Aliphatic Polyesters by ADMET Polymerization and Hydrogenation

The recent developments of the synthesis of bio-based long-chain aliphatic polyesters by the 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. The development of subsequent (one-pot) tandem hydrogenation produced saturated polyesters under mild conditions.

1. Introduction

The development of sustainable polymers from renewable feedstocks attracts considerable attention from the viewpoints of the circular economy as well as green sustainable chemistry. Hydrocarbon-rich molecular biomasses, 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 products [1][2][3][4][5][6][7][8][9][10][11]. A 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) of polyesters are generally influenced by the methylene length (and the direction of dipoles called the odd–even effect) [6][12][13][14]; the placement of longer methylene units should be effective for the obtainment of polyesters without softening them at elevated temperatures. It has been considered that the precise polymerization technique provides a new strategy and methodology for the design of 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) are considered for the synthesis from FAEs [6][8]. The ring-opening polymerization (ROP) approach from cyclic monomers can also be considered, but the method has a limited monomer scope; the method also faces the difficulty of catalysts enabling the synthesis of high molar mass polymers [15][16]. Studies on alternative approaches to polymers are also under investigation [17][18][19][20]. Moreover, the recent progress in the development of olefin metathesis catalysts for the conversion of plant oils (FAEs) is well known [21][22][23][24].
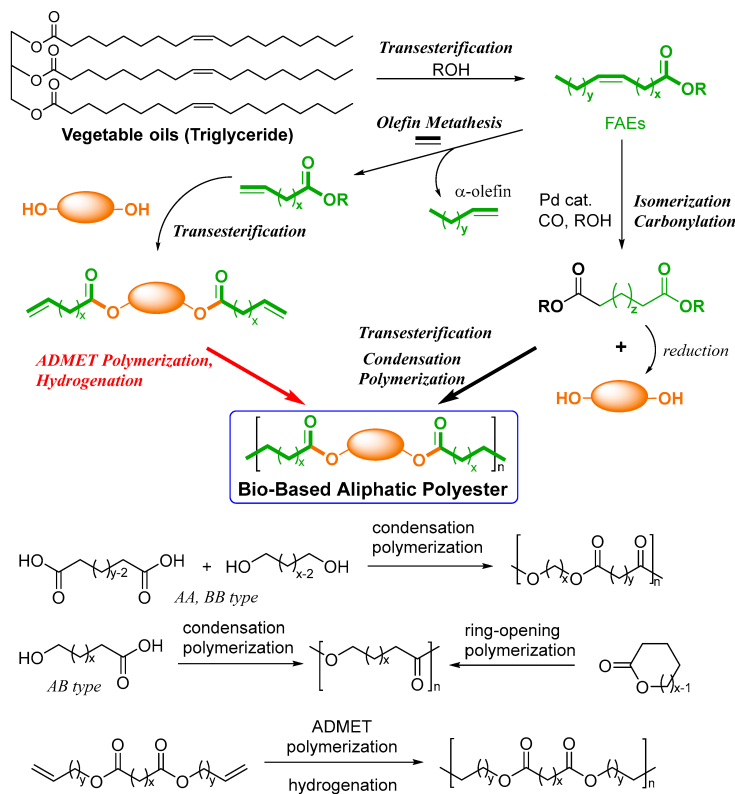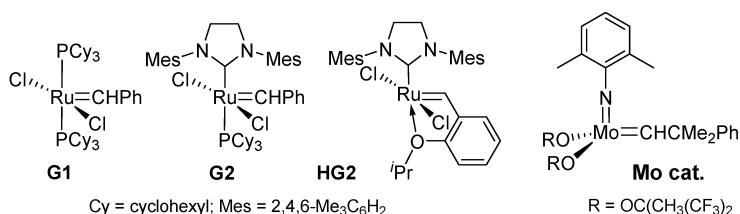
Scheme 1. Synthesis of bio-based polyesters from plant oil (triglycerides).

