well.

Experimental section

Computational Details. All DFT calculations were carried out using the Gaussian09 program suite,[16] employing the M06 functional,[17] and using a standard double-ξ polarized basis set, namely the 6-31(δ,π) set.[18] All stationary points were fully characterized via analytical frequency calculations as true minima (all positive eigen values). Enthalpies were obtained at T = 298 K within the harmonic approximation.

Methods and Instrumentation

NMR spectra were recorded on a AM-400 Bruker spectrometers at 298 K in $CDCl_3$. A relaxation delay of 3 s was used during the acquisition to yield quantitative ^{1}H NMR spectra. The chemical shifts were referenced to tetramethylsilane (TMS) using the residual protio-solvent (^{1}H) or the carbon (^{13}C) resonance of the deuterated solvent.

Monomer conversions were determined from ^{1}H NMR spectra of the crude polymer samples, from the integration (Int.) ratio $Int._{Polym}/[Int._{Polym}+Int._{Monom}]$, typically using the methine and methylene hydrogens.

Molar masses (M_n and M_w) and dispersities ($Đ_M = M_w/M_n$) of polymers and copolymers were determined by size exclusion chromatography (SEC) using a Polymer Laboratories PL-GPC 50 instrument equipped with a set of two ResiPore Mixed E 300 × 7.5 mm columns and a refractive index detector. The sample was eluted with $CHCl_3$ (PCHDC) or THF (copolymers) at 30 °C at 1.0 $mL{\cdot}min^{-1}$ and the calibration was carried out using 11 monodisperse polystyrene standards (M_n range from 580 to 380,000 $g{\cdot}mol^{-1}$).

Differential scanning calorimetry (DSC) analyses were performed on a Setaram DSC 131 apparatus calibrated with indium at a rate of 10 °C.min^{-1}, under continuous flow of helium (25 mL.min^{-1}), using aluminum capsules (typically 10 mg of polymer).

Syntheses

All manipulations were performed under inert atmosphere (argon, <3 ppm O_2) using standard Schlenk, vacuum line, and glovebox techniques. Benzyl alcohol and isopropanol were distilled over Mg turnings under argon atmosphere and kept over activated 3–4 Å molecular sieves. Complex [(NNO)ZnEt] was synthesized following the literature procedure.[21] 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) (98%, Aldrich) and $Y[N(SiMe_3)_2]_3$ (98%, Strem Chem.) were used as received. *Racemic trans*-cyclohexene carbonate (*rac*-CHC) was prepared as previously reported. Technical grade *L*-lactide (*L*-LA) was provided by Total Raffinage Chimie and purified by recrystallization from a hot (80 °C), concentrated isopropanol solution, followed by two subsequent recrystallizations in hot (105 °C) toluene. After purification, *L*-LA was stored at all times at a temperature of –30 °C in the inert atmosphere of the glove-box. *Trans-racemic*-1,2-cyclohex-4-enediol was prepared from cyclohexadiene following the reported literature procedure.[19]

***Trans*-(*R*,*R*)-1,2-cyclohex-4-ene-diol** (enantio-enriched, 83% ee) was obtained by resolution of the racemic product (Scheme 3) following the same procedure used for 1,2-cyclohexanediol.[20] A round-bottom flask was charged with dicyclohexylcarbodiimide (DCC; 2.00 g, 9.64 mmol), (±)-*trans*-cyclohex-4-ene-1,2-diol (1.00 g, 8.76 mmol) and *N*,*N*-dimethylaminopyridine (DMAP) (0.107 g, 8.76 mmol). Freshly distilled THF (20 mL) was introduced into the flask under an argon atmosphere, and the solution was cooled at –10 °C. A solution of (*S*)-(+)-*O*-acetylmandelic acid (1.70 g, 8.76 mmol) in THF (10 mL) was slowly added in. Stirring was maintained over 6 h until the completion of the reaction (TLC

monitoring). The reaction mixture was filtered to remove the urea derivative; the filtrate was evaporated under vacuum to obtain a colorless liquid, which was chromatographed using silica gel and 20% EtOAc/petroleum ether as eluent. The first fraction (minor fraction, the other one was discarded) was collected and the solvent was removed under vacuum (0.30 g, 30%). This product was stirred in a 1N methanolic NaOH solution (20 mL) at room temperature for 4 h. After disappearance of the ester (TLC monitoring), MeOH was evaporated, the crude product was purified through Kugelrohr distillation (200 °C, 4 mm Hg) and re-crystallized from benzene. *Trans*-(*R*,*R*)-1,2-cyclohex-4-ene-diol was obtained as a white solid (0.276 g, 92% for this step). Enantiomeric excess (83% ee) was measured by chiral GC using a Beta-dex column, helium (40.0 $cm.s^{-1}$), 90 °C to 160 °C at 2 $°C.min^{-1}$, R_t(*S*,*S*) = 19.6 min, R_t(*R*,*R*) = 20.1 min (Figure S1).

(±)-*Trans*-1,2-cyclohex-4-enyl cyclocarbonate (***rac*-CHDC**). A solution of triethylamine (10.8 mL, 79 mmol) in THF (30 mL) was added dropwise at 0 °C to a solution of (±)-*trans*-cyclohex-4-ene-1,2-diol (4.00 g, 35 mmol) and ethyl chloroformate (7.5 mL, 79 mmol) in THF (60 mL). Once the addition completed, the reaction mixture was stirred at 23 ± 2 °C over 6 h. The mixture was next filtered to remove the formed ammonium salt, and THF was removed under vacuum. The crude product was purified by flash column chromatography (pentane/ethyl acetate: 100:0 to 80:20), and then recrystallized three times from diethyl ether to give (±)-*trans*-CHDC as thin white crystalline needles (3.43 g, 70%). M_p = 128 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 23 °C, Figure S2): δ (ppm) 5.67 (d, 2H, CH_2*CH*=*CH*CH_2), 4.27 (m, 2H, CH_2*CH*OC(=O)O*CH*CH_2), 2.64–2.70 (m, 2H, *CH*HCH=CHC*H*H), 2.40–2.48 (m, 2H, *CH*HCH=CHC*H*H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 23 °C, Figure S3): δ (ppm) 154.9 (O*C*(=O)O), 124.1 (CH_2C*H*=*CH*CH_2), 79.8 (CH_2*C*H(CH)(OC(=O))), 29.6 (*CH_2*-CH=CH*CH_2*).

***Trans*-(*R,R*)-1,2-cyclohex-4-enyl cyclocarbonate ((*R,R*)-CHDC)** was obtained similarly**.** The product was recrystallized twice before use in ROP. M_p = 128 °C, $[\alpha]_D^{20}$ = –81.5 (*c* 0.36, CH_2Cl_2); ^{1}H NMR (Figure S4) and ^{13}C NMR (Figure S5) spectra are identical to those of *rac*-CHDC.

