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Synthesis of Polyesters Containing Long Aliphatic Methylene Units by ADMET Polymerization and Synthesis of ABA-Triblock Copolymers by One-Pot End Modification and Subsequent Living Ring-Opening Polymerization

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ABSTRACT: The synthesis of high-molecular-weight (M_n up to 62,000 g/mol) polyesters has been achieved by acyclic diene metathesis (ADMET) polymerization of α,ω-dienes prepared from biobased bis(undec-10-enoate) and diols [ethylene glycol (**M1**), propylene glycol (**M2**), 1,9-nonanediol (**M3**), 1,4-benzenedimethanol (**M4**), and hydroquinone (**M5**)] using ruthenium-carbene catalysts. Replacement of the solvent during the ADMET polymerization was effective for obtainment of the high-molecular-weight polymers (expressed as **P1−P5**). The melting temperatures (T_m) in the resultant polyesters were dependent upon the diol (middle) segment employed, and the polymer prepared from **M5** exceeded 100 °C (a T_m value of 122.5 °C). The polymerization of **M3** and **M4** in the presence of 1,4-cis-diacetoxy-2-butene (DAB, as the chain transfer agent) afforded the telechelic polyesters [**P3(OAc)₂** and **P4(OAc)₂**, respectively] containing acetoxy end groups exclusively. The resultant polymers containing hydroxy group termini [**P3(OH)₂** and **P4(OH)₂**], prepared by the selective deprotection of the acetoxy end groups, were treated with AlEt₃ followed by addition of ε-caprolactone to afford the ABA-type triblock copolymers exclusively, through a living ring-opening polymerization. The depolymerization (hydrolysis) under basic conditions (NaOH aqueous solution) of **P3** was explored.
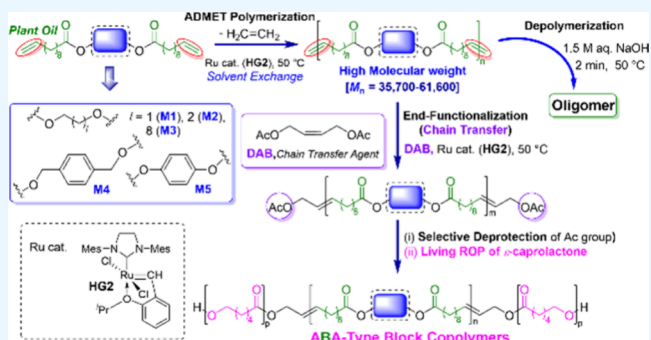
1. INTRODUCTION

The study on the development of polyesters containing long aliphatic chains derived from plant oil has been recognized as an important subject, especially due to a promising possibility as alternatives of petroleum-derived polymers.[1−7] In particular, the biobased aliphatic polyesters,[2,3,5−7] prepared from non-edible naturally abundant plant resources (plant oil, etc.), have been considered as an important subject in terms of not only efficient utilization of plant oils [fatty acids (FA) and the esters (FAEs)][8−10] but also of circular economy.[11−15] Two major approaches have been considered for the synthesis,[6,7] and the route by acyclic diene metathesis (ADMET) polymerization[16−20] with the subsequent hydrogenation seems to be more suitable than that by the polycondensation (with removal of water or alcohol) for better monomer scope.[7]

Despite many reports for synthesis of the (aliphatic) polyesters by ADMET polymerization of α,ω-diene monomers using ruthenium-carbene catalysts (**G2** and **HG2**, Scheme 1),[21−42] however, reports for synthesis of high-molecular-weight polymers (ca. M_n = >30,000 g/mol considered for better mechanical properties as films)[41,42] still have been limited (Scheme 1).[42] Indeed, in our recent study, the tensile

strength of certain biobased aliphatic polyesters in films increased with increasing the molar mass in the polymers.[42] A possibility of catalyst decomposition can be highly considered, as demonstrated previously,[22] when the metathesis polymerizations (reactions) were conducted at high temperatures (70−90 °C) and the subsequent isomerization and undesired side reaction caused by the formed radical species were known in this catalysis.[7,22,43−48] Recently, the synthesis of some high-molar-mass polymers was demonstrated by adopting ADMET polymerizations of α,ω-diene monomers of bis(undec-10-enoate) with isosorbide [dianhydro-D-glucityl bis(undec-10-enoate)], isomannide, 1,4-cyclohexanedimethanol, and 1,4-butanediol in the presence of a ruthenium-carbene catalyst in ionic liquids (ILs) such as 1-n-butyl-3-methyl imidazolium hexafluorophosphate, [Bmim]PF₆, and 1-n-hexyl-3-methyl
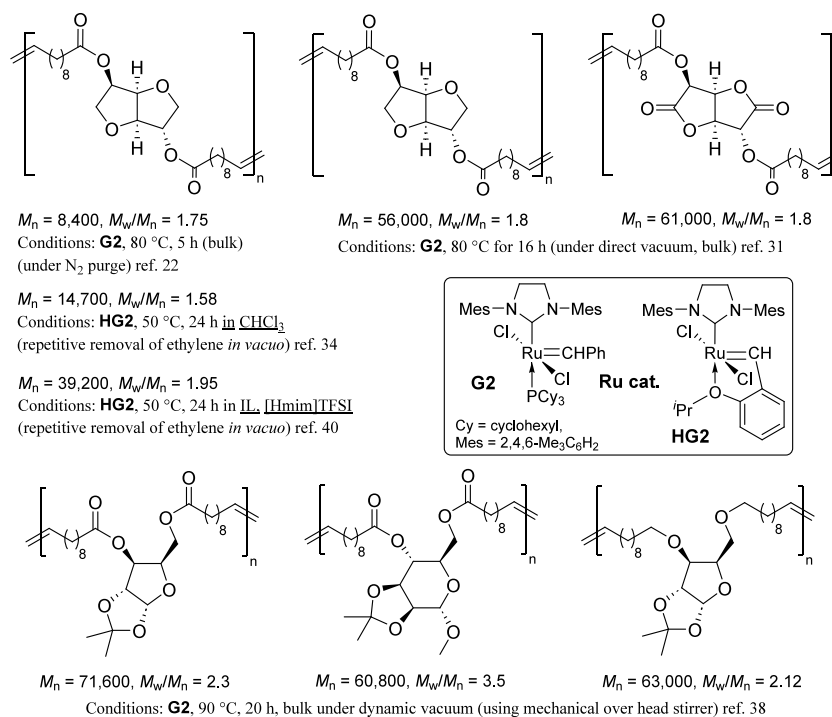
Scheme 1. Selected Reports for Synthesis of Aliphatic Polyesters by Acyclic Diene Metathesis Polymerization

