

Article

Synthesis of Network Biobased Aliphatic Polyesters Exhibiting Better Tensile Properties than the Linear Polymers by ADMET Polymerization in the Presence of Glycerol Tris(undec-10-enoate)

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Abstract: Development of biobased aliphatic polyesters with better mechanical (tensile) properties in film has attracted considerable attention. This report presents the synthesis of soluble network biobased aliphatic polyesters by acyclic diene metathesis (ADMET) polymerization of bis(undec-10-enyl)isobornide diester [**M1**, dianhydro-*D*-glucityl bis(undec-10-enoate)] in the presence of a tri-arm crosslinker [**CL**, glycerol tris(undec-10-enoate)] using a ruthenium-carbene catalyst, and subsequent olefin hydrogenation using RhCl(PPh₃)₃. The resultant polymers, after hydrogenation (expressed as **HCP1**) and prepared in the presence of 1.0 mol% **CL**, showed better tensile properties than the linear polymer (**HP1**) with similar molecular weight [tensile strength (elongation at break): 20.8 MPa (282%) in **HP1** vs. 35.4 MPa (572%) in **HCP1**]. It turned out that the polymer films prepared by the addition of **CL** during the polymerization (expressed as a 2-step approach) showed better tensile properties. The resultant polymer film also shows better tensile properties than the conventional polyolefins such as linear high density polyethylene, polypropylene, and low density polyethylene.

Keywords: olefin metathesis; polymerization; biobased; isobornide; polyesters; network; tensile property; chemical recycling



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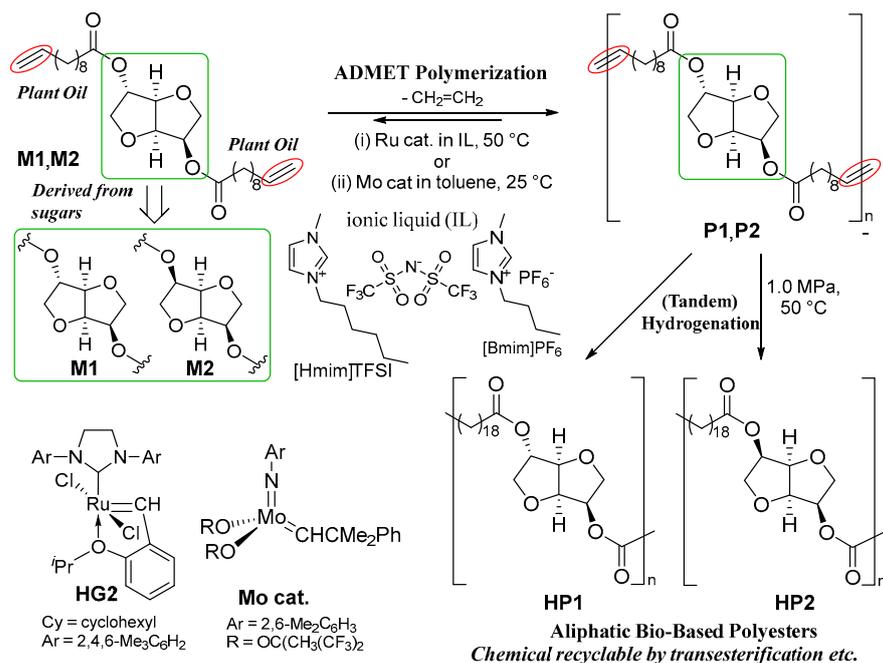


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1. Introduction

Development of biobased semicrystalline aliphatic polyesters derived from non-edible naturally abundant resources (plant oil, etc.) attracts considerable attention [1–8]. This is not only because these are considered alternatives to petroleum-based polymers but also because of their importance from the viewpoint of circular economy [9–11]. For example, these polyesters (including conventional polyesters) can be depolymerized by treating them with alcohols (via transesterification) in the presence of a catalyst to recover monomers exclusively (facile chemical recycling) [12–15]; one-pot closed-loop chemical recycling (depolymerization and repolymerization) was thus also demonstrated [13]. There have been thus many reports on the synthesis of polyesters derived from plant oil through polycondensation [7,15–19] and acyclic diene metathesis (ADMET) polymerization technique [7,17,20–36].

Recently, our laboratory demonstrated the synthesis of high molecular weight polyesters (expressed as **HP1** and **HP2**, Scheme 1) [14,36] exhibiting better tensile properties (tensile strength, elongation at break) than conventional polyolefins, and the polymers (**HP1**) reported previously [20,21,32]. These polymers were prepared by ADMET polymerization [37–40] and subsequent hydrogenation. The effect of molecular weight on the tensile property was demonstrated by exhibiting better tensile properties [36].



Scheme 1. Synthesis of high molecular weight aliphatic polyesters by acyclic diene metathesis (ADMET) polymerization [14,36].

In this paper, we focus on the synthesis of the soluble network polymers by ADMET polymerization. These polymers were prepared by conducting the polymerization in the presence of a crosslinker (CL) possessing three terminal olefins [31,41], as reported previously by us [31], and the resultant polymer should exhibit better tensile strength due to their network framework. We thus herein report the synthesis of network bio-based aliphatic polyesters, which show better tensile properties (tensile strengths and elongation at breaks) than the linear one (HP1). These polymers were also depolymerized to afford the corresponding diesters and diols (and triols) through transesterification with ethanol in the presence of CpTiCl₃ [12,14].

2. Materials and Methods

General Procedure. All synthetic experiments were conducted in a dry box or using standard Schlenk techniques under a nitrogen atmosphere. Anhydrous grade toluene, *n*-hexane, and dichloromethane (>99.5%, Kanto Chemical Co., Inc., Tokyo, Japan) were transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in a dry box. Isosorbide, 10-undecenoyl chloride, triethylamine, and glycerol of reagent grades (Tokyo Chemical Industry, Co., Ltd., Tokyo, Japan) were used without further purification. RuCl₂(IMesH₂)(CH-2-O^{*i*}Pr-C₆H₄) [HG2; IMesH₂ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene] obtained from Aldrich Chemical Co. (Milwaukee, WI, USA), was used as received. Monomer, dianhydro-*D*-glucityl bis(undec-10-enoate) (M1) was prepared according to the reported procedure [32].

All ¹H and ¹³C NMR measurements were performed at 25 °C on a Bruker AV500 spectrometer (500.13 MHz and 125.77 MHz, respectively) using CDCl₃ as solvent. Chemical shifts were reported as ppm with reference to SiMe₄ at 0.00 ppm. Gel permeation chromatography (GPC) was used for the analysis of molecular weights and molecular weight distributions for the resultant polymer. The GPC measurements were carried out at 40 °C on a SCL-10A (Shimadzu Co., Ltd., Kyoto, Japan) connected columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm diameter, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from <10² to 2 × 10⁷ MW, Kyoto, Japan), using a Shimadzu RID-10A detector in THF (>99.8%, Kanto Chemical Co., Inc., Tokyo, Japan) served as the eluent with a flow rate 1.0 mL/min.

