Synthesis of functionalized cyclic carbonate monomers using a versatile pentafluorophenyl carbonate intermediate.

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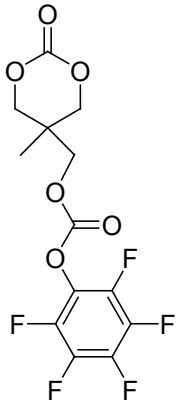
Supplemental Information

Materials: Reagents were available commercially from Aldrich and used as received unless otherwise noted. Bis(pentafluorophenyl)carbonate and 1,3-bis(1,1,1,3,3,3-hexafluoropropan-2-ol-yl)benzene (1,3-HFAB) were obtained from Central Glass Co., Ltd. (Japan). 1,1,1-tris(hydroxymethyl)ethane, cesium fluoride (anhydrous), (-)-sparteine, benzyl alcohol, and all other chemicals were obtained from Aldrich Chemical Co. (-)-sparteine was stirred over CaH_2, vacuum distilled, then stored over molecular sieves (3 Å). 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexyl-2-thiourea (TU) was prepared as previously reported in Pratt *et al. Macromolecules* **2006**, *39*, 7863. 1,3-HFAB was distilled under vacuum, them stored over molecular sieves (3 Å).

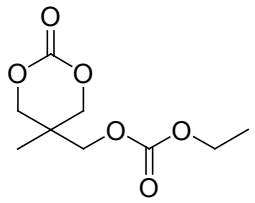
Methods: Melting points of small molecules were determined with a capillary tube melting point apparatus and are uncorrected. ^{19}F-, ^{1}H- and $\{^{1}H\}^{13}$C-NMR spectra were obtained on a Bruker Avance 400 instrument using $CDCl_3$ solutions unless noted otherwise. Gel permeation chromatography (GPC) was performed in THF at 30 °C using a Waters chromatograph equipped with four 5 μm Waters columns (300 mm x 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 10^5, 10^6 Å), a Waters 410 differential refractometer for refractive index (RI) detection and a 996 photodiode array detector, and calibrated with polystyrene standards (750 - (2 x 10^6) g/mol).

Preparation of (5-methyl-2-oxo-1,3-dioxan-5-yl)methyl pentafluorophenyl carbonate (MTC-PFPC) (**1**).



To a 100 mL round bottom flask, 1,1,1-tris(hydroxymethyl)ethane (2.0 g, 16.7 mmol) was combined with bis(pentafluorophenyl)carbonate (15.1 g, 38.3 mmol, 2.3 eq.) and cesium fluoride (0.76 g, 5.0 mmol, 0.3 eq.) in anhydrous tetrahydrofuran (THF) (11.9 mL) and stirred for over night at room temperature. Initially the reaction was heterogeneous, but after one hour the reaction formed a clear homogeneous solution. The reaction was concentrated *in vacuo* (100 mm Hg, 30° C) and the residue was dissolved in methylene chloride (~50 mL). Upon standing (~10 min), the pentafluorophenol byproduct precipitated from solution and was recovered by filtration. The mother liquor was washed with aqueous sodium bicarbonate (3 x 50 mL) until the pH of aqueous layer was ~8 and then with brine (1 x 50 mL). The organic layer was separated and dried over anhydrous sodium sulfate. The solution was concentrated to give the crude product that was purified by recrystallization. The crude product was dissolved in ethyl acetate (24 mL) at 65° C. *n*-Hexane (35 mL) was added at the same temperature, and the resulting solution was allowed to cool to room temperature. After stirring the solution overnight, the white crystalline product MTC-PFPC (**1**) was separated by filtration (4.0 g, 67% yield). m.p. 130-131° C. ^{1}H NMR ($CDCl_3$, 400Hz) 1.22(s, 3H), 4.23(d, 2H, J = 11Hz), 4.37(s, 2H), 4.38(d, 2H, J = 11Hz). ^{19}F NMR($CDCl_3$, 376Hz) -154.3~-154.3(m, 2F), -157.8(t, 1F, *J* = 22Hz), -162.6~-162.7(m, 2F). ^{13}C NMR($CDCl_3$, 100Hz) 16.8, 32.6, 70.3, 73.0, 125.4, 137.9, 140.1, 141.3, 147.4, 151.1. HRMS: $C_{13}H_9F_5O_6$, 356.0319; found, 356.0315.

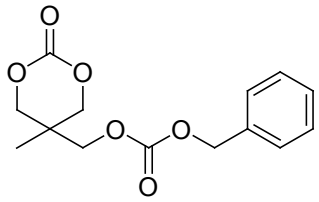
*Preparation of ethyl (5-methyl-2-oxo-1,3-dioxan-5-yl)methyl carbonate (**2a**).*



CsF catalyst: Under a dry nitrogen atmosphere, anhydrous ethanol (0.06 g, 1.26 mmol, 1.5 eq.) was added to the solution of MTC-PFPC (0.3 g, 0.84 mmol) and cesium fluoride (0.038 g, 0.25 mmol, 0.3 eq.) in THF (3 mL). The mixture was stirred for 1 day at room temperature. After the reaction, the solution was concentrated *in vacuo* and redissolved in methylene chloride. Upon standing (~10 min) the pentafluorophenol byproduct precipitated from solution and was removed by filtration. The crude product was purified by column chromatography (ethyl acetate/*n*-hexane = 1/3) to give **2a** as a white crystalline powder (0.11 g, 63% yield). m.p. 68-69° C. ^{1}H NMR($CDCl_3$, 400Hz) 1.15(s, 3H), 1.33(t, 3H, J = 7Hz), 4.14(s, 2H), 4.15(d, 2H, J = 11Hz), 4.23(q, 2H, J = 7Hz), 4.34(d, 2H, J = 11Hz). ^{13}C NMR($CDCl_3$, 100Hz) 14.2, 16.9, 32.3, 64.7, 67.8, 73.3, 147.7, 154.7. HRMS: $C_9H_{14}O_6$, 218.0790; found, 218.0788.

DMAP/pyridine catalyst: The reaction was performed using 1.0 eq. of ethanol and 4-(N,N-dimethylamino)pyridine (0.0031 g, 0.025 mmol, 0.03 eq.)/pyridine (0.67 g, 8.42 mmol, 10 eq.) instead of CsF. The mixture was stirred for 4 hours at room temperature. The reaction was worked up in a similar manner as above to afford **2b** in 93% yield.

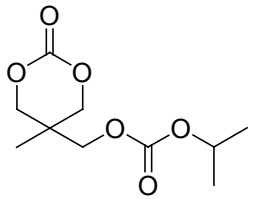
*Preparation of benzyl (5-methyl-2-oxo-1,3-dioxan-5-yl)methyl carbonate (**2b**).*



Pyridine catalyst: Under a dry nitrogen atmosphere, anhydrous benzyl alcohol (0.06 g, 0.55 mmol, 1.0 eq.) was added to the solution of MTC-PFPC (0.2 g, 0.55 mmol) and pyridine (0.04 g, 0.49 mmol, 0.89 eq.) in THF (2 mL). The mixture was stirred for 3 days at 55° C. After the reaction, the solution was concentrated and redissolved in methylene chloride. Upon standing (~10 min) the pentafluorophenol byproduct precipitated from solution. After removal of the byproduct by filtration, the mother liquor was washed with aqueous sodium bicarbonate (pH of aqueous layer ~8) and brine. The organic layer was separated and dried over anhydrous sodium sulfate. The solution was concentrated to give the crude product which was purified by recrystallization (ethyl acetate/*n*-hexane = 1/3) to give **2b** as a white crystalline powder (0.03 g, 20% yield). m.p. 72-75° C. ^{1}H NMR($CDCl_3$, 400Hz) 1.14(s, 3H), 4.13(d, 2H, J = 11Hz), 4.16(s, 2H), 4.32(d, 2H, J = 11Hz), 5.18(s, 2H), 7.38-7.39(m, 5H). ^{13}C NMR($CDCl_3$, 100Hz) 17.0, 32.4, 68.1, 70.3, 73.2, 128.6, 128.7, 128.9, 134.6, 147.5, 154.6. HRMS: $C_{14}H_{16}O_6$, 280.0947; found, 280.0940.

