APPENDIX A

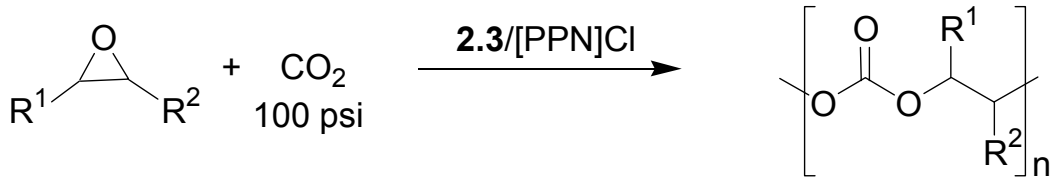
SYNTHESIS AND CHARACTERIZATION OF POLYCARBONATES USING HIGHLY ACTIVE CATALYST SYSTEM **2.3**/[PPN]Cl

A.1 Introduction

Appendix A describes preliminary work on the synthesis and characterization of a variety of polycarbonates using the highly active catalyst system **2.3**/[PPN]Cl.

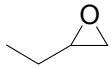
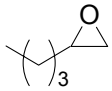
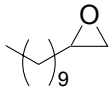
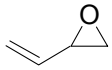
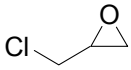
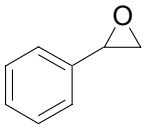
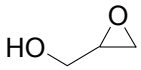
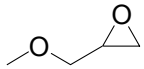
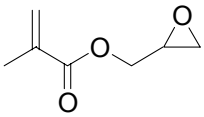
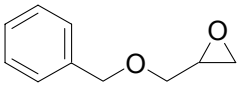
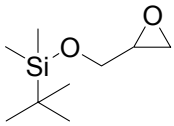
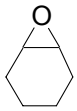
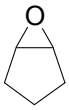
A.2 Synthesis and thermal properties of polycarbonates

We have described previously (Chapters 2, 3, and 4) that catalyst system **2.3**/[PPN]Cl is highly active for the copolymerization of both PO/CO_2 and CHO/CO_2. In an effort to explore the substrate scope for this catalyst system, we applied **2.3**/[PPN]Cl to a variety of epoxides while using previously optimized reaction conditions (Scheme A.1).



Scheme A.1. Epoxide and CO_2 copolymerization catalyzed by **2.3**/[PPN]Cl to yield poly(carbonate).

Table A.1. Epoxide/CO_2 copolymerization using catalyst system **2.3**/[PPN]Cl.[a]

Entry	Epoxide	Time (h)	Yield (%)[b]	TOF (h^{-1})[c]	Polymer: Cyclic[d]	M_n (kg/mol)[e]	M_w/M_n[e]
1		0.5	30	600	99:1	9.8	1.18
2		48	0	0	NA	NA	NA
3		2	37	185	95:5	24.1	1.15
4		6	43	72	74:26	20.7	1.22
5		48	0	0	NA	NA	NA
6		48	53	22	91:9	44.8	1.15
7		2	<1	<1	>1:99	NA	NA
8		48	0	0	NA	NA	NA
9		2	<1	<1	>1:99	NA	NA
10		6	48	80	85:15	4.7	1.42
11		24	28	12	nd	nd	nd
12		8	37	46	92:8	13.1	1.19
13		48	73	15	81:19	45.4	1.15
14		2	32	160	>99:1	14.9	1.14
15		48	0	0	0	NA	NA

[a] Copolymerizations run neat with **2.3**/[PPN]Cl at 100 psi CO_2 and [epoxide]:[**2.3**]:[[PPN]Cl] = 1000:1:1 except for entries 2 (500:1:1) and 4 (2000:1:1). [b] Based on isolated polymer yield. [c] Turnover frequency for polymer = (mol epoxide/(mol Co · h)) [d] Determined by ^{1}H NMR spectroscopy ($CDCl_3$, 300 MHz). [e] Determined by GPC relative to polystyrene standards in THF at 40 °C.

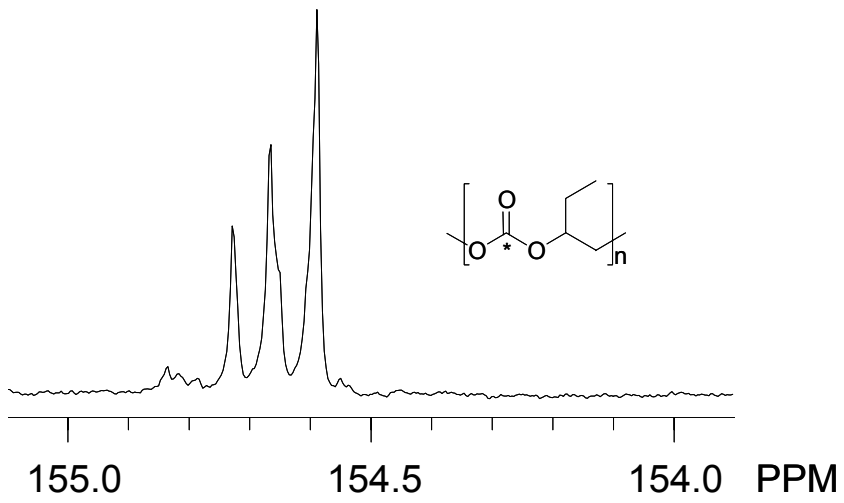


Figure A.1. Carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, d_1 = 10s) of poly(butylene carbonate) as synthesized from catalyst system **2.3**/[PPN]Cl.

