Review

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Review

Acyclic Diene Metathesis (ADMET) Polymerization for Synthesis of Chemically Recyclable Bio-Based Aliphatic Polyesters

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Abstract: Recent development for synthesis of bio-based long chain aliphatic polyesters by acyclic diene metathesis (ADMET) polymerization of α,ω-dienes, derived from plant oils and bio-based chemicals, like bis(10-undecenoate) with isosorbide, using ruthenium-carbene catalysts have been reviewed. Development of subsequent (one-pot) tandem hydrogenation afforded saturated polyesters under mild conditions. The polymerizations under bulk (without solvent, 80-90 ºC) or in ionic liquids (50 ºC) under vacuum conditions enabled synthesis of high molar mass polymers (M_n >30,000 g/mol). The polymerization by molybdenum-alkylidene catalyst afforded the highest molecular weight polyesters (44000–49400 g/mol, in toluene at 25 ºC) exhibiting promising tensile properties (strength and elongation at break) beyond polyethylene, polypropylene. Depolymerizations of these polyesters including closed loop chemical recycling were also demonstrated. Catalyst developments (more active, under mild conditions) play a key role for the efficient synthesis.

Keywords: bio-based; polyester; metathesis polymerization; plant oil; circular economy; chemical recycling; tensile properties; homogeneous catalysts

1. Introduction

Development of sustainable polymers from the renewable feedstocks attracts considerable attention from the viewpoints of circular economy as well as green sustainable chemistry. Hydrocarbon rich molecular biomass such as vegetable oils (castor, coconut, linseed, olive, palm, soybean, sunflower etc.) presented as triglycerides with fatty acids, or fatty acid esters (FAEs) are naturally abundant and are recognized as low-cost molecular biomass [1–11]. Study on bio-based advanced polyesters (exhibiting tunable mechanical properties and biodegradability), in particular long chain aliphatic polyesters (LCAPEs) are semicrystalline materials considered as a promising alternative of polyethylene [6,8]. The melting temperatures (T_m values) in the polyesters are generally influenced by the methylene length (and direction of dipoles called as odd-even effect) employed [6,12–14], placement of longer methylene units should be effective for obtainment of the polyesters without softening at elevated temperatures. It has been considered that the precise polymerization technique provides a new strategy and methodology for design of the macromolecular architectures.

Two condensation polymerization approaches, (i) condensation polymerization by transesterification (dicarboxylic acid and diol etc.) and (ii) acyclic diene metathesis (ADMET) polymerization (nonconjugated α,ω-dienes) and subsequent hydrogenation (Scheme 1) have been considered for the synthesis from FAEs [6,8]. The ring opening polymerization (ROP) approach from cyclic monomers can also be considered, but the method faces a limited monomer scope; the method would also face a difficulty of catalysts that enable synthesis of high molar mass polymers [15,16].

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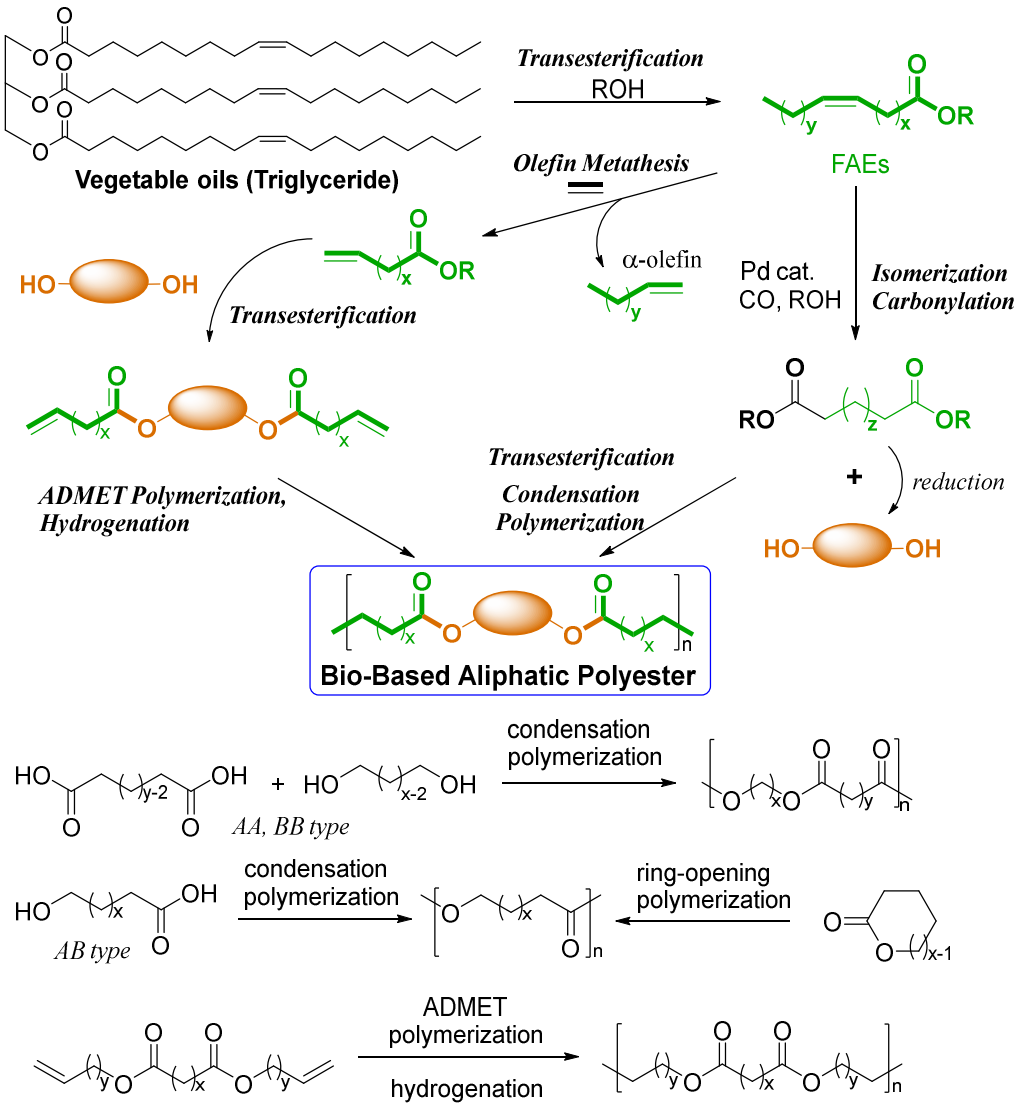

Scheme 1. Synthesis of bio-based polyesters from plant oil (triglycerides).

Conventional condensation polymerization approach through transesterification (ester bond exchange) requires high temperature with efficient removals of by product (such as alcohols, water) for obtainment of high molar mass polymers with high degree of polymerization (DP_n). For example, synthesis of poly(ethylene terephthalate) (PET), from terephthalic acid (must be purified) with excess ethylene glycol, requires high temperatures up to 290 °C under a reduced pressure [17]. The method, however, seems to be difficult to apply in synthesis of LCAPEs due to difficulty of removing diols with high boiling points (e.g., 1,12-dodecanediol, 189 °C/12 mmHg; 1,16-hexadecane diol 197-199 °C/3 mmHg). Moreover, a precise stoichiometric control (hydroxy and carboxylic groups) should be required for the purpose [6,18–20]; the polymerization with a precise stoichiometric ratio of diols (algae oil) and diesters (C_{17} and C_{19}) to afford high molar mass polymers ($M_n = 4.0\times10^4$) possessing T_m value of 99 °C [20].

