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Organocatalytic Synthesis and Postpolymerization Functionalization of Allyl-Functional Poly(carbonate)s

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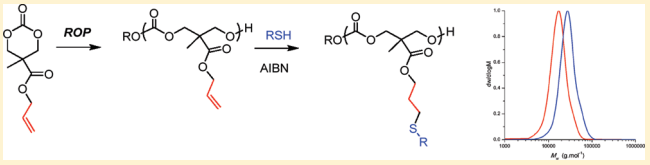
Supporting Information

ABSTRACT: Well-defined allyl-functional poly(carbonate)s were synthesized via the organocatalytic ring-opening polymerization of 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one using the dual 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea and (−)-sparteine catalyst system. The resulting allyl-functional poly(carbonate)s obtained showed low polydispersities and high end-group fidelity, with the versatility of the system being demonstrated by the synthesis of block copolymers and telechelic polymers. Further functionalization of homopolymers with degrees of polymerization of 11 and 100 were realized via the radical addition of thiols to the pendant allyl functional groups, resulting in a range of functional aliphatic poly(carbonate)s.



INTRODUCTION

Aliphatic poly(carbonate)s are excellent candidates for pharmaceutical applications as a consequence of their low toxicity, biocompatibility, and biodegradability. Tailoring of the poly(carbonate) structure by manipulation of pendant functionality on the polymer backbone enables precise control over the physical properties of the polymer or the addition of biologically active molecules. Poly(carbonate) synthesis is commonly realized either by the copolymerization of epoxides with carbon dioxide or by the ring-opening polymerization (ROP) of cyclic carbonate monomers.[1−6] The synthesis of poly(carbonate)s via CO_2/epoxide copolymerization is an exciting method of utilizing CO_2; however, the formation of five-membered cyclic carbonate byproduct, the presence of ether linkages, and the use of air-sensitive coordination compounds make its application synthetically challenging. Despite the requirement to synthesize the monomers, the ROP of cyclic carbonate monomers has received significantly more attention and consequently provides an attractive and versatile methodology for the synthesis of functionalized poly(carbonate)s that has been studied by many groups.

Monomer synthesis can be achieved in a number of ways although commonly involves multistep syntheses using toxic phosgene derivatives.[5,6] Recent examples from Hedrick and coworkers have demonstrated versatile routes to cyclic carbonate monomers via efficient routes from a single core scaffold based around 2,2-bis(hydroxymethyl)propionic acid (bisMPA) with the most recently reported approach being achieved in just two steps while avoiding the use of phosgene.[7,8] These routes have been used to prepare and subsequently polymerize a wide range of functional monomers including carbohydrate-,[9] RAFT CTA-,[10] and poly(ethylene glycol)-functional monomers,[11] with the latter being applied in hydrogel synthesis. While the synthesis of functional monomers from a single tunable monomer scaffold offers great versatility to tune the polymer functionality, the preparation and ROP of a functional monomer that can be functionalized postpolymerization in an efficient manner would provide an opportunity to yield a wide range of poly(carbonate)s with pendant functionalities including those that may not be compatible with the ROP process.[12−15] Notably, there are several reports in which degradable polymers bearing alkyne/azide[16−19] or (meth)acrylate[20−23] groups have been functionalized utilizing efficient chemistries. Chen et al. recently reported the synthesis and copolymerization of (meth)acrylate-functional cyclic carbonate monomers with either L-lactide or ε-caprolactone using tin-based catalysts at high temperatures.[23] Michael addition of a range of thiol-containing molecules (in excess) occurred readily to the acrylate-functional polymers with the conversion of these groups ranging between 30 and 100% depending on the substrate.

As a consequence of their unsaturation, allyl groups provide a versatile option for ready functionalization via radical addition of thiols, epoxidation, halogenation, and hydroboration, among others.[13,14,24−28] The introduction of a pendant carbon−carbon double bond in a poly(carbonate) backbone has previously been reported via the ring-opening polymerization of an allyl ester functional cyclic carbonate, 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC).[29−32] Previously reported homopolymerizations of MAC were either performed without added catalyst at elevated temperature (at 115 °C; M_n = 13 700 g mol^{-1}; PDI = 1.8),[31] in toluene at 95 °C using tin(II)-based poly(lactide) macroinitiator ([M]/[I] = 40; M_n = 9200 g mol^{-1}; PDI = 2.5),[31] or at 110 °C catalyzed by diethylzinc ([M]/[I] = 200; M_n = 19 000 g mol^{-1}; PDI = 1.61);[29] however, in all cases polymerizations showed

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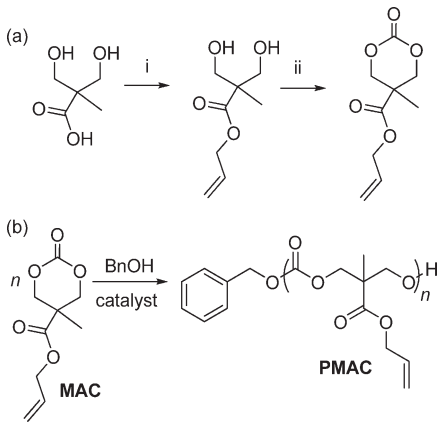
Scheme 1. (a) Synthesis and (b) Ring-Opening Polymerization of 5-Methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC)[a]



[a] Conditions: (i) allyl bromide, KOH, DMF, 100 °C for 1 h and then 45 °C for 16 h; (ii) ethyl chloroformate, THF, NEt_3, 0 °C for 16 h.

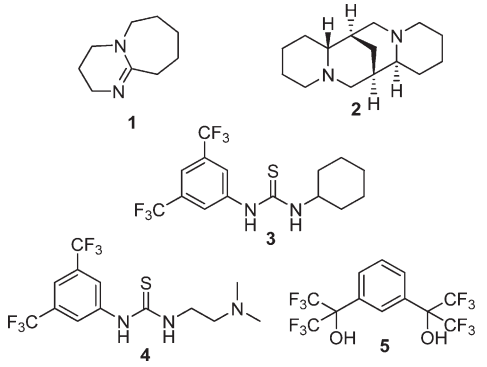


Figure 1. Organic catalysts screened for the ring-opening polymerization of MAC.

relatively poor control and resulted in branched polymers. Studies involving MAC or similar monomers have mostly focused on its copolymerization with lactide and include amphiphilic block copolymers of PMAC-*co*-PLA and poly(ethylene oxide) to form micelles and polycations from poly(ethylenimine)-grafted polycarbonate.[29−37]

A wide range of catalytic species have been studied in ROP reactions including cationic, anionic, coordination−insertion, enzymatic, and organocatalytic methods.[38−40] Recent advances, especially in organic catalysis, have led to marked improvements in selectivity and polymerization control.[40−46] Herein, we report the utilization of these highly specific organocatalysts for the controlled ROP of the allyl ester-functional cyclic carbonate, MAC, and describe its postpolymerization functionalization via radical addition of thiols to the pendant allyl groups, giving rise to a range of functional poly(carbonate)s through mild, versatile, and selective routes.

