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Synthesis of Semicrystalline Long Chain Aliphatic Polyesters by ADMET Copolymerization of Dianhydro-*D*-glucityl bis(undec-10-enoate) with 1,9-Decadiene and Tandem Hydrogenation

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Abstract: Acyclic diene metathesis (ADMET) copolymerization of dianhydro-*D*-glucityl bis(undec-10-enoate) (M1) with 1,9-decadiene (DCD) using ruthenium-carbene catalyst, $RuCl_2(IMesH_2)(CH\text{-}2\text{-}O^iPr\text{-}C_6H_4)$ [$IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene, **HG2**], afforded unsaturated polyesters (M_n = 9300–23,400) under the optimized conditions. Subsequent tandem hydrogenation (H_2 1.0 MPa, 50 °C) with the addition of a small amount of Al_2O_3 resulted in the saturated polymers having a melting temperature of 71.7–107.6 °C, depending on the molar ratio of M1 and DCD.

Keywords: olefin metathesis; polymerization; ruthenium catalyst; biobased; tandem synthesis; acyclic diene metathesis; copolymerization; hydrogenation

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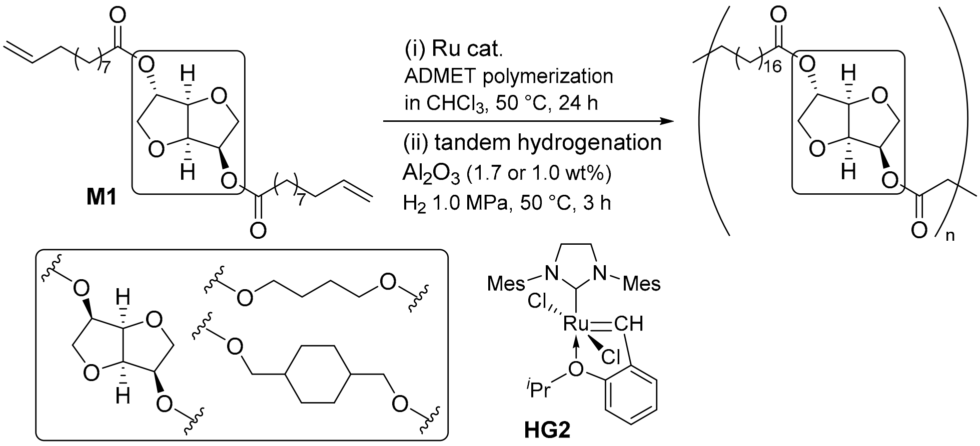
1. Introduction

