PAPER

Scope and limitations of ring-opening copolymerization of trimethylene carbonate with substituted γ-thiolactones†

M. Langlais,[a] O. Coutelier,[a] S. Moins,[b] J. De Winter,[c] O. Coulembier [iD] *[b] and M. Destarac [iD] *[a]

Functional (co)polymers are increasingly developed by ring-opening polymerization of functional cyclic esters and cyclic carbonates for a wide range of applications. Following this trend and aiming to challenge the polymerization of substituted γ-thiolactones, we studied the ring-opening copolymerization of recently developed γ-thiolactones with trimethylene carbonate in order to prepare new poly(carbonate-*co*-thioester)s with phosphonated or fluorinated pendant groups.
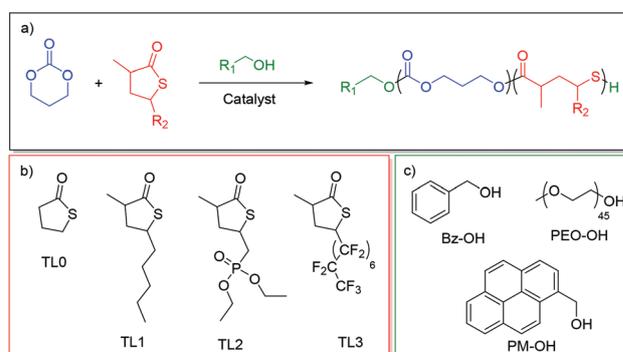
Introduction

Both cyclic esters and cyclic carbonates have been widely studied in ring-opening polymerization (ROP) leading to the synthesis of well-defined and functional materials using conventional metal-based catalysts or organocatalysts.[1–10] Poly(esters)s such as polylactide or poly(ε-caprolactone) (PCL) and poly(carbonate)s such as poly(trimethylene carbonate) (PTMC) have emerged as biocompatible and biodegradable polymers with applications in the biomedical field.[11–15] The ring-opening copolymerization (ROcP) of cyclic carbonates with cyclic esters leads to poly(carbonate-*co*-ester)s with tunable materials properties.[4,6,7,15–18]

In contrast to lactones, thiolactones have largely been ignored mainly because of their low polymerizability.[19] In their pioneering works, Overberger *et al.* reported the anionic ROP of 6- and 7-membered thiolactones, respectively δ-thiovalerolactone and ε-thiocaprolactone (tCL) and showed that 5-membered γ-thiobutyrolactone does not polymerize in the same conditions.[19,20] The thiol-initiated organocatalyzed ROP of tCL was recently reported[21] as well as its enzymatic ring-opening polymerization (*e*ROP) using lipase for the synthesis and chemical recycling of P(tCL).[22] One example of the copolymerization of ε-caprolactone (ε-CL) and tCL by *e*ROP with different ratios of both cyclic monomers was reported to produce poly(ester-*co*-thioester) with tunable properties.[23]

Due to their ring stability, γ-thiolactones were totally ignored in ROP. However in 2011, Du Prez and co-workers have found new applications of thiolactones in polymer chemistry with the one-pot amine-thiol–ene conjugation. The γ-thiolactone was ring-opened by a primary amine, releasing a thiol which can further react with thiol scavengers.[24,25] To extend this new chemistry, our group has recently developed a versatile xanthate-based synthetic procedure that allows easy access to a library of functional γ-thiolactones containing alkyl, phosphonated or fluorinated groups.[26]

In order to develop new copoly(thioester)s with functional pendant groups and to challenge the ROP of γ-thiolactones, we present in this report the scope and limitations of the ROcP of substituted γ-thiolactones with cyclic esters such as trimethyl-

[a]Laboratoire des IMRCP, Université de Toulouse, CNRS UMR 5623, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, Cedex 9, France. E-mail: destarac@chimie.ups-tlse.fr
[b]Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, Place du Parc 20, 7000 Mons, Belgium. E-mail: olivier.coulembier@umons.ac.be
[c]Organic Synthesis and Mass Spectrometry Laboratory (S2MOS), University of Mons, Place du Parc 20, 7000 Mons, Belgium
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c8py00127h

Scheme 1 (a) General synthetic procedure of the alcohol-initiated copolymerization of TMC with a substituted γ-thiolactone. Thiolactones (b) and alcohol initiators (c) used in this study.

ene carbonate (TMC) using different initiators and catalysts (Scheme 1).

