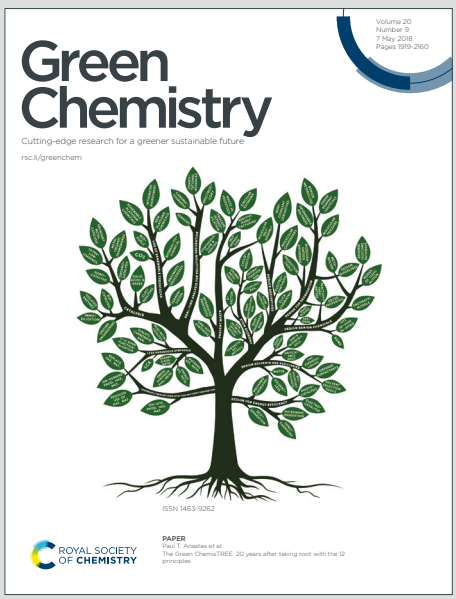
View Article Online
View Journal

Green Chemistry

Cutting-edge research for a greener sustainable future

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Dabral, U. Licht, P. Rudolf, G. Bollmann, S. Hashmi and T. Schaub, *Green Chem.*, 2020, DOI: 10.1039/C9GC04320A.



View Article Online
DOI: 10.1039/C9GC04320A

COMMUNICATION

Synthesis and polymerisation of α-alkylidene cyclic carbonates obtained from carbon dioxide, epoxides and the primary propargylic alcohol 1,4-butynediol

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Saumya Dabral,[a] Ulrike Licht,[b] Peter Rudolf,[b] Gérard Bollmann,[c] A. Stephen. K. Hashmi [a,c] and Thomas Schaub* [a,b]

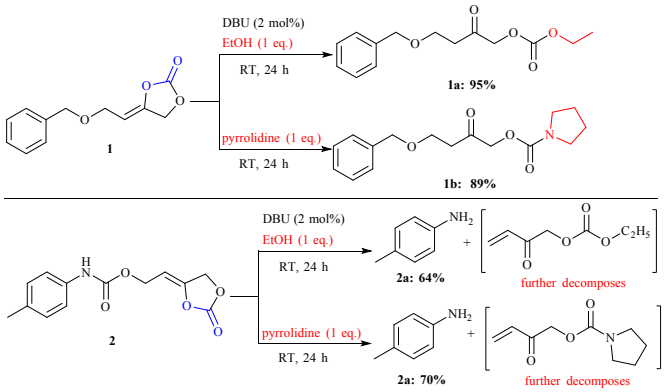
Based on the bulk chemical 1,4-butynediol, readily available epoxides and carbon dioxide, a new series of unsubstituted exovinylene carbonates were synthesised. Chemoselective additions of diamines or diols to these cyclic carbonates allow the regiocontrolled synthesis of new functionalised polyurethanes and polycarbonates under mild conditions. This route to polyurethanes avoids the use of toxic isocyanates.

Utilising carbon dioxide (CO_2) as a feedstock for industrial synthesis is not new, currently CO_2 is used on a significant scale (> 110 MT p.a.), mainly for the production of urea, carbonates, methanol or salicylic acid.[1,2] Among all products of the chemical industry, due to their diverse fields of application, polymers remain the most widely produced commodity chemicals. Traditionally, most of the commercial polymers and plastics are produced from non-renewable fossil resources. However, depleting fossil reservoirs and increasing consumer demands as well as environmental pollution and new legislative requirements, have initiated a significant increase of the efforts to find sustainable approaches for their synthesis.[3–10] In line with this, incorporating CO_2 into new monomers, offers an alternative way to achieve lower carbon footprints.

In the last years, significant advancements were made in catalyst development for integrating the inert greenhouse gas CO_2 as a renewable C_1 carbon feedstock, into valuable polymer-building blocks and directly into polymers with high CO_2 content (polycarbonates, polyols, polyurethanes (PU), polyureas and polyesters).[11–15] Amongst these, five-membered cyclic carbonates (5CCs) represent an important class of CO_2-based building blocks that are formed by reacting the corresponding oxirane with CO_2.[16–24] 5CCs, upon polyaddition with either diamines or diols, provided the two important classes of polymers, the poly(β-hydroxyurethane)s (PHUs)[25–30] and poly(carbonate)s (PCs).[31–35] Especially the PHUs obtained by this isocyanate-free route, offer an advantage of bypassing the handling of moisture sensitive reagents and toxic phosgene gas, thus making the overall process much safer than the classical isocyanate/alcohol synthesis.[25–31] However, the 5CCs ring opening reactions suffer from drawbacks such as poor reaction rate, lack of regiocontrol as well as generation of side products. Exovinylene carbonates (EVCs), produced by the catalytic carboxylative coupling of propargylic alcohols with CO_2, on the other hand, represent another emerging class of CO_2-derived cyclic carbonate building blocks.[36] Compared to the 5CCs, due to the establishment of a keto–enol equilibrium, the presence of an exocyclic olefinic group in the EVCs offers higher reactivity and regioselectivity for the ring-opening reactions. As a result of this, these α-alkylidene cyclic carbonates (αCCs) have allowed the synthesis of complex organic molecules such as β-oxo carbamates,[37] β-oxo-carbonates,[38] β-hydroxy-1,3-oxazolidin-2-ones,[38] α-hydroxyketones,[39,40] and 3-dialkyl amino-oxazolidin-2-ones.[41] Expanding this scope further, Detrembleur and coworkers recently reported on the application of the CO2-derived bis-EVCs as suitable building blocks for the synthesis of new regioregular functional isocyanate-free PUs and PCs.[42] The scope was further expanded to the organo-catalysed thiolation of αCCs to sulphur containing polymers.[43] These discoveries inspired us to investigate realted reaction pathways for our newly developed unique class of previously inaccessible and now industrially relevant unsubstituted αCCs, which are based on the cheap bulk chemical 1,4-butynediol.[44]