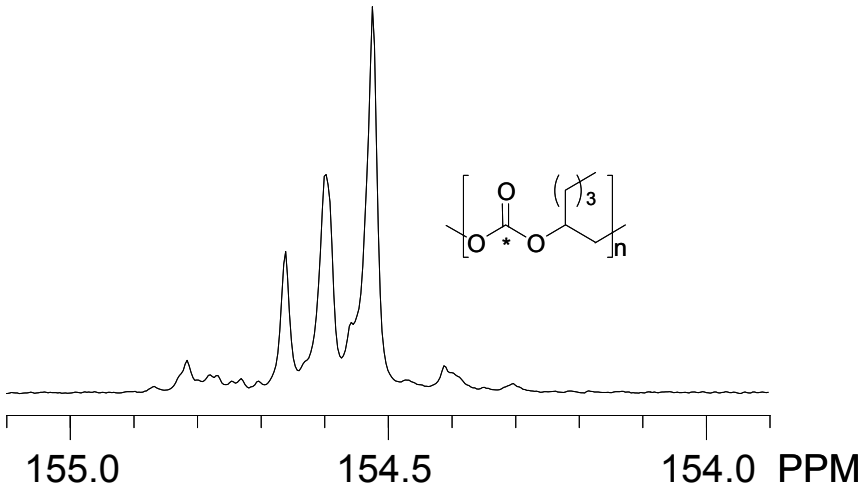


Figure A.2. Carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, d_1 = 10s) of poly(hexylene carbonate) as synthesized from catalyst system **2.3**/[PPN]Cl.

As discussed in chapter 3, catalyst system **2.3**/[PPN]Cl achieves a TOF of 600 h^{-1} for the copolymerization of *rac*-PO and CO_2 (Table A.1, entry 1). When the more sterically bulky isobutyleneoxide is used, however, no reaction occurs even when longer reaction times and higher catalyst loadings are applied (entry 2). When the pendant group (R^1) is an alkyl, increasing the number of carbons results in a slowing of catalyst activity (entries 3 and 4). The relative copolymerization activities follows the trend PO > 1,2-epoxybutane > 1,2-epoxyhexane > 1,2-epoxydodecane where 1,2-epoxydodecane is totally inactive (entry 5). The carbonyl region of the $^{13}C\{^1H\}$ NMR spectra of poly(butylene carbonate) (Figure A.1) and poly(hexylene carbonate) (Figure A.2) reveal that each of these polymers is highly regioregular, considering the same HT assignments as for previously characterized PPC (Chapter 2, Figure 2.6). Use of butadienemonoepoxide is slow compared to 1,2-epoxybutane, and in this case the polymer is regiorandom (entry 6 and Figure A.3). As this monomer is similar in sterics to 1,2-epoxybutane, we suspect that the electronic nature of the pendant functionality greatly influences the regioselectivity of the catalyst.

Addition of a pendant chloride, alcohol or phenyl group on the epoxide is detrimental for polycarbonate formation using catalyst system **2.3**/[PPN]Cl. Use of epichlorohydrin with CO_2 yielded predominantly cyclic carbonate with only trace polymer observed by ^1H NMR spectroscopy (entry 7). Alternatively, styrene oxide was found to be completely inactive (entry 8). Similar to results with epichlorohydrin, glycidyl and CO_2 yielded primarily cyclic carbonate (entry 9).

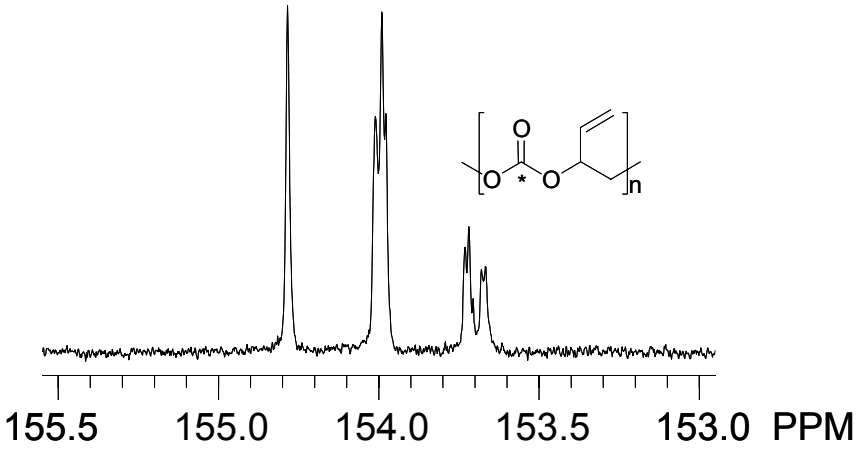


Figure A.3. Carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, d_1 = 10s) of poly(butadiene carbonate) as synthesized from catalyst system **2.3**/[PPN]Cl.

