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Synthesis and Functionalization of Sustainable Poly(ester-*co*-carbonate) from Carbon Dioxide, 1,3-Butadiene, and Biosourced Diols

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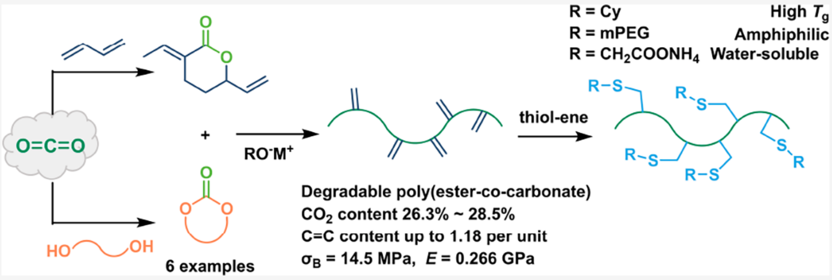

ABSTRACT: Chemical synthesis of polymers from carbon dioxide (CO_2) has been attracting a continuous amount of attention. This contribution explores the copolymerization of ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one (EVL) synthesized from CO_2 and 1,3-butadiene with various cyclic carbonates (CC) derived from CO_2 and biomass diols. Following the "scrambling polymerizations" mechanism, EVL units are incorporated into polycarbonate backbones, resulting in random poly(ester-*co*-carbonate) P(EVL-*co*-CC) with functionalizable C=C double bonds. Kinetic studies and characterizations are conducted by NMR, MALDI-ToF MS, and SEC techniques. The obtained degradable P(EVL-*co*-CC)s having varying topologies, CO_2 and C=C double bond contents, and glass transition temperatures are suitable for diverse applications. Modification in situ or via a postpolymerization "thiol−ene" reaction produces a copolymer with tunable tensile strength and amphiphilic and hydrophilic properties. This work presents an advancement in the utilization of CO_2 to synthesize functional poly(ester-*co*-carbonate)s, contributing to the development of sustainable and green polymer chemistry.

■ INTRODUCTION

Traditionally considered as an industrial byproduct, carbon dioxide (CO_2) is gaining recognition as a flexible and economical feedstock for chemical synthesis.[1−3] Polymer science researchers have made strides in utilizing CO_2 to synthesize a range of polymers, including polycarbonates,[4,5] polyureas,[6,7] polyurethanes,[8] and polyesters,[9,10] through the polycondensation of CO_2 with dinucleophiles. Yet, the most mature and widely adopted process is the copolymerization of CO_2 with epoxides, primarily producing aliphatic polycarbonates,[11,12] while the ring-opening polymerization (ROP) of cyclic carbonates (CC), a method that stands out for its low CO_2 pressure requirement during polymerization, presents an attractive alternative.[13] This ROP technique exhibits remarkable tolerance for diverse functional substitutions on CC and accommodates heteroatoms within the ring structures.[14] Recent extensive achievements have enabled the synthesis of CCs from diols, most of which are biosourced chemicals such as 1,3-propanediol, 1,4-butanediol, etc., under mild CO_2 pressure (down to 1 atm), intensifying the interest in CO_2-derived polycarbonates.[15,16]

Besides epoxides, alkenes, the starting materials of polyolefins, have also been developed for copolymerization with CO_2.[17] Despite the great promise of this approach, it has been confronted with obstacles attributed to kinetic and thermodynamic constraints. A groundbreaking development arrived in 2014 when Nozaki et al. harnessed ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one (EVL, also known as EVP), a diene-substituted lactone as an intermediate for copolymerization, resulting in CO_2/1,3-butadiene copolymers with a significant CO_2 incorporation of 29 wt %.[18] This advancement spurred a wave of research of EVL polymerization,[19] yielding a variety of polymers such as polysulfides,[20,21] functional polyolefins,[22,23] and (meth)acrylic polymers.[24−26] The ROP challenge of the inert lactone ring in EVL remained until our group unveiled a solution in 2021.[27,28] Employing scandium

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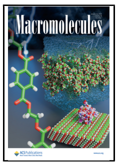

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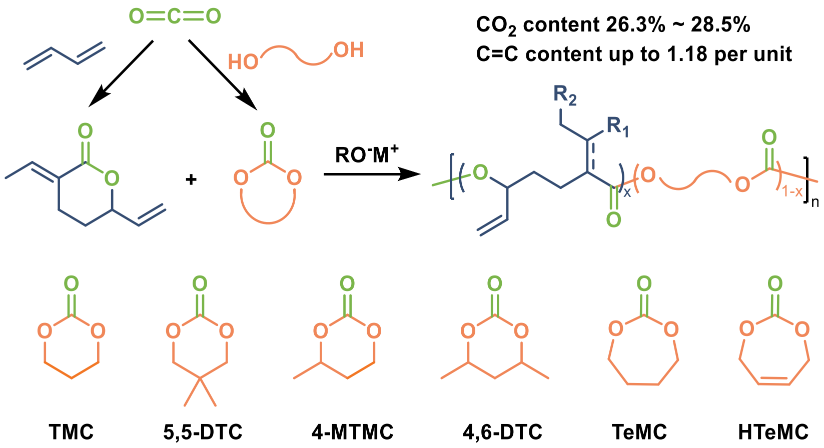
Scheme 1. Synthesis of Functionalizable Poly(ester-*co*-carbonate)s from CO_2, Diols, and 1,3-Butadiene



triflate as a catalyst, the copolymerization of EVL with β-butyrolactone, a lactone featuring high ring strain, resulted in copolymers with EVL content reaching an impressive 51 mol %. Further developments in the ROP of EVL and its derivatives have produced various functional (co)polyesters and poly(ester-*co*-ethers) suitable for postpolymerization modification.[29−37] Very recently, Lin and Li's groups individually developed the urea/phosphazene-based bifunctional catalyst system for the ROP of EVL at extremely low temperature, resulting in the homopolyester PEVL. The number-average molecular weight (M_n) was merely 2.6 kg/mol in Lin's work, while a higher molecular weight of 16.0 kg/mol was obtained using a diol initiator in Li's contribution.[38,39]

With the advancements in synthesizing diols and butadiene from biomass, EVL (from CO_2 and 1,3-butadiene) and CCs (from CO_2 and diols) are illuminated for green and sustainable chemistry.[15,40] They are considered as great candidates to produce random poly(ester-*co*-carbonate) bearing C=C double bonds. In this work, we copolymerize the two kinds of CO_2-derived monomers of EVL and CCs (six examples) catalyzed by alkali metal alkoxides which are abundant metal salts and easy to deal with (Scheme 1). Following the "scrambling polymerizations" mechanism,[33] EVL units are incorporated into polycarbonate backbones so that the CO_2-originated P(EVL-*co*-CC) is endowed with C=C double bonds suitable for postpolymerization modification. Cross-linked P(EVL-*co*-CC)s with remarkable tensile strength along with amphiphilic and water-soluble grafted P(EVL-*co*-CC)s are also prepared, highlighting the substantial potential for diverse applications.

