Article

Synthesis of High-Molecular-Weight Biobased Aliphatic Polyesters by Acyclic Diene Metathesis Polymerization in Ionic Liquids

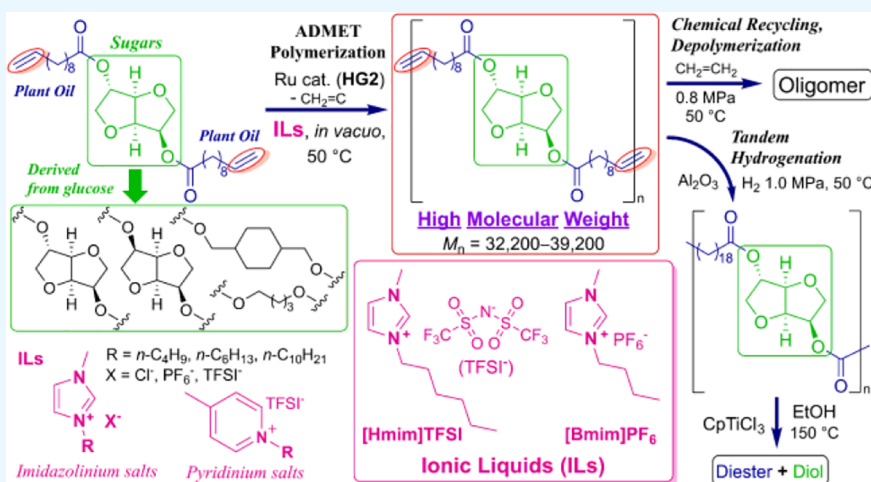Xiuxiu Wang, Weizhen Zhao, and Kotohiro Nomura*

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ABSTRACT: Acyclic diene metathesis (ADMET) polymerization of an α,ω-diene monomer of bis(undec-10-enoate) with isosorbide (**M1**) using a RuCl$_2$(IMesH$_2$)(CH-2-O^{i}Pr-C$_6$H$_4$) (**HG2**, IMesH$_2$ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene) catalyst and conducted at 50 °C (in vacuo) in ionic liquids (ILs) afforded higher-molecular-weight polymers (**P1**, M_n = 32 200−39 200) than those reported previously (M_n = 5600−14700). 1-n-Butyl-3-methyl imidazolium hexafluorophosphate ([Bmim]PF$_6$) and 1-n-hexyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide ([Hmim]TFSI) were suitable as effective solvents among a series of imidazolium salts and the pyridinium salts. The polymerization of α,ω-diene monomers of bis(undec-10-enoate) with isomannide (**M2**), 1,4-cyclohexanedimethanol (**M3**), and 1,4-butanediol (**M4**) in [Bmim]PF$_6$ and [Hmim]TFSI also afforded the higher-molecular-weight polymers. The M_n values in the resultant polymers did not decrease even under the scale-up conditions (300 mg to 1.0 g scale, **M1**, **M2**, and **M4**) in the polymerizations in [Hmim]TFSI; the subsequent reaction of **P1** with ethylene (0.8 MPa, 50 °C, and 5 h) gave oligomers (proceeded via depolymerization). Tandem hydrogenation of the resultant unsaturated polymers (**P1**) in a [Bmim]PF$_6$−toluene biphasic system upon the addition of Al$_2$O$_3$ (1.0 MPa H$_2$ at 50 °C) gave the corresponding saturated polymers (**HP1**), which was were isolated by a phase separation in the toluene layer. The [Bmim]PF$_6$ layer containing the ruthenium catalyst could be recycled without a decrease in the activity/selectivity of the olefin hydrogenation at least eight times.

INTRODUCTION

Acyclic diene metathesis (ADMET) polymerization is a widely used method in the synthesis of advanced functional polymers.[1−6] Condensation of the polymerization accompanies the byproduction of small molecules (such as ethylene, propylene), and the removal of the byproduct from the reaction medium is crucial to obtain high-molecular-weight polymers (to shift the equilibrium).[1−6] The method is useful for the synthesis of biobased aliphatic polyesters,[7−14] which have been considered not only as an important subjects in terms of the efficient conversion of plant oils (fatty acids and the esters, FAEs) but also as an alternative technology to petroleum-based chemical processes and in terms of a circular economy. There are number of reports on the synthesis of

(aliphatic) polyesters by the ADMET polymerization of α,ω-dienes in the presence of ruthenium-carbene catalysts;[15−32] however, the synthesis of high-molecular-weight polymers (ca. M_n > 30 000 considered for better mechanical properties as films) is still a challenging subject. Moreover, it has also been known that conducting the polymerization at high temper-
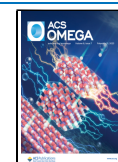
Scheme 1. Reported ADMET Polymerization in ILs[50,51]
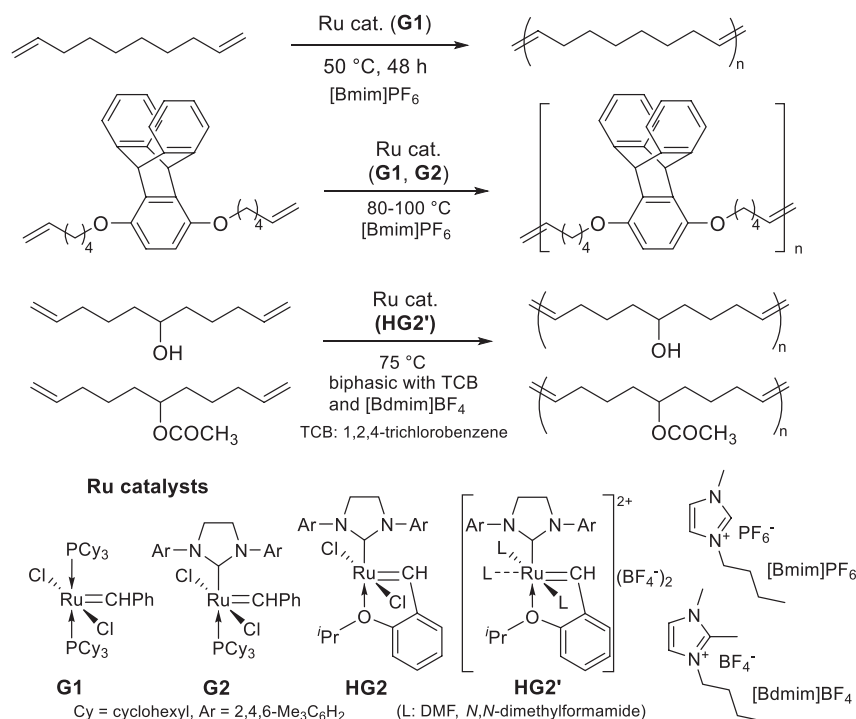
atures (70−90 °C) generally leads to catalyst decomposition, which causes olefin isomerization and/or radical-type side reactions.[7,16,33−38]

It was reported that the resultant polymers in the ADMET polymerization of dianhydro-D-glucityl bis(undec-10-enoate) (**M1**, shown below, Scheme 2) by RuCl$_2$(PCy$_3$)(IMesH$_2$)- (CHPh) (**G2**; IMesH$_2$ = 1,3-bis(2,4,6-trimethylphenyl)- imidazolin-2-ylidene, Cy = cyclohexyl) conducted at 60−90 °C (without solvent) afforded polymers (expressed as **P1**) with M_n values of 5600−8400 (60−80 °C, respectively), and the M_n value increased at high temperatures (until 80 °C).[16] Later, the M_n values in the resultant polymers (**P1**) increased (M_n = 7100−14700) when the polymerizations were conducted in (small amount of) CHCl$_3$ at 50 °C using RuCl$_2$(IMesH$_2$)(CH-2-O^{i}Pr-C$_6$H$_4$) (**HG2**) under high initial concentration conditions of **M1** (initial concentration of **M1** of 4.64 or 6.12 M) with the removal of ethylene from the reaction medium in vacuo.[27] Moreover, M_n values in the resultant copolymer of **M1** with 1,9-decadiene increased when the solvent (CHCl$_3$) in the reaction mixture was once removed and replaced during the polymerization run, probably because the remaining ethylene in the reaction mixture was removed during the solvent exchange event.[30,39] This information thus suggests that the development of the ADMET polymerization technique with the efficient removal of small molecules (e.g., ethylene) could be prerequisite for the purpose.