EXPERIMENTAL SECTION

Materials. *rac*-Lactide was purified from dry methylene chloride and sublimed twice before use and stored under inert atmosphere. Poly(ethylene oxide) methyl ether was dried in a desiccator over P_2O_5 and stored under inert atmosphere. $CDCl_3$, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), (−)-sparteine, α,α,α′,α′-tetrakis(trifluoromethyl)-1,3-benzenedimethanol (**5**), and dithiodiethanol were dried over CaH_2, distilled, degassed, and stored under inert atmosphere. Benzyl alcohol and 1,3-propanediol were dried and stored over 4 Å molecular sieves under inert atmosphere. 2-Hydroxyethyl disulfide was purchased from Aldrich and purified by distillation from CaH_2. Methylene chloride was purified over an Innovative Technology SPS alumina solvent column and degassed before use. 5-Methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC) was synthesized as reported,[32] recrystallized several times before use, and dried over CaH_2 in dry THF at 50−60 °C. Thiourea catalysts **3** and **4** were synthesized as previously reported[45] and then dried over calcium hydride in dry tetrahydrofuran and recrystallized from dry methylene chloride. Silica gel (pore size = 40 Å) was obtained from Fisher Scientific and used as received. All other solvents and chemicals were obtained from Sigma-Aldrich or Fisher Scientific and used as received.

Table 1. Catalyst Screening for the Ring-Opening Polymerization of MAC[a]

catalyst(s)	time (h)	monomer conv (%)[b]	M_n[c] (g mol^{-1})	PDI[c]
1[d]	4	90	10700	1.80
2[e] + **3**[f]	51.5	92	4600	1.12
2[e] + **4**[f]	768	94	4200	1.13
2[e] + **5**[f]	70	88	3530	1.12
1[d] + **3**[f]	4	92	10470	1.49

[a] Reactions were performed in $CDCl_3$ at 25 °C, [MAC] = 2.0 M, [M]/[I] = 20 using benzyl alcohol as the initiator. [b] Measured by ^{1}H NMR spectroscopy. [c] Determined by GPC analysis in THF. [d] Neopentanol was used as initiator with 5 mol % DBU. [e] 5 mol % (−)-sparteine, **2**. [f] 10 mol % cocatalyst (**3**−**5**).

General Considerations. Polymerizations were performed under inert atmosphere in a glovebox. Polymer functionalizations were carried out under oxygen-free conditions using standard Schlenk-line techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300, DPX-400, DRX-500, or AV II-700 spectrometer at 293 K. Chemical shifts are reported as δ in parts per million (ppm) and referenced to the residual solvent signal ($CDCl_3$: ^{1}H, δ = 7.26 ppm; ^{13}C, δ = 77.16 ppm; $(CD_3)_2SO$: ^{1}H, δ = 2.50; ^{13}C, δ = 39.52). Mass spectra were acquired by MALDI-TOF (matrix-assisted laser desorption ionization−time of flight) mass spectrometry using a Bruker Daltonics Ultraflex II MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with positive ion ToF detection performed using an accelerating voltage of 25 kV. Solutions of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB) as a matrix (0.3 μL of a 10 g L^{-1} solution in methylene chloride), sodium trifluoroacetate as a cationization agent (0.3 μL of a 10 g L^{-1} solution in methylene chloride), and analyte (0.3 μL of a 1 g L^{-1} solution in methylene chloride) were applied sequentially to the target followed by solvent evaporation to prepare a thin matrix/analyte film. The samples were measured in linear and reflectron ion mode and calibrated by comparison to 2 × 10^3 and 5 × 10^3 g mol^{-1} poly(ethylene oxide) monomethyl ether standards. Gel-permeation chromatography (GPC) was used to determine the molecular weights and polydispersities of the synthesized polymers. GPC in THF was conducted on a system composed of a Varian 390-LC-Multi detector suite fitted with differential refractive index (DRI), light scattering (LS), and ultraviolet (UV) detectors equipped with a guard column (Varian Polymer Laboratories PLGel 5 μM, 50 × 7.5 mm) and two mixed D columns (Varian Polymer Laboratories PLGel 5 μM, 300 × 7.5 mm). The mobile phase was either tetrahydrofuran eluent or tetrahydrofuran with 5% triethylamine eluent at a flow rate of 1.0 mL min^{-1}, and samples were calibrated against Varian Polymer Laboratories Easi-Vials linear poly(styrene) standards (162−3.7 × 10^5 g mol^{-1}) using Cirrus v3.3. GPC in DMF was

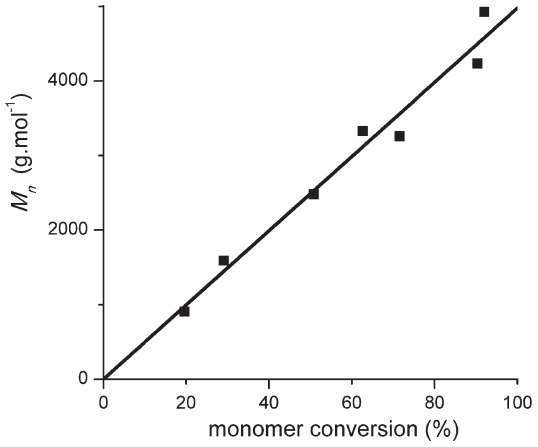


Figure 2. Plot of number-average molecular weight (M_n) against % monomer conversion in the ring-opening polymerization of MAC. Conditions: [MAC] = 2.0 M $CDCl_3$ at 25 °C, 5 mol % **2**, 10 mol % **3** [M]/[I] = 20 using benzyl alcohol as the initiator.