DMAP/pyridine catalyst: The reaction was performed using 4-(N,N-dimethylamino)pyridine (0.0021 g, 0.017 mmol, 0.03 eq) and pyridine (0.44 g, 5.61 mmol, 10 eq) instead of pyridine. The mixture was stirred for 4 hours at room temperature. The reaction was worked up in a similar manner as above to afford **2b** in 77% yield.

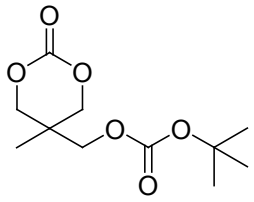
*Preparation of isopropyl (5-methyl-2-oxo-1,3-dioxan-5-yl)methyl carbonate (**2c**).*



CsF catalyst: Under a dry nitrogen atmosphere, anhydrous 2-propanol (0.025 g, 0.42 mmol, 1.5 eq.) was added to the solution of MTC-PFPC (0.1 g, 0.28 mmol) and cesium fluoride (0.013g, 0.084 mmol, 0.3 eq.) in THF (1 mL). The mixture was stirred for 1 day at room temperature. After the reaction, the solution was concentrated and redissolved in methylene chloride. Upon standing (~10 min) the pentafluorophenol byproduct precipitated from solution and was removed by filtration. The solvent was removed *in vacuo* to afford a crude product that was further purified by column chromatography (ethyl acetate/*n*-hexane = 1/3) to give **2c** as a white crystalline powder (0.03 g, 46% yield). m.p. 64~65° C. ^{1}H NMR($CDCl_3$, 400Hz) 1.18(s, 3H), 1.34(d, 6H, J = 6Hz), 4.14(s, 2H), 4.17(d, 2H, J = 11Hz), 4.36(d, 2H, J = 11Hz), 4.92(sep, 1H, J = 6Hz). ^{13}C NMR($CDCl_3$, 100Hz) 17.0, 21.7, 32.4, 67.6, 72.9, 73.3, 147.7, 154.2. HRMS: $C_{10}H_{16}O_6$, 232.0947; found, 232.0945.

DMAP/pyridine catalyst: The reaction was performed using 1.3 eq. of 2-propanol and 4-(N,N-dimethylamino)pyridine (0.0010 g, 0.0084 mmol, 0.03 eq.)/pyridine (0.22 g, 2.81 mmol, 10 eq.) instead of CsF. The mixture was stirred for 5 hours at room temperature. The reaction was worked up in a similar manner as above to afford **2c** in 80% yield.

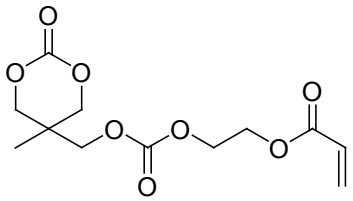
*Preparation of tert-butyl (5-methyl-2-oxo-1,3-dioxan-5-yl)methyl carbonate (**2d**).*



Under a dry nitrogen atmosphere, *tert*-butanol (0.062 g, 0.84 mmol, 3.0 eq.) was added to the solution of MTC-PFPC (0.1 g, 0.28 mmol) and cesium fluoride (0.013g, 0.084 mmol, 0.3 eq.) in THF (1 mL). The mixture was stirred for 3 days at room temperature. After the reaction, the solution was concentrated and redissolved in methylene chloride. Upon standing (~10 min) the pentafluorophenol byproduct precipitated from solution and was removed by filtration. The solvent was removed *in vacuo* to afford a 0 % yield of **2d**.

DMAP/pyridine catalyst: The reaction was performed using 1.3 eq. of *tert*-butanol and 4-(N,N-dimethylamino)pyridine (0.0010 g, 0.0084 mmol, 0.03 eq.)/pyridine (0.22 g, 2.81 mmol, 10 eq.) instead of CsF. The mixture was stirred for 1 day at room temperature. The reaction was worked up in a similar manner as above to afford **2d** in 0% yield.

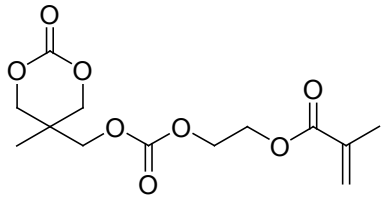
*Preparation of 2-(((5-methyl-2-oxo-1,3-dioxan-5-yl)methoxy)carbonyloxy)ethyl acrylate (**2e**).*



DMAP/pyridine catalyst: Under a dry nitrogen atmosphere, 2-hydroxyethyl acrylate (0.18 g, 1.4 mmol, 1.0 eq.) was added to the solution of MTC-PFPC (0.5 g, 1.4 mmol) and 4-(N,N-dimethylamino)pyridine (0.0051 g, 0.042 mmol, 0.03 eq.)/pyridine (1.11 g, 0.014 mmol, 10 eq.) in THF (1.4 mL). The mixture was stirred for 3 hours at room temperature. After the reaction, the solution was concentrated to afford a crude product

that was further purified by column chromatography (ethyl acetate/*n*-hexane = 1/2) to give **2e** as a white crystalline powder (0.22 g, 55% yield). ^{1}H NMR($CDCl_3$, 400Hz) 1.16(s, 3H), 4.16(d, 2H, *J* = 11Hz), 4.17 (s, 2H), 4.34(d, 2H, *J* = 11Hz), 4.41 (bs, 4H), 5.89(dd, 1H, *J* =10, 1Hz), 6.16(dd, 1H, *J* = 17, 10Hz), 6.46(dd, 1H, *J* = 17, 1Hz). ^{13}C NMR($CDCl_3$, 100Hz) 16.7, 32.2, 61.7, 66.0, 68.1, 73.0, 127.6, 131.6, 147.4, 154.4, 165.6. HRMS: $C_{12}H_{16}O_8$, 288.0845; found, 288.0841.

*Preparation of 2-(((5-methyl-2-oxo-1,3-dioxan-5-yl)methoxy)carbonyloxy)ethyl methacrylate (**2f**).*

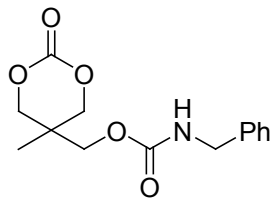


CsF catalyst: Under a dry nitrogen atmosphere, 2-hydroxyethyl methacrylate (0.037 g, 0.28 mmol, 1.0 eq.) was added to the solution of MTC-PFPC (0.1 g, 0.28 mmol) and cesium fluoride (0.013 g, 0.084 mmol, 0.3 eq.) in THF (1 mL). The mixture was stirred for 3 days at room temperature. After the reaction, the solution was concentrated and redissolved in methylene chloride. Upon standing (~10 min) the pentafluorophenol byproduct precipitated from solution and was removed by filtration. The solvent was removed *in vacuo* to afford a crude product that was further purified by column chromatography (ethyl acetate/*n*-hexane = 1/3) to give **2f** as a white crystalline powder (0.03 g, 35% yield). ^{1}H NMR($CDCl_3$, 400Hz) 1.16(s, 3H), 1.96(s, 3H), 4.16(d, 2H, *J* = 11Hz), 4.17 (s, 2H), 4.34(d, 2H, *J* = 11Hz), 3.39~4.43(m, 2H), 5.63(bs, 1H), 6.15(s, 1H). ^{13}C NMR($CDCl_3$, 100Hz) 17.0, 18.3, 32.4, 62.0, 66.2, 68.2, 73.2, 126.4, 135.7, 147.5, 154.6, 167.1. HRMS: $C_{13}H_{18}O_8$, 302.1002; found, 302.0998.

DMAP/pyridine catalyst: The reaction was performed using 4-(N,N-dimethylamino)pyridine (0.001 g, 0.0084 mmol, 0.03 eq.)/pyridine (0.22 g, 2.81 mmol,

10 eq.) instead of CsF. The mixture was stirred for 2 hours at room temperature. The reaction was worked up in a similar manner as above to afford **2f** in 64% yield.