Synthesis of crosslinker glycerol triundec-10-enoate (CL). In the dry box, glycerol (300 mg, 3.25 mmol) and triethylamine (2.0 g, 19.8 mmol, 2.0 eq.) were added to THF (30 mL) and then cooled to 0 °C. 10-undecenoyl chloride (2.0 g, 9.9 mmol) was then added dropwise to the cooled glycerol solution. The reaction was allowed to react at room temperature overnight until completion by confirmation via TLC. The THF solvent was then removed with a rotary evaporator and then diluted with chloroform and washed with 2M HCl, 5% NaHCO₃, deionized water, and brine. The washed product was then dried over MgSO₄, filtered through a filter paper, evaporated using a rotary evaporator, and further dried under vacuum. The crude product was then purified using column chromatography (9:1, *n*-hexane: ethyl acetate), collecting a colorless oil of CL (1.54 g, 80% yield). The resultant product was further purified inside the dry box by dissolving the crosslinker in hexane and passing through a short column of alumina and celite. ¹H NMR (CDCl₃): δ 1.28 (br s, 24H, -CH₂-), 1.37 (t, J = 6.9 Hz, 6H, -CH₂-), 1.60 (m, 6H, -CH₂CH₂COO-), 2.03 (dt, J = 8.15, 7.4 Hz, 6H, -CH₂CH=CH₂), 2.31 (t, J = 7.5 Hz, 6H, -CH₂COO-), 4.14 (dd, J = 11.95, 5.97 Hz, 2H, -OCH₂CHOCH₂O-), 4.29 (dd, J = 11.9, 4.31 Hz, 2H, -OCH₂CHOCH₂O-), 4.92 (d, J = 10.21 Hz, 3H, CH₂=CH-), 4.98 (d, J = 17.02 Hz, 3H, CH₂=CH-), 5.26 (tt, J = 5.84, 4.35 Hz, 1H, -CH(CH₂O)₂-), 5.80 (ddt, J = 17.02, 10.26, 6.71 Hz, 3H, -CH=CH₂) ¹³C{¹H} NMR (CDCl₃): δ 25.0 (-CH₂-), 29.0 (-CH₂-), 29.2 (-CH₂-), 29.4 (-CH₂-), 29.5 (-CH₂-), 33.9 (-CH₂CH=CH₂), 34.2 (-CH₂COO-), 34.4 (-CH₂COO-), 62.3 (-CH₂OCO-), 69.0 (-CH-OCO-), 114.3 (CH₂=CH-), 139.3 (-CH=CH₂), 173.0 (-COO-), 173.4 (-COO-). APCI-MS: calculated for C₃₆H₆₂O₆ *m/z*, 591.5 [M+H]⁺; found 591.4.

ADMET Polymerization. ADMET polymerizations were conducted by the analogous procedure reported previously [14,32]. In the dry box, the monomer (M1), crosslinker (CL), solvent, and ruthenium catalyst (HG2) were charged with the prescribed amounts in Table 1 into a sealed Schlenk-type tube (25 mL volume), and the reaction mixture was stirred for a specific time at 50 °C in an oil bath. The formed ethylene gas was removed continuously by freezing the reaction medium using liquid nitrogen, and the tube was shortly connected to the vacuum line with a certain time interval (each 15 min at the first 1 h, each 30 min in the following 2 h, and then each 1 h). The solvent exchange technique was conducted by solvent replacement [35,42] with a fresh solvent two or three times in the first two hours under N₂ atmosphere. Two drops of EVE were used to quench the ADMET polymerization and stirring for 1 h. The reaction mixture was diluted using 4 mL chloroform and precipitated in 100 mL cold methanol. The resultant polymers were collected via filtration and dried in vacuo and were characterized using ¹H (500.13 MHz) and ¹³C{¹H} (125.77 MHz) NMR spectra in CDCl₃ at 25 °C, GPC (SEC), and DSC.

CP1. ¹H NMR (CDCl₃): δ 1.28 (br s, 20H, -CH₂-), 1.61 (tt, J = 14.66, 7.42 Hz, 4H, -CH₂CH₂COO-), 1.97 (m, 4H, -CH₂CH=CH-), 2.30 (t, J = 7.46 Hz, 2H, -CH₂COO-), 2.36 (t, J = 7.57 Hz, 2H, -CH₂COO-), 3.79 (dd, J = 9.77, 5.45 Hz, 1H, -CH₂CHO-), 3.93–4.00 (m, 3H, -CH₂-CHO-, -CH₂CHO-), 4.14 (dd, J = 12.01, 5.93 Hz, 2H, -CH₂CHOCH₂O-), 4.29 (dd, J = 11.76 Hz, 3.97 Hz, 2H, -CH₂CHOCH₂O-), 4.47 (d, J = 4.54 Hz, 1H, -CH-CHO), 4.82 (t, J = 4.92 Hz, 1H, -CH-CHO), 5.14 (dt, J = 5.60, 5.60 Hz, 1H, -CHOCO-), 5.19 (d, J = 2.80 Hz, 1H, -CHOCO-), 5.37 (m, 2H, -CH=CH-). ¹³C{¹H} NMR (CDCl₃): δ 25.0 (-CH₂-), 29.2 (-CH₂-), 29.6 (-CH₂-), 29.4 (-CH₂-), 29.8 (-CH₂-), 32.7 (-CH₂CH=CH-), 34.1 (-CH₂COO-), 34.3 (-CH₂COO-), 62.2 (-CH₂OCO-), 69.0 (-CH-OCO-), 70.5 (-CH₂-CHO-), 73.6 (-CH₂-CHO-), 73.9 (-CHOCO-), 78.0 (-CHOCO-), 80.9 (-CH-CHO-), 86.1 (-CH-CHO-), 130.0 (-CH=CH-), 130.5 (-CH=CH-), 173.0 (-COO-), 173.3 (-COO-).

Olefin Hydrogenation. The resultant polymers (200 mg), toluene (3.0 mL), and RhCl(PPh₃)₃ (3 mg) were added into the autoclave (20 mL scale) [36]. The stainless steel autoclave was then pressurized with hydrogen (1.0 MPa) and was placed into a heating Al block preheated at 50 °C. The solution was magnetically stirred for 24 h. The reaction mixture was then poured into a mixed solution of MeOH. The polymer precipitates were collected on a filter paper, and the collected white precipitates were then dried in vacuo for several hours. No significant differences in the *M_n*, *D* (*M_w*/*M_n*) were observed in the polymer samples before/after the hydrogenation. The resultant polymers were identified

by NMR spectra (shown in Supplementary Materials), and the molecular weights and the distributions were analyzed by GPC.