Despite the lack of polymer formation with a pendant chloride, alcohol or phenyl group on the epoxide monomer, the copolymerization using catalyst system **2.3**/[PPN]Cl for glycidyl ethers and CO_2 proved more successful. The copolymerization of *tert*-butyldimethylsilyl glycidyl ether and CO_2 yielded highly regioregular poly(3-*tert*-butyl-dimethylsilyloxy-1-propylene carbonate) in 73% yield after prolonged reaction times (entry 10 and Figure A.3). Although both methyl, and benzyl glycidyl ethers likewise formed the corresponding polycarbonates, only low M_n poly(3-methoxy-1-propylene carbonate) was formed (entry 11 and Figure A.4), and the polymer poly(3-(benzyloxy)-1-propylene carbonate) slowly decomposed over a period of weeks (entry 12). Finally, the copolymerization of glycidyl methacrylate (GM) and CO_2 proceeded to 28% conversion although crosslinking occurred upon precipitation of this polymer, resulting in a highly insoluble material (entry 13).

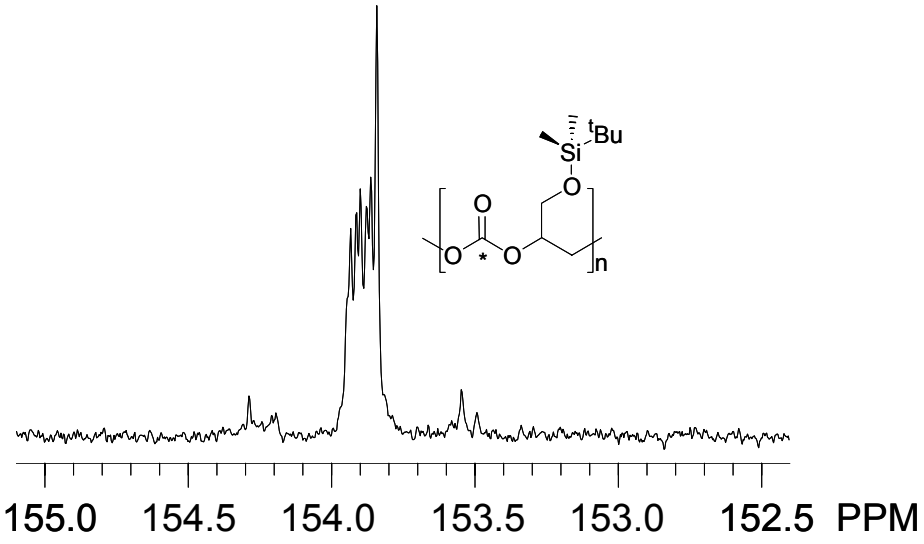


Figure A.4. Carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, d_1 = 10s) of poly(3-tert-butyl-dimethylsilyloxy-1-propylene carbonate) as synthesized from catalyst system **2.3**/[PPN]Cl.

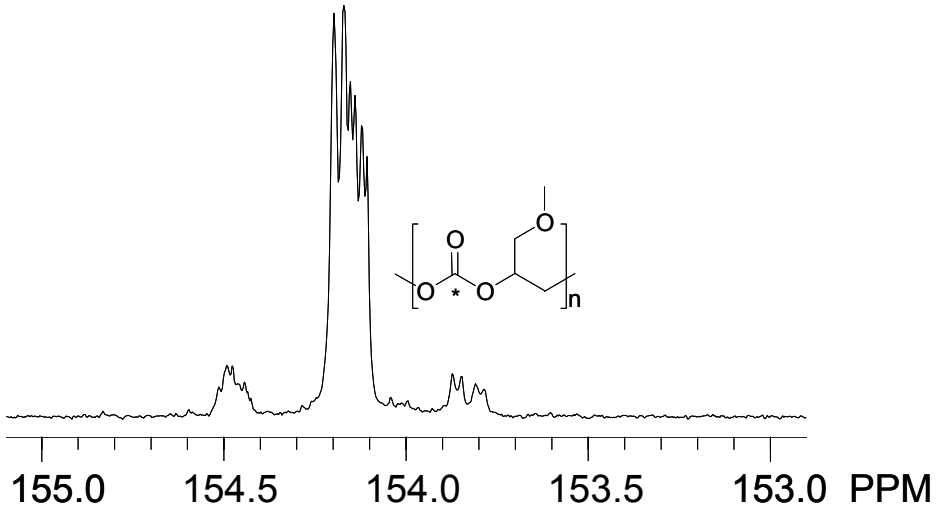
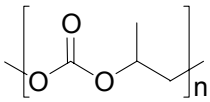
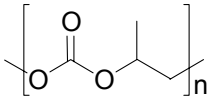
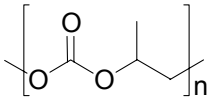
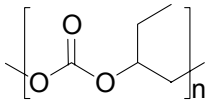
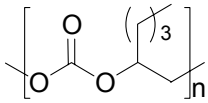
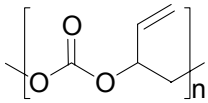
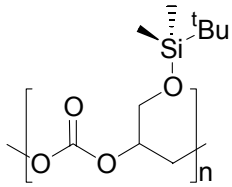
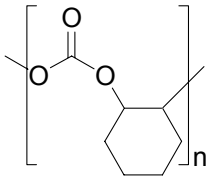
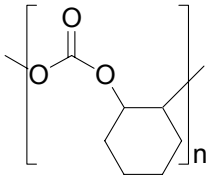


Figure A.5. Carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, d_1 = 10s) of poly(3-methoxy-1-propylene carbonate) as synthesized from catalyst system **2.3**/[PPN]Cl.

