

**Supplementary information**

**High molar mass poly(ricinoleic acid) *via* entropy-driven ring-opening metathesis  
polymerization**

Ryohei Ogawa\* and Marc A. Hillmyer\*

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## Experimental Details

**1. Materials.** Ricinoleic acid and methyl ricinoleate were supplied from Mitsui Chemicals Inc. Grubbs 2<sup>nd</sup> generation catalyst (Aldrich), and other commercially available reagents were used as received. Dichloromethane for PRA synthesis was purified by passing through an MBraun solvent purification column and then stored under an argon atmosphere. 4-(Dimethylamino)pyridinium-4-toluene-sulfonate (DPTS) was prepared according to the literature.<sup>1</sup>

**2. Characterization.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were collected using CDCl<sub>3</sub> solutions on the Bruker Advance III HD Nanobay AX-400. Chemical shifts are reported in  $\delta$  (ppm) relative to the <sup>1</sup>H and <sup>13</sup>C signals from the protic solvent (7.26 and 77.00 ppm, respectively, for CHCl<sub>3</sub>). Size-exclusion chromatography (SEC) was conducted on a liquid chromatograph (Agilent 1100 series) equipped with a Wyatt Technology DAWN DSP MALLS detector and a Wyatt optlab EX RI S11 detector. Polymer samples were diluted in THF (mobile phase) and passed through three Phenomenex Phenogel-5 columns at 35 °C under a constant volumetric flow rate (1 mL min<sup>-1</sup>). Molar mass characteristics of the samples were referenced to polystyrene standards (Polymer Laboratories) for RI detector. The dn/dc values were estimated by the in-line method, which using the total area of

the RI signal for samples of a known concentration and assumes 100% of the sample mass is recovered. Differential scanning calorimetry (DSC) was conducted on a TA Instruments Discovery Series DSC Q-1000. Samples were analyzed in hermetically sealed aluminum pans. The samples were equilibrated at 150 °C, cooled to -90 °C at 10 °C min<sup>-1</sup> followed by heating to 250 °C at 10 °C min<sup>-1</sup>. Glass transitions are reported upon the middle point of the second heating cycle, which was calculated using the *Trios* software. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 Analyzer at 10 °C min<sup>-1</sup> to 550 °C under nitrogen atmosphere. The Fourier transform infrared (FTIR) spectra were obtained on a Bruker Alpha Platinum spectrometer equipped with a diamond crystal in attenuated total reflection (ATR) mode at a resolution of 4 cm<sup>-1</sup>, and 32 scans were obtained for each spectrum. Dynamic mechanical thermal analysis (DTA) was performed on a TA Instruments Rheometric Series ARES rheometer using 8 mm parallel plate geometry. Experiments were performed in the linear viscoelastic regime. Horizontal shift factors ( $a_t$ ) were determined by aligning the curves of the loss tangent ( $\tan \delta$ ) and applied to the corresponding frequency sweep to generate a master curve *via* time-temperature superposition. The entanglement molar mass ( $M_e$ ) was calculated using the following equation:

$$M_e = \frac{\rho RT}{G_N^0}$$

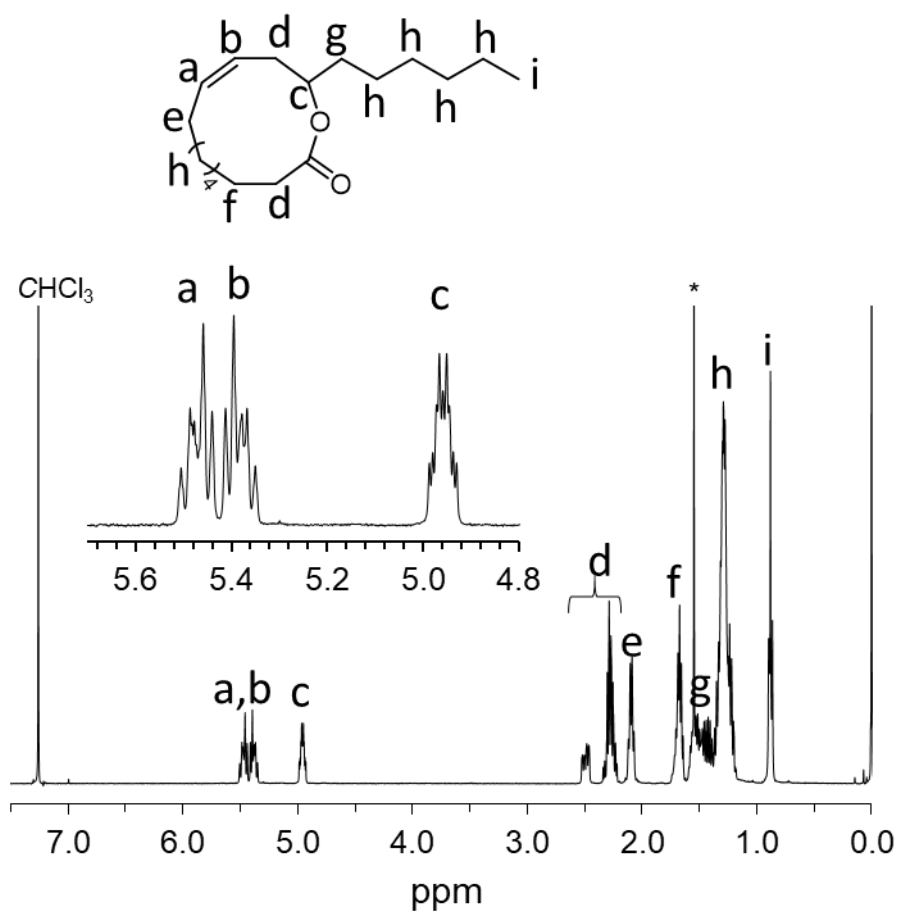
where  $\rho$  is the density of the PRA (assumed to be 1.0 kg/cm<sup>3</sup>),  $R$  is the universal gas constant,  $T$  is the reference temperature, and  $G_N^0$  is the plateau modulus. We estimated the plateau moduli for PRA *via* ED-ROMP at the minimum of  $\tan \delta$  for -40 °C experimental and PRA *via* SPC and at the minimum of  $\tan \delta$  for -20 °C experiment, respectively and these overall minima of  $\tan \delta$  respectively.

**3. Macrolactone synthesis.**<sup>2</sup> Mono-lactone (ML), di-lactone (DL), and mixed-lactone (MixL) were prepared according to the literature procedure. Chloroform was washed with deionized water two times to remove stabilizer (EtOH) and dried over CaCl<sub>2</sub>, and distilled under nitrogen atmosphere for use as a solvent. In the three-neck flask equipped with a reflux condenser and a dropping funnel, DCC (13.7 g, 66.4 mmol), DPTS (20.9 g, 71.0 mmol), DMAP (12.26 g, 100 mmol), and chloroform (0.9 L) was added and heated to reflux under nitrogen atmosphere to give a pale yellow solution. The solution of ricinoleic acid (10 g, 32 mmol) in CHCl<sub>3</sub> (0.10 L) was added to the reflux solution dropwise through the addition funnel for 5-8hrs, then cooled to room temperature and was continued to stir

another 18hr. The reaction was quenched by MeOH/Acetic acid, then, the solvent was evaporated. The crude product was extracted by the addition of diethyl ether (1 L), and the precipitate was removed by filtration. ML and DL was isolated by column chromatography on SiO<sub>2</sub> (Starting from hexane, then gradually added dichloromethane) to give 1.23 g of ML ( $R_f = 0.46$ , DCM/Hex = 1/1) and 3.3 g of DL ( $R_f = 0.26$ , DCM/Hex = 1/1). MixL was purified by column chromatography using dichloromethane as eluent until no longer any spots were detected by TLC analysis. Ricinoleic acid and the oligomers were not detected in MixL, which was also confirmed by TLC analysis (Hexan/EtOAc = 2/1,  $R_f = 0.45$  for ricinoleic acid,  $R_f = 0.86$  for MixL). NMR spectra of ML and DL were well consistent with the references.<sup>2,3</sup>

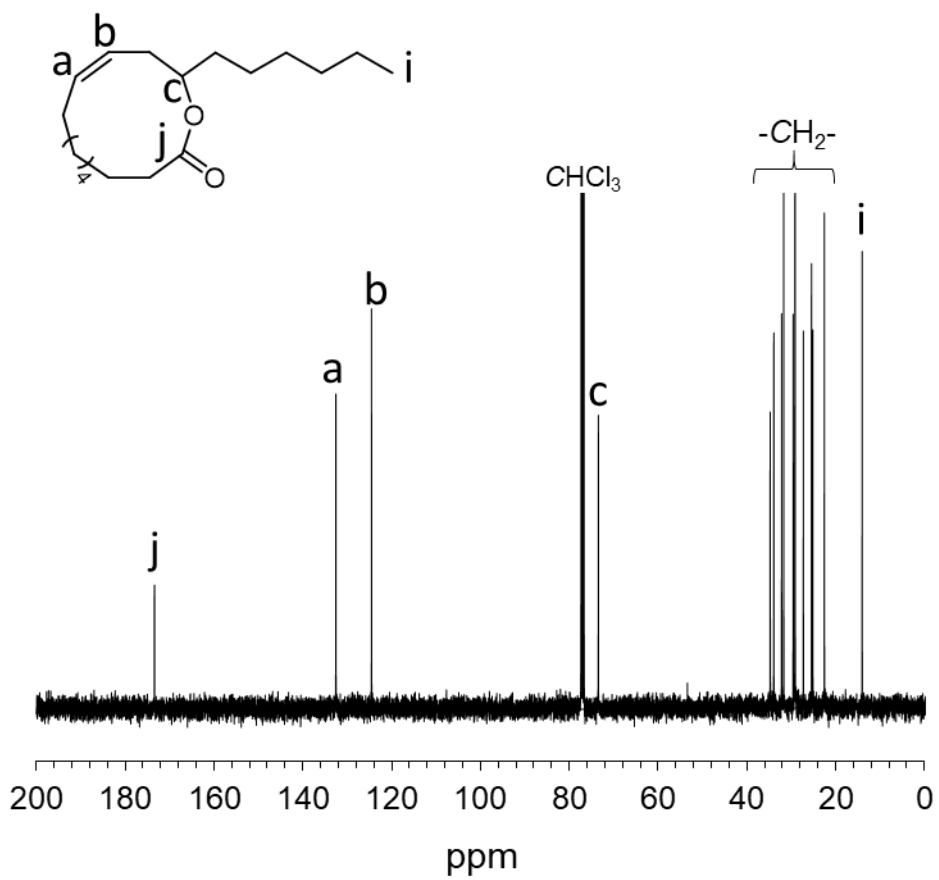
*(Z)-13-hexyloxacyclotridec-10-en-2-one (Mono-lactone, ML):* <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.86-0.90 (*m*, 3 H), 1.18 - 1.59 (*m*, 16 H), 1.67 (*m*, 3 H), 2.094 (*q*,  $J = 6.4$  Hz, 2 H), 2.22 – 2.34 (*m*, 3 H), 2.46 - 2.52 (*m*, 1 H), 4.958 (*dt*,  $J = 6.0$  Hz, 1 H), 5.41 - 5.35 (*m*, 1 H), 5.51 – 5.44 (*m*, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  174.38, 132.47, 124.84, 73.82, 35.19, 33.82, 31.83, 31.72, 29.47, 29.09, 27.35, 26.11, 25.72, 24.59, 23.47, 22.56, 14.04.

