Electronic Supplementary Information

Stereoregular cyclic poly(3-hydroxybutyrate) enabled by catalyst-controlled tacticity and topology

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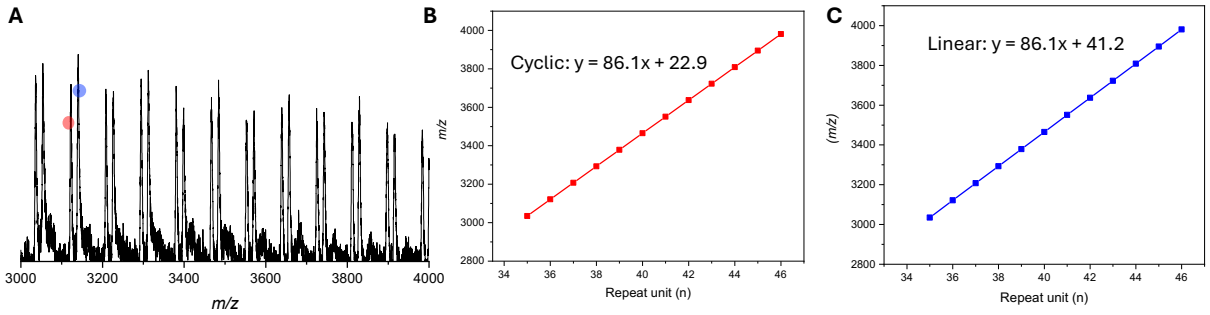
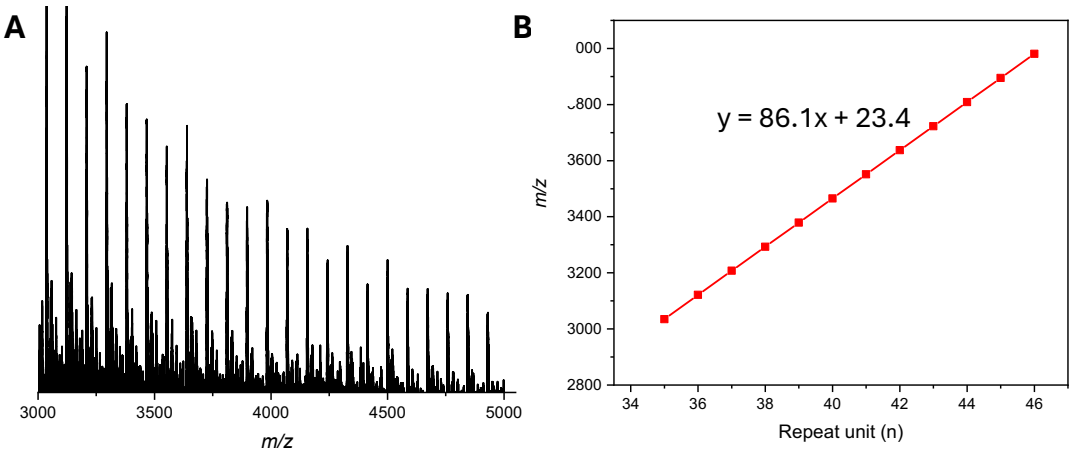


Figure S1. (**A**) MALDI-TOF-MS spectrum of *c*/*it*-P3HB produced directly using **1**. *c*/*it*-P3HB prepared using DCM (0.2 M) with a 20:1 ratio of *rac*-8DL^{Me} : **1** and quenched after stirring 7 h. Cyclic product indicated with red dot, linear product indicated with blue dot. (**B**) Plot of *m*/*z* values (y) vs the number of P3HB repeat units n (x) for first set of peaks showing no end groups. (**C**) Plot of *m*/*z* values (y) vs the number of P3HB repeat units n (x) for the second set of peaks showing an end group, indicating linear byproduct.



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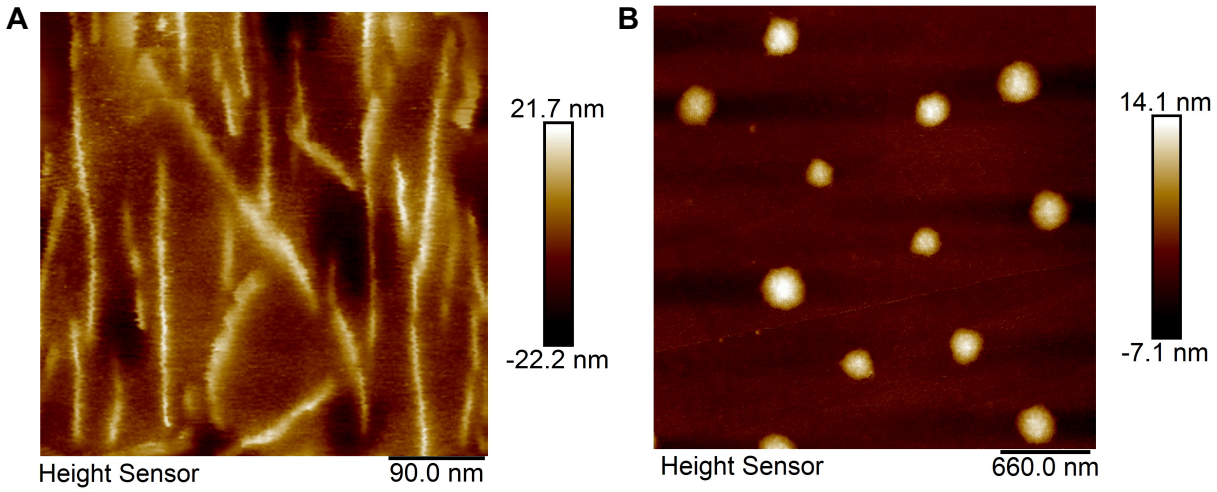