Synthesis of bio-based aliphatic polyesters by adopting the ADMET polymerization [21–23] approach especially using commercially available (called Grubbs type) ruthenium-carbene catalysts have been explored by many researchers, since the reactions do not require severe conditions conducted in the condensation polymerization through transesterification (described above). In this mini review, reports concerning synthesis of bio-based aliphatic polyesters by the ADMET approach have thus been summarized.

2. Synthesis of Bio-based Aliphatic Polyesters by the ADMET Polymerization.

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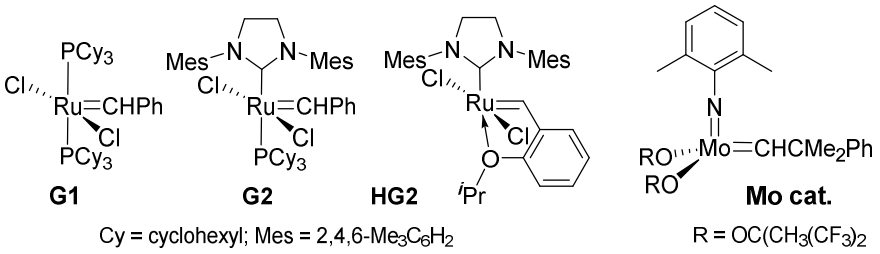
2.1. Synthesis of Aliphatic Polyesters by ADMET Polymerization and Hydrogenation.

There have been many reports concerning synthesis of bio-based polyesters by ADMET polymerization especially using commercially available (called Grubbs type) ruthenium-carbene catalysts, $RuCl_2(PCy_3)_2(CHPh)$ (**G1**; Cy = cyclohexyl), $RuCl_2(PCy_3)(IMesH_2)$-(CHPh) [**G2**; $IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene] and $RuCl_2(IMesH_2)(CH\text{-}2\text{-}O^iPr\text{-}C_6H_4)$ (**HG2**), shown in Scheme 2. The ruthenium catalysts have been employed for the purpose [8], because these complexes can be readily available and do not show strict Schlenk technique due to rather insensitivities toward water and oxygen (better functional group tolerance) [24–27]. More recently, the example by using molybdenum-alkylidene catalyst (**Mo cat.**) [28–30], shown below, was also demonstrated for synthesis of high molar mass polymers that exhibit good tensile properties [31].



Scheme 2. Ruthenium-carbene and molybdenum-alkylidene catalysts for synthesis of aliphatic polyesters by ADMET polymerization.

Synthesis of bio-based polyester, expressed as **PE1**, by the ADMET polymerization of undec-10-en-1-yl undec-10-enoate (**M1**), prepared by 10-undecenoic acid and 10-undecenol (derived from castor oil) was reported by the group of Meier in 2008 [32]. The resultant **PE1** prepared by **G2** (0.5 or 1.0 mol%, 80 ºC, 24 h, Scheme 3) possessed rather high molecular weight (M_n = 22000, 26500), and the M_n values were controlled by addition of terminal olefins, such as methyl 10-undecenoate, stearyl acrylate [32]. In contrast, the group reported that the polymerization of bis(undec-10-enoate) with isosorbide (**M2**, Scheme 3) conducted at 70-100 ºC under bulk conditions yielded rather low molecular weight polymers (**PE2**, Table 1) [33], whereas the M_n values seemed improving when the polymerizations were conducted at high temperature and/or under nitrogen purge (for removal of ethylene by-produced). This is probably due to catalyst decomposition by conducting the reaction at 70-100 ºC [34–39], because these ruthenium catalysts have been known to decompose under these conditions to afford ruthenium-hydride species [36] and/or nano particles [38], which induce olefin isomerization and/or certain side reactions by formed radicals [34–39]. **G2** showed more significant degree of olefin isomerization compared to **G1**, and the percentage of isomerization (estimated by GC-MS, after treating the mixture with MeOH-H_2SO_4 under reflux conditions) [33]. Later, degree of the isomerization could be extensively suppressed when the polymerizations were conducted in presence of benzoquinone [40].

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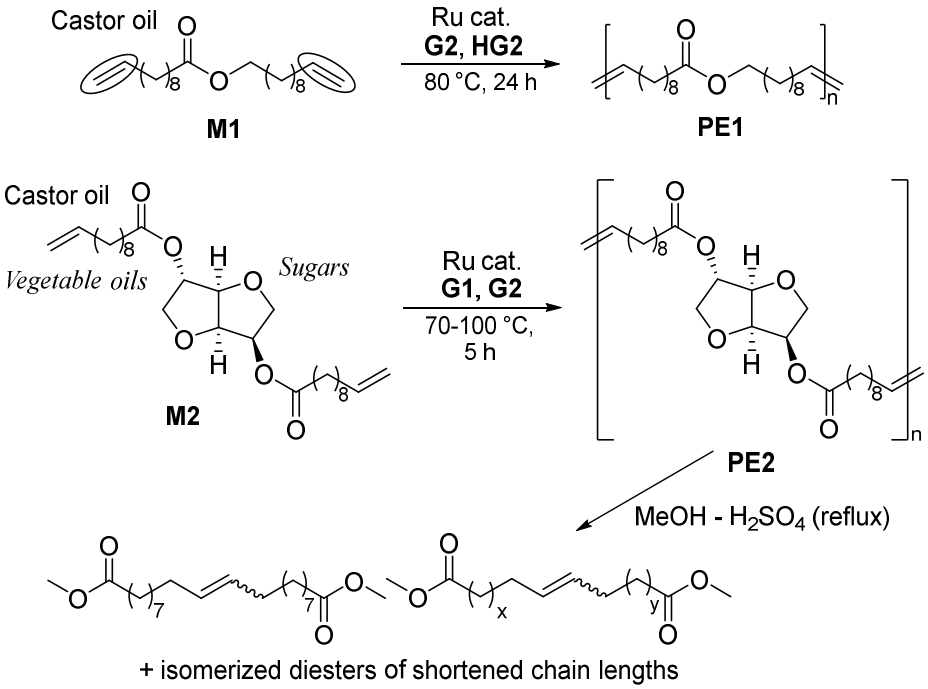

Scheme 3. ADMET polymerization of castor oil derived monomers (**M1**, **M2**) [32,33].

Table 1. Synthesis of **PE2** by ADMET polymerization using ruthenium catalysts [33].[1]

Ru cat.	temp. / °C	nitrogen purge[2]	M_n[3]	M_w/M_n[3]	isomerization[4] / %
G2	60	no	5600	1.65	48
G1	70	no	4400	1.57	3
G2	70	no	6000	1.71	49
G1	80	no	4750	1.56	4
G2	80	no	6100	1.61	69
G1	80	yes	6600	1.77	3
G2	80	yes	8400	1.75	76
G1	90	no	5450	1.69	3
G2	90	no	6200	1.65	66
G1	100	no	5000	1.61	42[5]

[1] Conditions: Ru cat 1.0 mol%, 5 h. [2] N_2 purge during polymerization. [3] GPC in THF vs polystyrene stds. [4] Isomerized diesters (%) estimated with GC-MS after transesterification. [5] Unidentified side-products.

