Highly Efficient Synthesis of Functionalizable Polymers from a CO₂/1,3-Butadiene-Derived Lactone

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Ⓢ *Supporting Information*
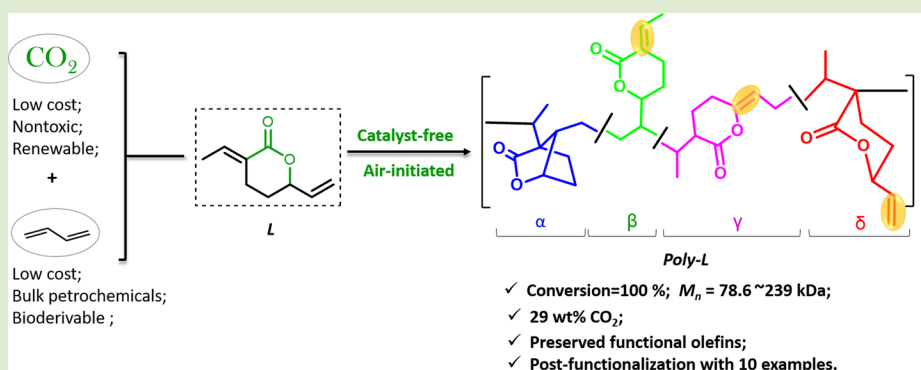
ABSTRACT: Making polymers from CO₂ and olefins has been long sought and is of particular significance for chemical utilizations of CO₂. Herein, high molecular-weight polymers with 29 wt % CO₂ were obtained by polymerizing a *δ*-lactone (**L**) synthesized from a C−C coupling reaction between CO₂ and 1,3-butadiene, an economical large-volume chemical that can also be derived from top biomass platform chemicals. Although **L** has been known for many years, little was investigated in its polymerization. We found that **L**'s polymerizability can be vitalized upon simply heating in the presence of O₂. The polymerization is additive/solvent-free with abundant preserved olefins and up to full monomer conversion, providing a convenient, economical, and scalable avenue to obtain CO₂-derived polymers with potentially tailorable properties via the readily modifiable olefins.

CO₂ is a highly attractive renewable C1 chemical feedstock due to its abundance, availability, recyclability, and nontoxicity.[1,2] To date, chemical utilizations of CO₂ are largely limited to the production of small molecules.[3,4] Polycarbonates derived from CO₂ and epoxides via the formation of C−O bonds are the only commercialized polymer that directly utilizes CO₂.[5−9] Considering that five of the current "big six" synthetic polymers (low-density polyethylene, high-density polyethylene, polyvinyl chloride, polystyrene, polypropylene, and polyethylene terephthalate) are made from olefins via C−C bond formations,[10] development of C−C bond forming strategies to utilize CO₂ and olefins as building blocks for polymers is highly desired for a more sustainable polymer industry but represents a major challenge. In spite of the long efforts seeking direct CO₂/olefin copolymerizations,[11−13] only low molecular weight (MW) oligomers have been obtained from reactions of CO₂ with dienes,[14] vinyl ethers,[15,16] or acrylonitrile.[17]

As one of the important components in the C4 fraction of oil cracking,[18,19] 1,3-butadiene is widely applied in the rubber industry as a major monomer.[19] It can also be derived from succinic acid,[20−22] which ranked as one of the top 12 biomass platform compounds best suited to replace the petrochemicals.[23] Thus, chemistry leading to polymers made from CO₂ and large-volume dienes, especially 1,3-butadiene, is of significant fundamental interest and promising large-scale industrial utility. In 1976, Inoue et al. synthesized a five-membered cyclic ester, 2-ethylidenehept-5-en-4-olide, via the catalytic coupling of CO₂ and 1,3-butadiene.[24] Musco et al. obtained a six-membered cyclic ester, 3-ethylidene-6-vinyl-tetrahydro-2*H*-pyran-2-one (**L**, 29 wt % CO₂), in the same coupling reaction.[25] Behr et al. optimized the selective synthesis of **L**[26−28] and developed a miniplant scale production.[29−32]

