PAPER

Check for updates

Functionalized polycarbonates *via* triphenylborane catalyzed polymerization-hydrosilylation†

Kori A. Andrea [ID] and Francesca M. Kerton [ID] *

Triphenylborane catalyzes the copolymerization and terpolymerization of epoxides and CO_2 to yield polycarbonates with excellent dispersity. *Via* assisted tandem catalysis, these materials could be hydrosilylated in a one-pot fashion yielding modified polymeric materials. Using only a few reagents, materials with glass transition temperatures ranging from 37–110 °C were obtained.

Transformation of carbon dioxide (CO_2) into useful organic materials is important from an economic and environmental viewpoint.[1,2] Specifically, the reaction of CO_2 and epoxides can yield either cyclic carbonates or polycarbonates, with product selectivity relying on several factors such as temperature, pressure, substrate and catalyst design. The polycarbonate product is attractive as it paves a new road towards the development of new sustainable polymeric materials that may serve as alternatives to the traditional petroleum-based products that dominate society today.[3–5] The use of catalysts that can incorporate a mixture of epoxide monomers into the final product has evolved in recent years, which can allow renewable functional epoxides to be incorporated into a biorenewable end product.[6,7] Furthermore, such functional epoxides including unsaturated building blocks allow for subsequent modification and tailoring of the polymer and its properties. This has been achieved previously,[8] for example, *via* olefin metathesis and thiol–ene crosslinking reactions.[8–14]

Copolymerization of epoxides and CO_2 is usually facilitated by metal-based catalytic systems,[6,15] but recently the use of organo- and non-metal catalysts has emerged,[16] including two examples making use of organoboranes. The first used triethylborane to yield polycarbonates with high carbonate content when either propylene oxide (PO) or cyclohexene oxide (CHO) were used as the substrate.[17] We recently reported the use of arylboranes, both triphenylborane (BPh₃) and the more Lewis acidic tris(pentafluorophenyl)borane (BCF), as catalysts for the production of either cyclic carbonate or polycarbonate products with substrate dependent selectivity.[18]

Triarylboranes, particularly BCF, either alone or as a Frustrated Lewis Pair (FLP) or within a complex ion-pair are known to catalyze a broad range of reactions,[19–24] including hydroelements that possess enormous potential for production of chemicals in a sustainable manner.[25,26]

Department of Chemistry, Memorial University of Newfoundland, St. John's, NL A1B 3X7, Canada. E-mail: fkerton@mun.ca

Specifically, hydrosilylation involves the addition of Si–H groups across C–C, C–O and C–N multiple bonds.[27] As hydrosilylation of alkenes by BCF had been reported,[21] along with our recent report of BPh₃ catalyzed copolymerization of CO_2 and vinylcyclohexene oxide (VCHO), we were motivated to combine these two reactions in one-pot to yield silylated-polycarbonates. Herein, we report the first example of an alkene hydrosilylation catalyzed by the less Lewis acidic BPh₃. Building on our previous findings regarding the ability of BPh₃ to produce perfectly alternating polycarbonates, we report sequential copolymerization-hydrosilylation in a one-pot manner *via* assisted tandem catalysis (Scheme 1). We anticipate that such processes can lead to CO_2-derived polymers with tailorable physical properties including glass transition temperatures. Also, these polymers may show enhanced solubility in organic solvents, which will facilitate film-casting, and if some Si–H bonds remain, it may allow polymers to be attached to surfaces *via* covalent bonding or grafted to other macromolecular species to form more complex architectures.

