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Electronic Supplementary Information

Sustainable block copolymers of poly(limonene carbonate)

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Terpolymerziation of *trans*-limonene-oxide, (*D/L*)-lactide and CO_2 (One Pot ROCP)

Table S1. Experimental details of one-pot simultaneous polymerization of DLLA, LO and CO_2 using [(BDI)Zn-(μ-OAc)] catalyst.

Lactide	Feed ratio	Polymer composition	Lactide		LO		Catalyst	THF/ Toluene	Yield	Yield
	DLLA/ LO	r-DLLA /r-LO	m	n	V	n	m			
	mol%	mol%	mg	mmol	mL	mmol	mg	%	%	g
D/L	9/91	21/79	264	1.8	3.0	18	24	-	75	2.76
D/L	17/83	39/61	538	3.7	3.0	18	24	-	76	2.90
D/L	23/77	41/59	792	5.5	3.0	18	24	-	79	3.90
D/L	29/71	54/46	1055	7.3	3.0	18	24	-	82	3.33
D/L	34/66	60/40	1318	9.1	3.0	18	24	-	82	3.42
D/L	77/23	99/1	1318	9.1	0.44	2.7	24	12	56	0.66
D/L	91/9	100/0	1318	9.1	0.15	0.9	24	12	7	0.06
L	20/80	29/71	650	4.5	3.0	18	19	30	72	2.77

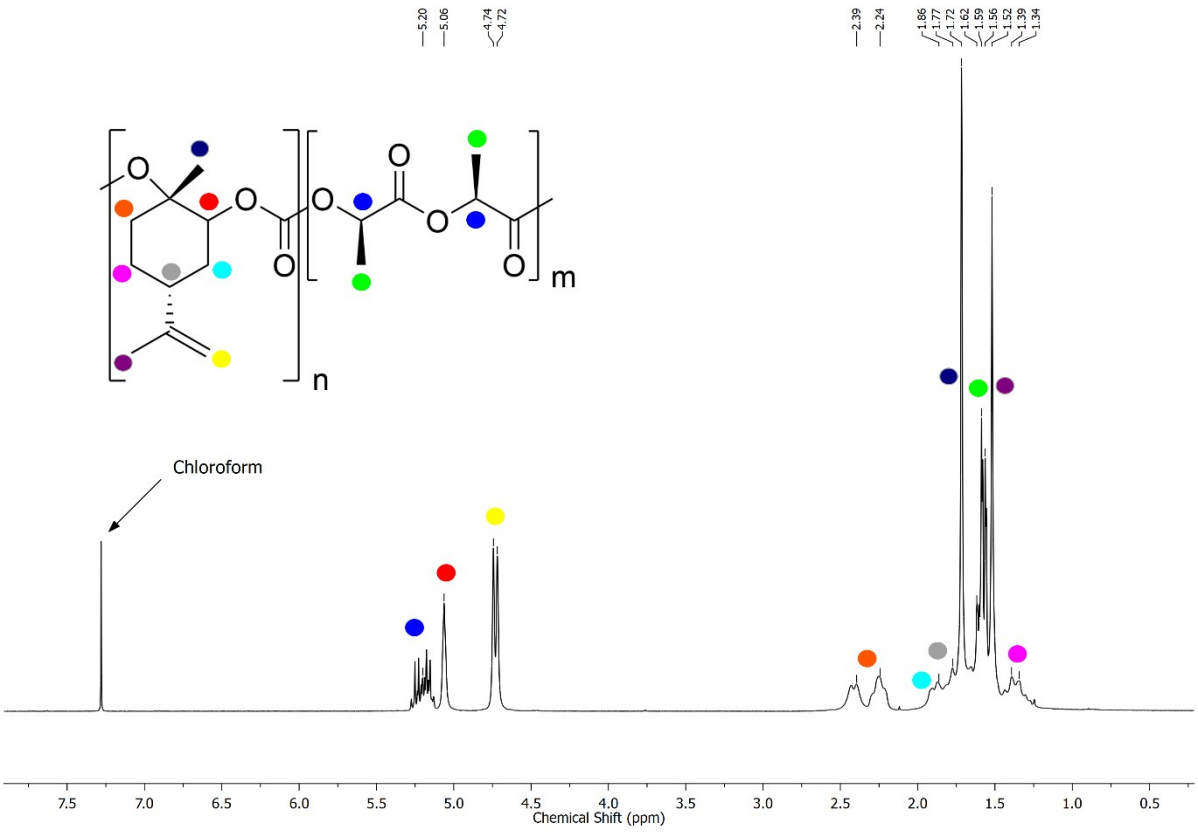


Fig. S1 ^{1}H-NMR (300 MHz) of copolymer prepared from DLLA:LO = 29/71 mol% (entry 4, Table 1) in the feed, measured in $CDCl_3$.

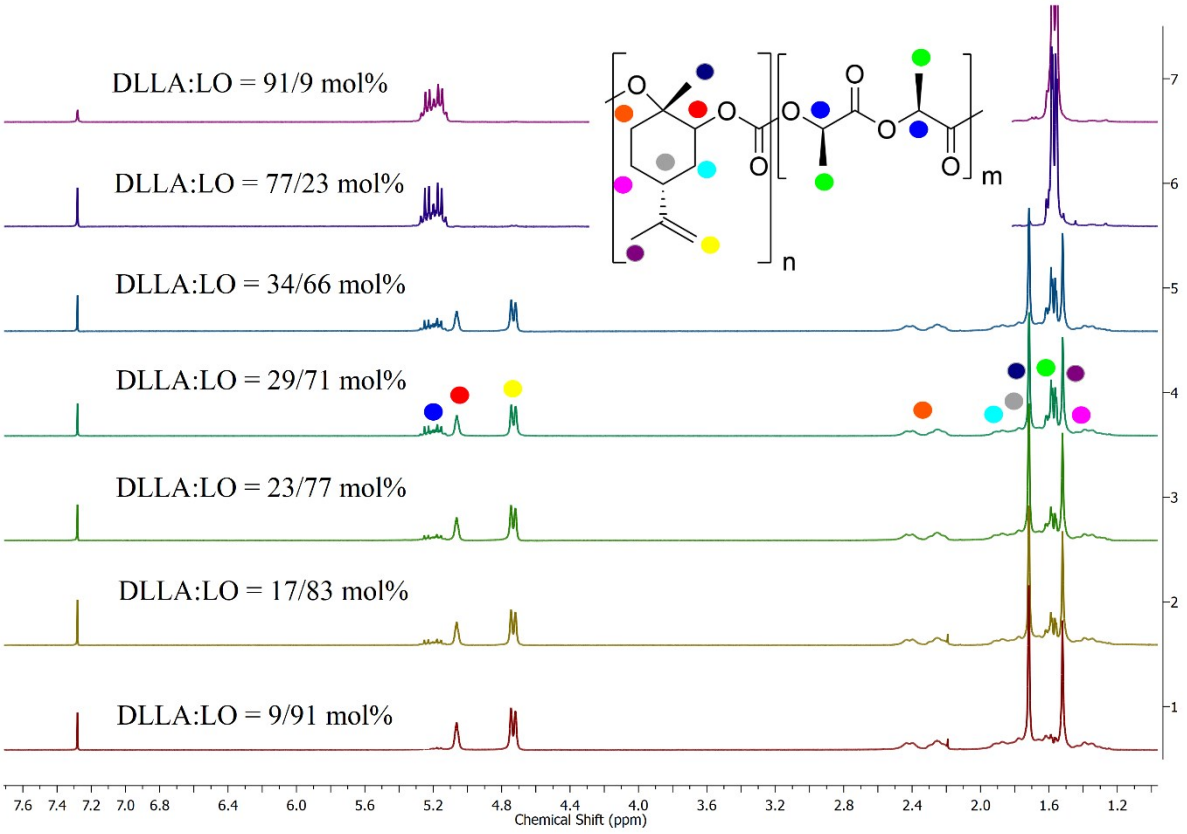
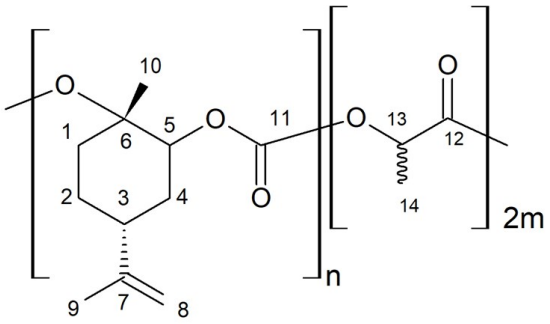


Fig. S2 ^{1}H-NMR (300 MHz) spectra of copolymer prepared from different molar ratio of DLLA and LO-CO_2 in the feed (Table 1), measured in $CDCl_3$.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.15-5.28 (m, 1H, C(13)-H), 5.06 (s, 1H, C(5)-H), 4.71-4.75 (d, *J = 9 Hz*, C(8)-H_2), 2.21-2.43 (m, 2H, C(1)-H_2), 1.86-1.91 (m, 2H, C(4)-H_2), 1.75-1.76 (m, 1H, C(3)-H), 1.69-1.73 (m, 3H, C(10)-H_3), 1.56-1.65 (m, 3H, C(14)-H_3), 1.50-1.52 (m, 3H, C(9)-H_3), 1.34-1.44 (m, 2H, C(2)-H_2) ppm.



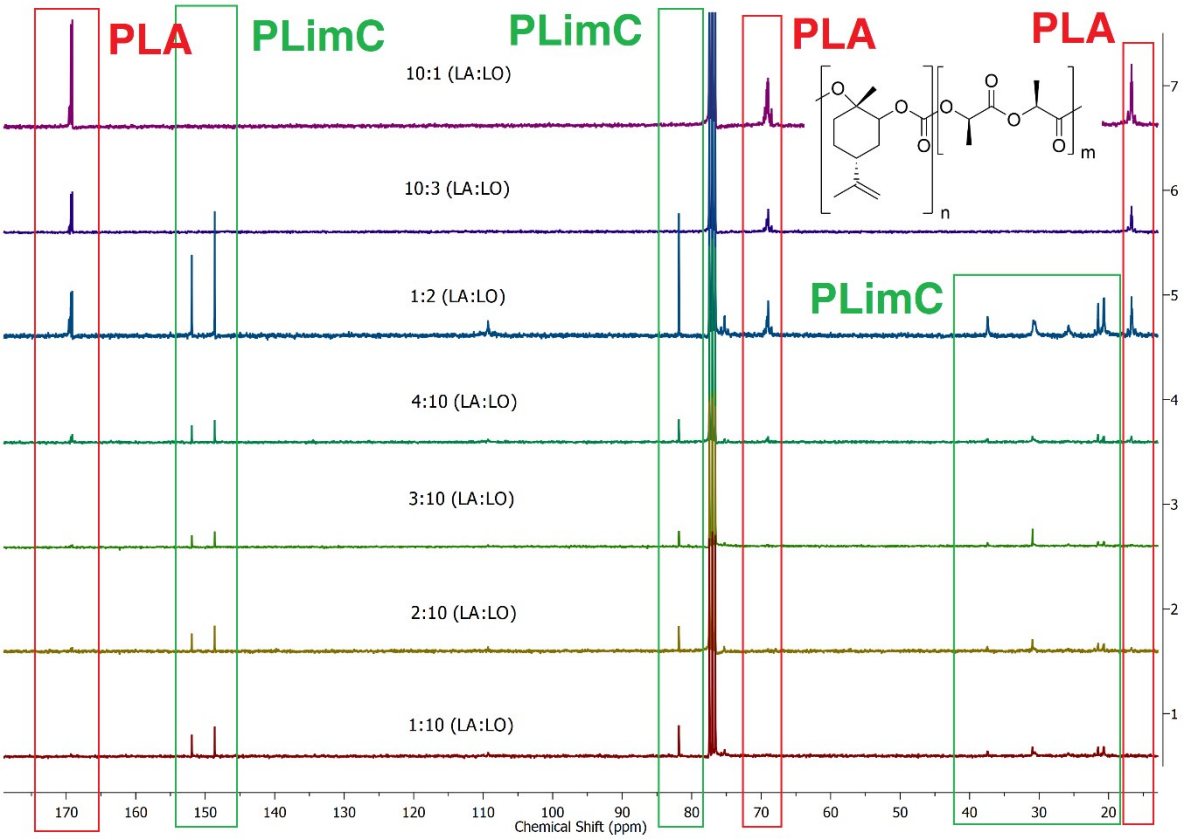


Fig. S3 ^{13}C-NMR spectra ($CDCl_3$, 75 MHz) of copolymers of DLLA and LO-CO_2 with different feed ratios.

