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

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High molar mass poly(ricinoleic acid) with a weight average molar mass over 400 kg/mol was synthesized *via* entropy-driven ring-opening metathesis polymerization of mono-, di- and mixed macrolactones of ricinoleic acid using Grubbs second-generation catalyst and fully characterized. High molar mass was achieved by reducing the catalyst loading, and the resultant polymer product had a very low level of ruthenium (36ppm as Ru based on G2 feed), was colorless and exhibited a high decomposition temperature without purification steps aimed at removing ruthenium.

Introduction

Given recent waste plastic problems which call for environmentally friendly materials, developing bio-based polymers has become prominent.[1] A series of oleochemicals derived from vegetable oil is of interest,[2] and we expect that ricinoleic acid (RA), which is derived from non-edible castor oil, is a promising candidate.[3] RA is an unsaturated fatty acid and with a pendant C6 alkyl group, a hydroxyl group, and a carboxyl group as well as a double bond. These derivatives are used in biocompatible consumer products such as cosmetics.[4] Poly(ricinoleic acid) (PRA) can be obtained from RA *via* the formation of ester linkages. One of the potential applications of PRA is as thermoset post crosslinking by vulcanization or treatment with oxidizers.[5,6] Synthesis of copolymers containing PRA or RA units as a soft segment for both of thermosets and thermoplastic elastomers and their properties have also been reported.[6–9]

The synthesis of high molar mass polymers is critical to expand PRA applications.[5] However, there are only two reports demonstrating high molar mass PRA homopolymer from RA.[8,10] Pathways to obtain PRA homopolymer include self-polycondensation (SPC),[9–12] ring-opening transesterification polymerization (ROTEP)[13] and ring-opening metathesis polymerization (ROMP)[8] (Scheme 1). Among them, ROMP is a particularly powerful method.

There are several studies of ROMP using Grubbs catalysts of olefin containing macrolactones.[8,14–21] For example, Gautrot and Zhu[8] demonstrated entropy-driven ROMP (ED-ROMP) of mixed cyclic macrolactones of RA from monomer to decamer using Grubbs 2nd generation catalyst (G2). They reported PRA
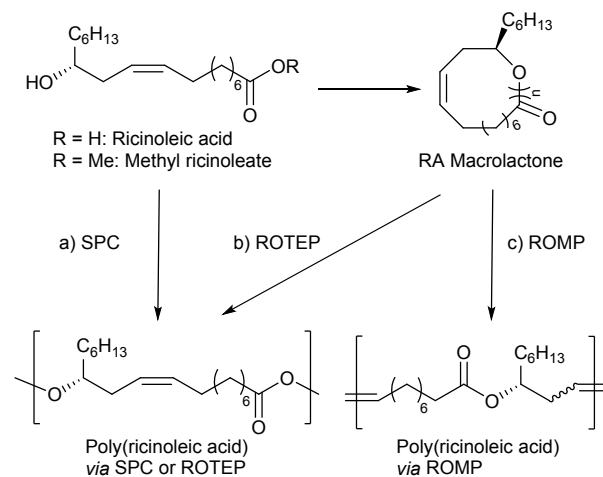
Scheme 1. Three synthetic approaches to high molar mass homopolymer of ricinoleic acid. (a) SPC: Self–polycondensation, (b) ROTEP: Ring-opening transesterification polymerization, (c) ROMP: Ring-opening metathesis polymerization.

homopolymer synthesized *via* ED-ROMP of RA macrolactone using 1 mol% G2 to give the weight average molar mass (M_w) of 150 kg/mol as a viscous oil having glass-transition temperature (T_g) of −60 °C. This work represents the largest molar mass of PRA homopolymer achieved to date. To demonstrate higher molar mass PRA to continue to improve material properties *via* ED-ROMP is one of the challenges to complement the previous report and to enable practical applications for PRA derived materials such as high strength crosslinked rubbers. In addition, the microstructural differences between the PRA *via* ED-ROMP and that of *via* SPC or ROTEP has not been reported. Finally, the remaining residual Ru catalysts in the polymer is generally assumed to cause thermal stability, toxicity, and color concerns that could also limit utility. Therefore, developing a well-defined high molar mass PRA homopolymer with a quite low catalyst that allowed for no subsequent purification is significant. In this report, we focused on synthesizing very high molar mass PRA through homopolymerization of RA macrolactone by ED-ROMP

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using G2, full assignment of its microstructure, and achieving high thermal stability at very low catalyst loadings.