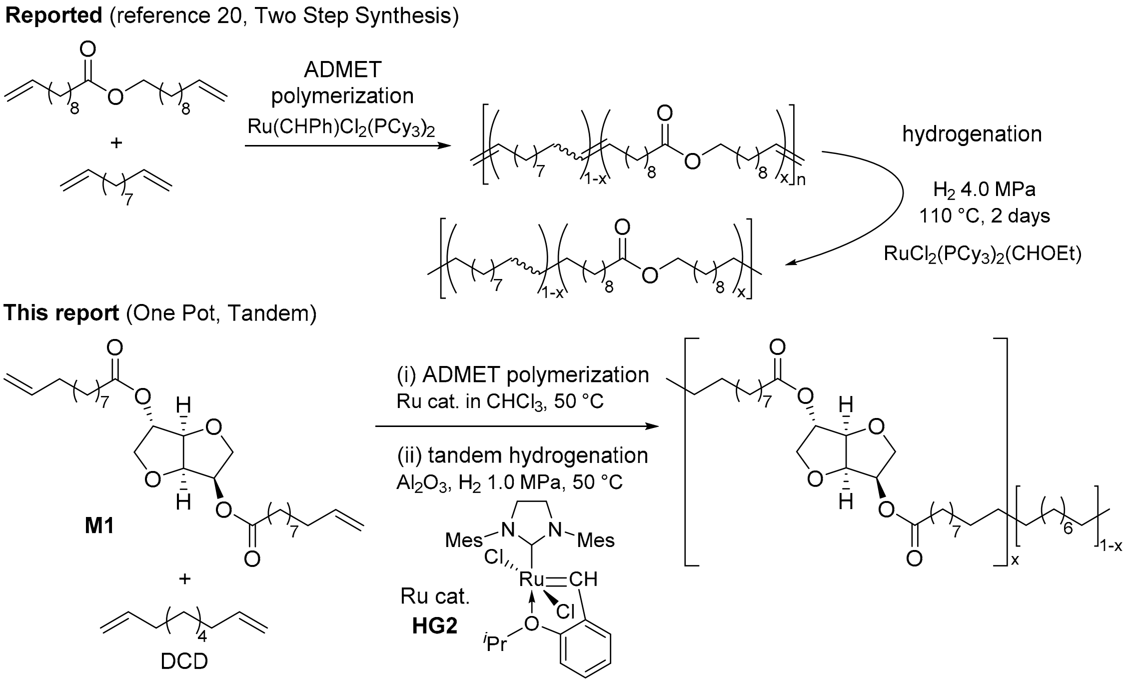
Development of advanced polymers from renewable feedstocks, as an alternative to petroleum-based polymers, attracts considerable attention, especially in terms of green sustainable chemistry [1–7]. Polyesters from bioderived monomers have been recognized as an important subject [7–12], and plant oils such as triglycerides of fatty acids are known as useful feedstock for synthesis of the aliphatic polyesters [7,9–12]. Two pathways, (i) polycondensation of the dicarboxylic acids with diols (mostly derived from the diacids by reduction) [11] and (ii) acyclic diene metathesis (ADMET) polymerization of α,ω-dienes (prepared by transesterification) have been considered as effective synthetic methods for the purpose [7].

ADMET polymerization has been an efficient method for synthesis of advanced functional polymeric materials with various architectures [7,13–16]. Synthesis of polyesters by adopting the polymerization of α,ω-dienes [7,17–28], especially derived from bio-based unsaturated fatty acids (such as ω-undecenoate, which consists of terminal olefinic double bond and carboxylate), is known. We recently reported one-pot synthesis of aliphatic polyesters by ruthenium-catalyzed tandem ADMET polymerizations of α,ω-dienes (prepared from castor oil and sugars by transesterification) and hydrogenation under mild conditions (Scheme 1) [28]. Moreover, depolymerization of the resultant unsaturated polymers by olefin metathesis with ethylene (as a reverse reaction of polycondensation) was demonstrated [28].

Synthesis of long chain aliphatic polyesters placing ester functionalities in different methylene spacing units by adopting ADMET copolymerization of undec-10-en-1-yl undec-10-enoate and undeca-1,10-diene (M_n = 7000–10,300, before hydrogenation) followed by hydrogenation of the olefinic double bonds in the presence of two different ruthenium catalysts (Scheme 2, top) has been reported [20]. The melting temperature (T_m) of the resultant polymer was depended upon the number of the methylene units employed. Hydrogenation of the isolated unsaturated copolymers by RuHCl(H$_2$)(PCy$_3$)$_2$ (Cy = cyclohexyl) catalyst required severe conditions (40 bar, 110 °C, 2 days) [20]. As in Scheme 1 above, we established a tandem system (one pot synthetic method) under mild conditions, and demonstrated one pot synthesis of bio-based saturated polyesters by tandem ADMET copolymerization of M1 with 1,9-decadiene (DCD) and subsequent hydrogenation (Scheme 2, bottom).



Scheme 1. One pot synthesis of bio-based long chain aliphatic polyesters by tandem ADMET polymerization and hydrogenation [28].



Scheme 2. (**Top**) Synthesis of aliphatic polyesters by copolymerization undec-10-en-1-yl undec-10-enoate and undeca-1,10-diene and subsequent hydrogenation [20]. (**Bottom**) One pot synthesis of polyesters by ADMET copolymerization of dianhydro-*D*-glucityl bis(undec-10-enoate) (M1) with 1,9-decadiene (DCD) and tandem hydrogenation (this report).

