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Ring-opening polymerization of functionalized aliphatic bicyclic carbonates†

Jixiang Ni,[a,b] Matteo Lanzi,*[a] David H. Lamparelli[a] and Arjan W. Kleij [ID] *[a,c]

A series of six-membered bicyclic carbonates has been prepared from an alcohol precursor through esterification, etherification and silyl-etherification methods to afford functional monomers with synthetically useful vinyl, allyl, alkynyl and polymerizable groups that allow for orthogonal polymerization strategies. Anionic ring-opening polymerization (AROP) of these monomers allows us to access densely functional aliphatic polycarbonates with M_n's and T_g's in the range of 3.2–11.7 kg mol^{-1} and 11–106 °C, respectively. Bifunctional monomers comprising two separate polymerizable groups can be selectively polymerized *via* AROP or radical based/ring-opening metathesis polymerization methods. Selected polycarbonates were post-modified *via* thiol–ene chemistry to further modulate their properties. Finally, base-mediated depolymerization of these new polycarbonates was attempted giving rise to an unusual bicyclic oxetane product, which may be upcycled through appropriate copolymerization methods.

Environmentally friendly and modular approaches to functional polymers are key to the development of sustainable materials.[1] Among the functional polymers developed to date, aliphatic polycarbonates (APCs) have received considerable consideration as a result of their low toxicity, high biocompatibility, and degradability.[2,3] These features are especially attractive in the context of applications that focus on medical devices and drug delivery systems.[4] Whereas the conventional way of polycarbonate synthesis relies on the use of phosgene derivatives, alternative strategies based on the use of carbon dioxide (CO$_2$) have recently emerged. The utilization of CO$_2$ as an abundant, cheap and safe reagent is considered to be a key factor for innovative process design towards APCs with biodegradation potential. APCs are typically prepared *via* two main approaches, either *via* ring-opening copolymerization (ROCOP) of epoxides and carbon dioxide[5,6] or through anionic ring-opening polymerization (AROP) of suitable cyclic carbonate monomers. Although the use of CO$_2$ as a monomer is attractive, the ROCOP approach using (acyclic) epoxides typically suffers from limitations in functional group diversity or compatibility, and is frequently accompanied by the formation of "ether" linkages (*i.e.*, structural defects) and the concomitant formation of five-membered cyclic carbonates as by-products affecting the overall chemo-selectivity.

The AROP reaction of 6- and 7-membered cyclic carbonates (abbreviated as 6MCCs and 7MCCs) has emerged as a more robust and versatile approach for the preparation of functional polycarbonates.[7,8] Larger ring cyclic carbonates such as 6MCCs over time have become popular monomers but are often prepared using harmful and low-atom economy reagents such as phosgene and its derivatives (Scheme 1a).[9]

Our group recently reported a simple catalytic CO$_2$-based approach towards bicyclic 6MCCs (Scheme 1b).[10,11] This approach benefits from a double and cooperative activation strategy with a pendent alcohol group activating CO$_2$ while an Al-complex promotes intramolecular ring-opening of the oxirane in the substrate through coordination. This approach allowed us to devise a structurally diverse range of novel bicyclic 6MCCs under mild conditions, and importantly enabled the isolation of compounds featuring a synthetically useful hydroxyl group. We envisioned that these –OH groups could be exploited such that different functionalities could be introduced in these 6MCC monomers. This would then offer a simple protocol to form functional carbonates for AROP leading ultimately to functionalized APCs (Scheme 1c), and herein we describe the advances we have made in the area.