The vinyl groups of the polyvinylcyclohexene carbonate (PVCHC) provide several potential routes to polymer modification, which could result in tuning of its physical and chemical properties. This has been done previously using methods such
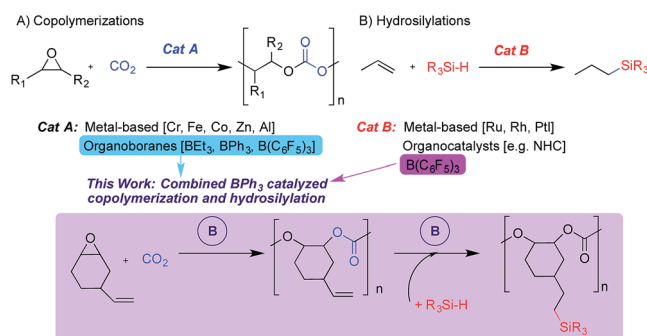
Scheme 1 Catalytic copolymerization and hydrosilylation.

as thiol–ene click chemistry[28] and metathesis.[10,18] BCF is known to activate Si–H bonds and facilitate their addition across unsaturated substrates,[21,29,30] whereas BPh$_3$ has been studied to a lesser extent. We envisioned that BPh$_3$ would be able to catalyze the addition of Si–H groups onto a vinyl-substituted polycarbonate. Therefore, we performed the following 'one-pot' sequence (Fig. 1): BPh$_3$ was used to catalyze the copolymerization of VCHO and CO$_2$, the CO$_2$ was vented and phenyldimethylsilane added to the reaction mixture so the BPh$_3$ present could then catalyze the hydrosilylation of the alkene within the polycarbonate. We did not attempt to perform the hydrosilylation reaction in the presence of CO$_2$, or prior to or during the copolymerization, as BPh$_3$ is able to hydrosilylate CO$_2$ but does not react with propylene carbonate,[31] and we presume other carbonates. We monitored the one-pot process *via in situ* IR spectroscopy. The formation of PVCHC was monitored *via* growth of the carbonate stretch at 1747 cm^{-1}. We observed no induction period and signal saturation occurred within approximately 1 h. After 24 h, we cooled and depressurized the vessel before injecting a mixture of phenyl-dimethylsilane in dichloromethane and heating to 40 °C. A trial hydrosilylation reaction (NMR scale) on isolated PVCHC was successful at this temperature. However, for the one pot process after 4 days, no new bands were observed in the IR spectrum. Upon increasing the temperature to 60 °C, within hours we saw a decrease in intensity of bands at 2122 and 882 cm^{-1} (PhMe$_2$SiH), and an increase in intensity of bands at 834 and 791 cm^{-1} demonstrating the successful addition of the silane across the alkene of the polycarbonate. The higher temperature for the one-pot process is likely needed to displace the Cl$^-$ anion from the boron centre and allow activation of the Si–H bond by the borane. Cl$^-$ is used as a co-catalyst in the CO$_2$ epoxide copolymerization process and the NMR scale trial reaction was performed in the absence of PPNCl. The successful one-pot reaction was confirmed with ^{1}H, ^{13}C, HSQC and refocused INEPT ^{29}Si NMR spectroscopy (Fig. S1–S6†), and integration of ^{1}H NMR signals for the residual vinyl protons and the silyl protons (Si–(CH$_3$)$_2$, Si–ArH) showed 10% of the vinyl groups

had been modified. In the refocused INEPT ^{29}Si NMR spectrum of the product, a new signal appeared at $\delta = -1.26$ ppm characteristic of a Si–C saturated bond *cf.* PhMe$_2$SiH $\delta = -17.27$ ppm. Gel permeation chromatography (GPC) traces show an increase in M_n for the product, while calculated Mark–Houwink–Sakurada (MHS) confirmation plots show an increased degree of branching in the product ($a = 0.697$ in PVCHC *vs.* silyl-PVCHC $a = 0.479$), further confirming successful functionalization (Fig. S7 and S8†).[32] As anticipated the silyl-modified polymer exhibited a lower glass transition temperature (T_g) 71.5 °C compared with PVCHC, 99.0 °C. This T_g may possibly be further decreased if a larger proportion of vinyl groups are converted or a different silane employed. Polycarbonates with relatively low T_g includes commercially available polypropylene carbonate that finds applications in films and coatings. This one-pot copolymerization-silylation process is an example of assisted tandem catalysis,[33] as the silane reagent triggers the mode of catalysis to change, and represents a new approach to functionalized polycarbonate.