^{13}C-NMR (300 MHz, $CDCl_3$): δ = 169.13 (C12), 151.92 (C11), 148.63 (C8), 109.3 (C7), 81.83 (C6), 75.32 (C5), 68.98 (C13), 37.43 (C3), 30.96 (C1), 21.54 (C4), 20.84 (C2), 20.65 (C10), 20.59 (C9), 16.07 (C14) ppm.

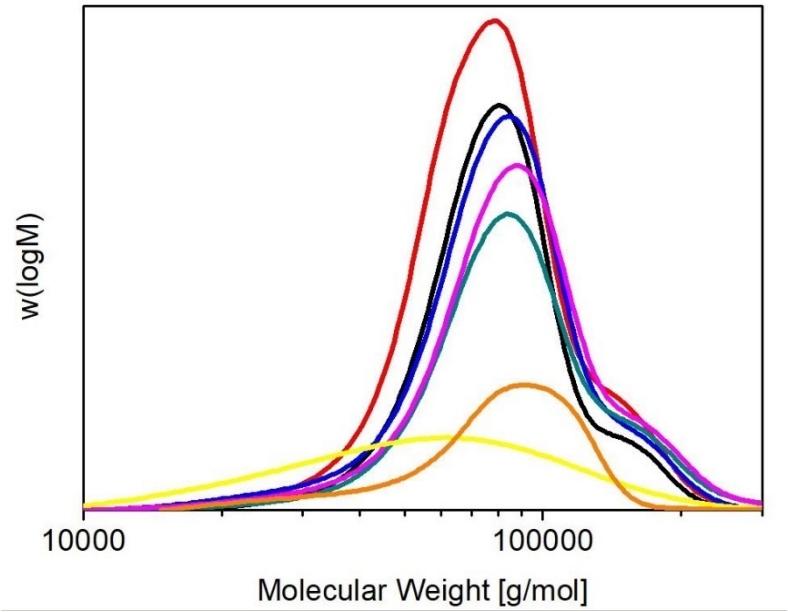


Fig. S4 $CHCl_3$-GPC traces of copolymers of DLLA and LO-CO_2 with different feed ratios. Molecular weight (M_n) and dispersity ($Đ$) were determined from these curves cannot be taken precisely due to the non-unimodal nature of the curves. DLLA:LO = 9/91 mol% (black), DLLA:LO = 17/83 mol% (red), DLLA:LO = 23/77 mol% (blue), DLLA:LO = 29/71 mol% (green), DLLA:LO = 34/66 mol% (pink), DLLA:LO = 77/23 mol% (yellow),), DLLA:LO = 91/9 mol% (orange).

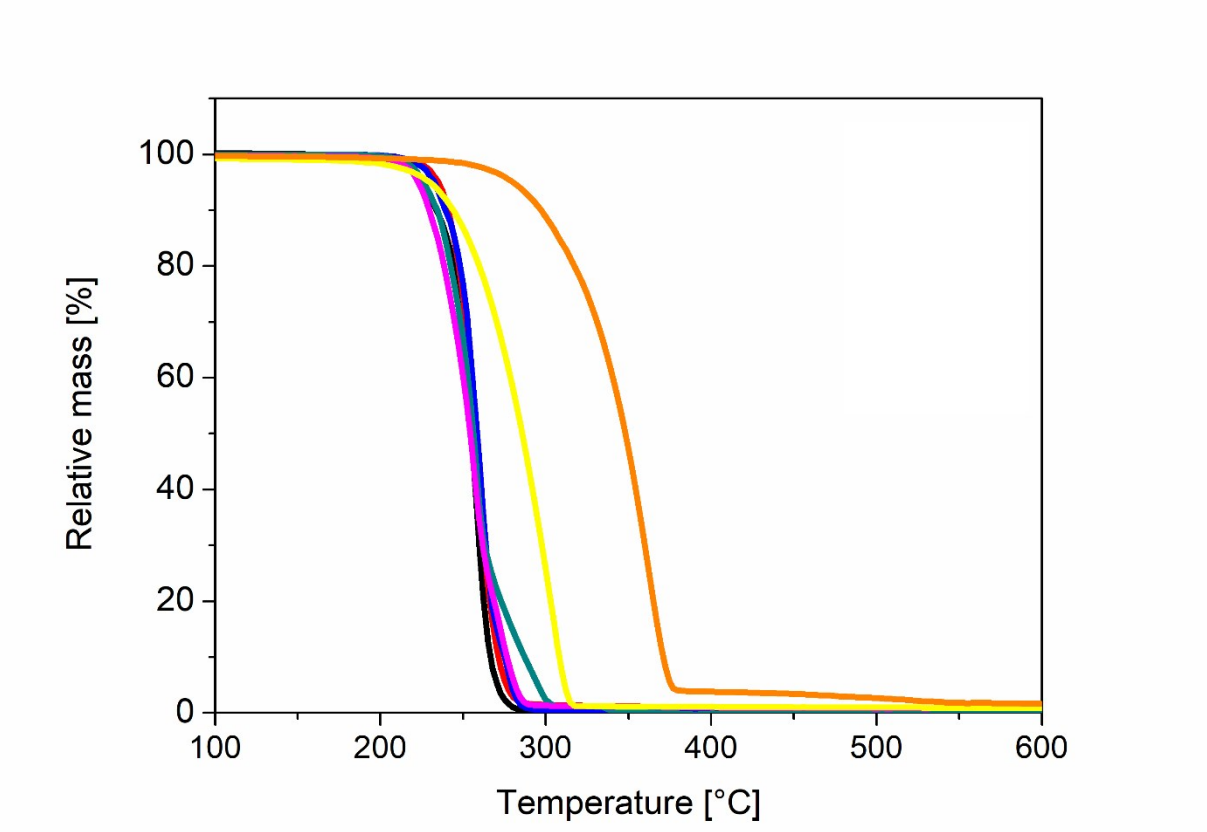


Fig. S5 TGA thermograms of copolymers of DLLA and LO-CO_2 with different feed ratios, measured under nitrogen with 10K/min. DLLA:LO = 9/91 mol% (black), DLLA:LO = 17/83 mol% (red), DLLA:LO = 23/77 mol% (blue), DLLA:LO = 29/71 mol% (green), DLLA:LO = 34/66 mol% (pink), DLLA:LO = 77/23 mol% (yellow),), DLLA:LO = 91/9 mol% (orange).

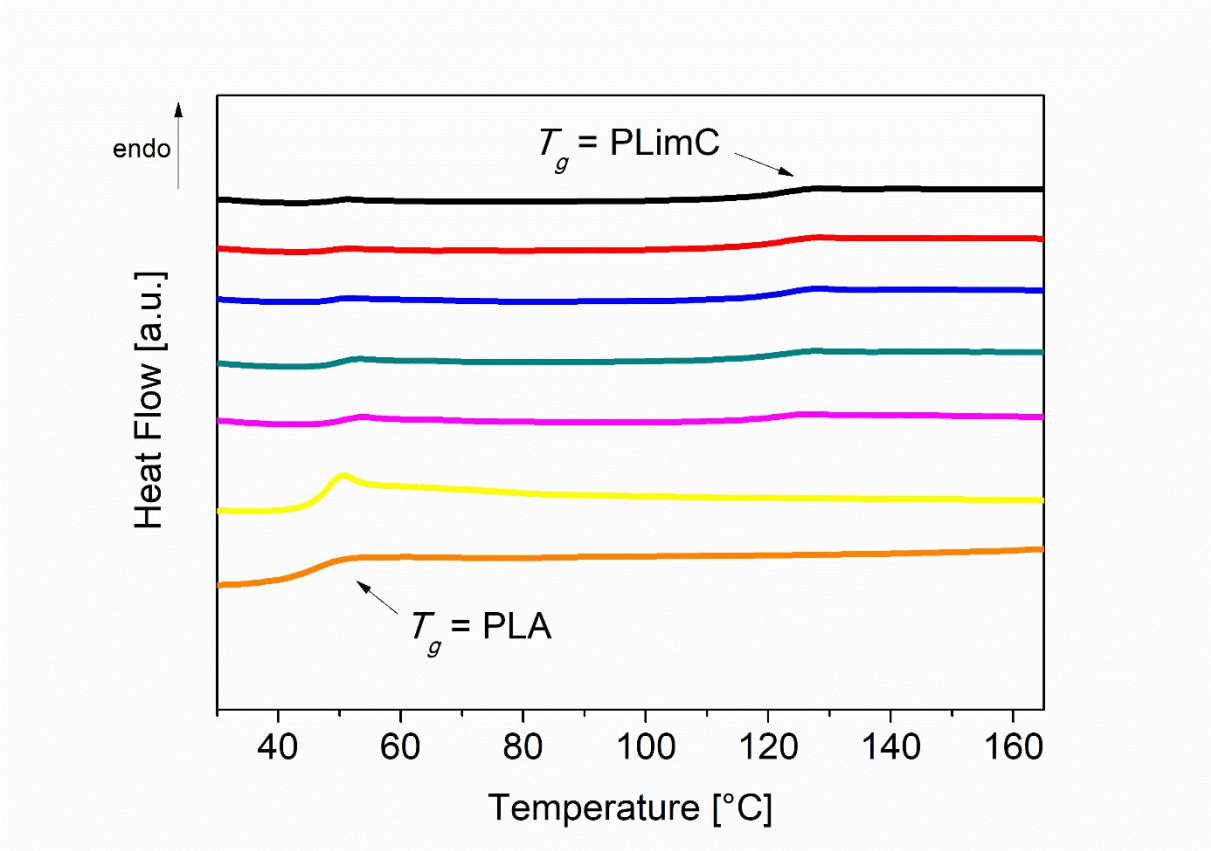


Fig. S6 DSC thermograms of copolymers of DLLA and LO-CO_2 with different feed ratios The displayed traces correspond to the second heating curve measured at 10 K min^{-1} under nitrogen. DLLA:LO = 9/91 mol% (black), DLLA:LO = 17/83 mol% (red), DLLA:LO = 23/77 mol% (blue), DLLA:LO = 29/71 mol% (green), DLLA:LO = 34/66 mol% (pink), DLLA:LO = 77/23 mol% (yellow),), DLLA:LO = 91/9 mol% (orange).