Taking advantage of the residual hydroxy group in **A–D**, we began our investigation with the synthesis of a small library of 6MCCs decorated with various synthetically useful moieties (Scheme 2). The silyl-ether derivatives **1–5** were all prepared using the respective silyl-chloride reagent and performing the coupling reaction in the presence of an excess of triethylamine
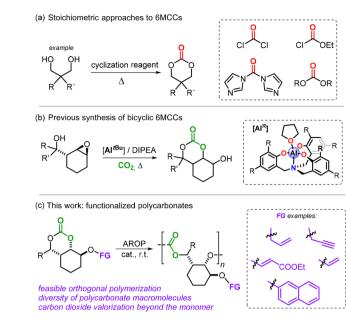
[a]Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science & Technology (BIST), Av. Països Catalans 16, 43007 – Tarragona, Spain. E-mail: akleij@iciq.es, mlanzi@iciq.es
[b]Universitat Rovira i Virgili (URV), Marcel·lí Domingo s/n, 43007 Tarragona, Spain
[c]Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluis Companys 23, 08010 – Barcelona, Spain
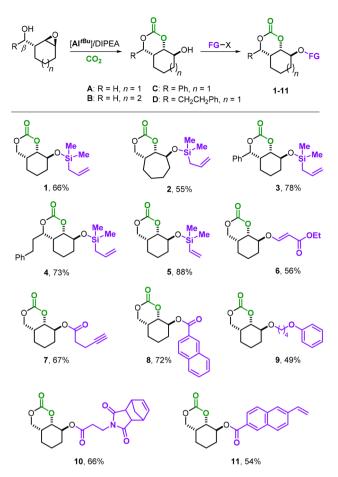
Scheme 1 (a) Common approach towards polymerizable six-membered cyclic carbonates. (b) Previously reported bicyclic monomer comprising a secondary alcohol. (c) Current approach towards functional polycarbonates through ROP of functional six-membered cyclic carbonates. 6MCCs stands for six-membered cyclic carbonates.

in dry CH_2Cl_2 at r.t. (see the ESI† for details). This approach allowed the introduction of either allyl (products **1–4**) or vinyl groups (compound **5**) in the different parent scaffolds (**A–D**) with appreciable yields of the isolated bicyclic 6MCCs. Monomers **3** and **4** are additionally equipped with an aryl/alkyl substituent at the other side of the bicycle allowing us to scrutinize their influence on the polymerizability of these 6MCCs. An oxo-Michael addition of precursor **A** to ethyl propiolate in the presence of *N*-methyl morpholine (NMM, 20 mol%) in CH_3CN at r.t. afforded monomer **6** in 56% yield, and this shows that also acrylic esters are feasible functional groups.

Steglich esterification (using DCC, dicyclohexyl-carbodiimide; see the ESI† for details) enables the coupling of various functional carboxylic acids with the secondary alcohol group of **A**. Homopropargylic carboxylic acid is smoothly coupled with **A** providing **7** in 67% yield, expanding the possible functionality pool to terminal alkynes. At this stage, we believed that the introduction of a rigid naphthyl moiety in the bicyclic 6MCC scaffold could be a way to produce, after AROP, APCs with larger aromatic groups favorable towards higher thermal resistance. Product **8** that comprises naphthyl ester groups could be isolated in 72% yield. To further modulate the thermal properties of the target APCs, a more flexible aliphatic chain could also be introduced (**9**, 49%) by performing a coupling between **A** and Kobayashi aryne precursors in THF.[12,13]

Finally, we aimed at designing bifunctional monomers that contain two distinct and polymerizable units (**10** and **11**) so that orthogonal polymerization strategies could be enabled. Monomer **10** was attained in 66% yield by esterification of **A**
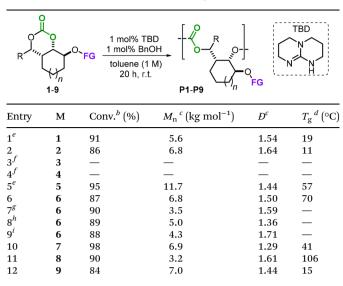
Scheme 2 General synthetic scheme for the functionalized bicyclic six-membered cyclic carbonate monomers **1–11** derived from precursor 6MCCs **A–D**. FG-X stands for the coupling agent used to produce the functionalized bicyclic 6MCC.

with 3-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2*H*-4,7-methano-iso-indol-2-yl)-propanoic acid, whereas **11** could be prepared in 54% yield by the treatment of **A** with 6-vinyl-2-naphthoic acid in the presence of DCC (see the ESI† for details). All new monomers **1–11** were fully characterized by ^{1}H NMR, ^{13}C NMR, high-resolution ESI(+)-MS, and IR spectroscopy.