Typical procedure for the ROP of *rac*-CHDC promoted by [(NNO)ZnEt] / BnOH. *A similar procedure was followed for the synthesis of PCHDC with $Y[N(SiMe_3)_2]_3$ or TBD as catalyst.* Typically, [(NNO)ZnEt] (4.0 mg, 9.3 µmol, 1 equiv.) was added to BnOH (1 equiv., as a stock solution in toluene) and stirred at room temperature over 15 min, just prior to the addition of *rac*-CHDC (64 mg, 0.46 mmol, 50 equiv) and the quantity of toluene necessary to reach a concentration of 4M (Table 1, entry 1). The mixture was then stirred at 60 °C over the appropriate time period (reaction times were not optimized). The polymerization was then stopped upon addition of an acetic acid solution (*ca.* 0.05 mL of a 1.6 mol.L^{-1} solution in toluene) and the volatiles removed under vacuum. After determination of the CHDC conversion by ^{1}H NMR analysis of this crude product, the resulting mixture was dissolved in CH_2Cl_2, and the polymer was purified upon precipitation (when a significant conversion could be achieved) in cold methanol, filtered and dried under vacuum. The isolated PCHC was then analysed by NMR, SEC, and DSC. ^{1}H and ^{13}C NMR spectra of PCHDC homopolymers are available in the Supporting Information (Figures S6-S11).

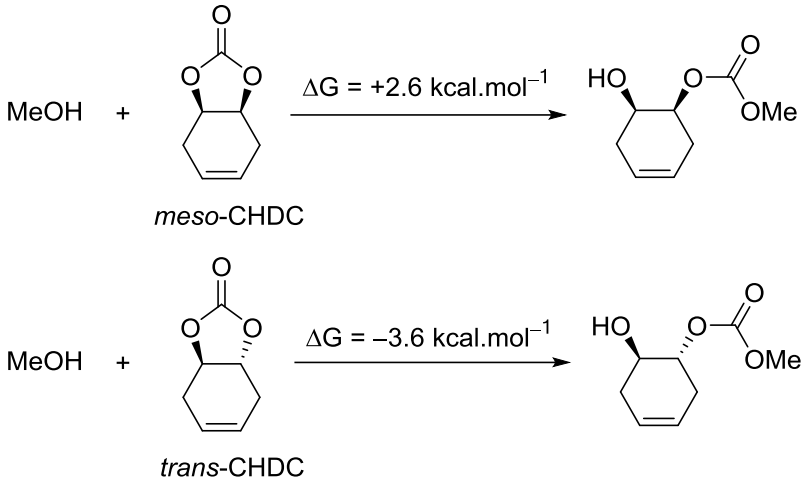
Simultaneous Copolymerization of *rac*-CHDC with *rac*-CHC or *L*-LA with [(NNO)ZnEt] / BnOH. The polymerizations were conducted as described above using a mixture of the two monomers. The P(CHC-*co*-PCHDC) and P(LLA-*co*-PCHDC) copolymers were isolated by re-precipitation with methanol from a CH_2Cl_2 solution and then analysed by ^{1}H NMR, ^{13}C NMR, SEC and DSC (see the Supporting Information).

Sequential Copolymerization of *rac*-CHC with *rac*-CHDC with [(NNO)ZnEt] / BnOH. The homopolymerization was conducted as described above for *rac*-CHDC. *Rac*-

CHC was polymerized first over 6 h. After this time period, a small aliquot was sampled under controlled atmosphere to determine the monomer conversion and the molecular mass of the formed PCHC, and *rac*-CHDC was then introduced in the reaction mixture. The reaction was continued for 3 h. The same workup as above was then applied. The P(CHC-*co*-PCHDC) and P(LLA-*co*-PCHDC) copolymers were isolated by re-precipitation with methanol from a CH_2Cl_2 solution and then analysed by ^{1}H NMR, ^{13}C NMR, SEC and DSC (see the Supporting information).

Results and Discussion

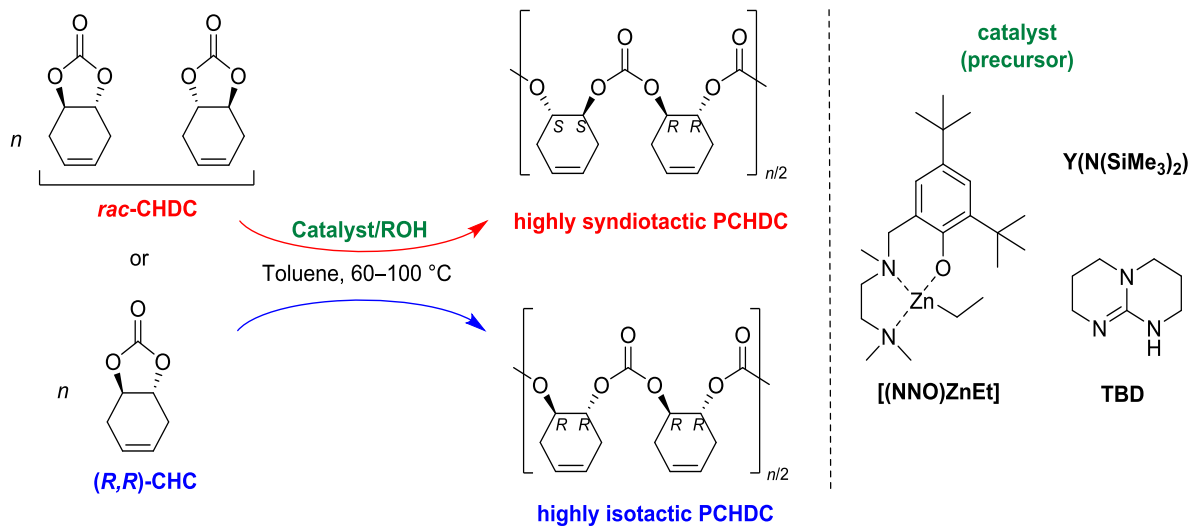
Preliminary DFT computations. In order to get a first hint, we assessed the polymerizability of the *trans* and *meso* diastereoisomers of CHDC *via* DFT computations. As for our prior work on the ROP of CHC,[13a] the ring-opening of these two molecules by methanol was used as a simple model (Scheme 2). Given the generally accepted uncertainty of ±2 kcal.mol^{-1} for DFT computations, the calculated $\Delta G°$ value of +0.8 kcal.mol^{-1} suggests that *trans*-CHDC may be thermodynamically ring-opened. In contrast, for *meso*-CHDC which is obviously less strained than the *trans* diastereomer, the clearly endergonic $\Delta G°$ value of +6.4 kcal.mol^{-1} indicates its non-polymerizability. These ring-opening energy values are unfavorably shifted from the corresponding ones determined for *trans*-CHC ($\Delta G° = -3.6$ kcal.mol^{-1}) and *meso*-CHC ($\Delta G° = +2.6$ kcal.mol^{-1}), suggesting a lower polymerizabilty of CHDC as compared to CHC;[13a] of note, the $\Delta G°_{trans}/\Delta G°_{meso}$ energy difference is similar for both CHDC and CHC (5.5–6.2 kcal.mol^{-1}). As we previously confirmed experimentally that *meso*-CHC is indeed not polymerizable in contrast to *trans*-CHC (in line with DFT computations),[13a] we thus decided to focus our experimental investigations on *trans*-CHDC.



