CO_2 Copolymers

DOI: 10.1002/anie.201403969

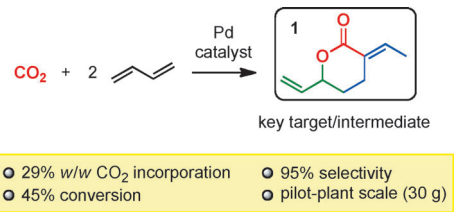
Preparation of CO_2/Diene Copolymers: Advancing Carbon Dioxide Based Materials**

*Giulia Fiorani and Arjan W. Kleij**

carbon dioxide · dienes · palladium · radical polymerization · telomerization

Despite its physical and chemical inertness, carbon dioxide (CO_2) continues to be an attractive and alternative carbon synthon as it is abundant, renewable, readily available, and inexpensive.[1] The inertness of CO_2 poses a huge challenge given the energy input that is required for its transformation and/or functionalization. A successful example of CO_2 reutilization is the development of atom-economic catalytic processes that are 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] Over the last ten years, various efficient catalysts that are active towards CO_2/epoxide couplings have been developed[2–4] for the stereocontrolled preparation of functional cyclic carbonates[5] as well as stereoregular functional polymers.[6] Furthermore, some of these promising catalytic systems are currently employed in commercially feasible industrial processes that exploit CO_2 fixation using ethylene and propylene oxide as reaction partners.[6c] These processes furnish poly(ethylene carbonate), poly(propylene carbonate), and polyethercarbonate–polyol mixtures with a tailored narrow molecular-weight distribution, which are of further (potential) use in polyurethane synthesis.[7] The applicability of this type of polymerization reaction is still limited to the synthesis of polycarbonates and polyethercarbonates and has not been extended to another ambitious and challenging (commercial) target, the preparation of polyesters by direct copolymerization of CO_2 with ethylene or dienes, thus far. This copolymerization reaction is particularly appealing as it represents a link between different renewable resources, such as CO_2, and inexpensive, widely available petroleum-derived alkenes, thus allowing a potential evolution towards more sustainable materials. The main obstacles that prevent a successful copolymerization of these monomers include 1) a high energy barrier associated with the alternating copolymerization between ethylene/polyene and CO_2, which requires excess ethylene insertion to ensure endergonic CO_2 insertion, and 2) a kinetic barrier that arises from the high activation energy for CO_2 insertion into the growing polymeric chain relative to polyethylene or polypropylene chain growth.[8]

Nozaki and co-workers have now reported a reproducible and highly customizable procedure for the preparation of CO_2/diene copolymers.[8b,c] Key to this success was the innovative use of an alternative polymerization strategy that circumvents the thermodynamic and kinetic barriers associated with direct CO_2/butadiene copolymerization. In particular, they have employed a known metastable δ-lactone, 3-ethylidene-6-vinyltetrahydro-2*H*-pyran-2-one (**1**),[9] which can be easily obtained by telomerization of CO_2 and butadiene in the presence of a palladium/phosphine ligand catalytic system (Scheme 1). Lactone **1** has been extensively studied by the groups of Behr and others over the past 30 years as a promising functional organic intermediate and versatile synthetic building block. The optimized preparation of **1** both on laboratory and pilot-plant scales, which minimizes the formation of undesired telomerization side products, should thus be regarded as a milestone in this area.[10]

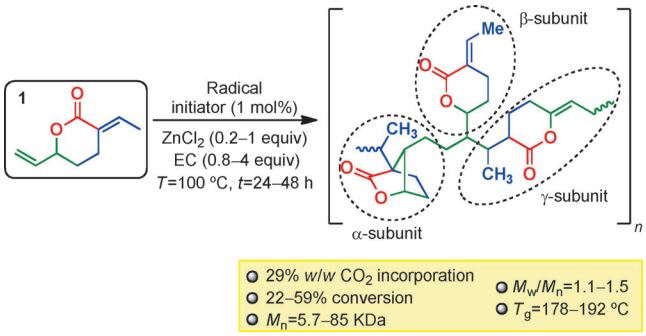


Scheme 1. Synthesis of δ-lactone **1**. The allylic moiety and the vinyl moiety are highlighted in blue and green, respectively.