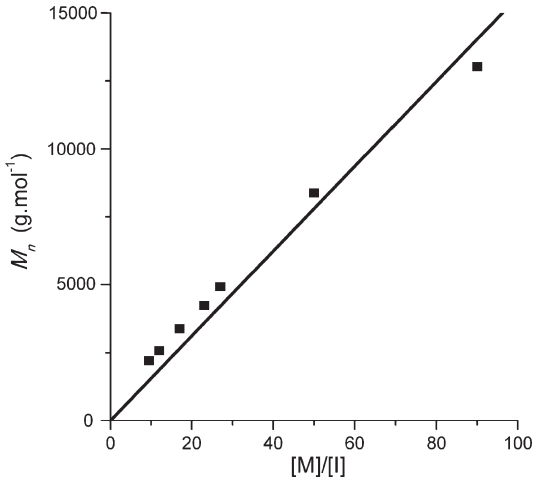


Figure 3. Plot of number-average molecular weight (M_n) against initial monomer-to-initiator ratio, $[M]_0/[I]_0$, in the ring-opening polymerization of MAC. Conditions: [MAC] = 2.0 M $CDCl_3$ at 25 °C, 5 mol % **2**, 10 mol % **3** using benzyl alcohol as the initiator.

conducted on a system composed of a Varian 390-LC-Multi detector suite fitted with differential refractive index (DRI) and ultraviolet (UV) detectors equipped with a guard column (Varian Polymer PLGel 5 μM, 50 × 7.5 mm) and two mixed D columns (Varian Polymer Laboratories PLGel 5 μM, 300 × 7.5 mm). The mobile phase was DMF with 5% LiBr eluent at a flow rate of 1.0 mL min^{-1}, and samples were calibrated against Varian Polymer Laboratories Easi-Vials linear poly(methyl methacrylate) standards (690−1.9 × 10^6 g mol^{-1}) using Cirrus v3.3. Differential scanning calorimetry (DSC) analyses in a T zero aluminum pan were performed under a flow of nitrogen using a Q2000 DSC from TA Instruments in a custom mode (stabilization at −90 °C, heating ramp of 10 °C/min from −90 to 80 °C, cooling ramp of 10 °C/min from 80 °C to −90 °C, stabilization at −90 °C, second heating ramp of 10 °C/min from −90 to 80 °C). Data were reported from the second scan. Thermogravimetric analysis (TGA) was performed under a nitrogen flow using a Q5000 TGA from TA Instruments with a conventional ramp of 20 °C/min from ambient to 700 °C.

Organocatalytic ROP of 5-Methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC). In a typical experiment, alcohol initiator, (−)-sparteine (5 mol % to monomer), and 1-(3,5-bis(trifluoromethyl) phenyl)-3-cyclohexylthiourea (10 mol % to monomer) catalyst were weighed and dissolved in dry $CDCl_3$ or dry methylene chloride. MAC was dissolved separately in the same solvent and added to the initiator/catalyst solution. After the desired time, the polymerizations were precipitated directly into hexanes. 1-(3,5-Bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea and (−)-sparteine impurities were removed by column chromatography on silica gel in hexanes/ethyl acetate (4:1). The polymer containing fractions were concentrated then dissolved in a minimal amount of methylene chloride and precipitated into hexanes. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.37 (m, OBn−Ar*H*), 5.87 (m, CH_{vinyl}), 5.37−5.20 (m, C$H_{2\text{-vinyl}}$), 5.15 (s, OBn−CH_2), 4.63 (m, OCH_2CH-CH_2), 4.45−4.24 (m, OC(O)OCH_2), 3.76−3.69 (m, CH_2OH), 2.46 (t, O*H*), 1.27 (s, CH_3), 1.22 (s, C(CH_3)CH$_2$OH). ^{13}C NMR (500 MHz, $CDCl_3$): δ 171.7 (CC(O)O), 154.4 (OC(O)O), 135.0 (ArC), 131.6 (CH_{vinyl}), 128.6 (ArC), 118.5 (C$H_{2\text{-vinyl}}$), 68.6 (OC(O)OCH_2), 68.4 (CH_2OH), 65.9 (OCH_2CHCH$_2$), 46.5 (CCH$_3$), 17.5 (CH_3). GPC (THF, RI): M_n (PDI) = 3440 g mol^{-1} (1.15). GPC (DMF, RI): M_n (PDI) = 3680 g mol^{-1} (1.10).

Synthesis of Block Copolymers. PEO-*b*-PMAC block copolymer was synthesized using the above-mentioned method with commercially available poly(ethylene oxide) monomethyl ether as initiator ([M]/[I] = 20).

For the synthesis of PLA-*b*-PMAC block copolymers, benzyl alcohol, (−)-sparteine, and thiourea were weighed and dissolved in dry $CDCl_3$. *rac*-Lactide (or MAC) was dissolved separately in $CDCl_3$ and added to the initiator/catalyst solution. After 2 h (>90% conversion), a small aliquot was taken from the mixture and used for GPC analysis, and the reaction mixture was poured in a vial containing MAC (or *rac*-lactide). The polymerization was carried out until >90% conversion was reached. The mixture was then precipitated in hexanes, purified by column chromatography on silica gel in hexanes/ethyl acetate (4:1). The polymer containing fractions were concentrated and then dissolved in a minimal amount of methylene chloride and precipitated into hexanes.

MeO-PEO$_{114}$-PMAC$_{20}$-OH. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.89 (CH_{vinyl}), 5.35−5.19 (C$H_{2\text{-vinyl}}$), 4.63 (OCH_2CHCH$_2$), 4.45−4.23 (OC(O)OCH_2), 3.64 (OCH_2CH_2), 3.37 (OCH$_3$), 2.49 (t, O*H*), 1.27 (s, CH_3), 1.22 (s, C(CH_3)CH$_2$OH). GPC (THF, RI): M_n (PDI) = 11 900 g mol^{-1} (1.06).

BnO-PMAC$_{16}$-PLA$_{23}$-OH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (OBn−Ar*H*), 5.89 (CH_{vinyl}), 5.42−5.11 (C$H_{2\text{-vinyl}}$, PLA−C*H* and OBn−CH_2), 4.63 (OCH_2CHCH$_2$), 4.41−4.25 (OC(O)OCH_2 and C*H*OH), 1.57 (PLA−CH_3), 1.27 (s, PMAC−CH_3). GPC (THF, RI): M_n (PDI) = 6620 g mol^{-1} (1.28).

BnO-PLA$_{20}$-PMAC$_{20}$-OH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (OBn−Ar*H*), 5.83 (CH_{vinyl}), 5.35−5.07 (C$H_{2\text{-vinyl}}$, PLA−C*H* and O-Bn−CH_2), 4.59 (OCH_2CHCH$_2$), 4.41−4.23 (OC(O)OCH_2), 3.68 (CH_2OH), 1.53 (PLA−CH_3), 1.23 (PMAC−CH_3), 1.19 (C(CH_3)CH$_2$OH). GPC (THF, RI): M_n (PDI) = 7130 g mol^{-1} (1.17).

