

Supporting information: (Experimental conditions, MALDI, NMR, pXRD and IR)

An air-stable Metal Organic Framework as an initiator for ring-opening polymerization of cyclic esters

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Experimental conditions:

For the preparation and characterization of complexes, all reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk or glove-box techniques and all solvents were freshly distilled over suitable drying agents and degassed prior to use. Ligands were purchased from Aldrich. $\text{Ti}(\text{O}^i\text{Pr})_4$ was purchased from Aldrich and purified by vacuum distillation prior to use. $^1\text{H}/^{13}\text{C}$ NMR spectra were recorded on a Bruker Advance 300 MHz spectrometer, referenced to residual solvent peaks. Coupling constants are given in Hertz. Elemental analysis was performed by Mr. A.K. Carver at the Department of Chemistry, University of Bath. Crystallography data were collected on a Nonius KappaCCD area detector diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), and all structures were solved by direct methods and refined on all F^2 data using the SHELXL-97 suite of programs hydrogen atoms, with the exception of those involved in hydrogen bonding, were included in idealised positions and refined using the riding model. For complex **1**: The hydrogen atoms involved in hydrogen bonding were located in the penultimate difference Fourier map and constrained at $0.86(2) \text{ \AA}$ away from the oxygen center. For complex **2**: H100 and H200 were located in the penultimate difference Fourier map and constrained at $0.86(2) \text{ \AA}$ away from the oxygen center, H300 and H400 were placed in calculated positions.

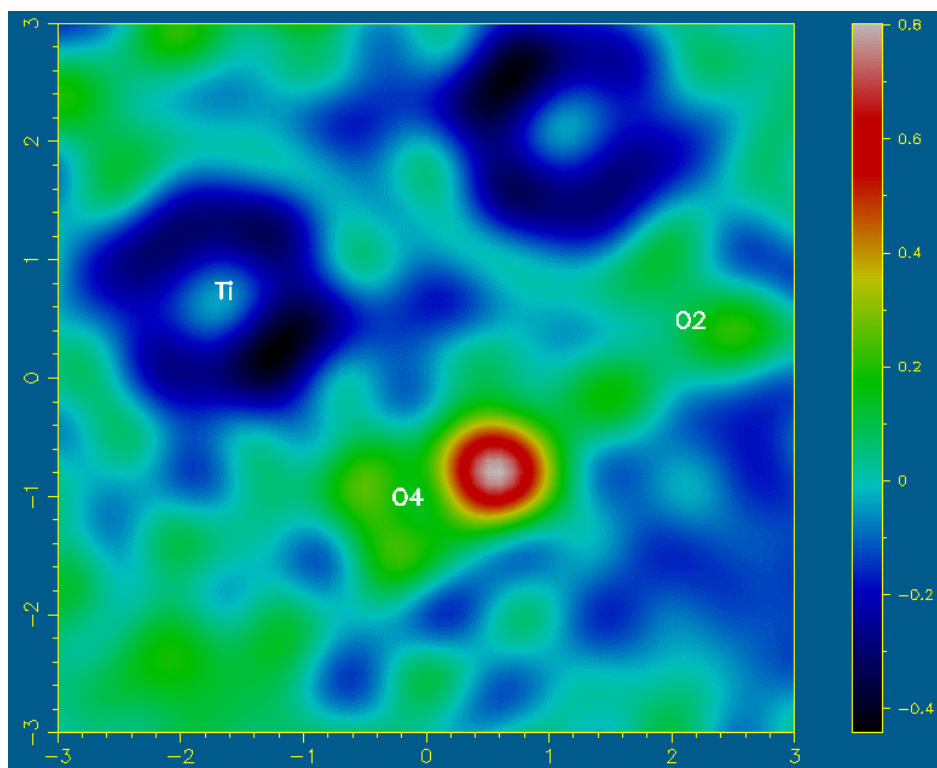
Complex synthesis:

$[\text{Ti}_2\text{L}_3(\text{LH})]_\infty$ ($\text{LH}_2 = 1,4\text{-butanediol}$)

1,4-butanediol (2.4 ml, 26.2 mmol) was added to $\text{Ti}(\text{O}^i\text{Pr})_4$ (2 ml, 6.6 mmol) in hexane (20 ml). CH_2Cl_2 (2 ml) was added and the solution stirred for 1 hour. After three days standing clear crystals were obtained. Yield 1.70 g, m.p. 128-134 °C. Elemental analysis: Calcd for $\text{C}_{20}\text{H}_{42}\text{O}_{10}\text{Ti}_2$: C, 44.63; H, 7.86. Found: C, 44.6; H,

