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From epoxide to cyclodithiocarbonate telechelic polycyclooctene through chain-transfer ring-opening metathesis polymerization (ROMP): precursors to non-isocyanate polyurethanes (NIPUs)

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Abstract

Telechelic polycyclooctenes (PCOEs) have been successfully synthesized by ring-opening metathesis polymerization (ROMP)/cross metathesis (CM) of cyclooctene (COE) using Grubbs' 2nd-generation catalyst (**G2**) in the presence of epoxide-functionalized chain-transfer agents (CTAs). The monofunctional epoxide oxiran-2-ylmethyl acrylate CTA (**1**) afforded the isomerized α-(glycidyl alkenoate),ω-propenyl functional (IMF) PCOEs. The use of 1,4-benzoquinone (BZQ) as additive completely inhibited the C=C isomerization process, thereby leading selectively to α-(glycidyl alkenoate),ω-vinyl telechelic (MF) PCOE. On the other hand, difunctional epoxide CTAs, bis(oxiran-2-ylmethyl) fumarate (**3**), bis(oxiran-2-ylmethyl) maleate (**4**), bis(oxiran-2-ylmethyl) (*E*)-hex-3-enedioate (**5**), and (*Z*)-1,4-bis(oxiran-2-ylmethoxy)but-2-ene (**6**), selectively afforded the corresponding α,ω-di(glycidyl alkenoate) telechelic PCOEs (DF), along with minor amounts of cyclic nonfunctional (CNF) PCOE. In presence of these difunctional symmetric CTAs, the mechanism is proposed to proceed through a tandem one-pot CM/ROMP/ring-closing metathesis (RCM) approach. CM was more effective with *Z*- than *E*-configurated CTAs (**4** > **6** >> **3** >> **5**), regardless of the presence of a methylene group in-between the C=C double bond and the glycidyl moiety. Subsequent dithiocarbonatation of the α,ω-diepoxide telechelic PCOEs upon reaction with CS_2 in the presence of LiBr quantitatively afforded the first examples of bis(cyclodithiocarbonate) end-functional PCOEs. Ensuing aminolysis of the bis(cyclodithiocarbonate) telechelic PCOEs with the polyether (triethyleneglycol) diamine JEFFAMINE EDR-148 quantitatively afforded, at room temperature without any added catalyst, the desired poly(mercaptothiourethane)s NIPUs, as evidenced from FTIR spectroscopy, TGA and DSC analyses.

Keywords: Chain-transfer agent, cyclodithiocarbonate, epoxide, NIPU, polycyclooctene, polyurethane, ring-opening metathesis polymerization (ROMP), telechelic

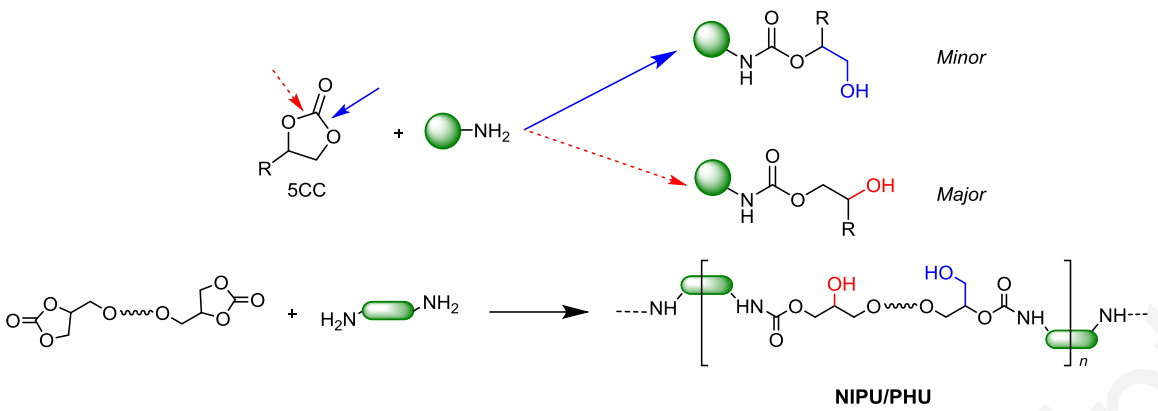
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Introduction

Conventional polyurethanes (PUs) are widely used in many applications such as foams, paintings, adhesives, or coatings.[1,2,3,4,5] Classically, PUs are synthesized from the polyaddition of a diol (or polyol) with a diisocyanate (or polyisocyanate) in the presence of a catalyst.[6,7,8,9] However, isocyanates require hazardous and toxic phosgene for their manufacture, and they are considered as toxic, hence limiting their use, in particular according to REACH European regulations. Current academic and industrial research thus aims at establishing safer and "greener" alternative routes to more environmentally friendly PUs. These more sustainable approaches mainly include the use of bio-based isocyanates, the valorization of renewable vegetable oils (natural oil polyols) or CO_2 feedstocks, and isocyanate-free methods. Among the latter ones, the aminolysis of a bis(cyclocarbonate) compound with a di- or polyamine to form non-isocyanate PUs (NIPUs) is nowadays the most investigated and promising strategy.[10,11,12,13,14,15,16,17,18]

Although six-, seven- and eight-membered cyclocarbonates react more readily with amines than five-membered cyclocarbonates (5CCs),[19,20,21,22,23] the latter have been more extensively used as they can be easily prepared in high yields and stored over long periods of time due to their high stability. Polyaddition between 5CCs and amines, typically bi-functional monomers, leads to polyhydroxyurethanes (PHUs) featuring both primary and secondary alcohols at the β-carbon atom of the urethane moiety, as depicted in Scheme 1.[4–17,24,25,26]

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Scheme 1. Typical aminolysis of a five-membered bis(cyclocarbonate).

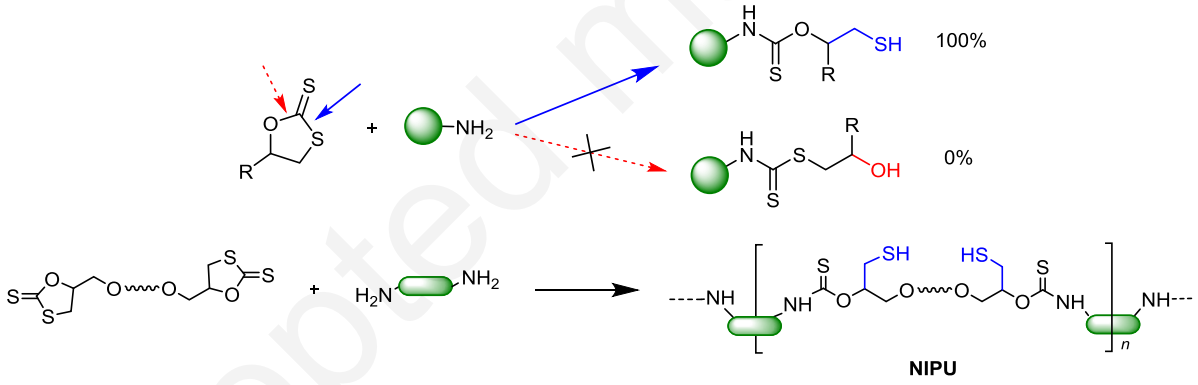
One first synthetic approach towards PHUs/NIPUs we have been investigating relies on the post-polymerization chemical modification of telechelic precursors such as α,ω-dihydroxy telechelic polycarbonate, polyesters or polyolefins, into their corresponding 5CC-functionalized polymers; this eventually enabled to reach high molar mass NIPU materials ($M_{n,SEC}$ up to 68 100 g.mol^{-1}).[27,28] Another more straightforward route we have been exploring towards the desired 5CC telechelic precursors of NIPUs relies on the direct synthesis of 5CC end-capped polymers through the ring-opening metathesis polymerization (ROMP) of a cyclic olefin using 5CC-based chain transfer agents (CTAs).[29,30] Indeed, the metathesis pathway enables, via bifunctional symmetric alkene CTAs (methacrylate, epoxide, carboxylate, acetoxy, amino, carbonate, hydroxy, halide and pseudo-halide, trialkoxysilyl), to access to well-defined telechelic polyolefins; as evidenced by Grubbs[31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48] later on by Hillmyer.[49,50,51,52,53,54,55,56,57] and recently by ourselves.[58,59] The resulting telechelic polyolefins next mainly served as macroinitiators towards the preparation of ABA triblock copolymers.

One drawback of the 5CCs is their high thermodynamic stability. Despite that several parameters can be tuned to improve the carbonate/amine reaction,[12,28] major current issues to tackle are the low reactivity of 5CCs at room temperature, the required presence of a catalyst,

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and the reaching of high molar mass polymers in relation with the ability to strictly control the functionality of the reactive telechelic precursors (both carbonate and amine).

Five-membered cyclothiocarbonates are promising, more reactive alternatives to their corresponding 5CC analogues. Endo and coworkers evidenced that the polyaddition of bis(cyclothiocarbonate)s with diamines under mild conditions (30 °C) afforded PUs featuring thiourethane groups along the polymer backbone.[60] The poly(mercaptothiourethane)s resulting from the polyaddition of bifunctional five-membered cyclodithiocarbonates (DTC) with diamines are then exempt of hydroxyl groups. On the other hand, the pendant thiol functions of the dithiourethane moieties can be advantageously crosslinked by oxidation into disulfide linkages, thus affording polymers with improved mechanical properties (Scheme 2).[61,62,63,64,65,66]



Scheme 2. Typical aminolysis of a five-membered bis(cyclodithiocarbonate).

In the present work, we expand our approach to NIPUs via the ROMP/cross metathesis (CM) strategy using Grubbs' second generation catalyst and epoxide-based CTAs to prepare α,ω-epoxide telechelic poly(cyclooctene)s (PCOEs); these next served as precursors to the corresponding α,ω-DTC telechelic PCOEs. Indeed, our preliminary investigations revealed that the direct approach consisting in using DTC-based CTAs in ROMP/CM could not be implemented due to catalyst deactivation upon its reaction with the

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thiol ring (Scheme S1).[67] Whereas monofunctional epoxide-based CTAs gave linear PCOEs end-capped by epoxide and vinyl groups, the symmetric epoxide-difunctional CTAs selectively afforded the desired α,ω-diepoxide functionalized PCOEs, possibly with some cyclic polyolefin, through a ROMP/ring-closing metathesis (RCM)/CM approach (Schemes 3, S2–S4). These diepoxide telechelic PCOEs complement the (to our knowledge) very rare such polyolefin examples previously reported from the ROMP of cyclooctadiene (COD),[39] from the acyclic diene metathesis of 1,9-decadiene with epoxide-containing monoolefins,[68] or from the chemical modification of a prepolymer.[69] Subsequent reaction of the PCOE epoxide end-functions with CS_2 smoothly and quantitatively afforded the five-membered bis(cyclodithiocarbonate) telechelic PCOEs, which successfully afforded poly(mercaptothiourethane) NIPUs following an ensuing aminolysis (Schemes 4–5). The polymers were thoroughly characterized by NMR, FTIR, DSC, TGA and MALDI-ToF MS.