HCPI. ^1H NMR (CDCl_3): δ 1.27 (br s, 28H, $-\text{CH}_2-$), 1.61 (tt, $J = 14.75, 7.12$ Hz, 4H, $-\text{CH}_2\text{CH}_2\text{COO}-$), 2.30 (t, $J = 7.56$ Hz, 2H, $-\text{CH}_2\text{COO}-$), 2.36 (t, $J = 7.51$ Hz, 2H, $-\text{CH}_2\text{COO}-$), 3.78 (dd, $J = 9.95, 5.40$ Hz, 1H, $-\text{CH}_2\text{CHO}-$), 3.92–4.00 (m, 3H, $-\text{CH}_2-\text{CHO}-$, $-\text{CH}_2\text{CHO}-$), 4.14 (dd, $J = 12.47, 5.92$ Hz, 2H, $-\text{OCH}_2\text{CHOCH}_2\text{O}-$), 4.28 (dd, $J = 11.77$ Hz, 4.10 Hz, 2H, $-\text{OCH}_2\text{CHOCH}_2\text{O}-$), 4.47 (d, $J = 4.55$ Hz, 1H, $-\text{CH}-\text{CHO}$), 4.82 (t, $J = 4.93$ Hz, 1H, $-\text{CH}-\text{CHO}$), 5.14 (dt, $J = 5.62, 5.55$ Hz, 1H, $-\text{CHOCO}-$), 5.19 (d, $J = 2.78$ Hz, 1H, $-\text{CHOCO}-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 25.0 ($-\text{CH}_2-$), 29.2 ($-\text{CH}_2-$), 29.4 ($-\text{CH}_2-$), 29.6 ($-\text{CH}_2-$), 29.7 ($-\text{CH}_2-$), 29.8 ($-\text{CH}_2-$), 34.1 ($-\text{CH}_2\text{COO}-$), 34.3 ($-\text{CH}_2\text{COO}-$), 62.2 ($-\text{CH}_2-\text{OCO}-$), 69.0 ($-\text{CH}-\text{OCO}-$), 70.5 ($-\text{CH}_2-\text{CHO}-$), 73.6 ($-\text{CH}_2-\text{CHO}-$), 73.9 ($-\text{CHOCO}-$), 78.0 ($-\text{CHOCO}-$), 80.9 ($-\text{CH}-\text{CHO}-$), 86.1 ($-\text{CH}-\text{CHO}-$), 173.0 ($-\text{COO}-$), 173.3 ($-\text{COO}-$).

Analysis of Tensile Properties. Stress/strain experiments were performed at 23 °C (speed 10 mm/min, humidity $50 \pm 10\%$) using a Shimadzu Universal Testing Instrument (Autograph AGS-10kNX, Kyoto, Japan) equipped with load cell (cell capacity 500 N). At least three specimens were tested for analysis of each polymer. The small dumbbell-shaped test specimens [width of parallel portion of 3 mm, distance between grippers (or gripping distance) of 10 mm, overall length of 25 mm and thickness of 0.1 mm] were cut from the polymer sheets prepared by a hot press. A toluene solution (2.0 mL) of **HP1** or **HCPI** (200 mg) sonicated for 10 min was placed into a PTFE petri dish ($\phi 50$ mm) and the sample films were prepared by removing the solvent upon heating (on a hot plate). The resultant solvent casted films were partly placed into a compression molding press machine (Shinto Metal Industries, Ltd., Osaka, Japan), and steel plates were heated up to 100 °C under 5.0 MPa for 2 min. The films were then obtained after cooling the steel plates to room temperature.

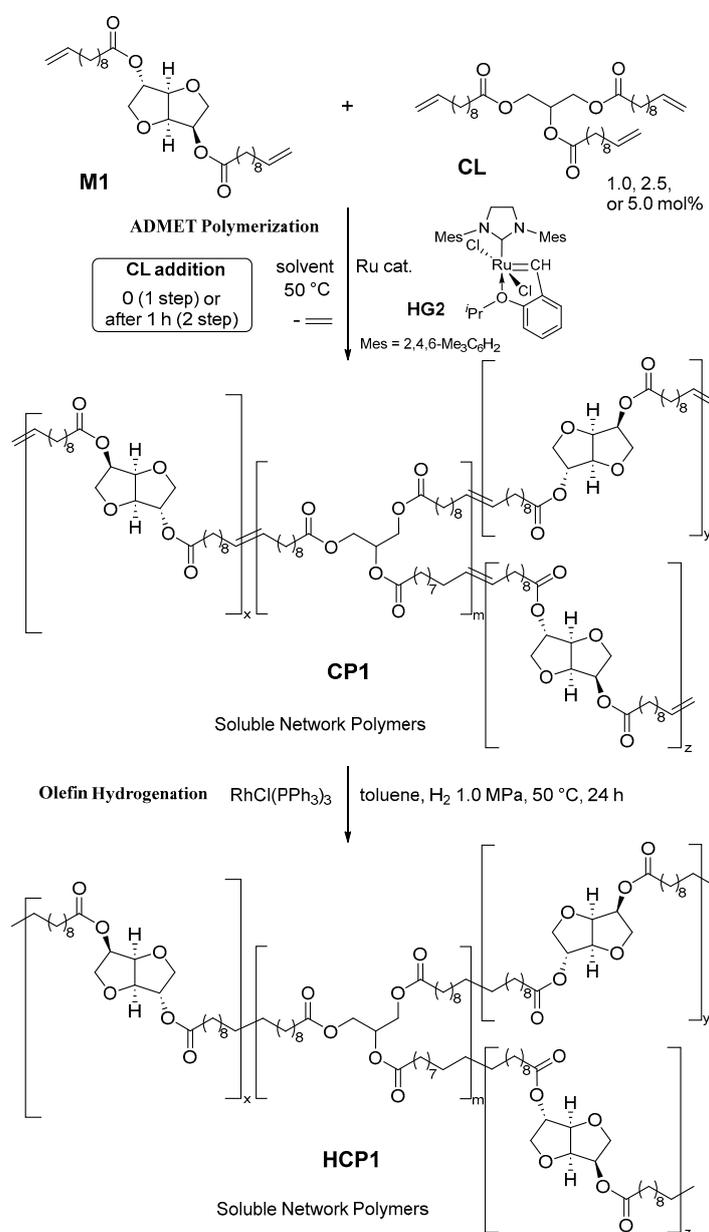
Table 1. ADMET polymerization of **M1** by **HG2** in the presence of the crosslinker (**CL**)¹.

Run	Solvent (Times of Solvent Replacement) ²	Polymerization			CP1		
		CL		Time (2) ⁴ /h	M_n^5 $\times 10^{-3}$	M_w/M_n^5	Yield ⁶ /%
		/mol%	Time (1) ³ /h				
1	chloroform (1)	--	--	24	30.3	2.11	96
2	chloroform (1)	0.5	0	24	36.5	2.20	92
3	chloroform (1)	1.0	0	24	36.6	3.00	97
4	chloroform (1)	1.0	0	24	34.8	3.11	92
5	chloroform (1)	1.0	0	24	32.2	2.64	91
6	toluene (1)	1.0	0	24	19.3	2.04	89
7	toluene (2)	1.0	0	24	26.0	2.82	94
8	tetrachloroethane (1)	1.0	0	24	20.1	1.99	98
9	chloroform (1)	2.5	0	24	29.6	4.11	98
10	chloroform (1)	2.5	0	24	29.6	4.14	91
11	toluene (1)	2.5	0	24	23.0	3.66	87
12	tetrachloroethane (1)	2.5	0	24	23.1	2.59	96
13	toluene (1)	5.0	0	24	20.0	4.63*	89
14	chloroform (1)	5.0	0	6	19.7	8.63*	77
15	chloroform (0)	5.0	0	6	6.70	1.67	75
16	chloroform (0)	5.0	0	12	7.50	1.83	89
17	chloroform (0)	5.0	0	24	20.0	4.64*	84
18	chloroform (1)	1.0	1	24	26.8	2.53	94
19	toluene (1)	1.0	1	24	21.0	2.18	88
20	tetrachloroethane (1)	1.0	1	24	17.6	1.95	97
21	chloroform (5)	1.0	1	24	36.6	2.79	91
22	chloroform (5)	1.0	1	24	35.8	3.00	90
23	chloroform (5)	2.5	1	24	31.1	4.13	90
24	chloroform (5)	2.5	1	24	32.0	4.48	91
25	chloroform (1)	2.5	1	24	25.0	5.94*	99
26	toluene (1)	2.5	1	24	19.5	2.61	90
27	chloroform (1)	5.0	1	24	16.4	5.45*	89
28	chloroform (5)	1.0	3	24	31.2	2.54	89

Table 1. Cont.