Ionic liquids (ILs) are thus the ideal solvents due to their lack of (or extremely low) vapor pressure, miscibility with polymers as well as organic compounds and metal catalysts (which makes most homogeneous catalytic reactions feasible), and high stability ranging from −30 to 300 °C.[40−47] These promising characteristics of ILs enable us to consider them as desirable solvents for synthesis of high-molecular-weight polyesters in the ADMET condensation polymerization.[48−52] Although olefin metathesis reactions in ILs have been

known,[53−62] the reported examples of ADMET polymerization have been limited so far.[50−52,63−65] For instance, the polymerization of 1,9-decadiene in 1-n-butyl-3-methyl imida-zolium hexafluorophosphate ([Bmim]PF$_6$) in the presence of RuCl$_2$(PCy$_3$)$_2$(CHPh) (**G1**) at 50 °C afforded rather high molecular weight polymers (Scheme 1, M_n = 1.08−1.92 × 10^4).[50] The polymerization of 1,4-bis(undec-10-en-1-yloxy)- triptycene conducted at 100 °C using **G2** (initially 80 °C for 24 h, total of seven days) also gave a rather high molecular weight polymer (M_n = 1.15 × 10^4).[50] Moreover, the molecular weight of the resultant polymer prepared by the ADEMT polymerization of 6-hydroxy-1,10-undecadiene using dicationic [Ru(DMF)$_3$(IMesH$_2$)(CH-2-O^{i}Pr−C$_6$H$_4$)](BF$_4$)$_2$ in a bipha-sic system consisting of 1-n-butyl-2,3-dimethylimidazolium tetrafluoroborate ([Bdmim]BF$_4$) and 1,2,4-trichlorobenzene (at 75 °C) was higher than that prepared by **HG2** in trichlorobenzene (Scheme 1),[51] and a significant reduction of the ruthenium contaminant in the polymer (extracted as 1,2,4-trichlorobenzene layer) was demonstrated.[51] These results strongly suggest that ADMET polymerization in ILs should provide a promising possibly for the synthesis of high-molecular-weight polymers of biobased aliphatic polyesters, as presented in this study.

In this paper, we thus first studied ADMET polymerizations of a biobased monomer, namely, α,ω-diene of bis(undec-10-enoate), with isosorbide (**M1**, Scheme 2),[16,27] using **HG2** in various ILs. We thus herein present that the method enables the synthesis of high-molecular-weight polymers from various biobased monomers (**M1**−**M4**, Scheme 2), even under gram scale conditions.[66] Since we developed a tandem hydro-genation system for synthesis of saturated polymers upon the addition of a small amount of alumina (Al$_2$O$_3$),[27] we thus explored the possibility of a biphasic system, namely, IL−toluene, to better separate polymers (dissolved in toluene) from the catalyst (present in IL layer), including the possibility

Scheme 2. Synthesis of High-Molecular-Weight Biobased Aliphatic Polyesters by ADMET Polymerization in ILs
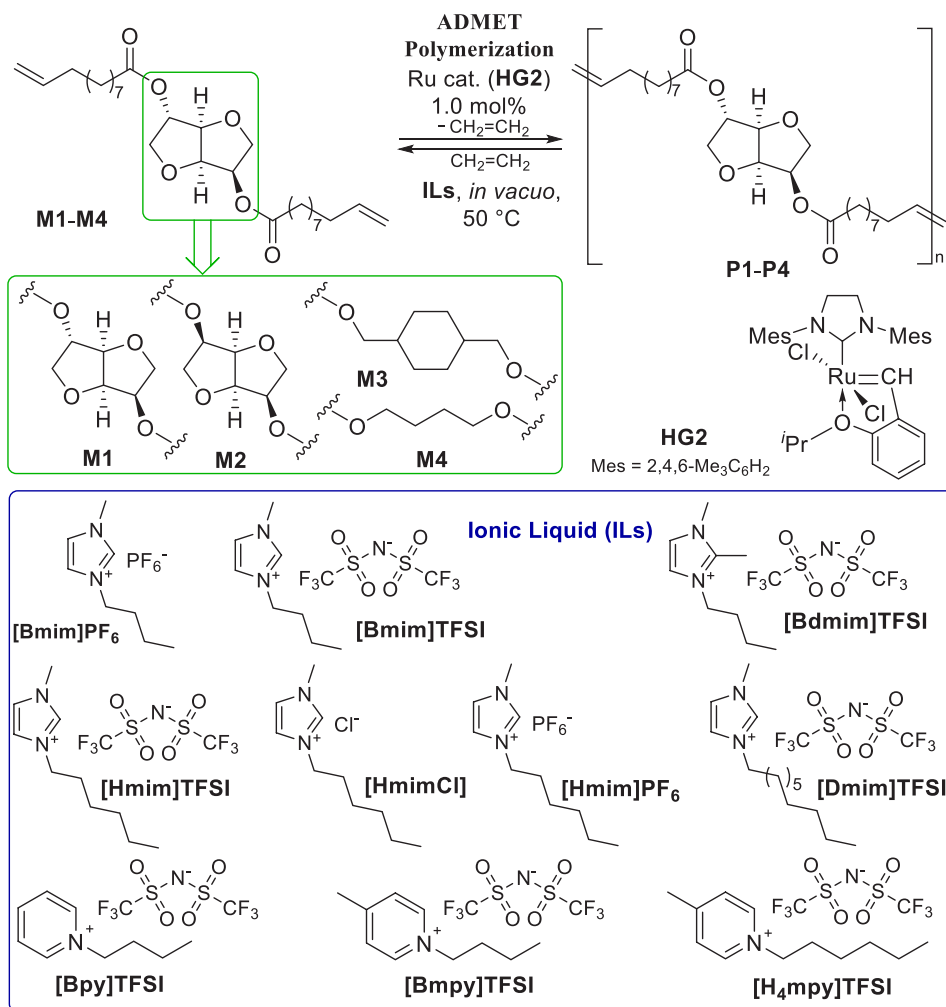
■ RESULTS AND DISCUSSION