Experimental section

Materials. All catalytic experiments were performed under inert atmosphere (argon, < 3 ppm O_2) using standard Schlenk line and glove box techniques. Grubbs' 2nd-generation catalyst, ([(IMesH_2)(Cy_3P)RuCl_2(=CHPh)], **G2**), acryloyl chloride, methacryloyl chloride, fumaroyl chloride, CH_2Cl_2 (stabilized with amylene), triethylamine (Et_3N), JEFFAMINE EDR-148 (triethyleneglycol diamine; Huntsman, primary amine content = 13.48 mequiv.g^{-1}), (*E*)-hex-3-enedioic acid, and all other reagents (Aldrich, unless otherwise mentioned), were used as received. Glycidol was distilled before use, and cyclooctene (COE, TCI Europe) was first dried over CaH_2 overnight, and then distilled before use. Acrylate cyclodithiocarbonate (DTC-Ac)[70,71] (^{1}H and ^{13}C{^{1}H}NMR Figures S1–S2; HRMS (ESI): $C_7H_8O_3NaS_2$ [M+Na]$^+$, calcd 226.9807; found 226.9806), bis(oxiran-2-ylmethyl) maleate[72,73] (**4**) (^{1}H and ^{13}C{^{1}H}NMR Figures S5–S6; HRMS (ESI): $C_{10}H_{12}O_6Na$ [M+Na]$^+$: calcd 251.05316; found

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251.0531), and (*Z*)-1,4-bis(oxiran-2-ylmethoxy)but-2-ene[31] (**6**) (Figures S7–S8; HRMS (ESI): $C_{10}H_{16}O_4Na$ $[M+Na]^+$: calcd 223.0946; found 223.0945) were synthesized according to the previously reported procedure, respectively.

Instrumentation and measurements. ^1H (500, 400 MHz) and $^{13}C\{^1H\}$ (125, 100 MHz) NMR spectra were recorded on Bruker Avance AM 500 and AM 400 spectrometers at 25 °C in $CDCl_3$. Chemical shifts (δ) are reported in ppm and were referenced internally relative to tetramethylsilane (δ 0 ppm) using the residual ^1H and ^{13}C solvent resonances of the deuterated solvent.

Monomer conversions were determined from ^1H NMR spectra of the crude polymer sample, from the integration (Int.) ratio $Int._{Polymer.}/[Int._{Polymer} + Int._{monomer}]$, using the methine hydrogens (–C*H*=C*H*– : δ 5.30 for PCOE, and 5.66 for COE).

The relative amounts of α-monofunctional (MF), isomerized α-monofunctional (IMF), and α,ω-difunctional (DF) polymers (neglecting linear non-functional (LNF), isomerized linear non-functional (ILNF) and cyclic non-functional (CNF) polymers – always found to be in minor amounts, *vide infra* –) were determined by ^1H NMR analysis of the precipitated polymer samples. The signal for the internal olefinic hydrogens adjacent to the CTA functional group (H^g, δ 7.02 Figure S9) was arbitrarily set to 1. The signal corresponding to the terminal methylene hydrogens of the vinyl group of a vinyl-end-functionalized polymer (H^7, δ 4.95, Figure S11) was used to determine the MF content as: MF (mol%) = Int.(δ 4.95) / 2 × 100%. The signal corresponding to the terminal methyl group adjacent to a propenyl end-functional polymer (H^6, δ 1.65, Figure S9) was used to determine the IMF content as: IMF (mol%) = Int.(δ 1.65) / 3 × 100%. The percentage of DF in the mixture is calculated from DF (mol%) = 100 – (MF + IMF)%.

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The molar mass values of the polymers samples were determined by ^{1}H NMR analysis in $CDCl_3$ ($M_{n,NMR}$) from the integral value ratio of the signals of end-groups' hydrogens (typically δ ca.7.02 (H^g)) to internal olefin hydrogens (δ ca. 5.36 (H^1)) (Figure S9).

The average molar mass ($M_{n,SEC}$) and dispersity ($Đ_M = M_w/M_n$) values of the PCOE samples were determined by size exclusion chromatography (SEC) in THF at 30 °C (flow rate = 1.0 mL.min^{-1}) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a set of two ResiPore PLgel 3 µm MIXED-E 300 × 7.5 mm columns. The polymer samples were dissolved in THF (2 mg.mL^{-1}). All elution curves were calibrated with 12 monodisperse polystyrene standards (M_n range = 580–380,000 g.mol^{-1}). $M_{n,SEC}$ values of polymers were uncorrected for their possible difference in hydrodynamic volume in THF vs polystyrene. The SEC traces of the polyolefins all exhibited a monomodal and symmetrical peak.

Flash chromatography was performed on a REVELERIS Prep purification system (Grace) using silica gel cartridges.

MALDI-ToF mass spectra were recorded at the CESAMO (Bordeaux, France) on a Voyager mass spectrometer (Applied Biosystems) equipped with a pulsed N_2 laser source (337 nm, 4 ns pulse width) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron mode and with an accelerating voltage of 20 kV. A freshly prepared solution of the polymer sample in THF (HPLC grade, 10 mg.mL^{-1}), a saturated solution of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (10 mg, DCTB) in THF (1 mL, HPLC grade) were prepared. A MeOH solution of the cationizing agent (NaI or $Ag(OCOCF_3)$ (AgTFA), 10 mg/mL) was also prepared. The solutions were combined in a 10:1:1 *v/v* of matrix-to-sample-to-cationizing agent. The resulting solution (1–2 µL) was deposited onto the sample target and vacuum-dried.

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FTIR spectra of the polymers were acquired (16 scans) with a resolution of 4 cm^{-1} on a Shimadzu IRAffinity-1 equipped with an ATR module.

Differential scanning calorimetry (DSC) analyses were performed with a Setaram DSC 131 apparatus calibrated with indium, at a rate of 10 °C.min^{-1}, under a continuous flow of helium (25 mL.min^{-1}), using aluminum capsules. The thermograms were recorded according to the following cycles: –70 to 120 °C at 10 °C.min^{-1}; 120 to –70 °C at 10 °C.min^{-1}; –70 °C for 5 min; –70 to 120 °C at 10 °C.min^{-1}; 120 to –70 °C at 10 °C.min^{-1}.

Thermogravimetric analyses (TGA) were performed on a Metler Toledo TGA/DSC1 by heating polymer samples at a rate of 10 °C.min^{-1} from +25 °C to +500 °C in a dynamic nitrogen atmosphere (flow rate = 50 mL.min^{-1}) (Figure S36).

Oxiran-2-ylmethyl acrylate (1). To a solution of glycidol (2.00 g, 27.0 mmol) and Et_3N (5.46 g, 54.0 mmol) in CH_2Cl_2 (27 mL), acryloyl chloride (2.44 g, 27.0 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 4 h, then filtered, and concentrated under reduced pressure. Separation by flash chromatography (pentane/ethyl acetate, gradient 100:0–60:40) afforded **1** as a colorless oil (2.90 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 2.66 (dd, *J* = 3, 5 Hz, 1H, OC*H*$_2$CHCH$_2$OC(O)), 2.85 (t, 1H, *J* = 5 Hz, OC*H*$_2$CHCH$_2$OC(O)), 3.25 (dq, *J* = 3, 6 Hz, 1H, OCH$_2$C*H*CH$_2$OC(O)), 4.01 (dd, *J* = 6, 12 Hz, 1H, OCH$_2$CHC*H*$_2$OC(O)), 4.49 (dd, *J* = 3, 12 Hz, 1H, OCH$_2$CHC*H*$_2$OC(O)), 5.87 (dd, *J* = 3, 10 Hz, 1H, C*H*$_2$CHC(O)), 6.15 (dd, *J* = 10, 17 Hz, 1H, CH$_2$C*H*C(O)), 6.45 (dd, *J* = 3, 17 Hz, 1H, C*H*$_2$CHC(O)) (Figure S13). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) 44.8 (OCH$_2$CHCH$_2$OC(O)), 49.5 (OCH$_2$*C*HCH$_2$OC(O)), 65.1 (OCH$_2$CH*C*H$_2$OC(O)), 128.0 (CH$_2$*C*HC(O)), 131.7 (*C*H$_2$CHC(O)), 165.9 (CH$_2$CH*C*(O)) (Figure S14). HRMS (ESI) (*m/z*): $C_6H_8O_3Na$ $[M+Na]^+$, calcd 151.0328; found 151.0327.

Oxiran-2-ylmethyl methacrylate (2). Compound **2** was synthesized following the same procedure as described for **1**, using glycidol (2.00 g, 0.027 mol), Et_3N (7.29 mL, 0.054 mol),

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CH_2Cl_2 (80 mL) and methacryloyl chloride (2.60 mL, 0.027 mol), and similarly purified by flash chromatography (pentane/ethyl acetate, 70:30) to give **2** as a colorless oil (1.03 g, 35%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm) 1.95 (s, 3H, $CH_2C(CH_3)C(O)$), 2.66 (dd, *J* = 3, 5 Hz, 1H, $OCH_2CHCH_2OC(O)$), 2.85 (t, *J* = 5, 1H, $OCH_2CHCH_2OC(O)$), 3.24 (dq, *J* = 3, 6 Hz, 1H, $OCH_2CHCH_2OC(O)$), 4.00 (dd, *J* = 6, 12 Hz, 1H, $OCH_2CHCH_2OC(O)$), 4.47 (dd, *J* = 5, 12 Hz, 1H, $OCH_2CHCH_2OC(O)$), 5.60 (s, 1H, $CH_2C(CH_3)C(O)$), 6.15 (s, 1H, $CH_2C(CH_3)C(O)$) (Figure S3). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) 18.2 ($CH_2C(CH_3)C(O)$), 44.5 ($OCH_2CHCH_2OC(O)$), 49.3 ($OCH_2CHCH_2OC(O)$), 65.1 ($OCH_2CHCH_2OC(O)$), 126.1 ($CH_2C(CH_3)C(O)$), 135.8 ($CH_2C(CH_3)C(O)$), 166.9 ($CH_2C(CH_2)C(O)$) (Figure S4). HRMS (ESI) (*m/z*): $C_7H_{10}O_3Na$ $[M+Na]^+$, calcd 165.0528; found 165.0527.

Bis(oxiran-2-ylmethyl) fumarate (3). Compound **3** was synthesized following the same procedure as described for **1** using glycidol (2.44 g, 33 mmol), Et_3N (8.5 mL, 33 mmol), CH_2Cl_2 (140 mL), and fumaroyl chloride (1.69 mL, 15 mmol). After 4 h of reaction at room temperature, the reaction mixture was filtered. The filtrate was washed with brine (2 × 30 mL), dried and concentrated. The recovered residue was purified by flash chromatography (pentane/ethyl acetate 100:0 to 0:100). Compound **3** was isolated as a colorless oil (0.85 g, 25%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 2.68 (dd, *J* = 3, 5 Hz, 2H, $OCH_2CHCH_2OC(O)$), 2.88 (t, *J* = 4 Hz, 2H, $OCH_2CHCH_2OC(O)$), 3.26 (dq, *J* = 3, 7 Hz, 2H, $OCH_2CHCH_2OC(O)$), 4.05 (ddd, *J* = 2, 6, 12 Hz, 2H, $OCH_2CHCH_2OC(O)$), 4.54 (dd, *J* = 3, 12 Hz, 2H, $OCH_2CHCH_2OC(O)$), 6.90 (s, 2H, $CHC(O)$) (Figure S15). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) = 44.7 ($OCH_2CHCH_2OC(O)$), 49.1 ($OCH_2CHCH_2OC(O)$), 66.0 ($OCH_2CHCH_2OC(O)$), 132.1 ($CHC(O)$), 164.8 ($OCH_2CHCH_2OC(O)$) (Figure S16). HRMS (ESI) (*m/z*): $C_{10}H_{12}O_6Na$ $[M+Na]^+$, calcd 251.0532; found 251.0533.