ADMET polymerization of **M1** by **G1** under high vacuum for two days gave **PE1** (M_n = 28000, M_w/M_n = 1.9) and subsequent hydrogenation (Pd/C, 50 bar H_2, 60 ºC) gave the saturated polyester (**HPE1**, PE-20.20, Scheme 4) [41]. The T_m value (103 ºC) observed was somewhat low compared to the **HPE1** prepared by condensation polymerization of 1,20-eicosanedioic acid with eicosane-1,20-diol (T_m = 108 ºC), to form 'regio-regular' ester groups, C(O)-O, alignment in the polymer chain (Scheme 4). It was thus suggested that the microstructural control directly affects the thermal property, as described above [6,14]. ADMET polymerizations of α,ω -dienes with different methylene chain length, di(icos-19-en-1-yl)tricosanedioate (**M3**), di(tricos-22-en-1-yl)tricosanedioate (**M4**), by using **G1** and the subsequent olefin hydrogenation by $Ru(CHOEt)Cl_2(PCy)_2$ (40 bar H_2, 70 ºC, 2 d), prepared from **G1**, yielded the corresponding PE-38.23 (**HPE3**), PE-44.23 (**HPE4**), respectively (Scheme 4) [42]. Polycondensation of 1,26-hexacosanedioate, prepared by cross metathesis of erucic acid, with the corresponding diol (prepared by the reduction with $LiAlH_4$) with $Ti(OBu)_4$ also gave the corresponding polyester (**HPE5**, PE-26.26, T_m = 114 ºC) [43]. The thermal property (T_m values) in the resultant LCAPEs with different methylene lengths, prepared by ADMET [42] and polycondensation [43,44] approaches, revealed that the T_m value reached to a constant value

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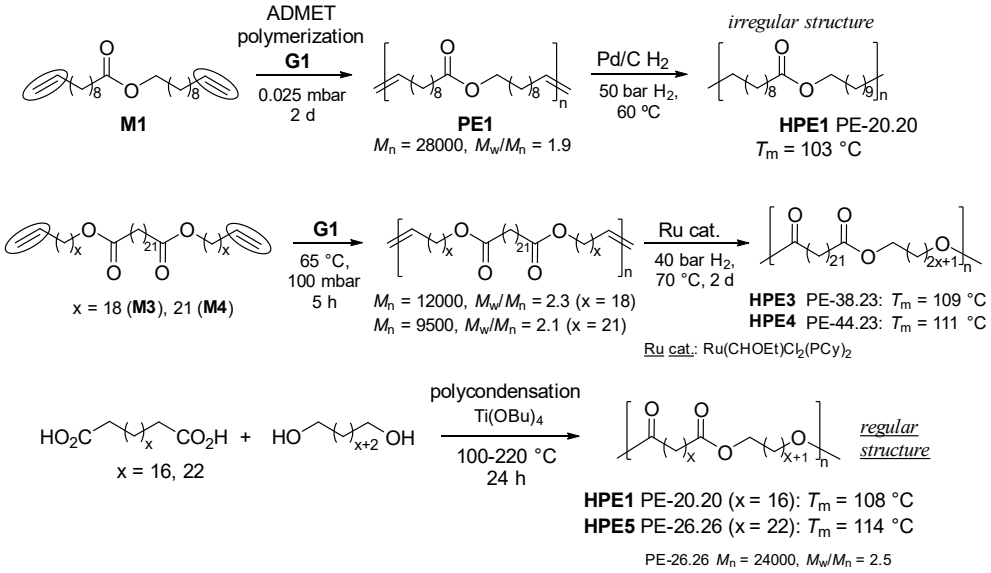
(Figure 1a) [42]. A linear relationship between the T_m values and the number of ester group in 1000 carbon was observed (Figure 1b) [42]. Polyesters, PE-26.26, PE-12.26 and PE-4.26 [43], PE-18,18 [45] were also prepared by the polycondensation.



Scheme 4. Synthesis of linear polyesters(LCAPEs) [41–43].

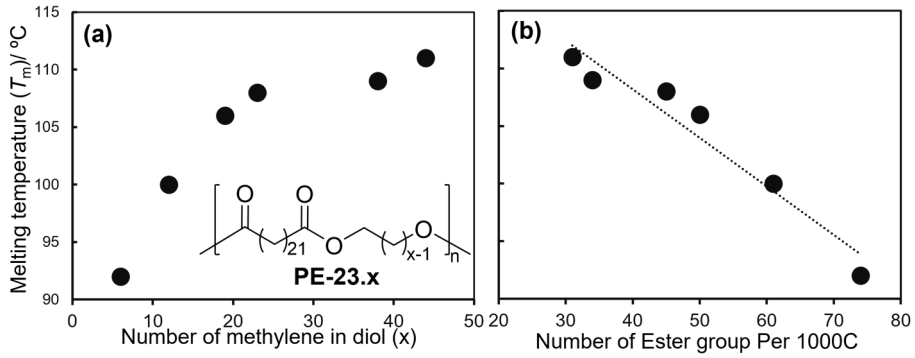


Figure 1. Plots of melting temperature (T_m) vs number of (a) methylene unit (x) in diol, (b) ester groups per 1000C (methylene) in PE-23.x [42].

Recently, one-pot synthetic method for the bio-based aliphatic polyesters by the ADMET polymerization and the subsequent hydrogenation was demonstrated (Scheme 5) [46]. The polymerization of bis(undec-10-enoate)s with isosorbide (**M2**), isomannide (**M6**), 1,3-propanediol (**M7**), 1,4-cyclohexanedimethanol (**M8**), derived from castor oil and glucose, in chloroform by **G2** or **HG2** under reduced pressure at 50 ºC gave unsaturated polymers (expressed as **PE2**, **PE6–PE8**, respectively) [46]. The M_n values in the resultant polymers (M_n = 11900-15900) were somewhat higher than those reported previously (M_n = 4400-8400) conducted at 70-100 ºC [33], and the M_n values did not change even under rather scale up conditions [46]. One reason for obtainment of high molecular weight could be due to that degree of the catalyst decomposition was significantly suppressed by conducting the polymerization at 50 ºC (and the polymerization was conducted under continuous reduced pressure) [46].

As described above (Scheme 4) and below [47], the conventional olefin hydrogenation requires high hydrogen pressure and high temperature after isolation of unsaturated polyesters after the ADMET polymerization [41,42,47]. In contrast, one-pot hydrogenation under rather mild conditions (1.0 MPa, 50 ºC, 3 h) was demonstrated upon addition of small amount of Al_2O_3 (ca. 1 wt%) into the reaction mixture (Scheme 5). The completion of the olefin hydrogenation was confirmed by DSC thermograms (uniform composition) due to difficulty (accuracy of integration of olefinic protons)