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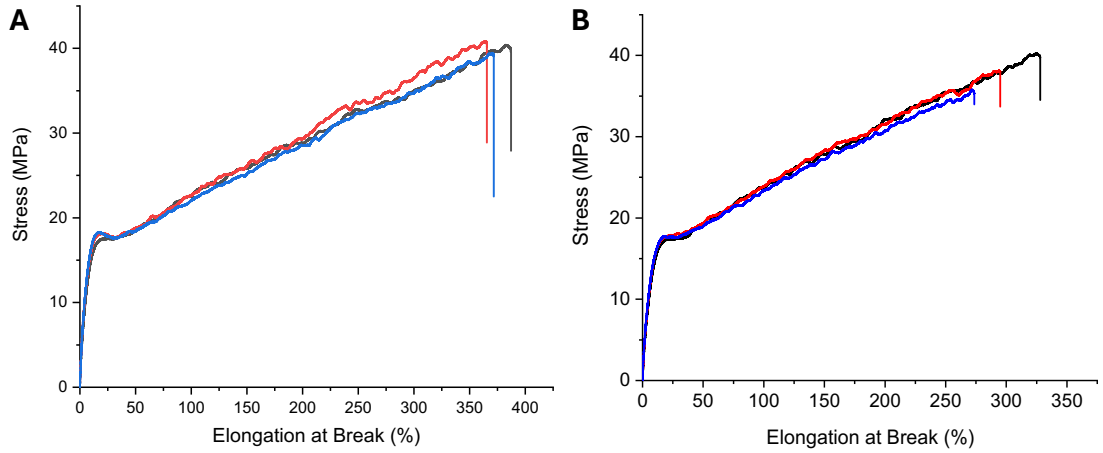

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Table S1. Triplicate tensile data for P3HB materials.

Polymer	M_n (kg mol^{-1})[a]	$Đ$[a]	Sample	Young's Modulus (E)	Standard Dev. (±)	Tensile strength (σ, MPa)	Standard Dev. (±)	elongation at break (ε, %)	Standard Dev. (±)
c/*sr*-P3HB	163	1.28	1	223		40		372	
			2	335		41		366	
			3	337		40		387	
			Average	298	65	40	0.8	375	11
l/*sr*-P3HB	283	1.26	1	207		35.8		274	
			2	231		38.1		295	
			3	251		40.2		328	
			Average	230	22	38.1	2.2	299	27

[a] M_n and $Đ$ were determined by size-exclusion chromatography (SEC) at 40 °C in $CHCl_3$ coupled with a DAWN HELEOS multi (18)-angle light scattering detector and an Optilab TrEX dRI detector.

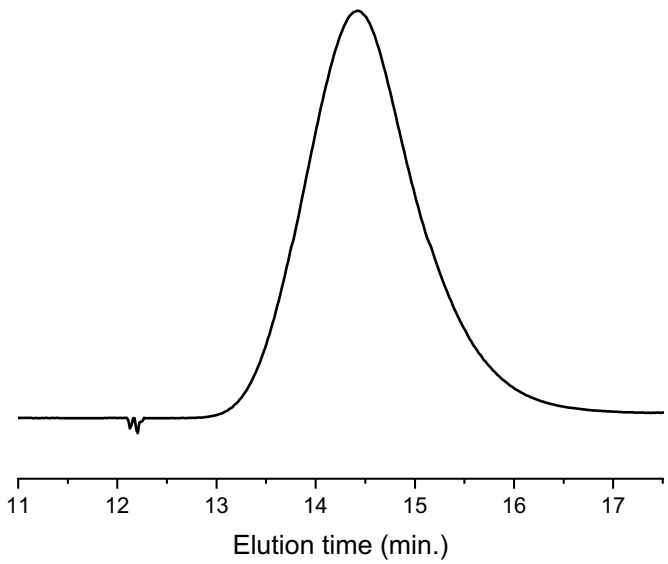


Figure S5. SEC trace of *c*/*it*-P3HB prepared from 200/1 *rac*-8DL^{Me}/**2** (M_n = 93.3 kg mol^{-1}, $Đ$ = 1.28).

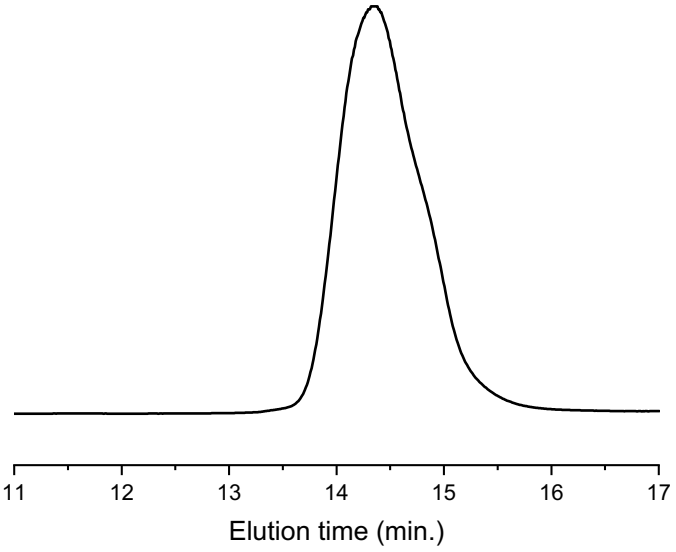
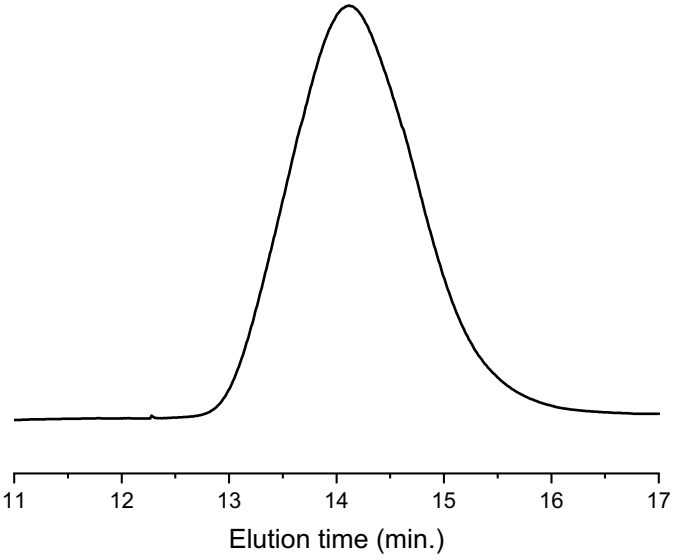


Figure S6. SEC trace of *l*/*it*-P3HB prepared from 600/1/1 *rac*-8DL^{Me}/**2**/BnOH (M_n = 141 kg mol^{-1}, $Đ$ = 1.07).