Run	Solvent (Times of Solvent Replacement) ²	Polymerization			CP1		
		CL /mol%	Time (2) ⁴		M_n^5 × 10 ⁻³	M_w/M_n^5	Yield ⁶ /%
			Time (1) ³ /h	/h			
29	chloroform (1)	1.0	3	24	26.7	3.04	94
30	toluene (1)	1.0	3	24	19.4	2.00	88
31	chloroform (1)	2.5	3	24	25.7	3.90	97
32	toluene (1)	2.5	3	21	15.1	2.60	92
33	toluene (2)	2.5	3	21	20.6	2.46	89

¹ Conditions: **M1** 300 mg (initial conc. 0.94 mmol/mL), 2.0 mol % **HG2**, 50 °C. ² Number of solvent replacements during the polymerization runs for every 30 min from the beginning. ³ Time (h) of addition of crosslinker (CL, Scheme 2). ⁴ Total polymerization time. ⁵ GPC data in THF vs. polystyrene standards. ⁶ Isolated yields as the methanol insoluble fraction. * Formation of gel.



Scheme 2. Synthesis of network polymers (**CP1** and **HCP1**) by ADMET polymerization and subsequent hydrogenation.

3. Results and Discussion

3.1. Synthesis of Network Polymers (CP1 and HCP1) by ADMET Polymerization and Subsequent Hydrogenation

ADMET polymerization of bis(undec-10-enyl)isobornide diester [**M1**, bis(undec-10-enoate) with isobornide] in the presence of glycerol tris(undec-10-enoate) (**CL**) was chosen because the resultant polymer film prepared by **M1** (expressed as **HP1**, Scheme 1) exhibited good tensile strength and elongation at break [36]. As shown in Scheme 2, two approaches involving adding **CL** from the beginning (1-step approach) or after 1 or 3 h (2-step approach) have been chosen for the synthesis since the approach might affect the network density or average polymer chain length between **CL**s (crosslinking point). The polymerizations of **M1** by the ruthenium–carbene catalyst (**HG2**, 2.0 mol%) were conducted in solvent (toluene, chloroform, or tetrachloroethane, initial **M1** conc. 0.94 mmol/mL) in the presence of **CL** (0.5–5.0 mol%), which were prepared by glycerol with 3.0 equiv of 1-undecenoyl chloride (see Materials and Methods). The selected results conducted under the various conditions are summarized in Table 1. For the obtainment of high molecular weight polymers under these conditions (300 mg **M1** scale), the solvent in the reaction mixture was removed in vacuo to replace the fresh one (called solvent replacement) every 30 min in certain experimental runs [42]. The method is effective for the purpose (removal of ethylene remained) of condensation polymerization [42], although the method would not be appropriate in terms of a green sustainable process, and alternative methods (conducted in IL [14] or a molybdenum catalyst [36]) should be studied.

It was revealed that the ADMET polymerizations of **M1** in the presence of 0.5–2.5 mol% **CL** (added at the beginning, called a 1-step approach) gave the highest molecular weight polymers (expressed as **CP1s**), and the M_n values became higher upon presence of **CL** (0.5 or 1.0 mol%, runs 1–5) compared to that in the absence of **CL** (run 1). The M_n value decreased upon further **CL** addition (2.5 mol%, runs 9 and 10), and the resultant polymers became swelled gels with stop stirring when the polymerizations were conducted in the presence of 5.0 mol% of **CL** (run 14). The results are highly reproducible, as demonstrated in runs 3–5, although the dispersity (PDI, M_w/M_n) values are somewhat large, probably due to the difficulty of stirring the reaction mixture owing to high viscosity (run 14) [14]. Indeed, the polymerizations in the presence of 5.0 mol% **CL** eventually afforded polymer gels irrespective of the kind of solvent employed (runs 13–17). It seems that the polymerization conducted in toluene and tetrachloroethane afforded polymers possessing rather low molecular weights compared to those conducted in chloroform, whereas the solvent replacement improved the M_n value in **CP1** [$M_n = 19,300$ (run 6) vs. 26,000 (run 7)].

In contrast, the M_n values in the resultant polymers (**CP1s**) were low when **CL** (1.0 mol%) was added after 1 h of the ADMET polymerization (expressed as a 2-step approach) irrespective of solvents ($M_n = 17,600$ – $26,800$, runs 18–20); the polymerization in chloroform gave **CP1** with the highest molecular weight (run 18). Although the M_w/M_n values in the resultant polymers in the presence of 2.5 mol% **CL** conducted in chloroform were rather large [$M_w/M_n = 4.13$ – 5.45 (runs 23–25)], the M_w/M_n values in **CP1** became rather low (unimodal) when **CL** was added after 3 h of the ADMET polymerization (runs 29–32). As observed above, an increase in the number of solvent replacements led to an increase in the M_n values because the ethylene that remained in the polymerization solution was removed in vacuo with the removal of solvent, which led to condensation polymerization [42]. Polymer samples with different molecular weights for the analysis of tensile properties (shown below, Figures 1 and 2) were thus prepared by adopting this method.