Experimental section

Materials

All following chemicals were stored in a glove box under dry nitrogen atmosphere before use. γ-Thiobutyrolactone (TL0, Sigma-Aldrich, 98%) was dried over molecular sieve (3 Å) before use. The other γ-thiolactones were synthesized following the reported procedure[26] and dried over molecular sieve (3 Å). ε-Caprolactone (ε-CL, Sigma-Aldrich, 97%) was dried over CaH_2 for 48 h at room temperature and distilled under reduced pressure. Trimethylene carbonate (TMC, Pugh & Co. International, 97%) was recrystallized twice from dried toluene. Benzyl alcohol (Bz–OH, Sigma Aldrich, 99%) and 1,8-diazabicyclo[5.4.0] under-7-ene (DBU, Sigma-Aldrich, 98%) were dried over CaH_2 for 48 hours at room temperature and distilled under reduced pressure. 1-Pyrenemethanol (PM, Sigma-Aldrich, 98%) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Sigma-Aldrich, 98%) were dried at 60 °C under reduced pressure for 24 h. OH terminated-poly(ethylene oxide) (PEO–OH, Sigma-Aldrich, M_n = 2000 g mol^{-1}) was purified by azeotropic distillations from dried toluene. Toluene was dried using a MBraun Solvent Purification System (model MB-SPS 800) equipped with alumina drying columns.

General techniques

Nuclear magnetic resonance (NMR) spectra (^{1}H and ^{31}P) were recorded at 298 K on a Bruker Avance 300 MHz instrument. ^{1}H NMR spectra were recorded at 300.13 MHz and ^{31}P NMR spectra were recorded at 121.49 MHz. Chemical shifts δ are reported in parts per million (ppm) and are referenced to the residual solvent peak ($CDCl_3$: H = 7.26 ppm).

Size-exclusion chromatography (SEC) analyses were performed in $CHCl_3$ at 35 °C at a flow rate of 1 mL min^{-1}, using a system composed of an isocratic pump (VE 1122, Viscotek), a set of two PLgel 5 μm MIXED-C ultra-high efficiency columns. Detections were conducted using a Shodex SE-61 differential refractometer and a variable wavelength UV detector (Spectra 100, Spectra-Physics). A volume of 100 μL of sample solution in chloroform (concentration 0.3% w/v) was injected. Polystyrene standards (Polymer Laboratories) with narrow molecular weight distributions were used to generate a calibration curve.

MALDI-ToF mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG (third harmonic) operating at 355 nm with a maximum output of 65 μJ delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10 000. All the samples were analyzed using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrix. That matrix was prepared as 40 mg mL^{-1} solution in $CHCl_3$. The matrix solution (1 μL) was applied to a stainless steel target

and air-dried. Polymer samples were dissolved in THF to obtain 1 mg mL^{-1} solutions and 50 μL of 2 mg mL^{-1} NaI solution in acetonitrile has been added to the polymer solution. Therefore, 1 μL of this solution was applied onto the target area already bearing the matrix crystals, and air-dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass all the ions of the distribution, and they were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time.

Differential scanning calorimetry (DSC) analyses were performed on a Mettler Toledo HSS8 apparatus using sealed aluminium capsules and under a continuous nitrogen flow (20 mL min^{-1}). The thermograms were recorded and repeated three times with the following cycle: +150 °C to −60 °C to 10 °C min^{-1}; −60 °C to +150 °C to 10 °C min^{-1}.

General (co)polymerization procedure

In a glove box, a dried vial was charged with TMC (77 mg, 7.5×10^{-4} mol) and TL2 (200 mg, 7.5×10^{-4} mol). Then Bz–OH initiator (1.6 μL, 1.5×10^{-5} mol) and $SnOct_2$ catalyst (7.6 μL, 1.5×10^{-5} mol) were added successively. The sealed vial was heated at 120 °C for 24 h. An aliquot was taken prior to precipitation for monomers conversions and analyzed by SEC. The result polymer was dissolved in a small amount of THF and then precipitated several times in cold *n*-hexane. The precipitated polymer was dried under vacuum at 60 °C for 16 h and analyzed by SEC and NMR.