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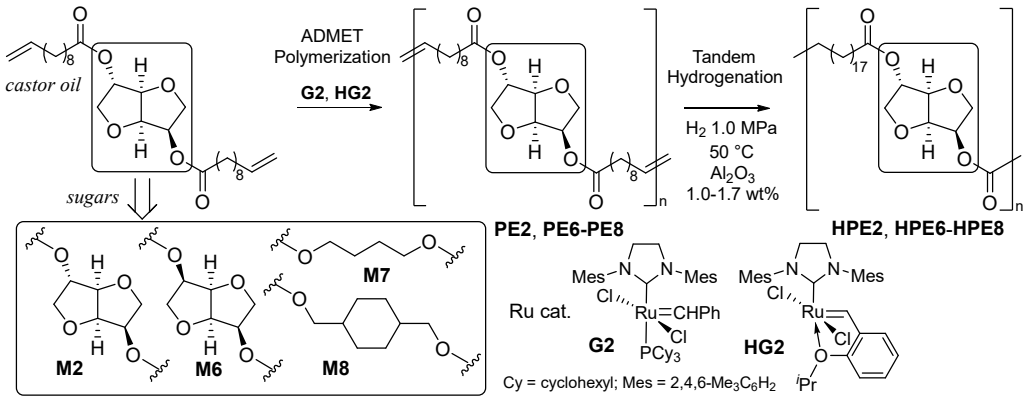
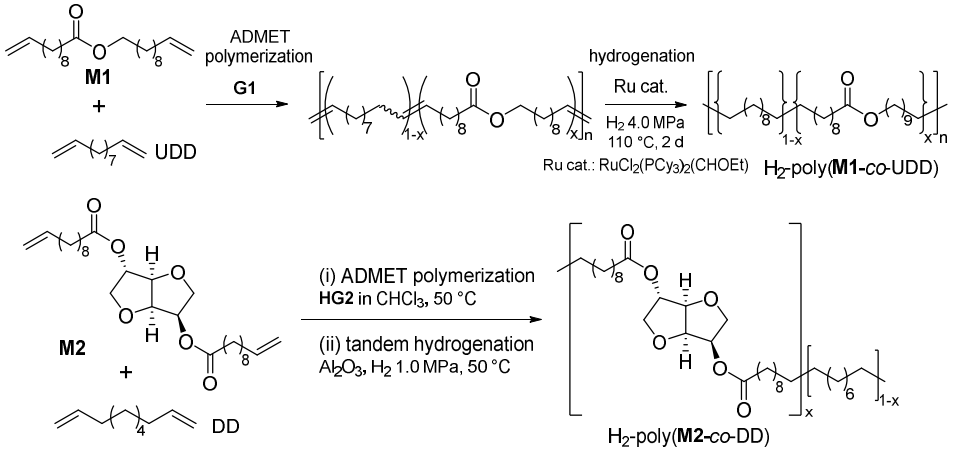
in the ^{1}H NMR spectra. No significant differences in the M_n values and M_w/M_n values were observed before/after hydrogenation [46].



Scheme 5. One-pot synthesis of bio-based polyesters by Ru-catalyzed ADMET polymerization and hydrogenation [46].

As shown in Figure 1b, melting temperature (T_m values) in the polyesters are influenced by number of the methylene unit (n). As shown in Scheme 6, the copolymerization of **M1** with undeca-1,10-diene (UDD) followed by olefin hydrogenation (H_2 40 bar, 110 °C, 2 d) gave various LCAPEs with different chain lengths (from 0.9 through 52.6 ester groups per 1000 carbon), expressed as H_2-poly(**M1**-*co*-UDD) [47]. A linear correlation of the melting temperature (T_m values) with average number of ester groups per methylene units was thus demonstrated, whereas the ester group was incorporated in a random manner. The similar trend was observed in the copolymerization of **M2** with 1,9-decadiene (DD) and the subsequent one-pot hydrogenation [48]. The saturated polymers possess a T_m value in range of 71.7–107.6 °C, depending on the molar ratio of **M2** and DD.



Scheme 6. ADMET Copolymerization undec-10-en-1-yl undec-10-enoate (**M1**) or bis(undec-10-enoate) with isosorbide (**M2**) with nonconjugated dienes, and subsequent hydrogenation [47,48]. .

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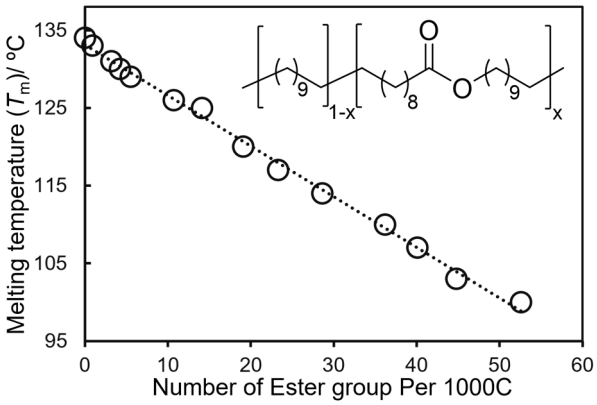

Figure 2. Plots of melting temperature (T_m) vs number of ester groups per 1000C (methylene units) in the hydrogenated copolymers, H2-poly(**M1**-*co*-UDD)s [47].

The polymerizations of bis(undec-10-enoate)s with *D*-xylose (1,2-*O*-isopropylidene-*α*-*D*-xylofuranose , **M9c**), *D*-mannose (**M10**) by **G2** were studied under dynamic vacuum (0.1 mbar) without solvent (bulk) conditions (60-90 ºC, 20 h, Scheme 7) [49]. The molecular weights in the resultant polymers (**PE9c**, **PE10**) were affected by the polymerization temperature employed as well as monomer/Ru molar ratios. Conducting the polymerization at 90 ºC under low Ru concentration (0.1 mol%) seemed to be the optimized conditions (**PE9c**: Ru, M_n = 7.14-7.16×10^4, M_w/M_n = 2.2-2.3, **PE10**: M_n = 3.24×10^4, M_w/M_n = 2.4) [49]. Due to the polymerization was conducted without solvent, the PDI (M_w/M_n) values became rather high due to difficulty to control stirring [49]. Later, the polymerizations of *D*-xylose diester analogues with different methylene length (**M9**, x = 0, 2, 8, Scheme 7) and the corresponding diether analogues (**M11**) were explored [50]. The M_n values in the resultant polymer decreased upon decreasing the methylene length, and the monomers that do not possess methylene spacer [50]. Some polymerization runs failed due to precipitation or difficulty for isolation [50]. The resultant unsaturated polymers were amorphous except **PE11a**, and both glass transition temperatures (T_g) increased after reducing the olefinic double bonds by treating with *p*-toluenesulfonyl hydrazide as a reducing agent; most of the resultant saturated polymers (**HPE9** and **HPE11**) are amorphous except **HPE9a** and **HPE11a** derived from castor oil (10-undecenoate), suggesting that placing the methylene spacer is important (as shown in Figures 1a, and 2) [50]. The resultant hydrogenated polymer films, especially **HPE11a** oriented film exhibited good tensile strength (43 MPa) with elongation at break of 155%, but the hot press film showed much less tensile strength (7.8 MPa) with improved elongation at break (667 %) [50].

Syntheses of polyesters containing vanillin (**PE12**) [51] afforded high molecular weight **PE12** (M_n = 10000, M_w/M_n = 1.6) possessing T_g value of 4 ºC (Scheme 7), whereas the polymerization of 4-allyl-2-methoxyphenyl 10-undecenoate (**M13**) by **G2** gave amorphous high molar mass polymers with low PDIs (M_w/M_n) with T_g at -9.6 ºC [52]. The ADMET polymerization of **M13** in the presence of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) gave rather high molar mass network polymers [52].