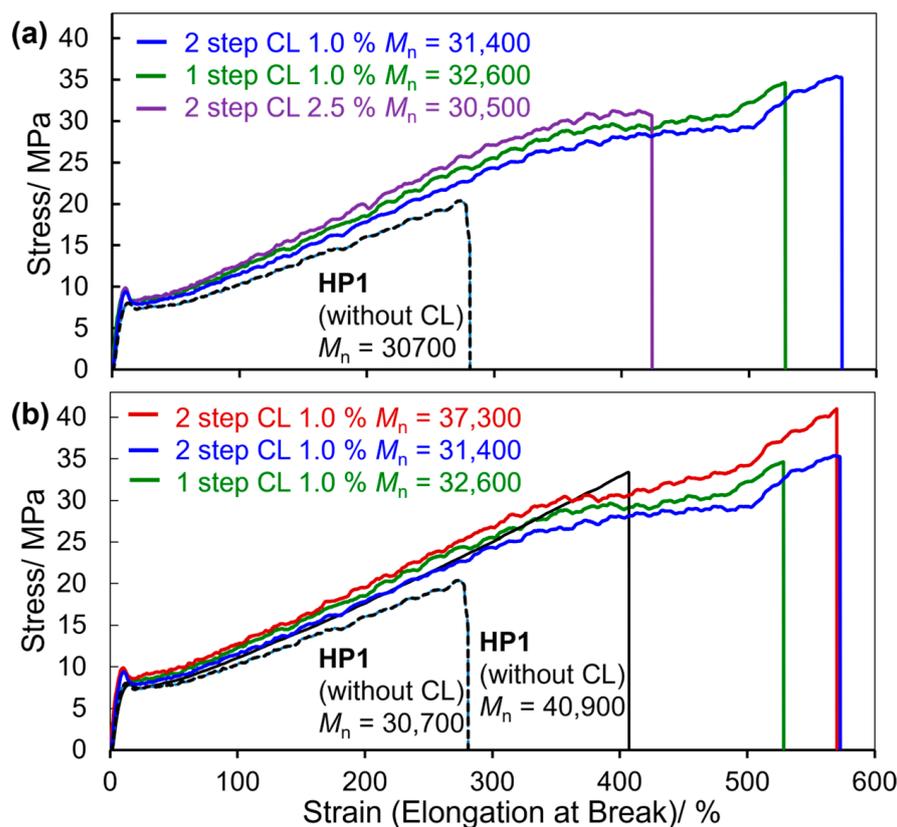


Figure 1. Tensile properties of HCP1 films (after hydrogenation). (a) Effect of approaches (1- or 2-step) and amount of CL. (b) Effect of molecular weight. Speed 10 mm/min at 23 °C.

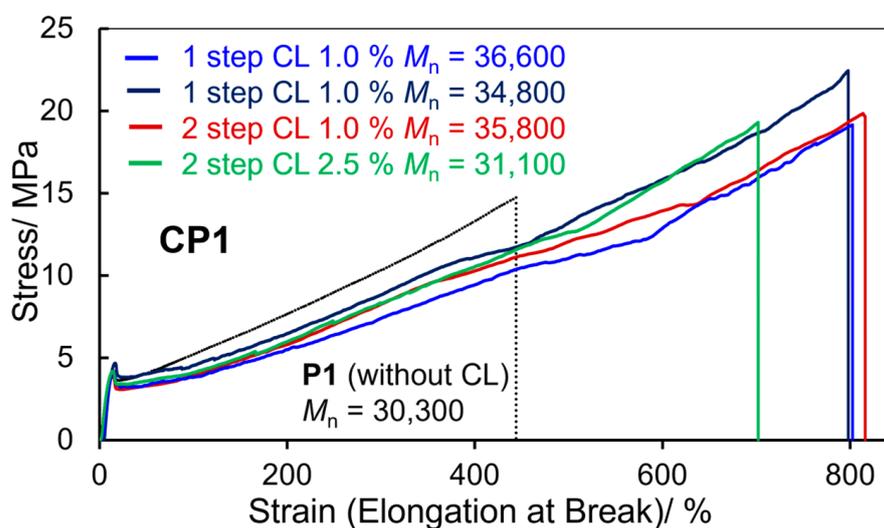


Figure 2. Tensile properties of CP1 films (before hydrogenation). Speed 10 mm/min at 23 °C.

According to the reported procedure [14], olefinic double bonds in the resultant polymers (CP1s) were hydrogenated by $\text{RhCl}(\text{PPh}_3)_3$ catalysts in toluene (Scheme 2, H_2 1.0 MPa, 50 °C, 24 h). The results are summarized in Table 2. It was revealed that, as reported previously [36], no significant changes in the M_n (as well as M_w/M_n) values were seen before/after hydrogenation, and resonances ascribed to the internal olefins disappeared in the polymer samples (HCP1s) after hydrogenation. Their uniform compositions (completion of hydrogenation) were also confirmed by DSC thermograms observed as sole melting temperatures [32]. As shown in Figure S20 (and Table S4), no significant differences in

the melting temperature were observed between linear and network polymers, whereas the T_m values in **HCP1** are higher than **CP1**, as reported previously by **P1** and **HP1** [32]. The resultant polymers are soluble in chloroform, THF, and toluene, regardless of their network structure.

Table 2. Olefin hydrogenation of the prepared polyesters (**CP1s**) by $\text{RhCl}(\text{PPh}_3)_3$ ¹.

Run	Before Hydrogenation			After Hydrogenation		
	Sample No. ²	$M_n^3 \times 10^{-4}$	M_w/M_n^3	$M_n^3 \times 10^{-4}$	M_w/M_n^3	Yield ⁴ /%
34	run 1	3.03	2.11	3.07	2.22	99
35	run 4	3.48	3.11	3.48	3.10	98
36	run 5	3.22	2.64	3.26	2.47	>99
37	run 10	2.96	4.11	2.83	4.05	98
38	run 21	3.66	2.79	3.73	2.92	96
39	run 22	3.58	3.00	3.53	2.98	97
40	run 23	3.11	4.13	3.05	3.91	>99
41	run 24	3.20	4.48	3.22	4.39	95
42	run 28	3.12	2.54	3.14	2.46	>99

¹ Conditions: 200 mg ADMET polymer, 3 mg $\text{RhCl}(\text{PPh}_3)_3$, toluene 5.0 mL, 1.0 MPa H_2 , 50 °C, 24 h. ² Run number in Table 1. ³ GPC data in THF vs. polystyrene standards. ⁴ Isolated yields by precipitation as the methanol insoluble fraction.

3.2. Tensile Properties in the Polymer Films (**CP1s**, **HCP1s**)

Small dumbbell-shaped test specimens in the resultant polymer samples were prepared by cutting the polymer sheet for measurement of their tensile properties. The polymer sheets were prepared using a hot press method according to the reported procedure [36]. The stress/strain experiments were conducted using a universal testing machine at 23 °C (speed of 10 mm/min, humidity 50 ± 10%). The selected results are shown in Figures 1 and 2, and the data are summarized in Table 3.

Table 3. Summary of the tensile properties of network polyesters (**CP1**, **HCP1**) at a speed of 10 mm/min (23 °C, humidity 50 ± 10%) ¹.

Sample	Run No. ²	CL /mol%	Method ³	M_n^4	M_w/M_n^4	Tensile Strength/MPa	Elongation at Break/%
HP1	ref ⁵	--	--	40.9	2.41	33.7 (±2.2)	413 (±13)
HP1	34	--	--	30.7	2.22	20.8 (±1.3)	282 (±14)
HCP1	36	1.0	1 step	32.6	2.47	34.7 (±0.6)	537 (±7)
HCP1	42	1.0	2 step	31.4	2.46	35.4 (±0.6)	572 (±1)
HCP1	38	1.0	2 step	37.3	2.92	36.9 (±3.8)	555 (±21)
HCP1	40	2.5	2 step	30.5	3.91	31.9 (±1.6)	457 (±65)
P1	1	--	--	30.3	2.11	15.4 (±1.2)	444 (±28)
P1	ref ⁵	--	--	39.6	1.89	17.3 (±2.2)	506 (±44)
CP1	4	1.0	1 step	34.8	3.11	18.6 (±0.5)	807 (±5)
CP1	21	1.0	2 step	36.6	2.79	24.6 (±1.1)	798 (±47)
CP1	22	1.0	2 step	35.8	3.00	21.3 (±2.0)	816 (±48)
CP1	23	2.5	2 step	31.1	4.13	19.7 (±1.5)	704 (±59)

¹ Experimental Details: see Supplementary Materials. ² Sample number in Tables 1 and 2. ³ Method in Scheme 2. ⁴ GPC data in THF vs. polystyrene standards. ⁵ Data cited from reference [16].