Results and discussion

Six- and seven-membered cyclic esters and carbonates such as lactide, ε-CL or TMC are the most common monomers polymerized by ROP. Alongside, few works on the ROP of the five-membered cyclic ester monomers such as γ-butyrolactone were reported.[27–29] The literature on ROP of thiolactones is mainly based on the β-thiolactone and tCL[19–23,30] while γ-thiolactone was not studied in ROP probably due to the insufficient nucleophilic character of the generated thiol, unable to open the thermodynamically stable 5-membered ring thiolactone. Similarly to the 5-membered lactone, *i.e.* the γ-butyrolactone (γ-BL), the inability of γ-thiolactone to give high molecular weight homopolymer does not prevent its homooligomerization or its ability to be incorporated into a copolymer. Such inability to homopolymerize is mainly due to a rate constant of depropagation (k_d) well higher than the rate constant of propagation (k_p) and the inequality between k_d and k_p [γ-BL] (k_p[γ-BL] ≪ k_d). On the other hand, kinetic schemes describing the γ-BL copolymerization suggest that such monomer can be introduced into a copolymer by a cross-propagation process with another reactive monomer. To date no general rule allows to predict the incorporation of unreactive monomer into a copolymer structure but a literature survey tends to indicate that the initial concentration of the unreactive monomer as well as the nature and the structure of the catalyst have an

impact on the level of incorporation into the final copolymer.[27,31–34]

The objective of this study was then to copolymerize to some extent various functional thiolactones with cyclic monomers (TMC or ε-CL) to access new functional copolymers from several well-known catalysts. Therefore, we selected three different functional thiolactones bearing alkyl, diethylphosphonate and perfluorinated substituents as well as γ-thiobutyrolactone as our reference. The choice of the substituents was driven by our will to introduce some functional groups of interest for the end-use properties of the resulting polymers as well as studying the steric and electronic contributions of these substituents on the rate of incorporation of the thiolactone into the final copolymer.

At first we copolymerized the commercially available γ-thiobutyrolactone (TL0) with TMC by using benzyl alcohol (Bz–OH) as initiator and tin(II) octoate (SnOct$_2$) as catalyst. The reaction was carried out for a [TMC]/[TL0]/[Bz–OH]/[SnOct$_2$] ratio of 50 : 50 : 1 : 1 in bulk at 120 °C during 24 h. The precipitated polymer was analyzed by size-exclusion chromatography (SEC) to obtain a molar mass M_n^{SEC} = 2800 g mol^{-1} with a dispersity Đ = 2.10 (Table 1, entry 1 and Fig. S1†). A conversion of 96% in TMC was determined by ^{1}H NMR. ^{1}H NMR analysis of the isolated polymer showed signals corresponding to the thioester backbone at 2.41–2.50 and 3.08–3.12 ppm (Fig. S2†). The incorporation of thiolactone units into the polymer was 9 mol%. Then, to compare different cyclic esters as comonomer, ε-CL was copolymerized with TL0 in the same conditions. A polymer was obtained with a molar mass M_n^{SEC} = 4320 g mol^{-1} and a dispersity Đ = 2.31 (Fig. S3†) with a lower fraction of thiolactone incorporated (6 mol%, Fig. S4†). We decided to continue our study with TMC as comonomer as it allowed a higher incorporation of γ-thiolactone units compared to ε-CL.

Following these initial results, we decided to screen the use of three substituted γ-thiolactones synthesized following the procedure described in our last work.[26] Firstly, the thiolactone with pentyl group in the γ-position (TL1) was copolymerized with TMC in the same conditions as for TL0. The obtained polymer was precipitated in hexane and analyzed by SEC. A monomodal and symmetrical chromatogram was obtained (Fig. S5†) with a M_n^{SEC} = 2350 g mol^{-1} and a dispersity of 1.83,
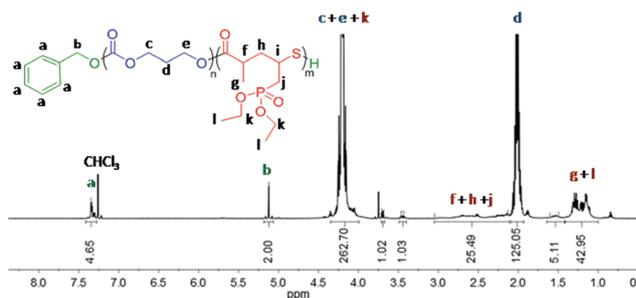