To obtain more examples of functional polycarbonates, while building upon past examples of mixed epoxide/CO$_2$ terpolymerizations,[34–38] we sought to investigate our BPh$_3$/PPNCl catalytic system for similar activity. In our previous research, when propylene oxide (PO) was used as the substrate neither polypropylene oxide nor polypropylene carbonate (PPC) was formed.[18] However, when an initial monomer mixture of 50 : 50 CHO : PO was used, we saw an incorporation ratio of 4 : 1 CHO : PO in the resulting polycarbonate *i.e.* 20% PPC linkages (Table 1, entry 1). Moving to a 10 : 90 CHO : PO monomer mixture, a terpolymer with 50% PPC linkages and a lower T_g, 37.3 °C, was obtained (Table 1, entry 2). From *in situ* IR monitoring, in addition to terpolymer, a notable amount of cyclic propylene carbonate formed. However, traces showed from a kinetic standpoint while the cyclic product formed quickly, once polymerization began there was no further cyclic formation (Fig. S13†). Instead the starting PO monomer continued to insert into the growing polymeric chain. When these ratios were reversed 90 : 10 CHO : PO (Table 1, entry 3), the polymer contained mostly PCHC linkages with a T_g similar to polycyclohexene carbonate. When CHO was replaced with VCHO in combination with PO (Table 1, entries 1 and 4), a larger proportion of PO was incorporated into the terpolymer. The BPh$_3$/PPNCl system did not give cyclic or polymer product when glycidol was used (Table 1, entry 6). Allyl glycidyl ether (AGE) in the presence of CHO or VCHO (Table 1, entries 7 and 9) could be incorporated into terpolymers but only modest amounts of AGE were found in the resulting polymer. All obtained terpolymers were characterized by ^{1}H and ^{13}C NMR spectroscopy, GPC and DSC (Fig. S9–S26†). DOSY NMR spectroscopy confirmed the incorporation of both epoxides within the same polymeric chain. The terpolymers with alkene functionality (*i.e.* those containing VCHO and AGE) are attractive as they introduce the potential to further modify the polymers.

Building upon our initial polycarbonate hydrosilylation results, we then performed 'one-pot' hydrosilylation using the CHO/VCHO terpolymer (Table 1, entry 8) following similar procedures to those discussed above (Fig. 2). For the
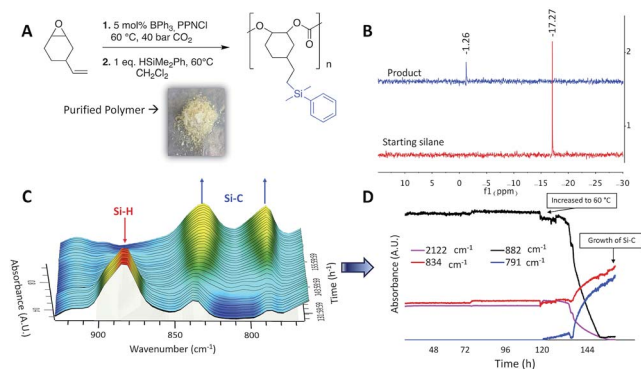

Fig. 1 One-pot assisted tandem catalysis to yield silane modified polycarbonates. (A) One-pot catalytic formation of silylated-PVCHC. (B) Refocused INEPT ^{29}Si NMR spectra of PhMe$_2$SiH and product. (C) *In situ* IR spectra of reaction mixture over time. (D) Reaction profile obtained from *in situ* IR data.