*Preparation of (5-methyl-2-oxo-1,3-dioxan-5-yl)methyl benzylcarbamate (**2g**).*

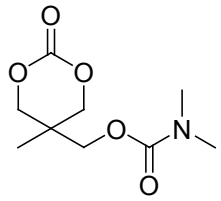


CsF catalyst: Under a dry nitrogen atmosphere, anhydrous benzyl amine (0.039 g, 0.37 mmol, 1.32 eq.) was added to the solution of MTC-PFPC (0.1g, 0.28 mmol) and cesium fluoride (0.013 g, 0.084 mmol, 0.3 eq.) in THF (1 mL). The mixture was stirred for 1 day at room temperature. After the reaction, the solution was concentrated and redissolved in methylene chloride. Upon standing (~10 min) the pentafluorophenol byproduct fell out of solution and was removed by filtration. The solvent was removed *in vacuo* to afford a crude product that was fnurther purified by column chromatography (ethyl acetate/*n*-hexane = 1/1) to give **2g** as a colorless oil (0.044g, 56% yield). ^{1}H NMR($CDCl_3$, 400Hz) 1.11(s,3H), 4.14(d, 2H, J = 11Hz), 4.15(s, 2H), 4.32(d, 2H, *J* = 11Hz), 4.38(d, 2H, *J* = 6Hz), 6.23 (bs, 1H), 7.28-7.36(m, 5H). ^{13}C NMR($CDCl_3$, 100Hz) 17.1, 32.4, 45.2, 66.1, 73.9, 127.6, 127.7, 128.7, 138.0, 148.0, 155.7. HRMS: $C_{14}H_{17}NO_5$, 279.1107; found, 279.1101.

DMAP/pyridine catalyst: The reaction was performed using 1.0 eq. of benzyl amine and 4-(N,N-dimethylamino)pyridine (0.03 eq.)/pyridine (10 eq.) instead of CsF. The mixture was stirred for 4 hours at room temperature. The reaction was worked up in a similar manner as above to afford **2g** in 0% yield.

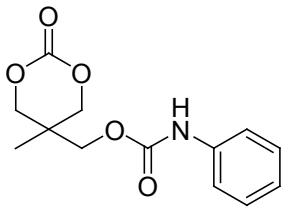
No catalyst: The reaction was performed using 1.1 eq. of benzyl amine without any additional catalyst. The mixture was stirred for 1 day at room temperature. The reaction was worked up in a similar manner as above to afford **2g** in 84% yield.

*Preparation of (5-methyl-2-oxo-1,3-dioxan-5-yl)methyl diethylcarbamate (**2h**).*



Under a dry nitrogen atmosphere, dimethyl amine (0.043 g, 0.590 mmol, 1.05 eq.) was added to the solution of MTC-PFPC (0.2 g, 0.56 mmol), 4-(*N,N*-dimethylamino)pyridine (0.021 g, 0.17 mmol, 0.03 eq.), and pyridine (0.44 g, 5.61 mmol, 10 eq.) in THF (1 mL). The mixture was stirred for 6 h at room temperature. After the reaction, the solution was concentrate to afford a crude product that was further purified by column chromatography (ethyl acetate/*n*-hexane = 1/1) to give **2h** as a colorless oil (0.10 g, 64% yield). ^{1}H NMR($CDCl_3$, 400Hz): 1.14(t, 6H, J = 7Hz), 1.15(s, 3H), 3.25(q, 2H, J = 7Hz), 3.31(q, 2H, J = 7Hz), 4.10(s, 2H), 4.15(d, 2H, J = 11Hz), 4.33(d, 2H, J = 11Hz) . ^{13}C NMR($CDCl_3$, 100Hz): 13.2, 14.0, 17.0, 32.3, 41.2, 41.9, 65.7, 73.6, 147.7, 154.8. HRMS: $C_9H_{15}NO_5$, 245.1263; found, 245.1265.

*Preparation of (5-methyl-2-oxo-1,3-dioxan-5-yl)methyl phenylcarbamate (**2i**).*



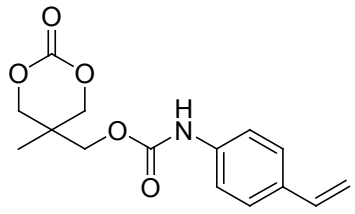
DMAP/pyridine catalyst: Under a dry nitrogen atmosphere, aniline (0.13 g, 0.0014 mmol, 1.0 eq.) was added to the solution of MTC-PFPC (0.5 g, 0.0014 mmol) and 4-(N,N-dimethylamino)pyridine (0.0051 g, 0.042 mmol, 0.03 eq.)/pyridine (1.11 g, 0.014 mmol, 10 eq.) in THF (2 mL). The mixture was stirred for 3 hours at room temperature. After the reaction, the solution was concentrated to afford a crude product that was

further purified by column chromatography (ethyl acetate/*n*-hexane = 1/1) to give **2i** as a colorless oil (0.30 g, 80% yield). ^{1}H NMR($CDCl_3$, 400Hz) 1.15(s, 3H), 4.19(d, 2H, *J* = 11Hz), 4.21(s, 2H), 4.38(d, 2H, *J* = 11Hz), 6.94(bs, 1H), 7.10(t, 1H, *J* = 7Hz), 7.30-7.40(m, 4H). ^{13}C NMR($CDCl_3$, 100Hz) 17.1, 32.4, 65.8, 73.8, 118.8, 123.8, 129.1, 137.4, 148.2, 152.7. HRMS: $C_{13}H_{15}NO_5$, 265.0950; found, 265.0952.

*Preparation of (5-methyl-2-oxo-1,3-dioxan-5-yl)methyl benzyl(ethyl)carbamate (**2j**).*

DMAP/pyridine catalyst: Under a dry nitrogen atmosphere, anhydrous *N*-ethyl-*N*-benzyl amine (0.088 g, 0.73 mmol, 1.3 eq.) was added to the solution of MTC-PFPC (0.2 g, 0.56 mmol) and 4-(N,N-dimethylamino)pyridine (0.0034 g, 0.028 mmol, 0.05 eq.)/pyridine (0.44 g, 5.61 mmol, 10 eq.) in THF (3 mL). The mixture was stirred for 16 days at room temperature. After the reaction, the solution was concentrated to give a 0% yield of **2j**.

*Preparation of (5-methyl-2-oxo-1,3-dioxan-5-yl)methyl 4-vinylphenylcarbamate (**2k**).*

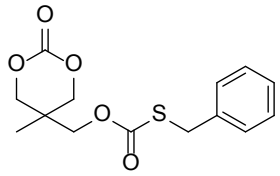


Under a dry nitrogen atmosphere, 4-vinylaniline (0.87 g, 7.3 mmol, 1.3 eq.) was added to the solution of MTC-PFPC (2.0 g, 5.6 mmol) and cesium fluoride (0.26 g, 1.7 mmol, 0.3 eq.) in THF (11.2 mL). The mixture was stirred for 2 days at room temperature. The solution was concentrated and the residue was redissolved in methylene chloride. Upon standing (~10 min) the pentafluorophenol byproduct precipitated from solution. After removal of the byproduct by filtration, the mother liquid was washed with aqueous sodium bicarbonate (pH of aqueous layer; ~8) and brine. The organic layer was separated and dried over anhydrous sodium sulfate. The solution was concentrated to

give the crude product which was purified by recrystallization from toluene (40 mL) to give **2k** as a crystalline powder (1.3 g, 81% yield). m.p. 120~121° C. ^{1}H NMR($CDCl_3$, 400Hz) 1.14(s, 3H), 4.19(d, 2H, *J* = 11Hz), 4.21(s, 2H), 4.38(s, 2H, *J* = 11Hz), 5.20(d, 1H, *J* = 11Hz), 5.68(d, 1H, *J* = 18Hz), 6.67(dd, 1H, *J* = 18, 11Hz), 6.98 (bs, 1H), 7.36(s, 4H). ^{13}C NMR($CDCl_3$, 100Hz) 17.0, 32.4, 65.8, 73.8, 112.9, 118.7, 126.9, 133.2, 136.0, 137.0, 148.3, 152.7. HRMS: $C_{15}H_{17}NO_5$, 291.1107; found, 291.1101.

DMAP/pyridine catalyst: The reaction was performed using 1.0 eq. of 4-vinylaniline and 4-(N,N-dimethylamino)pyridine (0.03 eq.)/pyridine (10 eq.) instead of CsF. The mixture was stirred for 3 hours at room temperature. The reaction was worked up in a similar manner as above to afford **2k** in 63% yield.