The conventional condensation polymerization approach through transesterification (ester bond exchange) requires high temperatures with the efficient removal of by-products (such as alcohols and water) to obtain high molar mass polymers with a high degree of polymerization (DP_n). For example, the synthesis of poly(ethylene terephthalate) from terephthalic acid (which must be purified) with excess ethylene glycol requires high temperatures up to 290 °C under a reduced pressure [25]. This method, however, seems to be difficult to apply for the synthesis of LCAPEs due to the difficulty of removing diols with high boiling points (e.g., 1,12-dodecanediol, 189 °C/12 Torr; 1,16-hexadecane diol 197–199 °C/3 mmHg). Moreover, precise stoichiometric control (hydroxy and carboxylic groups) is needed for this purpose [6][26][27][28]; polymerization with the precise stoichiometric ratios of diols (algae oil) and diesters (C_{17} and C_{19}) is required to create high molar mass polymers ($M_n = 4.0 \times 10^4$) possessing a T_m value of 99 °C [28].

2. Synthesis of Aliphatic Polyesters by ADMET Polymerization and Hydrogenation

Reports on the synthesis of bio-based polyesters by ADMET polymerization, especially using commercially available (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, are well known. These ruthenium catalysts have been employed [8] because these complexes can be readily available and do not require treatment with the strict Schlenk technique due to their insensitivities toward water and oxygen (better functional group tolerance) [29][30][31][32]. More recently, the example using a molybdenum-alkylidene catalyst (**Mo cat.**) [33][34][35], shown below, also demonstrates the synthesis of high molar mass polymers that exhibit good tensile properties [36].

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

The synthesis of a bio-based polyester, expressed as **PE1**, by the ADMET polymerization of undec-10-en-1-yl undec-10-enoate (**M1**), prepared by the reaction of 10-undecenoic acid with 10-undecenol (derived from castor oil) was reported by

the group of Meier in 2008 [37]. The resultant **PE1** synthesized by **G2** (0.5 or 1.0 mol%, 80 °C, 24 h, Scheme 3) possessed a rather high molecular weight (M_n = 22,000, 26,500), and the M_n values were controlled by the addition of terminal olefins, such as methyl 10-undecenoate and stearyl acrylate [37]. In contrast, the group reported that the polymerization of bis(undec-10-enoate) with isosorbide (**M2**, Scheme 3) conducted at 70–100 °C under bulk conditions yielded rather low-molecular-weight polymers (**PE2**) [38], whereas the M_n values seemed to improve when the polymerizations were conducted at high temperatures and/or under nitrogen-purge conditions (for the removal of by-produced ethylene). This was probably due to the catalyst decomposition caused by conducting the reaction at 70–100 °C [39][40][41][42][43][44], because these ruthenium catalysts are known to decompose under these conditions to produce ruthenium-hydride species [41] and/or nanoparticles [43], which induce olefin isomerization and/or certain side reactions by the formed radicals [39][40][41][42][43][44][45]. **G2** showed a more significant degree of olefin isomerization compared to **G1** and a higher percentage of isomerization (estimated by GC-MS, after treating the mixture with MeOH-H_2SO_4 under reflux conditions) [38]. Later, the degree of isomerization was extensively suppressed when the polymerizations were conducted in the presence of benzoquinone [45].
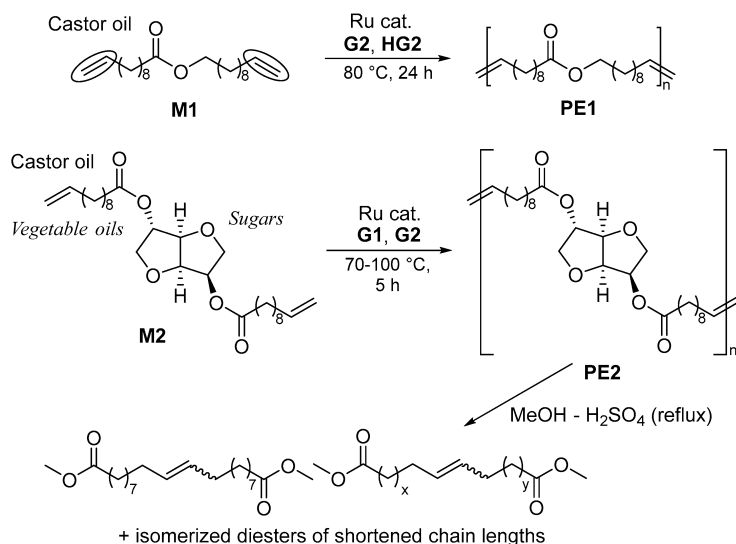
Scheme 3. ADMET polymerization of castor oil-derived monomers (**M1**, **M2**).