Postpolymerization Functionalization of PMAC. Stock solutions of polymer and AIBN (20%) in dioxane (50 mg polymer/mL) and stock solutions of thiol in dioxane were prepared and degassed prior to the reactions. In a typical experiment, an ampoule was charged with 0.78 mL of polymer/AIBN stock solution (i.e., 38.8 mg polymer), after which the dioxane was removed *in vacuo*. Under a nitrogen atmosphere, 0.15 mL of the degassed benzyl mercaptan stock solution (3.68 M) was added, and the ampule was placed in an oil bath at 90 °C and stirred for 24 h. The mixture was then concentrated *in vacuo*; the residue was dissolved in a minimal amount of methylene chloride and precipitated into petroleum ether.

7a: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (m, OBn−Ar*H*), 5.15 (s, OBn−CH_2), 4.44−4.25 (m, OC(O)OCH_2), 4.23 (m, OCH_2CH$_2$-CH$_2$S), 3.70 (m, CH_2OH), 2.55 (m, OCH$_2$CH$_2$CH_2S), 2.50 (m, SCH_2(CH$_2$)$_{10}$CH$_3$), 1.91 (m, OCH$_2$CH_2CH$_2$S), 1.58 (m, SCH$_2$CH_2-(CH$_2$)$_9$CH$_3$), 1.37 (m, S(CH$_2$)$_2$CH_2(CH$_2$)$_8$CH$_3$), 1.26 (m, CCH_3 and (CH$_2$)$_8$CH$_3$), 0.88 (s, (CH$_2$)$_8$CH_3). ^{13}C NMR (500 MHz, $CDCl_3$): δ

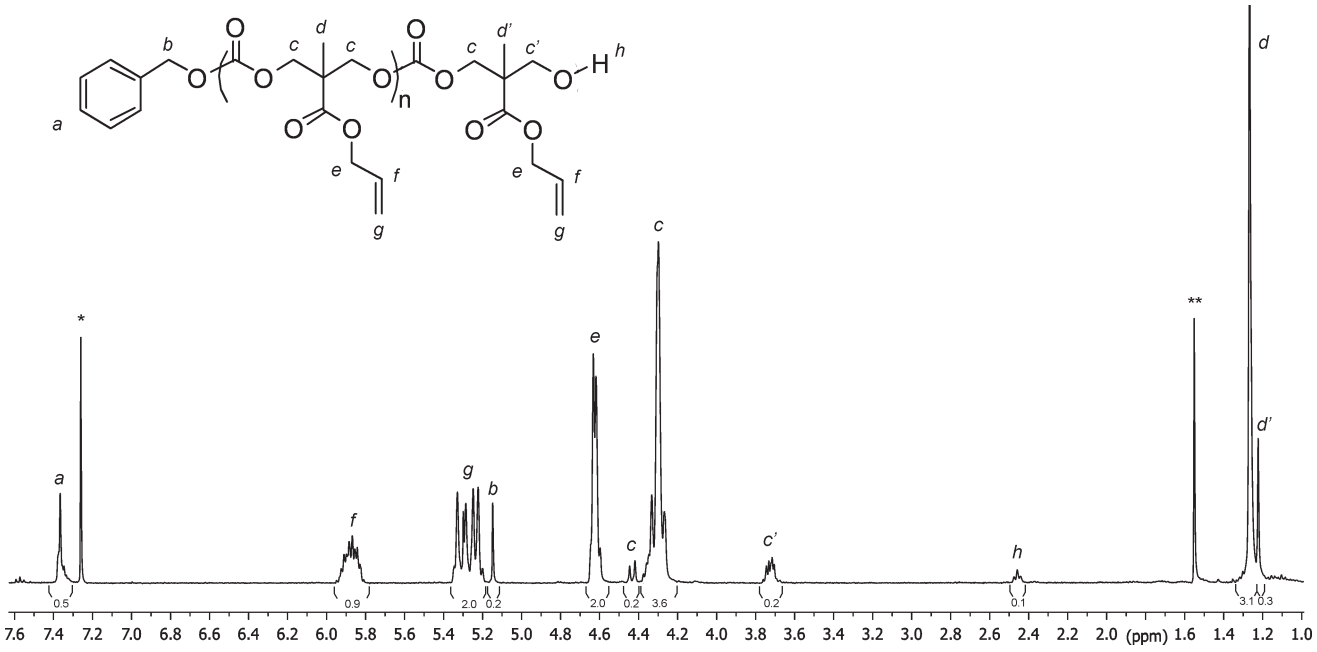


Figure 4. ^{1}H NMR in $CDCl_3$ of $PMAC_{11}$ initiated from benzyl alcohol using 5 mol % **2** and 10 mol % **3** (400 MHz, 293 K; ∗ = residual $CDCl_3$, ∗∗ = H_2O).

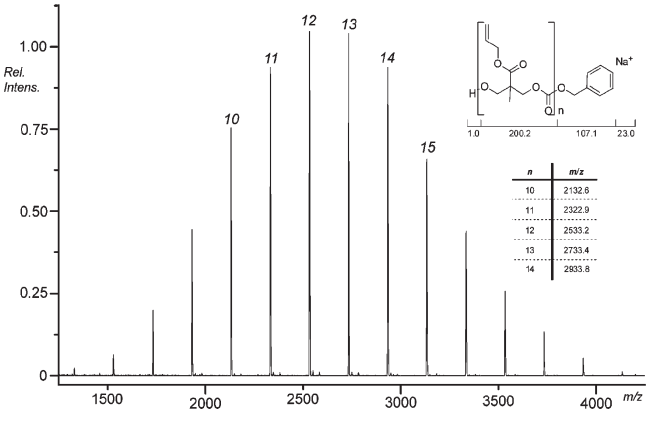


Figure 5. MALDI-TOF MS analysis of PMAC (DP = 11) initiated from benzyl alcohol using 5 mol % **2** and 10 mol % **3**.

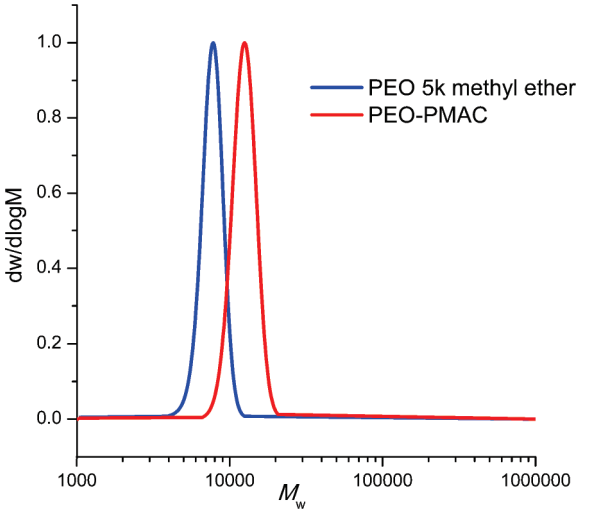


Figure 6. GPC traces of MeO-PEO_{114}-OH (M_n = 7520 g mol^{-1}, PDI = 1.03) and MeO-PEO_{114}-$PMAC_{20}$-OH block copolymer (M_n = 11 900, PDI = 1.06).