M_n = 8,400, M_w/M_n = 1.75
Conditions: **G2**, 80 °C, 5 h (bulk)
(under N$_2$ purge) ref. 22

M_n = 14,700, M_w/M_n = 1.58
Conditions: **HG2**, 50 °C, 24 h in CHCl$_3$
(repetitive removal of ethylene *in vacuo*) ref. 34

M_n = 39,200, M_w/M_n = 1.95
Conditions: **HG2**, 50 °C, 24 h in IL, [Hmim]TFSI
(repetitive removal of ethylene *in vacuo*) ref. 40

M_n = 56,000, M_w/M_n = 1.8
M_n = 61,000, M_w/M_n = 1.8
Conditions: **G2**, 80 °C for 16 h (under direct vacuum, bulk) ref. 31

Cy = cyclohexyl,
Mes = 2,4,6-Me$_3$C$_6$H$_2$

M_n = 71,600, M_w/M_n = 2.3 M_n = 60,800, M_w/M_n = 3.5 M_n = 63,000, M_w/M_n = 2.12
Conditions: **G2**, 90 °C, 20 h, bulk under dynamic vacuum (using mechanical over head stirrer) ref. 38

Scheme 2. Synthesis of Polyesters by ADMET Polymerization of M1−M5 and the End Modifications
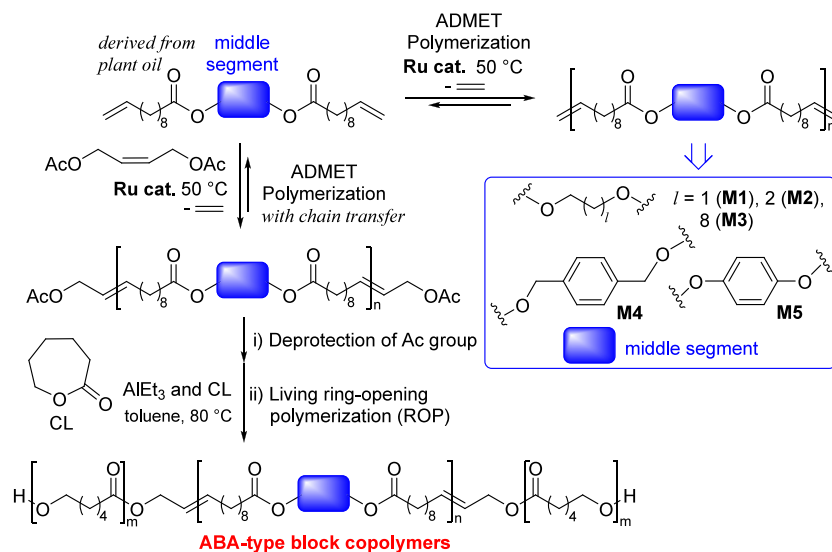
imidazolium bis(trifluoromethanesulfonyl)imide, [Hmim]-TFSI[40,49−52] (Scheme 1).

Another promising application by adopting the ADMET polymerization could be considered as a possibility of synthesis of end-functionalized polymers.[16−20] Reported examples for synthesis of end-functionalized polymers by ruthenium-catalyzed olefin metathesis polymerization in the presence of a chain transfer reagent [symmetric internal olefins, such as *cis*-1,4-diacetoxy-2-butene (DAB)][53−58] were limited to ROMP,[53−63] and, as far as we know, there is only one report for the synthesis of end-functionalized but rather rigid (rod and coil type) poly(9,9′-di-*n*-octyl-fluorene vinylene)s in the ADMET polymerization.[64] The precise synthesis of the end-functionalized polymers can be applied to exclusive prepara-

tion of (multi) block copolymers by adopting grafting-from and grafting-to approaches.[65,66]

We thus herein present the synthesis of the high-molecular-weight polyesters by the ADMET polymerization of five monomers with different middle (diol) segments (**M1−M5**) by adopting exchange (remove and refill) of the solvent (chloroform) and the synthesis of end-functionalized poly-esters in the presence of a chain transfer agent (DAB). The synthesis of ABA-type block copolymers was then demon-strated by deprotection of the acetoxy groups in the resultant polyester chain ends and subsequent Al-alkoxide-initiated ring-opening polymerization of ε-caprolactone (CL).[67−69]

