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Synthesis and Polymerization of Cyclobutenyl-Functionalized Polylactide and Polycaprolactone: A Consecutive ROP/ROMP Route to Poly(1,4-butadiene)-*g*-Polyesters

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Efficient preparation of cyclobutenyl end-functionalized polyester macromonomers bearing polylactide (PLA) or poly(ϵ -caprolactone) (PCL) arms was achieved by organocatalyzed ring-opening polymerization (ROP) of *L*-lactide or ϵ -caprolactone in the presence of *cis*-3,4-bis(hydroxymethyl)cyclobutene or *cis*-4-benzyloxymethyl-3-hydroxymethylcyclobutene acting as initiator. Cyclobutenyl end-functionalized PLA and PCL macromonomers having one or two arms were obtained in high yields with excellent control over molecular weights (up to 11 000 g.mol⁻¹) and dispersity (PDI < 1.25) by organocatalyzed ROP using 4-(*N,N*-dimethylamino)pyridine (DMAP) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), respectively. Ring-opening metathesis polymerization (ROMP) of the macromonomers using ruthenium-based Grubbs' second generation catalyst afforded well-defined polybutadiene-*g*-polyester copolymers having an exclusively linear polybutadiene backbone with a strictly 1,4-type microstructure, with molecular weights ranging from 20 000 to 170 000 g.mol⁻¹ and low dispersity (PDI \leq 1.30). The products resulting from this consecutive ROP/ROMP route represent the first examples of poly(1,4-butadiene)-*g*-polyesters through the macromonomer route.

Introduction

Ring-opening metathesis polymerization (ROMP) has emerged as a powerful tool to prepare graft copolymers (also denoted as bottlebrush copolymers) using the three well-known strategies: grafting-from, grafting-onto, and grafting-through routes.¹ The most often used method, namely the grafting-through (or macromonomer) route, relies on the ROMP of well-defined polymers bearing a "ROMP-able" strained ring such as norbornene² or oxanorbornene.³ In our group, we have developed a number of efficient synthetic strategies based on the cyclobutene ring as the "ROMP-able" functionality to prepare well-defined graft copolymers having a strictly 1,4-polybutadiene main chain with a high density of grafts.⁴⁻⁷ Cyclobutene derivatives have been much less investigated in ROMP compared to their (oxa)norbornene counterparts,^{4a,8} although this approach provides final polymers having an exclusively linear polybutadiene backbone with a strictly 1,4-type microstructure that is not easily attainable by other (ionic or radical) polymerization processes. We have previously demonstrated that the cyclobutenyl double bond survives various reversible deactivation radical polymerization processes such as atom transfer radical polymerization (ATRP),⁵ reversible addition-fragmentation transfer (RAFT) polymerization,⁶ and click copper-catalyzed azide-alkyne cycloaddition (CuAAC).^{6,7}

Driven by our interest in developing new efficient methodologies to prepare well-defined grafted poly(1,4-butadiene)s, we used in the present work a consecutive ring-opening polymerization (ROP)/ROMP route to prepare poly(1,4-butadiene)-*g*-polyesters from cyclobutenyl macromonomers bearing one or two polyester segment(s) derived from *L*-lactide (LA) or ϵ -caprolactone (CL).

Poly(lactide) (PLA) and poly(ϵ -caprolactone) (PCL) are important polymers as they are easily (bio)degradable and have tremendous applications as engineering plastics and within the biomedical field.⁹ An attractive feature of polyester-grafted copolymers is their potential to act as building blocks for nanomaterials synthesis thanks to the hydrolytically degradable polyester grafts.^{2b} Previously reported works devoted to the synthesis of polycycloalkene-*g*-polyesters by the grafting-through method have focused on the ROMP of (oxa)norbornenyl-functionalized PLA^{2b,2d,3a,10} and PCL^{2h,11} macromonomers using ruthenium-based catalysts. In the present study, we investigated the synthesis and ROMP of the first examples of cyclobutenyl-functionalized PLA and PCL macromonomers obtained from the ROP of the corresponding cyclic esters.

Over the past decade, the ROP of cyclic esters has been investigated using a large range of organocatalysts.¹² Organocatalyzed ROP has the distinct advantage over stannous octoate-catalyzed ROP to require lower reaction temperatures that are more compatible with the cyclobutene thermal stability.⁵ Following the pioneering work of Hedrick and Waymouth on the ROP of lactide and lactones,¹³ organic bases such as guanidine (e.g., 1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD), amidine (e.g., 1,8-

diazabicyclo[5.4.0]undec-7-ene, DBU), amine (4-(*N,N*-dimethylamino)pyridine, DMAP), thiourea (TU) derivatives, phosphines and phosphazenes (e.g., *tert*-butylimino-tris(dimethylamino)phosphorane, *t*-BuP₁ and 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,2,3-diazaphosphorinane, BEMP) or *N*-heterocyclic carbenes (NHCs) have enabled the ROP of lactides, lactones (CL, δ -valerolactone, β -butyrolactone) as well as of carbonates ((substituted) tri- and tetramethylene carbonates), reaching high polymerization rates and selectivities, and demonstrating tolerance to functional groups. As part of our ongoing efforts aimed at evaluating such organocatalysts in the ROP of cyclic esters,¹⁴ we focused the present study on TBD and DMAP. Both TBD and DMAP have successfully allowed the ROP of lactides and to a lesser extent of CL.^{13,15-18} TBD proved highly efficient in mediating the ROP of LA and CL. Indeed, associated (0.1% catalyst relative to monomer) to pyrenebutanol as the initiator (1%) in dichloromethane (DCM), as many as 475 LA units were converted at room temperature within 1 min affording well-defined PLAs with controlled number-average molecular weights (M_n up to 62 600 g.mol⁻¹) and low dispersity values (PDI < 1.2).¹⁵ TBD thus demonstrated a much higher reactivity toward the ROP of LA than its methyl-substituted analogue, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) (495 LA units were converted in 30 min with 0.5% catalyst).^{15a} Comparatively to LA, CL was polymerized more slowly by TBD with only 104 monomer units being consumed within 8h at room temperature from a more concentrated catalyst solution (0.5% relative to monomer).¹⁵ Similarly, MeTBD was found less efficient compared to TBD in the ROP of CL with only 78 CL units being consumed within 2h by 5% catalyst relative to CL. A possible rationalization of the heightened reactivity of TBD relative to MeTBD is that it acts as a bifunctional catalyst activating both the monomer and the alcohol group of the initiator/propagating species.^{15b,19} DMAP was also found active in the ROP of LA and CL, in solution or in bulk.^{13,16,17} Associated with an alcohol (isopropyl alcohol, ethanol, benzyl alcohol) or with a ruthenium tris-hydroxylated initiator, namely [Ru(bpyPLA₂)₃][PF₆]₂, DMAP enabled the synthesis of linear and three-arm stars PLAs. Under mild operating conditions (bulk at 135°C or in DCM solution at 35°C), using 0.1-4 equivalent(s) of amine relative to the initiating alcohol, polymers were recovered with M_n up to 57 000 g.mol⁻¹ and PDI < 1.26. A significant advantage of DMAP is its high selectivity during the propagation step. Also, as opposed to TBD, which was shown to catalyze transesterification reactions of the resulting aliphatic polyester if not quenched early enough before the completion of the polymerization,¹⁵ DMAP evidenced quite some resistance to undesirable inter- and/or intra-molecular transesterifications typically encountered in the ROP of cyclic esters (chain reshuffling and backbiting reactions, respectively).^{13,16,17,20,21}

In this contribution, we report on the synthesis of well-defined cyclobutenyl end-capped PLA and PCL from the organocatalyzed ROP of LA and CL, respectively, mediated by TBD or DMAP catalyst in the presence of a mono- or di-hydroxylated cyclobutene derivative as initiator. Subsequent ROMP of these PLA and PCL macromonomers using 2nd generation ruthenium-based Grubbs catalyst afforded well-defined poly(1,4-butadiene)-*g*-polyesters with controlled molecular weights and low dispersity.

Experimental

General Characterization

¹H Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 (200 MHz) and Bruker AC-400 (400 MHz) spectrometers. Chemical shifts are reported in ppm relative to the deuterated solvent resonances. Number-average degrees of polymerization (\overline{DP}_n) were determined by ¹H NMR analysis, based on the comparison of the integrations of the cyclobutene alkene protons at $\delta = 6.10$ -6.15 ppm (2H, labeled (a) in Figure 1) against the methine signals of PLA at $\delta = 5.10$ -5.20 ppm (2 × H × \overline{DP}_n , labeled (h) in Figure 1) (Table 1, Figure 1, Figures S3-S6 in Supporting Information). Similarly, $\overline{DP}_{n,NMR}$ values of PCL macromonomers were determined by the ratio of the integrations of the methylene group of PCL at 4.02-4.10 ppm (labeled (k) in Figure 5A) to the cyclobutene alkene protons at $\delta = 6.10$ -6.15 ppm (labeled (a) in Figure 5A) (Table 2, Figure 5A and Figures S10-S12 in Supporting Information). CL conversions were determined from ¹H NMR spectra of the crude PCL sample, from the integration (Int) ratio $\text{Int}_{\text{PCL}} / [\text{Int}_{\text{PCL}} + \text{Int}_{\text{CL}}]$, using the $\text{-CH}_2\text{OC(O)}$ methylene triplet ($\delta_{\text{PCL}} = 4.04$ ppm, $\delta_{\text{CL}} = 4.19$ ppm). Number-average molecular weight (M_n) and dispersity (PDI = M_w / M_n) values were measured by Size Exclusion Chromatography (SEC) using tetrahydrofuran (THF) as an eluent, and carried out using a system equipped with a SpectraSYSTEM AS 1000 autosampler, with a Guard column (Polymer Laboratories, PL gel 5 μm Guard column, 50 x 7.5 mm) followed by two columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2 x 300 x 7.5) and with a SpectraSYSTEM RI-150 detector. The instrument operated at a flow rate of 1.0 mL.min⁻¹ at 35 °C and was calibrated with narrow linear polystyrene (PS) standards with molecular weights ranging from 580 g.mol⁻¹ to 483 000 g.mol⁻¹. All elution curves were calibrated with polystyrene standards. Matrix-Assisted Laser Desorption and Ionization Time Of Flight (MALDI-TOF) mass spectrometry analysis was performed on a Bruker Biflex III MALDI-TOF instrument equipped with a nitrogen laser operating at 337 nm, a 2 GHz sampling rate digitizer, pulsed ion extraction source and reflectron. The laser pulse width is 3 ns and maximum power is 200 mJ. Spectra were recorded in the linear mode with an acceleration voltage of 19 kV and a delay of 200 ns. 100 single shot acquisitions were summed to give the spectra and the data were analyzed using Bruker XTOF software. Samples were prepared by dissolving the matrix (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, DCTB) in the solvent (dichloromethane, DCM, 30 mg.mL⁻¹) and mixing with the polymer (2 mg.mL⁻¹) in the ratio 1:50 (v/v). An aliquot of this solution (1 μL) was spotted directly onto a thin layer of sodium trifluoroacetate in acetone (concentration 19 mg.mL⁻¹) that had been deposited to act as a cationizing agent.