Initially, we performed our preliminary studies with EVC **1** (prepared by the AgOAc-Davephos catalysed carboxylative coupling of CO_2 to 4-(benzyloxy)but-2-yn-1-ol)[44] and EVC **2** (prepared by the AgOAc-Davephos catalysed carboxylative coupling of CO_2 to 4-hydroxybut-2-yn-1-yl *p*-tolylcarbamate). These 1,4-butynediol-based αCCs were chosen because they provided a variation in functionalisation of the alkylidene side chain. Scheme **1** shows the regioselective nucleophilic ring-opening of the unsubstituted αCCs **1** and **2** that were performed for 24 h at room temperature either with ethanol (EtOH, 1 eq.)

[a] *Catalysis Research Laboratory (CaRLa), Im Neuenheimer Feld 584, Heidelberg 69120, Germany.*
[b] *BASF SE, Carl-Bosch-Str. 38, Ludwigshafen 67056, Germany.*
[c] *Institute of Organic Chemistry, Heidelberg University, Im Neuenheimer Feld 270, Heidelberg 69120, Germany.*
*E-mail: thomas.schaub@basf.com.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



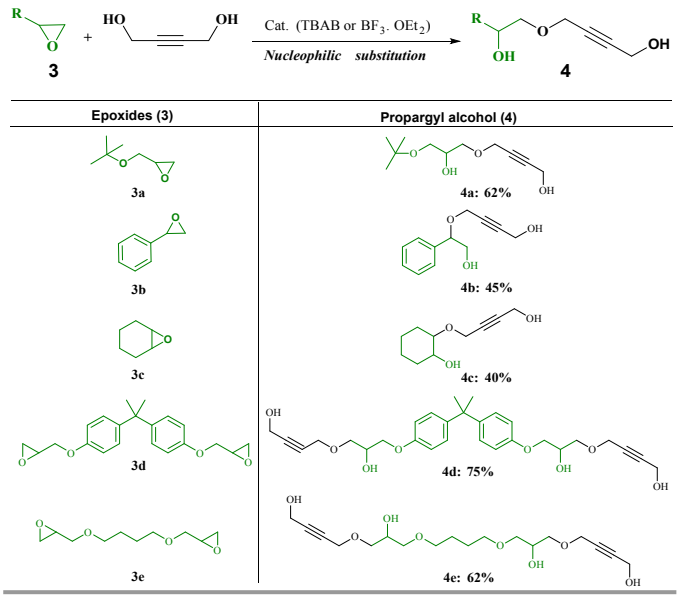
Scheme 1. EtOH and pyrrolidine initiated nucleophilic ring-opening of EVCs **1** and **2**.

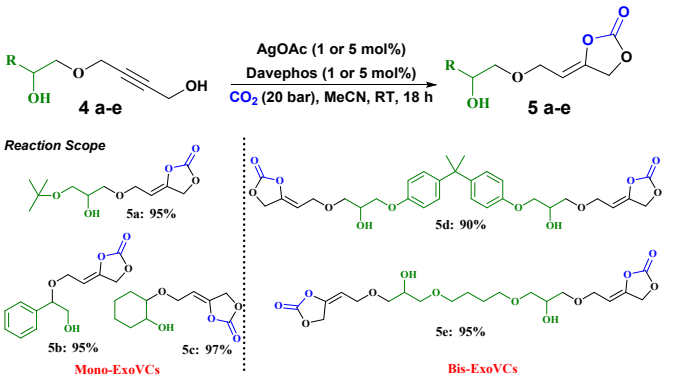
in the presence of 2 mol% 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) or with pyrrolidine (1 eq.). Pleasingly, the reaction of both nucleophiles with EVC **1** were quantitative and resulted in the desired carbonate **1a** and carbamate product **1b** in high yields of 95% and 89% respectively (Scheme **1**, Top). When 2 mol% of the related 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) instead of DBU were used in the ring-opening of 1, we observed the same reactivity. Moreover, the presence of isopropanol (secondary alcohol) did not influence the outcome of the ring opening reaction of EVC **1** with EtOH, hence highlighting the higher rate of reaction of primary alcohol over secondary (see Section **5.1** in the Supporting Information). EVC **2**, when subjected to these conditions however, afforded elimination product (*para*-toulidine) instead of the expected addition product (Scheme **1**, bottom, Section **5.2** Supporting Information). These results were especially interesting as they highlighted the stability of the ether bonds (R-O-R) of the alkylidene side-chain in EVC **1** over the carbamate functionality (RNH(CO)-OR) in EVC **2**, towards nucleophilic ring-opening rearrangement reactions.