2. Results and Discussion

2.1. One Pot Synthesis of Long Chain Polyesters by ADMET Copolymerization of Dianhydro-D-Glucityl bis(undec-10-enoate) (M1) with 1,9-Decadiene (DCD) and Tandem Hydrogenation

According to the reported procedure, ADMET copolymerizations of dianhydro-*D*-glucityl bis(undec-10-enoate) (M1) [18,28], with 1,9-decadiene (DCD) were conducted in the presence of Ru-carbene catalysts, RuCl$_2$(IMesH$_2$)(CH-2-O^{i}Pr-C$_6$H$_4$) [**HG2**; IMesH$_2$ = 1,3-

bis(2,4,6-trimethyl- phenyl)imidazolin-2-ylidene], which yielded high molecular weight unsaturated polyesters [7,16,26,28]. The polymerizations were conducted in a small amount of $CHCl_3$ using a sealed Schlenk tube equipped with a high-vacuum valve. The reaction tube was heated at 50 °C, and ethylene by-produced in the polycondensation was removed by cooling the solution with a liquid nitrogen bath followed by connecting a vacuum line (details, see Experimental section) [26,28]. The efficient ethylene removal is important for obtaining high molecular weight polymers in this type of polycondensation [16]. The results are summarized in Table 1. Selected GPC traces in the resultant polymers are also shown in Figure 1.

It was revealed that, as reported in the homopolymerization of M1, the average molecular weight (M_n) in the resultant copolymer, expressed as poly(M1-*co*-DCD), increased over the time course (runs 1–3, Figure 1a). The resultant copolymers possessed rather high molecular weights with unimodal molecular weight distributions (runs 2,3: M_n = 9300, 10,600, M_w/M_n = 1.78, 1.56, respectively). It was also revealed that the M_n values were affected by the amount of **HG2** loaded in the reaction mixture (run 2 vs. runs 4–6), as reported previously [26,28]. Although the polymerization of M1 yielded the high molecular weight polymer (M_n = 15,900), the M_n values in the copolymers were rather low and were somewhat affected by the M1:DCD molar ratios (runs 2,7,8, Figure 1b). The molar ratios (compositions) in the resultant polymers estimated by ^{1}H NMR spectra were close to the initial M1:DCD molar ratios (DCD/M1 = 9.9 (run 2), 4.8 (run 7), 2.1 (run 8), respectively), suggesting that the reaction took place with complete monomer conversion, as usually observed in the condensation polymerizations of this type [7,16–32].

It was noted that the M_n value increased when chloroform solvent in the reaction mixture was replaced during the polymerization (every 30 min), and repetitive replacement seemed more effective for obtaining high molecular weight copolymers (run 2 vs. runs 9–14, Table 1, Figure 1b). The effect was due to removal of ethylene that remained in the mixture by replacement of the solvent. The M_n value of 23,400 (M_w/M_n = 1.48) was attained by replacement of the solvent six times, although this is not be a productive method from a practical viewpoint.

Figure 2b shows the ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) for the resultant poly(M1-*co*-DCD), and the spectrum for poly(M1) is also placed for comparison (Figure 2a). Resonances assigned to protons of the internal olefins were observed at 5.29–5.38 ppm, whereas those assigned to the terminal olefins (at 4.84, 4.91, and 5.72 ppm) in M1 and DCD were no longer seen and other resonances were remained (resonances ascribed to protons in the internal olefins (5.29–5.38 ppm), protons adjacent to olefins (1.94 ppm) and methylene (1.43–1.21) overlapped with DCD, the other resonances corresponded to the protons from M1; details, see Materials and Methods). This result clearly indicates formation of polymers by the ADMET polymerization [13–28]. Moreover, resonances ascribed to the olefinic double bonds, and those to protons adjacent to the double bond (–CH_2-CH=CH–), disappeared in the sample after hydrogenation. The results also suggest conversion to the hydrogenated polymers.

We reported that the resultant polymer prepared by ADMET polymerization of M1 could be hydrogenated under mild conditions (1.0 MPa, 50 °C), compared to those reported previously (such as 4.0 MPa, 110 °C, 2 days, two-step process) [20,29–32], without isolation of unsaturated polymers, by adding small amount of alumina (Al_2O_3) into the reaction mixture. As reported previously [28], the completion of the hydrogenation of olefinic double bonds should be monitored (confirmed) by DSC thermograms (observed as single melting temperature with uniform composition), although disappearance of resonances ascribed to olefinic protons was observed after a short period [28]. Since we need to check whether the hydrogenation of the copolymer was complete under similar conditions, tandem hydrogenations were conducted under various conditions (hydrogen pressure, time; runs 9–11).