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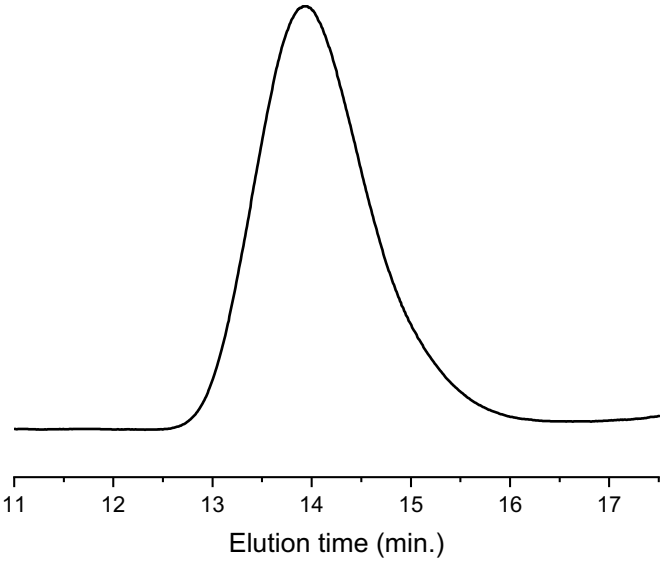

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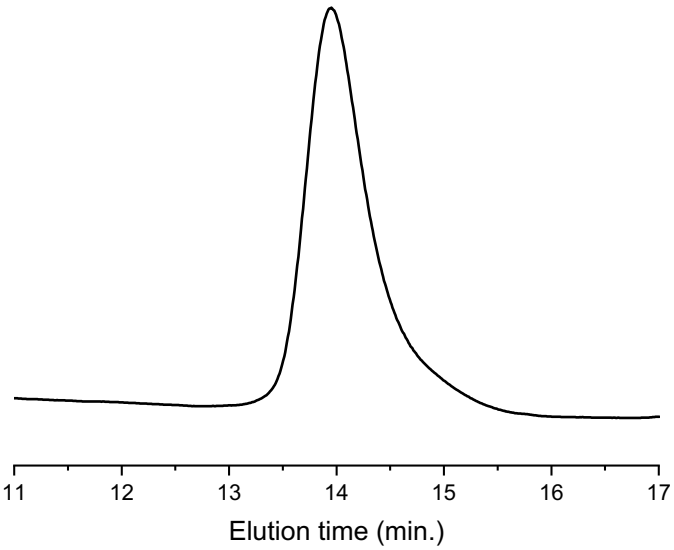

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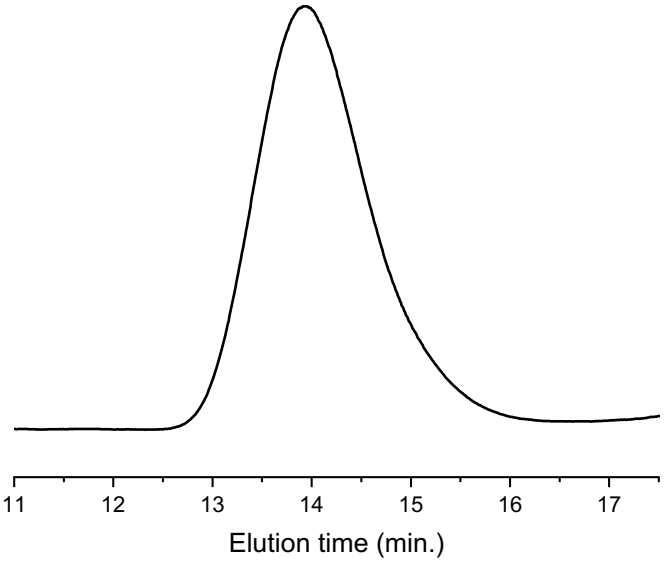

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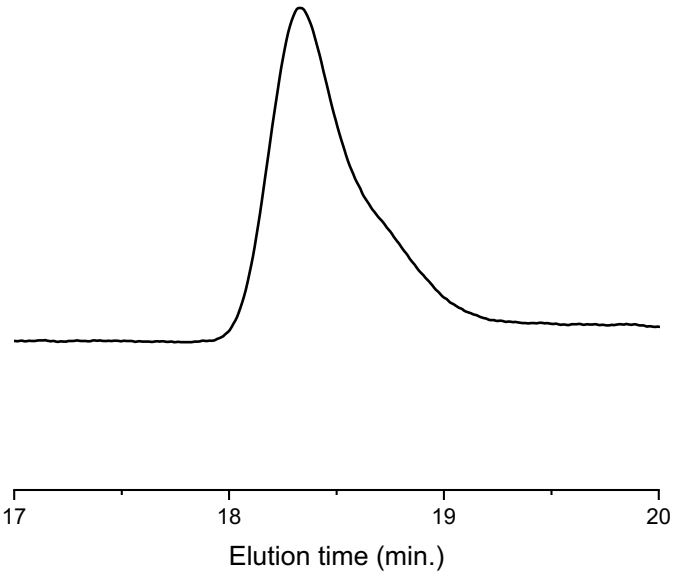

