Supporting Information

Two New approaches Based on Dynamic Carboxyl-Hydroxyl or Hydroxyl-Carboxyl Transformation for High Molecular Weight Poly(Butylene Maleate)

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Section S1. Results of model polyesterification using excess MA to BDO

Table S1 | Polyesterification of MA with BDO under different reaction conditions

entry	MA/BDO[a]	TsOH (mol%)	temperature (℃)	time to climb (h)	M_n (kDa)[c]	cis (%)[d]
1	1.05 : 1	0.5	135	N [b]	22	95.2
2	1.05 : 1	1	135	2.5	92	93.9
3	1.05 : 1	1.5	135	1.5	78	96.2
4	1.05 : 1	1	110	9	38	98.6
5	1.05 : 1	1	120	3.5	72	97.5
6	1.05 : 1	1	150	1.5	59	92.3
7	1.1:1	1	135	4	82	94.1

[a] MA/diol was the molar ratio of MA and diol. [b] No Weissenberg effect was observed within 8 h. [c] M_n obtained by gel permeation chromatography (GPC) in $CDCl_3$. [d] cis % was defined as cis/(cis+trans) and calculated from ^1H NMR.

Section S2. NMR spectra of maleic anhydride byproduct

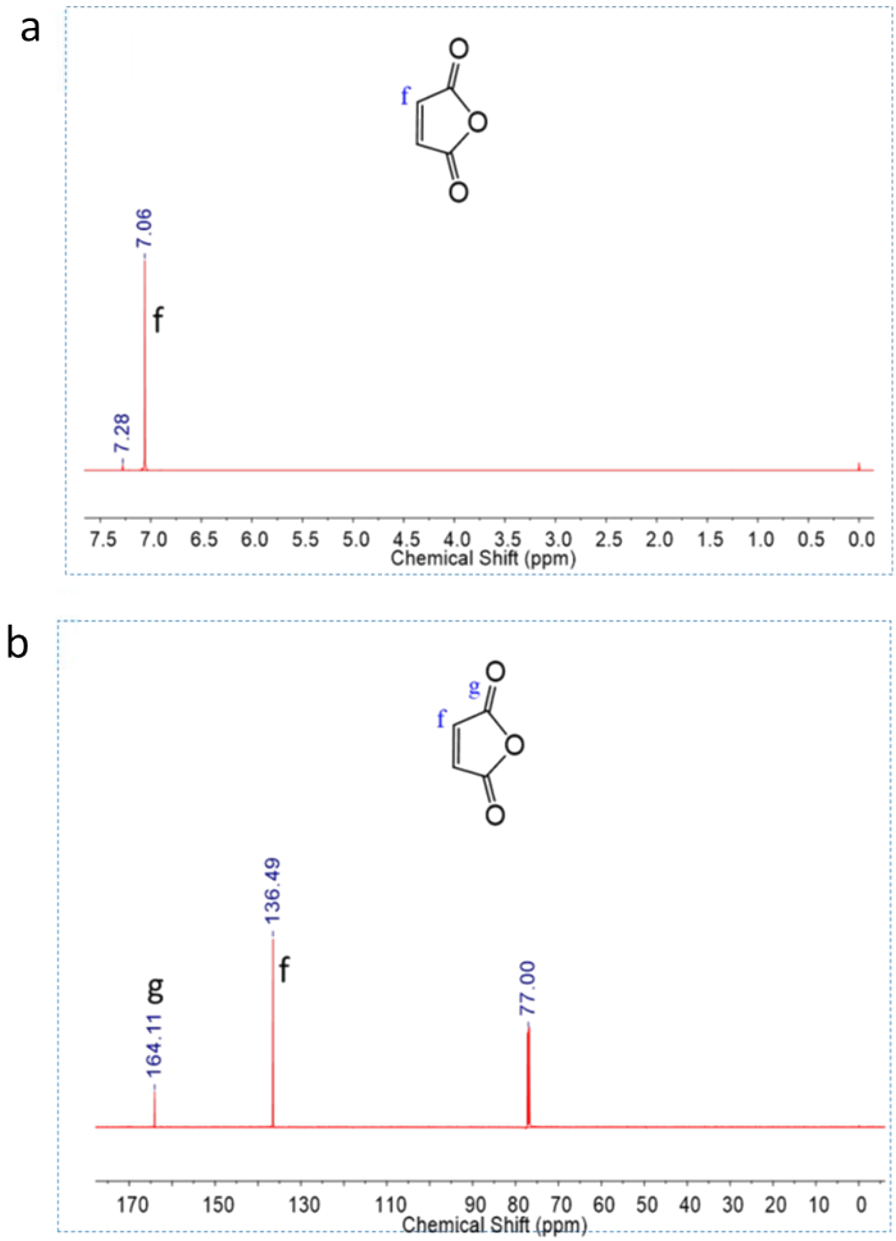


Fig. S1 | a, ^{1}H NMR spectrum of maleic anhydride. b, ^{13}C NMR spectrum of maleic anhydride.

Section S3. Characterizations of MA-based polyesters prepared with excess MA

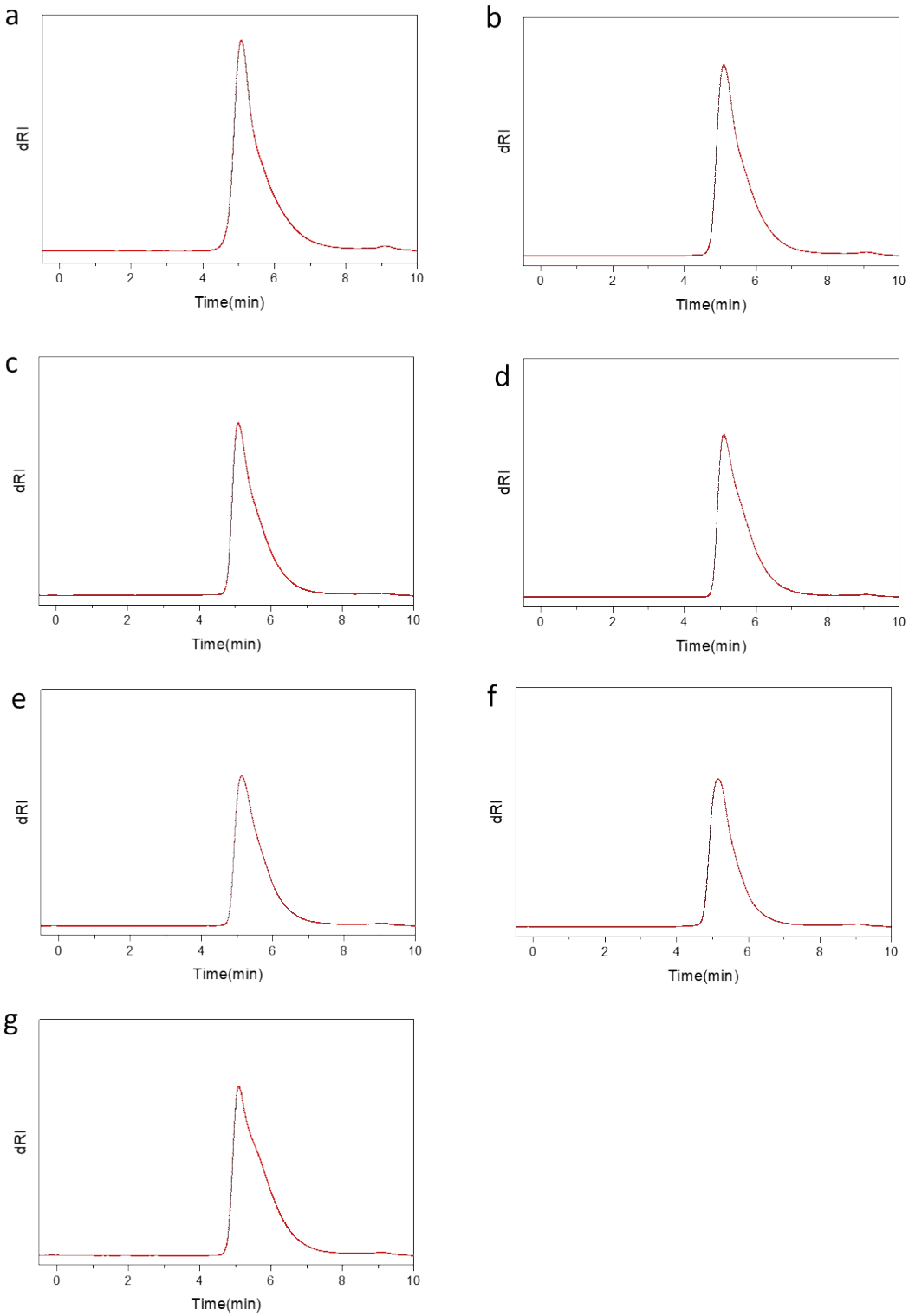


Fig. S2 | GPC curves of MA-based polyesters synthesized with MA/diol of 1.05:1. a, PBM. b, Poly(pentylene maleate). c, Poly(3-methylpentylene maleate). d, Poly(hexylene maleate). e, Poly(decylene maleate). f, Poly(dodecylene maleate). g, Poly(1,4-cyclohexandimethylene maleate).

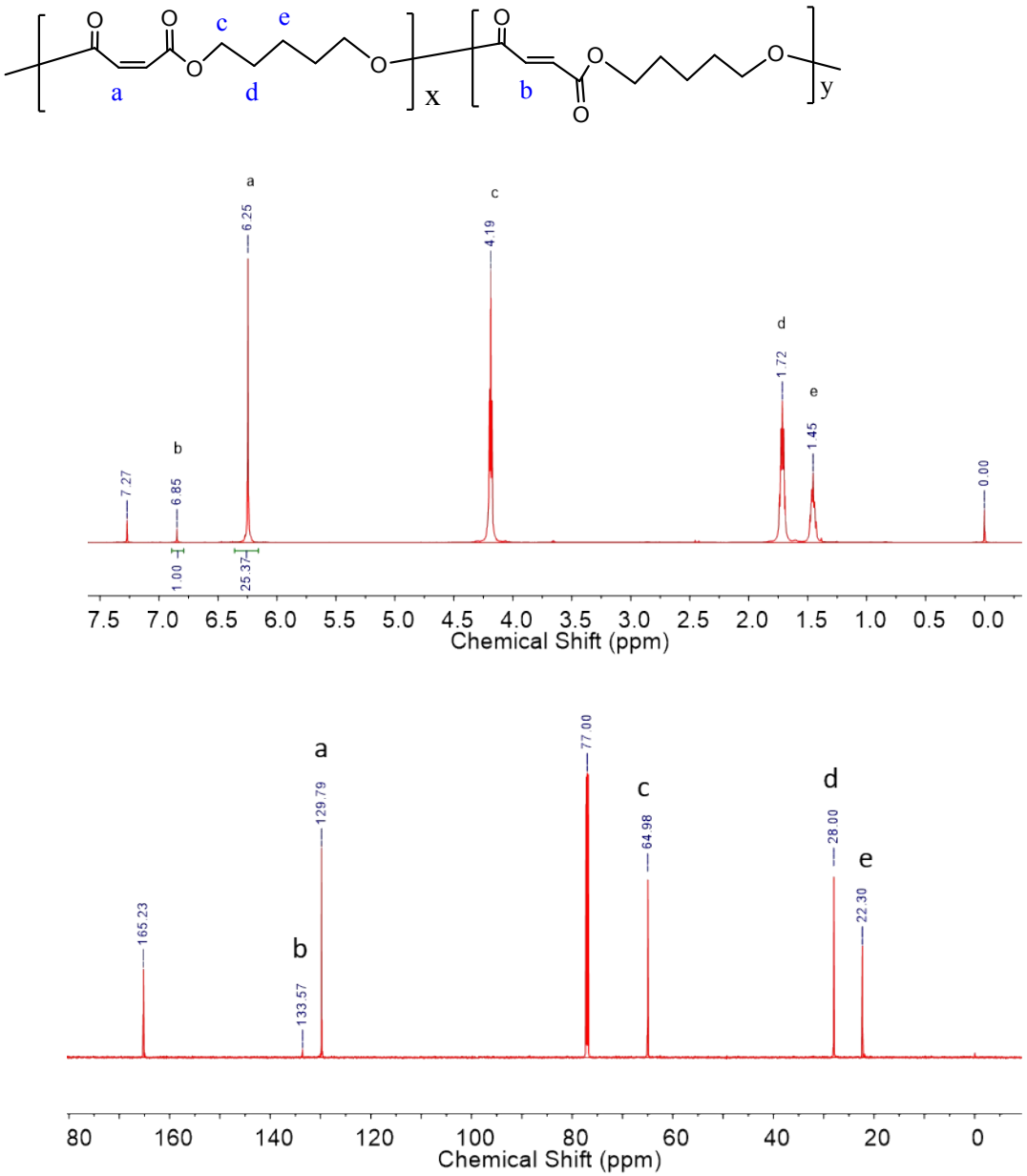
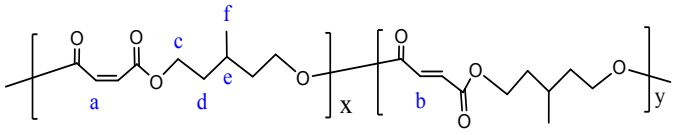