■ EXPERIMENTAL SECTION

Materials. CO_2 (>99.99%) and 1,3-butadiene were used as received. Toluene from Sinopharm Chemical Reagent was dried over sodium and then distilled under an argon atmosphere. Anhydrous tetrahydrofuran (THF), anhydrous dichloromethane (DCM), anhydrous acetonitrile (MeCN), anhydrous benzyl alcohol (BnOH), potassium *tert*-butoxide (*t*BuOK, 1.0 mol/L in THF), sodium methoxide (MeONa), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), chloroform-*d* ($CDCl_3$) purchased from J&K Scientific, and potassium methoxide (MeOK) bought from Aladdin were used as received. Sodium 2,6-di*tert*-butyl-4-methyl phenolate (NaOAr) was prepared following the literature procedure.[41] Trimethyl carbonate (TMC) purchased from Shanghai Titan Technology Co. Ltd. was recrystallized from THF and dissolved in DCM, and then the volatile was removed under reduced pressure after being dried over 4 Å molecular sieves for 2 days. EVL and other cyclic carbonates were synthesized according to literature procedures.[16,42] Prior to use, EVL and 4-methyl-[1,3]dioxan-2-one (4-methyl trimethylene carbonate, 4-MTMC) were dried over CaH_2 and distilled under reduced pressure. 5,5-Dimethyl-[1,3]dioxan-2-one (5,5-dimethyl trimethylene carbonate, 5,5-DTC) and 1,3-dioxepan-2-one (tetramethylene carbonate, TeMC) were recrystallized from toluene/*n*-hexane and dried under vacuum. 4,6-Dimethyl-[1,3]dioxan-2-one (4,6-dimethyl trimethylene carbonate, 4,6-DTC) was dried over molecular sieves 4 Å, and 4,7-dihydro-1,3-dioxepin-2-one (4,7-dihydrotetramethylene carbonate, HTeMC) was dried under vacuum. All other chemicals were purchased from Sinopharm Chemical Reagent and used as received.

Measurements. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE DMX 400 spectrometer or a Bruker AV4600 spectrometer. Chemical shifts were reported with reference to the internal solvent resonance. Molecular weights (MWs) and dispersities (Đs) of polymers were determined by an Agilent 1260 Infinity II size-exclusion chromatography (SEC) equipment composed of Vialsampler, Quat Pump VL, a refractive index detector, and two PLgel Mixed-B columns (MW between 500 and 10,000,000) when THF was employed as an eluent with a flow rate of 1 mL/min at 40 °C or a SEC equipment composed of a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, a Waters 2707 autosampler, and Ultrahydrogel series columns (Ultrahydrogel 250 and 1000, MW between 1000 and 1,000,000) when water containing 0.1 mol/L $NaNO_3$ was employed as the eluent with a flow rate of 1 mL/min at 35 °C. Commercial polystyrenes (PS) or poly(ethylene glycol)s (PEG) were used as calibration standards for the SECs in THF or water, respectively. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectra were recorded on a Bruker Ultraflextreme MALDI-ToF mass spectrometer with CF_3COOK as the cationic agent. Thermogravimetric analysis (TGA) was carried out on PerkinElmer Pyris 1 TGA instrument by heating in a nitrogen atmosphere from 35 to 600 °C at a heating rate of 10 °C/min. Glass transition temperatures (T_gs) of polymers were determined by differential scanning calorimetry (DSC) measurements on a TA DSC Q200 instrument from the second heating run at a heating and a cooling rate of 10 °C/min from −60 to 120 °C. Mass spectra were recorded by a Thermo Scientific ISQ EC single quadrupole mass spectrometer using negative ion electrospray ionization (ESI). Uniaxial tensile measurements were performed on a C41.104 universal testing machine of XinSanSi (Shanghai) Enterprise Development Co. Ltd. The stress at break, elongation at break, and Young's modulus were calculated according to GB/T 1040.2-2006/ISO 527-2:1993. The measurements were repeated for at least three specimens to report average values with confidence intervals at a 95% level. The hydrodynamic diameters were determined by dynamic light scattering (DLS) at 25 °C on a Zetasizer Nano Series of Malvern Instruments with a wavelength of 657 nm. The Fourier transform

Table 1. "Scrambling Polymerizations" of EVL with TMC Mediated by a Lewis Base (LB)[a]

entry	[EVL]:[TMC][b]	[M]:[LB][b]	temp. (°C)	conv. (EVL conjugated C=C, %)[c]	conv. (TMC, %)[c]	time (min)	M_n[d] (kg/mol)	Đ[d]	EVL content (mol %)[e]	CO_2 content (wt %)[e]	C=C content (per unit)[e]	T_g[f] (°C)
1[g]	1:0	50:1	25	88		60						
2	0:1	50:1	25		99	10	6.7	1.9	0	27.5	0	−26.6
3[h]	0.5:1	50:1	25	n.d	n.d	30	n.d	n.d	n.d	n.d	n.d	n.d
4	1:1	50:1	25	87	99	30	14.6	20.9	37.5	28.0	0.49	−13.0
5	2:1	50:1	25	92	99	60	13.4	17.9	55.6	28.3	0.71	13.7
6	3:1	50:1	25	90	98	60	8.6	2.84	58.5	28.3	0.75	7.2
7	4:1	50:1	25	88	98	60	6.6	2.19	62.8	28.4	0.82	13.1
8	4:1	50:1	−20	50	97	60	9.9	1.74	46.2	28.1	0.77	−17.3
9	4:1	50:1	0	59	98	60	8.2	1.96	47.9	28.2	0.72	−13.5
10	4:1	50:1	50	95	96	60	5.4	2.02	66.4	28.4	0.76	22.5
11	4:1	25:1	25	97	99	60	6.9	2.58	69.5	28.5	0.84	20.3
12	4:1	100:1	25	72	94	60	7.4	1.92	46.8	28.2	0.68	−6.9
13	4:1	200:1	25	17	96	60	7.2	1.67	8.3	27.6	0.14	−26.9
14[j]	4:1	50:1	25	46	96	60	5.8	1.47	34.2	28.0	0.49	−17.8
15[k]	4:1	50:1	25	n.d[m]	98	60	9.3	2.55	60.3	28.4	0.81	−0.7
16[n]	4:1	50:1	25	34	99	60	5.5	1.49	28.6	27.9	0.48	−23.8
17[o]	4:1	50:1	25	46	98	60	8.2	1.80	25.4	27.8	0.36	−24.2
18[p]	4:1	50:1	25	93	99	60	5.0	2.66	67.3	28.5	0.84	16.8