Scheme 2. Model reactions used for DFT computations of ring-opening of *meso*- and *trans*-CHDC.

Experimental investigations on the ROP of *trans*-CHDC

Homopolymerization. Homopolymerization of *trans*-CHDC was first investigated with a series of ROP catalyst systems that previously proved to be quite efficient towards cyclic esters and carbonates, and notably *trans*-CHC. These include the binary systems based on the zinc diaminophenolate complex [(NNO)ZnEt],[21] the simple homoleptic $Y(N(SiMe_3)_2)_3$,[22] or guanidine TBD, all combined to benzyl alcohol (BnOH) or isopropyl alcohol (*i*PrOH) as co-initiator (Scheme 3). In order to assess the stereoselectivity of the polymerizations, the ROP of *trans*-(*R*,*R*)-CHDC was investigated in parallel to that of the *trans-racemic* monomer. *Trans*-(*R*,*R*)-CHDC was first prepared by reaction of ethyl chloroformate with 1,2-cyclohex-4-enediol enantio-enriched (83% ee) through a resolution using (*S*)-(+)-*O*-acetyl-mandelic acid (refer to the Experimental section).



Scheme 3. ROP of *trans*-CHDC (*racemic* or (*R*,*R*)) towards highly isotactic PCHDC mediated by metal- or organo-based catalyst systems.

Table 1. ROP of *trans*-CHDC (*racemic* or (*R*,*R*)) mediated by metal- or organo-based catalyst systems.

Entry	Catalyst	ROH	$[CHDC]_0/[Cat.]_0/[ROH]_0$	Temp. (°C)	Time (h)	Conv.[c]	$M_{n,theo}$[d] (g.mol^{-1})	M_n[e] (g.mol^{-1})
1[a]	[(NNO)ZnEt]	BnOH	50:1:1	60	120	87	6200	4000/6300
2[a]	[(NNO)ZnEt]	BnOH	50:1:1	80	6	26[f]	1900	nd[f]
3[a]	[(NNO)ZnEt]	BnOH	100:1:1	80	120	61	8600	6100
4[a]	TBD	BnOH	100:1:1	80	120	37	5200	3800
5[a]	$Y[N(SiMe_3)_2]_3$	*i*PrOH	100:1:1	80	120	5[f]	800	nd[f]
6[a]	[(NNO)ZnEt]	BnOH	100:1:1	100	16	21[f]	3000	nd[f]
7[b]	[(NNO)ZnEt]	BnOH	50:1:1	60	72	25	1900	3500[g]

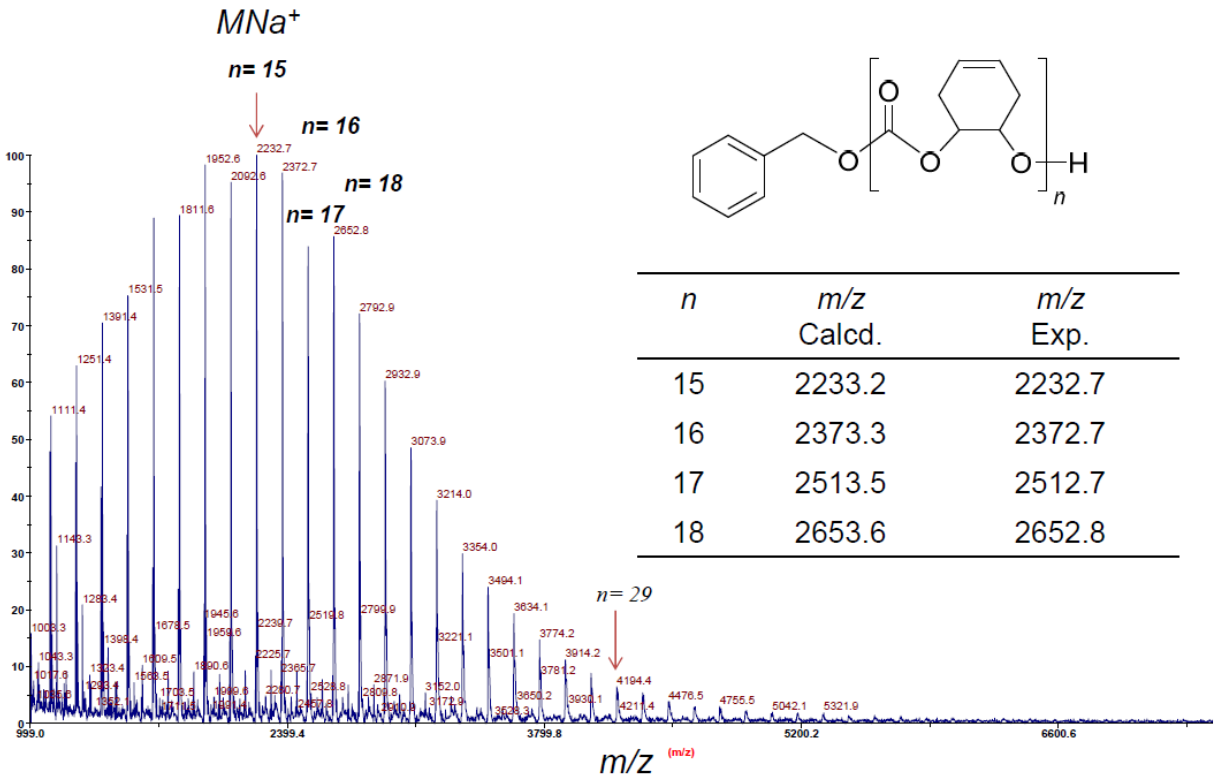
[a] *Trans-racemic* monomer. [b] *Trans*-(*R*,*R*) (83% ee) monomer. [c] Monomer conversion as determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Theoretical molar mass calculated from the relation: $M_{n,theo} = ([CHDC]_0/[ROH]_0) \times Conversion_{CHDC} \times M_{CHDC} + M_{ROH}$, with M_{CHDC} = 140 g.mol^{-1}, M_{BnOH} = 108 g.mol^{-1} and M_{iPrOH} = 60 g.mol^{-1}. [e] $M_{n,SEC}$ as determined by SEC in $CHCl_3$ calibrated *vs.* polystyrene standards with peak mass values of main signals in (multimodal) distribution(s), unless otherwise stated; see the Supporting Information. [f] Oily material which could not be isolated. [g] $M_{n,NMR}$ as determined from terminal groups.