Results and discussion

Starting from the synthesis of cyclic lactone from RA according to the literature,[13] polymerizations were carried out using 13-membered mono-lactone (ML), 26-membered di-lactone (DL), and mixed lactone (MixL) as monomers. These lactones were purified by column chromatography, and ED-ROMP was evaluated for each fraction. Polymerizations were carried out using G2 in dichloromethane at room temperature under an argon atmosphere at various monomer to G2 ratios ([M/n]/[G2], where n stands for n-mer of macrolactone). Table 1 summarized the results of the ED-ROMP of ML and DL. The reaction was quenched after 4 h by adding ethyl vinyl ether, and the resulting polymer was purified by precipitating twice in MeOH to give PRA in 60–90% yield. The monomer conversion reached over 90% and 80% for ML and DL, respectively, as calculated by ^{1}H NMR spectroscopy (Fig. S15). High molar mass PRAs were obtained from both ML and DL, and the M_w reached 480 kg/mol relative to polystyrene standards estimated by SEC in THF. The dispersity ($Đ$) values were 2–3, similar to previous reports for ED-ROMP.[22] The absolute molar mass obtained by light scattering measurements was about 0.8 times the number average molar mass (M_n) using polystyrene standards (Fig. S17). Although the M_n of the PRA increased with increasing the [M/n]/[G2] ratio, it was not well correlated with the calculated M_n from [M/n]/[G2] at ratios of more than 1000. Peng et al.[20] reported the good correlation between monomer-to-catalyst ratio and the M_n in the ED-ROMP of lactones from sophorolipids which polymerized at 60 °C and 45 °C for G2 at catalyst feeds ranging from 0.5–22mol% relative to monomer. However, low [M/n]/[G2] ratios showed similar molar masses to the expected molar mass based on conversion in our work, and molar masses were smaller than expected value at high [M/n]/[G2] ratios. The effect of trace impurities may be a cause of this limitation. Although these impurities have not been identified yet, it is possible that, for example, other fatty acids without hydroxyl groups in castor oil[3] or the presence of unintentionally ring-opened chains by adventitious water acting as chain transfer agents.

Simple precipitation into common poor solvents such as MeOH or hexane is not sufficient to completely remove Ru residue from polymer, and it can be necessary to reduce to several tens of ppm *via* a metal exchange for some applications.[23] For the ED-ROMP of macrolactone from RA, a high molar mass PRA was successfully obtained with a catalyst amount of 0.01mol% ([M/n]/[G2] = 10000). This ratio implies that only 36ppm Ru should remain even in the unpurified crude polymer; thus, the use without further purification may be acceptable in some applications.

A more practical way to produce PRA by ED-ROMP is to use MixL as a monomer mixture.[24] ED-ROMP was investigated using MixL purified by passing through a short column of silica gel in dichloromethane (Table 2). The range of monomer to G2 ratio was varied from 1000 to 10000. The polymerization proceeded

Table 1 ED-ROMP of RA macrolactone using G2[a]

Lactone	[M/n] /[G2][b]	M_n,[c] x10³	M_w,[c] x10³	Đ [c]	T_g,[d] °C	$T_{d5\%}$,[e] °C
ML (n=1)	100[f]	31	51	1.66	n.d.[g]	n.d.[g]
	1000	149	297	1.99	-65	278
	2000	196	411	2.10	-65	301
	5000	206	416	2.02	-65	322
	10000	228	464	2.04	-65	327[h]
DL (n=2)	500	112	306	2.72	-67	254
	1000	112	334	2.99	-66	261
	2000	148	483	3.27	-66	295

[a] Polymerizations were performed for 4h at room temperature in degassed dichloromethane (0.5 M). [b] Feed ratio of monomer to G2. [c] Precipitate in MeOH was estimated by SEC in THF as relative to monodisperse polystyrene standards. [d] Measured by DSC on the second heating at 10 °C/min under N₂. [e] Measured by TGA at 10 °C/min under N₂. [f] Polymerization was performed for 105 min. [g] Not determined. [h] 312 °C under air.