Figure 3 shows DSC thermograms of the resultant poly(M1-*co*-DCD)s (molar ratio of M1:DCD = 1:10) prepared under various conditions. It turned out that no significant differences in the thermograms, or the T_m (melting temperature) values, were observed irrespective of the hydrogenation conditions, clearly suggesting that the hydrogenation reached completion even after 3 h under 1.0 MPa of hydrogen in this catalysis (in the presence of Al_2O_3 at 50 °C). The resultant copolymers were, however, insoluble for ordinary GPC analysis (in THF at 40 °C, in *ortho*-dichlorobenzene at 145 °C), and were poorly soluble in chloroform in conventional NMR analysis.

Table 1. ADMET copolymerization of M1 with 1,9-decadiene (DCD) [a].

Run	ADMET Polymerization							Hydrogenation		
	DCD /mmol	Cat. /mol%	No. Solvent Exchange [b]	Yield [c] /%	Time /h	M_n [d]	M_w/M_n [d]	H_2 /MPa	Time /h	T_m [e] /°C
1	3.25	1.0	0	80.0	6	7000	1.46	1.0	24	100.9
2	3.25	1.0	0	65.5	24	9300	1.78	1.0	24	104.5
3	3.25	1.0	0	82.7	48	10,600	1.56	1.0	24	
4	3.25	2.0	0	70.9	24	5000	1.53	1.0	24	104.0
5	3.25	0.50	0	71.3	24	3100	1.47	1.0	24	103.4
6	3.25	0.25	0	52.1	24	3500	1.45	1.0	24	103.3
7	1.63	1.0	0	76.0	24	7300	1.66	1.0	24	98.2
8	0.65	1.0	0	72.2	24	9600	1.67	1.0	24	71.7
9	3.25	1.0	1	87.0	24	12,600	1.77	1.0	3	107.6
9-2 [f]								2.0	3	105.1
10	3.25	1.0	1	90.5	24	9800	1.61	1.0	6	105.9
10-2 [f]								1.0	24	106.8
11	3.25	1.0	1	70.1	24	9500	1.64	1.0	3	104.9
11-2 [f]								2.0	24	105.7
12	3.25	1.0	1	88.2	24	11,400	1.68	1.0	24	106.6
13	3.25	1.0	4	72.1	24	19,200	1.66	1.0	24	105.5
14	3.25	1.0	6	85.6	24	23,400	1.48	1.0	4	106.8

[a] Conditions (ADMET polymerization): M1 0.325 mmol, $CHCl_3$ 0.14 mL, 50 °C (see details in the Experimental section). Hydrogenation: addition of Al_2O_3 5 mg, 50 °C. [b] Number of solvent replacements during the polymerization (see details in Experimental section). [c] Isolated yields as MeOH insoluble fraction. [d] GPC data in THF vs. polystyrene standards (sample before hydrogenation). [e] By DSC thermograms (after hydrogenation). [f] Tandem hydrogenation under different conditions.

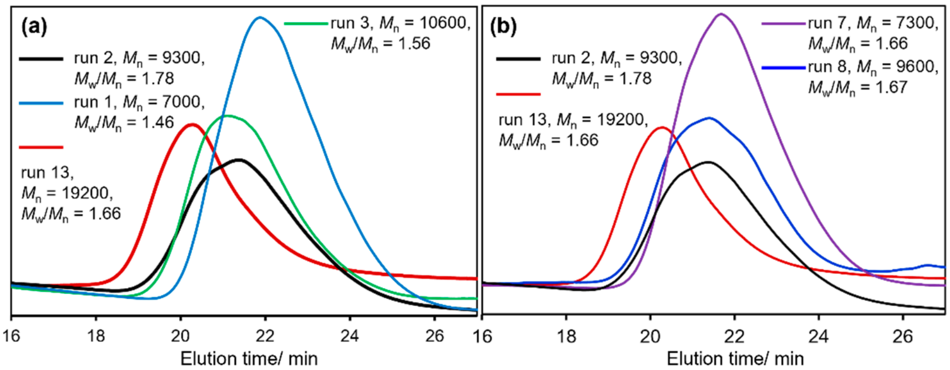


Figure 1. GPC traces in the resultant poly(M1-*co*-DCD)s. (**a**) Time course (runs 1–3), (**b**) effect of M1/DCD molar ration including GPC trace in run 13 (polymer after solvent exchange).