The ADMET polymerization of **M1** by **G1** under high-vacuum conditions for two days produced **PE1** (M_n = 28,000, M_w/M_n = 1.9) and a subsequent hydrogenation step (Pd/C, 50 bar H_2, 60 ºC) produced a saturated polyester (**HPE1**, PE-20.20, Scheme 4) [46]. The T_m value (103 °C) achieved was somewhat low compared to the **HPE1** prepared by the condensation polymerization of 1,20-eicosanedioic acid with eicosane-1,20-diol (T_m = 108 °C) to form 'regio-regular' ester groups, C(O)-O, aligned with the polymer chain (Scheme 4). It was thus suggested that the microstructural control directly affected the thermal property, as described above [6][14]. ADMET polymerizations of α,ω-dienes with different methylene chain lengths, di(icos-19-en-1-yl)tricosanedioate (**M3**) and di(tricos-22-en-1-yl)tricosanedioate (**M4**), using **G1** and the subsequent olefin hydrogenation conducted by Ru(CHOEt)Cl$_2$(PCy)$_2$ (40 bar H_2, 70 °C, 2 d), prepared from **G1**, yielded the corresponding values of PE-38.23 (**HPE3**) and PE-44.23 (**HPE4**), respectively (Scheme 4) [47]. The polycondensation of 1,26-hexacosanedioate, prepared by the cross-metathesis of erucic acid, with the corresponding diol (produced by a reduction with LiAlH$_4$) with Ti(OBu)$_4$ also produced the corresponding polyester (**HPE5**, PE-26.26, T_m = 114 °C) [48]. The thermal properties (T_m values) of the resultant LCAPEs with different methylene lengths, prepared by ADMET [47] and polycondensation [48][49] approaches, revealed that the T_m values achieved a constant value (**Figure 1**a) [47]. A linear relationship between the T_m values and the number of ester groups in 1000 carbon atoms was observed (**Figure 1**b) [47]. Polyesters PE-26.26, PE-12.26 and PE-4.26 [48], and PE-18,18 [50] were also prepared by polycondensation.
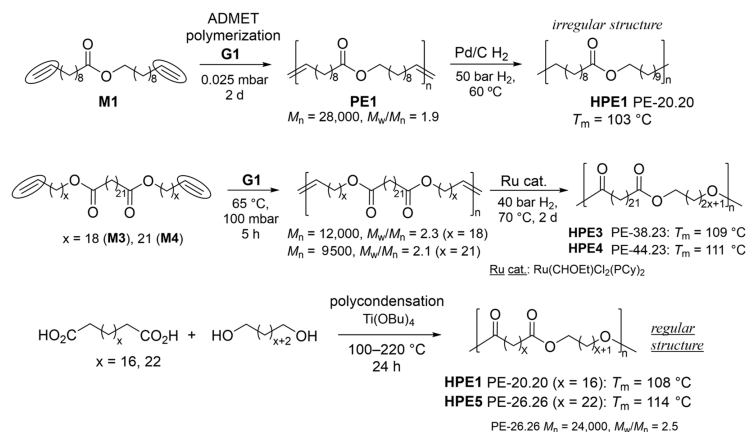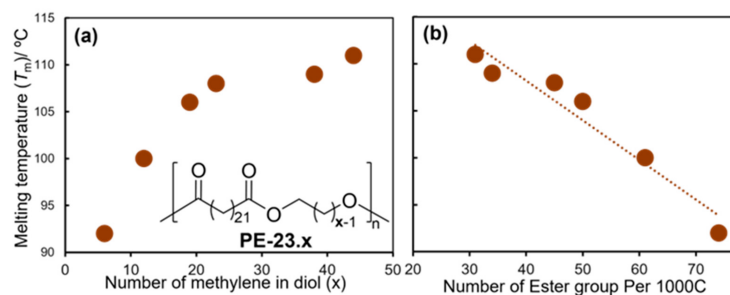
Scheme 4. Synthesis of linear polyesters (LCAPEs).

Figure 1. Plots of melting temperature (T_m) vs. number of (**a**) methylene units (x) in diol and (**b**) ester groups per 1000 C (methylene) in PE-23.x.