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Bis(oxiran-2-ylmethyl) (*E*)-hex-3-enedioate (5). A three neck flask (100 mL), equipped with a condenser and a magnetic bar, was charged with (*E*)-hex-3-enedioic acid (2.00 g, 14 mmol) and $SOCl_2$ (4.02 mL, 56 mmol). The resulting suspension was heated to 75 °C and stirred over 6 h. Gasses formed during the reaction were trapped with NEt_3. The resulting clear solution was cooled to room temperature and excess of $SOCl_2$ was eliminated under vacuum. The thus recovered (*E*)-hex-3-enedioyl chloride (2.53 g, 14 mmol) was used directly in the next step for the synthesis of **5**, following the same procedure as described for **3** using distilled glycidol (2.60 g, 35 mmol), Et_3N (7.6 mL, 56 mmol) and CH_2Cl_2 (130 mL). The recovered residue was purified by flash chromatography (pentane/ethyl acetate 90:10 to 0:100) to give **5** as a colorless oil (0.60 g, 17%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 2.64 (dd, *J* = 2, 5 Hz, 2H, $OCH_2CHCH_2OC(O)$), 2.84 (t, *J* = 5 Hz, 2H, $OCH_2CHCH_2OC(O)$), 3.14 (m, 4H, $CHCH_2C(O)O$), 3.20 (ddd, *J* = 3, 4, 7 Hz, 2H, $OCH_2CHCH_2OC(O)$), 3.92 (ddd, *J* = 2, 6, 12 Hz, 2H, $OCH_2CHCH_2OC(O)$), 4.42 (dd, *J* = 5, 12 Hz, 2H, $OCH_2CHCH_2OC(O)$), 5.71 (tt, *J* = 2, 4 Hz, 2H, $CHCH_2C(O)O$) (Figure S17). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) 37.6 ($CHCH_2C(O)O$), 44.7 ($OCH_2CHCH_2OC(O)$), 49.3 ($OCH_2CHCH_2OC(O)$), 65.3 ($OCH_2CHCH_2OC(O)$), 125.9 ($CHCH_2C(O)O$), 171.2 ($CHCH_2C(O)O$) (Figure S18). HRMS (ESI) (*m/z*): $C_{12}H_{16}O_6Na$ $[M+Na]^+$, calcd 279.0845; found 279.0841.

CTAs **1**, **2**, **3**, and **5** were stable in air at room temperature over at least 24 months.

General procedure for ROMP/CM of COE. All polymerizations were performed according to the following typical procedure (Table 2, entry 3). The only differences lie in the nature of the solvent, CTA and its initial concentration ($[CTA]_0$), and in the presence of an additive in some cases. Under argon atmosphere, a Schlenk flask equipped with a magnetic stir bar, was charged sequentially with CH_2Cl_2 (5.0 mL), COE (1.53 mL, 1.29 g, 11.7 mmol) and CTA **3** (27 mg, 0.12 mmol). The concentration of starting reagents (COE + CTA) was maintained at

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1.8 mol.L^{-1}. The resulting solution was placed at 40 °C and the polymerization was started upon addition of a fresh CH_2Cl_2 solution (2.0 mL) of **G2** (5.0 mg, 5.9 μmol). The reaction mixture turned highly viscous within 2 min. The viscosity then slowly decreased over the following 10 min. After the desired reaction time (typically 24 h), volatiles (solvent and ethylene) were removed under vacuum. The polymer was recovered upon precipitation in methanol (50 mL) (thereby allowing removal of the catalyst), filtration and drying at 25 °C under vacuum. All polymers were recovered as white powders, readily soluble in chloroform and THF, and insoluble in methanol (Tables 1–2). The isolated polymers were characterized by ^{1}H, $^{13}C\{^{1}H\}$ NMR, SEC, MALDI-ToF mass spectrometry and DSC analyses (Figures S9–S12, 1–3, S34).

General procedure for the chemical modification of PCOE epoxide chain-end groups into cyclodithiocarbonate ones. The reaction was carried out according to a modified literature procedure,[65] upon optimization of the initial stoichiometry, i.e. using PCOE-GA_2 (1 equiv.; GA = glycidyl alkenoate), LiBr (2 equiv.) and CS_2 (2.2 equiv.) (refer to the Supporting Information, Figures S30–34).

Synthesis of NIPUs from bis(cyclodithiocarbonate) telechelic PCOE. All syntheses of NIPUs were performed according to the following typical procedure. A Schlenk flask equipped with a magnetic stir bar was charged sequentially with CH_2Cl_2 (1.0 mL), PCOE-DTC_2 (0.130 g, 0.87 mmol (DTC).g^{-1}, 0.113 mmol DTC, as determined by ^{1}H NMR spectroscopy using benzene as internal standard), and a polyether diamine (JEFFAMINE EDR-148) (8 mg, 13.0 mmol (NH_2).g^{-1}; taking into account the primary amine content (mmol.g^{-1}), 0.104 mmol NH_2), and hydroxyethyl acrylate (13 mg, 8.6 mmol (C=C).g^{-1}). The resulting solution was stirred at 23 °C. The solution progressively turned slightly off white and precipitation of an off white solid was gradually observed over the reaction course. After the desired reaction time (typically 24 h; not optimized), the polymer was recovered upon

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complete precipitation in methanol (50 mL), filtration and drying at 25 °C under vacuum. All polymers were isolated as off white powders. The polymers, insoluble in common organic solvents ($CHCl_3$, THF, CH_2Cl_2, DMF), were characterized by FTIR, TGA and DSC analyses (Figures 6, S35).

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Results and Discussion

The ROMP/CM of cyclooctene (COE) catalyzed by Grubbs' second generation catalyst (**G2**), in the presence of several epoxide- and DTC-based CTAs, including both monofunctional (five-membered cyclodithiocarbonate acrylate (DTC-Ac), oxiran-2-ylmethyl acrylate (**1**), oxiran-2-ylmethyl methacrylate (**2**)), or difunctional (bis(oxiran-2-ylmethyl) fumarate (**3**), bis(oxiran-2-ylmethyl) maleate (**4**), bis(oxiran-2-ylmethyl) (*E*)-hex-3-enedioate (**5**), and (*Z*)-1,4-bis(oxiran-2-ylmethoxy)but-2-ene (**6**)) CTAs, has been investigated towards the synthesis of α,ω-diepoxide and -bis(cyclodithiocarbonate) telechelic PCOEs (Schemes 3, S1–S4), the latter ultimately serving as precursors towards NIPUs (Schemes 4–5).

Synthesis of CTAs 1, 2, 3, 5. CTAs **1**, **2**, **3**, and **5** were synthesized from the reaction of glycidol and acryloyl chloride, methacryloyl chloride, fumaroyl chloride or (*E*)-hex-3-enedioyl chloride, respectively, in the presence of triethylamine in CH_2Cl_2 (ca. 17–85% yield, Figures S3–S4, S13–S18).

Attempted direct synthesis of cyclodithiocarbonate difunctionalized PCOE. The ROMP/CM of COE mediated by **G2** in the presence of cyclodithiocarbonate acrylate (DTC-Ac) was attempted in THF and CH_2Cl_2 at 40 °C for 2 h with $[COE]_0/[DTC\text{-}Ac]_0/[\mathbf{G2}]_0$ = 1000:10:1 or 2000:20 or 80:1 (Scheme S1). However, whereas all COE was consumed, the PCOEs recovered did not feature any detectable alkenoate dithiocarbonate end-group; only linear non-functional PCOE (LNF) and possibly CNF was recovered, as evidenced by NMR (Figure S19). The same polymerization, carried out in the presence of an additional CTA known to be efficient in the ROMP of COE under similar conditions, namely the corresponding five-membered cyclocarbonate acrylate (5CC-Ac),[29,30] proceeded with full monomer consumption and gave the mono-(5CC-Ac) functional PCOE (Table S1, entry 2). The absence of DTC end-groups likely indicates partial deactivation of the ruthenium catalyst (most likely by C=S moieties)[67] after the fast ROMP stage, and the inability to perform the

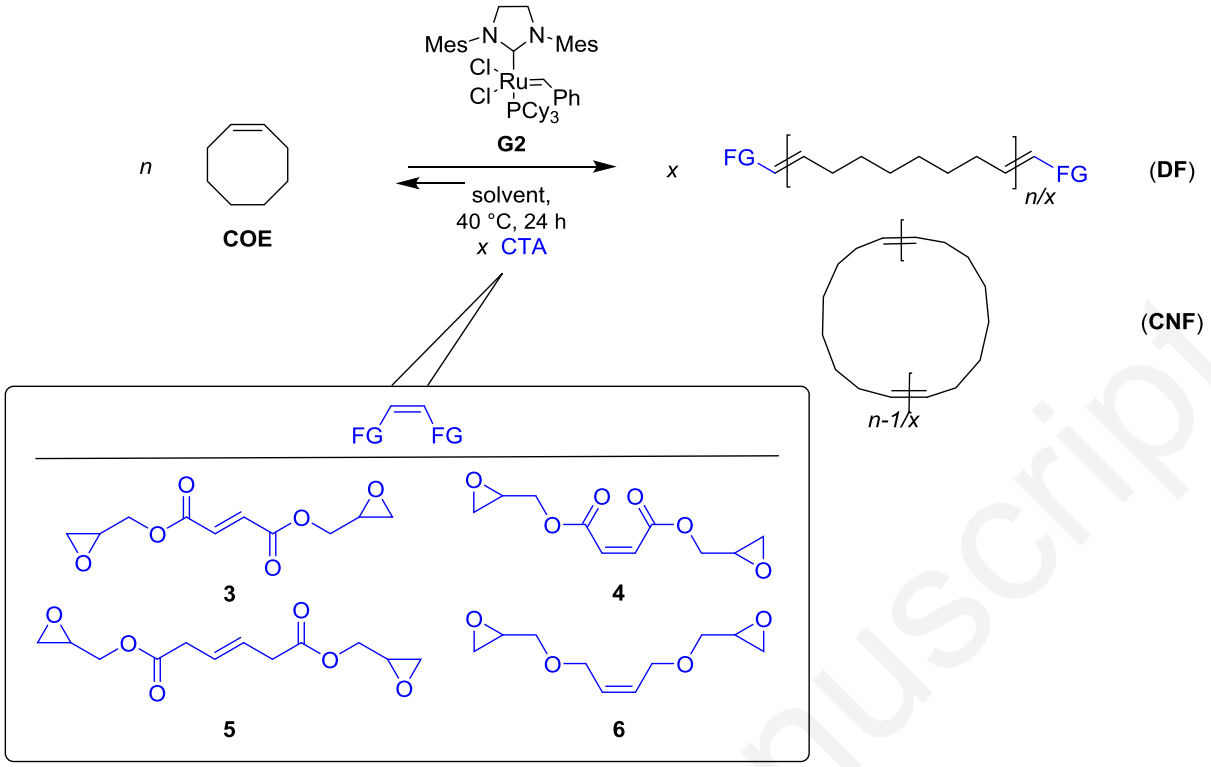
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CM step with DTC-Ac (*vide infra*),[58] while it could proceed to some extent with 5CC-AC. Given the difficulties in using a DTC-based CTA in the direct ROMP/CM of COE to prepare the corresponding bisDTC telechelic PCOE (PCOE-DTC_2) and subsequently the corresponding NIPU, we then undertook the synthesis of first diepoxide end-capped PCOEs, prior to their post-polymerization dithiocarbonatation.