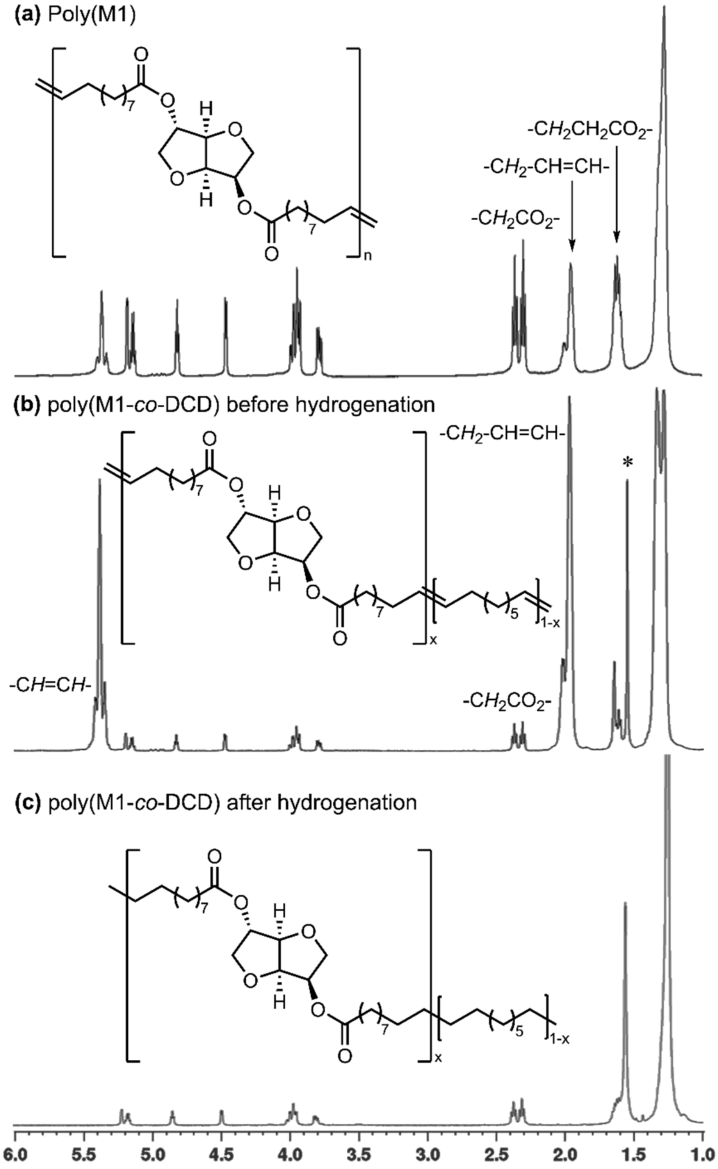


Figure 2. ^1H spectra (in $CDCl_3$ at 25 °C) for (**a**) poly(M1), (**b**) poly(M1-*co*-DCD) (before hydrogenation, run 6), and (**c**) hydrogenated poly(M1-*co*-DCD) (run 6). Resonance marked with * is water (impurity).