[a] Polymerization is conducted at a 2 mol/L initial total monomer concentration in THF. LB: *t*-BuOK. [b] Initial ratio. [c] Determined by in situ ^1H NMR. [d] Determined by SEC. [e] Determined by ^1H NMR of the copolymer. [f] Determined by DSC. [g] No product precipitated in Et_2O. [h] Not determined due to cross-linking. [j] In DCM. [k] In toluene. [m] Not determined due to the stacking of toluene and EVL conjugated C=C double bond signals. [n] LB: MeONa. [o] LB: NaOAr. [p] LB: MeOK.

infrared (FTIR) spectra were recorded on a Bruker VECTOR 22 spectrometer.

General Polymerization Procedure. Polymerizations were carried out on a standard Schlenk line or in a glovebox filled with nitrogen. The flasks were flame-dried or dried in a 110 °C oven for at least 3 h prior to use. In a general copolymerization procedure, a solution of EVL (304 mg, 2 mmol) and TMC (51 mg, 0.5 mmol) in THF (0.6 mL) was stirred for 15 min. 0.5 mL of *t*-BuOK (0.1 mol/L in THF) was added into the solution to start the polymerization. After a determined time, a 0.1 mL aliquot was taken out and quenched in 0.55 mL of "wet" $CDCl_3$ to determine the conversions of monomers. The residual was diluted in 1 mL of THF and precipitated in 19 mL of diethyl ether. The precipitate was dissolved in chloroform and precipitated in *n*-hexane twice to afford P(EVL-*co*-TMC). The obtained product was dried under vacuum overnight prior to characterization.

Polymerization Procedure to Synthesize Copolymers with a Low Molecular Weight for the MALDI-ToF MS Test. Polymerizations were carried out on a standard Schlenk line. The flasks were flame-dried or dried in a 110 °C oven for at least 3 h prior to use. A "one-pot-two-step" process was employed to ensure a low molecular weight. 0.3 mL of TBD solution in THF (16 mmol/L) was rapidly added into a solution of TMC (51 mg, 0.5 mmol) and BnOH (5 μL, 0.05 mmol) in 0.2 mL of THF to start the polymerization of TMC. After 5 min, 304 mg of EVL (2 mmol), 0.8 mL of THF, and 0.3 mL *t*-BuOK (0.2 mol/L in THF) were added into the solution. After 10 min, the solution was diluted in 1 mL of THF and precipitated in 19 mL of diethyl ether. The precipitate was dissolved in chloroform, then precipitated in *n*-hexane twice, and dried in vacuum overnight.

Preparation Procedure of Specimens for Tensile Measurements. Polymerizations were carried out in a glovebox filled with nitrogen. The flasks and PTFE models were dried in a 110 °C oven for at least 3 h prior to use. A solution of EVL (2.54 g, 16.7 mmol) and TMC (0.85 g, 8.3 mmol) in THF (5 mL) was stirred for 15 min. Under vigorous stirring, 5 mL of *t*-BuOK (0.1 mol/L in THF) was added rapidly into the solution to start the polymerization. After 5 min, the solution was transferred to a PTFE model. After the determined time, the cross-linked copolymer was immersed in a mixed solvent of THF and *n*-hexane (1:1) for 2 h to remove the unreacted components. The solvent was refreshed every 15 min. The product was dried in vacuum overnight and then cut into several dog-bone-shaped specimens for uniaxial tensile measurements.

Hydrolyzation Procedure of Copolymer and EVL. A 0.1 mL portion of KOH solution in water (10 mol/L) was added into a solution of 30 mg of P(EVL-*co*-TMC) or EVL in 0.9 mL of THF. The solution was stirred for 24 h, then diluted in water, and acidified with hydrochloric acid to a pH of 1. The solution was concentrated after the generated solid was filtered. The concentrated solution was extracted by DCM twice. The solvent of the collected organic phase was removed to afford the hydrolyzed product.

Postpolymerization Modification Procedure. 87 mg of cyclohexanethiol (120 mg for thiol-functionalized methoxy polyethylene glycol with an average molecular weight of 550 g/mol ($mPEG_{550}$-SH) or 115 mg for thioglycolic acid (TGAc)) was added into a solution of 30 mg of P(EVL-*co*-TMC) and 8 mg of 2,2-bimethoxy-2-phenylacetophenone in 1 mL of THF. The reaction was initiated by irradiation under UV light with a calibrated wavelength of 365 nm. After 6 h (24 h for $mPEG_{550}$-SH), the product was precipitated in 19 mL of *n*-hexane. It was redissolved in chloroform and then precipitated in *n*-hexane again (precipitated in diethyl ether for the copolymer modified by $mPEG_{550}$-SH and thioglycolic acid) to afford modified P(EVL-*co*-TMC).

P(EVL-*co*-TMC-*g*-mPEG) was dissolved in 5.0 mL of dimethyl sulfoxide (2 mg/mL), and 5.0 mL of deionized water was added dropwise overnight. The solution was dialyzed against deionized water for 3 days. The resulting solution was ready for DLS analysis.

To prepare the water-soluble copolymer, 0.66 mL of diluted ammonia in THF (1.5 mol/L) was added into a THF solution (2 mL) of 45 mg of P(EVL-*co*-TMC-*g*-TGAc) dropwise. The white precipitate was collected and dried in vacuum to afford the water-soluble copolymer P(EVL-*co*-TMC)-*g*-ammonium thioglycolate (P(EVL-*co*-TMC-*g*-ATG)).

■ RESULTS AND DISCUSSION

Nature of Copolymerization of EVL with TMC. The six-membered cyclic carbonate TMC that can be synthesized from carbon dioxide and 1,3-propanediol exhibits excellent reactivity in ROP (Table 1, entry 2), whereas the CO_2-derived lactone EVL remains inert under similar conditions (Table 1, entry 1).