To study the reactivity of the monomers **1–9**, we then directed our attention towards AROP using 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD) as a benchmark organocatalyst in the presence of an equimolar quantity of benzyl alcohol as an initiator at r.t. (Table 1, see the ESI† for experimental details).[14] These preferable mild temperature conditions were chosen as to avoid the possible depolymerization of the formed polycarbonates, which is feasible with TBD at elevated temperatures.[15] In nearly all cases, reasonable control of the polymerization process was achieved (*Đ* values in the range 1.29–1.64) delivering the functionalized APCs with low to moderately high molecular weights (M_n's 3.2–11.7 kg mol^{-1}). Allyl-functionalized monomers **1** and **2** were both ring-open polymerized to their APCs **P1** and **P2** with around 90% conversion (Table 1, entries 1 and 2). In contrast to these promising

Table 1 AROP of the monomers **1–9** using TBD/BnOH in toluene[a]

Entry	M	Conv.[b] (%)	M_n[c] (kg mol⁻¹)	Đ[c]	T_g[d] (°C)
1[e]	**1**	91	5.6	1.54	19
2	**2**	86	6.8	1.64	11
3[f]	**3**	—	—	—	—
4[f]	**4**	—	—	—	—
5[e]	**5**	95	11.7	1.44	57
6	**6**	87	6.8	1.50	70
7[g]	**6**	90	3.5	1.59	—
8[h]	**6**	89	5.0	1.36	—
9[i]	**6**	88	4.3	1.71	—
10	**7**	98	6.9	1.29	41
11	**8**	90	3.2	1.61	106
12	**9**	84	7.0	1.44	15

[a] Unless otherwise specified, the polymerization reactions were performed using 0.30 mmol of monomer, 1 mol% of TBD, and 1 mol% of BnOH in toluene (1 M) for 20 h at r.t. (20 °C). [b] Conversion of the monomer was determined by ^{1}H NMR (CDCl$_3$) spectroscopy. [c] Determined by GPC in THF calibrated with PPO standards. [d] Obtained from DSC analysis, the data refer to the second heating. [e] Reaction was performed at a 0.60 mmol scale. [f] Polymerization was performed both at 45 °C and 60 °C for 48 h with the same results. M stands for monomer. [g] TBD/BnOH loading was 0.5/0.5 mol%. [h] TBD/BnOH loading was 2.0/2.0 mol%. [i] TBD/BnOH loading was 2.0/1.0 mol%.

results, monomers **3** and **4** proved to be completely unreactive towards the formation of **P3** and **P4** even when raising the reaction temperature to 60 °C and extending the reaction time to 48 h (entries 3 and 4). This can be explained by the additional substitution on the carbonate ring, which apparently creates a too large steric impediment for the incoming TBD hydrogen-bond activator and BnOH initiator.
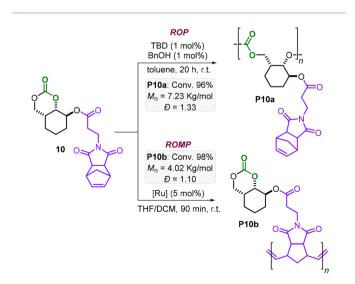
The AROP of the vinyl derivative **5** (entry 5) gave **P5** with the highest molecular weight (M_n = 11.7 kg mol⁻¹, Đ = 1.44) among the series. Other functional groups such as an acrylic ester (**6**) and a terminal alkyne (**7**) were compatible with the reaction conditions delivering **P6** and **P7** with modest M_n values and somewhat lower dispersities (entries 6 and 10). We used monomer **6** to examine the effect of the catalyst and initiator loading (cf., entries 6–9), but found that the best conditions (1 mol% of each) are most beneficial for these types of bicyclic carbonate monomers. Macromolecule **P8** showed a substantial decrease in molecular weight (M_n = 3.2 kg mol⁻¹, entry 11), which we ascribe to the more hindered carbonate ring upon activation by TBD following ring-opening by the initiator.