8.21. ^1H NMR (300 MHz, CDCl_3): 1.68 (4H, m, CH_2), 3.70 (4H, m, $\text{CH}_2\text{-O}$). ^{13}C NMR 29.8 (OCH_2CH_2), 62.9 (OCH_2CH_2). **Crystal data** for $[\text{Ti}_2\text{L}_3(\text{LH})]_\infty$: $\text{C}_{20}\text{H}_{42}\text{O}_{10}\text{Ti}_2$, $M = 538.34$, $0.25 \times 0.25 \times 0.13 \text{ mm}^3$, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.991(2)$, $b = 9.271(2)$, $c = 12.335(2) \text{ \AA}$, $\beta = 100.98(1)^\circ$, $V = 1233.91(4) \text{ \AA}^3$, $Z = 2$, $D_c = 1.449 \text{ g/cm}^3$, $\mu = 0.697 \text{ mm}^{-1}$ $F_{000} = 572$, $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 150(2)\text{K}$, $2\theta_{\text{max}} = 55.0^\circ$, 11188 reflections collected, 2800 unique ($R_{\text{int}} = 0.0329$). Final $\text{Goof} = 1.042$, $R_I = 0.0285$, $wR2 = 0.0756$, R indices based on 2568 reflections with $I > 2\sigma(I)$ (refinement on F^2), 149 parameters, 1 restraint. CCDC 601288.

The O-H hydrogen atom was located using a difference Fourier Map, and is clearly located on O4:



$\text{Ti}_3\text{L}'_4(\text{L}'\text{H})_4$ ($\text{LH}_2' = (2R,3R)\text{-2,3-butanediol}$)

A similar procedure was employed except (2R,3R)-2,3-butanediol was used. Elemental analysis: Calcd for $\text{C}_{32}\text{H}_{68}\text{O}_{16}\text{Ti}_3$: C, 45.09; H, 8.04. Found: C, 44.0; H, 7.86. ^1H NMR (300 MHz, CDCl_3): 1.02 (18H, m, CH_3), 1.09 (6H, d $J = 6\text{Hz}$, CH_3), 1.16 (6H, d $J = 6\text{Hz}$, CH_3), 1.23 (6H, d $J = 6\text{Hz}$, CH_3), 1.42 (6H, d $J = 6\text{Hz}$, CH_3), 1.52 (6H, d $J = 6\text{Hz}$, CH_3), 3.66 (4H, m, CH-O), 4.2 (4H, m, CH-O), 4.5 (8H, m, CH-O).

O). ^{13}C NMR 19.3, 19.5, 19.6, 19.7 (two overlapping peaks), 20.1, 20.2, 20.5 (CH_3), 75.7, 77.3, 82.3, 85.0, 86.7, 88.8, 90.4, 91.0 (CH-O). **Crystal data** for $\text{Ti}_3\text{L}'_4(\text{L}'\text{H})_4$: $\text{C}_{32}\text{H}_{68}\text{O}_{16}\text{Ti}_3$, $M = 852.56$, $0.22 \times 0.15 \times 0.10 \text{ mm}^3$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 9.149(1)$, $b = 16.139(1)$, $c = 29.014(3) \text{ \AA}$, $V = 4284.08(7) \text{ \AA}^3$, $Z = 4$, $D_c = 1.322 \text{ g/cm}^3$, $F_{000} = 1816$, MoK α radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 150(2)\text{K}$, $2\theta_{\text{max}} = 55.0^\circ$, 68871 reflections collected, 9765 unique ($R_{\text{int}} = 0.0572$). Final $\text{Goof} = 1.054$, $R_I = 0.0347$, $wR2 = 0.0780$, R indices based on 8378 reflections with $I > 2\sigma(I)$ (refinement on F^2), 486 parameters, 2 restraints, $\mu = 0.608 \text{ mm}^{-1}$. Absolute structure parameter = $-0.011(14)$ (Flack, H. D. *Acta Cryst.* **1983**, A39, 876-881). CCDC 609241