Based on these results, we considered exploring readily available epoxides (**3a**-**e**) as suitable precursors for the synthesis of primary propargylic alcohols (**4 a**-**e**) *via* epoxide ring-opening reactions initiated by the bulk chemical 1,4-butanediol, (Table **1**). These unprecedented nucleophilic additions of 1,4-butanediol to epoxides were initiated by either catalytic amounts of tetrabutylammonium bromide (TBAB) or boron trifluoride etherate (BF_3·OEt_2) (see Section **2.0** of the Supporting Information). The primary propargylic alcohols (**4 a**-**e**) were isolated in moderate yields (40-75%). These products **4** were subsequently subjected to our established AgOAc-DavePhos cyclisation conditions (Scheme **2**).[44]

At room temperature, using 1 mol% AgOAc-DavePhos catalyst loading, the propargylic alcohol **4a** was cyclised to the corresponding αCC **5a** in a high yield of 95% after 18 h reaction time under 20 bar of CO_2 pressure. Moreover, the secondary hydroxy group thus generated in **5a**, did not promote any inter- or intra-molecular ring-opening reaction under the described cyclisation conditions. Pleasingly, the product stability was further expanded to CO_2-based cycloadditon reactions of styrene oxide (**4b**) and cyclohexene oxide (**4c**) derived propargylic alcohols that, under similar reaction conditions, also afforded the corresponding αCCs **5b** and **5c**, bearing either a primary or a secondary -OH group, in excellent yields of 95% and 97%, respectively. Encouraged by the stability of these new

Table 1. Nucleophilic ring-opening of epoxides with bulk chemical 1,4-butynediol



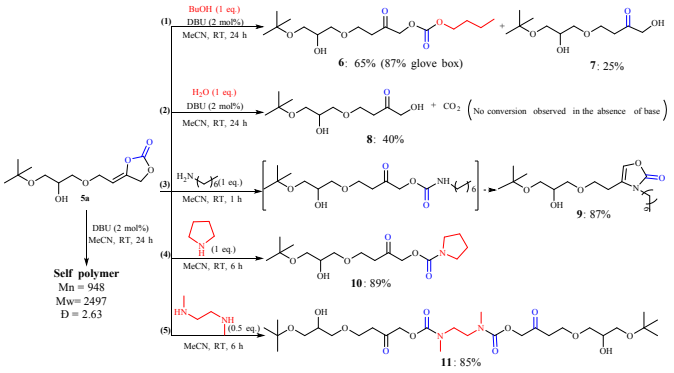


Scheme 2. Scope of the carboxylation cyclisation of propargyl alcohols (**4a**-**e**)

mono-EVCs, the methodology was next tested in the formation of bis-αCCs using 5 mol% catalyst loadings.

View Article Online
DOI: 10.1039/C9GC04320A

Starting from bisphenol-A diglycidyl ether and 1,4-butanediol diglycidyl ether propargylic alcohols **4d** and **4e**, the