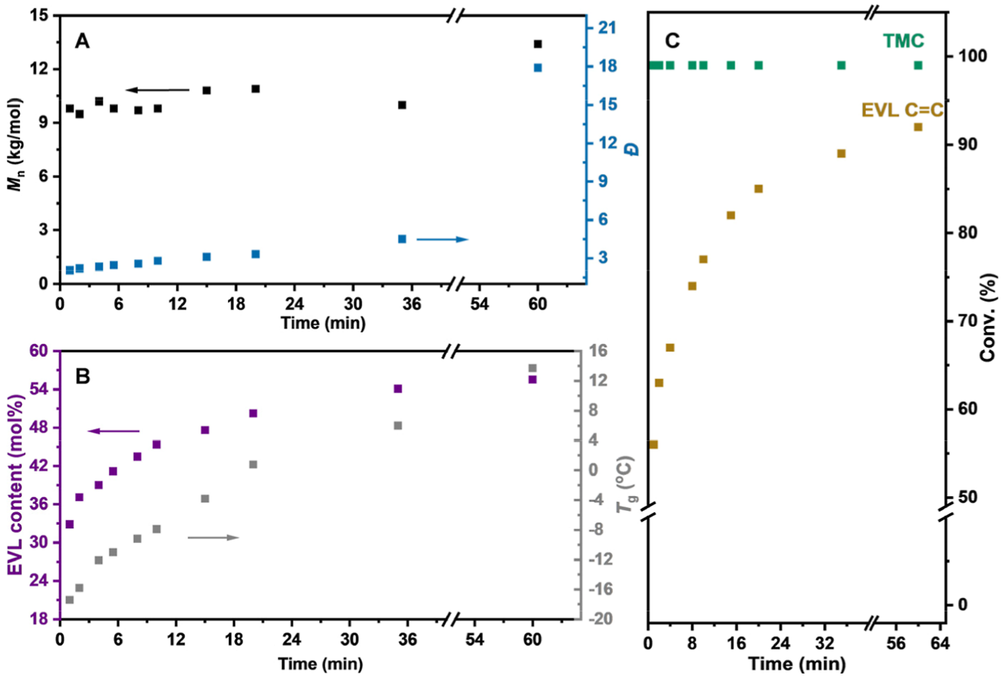


Figure 1. Kinetic plots of "scrambling polymerizations" of EVL with TMC ($[EVL]_0$:$[TMC]_0$:$[t\text{-BuOK}]_0$ = 33/16/1, $[M]_0$ = 2 mol/L, 25 °C in THF, cross-linked at 24 h).

Quantitative conversion of TMC within minutes is observed even during copolymerization (Figure 1C), suggesting that even if the ROP of EVL took place, it would result in a block copolymer. To achieve random poly(ester-*co*-carbonate) with uniformly distributed C═C double bonds, we decide to employ the "scrambling polymerizations" strategy.[33] In this method, an alkali metal alkoxide catalyst facilitates a frequent transesterification reaction, inserting EVL units into PTMC backbones generated by rapid ROP of TMC (Scheme S1). Therefore, kinetic studies reveal a sudden and complete conversion of TMC, followed by a gradual increase in the EVL content, which leads to an increase in the T_g of the copolymers. The high conversion of the conjugated C═C double bond of EVL suggests that most EVL monomers are activated to be oEVL forms (Scheme S2) ready for insertion into copolymers via transesterification. The almost constant M_n is due to a balance between the increase from the EVL unit incorporation and the decrease from the cleavage of PTMC chains. A topology transformation from linear to branched one occurs so that the yielded copolymer exhibits increasing dispersity (Đ) from 2.06 at 1 min to 17.9 at 60 min (Figure 1A). The transformation is caused by intermolecular transesterification between the main chain and pendent lactone rings in other chains, a phenomenon also observed in the case of CL.[33] Comprehensive copolymerization data of TMC with EVL are listed in Table 1. In the presence of *t*-BuOK, commercially available as THF solution, the copolymerization results in P(EVL-*co*-TMC) with a 63 mol % EVL content (Table 1, entry 7). Cross-linked copolymers are obtained in just 30 min when EVL is supplied in half the quantity of TMC (Table 1, entry 3). When EVL and TMC are fed equally, the resulting copolymer in 30 min displays a notably high Đ of 20.9, indicating a significant branching (Table 1, entry 4). An increase in Đ is observed as the EVL/TMC molar ratio decreases from 4:1 to 1:1 (Table 1, entries 4−7). This effect is attributed to the diminished availability of EVL and its oligomerized form oEVL for transesterification. Consequently, interchain transesterification is more favored, which in turn leads to branching and cross-linking. At a 4:1 EVL to TMC ratio, a copolymer with 63 mol % EVL content but a relatively low M_n of 6.6 kg/mol is produced (Table 1, entry 7). Reducing the temperature to −20 °C causes a decrease in EVL content from 66 mol % at 50 °C to 46 mol % (Table 1, entries 7−10) due to the constrained transesterification reactions and oligomerization at low temperatures. A minimal 0.5% Lewis base usage leads to the lowest EVL content of 8 mol % and a conjugated C═C double bond conversion of 17% (Table 1, Entry 13). In contrast, when a 4% Lewis base loading is utilized, the promoted oligomerization and transesterification reactions result in copolymers with EVL contents reaching a maximum of 70 mol % (Table 1, entry 11), which is much higher than that in the P(EVL-*co*-CL) copolymer.[33] The choice of solvent also plays a role. In the case of toluene, the copolymer with 60 mol % EVL content (Table 1, entry 15) is produced, maintaining M_n and Đ similar to those in THF, whereas DCM only allows for 34 mol % EVL incorporation (Table 1, entry 14). Switching the Lewis base to MeOK exhibits little influence on EVL incorporation (Table 1, entry 18). In contrast, replacing K^+ with Na^+ significantly decreases C═C double bond conversions to 46% and 34% and accordingly reduces the EVL content to 28 mol % and 25 mol % for MeONa and NaOAr, respectively (Table 1, entries 16−17).