171.9 (*C*C(O)O), 154.4 (OC(O)O), 68.7 (OC(O)O*C*H$_2$), 64.1 (O*C*H$_2$CHCH$_2$S), 46.6 (*C*CH$_3$), 32.2 (SCH$_2$(CH$_2$)$_{10}$CH$_3$), 31.9 (CH$_2$-*C*H$_2$CH$_3$), 29.7 (CH$_2$SCH$_2$*C*H$_2$(CH$_2$)$_9$CH$_3$), 29.3, 29.0, 28.7, 28.5, and 28.3 (*C*H$_2$)$_7$CH$_2$CH$_2$CH$_3$), 22.7 (CH$_2$*C*H$_2$CH$_3$), 17.4 (*C*H$_3$), 14.1 (S(CH$_2$)$_{11}$*C*H$_3$). GPC (THF, RI): M_n (PDI) = 25 000 g mol^{-1} (1.22).

7b: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40−7.22 (m, backbone Ar*H* and OBn−Ar*H*), 5.14 (s, OBn−C*H*$_2$), 4.39−4.13 (m, OC(O)OC*H*$_2$) and OC*H*$_2$CH$_2$CH$_2$S), 3.70 (s, CH$_2$(C$_5$H$_6$), 2.44 (m, OCH$_2$CH$_2$-C*H*$_2$S), 1.85 (m, OCH$_2$C*H*$_2$CH$_2$S), 1.19 (s, CC*H*$_3$). ^{13}C NMR (500 MHz, $CDCl_3$): δ 172.1 (*C*C(O)O), 154.4 (O*C*(O)O), 138.4 (CH$_2$*C*$_{Ar}$), 129.0 (*o*-Ar*C*), 128.6 (*m*-Ar*C*), 127.2 (*p*-Ar*C*), 68.8 (OC(O)O*C*H$_2$), 64.2 (O*C*H$_2$CHCH$_2$S), 46.7 (*C*CH$_3$), 36.7 (S*C*H$_2$(C$_6$H$_5$), 28.2 (OCH$_2$*C*HCH$_2$S), 27.6 (OCH$_2$*C*HCH$_2$S), 17.6 (*C*H$_3$). GPC (THF, RI): M_n (PDI) = 20 710 g mol^{-1} (1.19).

7c: ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 7.38 (m, OBn−Ar*H*), 5.14 (s, OBn−C*H*$_2$), 4.72 (m, CH(O*H*)CH$_2$OH), 4.53 (m, CH(OH)CH$_2$-O*H*), 4.34−4.08 (m, OC(O)OC*H*$_2$ and OC*H*$_2$CH$_2$CH$_2$S), 3.57 (m, C*H*(OH)CH$_2$OH), 3.34 (m, CH(OH)C*H*$_2$OH), 2.63−2.39 (m, OCH$_2$CH$_2$C*H*$_2$SC*H*$_2$), 1.81 (m, OCH$_2$C*H*$_2$CH$_2$S), 1.18 (m, CC*H*$_3$). ^{13}C NMR (500 MHz, $(CD_3)_2SO$): δ 171.7 (*C*C(O)O), 154.0 (O*C*(O)O), 71.5 (*C*HOH), 68.8 (OC(O)O*C*H$_2$), 64.9 (*C*H$_2$OH), 64.5 (O*C*H$_2$CHCH$_2$S), 46.2 (*C*CH$_3$), 35.1 (S*C*H$_2$CHOH), 28.2 (OCH$_2$*C*HCH$_2$S), 16.8 (*C*H$_3$). GPC (DMF, RI): M_n (PDI) = 29 340 g mol^{-1} (1.34).

7d: ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ 7.38 (m, OBn-Ar*H*), 5.14 (s, OBn−C*H*$_2$), 4.73 (m, O*H*), 4.31−4.17 (m, OC(O)OC*H*$_2$), 4.13 (m, OC*H*$_2$CH$_2$CH$_2$S), 3.52 (m, C*H*$_2$OH), 2.54 (m, OCH$_2$CH$_2$C*H*$_2$SCH$_2$), 1.81 (m, OCH$_2$C*H*$_2$CH$_2$S), 1.18 (m, CC*H*$_3$). ^{13}C NMR (500 MHz, $(CD_3)_2SO$): δ 171.7 (*C*C(O)O), 153.8 (O*C*(O)O), 68.8 (OC(O)OCH$_2$), 63.4 (OCH$_2$CHCH$_2$S), 60.8 (*C*H$_2$OH), 46.2 (*C*CH$_3$), 33.7 (SCH$_2$CHOH), 28.2 (OCH$_2$*C*HCH$_2$S), 27.6 (OCH$_2$*C*HCH$_2$S), 16.8 (*C*H$_3$). GPC (DMF, RI): M_n (PDI) = 26 050 g mol^{-1} (1.27).

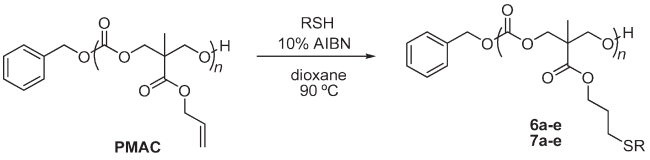
7e: ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ 12.62 (br s, COO*H*), 7.38 (m, OBn−Ar*H*), 5.13 (s, OBn−C*H*$_2$), 4.31−4.17 (m, OC(O)OC*H*$_2$),

Table 2. Telechelics and Block Copolymers of MAC[a]

polymer	DP[b]	M_n(NMR)[c] (g mol^{-1})	M_n(GPC)[d] (g mol^{-1})	PDI[d]
HO-PMAC-O$(CH_2)_3$O-PMAC-OH	9[f]	3670	5452	1.16
HO-PMAC-O$(CH_2)_2$S-S$(CH_2)_2$O-PMAC-OH	12[f]	4960	4050	1.23
MeO-PEO_{114}-*b*-PMAC-OH[e]	20[f]	12680	11900	1.06
BnO-PLA-OH	20[g]	1550	2020	1.17
BnO-PLA-*b*-PMAC-OH	20[f]	5550	7130	1.17
BnO-$PMAC_{16}$-OH	16[f]	3310	4260	1.34
BnO-PMAC-*b*-PLA-OH	23[g]	4970	6620	1.28

[a] Targeted degree of polymerization (DP) = 20 (block copolymers) or 10 (telechelics). Reactions were performed in $CDCl_3$ at 25 °C, [MAC] = 2.0 M, [M]/[I] = 20 using 5 mol % **2** and 10 mol % **3**. [b] Experimental degree of polymerization measured by ^{1}H NMR spectroscopy per OH group. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by GPC analysis in THF. [e] Poly(ethylene oxide) macroinitiator (DP = 114, determined as M_n = 7520 g mol^{-1}, PDI = 1.03 by GPC analysis in THF against poly(styrene) standards). [f] DP of PMAC block. [g] DP of PLA block.