Reagents

All chemicals were purchased from Aldrich unless otherwise noted. Acetic acid (98.0%, Merck), chloroform (CHCl_3 , > 99.8%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 99%), dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$, > 99%, Merck Schuchard), dichloromethane (DCM, HPLC grade, Fisher Chemical), 4-(*N,N*-dimethylamino)pyridine (DMAP, > 99%, Fluka), Grubbs' second generation catalyst (**G2**), *n*-hexane (> 97.0%), methanol (99%), silica gel for chromatography (SiO_2 , 0.035 - 0.070 mm, 60 Å, Acros Organics), tetrahydrofuran (THF, > 99.8%) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%) were used as received. ϵ -Caprolactone (CL, 99%, Acros) and toluene (99.9%) were distilled from CaH_2 . *L*-lactide (LA, 98%) was recrystallized in toluene three times prior to use. DCM and THF were dried over dry solvent stations GT S100. *cis*-Cyclobut-3-ene-1,2-dicarboxylic anhydride (**1**),²² *cis*-3,4-bis(hydroxymethyl)cyclobutene (**2**),²³ and *cis*-4-benzyloxymethyl-3-hydroxymethylcyclobutene (**3**)²⁴ were synthesized according to literature procedures.

General procedure for the preparation of cyclobutenyl-terminated PLA macromonomers via ROP

A dry 10 mL Schlenk flask equipped with a stirring bar, a rubber septum, LA, catalyst, inimer and degassed anhydrous DCM were introduced into a glovebox. LA (1.00 g, 6.94 mmol) and catalyst (TBD or DMAP) were added into the Schlenk flask. The desired quantity of inimer (**2** or **3**) was dissolved in degassed anhydrous DCM (2.90 mL). This solution was added to the Schlenk flask (which was then capped with the rubber septum) and allowed to stir. When an homogeneous solution was obtained, the Schlenk flask was removed from the glovebox and immersed in an oil bath preset at 35°C to allow the polymerization to proceed (initial reaction time, $t = 0$). The reaction mixture was stirred over the appropriate time. The polymerization was quenched by the addition of acetic acid solution in toluene (0.2 mL, 16.5 mmol/L). The resulting mixture was then concentrated to dryness under vacuum. The crude polymer was then dissolved in DCM (2 mL) and precipitated into cold methanol (10 mL), filtered and dried overnight under reduced pressure (typical isolated yield: 90-95%). The recovered polymer was then analyzed by NMR, SEC, and MALDI-TOF mass spectrometry.

Cyclobutenyl-terminated PLA initiated from 3. White powder. $[\text{LA}]_0/[\mathbf{3}]_0/[\text{DMAP}]_0 = 14/1/4$ (Table 1, run 3); $\overline{DP}_{n,NMR} = 18$; $M_{n,SEC} = 4\ 100\ \text{g}\cdot\text{mol}^{-1}$; PDI = 1.15. $^1\text{H NMR}$ (200 MHz, CDCl_3), δ (ppm): 7.35-7.30 (m, 5H, C_6H_5), 6.15-6.10 (m, 2H, $\text{CH}=\text{CH}$), 5.20-5.10 (q, $J = 7$ Hz, 48H, $\text{CH}-\text{CH}_3$ of the PLA repeating unit), 4.50 (s, 2H, $\text{CH}_2-\text{C}_6\text{H}_5$), 4.40-4.20 (m, 3H, $\text{CH}-\text{CH}_2-\text{O}-\text{CO}$, $\text{C}(\text{O})\text{CH}(\text{CH}_3)-\text{OH}$), 3.55 (m, 2H, $\text{CH}_2-\text{O}-\text{Bn}$), 3.20 (m, 2H, $=\text{CH}-\text{CH}-\text{CH}_2$), 1.55 (d, $J = 7$ Hz, 144H, $\text{CH}-\text{CH}_3$ of the PLA repeating unit), 1.50 (m, 3H, $\text{CH}(\text{CH}_3)-\text{OH}$) (Figure 1).

Cyclobutenyl-terminated PLA initiated from 2. White powder. $[\text{LA}]_0/[\mathbf{2}]_0/[\text{DMAP}]_0 = 14/1/8$ (Table 1, run 7); $\overline{DP}_{n,NMR} = 20$; $M_{n,SEC} = 4\ 600\ \text{g}\cdot\text{mol}^{-1}$; PDI = 1.09. $^1\text{H NMR}$ (200 MHz, CDCl_3), δ (ppm): 6.10 (s, 2H, $\text{CH}=\text{CH}$), 5.20-5.10 (q, $J = 7$ Hz, 40H, $\text{CH}-\text{CH}_3$ of the PLA repeating unit), 4.35-4.25 (m, 6H, $\text{CH}-\text{CH}_2-\text{O}-\text{C}(\text{O})$, $\text{C}(\text{O})\text{CH}(\text{CH}_3)-\text{OH}$), 3.25 (m, 2H, $=\text{CH}-\text{CH}$), 1.55 (d, $J = 7$ Hz, 120H, $\text{CH}-\text{CH}_3$ of the PLA repeating unit), 1.50 (m, 6H, $\text{CH}(\text{CH}_3)-\text{OH}$) (Figure S5 in Supporting Information).

General procedure for the preparation of cyclobutenyl-terminated PCL macromonomers via ROP

A dry 10 mL Schlenk flask equipped with a stirring bar, a rubber septum, CL, TBD, inimer and degassed anhydrous THF or toluene were introduced into a glovebox. The desired quantities of inimer (**2** or **3**) and TBD were added into the Schlenk flask and dissolved in degassed anhydrous THF or toluene (4.4 mL). The Schlenk flask was capped with a rubber septum and when an homogeneous solution was obtained, it was removed from the glovebox and immersed in an oil bath preset at 25°C. CL (1.00 g, 8.76 mmol) was added to the Schlenk flask *via* a syringe (initial reaction time, $t = 0$) and the polymerization allowed to proceed. The reaction mixture was stirred over the appropriate time. The polymerization was quenched by the addition of acetic acid solution in toluene (0.2 mL, 16.5 mmol/L). The resulting mixture was then concentrated to dryness under vacuum and the conversion determined by $^1\text{H NMR}$ analysis of the residue in CDCl_3 . Finally, the crude polymer was dissolved in DCM (2 mL) and purified upon precipitation into cold methanol (10 mL), filtered and dried overnight under reduced pressure (typical isolated yield 90-95%). The recovered polymer was then analyzed by NMR, SEC, and MALDI-TOF mass spectrometry.

Cyclobutenyl-terminated PCL initiated from 3. White powder. $[\text{CL}]_0/[\mathbf{3}]_0/[\text{TBD}]_0 = 18/1/0.34$ (Table 2, run 4); conversion > 99%; $\overline{DP}_{n,NMR} = 16$; $M_{n,SEC} = 3\ 900\ \text{g}\cdot\text{mol}^{-1}$; PDI = 1.10. $^1\text{H NMR}$ (200 MHz, CDCl_3), δ (ppm): 7.35 ppm (m, 5H, C_6H_5), 6.10 (s, 2H, $\text{CH}=\text{CH}$), 4.50 (s, 2H, $\text{O}-\text{CH}_2-\text{C}_6\text{H}_5$), 4.25 (m, 2H, $\text{CH}-\text{CH}_2-\text{O}-\text{C}(\text{O})$), 4.05 (t, $J = 7$ Hz, 32H, $\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(\text{O})$ of the PCL repeating unit), 3.70-3.55 (m, 4H, $\text{CH}_2-\text{O}-\text{Bn}$, CH_2-OH), 3.25 (m, 2H, $=\text{CH}-\text{CH}$), 2.30 (t, $J = 7$ Hz, 32H, $\text{O}-\text{C}(\text{O})-\text{CH}_2-\text{CH}_2$ of the PCL repeating unit), 1.80-1.50 (m, 64H, $\text{C}(\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2$ of the PCL repeating unit), 1.50-1.35 (m, 32H, $\text{C}(\text{O})-(\text{CH}_2)_2-\text{CH}_2$ of the PCL repeating unit) (Figure 5A).

