Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Thiol-substituted copolylactide: Synthesis, characterization and post-polymerization modification using thiol-ene chemistry

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Table of content

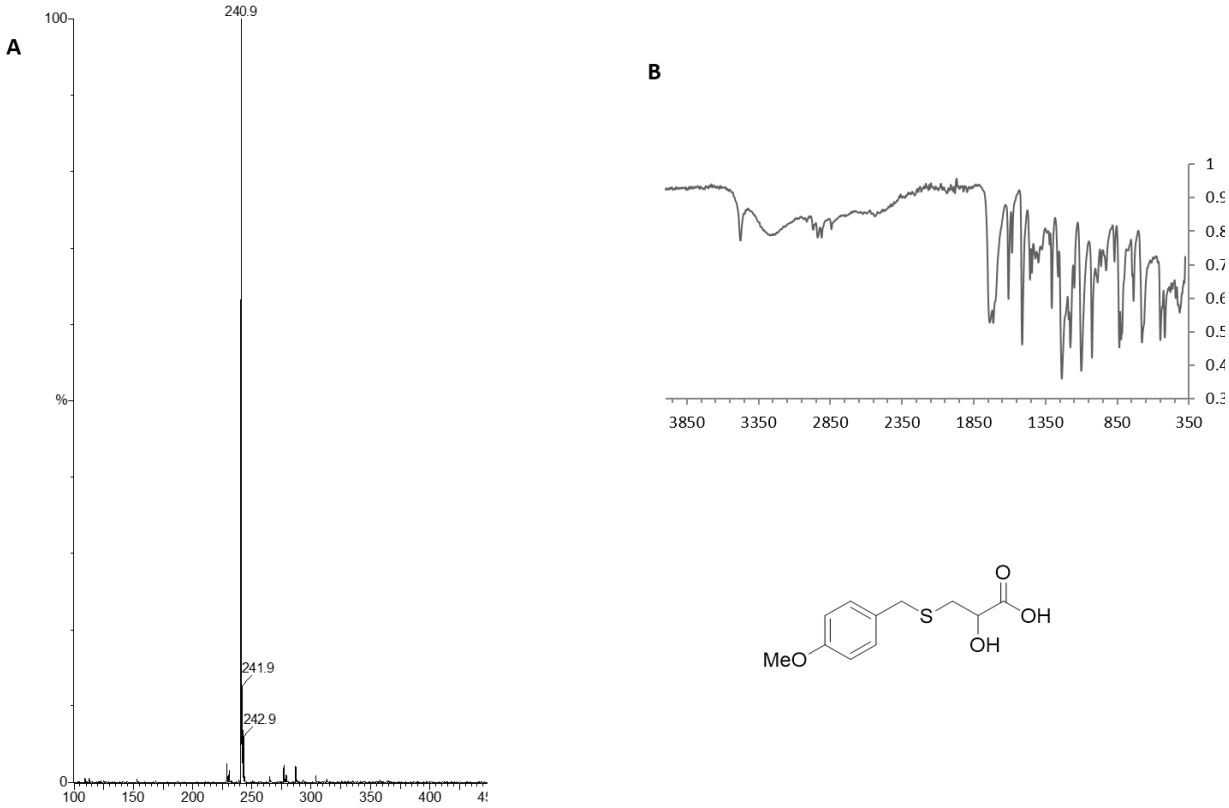

Figure S-1. 4-methoxybenzylthio-substituted lactic acid **2**. A, MS; B, IR spectrum.

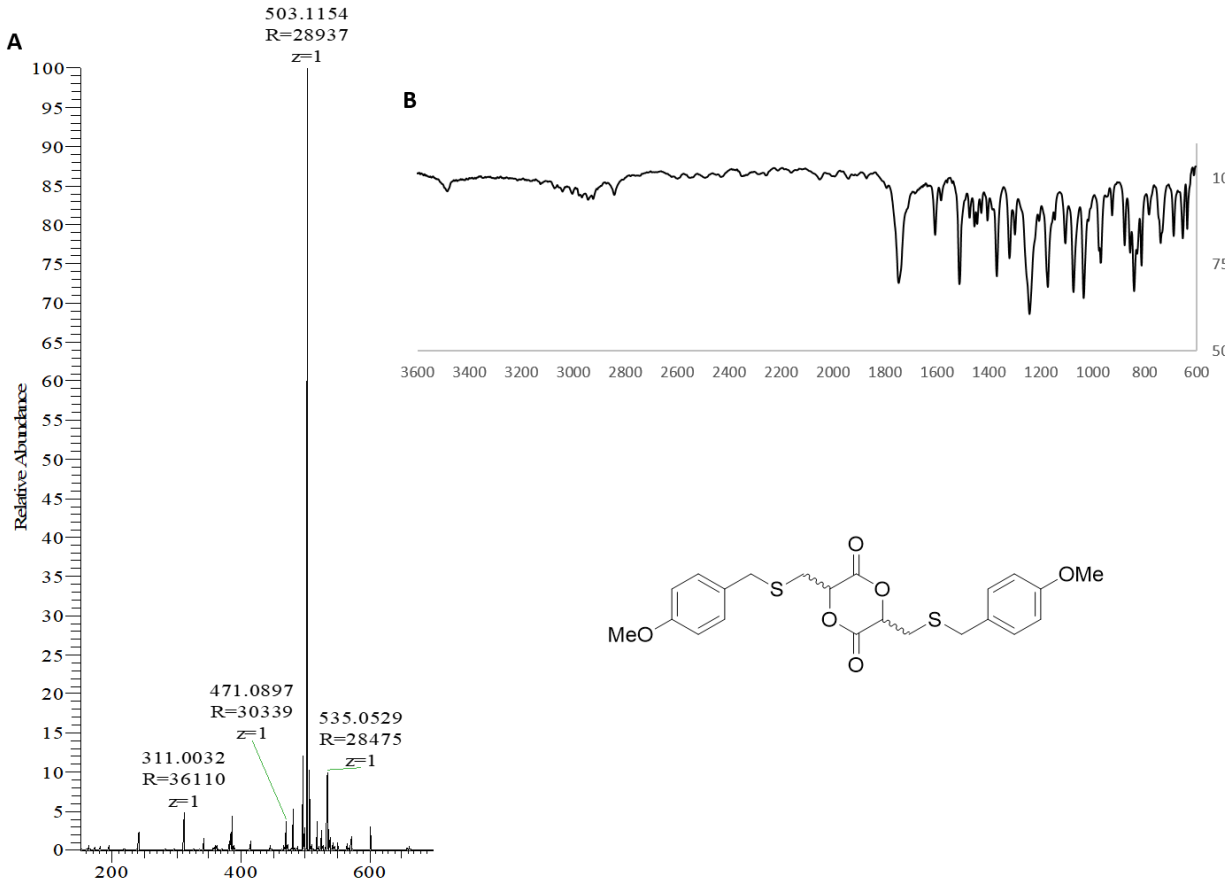

Figure S-2. 4-methoxybenzylthio-substituted lactide monomer **1** A, HRMS; B, IR spectrum.