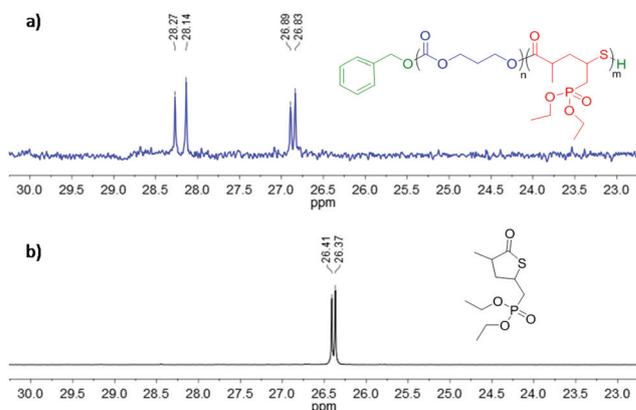Fig. 1 ^{1}H NMR of the isolated poly(TMC-co-TL2) in CDCl$_3$.

Fig. 2 ^{31}P NMR of (a) the isolated poly(TMC-co-TL2) and (b) the thiolactone TL2 in CDCl$_3$.

with incorporation of 9 mol% of TL1 units in the isolated copolymer (Table 1, entry 2).

We then copolymerized the bulkier diethyl phosphonate-functional thiolactone TL2 with TMC in the same experimental conditions as for the copolymerization of TL1 with TMC. The purified polymer was analyzed by ^{1}H NMR (Fig. 1) and ^{31}P NMR (Fig. 2). Signals at 1.0–1.5 and 2.2–3.0 ppm were observed in ^{1}H NMR and corresponding to the thioester units (Fig. 1). Phosphorus signals of the isolated polymer were observed at 26.83–26.89 and 28.14–28.27 ppm (Fig. 2a) with a shift compared to the thiolactone signals at 26.37–26.41 ppm

Table 1 Copolymerization data with [TL]$_0$/[TMC]$_0$/[initiator]$_0$/[catalyst]$_0$ = 50 : 50 : 1 : 1 in bulk at 120 °C for 24 h

Entry	Initiator R–OH	Thiolactone	Catalyst	mol% TL incorp.[a]	M_n^{SEC} [b] (g mol^{-1})	Đ[b]	T_g (°C)
1	Bz	TL0	SnOct$_2$	9	2800	2.10	−25.7
2	Bz	TL1	SnOct$_2$	9	2350	1.83	−29.3
3	Bz	TL2	SnOct$_2$	7	4920	1.97	−23.8
4	Bz	TL3	SnOct$_2$	3	4040	1.85	−28.7
5[c]	Bz	TL1	TBD	7.5	1660	1.86	−33.5
6[c]	Bz	TL1	DBU	4	4000	1.96	−26.1
7	PM	TL1	SnOct$_2$	9	3470	1.96	−30.1
8	PM	TL2	SnOct$_2$	6.5	4700	2.20	−23.8
9	PEO	TL2	SnOct$_2$	7.5	6210	2.08	—

Conversions TMC > 95% determined by ^{1}H NMR. [a] Percentage of thiolactone incorporation in the precipitated copolymer determined by ^{1}H NMR. [b] Determined by SEC in CHCl$_3$ (PS standards). [c] Polymerizations were carried out at 60 °C.

(Fig. 2b). M_n^{SEC} = 4920 g mol^{-1} and dispersity $Đ$ = 1.97 were obtained by SEC analysis, with an incorporation of 7 mol% of TL2 in the copolymer (Table 1, entry 3 and Fig. S6a†). Compared to TL1, the introduction of a bulky phosphonate group have no significant influence on the incorporation of thiolactone units in the copolymer, however the molar mass obtained was higher with comparable dispersities. Polymerizations of TMC with TL2 were also performed for a [TMC]/[TL2] ratio of 30 : 70 and 70 : 30 in order to investigate the influence of the initial monomers concentration. A higher initial concentration of TL2 did not allow a significant higher rate of incorporation of TL units into the copolymer backbone with 8 mol% while a lower initial concentration of TL2 decreased the incorporation of TL units to 3.5 mol% compared to a 50 : 50 feed ratio.