As previously described, the copolymerization of CHO and CO_2 using catalyst system **2.3**/[PPN]Cl proceeds with a TOF of 160 h^{-1} (entry 14). Interestingly, use of the smaller alicyclic cyclopentene oxide showed no activity, which we attribute to the higher thermodynamic stability of this monomer (entry 15). In summary, epoxides with pendant alkyl, vinyl, ether, and acrylate substituents were successfully copolymerized with CO_2 using catalyst system **2.3**/[PPN]Cl, however limited by the steric bulkiness of these groups.

The onset decomposition (T_d) and glass transition temperatures (T_g) for a series of the polycarbonates synthesized are presented in Table A.2. In all cases, no melting point transition temperature was observed, which is consistent with previously studied thermal properties in similar polymers.[1] Generally, varying the tacticity of PPC had little influence on the thermal properties of this polymer with T_gs ranging from 33 – 40 °C and T_ds ranging from 200 – 226 °C (entries 1 – 3). Similarly, *syndiotactic* PCHC had similar thermal properties to *atactic* PCHC with only a slightly lower T_d and T_g (entries 9 and 10). It has been shown by both Nozaki and coworkers and in our group that *isotactic* PCHC has a melting point transition (T_m) > 200 °C.[2, 3] Although the PCHCs we prepared are highly syndiotactic, these polymers are amorphous, with no observable T_m (see appendix A1). Furthermore, the possibility of crystalline syndiotactic PCHC may require increased % *r*-centered tetrads then that of the polymers presented herein (81%). Finally, in the case of polycarbonates with varying backbone structures, increasing the length of the alkyl chain decreases the T_g and increases the T_d slightly, consistent with previous accounts.[1]

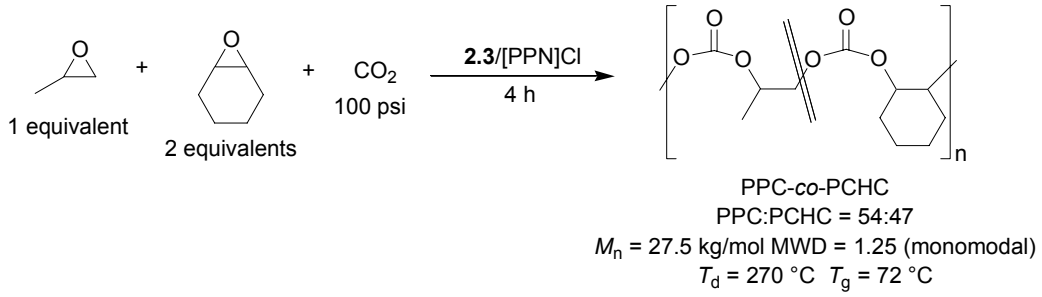
Table A.2. Thermal properties of various polycarbonates.

Entry	Polycarbonate	Tacticity[a]	M_n[b]	M_w/M_n[b]	T_g[c](°C)	T_d[d](°C)
1		atactic	21.0	1.14	39	221
2		isotactic[e]	22.2	1.15	40	200
3		syndiotactic[f]	21.8	1.22	33	226
4		atactic	32.2	1.15	16	222
5		atactic	20.7	1.22	-4	255
6		atactic	44.8	1.15	19	163
7		atactic	45.4	1.15	19	205
8		atactic	15.8	1.36	115	302
9		syndiotactic[g]	27.1	1.38	109	280

[a] Determined by $^{13}C\{^1H\}$ NMR spectroscopy (125 MHz, $CDCl_3$, d_1 = 10s) based on shifts assigned in Figures 2.11 and 4.9. [b] Determined by GPC relative to polystyrene standards in THF at 40 °C. [c] DSC on the 2nd heat, heating rate = 10 ºC·min^{-1}. [d] Onset decomposition temperature, heating rate = 20 ºC·min^{-1}. [e] >99 *mm* triads. [f] Tacticity depicted in figure 2.11. [g] 81% *r*-centered tetrads.

A.3 *rac*-PO/CHO/CO_2 terpolymerization

Although the **2.3**/[PPN]Cl catalyzed *rac*-PO/CO_2 copolymerization proceeds at a much faster rate than the CHO/CO_2 copolymerization under comparable reaction conditions, when *rac*-PO is combined with CHO and CO_2, a PPC-*co*-PCHC (random) copolymer is formed (Scheme A.2). Specifically, when a *rac*-PO:CHO loading of 1:2 is used, the polymer PPC-*co*-PCHC has a PPC to PCHC ratio of 54:47 and is atactic as determined by ^{1}H and ^{13}C NMR spectroscopy (Figure A.6). Interestingly, this indicates that incorporation of *rac*-PO into the polymer occurs approximately twice as fast as that for CHO, however the nature of the propagating end does not influence subsequent monomer addition. Furthermore, the ^{1}H NMR shifts of this polymer are broadened when compared to each polymer separately and a single T_d and T_g of 270 °C and 72 °C, respectively, are observed, indicative of PPC-*co*-PCHC rather than PPC-*b*-PCHC.