Polymerizations were run in toluene, at high monomer concentration ($[CHDC]_0$ = 4 M), in the temperature range 60–100 °C (Table 1). As anticipated from the DFT

computations, *trans*-CHDC is significantly less reactive than *trans*-CHC, whichever the catalyst system used. With [(NNO)ZnEt]/BnOH, which proved the most active among the three systems investigated, the reaction proceeded at 60 °C but required 5 days to convert 43 equiv. (apparent turnover frequency, TOF_{app} = 0.36 h^{-1}; entry 1). This is *ca*. 2 orders of magnitude lower than for *trans*-CHC under comparable conditions (TOF_{app} = 30–150 h^{-1}).[13a] Raising the temperature to 80 or 100 °C hardly increased the activity (TOF_{app} = 0.51 h^{-1}; entry 3 and TOF_{app} = 1.3 h^{-1}; entry 6, respectively). This is most likely due to the proximity to the ceiling temperature of PCHDC.[23] Although the detailed kinetics were not investigated, the ROP of (*R*,*R*)-CHDC appeared twice slower than that of the *racemic* monomer (TOF_{app} = 0.17 *vs.* 0.36 h^{-1}; entries 1 *vs.* 7). The commercially available, simple organic guanidine TBD catalyst combined with BnOH showed a lower activity than the zinc system (entry 4); this reactivity trend is in line with the results for *trans*-CHC.[13a] On the other hand, the yttrium-based system showed very poor productivity (entry 5).

When poor monomer conversions were reached, such as with the latter sluggish catalyst, only oily materials which could not be isolated were produced. Higher molar mass P(*rac*-CHDC)s (entries 1, 3 and 4) and P(*R*,*R*-CHDC) (entry 7) were isolated as white powders by precipitation from CH_2Cl_2/MeOH (1:15 *v/v*). These polymers are soluble in chlorinated solvents (CH_2Cl_2, $CHCl_3$) at room temperature and are insoluble in hydrocarbons (toluene, pentane) and ethers (THF, Et_2O). They were characterized by ^1H and ^{13}C NMR spectroscopy, MALDI-ToF mass spectrometry and DSC analysis.

The MALDI-ToF mass spectrum of a PCHDC prepared with the [(NNO)ZnEt]/BnOH catalytic system showed a single major population of macromolecules with the expected architecture of regular CHDC repeat units with benzyloxy and hydroxy end-groups (Figure 1); no evidence of decarboxylation products was observed.[24]

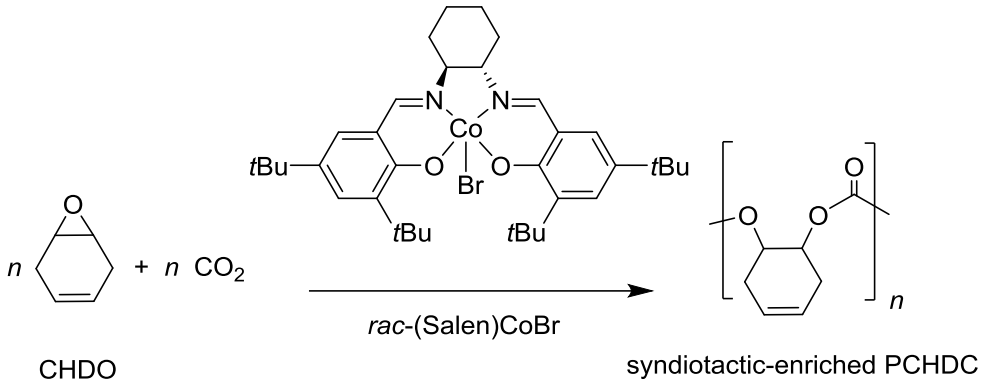


n	*m/z* Calcd.	*m/z* Exp.
15	2233.2	2232.7
16	2373.3	2372.7
17	2513.5	2512.7
18	2653.6	2652.8

Figure 1. MALDI-ToF mass spectrum of a PCHDC prepared by ROP of *trans-rac*-CHDC mediated by the [(NNO)ZnEt]/BnOH catalytic system (Table 1, entry 3) (the detected ions and calculated masses correspond to $[C_6H_5CH_2O(C_7H_8O_3)_nH].Na^+$).

The ^{1}H NMR spectra of P(*rac*-CHDC) and P(*R,R*-CHDC), synthesized by ROP of *trans-rac*-CHDC and *trans*-(*R,R*)-CHDC, respectively, in the presence of [(NNO)ZnEt] / BnOH or TBD/BnOH catalyst systems, showed the expected signals corresponding to the main chain olefinic, methine and methylene hydrogens (Figures S6, S8 and S10). No other signals which may reflect partial decarboxylation or other side processes could be noticed. For low molecular samples, the signals for the terminal benzyloxy group could generally[25] be observed (see *e.g.* Figures S10, S11), in agreement with the mass spectrometry results (*vide supra*). Also, the backbone signals in the three spectra are equally sharp, suggesting a well-defined microstructure in all samples.

Detailed microstructural analysis of the recovered PCHDCs was performed by $^{13}C\{^{1}H\}$ NMR spectroscopy (Figures 2 and S7, S9, S11 and S13). For comparison purposes, we also prepared a PCHD by copolymerization of CHDO and CO_2 in the presence of a catalyst which is known to provide slightly syndiotactic PCHCs from CHO and CO_2, that is *rac*-(Salen)CoBr (Scheme 4).[15a,26] The carbonyl region of the NMR spectra is indicative of the tacticity of the PCHDCs. The polymer recovered from ROP of *trans*-(*R,R*)-CHDC features a unique sharp resonance at δ 154.0 ppm assigned to pure isotactic PCHDC (Figures 2c and S11). This signal is also observed as the less intense one in the $^{13}C\{^{1}H\}$ NMR spectrum of the PCHDC prepared *via* ROCOP of CHDO and CO_2 with *rac*-(Salen)CoBr, in addition to a major, broad signal centered at δ 153.6 ppm, assigned to the syndiotactic sequences (*rr*, likely overlapping with *mr*) (Figures 2d and S13). Most interestingly, the latter resonance at δ 153.6 ppm is the only one observed, but then as a quite sharp signal, in the spectra of the PCHDCs prepared from *trans*-*rac*-CHDC, either with the [(NNO)ZnEt]/BnOH or TBD/BnOH catalyst systems (Figures 2a,b). This indicates that these polymers are highly syndiotactic PCHDCs. This is in striking contrast with the ROP of *trans*-*rac*-CHC which provided with the same catalyst systems PCHCs with 64–76% isoselectivity.[13a] The high syndioselectivity implies a type of "enantiomer-differentiating polymerization". Its origin is still unclear but the striking difference observed between the behavior of *rac*-CHDC and that of *rac*-CHC indicates that there are subtle effects imparted by the six-membered ring fused with the 5-membered cyclocarbonate.