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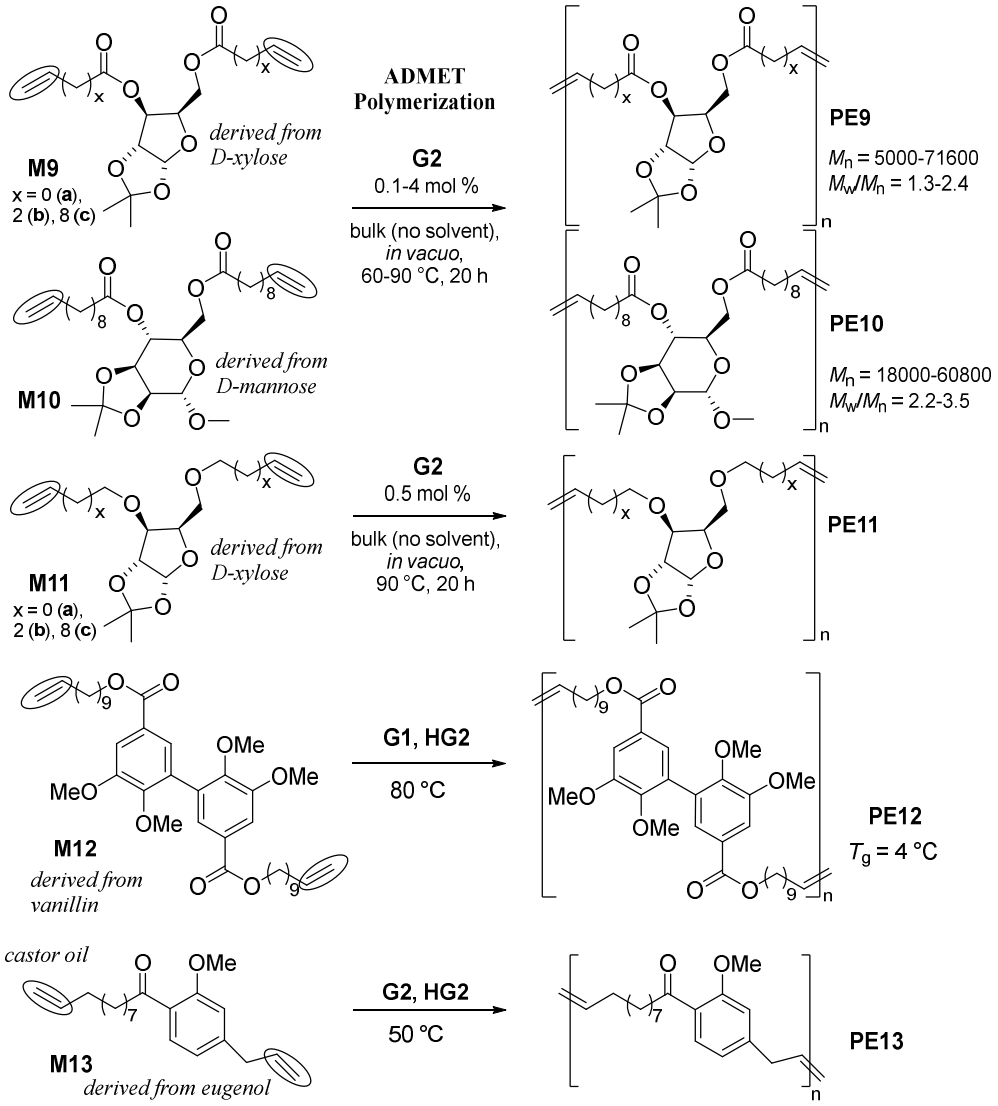

Scheme 7. ADMET polymerization of α,ω-dienes containing *D*-xylose, *D*-mannose, vanillin, and eugenol as the monomer unit [49–52].

Polymerization of trehalose bis(10-undecenoate) (**M14**) by **HG2** (4.0 mol%) in THF at 45 ºC for 24 h (Scheme 8) gave the semicrystalline polymers (**PE14**) possessing high molecular weight with unimodal molecular weight distribution (M_n = 13200, M_w/M_n = 2.1) with higher T_m value (156 ºC) [53]. Both molecular weight and the melting temperature (T_m values) in the resulting copolyesters with undec-10-en-1-yl undec-10-enoate (**M1**) decreased with increase of the percentage of **M1** [53].

Polymerization of bis(10-undecenoate)s with isosorbide (**M2**) and glucarodilactone (**M15**) and the copolymerization with different molar ratios were conducted in the presence of methyl-10-undecenoate (MU, 1.0 mol%) by using **G2** (1.0 mol%) at 80 ºC for 16 h under reduced pressure (Scheme 8) [54]. MU was employed as the monofunctional chain stoppers (chain transfer reagent by placement of MU unit as the end group) [54]. The resultant polymers possessed high molecular weights with unimodal molecular weight distributions. The copolymerizations with bis(hydroxymethylfuran) undecenoate (**M16**) were conducted [55]. The resultant **PE2** possessed the low T_g value (-10 ºC) compared to **PE15** (T_g = 32 ºC), and the homopolymers, **PE2** and **PE15**, were brittle materials, whereas these copolyesters were rubbery materials possessing better tensile properties, elastic behavior as well as shape memory properties.

Copolymerizations of α,ω-dienes (linear **M17** and *n*-hexyl branched **M18**), derived from castor oil and vernonia oil, by **G1** at 85 ºC, gave the LCAPEs containing branching in certain percentage (after subsequent hydrogenation by Pd/C, Scheme 8) [56]. These polymers were considered as

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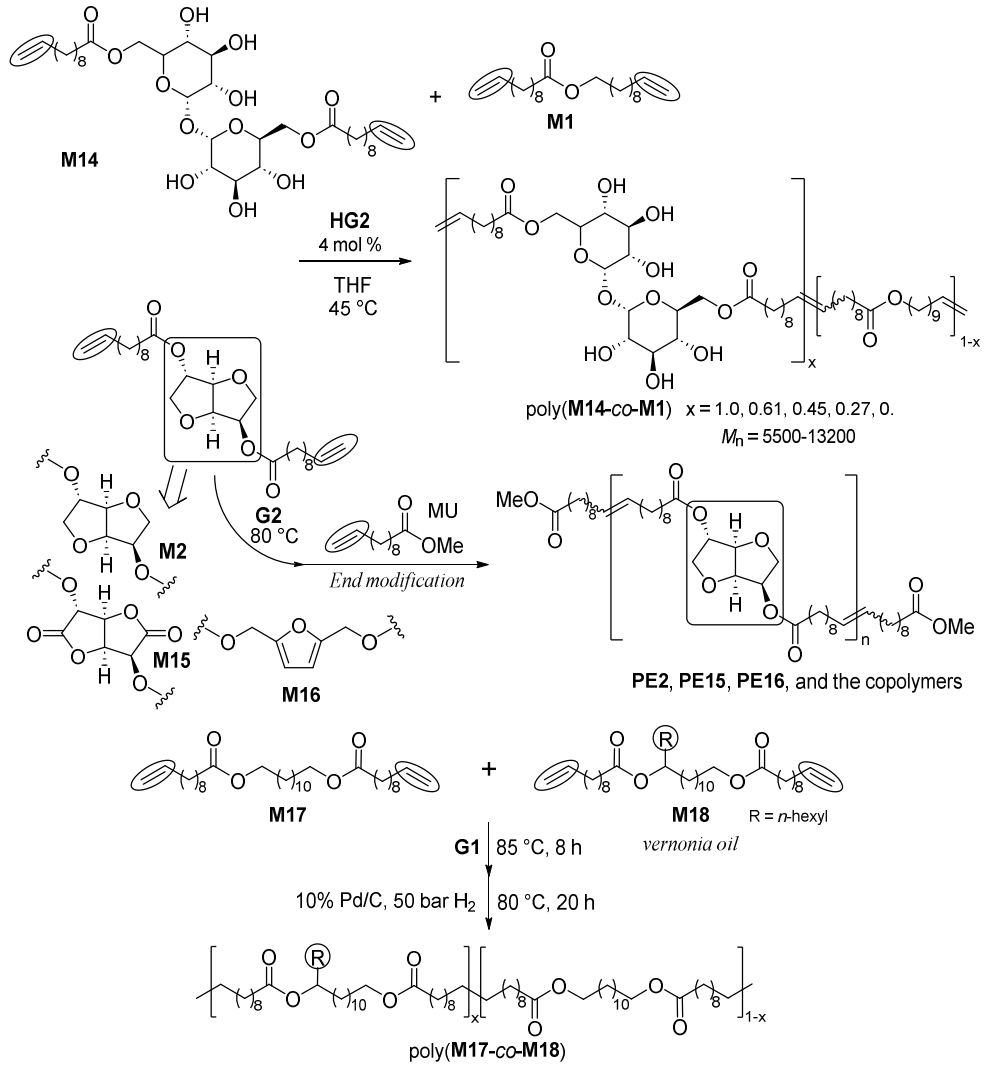
LLDPE (linear low-density polyethylene) and VLDPE very low-density polyethylene) mimics. However, their DSC thermograms possessed multiple melting temperatures, suggesting the composition in the resultant copolymers are not uniform [56].