Scheme A.2. Terpolymerization of *rac*-PO/CHO/CO_2 by catalyst system **2.3**/[PPN]Cl yielding PPC-*co*-PCHC.

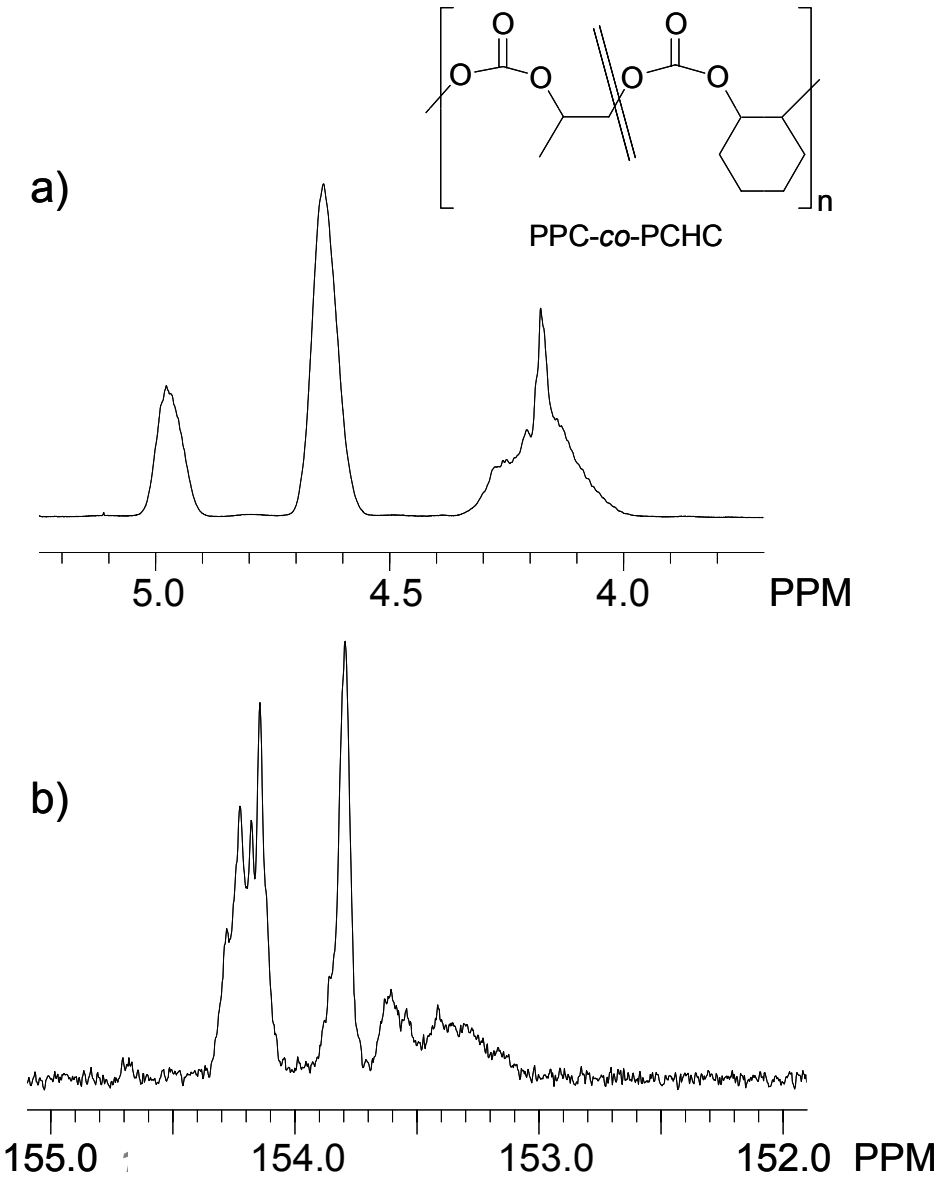
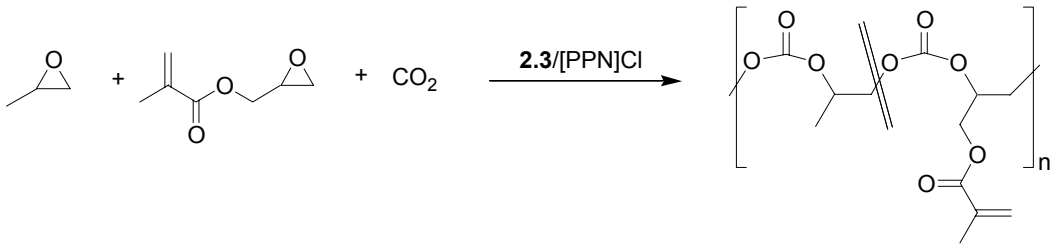


Figure A.6. a) ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of PPC-*co*-PCHC b) $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, d_1 = 10s) of PPC-*co*-PCHC as synthesized from catalyst system **2.3**/[PPN]Cl.