Figure S1 ^{1}H NMR of poly(pentene maleate)

Fig. S3 | Poly(pentylene maleate) (Table 1, entry 2), synthesized with MA/1,5-pentanediol of 1.05:1, in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=77 kDa, cis content=96.2%)



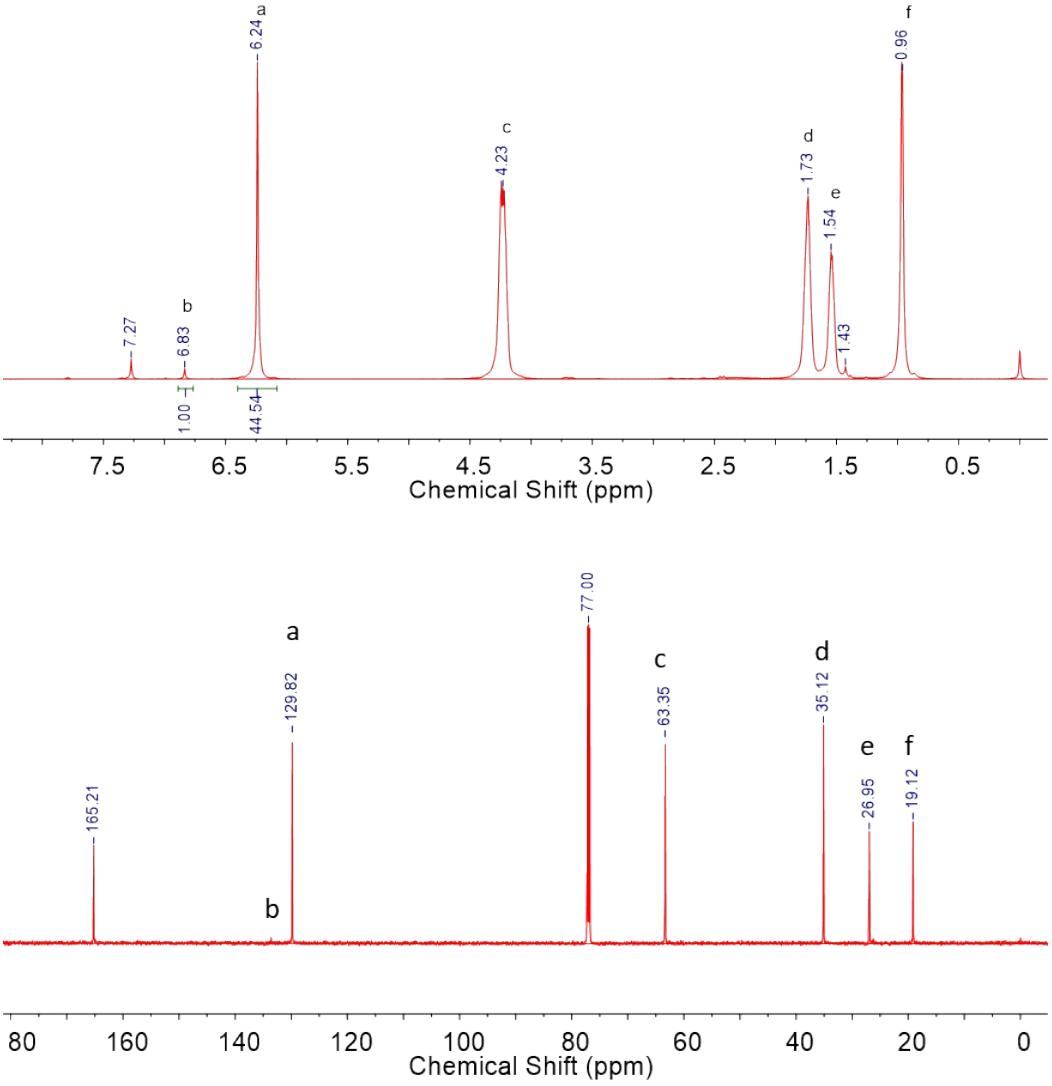
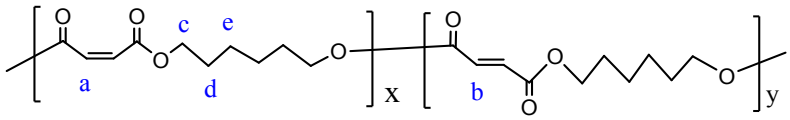
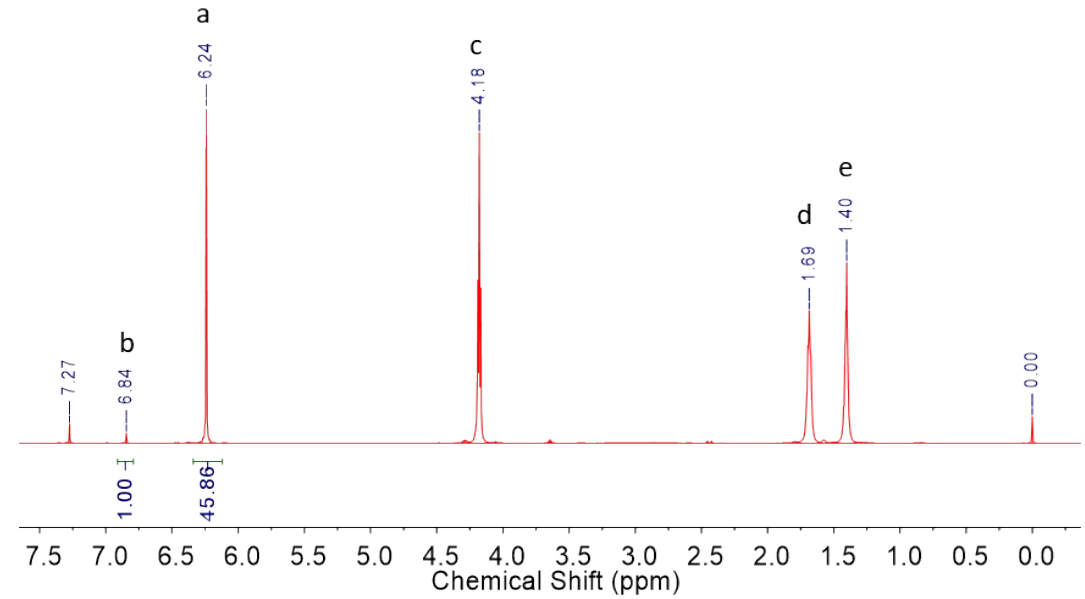


Fig. S4 | Poly(3-methylpentylene maleate) (Table 1, entry 3), synthesized with MA/3-methyl-1,5-pentanediol of 1.05:1, in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=53 kDa, cis content=97.8%)





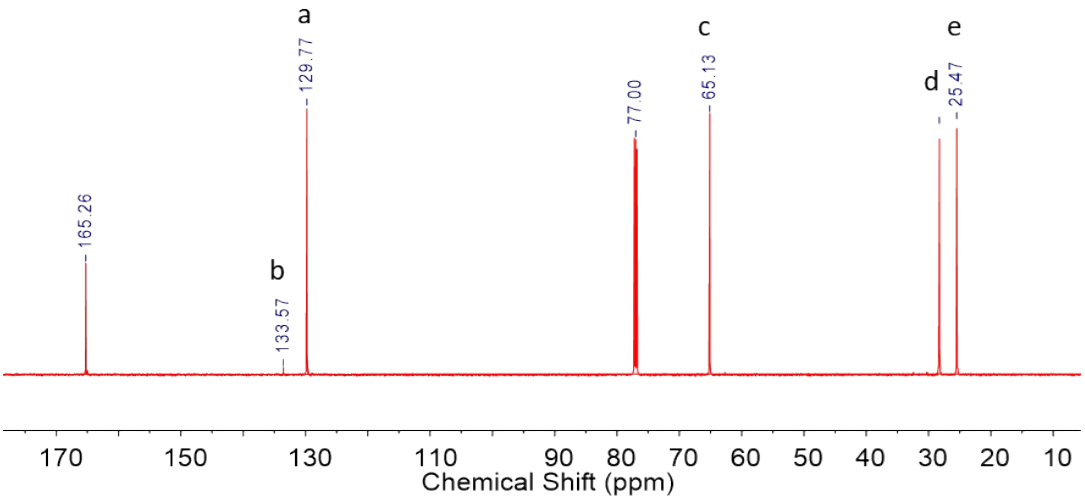


Fig. S5 | Poly(hexylene maleate) (Table 1, entry 4), synthesized with MA/1,6-hexanediol of 1.05:1, in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=52 kDa, cis content=97.9%)

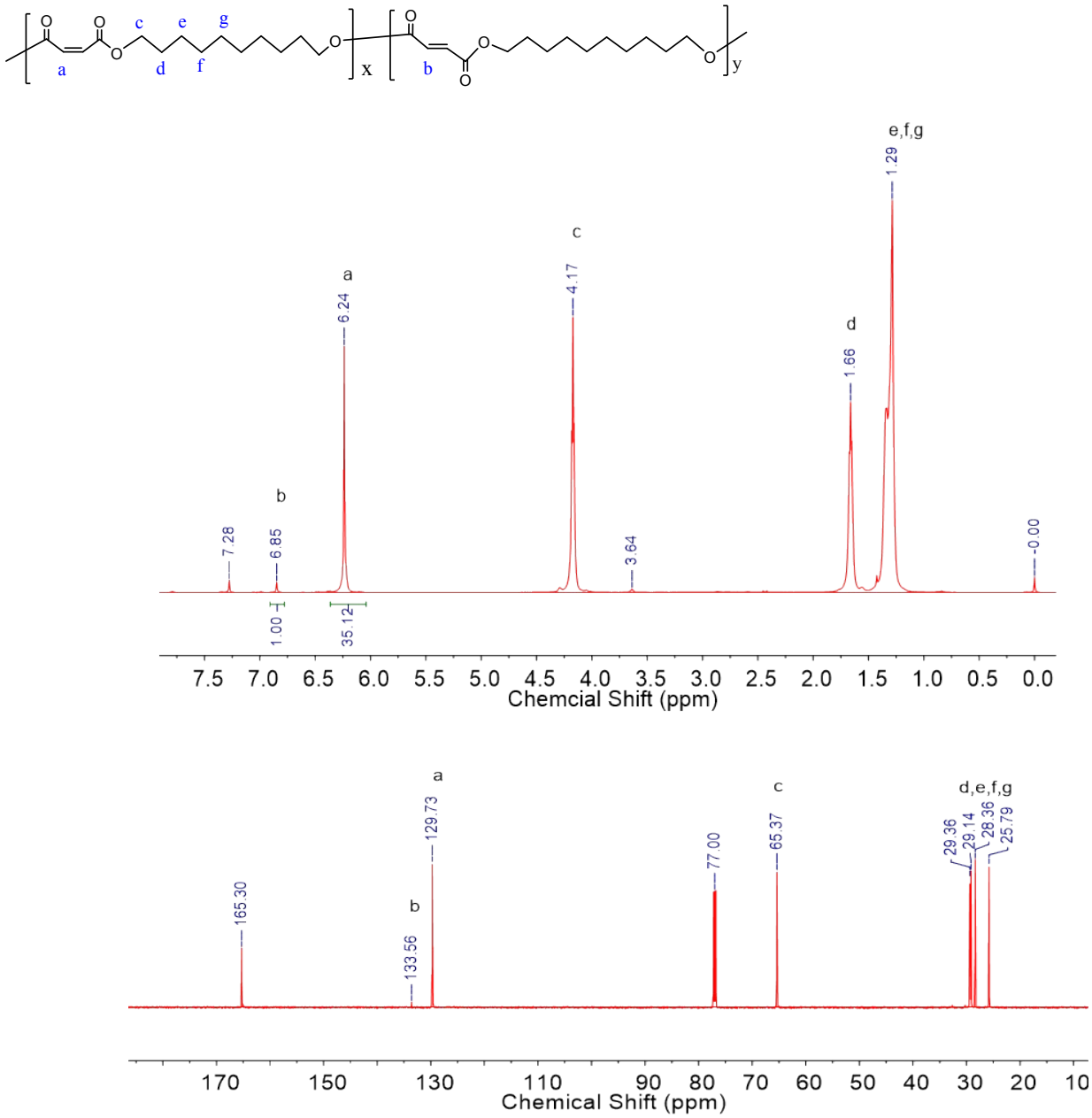
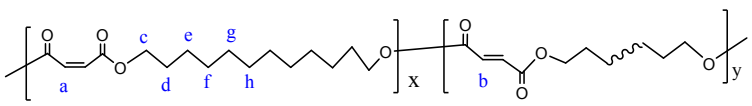