Table 1. ADMET Polymerization of α,ω-Diene Monomers (M1−M5) by Ruthenium-Carbene Catalysts (G2 and HG2)[a]

run	monomer (mmol)	cat. (mol %)	solvent (number of solvent exchange)[b]	time (h)	conc.[c] (M)	M_n[d] (g·mol^{-1})	M_w/M_n (Đ)[d]	yield[e] (%)	T_m[f] (°C)
1	M1 (0.76)	HG2 (1.0)	toluene (0)	24	4.3	11,700	1.52	93	41.5
2	M1 (0.76)	G2 (1.0)	chloroform (0)	24	2.5	11,600	1.50	92	44.3
3	M1 (0.76)	G2 (1.0)	chloroform (3)	24	3.0	36,000	1.69	92	49.0
4	M1 (0.76)	HG2 (1.0)	chloroform (2)	24	5.0	19,000	1.86	94	40.5
5	M1 (0.76)	HG2 (1.0)	chloroform (3)	24	5.0	40,000	1.74	95	49.0
6	M2 (0.73)	HG2 (1.0)	chloroform (0)	24	4.0	11,600	1.67	90	28.4
7	M2 (0.73)	HG2 (1.0)	chloroform (3)	24	4.0	35,700	1.70	95	32.9
8	M2 (0.73)	HG2 (1.0)	chloroform (3)	24	5.0	3200	1.65	93	31.1
9	M2 (0.73)	HG2 (2.0)	chloroform (3)	24	5.0	2000	1.87	90	31.0
10	M3 (0.61)	HG2 (1.0)	chloroform (0)	24	3.0	8300	1.41	88	51.9
11	M3 (0.61)	HG2 (1.0)	chloroform (3)	24	3.0	57,600	1.96	91	53.7
12	M3 (0.61)	HG2 (1.0)	chloroform (3)	16	3.0	47,800	1.59	95	55.0
13	M3 (0.61)	HG2 (1.0)	chloroform (4)	2	3.0	48,300	1.94	91	56.0
14	M3 (0.61)	HG2 (1.0)	chloroform (4)	6	3.0	6000	2.00	93	55.6
15	M3 (0.61)	HG2 (1.0)	chloroform (4)	24	3.0	61,600	1.82	93	56.1
16	M4 (0.64)	HG2 (1.0)	chloroform (3)	24	2.5	38,100	1.97	93	48.8
17	M4 (0.64)	HG2 (2.0)	chloroform (3)	24	2.5	22,300	1.62	89	32.9
18	M4 (0.64)	HG2 (1.0)	chloroform (4)	2	1.5	54,500	1.89	90	54.2
19	M4 (0.64)	HG2 (1.0)	chloroform (4)	6	1.5	59,500	1.97	93	58.1
20	M4 (0.64)	HG2 (1.0)	chloroform (4)	24	1.5	59,700	1.97	93	58.0
21	M5 (0.68)	HG2 (1.0)	tetrachloroethane (0)	24	1.0	5300	1.30	93	114.0
22	M5 (0.68)	HG2 (1.0)	tetrachloroethane (3)	24	1.0	2000	1.57	90	120.0
23	M5 (0.68)	HG2 (1.0)	chloroform (3)	24	1.0	3900	1.69	95	122.5
24	M5 (0.68)	HG2 (1.0)	chloroform (3)	6	1.0	36,300	1.87	92	120.0

[a]Conditions: 300 mg of the monomer in 0.15−0.68 mL of the solvent, 50 °C. [b]Conducted solvent replacements during the polymerization runs for every 30 min in the initial 1 h. [c]Initial monomer concentration in mmol/mL. [d]GPC (SEC) data in THF vs polystyrene standards. [e]Isolated yield by precipitation, as the methanol insoluble fraction. [f]Melting temperature measured by DSC thermograms.

Scheme 3. Synthesis of Polyesters by ADMET Polymerization of M1−M5 Using Ruthenium-Carbene Catalysts (G2 and HG2)
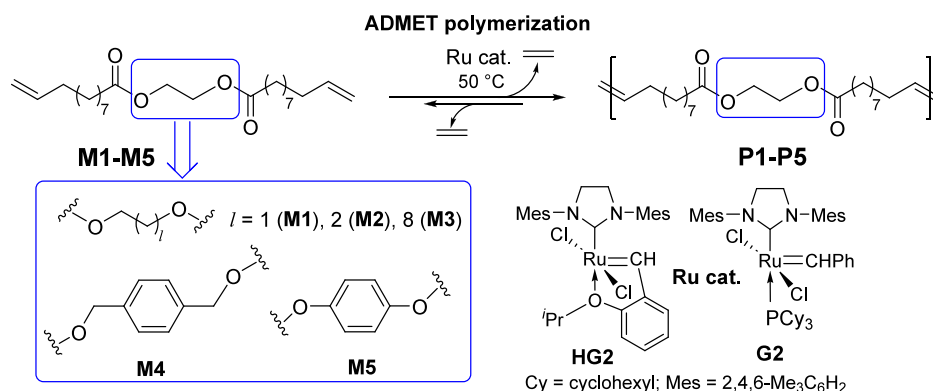
2. RESULTS AND DISCUSSION

2.1. ADMET Polymerization of α,ω-Dienes Using Ruthenium-Carbene Catalysts. α,ω-Diene monomers consisting of diesters of bis(undec-10-enoate) (derived from castor oil) with diols [ethylene glycol (M1),[70,71] propylene glycol (M2),[25] 1,9-nonanediol (M3), 1,4-benzenedimethanol (M4), and hydroquinone (M5),[24] shown in Scheme 2] have been chosen in this study. This is because their thermal (and mechanical) properties in the resultant polyesters should be affected by the middle segment (diol units, through the so-called interpolymer interactions) in these symmetric monomers.[6,7] These monomers were prepared according to the previous reports[7−9] by esterification of 10-undecenoyl chloride with various diols (detailed synthetic procedures are shown in the Supporting Information, SI)[24,25,70,71] and were identified

by ^1H and ^{13}C NMR spectra and atmospheric-pressure chemical ionization (APCI) mass spectrometry (Figures S1−S10, Supporting Information).