Epoxide functionalized PCOEs.

Mechanistic considerations. Depending on the functionality of the epoxide-based CTAs, a range of various epoxide or vinyl end-functionalized PCOEs may thus be prepared (Schemes 3, S2–S4). Indeed, asymmetric CTAs are well-known to give a statistical distribution of end-capped polymers during ROMP, including linear (isomerized) and/or cyclic non-functional (LNF, ILNF CNF), (isomerized) α-monofunctional (IMF, MF) and/or α,ω-difunctional (DF) PCOEs (Schemes S2–S3).[58,59] On the other hand, symmetrical alkene CTAs such as bis-epoxide CTAS **3**–**6** enable the selective formation of α,ω-difunctional (DF) PCOE possibly along with cyclic polymers (CNF; Schemes 3, S4). The functionality of PCOEs is thus essentially imparted by the nature of the CTA as well as by operating conditions.

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Scheme 3. Tandem ROMP/CM/RCM of COE catalyzed by Grubbs' second generation catalyst **G2** in the presence of a difunctional epoxide alkene CTA **3**, **4**, **5**, or **6**, showing the possible polymers (FG: glycidyl functional group; DF: α,ω-difunctional, CNF: cyclic non-functional).

Monoepoxide functionalized PCOEs: synthesis and characterization. The polymerization of COE mediated by **G2** in the presence of glycidyl acrylate **1** and glycidyl methacrylate **2** as CTAs (Scheme S2) was performed to assess any possible selectivity difference in the functionality of the formed PCOEs (Table 1). In our previous related works, NMR and MALDI-ToF MS analyses showed that the non-functionalized polymers (CNF, LNF and ILNF) were always formed in minor amounts (< 15%), if any, as compared to the functionalized polymers (MF, IMF, and DF).[58,59] Therefore, only MF, IMF and DF were considered to be formed in significant amounts in the present process.

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Table 1. ROMP/CM of COE catalyzed by **G2** using CTA **1** or **2**, and BZQ in CH_2Cl_2 and THF at 40 °C for 24 h.[a]

Entry	CTA	Solvent	$[COE]_0/[\mathbf{1}]_0/[\mathbf{G2}]_0$	$[BZQ]_0$	MF[b] (mol%)	IMF[b] (mol%)	DF[b] (mol%)	$M_{n,theo}$[c] ($g.mol^{-1}$)	$M_{n,NMR}$[d] ($g.mol^{-1}$)	$M_{n,SEC}$[e] ($g.mol^{-1}$)
1	**1**	THF	1000:20:1	0	0	100	0	5700	5000	12 300
2	**1**	THF	1000:100:1	0	1	99	0	1200	1500	6700
3	**1**	THF	2000:20:1	0	1	99	0	11 100	11400	26 300
4	**1**	CH_2Cl_2	1000:20:1	0	0	100	0	5700	5900	13 400
5	**1**	CH_2Cl_2	1000:50:1	50	90	10	0	2400	2800	7200
6	**1**	CH_2Cl_2	1000:50:1	100	100	0	0	2300	1900	6900
7	**2**	CH_2Cl_2	1000:50:1	0	0	0	0	110 000[f]	-	-
8	**2**	CH_2Cl_2	2000:50:1	0	0	0	0	220 000[f]	-	-

[a] General conditions: Catalyst = 5.9 µmol, $[COE + CTA]_0$ = 1.8 mol.L^{-1}; COE and CTA conversion observed by ^1H NMR analysis = 100% for 100% and 0% for **2**, respectively. [b] Relative molar ratio as determined by ^1H NMR analysis of MF = α-functionalized PCOE; IMF = α-func isomerized PCOE; DF = α,ω-difunctional PCOE (Scheme S2). [c] Theoretical molar mass value calculated from $M_{n,theo}$ = {DF% × ([CO Conv.$_{COE}$)× M_{COE} / (½ $[CTA]_0$ × Conv.$_{CTA}$)} + {(MF% + IMF%) × ($[COE]_0$ × Conv.$_{COE}$ × M_{COE}) / ($[CTA]_0$ × Conv.$_{CTA}$)}+ M_{CTA} with M_{COE} $g.mol^{-1}$, $M_{CTA\mathbf{1}}$ = 128 $g.mol^{-1}$, $M_{CTA\mathbf{2}}$ = 142 $g.mol^{-1}$, on the basis of the formation of only MF, IMF and DF without taking into account any LNF and ILNF. [d] Experimental molar mass value determined by ^1H NMR analysis (refer to the Experimental Se [e] Number-average molar mass ($M_{n,SEC}$) and dispersity ($Đ_M = M_w/M_n$) values determined by SEC vs polystyrene standards (uncorrected M_n valu THF at 30 °C. [f] Theoretical molar mass value calculated from $M_{n,theo}$ = $[COE]_0$ / $[\mathbf{G2}]_0$ × Conv.$_{COE}$ × M_{COE} with M_{COE} =110 $g.mol^{-1}$, on the basis formation of only LNF and CNF PCOE.

In the presence of CTA **1**, both the monomer and the CTA were completely consumed, as evidenced by ^1H NMR analyses (Figures S9, S11, S13). Similarly to CH_2Cl_2, THF was found to promote the undesired ISOM; the isomerized monofunctional PCOE (IMF) was then basically the only polymer recovered (Table 1, entries 1–4; Figures S20–S21). This detrimental isomerization was also observed during the ROMP/CM/RCM of COE catalyzed by **G2** in the presence of an unsymmetrical trimethoxysilyl acrylate CTA.[58,59] The experimental molar mass values of the polymers prepared from **G2**/CTA **1**, regardless of the solvent, as determined by ^1H NMR spectroscopy ($M_{n,NMR}$), generally varied inversely proportionally with the amount of initial CTA **1** loading, thus suggesting an effective chain-transfer process (Table 1). SEC analysis of the polymer samples gave molar mass values ($M_{n,SEC}$) in fair agreement with both the expected molar mass values ($M_{n,theo}$) and the experimental ones as determined by NMR ($M_{n,NMR}$), while displaying a single symmetrical

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peak ($Đ_M$ = ca. 1.5; Figure S22). The ^{1}H and ^{13}C{^{1}H} NMR spectra of an IMF PCOE prepared from [COE]$_0$/[**1**]$_0$/[**G2**]$_0$ = 1000:20:1 in THF (Table 1, entry 1) are illustrated in Figures S9 and S10, respectively. The ^{1}H NMR spectrum evidenced, along with the signals of the hydrogens of the repeating unit (H^1, H^2, H^3; in red), the presence of the isomerized C=C terminal bond ($H^{4,5}$, H^6; in green), and glycidyl α,β-unsaturated carboxylate chain-end (H^g, H^f, H^d, H^e, H^c, H^a, H^b, H^h, H^i; in black) (Figure S9). Correspondingly, the ^{13}C{^{1}H} NMR spectrum confirmed the presence of glycidyl α,β-unsaturated carboxylate end-group in IMF (H^d, H^f, H^e, H^c, H^b, H^a, $H^{g,h}$; in black) (Figure S10). Also, the distinctive ^{13}C{^{1}H} NMR signals of the terminal methyl group (C^{6trans}, C^{6cis}; in green; always displaying the same integration ratio (ca. 2:1), consistent with a set of *trans*/*cis* isomers), and its adjacent methylene hydrogens (C^4, C^5; in green) characteristic of the propenyl-end-functionalized polymers IMF, were observed (Figure S10). Remarkably, upon addition of 1,4-benzoquinone (BZQ), a hydrogen acceptor known to successfully impede undesirable isomerization process in various olefin metathesis reactions,[58,59,74,75,76] α-glycidyl,ω-vinyl telechelic (MF) PCOE could be isolated selectively (Table 1, entry 6). Indeed, the characteristic signal of IMF (H^6) is no longer observed, while the typical signal of α-glycidyl acrylate,ω-vinyl PCOE, namely (besides H^a–H^i) the methine H^g, H^f, and H^8, and methylene H^7 hydrogens, then display the relative integration values 1:1:1:2, respectively, supporting the monofunctionalization of PCOE. Correspondingly, the ^{13}C signals of the C^6 *cis/trans* isomers disappeared, whereas the characteristic resonance of the terminal methylene carbon atom C^7 showed up at δ 110.1 ppm (Figures S11–S12).

On the other hand, when using glycidyl methacrylate (CTA **2**) in CH_2Cl_2, ^{1}H NMR analysis of the recovered sample showed the presence of only non-functional PCOEs, as the characteristic methylene hydrogen signals of an α,β-unsaturated carboxylate chain-end (δ 7.1, 5.8 ppm $CH_2C\mathit{H}$=CHCOO) were not observed (Figure S23) (Table 1, entries 7–8). This

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indicates that CM did not take place during this polymerization. Control experiments carried out using a 1:1 mixture of **1** and **2** as CTAs gave a full COE conversion and consumption of **1**, whereas **2** remained unreacted (Table S2). The PCOEs thus formed only displayed a glycidyl α,β-unsaturated carboxylate and a vinyl chain-ends. Since CTA **2** did not inhibit these latter polymerizations, this suggests that the observed inactivity of the **G2**/**2** catalytic system did not arise from possible residual impurities which could deactivate **G2**, but rather from the intrinsic inefficiency of **2** in promoting the ROMP/CM of COE (Table 1, entries 7–8).[39]

Diepoxide functionalized PCOEs: synthesis and characterization. The polymerization of COE mediated by **G2** was investigated in the presence of a difunctional glycidyl CTA (**3**–**6**), at 40 °C for 24 h in CH_2Cl_2 (Scheme 3). All polymerizations proceeded with full monomer consumption and selectively afforded DF and possibly CNF PCOEs. The most significant results are gathered in Table 2.

Table 2. ROMP/CM of COE catalyzed by **G2** using CTAs **3–6** in CH_2Cl_2 at 40 °C for 24 h.