Cyclobutenyl-terminated PCL initiated from 2. White powder. $[\text{CL}]_0/[\mathbf{2}]_0/[\text{TBD}]_0 = 18/1/0.34$ (Table 2, run 1); conversion > 99%; $\overline{DP}_{n,NMR} = 19$; $M_{n,SEC} = 4\ 400\ \text{g}\cdot\text{mol}^{-1}$; PDI = 1.08. $^1\text{H NMR}$ (200 MHz, CDCl_3), δ (ppm): 6.10 (s, 2H, $\text{CH}=\text{CH}$), 4.20 (m, 4H, $\text{CH}-\text{CH}_2-\text{O}-\text{C}(\text{O})$), 4.05 (t, $J = 7$ Hz, 38H, $\text{CH}_2-\text{O}-\text{C}(\text{O})$ of the PCL repeating unit), 3.65 (t, $J = 6.5$ Hz, 4H, CH_2-OH), 3.20 (m, 2H, $=\text{CH}-\text{CH}$), 2.30 (t, $J = 7.4$ Hz, 38H, $\text{O}-\text{C}(\text{O})-\text{CH}_2$ of the PCL repeating unit), 1.80-1.50 (m, 76H, $\text{C}(\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2$ of the PCL repeating unit), 1.50-1.35 (m, 38H, $\text{C}(\text{O})-(\text{CH}_2)_2-\text{CH}_2$ of the PCL repeating unit) (Figure S11 in Supporting Information).

General procedure for the preparation of graft copolymers *via* ROMP

In a typical experiment, a dry Schlenk tube was charged with the desired quantity of macromonomer and a stir bar. The Schlenk flask

was capped with a rubber septum, and cycled three times between vacuum and argon to remove oxygen. The desired quantity of degassed, anhydrous toluene or dichloroethane ($[M]_0 = 0.01 - 0.04 \text{ mol/L}$) was added *via* a syringe under an argon atmosphere to dissolve the macromonomer. The Schlenk flask was immersed in an oil bath preset at 70°C and was stirred under argon for 10 min. A stock solution of catalyst **G2** in degassed anhydrous toluene or dichloroethane ($[\mathbf{G2}] = 47 \text{ mmol/L}$) was prepared in a separate vial. The desired quantity of catalyst was injected into the macromonomer solution to initiate the polymerization. The reaction mixture was stirred over 3 h. The polymerization was quenched by the addition of two drops of ethyl vinyl ether. The solvent was removed under reduced pressure for NMR and SEC measurements. The reaction mixture was then diluted in DCM and precipitated into 10 mL of stirred cold methanol. The crude PBu-*g*-PLA copolymers were dissolved in CHCl_3 and passed through a short SiO_2 column (5 g for a 0.2 g PBu-*g*-PLA sample). The resulting polymer solution volumes were reduced, and white or slightly yellow copolymers were recovered by precipitating into hexane.

1,4-Polybutadiene-*g*-poly(L-lactide) PBu₁₀-*g*-3-PLA₂₄. Brown plastic. $[\mathbf{3-PLA}_{24}]_0/[\mathbf{G2}]_0 = 10$ (Table 3, run 13); conversion : 88%; $M_{n,theo} = 36\,601 \text{ g}\cdot\text{mol}^{-1}$; $M_{n,SEC} = 30\,500 \text{ g}\cdot\text{mol}^{-1}$; PDI = 1.10. $^1\text{H NMR}$ (200 MHz, CDCl_3), δ (ppm): 5.10 (q, $J = 7.1 \text{ Hz}$, 212H, CH-CH_3 of the PLA repeating unit), 4.30 (q, $J = 7.2 \text{ Hz}$, 18H, $\text{C(O)CH(CH}_3\text{)-OH}$), 1.52 (d, $J = 7.2 \text{ Hz}$, 634H, CH-CH_3 of the PLA repeating unit), 1.42 (d, $J = 7.1 \text{ Hz}$, 52H, $\text{C(O)CH(CH}_3\text{)-OH}$) (Figure S22 in Supporting Information).

1,4-Polybutadiene-*g*-poly(L-lactide) PBu₁₀-*g*-2-PLA₂₀. Brown plastic. $[\mathbf{2-PLA}_{20}]_0/[\mathbf{G2}]_0 = 10$ (Table 3, run 17); conversion : 90%; $M_{n,theo} = 29\,901 \text{ g}\cdot\text{mol}^{-1}$; $M_{n,SEC} = 20\,900 \text{ g}\cdot\text{mol}^{-1}$; PDI = 1.05. $^1\text{H NMR}$ (200 MHz, CDCl_3), δ (ppm): 5.17 (q, $J = 7.1 \text{ Hz}$, 180H, CH-CH_3 of the PLA repeating unit), 4.36 (q, $J = 7.2 \text{ Hz}$, 18H, $\text{C(O)CH(CH}_3\text{)-OH}$), 1.65-1.53 (d, $J = 7.1 \text{ Hz}$, 540H, CH-CH_3 of the PLA repeating unit), 1.53-1.46 (m, 54H, $\text{C(O)CH(CH}_3\text{)-OH}$) (Figure S23 in Supporting Information).

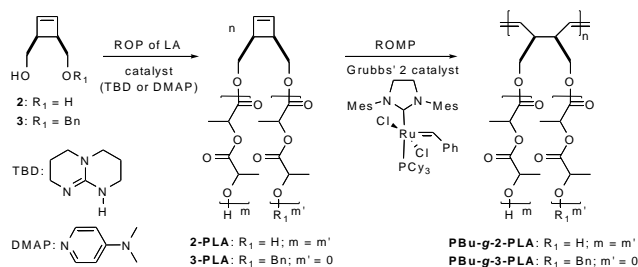
1,4-Polybutadiene-*g*-poly(ϵ -caprolactone) PBu₁₀-*g*-3-PCL₁₆. Brown plastic. $[\mathbf{3-PCL}_{16}]_0/[\mathbf{G2}]_0 = 10$ (Table 3, run 1); conversion : 97%; $M_{n,theo} = 20\,391 \text{ g}\cdot\text{mol}^{-1}$; $M_{n,SEC} = 30\,250 \text{ g}\cdot\text{mol}^{-1}$; PDI = 1.11. $^1\text{H NMR}$ (400 MHz, CDCl_3), δ (ppm): 7.30-7.16 ppm (m, 50H, C_6H_5), 5.10-5.60 (bs, 20H, CH=CH), 4.06 (t, $J = 6.6 \text{ Hz}$, 320H, $\text{CH}_2\text{-CH}_2\text{-O-C(O)}$ of the PCL repeating unit), 3.65 (t, $J = 6.3 \text{ Hz}$, 20H, $\text{CH}_2\text{-OH}$), 2.31 (t, $J = 7.4 \text{ Hz}$, 320H, $\text{O-C(O)-CH}_2\text{-CH}_2$ of the PCL repeating unit), 1.77-1.54 (m, 640H, $\text{C(O)-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$ of the PCL repeating unit), 1.48-1.28 (m, 320H, $\text{C(O)-(CH}_2\text{)}_2\text{-CH}_2$ of the PCL repeating unit) (Figure 5B).

1,4-Polybutadiene-*g*-poly(ϵ -caprolactone) PBu₁₀-*g*-2-PCL₁₉. Brown plastic. $[\mathbf{2-PCL}_{19}]_0/[\mathbf{G2}]_0 = 10$ (Table 3, run 7); conversion : 95%; $M_{n,theo} = 22\,891 \text{ g}\cdot\text{mol}^{-1}$; $M_{n,SEC} = 22\,950 \text{ g}\cdot\text{mol}^{-1}$; PDI = 1.06. $^1\text{H NMR}$ (200 MHz, CDCl_3), δ (ppm): 5.20-5.06 ppm (bs, 20H, CH=CH), 4.06 (t, $J = 6.8 \text{ Hz}$, 380H, $\text{CH}_2\text{-CH}_2\text{-O-C(O)}$ of the PCL repeating unit), 3.65 (t, $J = 6.8 \text{ Hz}$, 20H, $\text{CH}_2\text{-OH}$), 2.31 (t, $J = 7.3 \text{ Hz}$, 380H, $\text{O-C(O)-CH}_2\text{-CH}_2$ of the PCL repeating unit), 1.77-1.53 (m, 760H, $\text{C(O)-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$ of the PCL repeating unit), 1.50-1.29 (m, 380H, $\text{C(O)-(CH}_2\text{)}_2\text{-CH}_2$ of the PCL repeating unit) (Figure S24 in Supporting Information).

Results and Discussion

Synthesis of α -cyclobutenyl poly(L-lactide) (PLA) macromonomers

PLA macromonomers end-capped by a cyclobutenyl group were synthesized by ring-opening polymerization (ROP) of *L*-lactide (LA) promoted by a catalytic system composed of an organocatalyst of the guanidine or amine type, namely 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) or 4-(*N,N*-dimethylamino)pyridine (DMAP), in the presence of a di- or monohydroxylated derivative of cyclobutene, *i. e.*, *cis*-3,4-bis(hydroxymethyl)cyclobutene (**2**) or *cis*-4-benzyloxymethyl-3-hydroxymethylcyclobut-1-ene (**3**), used as initiator (Scheme 1). Representative results of these ROP experiments are summarized in Table 1.



Scheme 1 Synthesis of PLA macromonomers from mono- or dihydroxyl inimers and their subsequent ROMP.