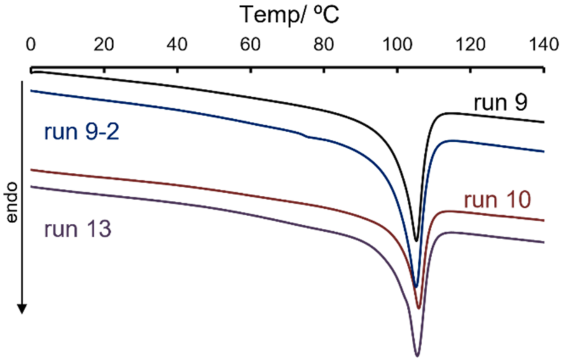


Figure 3. DSC thermograms of hydrogenated poly(M1-*co*-DCD)s (M1:DCD = 1:10, molar ratio) prepared under various hydrogenation conditions [H_2 1.0 MPa, 3 h (run 9), 6 h (run 10), and 24 h (run 13); H_2 2.0 MPa, 3 h (run 9-2)]. Detailed data are shown in Table 1.

Figure 4 shows DSC thermograms in the resultant poly(M1-*co*-DCD)s prepared under various M1:DCD molar ratios; the thermogram for poly(M1) is placed for comparison. It turned out that the T_m value in the resultant copolymer increased upon increasing the DCD molar ratios (the ratio was highly close to that charged in the reaction mixture). The resultant copolymer prepared with a DCD/M1 molar ratio of 10 possessed a T_m value of ca. 105–106 °C, and the value seemed rather low in the low molecular weight samples (runs 1,4–6). These results suggest that thermal resistant polymers (T_m higher than 100 °C) could be prepared by conducting copolymerization of biobased monomer (M1) with nonconjugated diene (DCD).

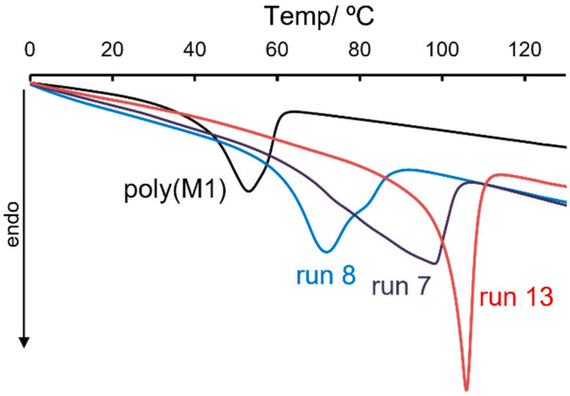


Figure 4. DSC thermograms of hydrogenated poly(M1-*co*-DCD)s prepared under various M1:DCD molar ratios [M1:DCD = 1:2 (run 8), 1:5 (run 7), 1:10 (run 13)]. Detailed data are shown in Table 1.

2.2. ADMET Copolymerization of M1 with 1,13-Tetradecadiene (TDCD) and Tandem Hydrogenation

Copolymerizations of M1 with 1,13-tetradecadiene (TDCD) were also conducted under similar conditions (TDCD:M1 = 10:1, molar ratio), and the results are summarized in Table 2. Although the polymerizations were conducted with different catalyst loading (1.0 and 0.5 mol%) as well as different numbers of solvent exchanges to remove ethylene by product in this polycondensation, the resultant polymers possessed rather low molecular weights and no improvements in the M_n values were attained.

Table 2. ADMET copolymerization of M1 with 1,3-tetradecadiene (TDCD) [a].

Run	Cat.	No. Solvent Exchange [b]	Yield [c]	M_n [d]	M_w/M_n [d]	T_m [e]
	/mol%		/%			/°C
15	1.0	1	80.2	4400	1.58	106.5
16	1.0	2	72.1	6700	1.67	105.2
17	1.0	4	84.1	6400	1.61	107.8
18	0.50	2	83.5	6100	1.61	107.0
19 [f]	0.50	4	82.8	6700	1.56	107.0

[a] Conditions (ADMET polymerization): 1,13-tetradecadiene 3.25 mmol, M1 0.325 mmol, $CHCl_3$ 0.14 mL, 50 °C. Hydrogenation: addition of Al_2O_3 5 mg, H_2 1.0 MPa, 50 °C, 24 h. [b] Number of solvent replacements during the polymerization (see details in Experimental Section). [c] Isolated yields as MeOH insoluble fraction. [d] GPC data in THF vs. polystyrene standards (sample before hydrogenation). [e] By DSC thermograms (after hydrogenation). [f] Composition of TDCD/M1 = 10.4 estimated by ^{1}H NMR spectrum.