A.4 Incorporation of GM into PPC

Incorporation of a small amount of a reactive pendant functional group into PPC provides for a readily crosslinked material upon post-polymerization modification. Furthermore, addition of the monomer GM to the *rac*-PO/CO_2 copolymerization using catalyst system **2.3**/[PPN]Cl yields PPC with an acrylate functionality (Scheme A.3 and Table A.3). Interestingly the amount of GM incorporated into the PPC is close to twice that of the feed ratio, suggesting that in the presence of PO, the reactivity of GM in the copolymerization is greatly enhanced. The ^{1}H NMR of PPC with 7% GM incorporation is shown in Figure A.7. The GM vinyl peaks integrate near equally to the remaining GM shifts, indicating that this polymer is not crosslinked. Additionally, the carbonyl region in the ^{13}C{^{1}H} NMR spectrum of this polymer reveals that the high regioselectivity of catalyst system **2.3**/[PPN]Cl is not compromised upon the addition of GM units (Figure A.8).



Scheme A.3. Incorporation of GM into PPC.

Table A.3. Incorporation of GM into PPC.[a]

Entry	% GM in PO	Yield[b](%)	% GM in PPC[c]	M_n[d] (kg/mol)	M_w/M_n[d]
1	2	35	4	15.8	1.19
2	4	35	7	16.5	1.16

[a] Polymerizations run neat with [PO]:[Co]:[[PPN]Cl] = 1000:1:1 at 22 °C with 100 psi of CO_2 for 1 h. [b] Based on isolated polymer yield. [c] Determined by ^{1}H NMR spectroscopy ($CDCl_3$, 300 MHz). [d] Determined by GPC relative to polystyrene standards in THF at 40 °C.

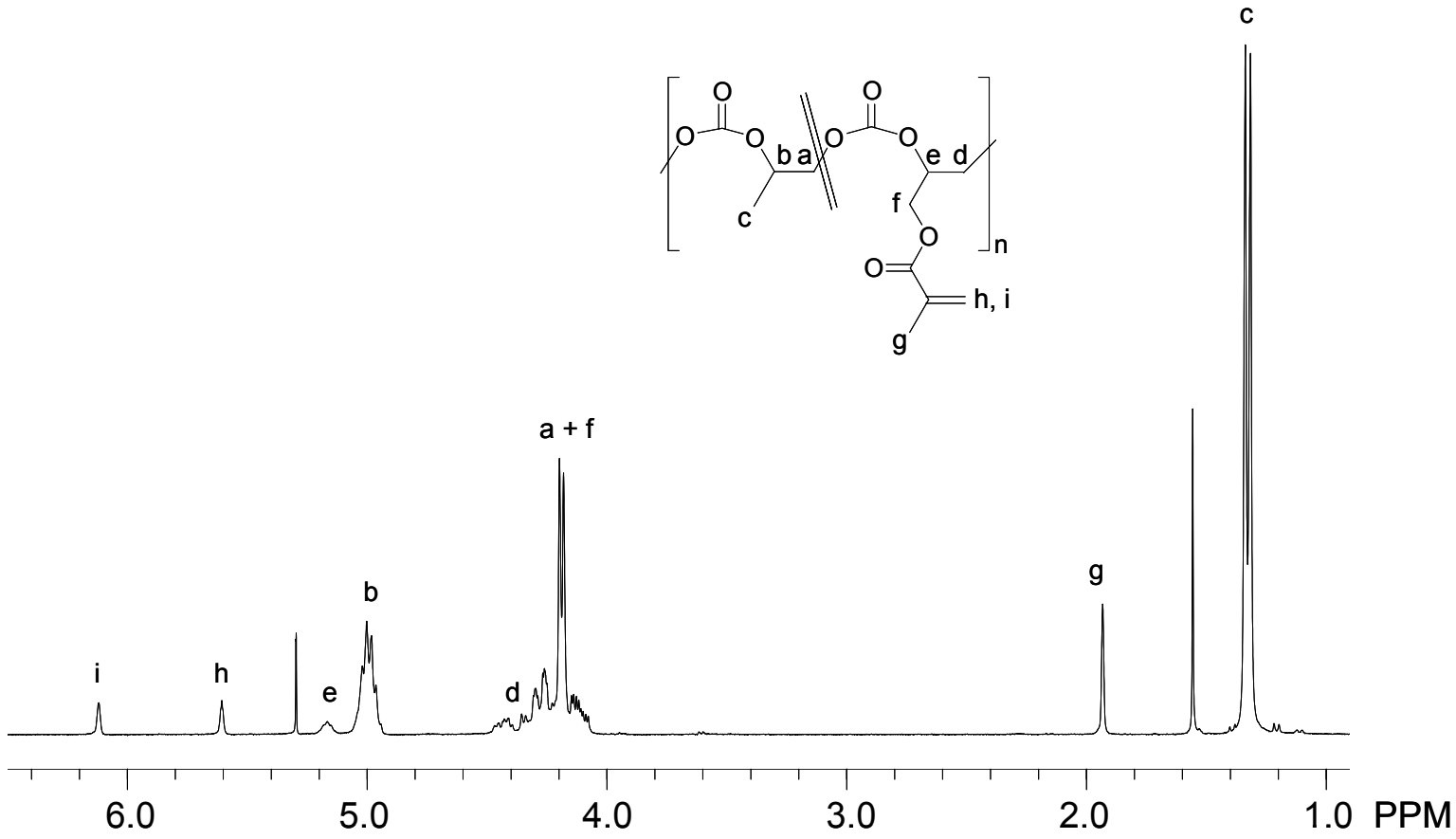


Figure A.7. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of PPC with 7% incorporation of GM as synthesized from catalyst system **2.3**/[PPN]Cl.

