Electronic Supplementary Information

Titanium complexes bearing oxa- and azacalix[4, 6]arenes: structural studies and use in the ring opening homo-/co-polymerization of cyclic esters.

Tian Xing,[a] Timothy J. Prior,[a] Kai Chen,[b] and Carl Redshaw[a*]

[a] *Plastics Collaboratory, Department of Chemistry, University of Hull, Cottingham Road, Hull, HU6 7RX, UK.*

[b] *Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, P. R. China.*

Crystallographic data

Bond lengths and angles for **1-7.**

ROP studies

Figure S1. Mass spectrum of PCL synthesized with **4**/BnOH (run 10, Table 1).

Figure S2. Mass spectrum of PVL synthesized with **7**/BnOH (run 13, Table 2).

Figure S3. Mass spectrum of PLA synthesized with **3**/BnOH (run 3, Table 3).

Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PCL synthesized with **1**/BnOH (run 17, Table 1).

Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PVL synthesized with **5**/BnOH (run 11, Table 2).

Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PLA synthesized with **2**/BnOH (run 2, Table 3).

Figure S7. ^1H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PLA-PCL synthesized with **4**/BnOH (run 4, Table 4).

Figure S8. 2D J-resolved ^1H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PLA synthesized with **1**/BnOH (run 1, Table 3).

Figure S9. Carbonyl range of ^{13}C NMR spectrum ($CDCl_3$, 25 ºC) of PLA-PCL co-polymer. Triads have been assigned according to the literature.

Equation S1. Determination of number-average sequence length for CL

Equation S2. Determination of number-average sequence length for LA.

Figure S10. Picture of complex **1-7**.

Crystallographic data

Selected bond lengths (Å) and angles (º):

For **1**·3.5MeCN: O(1)-Ti(1) 1.828(3), O(3)-Ti(1) 1.844(3), O(4)-Ti(2) 2.029(3), O(4)-Ti(1) 2.070(3), O(5)-Ti(2) 1.877(3), O(7)-Ti(2) 1.821(3), O(8)-Ti(2) 2.019(3), O(8)-Ti(1) 2.081(3), O(9)-Ti(1) 1.796(3), O(10)-Ti(2) 1.764(3), Ti(2)-O(4)-Ti(1) 106.35(13), Ti(2)-O(8)-Ti(1) 106.31(13), O(9)-Ti(1)-O(1) 99.39(14), O(9)-Ti(1)-O(3) 99.09(13), O(1)-Ti(1)-O(3) 102.70(13), O(9)-Ti(1)-O(4) 94.94(12) O(1)-Ti(1)-O(4) 159.26(12), O(3)-Ti(1)-O(4) 89.65(12).

For **2**·MeCN: O(9)-Ti(1) 2.313(6), O(1)-Ti (1) 1.785(3), O(2)-Ti (2) 1.814(3), O(3)-Ti (2) 1.818(3), O(4)-Ti(2) 1.803(3), O(5)-Ti(1) 1.788(3), O(10)-Ti(1) 1.890(3), O(6)-Ti(1) 2.032(3), C(1)-O(1)-Ti(1) 152.1(3), C(12)-O(2)-Ti(2) 147.4(3), C(23)-O(3)-Ti(2) 155.7(3), C(35)-O(4)-Ti(2) 163.6(3), C(46)-O(5)-Ti(1) 163.4(3), C(57)-O(6)-Ti(1) 122.3(2), O(1)-Ti(1)-O(5) 103.74(15), O(1)-Ti(1)-O(10) 95.97(14), O(5)-Ti(1)-O(10) 105.68(14), O(1)-Ti(1)-O(6) 95.53(12), O(5)-Ti(1)-O(6) 95.36(13), O(10)-Ti(1)-O(6) 152.80(12).

For **3**·2.5MeCN: Ti(1)-O(2) 1.762(2), Ti(1)-O(3) 1.822(2), Ti(1)-F(1) 1.8342(19), Ti(1)-F(14) 2.0018(18), Ti(1)-F(3) 2.0315(19), Ti(1)-F(2) 2.0326(19), Ti(2)-F(6) 1.771(2), Ti(2)-F(5) 1.780(2), Ti(2)-F(4) 1.781(2), Ti(2)-F(3) 1.944(2), Ti(2)-F(8) 1.9679(18), Ti(2)-F(12) 1.988(2), O(2)-Ti(1)-O(3) 95.06(11), O(2)-Ti(1)-F(1) 98.77(10), O(3)-Ti(1)-F(1) 97.97(9), O(2)-Ti(1)-F(14) 94.02(9), O(3)-Ti(1)-F(14) 91.73(9), F(1)-Ti(1)-F(14) 163.16(9), O(2)-Ti(1)-F(3) 87.41(10), O(3)-Ti(1)-F(3) 175.51(9), F(1)-Ti(1)-F(3) 85.33(8), F(6)-Ti(2)-F(5) 97.59(10), F(6)-Ti(2)-F(4) 96.63(10), F(5)-Ti(2)-F(4) 95.67(10), F(6)-Ti(2)-F(3) 167.61(9).

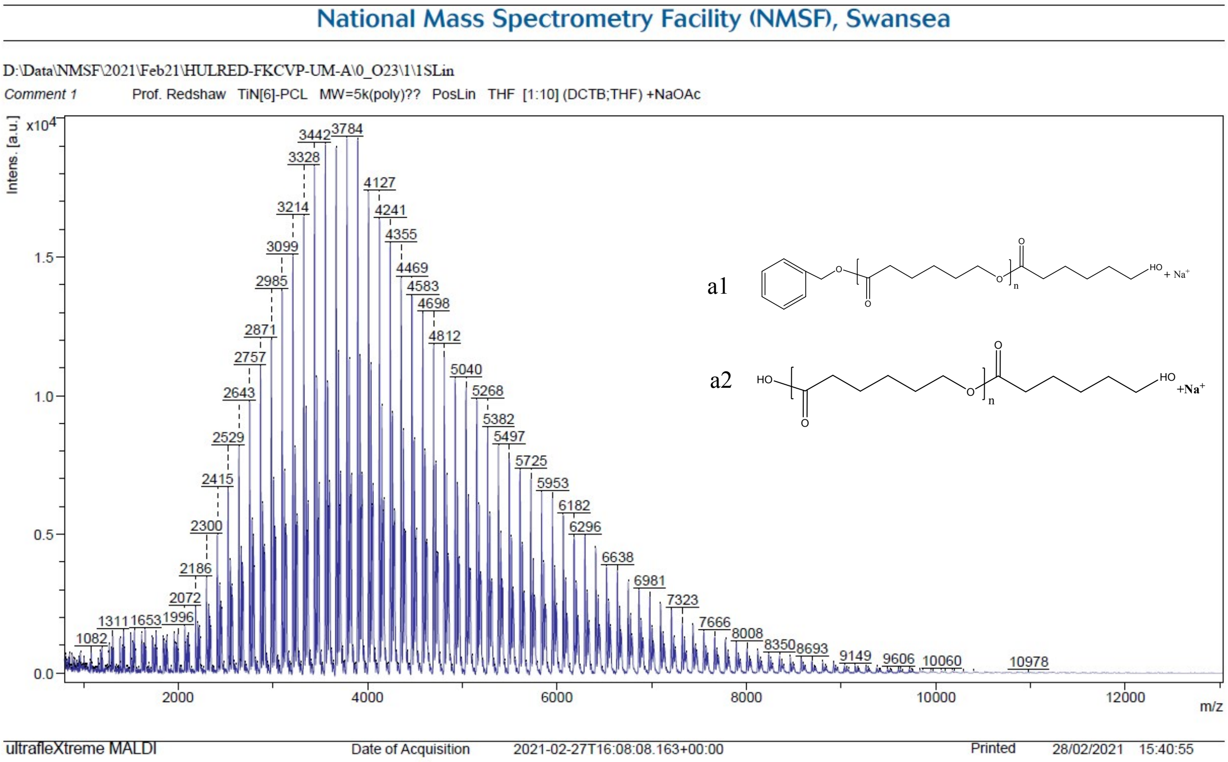
For **4**·3.5MeCN**:** O(1)-Ti(1) 1.8975(11), O(3)-Ti(2) 1.8341(11), O(4)-Ti(2) 1.8809(11), O(6)-Ti(1) 1.8324(11), O(7)-Ti(1) 1.8202(10), O(7)-Ti(2) 1.8245(10), Cl(1)-Ti(1) 2.4861(5), Cl(2)-Ti(1) 2.4311(5), Cl(3)-Ti(2) 2.4104(4), Cl(4)-Ti(2) 2.4863(5), Ti(1)-O(8) 2.1445(12), Ti(2)-O(9) 2.1570(11), Ti(1)-O(7)- Ti(2) 168.84(6), O(7)- Ti(1)-O(6) 99.11(5), O(7)-Ti(1)-O(1) 92.62(5), O(6)-Ti(1)-O(1) 98.13(5), O(7)-Ti(1)-O(8) 85.85(5), O(6)-Ti(1)-O(8) 172.84(5), O(1)-Ti(1)-O(8) 86.74(5) O(7)-Ti(1)-Cl(2) 170.03(4), O(6)-Ti(1)-Cl(2) 90.54(4), O(1)-Ti(1)-Cl(2) 88.45(3) O(8)-Ti(1)-Cl(2) 84.32(4).