(10Z,23Z)-13,26-dihexyl-1,14-dioxacyclohexacosa-10,23-diene-2,15-dione (Di-lactone, DL):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.81 - 0.92 (m, 3 H), 1.18 - 1.39 (m, 16 H), 1.47 - 1.66 (m, 4H), 1.94 - 2.10 (m, 2 H), 2.19 - 2.27 (m, 3 H), 2.30 - 3.38 (m, 1 H), 4.925 (m, 1 H), 5.28 - 5.35 (m, 1 H), 5.41 - 5.49 (m, 1 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.40, 132.55, 124.52, 73.45, 34.75, 34.74, 33.93, 32.18, 31.71, 29.57, 29.20, 29.16, 29.13, 27.28, 25.45, 25.16, 22.55, 14.04.

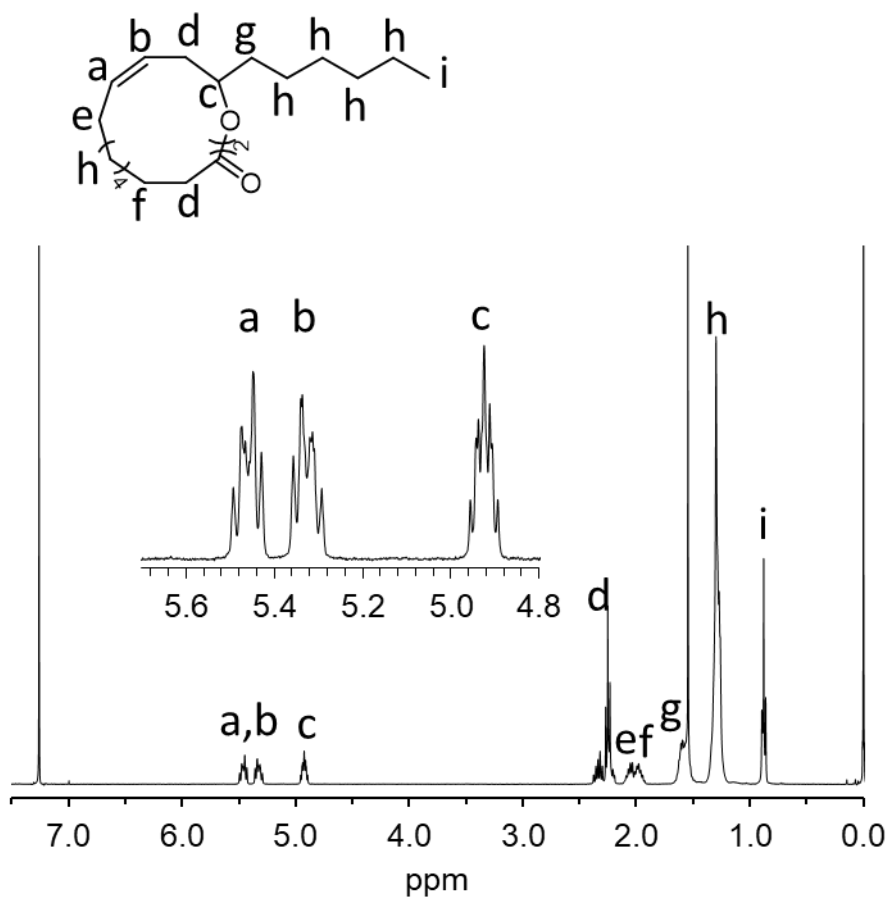


**Fig. S1.**  $^1\text{H}$  NMR spectrum of ML.

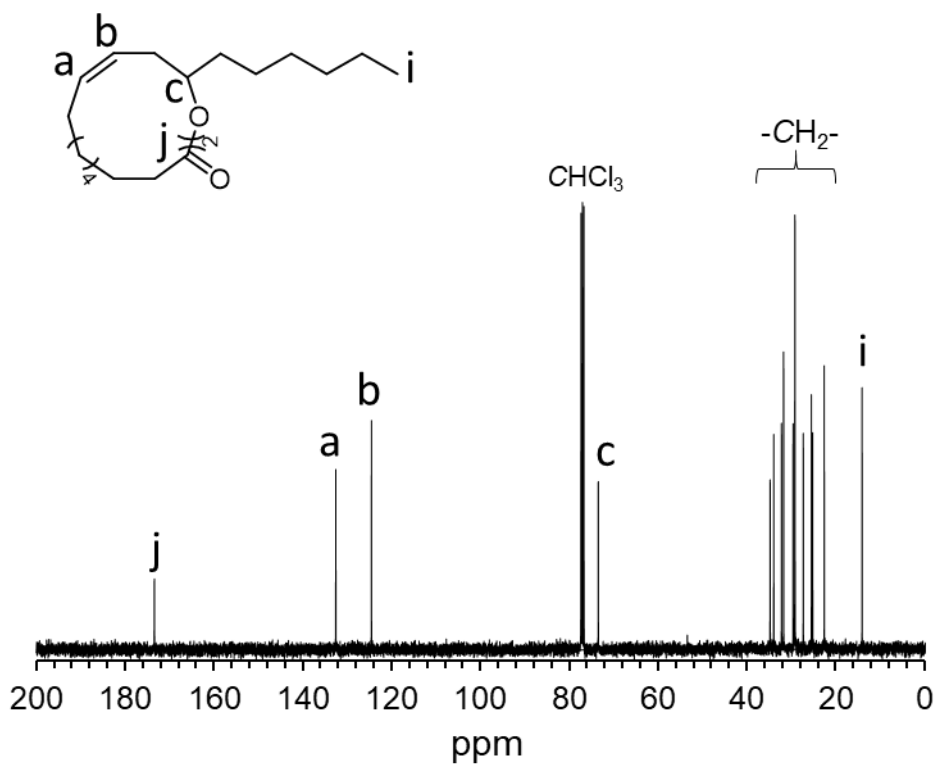




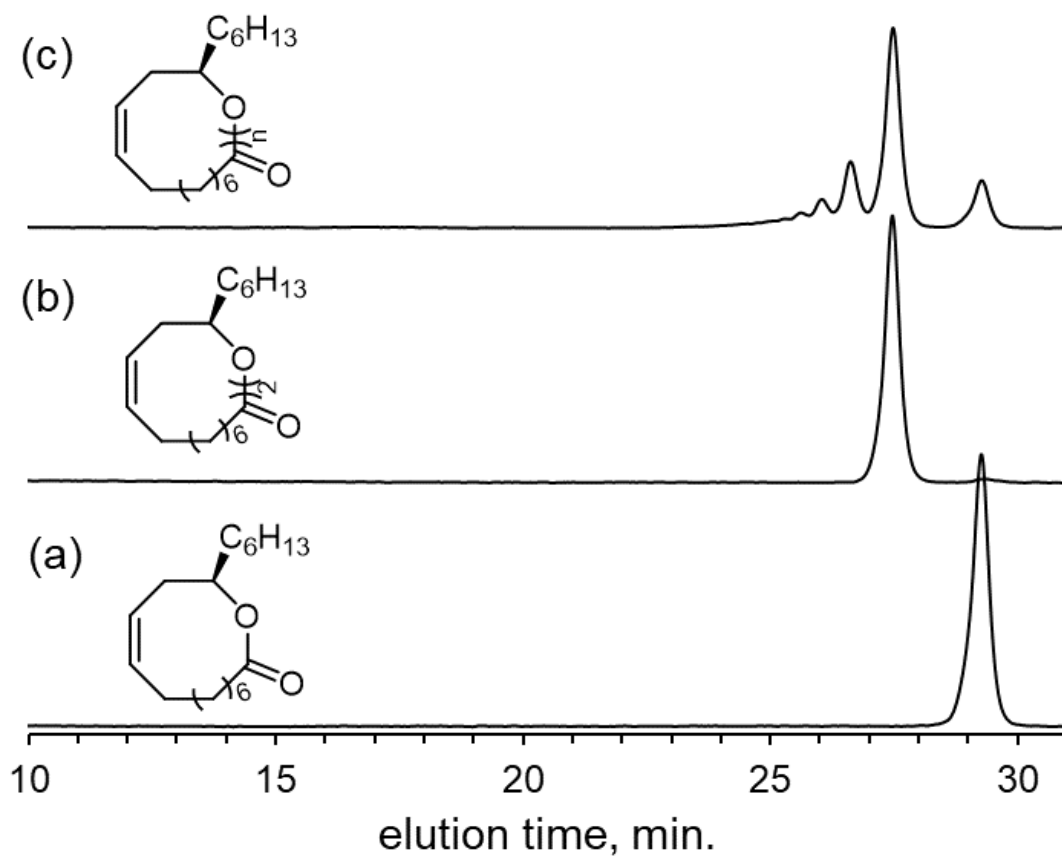
**Fig. S2.**  $^{13}\text{C}$  NMR spectrum of ML.