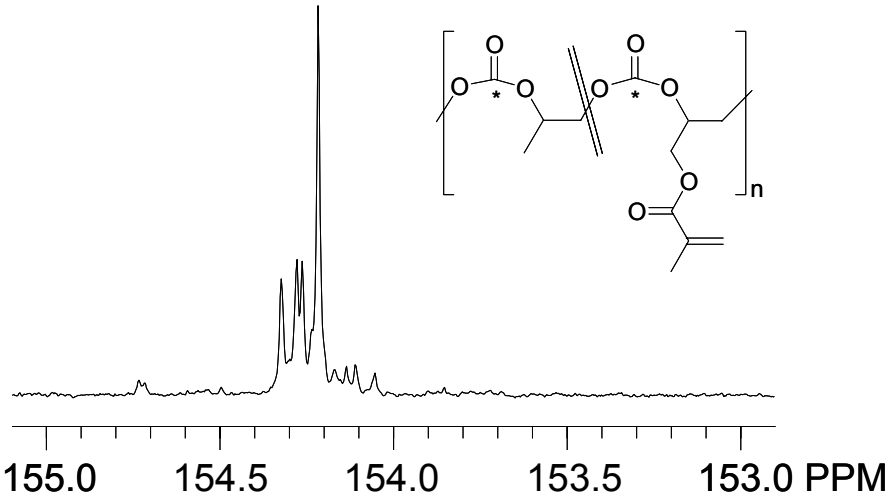


Figure A.8. Carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, d_1 = 10s) of PPC with 7% incorporation of GM as synthesized from catalyst system **2.3**/[PPN]Cl.

A.5 Conclusions

Using the highly active catalyst system **2.3**/[PPN]Cl a variety of polycarbonates can be synthesized. Generally, epoxides with pendant alky, or ether groups work well in the copolymerization with the exception of sterically bulky epoxides. In most cases, the polycarbonates generated are highly regioregular. Alteration of the polycarbonate backbone structure results in changes in thermal properties, however thermal properties are similar in each case when either PPC or PCHC microstructure is varied. Combination of *rac*-PO and CHO with CO_2 results in PPC-*co*-PCHC which is evidenced by broadened ^{1}H NMR polymer shifts and a T_d and T_g between pure PPC and PCHC. Finally, GM can be incorporated into PPC yielding a polycarbonate that can be readily cross-linked upon post-polymerization modification.

A.6 Experimental section

A.6.1 General procedures

All air or water sensitive reactions were carried out under dry N_2 using an MBraun Labmaster drybox or standard Schlenk-line techniques. All epoxides used are commercially available and were dried over calcium hydride and vacuum transferred before use except for glycidyl methacrylate which was used as received. CO_2 (99.998% purity) was purchased from Airgas and passed over a column of 4Å molecular sieves. Varian Mercury (300 MHz) and Varian Inova (500 MHz) spectrometers were used to record $^{13}C\{^1H\}$ (at 125 MHz) and ^1H NMR spectra, which were referenced versus residual nondeuterated solvent shifts. GPC analyses were carried out using a Waters instrument (M515 pump, U6K injector) equipped with Waters UV486 and Waters 2410 differential refractive index detector, and four 5 µm PL Gel columns (Polymer Laboratories; 100 Å, 500 Å, 1000 Å, and Mixed C porosities) in series. The GPC columns were eluted with THF at 40 ºC at 1 mL/min and were calibrated using 23 monodisperse polystyrene standards. DSC measurements were conducted using a TA MDSC Q1000 under N_2 atmosphere; data was collected on the second heating scan with a heating rate of 10 °C·min^{-1}. TGA measurements were conducted using a TA TGA Q50 under N_2 atmosphere with a heating rate of 20 ºC·min^{-1}.

A.6.2 Synthesis of catalysts

The synthesis of complex **2.3** has been described previously in Chapter 2.

A.6.3 Polymerizations

All polymers where characterized using ^1H NMR spectroscopy ($CDCl_3$, 300 MHz or 500 MHz), and in some cases with $^{13}C\{^1H\}$ NMR spectroscopy ($CDCl_3$, 125 MHz), GPC, TGA, and DSC (see above discussion). The characterization of both PPC

and PCHC has been discussed in detail in Chapters 2 – 4. The ^{1}H NMR data for additional polymers synthesized as well as the general polymerization procedures used are detailed below.