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]. Moderate conversion (17%) was observed, and the polymer poly-**1**, which exclusively contains

[*] Dr. G. Fiorani, Prof. Dr. A. W. Kleij
Institute of Chemical Research of Catalonia (ICIQ)
Av. Països Catalans 16, 43007 Tarragona (Spain)
E-mail: akleij@iciq.es
Homepage: http://www.iciq.es
Prof. Dr. A. W. Kleij
Catalan Institute of Advanced Studies (ICREA)
Pg. Lluís Companys 23, 08010 Barcelona (Spain)

[**] G.F. kindly acknowledges financial support from the European Community through FP7-PEOPLE-2013-IEF project RENOVACARB (622587). We thank the ICIQ, ICREA, and the Spanish MINECO (CTQ2011-27385) for financial support.



Scheme 2. Synthesis of and data for poly-**1** and poly-**1′**.

α-subunits formed by attack of the radical chain end on the allylic ester unit of **1**, was obtained (Scheme 2). Poly-**1** was characterized by a moderate M_n (5.7 kDa) and a narrow molecular weight distribution ($M_w/M_n \approx 1.3$). The presence of Lewis acid additives, such as $ZnCl_2$, and an additional solvent, such as ethylene carbonate (EC), accelerated the reaction rate and substantially improved the overall yield (48 %) and M_n values (62–85 kDa), while retaining a good M_w/M_n distribution. However, the morphology of the resulting polymer (poly-**1′**) was also significantly affected: Poly-**1′** comprises different isomeric subunits (α, β, and γ in Scheme 2), and their presence is due to Lewis acid stabilization of the radical in the α-position to the ester carbonyl group or hydrogen abstraction from the vinyl moiety of **1**. Both poly-**1** and poly-**1′** display relatively high CO_2 incorporation (29 % *w*/*w*) and high glass transition temperatures (T_g = 178–192 °C), so that these novel polymers are likely to be suitable materials for engineering plastics.

To simplify and speed up the synthetic procedure, poly-**1′** was also prepared in a one-pot fashion, starting from butadiene and CO_2. The scope of these one-pot polymerization reactions was extended to the incorporation of more complex diene structures (e.g., 1,3-pentadiene and isoprene) within the polymeric chain. The mixed telomerization of butadiene, CO_2, and other C_5 dienes was characterized by a lower reactivity, which was mainly ascribed to steric hindrance issues; however, after optimization, CO_2-rich terpolymers could be obtained in good yields (46 and 35 % for isoprene and 1,3-pentadiene, respectively) with relatively high CO_2 incorporation (20–24 % *w*/*w*) and different 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 that prevents direct CO_2/butadiene copolymerization, while expanding the library of useful high-energy CO_2 co-reactants. However, further characterization data, such as mechanical and thermal stability and biodegradability, are required to estimate the full potential and properties of the resulting CO_2-rich polymeric materials. Despite the slow reaction rates and the use of an excess amount of the Lewis acid co-catalyst, the possibility of obtaining CO_2/diene copolymers with a high CO_2 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 CO_2 as a chemical feedstock. Moreover, extensive studies on the optimization of the preparation procedures for intermediates of type **1** could be an excellent starting point for further process scale-up and providing new research opportunities. The use of new, (bio)renewable monomers and the concomitant development of one-pot polymerization strategies that are applicable to a discrete family of low-molecular-weight dienes could potentially lead to the preparation of new CO_2-based copolymers with novel innovative structures, enhancing their application potential in existing and new areas of polymer science.

Received: April 3, 2014
Published online: June 18, 2014

[1] a) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365 – 2387; b) M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T. E. Müller, *ChemSusChem* **2011**, *4*, 1216 – 1240; c) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem.* **2011**, *123*, 8662 – 8690; *Angew. Chem. Int. Ed.* **2011**, *50*, 8510 – 8537.

[2] a) M. North, R. Pasquale, C. Young, *Green Chem.* **2010**, *12*, 1514 – 1539; b) C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo, A. W. Kleij, *Chem. Eur. J.* **2014**, *20*, 2264 – 2275; c) T. Ema, Y. Miyazaki, S. Koyama, Y. Yano, T. Sakai, *Chem. Commun.* **2012**, *48*, 4489 – 4491.