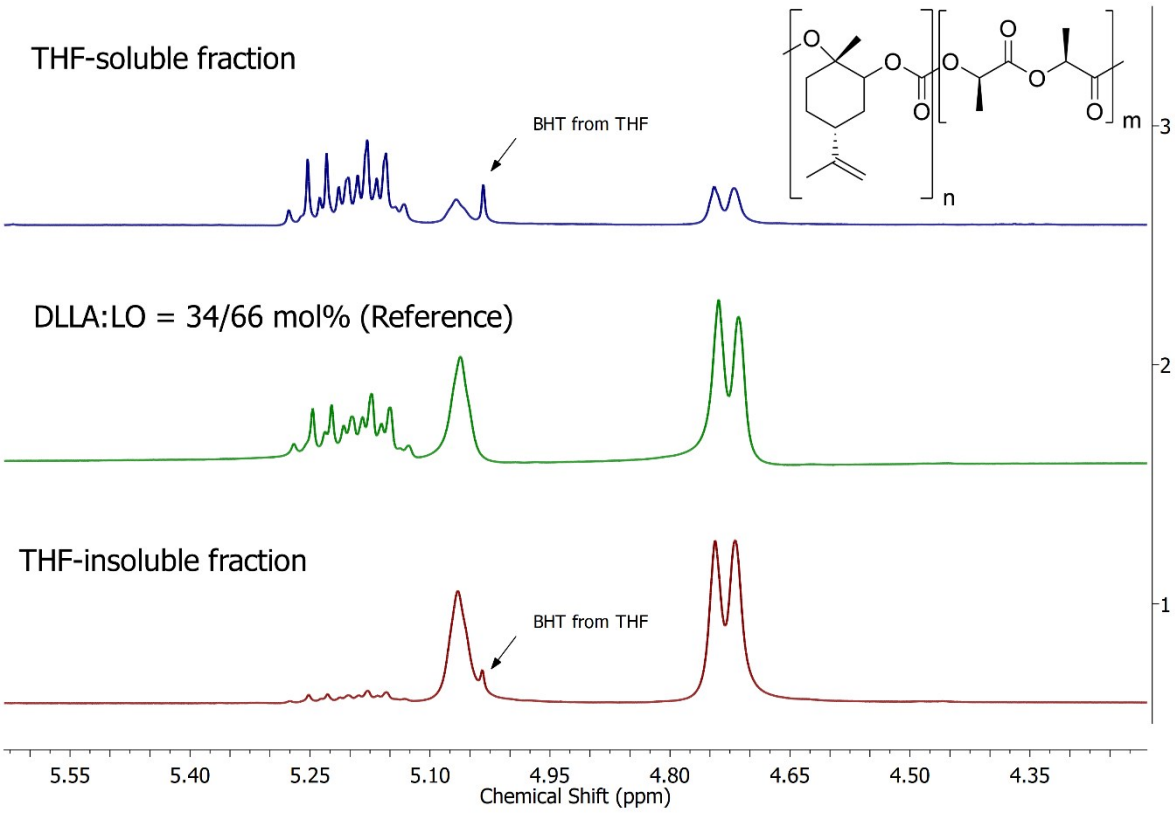


Fig. S7 ^{1}H-NMR spectrum ($CDCl_3$, 300 MHz) of copolymers (DLLA/ LO = 34/66 mol%) designated as reference in the figure) and the corresponding ^{1}H-NMR spectra of THF-soluble fraction and THF-insoluble fraction. Copolymer composition: DLLA/LO mol%: Reference: 60/40; THF soluble fraction: 87/13; THF insoluble fraction: 18/82.

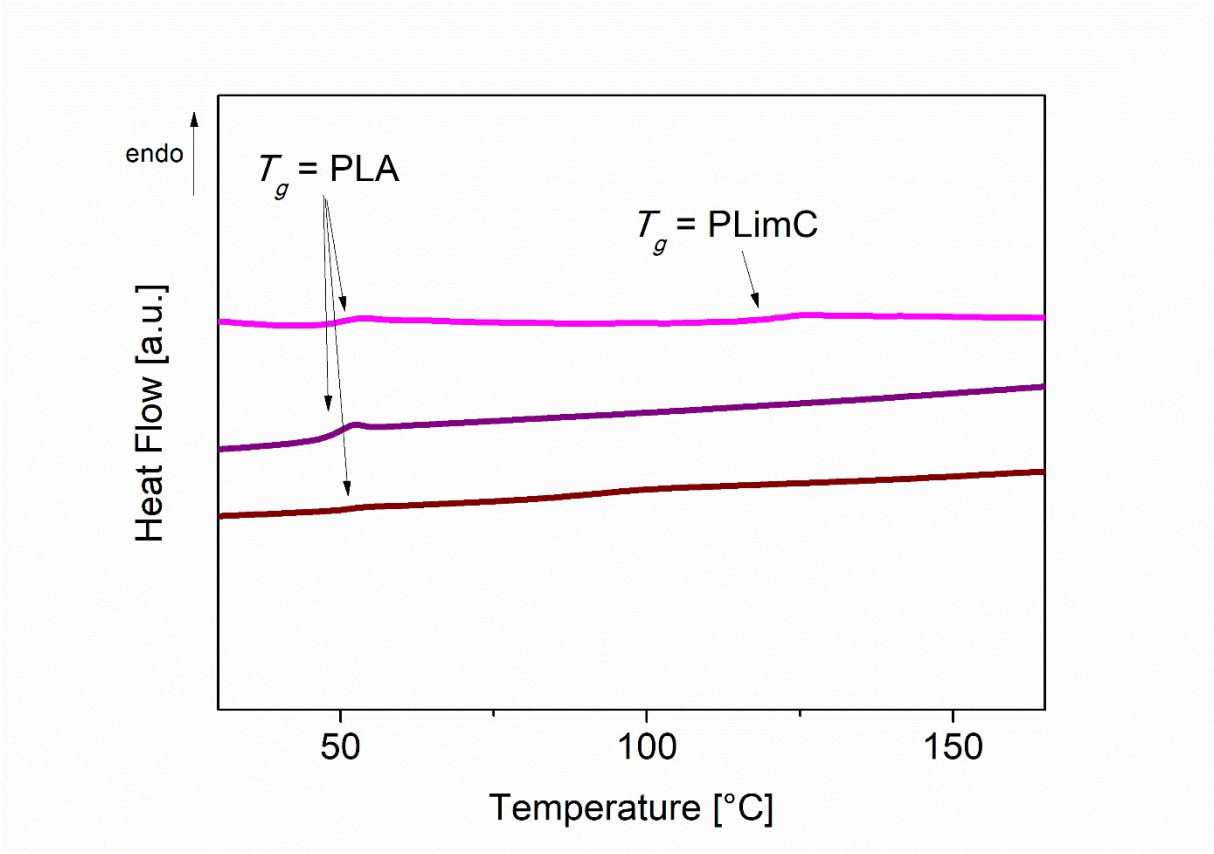


Fig. S8 DSC thermograms of PLimC-*b*-PDLLA block copolymers (DLLA/ LO = 34/66 mol%) and the corresponding DSC thermograms of THF-soluble fraction (brown) and THF-insoluble fraction (violet). The displayed traces correspond to the second heating curve measured at 10 K min^{-1}.

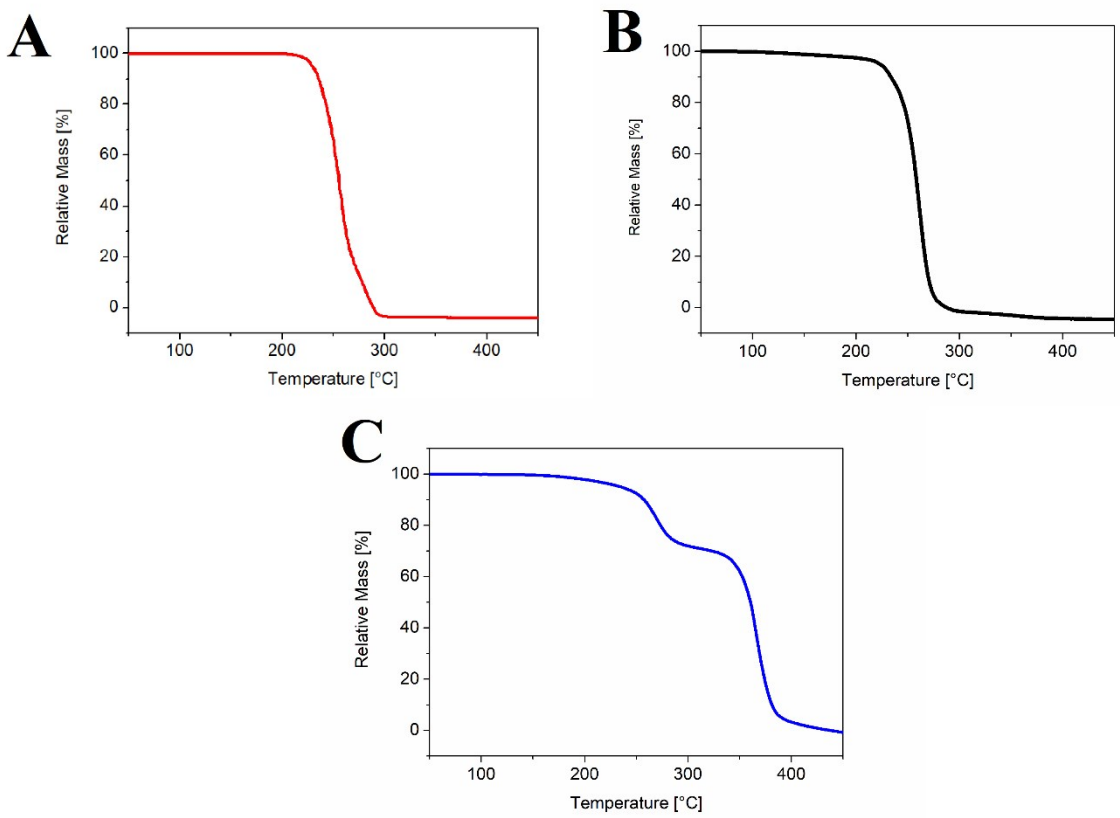


Fig. S9 TGA thermograms of PLimC-*b*-PDLLA block copolymers (DLLA/ LO = 34/66 mol%) and the corresponding TGA thermograms of the THF-soluble fraction and THF-insoluble fraction. A) Reference with 40 mol % PLimC/ 60 mol% PDLLA. B) THF-insoluble fraction with 82 mol% PLimC/18 mol% PDLLA. C) THF-soluble fraction with 13 mol% PLimC/ 87 mol % PDLLA.