Fig. S6 | Poly(decylene maleate) (Table 1, entry 5), synthesized with MA/1,10-decanediol of 1.05:1, in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=51 kDa, cis content=97.2%)



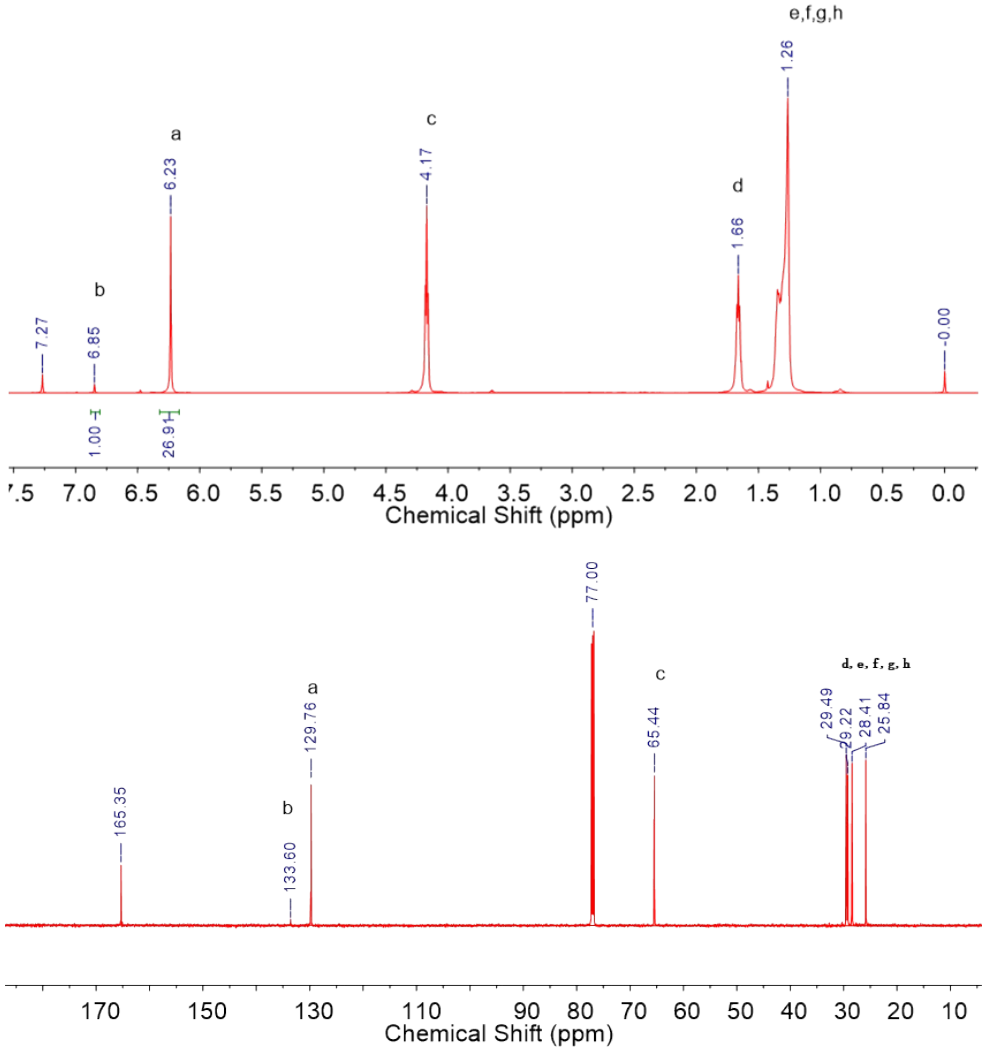


Fig. S7 | Poly(dodecylene maleate) (Table 1, entry 6), synthesized with MA/1,12-dodecanediol of 1.05:1, in $CDCl_3$. Top: ^1H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=80 kDa, cis content=96.4%)

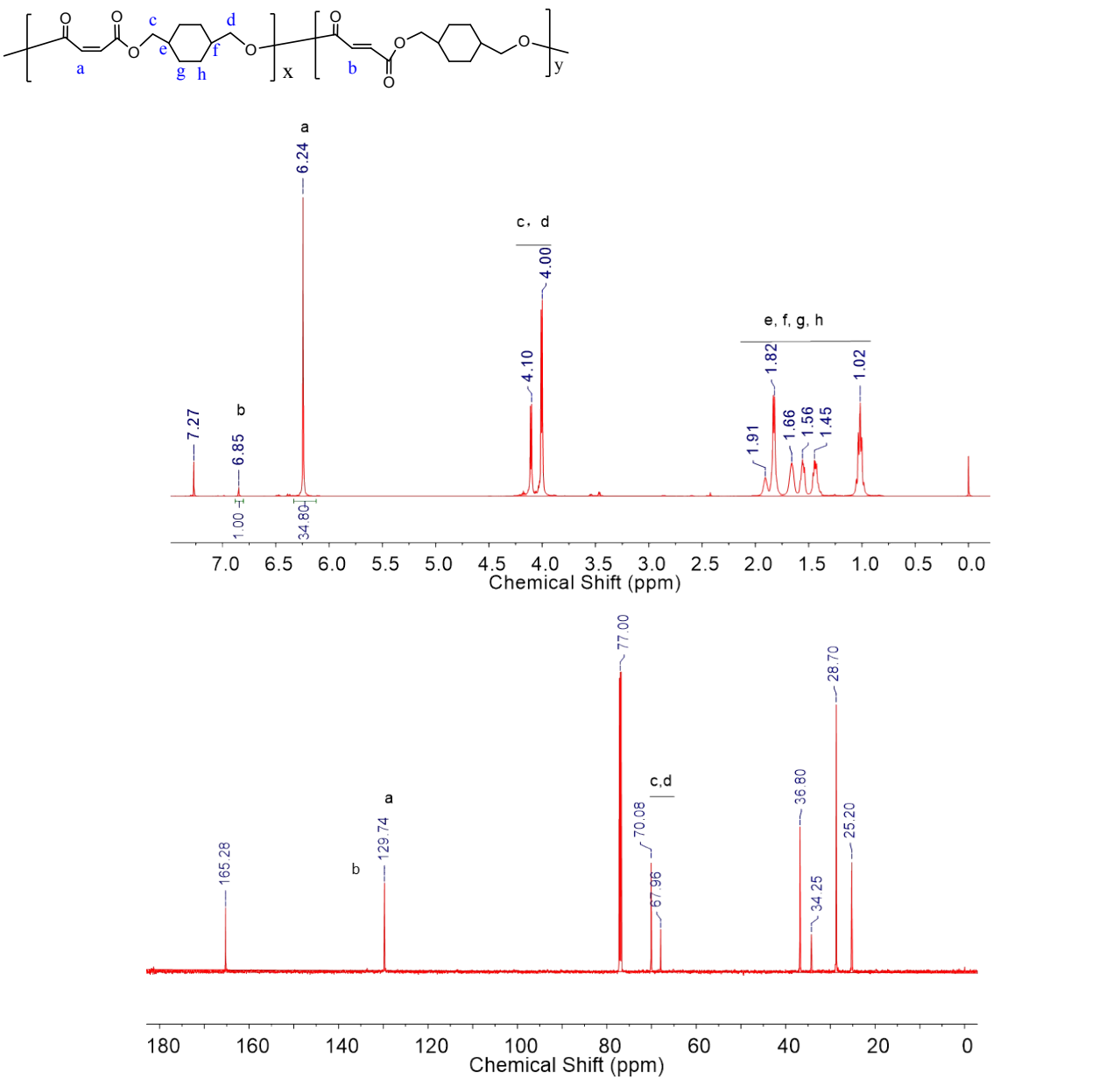


Fig. S8 | Poly(1,4-cyclohexanedimethylene maleate) (Table 1, entry 7), synthesized with MA/1,4-cyclohexanedimethanol of 1.05:1, in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=44 kDa, cis content=97.2%)

Section S4. PBM synthesis with conventional transesterification catalysts and dehydration of MA

Table S2 | Different catalysts applied for synthesis of PBM with excess MA

entry	MA:BDO[a]	catalyst	catalyst content (mol%)[f]	temp(℃)[b]	time(h)[c]	cis (%)[d]	M_n (kDa)[e]
1	1.05:1	$ZnCl_2$	0.5	135	6	88.1	1.9
2	1.05:1	$SnCl_2$	0.5	135	6	74.6	8.7
3	1.05:1	Sb_2O_3	0.5	135	6	91.6	1.5
4	1.05:1	GeO_2	0.5	135	6	91.0	1.3
5	1.05:1	$Ti(OBu)_4$	0.5	135	6	91.4	2.6

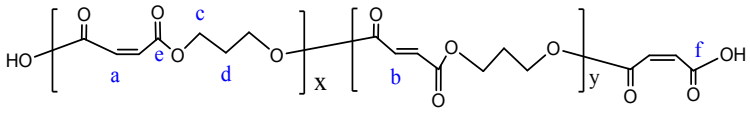
[a] In molar ratio. [b] Polycondensation temperature. [c] Polycondensation time. [d] cis % was defined as cis/(cis+trans) and calculated from ^{1}H NMR. [e] Mn was calculated from ^{1}H NMR. [f] Molar ratio of catalyst to BDO.

Table S3 | Conversion of maleic acid to maleic anhydride

entry	Feeding	temp(℃)[a]	time(h)[b]	Test description
1	maleic acid (0.2mol)	140	0.5	A large amount of maleic anhydride was collected in the cold trap.

[a] Polycondensation temperature. [b] Polycondensation time.