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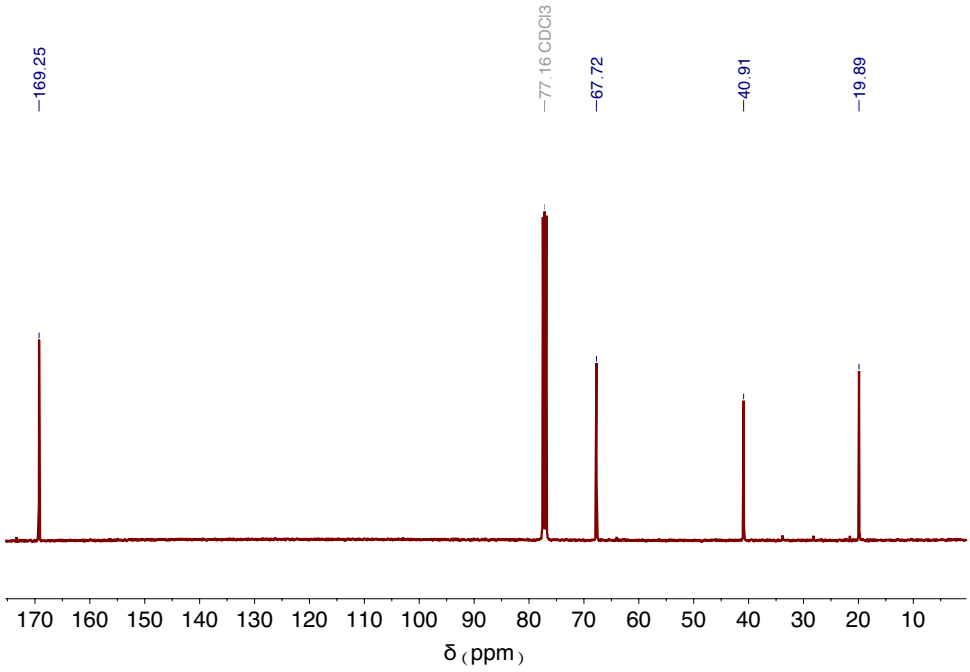

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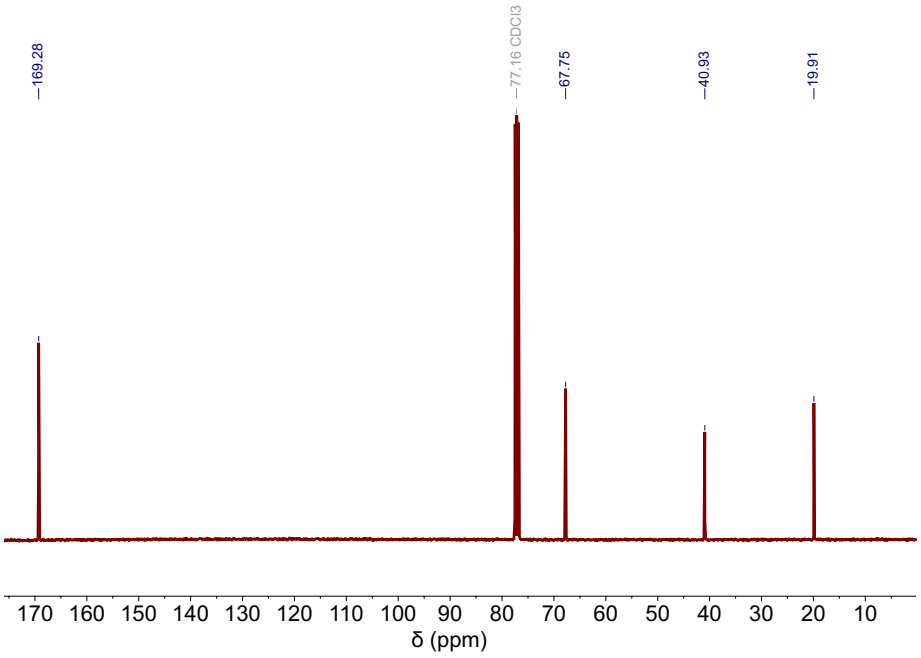

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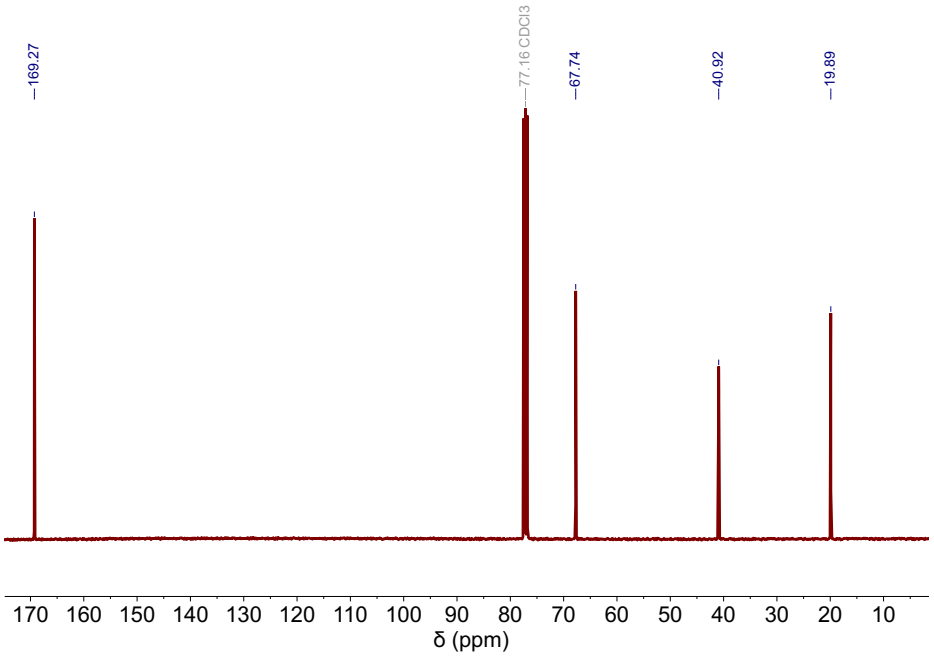

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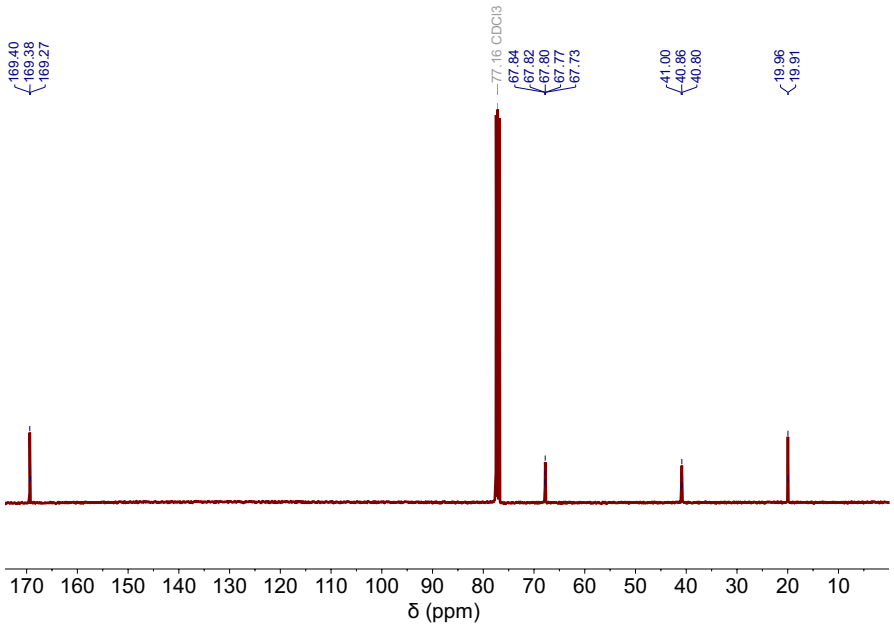