Entry	CTA	$[COE]_0/[\mathbf{CTA}]_0/[\mathbf{G2}]_0$ [a]	CTA Conv. [b] (%)	$M_{n,theo}$ [c] ($g.mol^{-1}$)	$M_{n,NMR}$ [d] ($g.mol^{-1}$)	$M_{n,sec}$ [e] ($g.mol^{-1}$)	$Đ_M$ [e]
1	**3**	1000:20:1	30	19 600	29 000	34 700	1.5
2	**3**	1000:100:1	85	1300	2200	9400	1.4
3	**3**	2000:20:1	37	30 100	32 400	49 150	1.7
4	**3**	2000:50:1	26	17 200	15 500	23 300	1.9
5	**3**	2000:90:1	45	5700	7600	10 600	1.5
6	**3**	2000:200:1	9	12 500	12 200	23 600	1.5
7	**4**	1 000:40:1	27	10 500	21 900	37 100	1.4
8	**4**	1 000:100:1	80	1600	1500	4700	1.5
9	**4**	2 000:20:1	78	11 000	11 600	18 400	1.2
10	**4**	2 000:50:1	80	5600	5700	7500	1.6
11	**4**	2 000:50:1	100	4600	4700	8200	1.4
12	**4**	2 000:100:1	68	3500	3900	9400	1.4
13	**4**	3 800:380:1	100	1300	1700	4300	1.5
14	**4**	5 000:500:1	33	3600	5 000	7400	1.6
15	**4**	8 000:800:1	100	1300	1700	7200	1.5
16	**4**	10 000:1000:1	95	1400	3000	8100	1.4
17	**5**	1000:40:1	10	27 800	26 400	29 000	1.5
18	**5**	1000:100:1	22	5300	5200	7800	1.4

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19	**5**	2000:50:1	20	22 300	27 000	27 200	1.6
20	**5**	2000:100:1	10	22 300	25 200	29 400	1.5
21	**6**	2000:20:1	62	18 000	26 600	31 200	1.4
22	**6**	2000:50:1	70	6300	6300	8400	1.6
23	**6**	2000:100:1	57	4100	4100	8200	1.5

[a] General conditions: Catalyst = 5.9 µmol, $[COE + CTA]_0$ maintained at 1.8 mol.L^{-1}, COE conversion determined by ^{1}H NMR analysis = 100% (refer to the Experimental Section). [b] CTA conversion determined by ^{1}H NMR analysis (refer to the Experimental Section). [c] Theoretical molar mass value calculated from $M_{n,theo} = \{M_{COE} \times ([COE]_0 \times Conv._{COE}) / ([CTA]_0 \times Conv._{CTA})\} + M_{CTA}$ with M_{COE}= 110 g.mol^{-1}, $M_{CTA\mathbf{3}} = M_{CTA\mathbf{4}}$ = 228 g.mol^{-1}, $M_{CTA\mathbf{5}}$ = 256 g.mol^{-1}, $M_{CTA\mathbf{6}}$ = 200 g.mol^{-1}, on the basis of the formation of only DF (i.e. without taking into account any NF, LNF, CNF, and ILNF). [d] Experimental molar mass value determined by ^{1}H NMR analysis (refer to the Experimental Section). [e] Number-average molar mass ($M_{n,SEC}$) and dispersity ($Đ_M = M_w/M_n$) values determined by SEC vs polystyrene standards (uncorrected M_n values) in THF at 30 °C.

While the polymerization of COE using the fumarate CTA **3** afforded only DF and possibly CNF PCOEs as evidenced from NMR analyses (Figures S24–S25), the consumption of **3** remained low (< ca. 40%), regardless of the $[COE]_0/[\mathbf{3}]_0$ feed ratio (Table 2, entries 1–6). Assuming that the analogous CTA featuring a *Z* configuration may facilitate its interaction with **G2**, as a result of the better accessibility of the C=C bond,[77] the ROMP/CM of COE was then comparatively investigated using the maleate CTA **4** (Table 2, entries 7–16). Monitoring the molar mass of the crude polymer sample as determined by NMR analysis, for a reaction carried out with CTA **4** and $[COE]_0/[CTA]_0/[\mathbf{G2}]_0$ = 2000:50:1, first revealed the sharp increase of $M_{n,NMR}$ within the first 10 min, in line with the visual increase of the viscosity of the reaction medium (Figure 1). The consecutive $M_{n,NMR}$ decrease, larger in the case of **4** vs **3**, is correlated to the CTA conversion (up to 80% with **4**, vs 34% with **3**), and thus to the better efficiency of the CM with **4**. Also, the molar mass of the polymers as determined by NMR ($M_{n,NMR}$) fairly matched the calculated value ($M_{n,theo}$) and decreased proportionally to the increasing amount of initial CTA loading, thus evidencing an efficient chain-transfer process (Table 2). The SEC traces showed only one symmetrical peak ($Đ_M$ = ca 1.65 Figure S26), suggesting that DF, and CNF if any, had a similar molar mass.

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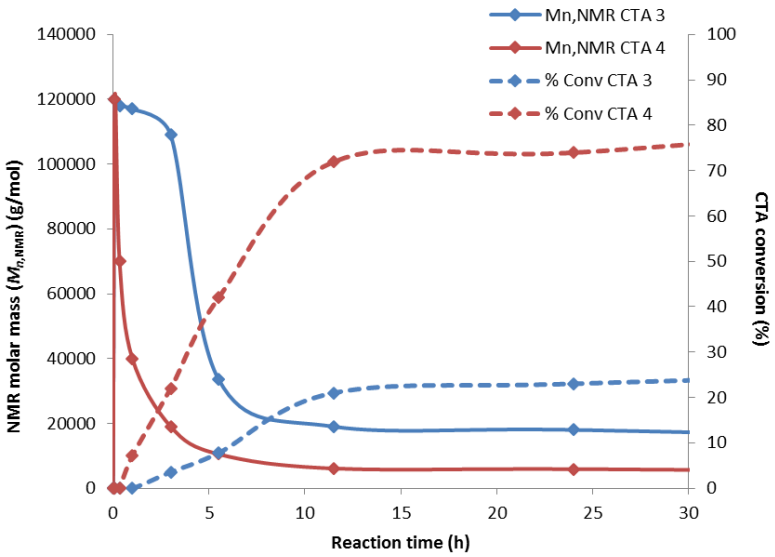


Figure 1. Monitoring of the molar mass determined by NMR over time of a polymer sample prepared by the ROMP/CM of COE in the presence of **G2**/CTA **3** or **4**, with $[COE]_0/[CTA]_0/[\mathbf{G2}]_0$ = 2000:50:1, in CH_2Cl_2 at room temperature (Table 2, entries 4, 10).

^{1}H and $^{13}C\{^{1}H\}$ NMR analyses of a PCOE prepared from **G2**/CTA **4** evidenced the sole formation of DF and possibly CNF (Figures 2, S27). Indeed, the main chain olefinic hydrogens (H^1–H^3, C^1–C^3) were clearly observed along with the signals typical of the glycidyl α,β-unsaturated carboxylate (H^a–H^i, C^a–C^h) end-groups (*vide supra*). The characteristic signals of LNF, MF (allyl methylene terminus, δ_{CH2} 5.15, 4.90 ppm) and their isomerized analogues ILNF and IMF (methyl group of the propenyl end-moiety, δ 1.64 ppm) were not observed. MALDI-ToF MS analyses were performed using a DCTB matrix and a silver salt as cationizing agent so as to assess the presence of both DF and CNF PCOEs (Figure 3). The mass spectra showed a major population of PCOE with a repeating unit of 110 $g.mol^{-1}$ end-capped with two glycidyl α,β-unsaturated carboxylate moieties, i.e. DF PCOE,

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with e.g. $m/z_{,experimental}$ = 1988.2 g.mol^{-1} vs $m/z_{,simulated}$ = 1988.6 g.mol^{-1} for n = 15. This was unequivocally supported by the close match of the simulated isotopic distribution of the DF PCOE with e.g. $m/z_{,simulated}$ = 1988.6 g.mol^{-1} for n = 15. A second minor population was attributed to the CNF PCOE with e.g. $m/z_{,experimental}$ = 1981.4 g.mol^{-1} for m = 17 *vs* $m/z_{,simulated}$ = 1980.8 g.mol^{-1}. The typical isomerization pattern previously observed with sets of signals separated by m/z = 14 g.mol^{-1} around each peak of DF corresponding to a given degree of polymerization (i.e. each n value),[58] was clearly not observed in the spectra of the present polymers, thereby evidencing the absence of isomerized COE units.