Section S5. Analysis of terminal groups by NMR during polyesterification with excess MA



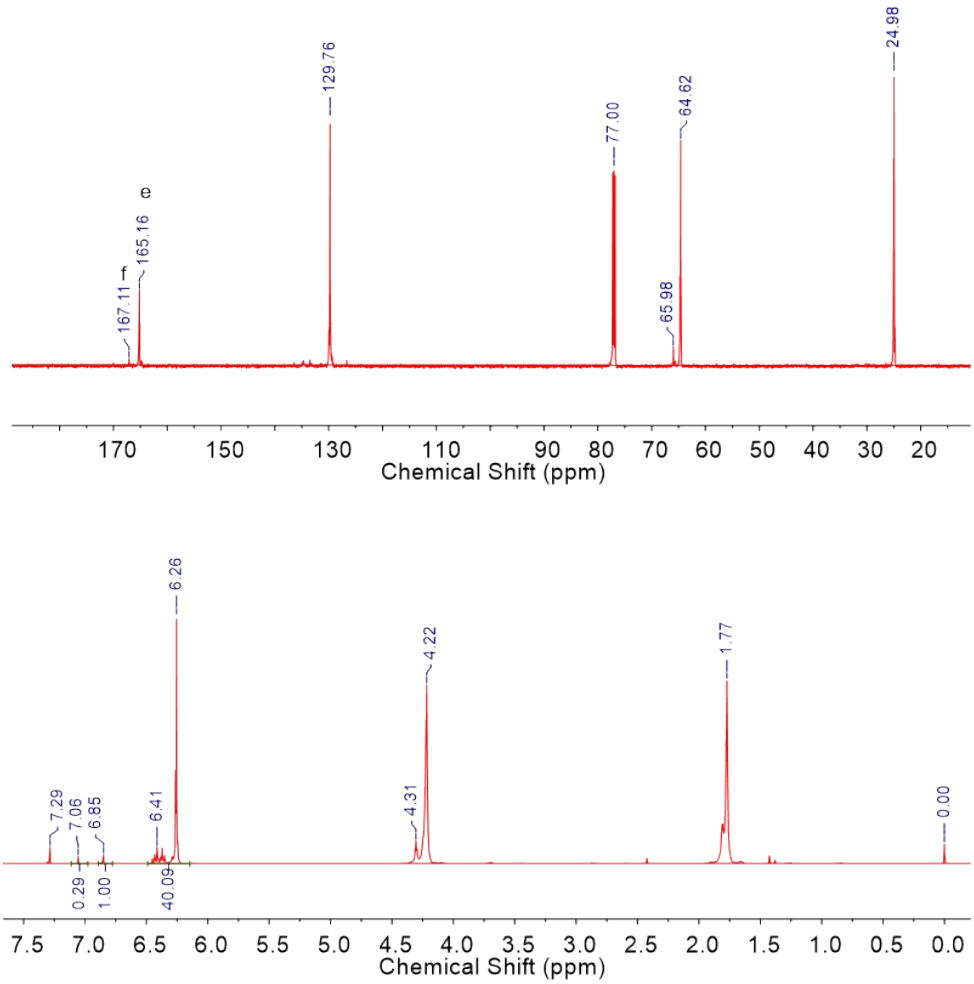
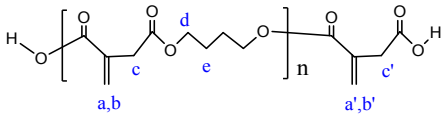


Fig.S9 | NMR analysis of the reaction mixture after 1 h at 110 ℃ (TsOH: 1 mol%, MA/BDO= 1.05:1). Top: ^{13}C NMR spectrum. Bottom: ^{1}H NMR spectrum in $CDCl_3$.

Section S6. Characterization of poly(butylene itaconate) by NMR



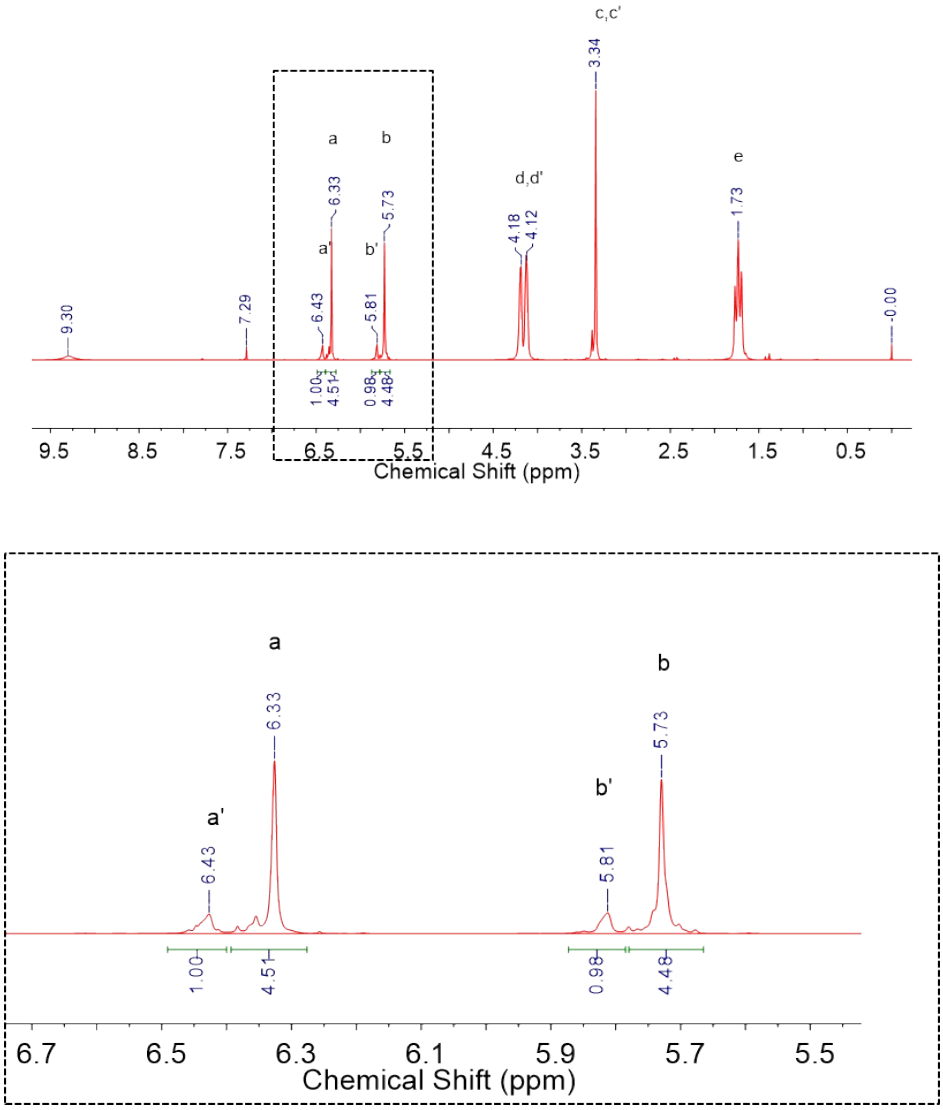


Fig. S10 | ^{1}H NMR spectrum of poly(butylene itaconate), synthesized under typical conditions (itaconic acid /BDO =1.05:1, 135 ℃, 1 mol% TsOH, 8 h), in $CDCl_3$. (Mn=960)

Section S7. NMR spectra of MA-based polyesters prepared with equimolar MA and diols

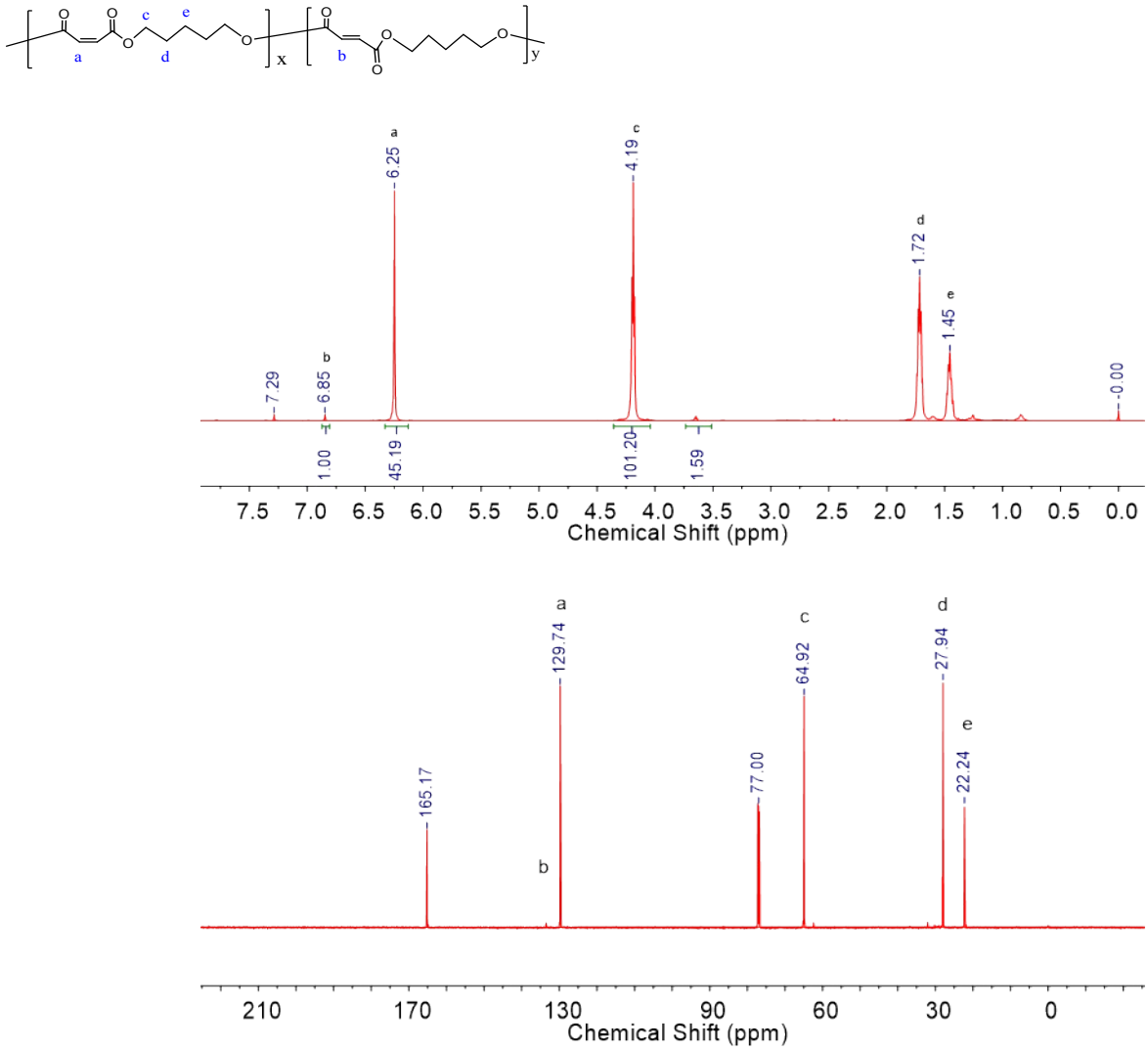
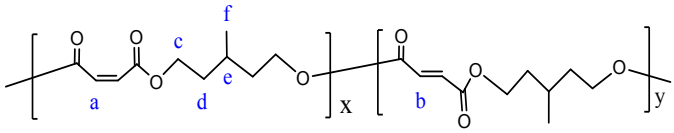


Fig. S11 | Poly(pentylene maleate) (Table 1, entry 9) in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=11.8 kDa, cis content=97.8%)