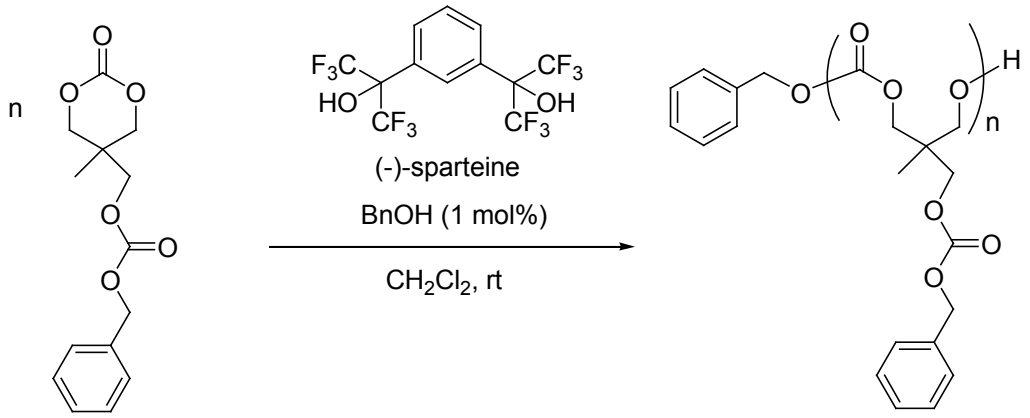
*Preparation of O-(5-methyl-2-oxo-1,3-dioxan-5-yl)methyl benzyl thiocarbonate (**2l**).*



Under a dry nitrogen atmosphere, benzyl thiol (0.349 g, 2.8 mmol) was added to the solution of MTC-PFPC (1.0 g, 2.8 mmol), 4-(N,*N*-dimethylamino)pyridine (0.2 g, 1.6 mmol) and pyridine (2 mL) in THF (10 mL). The mixture was stirred for 3 hours at room temperature. The solution was concentrated to afford a crude product that was further purified by column chromatography (ether) to give 0.64 g (77%) **2l** as a crystalline white powder ^{1}H NMR($CDCl_3$, 400Hz): 1.14(s, 3H), 4.15(m, 4H), 4.18(s, 2H), 4.26(s, 2H), 4.31(d, 2H, J = 11Hz), 7.33(m, 5H) ^{13}C NMR($CDCl_3$, 100Hz): 16.9, 32.4, 34.5, 67.6, 73.1, 122.6, 123.7, 129.6, 135.0, 139.2, 147.4, 148.3, 170.0. HRMS: $C_{14}H_{15}O_5S$, 296.0718; found, 296.0717.

Polymerization examples

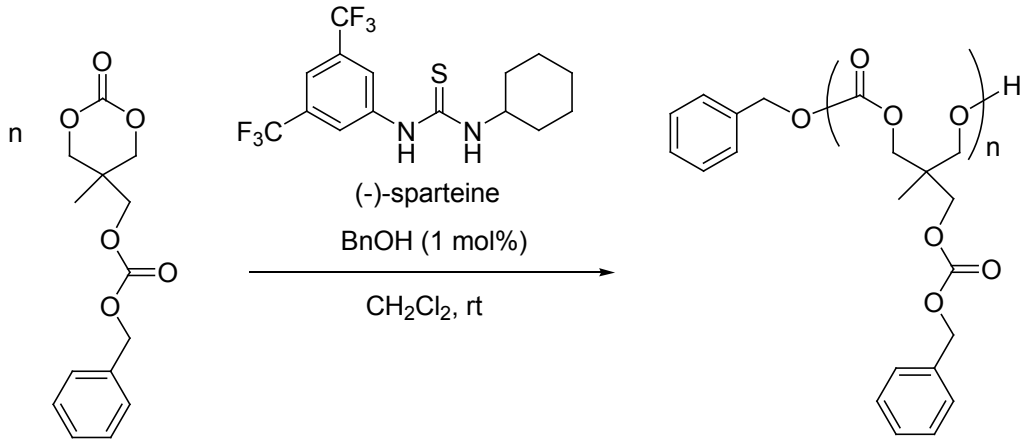
*Preparation of polymer **3a** by ring opening polymerization of **2b**.*



2b **3a**

Under a dry atmosphere, **2b** (0.28 g, 1.0 mmol), 1,3-bis(1,1,1,3,3,3-hexafluoro-2-hydroxy-prop-2-yl)benzene (0.041 g, 0.10 mmol, 0.10 eq), (-)-sparteine (23 microliters, 0.10 mmol, 0.10 eq.), benzyl alcohol (11 microliter, 0.01 mmol, 0.01 eq.), and methylene chloride (0.5 mL, 2.0M) were combined in a flask and stirred for 1 day at room temperature. ^{1}H NMR revealed the conversion to be >95%. The polymer **3a** was precipitated in *n*-hexane. M_n = 3390 g/mol. PDI = 1.81.

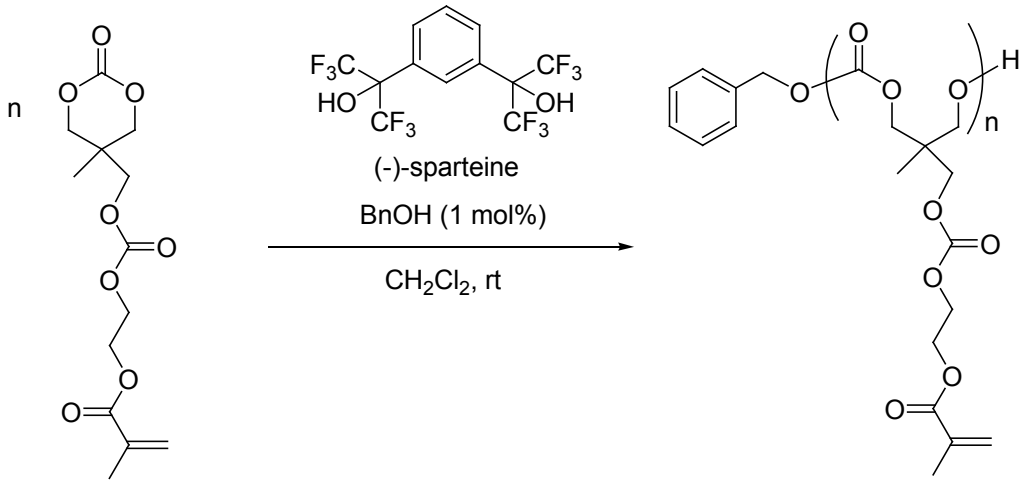
*Preparation of polymer **3b** by ring opening polymerization of **2b**.*



2b **3a**

Under a dry atmosphere, **2b** (0.21 g, 0.75 mmol), 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexyl-2-thiourea (0.015 g, 0.037 mmol, 0.05 eq), (-)-sparteine (4.2 mg, 0.018 mmol, 0.02 eq.), benzyl alcohol (0.8 mg, 0.007 mmol, 0.01 eq.), and methylene chloride (2.0M) were combined in a flask and stirred for 1 day at room temperature. ^{1}H NMR revealed the conversion to be 91%. The polymer **3b** was precipitated in *n*-hexane. M_n = 3500 g/mol. PDI = 2.32.

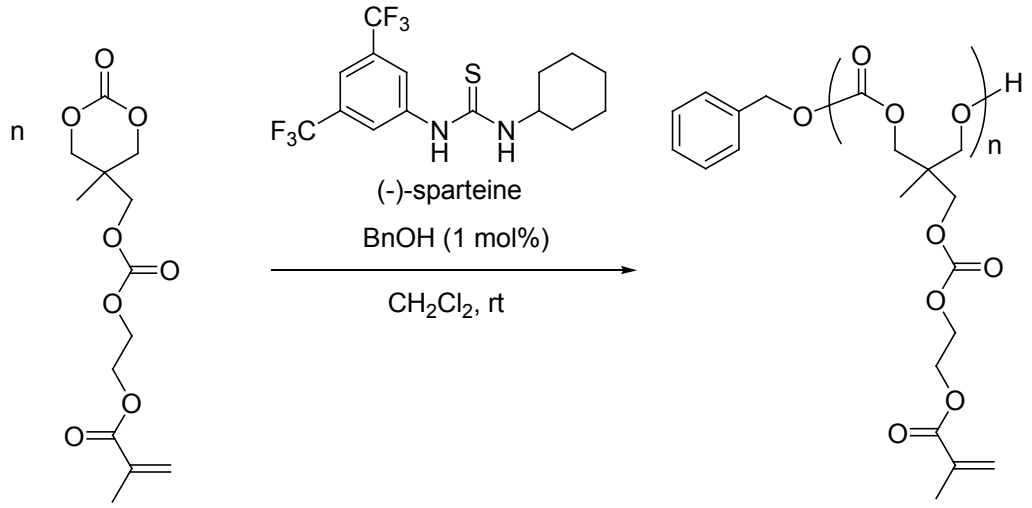
*Preparation of polymer **3c** by ring opening polymerization of **2f**.*



2f **3c**

Under a dry atmosphere, **2f** (0.12 g, 0.39 mmol), 1,3-bis(1,1,1,3,3,3-hexafluoro-2-hydroxy-prop-2-yl)benzene (0.016 g, 0.039 mmol, 0.10 eq), (-)-sparteine (9 microliters, 0.039 mmol, 0.10 eq.), benzyl alcohol (0.4 microliter, 0.0039 mmol, 0.01 eq.), and methylene chloride (0.2 mL, 2M) were combined in a flask and stirred for 1 day at room temperature. ^{1}H NMR revealed the conversion to be >95%. The polymer **3c** was precipitated in *n*-hexane. M_n = 4830 g/mol. PDI = 1.65.