Scheme 4. Preparation of slightly syndiotactic-enriched PCHDC *via* ROCOP of CHDO/CO_2.[15a]

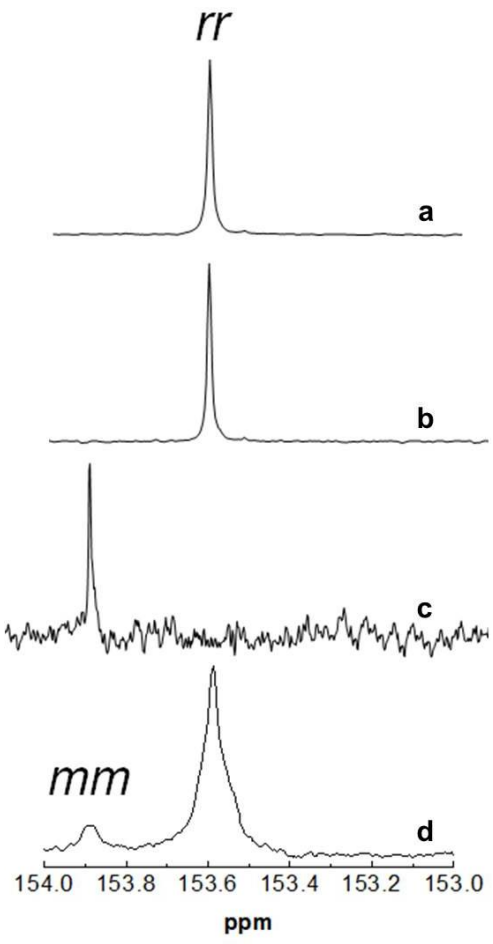


Figure 2. Detail of the carbonyl region of the $^{13}C\{^1H\}$ NMR spectra (100 MHz, $CDCl_3$, 23 °C) of PCHDCs synthesized by: [a] ROP of *trans*-*rac*-CHDC with [(NNO)ZnEt]/BnOH (Table 1, entry 3), [b] ROP of *trans*-*rac*-CHDC with TBD/BnOH (Table 1, entry 4), [c] ROP

of *trans*-(*R*,*R*)-CHDC with [(NNO)ZnEt]/BnOH (Table 1, entry 7), and [d] ROCOP of CHDO/CO_2 with *rac*-(Salen)CoBr.

The PCHDCs which could be recovered as solids were analyzed by SEC in $CHCl_3$ (as they are completely insoluble in THF). These analyses proved however erratic as the polymers were not always eluted, and the few chromatograms obtained often appeared bi/multimodal (Figures S14 and S15) for reasons we could not explain, possibly linked to the difficult elution and/or absorption of PCHDC on the columns. Similar problems were encountered previously with highly syndiotactic poly(3-hydroxybutyrate)s;[27] note that PCHDCs obtained by ROCOP of CHDO with CO_2, which are just slightly syndiotactic-enriched (Figure 2d) could be analyzed by SEC in THF.[15] Nevertheless, the SEC molar masses thus determined were roughly in agreement with the calculated ones. We assume that these SEC results do not reflect the real control achieved in the ROP of CHDC, as further evidenced by convincing SEC data obtained on CHDC copolymers (*vide infra*).

The thermal characteristics of syndiotactic PCHDCs prepared from *rac*-CHDC were determined by DSC (Figure 3). Independently of the catalyst used for their preparation ([(NNO)ZnEt]/BnOH or TBD/BnOH), these materials featured a crystallization at T_c = *ca.* 267 °C and a melting transition at T_m = *ca.* 318 °C; however, they already start to decompose at this temperature (Figure 3).[28] Slightly syndiotactic PCHDCs produced *via* ROCOP of CHDO and CO_2 exhibited no melting transition, only a glass transition at T_g = 115–123 °C.[15] This glass transition was not clearly observed in the syndiotactic PCHDCs prepared by ROP of *rac*-CHDC.

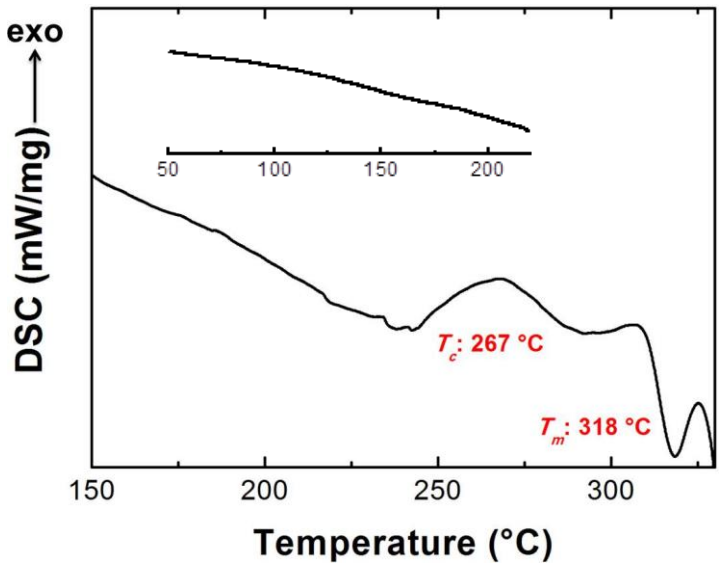
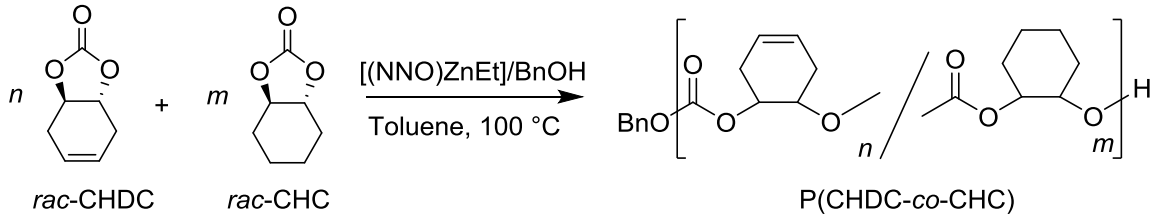


Figure 3. DSC thermogram (first heating cycle; heating rate = 10 °C.min^{-1}; argon flow) of a PCHDC prepared from the ROP of *trans-racemic*-CHDC (Table 1, entry 3).

Copolymerization of rac-CHDC. In order to explore the ability of *rac*-CHDC to copolymerize and eventually characterize the resulting materials, both simultaneous and sequential copolymerizations were attempted. Two cyclic ester comonomers were selected for this purpose: *trans*-cyclohexene carbonate (*rac*-CHC), for its obvious relationship with *rac*-CHDC, and *L*-lactide (*L*-LA), a monomer of topical interest.

Simultaneous Copolymerizations of rac-CHC and rac-CHDC: Preparation of Random P(CHC-co-CHDC) Copolymers. The simultaneous copolymerization of *rac*-CHC and *rac*-CHDC was performed in toluene at 100 °C with the [(NNO)ZnEt]/BnOH system (Scheme 5, Table 2). *Rac*-CHDC proved to be less reactive than *rac*-CHC, in line with the results of the DFT computations and homopolymerization experiments. The resulting P(CHC-*co*-CHDC) copolymers are insoluble in methanol but quite soluble in THF, $CHCl_3$, CH_2Cl_2 and were readily analyzed by SEC in THF. In contrast to the erratic SEC analyses of PCHDC homopolymers run in $CHCl_3$, the P(CHC-*co*-CHDC) copolymers all featured a monomodal

and symmetric trace (Figure S16). The number-average molar masses determined *vs.* polystyrene standards (uncorrected for a possible difference in hydrodynamic radii) were close to the theoretical values and the dispersity remained quite narrow, even after 16 h of reaction at this temperature (Table 2).