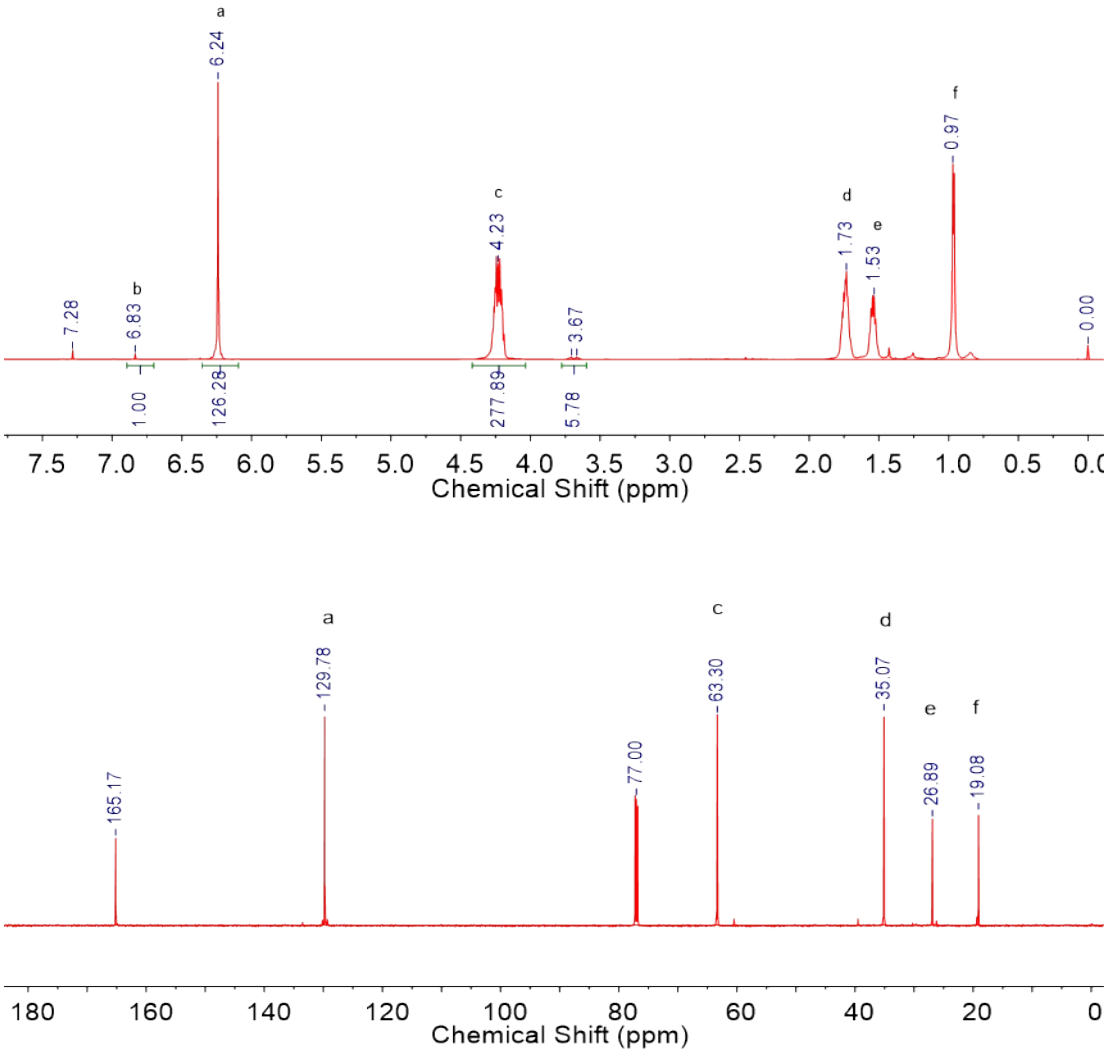
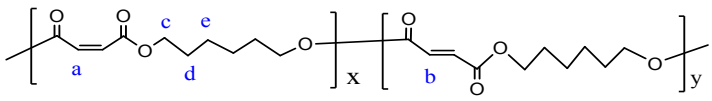
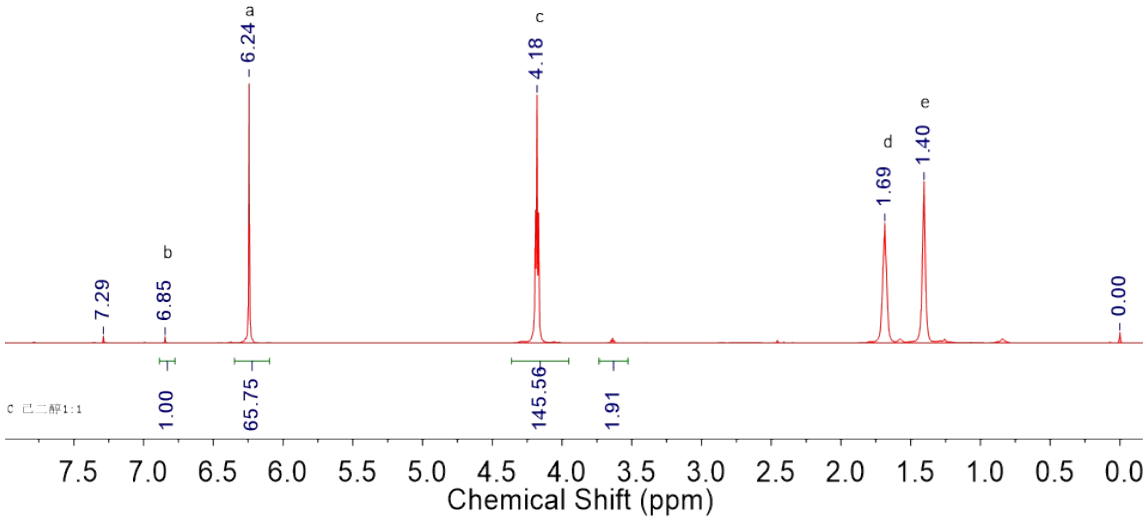


Fig. S12 | Poly(3-methylpentylene maleate) (Table 1, entry 10) in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=9.6 kDa, cis content=99.2%)





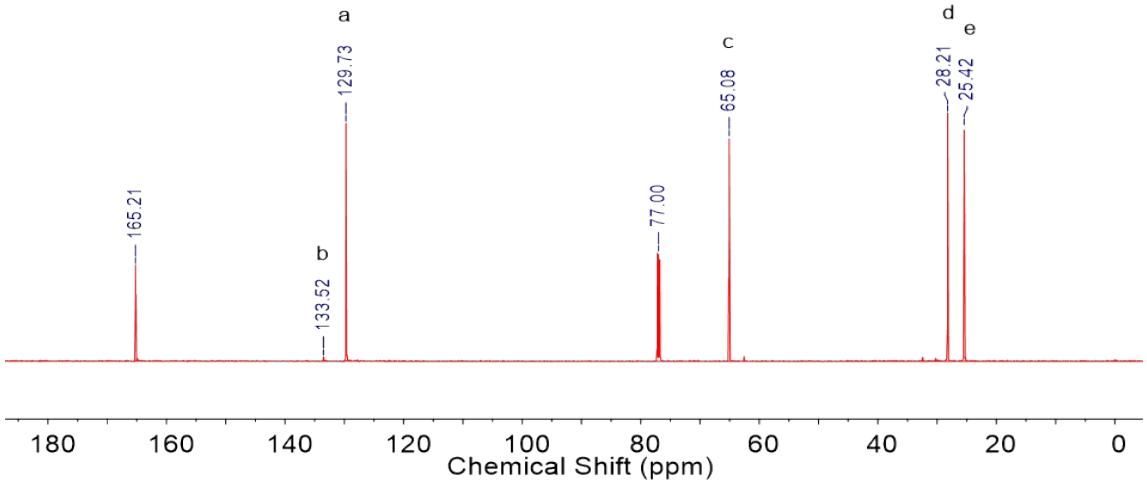
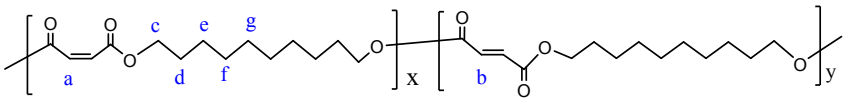


Fig. S13 | Poly(hexylene maleate) (Table 1, entry 11) in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=15.2 kDa, cis content=98.5%)



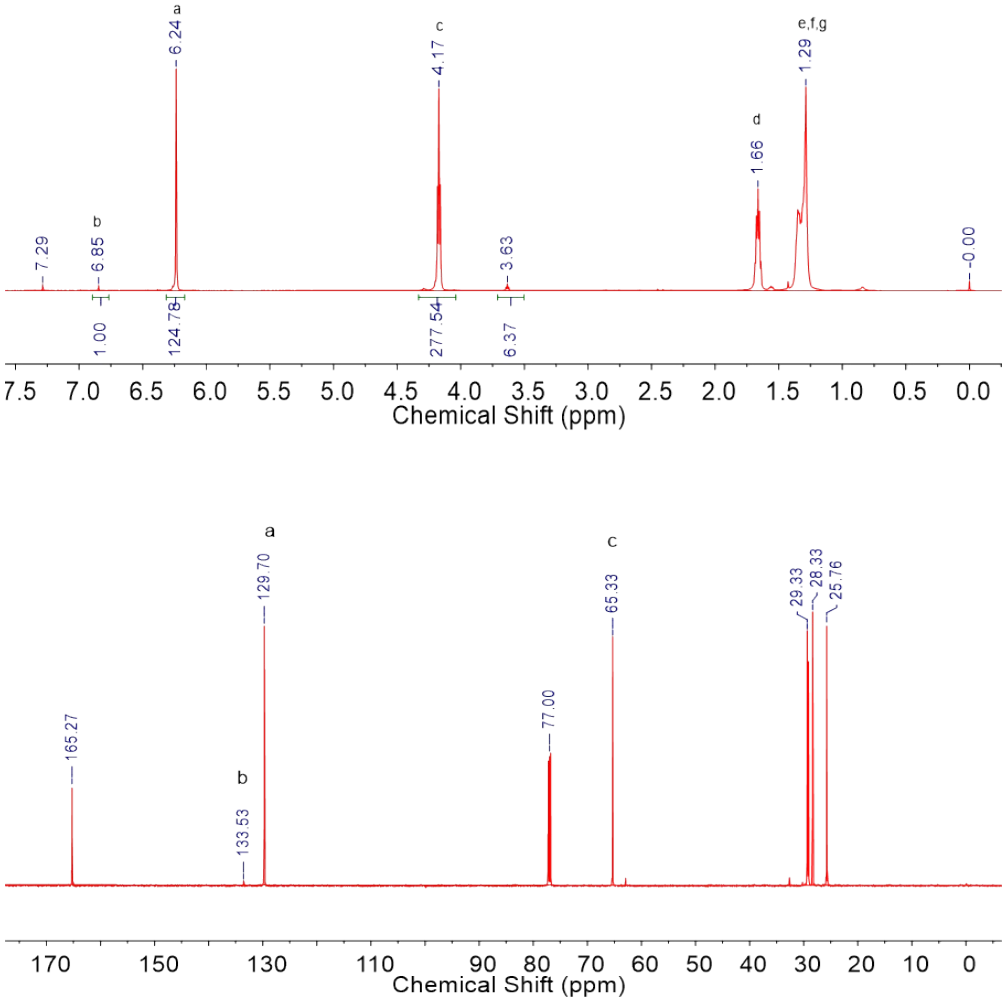
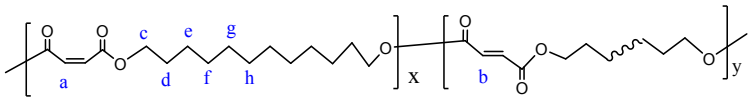


Fig. S14 | Poly(decylene maleate) (Table 1, entry 12) in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=11.2 kDa, cis content=99.2%)



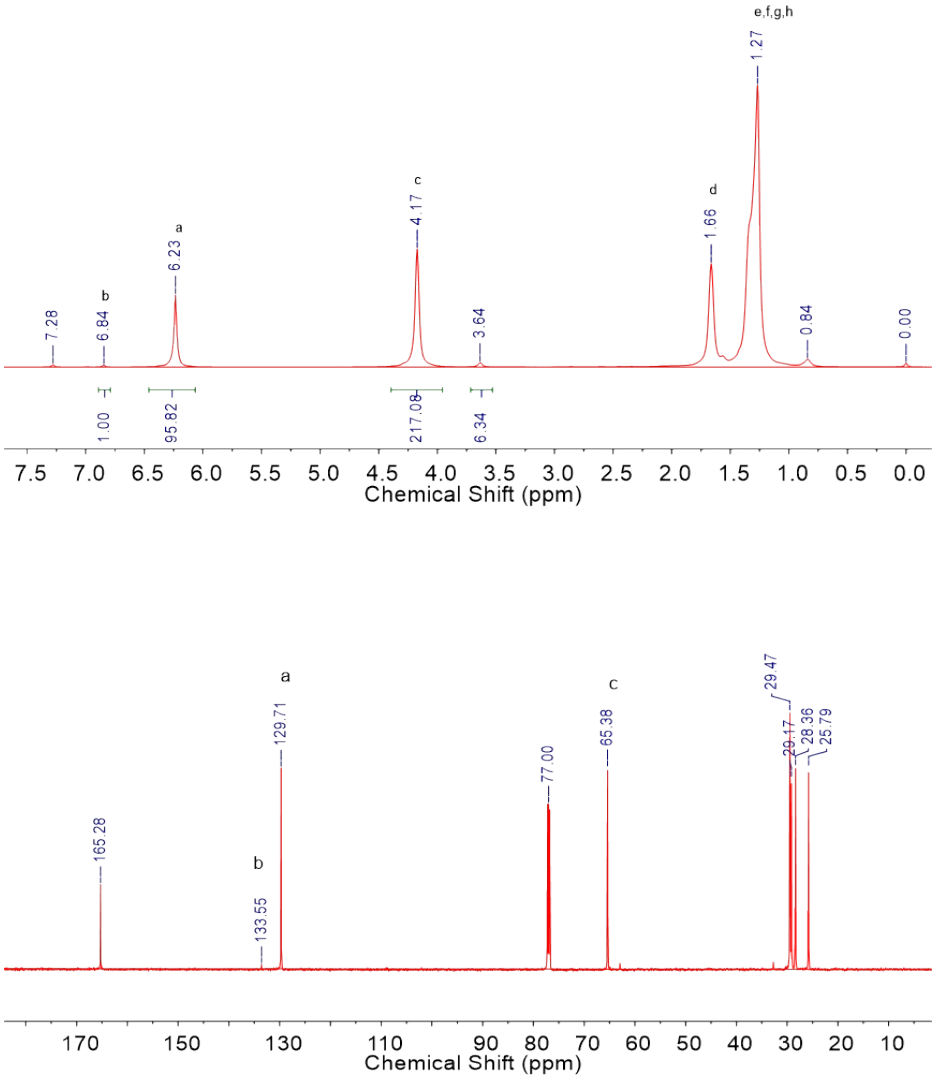
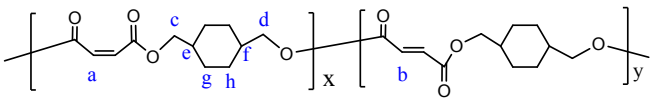