ADMET polymerizations of M1−M5 were conducted at 50 °C in the presence of the so-called Grubbs second-generation catalyst, $RuCl_2(PCy_3)(IMesH_2)(CHPh)$ [G2; IMesH$_2$ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene, Cy = cyclohexyl], and the so-called Hoveyda−Grubbs catalyst, $RuCl_2(IMesH_2)(CH-2-O^iPr-C_6H_4)$ (HG2), according to the reported procedure,[7−9] by removing ethylene in vacuo (by placing the sealed reaction tube into a liquid nitrogen bath to connect a vacuum line for a short period and then placing the tube into the oil bath heated at 50 °C). In certain experimental runs, chloroform or tetrachloroethane used as a solvent was removed in vacuo and was replaced every 30 min (three or four times) at the initial stage (noted as solvent exchange in Table
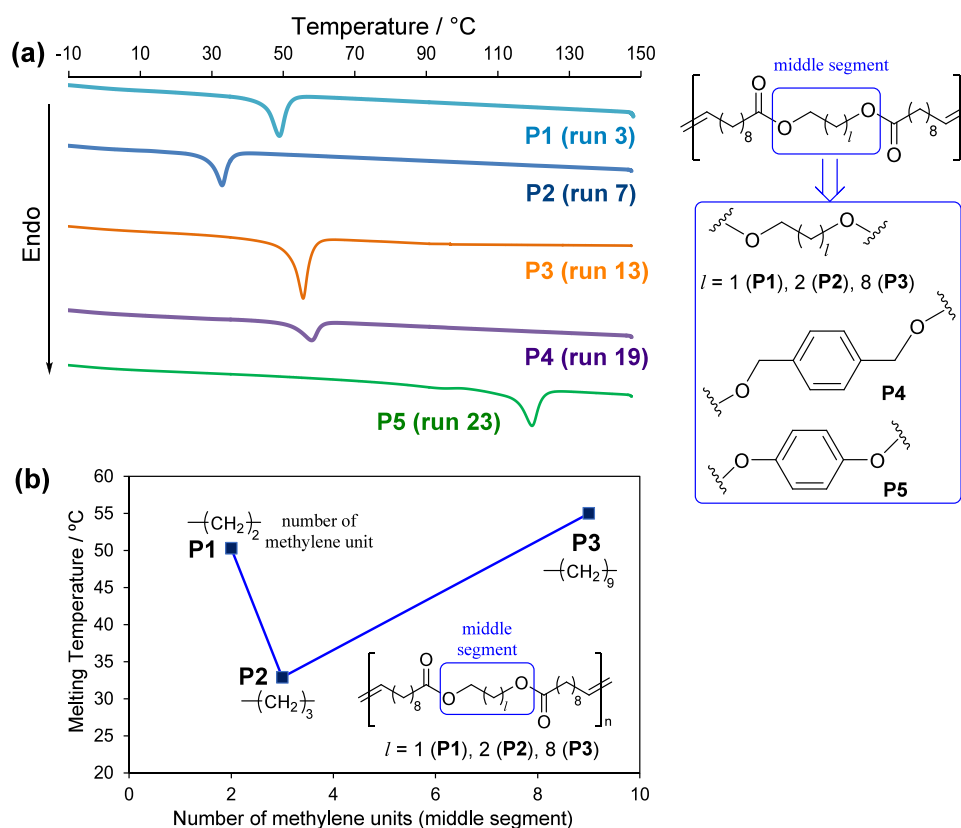
Figure 1. (a) DSC thermograms of polyesters (**P1−P5**) and (b) plots of melting temperatures (T_m) vs the number of methylene units in aliphatic polyesters (**P1−P3**).

1) to obtain the high-molecular-weight polymers (described below). The resultant polymers (expressed as **P1−P5**, Scheme 3) were identified by NMR spectra (Figures S12−S21, Supporting Information); resonances ascribed to protons (or carbons) corresponding to the terminal olefins in **M1−M5** were converted to those corresponding to the internal olefins, whereas most of the other resonances were unchanged significantly (Figure S11, Supporting Information). The molecular weights (M_w and M_n) and their distributions (M_w/M_n, Đ) were measured by GPC (SEC) in THF versus polystyrene standards (Figures S36−S40, Supporting Information), and their thermal properties were analyzed by DSC thermograms (Figures S30−S34, Supporting Information). The polymerizations were conducted under various conditions (solvent, catalyst, method, etc.) for obtainment of high-molecular-weight polymers, the selected results are summarized in Table 1, and additional results are also shown in Table S1 (SI).