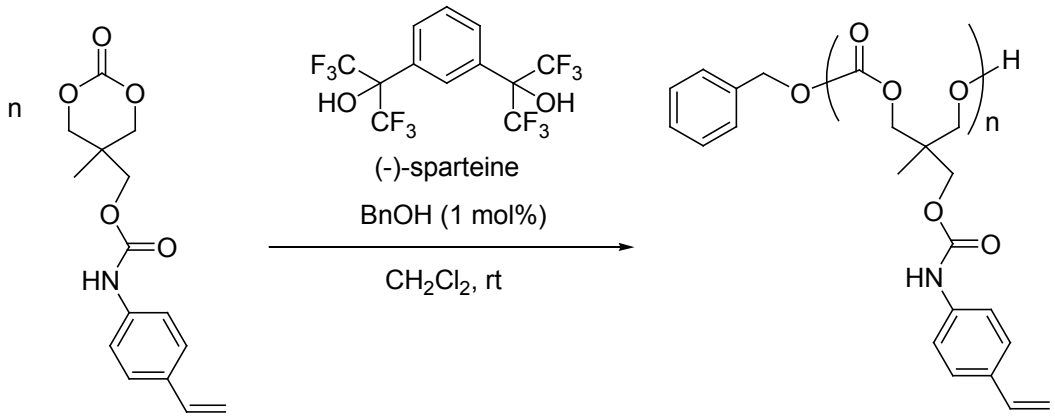
*Preparation of polymer **3d** by ring opening polymerization of **2f**.*



2f **3d**

Under a dry atmosphere, **2f** (0.23 g, 0.75 mmol), 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexyl-2-thiourea (0.016 g, 0.039 mmol, 0.05 eq), (-)-sparteine (4.2 microliters, 0.018 mmol, 0.02 eq.), benzyl alcohol (0.8 microliter, 0.0077 mmol, 0.01 eq.), and methylene chloride (0.4 g, 0.05M) were combined in a flask and stirred for 1 day at room temperature. ^{1}H NMR revealed the conversion to be 94%. The polymer **3d** was precipitated in *n*-hexane. M_n = 3350 g/mol. PDI = 1.66.

*Preparation of polymer **3e** by ring opening polymerization of **2k**.*

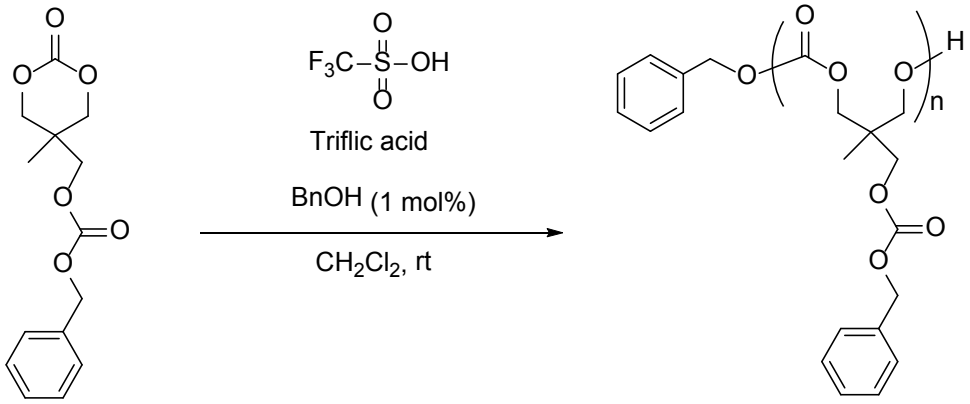


2k **3e**

Under a dry atmosphere, **2k** (296 mg, 0.924 mmol), 1,3-bis(1,1,1,3,3,3-hexafluoro-2-hydroxy-prop-2-yl)benzene (19 mg, 0.046 mmol, 0.05 eq), (-)-sparteine (11 microliters, 0.046 mmol, 0.05 eq.), benzyl alcohol (0.97 microliter, 0.009 mmol, 0.01 eq.), and methylene chloride (2 mL, 0.5M) were combined in a flask and stirred for 3 days at room temperature. ^{1}H NMR revealed the conversion to be >95%. The polymer **3e** was precipitated in methanol. M_n = 4270 g/mol. PDI = 1.62.

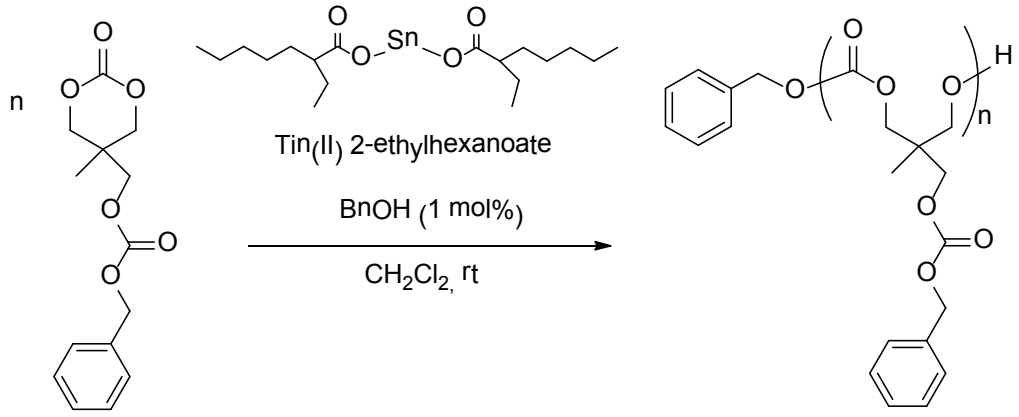
Representative Alternate Polymerization Procedures

Acid Catalysis



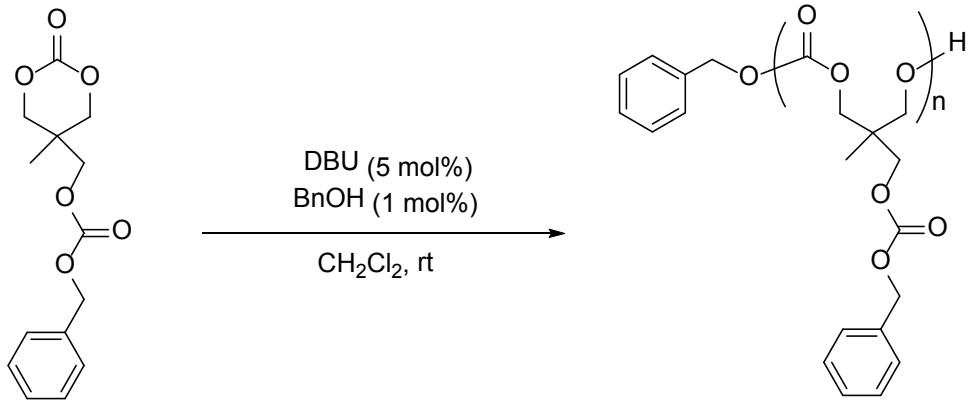
Under a dry atmosphere, **2b** (0.21 g, 0.75 mmol), triflic acid (5.5 mg, 0.037 mmol, 0.05 eq), benzyl alcohol (0.8 mg, 0.007 mmol, 0.01 eq.), and methylene chloride (2.0M) were combined in a flask and stirred for 1 day at room temperature. ^{1}H NMR revealed the conversion to be 98%. Characterization using GPC showed a polymodal distribution.