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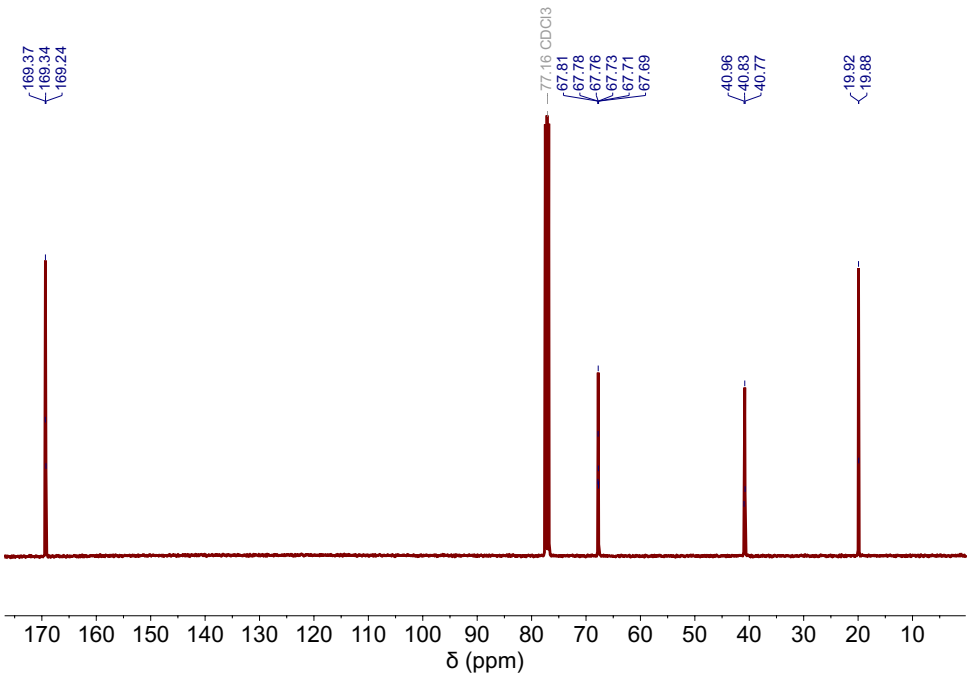

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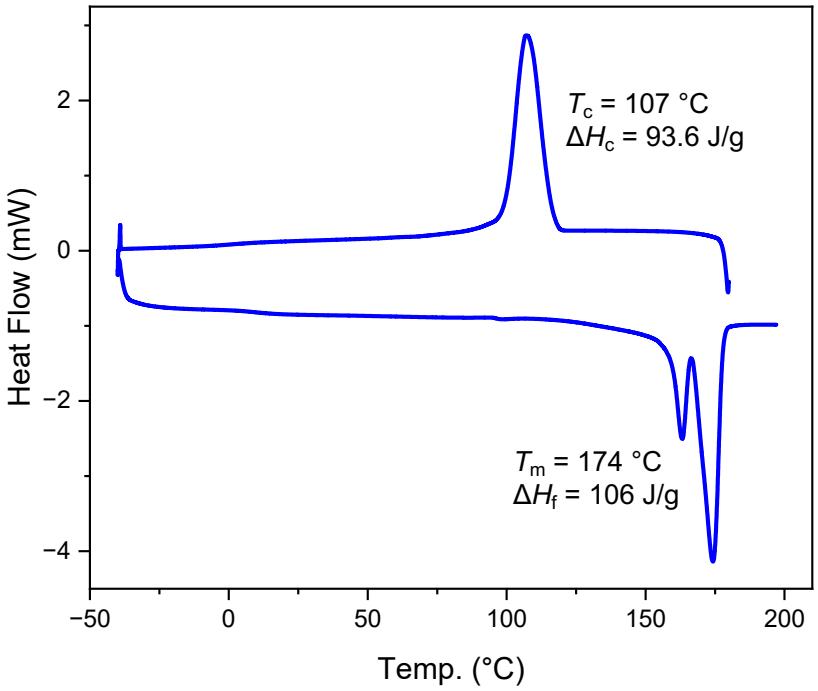

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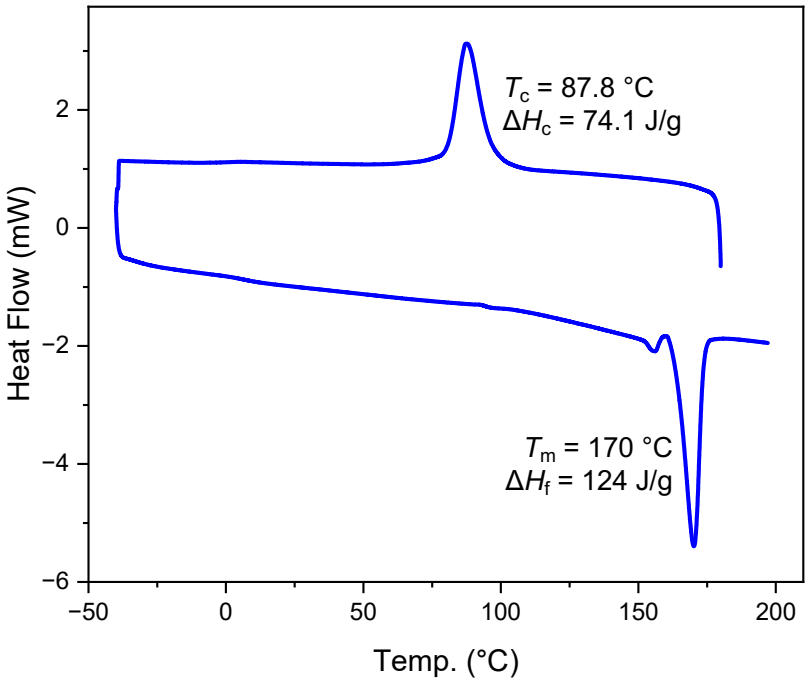