The one-pot synthetic method used for the bio-based aliphatic polyesters by ADMET polymerization and subsequent hydrogenation was demonstrated (Scheme 5) [51]. The polymerization of bis(undec-10-enoate)s with isosorbide (**M2**), isomannide (**M6**), 1,3-propanediol (**M7**), and 1,4-cyclohexanedimethanol (**M8**), derived from castor oil and glucose in chloroform by **G2** or **HG2** under a reduced pressure at 50 °C produced unsaturated polymers (expressed as **PE2** and **PE6**–**PE8**, respectively) [51]. The M_n values in the produced polymers (M_n = 11,900–15,900) were somewhat higher than those reported previously (M_n = 4400–8400), conducted at 70–100 °C [38], and the M_n values did not change, even under rather scaled-up conditions [51]. One reason for the obtainment of high-molecular-weight product could be that the degree of the catalyst decomposition was significantly suppressed by conducting the polymerization at 50 °C (and the polymerization was conducted under a continuously reduced pressure) [51].
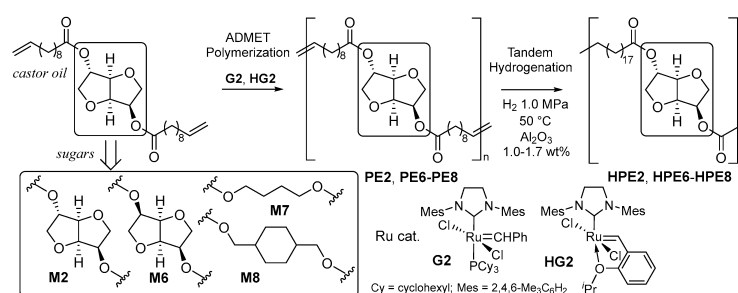

Scheme 5. One-pot synthesis of bio-based polyesters by Ru-catalyzed ADMET polymerization and hydrogenation.

As described above (Scheme 4) and below [52], conventional olefin hydrogenation requires a high hydrogen pressure and high temperature after the isolation of unsaturated polyesters after ADMET polymerization [46][47][52]. In contrast, one-pot hydrogenation under rather mild conditions (1.0 MPa, 50 °C, 3 h) was demonstrated following the addition of a small amount of Al$_2$O$_3$ (ca. 1 wt%) to the reaction mixture (Scheme 5). The completion of the olefin hydrogenation was confirmed by DSC thermograms (uniform compositions) due to the difficulty (accuracy of the integration of olefinic protons) of obtaining the ^{1}H NMR spectra. No significant differences in the M_n and M_w/M_n values were observed before/after hydrogenation [51].

As shown in **Figure 1**b, the melting temperatures (T_m values) of the polyesters are influenced by the methylene unit number (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) produced various LCAPEs with different chain lengths (ranging from 0.9 to 52.6 ester groups per 1000 carbon atoms), expressed as H$_2$-poly(**M1**-co-UDD) [52]. A linear correlation of the melting

temperatures (T_m values) with the average number of ester groups per methylene unit was thus demonstrated, whereas the ester group was incorporated in a random manner. A similar trend was observed in the copolymerization of **M2** with 1,9-decadiene (DD) and the subsequent one-pot hydrogenation [53]. The saturated polymers possessed T_m values in the range of 71.7–107.6 °C, depending on the molar ratios of **M2** and DD.
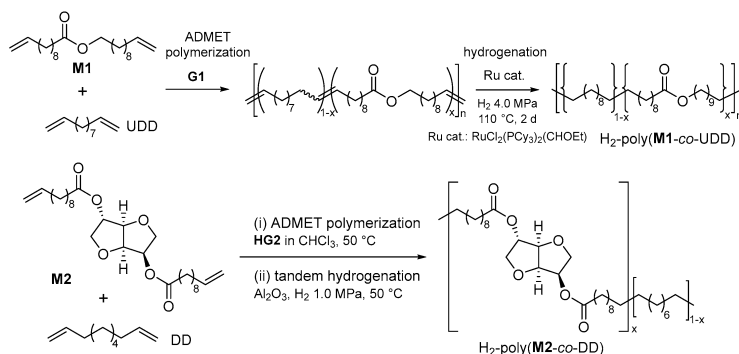
Scheme 6. ADMET copolymerization of undec-10-en-1-yl undec-10-enoate (**M1**) or bis(undec-10-enoate) with isosorbide (**M2**) with nonconjugated dienes, and subsequent hydrogenation.