It was revealed that the ADMET polymerization of **M1−M5** using a low **HG2** loading (1.0 mol %) with repetitive solvent replacements (3 times) afforded high-molecular-weight polyesters with unimodal molecular weight distributions [e.g., **P1** (run 5): M_n (M_w/M_n) = 40,000 g/mol (1.74); **P2** (run 7): 35,700 (1.70); **P3** (run 15): 61,600 (1.82); **P4** (run 20): 59,700 (1.97); **P5** (run 23): 39,000 (1.69)]. The apparent increase in the M_n values in the resultant polymers (**P1−P5**) was observed by conducting the replacement procedure [M_n = 11,600 g/mol (run 2) vs 36,000 (run 3), **P1**; 11,600 (run 6) vs 35,700 (run 7), **P2**; 8300 (run 10) vs 57,600 (run 11), **P3**; 5300 (run 21) vs 20,000 (run 22), **P5**]. This could be probably due to the fact that the remaining ethylene was removed with

the solvent (chloroform or tetrachloroethane) since the removal of ethylene is a prerequisite for obtainment of the high-molecular-weight polymers in this condensation polymerization, as demonstrated previously.[34,37,40] The assumption could also be confirmed by the facts that the M_n values were affected by the number of the replacement (2−4 times), and the repetitive replacement at the initial stage gave the high-molar-mass polymers [M_n = 19,000 g/mol (run 4) vs 40,000 (run 5), **P1**; 47,800 (run 12) vs 61,600 (run 15), **P3**; 38,100 (run 16) vs 59,700 (run 20), **P4**].

As also reported previously,[34,40] the M_n value was also affected by the **HG2** loading, and the values conducted with 1.0 mol % **HG2** were higher than those conducted with the 2.0 mol % loading (1.0−2.0 mol %, runs 3, 8, 9, 12, 16, 17, and S1−S3). The M_n value was also affected by the initial monomer concentration employed. Under the repetitive solvent replacement conditions (every 30 min for 2 h, a total of 4 times), the polymerization seems completed even after 6 h [M_n = 60,000 g/mol (run 14), **P3**; 59,500 (run 19), **P4**], and the further significant increases were not observed even if these polymerizations were continued for 24 h (runs 15 and 20).

The thermal behavior of the resultant polyesters was studied by using differential scanning calorimetry (DSC, Figures S30−S34, Supporting Information). As shown in Figure 1a, the resultant polymers possessed a sole melting temperature (T_m), suggesting that the resultant polymers are semicrystalline materials with uniform compositions. The T_m values were affected by the diol segment employed (Table 1); **P5**, prepared from bis(undec-10-enoate) with hydroquinone, possessed the highest T_m value (122.5 °C, run 23) among **P1−P5**. As described previously,[6,7] the T_m values were affected by the
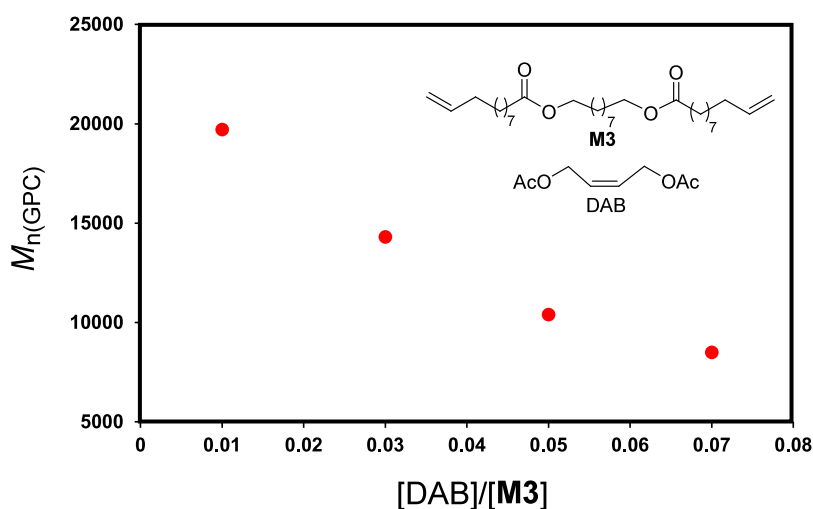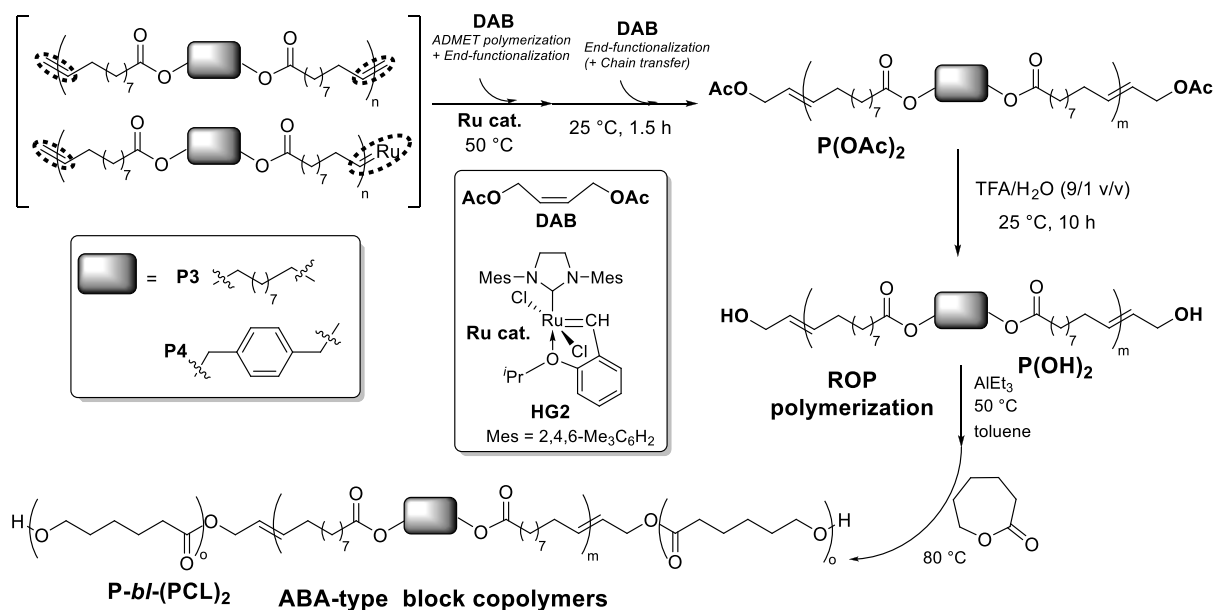
Scheme 4. Synthesis of ABA-Type Block Copolymers (P-*bl*-(PCL)$_2$) by One-Pot End Modification and Al-Alkoxide-Initiated Ring-Opening Polymerization of ε-Caprolactone