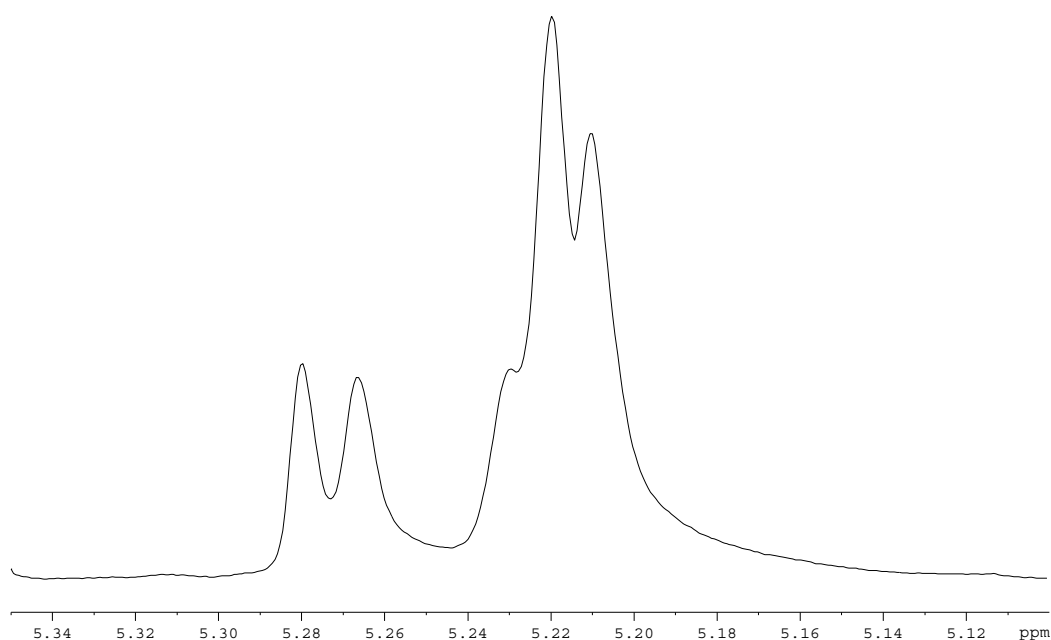
Catalysis:

Caprolactone/L-lactide

The catalyst (0.1 mmol) was added in toluene (10 ml) to which ϵ -caprolactone (10.0 mmol, 1.11 ml) was added. This was left to stir at room temperature for 48 hours during which time the viscosity of the solution significantly increased. The catalysis was quenched using 30 % acetic acid and water solution. The polymer was then precipitated using hexane, filtered, washed with copious amount of methanol and dried in-vacuo. For polylactide the conditions were 110 °C for 3 hours, with the same monomer:catalyst. ^1H NMR spectroscopy ($\text{CDCl}_3/\text{C}_6\text{D}_6$) and GPC (THF) were used to determine conversions and molecular weights (M_n and M_w) of the polymers produced, which were referenced to polystyrene.

Melt polymerization

For the melt reactions the monomer:catalyst ratio employed was 300:1 at a temperature of 130 °C. After the reaction time (2 hours) methanol was added to quench the reaction and the resulting solid was dissolved in dichloromethane. The solvents were removed in-vacuo and the resulting solid was washed with copious amounts of methanol to remove any unreacted monomer. The stereoselectivity was determined by analysis of the methine region of the ^1H homonuclear decoupled NMR spectrum, which is typical of an atactic polymer.



MALDI-TOF

Caprolactone:

Result of isotope pattern calculation

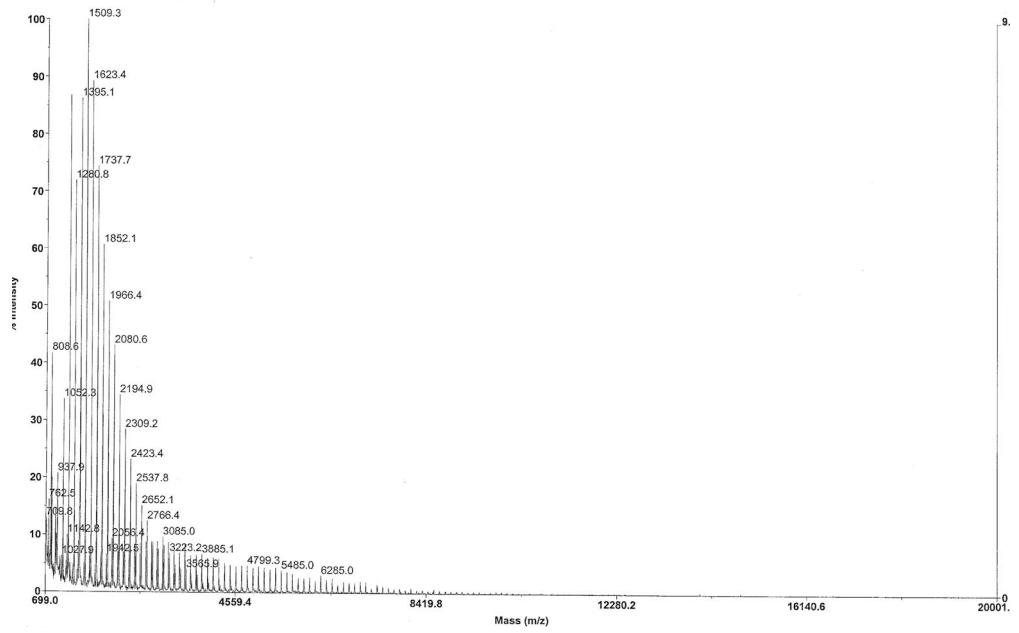
Formula: $C_{100}H_{170}O_{34}Na_1$ (1938 – polymer shown in scheme 1 o+p = 16)

mass	%	
1937	89.7	_____
1938	100.0	_____
1939	61.2	_____
1940	26.7	_____
1941	9.6	_____
1942	2.7	_____
1943	0.7	
1944	0.1	
1945	0.0	