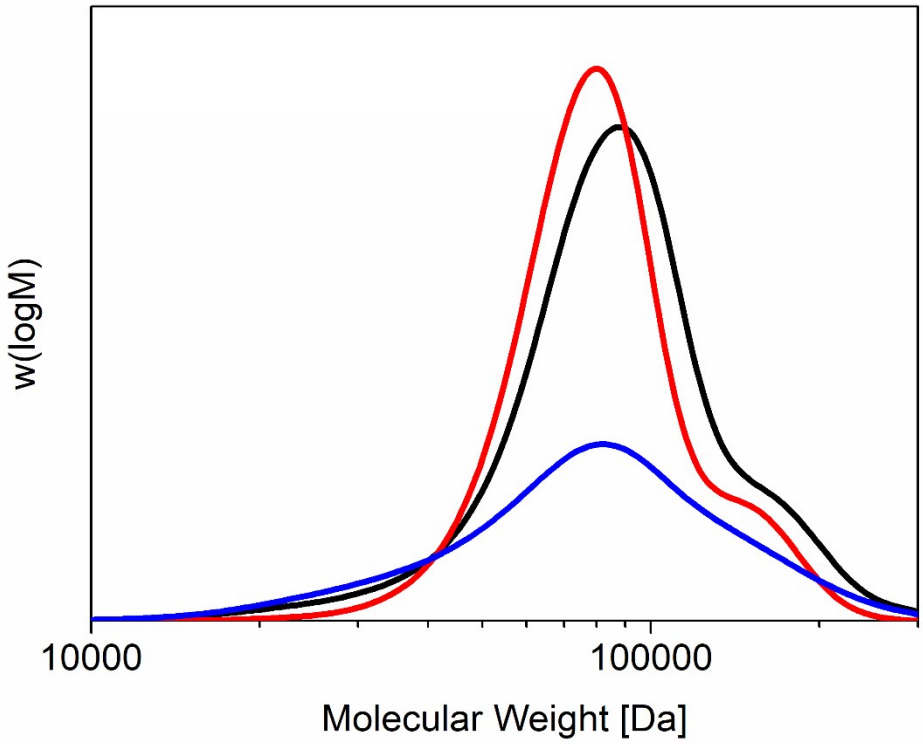


Fig. S10 $CHCl_3$-GPC traces of PLimC-*b*-PDLLA block copolymers (DLLA/ LO = 34/66 mol%) and the corresponding $CHCl_3$-GPC traces of the THF-soluble fraction and THF-insoluble fraction. Molecular weight (M_n) and dispersity ($Đ$) were determined by $CHCl_3$-GPC, calibrated with narrowly distributed polystyrene standards.

TEM micrographs of PLimC-b-PDLLA block copolymers

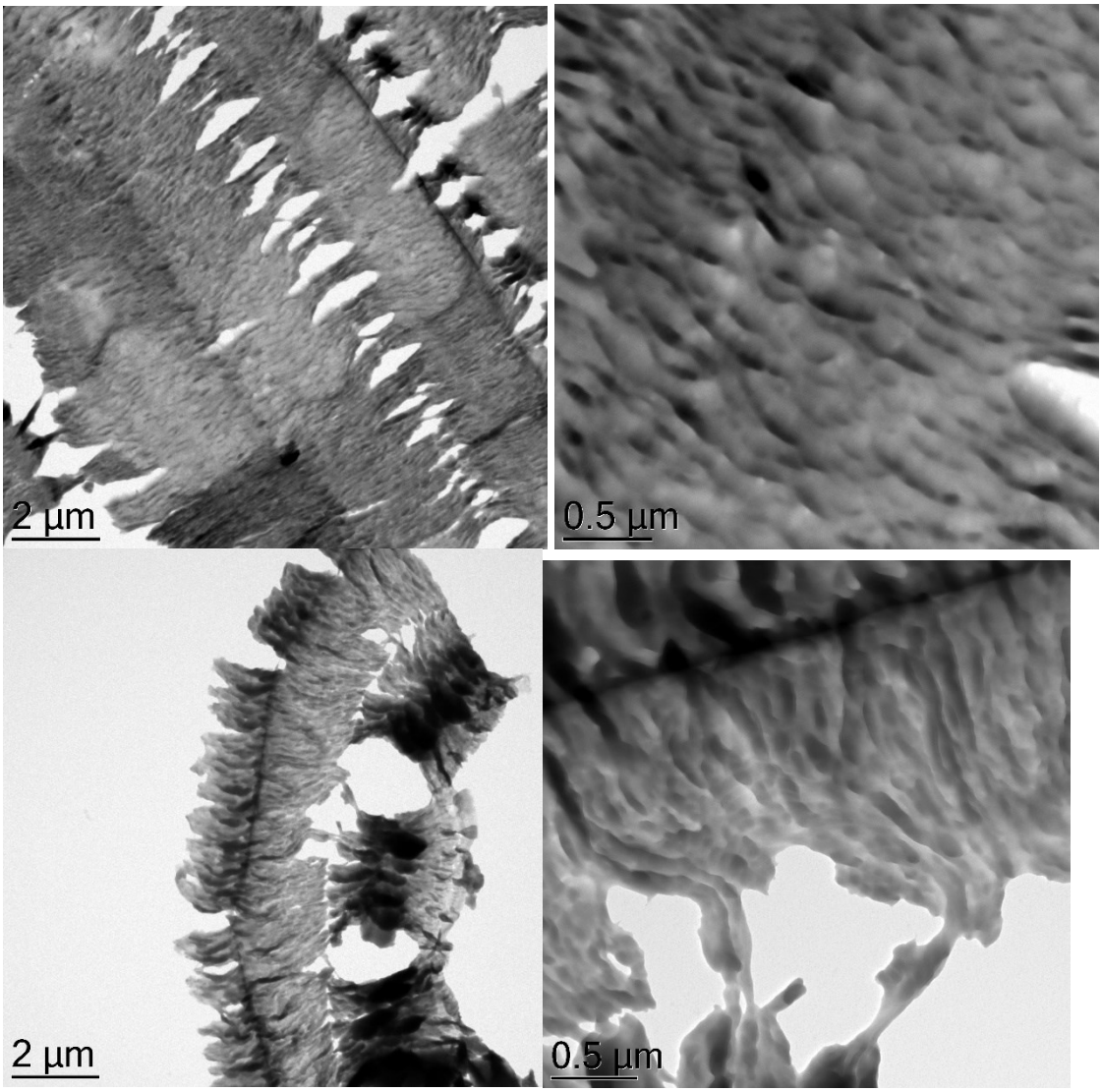


Fig. S11 TEM micrographs of PLimC-*b*-PDLLA block copolymers (DLLA/ LO = 17/83 mol%) with PLimC/PDLLA = 39/61 mol%.

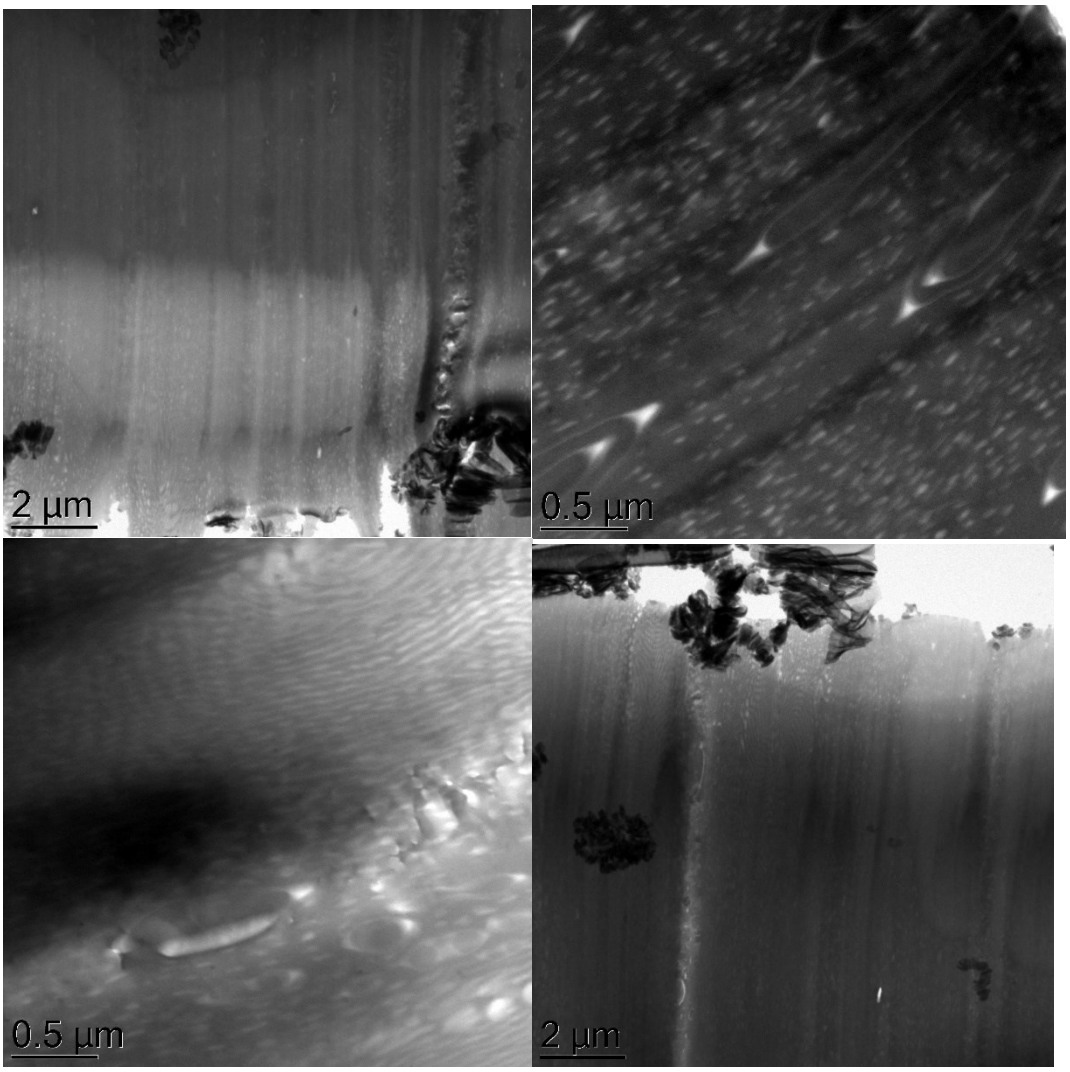


Fig. S12 TEM micrographs of PLimC-*b*-PDLLA block copolymers (DLLA/ LO = 23/77 mol%) with PLimC/PDLLA = 59/41 mol%.

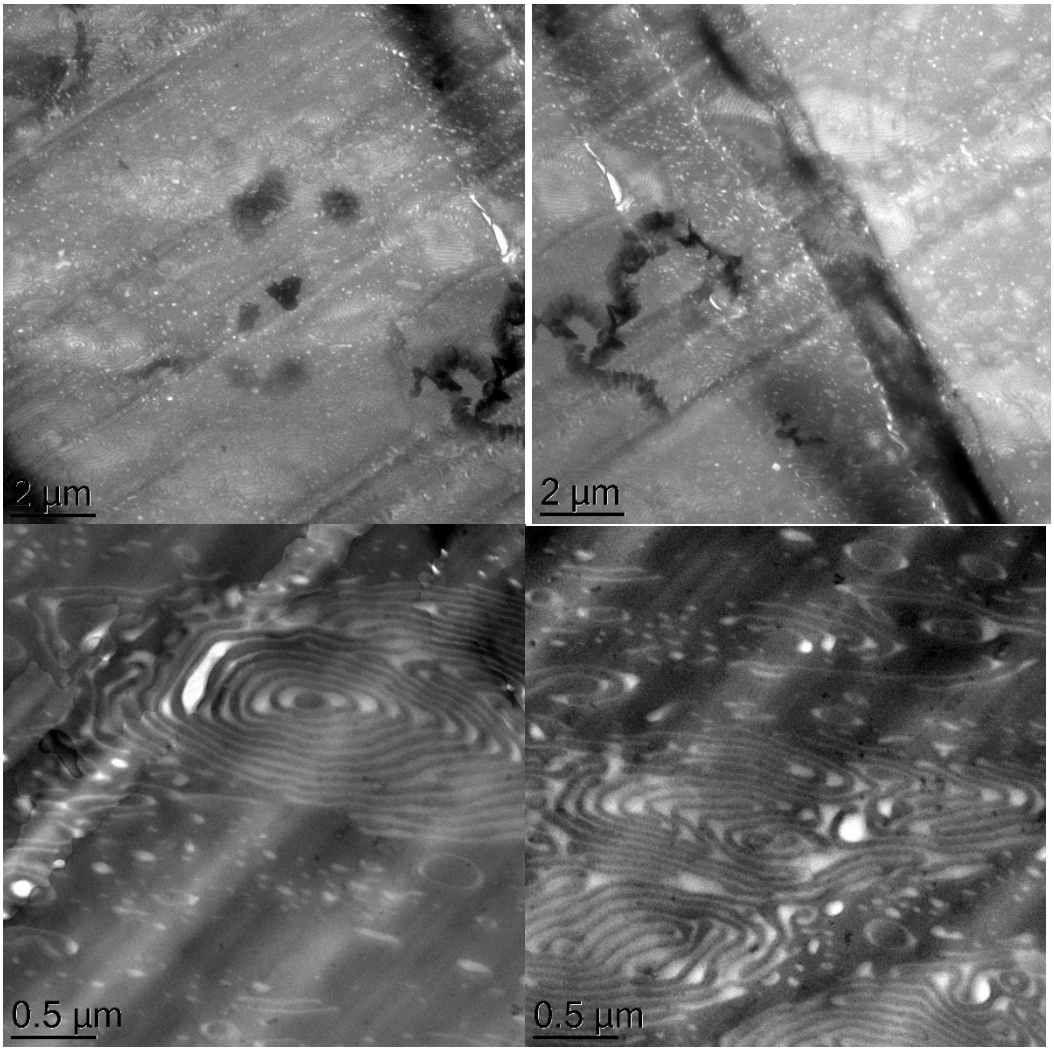


Fig. S13 TEM micrographs of PLimC-*b*-PDLLA block copolymers (DLLA/ LO = 29/71 mol%) with PLimC/PDLLA = 46/54 mol%.