Then we copolymerized TMC with TL3, which is substituted with a perfluorooctyl group. The copolymer after precipitation had a molar mass M_n^{SEC} = 4040 g mol^{-1} and dispersity $Đ$ = 1.85 (Table 1, entry 4 and Fig. S7†). However, the level of incorporation of TL3 in the final copolymer was very low with only 3 mol%. This observation could be related to the strong electron-withdrawing character of the perfluorooctyl group, which reduces the nucleophilic character of the thiolate active species.

As TL1 offered the highest rate of incorporation among the tested thiolactones, we decided to study the influence of the catalyst on the TL1/TMC copolymerization by using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as organocatalysts with Bz–OH as initiator. In both cases, reactions were carried out at 60 °C for 24 h to avoid the chain degradation by the catalyst that could appear with the use of high temperature.[35] When using TBD (Table 1, entry 5) the molar fraction of thiolactone incorporated in the copolymers was not improved (7.5 mol%) as compared to the one obtained from SnOct$_2$ while the molar mass decreased to M_n^{SEC} = 1660 g mol^{-1} and $Đ$ = 1.86 (Fig. S8a†). In the case of DBU (Table 1, entry 6), the molar mass of the polymer increased to a value of M_n^{SEC} = 4000 g mol^{-1} with a dispersity slightly broader with $Đ$ = 1.96 (Fig. S8b†). However the incorporation of thiolactone units was lower than the one obtained with SnOct$_2$ as a catalyst with a percentage of 4 mol%. As our study focused on the incorporation of γ-thiolactone into a polycarbonate copolymer, we concluded that SnOct$_2$ catalyst was the best choice with a good compromise for higher molar mass and higher incorporation of thiolactone units into the polymer backbone.

Finally we investigated the use of different initiators for thiolactone/TMC copolymerization with 1-pyrenemethanol (PM–OH) and a poly (ethylene oxide) (PEO–OH) macroinitiator. In the case of PM–OH, we copolymerized both TL1 and TL2 with TMC at 120 °C with SnOct$_2$ as catalyst. In the case of TL1, we obtained a copolymer with higher molecular weight and dispersity (3470 g mol^{-1} and $Đ$ = 1.96) with no difference in the incorporation of TL1 units compared to Bz–OH initiation (Table 1, entry 7). In the case of TL2, no difference was observed for the final polymer in terms of molar mass, disper-

sity and percentage of incorporation of TL2 (Table 1, entry 8 and Fig. S7b†). The use of PM–OH as initiator enabled fluorescent properties of the polymer under UV-light at 365 nm compared to polymers initiated by Bz–OH (Fig. S9†).

MALDI-ToF MS analyses performed on three TL1-based structures obtained in different conditions and from different initiators (Table 1, entries 2, 6 and 7) are presented (Fig. S10†). In accord with the ^{1}H NMR analyses, the incorporation of TL1 into the polymer structures has clearly been identified with MS signals spaced by 186 amu, *i.e.* the molar mass of the TL1 monomer (Fig. S10†). Note here than despite a deep investigation, the exact nature of the observed MS signals could not be elucidated since the obtained *m/z* ratios could correspond to different possible structures.

Differential scanning calorimetry (DSC) analyses were performed in order to determine the influence of the nature and concentration of γ-thiolactone on the glass transition (T_g) and melting point (T_m) temperatures of the synthesized poly(carbonate-co-thioester)s. In contrast with low molecular weight PTMC, for which a semi-crystalline character was reported (T_m = 36 °C, M_w ~ 7000 g mol^{-1}),[12] all the poly(TMC-co-TL)s of the series are purely amorphous (Table 1, entries 1–8). The incorporation of 9 mol% of the unsubstituted TL0 led to a copolymer with a T_g of −25.7 °C, which is in agreement with that of PTMC for a similar molecular weight (T_g = −26 °C, M_w ~ 7000 g mol^{-1}).[12] These values lie in the range of those determined for P(TMC-co-TL)s comprising a low fraction of substituted TL1, TL2 and TL3 units (−33.5 °C < T_g < −23.8 °C, Table 1 and Fig. S11†). The molar mass dependence of T_g for low M_w and the limited percentage of TL in the copolymers did not enable to reveal any trend in T_g values.