Table 2 ED-ROMP of MixL using G2[a]

[M/n] /[G2][b]	Conc., [M/n]₀[c]	Time, hr	M_n,[d] x10³	M_w,[d] x10³	Đ [d]	P/CO[e]
1000	0.5	4	74	155	2.0₉	77/23
2000	0.5	4	76	171	2.2₄	78/22
5000	0.5	4	83	195	2.3₄	75/25
10000	0.5	4	89	205	2.3₀	75/25
	1	2	137	314	2.2₉	80/20
	Bulk	1	141	496	3.5₁	92/8
	Bulk[f]	0.75	113	327	2.8₉	96/4

[a] Polymerizations were performed for 4h at room temperature in degassed dichloromethane. [b] Initial monomer to G2 ratio. [c] Initial monomer concentration. [d] Estimated by SEC in THF as relative to monodisperse polystyrene standards. [e] Calculated from area percentage of RI chromatographs of SEC. [f] at 80°C.
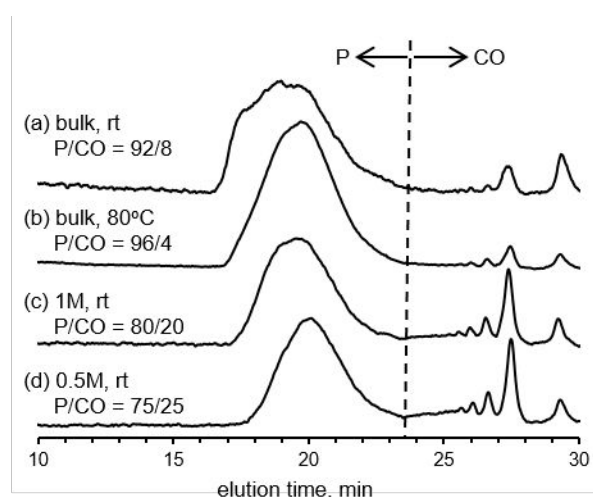

Fig. 1 SEC traces of PRA *via* ED-ROMP of MixL using 0.01mol% G2 at the monomer concentration of (a) 0.5M at rt for 4hr, (b) 1M at rt, (c) bulk at rt and (d) bulk at 80 °C in Table 2 (THF as eluenet, flow rate: 1mL/min, RI detector).
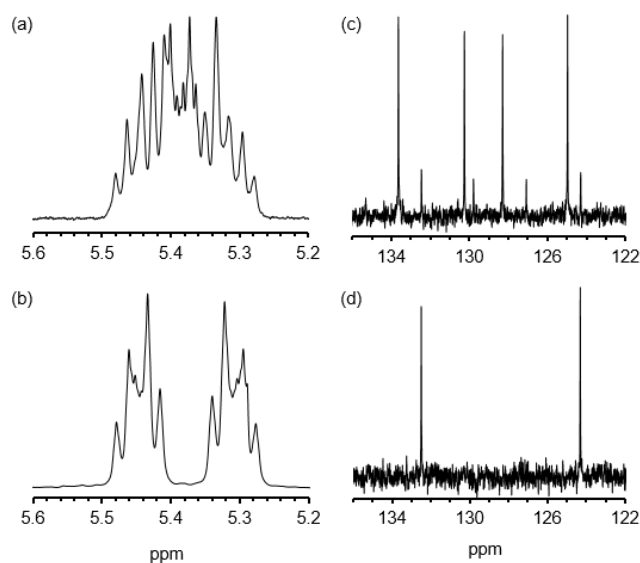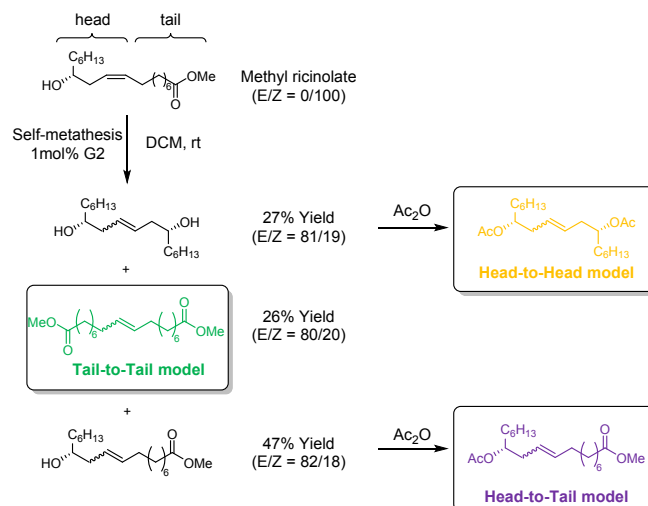
Fig. 2 ¹H (400MHz) and ¹³C (101MHz) NMR spectra in CDCl₃ of the olefin region of PRA synthesized *via* ED-ROMP ((a) and (c)) and *via* SPC ((b) and (d)). Steiglich coupling polymerization was used for the SPC (see ESI in detail).