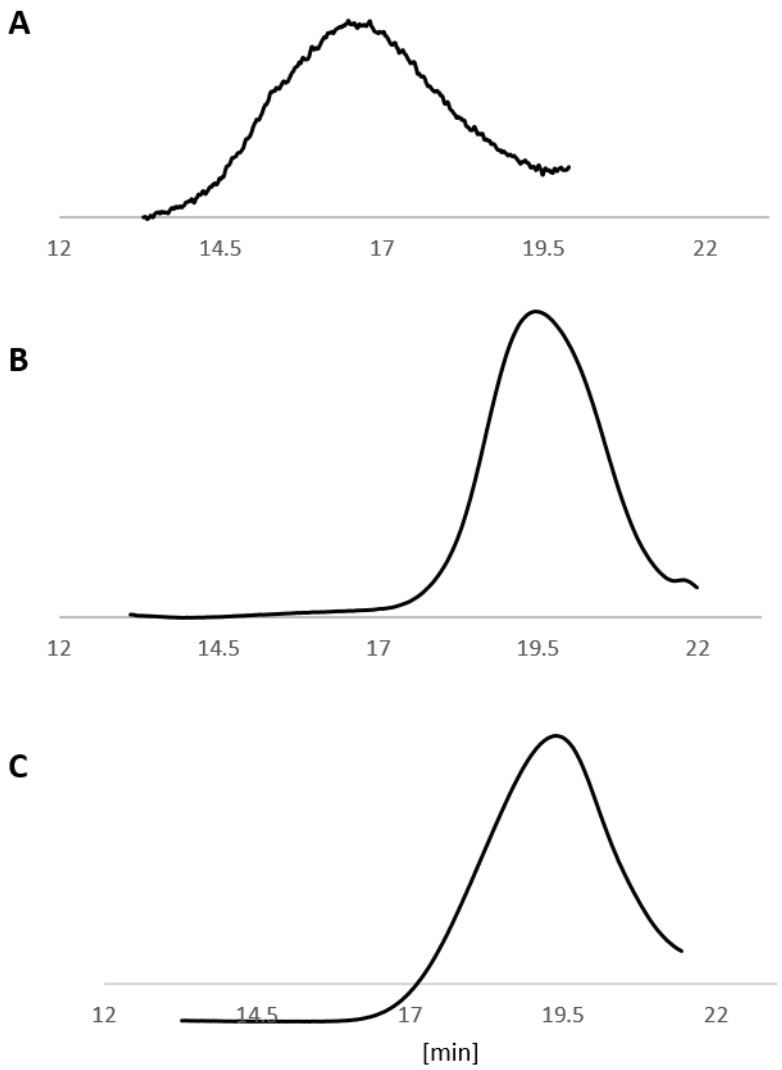

Figure S-3. GPC. A, 5 % MBT-PL obtained by copolymerization of trans MBT-lactide with L-lactide. B, 4 % thiol-PL. C, 4 % thiol-PL-phenylacrylate adduct.

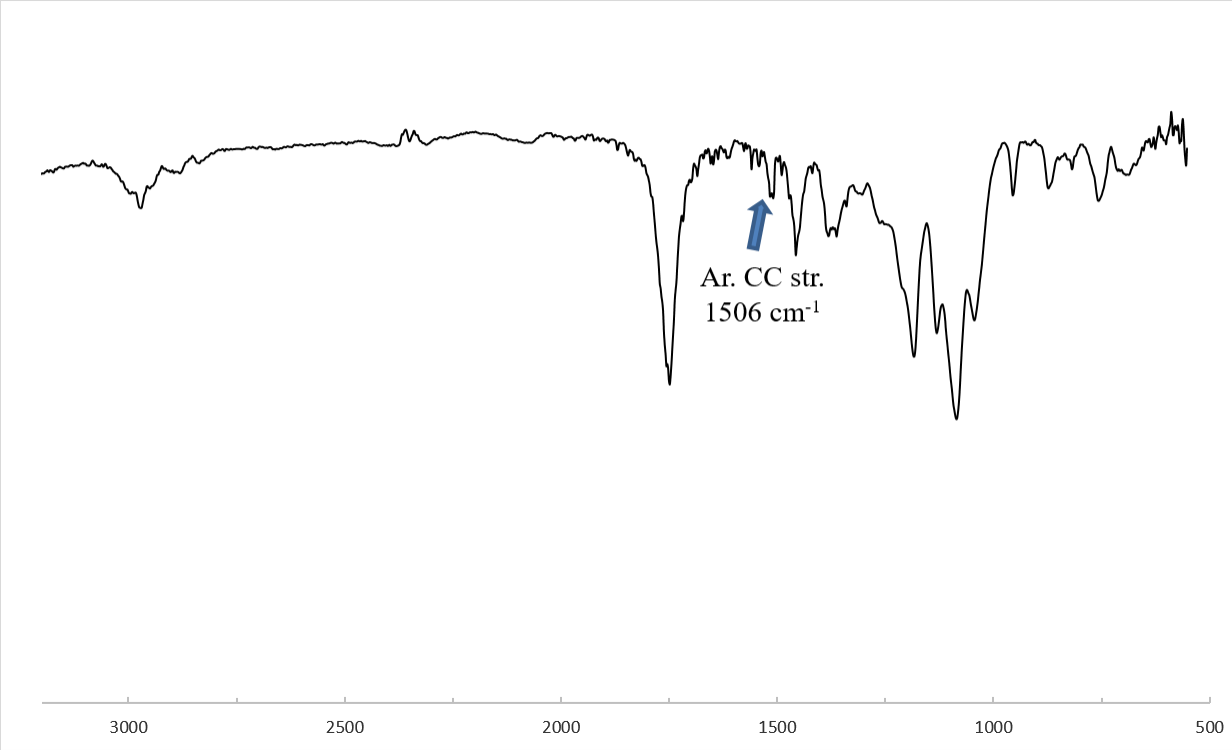

Figure S-4. IR spectrum of 5 % MBT-PL.