The copolymerization processes provide the capability to adjust the T_gs of the copolymers over a wide range. Homopolymer PTMC exhibits the lowest T_g of −26.6 °C (entry 2, Table 1). Over the course of copolymerization, the T_gs of copolymers gradually increase, starting from −17.4 °C at 1 min and reaching 0.8 °C after 20 min (Figure 1B). Then the highest T_g value of 20.3 °C is achieved for linear copolymers at 60 min. In the case of cross-linked copolymers, the T_g (30.5 °C) is even higher due to the limited segment mobility caused

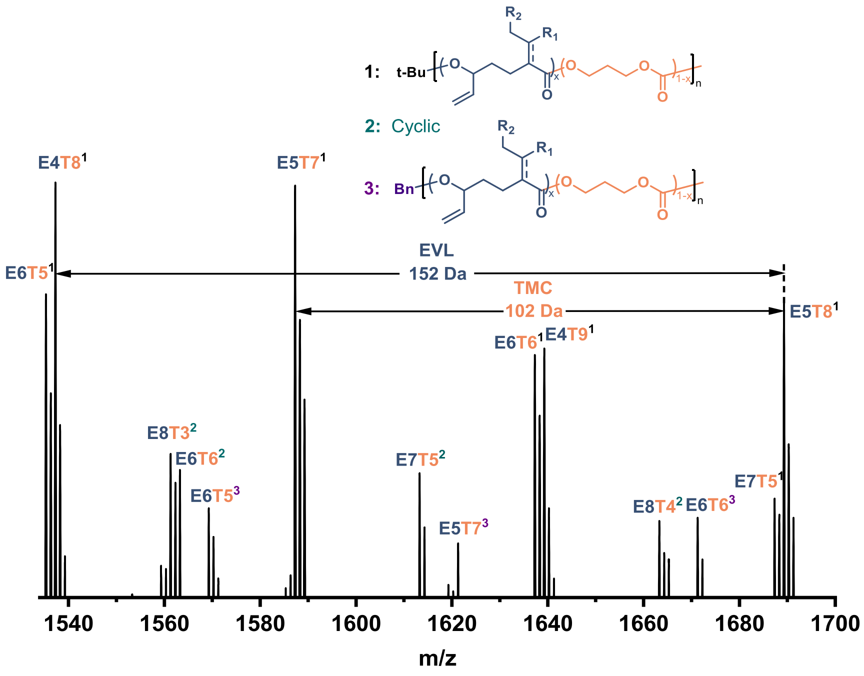


Figure 2. MALDI-ToF mass spectrum of P(EVL-*co*-TMC) (benzyloxy residual moiety (BnO−) resulting from the initiator benzyl alcohol, which initiated the ROP of TMC in the first step of the "one-pot-two-step" process for synthesizing copolymers suitable for the MALDI-ToF MS test).

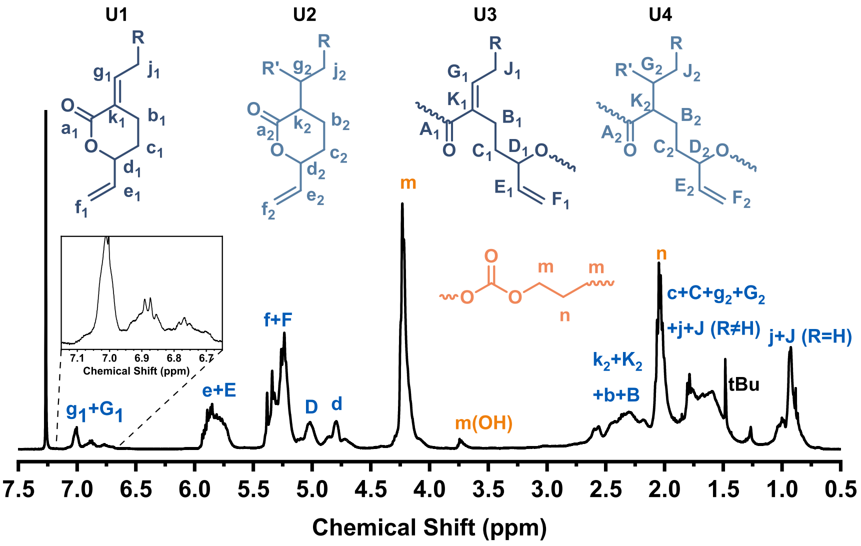


Figure 3. ^{1}H NMR spectrum of P(EVL-*co*-TMC) in $CDCl_3$ (Table 1, entry 7).

by cross-linking. TGA of P(EVL-*co*-TMC) reveals a decomposition temperature at a 5% mass loss ($T_{d,5\%}$) of 191 °C and a T_{max} (maximum degradation temperature, determined by the peak temperature in the relative derivative thermogravimetry) of 202 °C (Figure S1).

Microstructures of P(EVL-*co*-TMC). The MALDI-ToF mass spectrum of P(EVL-*co*-TMC) evidences the presence of both EVL and TMC units in the copolymer, exhibiting distinct mass intervals of 152 and 102 Da, respectively (Figure 2). Linear copolymers, containing a residual *tert*-butoxy initiator moiety, are determined to be the predominant species, alongside cyclic copolymers originating from intramolecular transesterification reactions. NMR spectroscopy is employed to further elucidate the copolymer structure. Characteristic signals assigned to EVL units ($H_{e,E}$ at 5.8 ppm, $H_{f,F}$ at 5.3 ppm) and TMC units (H_m at 4.2 ppm, H_n at 2.1 ppm) are observed in the ^{1}H NMR spectrum (Figure 3). Moreover, the ^{1}H diffusion-ordered spectroscopy (DOSY) NMR spectrum, illustrating identical diffusion coefficients for all protons, consistently confirms the coexistence of EVL and TMC units in the copolymer (Figure S2). Notably, the absence of a signal typically ascribed to the ether groups ($-ROCH_2$) at 3.45 ppm supports the conclusion that TMC decarboxylation does not occur during copolymerization.[43]

In the ^{13}C NMR spectrum (Figure S3), various carbonyl groups are specified, including 174 ppm for conjugated ester groups ($C_{a1,A1}$), 165 ppm for unconjugated ester groups ($C_{a2,A2}$), and 154 ppm for carbonate groups (C_p). The ring-opened EVL unit features a signal at 60 ppm (C_D), distinct from the one in the lactone ring at 78 ppm (C_d). The proposed P(EVL-*co*-TMC) structure is further verified by two-dimensional spectra (Figures S4−S6). Importantly, with ester and