**Fig. S3.** <sup>1</sup>H NMR spectrum of DL.

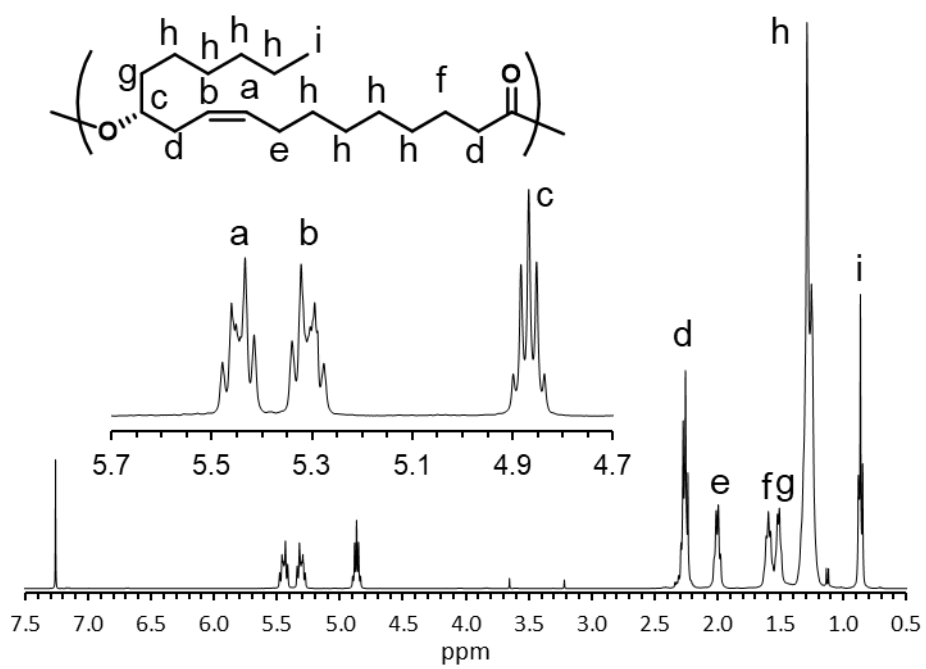


**Fig. S4.**  $^{13}\text{C}$  NMR spectrum of DL.

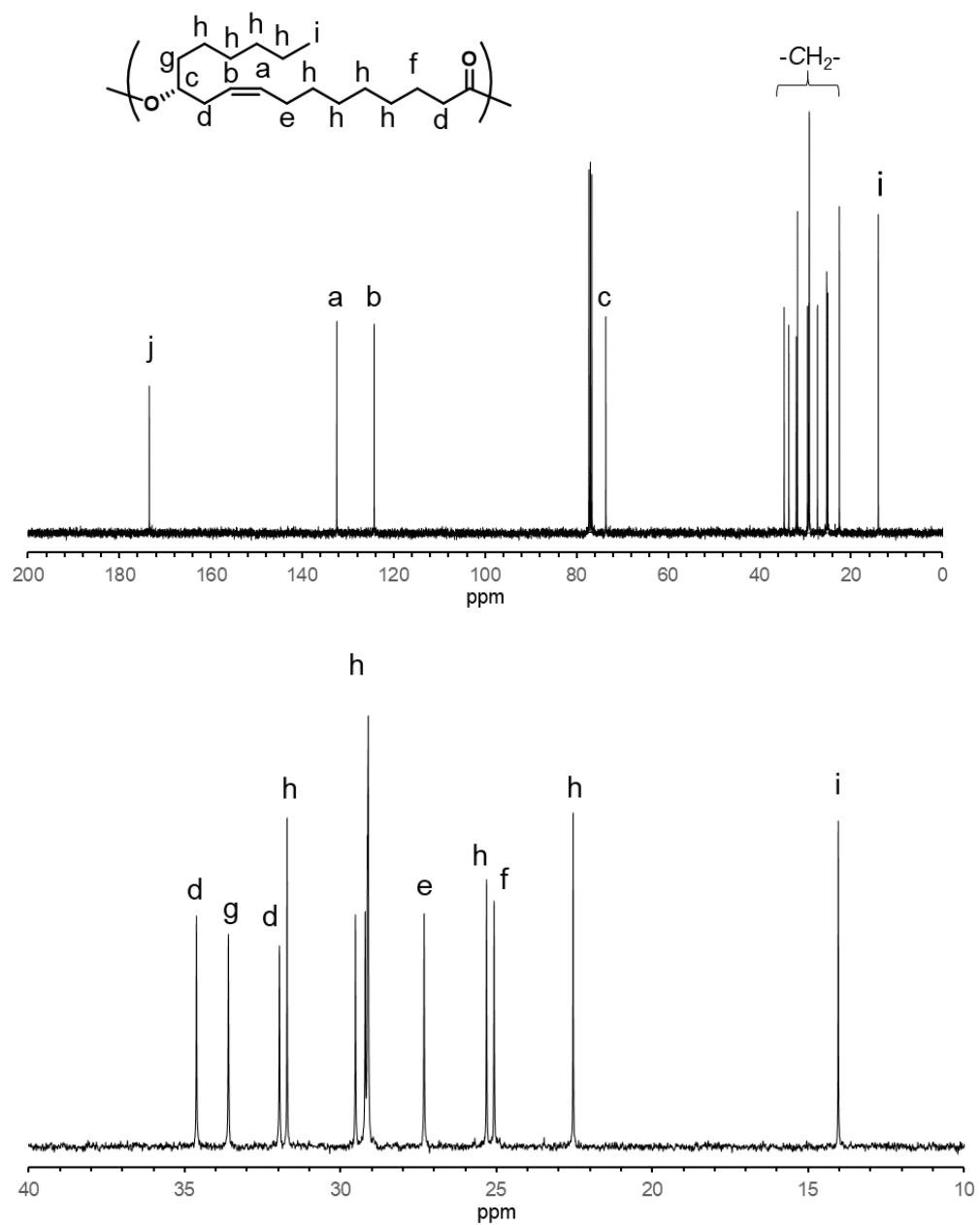


**Fig. S5.** SEC traces of (a) ML, (b) DL and (c) MixL.

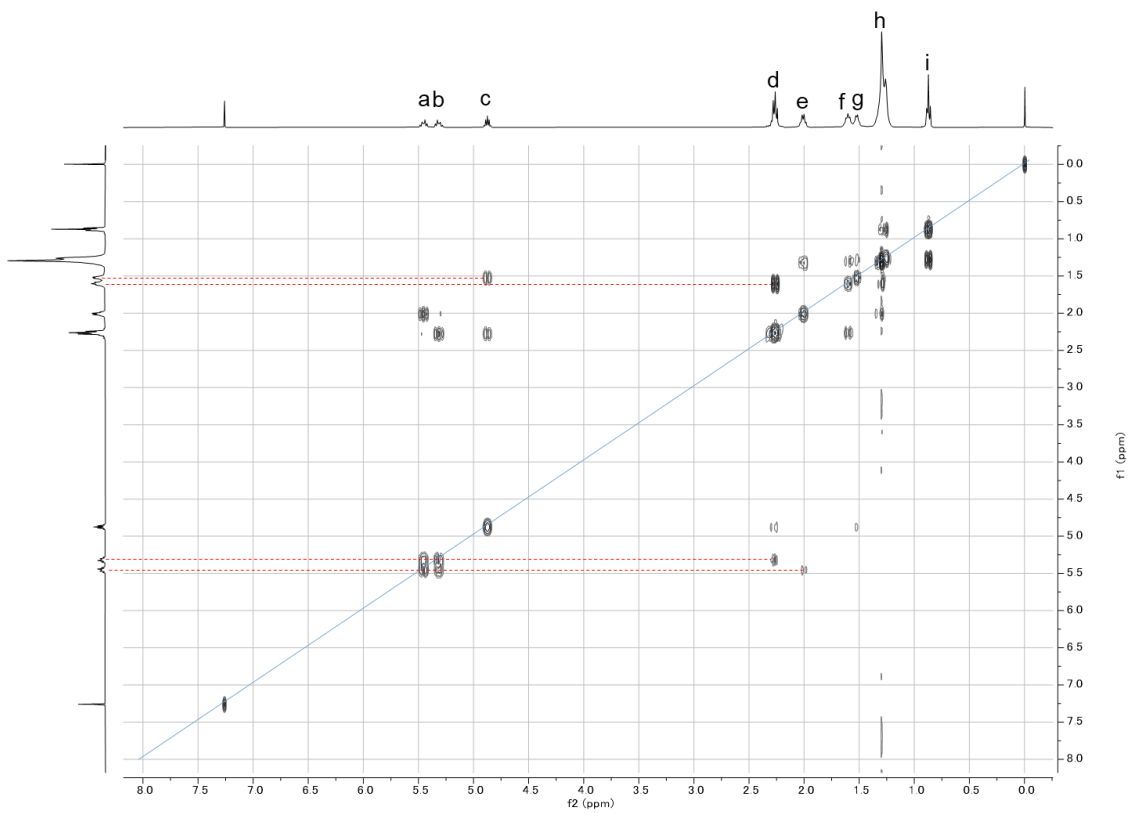
**4. Self Polycondensation (SPC) for the poly(ricinoleic acid).**<sup>1,4</sup> To the solution of ricinoleic acid (3.85 g, 12.9 mmol) and DPTS (707 mg, 2.58 mmol) in dichloromethane (6.45 mL) was added DIPC ( 2.5 mL, 16.15 mmol, 1.25 equiv.) dropwise at 0 °C for 1hr. After the addition of DIPC, the reaction was warmed to room temperature and stirred for 24h. The polymer was diluted and precipitated in cold methanol twice. The residual solvent was removed under vacuum (30 mTorr) at rt.  $M_w$  of the precipitated polymer was found to be 89.7 kg/mol by SEC with dispersity ( $\mathcal{D}$ ) of 5.76. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.87 (*m*, 3 H), 1.19 - 1.24 (*br m*, 24 H), 1.52 (*m*, 2 H), 1.60 (*m*, 2 H), 2.00 (*m*, 2 H), 2.25 (*m*, 4 H), 3.68 (*s*, 1 H), 4.87 (*q*, *J* = 6.0 Hz, 1 H), 5.28 - 5.34 (*dt*, *J* = 10.8 Hz, 1 H), 5.42 - 5.48 (*dt*, *J* = 10.8 Hz, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  173.46, 132.47, 124.28, 73.62, 34.62, 33.60, 31.96, 31.71, 29.52, 29.21, 29.14, 29.11, 27.32, 25.32, 25.08, 22.54, 14.03.