Scheme 5. Simultaneous copolymerization of *rac*-CHDC and *rac*-CHC

Table 2. Simultaneous copolymerization of *rac*-CHDC and *rac*-CHC mediated by [(NNO)ZnEt]/BnOH systems in toluene at 100 °C.

Entry	$[CHDC]_0/[CHC]_0/[Zn]_0/[BnOH]_0$	Time (h)	*rac*-CHDC Conv.[a] (%)	*rac*-CHC Conv.[a] (%)	$M_{n,theo}$[b] ($g.mol^{-1}$)	$M_{n,NMR}$[c] ($g.mol^{-1}$)	$M_{n,SEC}$[d] ($g.mol^{-1}$)	$Đ_M$
1	50:50:1:1	3	38	66	7500	7200	5000	1.12
2	50:50:1:1	16	50	85	9600	11 000	8400	1.18

[a] Calculated from the ^{1}H NMR of the crude product. [b] Theoretical molar mass value of P(CHDC-*co*-CHC) calculated from the relation: $M_{n,theo} = M_{CHDC} \times [CHDC]_0/[BnOH]_0 \times conv.(CHDC) + M_{CHC} \times [CHC]_0/[BnOH]_0 \times conv.(CHC) + M_{BnOH}$, with M_{CHDC} = 140 $g.mol^{-1}$, M_{CHC} = 142 $g.mol^{-1}$, M_{BnOH}= 108 $g.mol^{-1}$. [c] NMR molar mass of the copolymer calculated from the integral value ratio of the signals of OBn end-group hydrogens to methine/methylene hydrogens of the monomers. [d] Experimental number average molar mass (uncorrected) and dispersity values determined by SEC in THF at 30 °C using polystyrene standards.

The ^{1}H NMR spectra of P(CHC-*co*-CHDC) copolymers show readily distinguishable signals for PCHC and PCHDC units, notably those corresponding to the main chain methine hydrogens at δ 4.63 and 4.93 ppm, respectively, and the olefinic hydrogens of PCHDC at δ 5.56 ppm (Figure 4). No signal that could reflect decarboxylation was observed. Besides, the signals of the benzyloxy end-groups were clearly identified at δ 5.13 and 7.35 ppm. This enabled to determine the molar masses by NMR, which were found in good agreement with

the SEC and theoretical values (Table 2). The carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectrum showed several broadened signals at δ 153.4–153.9 ppm (Figure 5), suggesting a random enchainment of CHDC and CHC units (Figure 5).

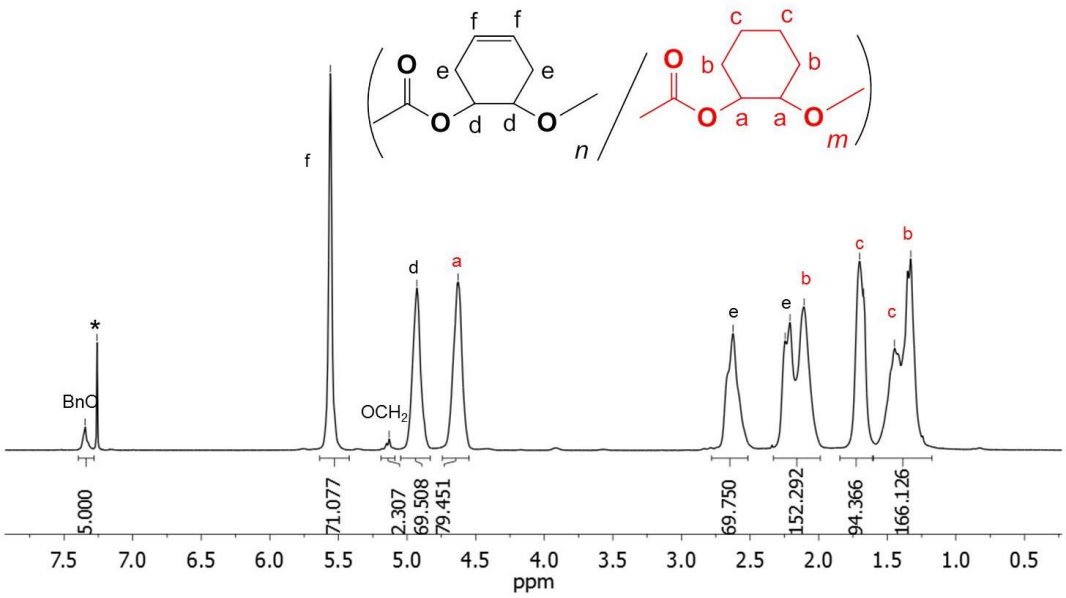


Figure 4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 23 °C) of a P(CHDC-*co*-CHC) prepared by ROP of *rac*-CHDC and *rac*-CHC with the [(NNO)ZnEt]/BnOH system (Table 2, entry 2) (* stands for residual $CHCl_3$ resonances).

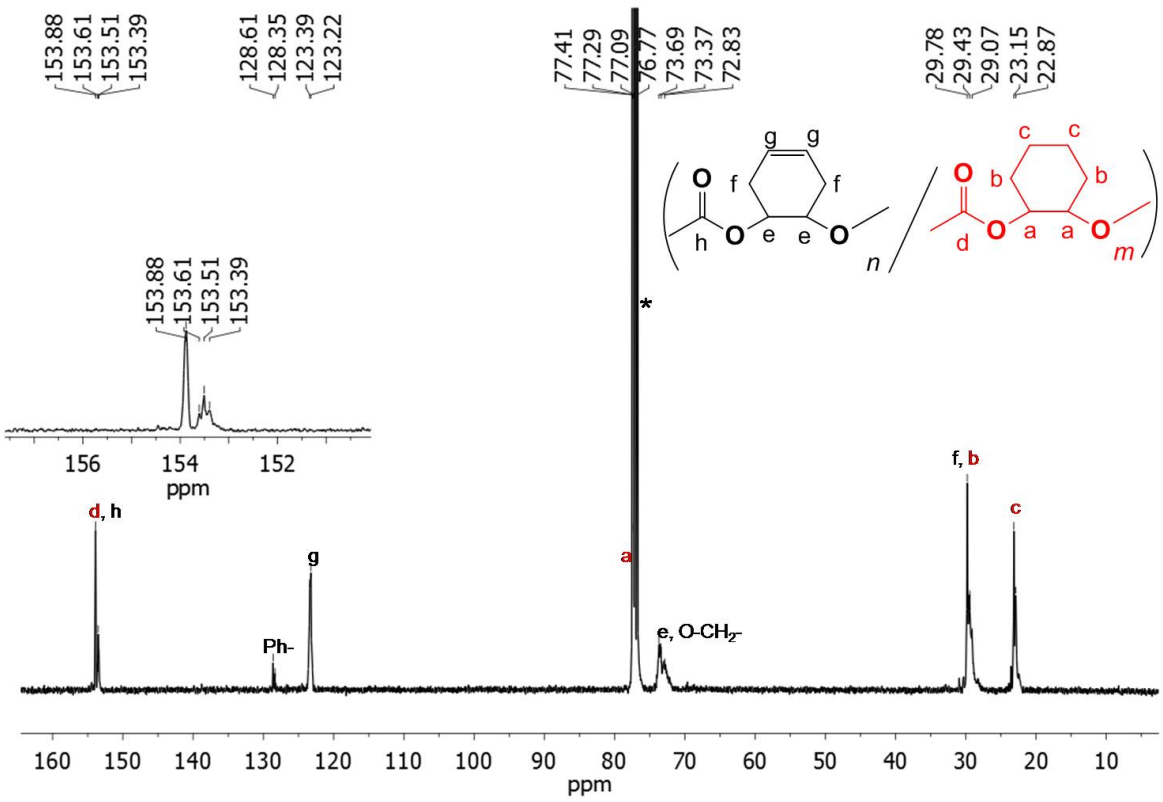
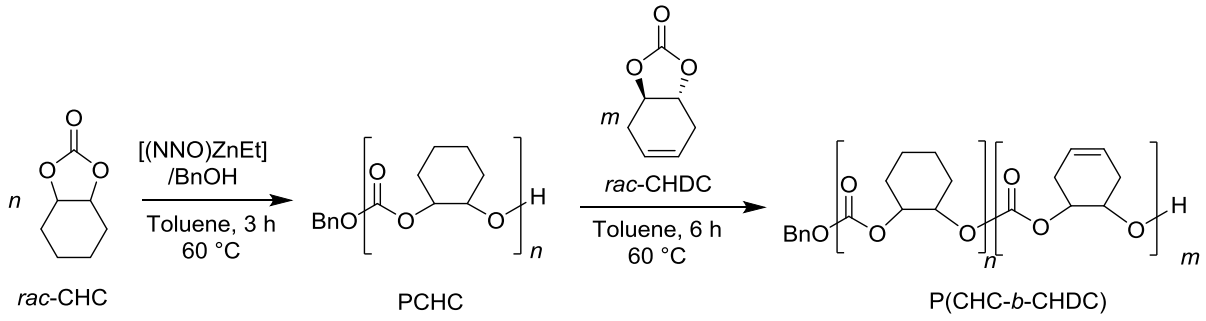