Scheme 8. Synthesis of bio-based copolyesters with different molar ratios [53–55].

2.2. Synthesis of High Molecular Weight Polymers Exhibiting Tensile Properties Beyond Polyethylene, Polypropylene.

In spite of many reports for synthesis of the bio-based aliphatic polyesters by ADMET polymerization of α,ω-diene monomers containing carbohydrate unit (such as **M2**, **M6**, **M9**, **M10**, **M14**, **M15**) using ruthenium catalysts [33,46,49,50,53–55], however, reports for synthesis of high molecular weight polymers (ca. M_n = >30,000 considered for better mechanical property as film, shown below) has been limited so far (Scheme 9) [50,54,55]. The catalyst decomposition can be highly considered, when the metathesis polymerizations (reactions) were conducted at high temperature (70–100 ºC) and the subsequent isomerization and/or undesired side reaction caused by the formed radicals were known [34–39]. The catalyst decomposition also causes a difficulty in separation of metal (present as the ruthenium metal, particles) from the resultant polymers, and this is often observed in metathesis polymerization chemistry especially using ruthenium catalysts. Moreover, the reported synthetic methods were conducted under direct vacuum and bulk conditions without solvent [50,54,55], the method would thus face a difficulty for stirring with high viscosity [50] and was applicable to process for synthesis of amorphous materials or semicrystalline materials with T_m values below 90 ºC. Therefore, development of the methods in the solution polymerization in

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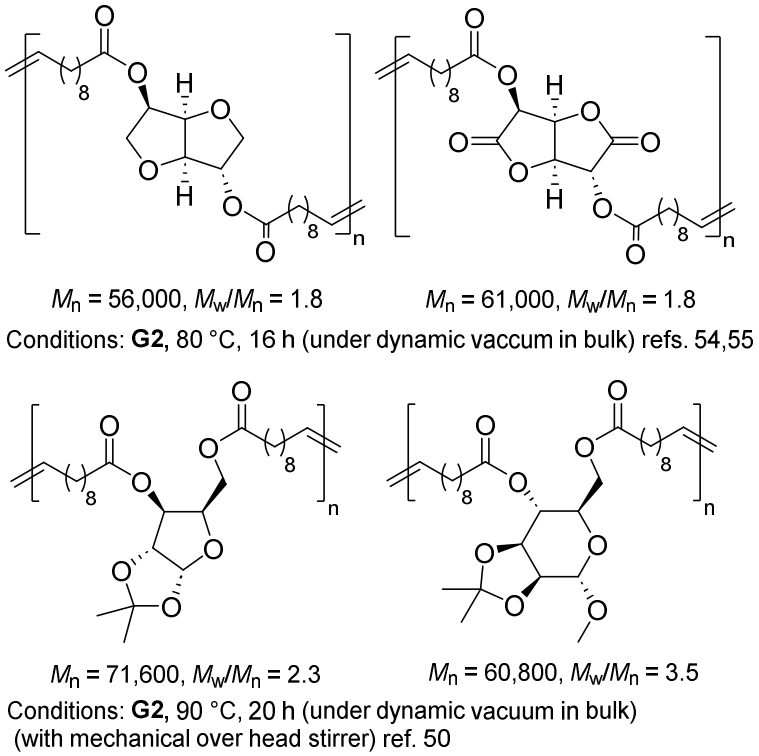
the presence of appropriate solvent seems to be better in terms of better process control (by lowering viscosity of the reaction mixture under rather mild conditions to avoid the catalyst decomposition) and of wide monomer scope.



Scheme 9. Selected reports for synthesis of high molecular weight aliphatic polyesters by acyclic diene metathesis (ADMET) polymerization of α,ω-diene monomers containing carbohydrate units [50,54,55].

The ADMET polymerization is the condensation polymerization by-producing small molecules (ethylene) and the removal is quite effective for obtainment of high molar mass polymers under certain equilibrated conditions. Conducting the polymerization under continuous dynamic vacuum and bulk conditions [50,54,55] is thus effective for the purpose. Consideration of these points, ionic liquids (ILs) can be thus considered as the ideal solvents not only due to their no (or extremely low) vapor pressure, ability for providing the homogeneous conditions with their good miscibility with polymers, organic compounds, and with metal catalysts, but also due to their high stability ranging from -30 to >300 ºC [57–64]. Although olefin metathesis reactions in ILs have been known, however, the reported examples in the ADMET polymerization still have been limited [65–70].

More recently, synthesis of high molecular weight polymers (**PE2**, M_n = 32,200–39,200) was demonstrated in the polymerization of α,ω-diene monomer [**M2**, dianhydro-*D*-glucityl bis(undec-10-enoate)] using **HG2** catalyst in ionic liquids (ILs) under continuous vacuum conditions at 50 ºC (Scheme 10) [71]. The M_n values were apparently higher than those reported previously (M_n = 5600–14700) [33,46]. 1-*n*-Butyl-3-methyl imidazolium hexafluorophosphate, [Bmim]PF_6, and 1-*n*-hexyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide, [Hmim]TFSI, were found to be effective as solvent among a series of the imidazolium salts and the pyridinium salts. As summarized in Table 2, the method is also effective for syntheses of high molar mass polymers containing isomannide (**PE6**), 1,4-cyclohexanedimethanol (**PE8**), and 1,4-butanediol (**PE7**) units as the diol segment in place of isosorbide (**PE2**); the M_n values did not decrease even under the scale-up conditions (300 mg → 1.0 g scale) [71]. Tandem hydrogenation of the resultant unsaturated polymers (**PE2**) in [Bmim]PF_6–toluene biphasic system upon addition of Al_2O_3 (H_2 1.0 MPa at 50 ºC) gave the corresponding saturated polymers (**HPE2**).