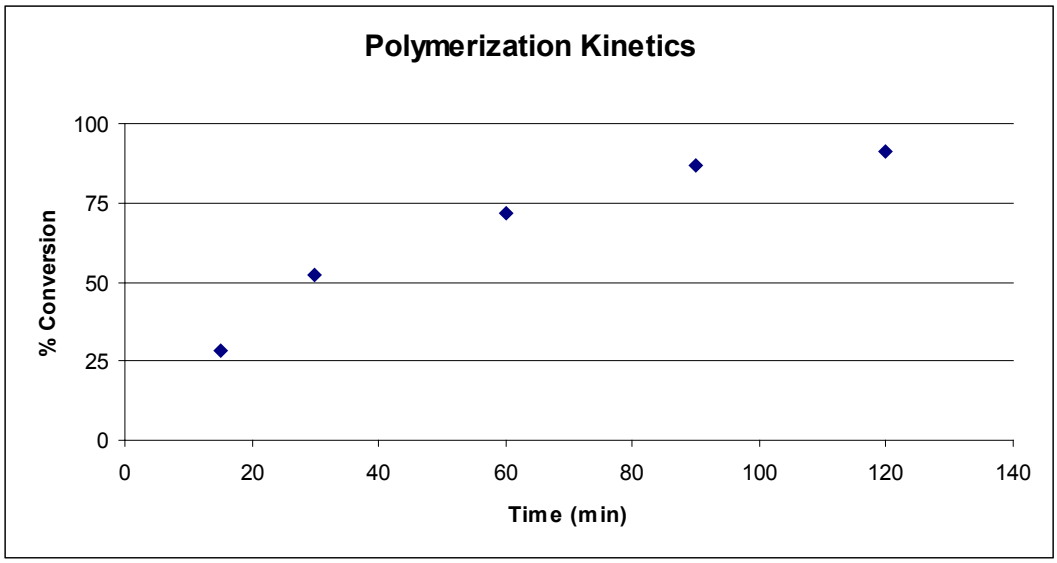
Organometallic Catalysis



Under a dry atmosphere, **2b** (0.21 g, 0.75 mmol), Tin(II) 2-ethylhexanoate (5.5 mg, 0.037 mmol, 0.05 eq), benzyl alcohol (0.8 mg, 0.007 mmol, 0.01 eq.), and toluene (2.0M) were combined in a flask and stirred for 1 day at 100ºC. ^{1}H NMR revealed the conversion to be 96%. Characterization using GPC showed a polymodal distribution.