Fig. S15 | Poly(dodecylene maleate) (Table 1, entry 13) in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=9.9 kDa, cis content=98.9%)



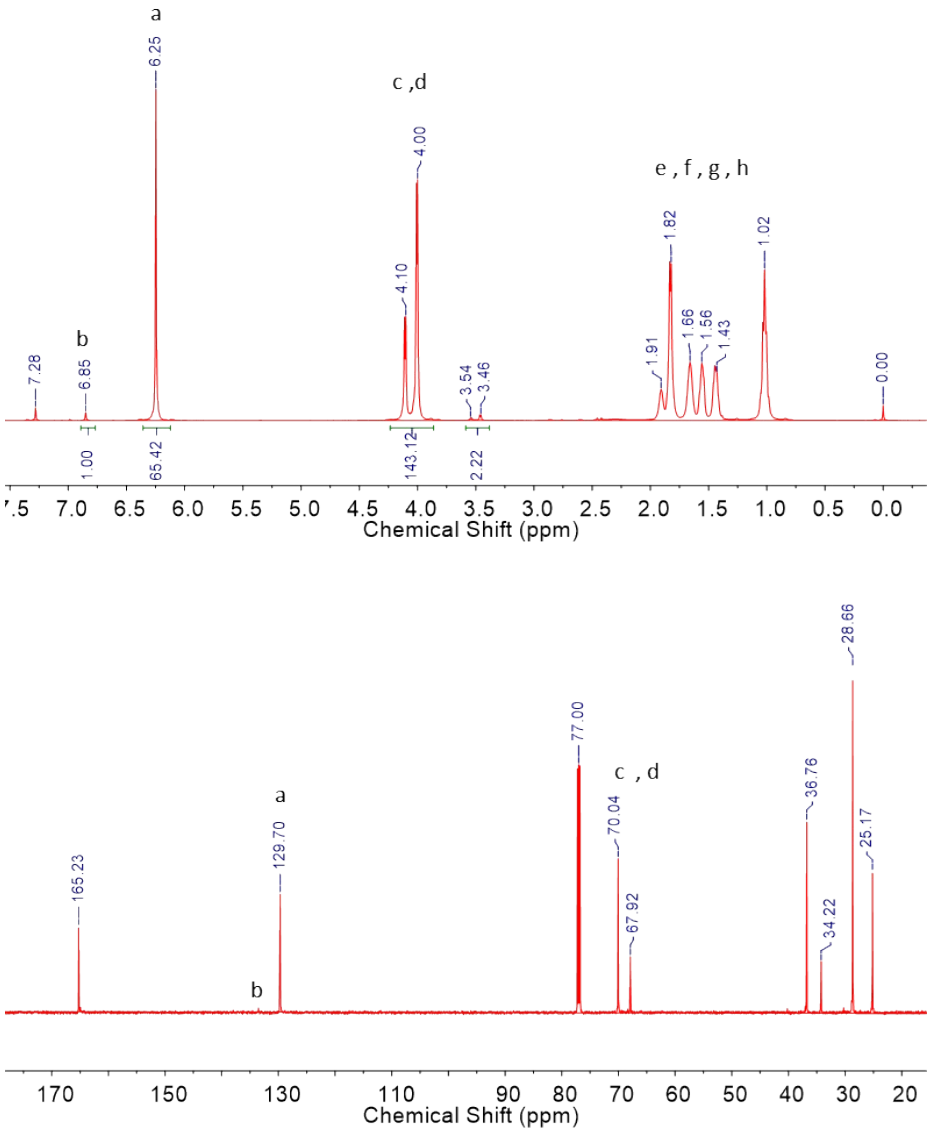
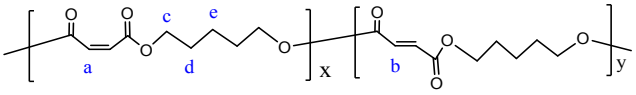


Fig. S16 | Poly(1,4-cyclohexanedimethylene maleate) (Table 1, entry 14) in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum. (M_n=12.9 kDa, cis content=98.4%)

Section S8. NMR Spectra of MA-based polyesters prepared with excess diols



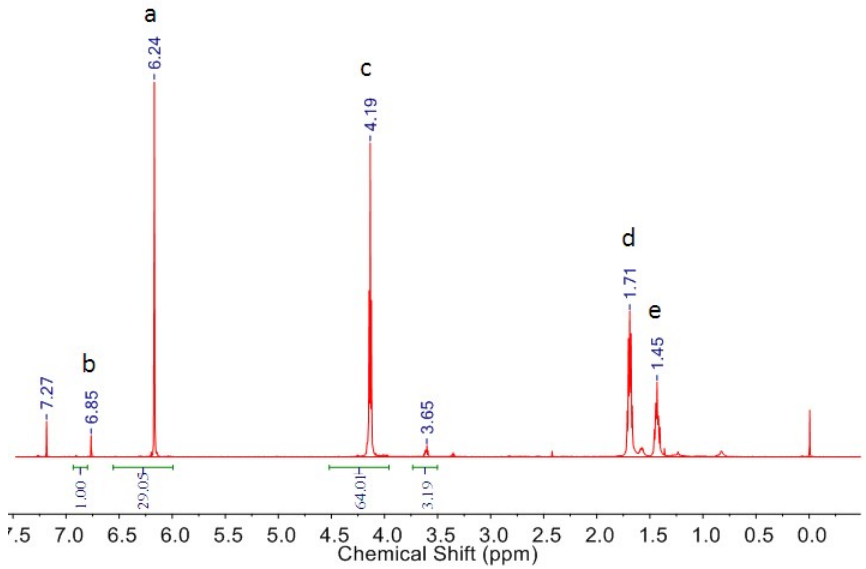
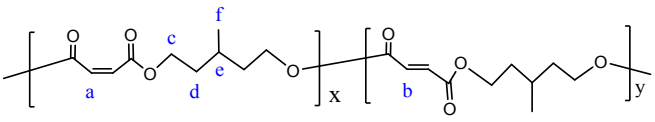


Fig. S17 | ^{1}H NMR spectrum of poly(pentylene maleate) (Table 1, entry 16) in $CDCl_3$. (Mn=3.8 kDa, cis content=96.7%)



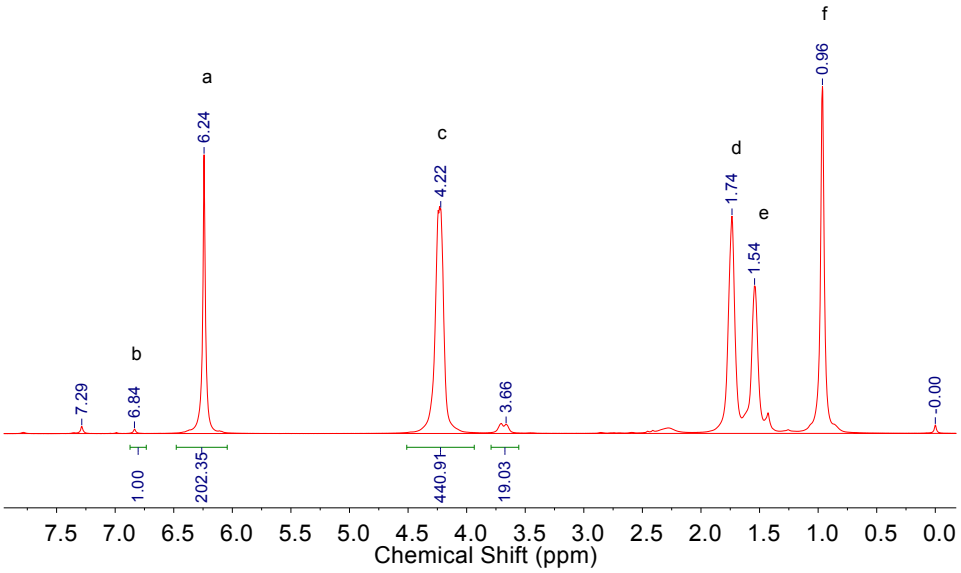
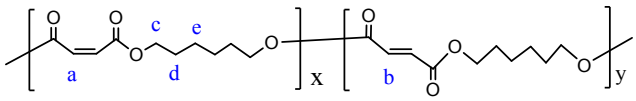


Fig. S18 | ^{1}H NMR spectrum of poly(3-methylpentylene maleate) (Table 1, entry 17) in $CDCl_3$. (Mn= 4.7 kDa, cis content=99.5%)



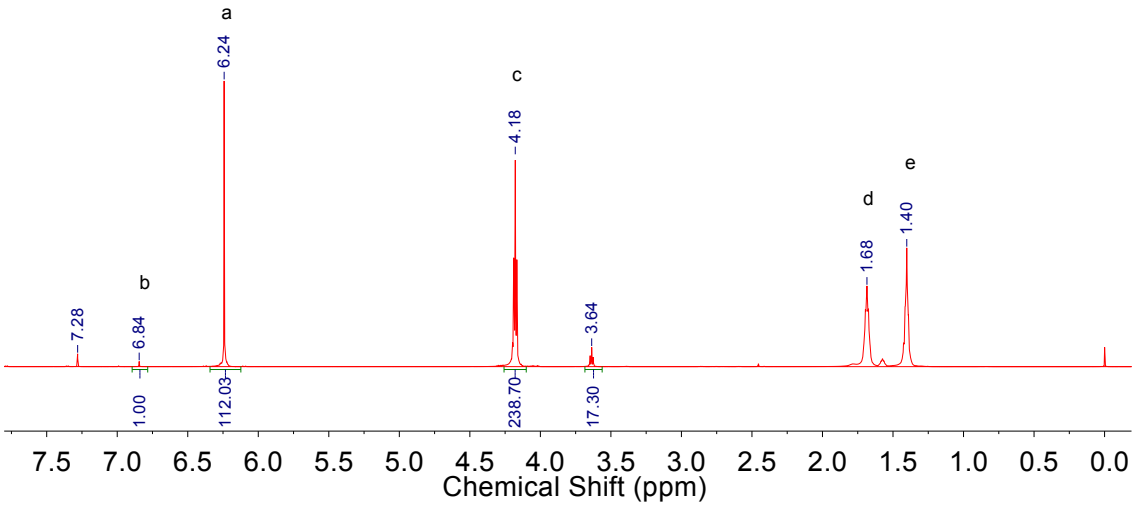
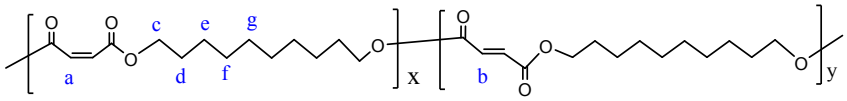


Fig. S19 | ^{1}H NMR spectrum of poly(hexylene maleate) (Table 1, entry 18) in $CDCl_3$. (Mn=2.8 kDa, cis content=99.1%)