Figure 5. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 23 °C) of a P(CHC-*co*-CHDC) prepared by ROP of *rac*-CHC and *rac*-CHDC with the [(NNO)ZnEt]/BnOH system (Table 2, entry 2) (* stands for residual $CHCl_3$ resonances).

The DSC trace (Figure S17) of these P(CHDC-*co*-CHC) copolymers showed a single glass transition at T_g = 102 °C. This value is lower than that reported for PCHDC and PCHC homopolymers (T_g = *ca.* 115–123 °C[15] and 121 °C,[13] respectively), but similar to that observed in polycarbonates derived from the terpolymerization of CHO, CHDO and CO_2.[15a] No melting transition was detected, which is consistent with the above mentioned random rather than blocky structure of these copolymers.

Sequential Copolymerization of rac-CHC and rac-CHDC: Preparation of Block P(CHC-b-CHDC) Copolymers. The preparation of a diblock P(CHC-*b*-PCHDC) copolymer

was attempted via the sequential polymerization of *rac*-CHC followed by that of *rac*-CHDC in the presence of [(NNO)ZnEt]/BnOH system at 60 °C in toluene (Scheme 6; Table 3). The reaction proceeded with almost complete conversion of *rac*-CHC and *ca*. 50% conversion of *rac*-CHDC; even though this would lead to a larger conversion of *rac*-CHDC, the reaction time for the second stage was not further extended to avoid side processes (transcarbonatation, etc). Thanks to the ^{1}H NMR signals of the benzyloxy end-groups (δ 5.06 and 7.28 ppm), the molar mass could be monitored and was shown to increase expectedly from the first ($M_{n,NMR}$ = 6600 g.mol^{-1}) to the second block ($M_{n,NMR}$ = 10 800 g.mol^{-1}). In fact, the ^{1}H and ^{13}C NMR spectra of this copolymer (Figures S18 and S19), isolated after precipitation in methanol, resemble much that of the random copolymer obtained by simultaneous copolymerization (*vide supra*). However, the materials could be differentiated by their thermal properties. The DSC trace of the P(CHC-*b*-PCHDC) copolymer features, in addition to a glass transition at T_g = 109 °C similar to that of the random copolymer, a melting transition at T_m = 262 °C (ΔH_m = 22.1 J.g^{-1}) assignable to the syndiotactic PCHDC block (Figure S20).



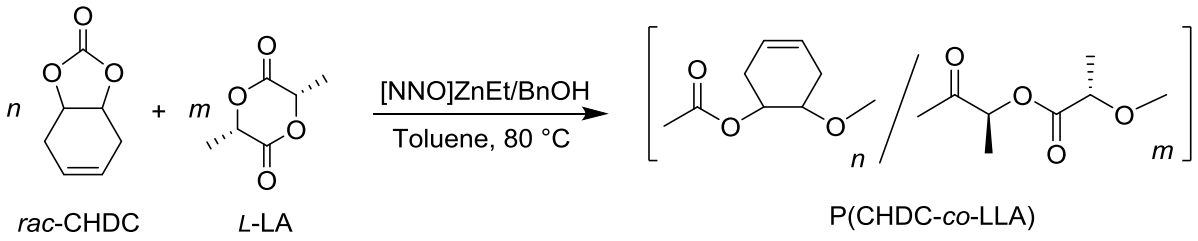
Scheme 6. Sequential copolymerization of *rac*-CHC followed by *rac*-CHDC.

Table 3. Sequential copolymerization of *rac*-CHC followed by *rac*-CHDC mediated by the [(NNO)ZnEt]/BnOH system at 60 °C (Scheme 6).

				PCHC		PCHC-*b*-PCHDC			
Entry	[*rac*-CHC]$_0$/ [*rac*-CHDC]$_0$/ [Zn]$_0$/[BnOH]$_0$	CHC Conv.[a] (%)	CHDC Conv.[a] (%)	$M_{n,theo}$[b] (g.mol^{-1})	$M_{n,NMR}$[c] (g.mol^{-1})	$M_{n,theo}$[d] (g.mol^{-1})	$M_{n,NMR}$[c] (g.mol^{-1})	$M_{n,SEC}$[e] (g.mol^{-1})	$Đ_M$[e]
1	50:50:1:1	95	53	6800	6600	10 600	10 800	9800	1.22

[a] Calculated from the ^{1}H NMR of the crude product at the intermediary and final stages. [b] Theoretical molar mass calculated from the relation: $M_{n,theo}$= ([CHC]$_0$/[BnOH]$_0$) × Conv.$_{CHC}$ × M_{CHC} + M_{BnOH}, with M_{CHC} = 142 g.mol^{-1} and M_{BnOH} = 108 g.mol^{-1}. [c] NMR molar mass of the copolymer calculated from the integral value ratio of the signals of OBn end-group hydrogens to methine / methylene hydrogens of the monomers. [d] Theoretical molar mass value of P(CHC-*co*-CHDC) calculated from the relation: $M_{n,theo}$ = M_{CHC} × [CHC]$_0$/[BnOH]$_0$× conv.$_{CHC}$ + M_{CHDC} × [CHDC]$_0$/[BnOH]$_0$× conv.$_{CHDC}$ + M_{BnOH}, with M_{CHDC} = 140 g.mol^{-1}. [e] Experimental number average molar mass (uncorrected) and dispersity values determined by SEC in THF at 30 °C using polystyrene standards.