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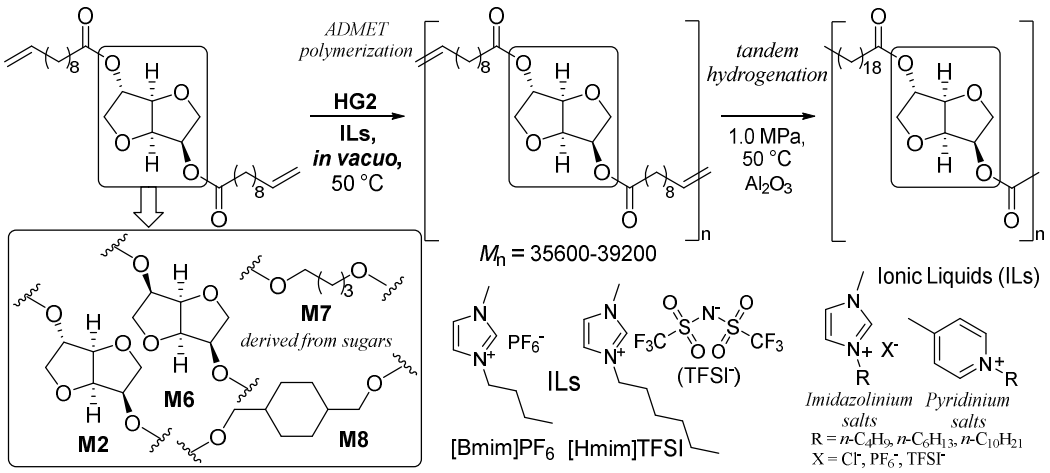

Scheme 10. Synthesis of high molecular weight bio-based polyesters by ADMET polymerization in ionic liquids (ILs) and tandem hydrogenation, and depolymerization by olefin metathesis, transesterification [71].

Table 2. ADMET polymerization of **M2**, **M6**–**M8** by **HG2** in [Hmim]TFSI.[1]

monomer	yield[2]/ %	M_n[3]	M_w/M_n[3]
M2	93	39,200	1.95
M2[4]	86	37,500	1.91
M6	92	26,000	1.95
M7	89	33,400	2.30
M7[4]	87	34,900	1.82
M8	94	38,800	3.38

[1] Conditions: Monomer 300 mg in IL 0.14 mL [initial conc. 4.48 M (**M2**), 4.48 M (**M6**), 5.07 M (**M7**), 4.69 M (**M8**)], **HG2** 1.0 mol%, 50 ℃ *in vacuo*. [2] Isolated yield. [3] GPC data in THF versus polystyrene standards. [4] Reaction scale: monomer 1.0 g in [Hmim]TFSI 0.30 mL [initial concentration: 6.97 M (**M2**), 7.80 M (**M7**)].

As described above, the polymerization of **M2** conducted in ILs with continuous removal of ethylene by-produced afforded high molar mass polymers (Scheme 10) [71], whereas the polymerization conducted in toluene or $CHCl_3$ (even under optimized conditions with careful removal of ethylene) afforded polymers of M_n values up to 15000 [46]. Development of the method without using (expensive) ILs could be favored from the practical point of view.

We demonstrated more recently that synthesis of higher molar mass polymers (M_n = 44000–49400 g/mol) has been achieved by the polymerization in toluene by using the molybdenum-alkylidene catalyst, $Mo(CHCMe_2Ph)(2,6\text{-}Me_2C_6H_3)[OC(CH_3)(CF_3)_2]$ (**Mo cat.**, Scheme 11) [31]. As summarized in the selected results in Table 3, the M_n values were affected by the **M2**/Mo molar ratios and amount of toluene employed. As observed in the conventional ADMET polymerization, the polymerization with low catalyst loading under high initial monomer conditions should be suited to this condensation polymerization; it seemed that the M_n value in **PE2** increased with increasing the reaction scale [90.5 (43.5 mg) → 261 μmol (543 mg)] with increasing the initial monomer concentration (by varying the amount of toluene) [31]. The method is applicable to the other monomers (**M6**, **M19**). Olefinic double bonds in the resultant polymers were hydrogenated by using rhodium catalyst under mild conditions (1.0 MPa, 50 ºC), and no significant changes in the M_n values as well as the PDI values in the polymers after hydrogenation were observed.

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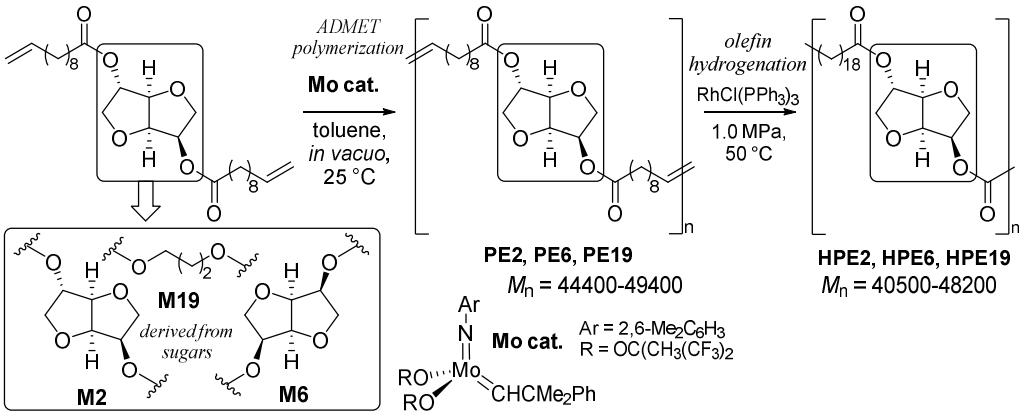

Scheme 11. Synthesis of high molecular mass polyesters by ADMET polymerization using molybdenum catalyst [31].

Table 3. ADMET polymerization of **M2**, **M6**, and **M19** by molybdenum catalyst (25 ºC, 6 h) [31]. [1]

monomer (μmol)	cat./ mol%	yield [2]/ %	M_n [3] / g·mol^{-1}	M_w/M_n [3]
M2 (90.5)	5.0	99	16000	1.79
M2 (90.5)	2.5	90	25100	1.43
M2 (90.5)	1.0	88	34400	1.49
M2 (272)	1.0	88	46100	2.08
M2 (272)	1.0	91	46100	1.84
M6 (272)	1.0	87	34800	1.87
M19 (272)	1.0	99	67200	2.27
M2 (272)	0.5	90	48700	2.04
M2 (543) [4]	0.5	91	49400	2.47

[1] Conditions: Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)[OC(CH$_3$)(CF$_3$)$_2$]$_2$ (**Mo**), toluene 0.72 mL, quenched by C$_6$H$_5$CHO or 4-Me$_3$SiOC$_6$H$_3$CHO (for termination through Wittig-type cleavage). [2] Isolated yield (as MeOH insoluble fraction). [3] GPC data in THF (at 40 ºC) *vs* polystyrene standards. [4] Toluene 1.0 mL.

It should be noted that both tensile strength (stress) and elongation at break (strain) in the prepared polymer films of **HPE2** increased remarkably upon increasing the M_n value (Figure 3) [31]; a fairly good linear correlation was observed between the stress and the strain; the **HPE2** sample with the highest M_n value (M_n = 48200) exhibited the tensile strength of 39.7 MPa along with the elongation at break of 436 %. The value is higher than not only PE-18,18, prepared from C$_{18}$ dimethyl dicarboxylate and the corresponding diol by a condensation polymerization [9], but also poly(lactic acid) (PLA), poly(ethylene terephthalate) (PET), high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP) [31,72]. The **PE2** sample before hydrogenation showed higher strain (elongation at break) with less stress (tensile strength) compared to **HPE2**, and the isomannide-based **HPE6** showed similar tensile property to the isosorbide-based **HPE2** [31]. Importance of development of synthetic method for synthesis of high molar mass polymer by the ADMET polymerization has thus been demonstrated [31].