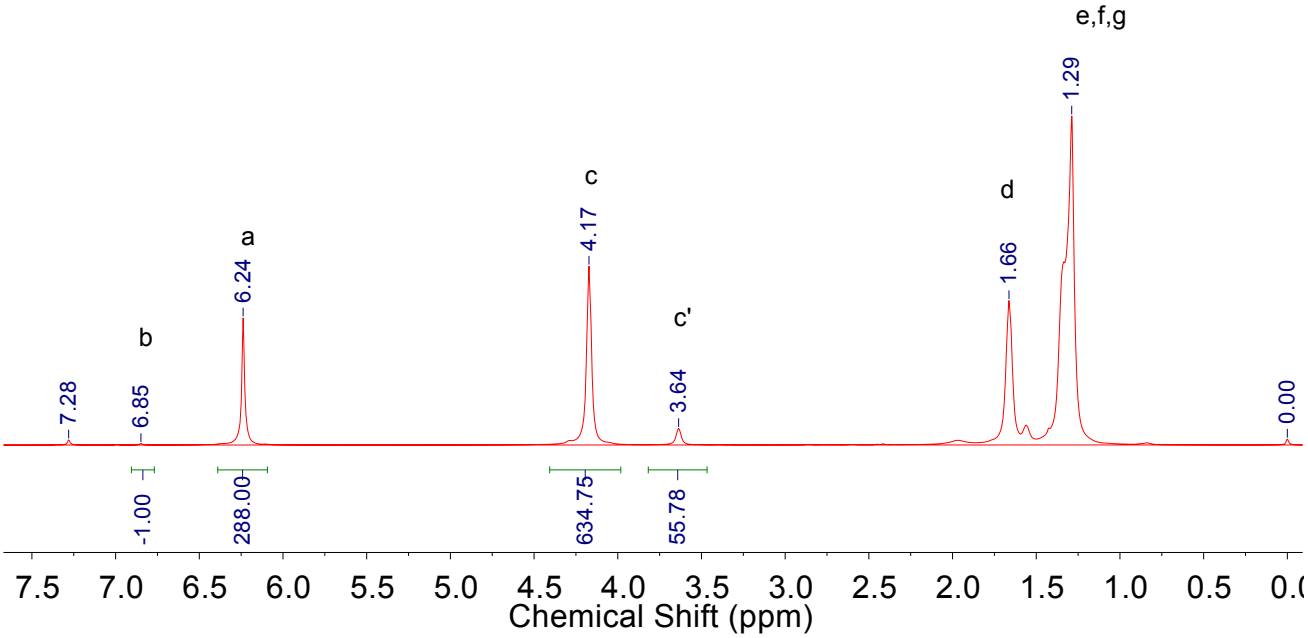
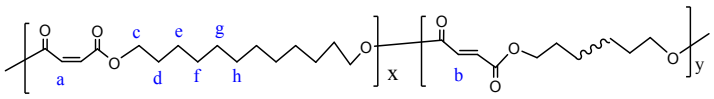


Fig. S20 | ^{1}H NMR spectrum of poly(decylene maleate) (Table 1, entry 19) in $CDCl_3$. (Mn=3.1 kDa, cis content=99.7%)



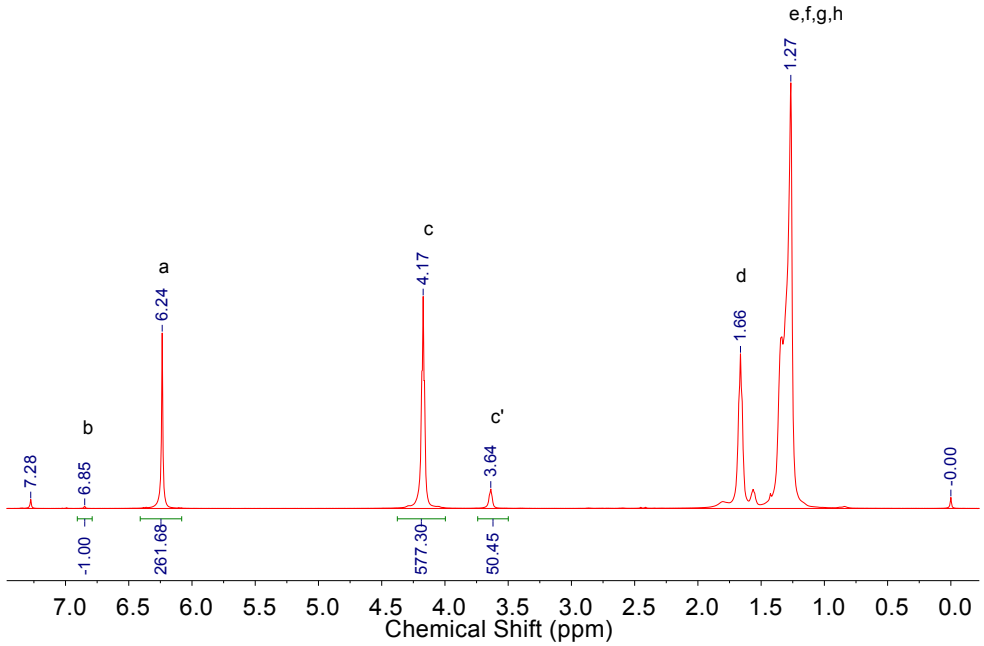
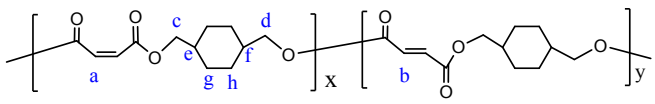


Fig. S21 | ^{1}H NMR spectrum of poly(dodeylcene maleate) (Table 1, entry 20) in $CDCl_3$. (M_n=3.4 kDa, cis content=99.6%)



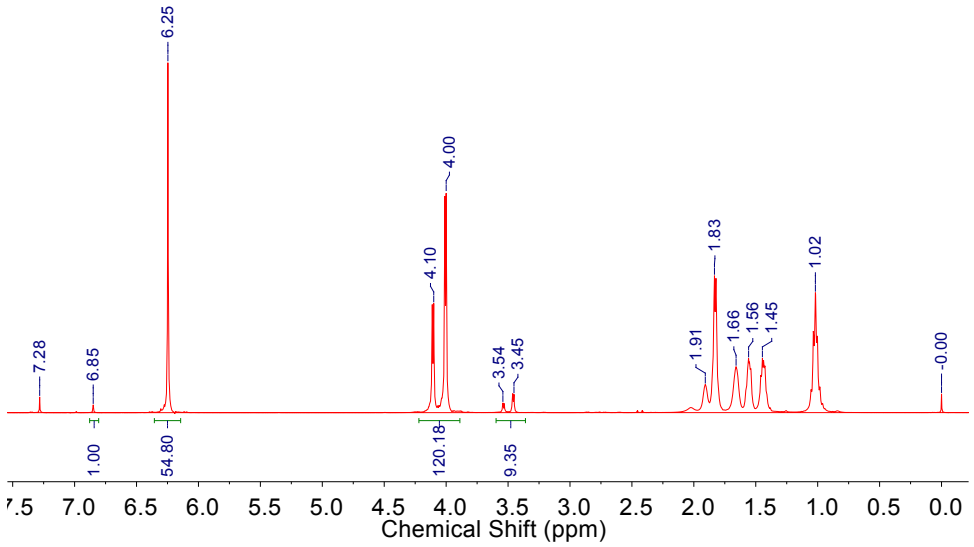


Fig. S22 | ^{1}H NMR spectrum of poly(1,4-cyclohexanedimethylene maleate) (Table 1, entry 21) in $CDCl_3$. (M_n=2.7 kDa, cis content=98.2%)

Section S9. PBM synthesis with conventional transesterification catalysts with excess BDO and PBM synthesis using Dimethyl maleate and BDO

Table S4 | Different catalysts applied for the synthesis of PBM with excess BDO

entry	MA: BDO[a]	catalyst	catalyst content (mol%)[f]	temp(℃)[b]	time(h)[c]	cis (%)[d]	M_n (kDa)[e]	ref
1	1:1.1	$ZnCl_2$	0.5	160	6	77.1	7[d]	this work
2	1:1.1	$SnCl_2$	0.5	160	6	72.5	10.3[d]	this work
3	1:1.1	Sb_2O_3	0.5	160	6	78.9	2.2[d]	this work
4	1:1.1	GeO_2	0.5	160	6	88.6	1.2[d]	this work
5	1:1	$Ti(OBu)_4$	0.6	160	-	88.9	4.2	[1]

[a] In molar ratio. [b] Polycondensation temperature. [c] Polycondensation time. [d] cis % was defined as cis/(cis+trans) and calculated from ^{1}H NMR. [e] Mn was calculated from ^{1}H NMR. [f] Molar ratio of catalyst to MA.

Table S5 | Synthesis of PBM using dimethyl maleate and BDO

entry	Feeding	catalyst	catalyst content (mol%)[d]	temp(℃)[b]	time(h)[c]	Test description
1	dimethyl maleate : BDO=1:1.1 [a]	TsOH	1	140	8	In the esterification stage, no liquid was collected in the water trap

[a] In molar ratio. [b] Esterification temperature. [c] Esterification time. [d] Molar ratio of catalyst to dimethyl maleate.

Section S10. Analysis of byproduct in the cold trap by NMR

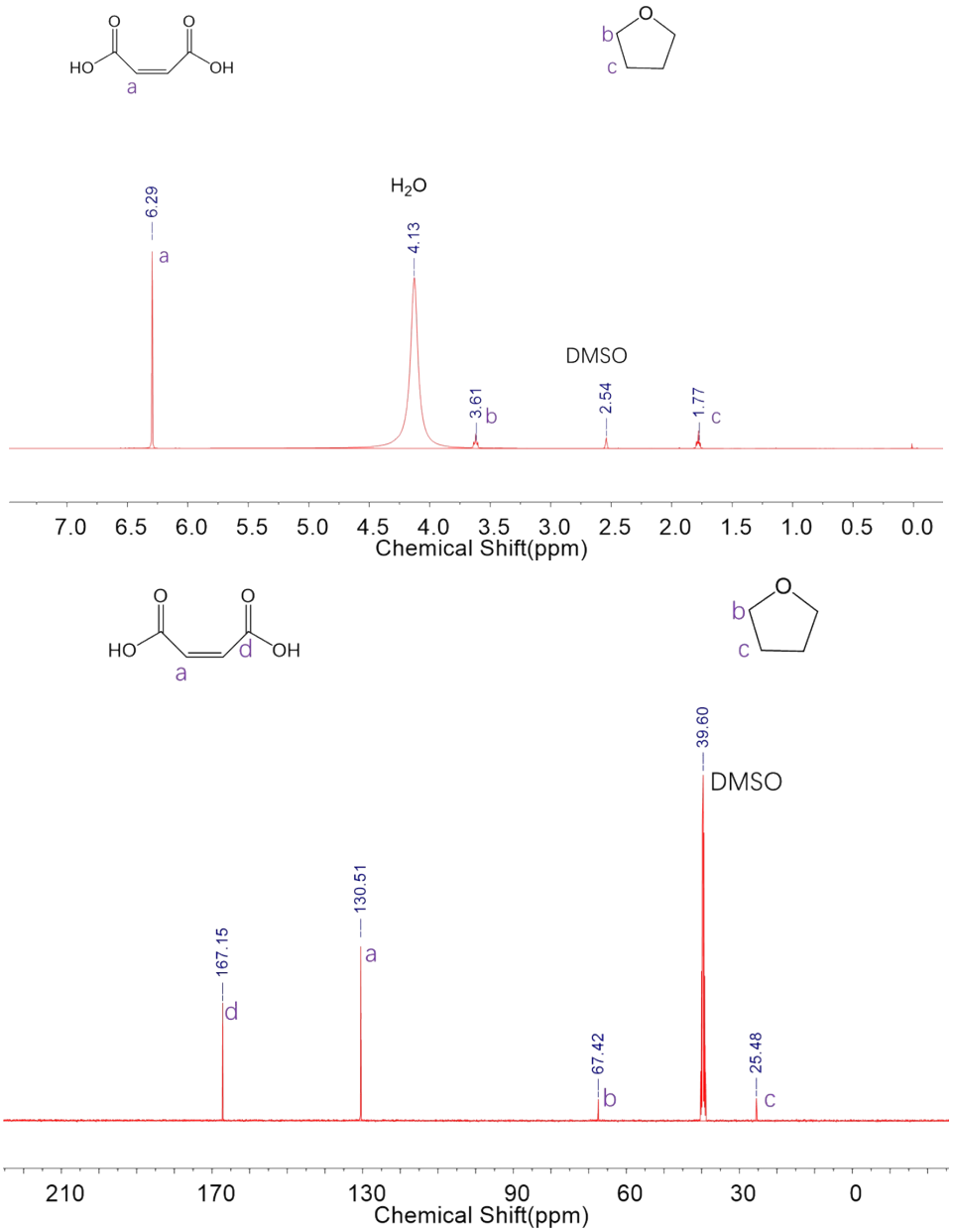
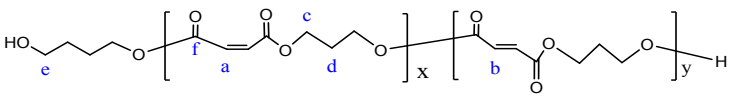


Fig.S23 | NMR analysis of liquid byproducts mixture in the cold trap (MA/BDO= 1:1.1). Top: ^{13}C NMR spectrum. Bottom: ^{1}H NMR spectrum in DMSO.