Table 1 Tepolymerizations of epoxides and CO_2 catalyzed by BPh_3[a]

Entry	Epoxide A equiv. (%)	Epoxide B equiv. (%)	Monomer incorporation[b] (A : B)	M_n[c] (g mol^{-1})	$Đ$[c]	T_g[d] (°C)
1	CHO (50)	PO (50)	4 : 1	7990	1.03	79.9
2	CHO (10)	PO (90)	1 : 2	7310	1.06	37.3
3	CHO (90)	PO (10)	25 : 1	3760	1.03	110.2
4	VCHO (50)	PO (50)	1.5 : 1	9660	1.08	78.4
5	CHO (50)	Glycidol (50)	No reaction	—	—	—
6	CHO (50)	AGE (50)	1 : 0.1	6080	1.07	72.5
7	CHO (50)	VCHO (50)	1 : 0.5	5120	1.10	109.1
8	VCHO (50)	AGE (50)	2.2 : 1	7540	1.09	76.6

[a] General reaction conditions unless otherwise indicated: total epoxide (A + B) (0.025 mol), PPNCl (0.124 mmol), BPh_3 (0.124 mmol), 60 °C, 40 bar CO_2. All obtained terpolymers contained >99% CO_3 linkages, no evidence of polyether formation. [b] Determined by ^{1}H NMR spectroscopy. [c] $Đ$, dispersity = M_w/M_n. Determined in THF by GPC equipped with a multiangle light-scattering detector. [d] Determined from DSC.

copolymerization step, a catalyst loading of 2.5 mol% BPh_3 was used, which corresponds to 5 mol% BPh_3 for the hydrosilylation step (as only 50% VCHO was present). After 24 h the vessel was cooled, depressurized and a mixture of diphenylsilane in dichloromethane was injected into the vessel. The mixture was then heated to 60 °C for 24 h. *Via in situ* IR spectroscopy, we observed a decreased in intensity of the silane bands (2144 and 845 cm^{-1}), which plateaued after approx. 12 h and growth of a band at 830 cm^{-1} corresponding to the hydrosilylated product. The hydrosilylated polymer was further characterized by ^{1}H, ^{13}C, HSQC and refocused INEPT ^{29}Si NMR spectroscopy (Fig. S27–S32†). From ^{1}H NMR integration of signals for the residual vinyl protons and the aromatic protons (–SiPh$_2$), 36% of vinyl groups had been modified. The refocused INEPT ^{29}Si NMR spectrum of the product had a resonance at $\delta = -19.32$ ppm, *cf.* $\delta = -33.18$ ppm (Ph$_2$SiH$_2$). From both ^{1}H and refocused INEPT ^{29}Si NMR it is evident that only one Si–H bond added across the alkene of the terpolymer and hence no cross-linking occurred. From DSC data, a decline in T_g from 111.6 °C to 47.8 °C was observed for the silylated product (Fig. S33†). From GPC, an increase in molecular weight from 4.31×10^3 g mol^{-1} ($Đ = 1.07$) to 6.20×10^3 g mol^{-1} ($Đ = 1.12$) was observed as well as increased branching in MHS confirmation plots (Fig. S34†).

Finally, we set out to evaluate the substrate scope of these transformations by evaluating the reactivity of a hydride terminated polydimethylsiloxane. For the hydride terminated polydimethylsiloxane (DMS-HO3) and PVCHC, the resulting polymer was characterized by ^{1}H, ^{13}C, refocused INEPT ^{29}Si, and H–Si HMQC NMR spectroscopy (Fig. S35–S37†). *Via* integration of the ^{1}H NMR spectrum, hydrosilylation has occurred to a similar extent to other hydrosilylations reported herein. We note that only one Si–H group per DMS-HO3 has undergone reaction and no cross-linking between polycarbonate chains was indicated by NMR and DSC data. IR spectra of the hydrosilylated-polycarbonate showed new bands at $\nu = 1013$, 907 and 788 cm^{-1} corresponding to O–Si–O, Si–H and Si–CH$_3$ groups respectively (Fig. S38†). From GPC, there was a moderate increase in molecular weight and no significant change in $Đ$. There was a decline in the slope of the MHS plot indicating a higher degree of branching in the final product (Fig. S39†). DSC analysis demonstrated a slight increase in T_g from 99.0 °C to 104.6 °C. The residual unreacted Si–H bonds in the functionalized polymer introduces further functionality potential. For example, BCF has been reported to catalyze the addition of Si–H bonds onto silica derived materials.[39]