Table 1 Characteristics of the **2-PLA** and **3-PLA** macromonomers synthesized upon ROP of LA mediated by TBD or DMAP catalysts and inimer **2** or **3** at 35 °C

Run	Sample ^a	Catalyst	[LA] ₀ /[inimer] ₀ /[catalyst] ₀	Reaction time ^b (h)	$\overline{DP}_{n,NMR}$ ^c	$\overline{M}_{n,NMR}$ ^d (g.mol ⁻¹)	$\overline{M}_{n,SEC}$ ^e (g.mol ⁻¹)	PDI ^e
1	3-PLA ₂₄	TBD	14/1/0.5	1	24	3 660	4 400	1.50
2	3-PLA ₂₄	TBD	14/1/0.5	0.3	24	3 660	4 400	1.34
3	3-PLA ₁₈	DMAP	14/1/4	24	18	2 800	4 100	1.15
4	3-PLA ₂₄	DMAP	14/1/4	24	24	3 660	4 400	1.18
5	3-PLA ₄₁	DMAP	35/1/4	48	41	6 110	6 600	1.16
6	3-PLA ₇₆	DMAP	70/1/4	72	76	11 150	7 500	1.17
7	2-PLA ₂₀	DMAP	14/1/8	22	20	2 990	4 600	1.09
8	2-PLA ₄₀	DMAP	34.5/1/8	24	40	5 870	9 500	1.10
9	2-PLA ₇₇	DMAP	70/1/8	24	77	11 200	12 200	1.14

^a In the sample name, the first number denotes the inimer and the last number in subscript refers to the number of LA repeating units determined by ¹H NMR. ^b The reaction time was not necessarily optimized. ^c Calculated from ¹H NMR spectra of precipitated macromonomer by comparing the peaks areas of the cyclobutene alkene protons at $\delta = 6.10$ -6.15 ppm and the methine proton of the PLA at $\delta = 5.10$ -5.20 ppm. ^d Determined by NMR analysis of precipitated macromonomer from $\overline{M}_{n,NMR} = (\overline{DP}_{n,NMR} \times M_{LA}) + M_{inimer}$ with $M_{LA} = 144$ g.mol⁻¹, $M_{inimer 2} = 114$ g.mol⁻¹ and $M_{inimer 3} = 204$ g.mol⁻¹. ^e Determined by SEC in tetrahydrofuran (THF) with RI detector, calibrated with linear polystyrene standards.

The polymerization of LA was first investigated from the TBD/**3** catalytic system with a LA-to-initiator molar ratio of 14 in dichloromethane (DCM) at 35°C (Table 1, runs 1-2). The NMR spectra of the recovered PLAs showed the downfield shift of the signal of the methylene protons of the initiating group from $\delta = 3.60$ -3.80 ppm in **3** to $\delta = 4.20$ -4.40 ppm in **3-PLA₂₄** (Figure S1 in Supporting Information). SEC analysis of the crude products featured an unsymmetrical trace (Figure S2A in the Supporting Information) together with a rather broad dispersity (PDI = 1.50). A shorter reaction time allowed to decrease the PDI down to 1.34 while retaining a quantitative conversion (Table 1, run 2 vs 1). Nevertheless, SEC analysis of the crude product still displayed an unsymmetrical trace (Figure S2B in Supporting Information). These preliminary experiments suggested the occurrence of adverse side transesterification reactions - as quite often encountered in the TBD-catalyzed ROP of LA,^{15,20,21} and thus prompted the search for a better catalyst.

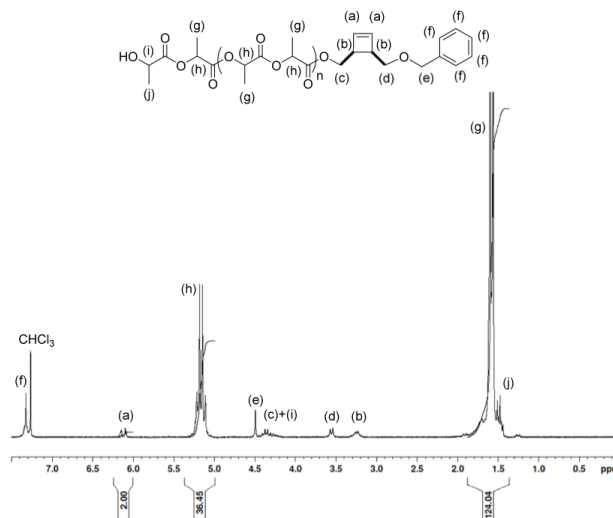


Fig. 1 ¹H NMR (200 MHz, CDCl₃, 25 °C) spectrum of precipitated **3-PLA₁₈** issued from the ROP of LA in DCM at 35°C using inimer **3** as the initiator and DMAP as the catalyst with [LA]₀/[**3**]₀ = 14 (Table 1, run 3).

DMAP, a catalyst known to limit such transesterification reactions,^{12b,12e,13a,16} was then evaluated in the ROP of LA carried out in DCM at 35 °C (Table 1, runs 3-9). A series of cyclobutene-capped PLA macromonomers were thus synthesized from the DMAP-promoted ROP of LA, in the presence of cyclobutenes **2-3** featuring one or two hydroxyl initiating groups, respectively, with targeted number-average molecular weights (M_n) of 2 000, 5 000 and 10 000 g.mol⁻¹. Number-average degrees of polymerization (\overline{DP}_n) were determined by ¹H NMR analysis of the precipitated macromonomers, based on the comparison of the integrations of the cyclobutene alkene protons at $\delta = 6.10$ - 6.15 ppm (labeled (a) in Figure 1) against the methine signals of the PLA at $\delta = 5.10$ - 5.20 ppm (labeled (h) in Figure 1) (Table 1, Figure 1, Figures S3-S6 in Supporting Information). The experimental \overline{DP}_n values determined from NMR analysis increased with increasing [LA]₀/([**2**]₀ or [**3**]₀) ratio. SEC analyses indicated that the resulting

macromonomers showed increasing \overline{M}_n with increasing $[LA]_0/[2]_0$ or $[3]_0$ ratios, as evidenced by a shift of the SEC traces to the higher molar mass values, while retaining a narrow and unimodal elution peak with PDI in the range 1.16-1.18 (Figure 2 for **3-PLA** macromonomers, Figure S7 in Supporting Information for **2-PLA** macromonomers).

The end-group fidelity of the PLA macromonomers was confirmed by Matrix-Assisted Laser Desorption and Ionization Time Of Flight (MALDI-TOF) mass spectrometry analysis of a low molar mass sample of **3-PLA₁₈** macromonomer (Table 1, run 3) (Figure 3; Figure S8 in Supporting Information for **2-PLA₂₀** macromonomer). The spectrum displayed a major distribution spaced by $m/z = 144$, corresponding to the molar mass of the LA repeating unit (calculated value = 144.04 g.mol⁻¹). The most intense signal detected at m/z ($[M + Na^+]$) = 2819.69 is assignable to a sodium charged PLA chain with an even number of lactoyl repeating units (C(O)CH(CH₃)O) of 36, and with a 4-benzyloxymethyl-3-methylcyclobutene group and a hydroxyl group termini, which well-agrees with the calculated value (calculated isotopic mass for ¹²C₁₂₁¹H₁₆₀¹¹Na¹⁶O₇₄ = 2819.86 g.mol⁻¹). Moreover, the other lower intensity series (m/z ($[M + Na^+]$) = 2747.67) corresponds to an analogous series depleted from one lactoyl fragment of the LA (calculated isotopic mass for 35 lactoyl repeating units: ¹²C₁₁₈¹H₁₅₆¹¹Na¹⁶O₇₂ = 2747.84 g.mol⁻¹), consistent with the occurrence of minor intermolecular transesterification side-reactions (backbiting),²⁰ as hinted from the PDI of 1.18 measured by SEC.

Synthesis of α -cyclobutenyl poly(ϵ -caprolactone) (PCL) macromonomers

PCL macromonomers end-terminated by a cyclobutenyl group were then similarly synthesized *via* ROP of ϵ -caprolactone (CL) initiated by inimer **2** or **3** with $[CL]_0/[2]_0$ or $[3]_0$ feed ratios ranging from 14/1 to 70/1 (Scheme 2). The polymerization was performed at 25 °C in THF or toluene, selecting TBD as the catalyst for its efficiency in promoting the ROP of CL and for its wider use relative to DMAP in reported procedures for the ROP of CL.¹⁵ Representative results of these ROP experiments are summarized in Table 2.

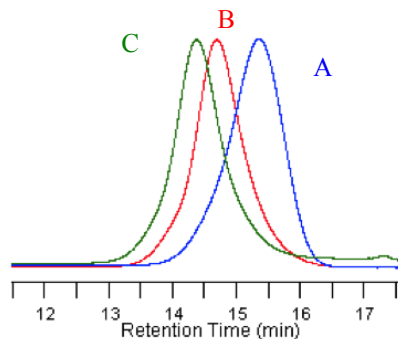


Fig. 2 SEC traces for (A) **3-PLA₁₈** (Table 1, run 3), (B) **3-PLA₄₁** (Table 1, run 5), and (C) **3-PLA₇₆** (Table 1, run 6).

Table 2 Characteristics of the **2-PCL** and **3-PCL** macromonomers synthesized upon ROP of CL mediated by TBD catalyst and inimer **2** or **3** at 25 °C

Run	Sample ^a	$[CL]_0/[inimer]_0/[TBD]_0$	Solvent	Reaction time ^b (h)	Conv. ^c (%)	$\overline{DP}_{n,NMR}$ ^d (g.mol ⁻¹)	$\overline{M}_{n,NMR}$ ^e (g.mol ⁻¹)	$\overline{M}_{n,SEC}$ ^f (g.mol ⁻¹)	PDI ^f
1	2-PCL ₁₉	18/1/0.34	THF	4.5	> 99	19	2 280	4 400	1.08
2	2-PCL ₄₇	48/1/0.65	Toluene	5	> 99	47	5 470	8 200	1.16
3	2-PCL ₈₁	96/1/0.65	Toluene	5	81	81	9 350	13 700	1.18
4	3-PCL ₁₆	18/1/0.34	THF	4.5	> 99	16	2 030	3 900	1.10
5	3-PCL ₃₈	48/1/0.65	THF	20	83	38	4 300	5 670	1.13
6	3-PCL ₃₈	48/1/0.65	Toluene	5	79	38	4 340	5 870	1.16
7	3-PCL ₈₄	96/1/0.65	Toluene	5	62	84	9 780	10 200	1.22

^a In the sample name, the first number denotes the inimer and the last number in subscript refers to the number of CL repeating units determined by ¹H NMR. ^b The reaction time was not necessarily optimized. ^c The CL monomer conversions were determined by comparing the peak areas of the methylene triplet of PCL at $\delta = 4.02$ -4.10 ppm and the methylene group of CL at $\delta = 4.21$ ppm from ¹H NMR spectra of the crude mixture. ^d Calculated from ¹H NMR spectra by comparing the peak areas of the cyclobutene alkene protons at $\delta = 6.10$ -6.15 ppm and the -CH₂CH₂OC(O) methylene triplet at $\delta = 4.02$ -4.10 ppm. ^e Determined by NMR analysis from $\overline{M}_{n,NMR} = (\overline{DP}_{n,NMR} \times M_{CL}) + M_{inimer}$ with $M_{CL} = 114$ g.mol⁻¹, $M_{inimer 2} = 114$ g.mol⁻¹ and $M_{inimer 3} = 204$ g.mol⁻¹. ^f Determined by SEC in tetrahydrofuran (THF) with RI detector, calibrated with linear polystyrene standards.