ADMET Polymerization of Biobased Monomers (M1–M4) in ILs. Table 1 summarizes results for ADMET polymerization of dianhydro-D-glucityl bis(undec-10-enoate) (M1, Scheme 2),[27] an α,ω-diene of bis(undec-10-enoate) with isosorbide, using the $RuCl_2(IMesH_2)(CH-2-O^i Pr-C_6H_4)$ (HG2) catalyst in various ionic liquids (ILs). A series of imidazolium salts with different alkyl substituents and counteranions, such as PF_6^-, Cl^-, and bis-(trifluoromethanesulfonyl)imide ($TFSI^-$), and pyridinium salts containing TFSI anions have been chosen. This is because these ILs (featuring delocalized cations compared to the ammonium salts)[49] are commercially available and could be suited for the initial screening to explore the effect of ILs. ILs containing TFSI anions (low viscosity, hydrophobic) have also been chosen because, as described below, the polymerization proceeded under homogeneous conditions (pictures of the reaction mixtures are shown in the Supporting Information (SI)). These polymerizations were conducted at 50 °C in a sealed Schlenk tube (300 mg of M1 in 0.14 mL of the IL under

the same initial monomer concentration reported previously[27] in CHCl₃ for comparison) connected to a vacuum line. It has been known that ADMET polymerization conducted under high-monomer-concentration conditions should be favored in this type of condensation polymerization;[1–6] polymerization under reduced pressure should also be favored for the effectiveremoval of ethylene byproduct, as demonstrated in synthesis of arylene vinylene-type conjugated polymers.[67–69] Additional results, including confirmation of reproducibility of the polymerization, are summarized in Table S1 in the SI.

It should be noted that the polymerization reactions in ILs afforded high-molecular-weight polymers (expressed as P1) in most cases, except the runs conducted in 1-n-hexyl-3-methyl imidazolium chloride, expressed as [Hmim]Cl. The M_n values in the resultant polymers (P1s) were higher than those of the polymers from reactions conducted in CHCl₃ reported previously under optimized (similar) conditions (M_n = 10 300–14 700; 300 mg of M1, initial M1 conc. in CHCl₃ of 4.64 M at 50 °C).[27] It was revealed that the M_n values in the resultant polymers were affected by the ILs employed. For instance in the 1-n-hexyl-3-methyl imidazolium salts, [Hmim]⁺, the M_n values increased in the order [Hmim]Cl (M_n = 7800 and 11 200, after 6 and 16 h, respectively, runs 8 and 9) < [Hmim]PF₆ (M_n = 11 600 and 15 300 after 6 and 16 h, respectively, runs 10 and 11) < [Hmim]TFSI (M_n = 23 200

Table 1. ADMET Polymerization of M1 by HG2 in ILs: Effect of ILs[a]

run	IL[b]	time (h)	yield[c] (%)	M_n[d]	M_w/M_n[d]
1	[Bmim]PF$_6$	6	87	24 700	1.97
2	[Bmim]PF$_6$	6	87	23 500	1.79
3	[Bmim]PF$_6$	16	89	32 200	1.87
4	[Bmim]TFSI	6	86	17 700	1.79
5	[Bmim]TFSI	16	93	23 000	1.94
6	[Bdmim]TFSI	6	87	20 000	1.73
7	[Bdmim]TFSI	16	92	23 600	1.88
8	[Hmim]Cl	6	82	7800	1.65
9	[Hmim]Cl	16	91	11 200	1.65
10	[Hmim]PF$_6$	6	87	11 600	2.15
11	[Hmim]PF$_6$	16	90	15 300	1.73
12	[Hmim]TFSI	6	87	23 200	1.89
13	[Hmim]TFSI	6	84	23 200	1.79
14	[Hmim]TFSI	16	90	35 600	1.91
15	[Hmim]TFSI	16	93	39 200	1.95
16	[Hmim]TFSI	16	89	35 700	1.78
17	[Dmim]TFSI	6	92	20 600	1.74
18	[Dmim]TFSI	16	88	23 100	1.78
19	[Bpy]TFSI	6	84	12 000	1.56
20	[Bpy]TFSI	16	80	18 000	1.72
21	[B$_4$mpy]TFSI	6	93	12 100	1.67
22	[B$_4$mpy]TFSI	16	78	21 500	1.75
23	[H$_4$mpy]TFSI	6	81	25 300	1.79
24	[H$_4$mpy]TFSI	16	92	25 700	1.94

[a]Conditions are as follows: 300 mg of **M1** (0.63 mmol) in 0.14 mL of the IL (initial **M1** conc. of 4.48 M) with 1.0 mol % Ru catalyst (**HG2**) at 50 °C in vacuo. [b]ILs are listed in Scheme 2. [c]Isolated yield. [d]GPC data in THF versus polystyrene standards.

and 35 600−39 200 after 6 and 16 h, respectively, runs 12−16). The polymerization in [Hmim]TFSI proceeded under homogeneous conditions, whereas the reaction mixture in [Hmim]Cl became heterogeneous (precipitation), probably due to its rather hydrophilic nature[49] compared to [Hmim]-TFSI (hydrophobic).[49] The M_n values of the resultant polymer from the reaction conducted in [Bmim]PF$_6$ (M_n = 23 500− 32 400, runs 1−3 and S1, Table S1) were higher than those conducted in [Bmin]TFSI (M_n = 17 100−23 000, runs 4, 5, S2, and S3). In the polymerization in ILs containing TFSI anion, the M_n values in the resultant polymers from reactions conducted in 1-*n*-hexyl-3-methyl imidazolium salts, [Hmim]-TFSI (M_n = 35 600−39 200 after 16 h, runs 14−16), were higher than those of the resultant polymers from reactions conducted in the 1-*n*-butyl-3-methyl analogue [Bmim]TFSI (M_n = 23 000, run 5), the 1-*n*-butyl-2,3-dimethyl analogue [Bdmim]TFSI (M_n = 23 600, run 7), and the 1-*n*-decyl-3-methyl analogue [Dmim]TFSI (M_n = 23 100, run 18). We assume that these differences are due to increase in the viscosity of the reaction mixture over the polymerization time course. As also shown in Table S1, these polymerization results were reproducible.

It was also revealed that the ADMET polymerizations in the pyridinium salts also afforded the high-molecular-weight polymers (M_n = 18 000−25 700 after 16 h). The polymerization conducted in the *N*-hexyl-4-methylpyridinium salt, [H$_4$mpy]TFSI, afforded the highest molecular weight polymer even after 6 h (M_n = 25 300, run 23), but the M_n value was rather low compared to those of the resultant polymers from reactions conducted in [Hmim]TFSI (M_n = 35 600−39 200

after 16 h, runs 14−16). It is thus concluded that the polymerizations in [Bmim]PF$_6$ and [Hmim]TFSI are suitable for further study in terms of the synthesis of high-molecular-weight polymers.