**Fig. S6.**  $^1\text{H}$  NMR spectrum of PRA synthesized *via* SPC.

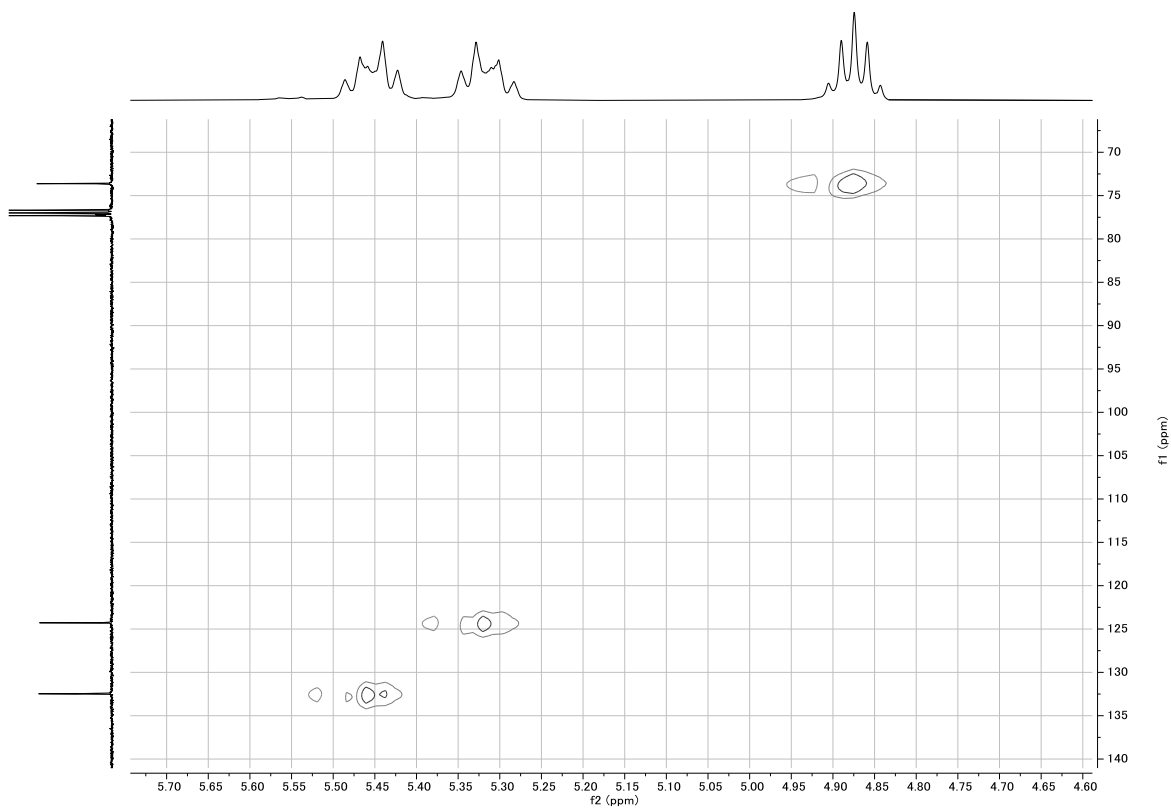


**Fig. S7.**  $^{13}\text{C}$  NMR spectrum of PRA synthesized *via* SPC.



**Fig. S8.** H-H COSY spectrum of PRA synthesized *via* SPC.



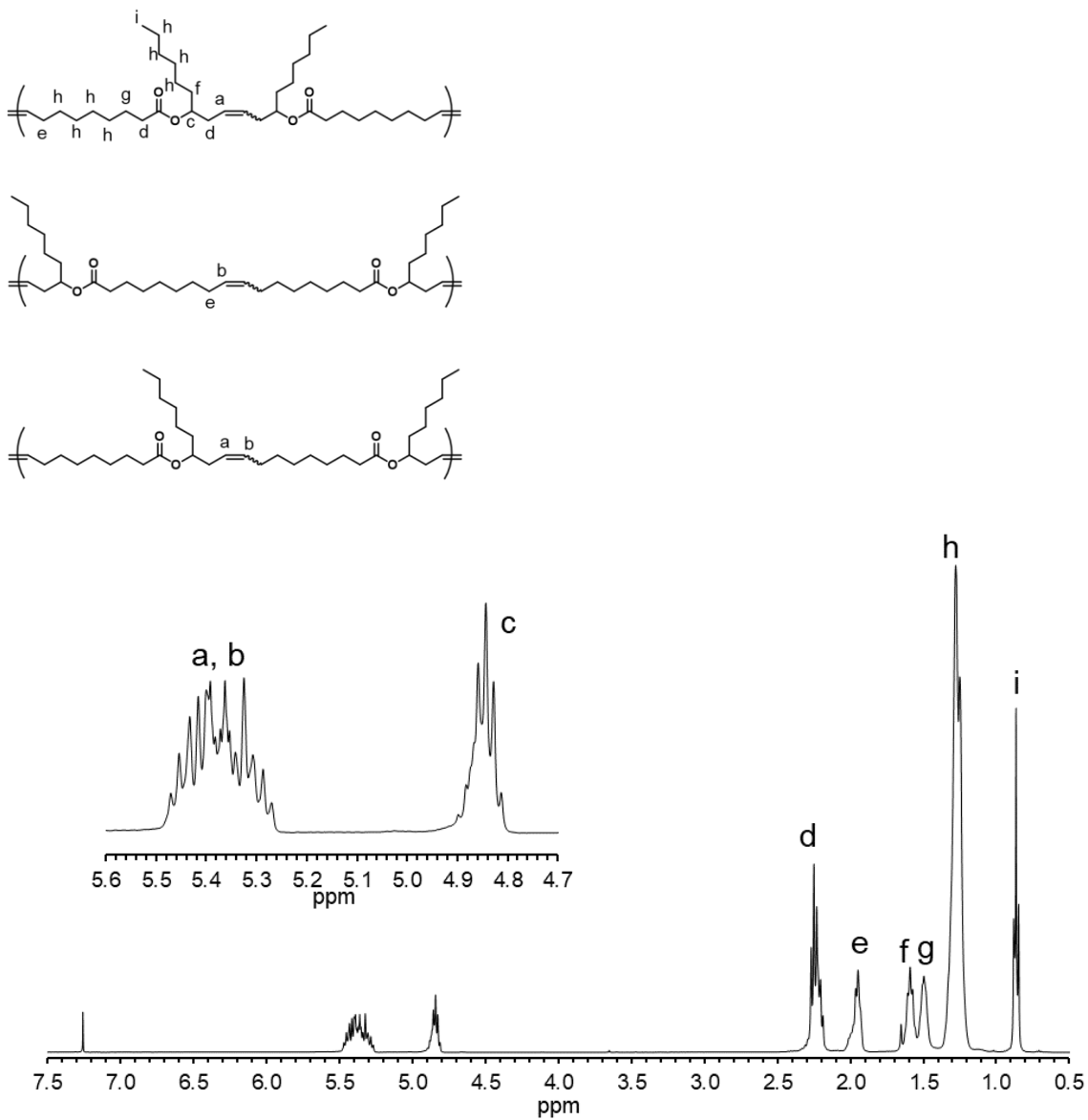


**Fig. S9.** HSQC spectrum of olefin and methine region PRA synthesized *via* SPC.

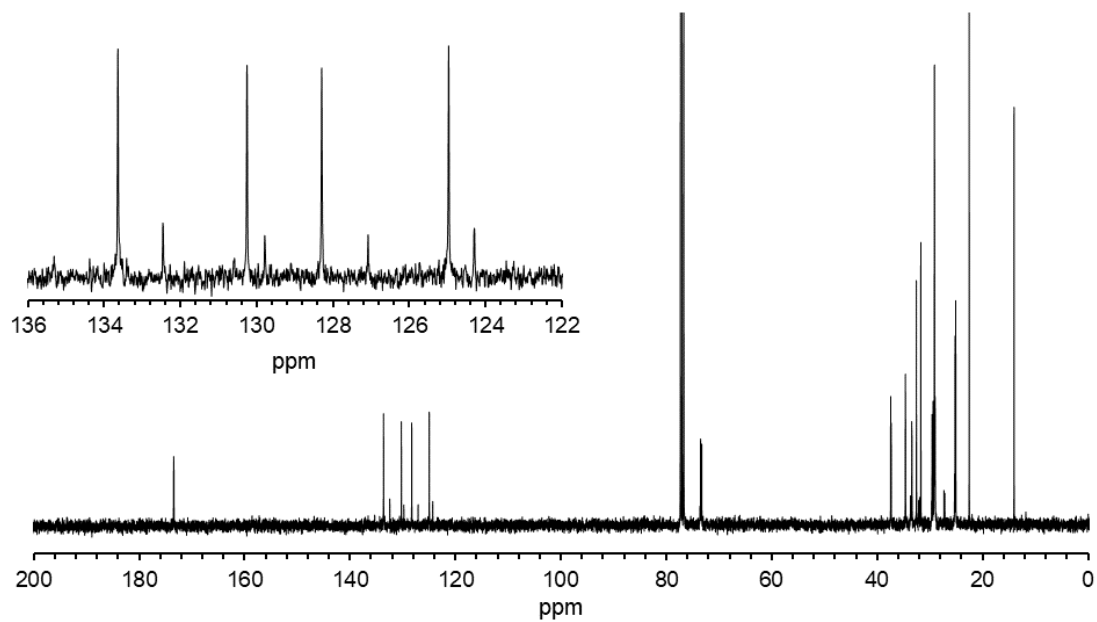
## 5. General procedure for the preparation of poly(ricinoleic acid) *via* ED-ROMP.

The following is a specific example of the general procedure we used to prepare poly(ricinoleic acid) [Table1, ML,  $[M]/[G2] = 10000$ ]. Dichloromethane was degassed by argon bubbling for 30min prior to the reaction. ML (0.280 g, 1.0 mmol) and degassed dichloromethane (1.8 mL) were charged in a 15 mL glass vessel equipped with a magnetic stir bar under argon. The solution of G2 in dichloromethane (0.50 mM, 0.2 mL, 0.00010 mmol) was added to the solution. The mixture was stirred for 4h. An excess amount of ethyl vinyl ether was added to quench the reaction and stirred for 30min. The polymer was precipitated in cold methanol twice. The residual solvent was removed under vacuum (30 mTorr) at rt. Conversion by  $^1\text{H}$  NMR spectroscopy of the crude mixture was  $> 98\%$ , and gravimetric yield after precipitation was 90%. Monomer conversion was also calculated by the SEC trace based on the area of ML and polymer (oligomer).  $M_w$  of the precipitated polymer was found to be  $484.8 \text{ kg mol}^{-1}$  by SEC with a PDI of 2.02.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86 (*m*, 3 H), 1.18 - 1.37 (*br m*, 16 H), 1.50 (*m*, 2 H), 1.59 (*m*, 2 H), 1.90 - 2.04 (*m*, 2 H), 2.16-2.35 (*m*, 4 H), 4.80 - 4.90 (*m*, 1 H), 5.25 - 5.49 (*m*, 2 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.43, 173.39, 133.64, 132.46, 130.25, 129.79, 128.30, 127.08,

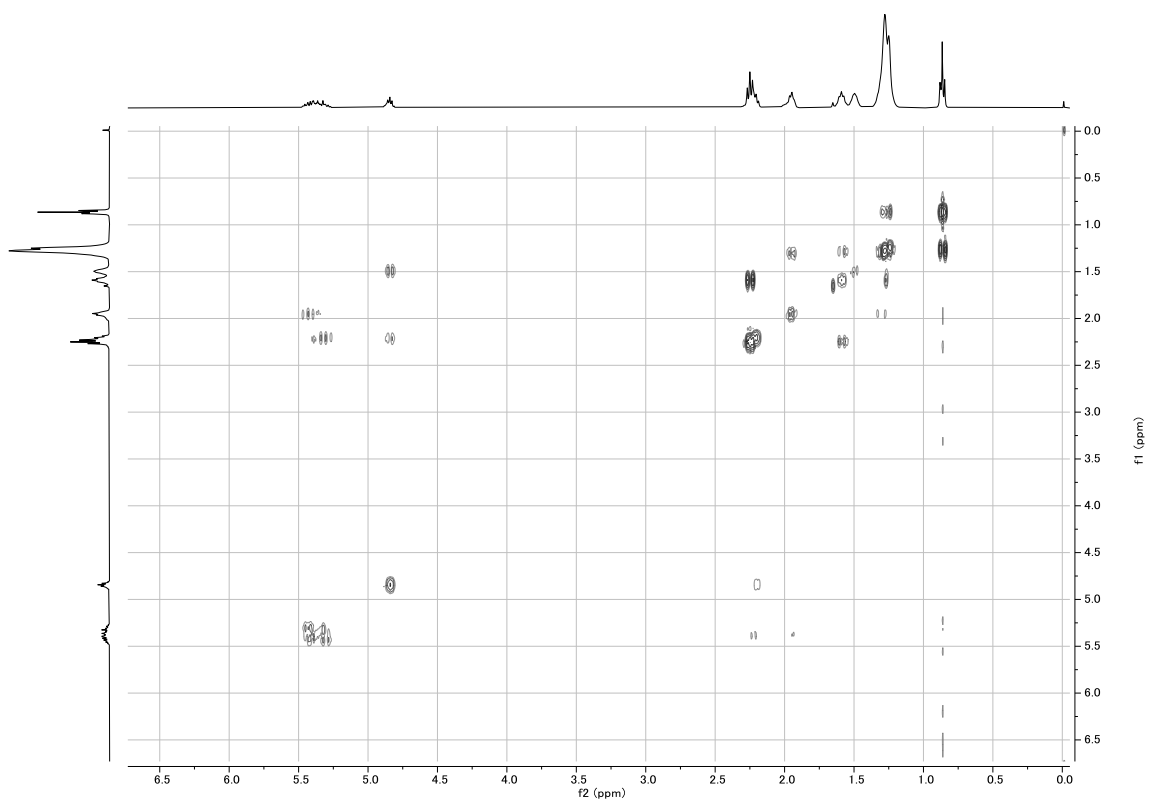
124.97, 124.30, 73.50, 73.29, 37.44, 37.34, 34.66, 34.64, 34.61, 33.69, 33.60, 33.44,  
33.39, 32.56, 32.14, 31.96, 31.72, 31.71, 29.59, 29.53, 29.39, 29.22, 29.14, 29.11,  
29.01, 28.99, 27.32, 27.17, 25.32, 25.23, 25.21, 25.10, 22.54, 14.03.