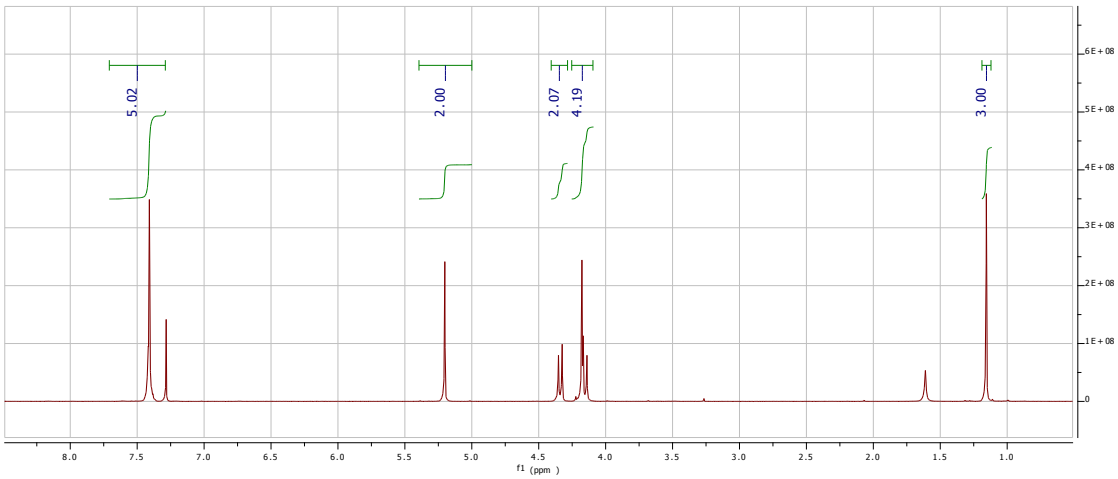
Representative Polymerization Kinetics



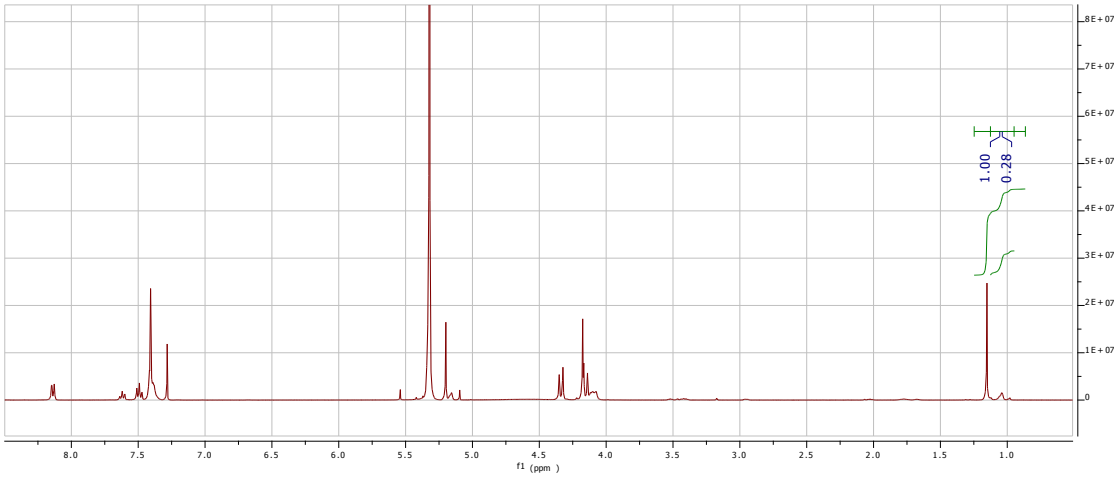


NMR Spectra at Various Time Points

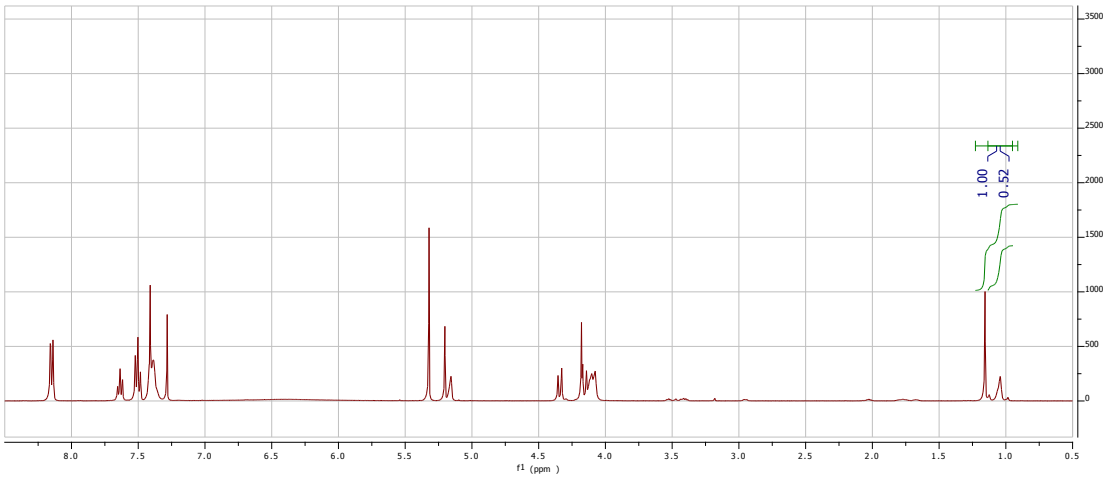
$t = 0$ min



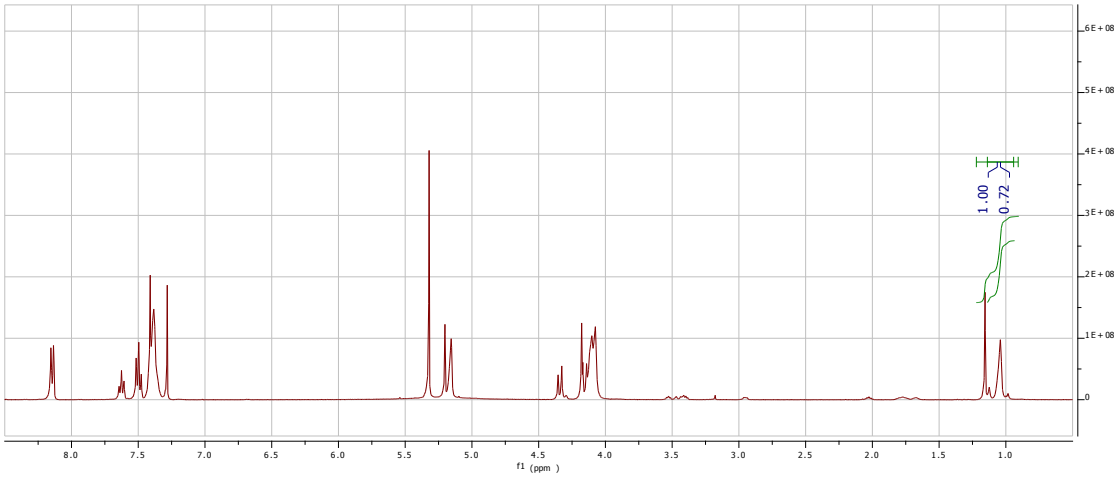
t = 15 min



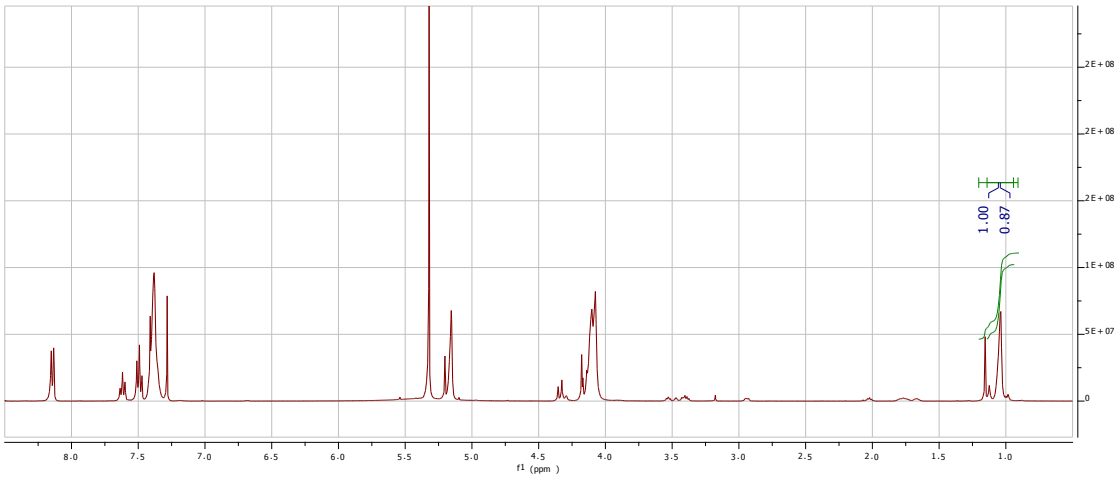
t = 30 min



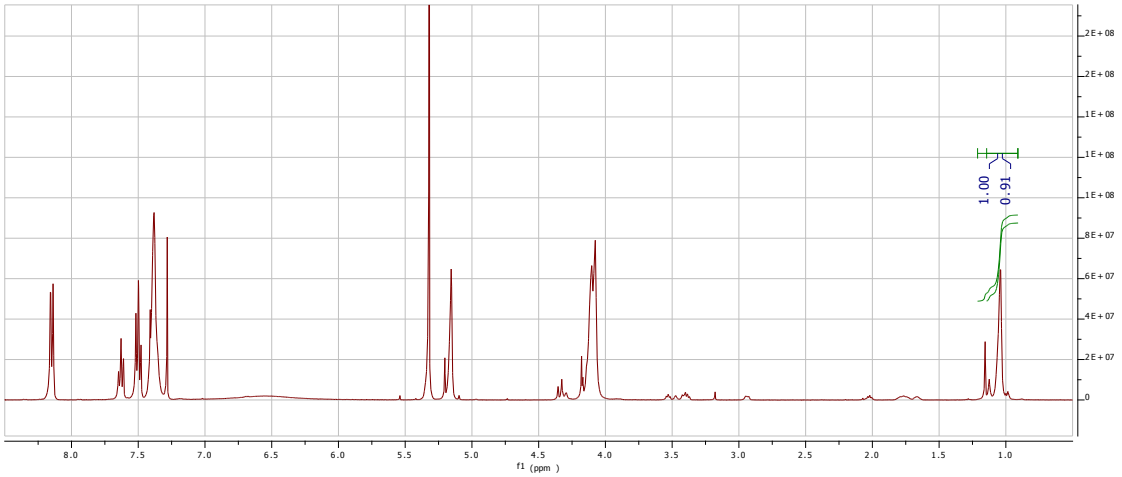
t = 60 min



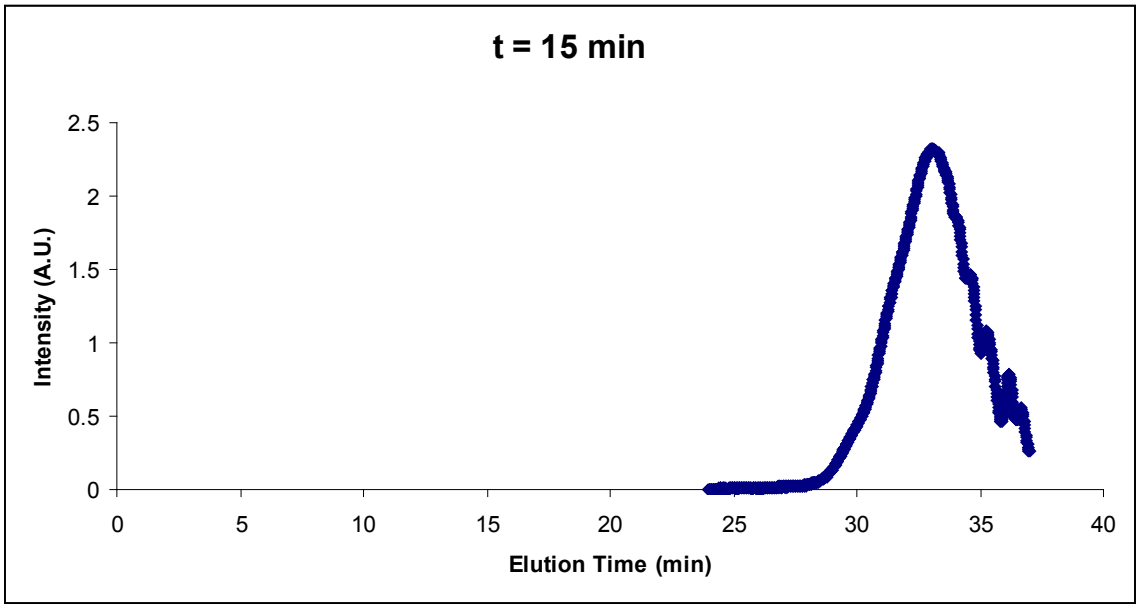
t = 90 min