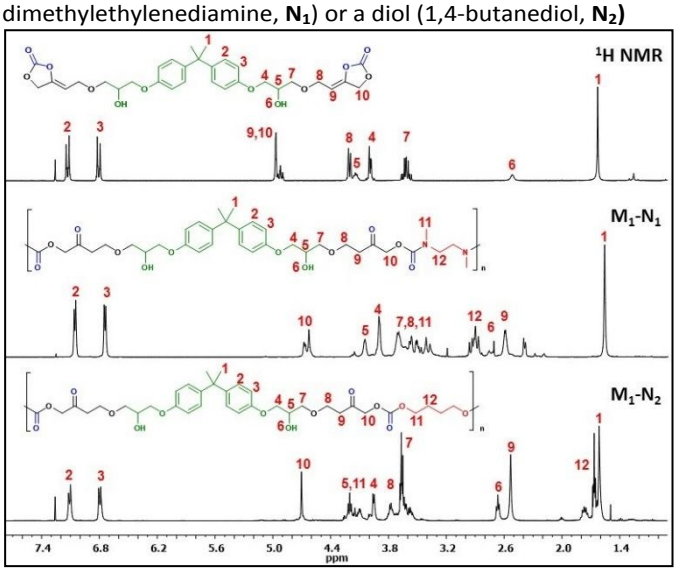
corresponding symmetrical bis-EVCs **5d** and **5e** were also isolated in high yields of 90% and 95%, respectively. These new CO_2-derived bis-exovinylene carbonates were then studied in co-polymerisation reactions. Based on our observations with EVCs **1** and **2**, the regio-controlled ring-opening reactions were first studied on the mono-EVC **5a**, bearing an ether linkage on the side chain of the exocyclic olefin (Scheme **3**) Subjecting **5a** to 2 mol% DBU, even in the absence of an external alcohol as nucleophile, resulted in its self-polymerisation (due to presence of secondary -OH groups) to give a dark coloured sticky macromolecule with a weight average molecular mass (M_w) of 2497 g mol^{-1} (see Section **5.3** in the Supporting Information). However, the addition of a primary alcohol (butane-1-ol) to **5a** in the presence of DBU (2 mol%) led to a regio-selective ring-opening to afford 65% of the β-oxo-carbonate product **6** (a β-

Scheme 3: Nucleophilic ring-opening reactions of EVC **5a**

keto tautomer)[42] along with the formation of the decarboxylated product **7** in 25% yield after a 24 h reaction time (Scheme **3**, reaction **1**). Since **7** could be formed due to the presence of water (H_2O) in the reaction mixture, the reaction was repeated in the glove box, which increased the yield of **6** to 87%. It is important to mention here that in the absence of DBU no conversion wasobserved for the above reaction. This underlines the catalytic activity of DBU, that possibly activates the alcohol by hydrogen bonding which in turn increases its nucleophilicity towards the EVC. Furthermore, a separate reaction of EVC **5a** with stoichiometric amounts of H_2O in the presence of DBU (2 mol%) as catalyst gave the decarboxylation product **7** in 40% yield (Scheme **3**, reaction **2**). This observation is especially interesting as parallels could be drawn to the reactivity of αCCs with H_2O to the blowing process (an important competing reaction) occurring between isocyanate and H_2O during the production of rigid polyurethane foams, hence opening similar opportunities for future application of EVCs to be looked into.[45]

Next the stability of the side-chain in EVC **5a** towards primary (1-hexylamine) and secondary (pyrrolidine) amines as nucleophiles was tested. While the reaction of **5a** with 1-hexylamine in just 1 h at room temperature led to the formation of the oxazolidone (formed by intramolecular ring-cyclisation of the corresponding β-oxo-urethane intermediate), which on further dehydrated gave **9** in 87% yield (Scheme **3**, reaction **3**), the reaction of **5a** with pyrrolidine took place at a slower rate, afforded the desired β-oxo-urethane product **10** in very good yield of 89% after performing the reaction for 6 h at room temperature (Scheme **3**, reaction **4)**. Furthermore, under similar reaction conditions, reacting 1.0 equivalent of **5a** with 0.5 equivalent of *N*,*N*-dimethylethylamine led to the formation of a bis-β-oxo-urethane product **11** in a yield of 85% (Scheme **3**, reaction **5**). Having successfully formed the corresponding urethane and carbonate bonds from **5a**, the reactions were then extended onto bis-EVCs **5d**/**5e**, which on reaction with either two equivalents of pyrrolidine or butane-1-ol resulted in the corresponding di-ring opened products (see Section **5.4** and **5.5** of the Supporting Information).

Based on the above regioselective ring-opening reactions, the polyaddition of bis-αCCs (**5d** = $\mathbf{M_1}$ and **5e** = $\mathbf{M_2}$) were finally attempted with equimolar amounts of either a diamine (*N*,*N'*-dimethylethylenediamine, $\mathbf{N_1}$) or a diol (1,4-butanediol, $\mathbf{N_2}$)



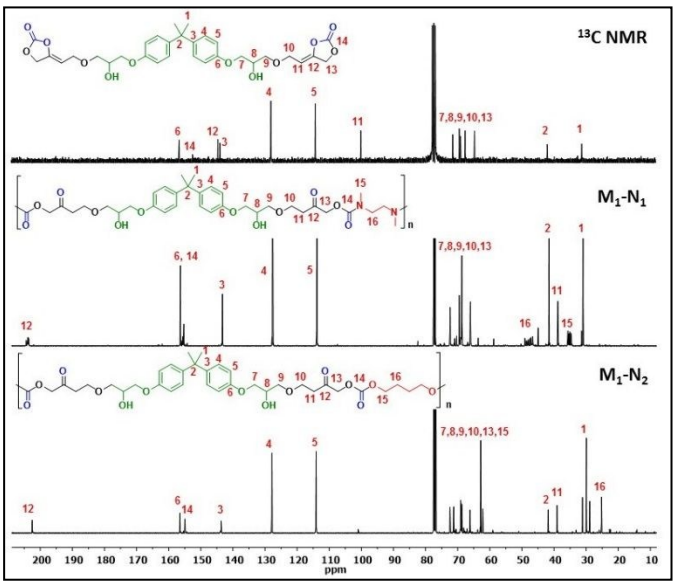


Figure 1: Comparison of ^{1}H (Top) and ^{13}C NMR (Bottom) for the reaction of **5d** with *N*,*N'*-dimethyl-1,4-butanediamine ($\mathbf{N_1}$) and 1,4-butanediol ($\mathbf{N_2}$)