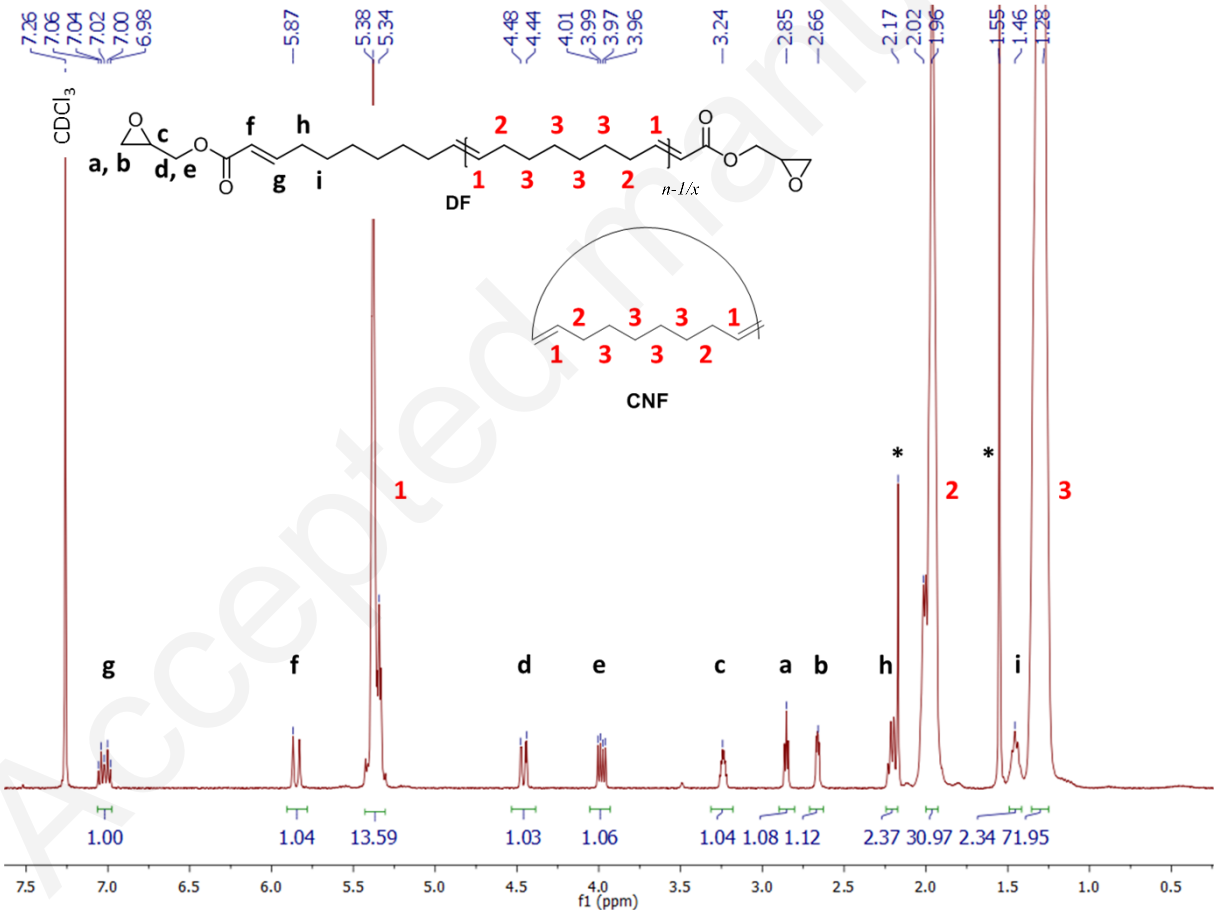
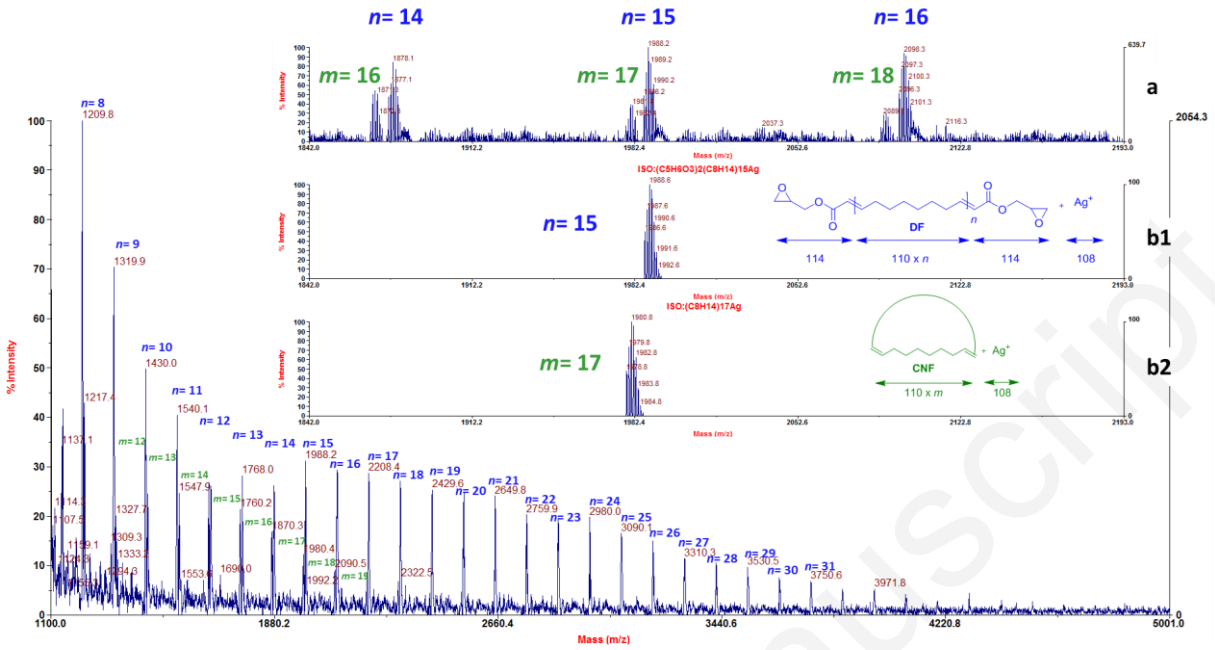


Figure 2. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of the polymer sample prepared by ROMP/CM of COE in the presence of **G2**/CTA **4** showing DF and possibly CNF PCOEs (Table 2, entry 15) (* stands for residual solvent (acetone δ 2.10 ppm), water (δ 1.55 ppm)).

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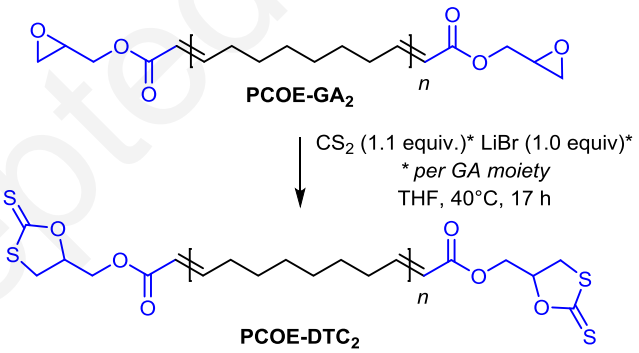
showing a mixture of DF and CNF PCOEs; see top zoomed region and the corresponding middle and bottom simulations for n = 15 and m = 17, respectively.

Given the difference in the efficiency of CTAs **3**–**4** in the ROMP/CM of PCOE resulting from the *E* vs *Z* configuration, respectively, with the less sterically encumbered double bond of the alkene CTA **4** providing more efficient chain-transfer, we next evaluated CTAs **5**–**6**, structurally related to **3**–**4**.[78] The effect of the distance between the double bond and the functional group within a CTA, studied for hydroxy, carboxylic, ester, ether, nitrile and halide functions, revealed no general trend in literature reports.[79,80,81] Experimentally, in our case, the CM efficiency based on the CTA conversion was in the order **4** > **6** >> **3** >> **5**, with CTAs with a *Z* configuration being more effective than those with an *E* configuration (similarly to **4** vs **3**, *vide supra*), regardless of the presence of methylene group in-between the C=C double bond and the glycidyl α,β-unsaturated carboxylate/ether moiety, as previously reported[53] (Table 2). The polymerization of COE mediated by **G2** in the presence of CTA **5** or **6** similarly afforded the corresponding DF and possibly CNF PCOEs end-capped by the

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CTA's functional group, as evidenced by ^{1}H and $^{13}C\{^{1}H\}$ NMR analyses (Figures S28–29).[39] Note that the ROMP of cyclooctadiene (COD) mediated by the catalyst [$(PCy_3)_2Cl_2Ru$=CHPh)]/CTA **5** with $[COD]_0/[\mathbf{5}]_0/[catalyst]_0$ = 4000:50–267:1, at 45 °C in 48 h, similarly afforded the diepoxide telechelic polybutenylene.[39]

Chemical modification of diepoxide telechelic PCOE into bis(cyclodithiocarbonate) telechelic PCOE. Since the PCOE-DTC_2 could not be directly synthesized by the polymerization of COE in the presence of DTA-Ac (*vide supra*), the post-polymerization chemical modification of the diepoxide PCOE (PCOE-GA_2) into PCOE-DTC_2 was then performed. The reaction with CS_2 proceeded at 40 °C for 17 h in quantitative yield upon optimizing the quantity of LiBr to a stoichiometric amount (an excess led to the formation of unidentified side-products) and lowering the CS_2 excess to 1.1 equiv. (instead of the original 1.8 equiv.;[65] Scheme 4, Table S3). This is, to our knowledge, the first example of cyclo(di)thiocarbonate end-functionalized PCOE. The reaction proceeded without alteration of the molar mass ($M_{n,NMR}$, Table 3).



Scheme 4. Chemical modification of diepoxide telechelic PCOE (PCOE-GA_2) into bis(cyclodithiocarbonate) telechelic PCOE (PCOE-DTC_2).

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Table 3. Macromolecular characteristics of PCOE-GA_2, PCOE-DTC_2 synthesized upon dithiocarbonatation reaction of PCOE-GA_2, and of the resulting poly(mercaptothiourethane) NIPU synthesized upon aminolysis of PCOE-DTC_2 with JEFFAMINE EDR-148.

	PCOE-GA_2						**PCOE-DTC_2**						**NIPU**	
Entry	$M_{n,NMR}$ [a] ($g.mol^{-1}$)	$M_{n,sec}$ [b] ($g.mol^{-1}$)	$Đ_M$ [b]	T_g (°C)	T_m (°C)	T_c (°C)	$M_{n,NMR}$ [a] ($g.mol^{-1}$)	$M_{n,sec}$ [b] ($g.mol^{-1}$)	$Đ_M$ [b]	T_g [c] (°C)	T_m [c] (°C)	T_c [c] (°C)	T_g [c] (°C)	T_m [c] (°C)
1	2200	4400	1.4	*n.o.*	60	46	2300	4800	1.6	*n.o.*	57	45	*n.o.*	51
2	4500	7200	1.5	*n.o.*	60	45	4500	7300	1.5	*n.o.*	56	46	*n.o.*	50
3	6500	19 000	1.5	*n.o.*	57	45	6500	19 500	1.3	*n.o.*	56	43	*n.o.*	51
4	7600	20 300	1.4	*n.o.*	59	46	7700	20 400	1.3	*n.o.*	57	44	*n.o.*	49

[a] Experimental molar mass value determined by ^{1}H NMR analysis (refer to the Experimental Section). [b] Number-average molar mass ($M_{n,SEC}$ dispersity ($Đ_M = M_w/M_n$) values determined by SEC vs polystyrene standards (uncorrected M_n values) in THF at 30 °C. [c] Thermal transition temper measured by DSC (second heating scan). *n.o.* not observed.

^{1}H NMR monitoring of the dithiocarbonatation reaction showed, besides the main chain olefinic hydrogens (H^1, H^2, H^3; in red), the disappearance of the GA end-groups (*vide supra* with **1**) concomitantly to the appearance of the characteristic DTC signals (H^a– H^i; in black) (Figure S30), up to the quantitative formation of the α,ω-bisDTC telechelic PCOE (Figure 4). Correspondingly, $^{13}C\{^1H\}$ NMR spectroscopy confirmed the presence of the DTC termini on the PCOE backbone (C^a–$C^{h,i}$; in black) (Figure S31). FTIR analysis of the PCOE-DTC_2 sample showed the DTC characteristic $\upsilon_{C=S}$ (1192 cm^{-1}), $\upsilon_{C=O}$ (1726 cm^{-1}) (Figure S32). Furthermore, MALDI-ToF MS analyses performed using a DCTB matrix and a sodium or silver salt as cationizing agent, evidenced the presence of DF PCOE-DTC_2 and CNF PCOE, respectively (Figure 5a and b). The mass spectra showed two major populations of PCOE with a repeating unit of 110 $g.mol^{-1}$ corresponding to COE. As unequivocally supported by the close match of the simulated isotopic distributions, one population is end-capped with two DTC moieties, i.e. DF PCOE, with e.g. $m/z_{,experimental}$ = 1283.8 $g.mol^{-1}$ vs $m/z_{,simulated}$ = 1283.8 $g.mol^{-1}$ for n = 8 (Figure 5a), and the other one corresponds to the CNF PCOE with e.g. $m/z_{,experimental}$ = 1210.2 $g.mol^{-1}$ for m = 10 vs $m/z_{,simulated}$ = 1210.0 $g.mol^{-1}$, and

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with e.g. $m/z_{,experimental}$ = 1337.8 g.mol^{-1} for p = 11 vs $m/z_{,simulated}$ = 1338.1 g.mol^{-1} (Figure 5b). Finally, DSC analyses of PCOE-DTC$_2$ samples revealed a thermal behavior similar to that of PCOE-GA$_2$ precursors, with a melting and a crystallization temperatures at T_m = +56 °C and T_c = +45 °C, respectively (Table 3) (Figures S33–S34).