With two C=C bonds and a cyclic ester, **L** appears as a tantalizing monomer for polymeric materials. However, only limited success has been achieved in the oligomerizations of **L**

through radically, cationically, or anionically initiated polymerizations in the past decades,[33] mainly owing to the well-known difficulty in polymerizing sterically hindered olefins such as tiglate-type olefins.[34−36] Nozaki et al. recently reported the only successful polymerization of *L* using various radical initiators (V-40 or AIBN) and metal additives (MX_n, M = Zr, Cu, Fe, Zn; X = Cl, Br) with relatively low yields (up to 59%),[37] providing the first methodology to allow a stepwise formal copolymerization of CO_2 and 1,3-butadiene. Methodological development to improve the efficiency of polymerizing *L* is a major challenge that may allow the application of the copolymerization as a new strategy for large-scale chemical utilization of CO_2.

Herein, we report a formal copolymerization of CO_2 and 1,3-butadiene via a surprisingly efficient air-initiated bulk polymerization of *L* derived from CO_2 and 1,3-butadiene (Figure. 1).
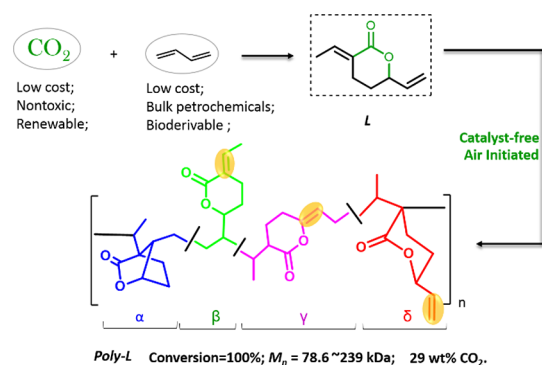

Figure 1. Synthetic route for CO_2/1,3-butadiene-derived polymer. The structures of *L* and poly-*L* are shown. Poly-*L* was obtained by simply heating *L* under air without any additives and solvents. Four different repeating units (**α, β, γ,** and **δ**) were observed in the poly-*L*.

The polymerization did not need any additive/solvent and high molar mass (up to 239 kDa) polymers with up to a quantitative conversion (up to 100%) of monomer as well as high contents of CO_2 (29 wt %) and preserved functional olefins were obtained. Comparing with the previous work,[37] a new repeating unit (**δ**) was found in poly-*L* with higher conversion and MW. Postpolymerization modification of the obtained poly-*L* was achieved via thiol−ene click reactions with a wide substrate scope.

We began our explorations by heating CO_2-derived dry *L* at temperatures up to 180 °C with dibutyltin dilaurate (DBTDL) as an additive, initially hoping to trigger ring-opening reactivity, but no reaction was observed after performing the experiments under a rigorous N_2 atmosphere in a glovebox (entry 1, Table 1). To our surprise, polymerization was observed using the same reagents at 180 °C but conducted outside the glovebox. This serendipitous result suggested that the reaction might be promoted by diffusion of an adventitious amount of air. We repeated the reaction in a sealed vial after a purposeful exposure of *L* to air for 10 s and observed a 37% monomer conversion by ^1H NMR spectroscopy after heating at 180 °C for 24 h (entry 2, Table 1). With this encouraging result, the reaction was repeated again in an unsealed vial under air. To our delight, the conversion of monomer increased to 88% (entry 3, Table 1). These unexpected results encouraged us to further investigate the nature of the polymerization. Surprisingly, a quantitative conversion of *L* to a solid material was observed under air in the absence of DBTDL, suggesting that the metal compound is an inhibitor instead of a promoter for the polymerization of *L*

Table 1. Condition Screening for the Bulk Polymerization of L^a

entry	additives	atmosphere	t (h)	conversion[d] (%)
1[a]	DBTDL	N_2	48	0
2[b]	DBTDL	limited air	24	37
3[b]	DBTDL	air	24	88
4		air	24	100
5		N_2	72	0
6[c]	water	N_2	72	0
7	TEMPO	air	24	0
8	1,4-benzoquinone	air	24	0
9		O_2	24	83

[a]The reaction was conducted with dry *L* under 180 °C in a glovebox. $[M]_0/[additive] = 100:1$. [b]Reagents were first mixed in a glovebox and then heated in the presence of or under air at 180 °C. [c]The reaction was conducted in a glovebox with 5 mol % DI water. [d]Conversion was determined by ^1H NMR spectroscopy.