nucleophile to afford a novel class of CO_2-based isocyanate-free poly(β-oxo-urethane)s and poly(β-oxo-carbonate)s (Figure **2**). Figure **1** shows the crude ^{1}H NMR and ^{13}C NMR spectra for the co-polymerisation of bis-EVC $\mathbf{M_1}$ with nucleophiles $\mathbf{N_1}$ and $\mathbf{N_2}$. The comparison of the ^{1}H NMR spectra showed the full consumption of the starting EVC **5d** ($\mathbf{M_1}$) at room temperature, after 24 h reaction time, while the comparison of ^{13}C NMR spectra for the polymers ($\mathbf{M_1}$-$\mathbf{N_1}$ and $\mathbf{M_2}$-$\mathbf{N_2}$) with the starting monomer $\mathbf{M_1}$ indicated the appearance of new resonance peaks for the β-keto group at δ = 207 ppm and the urethane and carbonate carbonyl peaks at δ = 156 and 155 ppm respectively. Further peaks in the NMR were assigned on the basis of the similarity of these regions with the products isolated for the individual reaction of **5d** with pyrrolidine and butan-1-ol. Similar studies were also performed on bis-EVC **5e** (see Section **5.5** of the Supporting Information). Size exclusion chromatography (SEC) was also performed on newly formed polymers, that indicated the weight average molar mass (M_w) of 5701 g mol^{-1} and 7656 g mol^{-1} for poly(β-oxo-urethane)s ($\mathbf{M_1}$-$\mathbf{N_1}$) and ($\mathbf{M_2}$-$\mathbf{N_1}$) respectively (Table **2** entries **1** and **2**). On the other hand the M_w values for the poly(β-oxo-carbonate)s ($\mathbf{M_1}$-$\mathbf{N_2}$) and ($\mathbf{M_2}$-$\mathbf{N_2}$) were found to be 2144 g mol^{-1} and 1971 g mol^{-1} respectively (Table **2**, entries **3** and **4**). Further studies pertaining to the effect of solvents and the nature of the base-catalyst on the molecular weight of the polymers are currently underway in our laboratory.

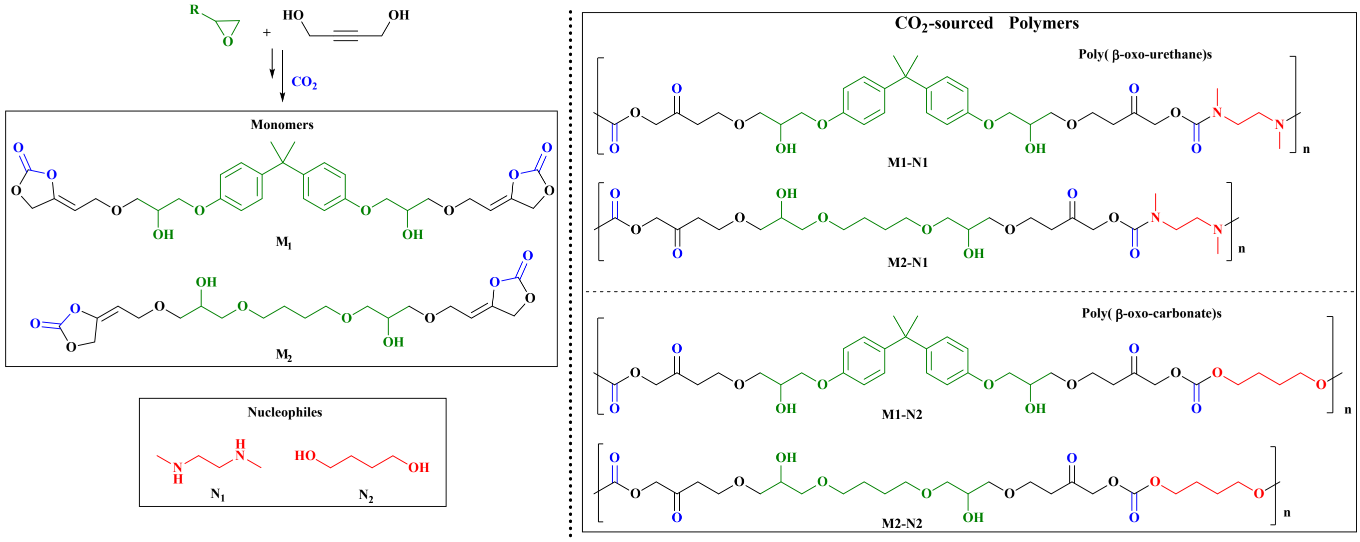


Figure 2: Representative structures of the monomers used and the corresponding polymers formed.

