

New CO₂ copolymers

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Preparation of CO₂-diene copolymers: advancing carbon-dioxide based materials**

Giulia Fiorani and Arjan W. Kleij*

((Dedication----optional))

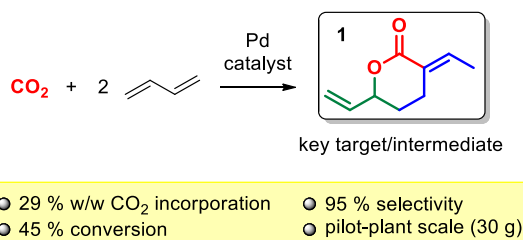
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Carbon dioxide · dienes · radical polymerization · CO₂ telomerization · Pd catalysis

Despite its physical and chemical inertness, carbon dioxide (CO₂) continues to be an attractive and alternative carbon synthon being abundant, renewable, readily available and cheap.^[1] The inertness of CO₂ poses a huge challenge given the energy input required for its transformation and/or functionalization. A successful example of CO₂ reutilization is represented by the development of atom-economical catalytic processes based on high-energy reactants (such as epoxides and oxetanes) leading to new functional molecules such as organic carbonates,^[2] polycarbonates and polyether-polycarbonate based polymers.^[3] Various efficient catalysts active towards CO₂/epoxide couplings have been developed in the last ten years,^[2-4] aiming at the stereo-controlled preparation of functional, cyclic carbonates^[5] as well as stereo-regular functional polymers.^[6] Further to this, some of these promising catalytic systems are currently employed in commercially feasible, industrial processes exploiting CO₂ fixation using ethylene and propylene oxide as reaction partners.^[6c] These processes furnish polyethylene carbonate, polypropylene carbonate and poly(ether)carbonate-polyols mixtures with a tailored, narrow molecular weight distribution of further (potential) use in polyurethane synthesis.^[7] The applicability of this type of polymerization reaction is still limited to polycarbonates/poly(ether)carbonates synthesis and, so far, has not been extended to another ambitious and challenging (commercial) target, the preparation of polyesters by direct copolymerization of CO₂ with ethylene or dienes. This copolymerization reaction is particularly appealing since it represents a link between different renewable resources such as CO₂, and cheap, widely available petroleum-derived alkenes allowing a potential evolution towards more sustainable materials. The principal obstacles preventing a successful copolymerization of these monomers include (1) a high energy barrier associated to the alternating copolymerization between ethylene/polyene and CO₂ requiring excess ethylene insertion to

ensure endergonic CO₂ insertion, and (2) a kinetic barrier represented by the high activation energy for CO₂ insertion in the growing polymeric chain *versus* chain growth of the poly(ethylene) or poly(propylene).^[8]

Nozaki and co-workers have now reported a reproducible and highly customizable procedure for the preparation of CO₂-diene copolymers.^[8b,c] Key to this success is the innovative use of an alternative polymerization strategy, circumventing the thermodynamic and kinetic barriers associated to direct CO₂-butadiene co-polymerization. In particular, they have employed a known *meta*-stable δ -lactone, 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (**1**)^[9] that can be easily obtained by telomerization of CO₂ and butadiene in the presence of a Pd/phosphine ligand catalytic system (Scheme 1). Lactone **1** has been extensively studied by Behr and others in the past 30 years as a promising functional organic intermediate and versatile synthetic building block. The optimized preparation of **1** both on lab and pilot-plant scale, thereby minimizing the formation of undesired telomerization side-products, should thus be regarded as a milestone in this area.^[10]



Scheme 1. Synthesis of δ -lactone **1**; the allylic moiety and the vinyl moiety are highlighted in blue and green, respectively.