Though a low(er) molecular weight was attained for **P8**, the measured glass transition temperature (T_g = 106 °C) was significantly higher compared to those of the other APCs, which is likely due to an increase in pi–pi stacking in the solid state. The poly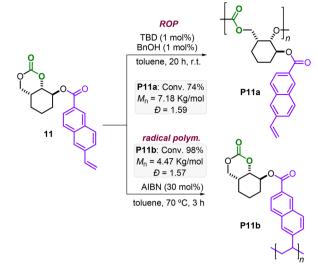merization of monomer **9** provided a molecular weight, polymer dispersity and T_g (entry 12) similar to those of polymers **P1** and **P2**. Purified samples of all the APCs (white powders) reported in Table 1 were obtained through simple precipitation of the crude reaction mixtures from methanol, and the analytical data and spectra are provided in the ESI.† All PCs reported here are likely regio-irregular on the basis of their ^{13}C NMR spectra (see the ESI†) and display monomodal peak distributions in their GPCs. On the basis of our previous experience with ring-opening of substituted cyclic carbonates, the initiator (BnOH) most likely approaches from the least hindered side, thereby leaving a primary alcohol as an end-group.[16]

Additionally, bifunctional monomers **10** and **11** bearing orthogonal polymerizable groups were tested (Schemes 3 and 4). Under the AROP reaction conditions reported in Table 1, the monomers **10** and **11** are smoothly transformed delivering **P10a** and **P11a** with appreciable molecular weight (M_n = 7.23 and 7.18 kg mol⁻¹, respectively) and reasonable polydispersities (Đ = 1.33 and 1.59, respectively).

Monomer **10** has, apart from the 6MCC fragment, an additional strained cyclohexene moiety, which is suitable for ring-opening metathesis polymerization (ROMP). ROMP is nowadays a robust and selective approach for the controlled preparation of polyolefins, especially starting from strained structures.[7b,17–19] By treatment of **10** with a Grubbs 3rd generation catalyst, a complete conversion was obtained within 90 min at r.t. yielding the desired polyolefin **P10b** (Scheme 3) with a low polydispersity (Đ = 1.10) and a modest molecular weight (M_n = 4.02 kg mol⁻¹). It should be noted that lower amounts of Ru-catalyst also worked well leading to gel-like products. However, in these cases, solubility issues did not allow further characterization. Azobisisobutyronitrile (AIBN) initiated radical polymerization of the vinyl moiety present in monomer **11** led to full conversion in 3 h at 70 °C yielding the poly-naphthalene product **P11b** (M_n = 4.47 kg mol⁻¹, Đ = 1.57). Noteworthily, complete chemoselectivity is observed in all
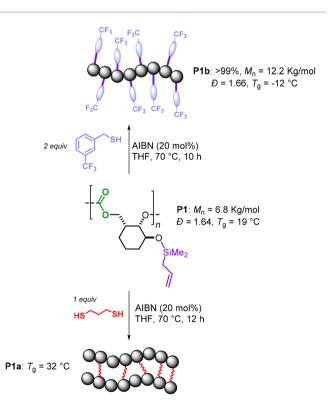

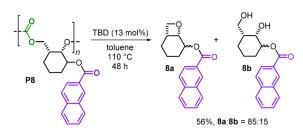**Scheme 3** Synthesis of polymers **P10a** and **P10b**.

Scheme 4 Synthesis of polymers **P11a** and **P11b**.

transformations of **P10** and **P11** preserving the other functional groups (*i.e.*, the 6MCC, norbornene and vinyl moieties) as additional handles for further transformations.