Figure 2. Plots of $M_{\text{n(GPC)}}$ values in **P3(OAc)$_2$** vs the initial molar ratios of DAB to **M3** (runs 25−28).

methylene chain length (n = 1, 2, and 8, Figure 1b), probably explained as due to the difference in the direction of dipoles between ester groups in close layers of the crystalline phase of aliphatic polyesters.[6] It also seems that the T_{m} values were also affected by the M_{n} values, and the values initially increased upon increasing the M_{n} value.

2.2. One-Pot Synthesis of End-Functionalized Unsaturated Polyesters and Synthesis of the ABA-Type Block Copolymers by Grafting from the Chain Ends. A possibility of synthesis of the end-functionalized polymer was explored by adopting the ADMET polymerization in the presence of a chain transfer reagent, 1,4-*cis*-diacetoxy-2-butene (DAB), according to the reported one-pot procedure for synthesis of the end-functionalized (rather rigid, rod and coil type) poly(9,9′-di-*n*-octyl-fluorene vinylene)s.[64] As shown in Scheme 4, DAB (with different molar ratios) was added after the initial ADMET polymerization of **M3** (or **M4**) by **HG2** (1.0 mol %, 50 °C, 2 h) with replacement of chloroform [every 30 min, twice (**M3**) or three times (**M4**)]. The subsequent

olefin metathesis reactions with DAB with various molar ratios were conducted at 50 °C for 2 h, and DAB was then further added with a rather excess amount at 25 °C for completion of the olefin metathesis of the polymer chain ends with DAB (1.5 h, detailed synthetic procedures are shown in the Experimental Section).

Introduction of the acetoxy end group could be confirmed by ^{1}H NMR spectra (in CDCl$_3$ at 25 °C) as the disappearance of resonances ascribed to the terminal vinyl groups (5.82, 5.0, and 4.94 ppm) along with observation of new resonances corresponding to the terminal acetoxy group [2.08 (methyl), 4.63 and 4.52 (methylene), etc.], as shown in Figure 3 and Figure S22, Supporting Information. The resultant end-functionalized polyesters, expressed as **P3(OAc)$_2$** and **P4-(OAc)$_2$** (Scheme 4), were thus identified by ^{1}H NMR spectra (Figures S22−S25, Supporting Information) and GPC traces [unimodal molecular weight distribution without a significant increase of PDI ($M_{\text{w}}/M_{\text{n}}$) values, Figures S41−S43, Supporting Information]. More data including the reaction of **M3** using

Table 2. One-Pot Catalytic Synthesis of End-Functionalized Polyesters Using ADMET Polymerization of M3 and M4 in the Presence of 1,4-*cis*-Diacetoxy-2-butene (DAB) as a Chain Transfer Agent[a]

run	monomer (mmol)	ADMET polymer[b]		first reaction[c]	second reaction[c]	end-functionalized polyester P(OAc)₂			
		$M_n{}^g$ (g·mol⁻¹)	$M_w/M_n(Đ)^g$	[DAB]/[M][d]	[DAB]/[M][d]	conv.[e] (%)	$M_n{}^g$ (g·mol⁻¹)	$M_w/M_n(Đ)^g$	yield[f] (%)
25	**M3** (0.61)	27,600[h]	1.70	0.07	0.54	>98	8500	1.82	90
26	**M3** (0.61)			0.05	0.54	>98	10,400	1.80	92
27	**M3** (0.61)			0.03	0.54	>98	14,300	1.72	91
28	**M3** (0.61)			0.01	0.54	>98	19,700	1.80	93
29	**M4** (0.64)	38,100[h]	1.97	0.05	0.54	>98	12,900	1.80	92
30	**M4** (0.64)			0.05	0.54	>98	13,200	1.81	92

[a]Conditions: 300 mg of the monomer in 0.25 mL of chloroform, 1.0 mol % HG2, 1.0 mol % benzoquinone, 50 °C, 2 h, solvent exchanges (twice for runs 25−28 and 3 times for runs 29−30). [b]Initial ADMET polymerization before addition of DAB: 300 mg of the monomer in 0.25 mL of chloroform, 1.0 mol % HG2, 1.0 mol % benzoquinone, 50 °C, 2 h, solvent exchanges (twice for runs 25−28 and 3 times for runs 29−30). [c]Conditions after addition of DAB: 1st reaction 2 h, 50 °C, 2nd reaction 1.5 h at 25 °C. [d]Initial molar ratio of DAB to the monomer (**M3** or **M4**). [e]Estimated by ¹H NMR spectra (percentage of end functionalization, consumption of vinyl groups). [f]Isolated yield, as the methanol insoluble fraction. [g]GPC (SEC) data in THF vs polystyrene standards. [h]Independent runs in the polymerization at 50 °C (before the addition of DAB).