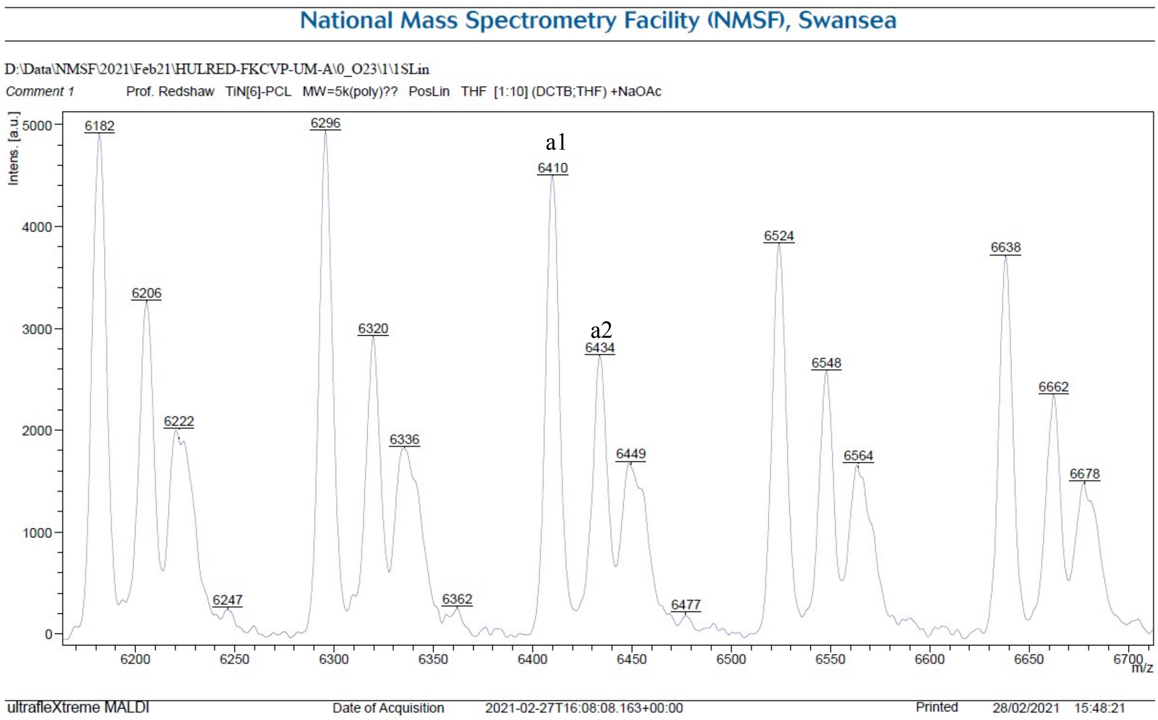
For **5**·4.5MeCN: O(1)-Ti(1) 1.883(3), O(3)-Ti(2) 1.825(3), O(4)-Ti(2) 1.869(3), O(6)-Ti(1) 1.828(3), O(7)-Ti(2) 1.817(3), O(7)-Ti(1) 1.817(3), Br(1)-Ti(1) 2.6748(8), Br(2)-Ti(1) 2.6040(9), Br(3)-Ti(2) 2.5796(9), Br(4)-Ti(2) 2.6647(9), Ti(1)-O(8) 2.134(3), Ti(2)-O(9) 2.152(3), Ti(2)-O(7)-Ti(1) 172.65(17), O(7)-Ti(1)-O(6) 100.63(13), O(7)-Ti(1)-O(1) 94.90(12), O(6)-Ti(1)-O(1) 99.19(13), O(7)-Ti(1)-O(8) 86.50(13), O(6)-Ti(1)-O(8) 171.03(13), O(1)-Ti(1)-O(8) 85.49(13), O(7)-Ti(1)-Br(2) 168.80(9), O(6)-Ti(1)-Br(2) 89.29(9), O(1)-Ti(1)-Br(2) 88.59(9), O(8)-Ti(1)-Br(2) 83.15(9), O(7)-Ti(1)-Br(1) 88.29(8), O(6)-Ti(1)-Br(1) 91.97(8), O(1)-Ti(1)-Br(1)167.59(10), O(8)-Ti(1)-Br(1) 82.74(9).

For **6**·7MeCN: Ti(1)-O(1) 1.779(4), Ti(1)-N(2) 2.236(6), Ti(1)-Br(2) 2.4939(13), Ti(1)-Br(1) 2.5058(15), Ti(1)-Br(3) 2.5064(15), Ti(1)-Br(4) 2.5423(13), Ti(2)-O(2) 1.755(4), Ti(2)-O(3) 1.820(4), Ti(2)-N(4) 2.194(5), Ti(2)-N(3) 2.245(5), Ti(2)-Br(6) 2.4998(11), Ti(2)-Br(5) 2.5280(11), O(1)-Ti(1)-N(2) 176.3(2), O(1)-Ti(1)-Br(2) 98.72(14), N(2)-Ti(1)-Br(2) 82.18(15), O(1)-Ti(1)-Br(1) 97.79(15), N(2)-Ti(1)-Br(1) 85.75(17), Br(2)-Ti(1)-Br(1) 90.42(5), O(1)-Ti(1)-Br(3) 91.34(15), O(2)-Ti(2)-O(3) 98.68(18), O(2)-Ti(2)-N(4) 94.27(19), O(3)-Ti(2)-N(4) 165.59(19), O(2)-Ti(2)-N(3) 175.84(18), O(3)-Ti(2)-N(3) 85.48(17), N(4)-Ti(2)-N(3) 81.58(19), O(2)-Ti(2)-Br(6) 95.06(14).

For **6**·7MeCN: O(1)-Ti(1) 1.792(5), O(2)-Ti(1) 1.801(4), O(3)-Ti(2) 1.789(4), O(4)-Ti(2) 1.791(5), F(1)-Ti(1) 1.802(3), F(2)-Ti(1) 2.035(3), F(2)-Ti(2) 2.064(3), F(3)-Ti(2) 2.023(4), F(3)-Ti(1) 2.049(4), F(4)-Ti(1) 2.012(4), F(4)-Ti(2) 2.055(4), F(5)-Ti(2) 1.799(3), O(1)-Ti(1)-O(2) 97.67(19), O(1)-Ti(1)-F(1) 100.70(19), O(2)-Ti(1)-F(1) 101.88(19), O(1)-Ti(1)-F(4) 162.69(19), F(1)-Ti(1)-F(4) 90.92(16), O(1)-Ti(1)-F(2) 91.46(18), F(1)-Ti(1)-F(2) 159.36(16), O(2)-Ti(1)-F(4) 92.36(18), (4)-Ti(1)-F(2) 73.92(15), O(2)-Ti(1)-F(2) 92.85(17).

ROP studies

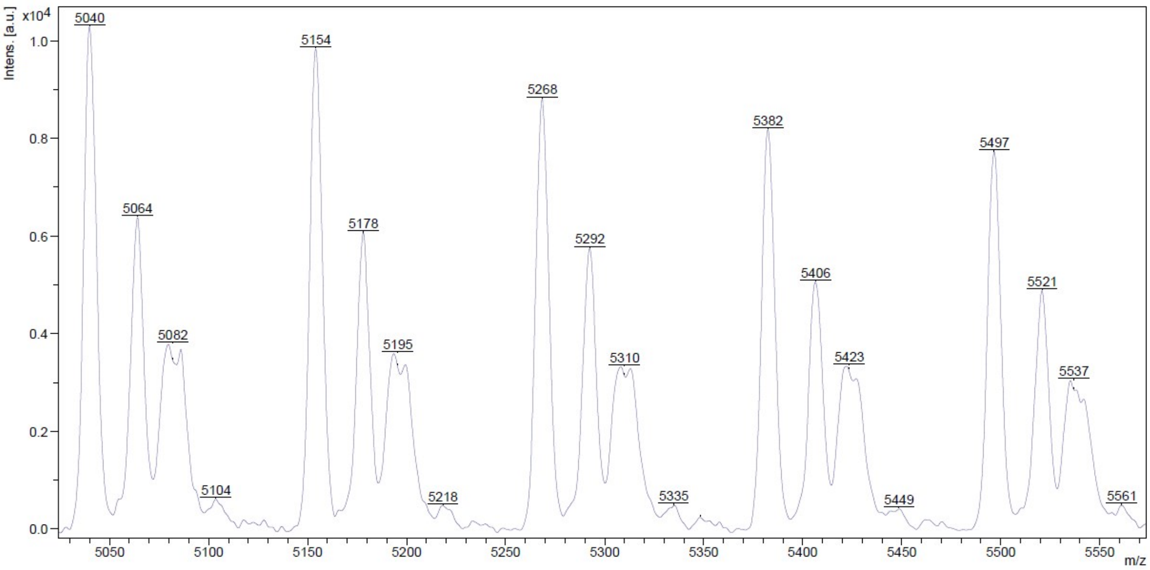

National Mass Spectrometry Facility (NMSF), Swansea
D:\Data\NMSF\2021\Feb21\HULRED-FKCVP-UM-A\0_O23\1\1SLin
Comment 1 Prof. Redshaw TiN[6]-PCL MW=5k(poly)?? PosLin THF [1:10] (DCTB;THF) +NaOAc
Intens. [a.u.]
x10^4
1.5
1.0
0.5
0.0
1082 1311 1653 1996 2072 2186 2300 2415 2529 2643 2757 2871 2985 3099 3214 3328 3442 3784 4127 4241 4355 4469 4583 4698 4812 5040 5268 5382 5497 5725 5953 6182 6296 6638 6981 7323 7666 8008 8350 8693 9149 9606 10060 10978
2000 4000 6000 8000 10000 12000
m/z
a1
a2
HO
+ Na+
+Na+
O
n
ultrafleXtreme MALDI
Date of Acquisition 2021-02-27T16:08:08.163+00:00
Printed 28/02/2021 15:40:55