Table 2: Molecular weight characterisation of the poly(β-oxo-urethane)s and poly(β-oxo-carbonate)s[a]

Entry	Polymer	Solvent	Cat. [b]	Time (h)	M_n (g mol^{-1})	M_w (g mol^{-1})	Conv[c]	Đ
1	M_1-N_1	MeCN	-	24	5204	5701	99	1.09
2	M_2-N_1	MeCN	-	24	3852	7656	99	1.98
3	M_1-N_2	MeCN	DBU	24	2113	2144	99	1.01
4	M_2-N_2	MeCN	DBU	24	1905	1971	99	1.03

[a] Determined by GPC in EtOH-stabilised $CHCl_3$ eluent using polystyrene standards for calibration. [b] 3 mol% DBU. [c] Monomer conversions determined by ^{1}H NMR spectroscopy

Conclusions

In conclusion, for the first time we demonstrated the synthesis of new CO_2-based unsubstituted mono- and di-α-alkylidene cyclic carbonates using readily available epoxides and 1,4-butynediol as starting materials. These EVCs are envisioned as cheap building-blocks for the synthesis of new region-regular isocyanate-free polyurethanes and polycarbonates along with incorporating CO_2 as a chemical feedstock in the polymer backbone. The synthesis of EVCs (**5a**-**e**) were based on the nucleophilic ring-opening studies performed on EVC **1** and **2,** which highlight that stability of the ethereal side chain substituent of the exocyclic olefinic group effected the successful formation of the corresponding β-oxo-urethane and β-oxo-carbonate. Preliminary ring-opening reactions performed on mono-EVC **5a** and bis-EVC **5d** and **5e** in the presence of either mono-amines or mono-alcohols as nucleophiles (pyrrolidine, 1-hexylamine and butanol) thus led to the of the corresponding β-oxo-urethane, oxazolidone and β-oxo-carbonate products in very good yields and under mild reaction conditions. The robustness of this system was then extended to the synthesis of regioregular poly(β-oxo-urethane)s and poly(β-oxo-carbonates)s obtained *via* co-polymerisation of bis-EVC **5d** and **5e** with a diamine or a diol respectively. The presence of the -OH groups in the polymer is of special importance as they could potentially initiate secondary hydrogen bonding interactions, similar to those found in PU adhesives thereby opening new avenues for their application in the industry. The current protocol for the synthesis of epoxide-based propargylic alcohols and the catalyst recycling after the formation of the EVCs have to be further

optimised in order to facilitate the scale-up synthesis of the regioregular polymers at a reasonable cost.

Conflicts of interest

Two patents from the authors disclosing the catalyst system and the new monomers are published (see ref 44b and 44c).

Acknowledgements

CaRLa (Catalysis Research Laboratory) is co-financed by the Heidelberg University and BASF SE.

Notes and references

1 T. Schaub, R. A. Paciello and M. Limbach, in *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Four Volumes*, eds. B. Cornils, W. A. Herrmann, M. Beller and R. A. Paciello, WILEY-VCH Weinheim, 2018, pp. 1601–1614.

2 S. Topham, A. Bazzanella, S. Schiebahn, S. Luhr, L. Zhao, A. Otto and D. Stolten, *Ullmann's Encycl. Ind. Chem.*, 2014, 1–43.