Scheme 2. Radical Addition of a Thiol (RSH) to the PMAC



4.13 (m, $OCH_2CH_2CH_2S$), 3.21 (s, SCH_2CO_2H), 2.61 (m, $OCH_2CH_2CH_2S$), 1.84 (m, $OCH_2CH_2CH_2S$), 1.17 (m, CCH_3). ^{13}C NMR (500 MHz, $(CD_3)_2SO$): δ 171.6 (CC(O)O), 171.5 (COOH), 153.8 (OC(O)O), 68.8 (OC(O)OCH_2), 63.4 (OCH_2CHCH_2S), 46.3 (CCH_3), 33.0 (SCH_2COOH), 28.0 (OCH_2CHCH_2S), 27.5 (OCH_2CHCH_2S), 16.7 (CH_3).

RESULTS AND DISCUSSION

Monomer Synthesis and Polymerization. Owing to the electrophilic nature of allyl bromide, 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC) was able to be synthesized in a simple two-step procedure as previously reported (Scheme 1a).[29] The organocatalytic ROP of MAC was investigated using a range of organic catalysts, previously studied for the ring-opening polymerization of lactide and trimethylene carbonate (Figure 1).[41,44,45,47,48]

Initial polymerization studies were carried out in $CDCl_3$ or CH_2Cl_2 (2.0 M MAC) at 25 °C with [M]/[I] = 20 (Table 1). Application of the highly active 1,8-diazabicyclo[5.4.0]undec-7-ene (**1**, DBU) as catalyst (5 mol %) revealed a linear increase of monomer conversion against time until ca. 70% monomer conversion, at which point the polymerizations became severely retarded with isolated polymers displaying broadening molecular weight distributions (from PDI = 1.15 to >1.80) ultimately leading to bimodal GPC traces (see Supporting Information). As such, our focus turned to the bifunctional catalyst systems. For the ROP of MAC using (−)-sparteine, **2** (5 mol %), in combination with either thiourea, **3** or **4**, or α,α,α′,α′-tetrakis-(trifluoromethyl)-1,3-benzenedimethanol (**5**) (10 mol %), good control of the polymerization was observed. Of these systems, the **2**/**3** system had the highest activity and was therefore chosen as catalyst system for the ROP of MAC.

Investigation of the living characteristics of the polymerization catalyzed by **3** and (−)-sparteine (**2**) led to the observation of a linear correlation between number-average molecular weight (M_n) against monomer conversion (Figure 2) and initial monomer-to-initiator ratio ($[M]_0/[I]_0$) while retaining low PDI values throughout the polymerization (Figure 3). After precipitation from CH_2Cl_2 into cold hexanes, residual catalyst could be removed by column chromatography to yield pure polymers. Analysis of DP10 and DP100 polymer using ^{1}H NMR spectroscopy confirmed degrees of polymerization (DP) of 11 and 100, respectively, by comparison of the integration of the resonances at δ = 7.37 and 5.15 ppm originating from the benzyl alcohol initiator group and unsaturated allyl functionality on the polymer, respectively (Figure 4). Further analysis of the DP10 polymer by MALDI-ToF MS revealed a single distribution with a spacing of 200 *m*/*z*, which is equal to that of a monomer unit (Figure 5). The main peak at *m*/*z* = 2533 corresponds to a sodium charged polymer chain of DP12 with a benzyl alcohol end group.

Table 3. Postpolymerization Radical Thiol−Ene Functionalization of Poly(carbonates)[a]

polymer	thiol	M_n (g mol^{-1})	PDI
BnO-$PMAC_{11}$-OH (**6**)		3440[b]/3680[c]	1.15[b]/1.10[c]
BnO-$PMAC_{100}$-OH (**7**)		15100[b]/17160[c]	1.23[b]/1.18[c]
6a	1-dodecanethiol	5320[b]	1.16[b]
7a	1-dodecanethiol	25000[b]	1.22[b]
6b	benzyl mercaptan	3530[b]	1.18[b]
7b	benzyl mercaptan	20710[b]	1.19[b]
6c	1-thioglycerol	6750[c]	1.16[c]
7c	1-thioglycerol	29340[c]	1.34[c]
6d	mercaptoethanol	6170[c]	1.17[c]
7d	mercaptoethanol	26050[c]	1.27[c]

[a] [PMAC] = ca. 0.15 M in 1,4-dioxane, 2 equiv of thiol, 10 mol % AIBN, 90 °C, 24 h. [b] Measured by GPC analysis using THF as eluent. [c] Measured by GPC analysis using DMF as eluent.

Initiator Versatility and Block Copolymer Synthesis. Initiator versatility was investigated by the synthesis of telechelic PMAC ([M]/[I] = 10 per alcohol group) initiated from 1,3-propanediol and 2-hydroxyethyl disulfide. ^{1}H NMR analysis of these polymers revealed resonances expected for the initiating alcohols with integration against the main chain polymer resonances being consistent with DP20 polymers in both cases. MALDI-ToF MS analysis of these polymers both showed distributions with a spacing of 200 *m*/*z*. The main peaks at *m*/*z* 3502 (DP17) and *m*/*z* 4380 (DP21) both correspond to the values expected for telechelic PMAC initiated from 1,3-propanediol and dithiodiethanol, respectively. In both cases, however, a second smaller distribution could be observed by MALDI-TOF