Scheme 2. Self-metathesis reaction of methyl ricinoleate and following acetylation to synthesis of model compound

even when 0.01mol% G2 was used ([M/n]/[G2] = 10000). Although the molar mass was smaller than the results of ML and DL on the same ratios of [M/n]/[G2], impurities (not identified) may be acting as chain transfer agents. Cyclic oligomers, whose putative contents were estimated by SEC (THF, 1.0 mL min⁻¹, 25 °C) using an RI detector (Fig. S18), were formed as a result of the equilibrium state at 0.5M of initial monomer concentration from the crude samples. Higher concentrations of ED-ROMP were tested using MixL to suppress oligomer formation. The reaction was carried out for several hours using 0.01mol% G2 to ensure sufficient time to reach equilibrium. As a result, higher concentrations afforded higher molar mass with lower oligomer content. The SEC traces of the obtained unpurified polymer are shown in Fig. 1. In the bulk polymerization, the viscosity increased, and the reaction did not stir after a few minutes. As seen in Fig. 1(a), the bulk polymerization at room temperature lead to an increased Đ value possibly due to inadequate mixing in the high molar mass melt of polymer. We note that every polymer obtained using 0.01mol% G2 was essentially colorless (*i.e.*, no visible color from G2 residue, Fig. S14) even without further purification.

We expect that the polymerization proceeds with ring-chain equilibrium and intra- and inter-molecular metathesis, which will lead to scrambling the sequence. Fig. 2a and 2b show ¹H NMR spectra of PRA obtained *via* ROMP (Table 1, M = DL, [M/n]/[G2] = 500) and the PRA synthesized by SPC (M_n 1.6 x 10⁴, M_w 9.0 x 10⁴, see ESI for the synthesis),[25] respectively. The characteristic difference between the two PRAs was in the olefin region from 5.26 to 5.50 ppm. Since the PRA from SPC should retain the *cis* structure of the polymer, in the ¹³C NMR spectra (Fig. 2d), the olefin region showed only two peaks at 124.2 and 132.5 ppm corresponding to C9 and C10 (confirmed by HSQC, Fig. S9). The PRA *via* ED-ROMP showed a total of eight distinct carbons in the ¹³C NMR spectrum, which should
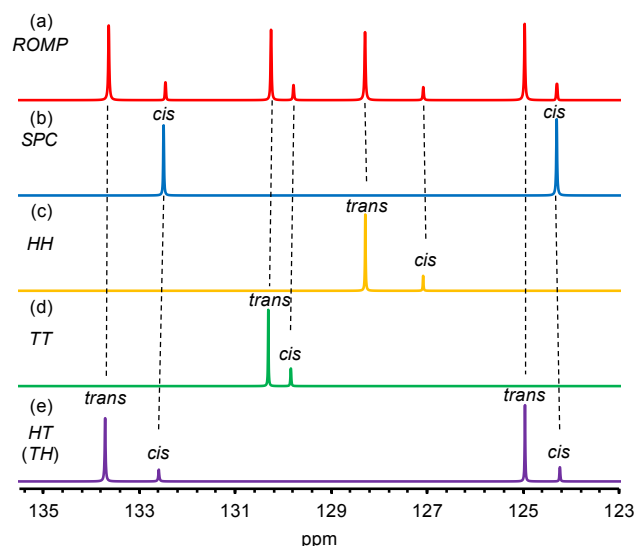