3 S. A. Miller, *Polym. Chem.*, 2014, **5**, 3117–3118.

4 D. Esposito and M. Antonietti, *Chem. Soc. Rev.*, 2015, **44**, 5821–5835.

5 T. Iwata, *Angew. Chemie Int. Ed.*, 2015, **54**, 3210–3215.

6 V. Froidevaux, C. Negrell, S. Caillol, J.-P. Pascault and B. Boutevin, *Chem. Rev.*, 2016, **116**, 14181–14224.

7 C. Zhang, T. F. Garrison, S. A. Madbouly and M. R. Kessler, *Prog. Polym. Sci.*, 2017, **71**, 91–143.

8 S. Lambert and M. Wagner, *Chem. Soc. Rev.*, 2017, **46**, 6855–6871.

9 Z. Sun, B. Fridrich, A. de Santi, S. Elangovan and K. Barta, *Chem. Rev.*, 2018, **118**, 614–678.

10 G. John, S. Nagarajan, P. K. Vemula, J. R. Silverman and C. K. S. Pillai, *Prog. Polym. Sci.*, 2019, **92**, 158–209.

11 Q.-W. Song, Z.-H. Zhou and L.-N. He, *Green Chem.*, 2017, **19**, 3707–3728.

12 R. Muthuraj and T. Mekonnen, *Polymer (Guildf).*, 2018, **145**, 348–373.

13 J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow and W. Leitner, *Chem. Rev.*, 2018, **118**, 434–504.

14 B. Grignard, S. Gennen, C. Jérôme, A. W. Kleij and C. Detrembleur, *Chem. Soc. Rev.*, 2019, **48**, 4466–4514.

15 S. Dabral and T. Schaub, *Adv. Synth. Catal.*, 2019, **361**, 223–246.

16 M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514–1539.

17 C. Martín, G. Fiorani and A. W. Kleij, *ACS Catal.*, 2015, **5**, 1353–1370.

18 G. Fiorani, W. Guo and A. W. Kleij, *Green Chem.*, 2015, **17**, 1375–1389.

19 M. Alves, B. Grignard, S. Gennen, R. Mereau, C. Detrembleur, C. Jerome and T. Tassaing, *Catal. Sci. Technol.*, 2015, **5**, 4636–4643.

20 S. Gennen, M. Alves, R. Méreau, T. Tassaing, B. Gilbert, C. Detrembleur, C. Jerome and B. Grignard, *ChemSusChem*, 2015, **8**, 1845–1849.

21 M. Alves, B. Grignard, R. Mereau, C. Jerome, T. Tassaing and C. Detrembleur, *Catal. Sci. Technol.*, 2017, **7**, 2651–2684.

22 H. Büttner, J. Steinbauer and T. Werner, *ChemSusChem*, 2015, **8**, 2655–2669.

23 W. Desens and T. Werner, *Adv. Synth. Catal.*, 2016, **358**, 622–630.

24 H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf and T. Werner, *Top. Curr. Chem.*, 2017, **375**, 50.

25 L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau and H. Cramail, *Chem. Rev.*, 2015, **115**, 12407–12439.

26 L. Poussard, J. Mariage, B. Grignard, C. Detrembleur, C. Jérôme, C. Calberg, B. Heinrichs, J. De Winter, P. Gerbaux, J.-M. Raquez, L. Bonnaud and P. Dubois, *Macromolecules*, 2016, **49**, 2162–2171.

27 B. Grignard, J.-M. Thomassin, S. Gennen, L. Poussard, L. Bonnaud, J.-M. Raquez, P. Dubois, M.-P. Tran, C. B. Park, C. Jerome and C. Detrembleur, *Green Chem.*, 2016, **18**, 2206–2215.

28 S. Samanta, S. Selvakumar, J. Bahr, D. S. Wickramaratne, M. Sibi and B. J. Chisholm, *ACS Sustain. Chem. Eng.*, 2016, **4**, 6551–6561.

29 G. Liu, G. Wu, S. Huo, C. Jin and Z. Kong, *Prog. Org. Coatings*, 2017, **112**, 169–175.

30 K. Błażek and J. Datta, *Crit. Rev. Environ. Sci. Technol.*, 2019, **49**, 173–211.

31 N. Yadav, F. Seidi, D. Crespy and ValerioD'Elia, *ChemSusChem,* 2019, **12**, 724 –754.

32 J.-C. Lee and M. H. Litt, *Macromolecules*, 2000, **33**, 1618–1627.

33 S. Tempelaar, L. Mespouille, O. Coulembier, P. Dubois and A. P. Dove, *Chem. Soc. Rev.*, 2013, **42**, 1312–1336.

34 W. Guerin, A. K. Diallo, E. Kirilov, M. Helou, M. Slawinski, J.-M. Brusson, J.-F. Carpentier and S. M. Guillaume, *Macromolecules*, 2014, **47**, 4230–4235.

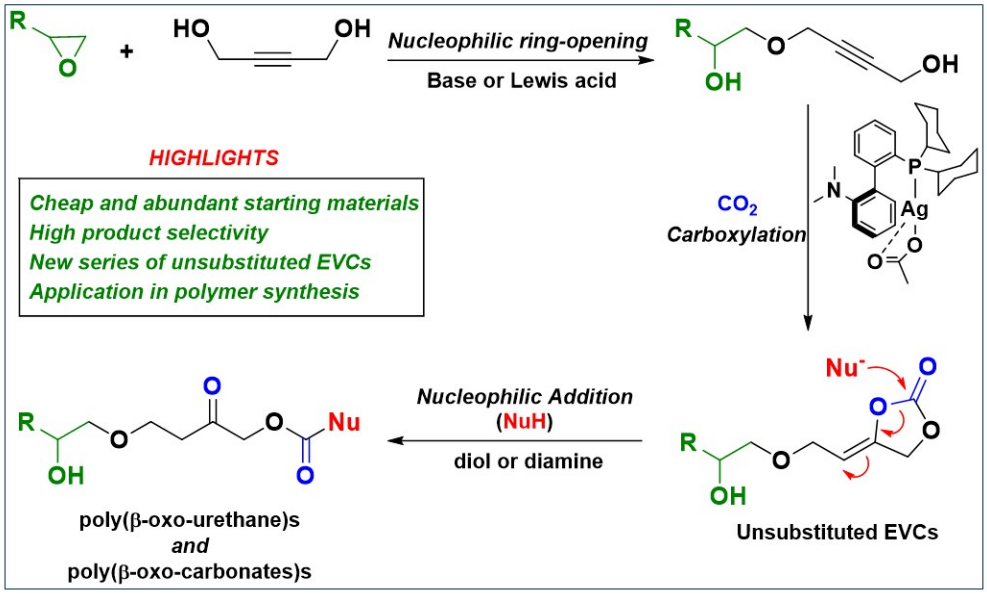
35 S. Paul, Y. Zhu, C. Romain, R. Brooks, P. K. Saini and C. K. Williams, *Chem. Commun.*, 2015, **51**, 6459–6479.