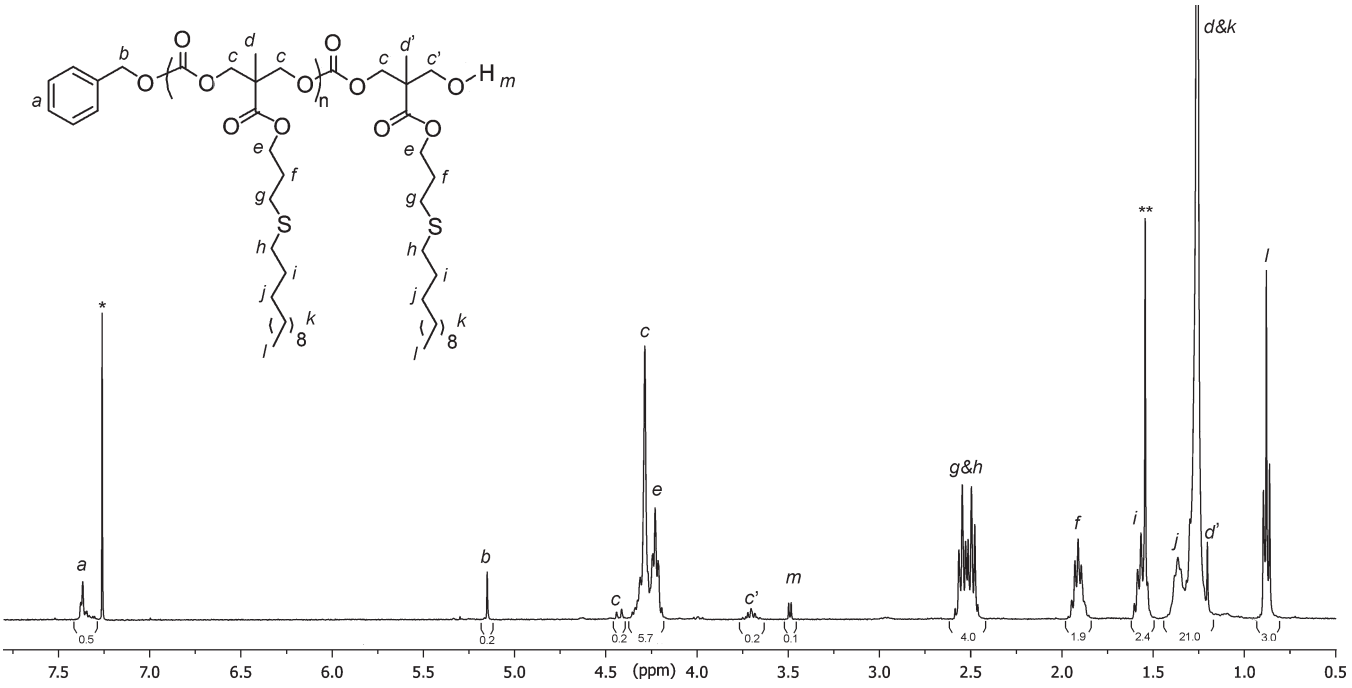


Figure 7. ^{1}H NMR in $CDCl_3$ of $PMAC_{11}$ after postpolymerization radical "thiol−ene" functionalization with 1-dodecanethiol (400 MHz, 293 K; ∗ = residual $CDCl_3$, ∗∗ = H_2O).

MS. This distribution could originate either by initiation from residual water within the system or by monomer initiated ROP according to an active chain-end mechanism as recently proposed by Delcroix et al.[49] Initiator versatility was further demonstrated by the synthesis of a MeO-PEO_{114}-*b*-$PMAC_{20}$-OH block copolymer by initiation of MAC polymerization from commercially available poly(ethylene oxide) monomethyl ether-5K that when characterized by GPC analysis in THF against poly(styrene) standards (comparable to the PMAC polymers) revealed a M_n = 7520 g mol^{-1} (PDI = 1.03). Chain growth was confirmed by GPC analysis with the block copolymer revealing a shift to higher molecular weight (M_n = 11 900 g mol^{-1}; PDI = 1.06; Figure 6). To further demonstrate the living nature of the system, block copolymers of PMAC with poly(lactide), PLA, were synthesized both by chain growth of PMAC from a PLA synthesized using the same catalyst system, initiated from benzyl alcohol in a one-pot process, and by lactide ROP from a PMAC macroinitiator. BnO-PLA_{20}-*b*-$PMAC_{20}$-OH and BnO-$PMAC_{16}$-*b*-PLA_{23}-OH block copolymer synthesis was confirmed by ^{1}H NMR showing resonances corresponding to both PLA and PMAC, only differing in the resonances of the final monomer unit (hydroxyl chain end, δ = 3.68 and 1.19 ppm for MAC monomer unit; δ = 4.27 ppm for PLA monomer unit). Furthermore, in both cases an increase in molecular weight was observed by GPC, while maintaining a low polydispersity (Table 2).

Postpolymerization Functionalization. Optimization of the required conditions for the radical addition of thiols to the allyl esters (Scheme 2) was undertaken using a model system consisting of allyl acetate and thiophenol, with azobis(isobutyronitrile), AIBN, as the radical initiator. These reactions were performed at 90 °C in a range of solvents. While dimethylformamide and dimethyl sulfoxide led to no conversion being observed, 1,4-dioxane resulted in almost a doubling in conversion over 24 h compared to reactions in which other solvents were applied (chloroform, ethyl acetate, etc.). As an excellent solvent for the poly(carbonate)s, 1,4-dioxane was

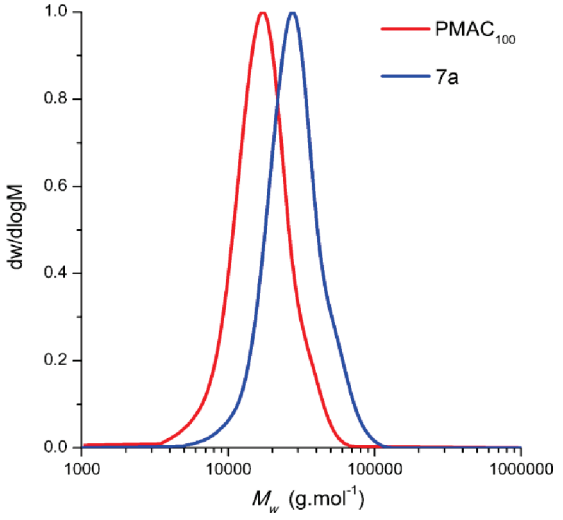


Figure 8. GPC traces of $PMAC_{100}$ before (M_n = 15 100 g mol^{-1}, PDI = 1.23) and after postpolymerization radical "thiol−ene" functionalization with 1-dodecanethiol (M_n = 25 000 g mol^{-1}, PDI = 1.22).

hence used in further thiol−ene reactions. As expected, the amount of radical initiator did not greatly influence the reaction whereas increased concentration of the reagents led to decreased reaction times. Under optimal conditions (0.15 M PMAC in dioxane at 90 °C for 24 h) with 1 equiv of benzyl mercaptan, initial reactions led to the observation of a high molecular weight tail by GPC analysis, most likely a consequence of cross-linking of some pendant allyl groups. Variation of the equivalents of benzyl mercaptan between 0.5 and 3 equiv observed cross-linked chloroform-insoluble product with 0.5 equiv, whereas increasing the equivalents of thiol to 2 or more resulted in the observation of monomodal GPC traces with the narrow molecular weight distributions of the initial PMAC retained.