Table 2 summarizes the results for polymerization of α,ω-dienes of bis(undec-10-enoate) with diols (isomannide (**M2**),

Table 2. ADMET Polymerization of M1−M4 by HG2 in ILs[a]

run	IL[b]	monomer	time (h)	yield[c] (%)	M_n[d]	M_w/M_n[d]
1	[Bmim]PF$_6$	**M1**	6	87	24 700	1.97
3	[Bmim]PF$_6$	**M1**	16	89	32 200	1.87
25	[Bmim]PF$_6$	**M2**	6	90	21 000	1.85
26	[Bmim]PF$_6$	**M2**	16	90	24 400	1.78
27	[Bmim]PF$_6$	**M3**	6	78	23 400	7.5
28	[Bmim]PF$_6$	**M3**	6	77	23 300	5.2
29	[Bmim]PF$_6$	**M3**	16	82	29 900	5.5
30	[Bmim]PF$_6$	**M4**	6	89	22 500	1.88
31	[Bmim]PF$_6$	**M4**	16	87	26 000	2.44
12	[Hmim]TFSI	**M1**	6	87	23 200	1.89
15	[Hmim]TFSI	**M1**	16	93	39 200	1.95
32	[Hmim]TFSI	**M2**	6	97	18 400	1.84
33	[Hmim]TFSI	**M2**	16	92	26 000	1.95
34	[Hmim]TFSI	**M3**	6	79	24 200	4.33
35	[Hmim]TFSI	**M3**	16	94	38 800	3.38
36	[Hmim]TFSI	**M4**	6	91	28 300	2.38
37	[Hmim]TFSI	**M4**	16	89	33 400	2.30

[a]Conditions are as follows: 300 mg of monomer (0.63 mmol) in 0.14 mL of IL [initial conc. of 4.48 (**M1**), 4.48 (**M2**), 4.69 (**M3**), or 5.07 M (**M4**)] with 1.0 mol % Ru catalyst (**HG2**) at 50 °C in vacuo. [b]ILs are listed in Scheme 2. [c]Isolated yield. [d]GPC data in THF versus polystyrene standards.

1,4-cyclohexanedimethanol (**M3**), and 1,4-butanediol (**M4**), Scheme 2), as reported previously in CHCl$_3$,[27] using **HG2** in [Bmim]PF$_6$ and [Hmim]TFSI, which were chosen on the basis of the results in Table 1. In all polymerization runs conducted in two ILs, the resultant polymers possessed higher molecular weights (M_n = 24 400−38 800 after 16 h) than those for previously reported reactions conducted in CHCl$_3$ (M_n = 9800−10 900 (**P2**), 9400 (**P3**), and 12 400−16 400 (**P4**) after 24 h);[27] the M_n values increased over the time course, as observed in the polymerization of **M1** (runs 1, 3, 12, and 15, Table 2).

It was revealed that the polymerizations of **M3** and **M4** conducted in [Hmim]TFSI afforded polymers with higher molecular weights than those conducted in [Bmim]PF$_6$ (**P3**, M_n = 38 800 (run 35) vs 29 900 (run 29); **P4**, M_n = 33 400 (run 37) vs 26 000 (run 31)). The PDI ($Đ$, M_w/M_n) values in the polymer from **M3** were, however, somewhat large (M_w/M_n = 4.33 and 3.38, runs 34 and 35, respectively), probably due to increased viscosity (difficult to conduct stirring under homogeneous conditions). The $Đ$ (PDI) values in the resultant polymers from **M3** in [Bmim]PF$_6$ also became larger (M_w/M_n = 5.2−7.5, runs 27−29) due to more difficult stirring. It was revealed that the M_n values in the polymerization of **M2** were rather low compared to those for **M1**, **M3**, and **M4**, and no significant differences were observed between [Bmim]PF$_6$ and [Hmim]TFSI as solvents. The M_n values in the resultant polymers (**P2**, M_n = 18 400−26 000, runs 25, 26, 32, and 33) were apparently higher than those for previously reported reactions conducted in CHCl$_3$ (M_n = 6700−10 900).[27]

Table 3. ADMET Polymerization of M1 by HG2 in ILs under Scale-Up Conditions[a]

run	IL[b]	$[\mathbf{M1}]_0$[b]	reactor[c]	HG2 (mol %)	time (h)	yield[d] (%)	M_n[e]	M_w/M_n[e]
1[f]	[Bmim]PF$_6$	4.48	A	1.0	6	87	24 700	1.97
3[f]	[Bmim]PF$_6$	4.48	A	1.0	16	89	32 200	1.87
38	[Bmim]PF$_6$	5.23	A	1.0	6	87	11 100	1.78
39	[Bmim]PF$_6$	5.23	A	1.0	16	88	19 300	1.74
40	[Bmim]PF$_6$	6.97	A	0.5	6	89	11 000	2.25
41	[Bmim]PF$_6$	6.97	A	0.5	16	90	16 200	2.42
42	[Bmim]PF$_6$	6.97	A	1.0	6	87	17 600	1.72
43	[Bmim]PF$_6$	6.97	A	1.0	16	90	26 000	1.74
44	[Bmim]PF$_6$	6.97	B	1.0	16	85	27 100	2.67
45	[Bmim]PF$_6$	8.36	A	1.0	6	92	15 400	2.17
46	[Bmim]PF$_6$	8.36	A	1.0	16	88	25 900	2.16
12[f]	[Hmim]TFSI	4.48	A	1.0	6	87	23 200	1.89
47	[Hmim]TFSI	6.97	A	0.5	6	92	19 400	1.96
48	[Hmim]TFSI	6.97	A	1.0	6	87	18 300	1.64
49	[Hmim]TFSI	6.97	A	2.0	6	90	15 100	1.60
15[f]	[Hmim]TFSI	4.48	A	1.0	16	93	39 200	1.95
50	[Hmim]TFSI	6.97	A	0.5	16	89	21 300	1.78
51	[Hmim]TFSI	6.97	A	1.0	16	91	22 500	2.13
52	[Hmim]TFSI	6.97	A	1.0	16	91	22 900	1.74
53	[Hmim]TFSI	6.97	A	2.0	16	96	16 200	1.66
54	[Hmim]TFSI	6.97	B	1.0	6	95	24 500	1.94
55	[Hmim]TFSI	6.97	B	1.0	16	86	37 500	1.91
56	[Hmim]TFSI	6.97	B	1.0	16	86	38 800	2.60
57	[Hmim]TFSI	8.36	A	1.0	6	95	11 800	2.21
58	[Hmim]TFSI	8.36	A	1.0	16	79	14 500	1.81

[a]Conditions are as follows: 1.00 g of **M1** (2.09 mmol) in 0.25, 0.30, or 0.40 mL of the IL (**M1** conc. of 8.36, 6.97, or 5.23 mmol/mL, respectively) with 0.5−2.0 mol % Ru catalyst (**HG2**) at 50 °C in vacuo. [b]ILs are listed in Scheme 2, and the initial **M1** concentration is in mmol/mL (M). [c]The reactor is a sealed tube (100 mL scale, reactor A) or a round-bottom flask with a three-way stopcock (25 mL scale, reactor B), as shown in the SI. [d]Isolated yield. [e]GPC data in THF versus polystyrene standards. [f]Reaction scale was 300 mg of **M1** (Table 1).

Synthesis of High-Molecular-Weight Polymers under Scale-Up Conditions. Table 3 summarizes results of the ADMET polymerization of **M1** by the **HG2** catalyst under scale-up (**M1**, 300 mg to 1.0 g) conditions in [Bmim]PF$_6$ and [Hmim]TFSI.[63] These polymerizations were explored under conditions of different initial **M1** concentrations (amount of IL charged), Ru catalyst loadings, and reaction times to explore the effects toward the M_n values of the resultant polymers. The additional polymerization results, including the confirmation of reproducibility, are shown in Table S3.