National Mass Spectrometry Facility (NMSF), Swansea
D:\Data\NMSF\2021\Feb21\HULRED-FKCVP-UM-A\0_O23\1\1SLin
Comment 1 Prof. Redshaw TiN[6]-PCL MW=5k(poly)?? PosLin THF [1:10] (DCTB;THF) +NaOAc
Intens. [a.u.]
5000
4000
3000
2000
1000
0
6182 6206 6222 6247 6296 6320 6336 6362
a1
6410
a2
6434 6449 6477 6524 6548 6564 6638 6662 6678
6200 6250 6300 6350 6400 6450 6500 6550 6600 6650 6700
m/z
ultrafleXtreme MALDI
Date of Acquisition 2021-02-27T16:08:08.163+00:00
Printed 28/02/2021 15:48:21

National Mass Spectrometry Facility (NMSF), Swansea

D:\Data\NMSF\2021\Feb21\HULRED-FKCVP-UM-A\0_O23\1\1SLin

Comment 1 Prof. Redshaw TiN[6]-PCL MW=5k(poly)?? PosLin THF [1:10] (DCTB;THF) +NaOAc

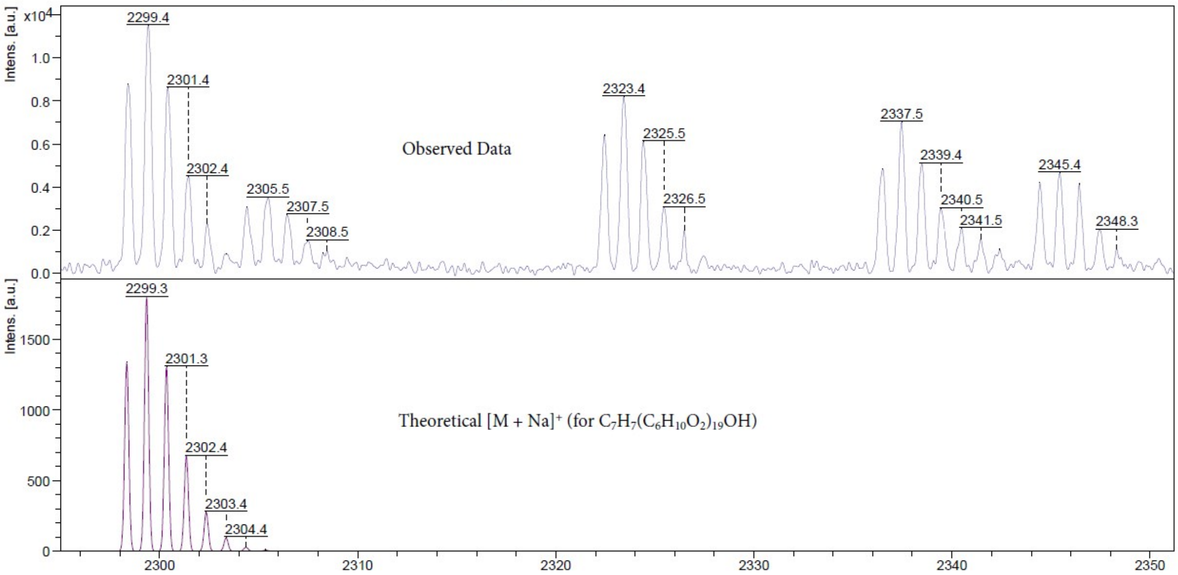


ultrafleXtreme MALDI Date of Acquisition 2021-02-27T16:08:08.163+00:00 Printed 28/02/2021 15:48:01

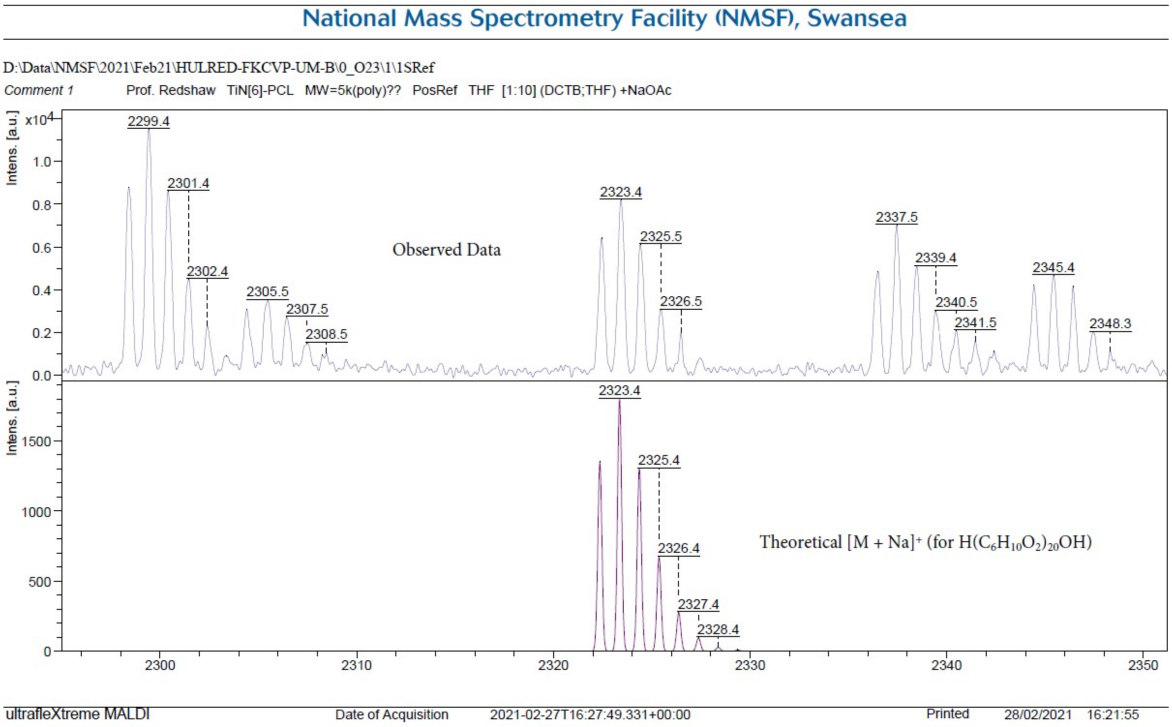
National Mass Spectrometry Facility (NMSF), Swansea

D:\Data\NMSF\2021\Feb21\HULRED-FKCVP-UM-B\0_O23\1\1SRef

Comment 1 Prof. Redshaw TiN[6]-PCL MW=5k(poly)?? PosRef THF [1:10] (DCTB;THF) +NaOAc



ultrafleXtreme MALDI Date of Acquisition 2021-02-27T16:27:49.331+00:00 Printed 28/02/2021 16:24:37



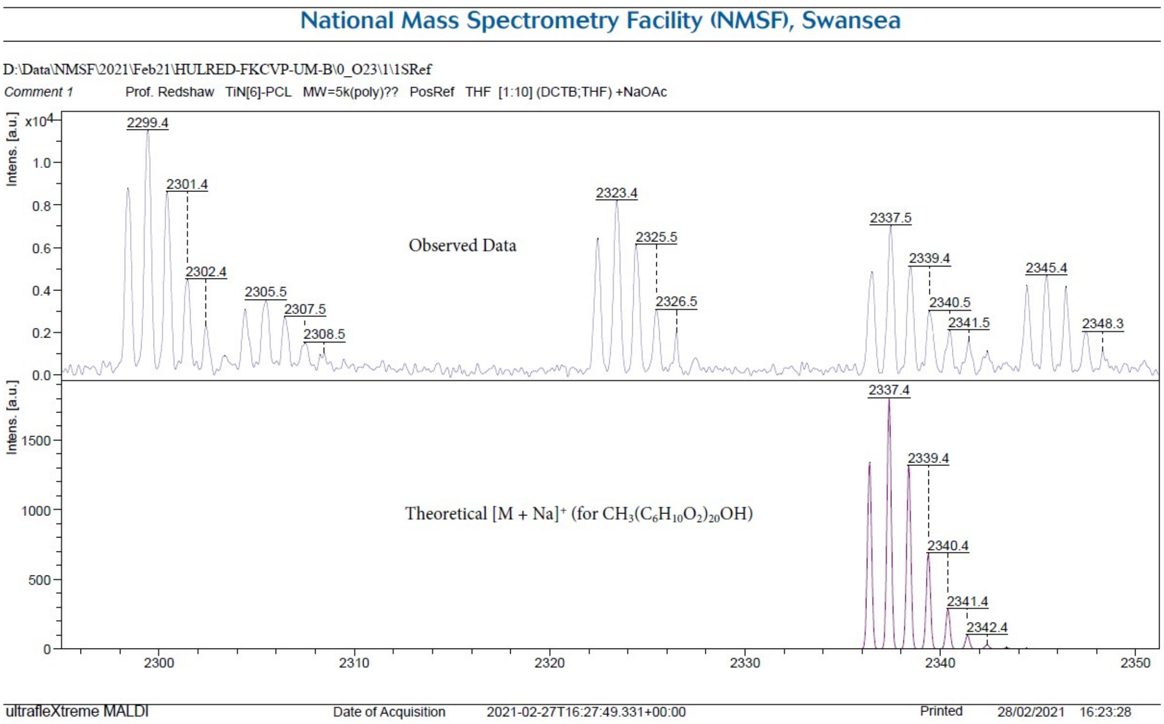
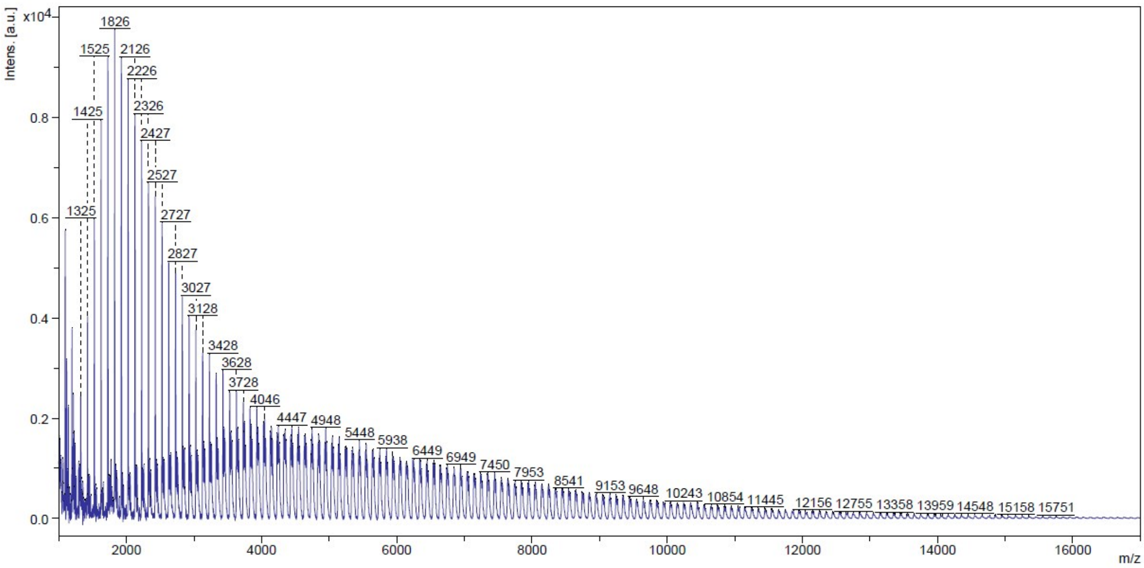