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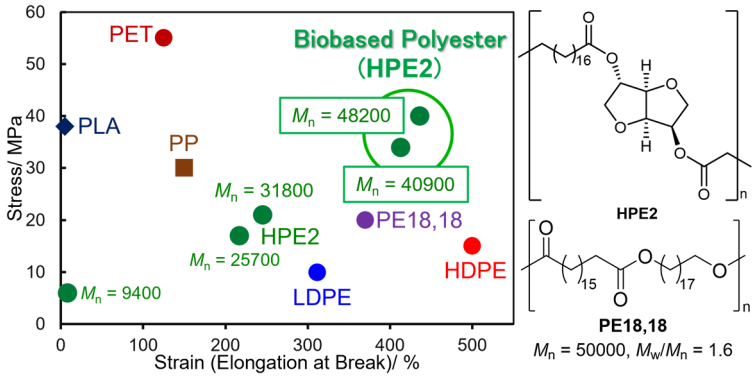

Figure 3. Plots of tensile (fracture) strengths and strains (elongation at breaks) of **HPE2** with different M_n values. The plots of PE18.18 (polyester-18.18) [9], commercially available polyethylene terephthalate (PET), poly(lactic acid) (PLA), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) [31].

2.3. Chemical Recycling of Polyesters.

PE18,18, prepared by condensation polymerization of 1,18-octadeca dicarboxylic acid with 1,18-octadecanediol, was treated with MeOH (150 ºC, 12 h) to give a solid mixture consisting of dicarboxylic acid and diol after MeOH removal. The resultant solid was used for the subsequent condensation polymerization with $Ti(O^nBu)_4$ to yield recycled PE18,18 with high molecular weight (M_n = 79000, M_w/M_n = 1.9, Scheme 12) [9]. Moreover, treatment of polycarbonate (PC18, M_n = 90000, M_w/M_n = 2.7), prepared by condensation polymerization of 1,18-octadecane diol with diethyl carbonate (DEC) in the presence of LiH, with 10 wt% KOH ethanol solution (at 120 ºC, 24 h) gave 1,18-octadecanediol exclusively (yield 98 %, purity 99 % after recrystallization from MeOH). The subsequent polycondensation with DEC gave recycled PC18 without loss of the M_n value (M_n = 70000, M_w/M_n = 3.4), which exhibited similar properties as the fresh one [9]. These results indicate a possibility of closed loop chemical recycling.

More recently, exclusive acid-, base-free chemical conversions of polyesters [poly(ethylene adipate) (PEA), poly(butylene adipate) (PBA), poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT)] to the corresponding monomers (diethyl adipate, diethyl terephthalate, ethylene glycol, 1,4-butane diol) by transesterification with ethanol using $Cp'TiCl_3$ (Cp' = Cp, Cp*) catalyst were demonstrated [73,74]. The depolymerizations proceeded completed conversions (>99 %) of PET, PBT to afford diethyl terephthalate and ethylene glycol or 1,4-butanediol exclusively (selectivity >99 %, 150-170 ºC, Ti 1.0 or 2.0 mol%) [74]. The resultant reaction mixture after the depolymerization of PBA with ethanol by $CpTiCl_3$ catalyst (1.0 mol%, 150 ºC, 3 h), consisting of diethyl adipate and 1,4-butanediol, was heated at 150 ºC *in vacuo* for 24 h to afford high molecular weight recycled PBA with unimodal molecular weight distribution (M_n = 11800, M_w/M_n = 1.6, Scheme 12), strongly demonstrating a possibility of one pot (acid-, base-free) closed loop chemical recycling [74]. The method can also be applicable to the bio-based aliphatic polyesters, reaction of **HPE2** with ethanol by $CpTiCl_3$ afforded the corresponding dicarboxylic acid and isosorbide exclusively [71].

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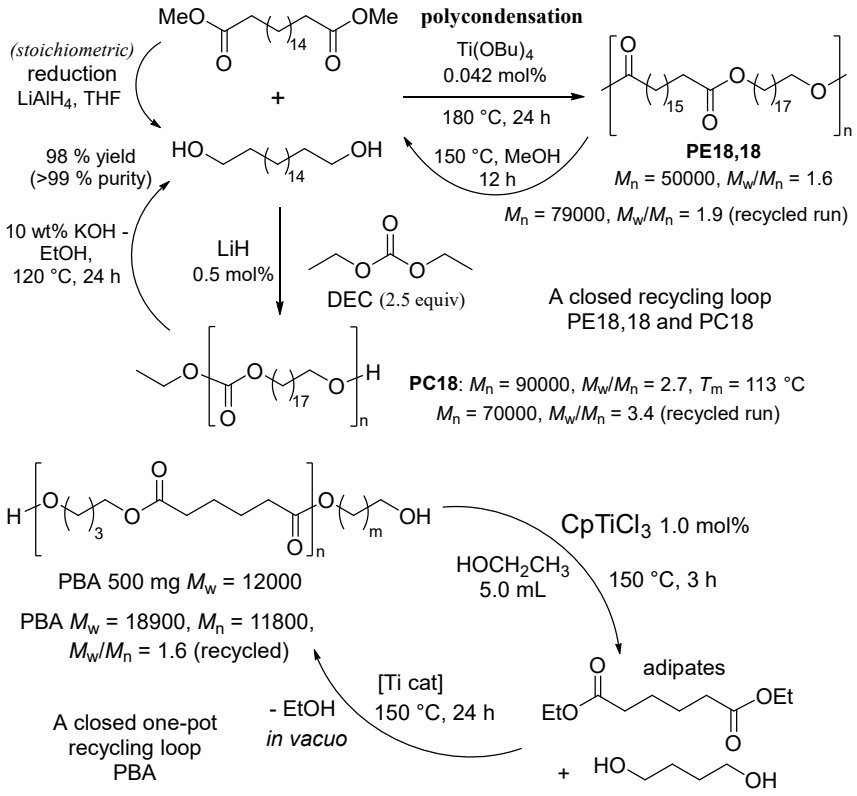

Scheme 12. Closed loop chemical recycling of polyesters [9,74].

3. Concluding Remarks

This review summarizes recent development for synthesis of bio-based LCAPEs by acyclic diene metathesis (ADMET) polymerization of α,ω-dienes, derived from plant oils and bio-based chemicals (carbohydrate and the derivatives etc.) in the presence of ruthenium-carbene catalysts (**G1**, **G2**, **HG2**, Scheme 2). Development of subsequent (one-pot) tandem hydrogenation afforded saturated polyesters under mild conditions. Reported examples for synthesis of high molecular weight polymers still have been limited; the polymerizations under bulk (without solvent, 80-90 ºC) or in ionic liquids (50 ºC) under vacuum conditions enabled synthesis of high molar mass polymers (M_n >30,000), that exhibit better mechanical properties as film. However, the high temperature polymerization (at 70-100 ºC) caused possibility of catalyst decompositions. The polymerization by using molybdenum-alkylidene catalyst afforded the highest molecular weight polyesters (44000–49400 g/mol) even in toluene at 25 ºC). Hydrogenated polyester films, prepared by polymerization of bis(10-undecenoate) with isosorbide and the subsequent hydrogenation, exhibited promising tensile properties (strength and elongation at break) beyond polyethylene, polypropylene. Significant effect of molecular weight toward the tensile properties were demonstrated, clearly indicating an importance of synthesis of high molar mass polymers for the better materials properties. Reported procedure for closed loop chemical recycling of polyesters by the depolymerizations and the re-polymerization were also introduced. The depolymerization of poly(butylene adipate) (PBA) with ethanol using $CpTiCl_3$ catalyst afforded diethyl adipate and 1,4-butandiol exclusively, and the subsequent polycondensation gave PBA without loss of the M_n value. Catalyst developments (more active, under mild conditions) play a key role for the efficient synthesis.

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