In the ADMET polymerization of **M1** in [Bmim]PF$_6$, it was revealed that the M_n values for reactions conducted under 1.0 g scale conditions using a sealed Schlenk tube (reactor A, runs 38−46) were lower than those for reactions conducted under 300 mg scale conditions (runs 1 and 3, Table 1). The value was affected by the initial monomer concentration (amount of solvent employed, higher than 6.97 M) and the Ru loading (1.0 mol % seemed to be the optimized condition), whereas the M_n values after 16 h were higher than those after 6 h in all cases. Two factors, namely, the remaining ethylene in the solution and the viscosity of the reaction mixture, could be probably assumed because the M_n values after 6 h increased in the order M_n = 11 100 (run 38, 5.23 M **M1**) < 15 400 (run 45, 8.36 M **M1**) < 17 600 (run 42, 6.97 M **M1**). Since the M_n values after 16 h were close under rather high **M1** concentration conditions (M_n = 26 000 (run 43) and 25 900 (run 46)], it was thus assumed that removal of ethylene from the mixture could be more important for the synthesis of high-molecular-weight polymers. However, probably due to the increased viscosity of the reaction mixture in [Bmim]PF$_6$

(shown Figure S28 and S30, high viscosity) compared to that in [Hmim]TFSI (Figure S29 and S30, generally low viscosity with a hydrophobic nature compared to PF$_6^-$ salt),[49] obtaining high-molecular-weight polymers from reactions conducted under a 300 mg scale (M_n = 32 200, run 3 after 16 h) seemed difficult even under the optimized reaction conditions.

As observed in the ADMET polymerization of **M1** in [Bmim]PF$_6$, the M_n values from reactions conducted in [Hmim]TFSI under 1.0 g scale conditions using a sealed Schlenk tube (runs 47−53, 57, and 58 in vacuo) were lower than those for reactions conducted under 300 mg scale conditions (runs 12 and 15, Table 1). Although the trend was somewhat different, as described below, the value was also affected by the initial monomer concentration and Ru loading, whereas in all cases the M_n values after 16 h were higher than those after 6 h. In contrast to the polymerization in [Bmim]PF$_6$, the polymerization conducted under high **M1** concentration (runs 57 and 58, 1.0 g/0.25 mL solvent) gave the polymers with low M_n values; an appropriate amount of **HG2** catalyst (0.5 or 1.0 mol %) was required (runs 47−49 and runs 50−53). Under these polymerization conditions (**M1**, 1.0 g scale polymerization) for the reaction conducted using sealed Schlenk tube (reactor A, Table 3), the synthesis of high-molecular-weight polymers as obtained under 300 mg of **M1** conditions seemed difficult (M_n (conducted using reactor A, Schlenk tube) = 21 300−22 900 (1.0 g scale, runs 50−52) vs 39 200 (300 mg scale after 16 h, run 15)].

In contrast, it should be noted that synthesis of high-molecular-weight polymers (M_n = 37 500 and 38 800, runs 55

and 56, respectively) could be achieved when these polymerizations were conducted in a round-bottom flask (25 mL scale, express as reactor B) connected to three-way stopcock in the presence of a football-type stir bar (the picture of the apparatus was shown in Figure S29). The M_n value after 6 h (M_n = 24 500, run 54) was apparently higher than those for reactions conducted in a Schlenk tube (reactor A, runs 12, 47−49). It was thus revealed that the synthesis of the high-molecular-weight polymer (P1) could be possible even under scale-up conditions after the optimization.

As summarized in Table 4, by adopting the optimized conditions under the 1.0 g scale polymerization of M1 (runs 55

Table 4. ADMET Polymerization of M1−M4 by HG2 in [Hmim]TFSI under the Scale-Up Conditions[a]

run	monomer	yield[b] (%)	M_n[c]	M_w/M_n[c]
15[d]	M1	93	39 200	1.95
55	M1	86	37 500	1.91
33[d]	M2	92	26 000	1.95
59	M2	90	23 000	1.75
60	M2	89	23 900	1.81
35[d]	M3	94	38 800	3.38
61	M3	81	24 900	2.67
62	M3	80	26 900	2.97
37[d]	M4	89	33 400	2.30
63	M4	87	34 900	1.82

[a]Conditions are as follows: the reaction of 1.00 g of monomer in 0.03 mL of [Hmim]TFSI [initial conc. of 6.97 (M1 and M2), 7.00 (M3), or 7.80 mmol/mL (M4)]) was conducted a round-bottom flask with a three-way stopcock (25 mL scale) with 1.0 mol % HG2 at 50 °C for 16 h in vacuo. [b]Isolated yield. [c]GPC data in THF versus polystyrene standards. [d]Reaction scale was 300 mg of monomer (Tables 1 and 2).

and 56), the synthesis of high-molecular-weight polymers could also be achieved in the polymerizations of M2 and M4. The M_n values in the resultant polymers (P2, P4, respectively; M_n = 23 900 (P2, run 60) and 34 900 (P4, run 63), Table 4) were very close to those of the resultant polymers from reactions conducted under 300 mg scale polymerization conditions (M_n = 26 000 (P2, run 33) and 33 400 (P4, run 37), Table 2). However, the M_n values in the polymerization of

M3 (runs 61 and 62) were rather low, although we may need further optimization for this purpose.

Hydrogenation of Olefinic Double Bonds in the Biobased Polymers by a Recyclable Ruthenium Catalyst under Biphasic Conditions. After the ADMET polymerization of M1 (1.0 g) by HG2 (1.0 mol %) at 50 °C for 16 h in [Bmim]PF6 (0.30 mL, conducted under the same conditions as those in run 43), the IL solution was carefully transferred into an autoclave (20 mL scale), and to the mixture were added toluene (8.0 mL) and Al2O3 (30 mg). As reported previously in CHCl3,[27] the subsequent tandem hydrogenation gave the saturated polymers (expressed as HP1), which were isolated by carefully and cleanly separating the toluene layers from the [Bmim]PF6 layer to afford HP1 as the white precipitate (Scheme 3); the clean separation from [Hmim]-TFSI, however, seemed difficult (Figure S30, P1). Completion of the hydrogenation was confirmed by the ^{1}H NMR spectra (shown in the Figure S17) and DSC thermograms (increase of the T_m value in addition to the observation of a sole T_m value as confirmation of uniform composition), as established in the previous report.[27]

The [Bmim]PF6 layer after the separation was thus reused without further purification for olefin hydrogenation by adding P1 (1.0 g), prepared independently the ADMET polymerization of M1, and toluene (8.0 mL) to explore the possibility of catalyst recycling. It should be noted that no significant changes in the catalyst performance was observed, and the hydrogenation completed even after an additional eight recycled runs, as confirmed by GPC data (M_n, M_w/M_n values in Table 5), NMR spectra (Figure 1), and DSC thermograms (Figure 2) of the hydrogenated polymers (selected ^{1}H NMR spectra and the DSC thermograms are shown in Figures 1 and 2, and additional data are shown in the SI). The results thus clearly indicate that the hydrogenation catalyst can be recycled without any reactivation by adopting a two-phase hydrogenation system (toluene containing the polymer and IL containing the catalyst).