Figure S1. Mass spectrum of PCL synthesized with **4**/BnOH (run 10, Table 1).

National Mass Spectrometry Facility (NMSF), Swansea

D:\Data\NMSF\2021\Feb21\HULRED-FKCV7-UM-A\0_O24\1\1SLin

Comment 1 Prof. Redshaw TiCIN[6]-PVL MW=6k(poly)?? PosLin THF [1:10] (DCTB;THF) +NaOAc

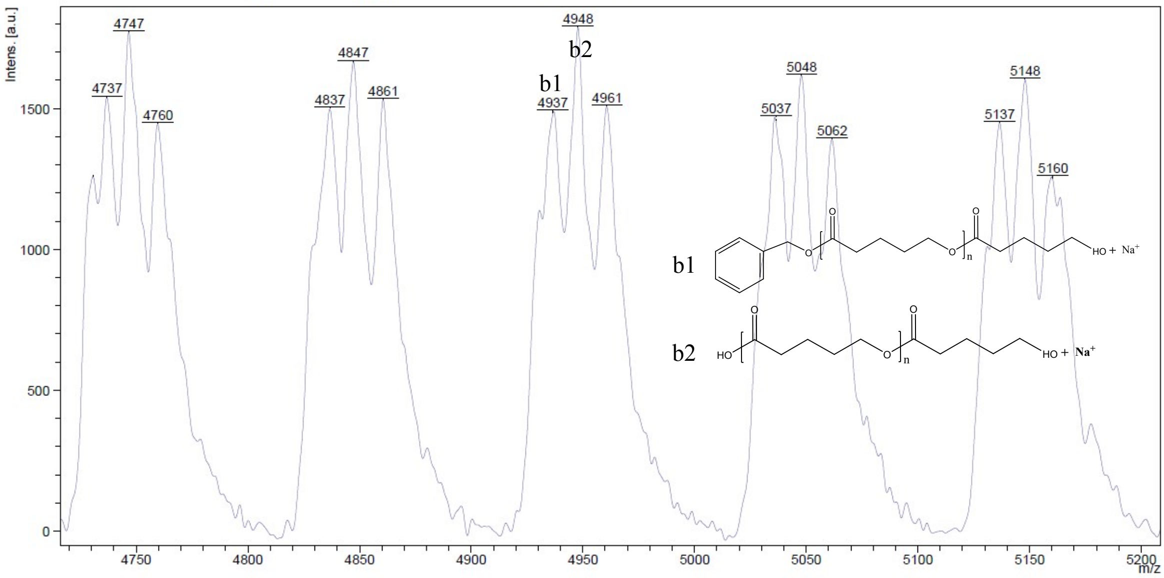


ultrafleXtreme MALDI Date of Acquisition 2021-02-27T16:13:37.043+00:00 Printed 28/02/2021 17:03:45

National Mass Spectrometry Facility (NMSF), Swansea

D:\Data\NMSF\2021\Feb21\HULRED-FKCV7-UM-A\0_O24\1\1SLin

Comment 1 Prof. Redshaw TiCIN[6]-PVL MW=6k(poly)?? PosLin THF [1:10] (DCTB;THF) +NaOAc

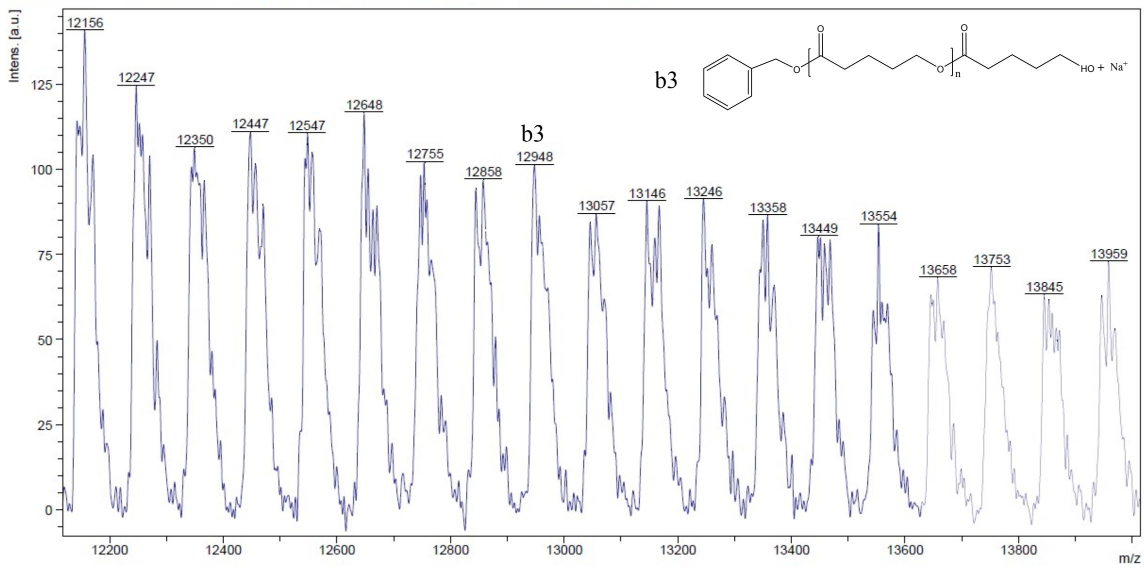


ultrafleXtreme MALDI Date of Acquisition 2021-02-27T16:13:37.043+00:00 Printed 28/02/2021 17:07:22

National Mass Spectrometry Facility (NMSF), Swansea

D:\Data\NMSF\2021\Feb21\HULRED-FKCV7-UM-A\0_O24\1\1SLin

Comment 1 Prof. Redshaw TiCIN[6]-PVL MW=6k(poly)?? PosLin THF [1:10] (DCTB;THF) +NaOAc

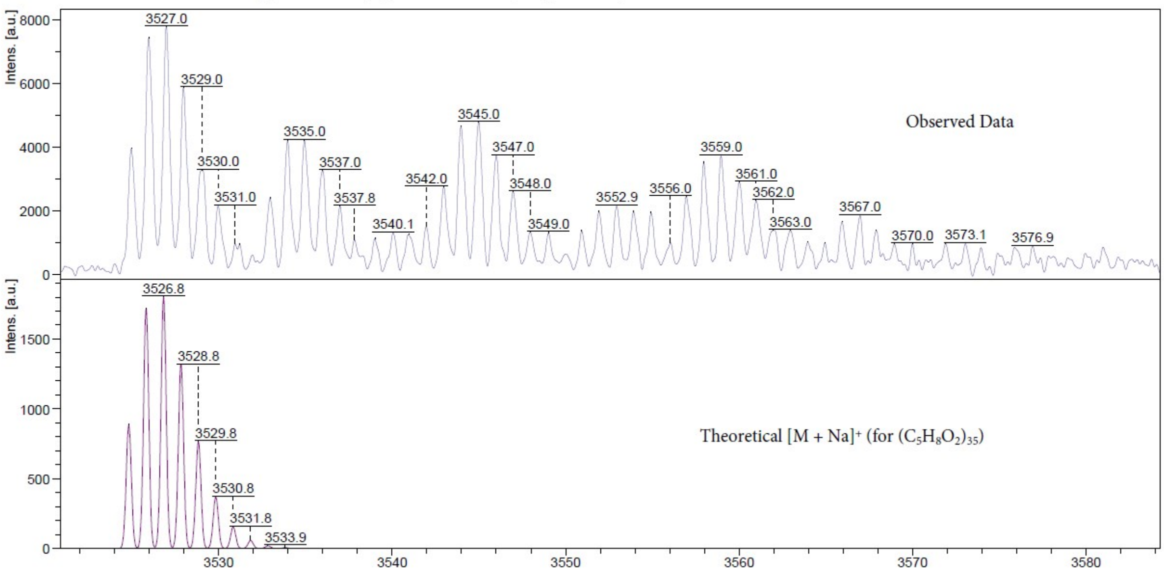


ultrafleXtreme MALDI Date of Acquisition 2021-02-27T16:13:37.043+00:00 Printed 28/02/2021 17:09:17