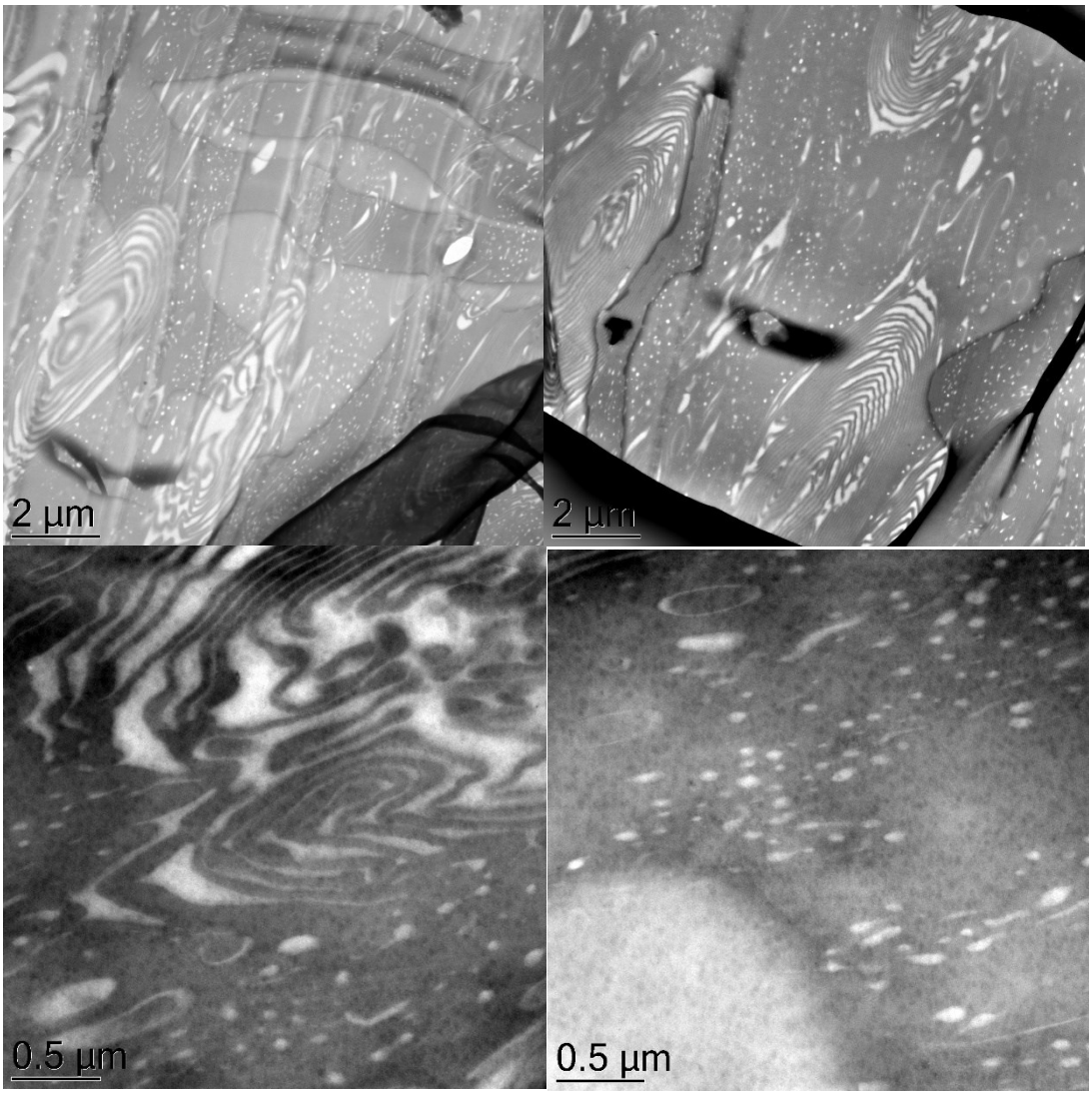


Fig. S14 TEM micrographs of PLimC-*b*-PDLLA block copolymers (DLLA/ LO = 34/66 mol%) with PLimC/PDLLA = 40/60 mol%.

Sequential terpolymerziation of *trans*-limonene-oxide, (*L*)-lactide and CO_2

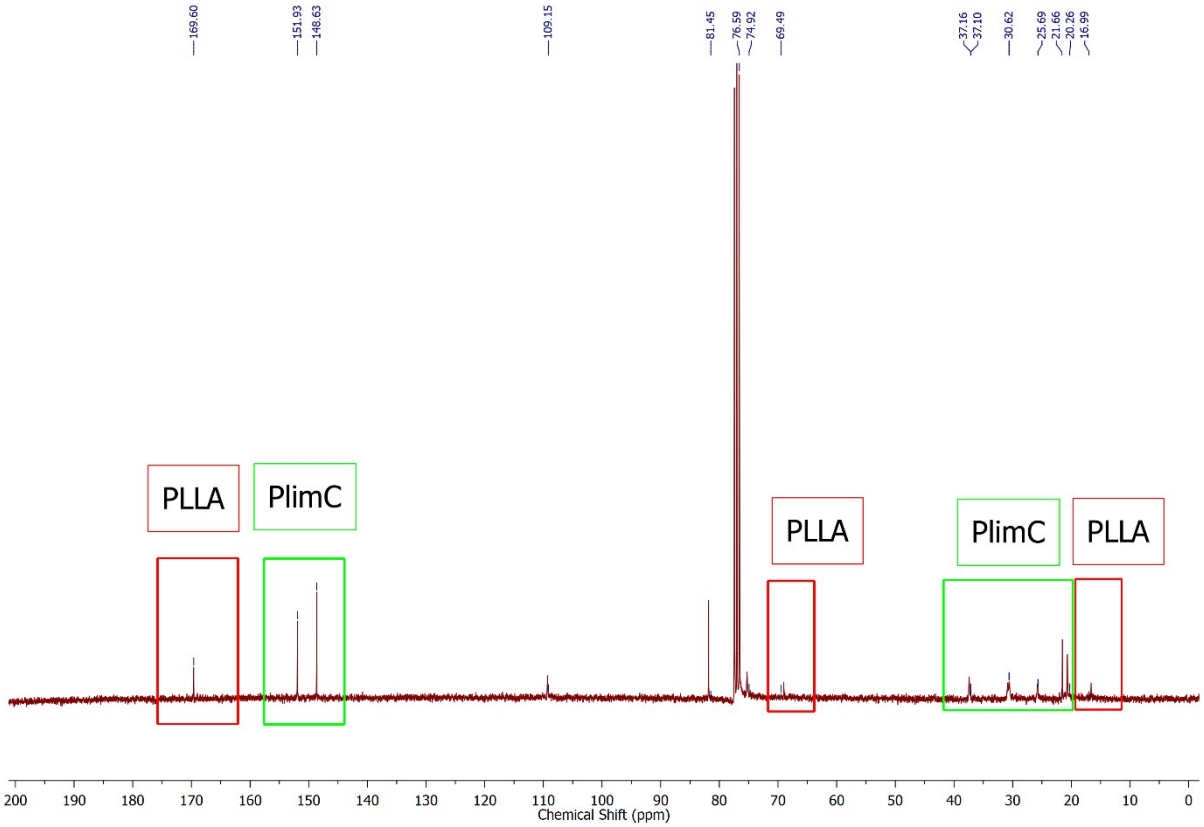


Fig. S15 ^{13}C-NMR ($CDCl_3$, 75 MHz) spectrum of PLimC-*b*-PLLA block copolymer (feed ratio: LA/LO = 20/80 mol%) with a composition of PLimC/PLLA = 29/71 mol%, measured in $CDCl_3$.

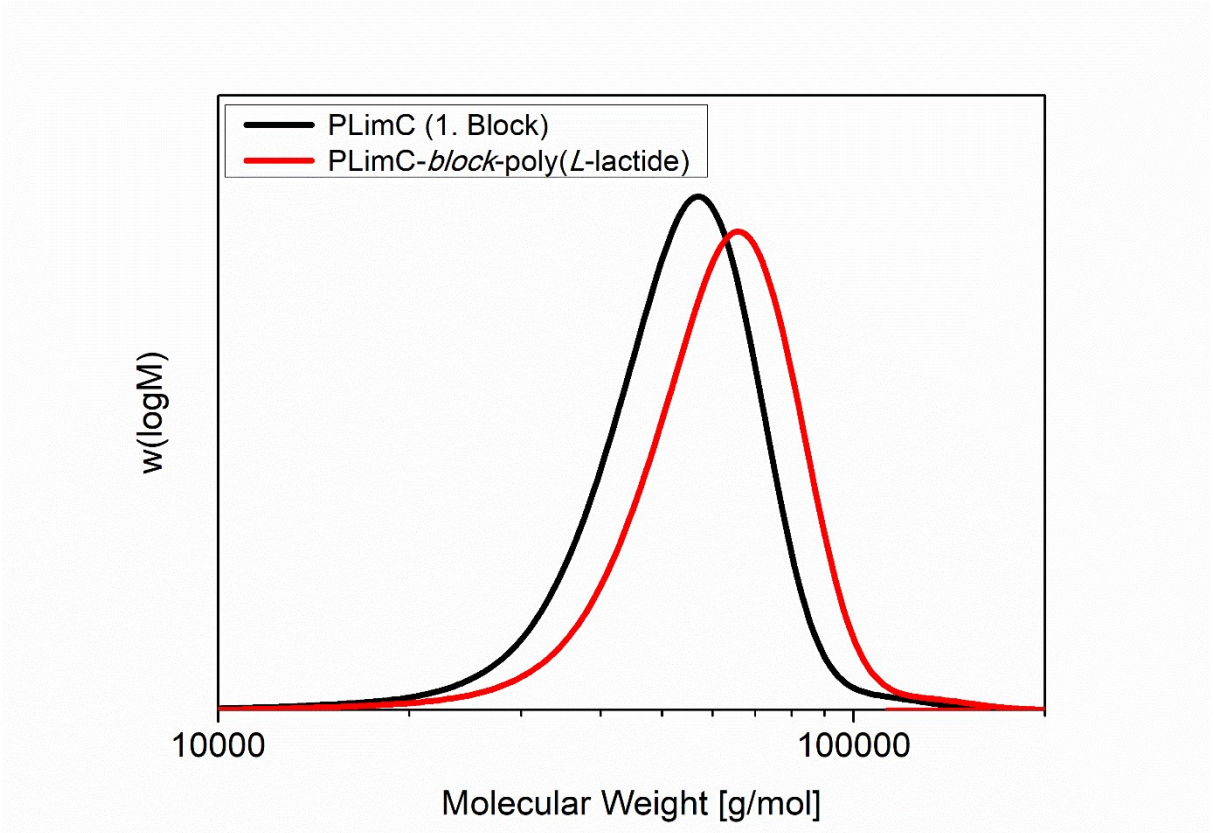


Fig. S16 $CHCl_3$-GPC traces of PLimC-*b*-PLLA block copolymer (feed ratio: LA/LO = 20/80 mol%) with a composition of PLimC/PLLA = 29/71 mol%. Molecular weight (M_n) and dispersity ($Đ$) were determined by $CHCl_3$-GPC, calibrated with narrowly distributed polystyrene standards.