Table 4. Thermal Analysis of Functionalized Poly(carbonates)

polymer	thiol	T_g [a] (°C)	T_m [b] (°C)	ΔH_m (J g^{-1})	$T_{5\%}$ [d] (°C)	$T_{50\%}$ [d] (°C)
BnO-PMAC$_{100}$-OH		−26.4			307	355
7a	1-dodecanethiol	−15.7[c]	−2.9	27.0	282	313
7b	benzyl mercaptan	−5.1			280	347
7c	1-thioglycerol	−28.5			229	275
7d	mercaptoethanol	−16.3			284	329
7e	mercaptoacetic acid	−33.2			261	343

[a] Glass transition temperature, measured by DSC analysis at the second scan. [b] Melting point, measured by DSC analysis. [c] Loss of accuracy due to proximity to the melting endotherm. [d] Temperatures at 5 and 50% weight degradation.

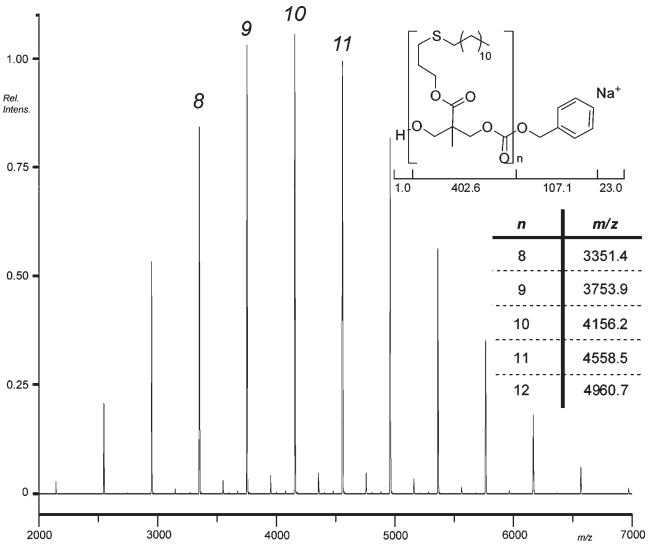


Figure 9. MALDI-ToF-MS of PMAC (DP = 11) after postpolymerization radical "thiol−ene" functionalization with 1-dodecanethiol. The second lower distribution represents a PMAC chain that is not fully functionalized and has one pendant allyl group left.

In order to demonstrate the versatility of this system, PMAC homopolymers (DP11 and DP100) were functionalized with a range of thiol-containing molecules (Table 3). ^{1}H NMR spectroscopic analysis revealed >99% conversion of the allyl groups had occurred, evidenced by the disappearance of the vinyl resonances at δ = 5.87 and 5.37−5.20 ppm (Figure 7) and the appearance of new signals consistent with the corresponding thiol groups. Furthermore, in all cases, analysis by GPC revealed a shift to higher molecular weight while maintaining narrow, unimodal distributions with polydispersity indices similar to that of the unmodified PMAC (Figure 8). MALDI-ToF MS analysis of the polymers (Figure 9) revealed a new distribution with repeat units that were consistent with the new polymer structure; for example, addition of 1-dodecanethiol across the double bonds resulted in an increase in the repeating unit from m/z = 200 to m/z = 402. In most cases, additional peaks corresponding to a polymer chain with a single residual unfunctionalized allyl group is also observed, although in notably lower intensity.

The radical "thiol−ene" process was repeated for a range of thiol-containing molecules including some with functional groups that are not compatible with ring-opening polymerization such as alcohol and carboxylic acid groups (Table 3). In all cases ^{1}H NMR analysis of the modified polymers (Supporting Information) demonstrated that addition of the thiol to the allyl groups was occurring to >99% with data consistent with those expected for the modified side-chain groups. GPC data were also consistent with the absence of adverse side reactions; however, addition of mercaptoacetic acid resulted in the isolation of a polymer that was not soluble in any available GPC solvents.

Thermal Analysis. Analysis of the DP100 functional polymers by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was undertaken to investigate the effect of chemical structure on the thermal properties and degradation of the functional polymers. Notably, DSC analysis of the DP100 PMAC prefunctionalization revealed a lower glass transition temperature (T_g) of −26.4 °C than those previously reported (−12.0 °C; M_n = 19 000 g mol^{-1}, PDI = 1.6 and M_n = 9200 g mol^{-1}, PDI = 1.8).[29,31] Postpolymerization functionalization of the PMAC homopolymers revealed subtle changes in the T_g values of the polymers with respect to DP100 PMAC displaying a glass transition temperature (T_g) of −26.4 °C (Table 4). While the addition of linear alkyl groups (1-dodecanethiol and mercaptoethanol) led to a slight increase in T_g, the addition of benzyl mercaptan led to the highest increase to −5.0 °C, attributed to the steric hindrance and aromatic interactions. Notably, the 1-dodecanethiol-functionalized polymer also displayed a melting transition at T_m = −2.9 °C, likely a consequence of crystallization of the linear alkyl side chains.

The thermal degradation of PMAC$_{100}$ and functionalized PMAC$_{100}$ samples (**12a**−**12e**) was also studied using TGA (Table 4). Again, the initial degradation values were shown to be largely invariant with polymer structure ranging from 311 to 360 °C, attesting for a good thermal stability whatever the nature of the pendant functional groups. The most notable outlier was the 1-thioglycerol-functionalized polymer which degraded at significantly lower temperature (initial degradation temperature = 247.5 °C) most likely attributed to the dehydratation of this polyol derivative. Notably, all investigated (functionalized) poly(carbonate)s display higher thermal stability than poly(trimethylene carbonate) (PTMC), which has a reported degradation temperature of ca. 230 °C.[11]

■ CONCLUSIONS

In conclusion, the controlled ring-opening polymerization of 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one was achieved successfully by using a range of organic catalysts under mild conditions. Using the preferred system of thiourea and (−)-sparteine, the living nature of the polymerizations was demonstrated by the observation of a linear evolution of molecular weight with both monomer conversion and monomer to initiator ratio, low PDIs, and the synthesis of telechelic polymers and block copolymers of PMAC with PEO and PLA. Postpolymerization functionalization of the pendant allyl groups in the polymer

backbone by facile free radical "thiol−ene" addition led to the isolation of aliphatic poly(carbonate)s with a range of pendant functionalities, without notable polymer degradation leading to precise control over the thermal properties of the polymers. Such a facile and versatile methodology provides an attractive route to the synthesis of functional aliphatic poly(carbonates).

■ ASSOCIATED CONTENT

Supporting Information. Additional spectral and chromatographic data of the functionalized polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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