It should be noted that, as shown in Figure 1a, the tensile strength (stress) in the resultant network polymer films after hydrogenation (**HCP1**) became higher than that prepared in the absence of **CL** (**HP1**, linear polymer). The elongation at break (strain) was affected by the method prepared, whereas no significant effects toward the stress were observed; the polymer film prepared by the 2-step approach (addition of **CL** after 1 h polymerization) showed higher strain compared to that prepared by the 1-step approach. This might be probably due to the difference in the average length of each polymer chain between **CL** units, although we do not have clear evidence at this moment. Increased **CL** (from 1.0 mol to 2.5 mol%) led to a decrease in the strain, probably due to increased network density. As reported previously [36], both the tensile strength and the elongation break in the linear polymer (**HP1**) are affected by the M_n value [**HP1**, $M_n = 30,700$ vs. 40,900.

Figure 1b]. In contrast, in the network polymer (**HCP1**), an increase in the tensile strength (strain) was observed upon an increase in the M_n value [**HCP1**, $M_n = 31,400$ vs. $37,300$. Figure 1b].

Figure 2 shows tensile properties in the resultant unsaturated polyester films (**CP1**, before hydrogenation) prepared by the ADMET polymerization. It was also noted that both the tensile strength (stress) and the elongation at break in the resultant network polymer films (**CP1**) became higher than that prepared in the absence of **CL** (**P1**, linear polymer). As reported previously in **HP1** [36], the resultant polymer films (**CP1**) showed higher stress (elongation at break) than the saturated ones (**HCP1**), although the tensile strengths (strain) were somewhat low. In contrast to the results in the saturated polymer films (**HCP1**), it seems that the tensile properties were not affected by the method employed (1-step or 2-step), whereas the strain (elongation at break) in **CP1** decreased upon increasing the **CL** (from 1.0 mol to 2.5 mol%).

Figure 3 summarizes plots of tensile (fracture) strengths and strains (elongation at breaks) of **HP1** and **CHP1** for comparison with the conventional polymers such as linear high density polyethylene (HDPE), polypropylene (PP) and low density polyethylene (LDPE) [43]. It is clear that the resultant polymer film shows better tensile properties (tensile strength, elongation at break) than the conventional polyolefins as well as the other conventional polymers.

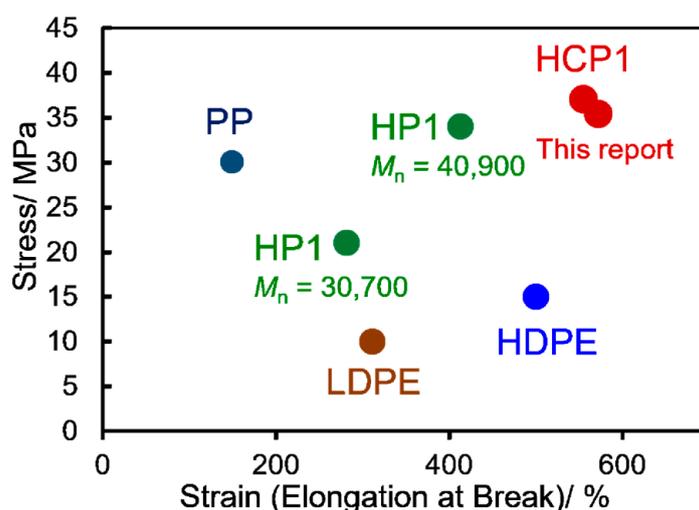


Figure 3. Plots of tensile (fracture) strengths and strains (elongation at breaks) of **HP1** and **CHP1** in this study. The plots of high density polyethylene (HDPE), low density polyethylene (LDPE), and polypropylene (PP) [43]. Tensile strength (MPa) and the elongation at break of the reference polymers are as follows: HDPE (15, 500), LDPE (10.0, 312), and PP (30, 150), respectively.

Figure 4 shows temperature dependence in the storage module (E'), loss module (E''), and loss factor, $\tan \delta$, for **HP1** and **HCP1**s measured by dynamic mechanical analyses (DMA, 1.0 Hz). The resultant polymers possessed $\tan \delta$ values with relatively narrow widths, suggesting that the resultant polymer possessed uniform composition, and the results may also suggest that the crosslinking distributions in **HCP1** were uniform [44]. However, no significant differences in their temperature dependences toward E' , E'' , and $\tan \delta$ were observed between linear (**HP1**) and network polymers (**HCP1**). It seems likely that the resultant polymers possessed relatively low crosslinking density, and polymer units between the crosslinking points are relatively long (reflect the polymer property measured by DMA analysis).

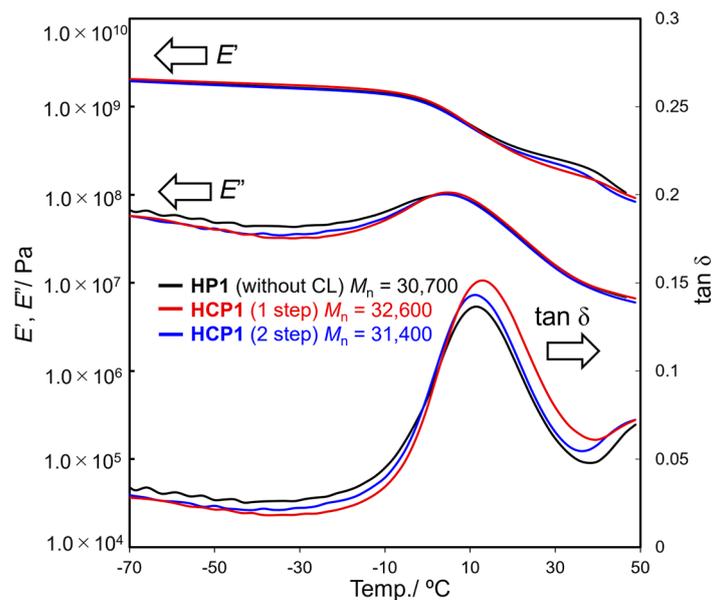


Figure 4. Temperature dependence in the storage module (E'), loss module (E''), and loss factor, $\tan \delta$, for HP1 and HCP1s (measured by DMA, 1.0 Hz).