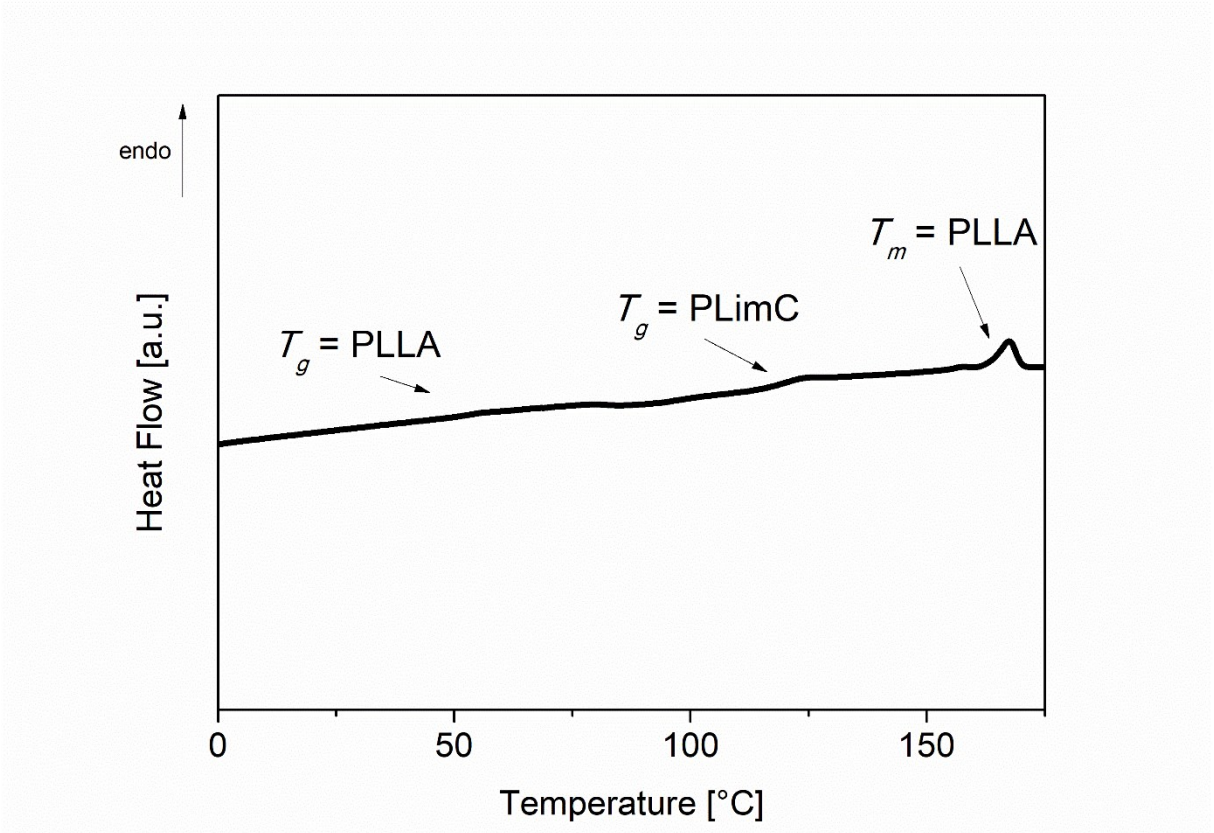


Fig. S17 DSC thermogram of PLimC-*b*-PLLA block copolymer (feed ratio: LA/LO = 20/80 mol%) with a composition of PLimC/PLLA = 29/71 mol%. The displayed trace corresponds to the second heating curve measured at 10 K min^{-1} under nitrogen.

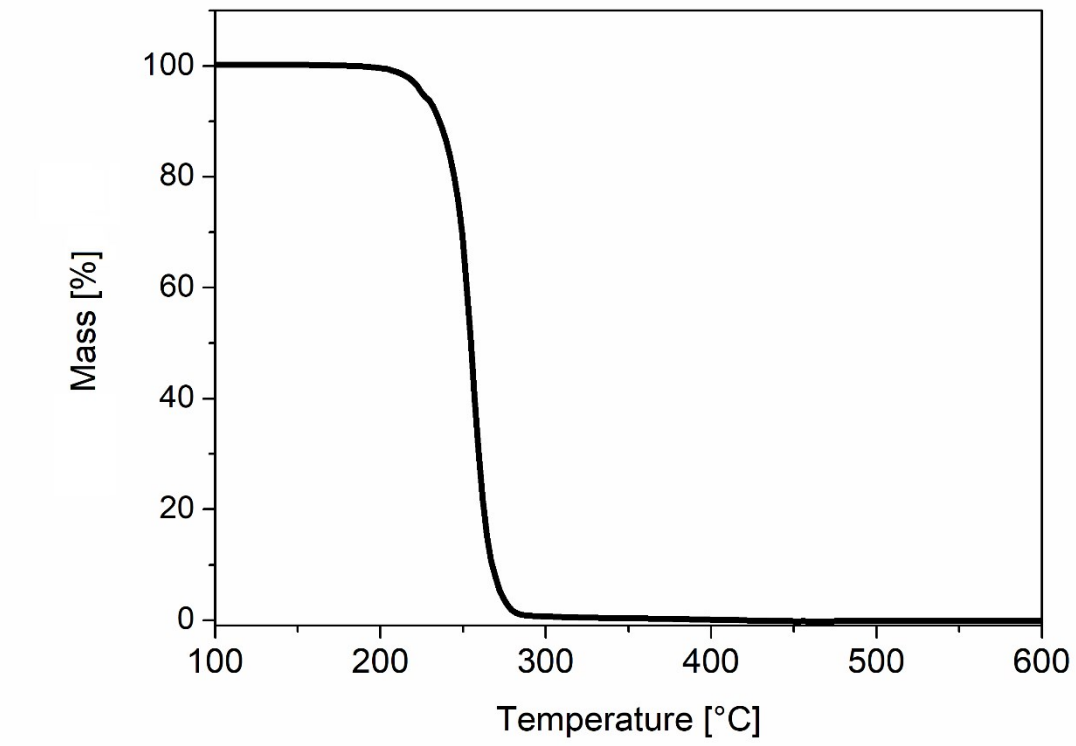
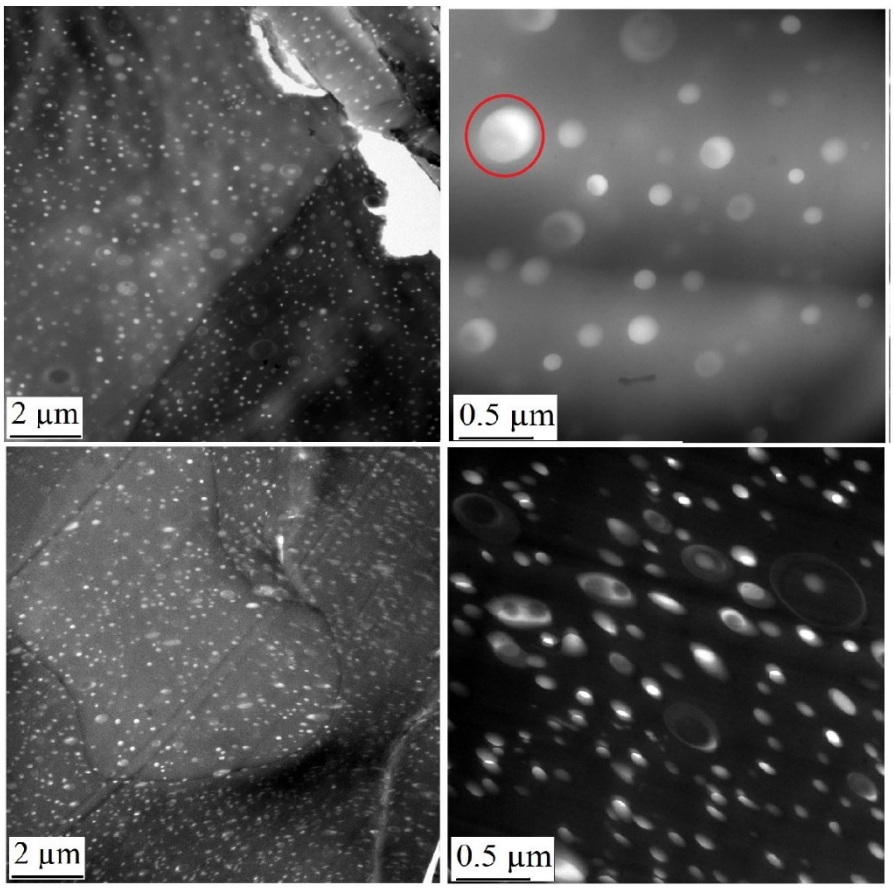


Fig. S18 TGA thermogram for PLimC-*b*-PLLA block copolymer (feed ratio: LA/LO = 20/80 mol%) with a composition of PLimC/PLLA = 29/71 mol%, measured under nitrogen with 10K/min.



Spheres (S)

Fig. S19 TEM micrographs of PLimC-*b*-PLLA block copolymer with PLimC/PLLA = 71/29 mol%. PLimC is selectively stained with OsO4 vapor.

Terpolymerziation of *trans*-limonene-oxide, dihexyl-substituted lactide and CO_2 (Sequential ROCP)

Table S2. Experimental details of sequential polymerization of diHLA, LO and CO_2 using [(BDI)Zn-(μ-OAc)] catalyst.

Sample	Feed Ratio	Polymer Composition	Lactide		LO		Catalyst	Toluene	Yield
	diHLA/ LO	r-diHLA /r-LO	m	n	V	n	m	V	
Unit	mol%	mol%	mg	mmol	mL	mmol	mg	mL	%
10	23/77	29/71	511	1.80	1.0	6.1	33	6	89
11	13/87	50/50	260	0.91	1.0	6.1	33	11	n.d.
12	50/50	62/38	993	3.49	0.57	3.5	20	5	74

Table S3. Overview of the synthesized PLimC and PdiHLA block copolymers in terms of feed ratio, polymer composition, molecular weight, and thermal properties.