36 Recent publications for the synthesis of EVCs by reacting propargyl alcohols with CO_2: [*a*] J. Qiu, Y. Zhao, Z. Li, H. Wang, M. Fan and J. Wang, *ChemSusChem*, 2017, **10**, 1120–1127; [*b*] H. Zhou, G.-X. Wang and X.-B. Lu, *Asian J. Org. Chem.*, 2017, **6**, 1264–1269; [*c*] Y. Yuan, Y. Xie, C. Zeng, D. Song, S. Chaemchuen, C. Chen and F. Verpoort, *Green Chem.*, 2017, **19**, 2936–2940; [*d*] Y. Yuan, Y. Xie, C. Zeng, D. Song, S. Chaemchuen, C. Chen and F. Verpoort, *Catal. Sci. Technol.*, 2017, **7**, 2935–2939; [*e*] Z. Zhou, C. He, L. Yang, Y. Wang, T. Liu and C. Duan, *ACS Catal.*, 2017, **7**, 2248–2256; [*f*] Z.-H. Zhou, Q.-W. Song and L.-N. He, *ACS Omega*, 2017, **2**, 337–345; [*g*] Y. Yuan, Y. Xie, D. Song, C. Zeng, S. Chaemchuen, C. Chen and F. Verpoort, *Appl. Organomet. Chem.*, 2017, **31**, e3867; [*h*] S.-L. Hou, J. Dong, X.-L. Jiang, Z.-H. Jiao and B. Zhao, *Angew. Chemie Int. Ed.*, 2019, **58**, 577–581; [*i*] H. Zhou, R. Zhang and X. -B. Lua, *Adv. Synth. Catal.* 2019, **361**, 326–334.

View Article Online
DOI: 10.1039/C9GC04320A

37 C.-R. Qi and H.-F. Jiang, *Green Chem.*, 2007, **9**, 1284–1286.
38 P. Toullec, A. Carbayo Martin, M. Gio-Batta, C. Bruneau and P. H. Dixneuf, *Tetrahedron Lett.*, 2000, **41**, 5527–5531.
39 Y. Zhao, Z. Yang, B. Yu, H. Zhang, H. Xu, L. Hao, B. Han and Z. Liu, *Chem. Sci.*, 2015, **6**, 2297–2301.
40 Q.-W. Song, Z.-H. Zhou, M.-Y. Wang, K. Zhang, P. Liu, J.-Y. Xun and L.-N. He, *ChemSusChem*, 2016, **9**, 2054–2058.
41 N. B. Chernysheva, A. A. Bogolyubov and V. V Semenov, *Chem. Heterocycl. Compd.*, 2003, **39**, 1057–1064.
42 S. Gennen, B. Grignard, T. Tassaing, C. Jérôme and C. Detrembleur, *Angew. Chemie Int. Ed.*, 2017, **56**, 10394–10398.
43 F. Ouhib, B. Grignard, E. Van Den Broeck, A. Luxen, K. Robeyns, V. Van Speybroeck, C. Jerome and C. Detrembleur, *Angew. Chemie Int. Ed.*, 2019, **58**, 11768–11773.
44 [*a*] S. Dabral, B. Bayarmagnai, M. Hermsen, J. Schießl, V. Mormul, A. S. K. Hashmi and T. Schaub, *Org. Lett.*, 2019, **21**, 1422–1425; [*b*] B. Bayarmagnai, T. Schaub, V. Mormul, P. Rudolf, WO 2019034648, 2017; [*c*] T. Schaub, P. Rudolf, U. Licht, V. Mormul, S. Dabral, WO 2019219469A1, 2019.
45 E. Delebecq, J. -P. Pascault, B. Boutevin and F. Ganachaud, *Chem. Rev.,* 2013, **113**, 80−118.

View Article Online
DOI: 10.1039/C9GC04320A



275x190mm (96 x 96 DPI)