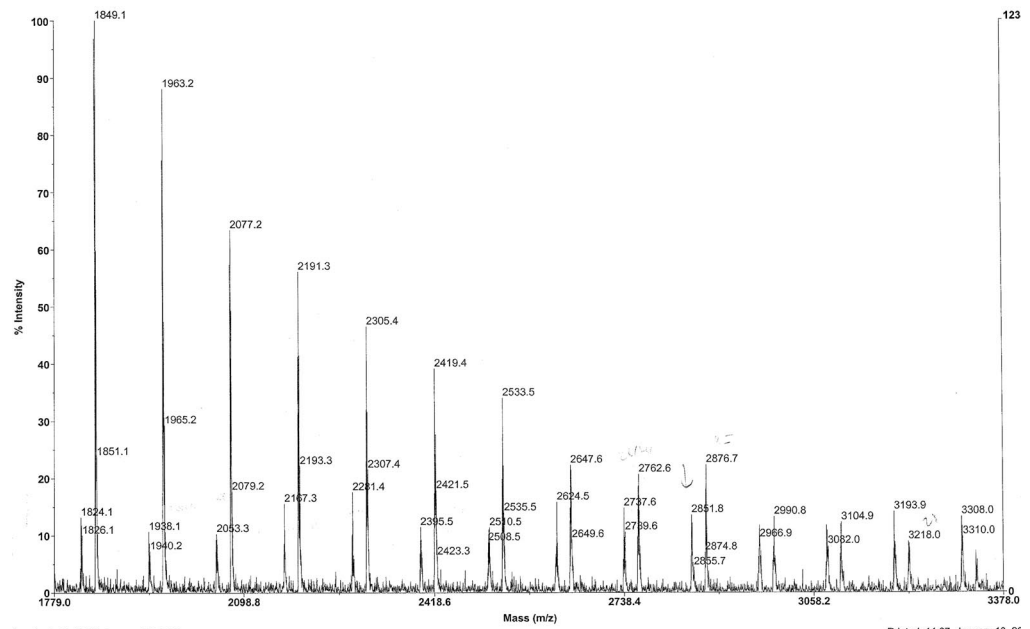
Formula: $C_{102}H_{170}O_{34}Na_1$ (1963 - cyclic PCL 17 repeat units ($C_6H_{10}O_2$))

mass	%	
1961	87.9	_____
1962	100.0	_____
1963	62.1	_____
1964	27.5	_____
1965	9.9	_____
1966	2.8	_____
1967	0.7	
1968	0.1	
1969	0.0	

A (linear + Cyclic PCL)



B (linear +cyclic PCL)



A – PosLin mode, ionised with NaI
 B – PosRef mode, ionised with NaI

Poly lactide

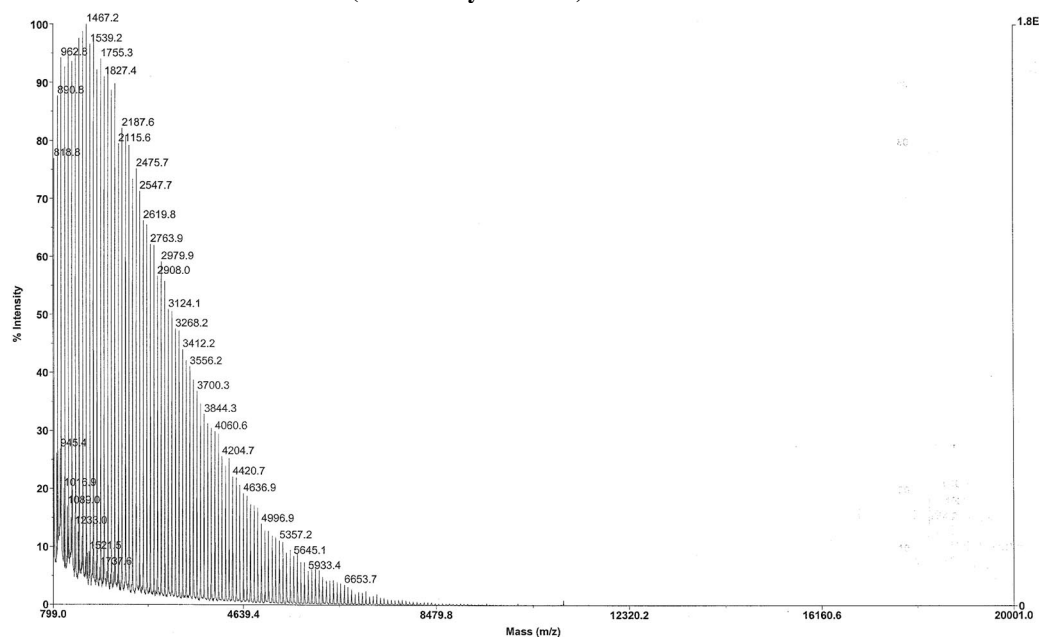
Formula: $C_{42}H_{56}O_{28}Na_1$ (1031 – cyclic PLA 14 repeat units ($C_3H_4O_2$))