[3] a) M. R. Kember, A. Buchard, C. K. Williams, *Chem. Commun.* **2011**, *47*, 141 – 163; b) P. P. Pescarmona, M. Taherimehr, *Catal. Sci. Technol.* **2012**, *2*, 2169 – 2187; c) D. J. Darensbourg, S. J. Wilson, *Green Chem.* **2012**, *14*, 2665 – 2671; d) D. J. Darensbourg, *Chem. Rev.* **2007**, *107*, 2388 – 2410; e) G. W. Coates, D. R. Moore, *Angew. Chem.* **2004**, *116*, 6784 – 6806; *Angew. Chem. Int. Ed.* **2004**, *43*, 6618 – 6639; f) X.-B. Lu, W.-M. Ren, G.-P. Wu, *Acc. Chem. Res.* **2012**, *45*, 1721 – 1735.

[4] a) G.-P. Wu, S.-H. Wei, W.-M. Ren, X.-B. Lu, T.-Q. Xu, D. J. Darensbourg, *J. Am. Chem. Soc.* **2011**, *133*, 15191 – 15199; b) M. R. Kember, P. D. Knight, P. T. R. Reung, C. K. Williams, *Angew. Chem.* **2009**, *121*, 949 – 951; *Angew. Chem. Int. Ed.* **2009**, *48*, 931 – 934; c) K. Nakano, K. Nozaki, T. Hiyama, *J. Am. Chem. Soc.* **2003**, *125*, 5501 – 5510; d) S. I. Vagin, R. Reichardt, S. Klaus, B. Rieger, *J. Am. Chem. Soc.* **2010**, *132*, 14367 – 14369; e) C. T. Cohen, T. Chu, G. W. Coates, *J. Am. Chem. Soc.* **2005**, *127*, 10869 – 10878; f) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, *J. Am. Chem. Soc.* **2013**, *135*, 1228 – 1231.

[5] a) W.-M. Ren, G.-P. Wu, F. Lin, J.-Y. Jiang, C. Liu, Y. Luo, X.-B. Lu, *Chem. Sci.* **2012**, *3*, 2094 – 2102; b) C. J. Whiteoak, E. Martin, E. Escudero-Adán, A. W. Kleij, *Adv. Synth. Catal.* **2013**, *355*, 2233 – 2239.

[6] a) Y. Liu, M. Wang, W.-M. Ren, K.-K. He, Y.-C. Xu, J. Liu, X.-B. Lu, *Macromolecules* **2014**, *47*, 1269 – 1276; b) K. Nakano, S. Hashimoto, M. Nakamura, T. Kamada, K. Nozaki, *Angew. Chem.* **2011**, *123*, 4970 – 4973; *Angew. Chem. Int. Ed.* **2011**, *50*, 4868 – 4871; Bayer and Novomer have commercialized such processes; see: c) *Chem. Eng. News* **2013**, *91*(8), 15.

[7] a) J. Langanke, A. Wolf, J. Hofmann, K. Bohm, M. A. Subhani, T. E. Muller, W. Leitner, C. Gurtler, *Green Chem.* **2014**, *16*, 1865 – 1870; b) M. R. Kember, C. K. Williams, *J. Am. Chem. Soc.* **2012**, *134*, 15676 – 15679.

[8] a) C. J. Price, B. J. E. Reich, S. A. Miller, *Macromolecules* **2006**, *39*, 2751 – 2756; b) R. Nakano, S. Ito, K. Nozaki, *Nat. Chem.* **2014**, *6*, 325 – 331; c) A. P. Dove, *Nat. Chem.* **2014**, *6*, 276 – 277.

[9] For the first synthesis of this lactone, see: A. Musco, C. Perego, V. Tartiari, *Inorg. Chim. Acta* **1978**, *28*, L147 – L148.
[10] a) A. Behr, K.-D. Juszak, *J. Organomet. Chem.* **1983**, *255*, 263 – 268; b) A. Behr, M. Heite, *Chem. Ing. Tech.* **2000**, *72*, 58 – 61; c) A. Behr, P. Bahke, M. Becker, *Chem. Ing. Tech.* **2004**, *76*, 1828 – 1832; d) A. Behr, M. Becker, *Dalton Trans.* **2006**, 4607 – 4613; e) A. Behr, P. Bahke, B. Klinger, M. Becker, *J. Mol. Catal. A* **2007**, *267*, 149 – 156; f) A. Behr, G. Henze, *Green Chem.* **2011**, *13*, 25 – 39.