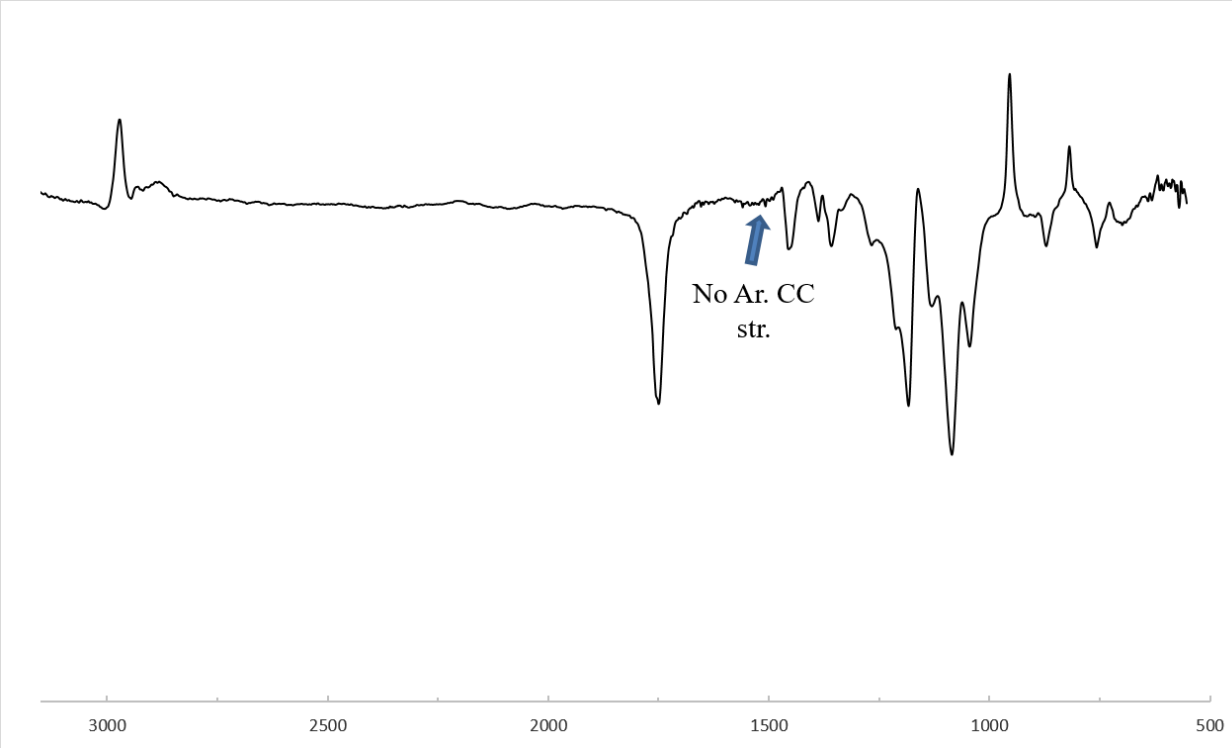

Figure S-5. IR spectrum of 4 % thiol-PL.

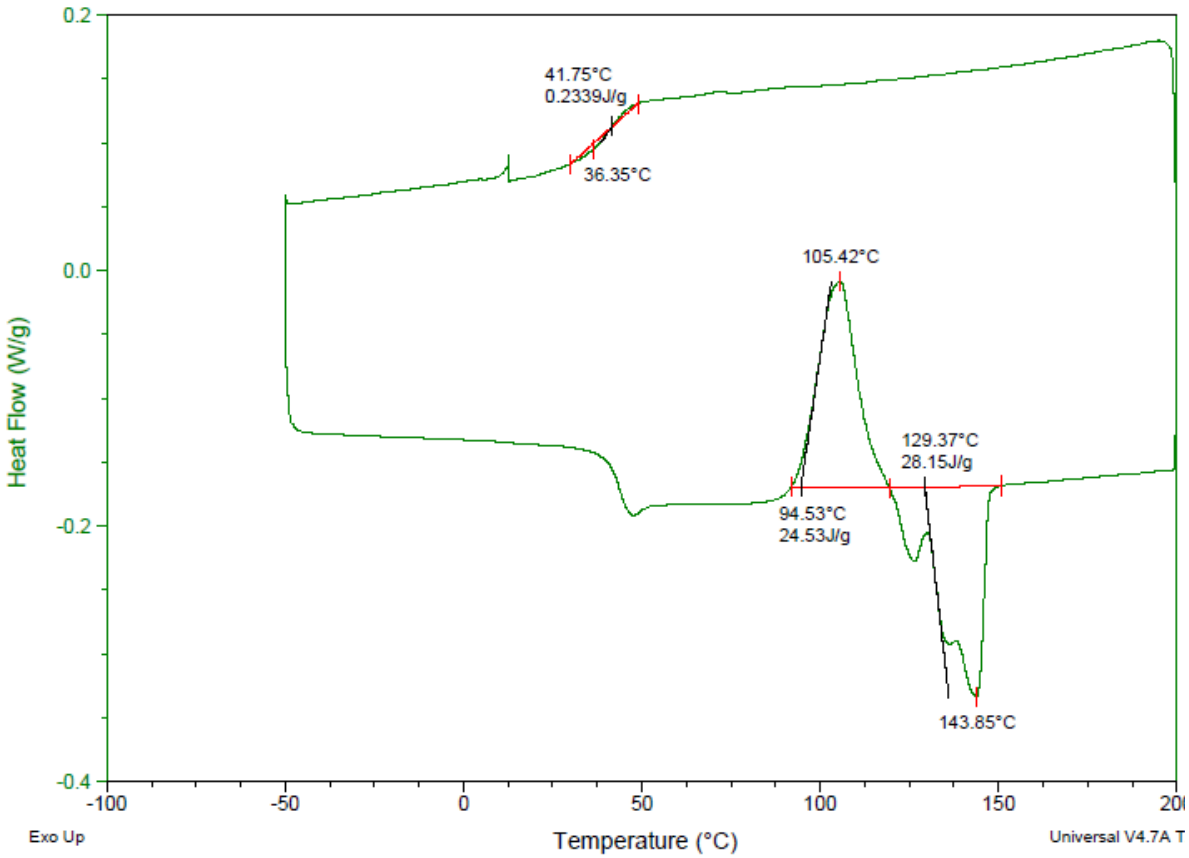

Figure S-6. DSC thermogram of 5 % MBT-PL obtained by copolymerization of the cis stereoisoform of monomer **1** with L-lactide. 5 °C/min, -50 °C to 200 °C.