	mass %
1031	100.0
1032	47.1
1033	16.5
1034	4.2
1035	0.9
1036	0.2
1037	0.0

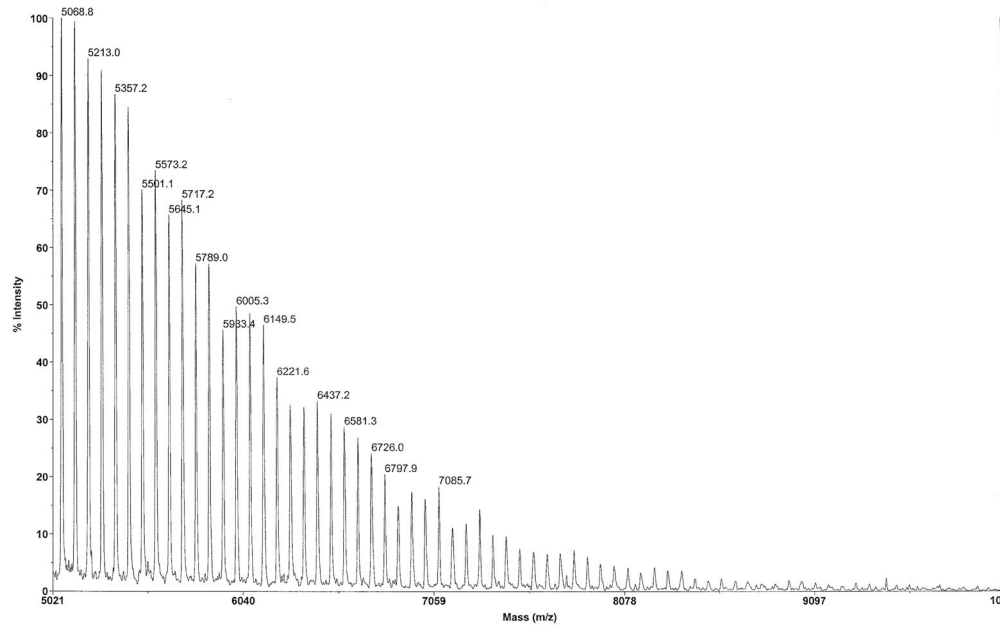
Formula: $C_{43}H_{62}O_{28}Na_1$ (peak at 1049 – linear PLA $m+n = 13$)