Fig. 3 ¹³C NMR spectra (CDCl₃, 101MHz) in olefin region (a) PRA *via* ED-ROMP (b) PRA *via* SPC, (c) *HH* model, (d) *TT* model and (e) *HT* (*TH*) model in Scheme 2. Data created by MestReNova line fitting tool.

correspond to the three regioisomers (head-to-head (*HH*), head-to-tail (*HT*), tail-to-tail (*TT*)) with the stereoisomers Z and E (Fig. 2c).

To clarify each carbon peak, syntheses of model compounds of *HH*, *HT* (*TH*) and *TT* were performed as shown in Scheme 2.[26–28] The self-metathesis reaction of methyl ricinoleate afforded three spots by TLC analysis, and these were collected by column chromatography in quantitative yield. Then acetylation of the remaining hydroxyl groups gave model compounds for *HH*, *HT* (*TH*) and *TT* structure. These structures were characterized by ¹H and ¹³C NMR spectroscopy (see ESI Section10 in detail). The corresponding chemical shifts in the olefin region of ¹³C NMR were compared to PRA *via* ED-ROMP in Fig. 3. The *HT* (*TH*) model provided a total of four carbon peaks at 124.2, 124.9,

132.5 and 133.7 ppm (Fig. 3e). The peaks at 124.9 and 133.7 ppm corresponded to PRA *via* SPC which retains *cis* structure. Thus, the peaks at 124.2 and 132.5 ppm correspond to the *trans* structure. The *HH* model (Fig. 3c) also provided 130.3 ppm as *trans* and 129.8 ppm as *cis* structure as well as the *TT* model did 128.27 ppm as *trans* and 127.7 ppm as *cis* structure (Fig. 3b). These assignments clearly demonstrated the microstructure of PRA *via* ED-ROMP with a mixture of *HH*, *HT* (*TH*), and *TT*, in which *E*:*Z* ratios were calculated to be 81:19, 80:20, and 82:18, respectively, from each carbon intensity. This result indicates that methyl ricinoleate predominantly isomerized to the *trans* configuration as a result of equilibration during the self-metathesis reaction. The corresponding carbon intensity in the PRA *via* ED-ROMP shown in Fig. 3a was calculated as 77–82% *trans*-dominant as in these model compounds. It was also estimated from each carbon intensity that *HH*, *HT* (*TH*), and *TT* ratio of 26:49:25 was statistically close to random ratios corresponding to the associated data for the model compounds (27:46:26 in Scheme 2). All of the obtained PRA *via* ED-ROMP in Table 1 and 2 showed almost identical microstructure (Table S2, Fig. S22).

The thermal properties of RRA *via* ED-ROMP were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results of DSC (Table 1 and Fig. S22) showed all of the obtained polymers were amorphous and had −65 °C of the glass transition temperature (T_g), which were similar to the reported value of −60 °C.[8] In Fig. 4, TGA traces under the nitrogen atmosphere and the relationship between the reciprocal of [M/n]/[G2] ratio and the 5% thermogravimetric loss temperature ($T_{d5\%}$) of the purified PRA by precipitation in MeOH are plotted. Interestingly, even in methanol-purified PRA, $T_{d5\%}$ decreased with decreasing [M/n]/[G2] ratios. These data implied that the precipitation of PRA *via* ED-ROMP using G2 from MeOH was not efficient at removing Ru catalyst to ultralow levels and the residual Ru induced the thermal degradation. The data at low catalyst loading, *i.e.,* [M/n]/[G2] = 5000 and 10,000 imply that the polymer does not require purification to achieve high thermal stability. Actually, [M/n]/[G2] = 5000 and 10,000 (Table 2, rows 3 and 5) showed a very high decomposition temperature without any precipitation, where $T_{d5\%}$ were 306 and 321 °C, respectively (Fig. S23). We note that the sample by [M/n]/[G2] = 10000 in Table 1, row 5 showed high decomposition temperature ($T_{d5\%}$ = 312 °C) even under air (Fig. S24).