3. Concluding Remarks

Copolymerizations of bio-based dianhydro-*D*-glucityl bis(undec-10-enoate) (M1) with 1,9-decadiene (DCD) by tandem acyclic diene metathesis (ADMET) copolymerization, and subsequent tandem hydrogenation (H_2 1.0 MPa, 50 °C) by adding a small amount of Al_2O_3, were explored. The copolymerizations, conducted under optimized conditions yielded high molecular weight unsaturated polyesters (M_n = 9300–23,400) with melting temperatures of 71.7–107.6 °C depending on the ratio of M1 and DCD. An efficient tandem hydrogenation system under rather mild conditions (1.0 MPa, 3 h at 50 °C) was also demonstrated in this catalysis. The attempted copolymerization with 1,13-tetradecadiene in place of DCD yielded rather low molecular weight polymers, suggesting that further improvements should be considered as a future project. Synthesis of rather thermal resistant polymers (T_m higher than 100 °C) containing isosorbide (derived from a glucose) unit was demonstrated by copolymerization of a biobased monomer (M1) with nonconjugated diene (DCD). The approach adopted here should be beneficial to development of a green sustainable process with materials that should be promising alternatives to those based on fossil fuels.

4. Materials and Methods

General Procedure. Dianhydro-*D*-glucityl bis(undec-10-enoate) (M1) was prepared according to the reported procedure [28], and $RuCl_2(IMesH_2)(CH\text{-}2\text{-}O^iPr\text{-}C_6H_4)$ [**HG2**; Cy = cyclohexyl, $IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene, Aldrich Chemical Co., Milwaukee, WI, USA] was used as received. Anhydrous grade dichloromethane (>99.5%, Kanto Chemical Co., Inc., Tokyo, Japan), 1,9-decadiene (TCI Co., Ltd., Tokyo, Japan), ethyl vinyl ether (>98%), alumina (activated Al_2O_3), and Celite (Fujifilm Wako Pure Chemical Ind., Inc., Tokyo, Japan), and other chemicals of reagent grade were used as received. All ^1H NMR spectra (in $CDCl_3$ at 25 °C) were recorded on a Bruker AV500 spectrometer (500.13 MHz for ^1H). All chemical shifts were presented in ppm (reference $SiMe_4$ at 0.00 ppm) and obvious multiplicities and routine coupling constants are not listed. Molecular weights and the molecular weight distributions of resultant polymers were measured by gel-permeation chromatography (GPC), equipped with columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm diameter, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from $<10^2$ to 2×10^7 MW). The measurements were performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co., Ltd., Kyoto, Japan) in THF (HPLC grade, Fujifilm Wako Pure Chemical Ind., Inc., Tokyo, Japan, containing 0.03 wt% of 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). DSC (Differential scanning calorimetric) data for the polymers were measured using a Hitachi DSC 7020 analyzer. All samples (5–7 mg) were placed in standard aluminum pans under a nitrogen atmosphere and were first heated from 25 to 150 °C then cooled to -100 °C at a rate of 10 °C/min. The melting (T_m) temperature was determined upon a second heating cycle.

Acyclic diene metathesis (ADMET) polymerization. The typical polymerization procedure is as follows. In the drybox, a prescribed amount of 1,9-decadiene (DCD), and a $CHCl_3$ solution (0.14 mL, anhydrous) containing a prescribed amount of ruthenium catalyst (**HG2**) was placed into a 50 mL scale sealed Schlenk tube. After stirring the solution for 10 min at 25 °C under a nitrogen atmosphere in the drybox, dianhydro-*D*-glucityl bis(undec-10-enoate) (M1 0.325 mmol, 150 mg) was added to the reaction mixture. The reaction tube was taken out and was magnetically stirred in an oil bath at 50 °C. The mixture was then placed into a liquid nitrogen bath to remove ethylene from the reaction by opening the valve connected to the vacuum line for a short period (1 min). The valve was then closed, and the tube was returned into the oil bath to continue the reaction [26,28]. The procedure removing ethylene was repeated after a measured period (30 min for the first time then every 1.0 h until 6 h). The polymerization mixture was then cooled to room temperature and was quenched with excess ethyl vinyl ether (two drops, ca. 100 mg) while stirring for 1.0 h. The resultant solution was then dissolved in chloroform (2.0 mL) for dilution, and the solution was added dropwise into the stirred cold methanol (50 mL). The solution was stirred for ca. 15 min, and the precipitates were then collected by filtration and dried in *vacuo* to yield poly(M1-*co*-DCD) as a white solid. During the reaction in certain experimental runs, $CHCl_3$ was removed in vacuo and was replaced every 30 min at the initial stage (noted as solvent exchange in Table 1).