Simultaneous Copolymerization of rac-CHDC and L-LA: Preparation of Random P(CHDC-co-LLA) Copolymers. Random copolymerizations of *rac*-CHDC and *L*-LA in various ratios were carried out with the [(NNO)ZnEt]/BnOH system at 80 °C in toluene (Scheme 7, Table 4). Figure 6 shows the representative SEC trace of a P(CHDC-*co*-LLA) copolymer with a $M_{n,SEC}$ of 17 100 g.mol^{-1} and a dispersity of 1.39 (Table 4, entry 2). The monomodal, symmetric SEC trace reveals that both monomers copolymerize quite effectively, although monitoring of monomers' conversion indicate that, as anticipated, *L*-LA is much more reactive than *rac*-CHDC.



Scheme 7. Simultaneous copolymerization of *rac*-CHDC and *L*-LA

Table 4. Simultaneous copolymerization of *rac*-CHDC and *L*-LA mediated by the [(NNO)ZnEt]/BnOH system at 80 °C.

Entry	[*rac*-CHDC]$_0$/ [*L*-LA]$_0$/ [Zn]$_0$/[BnOH]$_0$	Time (h)	*rac*-CHDC Conv.[a] (%)	*L*-LA Conv.[a] (%)	$M_{n,theo}$[b] (g.mol^{-1})	$M_{n,NMR}$[c] (g.mol^{-1})	$M_{n,SEC}$[d] (g.mol^{-1})	$Đ_M$	T_g (°C)
1	50:150:1:1	6	77	100	27 100	23 200	8800	1.35	nd
2	100:100:1:1	24	74	100	24 900	18 600	17 100	1.39	74
3	150:50:1:1	6	56	100	19 100	17 400	6300	1.43	87

[a] Calculated from the ^{1}H NMR of the crude product. [b] Theoretical molar mass value of P(CHDC-*co*-LLA) calculated from the relation: $M_{n,theo} = M_{rac\text{-CHDC}} \times [rac\text{-CHDC}]_0/[BnOH]_0 \times conv._{rac\text{-CHDC}} + M_{LLA} \times [LLA]_0/[BnOH]_0 \times conv._{LLA} + M_{BnOH}$ with $M_{rac\text{-CHDC}}$ = 140 g.mol^{-1}, M_{LLA} = 144 g.mol^{-1}, and M_{BnOH}= 108 g.mol^{-1}. [c] NMR molar mass value of P(CHDC-*co*-LLA) calculated from the integral value ratio of the signals of OBn end-group hydrogens to internal methine or methylene hydrogens. [d] Experimental number average molar mass (uncorrected) and dispersity values determined by SEC in THF at 30 °C using polystyrene standards. [e] Glass transition temperature determined by DSC (2nd heating cycle, 10 °C.min^{-1}).

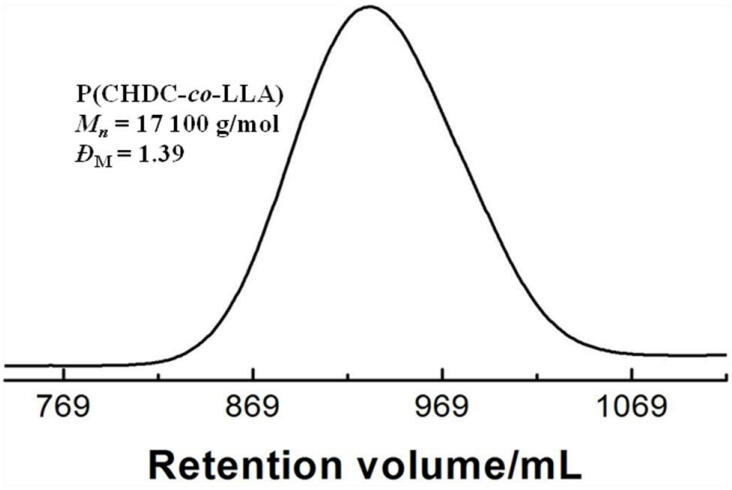


Figure 6. SEC trace (THF, 30 °C) of a P(CHDC-*co*-LLA) prepared by simultaneous copolymerization of *rac*-CHDC and *L*-LA with the [(NNO)ZnEt]/BnOH system (Table 4, entry 2).

The ^{1}H and ^{13}C{^{1}H} NMR spectra of these P(CHDC-*co*-LLA) copolymers show the expected signals for the two monomers (Figures S21 and S22). The ^{1}H signals for the phenyl hydrogens of the benzyloxy end-groups can be discerned and then used to determine the molar mass. The $M_{n,NMR}$ values thus determined agreed well with the theoretical $M_{n,theo}$ ones. The (uncorrected) $M_{n,SEC}$ values differ much according to the relative amount of CHDC-LLA units, suggesting quite different hydrodynamic volumes.

The DSC traces of the copolymers feature only a glass transition; no melting transition was observed. The copolymers with a significant fraction of CHDC have a higher T_g (74 °C, entry 2; 87 °C, entry 3; Figures S23 and S24) than that of the PLLA homopolymer (*ca.* 60–65 °C).

Conclusions

We have shown for the first time that *trans*-cyclohexadiene carbonate (CHDC) can be polymerized with regular ROP catalyst systems made of a zinc-based complex or a guanidine, associated with an alcohol. As anticipated by DFT computations, its reactivity is however significantly lower than that of *trans*-cyclohexene carbonate (CHC). This is exemplified both in homopolymerizations of CHDC and copolymerizations of CHDC with CHC and *L*-LA. The [(NNO)ZnEt]/BnOH system proved to be a more active catalyst than TBD for these ROP reactions, which proceeded without decarboxylation. Quite interestingly, even though no chiral catalyst was used, ROP of *rac*-CHDC proceeded in a stereoselective fashion: highly syndiotactic PCHDC was obtained with both the zinc and TBD-based catalysts, as revealed by ^{13}C NMR studies. ROP of *rac*-CHDC thus provides a new entry toward engineering polycarbonates that is much complementary to ROCOP of cyclohexadiene oxide with CO_2. Indeed, the latter route thus far only yielded atactic or slightly syndiotactic PCHDC.[15] The high syndioselectivity observed in the ROP of *rac*-CHDC contrasts with the modest isoselectivity (P_m = *ca.* 75%) for the ROP of *rac*-CHC with the same catalyst systems.[13a] This evidences subtle effects induced by the adjacent ring fused to the 5-membered cyclocarbonate moiety.

Acknowledgements

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Supporting information includes NMR, SEC and DSC data for monomer and polymers. This information is available free of charge via the Internet.

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