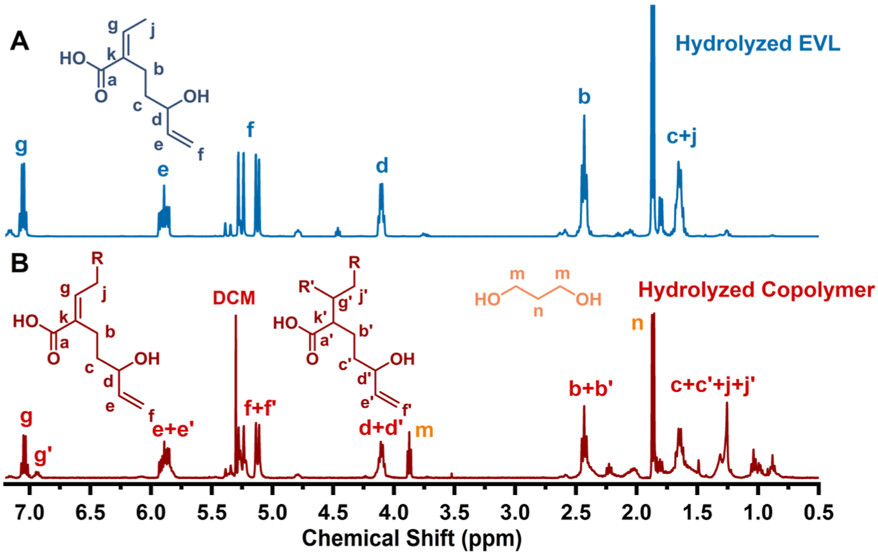


Figure 4. ^1H NMR spectrum of hydrolyzed EVL (A) and P(EVL-*co*-TMC) (B) in $CDCl_3$.

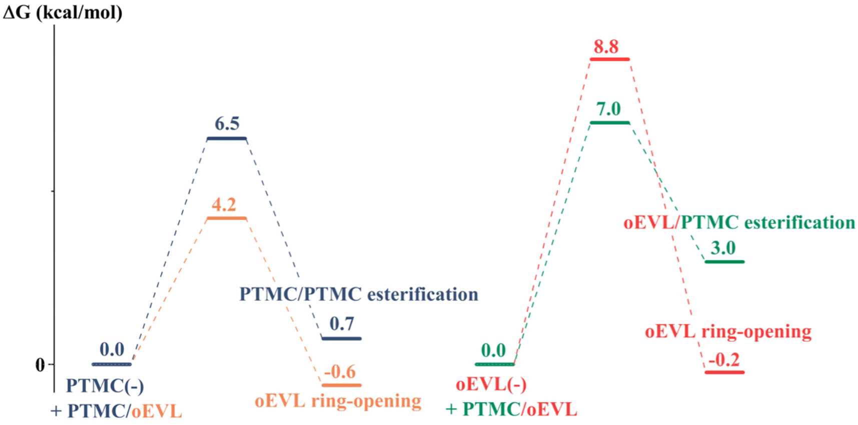


Figure 5. DFT-calculated energy profiles of the four transesterification reactions under M06-2X/6-31+G(d,p).

carbonate linkages, P(EVL-*co*-TMC) is hydrolytically degradable, facilitating the recovery of diols and hydroxy acids from EVL derivates, whose structure will be discussed in detail below (Figure 4B).

In the zoom-in view of the ^1H NMR spectrum, a strong quadruple peak is observed at 6.9 ppm (Figures 3 and S7). The signal can be attributed to the ring-opened and conjugated EVL-derived units (U3) in the copolymer. Its chemical shift matches the one detected in copolymer P(EVL-*co*-beta-butyrolactone), where EVL is incorporated into the polyester as U3 (R = H).[28] Methanolized EVL, which structurally resembles U3, also displays this quadruple peak (Figure S7), spectrally confirming the ring-opened EVL unit in the copolymer.

To gain deeper insights, both P(EVL-*co*-TMC) and EVL are hydrolyzed in THF containing 10% water and 1.0 mol/L KOH. Subsequent acidification and chloroform extraction resulted in unconjugated acid (from U2 and U4) and 1,3-propanediol (from TMC unit) (Figure 4B). Remarkably, the quadruple peak at 6.9 ppm is assigned to the conjugated acid (from U1 and U3), consistent with the observations in the spectrum of hydrolyzed EVL (Figure 4A). The peaks of hydrolyzed EVL and hydrolyzed oEVL ($x = 0$) are identified by ESI-MS (Figure S8). These observations indicate that not only unconjugated lactones in oEVL but also conjugated lactones in EVL or oEVL are involved in transesterification with carbonate groups in the PTMC. DFT calculation reveals that the coordination of carbonyl groups with potassium cations reduces the Gibbs energy barriers of the ring-opening of lactone in oEVL to all below 5.0 kcal/mol, indicating the enhanced ring-opening reactivities of all the three lactone rings (Figure S9). The rapid transesterifications lead to 33 mol % EVL incorporation in 1 min (Figure 1A). It is also supported by DFT calculation results that the Gibbs free energy change barriers ($\Delta G^{\ddagger}$) of the transesterification reactions between oEVL and PTMC are both less than 10 kcal/mol, specifically 4.2 kcal/mol for PTMC end with oEVL and 7.0 kcal/mol for oEVL end with PTMC (Figure 5). Building upon this evidence, we propose various structures for EVL-related units, depicted in Scheme S3. Specifically, ES1 and ES2 originate from the ring-cleavage of conjugated lactone of EVL and oEVL, respectively, while ES3 results from either the conjugated addition of (o)EVL with ES1 or the ring-opening of the unconjugated lactone of oEVL.

In conclusion, in the copolymerization of EVL with TMC, the "scrambling polymerizations" mechanism is quite different from the case of CL.[33] Although the ROP of TMC and conjugated addition of EVL still proceed rapidly in stage I

Table 2. "Scrambling Polymerizations" of EVL with Various CCs Mediated by *t*-BuOK[a]

entry	cyclic carbonate	[EVL]:[TMC][b]	conv. (EVL conjugated C=C, %)[c]	conv. (CC, %)[c]	time (min)	M_n[d] (kg/mol)	Đ[d]	EVL content (mol %)[e]	CO_2 content (wt %)[e]	C=C content (per unit)[e]	T_g[f] (°C)
1	5,5-DTC	4:1	96	n.d[g]	60	4.2	1.70	76.3	27.2	0.90	14.7
2[h]	4,6-DTC	2:1	96	62	20	5.1	3.11	81.6	27.6	0.94	34.5
3	4-MTMC	2:1	96	90	60	5.4	1.97	61.4	27.1	0.75	27.7
4	TeMC	4:1	97	99	60	9.7	1.92	44.2	26.3	0.59	−4.6
5	HTeMC	4:1	93	n.d[g]	15	7.1	3.45	64.9	27.4	1.18	10.7

[a]Polymerization is conducted at a 2 mol/L initial total monomer concentration in THF, 25. °C. [M]:[*t*-BuOK] = 25:1. [b]Initial ratio. [c]Determined by in situ ^{1}H NMR. [d]Determined by SEC. [e]Determined by ^{1}H NMR of the copolymer (Figures S10−S14). [f]Determined by DSC. [g]Not determined due to the stacking of signals. [h]Polymerization at 60 °C.