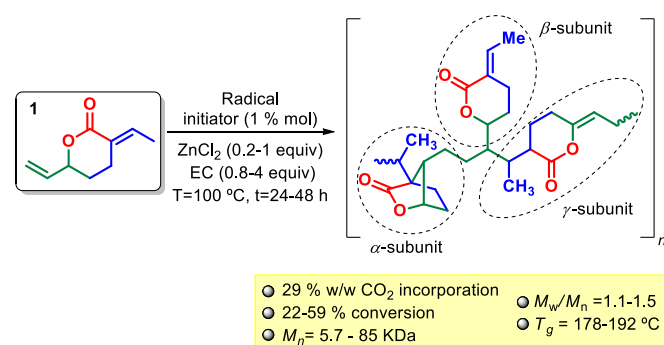
Nozaki and co-workers have found that δ -lactone **1** can easily undergo thermally initiated radical polymerization under aerobic conditions in the presence of an appropriate, thermally activated radical initiator [1,1'-azobis(cyclohexane-1-carbonitrile), V-40], observing a moderate conversion (17%) and producing a polymer, poly-**1** (Scheme 2), containing exclusively α -subunits formed by attack of the radical chain-end on the allylic ester unit of **1** (Scheme 2). Poly-**1** was characterized by a moderate M_n (5.7 kDa) and a narrow polydispersity M_w/M_n of around 1.3. The presence of Lewis acid additives such as ZnCl₂ and additional solvent such as ethylene carbonate (EC) accelerated the reaction rate and improved substantially the overall yield (48%) and M_n values (62–85 kDa) while retaining a good M_w/M_n distribution, but affected significantly the morphology of the resulting polymer (poly-**1'**); poly-**1'** comprises different isomeric subunits (α , β and γ in Scheme 2) and their presence is mediated by Lewis acid stabilization of the radical in the

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α -position to the ester carbonyl group or hydrogen abstraction in the vinyl moiety of **1**. Both poly-**1** and poly-**1'** polymers display relatively high CO₂ incorporation (29% w/w) and high glass transition temperatures ($T_g = 178$ – 192 °C) making these novel polymers likely suitable as engineering plastics.



Scheme 2. Synthesis of and details for poly-**1** and poly-**1'**.

To simplify and speed up the synthetic procedure, poly-**1'** was also prepared in a one-pot fashion, starting from butadiene and CO₂. The scope of these one-pot polymerization reactions was extended to the incorporation of more complex diene structures (*viz.* 1,3-pentadiene and isoprene) within the polymeric chain. The mixed telomerization of butadiene, CO₂ and other C₅ dienes was characterized by a lower reactivity, mainly ascribed to steric hindrance issues; however, after optimization, CO₂-rich terpolymers could be obtained in good yields (46 and 35% yield for isoprene and 1,3-pentadiene, respectively) with relative high CO₂ incorporation (20–24% w/w) and varying polymer properties ($M_n = 5.5$ – 16 KDa, $M_w/M_n = 2.0$ – 2.5 ; $T_g = 33$ – 63 °C).

By exploiting this facile aerobic radical homo-polymerization of δ -lactone **1**, Nozaki and co-workers have elegantly overcome the thermodynamic barrier preventing direct CO₂/butadiene co-polymerization, while expanding the library of useful high-energy CO₂ co-reactants. However, further characterization data (*cf.*, mechanical and thermal stability, biodegradability) of the resulting CO₂-rich polymeric materials is required to estimate their full potential and properties. Despite the slow reaction rates and the use of an excess Lewis acid co-catalyst, the possibility of obtaining CO₂/diene copolymers with a high CO₂ content (between 20–29 % w/w) is a significant step forward towards the preparation of more sustainable plastics and could potentially lead to a bulk utilization of CO₂ as a chemical feedstock. Moreover, extensive studies on the optimization of preparation procedures for intermediates of type **1** could be an excellent starting point for further process scale-up and providing new research opportunities. The combination of new, (bio)renewable based monomers with the concomitant development of one-pot polymerization strategies applicable to a discrete family of low molecular weight dienes could potentially lead to the preparation of new CO₂-based copolymers with novel innovative structures, enhancing their application potential in existing and new areas of polymer science.

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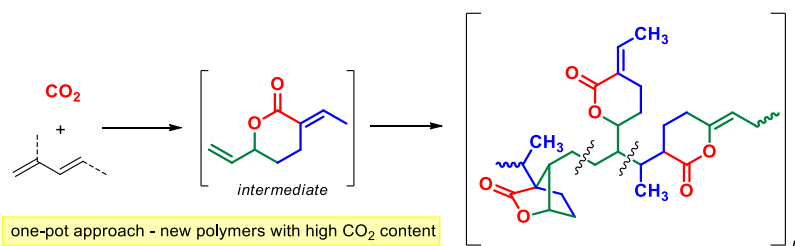
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Preparation of CO₂-diene copolymers:
advancing carbon-dioxide based
materials

Expanding the family of CO₂ based materials: *meta*-stable CO₂-diene based lactones, prepared by Pd-catalyzed telomerization of CO₂ and dienes, easily undergo aerobic radical homo-polymerization to give novel CO₂-rich polymers (see Scheme). This two-step reaction set-up expands the potential applications of CO₂-based copolymers adding innovative compositions, structures and properties.