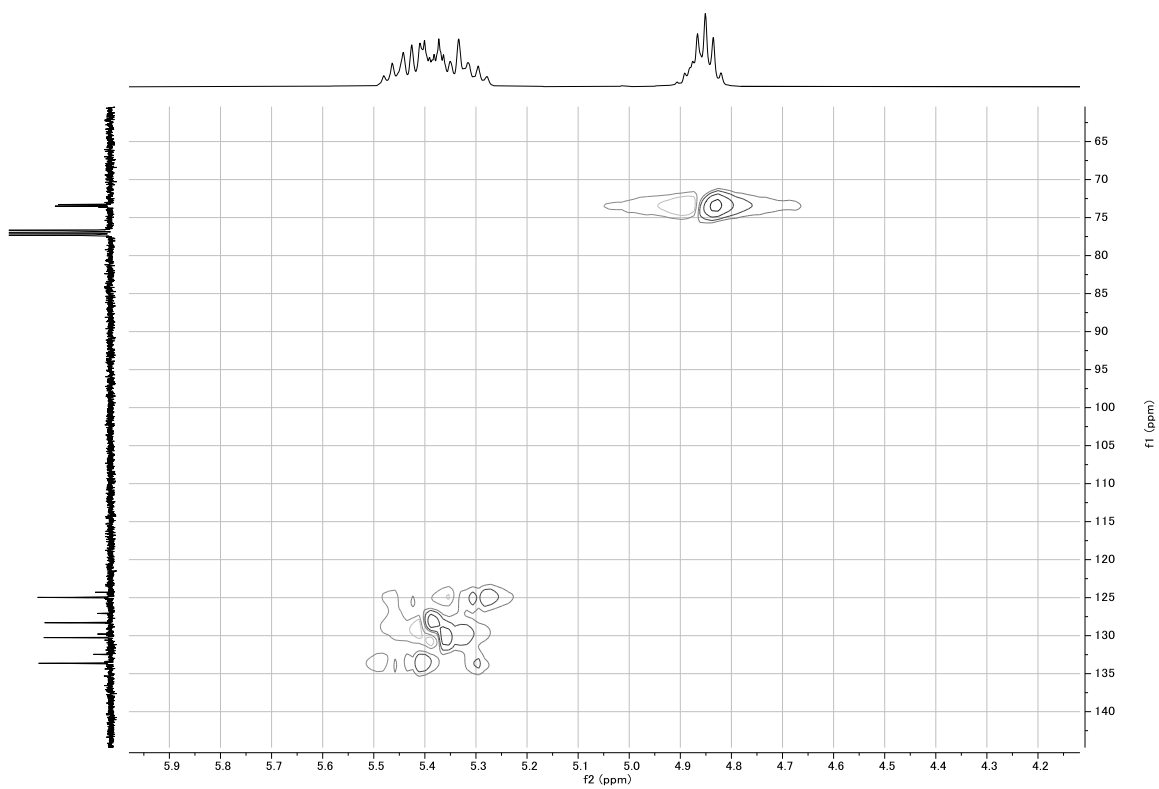
**Fig. S10.**  $^1\text{H}$  NMR spectrum of PRA synthesized *via* ED-ROMP.



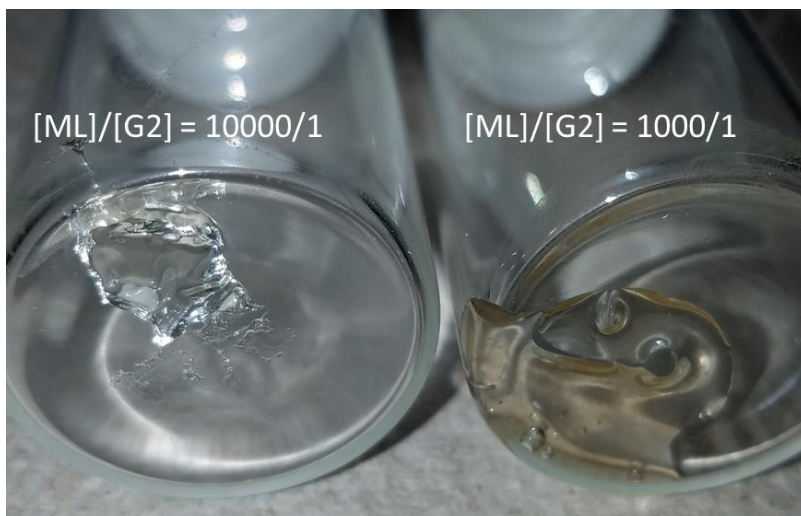
**Fig. S11.**  $^{13}\text{C}$  NMR spectrum of PRA synthesized *via* ED-ROMP.



**Fig. S12.** H-H COSY spectrum of PRA synthesized *via* ED-ROMP.



**Fig. S13.** HSQC spectrum of olefin and methine region PRA synthesized *via* ED-ROMP.

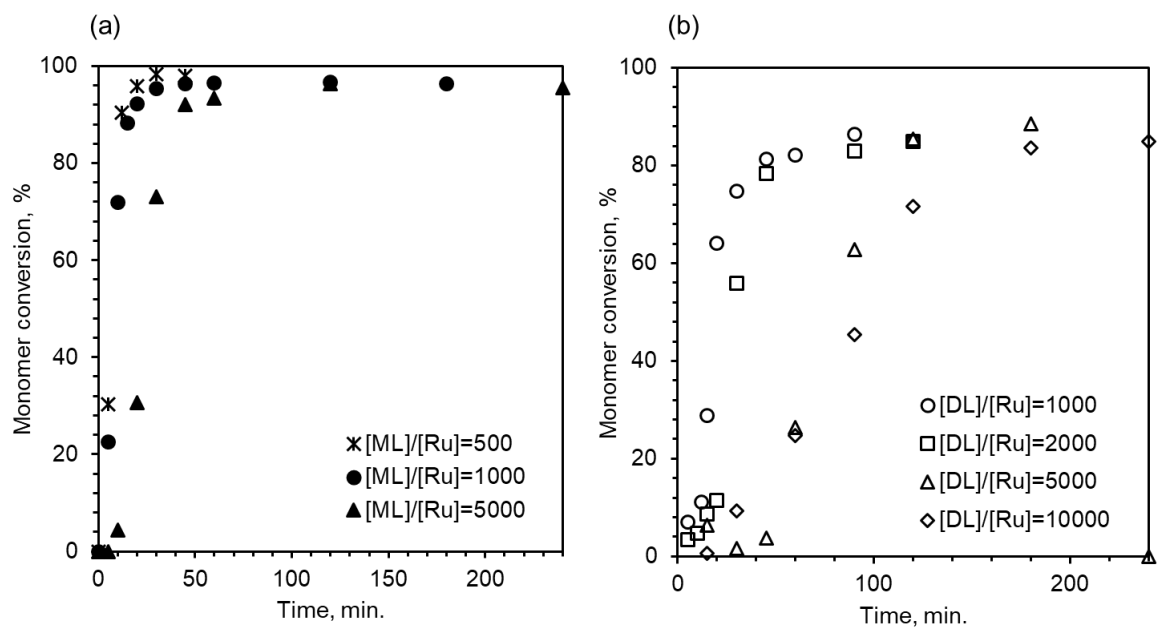


**Fig. S14.** Photos of PRA precipitated from MeOH. Left:  $[ML]/[Ru] = 10000/1$ , Right:  $[ML]/[G2] = 1000/1$ .

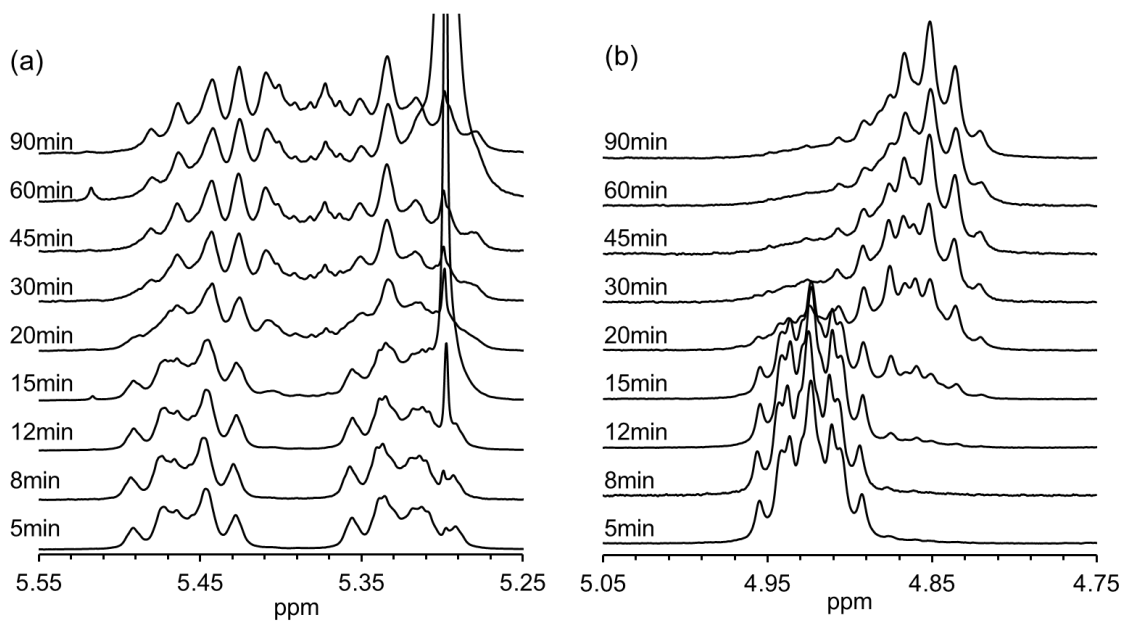


**6. Calculation of the monomer conversion by  $^1\text{H}$  NMR.** The monomer conversions for ML and DL were calculated by  $^1\text{H}$  NMR spectra using the methine regions of polymer and monomer peaks. Because of the partially overlapping the methine peaks, the half-intensity of monomer was used according to the literature.<sup>5</sup> The peak tops of 4.958 for ML and 4.925 for DL were used for the half intensities.