OH-terminated poly(ethylene oxide) (PEO–OH) macroinitiator with a M_n^{SEC} = 2700 g mol^{-1} ($Đ$ = 1.14) was considered with a view of preparing a PEO-poly(TMC-co-TL2) diblock copolymer. The isolated copolymer was characterized with M_n^{SEC} = 6210 g mol^{-1} and dispersity $Đ$ = 2.08, and the incorporation of

Legend:
- - - PEO-OH
——— PEO-poly(TMC-*co*-TL2)

M_n = 6210 g.mol^{-1}
$Đ$ = 2.08

M_n = 2700 g.mol^{-1}
$Đ$ = 1.14
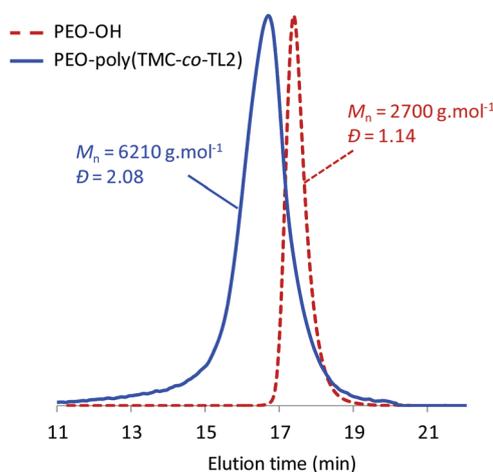
Elution time (min)

Fig. 3 SEC-RI analysis of the macroinitiator (PEO–OH, dotted trace) and the isolated PEO-*b*-poly(TMC-*co*-TL2) (solid trace).
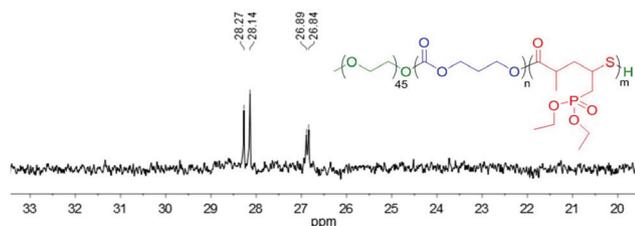
Fig. 4 ^{31}P NMR of the isolated PEO-*b*-poly(TMC-*co*-TL2) in CDCl$_3$.

thiolactone units (7.5 mol%) was similar to those determined for the other tested initiators (Table 1, entry 9). The SEC chromatograms showed a shift of PEO–OH chromatogram toward lower elution times, which is characteristic of a chain extension by ROcP and formation of a diblock copolymer (Fig. 3). ^{31}P NMR analysis of the precipitated polymer showed the phosphonate group signals at 28.27–28.14 and 26.89–26.84 ppm (Fig. 4) shifted compared to the thiolactone monomer TL2 at 26.41–26.37 ppm (Fig. 2b) attesting the incorporation of TL2 units into the block copolymer.

Conclusions

In summary, we report the synthesis of new functional poly(carbonate-*co*-thioester)s by ring-opening copolymerization of trimethylene carbonate with recently developed functional γ-thiolactones. Although stable γ-thiolactones are not prone to polymerizing, the incorporation of functional thiolactone units into the copolymer backbone was achieved and proved by NMR and MALDI-TOF MS analysis. Similarly to γ-lactones, γ-thiolactones have been demonstrated to cross-propagate with the reactive trimethylene carbonate, nevertheless, the percentage of thiolactone incorporation was limited to 9 mol% due to the much greater reactivity of trimethylene carbonate. Unlike previous studies on other ROcP systems, the level of incorporation of the unreactive γ-TL was not affected by the comonomer feed composition and the nature of the catalyst, and only a slight influence of the thiolactone substituent was demonstrated. PEO-poly(TMC-*co*-TL) diblock polymers with diethyl phosphonate pendant groups were synthesized from a hydroxyl-terminated PEO macroinitiator. Considering the rich chemistry of γ-thiolactones, these findings open new perspectives for the direct incorporation of specific functional groups in biodegradable polymers for targeted applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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