(entry 4, Table 1). In contrast, no reaction was observed for the same conditions under N_2 (entry 5, Table 1).

All observations above suggested that air, most likely O_2 or moisture, should be the initiating component for the polymerization. Since O_2 is a well-known inhibitor for radical polymerizations,[38] it was first assumed that water might be the active component. However, no reaction was observed upon heating *L* with a catalytic amount of water in the glovebox (entry 6, Table 1), suggesting that O_2 acts as a radical promoter in the present reaction. We next probed this possibility by performing the reaction under air in the presence of 2 mol % free radical inhibitor, including 2,2,6,6-tetramethylpiperidine (TEMPO) and 1,4-benzoquinone (entries 7 and 8, Table 1). No measurable polymerization took place, clearly supporting a free-radical polymerization mechanism initiated by O_2. Interestingly, increasing the concentration of O_2 was not always beneficial to the polymerization; a lower conversion was observed if the reaction was carried out under pure O_2 instead of air (entry 9, Table 1), suggesting that O_2 can also act as a radical inhibitor once its concentration in the reacting system is sufficiently high.

The chemical structure of the obtained poly-*L* was characterized by ^1H NMR (Figure 2),^{13}C NMR, and ^1H−^1H COSY spectroscopies (Figures S2 and S3). The ^1H NMR spectrum shows multiple downfield signals in the region of 5−7 ppm, indicating that a fair amount of conjugated and nonconjugated olefins of *L* are preserved in the polymerization. This structural feature is highly desirable because it has been widely demonstrated that polymers with abundant C=C bonds can be conveniently postmodified to install functionalities for various applications.[39−41] Both **β** and **δ** units partially reserved the characteristic ^1H NMR features of *L* in the olefinic region. The new signal at about 6.2 ppm indicated the appearance of the nonconjugated internal olefin in the **γ** unit due to an intramolecular H atom abstraction (HAA) reaction. The significantly increased signals in the area of 0−3 ppm is characteristic of the formation of the **α** unit in which both C=C bonds of *L* became saturated. Other notable feature is the broad signal in the area of 4.4−5.0 ppm corresponding to the tertiary C−H bond adjacent to the ester. That bond was lost in the **γ** unit due to the HAA reaction. ^1H and ^{13}C NMR signals corresponding to **α, β,** and **γ** repeating units are consistent with the literature data.[37] Another set of signals was observed in the downfield region of the ^1H NMR spectrum, indicating the
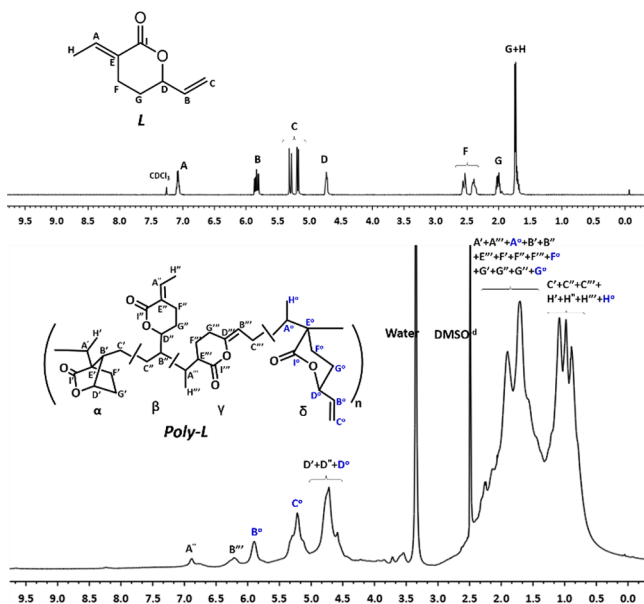
Figure 2. ^1H NMR spectra of L (in CDCl$_3$) and poly-L (in DMSO-d^6). Chemical shifts in the ^1H NMR spectrum of poly-L were assigned to each repeating unit (α, β, γ, or δ). Signals in the area of 5−7 ppm indicated a fair amount of conjugated and nonconjugated olefins of L were preserved in poly-L.