In summary, we report the first example of BPh_3 catalyzed hydrosilylation of perfectly alternating PVCHC in a tandem catalytic manner. These reactions were monitored by *in situ* IR spectroscopy, which demonstrated the addition of the Si–H bond across the pendent alkenes in the polymer. In an attempt to build new classes of polymeric materials, we showed the ability of BPh_3 to catalyze the terpolymerization of CO_2 and several epoxide combinations, yielding products with T_g values from 37.3 °C to 110.2 °C, which we could then functionalize in a similar one-pot manner as above. Finally, we evaluated the reactivity of a polymeric hydride terminated siloxane which can serve as a precursor for silica surface modification. Using the results in-hand, we will work towards developing sustainable surface functionalized materials in the future.
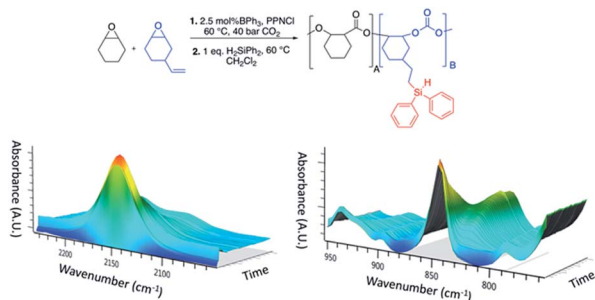

Fig. 2 One-pot assisted tandem catalysis to yield silylated-terpolymers. General reaction scheme (top) and three-dimensional plots obtained *via in situ* IR spectroscopy showing a decreased for silane bands and growth of product bands (bottom).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1 J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow and W. Leitner, Sustainable Conversion of Carbon Dioxide: An Integrated Review of Catalysis and Life Cycle Assessment, *Chem. Rev.*, 2018, **118**, 434–504.

2 M. Aresta, A. Dibenedetto and A. Angelini, Catalysis for the Valorization of Exhaust Carbon: from CO_2 to Chemicals, Materials, and Fuels. Technological Use of CO_2, *Chem. Rev.*, 2014, **114**, 1709–1742.

3 M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, Transformation of Carbon Dioxide with Homogeneous Transition-Metal Catalysts: A Molecular Solution to a Global Challenge?, *Angew. Chem., Int. Ed.*, 2011, **50**, 8510–8537.

4 Q. Liu, L. Wu, R. Jackstell and M. Beller, Using Carbon Dioxide as a Building Block in Organic Synthesis, *Nat. Commun.*, 2015, **6**, 5933.

5 M. North and P. Styring, Perspectives and Visions on CO_2 Capture and Utilisation, *Faraday Discuss.*, 2015, **183**, 489–502.

6 G. Trott, P. K. Saini and C. K. Williams, Catalysts For CO_2/epoxide Ring-opening Copolymerization, *Philos. Trans. R. Soc., A*, 2016, **374**, 20150085.

7 O. Hauenstein, S. Agarwal and A. Greiner, Bio-based Polycarbonate as Synthetic Toolbox, *Nat. Commun.*, 2016, **7**, 11862.

8 Y. Wang and D. J. Darensbourg, Carbon Dioxide-based Functional Polycarbonates: Metal Catalyzed Copolymerization of CO_2 and Epoxides, *Coord. Chem. Rev.*, 2018, **372**, 85–100.

9 S. Liu, X. Zhao, H. Guo, Y. Qin, X. Wang and F. Wang, Construction of Well-Defined Redox-Responsive CO_2-Based Polycarbonates: Combination of Immortal Copolymerization and Prereaction Approach, *Macromol. Rapid Commun.*, 2017, **38**, 1600754.

10 A. E. Cherian, F. C. Sun, S. S. Sheiko and G. W. Coates, Formation of Nanoparticles by Intramolecular Cross-Linking: Following the Reaction Progress of Single Polymer Chains by Atomic Force Microscopy, *J. Am. Chem. Soc.*, 2007, **129**, 11350–11351.