4. Conclusions

The present report demonstrates synthesis of soluble network biobased aliphatic polyesters by ADMET polymerization of bis(undec-10-enoate) with isosorbide [M1, bis(undec-10-enyl)isosorbide diester] in the presence of tri-arm crosslinker (CL), glycerol tris(undec-10-enoate). The resultant polymers, after hydrogenation (expressed as HCP1) and prepared in the presence of 1.0 mol% CL, showed better tensile properties than the linear polymer (HP1) with similar molecular weight. The addition of CL during the polymerization (expressed as a 2-step approach) was effective for the preparation of polymer films with better tensile properties. As shown in Figure 3, the resultant polymer film shows better tensile properties than the conventional polyolefins such as linear high density polyethylene (HDPE), polypropylene (PP), and low density polyethylene (LDPE) as well as the other conventional polymers. The approach should be effective for the synthesis of other biobased polyesters to improve especially the elongation at break.

Moreover, as demonstrated in HP1 [14], the resultant polymers (HCP1s) could be depolymerized with ethanol in the presence of CpTiCl_3 (1.0 mol%, 150 °C, 24 h) to afford isosorbide and the dicarboxylic acids confirmed by NMR spectra (details are shown in the Supplementary Materials, Figures S18 and S19, and Table S3). Therefore, these polyesters could demonstrate a promising possibility of chemical recyclable, biobased aliphatic polyesters not only as alternatives to conventional polyolefins but also as functional polymers suited to a circular economy.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym16040468/s1>, (1) Selected NMR spectra of the prepared monomer, crosslinker, and polymers. (2) Selected GPC traces of the prepared polymers. (3) Additional results for the mechanical properties of the prepared polymers. (4) Depolymerization of the prepared polyesters by catalytic transesterification using CpTiCl_3 . (5) Thermal properties of the prepared polyesters.

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References

1. Stempfle, F.; Ortmann, P.; Mecking, S. Long-chain aliphatic polymers to bridge the gap between semicrystalline polyolefins and traditional polycondensates. *Chem. Rev.* **2016**, *116*, 4597–4641. [[CrossRef](#)]
2. Meier, M.A.R.; Metzger, J.O.; Schubert, U.S. Plant oil renewable resources as green alternatives in polymer science. *Chem. Soc. Rev.* **2007**, *36*, 1788–1802. [[CrossRef](#)]
3. Xia, Y.; Larock, R.C. Vegetable oil-based polymeric materials: Synthesis, properties, and applications. *Green Chem.* **2010**, *12*, 1893–1909. [[CrossRef](#)]
4. Biermann, U.; Bornscheuer, U.; Meier, M.A.R.; Metzger, J.O.; Schäfer, H.J. Oils and fats as renewable raw materials in chemistry. *Angew. Chem. Int. Ed.* **2011**, *50*, 3854–3871. [[CrossRef](#)] [[PubMed](#)]
5. Hillmyer, M.A.; Tolman, W.B. Aliphatic polyester block polymers: Renewable, degradable, and sustainable. *Acc. Chem. Res.* **2014**, *47*, 2390–2396. [[CrossRef](#)]
6. Gandini, A.; Lacerda, T.M. Monomers and polymers from chemically modified plant oils and their fatty acids. In *Polymers from Plant Oils*, 2nd ed.; Gandini, A., Lacerda, T.M., Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, USA; Scrivener Publishing LLC: Beverly, MA, USA, 2019; pp. 33–82.
7. Nomura, K.; Awang, N.W.B. Synthesis of bio-based aliphatic polyesters from plant oils by efficient molecular catalysis: A selected survey from recent reports. *ACS Sustain. Chem. Eng.* **2021**, *9*, 5486–5505. [[CrossRef](#)]
8. Biermann, U.; Bornscheuer, U.T.; Feussner, I.; Meier, M.A.R.; Metzger, J.O. Fatty acids and their derivatives as renewable platform molecules for the chemical industry. *Angew. Chem. Int. Ed.* **2021**, *60*, 20144–20165. [[CrossRef](#)]
9. Coates, G.W.; Getzler, Y.D.Y.L. Chemical recycling to monomer for an ideal, circular polymer economy. *Nat. Rev. Mat.* **2020**, *5*, 501–516. [[CrossRef](#)]
10. Häußler, M.; Eck, M.; Rothauer, D.; Mecking, S. Closed-loop recycling of polyethylene-like materials. *Nature* **2021**, *590*, 423–427. [[CrossRef](#)] [[PubMed](#)]
11. Worch, J.C.; Dove, A.P. 100th Anniversary of macromolecular science viewpoint: Toward catalytic chemical recycling of waste (and future) plastics. *ACS Macro Lett.* **2020**, *9*, 1494–1506. [[CrossRef](#)] [[PubMed](#)]
12. Nomura, K.; Aoki, T.; Ohki, Y.; Kikkawa, S.; Yamazoe, S. Transesterification of methyl-10-undecenoate and poly(ethylene adipate) catalyzed by (cyclopentadienyl)titanium trichlorides as model chemical conversions of plant oils and acid-, base-free chemical recycling of aliphatic polyesters. *ACS Sustain. Chem. Eng.* **2022**, *10*, 12504–12509. [[CrossRef](#)]
13. Ohki, Y.; Ogiwara, Y.; Nomura, K. Depolymerization of polyesters by transesterification with ethanol using (cyclopentadienyl)titanium trichlorides. *Catalysts* **2023**, *13*, 421. [[CrossRef](#)]
14. Wang, X.; Zhao, W.; Nomura, K. Synthesis of high molecular weight biobased aliphatic polyesters by acyclic diene metathesis polymerization in ionic liquids. *ACS Omega* **2023**, *8*, 7222–7233. [[CrossRef](#)]
15. Roesle, P.; Stempfle, F.; Hess, S.K.; Zimmerer, J.; Río Bartulos, C.; Lepetit, B.; Eckert, A.; Kroth, P.G.; Mecking, S. Synthetic polyester from Algae oil. *Angew. Chem. Int. Ed.* **2014**, *53*, 6800–6804. [[CrossRef](#)]
16. Quinzler, D.; Mecking, S. Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. *Angew. Chem. Int. Ed.* **2010**, *49*, 4306–4308. [[CrossRef](#)] [[PubMed](#)]
17. Stempfle, F.; Quinzler, D.; Heckler, I.; Mecking, S. Long-chain linear C₁₉ and C₂₃ monomers and polycondensates from unsaturated fatty acid esters. *Macromolecules* **2011**, *44*, 4159–4166. [[CrossRef](#)]
18. Roumanet, P.-J.; Laflèche, F.; Jarroux, N.; Raoul, Y.; Claude, S.; Guégan, P. Novel aliphatic polyesters from an oleic acid based monomer. Synthesis, epoxidation, cross-linking and biodegradation. *Eur. Polym. J.* **2013**, *49*, 813–822. [[CrossRef](#)]
19. Roumanet, P.-J.; Jarroux, N.; Goujard, L.; Le Petit, J.; Raoul, Y.; Bennevault, V.; Guégan, P. Synthesis of linear polyesters from monomers based on 1,18-(Z)-octadec-9-enedioic acid and their biodegradability. *ACS Sustain. Chem. Eng.* **2020**, *8*, 16853–16860. [[CrossRef](#)]
20. Rybak, A.; Meier, M.A.R. Acyclic diene metathesis with a monomer from renewable resources: Control of molecular weight and one-step preparation of block copolymers. *ChemSusChem* **2008**, *1*, 542–547. [[CrossRef](#)]
21. Fokou, P.A.; Meier, M.A.R. Use of a renewable and degradable monomer to study the temperature-dependent olefin isomerization during ADMET polymerizations. *J. Am. Chem. Soc.* **2009**, *131*, 1664–1665. [[CrossRef](#)] [[PubMed](#)]