Section S11. Analysis of terminal groups by NMR during polyesterification with excess diol



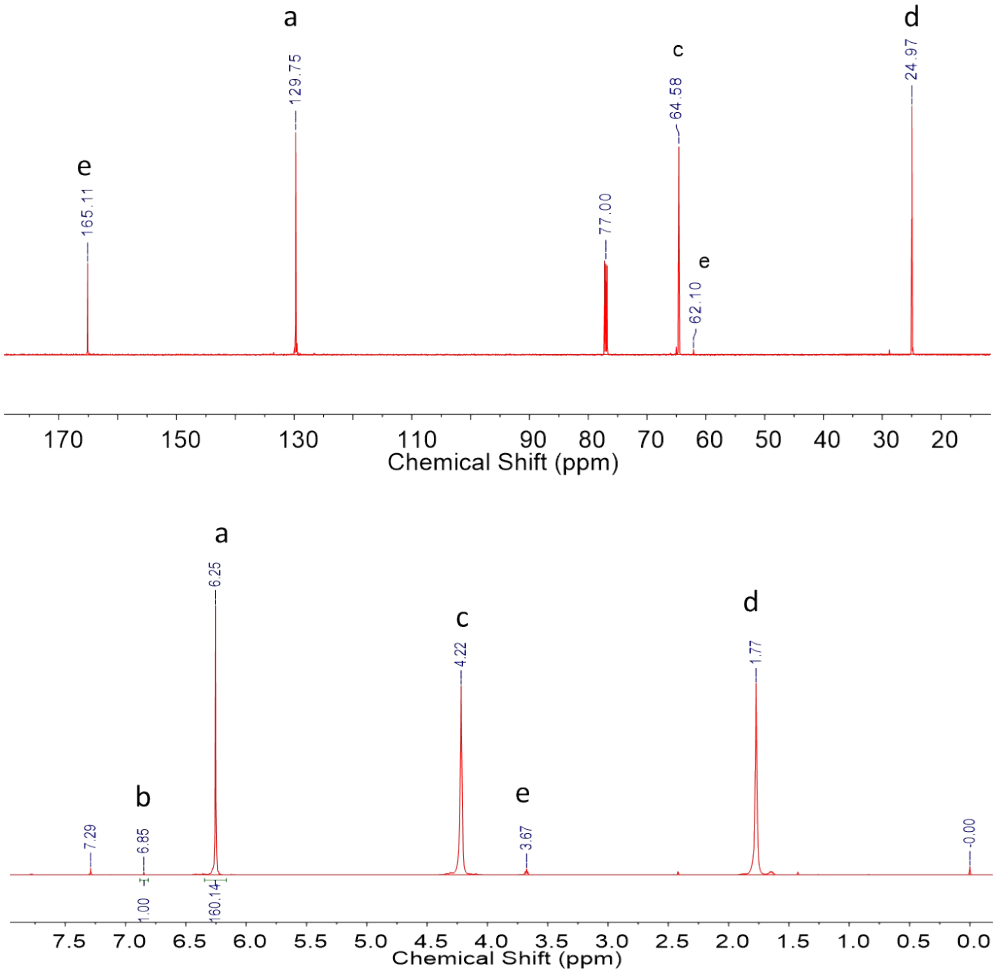


Fig.S24 | NMR analysis of the reaction mixture after 1 h at 120 ℃ (TsOH: 1 mol%, MA/BDO= 1:1.2). Top: ^{13}C NMR spectrum. Bottom: ^{1}H NMR spectrum in $CDCl_3$.

Section S12. Characterizations of the cyclic byproducts obtained with excess BDO

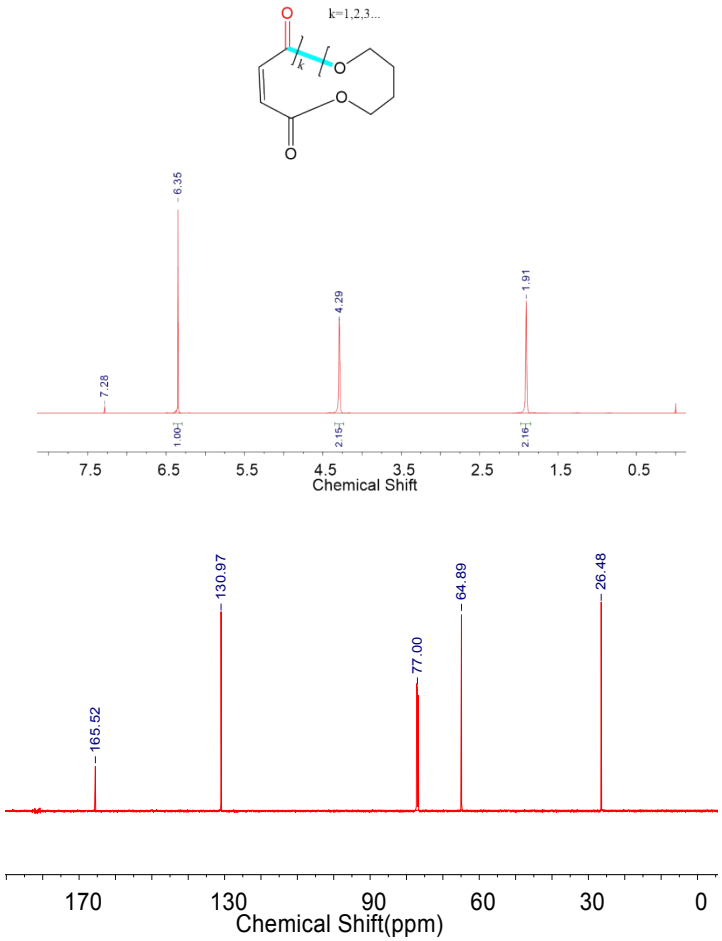


Fig. S25 | Cyclic poly(butylene maleate) byproduct in $CDCl_3$. Top: ^{1}H NMR spectrum. Bottom: ^{13}C NMR spectrum.

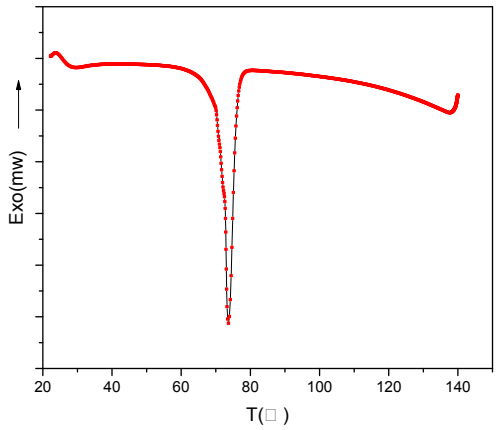


Fig. S26 | DSC curve of the cyclic byproduct. T_m is 73.6 ℃.

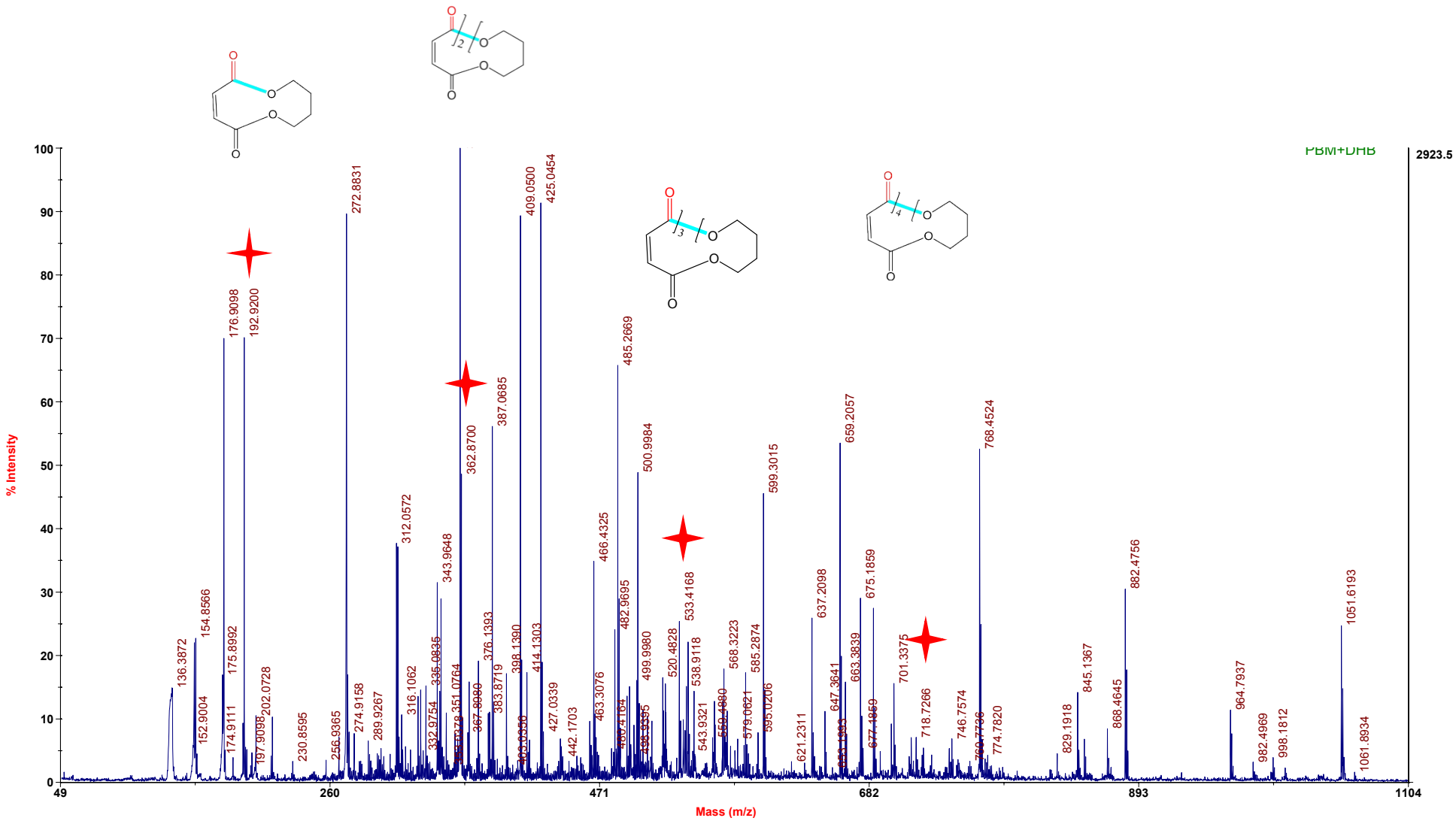


Fig. S27 | MALDI-TOF MS of the cyclic byproduct

1. Yu, Y.; Wei, Z.; Leng, X.; Li, Y. J. P. C., Facile preparation of stereochemistry-controllable biobased poly (butylene maleate-co-butylene fumarate) unsaturated copolyesters: a chemoselective polymer platform for versatile functionalization via aza-Michael addition. **2018,** *9* (45), 5426-5441.