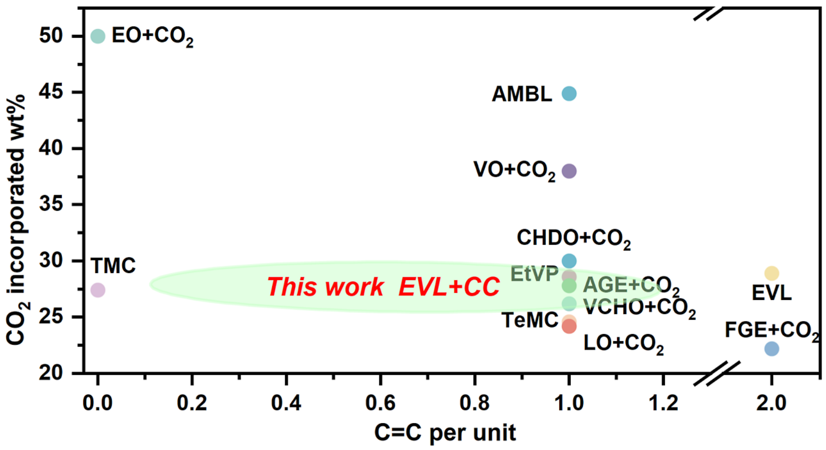


Figure 6. Incorporated CO_2 and the amount of C=C double bonds of CO_2-derived polyesters and polycarbonates (labeled with monomer names). AGE: allyl glycidyl ether,[46] AMBL: *α*-methylene-*β*-butyrolactone,[47] CHDO: cyclohexadiene oxide,[48] EO: ethylene oxide,[49] FGE: furfuryl glycidyl ether,[50] LO: limonene oxide,[51] VCHO: 4-vinyl cyclohexene oxide,[52] and VO: vinyloxirane.[53]

(Figure 1C), during stage II, not only unconjugated lactone rings in oEVL but also conjugated lactone rings in EVL and oEVL participate in transesterification reactions, resulting in various EVL-derived units (U1−U4, Figure 3). Concurrently, U1 and U3 undergo conjugated addition with EVL, transforming into U2 and U4. Both transesterification and conjugated addition contribute to the increase in the EVL content (Figure 1B). It explains the much higher EVL content (70 mol %) in P(EVL-*co*-TMC) than that in P(EVL-*co*-CL) (up to 50 mol %).[33] Furthermore, in stage III, intermolecular transesterification continues to play a significant role in the branching and cross-linking processes, generating copolymers with broad molecular weight distribution.

Obtaining Copolymers of Various CCs with EVL. In addition to TMC, five kinds of six- and seven-membered CCs are prepared from the corresponding diols and CO_2 at atmospheric pressure, following established protocols in the literature.[16] Prior studies have investigated the ROP of several CCs, highlighting the feasibility of producing copolymers with EVL via the "scrambling polymerizations" strategy.[44,45] As presented in Table 2, the copolymer of EVL with 5,5-DTC contains 76 mol % EVL units and has a M_n of 4.2 kg/mol (Table 2, entry 1). For another instance, the ROP of EVL with 4-MTMC generates a copolymer with 62 mol % EVL (Table 2, entry 2). However, an attempt to copolymerize EVL with 4,6-DTC yields a trace product even after 24 h at room temperature due to the poor ROP activity of 4,6-DTC with merely 20% conversion. P(EVL-*co*-4,6-DTC) with a M_n of 5.1 kg/mol and 82 mol % EVL incorporation is obtained at 60 °C (Table 2, entry 3). The seven-membered cyclic carbonate TeMC, known for its higher ring strain, provides a copolymer with a relatively high M_n of 9.7 kg/mol (Table 2, entry 4). Additionally, employing HTeMC, featuring a vinyl group, as a comonomer results in a copolymer with the highest C=C content (1.18 per unit; Table 2, entry 5) among all the copolymers in this research. The T_g of P(EVL-*co*-4,6-DTC) reaches a peak of 34.5 °C, demonstrating a significant expansion in the achievable range of thermal properties (Table 2, entry 2).

Figure 6 illustrates the CO_2 content and the number of functional group counts per unit of the reported CO_2-derived polyesters/polycarbonates. Most of the copolymers from CO_2 and epoxides containing C=C double bonds maintain a consistent 1.0 C=C double bond per repeating unit when 100% carbonate linkage selectivity is achieved, with the highest CO_2 content being 38 wt % for poly(2-vinyloxirane carbonate) (PVIC). In contrast, P(EVL-*co*-TMC)s exhibit flexibility in the CO_2 content and C=C double bond incorporation. The homopolymer PTMC stands out with a CO_2 content of 27 wt % (Table 1, entry 2). However, these copolymers lack C=C double bonds for postpolymerization modifications. EVL, on the other hand, offers 29 wt % CO_2 along with more than one C=C double bond. As a result, P(EVL-*co*-TMC) contains up to 0.82 C=C double bonds per unit, enhancing its availability in facile postpolymerization modification. The average number of C=C double bonds per unit attains a maximum of 1.18 when using HTeMC as the comonomer; meanwhile, it is accompanied by a CO_2 content of 27 wt % (entry 5, Table 2).

Mechanical Properties of the Cross-Linked Copolymer. By employing the "scrambling polymerizations" strategy, cross-linked copolymers are successfully produced by a convenient "one-pot-one-step" procedure. In the P(EVL-*co*-CL) case, 72 h is necessary for a well-cross-linked copolymer with merely 1.7 MPa stress at break (σ_B).[33] With TMC, the copolymerizations carried out for 4 and 12 h at an initial EVL/TMC ratio of 2:1 result in P(EVL-*co*-TMC) networks with σ_B values of 8.5 ± 5.7 and 9.7 ± 2.2 MPa, respectively (Figure 7).

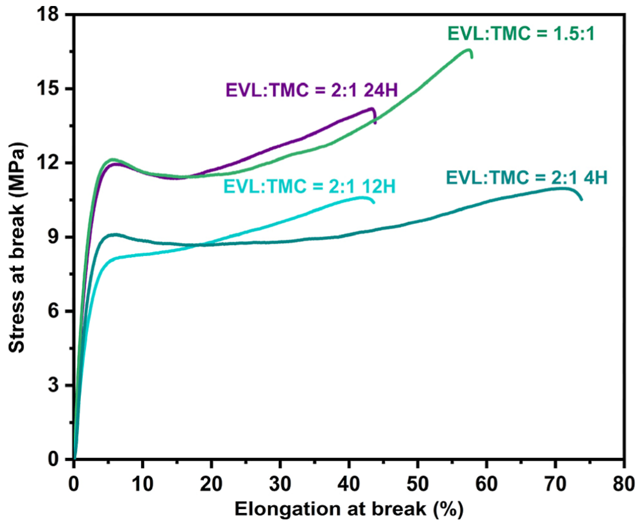


Figure 7. Strength−strain plots of cross-linked P(EVL-*co*-TMC).