11 D. J. Darensbourg, W.-C. Chung, C. J. Arp, F.-T. Tsai and S. J. Kyran, Copolymerization and Cycloaddition Products Derived from Coupling Reactions of 1,2-Epoxy-4-cyclohexene and Carbon Dioxide. Postpolymerization Functionalization via Thiol–Ene Click Reactions, *Macromolecules*, 2014, **47**, 7347–7353.

12 G.-W. Yang, Y.-Y. Zhang, Y. Wang, G.-P. Wu, Z.-K. Xu and D. J. Darensbourg, Construction of Autonomic Self-Healing CO_2-Based Polycarbonates via One-Pot Tandem Synthetic Strategy, *Macromolecules*, 2018, **51**, 1308–1313.

13 C. Martín and A. W. Kleij, Terpolymers Derived from Limonene Oxide and Carbon Dioxide: Access to Cross-Linked Polycarbonates with Improved Thermal Properties, *Macromolecules*, 2016, **49**, 6285–6295.

14 T. Stößer, C. Li, J. Unruangsri, P. K. Saini, R. J. Sablong, M. A. R. Meier, C. K. Williams and C. Koning, Bio-derived Polymers for Coating Applications: Comparing Poly(Limonene Carbonate) and Poly(Cyclohexadiene Carbonate), *Polym. Chem.*, 2017, **8**, 6099–6105.

15 C. M. Kozak, K. Ambrose and T. S. Anderson, Copolymerization of Carbon Dioxide and Epoxides by Metal Coordination Complexes, *Coord. Chem. Rev.*, 2018, **376**, 565–587.

16 R. R. Shaikh, S. Pornprapom and V. D'Elia, Catalytic Strategies for the Cycloaddition of Pure, Diluted, and Waste CO_2 to Epoxides under Ambient Conditions, *ACS Catal.*, 2018, **8**, 419–450.

17 D. Zhang, S. K. Boopathi, N. Hadjichristidis, Y. Gnanou and X. Feng, Metal-Free Alternating Copolymerization of CO_2 with Epoxides: Fulfilling "Green" Synthesis and Activity, *J. Am. Chem. Soc.*, 2016, **138**, 11117–11120.

18 K. A. Andrea and F. M. Kerton, Triarylborane-Catalyzed Formation of Cyclic Organic Carbonates and Polycarbonates, *ACS Catal.*, 2019, **9**, 1799–1809.

19 D. W. Stephan, The Broadening Reach of Frustrated Lewis Pair Chemistry, *Science*, 2016, **354**, aaf7229.

20 J. R. Lawson and R. L. Melen, Tris(pentafluorophenyl)-borane and Beyond: Modern Advances in Borylation Chemistry, *Inorg. Chem.*, 2017, **56**, 8627–8643.

21 M. Rubin, T. Schwier and V. Gevorgyan, Highly efficient $B(C_6F_5)_3$-catalyzed hydrosilylation of olefins, *J. Org. Chem.*, 2002, **67**, 1936–1940.

22 M. Pérez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky and D. W. Stephan, Olefin Isomerization and Hydrosilylation Catalysis by Lewis Acidic Organofluorophosphonium Salts, *J. Am. Chem. Soc.*, 2013, **135**, 18308–18310.

23 M. H. Holthausen, M. Mehta and D. W. Stephan, The Highly Lewis Acidic Dicationic Phosphonium Salt: [(SIMes)PFPh$_2$][B(C$_6$F$_5$)$_4$]$_2$, *Angew. Chem., Int. Ed.*, 2014, **53**, 6538–6541.

24 A. Simonneau and M. Oestreich, 3-Silylated Cyclohexa-1,4-dienes as Precursors for Gaseous Hydrosilanes: The $B(C_6F_5)_3$-Catalyzed Transfer Hydrosilylation of Alkenes, *Angew. Chem., Int. Ed.*, 2013, **52**, 11905–11907.