	mass %
1049	100.0
1050	48.2
1051	17.1
1052	4.4
1053	1.0
1054	0.2
1055	0.0

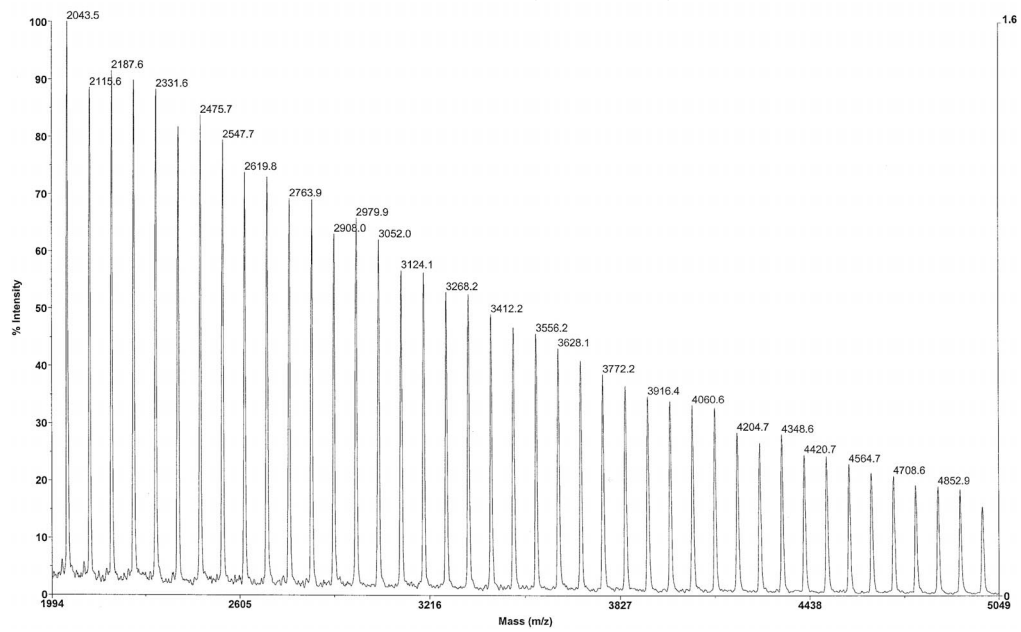
A (linear + Cyclic PLA)



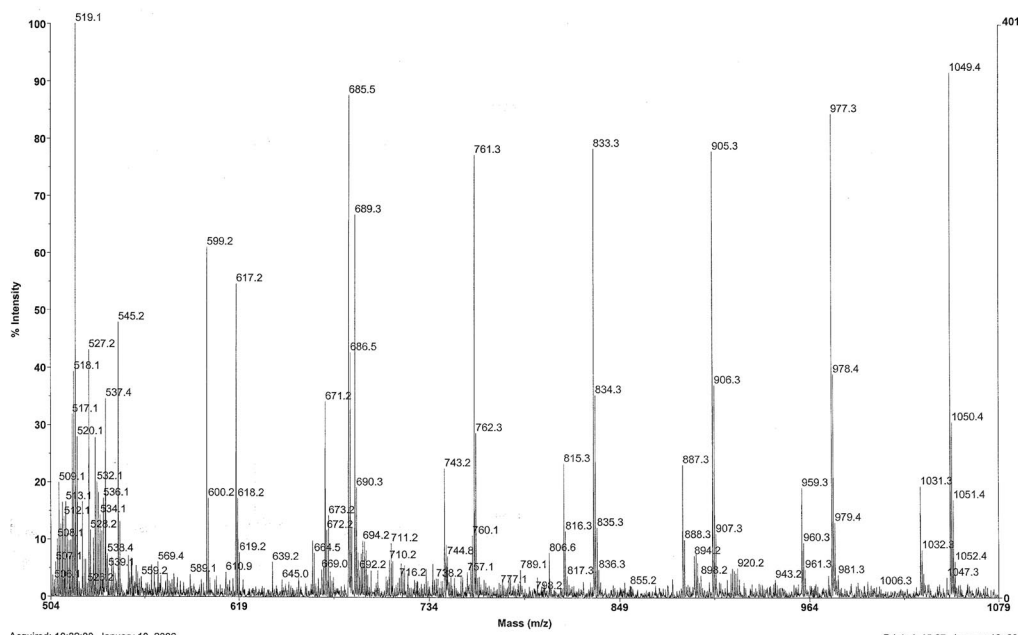
B (linear PLA)