Depolymerization by Olefin Metathesis and Transesterification. As demonstrated previously in CHCl3,[27] the resultant unsaturated polymer (P1), prepared by the ADMET polymerization of M1 (HG2 1.0 mol %, 50 °C, 6 h, M1 1.0 g scale) in [Bmim]PF6 or [Hmim]TFSI, was treated with ethylene (0.8 MPa) at 50 °C for 5 h (Scheme 4) with the

Scheme 3. Hydrogenation of the Unsaturated Polymer Prepared by ADMET Polymerization of M1 and the Recyclability of the Catalyst Solution in the [Bmim]PF6 IL under Biphasic Conditions
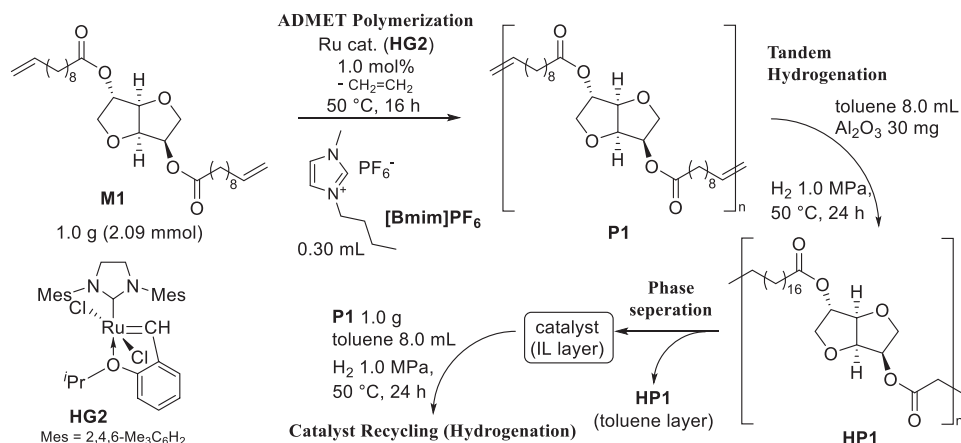
Table 5. Tandem Hydrogenation after ADMET Polymerization of M1 by HG2 in [Bmim]PF₆: The Catalyst Recycling Experiments in the Olefin Hydrogenation of P1[a]

run	recycled runs	before hydrogenation		after hydrogenation			
		M_n[b]	M_w/M_n[b]	M_n[b]	M_w/M_n[b]	yield[c] (%)	T_m[d] (°C)
41	0	16 200	2.12	14 900	2.42	95	73
64[e]	0	19 900	1.86	21 200	1.66	88	
65[f]	1	15 900	1.71	15 600	1.96	82	74
66[f]	2	15 900	1.71	14 200	2.04	84	74
67[f]	3	15 900	1.71	15 400	2.20	93	73
68[f]	4	19 000	1.71	19 700	1.73	92	72
69[f]	5	19 000	1.71	20 700	1.75	94	73
70[f]	6	19 000	1.71	20 500	1.78	93	73
71[f]	7	19 000	1.71	19 400	1.79	93	73
72[f]	8	19 000	1.71	20 900	1.72	92	73

[a]Hydrogenation conditions are as follows: 1.0 g of **P1** (1.0 g of **M1** for runs 41 and 64), 1.0 mol % **HG2** (0.5 mol % for run 41), 0.30 mL of [Bmim]PF₆, 30 mg of Al₂O₃, and 8.0 mL of toluene under 1.0 MPa H₂ at 50 °C for 24 h. In the recycled runs (runs 65–72), no additional [Bmim]PF₆, Al₂O₃, or ruthenium catalyst was added. [b]GPC data in THF versus polystyrene standards. [c]Isolated yield. [d]Determined by DSC thermograms. [e]Polymerization conditions are as follows: the reaction of 1.0 g of **M1** and [Bmim]PF₆ was conducted in sealed Schlenk tube at 50 °C for 16 h (same conditions as in run 43, Table 3). [f]Recycling experiment conditions are as follows: after the hydrogenation, the toluene layer (containing polymer) was separated from [Bmim]PF₆ (containing the ruthenium catalyst), and **P1** and toluene (8.0 mL) were added without the addition of [Bmim]PF₆, Al₂O₃, and **HG2**.

addition of toluene (3.0 mL). The resultant mixture was extracted with toluene and analyzed by ¹H NMR spectroscopy (and GPC trace, Figure S25 and S26, SI), as summarized in Table 6. It was revealed that the resultant solution was a mixture of oligomers (expressed as **DP1**), which were
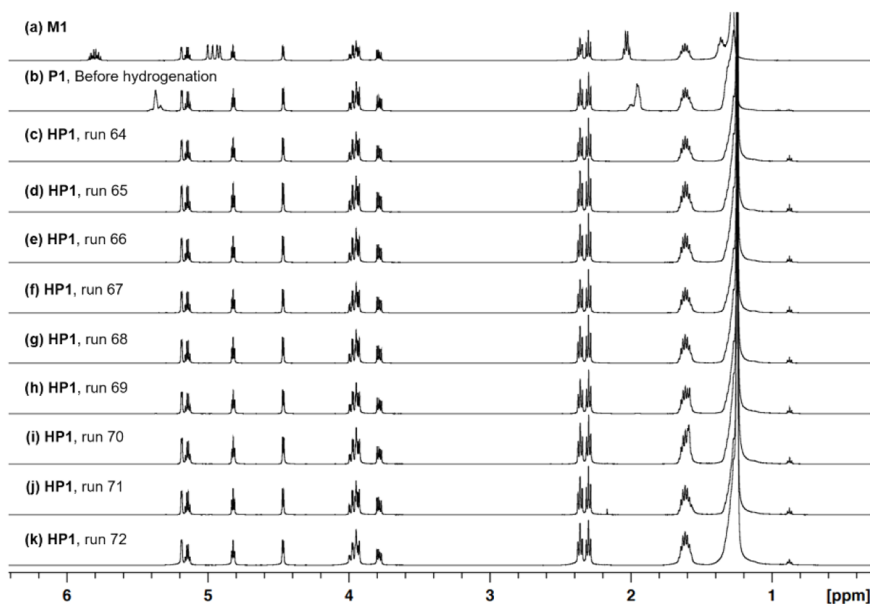

Figure 2. DSC thermograms of the unsaturated polymer after ADMET polymerization (**P1**) and saturated polymers after hydrogenation (**HP1**s) in the recycled runs (runs 65–72).

identified by the ¹H NMR spectra (Figures S19, S20, S22, and S23), clearly suggesting that the resultant polymer reacted with ethylene to give oligomers by depolymerization. As reported previously,[27] ¹H NMR spectra of the resultant reaction mixture showed resonances ascribed to both internal and terminal olefins, suggesting the formation of oligomers (tetramer on the basis of integration ratios of protons in terminal and internal olefins); this was also suggested by the GPC data (Figures S25).