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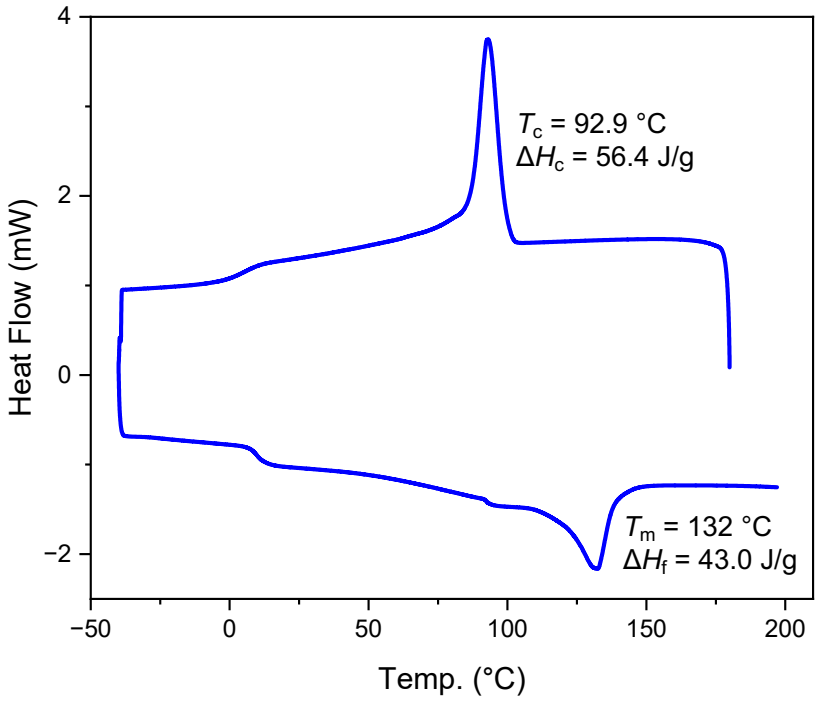

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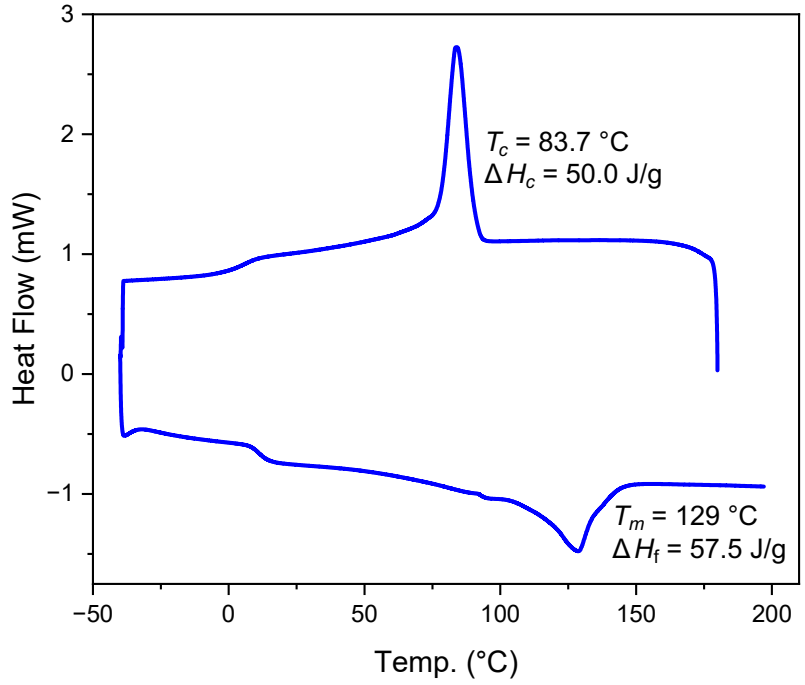

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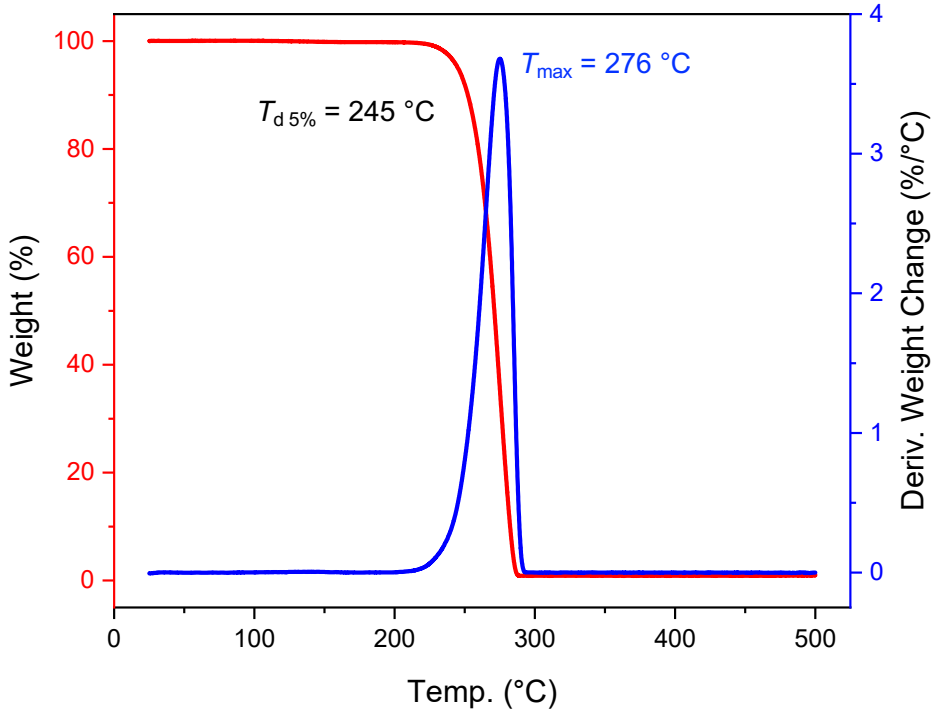