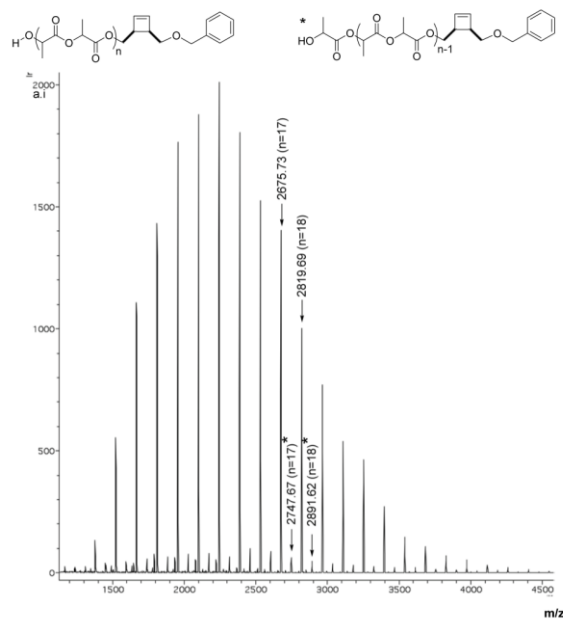
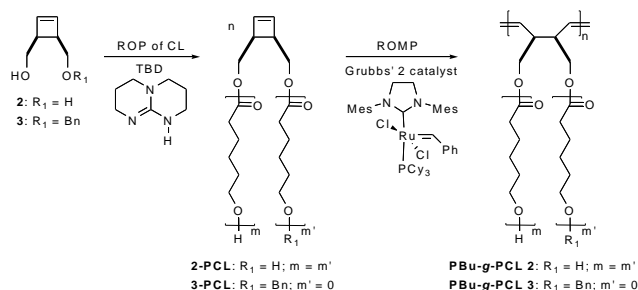


Fig. 3 MALDI-TOF mass spectrum (matrix: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) + sodium trifluoroacetate (NaTFA)) of the cyclobutenyl-functionalized PLA synthesized by ROP using inimer **3** as the initiator and DMAP as the catalyst in DCM at 35 °C with $[LA]_0/[3]_0 = 14/1$ (Table 1, run 3).



Scheme 2 Synthesis of PCL macromonomers from mono- or dihydroxyl inimers and their subsequent ROMP.

The ROP of CL in solution proceeded within a few hours (typically 5 hours) affording moderate-to-high CL conversions resulting in quite well-defined PCLs. Although the operating conditions were not strictly the same, the ROP of LA promoted by DMAP was found slower than that of CL mediated by TBD, whichever the inimer. For instance, TBD enabled the almost quantitative conversion of 48 CL units in toluene within 5 hours thereby affording PCLs of molar mass up to $M_{n,SEC} = 13\,700\text{ g}\cdot\text{mol}^{-1}$ in comparison with DMAP which required 48 h to afford a quantitative conversion of 41 LA units. All PCLs featured controlled molar mass values with molar mass values determined experimentally in good agreement with the calculated data. The SEC traces of the PCL macromonomers displayed a monomodal distribution with rather narrow dispersity values ranging from PDI = 1.08 to 1.22 as depicted Figure 4 for **3-PCL** macromonomers (Figure S9 in Supporting Information for **2-PCL** macromonomers).

The resulting PCL macromonomers were further characterized by ^1H NMR spectroscopy and MALDI-TOF mass spectrometry. The end-capping of the PCL chains by cyclobutene was first demonstrated by ^1H NMR spectrum, which clearly showed the downfield shift of methylene protons of the initiating ROP group from $\delta = 3.60\text{--}3.80\text{ ppm}$ in **3** to $\delta = 4.25\text{ ppm}$ in **3-PCL** macromonomers, as illustrated in Figure 5A (Figures S10-S12 in Supporting Information). DP_n were determined by ^1H NMR analysis, based on the comparison of the integrations of the cyclobutene alkene protons at $\delta = 6.10\text{--}6.15\text{ ppm}$ (labeled (a) in Figure 5A) against the $-\text{CH}_2\text{CH}_2\text{OC(O)}$ methylene triplet of the PCL at $\delta = 4.02\text{--}4.10\text{ ppm}$ (labeled (k) in Figure 5A) (Table 2, Figure 5A, Figures S10-S12 in Supporting Information). The $DP_{n,NMR}$ values of PCL macromonomers, determined by ^1H NMR, gave molar mass values in agreement with the ones predicted from the monomer feed ratios. Toluene was the favored solvent for the synthesis of higher molecular weight macromonomers, as it allows decreasing the reaction time while retaining a narrow dispersity (Table 2, runs 5-6). Quantitative chain-end functionalization of PCLs by the initiator was further confirmed by MALDI-TOF mass spectrometry analysis. The spectrum of a low molar mass sample of **3-PCL**₁₆ macromonomer illustrated in Figure 6 revealed a unique distribution

mode with a constant mass difference of 114 between each signal, corresponding to the molar mass of CL repeating unit (calculated value = 114.07 g.mol⁻¹) (Figure S13 in Supporting Information for **2-PCL**₁₉ macromonomer). The most intense peak at *m/z* = 1824.06 corresponds to a polymer chain consisting of 14 CL units, end-capped by 4-benzyloxymethyl-3-methylcyclobutene and hydroxyl groups, and a sodium atom responsible for ionization (calculated isotopic mass for ¹²C₉₇¹H₁₅₆¹¹Na¹⁶O₃₀ = 1824.06 g.mol⁻¹).

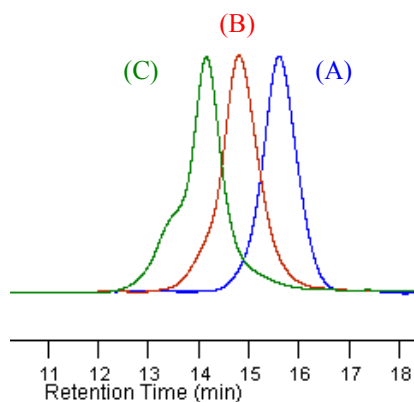


Fig. 4 SEC traces for (A) **3-PCL**₁₆ (Table 2, run 4), (B) **3-PCL**₃₈ (Table 2, run 6) and (C) **3-PCL**₈₄ (Table 2, run 7).

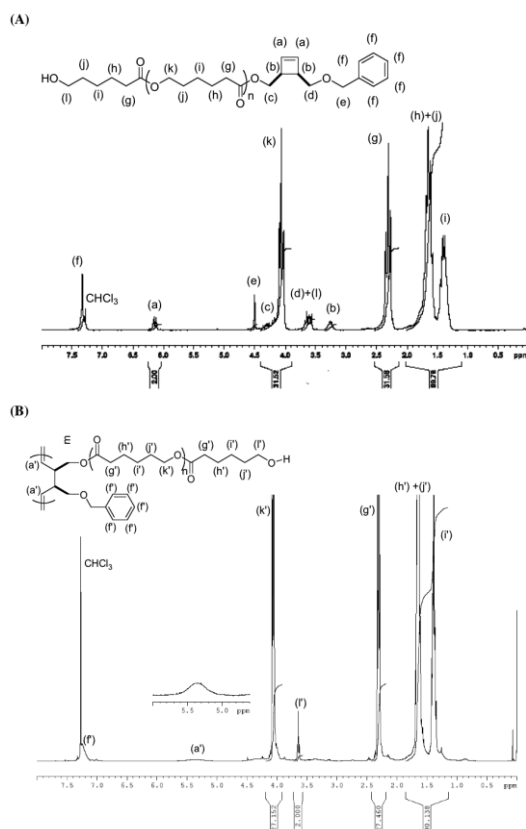


Fig. 5 ¹H NMR spectra (200 MHz, CDCl₃, 25 °C) of precipitated (A) **3-PCL**₁₆ from the ROP of CL in THF at 25°C using inimer **3** as the initiator and TBD as the catalyst with [CL]₀/[**3**]₀ = 18 (Table 2, run 4), and (B) **PBu**₁₀-**g-3-PCL**₁₆ issued from the ROMP of **3-PCL**₁₆ in toluene at 70°C using **G2** as the catalyst with [**3-PCL**₁₆]/[**G2**] = 10 for a reaction time of 3 h (Table 3, run 1).

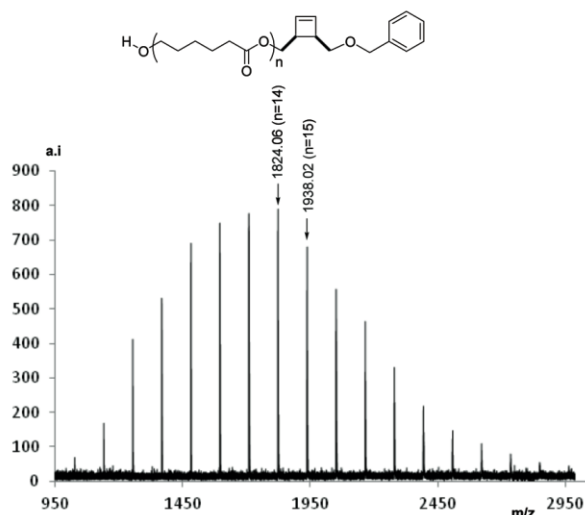


Fig. 6 MALDI-TOF mass spectrum (matrix: DCTB + NaTFA) of the cyclobutenyl-functionalized PCL synthesized by ROP using inimer **3** as the initiator and TBD as the catalyst in THF at 25°C with $[CL]_0/[3]_0 = 18/1$ (Table 2, run 4).