Moreover, the resultant saturated polymer (**HP1**) could be depolymerized by transesterification with ethanol (150 °C and 6 h) in the presence of CpTiCl₃ (1.0 mol %), as reported previously[71] for the depolymerization of poly(ethylene adipate) and poly(butylene adipate). The resultant reaction mixture consisted of isosorbide and diethyl eicosane dioate

Figure 1. ¹H NMR spectra (in CDCl₃ at 25 °C) of (a) **M1**, (b) the unsaturated polymer after ADMET polymerization (**P1**), (c) the hydrogenated polymer (**HP1**, 64), and (d–k) **HP1** in the recycled runs (runs 65–72, respectively). Resonances observed at ca. 0.9 ppm in some runs are due to an impurity in the NMR solvent.
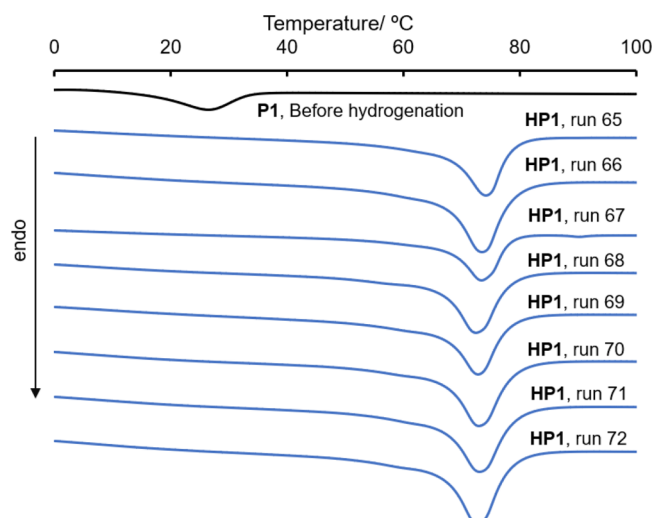
Scheme 4. Depolymerization of the Unsaturated Polymer (P1) with Ethylene by Olefin Metathesis
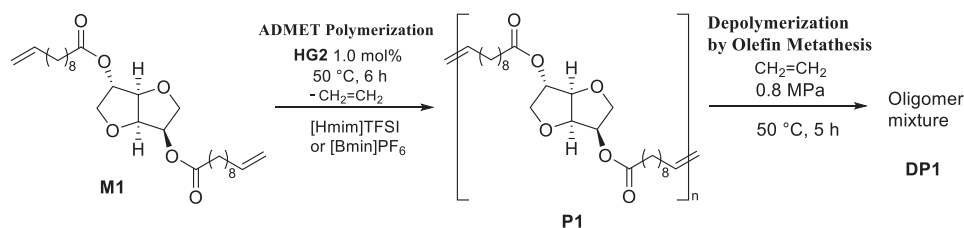

Table 6. Reaction of P1, Prepared by the ADMET Polymerization of M1 by HG2, with Ethylene

run	IL	P1 (ADMET polymerization)[a]		DP1 (after reaction with ethylene)[c]		
		M_n[b]	M_w/M_n[b]	M_n[b]	M_w/M_n[b]	yield[e] (%)
73	[Bmim]PF$_6$	17 100	2.22	1600	2.02	86
74	[Bmim]PF$_6$	17 100	2.05	1700	2.15	83
75[d]	[Hmim]TFSI	27 900	1.79	3000	2.10	88
76	[Hmim]TFSI	18 300	1.76	4400	1.97	92

[a]Conditions are as follows: the reaction of 1.00 g of **M1** (2.09 mmol) in 0.30 mL of the IL with 1.0 mol % Ru catalyst (**HG2**) was performed in a 100 mL scale sealed Schlenk tube (reactor A, Table 3) at 50 °C for 6 h in vacuo. [b]GPC data in THF versus polystyrene standards. [c]Conditions are as follows: 3.0 mL of toluene and 0.8 MPa ethylene at 50 °C for 5 h. [d]The reaction was conducted with a round-bottom flask connected with a three-way stopcock (25 mL scale, reactor B, Table 3). [e]Isolated yield.

(EtO$_2$C(CH$_2$)$_{18}$CO$_2$Et) exclusively with the isolation of the diester (96% isolated yield), which was confirmed by the ^{1}H NMR spectra (Scheme 5, the procedure and the NMR spectra

Scheme 5. Transesterification of HP1 with Ethanol in the Presence of CpTiCl$_3$
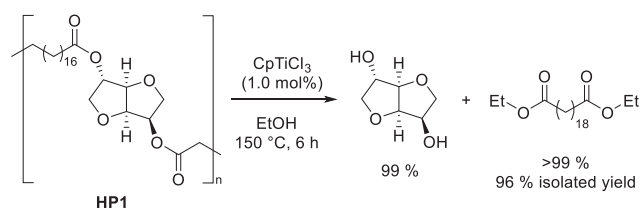
are shown in the Supporting Information).[72] The preliminary result suggest that the resultant polymers could be converted to isosorbide and diethyl eicosane dioate by transesterification in the presence of CpTiCl$_3$.[72]

■ CONCLUDING REMARKS

ADMET polymerization of the α,ω-diene of bis(undec-10-enoate) with isosorbide (**M1**) using a RuCl$_2$(IMesH$_2$)(CH-2-O^{i}Pr−C$_6$H$_4$) (**HG2**, IMesH$_2$ = 1,3-bis(2,4,6-trimethylphenyl)-imidazolin-2-ylidene) catalyst in ionic liquids (ILs, 50 °C under vacuum conditions) afforded high-molecular-weight polymers (**P1**, M_n = 32 200−39,200) compared to those reported previously (M_n = 5600−14700). Both 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 suitable as effective solvents among a series of the imidazolium salts and the pyridinium salts. The polymerization of α,ω-dienes of

bis(undec-10-enoate) with isomannide (**M2**), 1,4-cyclohex-ane-dimethanol (**M3**), and 1,4-butanediol (**M4**) also afforded the higher molecular weight polymers. The M_n values in the resultant polymers did not decrease even under scale-up conditions (300 mg →1.0 g scale) in the polymerizations of **M1**, **M2**, and **M4** in [Hmim]TFSI.

The subsequent reaction of **P1** with ethylene (0.8 MPa at 50 °C for 5 h) gave oligomers (proceeded depolymerization). Tandem hydrogenation of the resultant unsaturated polymers (**P1**) in a [Bmim]PF$_6$−toluene biphasic system upon the addition of Al$_2$O$_3$ (1.0 MPaH$_2$ at 50 °C) gave the corresponding saturated polymers (**HP1**). The resultant polymer was isolated by a phase separation of the toluene layer. The [Bmim]PF$_6$ layer containing the ruthenium catalyst could be recycled without a decrease in the activity/selectivity for the olefin hydrogenation at least eight times. The transesterification of **HP1** with ethanol by CpTiCl$_3$ gave the corresponding diesters and isosorbide.

Synthesis of high-molecular-weight aliphatic polyesters is in fact very important in terms of the preparation of polymer films with better mechanical properties (possessing a better tensile strength and elongation at break),[66] because the reported M_n values (M_n = 5600−14700) are not suitable for this purpose.[13,66,70] Indeed, in our preliminary results,[66] the elongation at break of the films in the hydrogenated polymer (**HP1**) was strongly affected by the M_n value (e.g., elongation at break of the hot-pressed film of 8.5% (M_n = 9400)[16,27] < 22.6% (M_n = 21800) < 253% (M_n = 29800), determined using Shimadzu Universal Testing Instruments (Autograph AGS-10kNX) equipped with a load cell (cell capacity 500 N) at 10 mm/min and 25 °C) as the tensile strength increased, suggesting that the film requires certain threshold of the M_n value to exhibit better mechanical properties.[66] We strongly believe that the results could provide a new possibility of biobased polyesters prepared by the olefin metathesis approaches, and the manuscript also provides information concerning factors presented in this method for the purpose even under scale-up conditions. The results also provide the possibility of developing functional polyesters from biorenew-ables. The study for development of alternative methods/methodology for the synthesis of high-molecular-weight polymers by the ADMET polymerization could also be considered as a subject of interest, and we believe that catalyst development may provide a new possibility.