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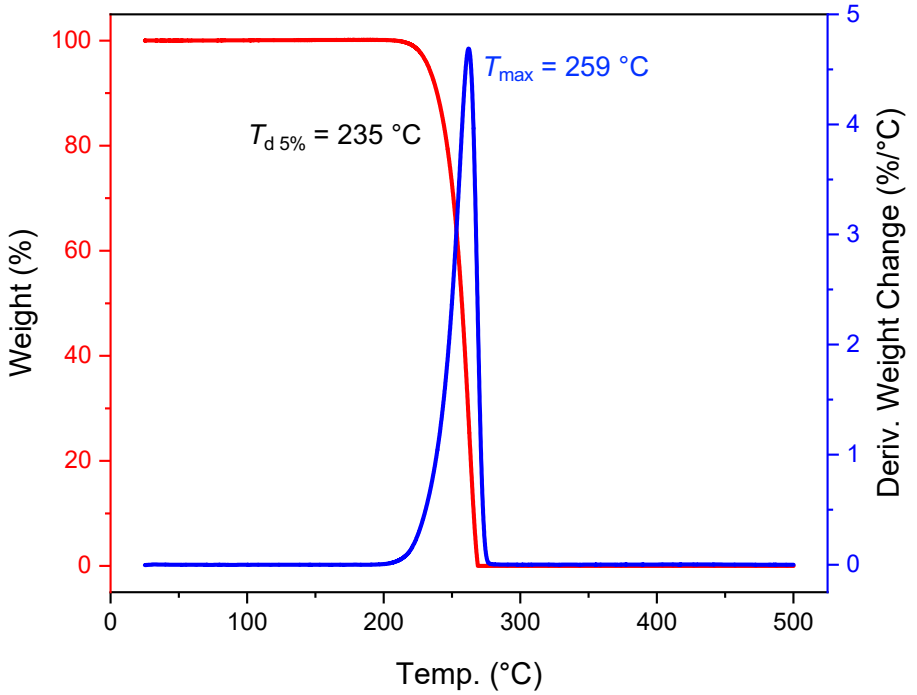

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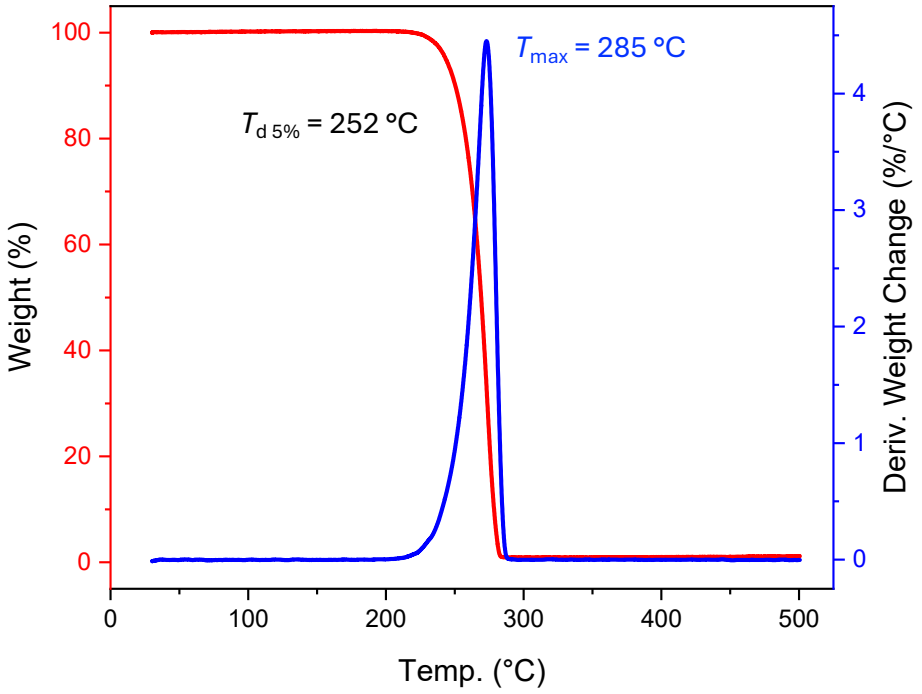

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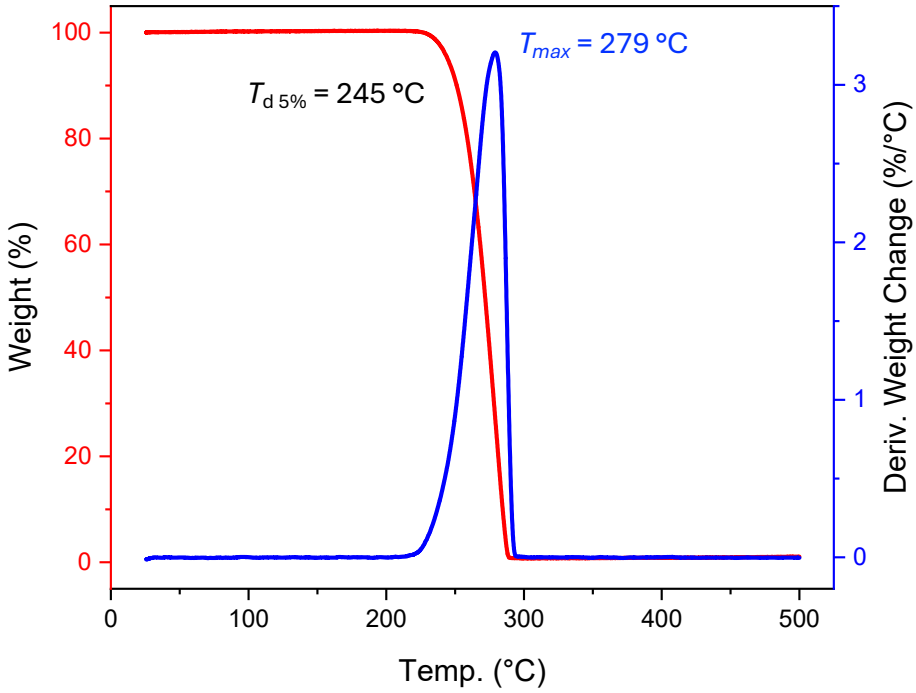