G2 (in place of **HG2**) in the presence of DAB are also summarized in Table S2 (SI); the optimized conditions for the first and second DAB additions were 2 h at 50 °C and 1.5 h at 25 °C, respectively.

As shown in Figure 2 and Table 2, the M_n values in the resultant polymers, expressed as **P3(OAc)₂**, were varied by the DAB/**M3** initial molar ratios since a fairly good linear correlation was thus observed between the M_n values and the molar ratios along with high conversions of vinyl groups (>98%, by ¹H NMR spectra, Figure S24). The results thus suggest that the M_n value could be controlled by the amount of the chain transfer agent (DAB) charged. For instance, the ADMET polymerization of **M3** conducted with the molar ratios of [DAB]/[M] = 0.01, 0.03, 0.05, and 0.07 afforded the corresponding polymers, **P3(OAc)₂**, with M_n (M_w/M_n) values of 19,700 (1.80, run 28), 14,300 (1.72, run 27), 10,400 (1.80, run 26), and 8,500 g/mol (1.82, run 25), respectively (their GPC traces are shown in Figure S42, Supporting Information). Similarly, the end-functionalized polyesters, **P4(OAc)₂**, could also be prepared from **M4** under the optimized conditions (runs 29 and 30, Table 2) with high consumption of the vinyl end groups (>98%) confirmed by ¹H NMR spectra (Figure 2). Their GPC traces in the resultant polymers possessed unimodal molecular weight distributions (Figure S43, Supporting Information). As described below, their quantitative end modifications were confirmed by grafting ring-opened poly(ε-caprolactone).

2.3. Synthesis of ABA-Type Block Copolymers by Combination of ADMET with Al-Alkoxide-Initiated Ring-Opening Polymerization of ε-Caprolactone. The hydroxy group-terminated telechelic polyesters, expressed as **P3(OH)₂** and **P4(OH)₂**, could be obtained via an exclusive hydrolysis of the acetoxy end groups in **P3(OAc)₂** or **P4(OAc)₂**. The hydrolysis of the acetoxy chain ends without degradation of the main chain (ester linkage) could be attained by treating the acetoxy-functionalized polymers with a mixed solution of trifluoroacetic acid and water (9/1 v/v) at room temperature (25 °C) for 10 h (Scheme 4, the selected results are summarized in Table S3, Supporting Information). The selective deprotection could be confirmed by ¹H NMR spectra as the disappearance of the acetyl methyl proton (2.08 ppm) with retaining of the other resonances (Figure 3 and Figure S26), in addition to the fact that no significant differences in the M_n values (without increasing the M_w/M_n values by GPC data) were observed before/after the deprotection event. As

described below, the fact can also be confirmed by the (quantitative) postmodification. The selective hydrolysis of **P3(OAc)₂** and **P4(OAc)₂** was also attempted under mild basic conditions (0.01 N NaOH solution in methanol) after 1 h at room temperature,[72] but a certain degree of degradation (hydrolysis of the ester linkage in the main chain) was observed (Table S3 and Figures S26−S27, Supporting Information).

The M_n values in **P3(OH)₂** and **P4(OH)₂** were estimated by treating the OH group with Me₃SiCl in THF (for experimental details, see the Experimental section). On the basis of the integration ratios of protons between the internal olefins and SiMe₃ end groups (Table 3, ¹H NMR spectra, Figure S29), the $M_{n(NMR)}$ values were 5400 [run 31, **P3(OH)₂**] and 14,700 [run 34, **P4(OH)₂**], respectively, which are close to those (5500 and 14,900, respectively) estimated by the integration ratios between the protons of internal olefins and the methylene protons bound to the hydroxyl groups at 3.76 ppm (Figure 3). These also suggest the exclusive end functionalization and the deprotection.

The hydroxy groups in the resultant polyesters [**P3(OH)₂** and **P4(OH)₂**] were thus used as macroinitiators for the subsequent reaction of Al-alkoxide-initiated ring-opening polymerization (ROP) of ε-caprolactone (CL), according to the reported procedure.[67,68] For instance, as shown in Scheme 4, the OH group was treated with 2.1 equiv of AlEt₃ (vs OH groups) in toluene at 50 °C (to form the Al-alkoxide *in situ*), and the subsequent reaction was conducted with CL at 80 °C to afford the corresponding ABA-type triblock copolymers, expressed as **P3-*bl*-(CL)₂** or **P4-*bl*-(CL)₂**, respectively (Table 3). As shown in Table 3, the M_n values in the resultant graft copolymer (by GPC) increased with increasing the reaction time (30 min to 1 h, Figure 4) along with an increase in the CL conversion; no significant differences in their M_w/M_n values were also seen. Linear relationships between M_n values (estimated by ¹H NMR) and the conversion were thus observed (Figure S44, Supporting Information), suggesting the possibility of living polymerization, as reported previously.[67,68]