25 M. Oestreich, Transfer Hydrosilylation, *Angew. Chem., Int. Ed.*, 2016, **55**, 494–499.

26 X. Zeng, Recent Advances in Catalytic Sequential Reactions Involving Hydroelement Addition to Carbon-Carbon Multiple Bonds, *Chem. Rev.*, 2013, **113**, 6864–6900.

27 Y. Nakajima and S. Shimada, Hydrosilylation Reaction of Olefins: Recent Advances And Perspectives, *RSC Adv.*, 2015, **5**, 20603–20616.

28 D. J. Darensbourg and Y. Wang, Terpolymerization of Propylene Oxide and Vinyl Oxides With CO_2: Copolymer Cross-Linking and Surface Modification via Thiol–Ene Click Chemistry, *Polym. Chem.*, 2015, **6**, 1768–1776.

29 A. Berkefeld, W. E. Piers and M. Parvez, Tandem Frustrated Lewis Pair/Tris(Pentafluorophenyl)Borane-Catalyzed Deoxygenative Hydrosilylation of Carbon Dioxide, *J. Am. Chem. Soc.*, 2010, **132**, 10660–10661.

30 L. C. Wilkins, J. L. Howard, S. Burger, L. Frentzel-Beyme, D. L. Browne and R. L. Melen, Exploring Multistep Continuous-Flow Hydrosilylation Reactions Catalyzed by Tris(Pentafluorophenyl)Borane, *Adv. Synth. Catal.*, 2017, **359**, 2580–2584.

31 D. Mukherjee, D. F. Sauer, A. Zanardi and J. Okuda, Selective Metal-Free Hydrosilylation of CO_2 Catalyzed by Triphenylborane in Highly Polar, Aprotic Solvents, *Chem.– Eur. J.*, 2016, **22**, 7730–7733.

32 S. Mori and H. G. Barth, *Size Exclusion Chromatography*, Springer-Verlag, Berlin-Heidelberg-New York, 1999.

33 D. E. Fogg and E. N. dos Santos, Tandem Catalysis: A Taxonomy and Illustrative Review, *Coord. Chem. Rev.*, 2004, **248**, 2365–2379.

34 H. Li and Y. Niu, Alternating Copolymerization of CO_2 with Propylene Oxide and Terpolymerization with Aliphatic Epoxides by Bifunctional Cobalt Salen Complex, *Polym. J.*, 2010, **43**, 121–125.

35 J. E. Seong, S. J. Na, A. Cyriac, B. W. Kim and B. Y. Lee, Terpolymerizations of CO_2, Propylene Oxide, and Various Epoxides Using a Cobalt(III) Complex of Salen-Type Ligand Tethered by Four Quaternary Ammonium Salts, *Macromolecules*, 2010, **43**, 903–908.

36 G. P. Wu, P. X. Xu, Y. P. Zu, W. M. Ren and X. B. Lu, Cobalt(III)-Complex-Mediated Terpolymerization of CO_2, Styrene Oxide, and Epoxides with an Electron-Donating Group, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 874–879.

37 D. J. Darensbourg, R. R. Poland and A. L. Strickland, (Salan) CrCl, An Effective Catalyst for the Copolymerization and Terpolymerization of Epoxides and Carbon Dioxide, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 127–133.

38 K. Deng, S. Wang, S. Ren, D. Han, M. Xiao and Y. Meng, A Novel Single-Ion-Conducting Polymer Electrolyte Derived from CO_2-Based Multifunctional Polycarbonate, *ACS Appl. Mater. Interfaces*, 2016, **8**, 33642–33648.

39 N. Moitra, S. Ichii, T. Kamei, K. Kanamori, Y. Zhu, K. Takeda, K. Nakanishi and T. Shimada, Surface Functionalization of Silica by Si–H Activation of Hydrosilanes, *J. Am. Chem. Soc.*, 2014, **136**, 11570–11573.