ROMP of α -cyclobutenyl PCL and PLA macromonomers

PCL and PLA macromonomers with one (**3-PCL**, **3-PLA**) and two (**2-PCL**, **2-PLA**) arms of varying lengths were subjected to ROMP (Schemes 1 & 2) using 2nd generation Grubbs' catalyst, which is one of the most active and thermally stable ROMP initiators^{2h,3a-c} especially for the ROMP of cyclobutene macromonomers^{4a,5a,7} and other sterically hindered macromonomers.^{3a,10a}

ROMP of cyclobutenyl macromonomers bearing one PCL or PLA arm

In order to have the macromonomer entirely polymerized, cyclobutene macromonomer with one PCL chain **3-PCL**₁₆ with a \overline{DP}_n of 16 and a low macromonomer-to-catalyst ratio of 10 was applied (Table 3, run 1). ROMP was carried out in toluene at 70°C with an olefin concentration of 0.01 mol.L⁻¹. The final macromonomer conversion was measured by SEC. It was shown that ROMP of **3-PCL**₁₆ could afford well-defined brush copolymers with high overall macromonomer conversions (> 97%) and a uniform size distribution, with a low PDI (1.11), similar to that of the macromonomer (PDI = 1.10) (Figure 7A vs 7B), which demonstrated the living characteristics and high efficiency of "ROMP-able"-terminated macromonomers. The high conversion of **3-PCL**₁₆ in ROMP was also revealed by ¹H NMR spectroscopic analysis. Indeed, in the spectrum of **PBu**_{10-g-3-PCL₁₆ (Figure 5B), the total disappearance of the characteristic macromonomer olefinic protons resonance at $\delta = 6.10$ ppm and the concomitant appearance of the 'ene' protons resonance of the PBu backbone at $\delta = 5.10$ -5.60 ppm confirms the quantitative consumption of the macromonomers, in good agreement with the SEC analysis. These results from SEC and NMR measurements indicated that a well-defined graft copolymer has been prepared. The \overline{M}_n determination was complicated by ¹H NMR spectroscopy as the chain-ends are not observable. However, SEC measurements give access to the molecular weight values using a calibration with linear PS standards; these values were used for comparison only.}

Table 3 ROMP of PCL and PLA macromonomers using 2nd generation Grubb's catalyst at 70°C during 3h

Run	Grafted copolymer	[M] ₀ /[I] ₀ ^a	[M] ₀ (mol.L ⁻¹)	Solvent	$\overline{M}_{n,theo}$ ^b (g.mol ⁻¹)	Conv. ^c SEC (%)	$\overline{M}_{n,SEC}$ ^d (g.mol ⁻¹)	PDI ^d
1	PBu _{10-g-3} -PCL ₁₆	10	0.01	Toluene	20 391	97	30 250	1.11
2	PBu _{50-g-3} -PCL ₁₆	50	0.01	Toluene	101 591	85	84 200	1.19
3	PBu _{50-g-3} -PCL ₁₆	50	0.04	Toluene	101 591	95	97 400	1.08
4	PBu _{100-g-3} -PCL ₁₆	100	0.04	Toluene	203 091	65	- ^e	- ^e
5	PBu _{10-g-3} -PCL ₃₈	10	0.01	Toluene	43 131	79	43 800	1.10
6	PBu _{10-g-3} -PCL ₈₄	10	0.01	Toluene	97 891	80	80 700	1.08
7	PBu _{10-g-2} -PCL ₁₉	10	0.01	Toluene	22 891	95	22 950	1.06
8	PBu _{50-g-2} -PCL ₁₉	50	0.04	Toluene	114 091	95	79 300	1.30
9	PBu _{100-g-2} -PCL ₁₉	100	0.04	Toluene	228 091	70	- ^e	- ^e
10	PBu _{10-g-2} -PCL ₄₇	10	0.01	Toluene	54 791	95	47 100	1.11
11	PBu _{50-g-2} -PCL ₄₇	50	0.04	Toluene	273 591	92	172 200	1.30
12	PBu _{10-g-2} -PCL ₈₁	10	0.01	Toluene	93 591	92	80 100	1.05
13	PBu _{10-g-3} -PLA ₂₄	10	0.01	C ₂ H ₄ Cl ₂	36 601	88	30 500	1.10
14	PBu _{50-g-3} -PLA ₂₄	50	0.04	C ₂ H ₄ Cl ₂	183 001	55	61 650	1.09
15	PBu _{10-g-3} -PLA ₄₁	10	0.01	C ₂ H ₄ Cl ₂	61 101	68	43 600	1.10
16	PBu _{10-g-3} -PLA ₇₆	10	0.01	C ₂ H ₄ Cl ₂	111 501	0	- ^e	- ^e
17	PBu _{10-g-2} -PLA ₂₀	10	0.01	C ₂ H ₄ Cl ₂	29 901	90	20 900	1.05
18	PBu _{50-g-2} -PLA ₂₀	50	0.04	C ₂ H ₄ Cl ₂	149 501	94	56 350	1.17
19	PBu _{10-g-2} -PLA ₄₀	10	0.01	C ₂ H ₄ Cl ₂	58 701	75	41 000	1.08
20	PBu _{10-g-2} -PLA ₇₇	10	0.01	C ₂ H ₄ Cl ₂	112 001	32	60 600	1.05

^a Macromonomer-to-catalyst molar ratio. ^b $\overline{M}_{n,theo} = \overline{M}_{n,NMR} + [M]_0/[I]_0 + M_{extr.}$. ^c Determined by comparing the peak areas of grafted copolymer and residual macromonomer from SEC measurement of the crude product. ^d Determined by SEC in THF with RI detector, calibrated with linear polystyrene standards. ^e Not determined.

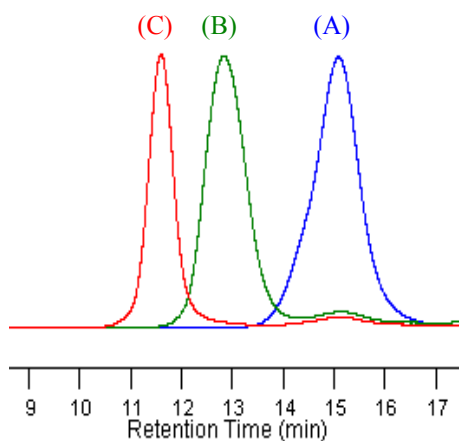


Fig. 7 SEC traces for (A) **3-PCL₁₆** after purification (Table 2, run 4), (B) **PBu_{10-g-3}-PCL₁₆** without purification (Table 3, run 1) and (C) **PBu_{50-g-3}-PCL₁₆** without purification (Table 3, run 3).

The influence of the macromonomer-to-catalyst ratio on the ROMP efficiency was then investigated. **3-PCL₁₆** (Table 2, run 4) was first engaged in ROMP with a macromonomer-to-catalyst ratio of 50 (Table 3, runs 2-3). The ROMP proceeded almost to completion as ascertained by the SEC trace (Figure 7C), although a higher macromonomer concentration of 0.04 M was necessary to achieve reasonable yield (Table 3, run 3 vs run 2, Figure S14A vs. S14B in Supporting Information). The line profile of the resulting **PBu_{50-g-3}-PCL₁₆** is perfectly symmetrical together with a low dispersity (PDI = 1.08), supporting the controlled nature of the ROMP (Figure 7C). However, ROMP of **3-PCL₁₆** (Table 2, run 4) with a macromonomer-to-catalyst ratio of 100 (Table 3, run 4) led to an incomplete conversion as observed by SEC (Figure S15B in Supporting Information). The extension of the reaction time to 24 h did not allow to increase the conversion (Figure S15C in Supporting Information). Steric hindrance from the growing polymacromonomer is probably the limiting factor of the polymerization. As the backbone length increases, the reactivity of the propagating center decreases, making more difficult the incorporation of new macromonomers. Feast *et al.* have demonstrated that the ROMP at high molar macromonomer-to-catalyst ratio ceases as a consequence of steric hindrance.²⁵

ROMP performance of cyclobutene macromonomer with one PLA chain **3-PLA₂₄** (Table 1, run 4) with a \overline{DP}_n of 24 was then studied. Polymerizations have been conducted in dichloroethane (C₂H₄Cl₂) as the PLA macromonomers are insoluble in toluene. The results show a decrease of reactivity compared to their PCL macromonomers analogs as the resulting copolymers issued from ROMP

with macromonomer-to-catalyst ratios of 10 and 50 show a bimodal distribution of the SEC traces consistent with the presence of unreacted macromonomer (Table 3, runs 13-14, Figure S16 in Supporting Information). This difference in reactivity could be ascribed to a lack of solubility of the PLA macromonomers as it was necessary to heat the macromonomer solutions at 50°C for 5 min before adding the catalyst to ensure complete solubilization.

High molecular weight macromonomers with one PCL or PLA arm per cyclobutene have then been subjected to ROMP (Table 3, 5-6, 15-16). Conversions decreased noticeably with increasing M_n of the macromonomers even with a targeted low degree of polymerization ($DP_n = 10$), as observed on the SEC traces (Figures S17, S18 and S19 in Supporting Information). The macromonomer chain length is a critical factor toward the conversion, probably due to the limiting effect of the macromonomer steric hindrance during the propagation step.^{5a,10}

ROMP of cyclobutenyl macromonomers bearing two PCL or PLA arms

ROMP of PCL macromonomers bearing two arms per cyclobutene was next studied. As determined by SEC analysis, high conversions (> 92%) were obtained for macromonomer-to-catalyst ratios of 10 and 50 (Table 3, runs 7-8 and 10-12). Comparison of results obtained during ROMP of macromonomers having similar arm lengths (runs 10 vs. 1 and 11 vs. 3) suggests no influence of the side chain density. Nevertheless, the SEC trace of the crude **PBu₅₀-g-2-PCL₁₉** (Table 3, run 8, Figure 8C) is unsymmetrical with a small shoulder at higher molecular weights originating most likely from polymer chains which were formed by chain-coupling reactions, and a spreading toward lower molecular weights issued from backbiting²⁶ revealing a loss of control of the polymerization as ascertained by the increase of the dispersity value (PDI = 1.30).