**7. Time-conversion plots for polymerization.** The monomer conversion using various catalytic amounts of G2 was monitored during the reaction by taking aliquots at certain intervals. The plots of time vs. conversion were shown in Fig. S16. Both ML and DL were consumed within 2 h, which was confirmed by  $^1\text{H}$  NMR. Since the monomer and polymer methine peaks were overlapped in  $^1\text{H}$  NMR, the tendency for the MixL was not evaluated.



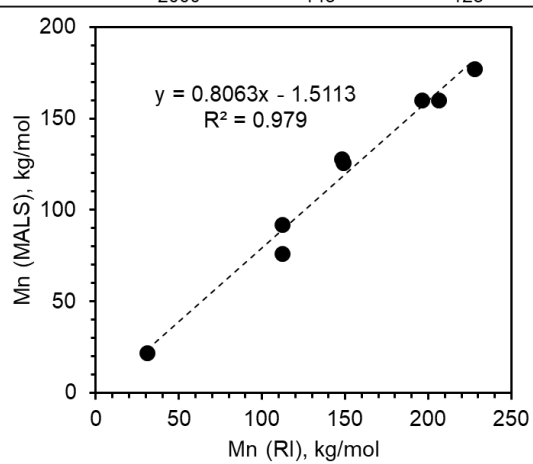
**Fig. S15.** Plots of time-conversion for the ED-ROMP of (a) ML and (b) DL.



**Fig. S16.**  $^1\text{H}$  NMR spectra (400MHz,  $\text{CHCl}_3$ ) of (a) olefin region and (b)  $\alpha$  position of ester during the ROMP of DL using 0.1mol% G2.

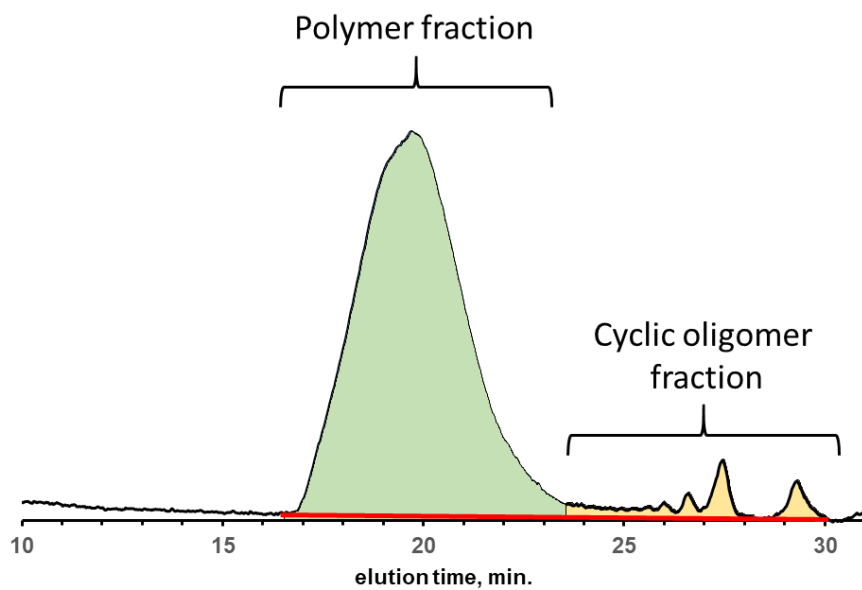
## 8. Absolute molar mass

Lactone	[M/n]/[G2]	$M_{n(RI)}, \times 10^3$	$M_{n(MALS)}, \times 10^3$
ML (n=1)	100	31	22
	1000	149	126
	2000	196	160
	5000	206	160
	10000	228	177
DL (n=2)	500	112	76
	1000	112	92
	2000	148	128

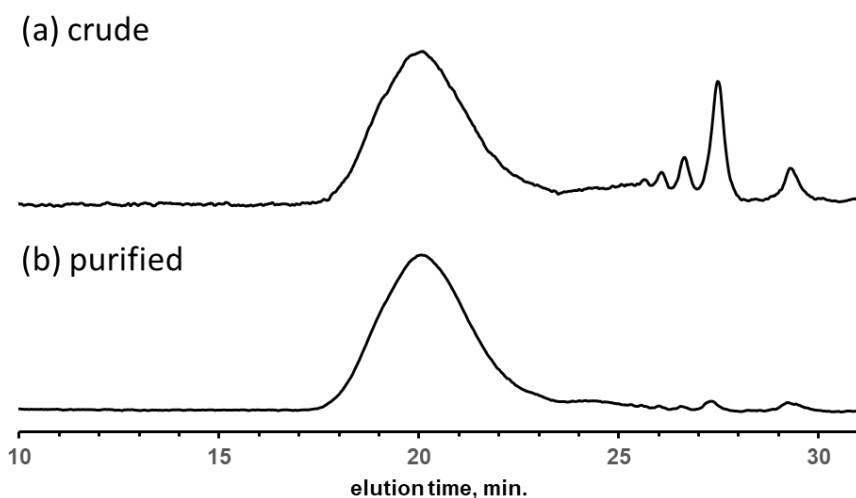


**Fig. S17.** Plots of  $M_n$  of RI vs.  $M_n$  of MALS.

**9. Polymerization results of mixed lactone.** Calculation of Polymer/Cyclic Oligomer ratio: P/CO ratio was calculated from the area percentage of RI chromatographs of SEC (Fig. S19). Polymer fraction defined as retention time less than 23.53min., and the cyclic oligomer is defined as retention time from 23.54 to 30.0min. Fig S19 illustrated SEC traces for before/after purification.



**Fig. S18.** A typical SEC trace of a reaction mixture of PRA *via* ED-ROMP (Fig. 1b).



**Fig. S19.** SEC traces of PRA via ED-ROMP: (a) before purification (Fig. 1d), (b) after purification.

**Table S1. ED-ROMP of mixed macrolactone of RA using G2.<sup>a</sup>**

$[M/n]/[G2]^b$	Conc., $[M/n]^c$	Time, hr	$M_n^d$ $\times 10^3$	$M_w^d$ $\times 10^3$	$\bar{D}^d$	P/CO <sup>e</sup>	$T_{d5\%}^f$ $^{\circ}C$	$M_n^g$ $\times 10^3$	$M_w^g$ $\times 10^3$	$\bar{D}^g$	$T_{d5\%}^g$ $^{\circ}C$
1000	0.5	4	74	155	2.09	77/23	250	81	218	2.71	-
2000	0.5	4	76	171	2.24	78/22	281	91	203	2.23	-
5000	0.5	4	83	195	2.34	75/25	306	84	202	2.39	326
10000	0.5	4	89	205	2.3	75/25	319	88	205	2.33	328
	1	2	137	314	2.29	80/20	321	110	316	2.86	328
	Bulk	1	141	496	3.51	92/8	335	145	488	3.36	327
	Bulk <sup>h</sup>	0.75	113	327	2.89	96/4	337	118	310	2.63	326

<sup>a</sup> Polymerizations were performed at room temperature in degassed dichloromethane. <sup>b</sup> Initial monomer to G2 ratio. <sup>c</sup> Initial monomer concentration. <sup>d</sup> Estimated by SEC in THF as relative to monodisperse polystyrene standards for crude samples. <sup>e</sup> Calculated from area percentage of RI chromatographs of SEC. <sup>f</sup> 5% weight loss temperature measured by TGA at 10  $^{\circ}C/min$  under  $N_2$  for crude samples. <sup>g</sup> Data for purified samples. <sup>h</sup> at 80  $^{\circ}C$ .

**10. Model reaction (self-metathesis reaction of methyl ricinoleate).**<sup>6-8</sup> To the solution of methyl ricinoleate (1.0 g, 3.2 mmol) in DCM (6.4 mL) was added the solution of G2 (27 mg, 0.032 mmol) under an argon atmosphere at room temperature. After stirring for 24hr, an excess amount of ethyl vinyl ether was added and stirred for 30 minutes to quench the reaction. The TLC analysis (hexane/EtOAc = 2/1) shows 3 spots ( $R_f = 0.77, 0.65$  and  $0.31$ , respectively), and these were separated by column chromatography (hexane then hexane/EtOAc = 4/1 to 3/2). The first, second, and third elutes were dimethyl octadec-9-enedioate, methyl 12-hydroxyoctadec-9-enoate, and octadec-9-ene-7,12-diol, respectively. These were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses. Then, corresponding hydroxyl groups of methyl 12-hydroxyoctadec-9-enoate and octadec-9-ene-7,12-diol were converted to an acetyl group using acetic anhydride in pyridine at room temperature. The ratio of trans/cis was 80/20 which were calculated by the intensities of olefin region of  $^{13}\text{C}$  NMR.

*Dimethyl octadec-9-enedioate:*  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.24 -1.37 (*br m*, 8 H), 1.61 (*t*,  $J = 7.2$  Hz, 2 H), 1.92 - 2.03 (*m*, 2 H), 2.23 (*t*,  $J = 7.6$  Hz, 4 H), 3.66 (*s*, 3 H), 5.28 - 5.43 (*m*, 1 H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  24.94, 27.16, 28.93, 29.10, 29.15, 29.54, 32.54, 34.10, 51.43, 129.84, 130.31, 174.32.

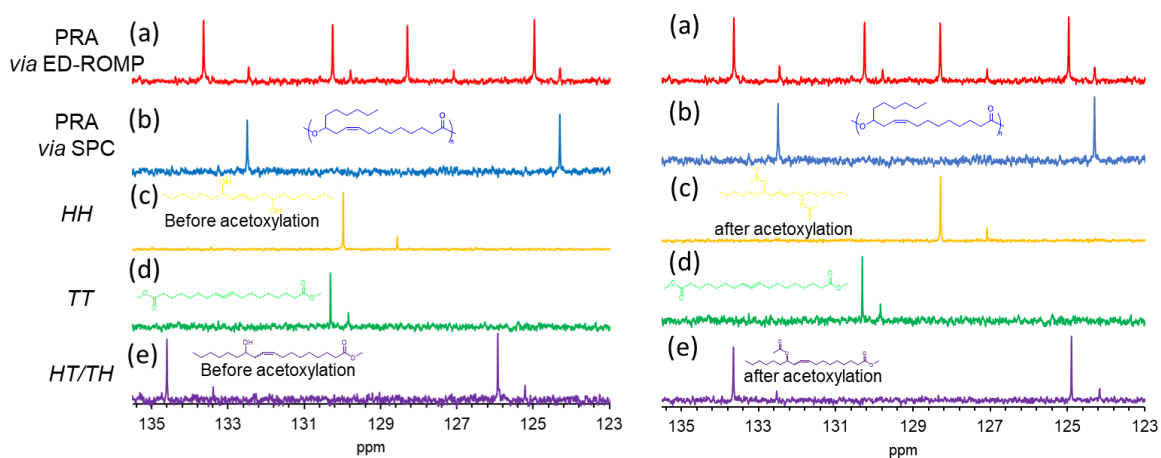
*Methyl 12-hydroxyoctadec-9-enoate*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (m, 3 H), 1.21 - 1.39 (m, 16 H), 1.44 (m, 3 H), 1.51 - 1.65 (m, 3 H), 1.97 - 2.27 (m, 4 H), 2.30 (t,  $J = 7.6$  Hz, 2 H), 3.58 (m, 1 H), 3.66 (s, 3H), 5.34 - 5.45 (m, 1 H), 5.48 - 5.60 (m, 1 H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  14.08, 22.61, 22.64, 24.91, 25.65, 28.92, 29.07, 29.35, 31.83, 32.61, 34.08, 36.74, 40.7, 51.44, 70.90, 71.49, 125.21, 125.93, 133.38, 134.60, 174.30.