The polymerization of bis(undec-10-enoate)s with *D*-xylose (1,2-*O*-isopropylidene-α-*D*-xylofuranose, **M9c**), and *D*-mannose (**M10**) by **G2** was studied under a dynamic-vacuum (0.1 mbar) condition without solvent (bulk) conditions (60–90 °C, 20 h, Scheme 7) [54]. The molecular weights of the resultant polymers (**PE9c**, **PE10**) were affected by the polymerization temperature employed and the monomer/Ru molar ratios. Conducting the polymerization at 90 ºC under a low Ru concentration (0.1 mol%) seemed to be the optimized condition (**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) [46]. Due to the fact that the polymerization was conducted without a solvent, the PDI (M_w/M_n) values were rather high due to the difficulty pf controlling the stirring [54]. Later, the polymerizations of *D*-xylose diester analogs with different methylene lengths (**M9**, x = 0, 2, 8, Scheme 7) and the corresponding diether analogs (**M11**) were explored [55]. The M_n values of the resultant polymers decreased upon decreasing the methylene length, and the monomers did not possess a methylene spacer [55]. Some polymerization runs failed due to precipitation or the difficulty of performing isolations [55]. The resultant unsaturated polymers were amorphous, except **PE11a**, and both glass transition temperatures (T_g) increased after reducing the olefinic double bonds by treating them with *p*-toluenesulfonyl hydrazide as a reducing agent; most of the resultant saturated polymers (**HPE9** and **HPE11**) were amorphous, except **HPE9a** and **HPE11a** derived from the castor oil (10-undecenoate), suggesting that the placement of the methylene spacer was important (as shown in **Figure 1**a and **Figure 2**) [55]. The resultant hydrogenated polymer films, especially the **HPE11a**-oriented film, exhibited a good tensile strength (43 MPa) with an elongation at a break of 155%; but, the hot-press film showed a much weaker tensile strength (7.8 MPa) with and improved elongation at the break (667%) [55].
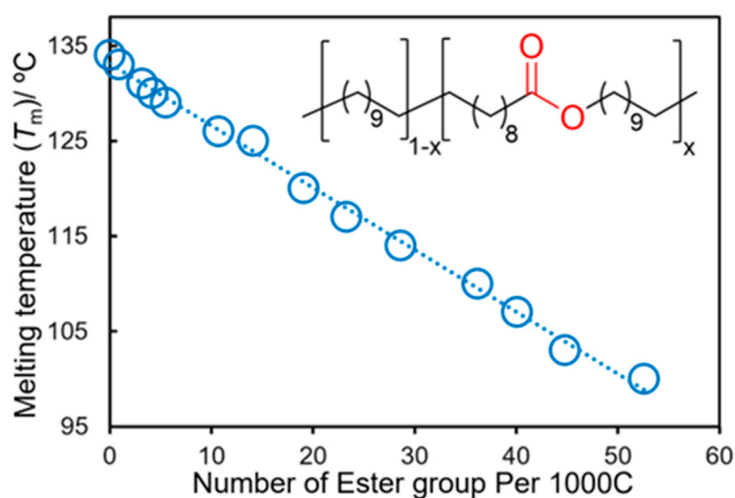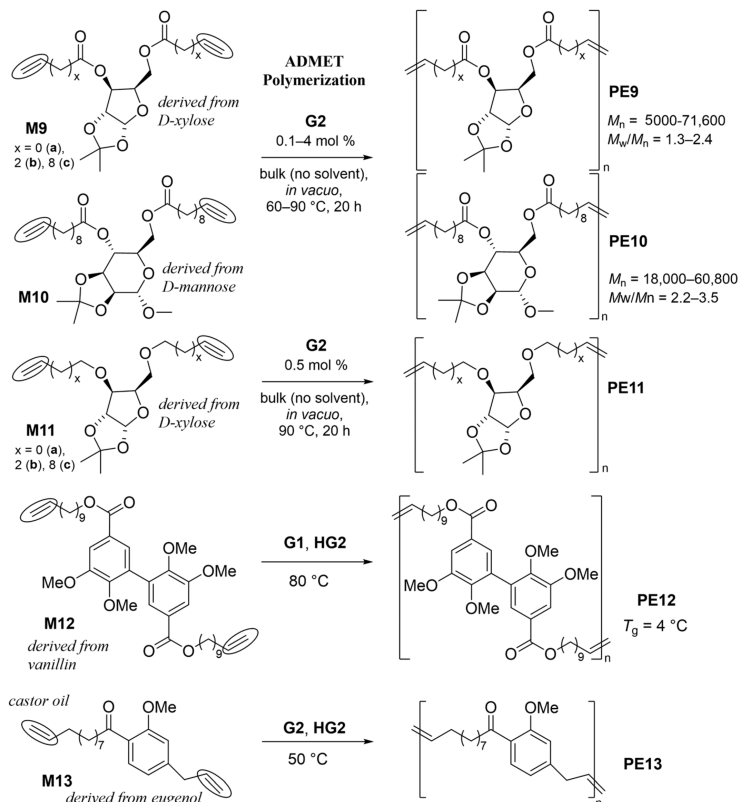