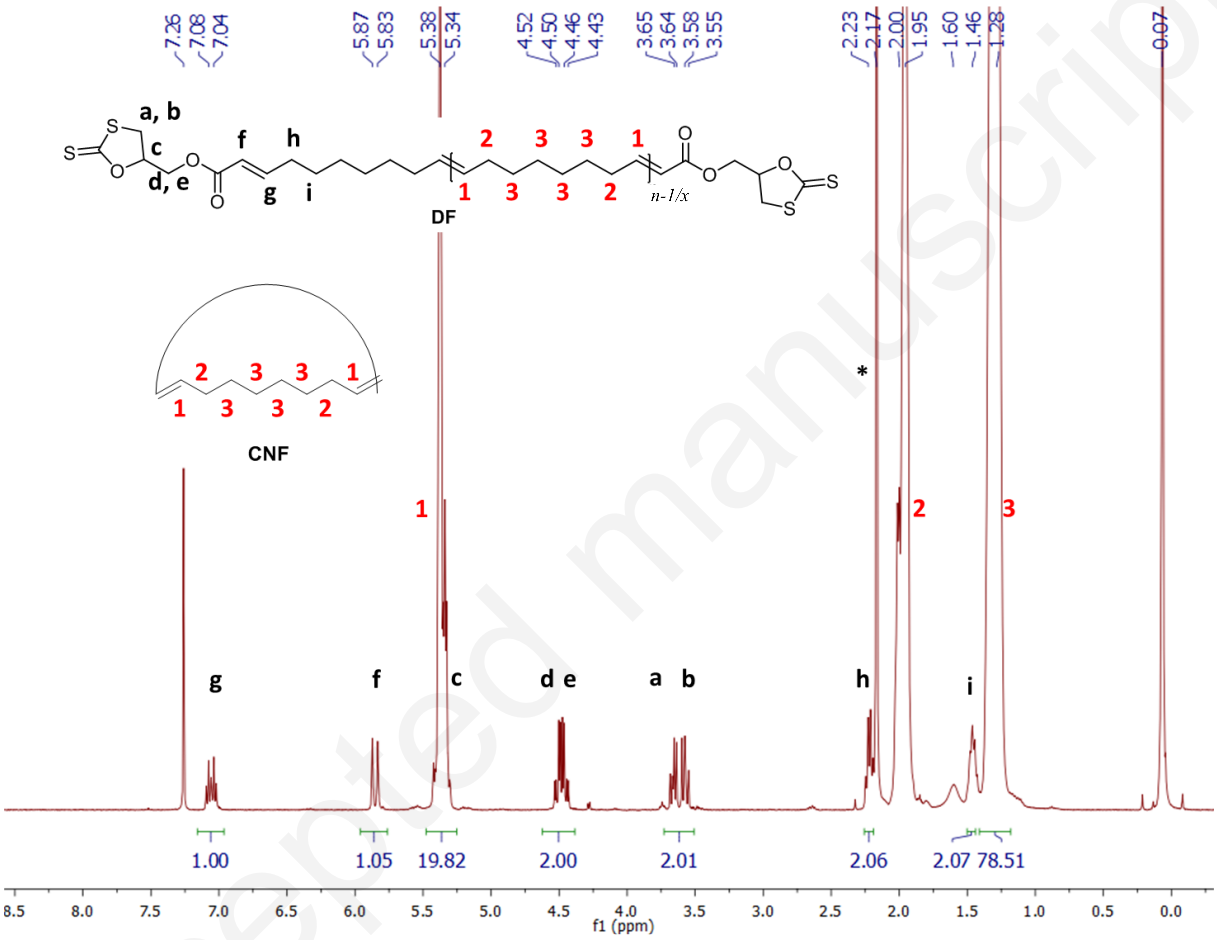
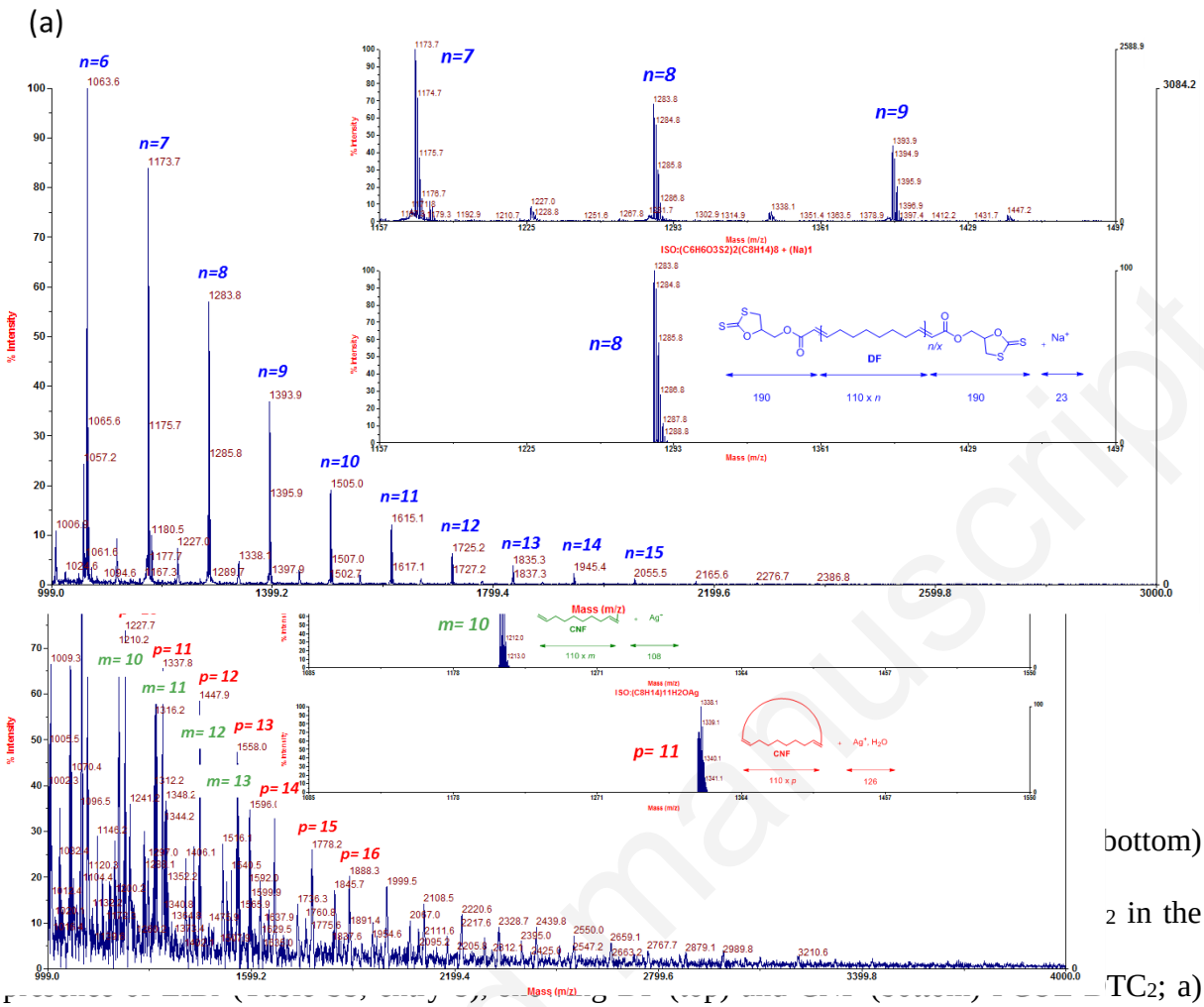


Figure 4. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of a PCOE-DTC$_2$ sample prepared by reaction of PCOE-GA$_2$ with CS_2 in the presence of LiBr (Table S3, entry 5).

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bottom)

2 in the

TC2; a) see top zoomed region and the corresponding bottom simulation for *n* = 8; b) see top zoomed region and the corresponding middle and bottom simulations for *m* = 10 and *p* = 11, respectively.

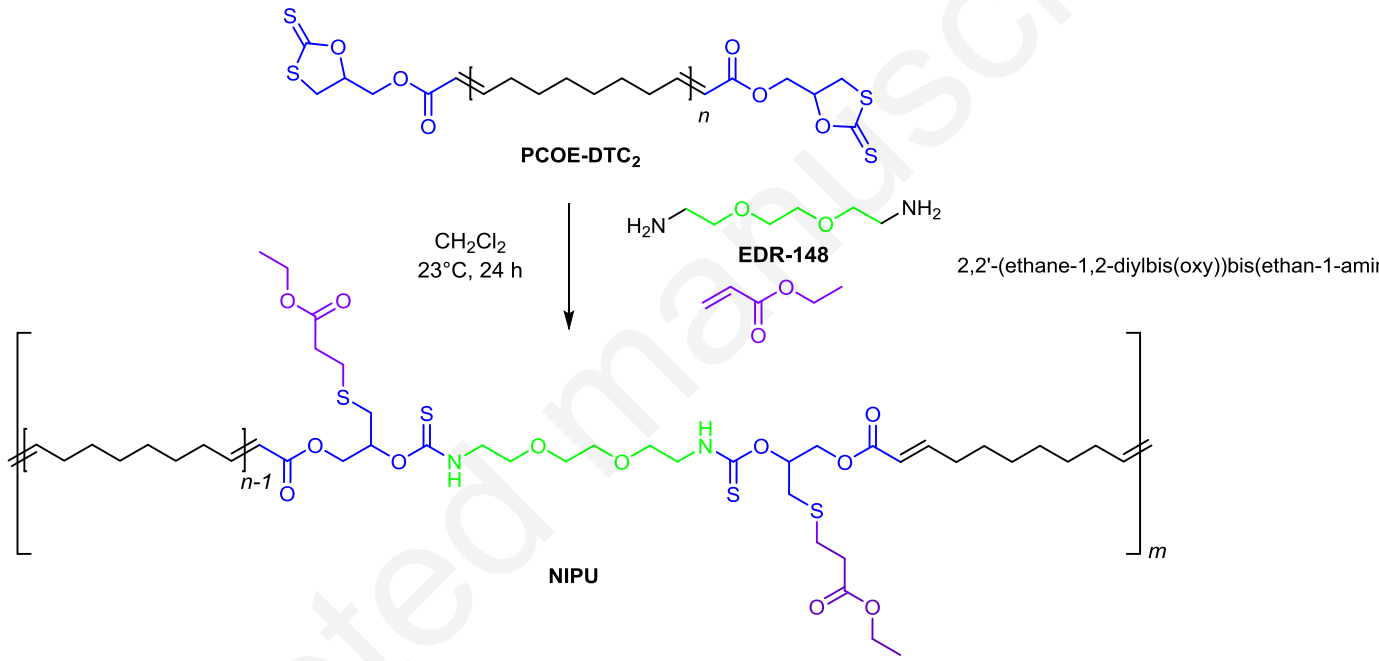
Aminolysis of bis(cyclodithiocarbonate) telechelic PCOE into NIPU. The stoichiometric aminolysis of PCOE-DTC$_2$ with a polyether diamine (JEFFAMINE EDR-148) was investigated towards the formation of poly(mercaptothiourethane)s as NIPUs. Ethyl acrylate, known to favor the thiol/acrylate Michael reaction,[82] was used as an additive to prevent the formation of disulfide bridges, so as to provide a priori linear polymer samples (Scheme 5). The ring-opening of PCOE DTC chain-ends was quantitative at room temperature over 24 h, as evidenced by the decreasing intensity of the $\nu_{C=S(DTC)}$ concomitant with the increasing intensity of $\nu_{C-N(NIPU)}$.[83] The formed NIPU materials were unexpectedly recovered as insoluble