22. Trzaskowski, J.; Quinzler, D.; Bährle, C.; Mecking, S. Aliphatic long-chain C₂₀ polyesters from olefin metathesis. *Macromol. Rapid Commun.* **2011**, *32*, 1352–1356. [[CrossRef](#)] [[PubMed](#)]
23. Vilela, C.; Silvestre, A.J.D.; Meier, M.A.R. Plant oil-based long-chain C₂₆ monomers and their polymers. *Macromol. Chem. Phys.* **2012**, *213*, 2220–2227. [[CrossRef](#)]
24. Stempfle, F.; Ortmann, P.; Mecking, S. Which polyesters can mimic polyethylene? *Macromol. Rapid Commun.* **2013**, *34*, 47–50. [[CrossRef](#)] [[PubMed](#)]
25. Ortmann, P.; Mecking, S. Long-spaced aliphatic polyesters. *Macromolecules* **2013**, *46*, 7213–7218. [[CrossRef](#)]
26. Lebarbé, T.; Neqal, M.; Grau, E.; Alfos, C.; Cramail, H. Branched polyethylene mimicry by metathesis copolymerization of fatty acid-based α,ω -dienes. *Green Chem.* **2014**, *16*, 1755–1758. [[CrossRef](#)]
27. Shearouse, W.C.; Lillie, L.M.; Reineke, T.M.; Tolman, W.B. Sustainable Polyesters Derived from Glucose and Castor Oil: Building Block Structure Impacts Properties. *ACS Macro Lett.* **2015**, *4*, 284–288. [[CrossRef](#)] [[PubMed](#)]
28. Llevot, A.; Grau, E.; Carlotti, S.; Greliera, S.; Cramail, H. ADMET polymerization of bio-based biphenyl compounds. *Polym. Chem.* **2015**, *6*, 7693–7700. [[CrossRef](#)]
29. Hibert, G.; Grau, E.; Pintori, D.; Lecommandoux, S.; Cramail, H. ADMET polymerization of α,ω -unsaturated glycolipids: Synthesis and physico-chemical properties of the resulting polymers. *Polym. Chem.* **2017**, *8*, 3731–3739. [[CrossRef](#)]
30. Lillie, L.M.W.; Tolman, B.T.; Reineke, M. Structure/property relationships in copolymers comprising renewable isosorbide, glucarodilactone, and 2,5-bis(hydroxymethyl)-furan subunits. *Polym. Chem.* **2017**, *8*, 3746–3754. [[CrossRef](#)]
31. Le, D.; Samart, C.; Kongparakul, S.; Nomura, K. Synthesis of new polyesters by acyclic diene metathesis polymerization of bio-based α,ω -dienes prepared from eugenol and castor oil (undecenoate). *RSC Adv.* **2019**, *9*, 10245–10252. [[CrossRef](#)]
32. Nomura, K.; Chaijaroen, P.; Abdellatif, M.M. Synthesis of biobased long-chain polyesters by acyclic diene metathesis polymerization and tandem hydrogenation and depolymerization with ethylene. *ACS Omega* **2020**, *5*, 18301–18312. [[CrossRef](#)]
33. Piccini, M.; Leak, D.J.; Chuck, C.J.; Buchard, A. Polymers from sugars and unsaturated fatty acids: ADMET polymerisation of monomers derived from d-xylose, d-mannose and castor oil. *Polym. Chem.* **2020**, *11*, 2681–2691. [[CrossRef](#)]
34. Piccini, M.; Lightfoot, J.; Castro, D.B.; Buchard, A. Xylose-Based Polyethers and Polyesters via ADMET Polymerization toward Polyethylene-like Materials. *ACS Appl. Polym. Mater.* **2021**, *3*, 5870–5881. [[CrossRef](#)]
35. Kojima, M.; Abdellatif, M.M.; Nomura, K. Synthesis of semi-crystalline long chain aliphatic polyesters by ADMET copolymerization of dianhydro-D-glucityl bis(undec-10-enoate) with 1,9-decadiene and tandem hydrogenation. *Catalysts* **2021**, *11*, 1098. [[CrossRef](#)]
36. Kojima, M.; Wang, X.; Go, L.O.P.; Makino, R.; Matsumoto, Y.; Shimoyama, D.; Abdellatif, M.M.; Kadota, J.; Higashi, S.; Hirano, H.; et al. Synthesis of high molecular weight biobased aliphatic polyesters exhibiting tensile properties beyond polyethylene. *ACS Macro Lett.* **2023**, *12*, 1403–1408. [[CrossRef](#)] [[PubMed](#)]
37. Schulz, M.D.; Wagener, K.B. ADMET Polymerization. In *Handbook of Metathesis*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2015; Volume 3, pp. 315–355.
38. da Silva, L.C.; Rojas, G.; Schulz, M.D.; Wagener, K.B. Acyclic diene metathesis polymerization: History, methods and applications. *Prog. Polym. Sci.* **2017**, *69*, 79–107. [[CrossRef](#)]
39. Chen, Y.; Abdellatif, M.M.; Nomura, K. Olefin metathesis polymerization: Some recent developments in the precise polymerizations for synthesis of advanced materials (by ROMP, ADMET). *Tetrahedron* **2018**, *74*, 619–692. [[CrossRef](#)]
40. Pribyl, J.; Wagener, K.B.; Rojas, G. ADMET polymers: Synthesis, structure elucidation, and function. *Mater. Chem. Front.* **2021**, *5*, 14–43. [[CrossRef](#)]
41. Go, L.O.P.; Nomura, K. Functional Bio-based Polymer Network Synthesis via ADMET Polymerization. In Proceedings of the 11th The International Symposium on Feedstock Recycling of Polymeric Materials, ISFR, Pattaya, Thailand, 29 November–2 December 2022.
42. Abdellatif, M.M.; Nomura, K. Synthesis of polyesters containing long aliphatic methylene units by ADMET polymerization and synthesis of the ABA-triblock copolymers by one-pot end modification and the subsequent living ring-opening polymerization. *ACS Omega* **2024**, *accepted*.
43. Wang, X.; Chin, A.L.; Zhou, J.; Wang, H.; Tong, R. Resilient poly(α -hydroxy acids) with improved strength and ductility via scalable stereosequence-controlled polymerization. *J. Am. Chem. Soc.* **2021**, *143*, 16813–16823. [[CrossRef](#)]
44. Nomura, K.; Hatanaka, Y.; Okumura, H.; Fujiki, M.; Hasegawa, K. Polymerization of 1,5-hexadiene by the nonbridged half-titanocene complex-MAO catalyst system: Remarkable difference in the selectivity of repeated 1,2-insertion. *Macromolecules* **2004**, *37*, 1693–1695. [[CrossRef](#)]

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