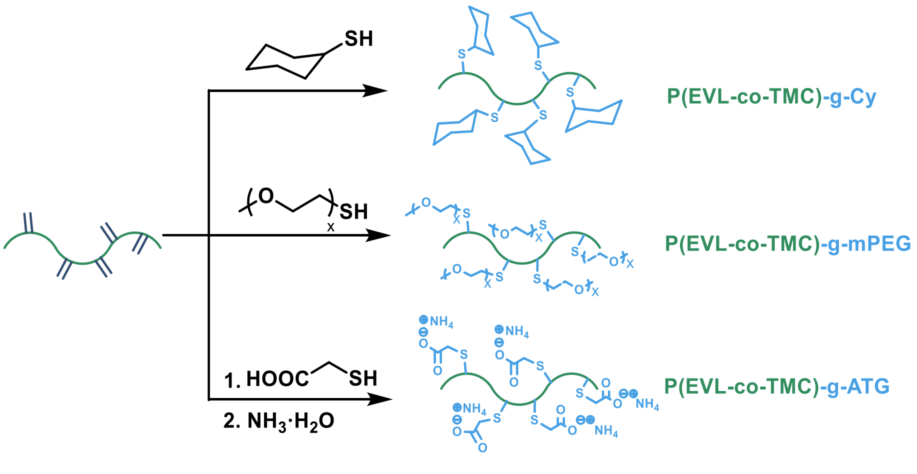
Extending the polymerization to 24 h further increases σ_B of the well-cross-linked network to 13.9 ± 0.9 MPa. However, it reduces the elongation at break (ε_B) to 52.2 ± 5.3% from 74.1 ± 12.2% (observed for 4 h). When 1.5 times EVL is fed compared to TMC, the P(EVL-*co*-TMC) obtained after 24 h exhibits a similar σ_B of 14.5 ± 3.1 MPa but a higher ε_B of 69.5 ± 3.5% and Young's modulus (E = 0.266 ± 0.078 GPa). P(EVL-*co*-TMC)s possess mechanical properties comparable to those of commercial LDPE (σ_B = 10 MPa, E = 0.10 GPa) enabling their application as universal materials.[54]

Postpolymerization Modification of Copolymers via Preserved C═C Double Bonds. The abundant C═C double bonds preserved in the copolymers enable postpolymerization modification, particularly through thiol−ene click reactions with thiols, for facile installation of pendant groups (Scheme 2). Employing cyclohexyl mercaptan, a cyclohexyl group is successfully introduced into P(EVL-*co*-TMC), which is confirmed by the ^{1}H NMR spectrum (Figures S15). The modification results in an increase in T_g from the original 13.1 to 23.8 °C, showing the impact of bulk side groups (Figure S16). In the second modification, mPEG$_{550}$-SH is grafted onto P(EVL-*co*-TMC) (Figure S17), which remarkably raises the peak molecular weight (MP) from 8.8 to 15.3 kg/mol (Figure S18), indicating the successful grafting of mPEG. DSC analysis reveals a reduced T_g of −19.7 °C due to the attached PEG segments with a low T_g (Figure S16). P(EVL-*co*-TMC-*g*-mPEG) in aqueous environments exhibits nanoparticles with hydrodynamic diameters ($D_{h,intensity}$) of 8.1 and 49 nm (Figure S19). The third modification introduces carboxyl groups into P(EVL-*co*-TMC) by grafting thioglycolic acid (TGAc). Subsequently, the obtained P(EVL-*co*-TMC)-*g*-TGAc is transformed into water-soluble P(EVL-*co*-TMC)-*g*-ATG through ammonia deprotonation, with the methylene protons (−S−CH_2−COONH$_4$) observed in the ^{1}H NMR spectrum (in D_2O, Figure S20). The absence of signals at 5.5−7.5 ppm, which is assigned to C═C double bonds, suggests high grafting efficiency. The conversion from carboxyl groups to carboxylates is further confirmed by Fourier transform infrared (FTIR) spectra, with the peaks of C═O stretching vibration of carboxyl groups shifting from 1634 to 1582 cm^{-1} and 1385 cm^{-1} (Figure S21). The M_n and $Đ$ of P(EVL-*co*-TMC)-*g*-ATG are determined as 5.0 kg/mol and 1.2, respectively, according to the SEC measurement in water (Figure S22). Additionally, the ammonium salt P(EVL-*co*-TMC)-*g*-ATG with a strong interchain interaction shows a high T_g of 42 °C in DSC (Figure S16). In short, various functional polymers are accessible after postpolymerization modifications, demonstrating the great potential of P(EVL-*co*-TMC)-derived materials.

■ CONCLUSIONS

CO$_2$-derived poly(ester-*co*-carbonate)s have been successfully synthesized via copolymerization of EVL with various CCs. Mediated by tBuOK, P(EVL-*co*-TMC)s are obtained following a "scrambling polymerizations" strategy. The incorporations of both TMC and EVL-derived units, in which the conjugated and ring-opened structure is first observed, are confirmed by NMR spectra and the MALDI-ToF mass spectrum. The resulting P(EVL-*co*-TMC)s, featuring CO$_2$ contents exceeding 27 wt %, exhibit T_gs in the range of −26.9 to 22.5 °C. Moreover, copolymerizations of alternative CCs with EVL

Scheme 2. Post-polymerization Modification of P(EVL-*co*-TMC) via the Thiol−Ene "Click" Reaction



yield copolymers with average C═C double bonds per unit up to 1.18. These C═C double bonds originating from EVL are modified through "thiol−ene" reactions, resulting in high T_g, amphiphilic, and water-soluble poly(ester-*co*-carbonate)s. Cross-linked P(EVL-*co*-TMC)s are facilely produced by a "one-pot-one-step" process, achieving an impressive tensile strength of 14.5 MPa. The work presents a universal approach to prepare customizable functional poly(ester-*co*-carbonate) materials from CO_2, 1,3-butadiene, and diols.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c02023.

Schemes with chemical structures and characterization results including NMR, TGA, DSC, ESI-MS, and DLS (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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