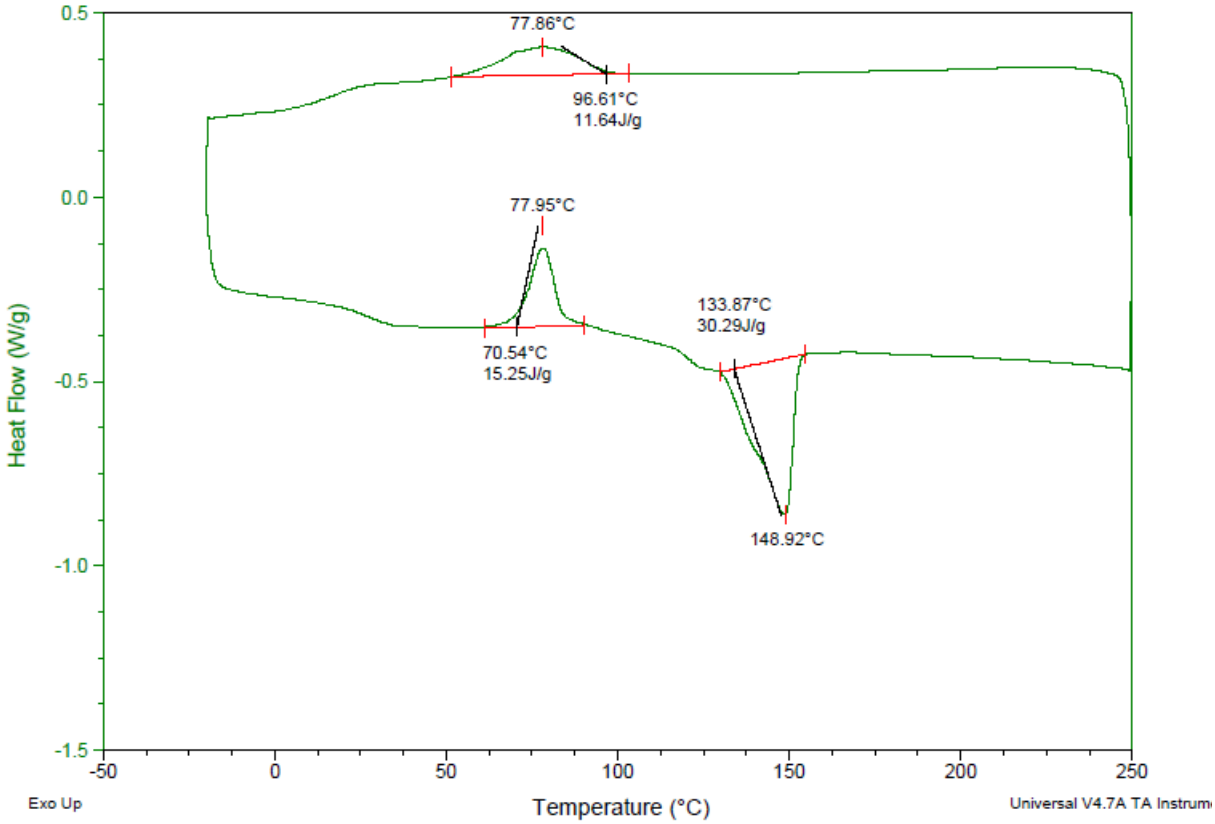

Figure S-7. DSC thermogram of 5 % MBT-PL obtained by copolymerization of the trans stereoisoform of monomer **1** with L-lactide. 5 °C/min, -10 °C to 250 °C

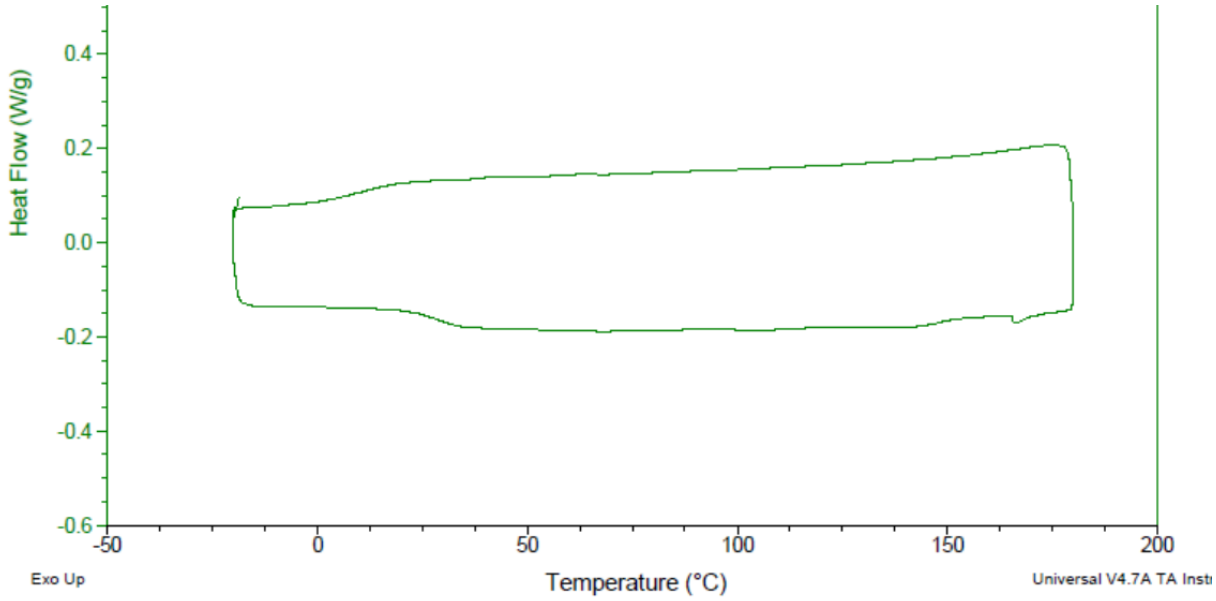

Figure S-8. DSC thermogram of 5 % MBT-PL obtained by copolymerization of the diasteriomeric mixture of monomer **1** with L-lactide. 5 °C/min, -10 °C to 180 °C