Monomer Lactide	Reaction Type	Feed Ratio diHLA/ LO	r-diHLA /r-LO	M_n[a]	$Đ$[a]	T_g[b] PLimC	T_g[b] PE	T_m[b] PE	$T_{5\%}$[c]	$T_{max,1}$[d] PLimC	$T_{max,2}$[d] PE
		mol%	mol%	kDa		°C	°C	°C	°C	°C	°C
diHLA	Sequential	23/77	29/71	35	1.40	-	-36	-	228	254	329
diHLA	Sequential	13/87	50/50	14	1.20	-	-39	-	224	247	299
diHLA	Sequential	50/50	62/38	49	1.40	106	-38	-	229	254	289

[a]GPC: M_n and $Đ$ were determined by $CHCl_3$-GPC, calibrated with narrowly distributed polystyrene standards.
[b]DSC: T_g and T_m were determined from the second heating traces (scanning rate 10 K min^{-1}).
[c]TGA: $T_{5\%}$ was determined with a heating rate of 10 K min^{-1} under N_2 atmosphere.
[d]TGA: $T_{max,1}$ and $T_{max,2}$ were determined from the 1st derivative of the TGA trace.

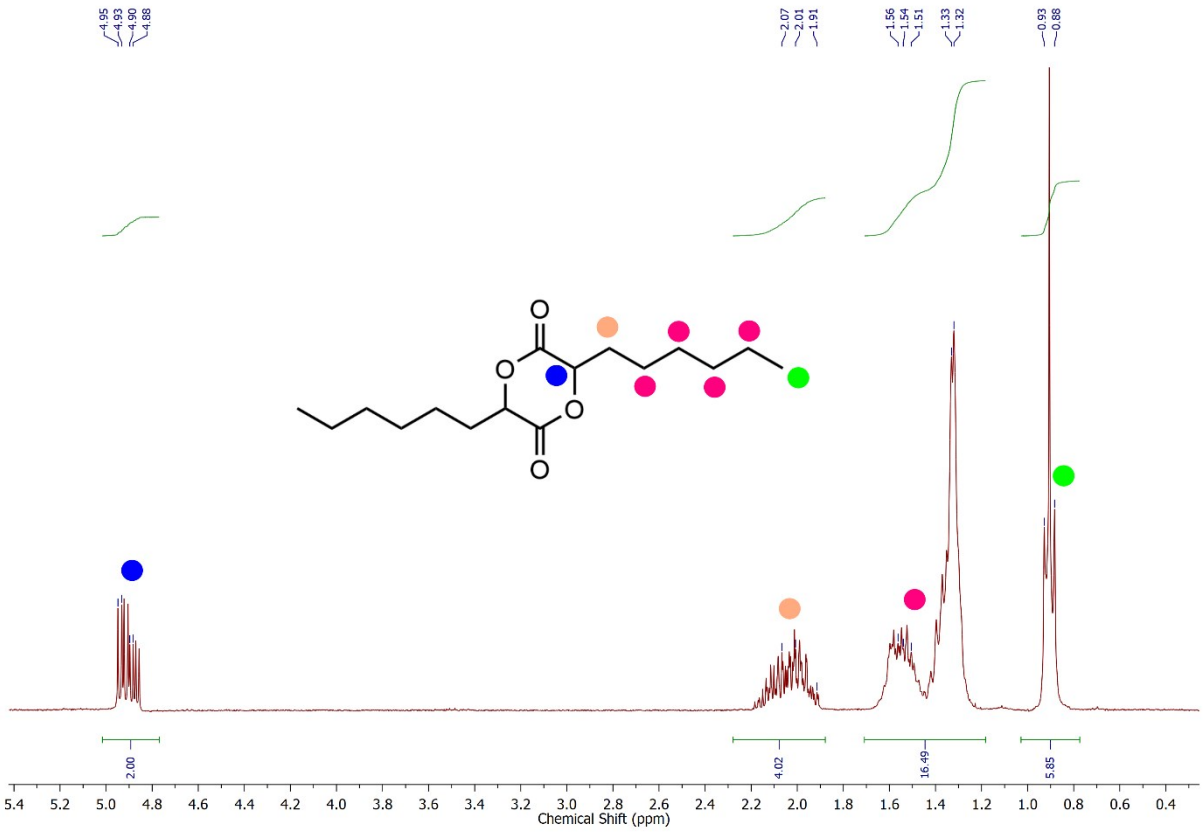


Fig. S20 ^{1}H-NMR spectrum ($CDCl_3$, 300 MHz) of monomer dihexyl-substituted lactide (diHLA).

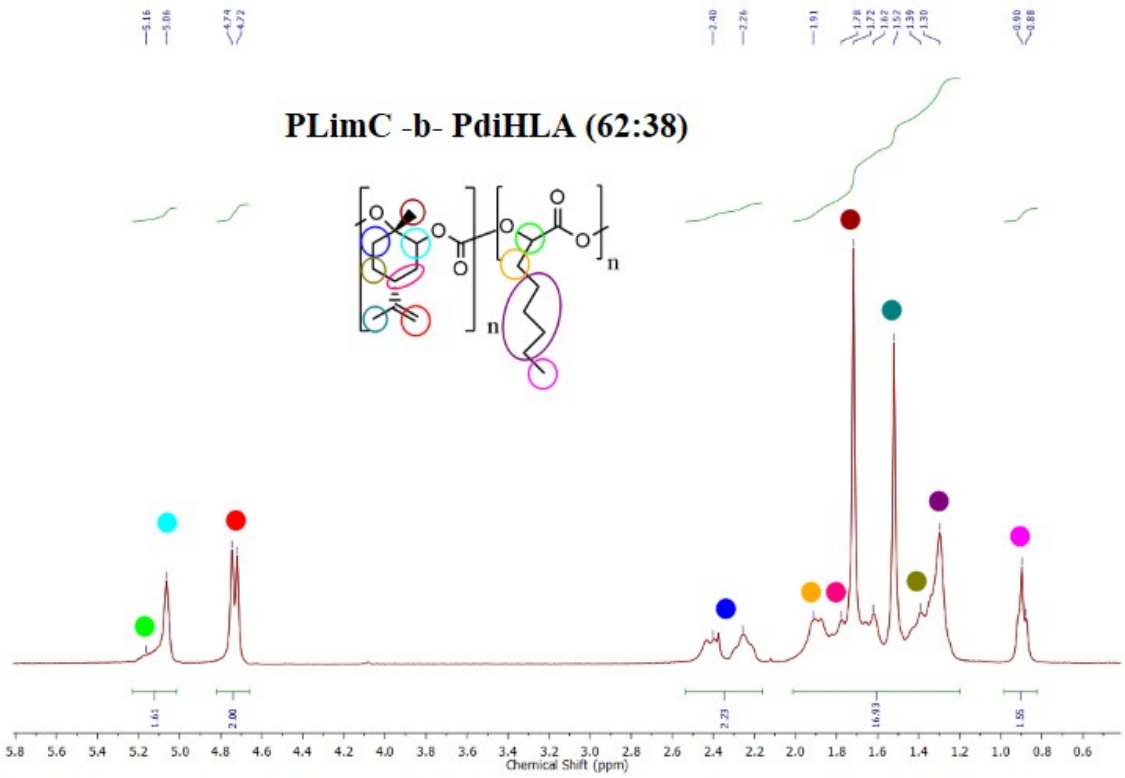


Fig. S21 ^{1}H-NMR spectrum ($CDCl_3$, 300 MHz) of PLimC-*b*-PdiHLA block copolymer (feed ratio: diHLA/LO = 50/50 mol%) with a composition of PLimC/PdiHLA = 62/38 mol%.

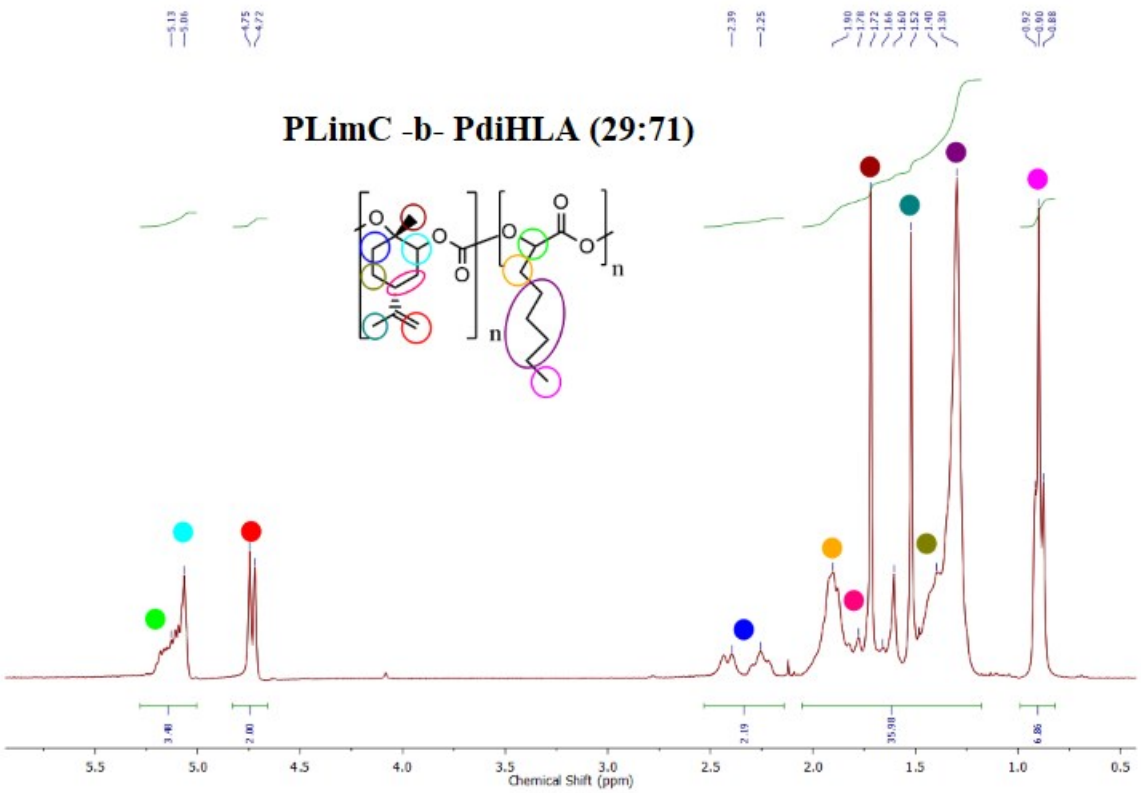


Fig. S22 ^{1}H-NMR spectrum ($CDCl_3$, 300 MHz) of PLimC-*b*-PdiHLA block copolymer (feed ratio: diHLA/LO = 22/78 mol%) with a composition of PLimC/PdiHLA = 29/71 mol%.