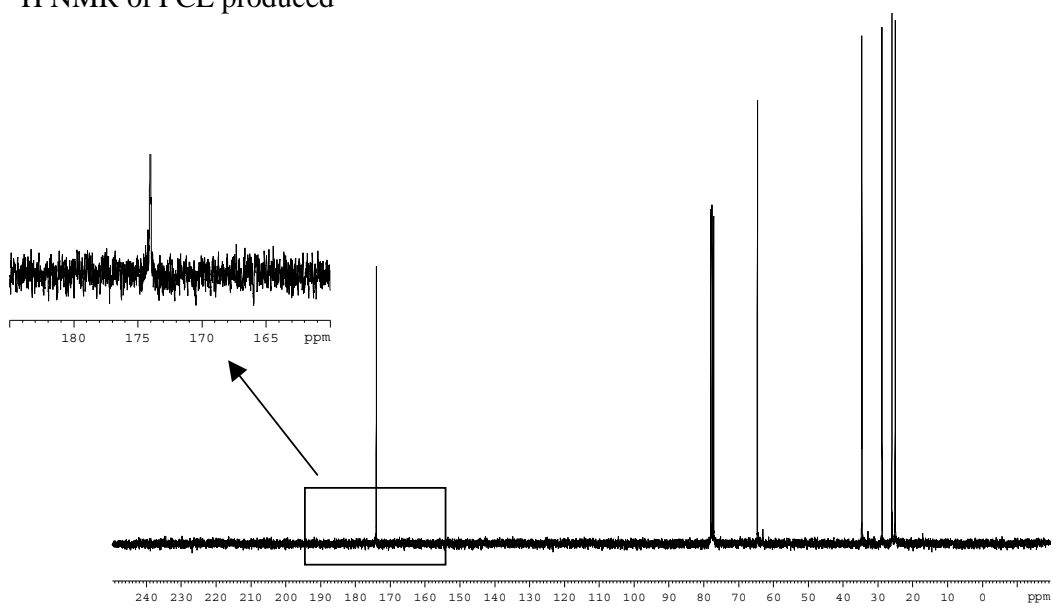
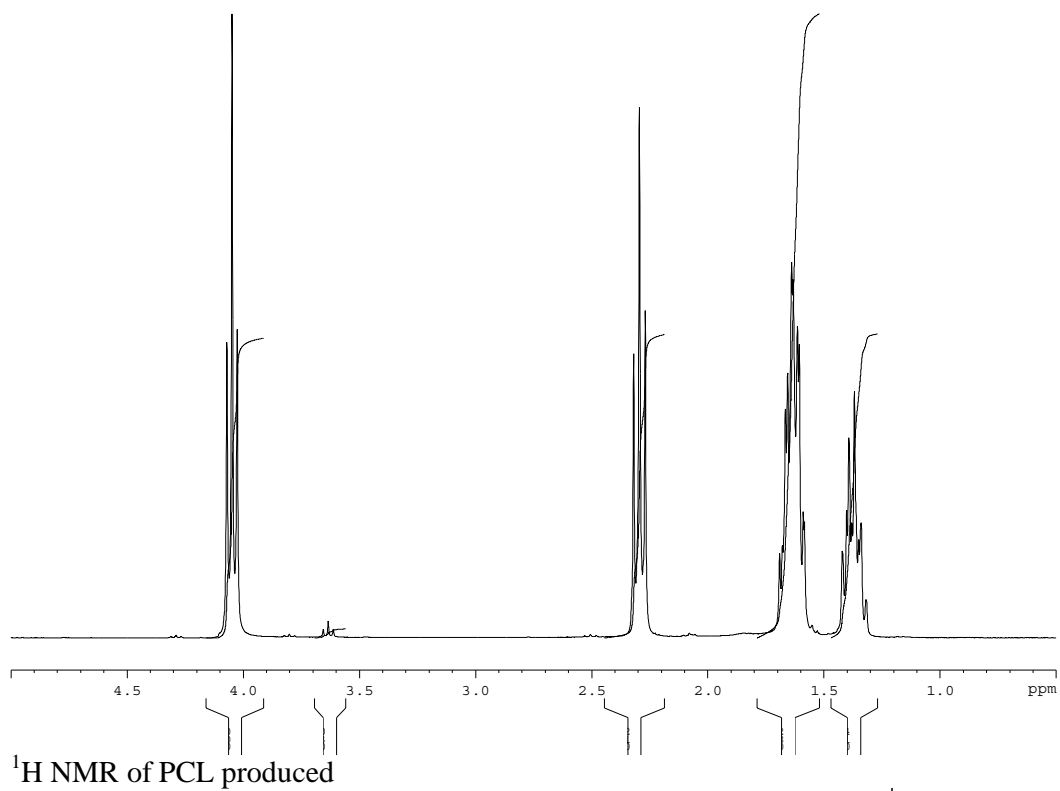


C (Linear PLA)

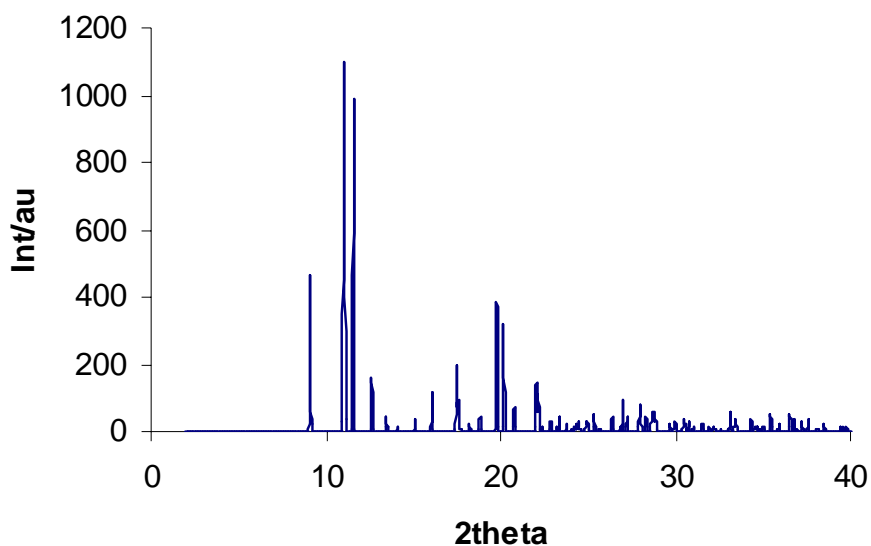


D (linear + cyclic PLA)