Post-polymerization modification of **P1** was also conducted to show the robustness of the polycarbonate macromolecules (Scheme 5). Two approaches were considered: a "click" reaction using a mono-thiol and a cross-linking reaction using a di-thiol reagent.[20] First, **P1** was subjected to cross-linking in the presence of 1,3-propanedithiol and AIBN as the radical

Scheme 5 Thiol–ene based functionalization and cross-linking of **P1**.

Scheme 6 Depolymerization of **P8** using TBD as a catalyst.

initiator at 70 °C. Under these conditions, full conversion of the alkene moieties was observed after 12 h. Due to the high level of crosslinking, **P1a** was insoluble in the typical organic solvents, thus preventing further characterization by NMR and GPC. IR analysis of **P1a** showed a disappearance of the initial =C–H and C=C (stretch) absorptions for **P1** at 3077 and 1631 cm^{-1}, respectively, suggesting that most of the double bonds had reacted. Differential scanning calorimetry (DSC) analysis showed that **P1a** has a T_g of 32 °C, which is 12° higher than that of the parent polymer **P1**, thus implying that at least a part of the silyl-allyl fragments took part in the crosslinking event. The same silyl-allyl groups were also allowed to react with trifluorobenzyl thiol under similar reaction conditions to quantitatively afford (soluble) **P1b**. Gel-permeation chromatography analysis (GPC) of **P1b** displayed a significant increase in the polymer weight (the M_n rose to 12.2 kg mol^{-1}) while the polydispersity remained virtually the same. This seems to corroborate with a high functionalization degree of **P1** and a substantial mass increase of the repeat units (270 → 462 g mol^{-1}, ΔM = 42%), and thus the polymer as a whole.

Finally, chemical degradation studies were conducted to examine whether these new polycarbonates could be selectively depolymerized. Depolymerization of **P8** was assessed using TBD as a catalyst in toluene at 110 °C (Scheme 6), as previously a bio-based polycarbonate was reported to fully decompose towards its original monomers under such conditions.[15] In the present case, a similar catalytic degradation was performed and the reaction delivered two new products: a fused bicyclic oxetane **8a** and the diol **8b** as an inseparable 85 : 15 mixture in a combined 56% yield. Whilst basic conditions for the degradation of polycarbonates often release the corresponding diol as a byproduct,[14] to the best of our knowledge, the formation of a fused bicyclic oxetane **8a** from the decomposition of polycarbonate is a new observation.[21] Recently, both Buchard and Wooley showed that similar types of bicyclic oxetanes can be used to prepare different kinds of polymers including polycarbonates and polyethers,[22] thus providing a potential recycling or repurposing route for **8a**.

Conclusions

In summary, we have prepared a family of functional, bicyclic 6MCC monomers bearing synthetically useful groups. The catalytic AROP provides straightforward access to densely sub-

stituted macromolecular aliphatic carbonates. Bifunctional monomers were also designed allowing the triggering of two different types of polymerizations and offering orthogonal polymerization/crosslinking strategies. Post-synthetic functionalization of these APCs was also demonstrated, which permits the change and modulation of the (thermal) properties. A TBD-catalyzed degradation of one selected oligocarbonate led to a new fused bicyclic oxetane, which had the potential to be recycled or repurposed to different kinds of polymeric materials. This work exemplifies that properly equipped carbonate monomers can be designed to extend the pool of functionality eventually present in APCs. We expect that this gives new impetus to different curing opportunities and post-polymerization adjustment of relevant physical properties such as hydrophobicity/philicity, polymer processability and miscibility.

Author contributions

JN, ML and DHL carried out all the experiments and the analytical interpretation, ML assisted JN during the project with feedback and scientific input, and AWK and ML designed the project, provided continuous feedback on the results and wrote the manuscript in collaboration with JN and DHL.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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