*Methyl 12-acetoxyoctadec-9-enoate*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.85 (m, 3 H), 1.26 (m, 16 H), 1.39 (m, 3 H), 1.58 (m, 3 H), 1.99 (s, 3 H), 2.27 (t,  $J = 7.6$  Hz, 2 H), 3.63 (s, 3 H), 5.24 - 5.43 (m, 1 H), 5.45 - 5.56 (m, 1 H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  8.61, 13.98, 21.18, 22.09, 22.49, 25.17, 25.27, 25.65, 27.22, 27.29, 28.82, 29.07, 29.43, 29.49, 31.65, 31.86, 32.46, 33.41, 33.53, 35.30, 37.33, 40.65, 45.71, 53.36, 73.78, 73.92, 125.21, 124.17, 124.90, 133.65, 166.31, 170.68.

*Octadec-9-ene-7,12-diol*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (m, 3 H), 1.21 - 1.37 (br m, 8 H), 1.44 (m, 3 H), 2.05 - 2.33 (m, 2 H), 3.54 - 3.69 (m, 1 H), 5.45 - 5.67 (m, 1 H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  14.06, 22.60, 25.64, 25.77, 29.32, 31.81, 34.95, 36.93, 40.73, 70.86, 71.27, 128.57, 129.98.



*Octadec-9-ene-7,12-diyl diacetate*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (*m*, 3 H), 1.17 - 1.36 (*br m*, 9 H), 1.41 (*t*,  $J = \text{Hz}$ , 1 H), 1.45-1.56 (*m*, 2 H), 2.01 (*s*, 3 H), 2.16 - 2.32 (*m*, 2 H), 4.79 - 4.90 (*m*, 1 H), 5.29 - 5.49 (*m*, 1 H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  8.60, 14.02, 21.22, 22.54, 25.23, 25.33, 29.11, 31.70, 32.05, 33.42, 33.66, 37.25, 45.74, 73.62, 73.75, 127.08, 128.29, 170.71, 170.75.



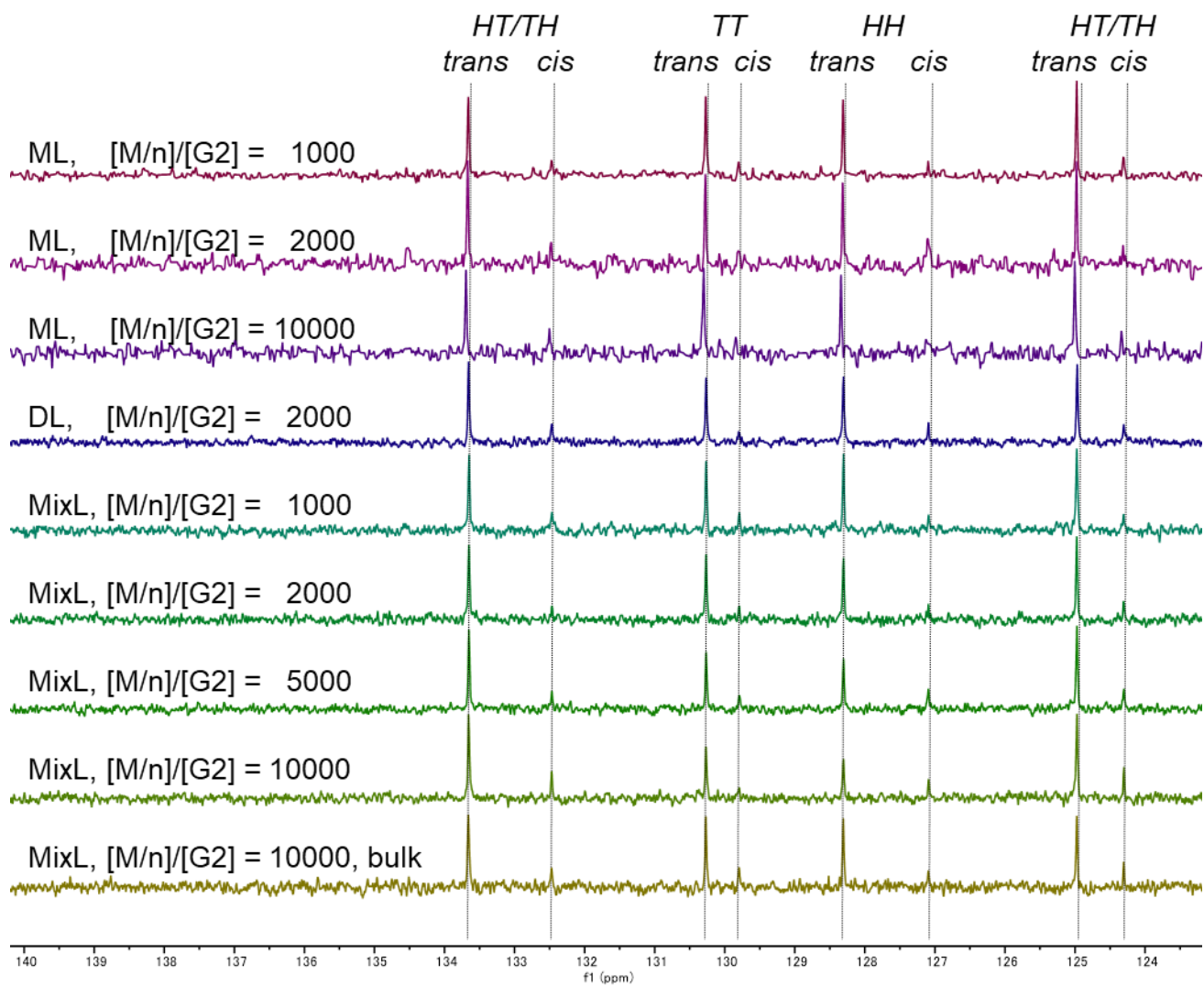
**Fig. S20.**  $^{13}\text{C}$  NMR spectra ( $\text{CDCl}_3$ , 101MHz) in olefin region of (a) PRA *via* ED-ROMP, (b) PRA *via* SPC, (c) *HH* model, (d) *TT* model and (e) *HT* (*TH*) model in Scheme 2. Left :before acetoxylation of *HH* and *HT/TH* models. Right: after acetoxylation of *HH* and *HT/TH* models.

## 11. Regioselectivity data

**Table S2. Selective regioselectivity data<sup>a</sup>**

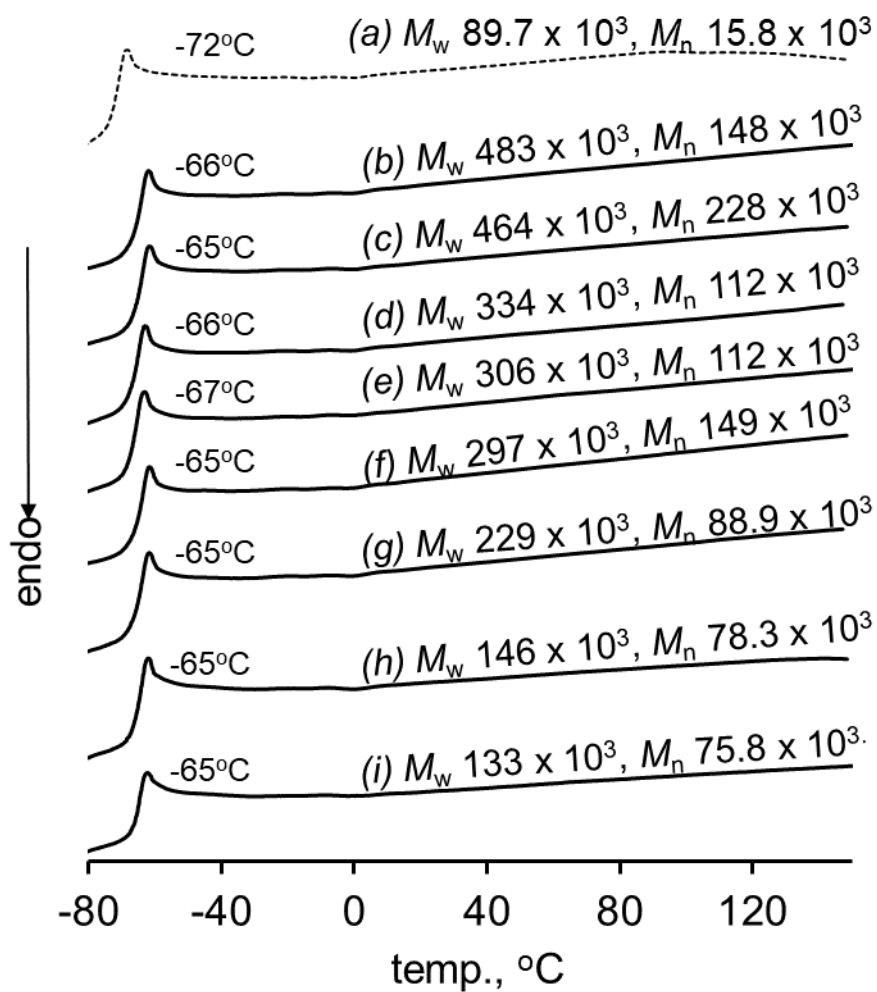
Lactone	[M/n]/ [G2] <sup>b</sup>	Time, hr	$M_n^c$ $\times 10^3$	$M_w^c$ $\times 10^3$	$\mathcal{D}^c$	$HT^d$	HH	TT	$HT$ - <i>trans</i> <sup>d</sup>	$HT$ - <i>cis</i> <sup>d</sup>	HH- <i>trans</i>	HH- <i>cis</i>	TT- <i>trans</i>	TT- <i>cis</i>
ML	1000	4	149	297	1.99	54	24	22	76	24	81	19	85	15
	2000	4	196	411	2.10	54	24	23	80	20	84	16	84	16
	10000	4	228	464	2.04	52	25	23	85	15	82	18	76	24
DL	2000	4	148	483	3.27	55	21	24	81	19	86	14	78	22
MixL	1000	4	81	218	2.71	52	24	24	82	18	80	20	85	15
	2000	4	91	203	2.23	55	24	21	83	17	84	16	83	17
	5000	4	84	202	2.39	59	21	21	82	18	80	20	71	29
	10000	4	88	205	2.33	66	18	16	76	24	87	13	67	33
	10000 <sup>e</sup>	1	145	488	3.36	52	25	23	77	23	79	21	82	18