t = 120 min



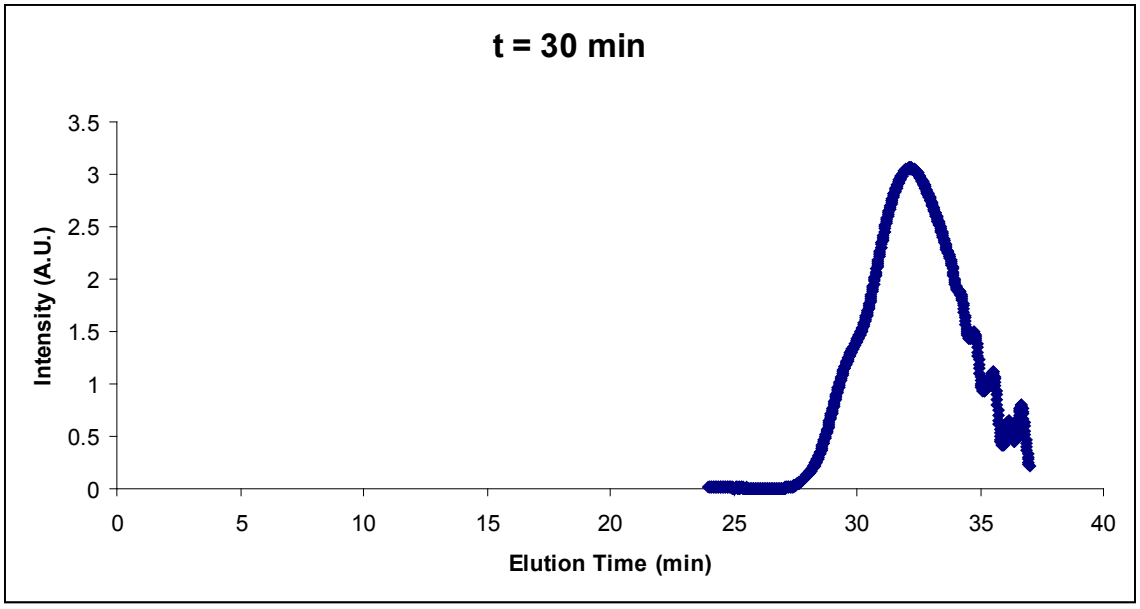
Molecular Weight Characterization



Mn – 2.75 kDa

PDI – 1.37

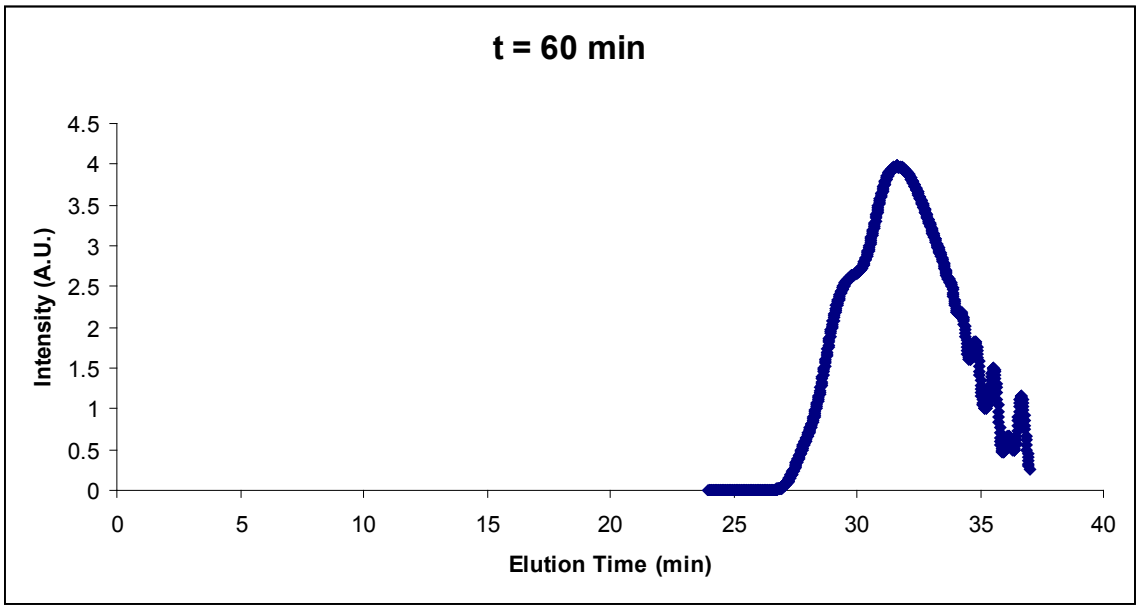
Conversion – 28 %



Mn – 3.44 kDa

PDI – 1.67

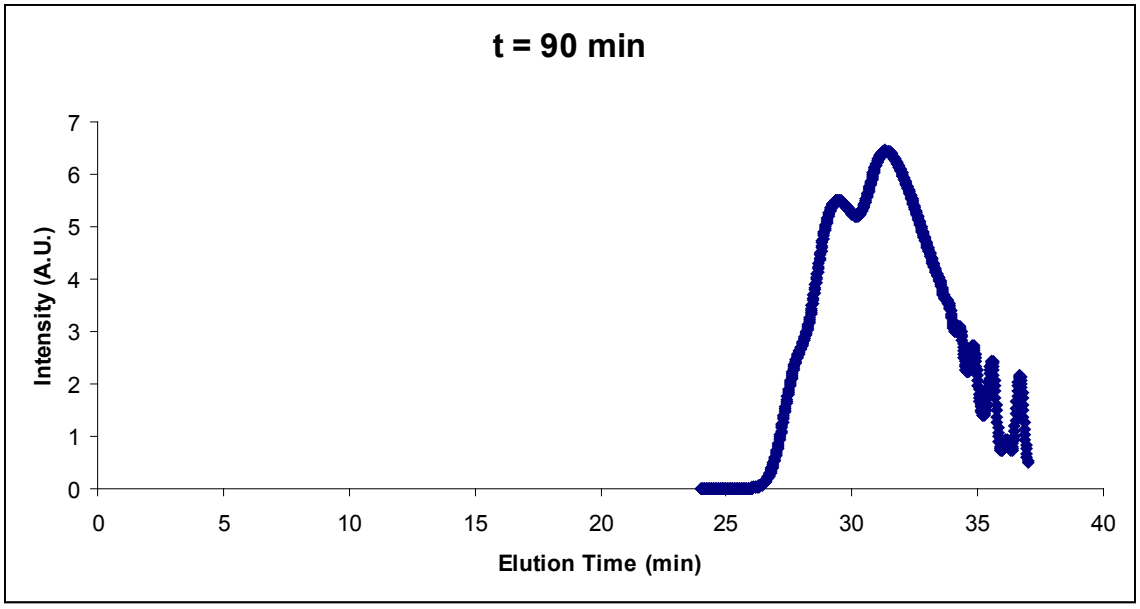
Conversion – 52 %



Mn – 5.22 kDa

PDI – 1.67

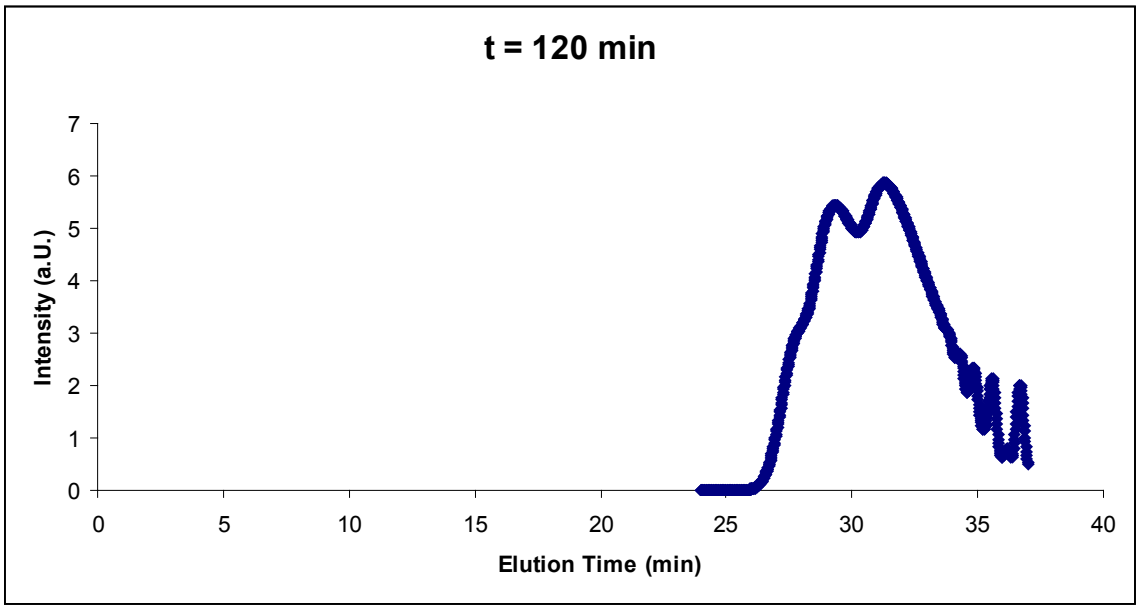
Conversion – 72 %



Mn – 6.38 kDa

PDI – 2.04

Conversion – 87 %



Mn – 6.38 kDa

PDI – 2.04

Conversion – 87 %