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solids, thus precluding NMR and SEC analyses (and the subsequent evaluation of the molar mass values). Considering the implemented stoichiometric polyaddition towards the formation of the NIPU, a linear polymer was anticipated (Scheme 5). However, the insolubility of the produced polymers most likely hints crosslinked, final structures. Several origins may be envisioned for such crosslinking: i) possible presence of small amounts of triamines or higher functionality polyamines in the commercial grade of JEFFAMINE EDR-148 used; ii) formation of small amounts of disulfide bridges despite the use of thiol-acceptors; iii) possible crosslinking via thiol-ene reaction involving C=C bonds of the polyene backbone. A control click reaction of a linear PCOE-DTC_2 with an excess of 2-mercaptoethanol, performed under the same conditions as those used for the NIPUs synthesis (CH_2Cl_2, 23 °C, 24 h), showed the stability of the polyolefin backbone, thus ruling out this latter scenario. The latter NIPUs were thus characterized by FTIR spectroscopy, DSC and TGA analyses (Figures 6, S35, S36; Table 3). FTIR analyses showed the absence of the $\nu_{C=S(DTC)}$ (1193 cm^{-1}), along with the apparition of the distinctive ν_{N-H} (3385 cm^{-1}) and ν_{C-N} (1539 cm^{-1}) (Figure 6).[19,20,21] These results thus support the complete conversion of PCOEs-DTC_2 into the corresponding NIPUs. DSC analyses showed the semi-crystallinity of the poly(mercaptothiourethane)s NIPUs, alike PCOE-DTC_2 and PCOE-GA_2 (Table 3, Figure S35). The NIPU materials did not display a T_g while both their T_m = ca. 51 °C and T_c = ca. 32 °C were significantly lower than those of PCOE-GA_2 and PCOE-DTC_2 (T_m > 56 °C, T_c = 30–46 °C). TGA analyses revealed that PCOE-NIPU remained stable up to *ca.* 400 °C while the onset of the degradation temperature of PCOE-DTC_2 was observed at *ca.* 310 °C. A lower degradation temperature of the PCOE-DTC_2 (T_d^{50} = temperature at which 50% of mass loss occurs = 437 °C) precursor was observed as compared to that of the resulting NIPU which displayed a slightly better temperature stability (T_d^{50} = 451 °C) (Figure S36). Both copolymers were fully degraded (96–98%) at *ca.* 480–487 °C. Polythiourethanes reported in

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literature are very scarce and feature different soft segments, making the comparison of thermal characteristics delicate.[65,8284,85] Thermal properties of known polythiourethanes generally revealed T_g values (–29 °C–+57 °C) without any melting or crystallization temperatures being mentioned. The reported thermal stability of these materials was also lower (T_d^{50} < ca. 370 °C) than that of the PCOE-NIPU reported in the present work. The thermal behavior of the PCOE-NIPU thus revealed these materials promising for industrial applications.[88]



Scheme 5. Aminolysis of bis(cyclodithiocarbonate) telechelic PCOE (PCOE-DTC$_2$) into the corresponding poly(mercaptothiourethane) NIPU.

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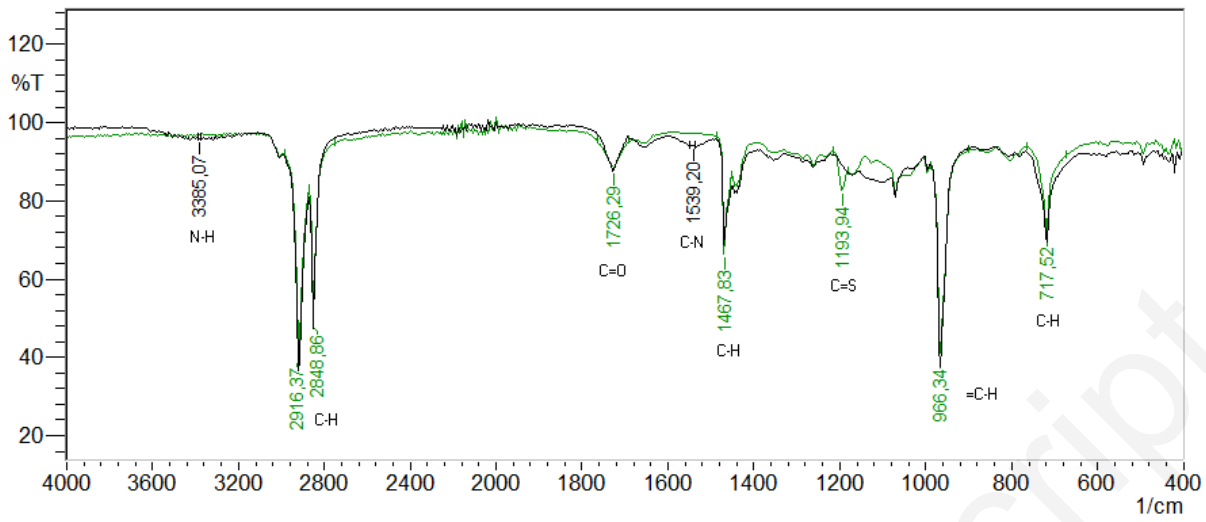


Figure 6. FTIR spectrum of a polymer sample (black trace) prepared by reaction of PCOE-DTC_2 (green trace) with JEFFAMINE EDR-148 in the presence of ethyl acrylate at 23 °C for 24 h in CH_2Cl_2 (Table 3, entry 3).

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Conclusion

Telechelic PCOEs have been successfully synthesized by tandem ROMP/CM of COE using Grubbs' 2nd-generation catalyst in the presence of various epoxide functionalized CTAs. The monofunctional epoxide CTA **1** selectively gave the isomerized α-epoxy-ω,propenyl monofunctionalized PCOE (IMF), but the use of 1,4-benzoquinone as additive allowed inhibiting completely the isomerization process, thus selectively affording α-glycidyl alkenoate,ω-vinyl telechelic PCOE (MF). The methacrylate CTA **2** related to **1** only afforded non-functionalized PCOE. As anticipated, the difunctional epoxide CTAs **3**–**6** selectively afforded the corresponding α,ω-diepoxide telechelic PCOEs (DF), and possibly CNF, through a proposed tandem one-pot CM/ROMP/RCM mechanism. *Z*-configurated CTAs were more effective than the *E* analogues (**4** > **6** >> **3** >> **5**). Subsequent cyclodithiocarbonatation of the α,ω-diepoxide telechelic PCOE (PCOE-GA_2) from CS_2/LiBr quantitatively provided the first example of cyclo(di)thiocarbonate end-functionalized PCOE, PCOE-DTC_2. Although, CS_2 is a rather toxic compound, it is yet used herein as an intermediate reagent (fully consumed under stoichiometric conditions) in the preparation of safe cyclodithiocyclocarbonate end-capped NIPU pre-polymers. CS_2 has also otherwise been used as a resource towards functional polymers.[86]

Finally, aminolysis of the PCOE-DTC_2 with JEFFAMINE EDR-148 quantitatively afforded the desired poly(mercaptothiourethane)s as NIPUs. To our knowledge, NIPUs were thus prepared in high yield, for the first time from the room temperature reaction of a dithiocarbonate α,ω-end-capped prepolymer with a diamine and without any added catalyst. Being able to prepare NIPUs from a room temperature reaction is a significant achievement in comparison to the prior approach through the opening of the five-membered carbonates which required heating at typically 50–80 °C.[8,12,27,28] Also noteworthy, the aminolysis was, in the present work, carried out without any catalyst, another major improvement. Indeed, to our

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knowledge, a five-membered carbonate ring was reported to be successfully ring-opened at room temperature, yet in the presence of triazabicyclodecene guanidine (TBD) or LiOTf as catalyst/additive.[87] These solid NIPUs and their forthcoming liquid congeners to be published in due time, are envisaged as valuable synthons for adhesive, mastic or surface coating industrial applications.[88]

Acknowledgements

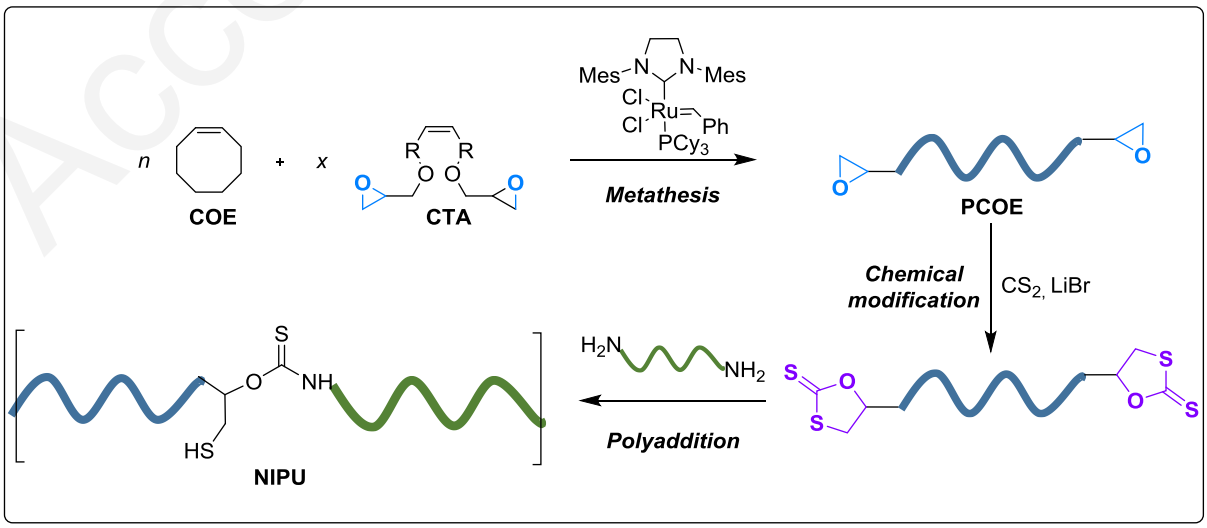
Financial support of this research by the ANR, project CYRRENAS (Ph.D. grant to E.V.) is gratefully acknowledged.

Electronic supplementary information (ESI) available: Complementary synthetic procedures and macromolecular data, ^{1}H and $^{13}C\{^{1}H\}$ NMR and FTIR spectra, DSC traces of CTAs and polymers. (PDF)

Notes

The authors declare no competing financial interest.

Graphical Abstract



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[83] Note that reaction of the acrylate with the amine may also be envisioned. However, under very similar conditions to those used in the present study, acrylates have been reported to preferentially react with thiol rather than with amine functions.[82] Also, FTIR analyses support the absence of such an acrylate/amine reaction since the $\nu_{C\text{-}N}$ = 1220 cm^{-1} absorption (characteristic of the formation of the resulting secondary amine) was not observed (Figure 6).

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