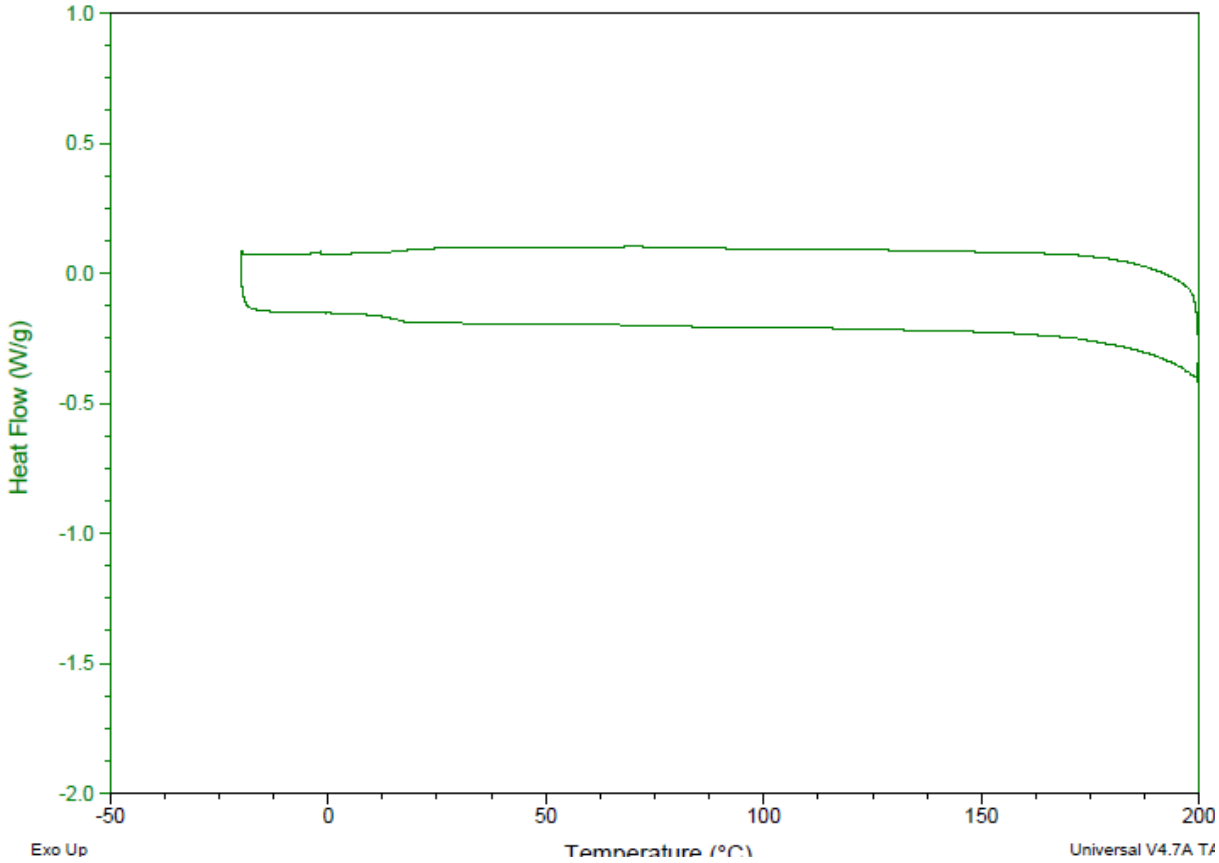

Figure S-9. DSC thermogram of 4 % thiol-PL showing the second thermal cycle. 5 °C/min, -20 °C to 200 °C.

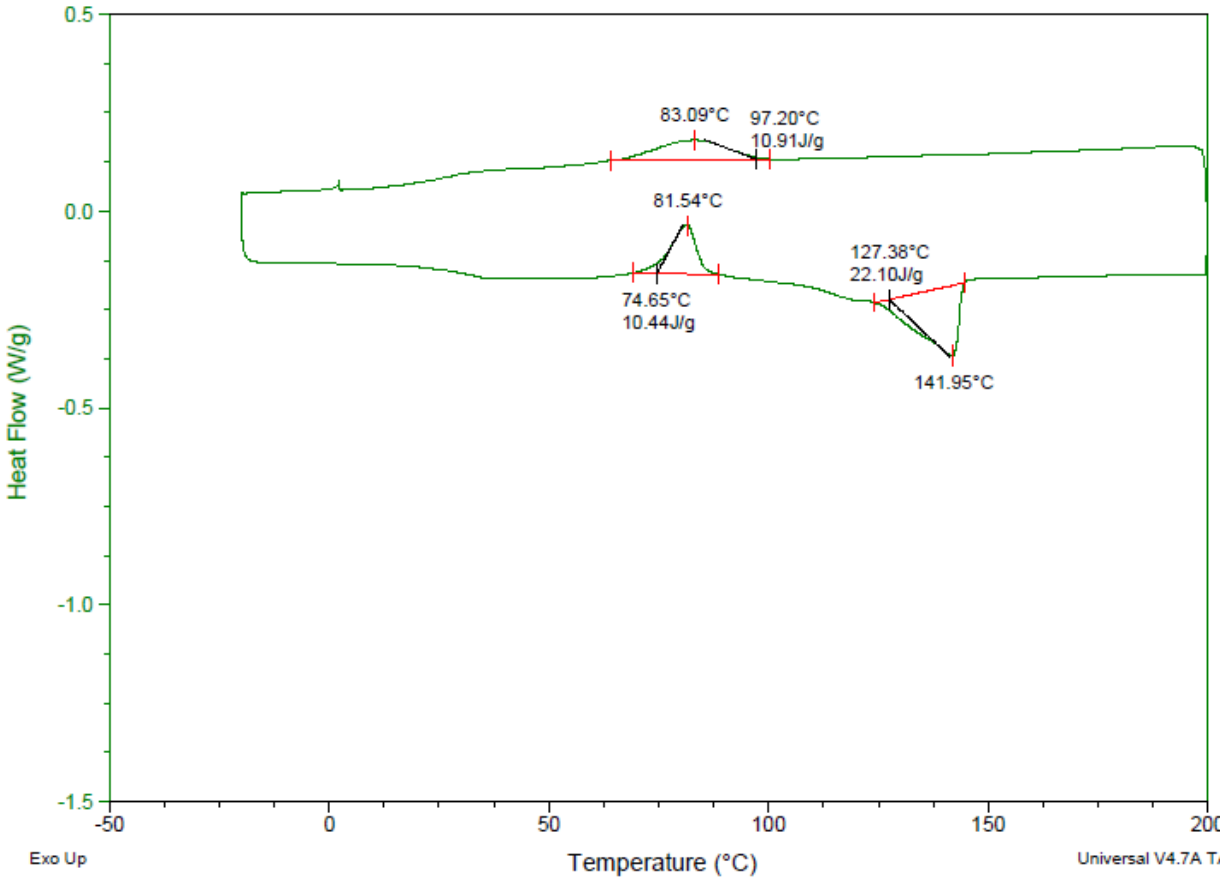

Figure S-10. DSC thermogram of phenyl acrylate adduct of 4 % thiol-PL copolymer showing the second thermal cycle. 5 °C/min, -10 °C to 200 °C.