GPC traces of PLimC-b-PdiHLA block copolymers

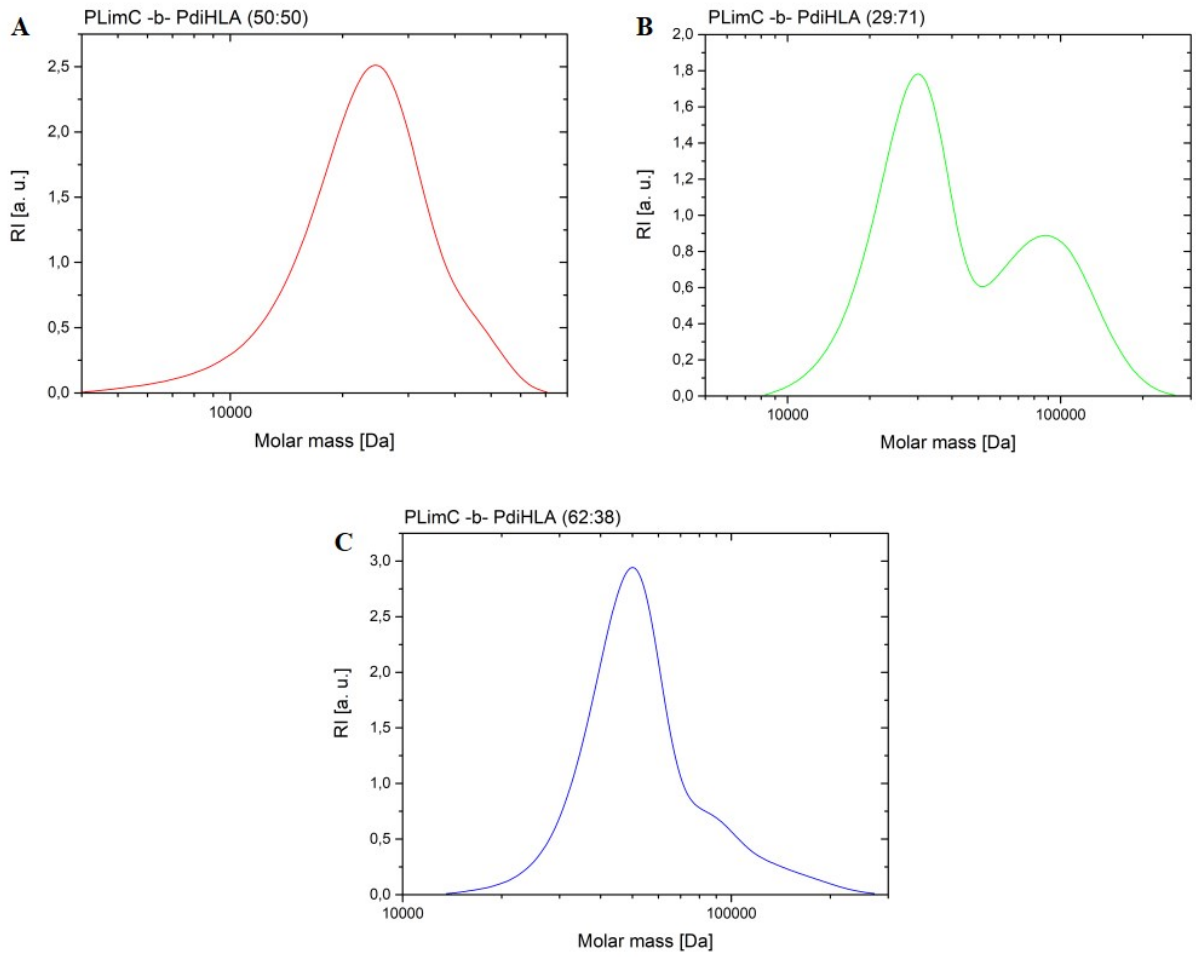


Fig. S23 $CHCl_3$-GPC traces of PLimC-*b*-PdiHLA block copolymers. A) PLimC-*b*-PdiHLA (50:50) block copolymer, M_n = 14.210 g/mol, $Đ$ = 1.4. B) PLimC-*b*-PdiHLA (29:71) block copolymer, M_n = 35.070 g/mol, $Đ$ = 1.5. C) PLimC-*b*-PdiHLA. (62:38) block copolymer, M_n = 48.980 g/mol, $Đ$ = 1.2. Molecular weight (M_n) and dispersity ($Đ$) were determined by $CHCl_3$-GPC, calibrated with narrowly distributed polystyrene standards.

DSC thermogram of PLimC-b-PdiHLA block copolymer

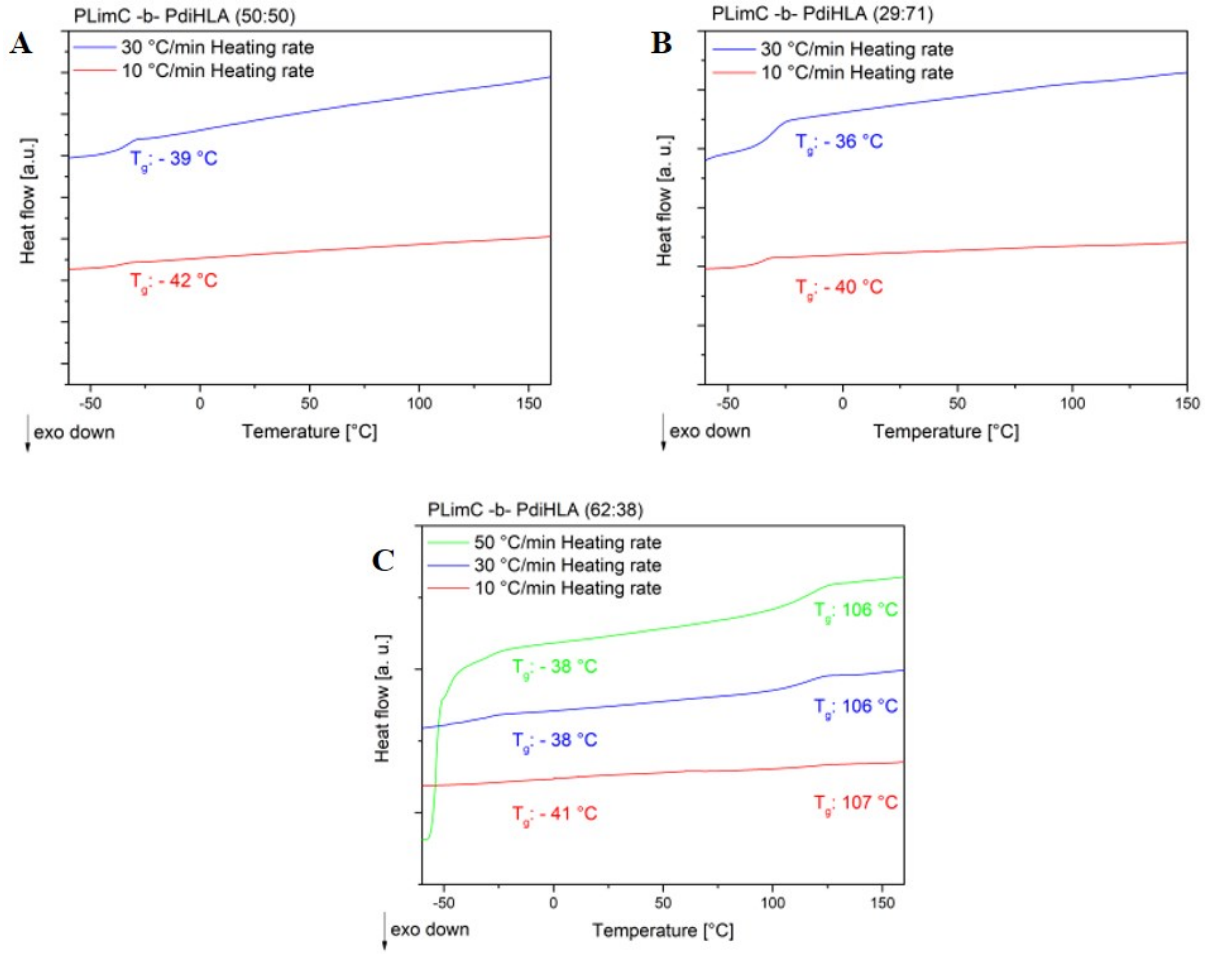


Fig. S24 DSC thermograms of PLimC-*b*-PdiHLA block copolymers. A) PLimC-*b*-PdiHLA (50:50) block copolymer. B) PLimC-*b*-PdiHLA (29:71) block copolymer. C) PLimC-*b*-PdiHLA (62:38) block copolymer with a heating rate of 10, 30 and 50 °C/min.

TGA thermograms of PLimC-b-PdiHLA block copolymer

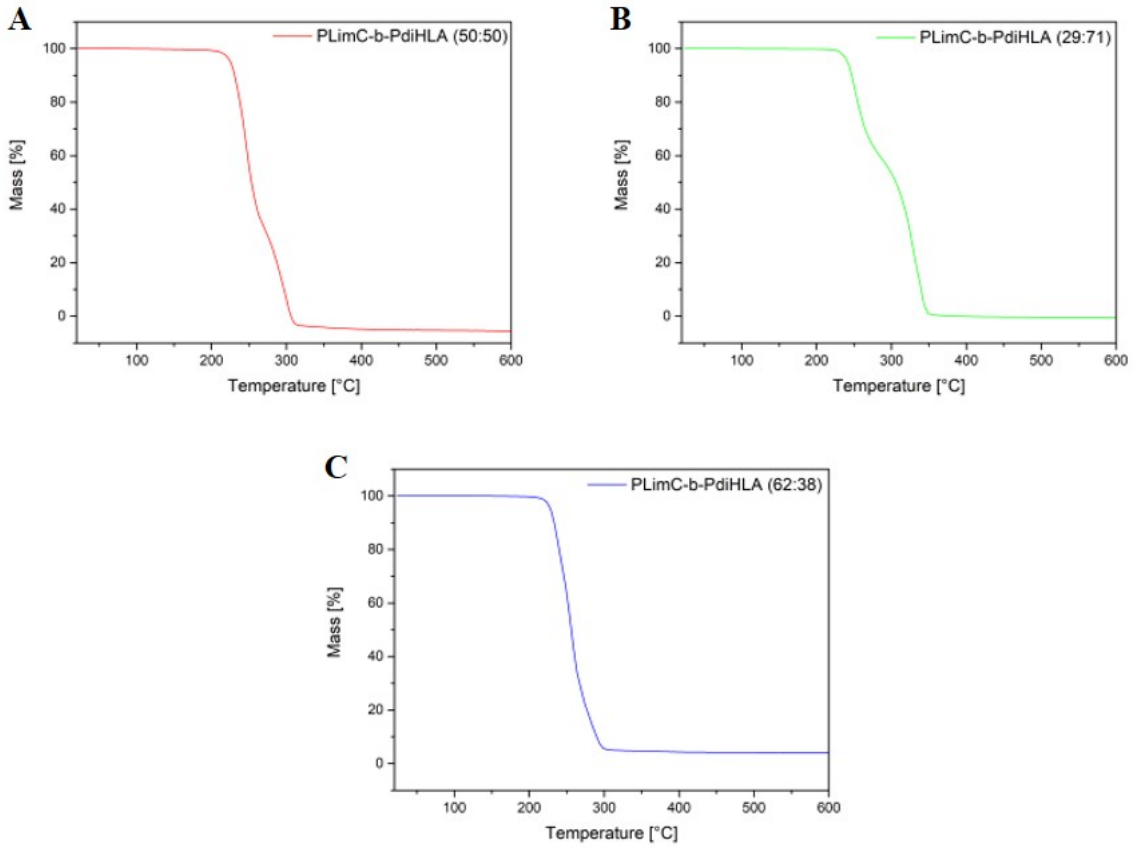


Fig. S25 TGA thermograms of PLimC-*b*-PdiHLA block copolymer. A) PLimC-*b*-PdiHLA (50:50) block copolymer, T_{onset} of PLimC degradation: 226 °C, T_{onset} of PdiHLA degradation: 260 °C. B) PLimC-*b*-PdiHLA (29:71) block copolymer, T_{onset} of PLimC degradation: 247 °C, T_{onset} of PdiHLA degradation: 306 °C. C) PLimC-*b*-PdiHLA (62:38) block copolymer, T_{onset} of PLimC degradation: 226 °C, T_{onset} of PdiHLA degradation: 260 °C. The displayed traces were measured under nitrogen with 10K/min.