■ EXPERIMENTAL SECTION

General Procedure. All synthetic experiments were carried out under a nitrogen atmosphere in a drybox or using standard Schlenk techniques. Anhydrous-grade toluene, n-hexane, and dichloromethane (DCM) (>99.5%, Kanto Chemical Co., Inc.) were transferred into a bottle containing molecular sieves (mixture of 3Å 1/16, 4 Å 1/8, and 13X 1/16)

in a drybox. Chemicals (Tokyo Chemical Industry, Co., Ltd.) such as triethylamine (>99.0%), ethyl vinyl ether (>98.0%), 10-undecenoyl chloride (>98.0%), isomannide (>98.0%), isosorbide (>98.0%), 1,4-cyclohexanedimethanol (>99.0%), and 1,4-butanediol (>99.0%) were used without further purification. $RuCl_2(IMesH_2)(CH-2-O^i Pr-C_6H_4)$ (**HG2**, 97.0%) was obtained from Aldrich Chemical Co. and was used as received. Ionic liquids (ILs) such as 1-hexyl-3-methylimidazolium hexafluorophosphate expressed as $[Hmim]PF_6$, 1-butylpyridinium bis(trifluoromethanesulfonyl)-imide expressed as $[Bpy]TFSI$ (>98.0%, Tokyo Chemical Industry, Co., Ltd.), 1-hexyl-3-methylimidazolium chloride expressed as $[Hmim]Cl$ (>95.0%, Wako Pure Chemical Industries, Ltd.), 1-hexyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)imide expressed as $[Hmim]TFSI$, 1-butyl-3-methylimidazolium hexafluorophosphate expressed as $[Bmim]PF_6$, 1-butyl-2,3-dimethylimidazolium bis-(trifluoromethanesulfonyl)imide expressed as $[Bdmim]TFSI$, 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide expressed as $[Dmim]TFSI$ (>97.0%, Wako Pure Chemical Industries, Ltd.), 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide expressed as $[Bmim]TFSI$, 1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide expressed as $[B_4mpy]TFSI$, and 1-hexyl-4-methylpyridinium bis(trifluoromethanesulfonyl)imide expressed as $[H_4mpy]$-TFSI (>98.0%, Wako Pure Chemical Industries, Ltd.) were purified by passing a mixed solution (dichloromethane and ILs) through a microflush column of Celite and alumina (Wako Pure Chemical Industries, Ltd.) and dried under reduced pressure before use in a drybox. Monomers employed in this study such as dianhydro-*D*-glucityl bis(undec-10-enoate) (**M1**), dianhydro-*D*-mannityl bis(undec-10-enoate) (**M2**), cyclohexane-1,4-dimethanol bis(undec-10-enoate) (**M3**), and butane-1,4-diyl bis(undec-10-enoate) (**M4**) were prepared according to the reported procedure.[27]

All ^1H and ^{13}C NMR measurements were performed at 25 °C on a Bruker AV500 spectrometer (500.13 and 125.77 MHz, respectively) using $CDCl_3$ as the solvent. Chemical shifts were reported as ppm with reference to $SiMe_4$ at 0.00 ppm. Gel permeation chromatography (GPC) was used to analyze the molecular weights and molecular weight distributions of the resultant polymer. The GPC measurements were carried out at 40 °C on SCL-10A (Shimadzu Co., Ltd.) 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) using a Shimadzu RID-10A detector in THF (>99.8%, Kanto Chemical Co., Inc.), which served as the eluent with a flow rate 1.0 mL/min. Differential scanning calorimetric (DSC) data for the resultant polymers was measured using a Hitachi DSC-7000X analyzer under a nitrogen atmosphere. All samples (3−5 mg) were placed in standard aluminum pans. These samples were first heated from 30 to 150 °C at 20 °C/min and then cooled to −100 °C at 10 °C/min. The melting (T_m) temperature was determined upon the second heating cycle.

ADMET Polymerization of Biobased Monomers (M1−M4) in ILs. The ADMET polymerizations of α,ω-diene monomers (**M1−M4**) were conducted using a second-generation Hoveyda−Grubbs catalyst (**HG2**) in various ILs in vacuo. Typical procedure is as follows. To as sealed Schlenk tube (25 mL scale) were added monomer (**M1**, 300 mg, 0.63 mmol), ILs (0.14 mL), and a dichloromethane solution containing a prescribed amount of **HG2** in the drybox. The

tube was placed in a liquid nitrogen bath to remove ethylene and nitrogen by opening the valve connected to the vacuum line for 1 min, and the solution was warmed with stirring to room temperature. The CH_2Cl_2 was then immediately removed under vacuum conditions at room temperature, and the tube was placed into an oil bath to perform the polymerization at 50 °C under vacuum conditions. Ethylene produced as a byproduct from the condensation polymerization was continuously removed. After the reaction, the reaction mixture was cooled to room temperature and quenched with a solution of ethyl vinyl ether and toluene (6.0 mL) under a nitrogen atmosphere while stirring for 3 h, and the toluene layer was separated from the IL layer. The IL layer was further extracted with toluene (2.0 mL) if necessary. The toluene solution was then poured into cold methanol (ca. 100 mL), and the precipitates were then collected by filtration and dried in vacuo. The polymerizations of **M2−M4** (300 mg) were conducted similarly to give **P2−P4**, respectively. The amount of toluene and methanol for extraction and precipitation can be optimized.

Tandem Olefin Hydrogenation under Biphasic Conditions. After Athe DMET polymerization, the mixture dissolved in toluene (8.0 mL) was transferred to an autoclave with the addition of a small amount of Al_2O_3, and the reactor was then pressurized with H_2 at 1.0 MPa. Hydrogenation occurred at 50 °C, then the toluene solution was separated from the IL, passed through a microcolumn of Celite and alumina, and precipitated in cold methanol (100 mL) while stirring for 15 min. The product was obtained by filtration and dried in vacuo. After tandem hydrogenation, the obtained IL mixture was transferred to the same autoclave with the addition of the selected **P1** dissolved in toluene. Hydrogenation of a subsequent batch of **P1** occurred at 50 °C, and the process can be recycled multiple times under the same conditions. The product was obtained by filtration and dried in vacuo.

Reaction of Unsaturated Polymers with Ethylene. The basic reaction procedure is the same as that reported previously.[27] After the ADMET polymerization of **M1**, the IL solution containing **P1** and the ruthenium catalyst was transferred to an autoclave (20 mL scale, stainless steel) with the addition of toluene (3.0 mL). The reaction was carried out under ethylene (0.8 MPa) at 50 °C for the prescribed time. The toluene solution was separated from the IL, and the product was separated by evaporation for GPC and NMR analyses.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c00390.

> Additional polymerization results in various ILs, including typical experimental procedures, the reaction apparatus, and a picture in the reaction solution; selected NMR spectra and DSC thermograms in the resultant polymers; and additional olefin hydrogenation results, including the recycling experiment, additional data (NMR spectra) for the reaction with ethylene, and the transesterification of ethanol (PDF)

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Notes

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