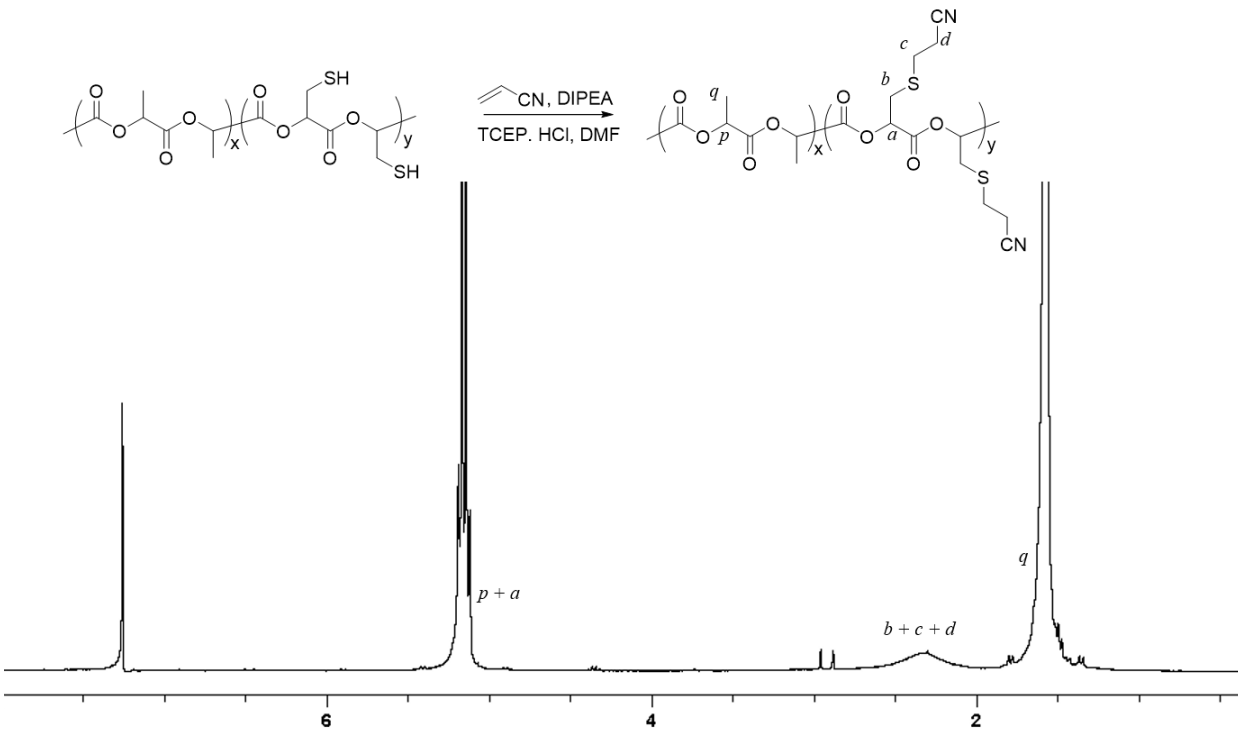

Figure S-11.^{1}H NMR spectrum (300 MHz, $CDCl_3$) of acrylonitrile adduct of 4 % thiol-PL.

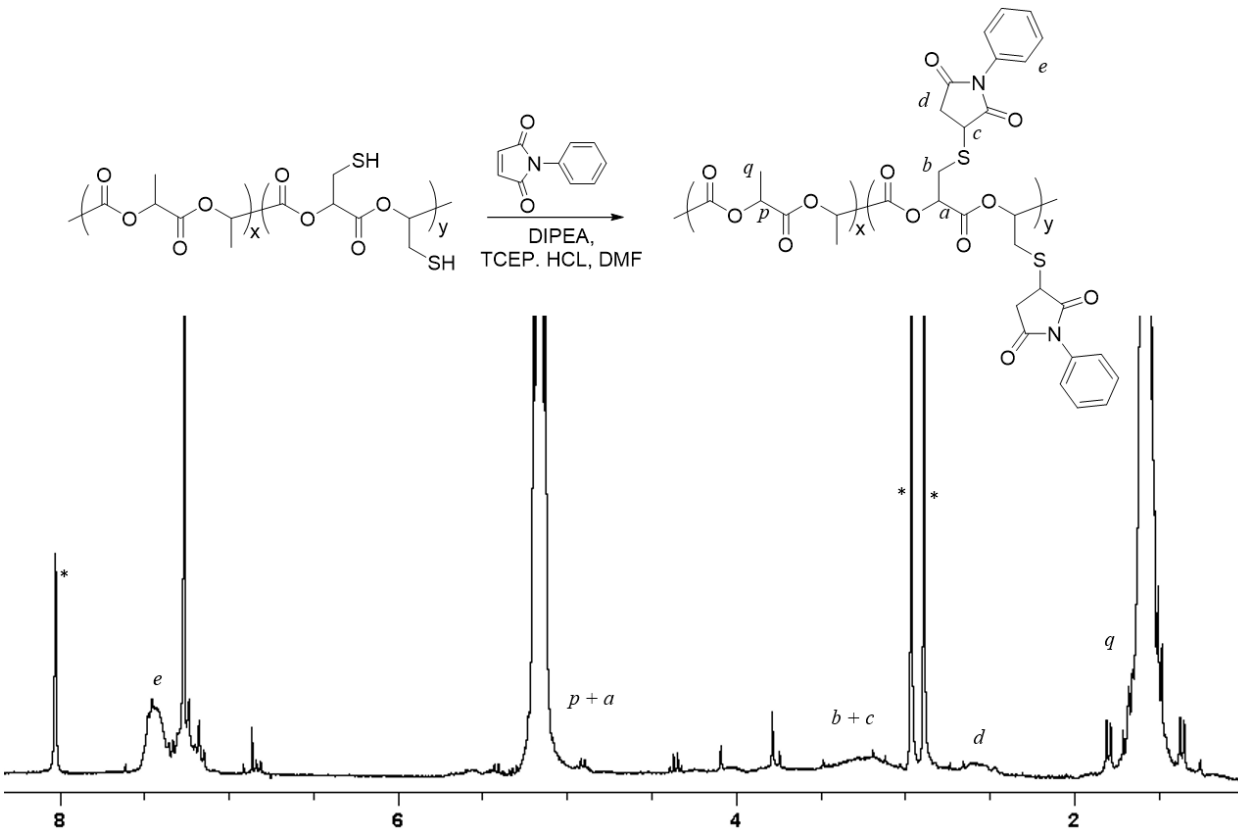

Figure S-12.[1]H NMR spectrum (300 MHz, $CDCl_3$) of *N*-phenylmaleimide adduct of 4 % thiol-PL. * residual DMF