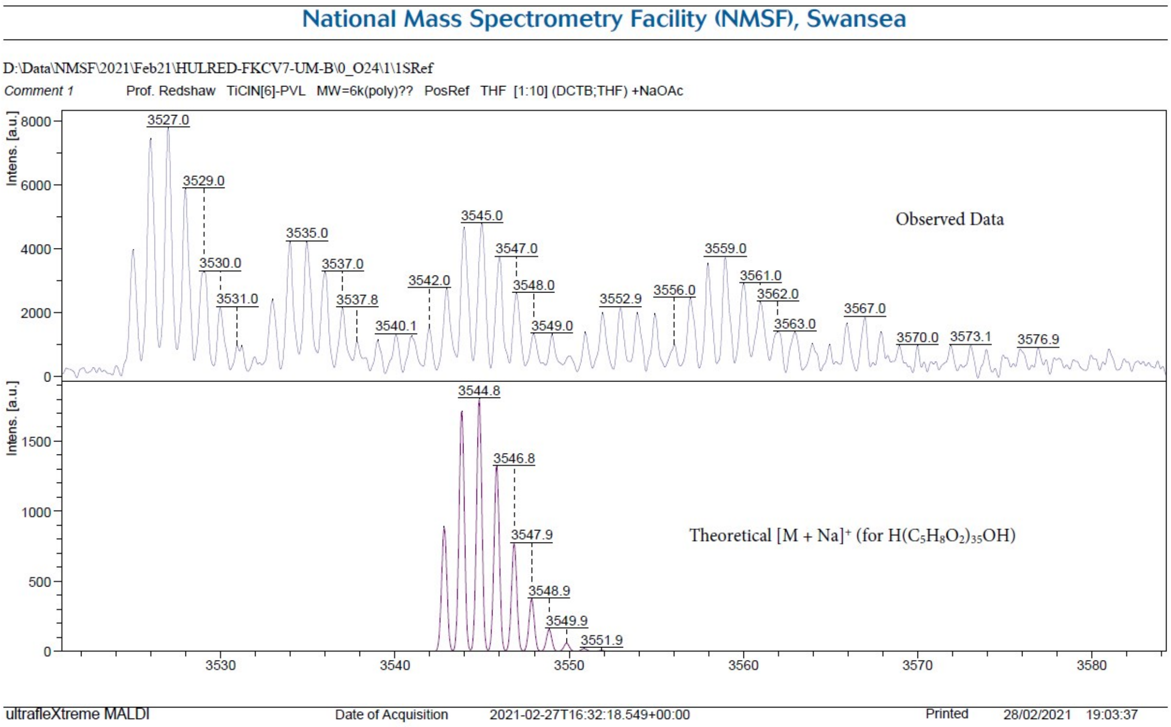
National Mass Spectrometry Facility (NMSF), Swansea

D:\Data\NMSF\2021\Feb21\HULRED-FKCV7-UM-B\0_O24\1\1SRef

Comment 1 Prof. Redshaw TiCIN[6]-PVL MW=6k(poly)?? PosRef THF [1:10] (DCTB;THF) +NaOAc



ultrafleXtreme MALDI Date of Acquisition 2021-02-27T16:32:18.549+00:00 Printed 28/02/2021 19:03:04



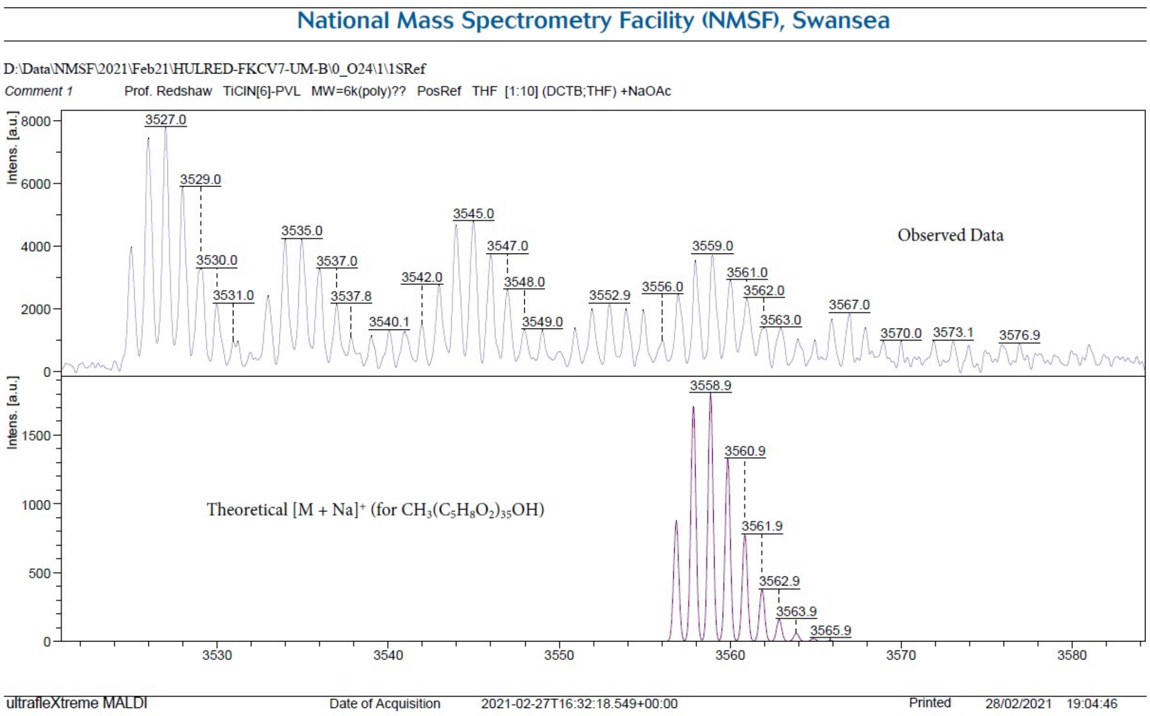
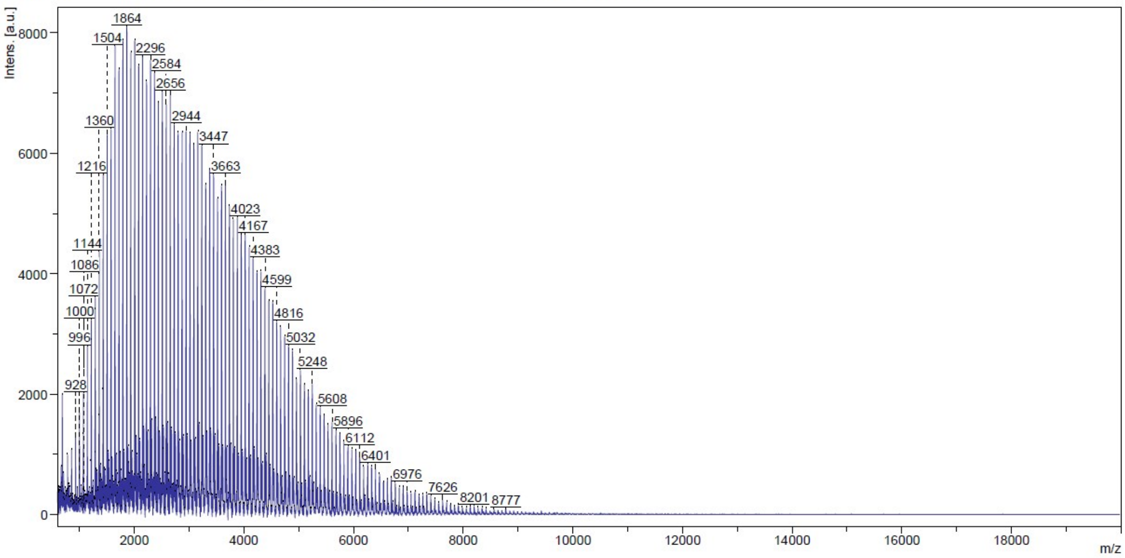


Figure S2. Mass spectrum of PVL synthesized with **7**/BnOH (run 13, Table 2).

National Mass Spectrometry Facility (NMSF), Swansea

D:\Data\NMSF\2020\December\HULRED-FJXFX-UM-A\0_M1\1\1SLin

Comment 1 Prof. Redshaw TiCIN[6]-PLA MW=5k(poly)?? PosLin THF? [1:5] (DCTB;THF) +NaOAc

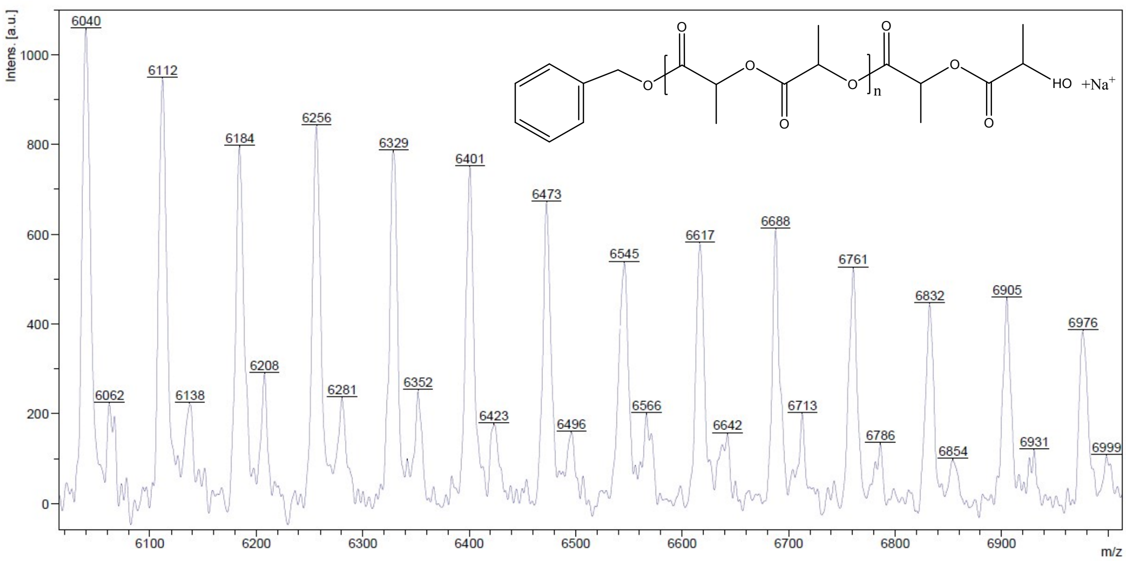


ultrafleXtreme MALDI Date of Acquisition 2020-12-20T16:31:45.484+00:00 Printed 22/12/2020 21:55:12