Representative copolymerization procedure (NOV-3-40). A Fischer-Porter bottle (FPB) was charged with a Teflon stirbar, heated to 150 °C in an oven for 4 h, then moved to a drybox. Once cooled to 22 °C, catalyst **2.3** (11.6 mg, 0.0143 mmol), [PPN]Cl (8.2 mg, 0.014 mmol), and *rac*-PO (1.00 mL, 14.3 mmol) were added to the FPB in the drybox. The FPB was pressurized to 100 psi of CO_2 and was left to stir at 22 °C for 0.5 h. The FPB was vented at 22 °C. A small aliquot of the product mixture was removed from the FPB for ^{1}H NMR analysis. The remaining product mixture was dissolved in methylene chloride (5 mL), quenched with 5% HCl solution in methanol (0.2 mL), and transferred to a pre-weighed vial. The product mixture was dried *in vacuo* to constant weight, and the crude yield was determined after subtracting out the catalyst weight (470 mg, 32%). The product was dissolved in methylene chloride (3 mL) and precipitated from methanol (30 mL). The polymer was collected and dried *in vacuo* to constant weight and the polymer yield was determined (440 mg, 30%).

Poly(1-butene carbonate) (CTC-4-237). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.93 – 1.01 ppm (m, 3 equiv), 1.67 (quintet, ^3J = 7.2 Hz, 2 equiv), 4.05 - 4.40 (m, 2 equiv), 4.80 – 4.91 (m, 1 equiv).

Poly(1-hexene carbonate) (CTC-4-235). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.78 – 0.91 ppm (m, 3 equiv), 1.21 – 1.37 (m, 4 equiv), 1.50 – 1.68 (m, 2 equiv), 3.99 – 4.34 (m, 2 equiv), 4.80 – 4.91 (m, 1 equiv).

Poly(vinylethylene carbonate) (CTC-4-230). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.12 – 4.38 (m, 2 equiv), 5.28 – 5.38 (m, 2 equiv), 5.40 – 5.48 (m, 1 equiv), 5.75 – 5.86 (m, 1 equiv).

Poly(3-methoxy-1-propylene carbonate) (CTC-4-223). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.37 (s (broad), 3 equiv), 3.58 (d, ^3J = 5 Hz, 2 equiv), 4.23 – 4.46 (m, 2 equiv), 5.00 – 5.70 (m, 1 equiv).

Poly(3-(benzyloxy)-1-propylene carbonate) (CTC-4-249). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.53 – 3.66 (m, 2 equiv), 3.55 – 3.64 (m, 2 equiv), 4.16 – 4.56 (m, 4 equiv), 7.20 – 7.37 (m, 5 equiv).

Poly(3-tert-butyl-dimethylsilyloxy-1-propylene carbonate) (CTC-4-241). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.05 (s (broad), 6 equiv), 0.88 (s (broad), 9 equiv), 3.75 – 3.81 (m, 2 equiv), 4.17 – 4.50 (m, 2 equiv), 4.87 – 4.93 (m, 1 equiv).

Poly(3-methyacrylate-1-propylene carbonate) (NOV-3-215). ^{1}H NMR (from crude reaction mixture, $CDCl_3$, 300 MHz) δ 1.92 (s (broad), 3 equiv), 4.15 – 4.55 (m, 4 equiv), 5.16 (s (broad), 1 equiv), 5.60 (s (broad), 1 equiv), 6.11 (s (broad), 1 equiv).

***rac*-PO/CHO /CO_2 Terpolymerization (CTC-4-208).** This procedure was carried out according to the representative procedure for the copolymerization of epoxide/CO_2 described above, however **2.3** (23.9 mg, 0.0293 mmol), [PPN]Cl (16.8 mg, 0.0293 mmol), *rac*-PO (0.70 mL, 9.8 mmol) and CHO (1.95 mL, 19.5 mmol) were added to the FPB and stirred for 4 h to yield the product polymer (2.4 g, 64%).

Incorporation of GM in PPC Representative polymerization procedure (NOV-3-207). A FPB was charged with a Teflon stirbar, heated to 150 °C in an oven for 4 h, then moved to a drybox. Once cooled to 22 °C, catalyst **2.3** (11.6 mg, 0.0143 mmol) and [PPN]Cl (8.2 mg, 0.014 mmol) were added to the FPB in the drybox. To a Schlenk tube charged with *rac*-PO (10.0 mL, 143 mmol) was added *rac*-GM (0.390 mL, 2.86 mmol) under N_2. The solution was cooled to 0 °C and 1.0 mL was added to the FPB under N_2. The FBP was pressurized to 100 psi of CO_2 and was left to stir at 22 °C for 1 h. The FPB was vented at 22 °C. A small aliquot of the product mixture was removed from the FPB for ^{1}H NMR analysis. The remaining product mixture was

then dissolved in methylene chloride (5 mL), quenched with 5% HCl solution in methanol (0.2 mL), and precipitated from methanol (30 mL). The polymer was collected and dried *in vacuo* to constant weight and the polymer yield was determined (530 mg, 36%). The polymer was then characterized using ^{1}H NMR spectroscopy and GPC.

A.7 References

(1) Allen, S. D. PhD Dissertation, Cornell University, May **2004** and references therein.

(2) Nozaki, K.; Nakano, K.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 11008-11009.

(3) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Chem. Comm.* **2000**, 2007-2008.