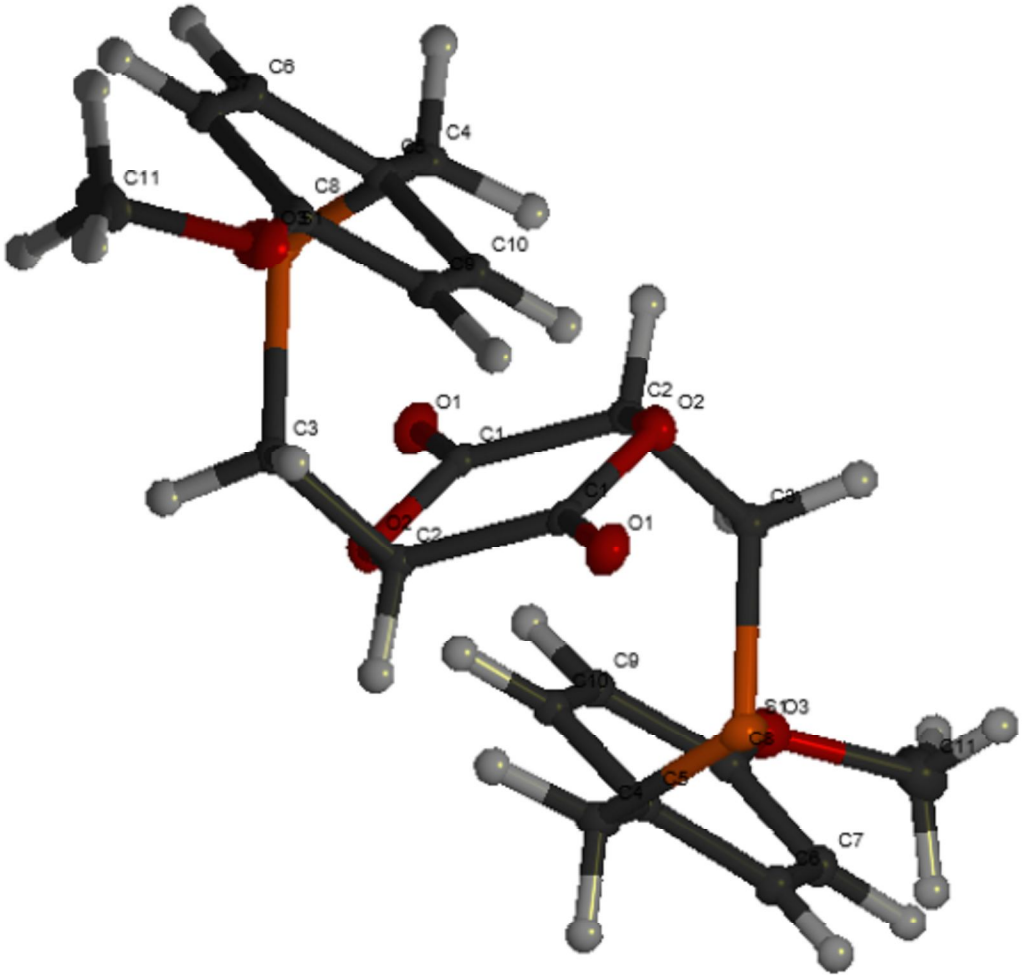

Figure S-13. Crystal structure of trans MBT-lactide**.**

Table S-1 Crystal data and structure refinement for MBT-lactide.

Identification code	MBT-lactide
Empirical formula	$C_{22}H_{24}O_6S_2$
Formula weight	448.53
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	5.5834(9)
b/Å	7.3620(11)
c/Å	12.537(2)
α/°	91.1515(18)
β/°	93.4047(17)
γ/°	100.6667(17)
Volume/Å^3	505.29(14)
Z	1
ρ_{calc}g/cm^3	1.474
μ/mm^{-1}	0.302
F(000)	236.0
Crystal size/mm^3	0.658 × 0.566 × 0.559
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.256 to 59.146
Index ranges	$-7 \leq h \leq 7, -10 \leq k \leq 10, -17 \leq l \leq 17$
Reflections collected	8401
Independent reflections	2818 [R_{int} = 0.0253, R_{sigma} = 0.0252]
Data/restraints/parameters	2818/0/137
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0336, wR_2 = 0.0839
Final R indexes [all data]	R_1 = 0.0374, wR_2 = 0.0871
Largest diff. peak/hole / e Å^{-3}	0.45/-0.26

Table S-2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for thiol-lactide. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	3447.8(5)	1540.6(4)	2040.3(2)	14.22(9)
O2	4760.9(16)	-1602.1(11)	628.7(6)	12.43(17)
O1	1093.4(16)	-2610.5(13)	-139.8(7)	16.82(19)
O3	11827.4(17)	8299.4(13)	4283.5(7)	19.1(2)
C5	6133(2)	5142.9(15)	2363.2(9)	11.2(2)
C1	2927(2)	-1449.5(16)	-81.1(9)	11.2(2)
C2	6724(2)	-65.9(15)	886.3(9)	10.6(2)
C10	8398(2)	5857.3(16)	1974.2(9)	11.7(2)
C9	10244(2)	6926.7(16)	2630.1(9)	13.1(2)
C3	6321(2)	742.7(16)	1982.4(9)	11.6(2)
C7	7588(2)	6637.2(17)	4089.5(9)	14.7(2)
C6	5751(2)	5574.2(17)	3420.0(9)	13.6(2)
C8	9868(2)	7286.7(16)	3696.1(9)	13.2(2)
C4	4190(2)	3947.9(16)	1643.3(10)	13.1(2)
C11	11752(3)	8296(2)	5421.8(11)	23.3(3)