<sup>a</sup> All of regeoselectivity data were collected from the intensity of olefin regions after curve fitting of the <sup>13</sup>C NMR spectra of PRA listed in Table 1 and 2 in the manuscript. <sup>b</sup> Initial monomer to G2 ratio. <sup>c</sup> Estimated by SEC in THF as relative to monodisperse polystyrene standards for purified samples. <sup>d</sup> Calculated as an average of four peaks in 133.64, 132.46, 124.97, and 124.30ppm, respectively. <sup>e</sup> in bulk reaction



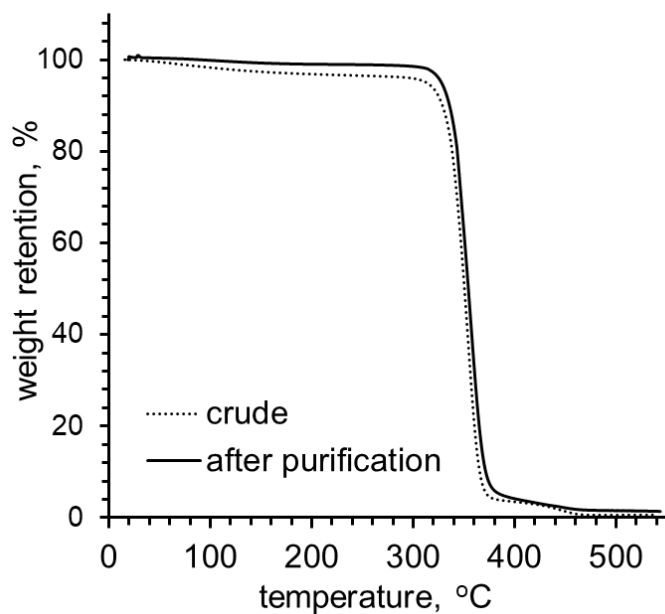
**Fig. S21.**  $^{13}C$  NMR spectra in the olefin region of PRA *via* ED-ROMP.

## 12. DSC traces

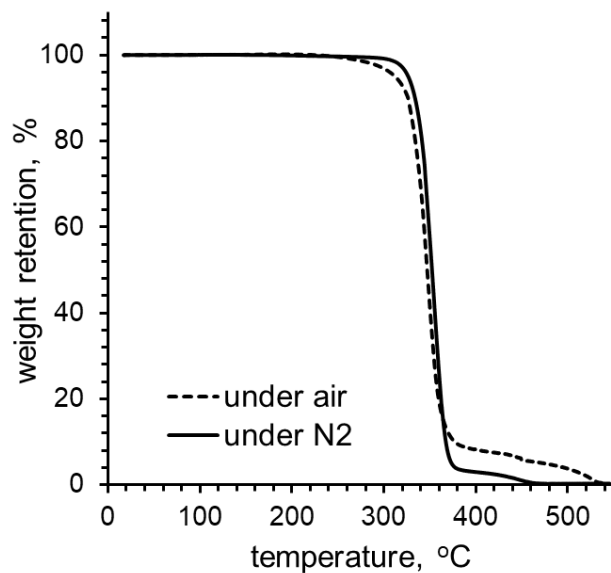


**Fig. S22.** DSC traces of PRA from (a) SPC and (b – i) ED-ROMP.

### 13. TGA curves

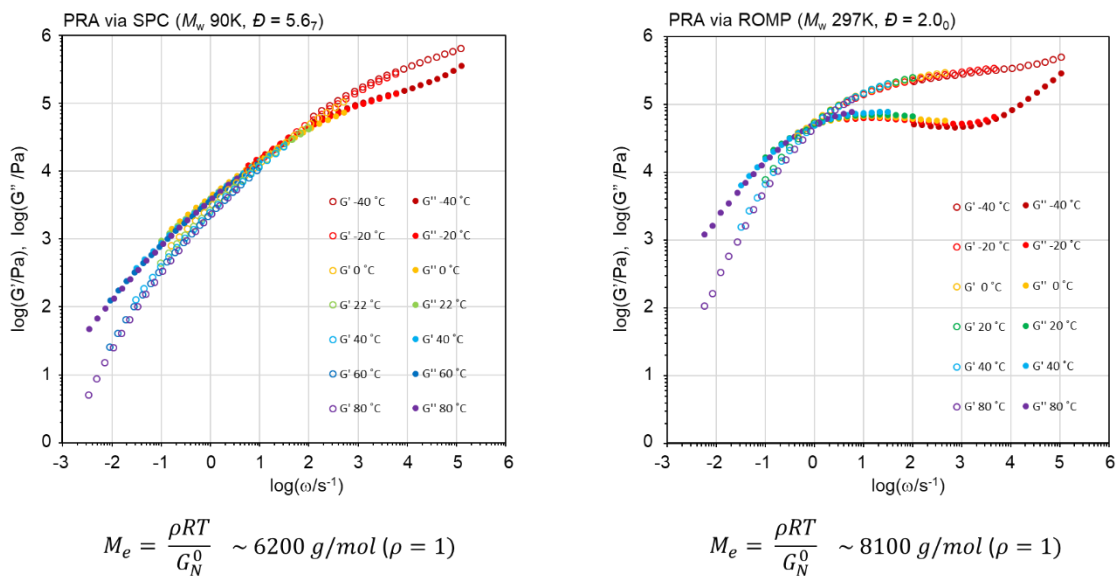


**Fig. S23.** TGA curves before and after purification of PRA *via* ED-ROMP. PRA was prepared using MixL as a monomer ( $[M/n]/[Ru] = 10000/1$ , 1.0M in DCM, 4hr).  $T_{d5\%}$  were 321°C and 328°C for the crude and purified samples, respectively.

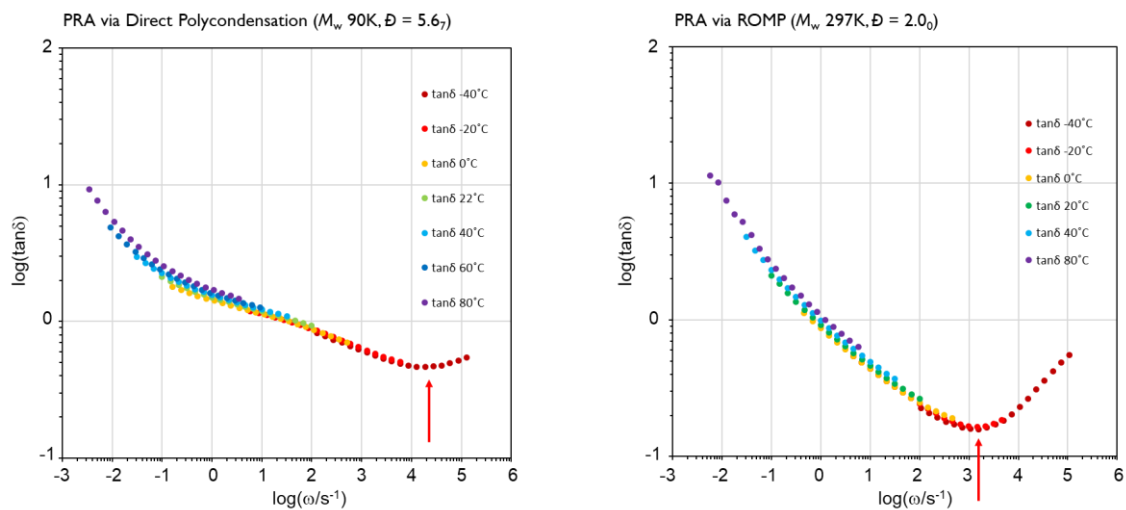


**Fig. S24.** TGA curves of PRA *via* ED-ROMP under N<sub>2</sub> (solid line) and air (dash line). PRA was prepared using DL as a monomer ( $[M/n]/[Ru] = 10000/1$ , 1.0M in DCM, 4hr).  $T_{d5\%}$  were 327°C and 312°C, respectively.

## 14. Rheology data



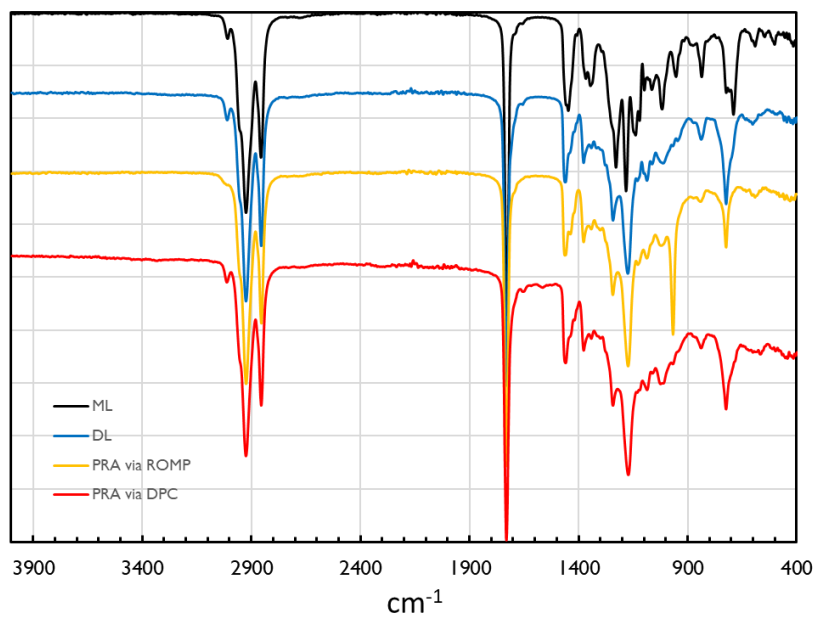
**Fig. S25.** Master curves for PRA *via* SPC and ED-ROMP. Curves were acquired by applying shift factors to dynamic frequency sweep data. The reference temperatures are 22 °C for PRA *via* SPC and 20 °C for PRA *via* ED-ROMP. The molar mass of entanglement ( $M_e$ ) was calculated using the value for the plateau of  $G'$  where  $\tan \delta$  is at a minimum in the -40°C experiment for PRA *via* SPC and the -20°C experiment for PRA *via* ED-ROMP in Fig. S26.



**Fig. S26.** Plots of  $\tan \delta$  corresponding to the master curve for PRA shown in Fig. S25.



## 15. FT-IR



**Fig. S27.** FT-IR Spectra for ML, DL, PRA *via* ED-ROMP, and PRA *via* SPC.

## 16. References

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