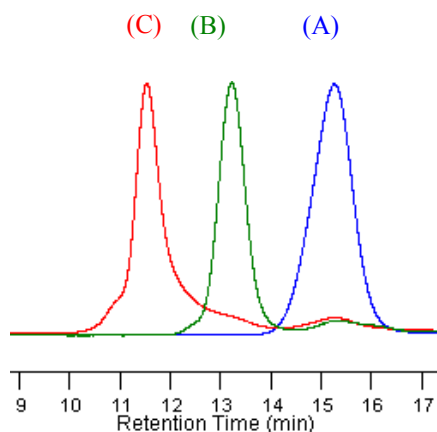


Fig. 8 SEC traces of (A) **2-PCL₁₉** after purification (Table 2, run 4), (B) **PBu₁₀-g-2-PCL₁₉** without purification (Table 3, run 7) and (C) **PBu₅₀-g-2-PCL₁₉** without purification (Table 3, run 8).

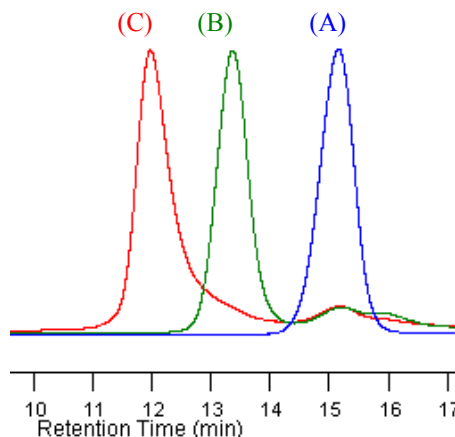


Fig. 9 SEC traces of (A) **2-PLA₂₀** after purification (Table 1, run 6), (B) **PBu₁₀-g-2-PLA₂₀** without purification (Table 3, run 17) and (C) **PBu₅₀-g-2-PLA₂₀** without purification (Table 3, run 18).

For comparison, the reactivity of PLA macromonomers bearing two arms per cyclobutene toward ROMP was also investigated. As shown in Figure 9, conversion of **2-PLA**₂₀ (Table 1, run 7) to brush polymer was very high (*i.e.*, > 90%) for a macromonomer-to-catalyst ratio of 10 (Table 3, run 17, Figure 9B). The well-defined structure of **PBu**₁₀-*g*-**2-PLA**₂₀ was supported by SEC, with a monomodal molecular weight distribution and low dispersity (PDI < 1.05). Use of a macromonomer-to-catalyst ratio of 50 (Table 3, run 18) has resulted in a similar conversion. Although the unpurified **PBu**₅₀-*g*-**2-PLA**₂₀ showed a monomodal distribution with low dispersity (1.17), increasing macromonomer-to-catalyst ratio entailed tailing of the elution profile in the SEC trace (Figure 9C) toward lower molecular weights, that can be ascribed to backbiting, confirming an ill-controlled polymerization.²⁶ Crude copolymers were purified by passing the crude material through a silica column which allowed the removal of unreacted macromonomer as evidenced by the SEC profiles (Figure 10). As expected, ROMP of **2-PLA** macromonomers with longer side chains (Table 3, runs 19-20) resulted in an incomplete conversion as shown by the multimodal SEC traces (Figures S20 and S21 in Supporting Information).

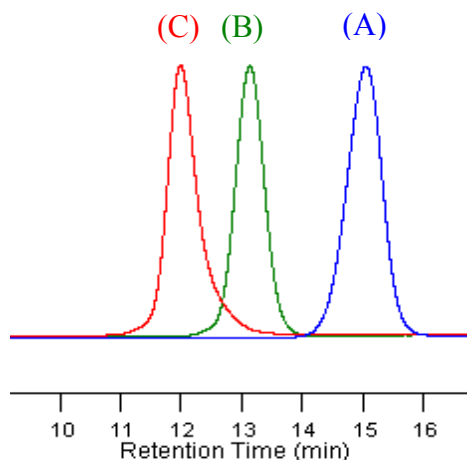


Fig. 10 SEC traces of (A) **2-PLA**₂₀ (Table 1, run 6), (B) **PBu**₁₀-*g*-**2-PLA**₂₀ (Table 3, run 17) and (C) **PBu**₅₀-*g*-**2-PLA**₂₀ (Table 3, run 18) after purification.

Conclusions

Cyclobutenyl-terminated polyester macromonomers bearing one or two PCL or PLA arms have been successfully prepared by organocatalyzed ROP of CL or LA by DMAP or TBD combined with a cyclobutenyl alcohol acting as an initiator. This approach easily provides in high yields cyclobutenyl end-functionalized macromonomers with predictable molecular weights (up to 11 000 g.mol⁻¹) and narrow molecular weight distributions, and the length of the polyester block(s) can be easily tuned. Subsequent “grafting-through” by ROMP using Grubbs’ second generation catalyst afforded polybutadiene brushes featuring pendant polyester (PLA or PCL) side-chains. This efficient ROP/ROMP two-step approach thus allowed the synthesis of well-defined poly(1,4-butadiene)-*g*-polyesters copolymers. To the best of our knowledge, the products resulting from this strategy represent the first examples of poly(1,4-butadiene)-*g*-polyesters through the macromonomer route. These results pave the way to more complicated macromolecular architectures, *e.g.*, by modification of the side-chain termini. Moreover, the hydrolytic (bio)degradation potential of the side chains (that can be used as sacrificial domains) of those bottlebrush copolymers makes them attractive candidates to be used for the preparation of complex hollowed nanostructures.²⁷

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Notes and references

- (a) C. Tsitsilianis, Synthesis of Block and Graft Copolymers. In *Controlled/Living Polymerizations*; K. Matyjaszewski, A. H. E. Müller, Eds.; Wiley-VCH: Weinheim, 2009; pp 445–492. (b) R. Iha, K. L. Wooley, A. M. Nyström, D. J. Burke, M. J. Kade, C. J. Hawker, *Chem. Rev.* 2009, **109**, 5620–5686. (c) S. S. Sheiko, B. S. Sumerlin, K. Matyjaszewski, *Prog. Polym. Sci.* 2008, **33**, 759–785. (d) M. Zhang, A. H. E. Müller, *J. Polym. Sci., Part A: Polym. Chem.* 2005, **43**, 3461–3481. (e) N. Hadjichristidis, M. Pitsikalis, H. Iatrou, S. Pispas, *Macromol. Rapid Commun.* 2003, **24**, 979–1013.
- For recent examples, see: (a) A. Li, J. Ma, G. R. Sun, Z. Li, S. H. Cho, C. Clark, K. L. Wooley, *J. Polym. Sci., Part A: Polym. Chem.* 2012, **50**, 1681–1688. (b) A. Li, Z. Li, S. Y. Zhang, G. R. Sun, D. M. Policarpio, K. L. Wooley, *ACS Macro Lett.* 2012, **1**, 241–245. (c) Y. K. Li, E. Themistou, J. Zou, B. P. Das, M. Tsianou, C. Cheng, *ACS Macro Lett.* 2012, **1**, 52–56. (d) Y. K. Li, J. Zou, B. P. Das, M. Tsianou, C. Cheng, *Macromolecules* 2012, **45**, 4623–4629. (e) A. O. Burts, Y. Li, A. V. Zhukhovitskiy, P. R. Patel, R. H. Grubbs, M. F. Ottaviani, N. J. Turro, J. A.