Table S-3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for MBT-lactide. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	11.63(14)	11.23(14)	19.49(15)	-1.18(10)	5.26(10)	0.16(10)
O2	15.8(4)	8.6(4)	11.7(4)	1.0(3)	-0.7(3)	-0.2(3)
O1	15.4(4)	16.5(4)	16.3(4)	0.1(3)	3.7(3)	-3.6(3)
O3	19.3(4)	19.6(5)	17.3(4)	-6.9(3)	-5.0(3)	3.4(4)
C5	12.8(5)	8.4(5)	13.0(5)	0.5(4)	0.7(4)	3.7(4)
C1	12.7(5)	11.1(5)	9.9(5)	-1.5(4)	3.8(4)	2.1(4)
C2	10.2(5)	9.7(5)	11.7(5)	0.1(4)	0.1(4)	1.3(4)
C10	14.5(5)	10.4(5)	10.9(5)	-0.2(4)	2.2(4)	3.6(4)
C9	13.4(5)	10.8(5)	15.2(5)	-0.2(4)	2.2(4)	2.4(4)
C3	12.4(5)	11.7(5)	10.8(5)	0.6(4)	-0.1(4)	2.5(4)
C7	21.2(6)	14.1(5)	10.5(5)	0.5(4)	2.9(4)	6.8(4)
C6	15.0(5)	13.3(5)	13.3(5)	1.5(4)	3.9(4)	3.8(4)
C8	16.0(5)	9.8(5)	14.1(5)	-1.5(4)	-2.5(4)	4.7(4)
C4	11.8(5)	10.2(5)	17.2(5)	-0.9(4)	-0.6(4)	2.7(4)
C11	33.7(7)	20.7(6)	16.2(6)	-6.1(5)	-10.1(5)	11.6(6)

Table S-4 Bond Lengths for MBT-lactide.

Atom	Atom	Length/Å
S1	C3	1.8122(12)
S1	C4	1.8299(12)
O2	C1	1.3383(14)
O2	C2	1.4383(14)
O1	C1	1.2037(14)
O3	C8	1.3696(15)
O3	C11	1.4303(16)
C5	C10	1.3972(16)
C5	C6	1.3940(15)
C5	C4	1.5047(16)
C1	C2[1]	1.5133(16)
C2	C1[1]	1.5133(16)
C2	C3	1.5319(15)
C10	C9	1.3894(16)
C9	C8	1.3929(16)
C7	C6	1.3937(17)
C7	C8	1.3969(17)

[1]1-X,-Y,-Z

Table S-5 Bond Angles for MBT-lactide.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	S1	C4	103.53(5)	C1[1]	C2	C3	109.92(9)
C1	O2	C2	121.08(9)	C9	C10	C5	120.96(10)
C8	O3	C11	117.27(11)	C10	C9	C8	120.23(11)
C10	C5	C4	119.84(10)	C2	C3	S1	113.94(8)
C6	C5	C10	118.15(11)	C6	C7	C8	119.43(10)
C6	C5	C4	122.01(10)	C7	C6	C5	121.55(11)
O2	C1	C2[1]	119.68(10)	O3	C8	C9	115.66(11)
O1	C1	O2	119.91(11)	O3	C8	C7	124.75(11)
O1	C1	C2[1]	120.07(10)	C9	C8	C7	119.59(11)
O2	C2	C1[1]	116.16(9)	C5	C4	S1	114.06(8)
O2	C2	C3	107.88(9)				

[1]1-X,-Y,-Z

Table S-6 Torsion Angles for MBT-lactide.

A	B	C	D	Angle/°
O2	C2	C3	S1	-59.29(10)
C5	C10	C9	C8	0.75(17)
C1	O2	C2	C1[1]	-19.89(15)
C1	O2	C2	C3	103.99(11)
C1[1]	C2	C3	S1	68.28(11)
C2	O2	C1	O1	-166.06(10)
C2	O2	C1	C2[1]	20.57(16)
C10	C5	C6	C7	-2.04(17)
C10	C5	C4	S1	113.17(11)
C10	C9	C8	O3	177.81(10)
C10	C9	C8	C7	-2.90(17)
C3	S1	C4	C5	-60.13(9)
C6	C5	C10	C9	1.70(17)
C6	C5	C4	S1	-66.94(13)
C6	C7	C8	O3	-178.22(11)
C6	C7	C8	C9	2.56(17)
C8	C7	C6	C5	-0.08(18)
C4	S1	C3	C2	-89.00(9)
C4	C5	C10	C9	-178.41(10)
C4	C5	C6	C7	178.08(11)
C11	O3	C8	C9	-164.19(11)
C11	O3	C8	C7	16.56(17)

[1]1-X,-Y,-Z

Table S-7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for MBT-lactide.

Atom	*x*	*y*	*z*	U(eq)
H2	8272	-564	958	13
H10	8682	5608	1251	14
H9	11767	7414	2351	16
H3A	7673	1792	2175	14
H3B	6385	-213	2523	14
H7	7291	6918	4807	18
H6	4203	5133	3690	16
H4A	4740	3973	907	16
H4B	2687	4483	1633	16
H11A	10472	8948	5638	35
H11B	13335	8921	5751	35
H11C	11400	7018	5656	35

Experimental

Single crystals of $C_{22}H_{24}O_6S_2$ (MBT-lactide) were recrystallized from chloroform. A suitable crystal was selected and the crystal was mounted on a loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of MBT-lactide

Crystal Data for $C_{22}H_{24}O_6S_2$ (*M* =448.53 g/mol): triclinic, space group P-1 (no. 2), *a* = 5.5834(9) Å, *b* = 7.3620 (11) Å, *c* = 12.537(2) Å, *α* = 91.1515(18)°, *β* = 93.4047(17)°, *γ* = 100.6667(17)°, *V* = 505.29(14) Å^3, *Z* = 1, *T* = 100(2) K, μ(MoKα) = 0.302 mm^{-1}, *Dcalc* = 1.474 g/cm^3, 8401 reflections measured (3.256° ≤ 2Θ ≤ 59.146°), 2818 unique (R_{int} = 0.0253, R_{sigma} = 0.0252) which were used in all calculations. The final R_1 was 0.0336 (I > 2σ(I)) and wR_2 was 0.0871 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C2(H2)
2.b Secondary CH2 refined with riding coordinates:
 C3(H3A,H3B), C4(H4A,H4B)
2.c Aromatic/amide H refined with riding coordinates:
 C10(H10), C9(H9), C7(H7), C6(H6)
2.d Idealised Me refined as rotating group:
 C11(H11A,H11B,H11C)
```