Poly(M1-co-DCD) (before hydrogenation). ^1H NMR ($CDCl_3$): δ 1.43–1.21 (m, $\text{-C}H_2\text{-}$), 1.61 (t, J = 6.6 Hz, $\text{-C}H_2CH_2COO\text{-}$), 1.94 ($\text{-C}H_2CH = CH\text{-}$), 2.30 (t, J = 7.7 Hz, $\text{-C}H_2COO\text{-}$), 2.34 (t, J = 7.1 Hz, $\text{-C}H_2COO\text{-}$), 3.78 (dd, J = 9.8, 5.4 Hz, $\text{-CH}_2OC H\text{-}$), 3.92–4.03 (m, $\text{-C}H_2\text{-}$

OCH-,-CH_2-OC*H*-), 4.46 (d, *J* = 4.6 Hz, -CH_2-OCH-), 4.82 (t, *J* = 5.0 Hz, -CH_2-OCH-), 5.13 (dd, *J* = 5.6 Hz, -C*H*OCO-), 5.18 (d, *J* = 3.2 Hz, -C*H*OCO-), 5.37 (-C*H*=C*H*-). The assignments of chemical shifts were almost identical with that of poly(M1) reported previously [28], except the integration ratio of protons of internal olefins (5.37 ppm, -C*H*=C*H*-), methylene (1.43–1.21 ppm, -CH_2-) and of that observed at 1.94 ppm (-CH_2CH=CH-), ascribed from incorporation of DCD. ^{13}C NMR ($CDCl_3$): δ 17.9, 24.8, 27.2, 28.7, 28.9, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.8, 32.5, 32.6, 34.0, 34.2, 70.3, 73.5, 73.7, 73.7, 80.7, 86.0, 124.5, 124.6, 129.9, 130.4, 131.8, 172.9, 173.1. Compositions of DCD/M1 were estimated by integration of protons resonances at 1.94 (-CH_2CH=CH-), 2.30 and 2.34 ppm (-CH_2COO-).

Tandem hydrogenation. After polymerization, the reaction mixture was placed into an autoclave, and a prescribed amount of Al_2O_3 powder (5 mg) was added. The reactor was then pressurized with hydrogen at 1.0 MPa. The reactor was then placed into aluminum heating blocks set at 50 °C, and was stirred for 24 h (or 3 h). The resultant mixture was diluted in chloroform (2.0 mL), and the solution (after filtration through Celite pad) was added dropwise into the stirred cold methanol (50 mL). The precipitates were collected by filtration and dried in *vacuo*. In runs 9–11, the reaction mixtures were separated into two portions to conduct hydrogenation under various hydrogenation conditions.

Poly(M1-co-DCD) (after hydrogenation). ^{1}H NMR ($CDCl_3$): δ 1.27 (m, -CH_2-), 1.64 (m, -CH_2CH$_2$COO-), 2.33 (t, *J* = 7.7 Hz, -CH_2COO-), 2.39 (t, *J* = 7.1 Hz, -CH_2COO-), 3.81 (dd, *J* = 9.8 and 5.4 Hz, -CH_2OC*H*-), 3.96–4.02 (m, -CH_2-OCH-,-CH_2-OC*H*-), 4.49 (d, *J* = 4.6 Hz, -CH_2-OCH-), 4.84 (t, *J* = 5.0 Hz, -CH_2-OCH-), 5.16 (dd, *J* = 5.6 Hz, -C*H*OCO-), 5.20 (d, *J* = 3.2 Hz, -C*H*OCO-).

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Conflicts of Interest: The authors declare no conflict of interest.

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