presence of a new type of repeating unit, δ. In contrast to α and γ units, the δ unit showed ^1H NMR signals similar to corresponding hydrogens of L, except for the disappearance of the conjugated olefinic hydrogen, indicating the participation of conjugated olefin into the backbone formation of the polymer. ^{13}C NMR spectroscopy, especially comparisons of the NMR data of the δ unit with an analogous small molecule, further confirmed the structural assignments (see Supporting Information for details, Tables S2 and S3). Strong couplings of the two signals assigned to the terminal olefin in δ unit were observed in the $^1H-^1H$ COSY spectrum. It should be noted that strong steric repulsions between trisubstituted repeating olefins typically prohibits the formation of poly-δ, while in the present system, such an inhibiting factor is presumably absent due to its copolymerization with other units (α, β, or γ).

The initiation and propagation process were proposed in Figure 3 to rationalize the four different units in poly-L. The
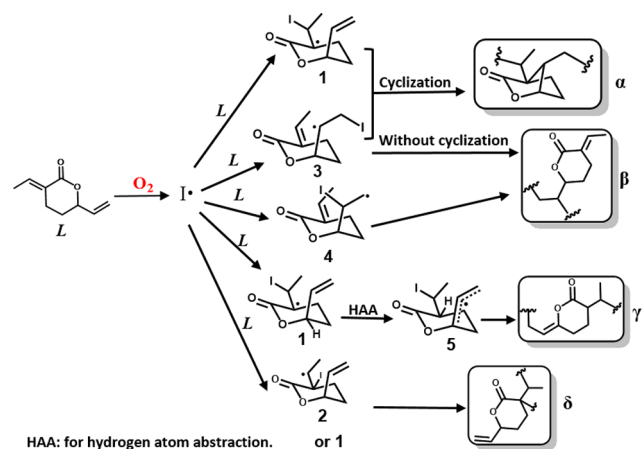

Figure 3. Proposed mechanism to form four different repeating units.

reaction between the monomer (L) and O$_2$ upon heating presumably produced the radical initiator ($I^\bullet$), which can attack either of the two different C=C bonds of L to form two pairs of radical regio-isomers ($1/2$ and $3/4$). Direct chain propagation from $1/2$ and $3/4$ resulted in the formation of the δ unit and the β unit, respectively. In contrast, the *exo*-cyclization reactions from 1 and 3 led to the formation of the α repeating unit. Finally, an intramolecular HAA of 1 could lead to the allyl radical species (5) and produced the γ unit.

The air-initiated polymerization of L was next systematically probed with different amounts of air at various temperatures. The impact of reaction time was also studied. Higher reaction temperatures and more air were expected to increase the amount of radicals in the reaction mixture, which should lead to a faster consumption of the monomer and a higher probability of chain transfer and chain termination. Experimentally, it was observed that the conversion of L increased as the amount of air and the temperature increased, consistent with the proposed O$_2$-promoted free-radical mechanism and suggesting that the initiation role of O$_2$ should outweigh its inhibition role for concentrations of O$_2$ not exceeding that of air. Too much oxygen can cause obvious inhibition process by the competing reaction of the living chain radicals with O$_2$, thus there was a balance considering the concentration of O$_2$. Polymers with higher MWs and moderate to wide dispersity values (M_n up to ca. 240 kDa, PDI ≈ 1.4−3.2) were obtained (Table 2; Figure