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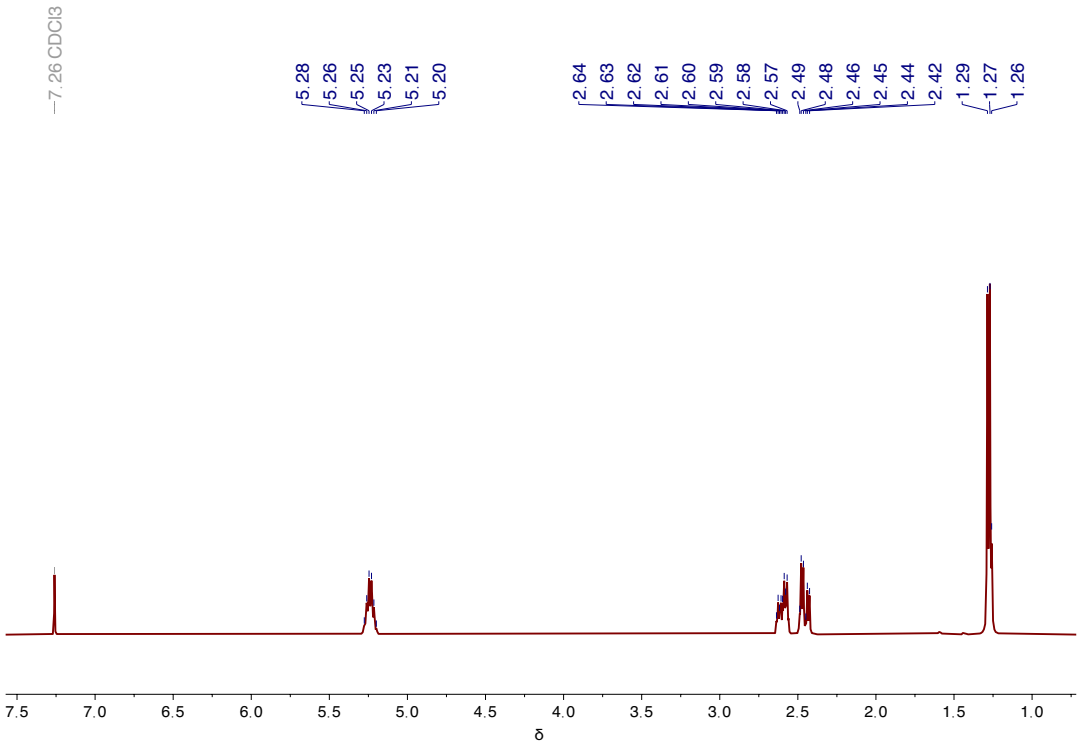

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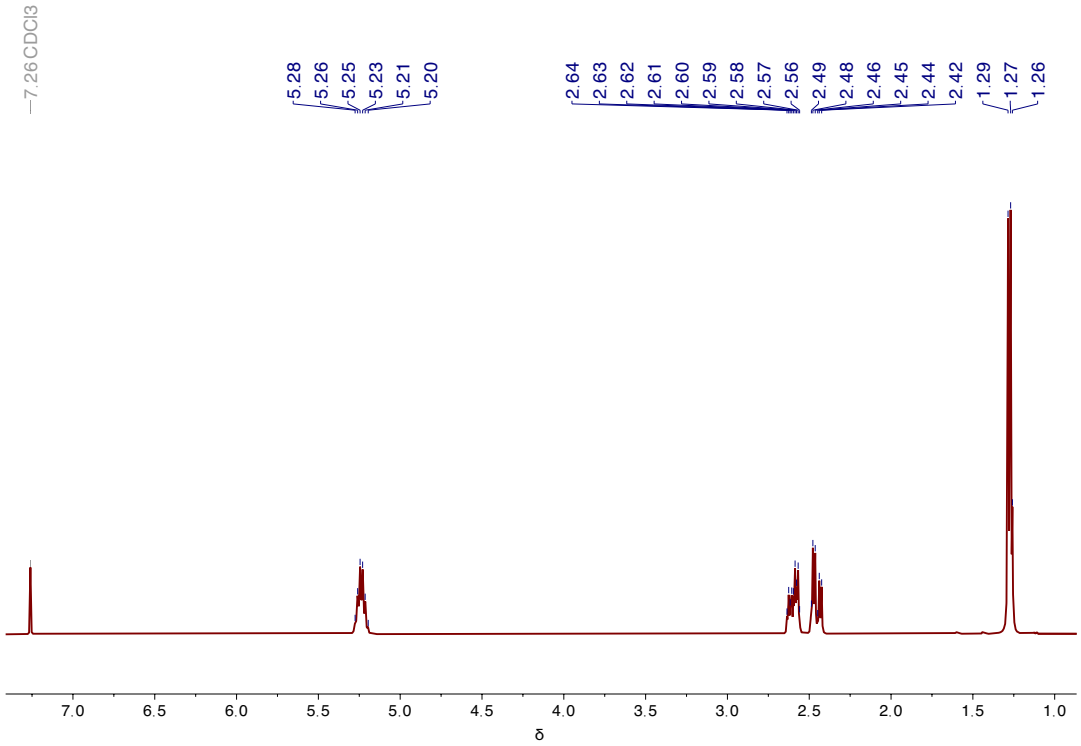

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Supplementary Note 1.

The crystallinity of the resulting P3HB was calculated using the equation X_c (%) = ($\Delta H_f/\Delta H_f^0$) · 100, where ΔH_f and ΔH_f^0 is the heat of fusion (J g^{-1}) of the synthesized P3HB and the 100% crystalline P3HB (146 J g^{-1})[1] respectively.

Bibliography:

1. Barham, P. J., Keller, A., Otun, E. L., and Holmes, P. A, *Journal of Materials Science,* **1984**, *19*, 2781–2794.