- Johnson, *Macromolecules* 2012, **45**, 8310–8318. (f) A. M. Anderson-Wile, G. W. Coates, F. Auriemma, C. De Rosa, A. Silvestre, *Macromolecules* 2012, **45**, 7863–7877. (g) J. G. Kim, G. W. Coates, *Macromolecules* 2012, **45**, 7878–7883. (h) Q. Fu, J. M. Ren, G. G. Qiao, *Polym. Chem.* 2012, **3**, 343–351. (i) F. Collette, R. Delatouche, C. Blanquart, F. Gueugnon, M. Gregoire, P. Bertrand, V. Heroguez, *J. Polym. Sci., Part A: Polym. Chem.* 2013, **51**, 176–189. (j) F. Gueugnon, I. Denis, D. Pouliquen, F. Collette, R. Delatouche, V. Heroguez, M. Gregoire, P. Bertrand, C. Blanquart, *Biomacromolecules* 2013, **14**, 2396–2402.
- 3 (a) I. Czelusniak, E. Khoshravi, A. M. Kenwright, C. W. G. Ansell, *Macromolecules* 2007, **40**, 1444–1452. (b) G. Morandi, G. Mantovani, V. Montebault, D. M. Haddleton and L. Fontaine, *New J. Chem.* 2007, **31**, 1826–1829. (c) M. R. Xie, J. Y. Dang, H. J. Han, W. Z. Wang, J. W. Liu, X. H. He, Y. Q. Zhang, *Macromolecules* 2008, **41**, 9004–9010. (d) D. Le, V. Montebault, J.-C. Soutif, M. Rutnakornpituk, L. Fontaine, *Macromolecules* 2010, **43**, 5611–5617.
- 4 (a) D. Le, G. Morandi, S. Legoupy, S. Pascual, V. Montebault and L. Fontaine, *Eur. Polym. J.* 2013, **49**, 972–983. (b) G. Morandi, S. Pascual, V. Montebault, S. Legoupy, N. Delorme, L. Fontaine, *Macromolecules* 2009, **42**, 6927–6931. (c) P. de Fremont, H. Clavier, V. Montebault, L. Fontaine, S. P. Nolan, *J. Mol. Catal. A: Chem.* 2008, **283**, 108–113. (d) V. Lapinte, P. de Fremont, V. Montebault, L. Fontaine, *Macromol. Chem. Phys.* 2004, **205**, 1238–1245. (e) V. Lapinte, L. Fontaine, V. Montebault, I. Campistrone, D. Reyx, *J. Mol. Catal. A: Chem.* 2002, **190**, 117–129.
- 5 (a) G. Morandi, V. Montebault, S. Pascual, S. Legoupy and L. Fontaine, *Macromolecules* 2006, **39**, 2732–2735. (b) S. Pioge, G. Morandi, S. Legoupy, V. Montebault, S. Pascual, L. Fontaine, *Macromolecules* 2008, **41**, 9595–9601. (c) G. Morandi, S. Piogé, S. Pascual, V. Montebault, S. Legoupy and L. Fontaine, *Mater. Sci. Eng. C* 2009, **29**, 367–371.
- 6 D. Le, V. Montebault, S. Pascual, S. Legoupy and L. Fontaine *Macromolecules* 2012, **45**, 7758–7769.
- 7 D. Le, V. Montebault, S. Pascual, F. Collette, V. Heroguez, L. Fontaine, *Polym. Chem.* 2013, **4**, 2168–2173.
- 8 (a) Z. Wu, D. R. Wheeler, R. H. Grubbs, *J. Am. Chem. Soc.* 1992, **114**, 146–151. (b) Z. Wu, R. H. Grubbs, *Macromolecules* 1995, **28**, 3502–3508. (c) R. B. Maughon, R. H. Grubbs, *Macromolecules* 1997, **30**, 3459–3469. (d) M. G. Perrott, B. M. Novak, *Macromolecules* 1995, **28**, 3492–3494. (e) M. G. Perrott, B. M. Novak, *Macromolecules* 1996, **29**, 1817–1823. (f) J. C. Lee, K. A. Parker, N. S. Sampson, *J. Am. Chem. Soc.* 2006, **128**, 4578–4579. (g) A. R. Song, K. A. Parker, N. S. Sampson, *J. Am. Chem. Soc.* 2009, **131**, 3444–3445. (h) A. R. Song, K. A. Parker, N. S. Sampson, *Org. Lett.* 2010, **12**, 3729–3731. (i) A. R. Song, J. C. Lee, K. A. Parker, N. S. Sampson, *J. Am. Chem. Soc.* 2010, **132**, 10513–10520. (j) K. Lee, T. L. Choi, *Org. Lett.* 2011, **13**, 3908–3911.
- 9 (a) R. M. Rasal, A. V. Janorkar, D. E. Hirt, *Prog. Polym. Sci.* 2010, **35**, 338–356. (b) A. P. Gupta, V. Kumar, *Eur. Polym. J.* 2007, **43**, 4053–4074. (c) S. Mecking, *Angew. Chem., Int. Ed.* 2004, **43**, 1078–1085. (d) A.-C. Albertsson, I. K. Varma, *Biomacromolecules* 2003, **4**, 1466–1486. (e) *Poly(Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications*; R. Auras, L.-T. Lim, S. E. M. Selke, H. Tsuji, Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, 2010.
- 10 (a) S. Jha, S. Dutta, N. B. Bowden, *Macromolecules* 2004, **37**, 4365–4374. (b) Y. Xia, B. D. Olsen, J. A. Kornfield, R. H. Grubbs, *J. Am. Chem. Soc.* 2009, **131**, 18525–18532.
- 11 (a) D. Yang, W. Huang, J. H. Yu, J. S. Jiang, L. Y. Zhang, M. R. Xie, *Polymer* 2010, **51**, 5100–5106. (b) M. Xie, J. Dang, H. Han, W. Wang, J. Liu, X. He, Y. Zhang, *Macromolecules* 2008, **41**, 9004–9010. (c) D. Mecerreyes, D. Dahan, P. Lecomte, P. Dubois, A. Demonceau, A. F. Noels, R. Jerome, *J. Polym. Sci., Part A: Polym. Chem.* 1999, **37**, 2447–2455.
- 12 (a) M. Fevre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, *Chem. Soc. Rev.* 2013, **42**, 2142–2172. (b) M. Fevre, J. Vignolle, Y. Gnanou, D. Taton, *Polymer Science: A Comprehensive Reference* 2012, **4**, 67–115. (c) A. P. Dove, *ACS Macro Lett.* 2012, **1**, 1409–1412. (d) M. K. Kiesewetter, E. J. Shin, J. L. Hedrick, M. R. Waymouth, *Macromolecules* 2010, **43**, 2093–2107. (e) N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer, J. L. Hedrick, *Chem. Rev.* 2007, **107**, 5813–5840. (f) D. Bourissou, S. Moebs-Sanchez, B. Martin-Vaca, *C. R. Chimie* 2007, **10**, 775–794. (g) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* 2004, **104**, 6147–6176.
- 13 (a) F. Nederberg, E. F. Connor, M. Moeller, T. Glauser, J. L. Hedrick, *Angew. Chem., Int. Ed.* 2001, **40**, 2712–2715. (b) F. Nederberg, E. F. Connor, T. Glauser, J. L. Hedrick, *Chem. Commun.* 2001, 2066–2067.
- 14 (a) S. M. Guillaume, J.-F. Carpentier, *Catal. Techn.* 2012, **2**, 898–906; (b) N. Ajellal, J.-F. Carpentier, C. Guillaume, S. M. Guillaume, M. Helou, V. Poirier, Y. Sarazin, A. Trifonov, *Dalton Trans.* 2010, **39**, 8363–8376; (c) M. Helou, O. Miserque, J.-M. Brusson, J.-F. Carpentier, S. M. Guillaume, *Chem.-Eur. J.* 2010, **16**, 13805–13813; (d) P. Brignou, J.-F. Carpentier, S. M. Guillaume, *Macromolecules* 2011, **44**, 5127–5135; (e) P. Brignou, M. Priebe Gil, O. Casagrande, J.-F. Carpentier, S. M. Guillaume, *Macromolecules* 2010, **43**, 8007–8017; (f) M. Helou, J.-M. Brusson, J.-F. Carpentier, S. M. Guillaume, *Polym. Chem.* 2011, **2**, 2789–2795; (g) C.-G. Jaffredo, J.-F. Carpentier, S. M. Guillaume, *Macromol. Rapid Commun.* 2012, **33**, 1938–1944; (h) C.-G. Jaffredo, J.-F. Carpentier, S. M. Guillaume, *Polym. Chem.* 2013, **4**, 3837–3850.
- 15 (a) B. G. G. Lohmeijer, R. C. Pratt, F. Leibfarth, J. W. Logan, D. A. Long, A. P. Dove, F. Nederberg, J. Choi, C. Wade, R. M. Waymouth, J. L. Hedrick, *Macromolecules* 2006, **39**, 8574–8583; (b) R. C. Pratt, B. G. G. Lohmeijer, D. A. Long, R. M. Waymouth, J. L. Hedrick, *J. Am. Chem. Soc.* 2006, **128**, 4556–4557.
- 16 M. Bouyahyi, M. P. F. Pepels, A. Heise, R. Duchateau, *Macromolecules* 2012, **45**, 3356–3366.
- 17 (a) J. Kadota, D. E. Pavlovic, J.-P. Desvergne, B. Bibal, F. Peruch, A. Deffieux, *Macromolecules* 2010, **43**, 8874–8879; (b) O. Coulembier, P. Dubois, *Polym. Chem.* 2012, **2**, 1672–1680; (c) H. Feng, C.-M. Dong, *J. Polym. Sci.; Part A: Polym. Chem.* 2006, **44**, 5353–5361.
- 18 G. Theryo, F. Jing, L. M. Pitet, M. A. Hillmyer, *Macromolecules* 2010, **43**, 7394–7397.
- 19 (a) A. Chuma, H. W. Horn, W. C. Swope, R. C. Pratt, L. Zhang, B. G. G. Lohmeijer, C. G. Wade, R. M. Waymouth, J. L. Hedrick, J. E. Rice, *J. Am. Chem. Soc.* 2008, **130**, 6749–6754; (b) L. Zhang, R. C. Pratt, F. Nederberg, H. W. Horn, J. E. Rice, R. M. Waymouth, C. G. Wade, J. L. Hedrick, *Macromolecules* 2010, **43**, 1660–1664.
- 20 S. Penczek, R. Szymanski, A. Duda, J. Baran, *Macromol. Symp.* 2003, **201**, 261–269.
- 21 A. Buchard, C. M. Bakewell, J. Weiner, C. K. Williams, *Top. Organomet. Chem.* 2012, **39**, 175–224.
- 22 N. Gauvry, C. Comoy, C. Lescop, F. Huet, *Synthesis* 1999, 574–576.
- 23 L. Mevellec, F. Huet, *Tetrahedron* 1994, **50**, 13145–13154.
- 24 L. Mevellec, M. Evers, F. Huet, *Tetrahedron* 1996, **52**, 15103–15116.
- 25 W. J. Feast, V. C. Gibson, A. F. Johnson, E. Khosravi M. A. Mohsin, *J. Mol. Catal. A: Chem.* 1997, **115**, 37–42.
- 26 (a) C. W. Bielawski, R. H. Grubbs, *Prog. Polym. Sci.* 2007, **32**, 1–29. (b) *Handbook of Metathesis*; R. H. Grubbs, Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 3.
- 27 (a) J. Rzaev, *ACS Macro Lett.* 2012, **1**, 1146–1149. (b) M. Seo, M. A. Hillmyer, *Science* 2012, **336**, 1422–1425. (c) D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, *Chem. Rev.* 2012, **112**, 3959–4015.