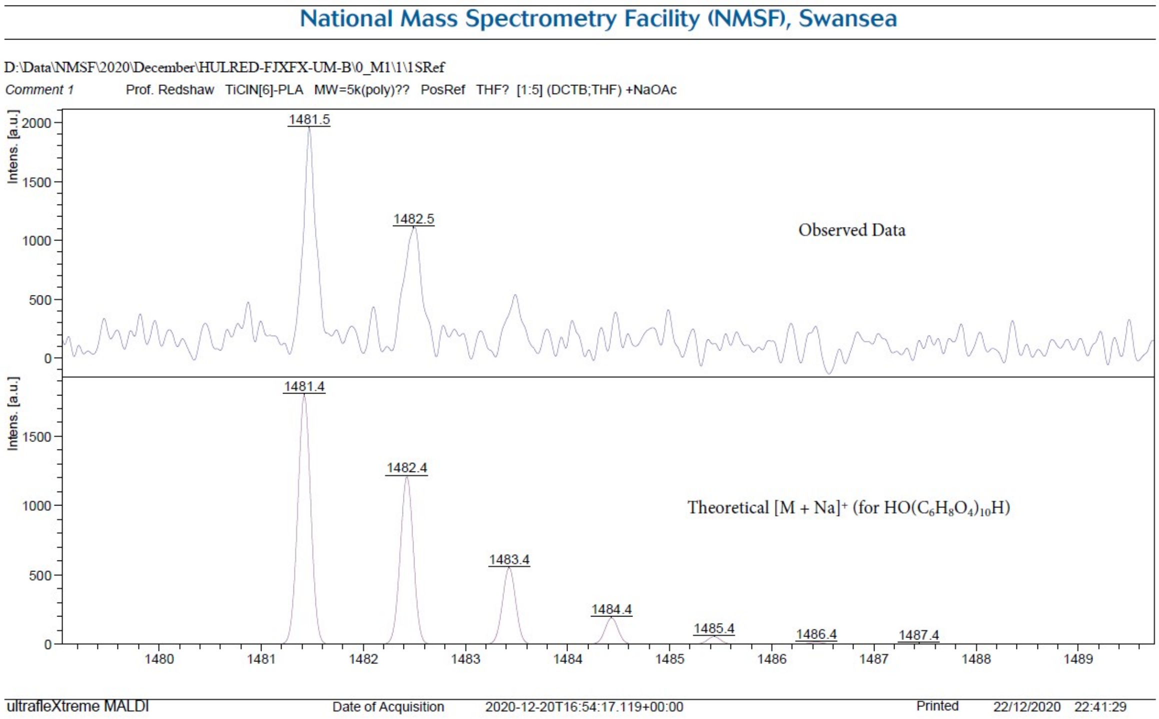
National Mass Spectrometry Facility (NMSF), Swansea

D:\Data\NMSF\2020\December\HULRED-FJXFX-UM-A\0_M1\1\1SLin

Comment 1 Prof. Redshaw TiCIN[6]-PLA MW=5k(poly)?? PosLin THF? [1:5] (DCTB;THF) +NaOAc



ultrafleXtreme MALDI Date of Acquisition 2020-12-20T16:31:45.484+00:00 Printed 22/12/2020 21:58:50



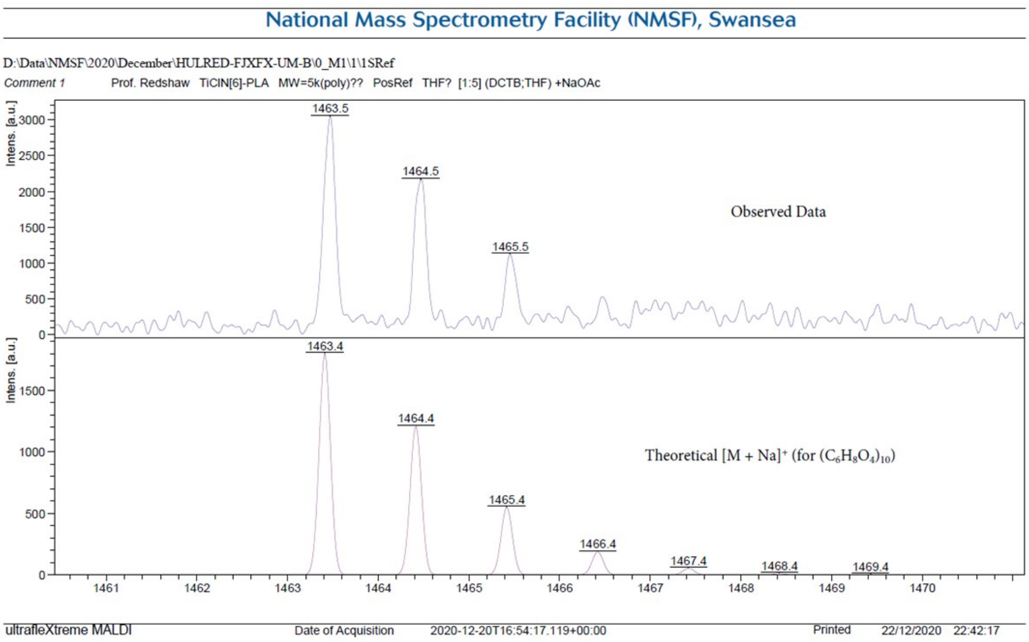


Figure S3. Mass spectrum of PLA synthesized with **3**/BnOH (run 3, Table 3).

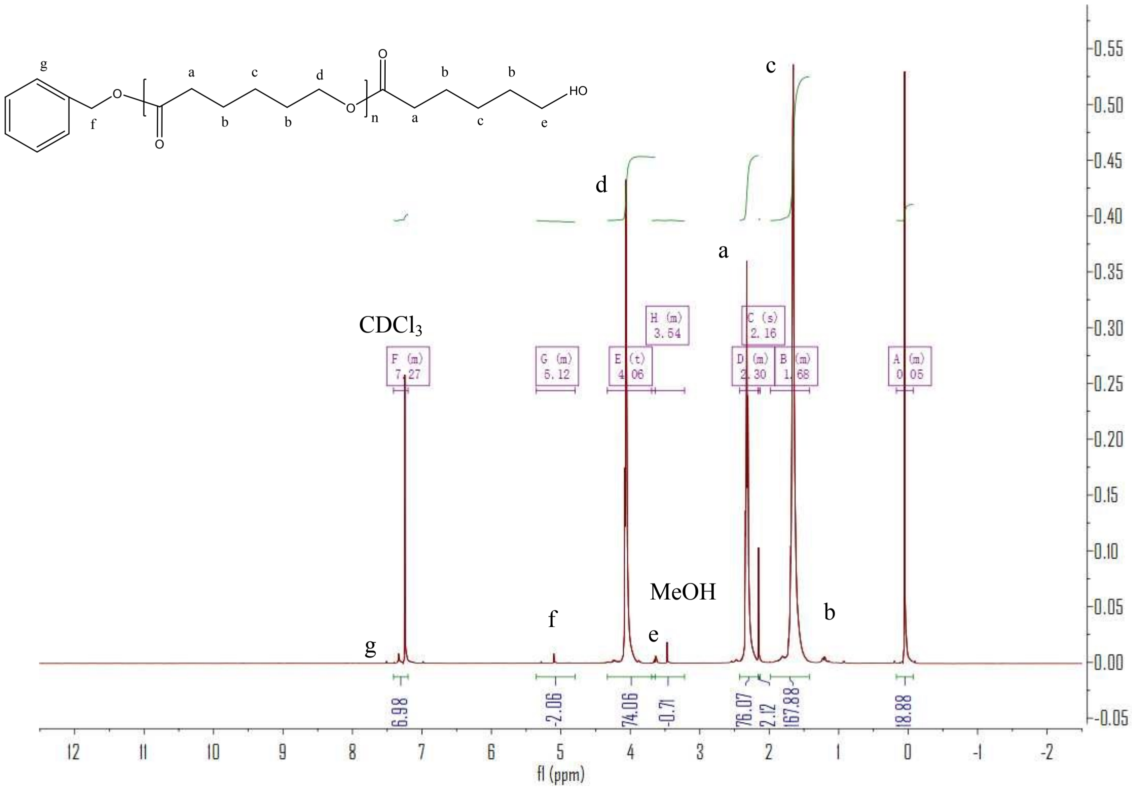


Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PCL synthesized with **1**/BnOH (run 17, Table 1).