Table 2. Effect of Temperature and the Amount of Air on the O$_2$-Initiated Bulk Polymerization of L^a

entry	T (°C)	air (mL)	conv.^{a} (%)	M_n^c (kDa)	PDI^c	$\alpha/\beta/\gamma/\delta^a$
1	180	in air	100	78.6	3.29	4:1.8:1.3:2.9
2^b	180	in air	60	67.8	2.77	n.d.
3	150	in air	80	106	2.91	4.2:1.6:1.3:2.9
4	120	in air	69	122	1.44	4.8:1.5:0.8:2.9
5	100	in air	59	175	2.57	4:1.5:0.9:3.6
6	90	in air	37	167	2.70	n.d.
7	60	in air	9	216	2.33	n.d.
8	180	40	74	203	2.78	6.5:1.2:0.7:1.6
9	180	30	46	239	1.75	5.9:1.6:0.7:1.8

^{a}Conversion was determined by ^1H NMR spectroscopy. ^{b}The reaction was conducted for 1 h. ^{c}Determined by GPC in DMF (entries 1, 3, 4) or THF (entries 2, 5−8) with RI, UV, and LS detector. MW was calculated using PS as standards. n.d. for no detection.

S4). The related polymers in the previous work showed lower MWs (up to 85 kDa[37]) and similar PDIs. In the present system, the MW decreased as the amount of air and the temperature increased, as lower steady state radical concentration lowered the termination rate much more significantly than that of the propagating rate which led to a longer kinetic chain length with less O$_2$ concentration and lower reaction temperature. The chain transfer reaction was more likely to take place when there was no more monomer available for propagation, that explained why the PDI was much wider at high conversion. Such behavior is in good agreement with typical radical polymerization.[43,45] Polymerization was observed at a temperature as low as 60 °C with a high M_n = 216 kDa (entry 6, Table 2), presumably due to the allylic moiety that can form radicals relatively easily. In contrast to monomer conversion rate as well as MW and PDI, no significant effect onto the percentage of $\alpha/\beta/\gamma/\delta$ was observed by varying temperatures and the amount of air. Under

all conditions, the formation of α/δ was always only slightly more favorable than β/γ. In comparison, exclusive formations of α were observed previously with AIBN or V-40 as the initiator.[37] The factors controlling the selectivity remains unclear.

Though O_2 is a well-known inhibitior for radical polymerizations, examples of O_2 initiated radical polymerization were also reported in literature.[42−44] The complicated dependence of the conversion rate on O_2 might be attributed to the dual roles of O_2 in the polymerization. In present system, **L** presumably provides abundant weak allylic C−H bonds that can react with O_2 via HAA to produce the active radical species ($I^\bullet$) for the initiation of the polymerization, which is consistent with the positive correlation between polymerization rates and O_2 concentrations under relatively low-O_2 conditions. On the other hand, O_2 can trap the active radical species during the initiation or propagation stage to produce peroxyl radicals that are well-known as less active species for chain propogation.[38] This inhibition behavior becomes important as the concentration of O_2 is sufficiently high, which might account for the lower conversion rate under O_2 as compared to that under air.

The crude products were in solid state at 180 °C, which indicated a high melting temperature for the obtained materials. But no melting endotherms were observed by differential scanning calorimetry, which indicated an amorphous nature. The noncrystalline structure was also supported by powder X-ray diffraction analysis (Figures S16 and S17). The glass-transition temperatures (T_g) were in the range of 111−129 °C (Figures S18−S20) and thermogravimetric analyses showed that the decomposition temperatures (T_d) were at 350 °C−450 °C (Figures S21−S28). Comparing with the poly-α obtained in the previous work,[37] the present poly-**L** showed lower T_g and similar T_d. The lower T_g may result from the smaller percentage of the rigid α unit in poly-**L** than poly-α.