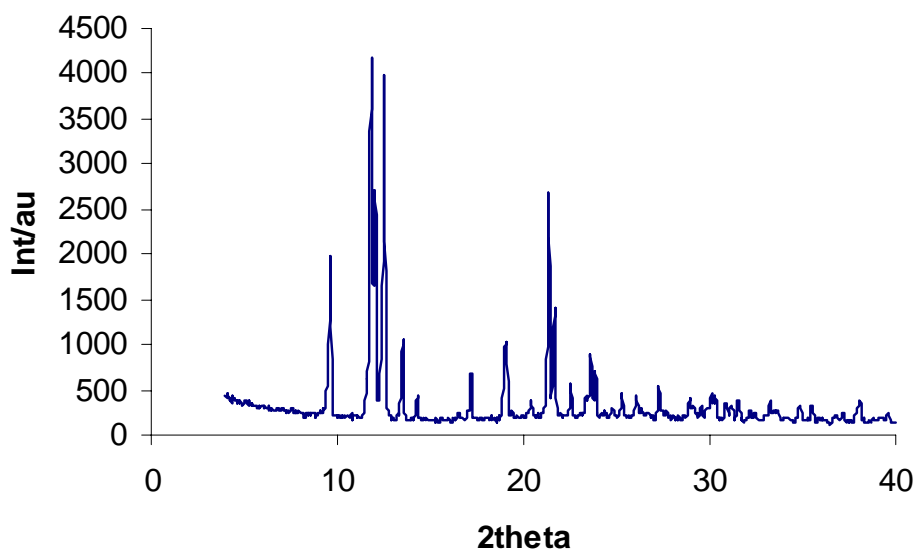




Calculated pXRD pattern



Observed pXRD pattern

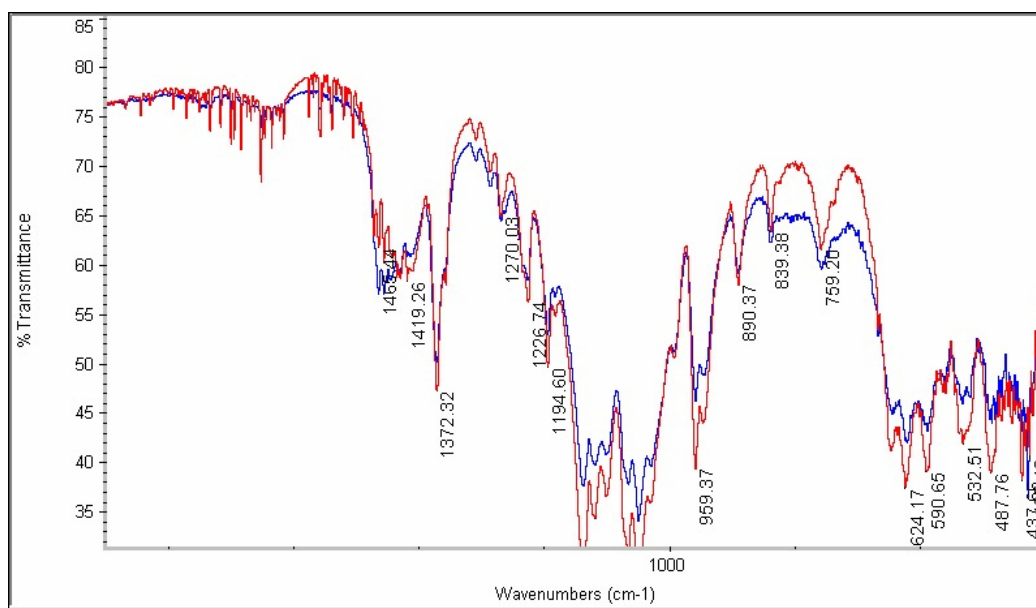


The observed pXRD pattern was taken after 5 days exposed to the atmosphere.

Conditions:

pXRD measurements were performed on a Bruker DX axes diffractometer, with a step of 0.050 ° and step time of 5 s.

FT-IR (KBr) for the finger-print region:



Red – fresh sample

Blue – exposed to atmosphere for 5 days