Conclusions

We have demonstrated high molar mass homopolymers of PRA from ML, DL and MixL, which are cyclic macrolactones of ricinoleic acid, *via* ED-ROMP using G2 as a catalyst. Even at as low as 0.01mol% (36ppm as Ru), a high molar mass PRA was obtained within 4 h. Oligomers were suppressed by utilizing high concentration conditions (*i.e.*, bulk polymerization), resulting in up to 98% of the monomer conversion. Although it is known that it can be difficult to remove Ru residue from the polymer,[23] the result that the catalyst amount reduced to 0.01mol% demonstrated the effectiveness giving higher
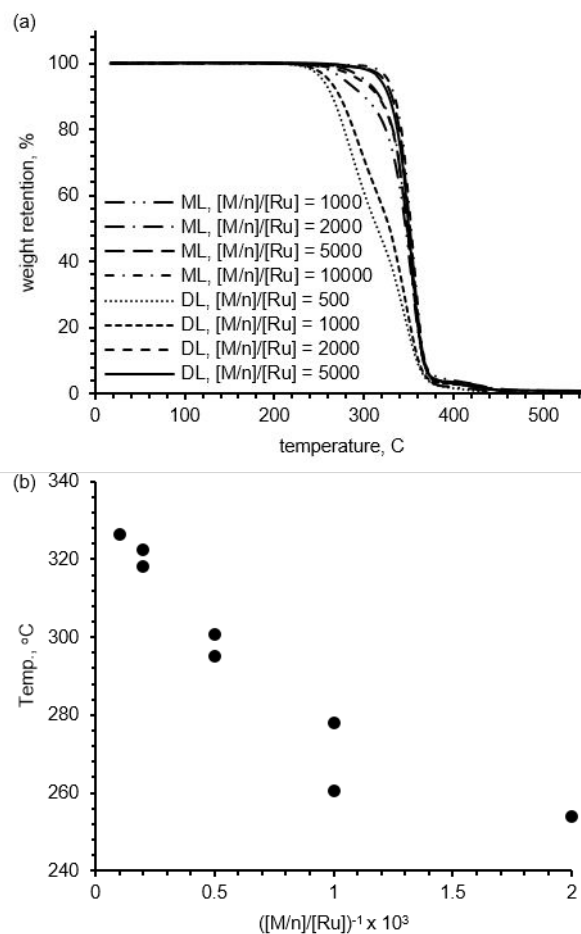

Fig. 4 (a) TGA traces of PRA in table 1 and (b) the relationship between catalyst loading ([M/n]/[G2]$^{-1}$ x 10^3) to 5% weight loss temperature after precipitation in MeOH.

thermal stabilities and colorless polymers without removal of the catalyst, which is beneficial to industrial applications. The microstructure was revealed by comparing model compounds of *HH*, *HT* (*TH*) and *TT*, and PRA *via* ED-ROMP, where a mixture of the statistically nearly random regioisomers and trans-enriched geometric isomer was formed as a result of ring-closing and secondary metathesis. High molar mass PRA homopolymers were physical gel-like materials (Fig. S14) since the molar mass might be high enough to entangle to decrease the relaxation (Fig. S25 and S26). Therefore, it should be noted that the properties differ from those of the previously reported viscous oil. Since the PRA obtained by ED-ROMP is different from the PRA from SPC with *cis* and *HT* (*TH*) structure, further investigation on the properties such as crosslinking with sulfur or peroxide for thermoset, conversion into saturated polyesters by hydrogenation and copolymerization with other cyclic olefins are expected to give high performing bio-based elastomeric materials.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

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