Figure 2. Plots of melting temperature (T_m) vs. number of ester groups per 1000 C (methylene units) in the hydrogenated copolymers, H₂-poly(**M1**-*co*-UDD)s.

Scheme 7. ADMET polymerization of α,ω-dienes containing *D*-xylose, *D*-mannose, vanillin, and eugenol as the monomer units.

The syntheses of polyesters containing vanillin (**PE12**) [56] afforded high-molecular-weight **PE12** (M_n = 10,000, M_w/M_n = 1.6) possessing a T_g value of 4 °C (Scheme 7), whereas the polymerization of 4-allyl-2-methoxyphenyl 10-undecenoate (**M13**) by **G2** produced amorphous high molar mass polymers with low PDIs (M_w/M_n) with T_g at −9.6 °C [57]. The ADMET polymerization of **M13** in the presence of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) produced rather high molar mass network polymers [57].

The polymerization of trehalose bis(10-undecenoate) (**M14**) by **HG2** (4.0 mol%) in THF at 45 ºC for 24 h (Scheme 8) produced semicrystalline polymers (**PE14**) possessing high molecular weights with unimodal molecular-weight distributions (M_n = 13,200, M_w/M_n = 2.1) with higher T_m values (156 °C) [58]. Both the molecular weights and melting temperatures (T_m values) of the resulting copolyesters with undec-10-en-1-yl undec-10-enoate (**M1**) decreased with the increase in the percentage of **M1** [58].
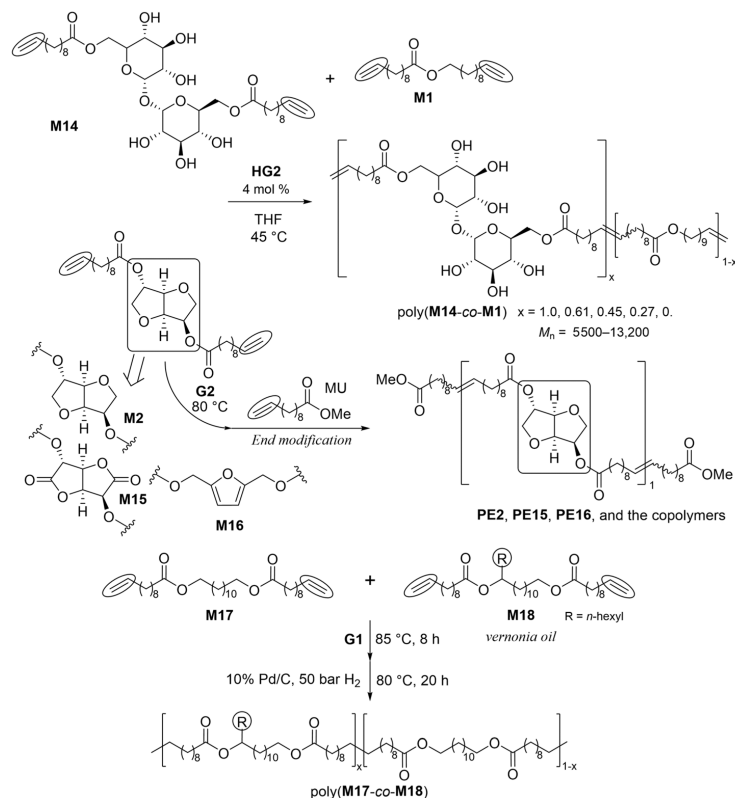
Scheme 8. Synthesis of bio-based copolyesters with different molar ratios.

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