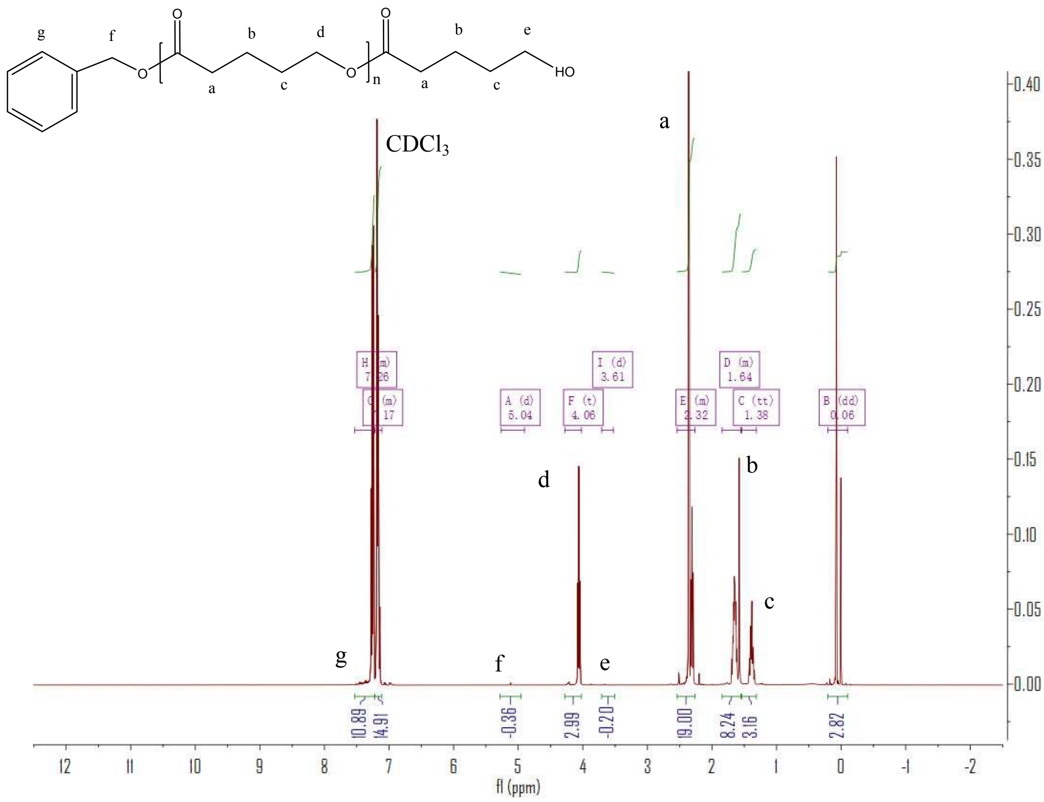
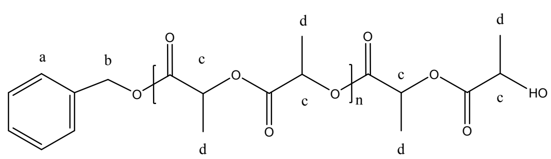


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PVL synthesized with **5**/BnOH (run 11, Table 2).



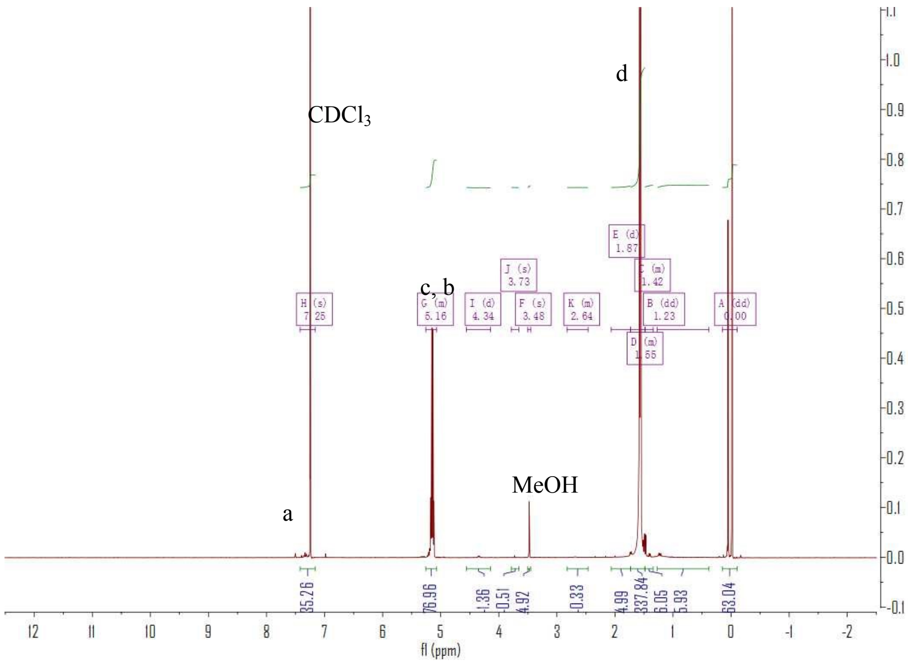


Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PLA synthesized with **2**/BnOH (run 2, Table 3).

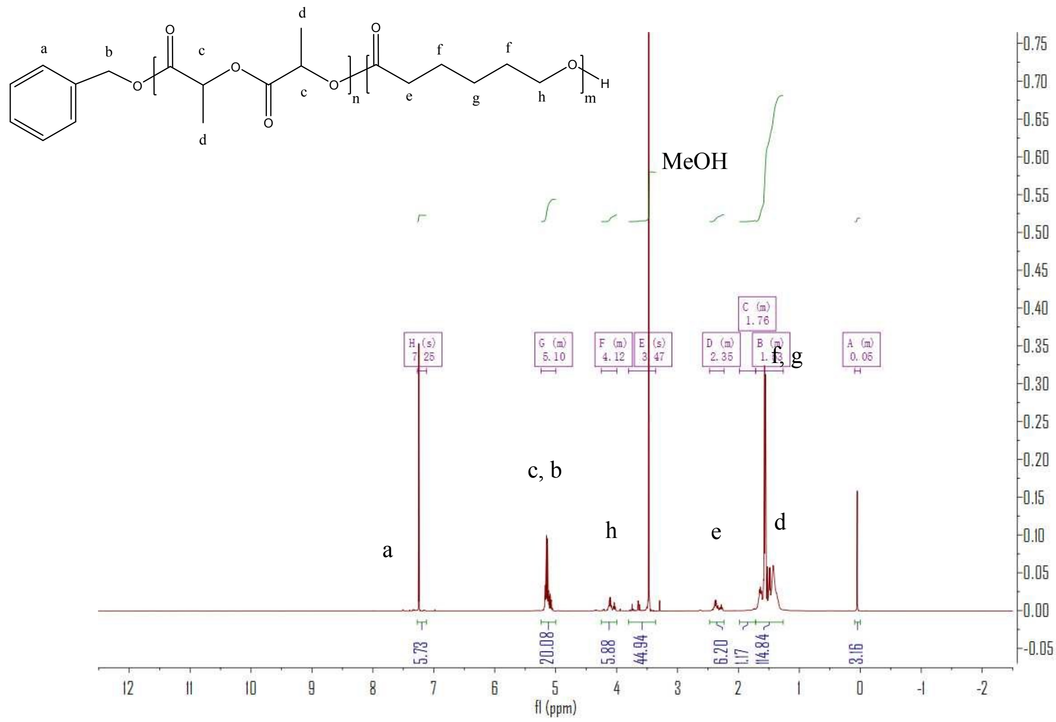


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PLA-PCL copolymer synthesized with **6**/BnOH (run 6, Table 4).