Postpolymerization modifications of poly-**L** can be readily achieved taking advantage of the abundant C=C bonds present in the polymeric structures. We tested commonly used thiol−ene reaction that has been widely applied in functional installations to the formed polymers.[39−41] For example, the functionalization of poly-**L** ($M_n = 7.86 \times 10^4$ kDa) was realized with benzyl mercaptan (**R₁SH**) using photoinitiator DMPA in CHCl₃ under UV light (254 and 365 nm) light at room temperature for 24 h (Scheme 1). ^{1}H NMR spectra of the resultant poly(**L-SR₁**) showed a significant decrease in the pendant alkene (δ = 5.0−7.0 ppm) and the appearance of signals in the aromatic region (δ = 7.1−7.5 ppm), thioester group − CH₂S− at δ = 2.75 ppm, 3.73 ppm (Figure S31) compared with the ^{1}H NMR spectra of poly-**L** (Supporting Information, Figure S29). Molecular weight of poly(**L-SR₁**) was measured to be 10.9×10^4 kDa after postpolymerization functionalization. Except for benzyl mercaptan, other thiols containing different groups such as carboxyl, hydroxyl and amine were also employed using DMAP as catalyst under ultraviolet light at room temperature in the thiol−ene postpolymerization modification of poly-**L** in Scheme 1. Most thio-ene reactions of poly-**L** with both aryl- and alkyl- thiols showed moderate conversions with about 50−84% with good functional compatibility. Poly-**L** can also be modified by both cysteine (**R₉SH**) and PEG-dithiol (**R₁₀SH**) with conversion of 69% and 53%, respectively. Detailed ^{1}H NMR and FTIR data are in the Supporting Information (Figures S31−S50). The conversions of all three different types of olefinic units for thiol−ene reactions were estimated by ^{1}H NMR and

Scheme 1. Substrate Scope for Post-Polymerization Modifications of Poly-L
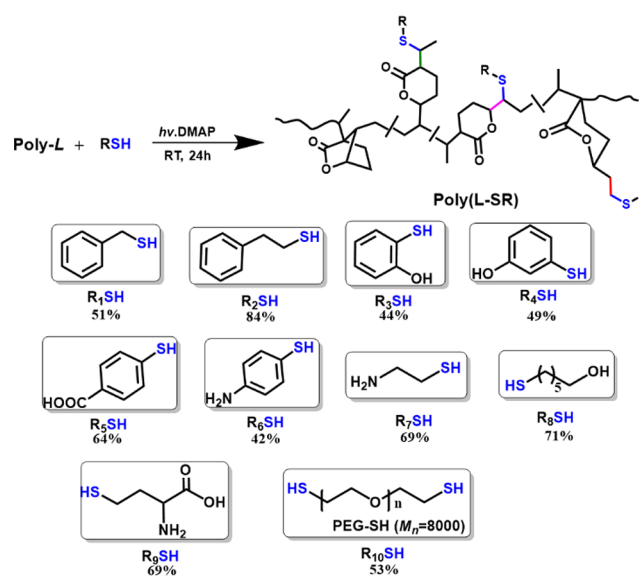
normalized to the initial amount of each corresponding olefinic unit (Table S4). The nonconjugated internal olefin (γ unit) showed the highest activity for most of the thiols in the present system. Further modification and more applications of poly-**L** are currently under exploration.

In summary, we have discovered a simpler and more convenient method to produce high-molecular-weight polymers from CO_2−BD-derived monomer with high contents of CO_2 and preserved olefins. Experimental results support an O_2-promoted radical polymerization mechanism through radical intermediates generated at two C=C groups. The resulting polymers can be easily functionalized using thiol−ene reactions. The simplicity and high efficiency of the present method, the renewability and large-scale availability of the feedstock as well as the abundant C=C bonds in the polymers should enable researchers to conveniently obtain scalable and economical CO_2-derived polymers that can be readily modified for various applications. This work demonstrates the great potential of using CO_2 as a renewable carbon feedstock to make polymers with olefins via C−C bond formations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.7b00774.

Experimental details and supporting figures (PDF).

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Dong and Professor Junxia Lu of ShanghaiTech University for the ^{13}C NMR data of the polymer.

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