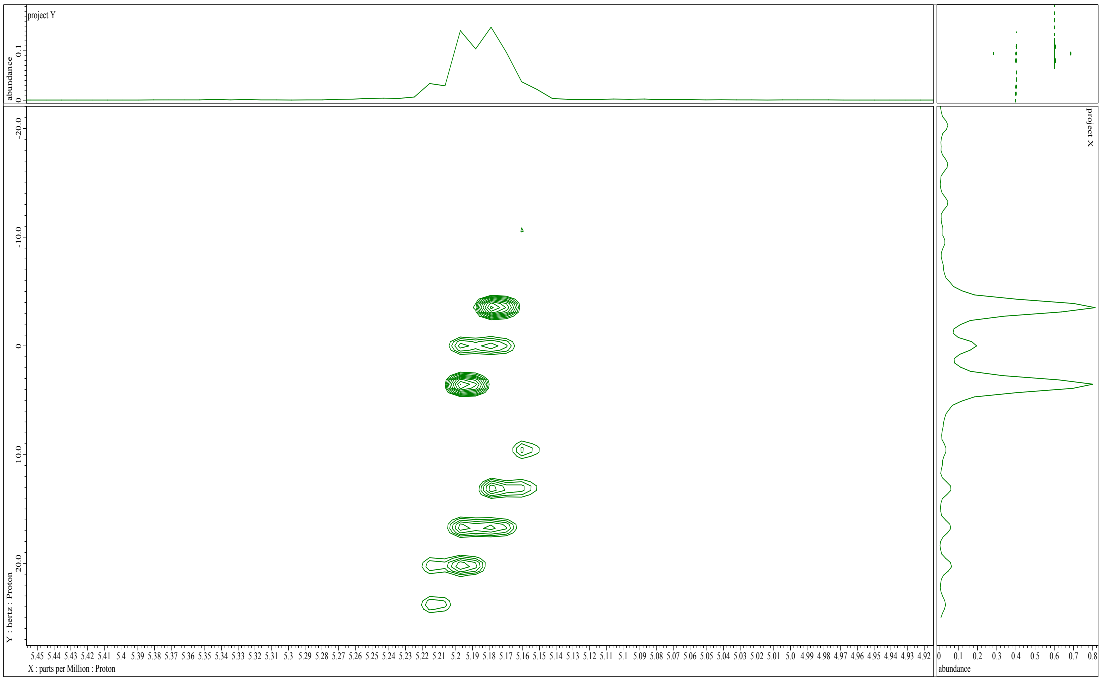
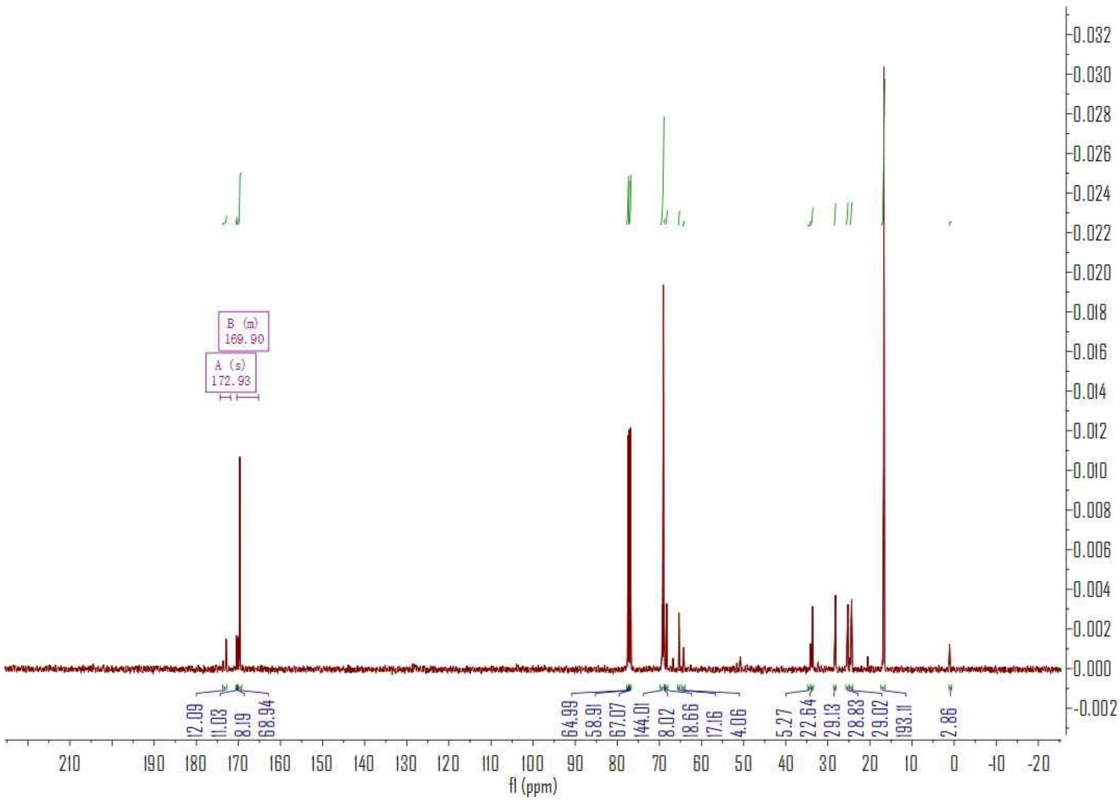


Figure S8. 2D *J*-resolved ^1H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PLA synthesized with **1**/BnOH (run 1, Table 3).



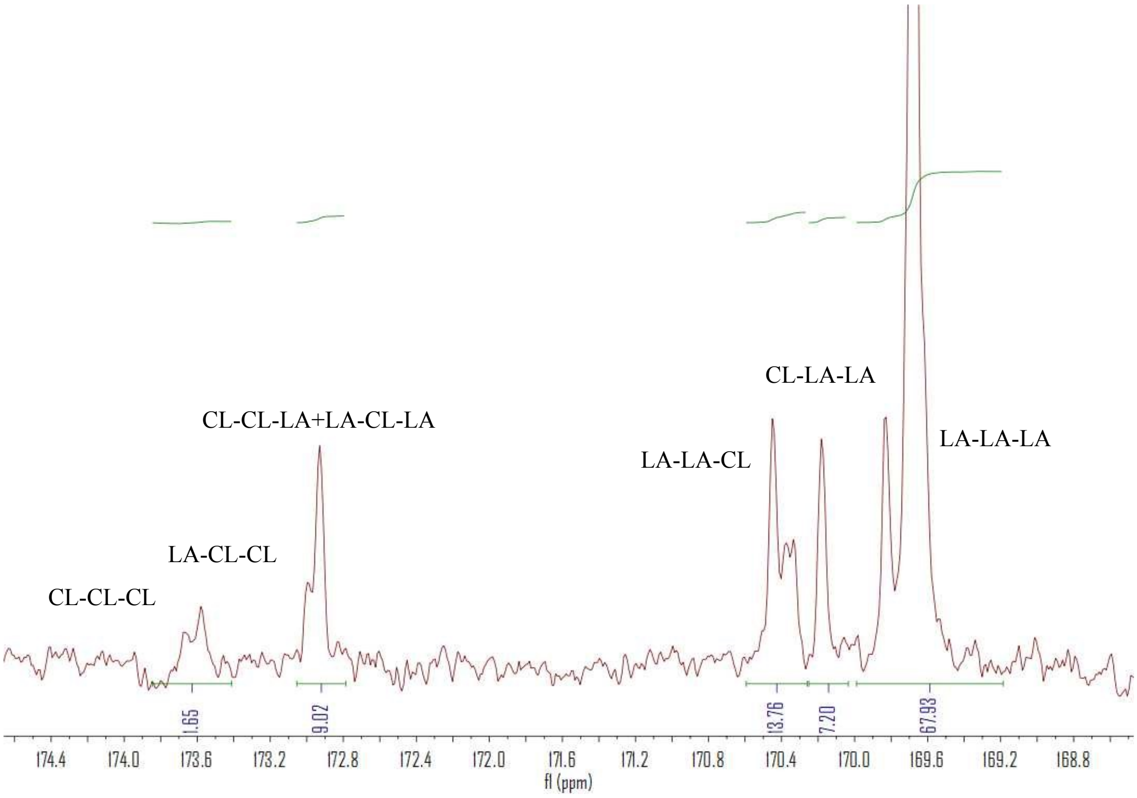


Figure S9. Carbonyl range of ^{13}C NMR spectrum ($CDCl_3$, 25 ºC) of PLA-PCL co-polymer. Triads have been assigned according to the literature.[1]

Equation S1. Determination of number-average sequence length for CL[1]

$$L_{CL}=[(I_{CL\text{-}CL\text{-}CL}+I_{LA\text{-}CL\text{-}CL})/(I_{CL\text{-}CL\text{-}LA}+I_{LA\text{-}CL\text{-}LA})]+1$$

Equation S2. Determination of number-average sequence length for LA. [1]

$$L_{LA}=\{[(I_{LA\text{-}LA\text{-}LA}+(I_{LA\text{-}LA\text{-}CL} + I_{CL\text{-}LA\text{-}LA})/2]/[I_{CL\text{-}LA\text{-}CL}+(I_{LA\text{-}LA\text{-}CL}+ I_{CL\text{-}LA\text{-}LA})/2]+1\}/2$$

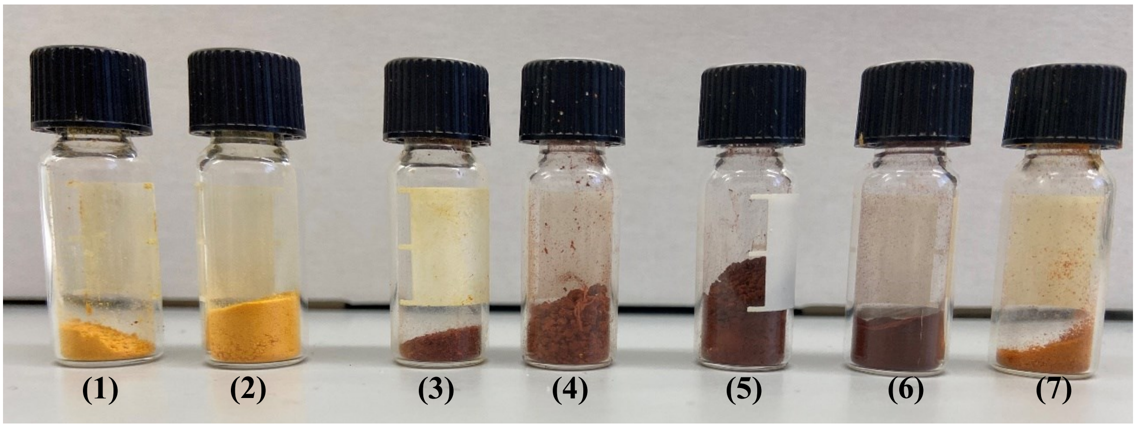


Figure S10. Picture of complexes **1-7**.

[1] (a) F. Della Monica, E. Luciano, A. Buonerba, A. Grassi, S. Milione and Carmine Capacchione, *RSC Adv*. 2014, **4**, 51262−51267; (b) P. Vanhoorne, P. Dubois, R. Jerome and P. Teyssie, *Macromolecules* 1992, **25**, 37–44; (c) J. Kasperczyk and M. Bero, *Makromol. Chem*. 1991, **192**, 1777–1787; (d) J. Kasperczyk and M. Bero, *Makromol. Chem*. 1993, **194**, 913–925; (e) N. Nomura, A. Akita, R. Ishii and M. Mizuno, *J. Am. Chem. Soc*. 2010, **132**, 1750–1751; (f) G. Li, M. Lamberti, D. Pappalardo and Claudio Pellecchia *Macromolecules*, 2012, **45**, 8614−8620.