The resultant copolymers were characterized by NMR spectra, GPC analysis, and DSC thermograms. Resonances ascribed to ring-opened poly(CL) (4.16, 3.76, 2.32, 1.67, and 1.3 ppm) were observed in the ¹H NMR spectra, whereas the other resonances (except OH) corresponding to the hydroxy group-terminated polymers remained (Figure 3 and Figure S28, Supporting Information). The M_n values in the resultant
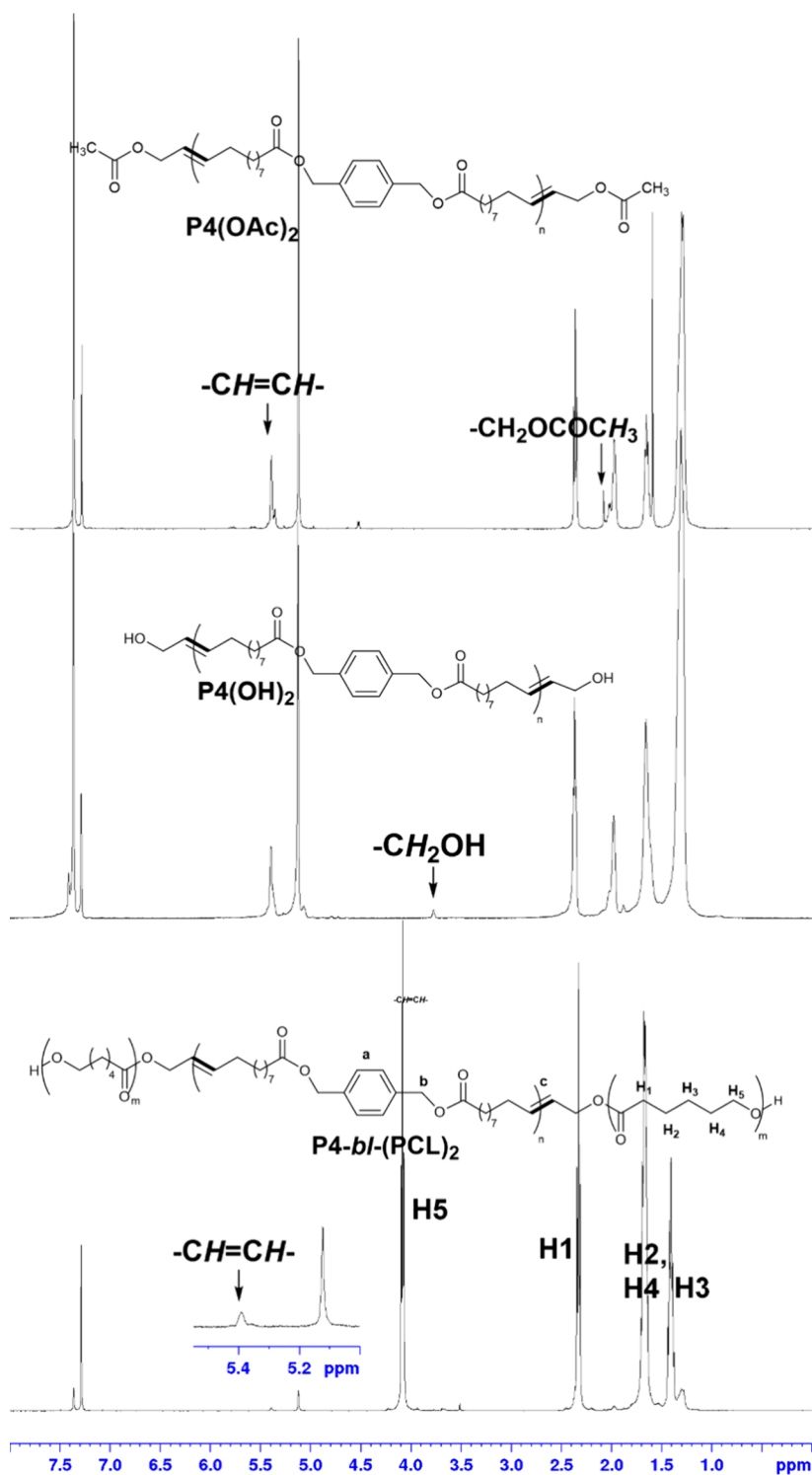
Figure 3. ^{1}H NMR spectra (in CDCl$_3$ at 25 °C) for preparation of the block copolymer, **P4**-*bl*-(**PCL**)$_2$.

block copolymers, **P3**-*bl*-(**CL**)$_2$ and **P4**-*bl*-(**CL**)$_2$, were estimated on the basis of integration ratios of the proton in the internal olefins and the methylene proton of poly(CL) at 4.16 ppm (Table 3). The resultant triblock copolymers showed melting temperatures corresponding to the ring-opened poly(CL) in their DSC thermograms (Figure S35, Supporting Information), suggesting the presence of the block copolymers as well as uniform compositions. The appearance of sole T_m values would be due to the low molecular weight (present as

amorphous in the copolymer expressed as the B segment).[73−75] In addition to their M_n values over the time course, the results thus suggest that the resultant polymers are ABA-type triblock copolymers. Moreover, diffusion-ordered spectroscopy (DOSY) analysis of the resultant block copolymers also revealed that the polyester macroinitiator [P(OH)$_2$] and polycaprolactone blocks (PCL) possess the same diffusion coefficients, indicating the successful prepara-

Table 3. Synthesis of ABA-Type Block Copolymers (P-*bl*-(PCL)$_2$) by Combination of ADMET with Ring-Opening Polymerization[a]

		macroinitiators				ABA-triblock copolymers (P-*bl*-(PCL)$_2$)				
run		$M_{n(GPC)}$[b] (g·mol^{-1})	$M_{n(NMR)}$[c] (g·mol^{-1})	$M_{n(NMR)}$[d]	M_w/M_n (Đ)[b]	time (min)	$M_{n(GPC)}$[b] (g·mol^{-1})	$M_{n(NMR)}$[e] (g·mol^{-1})	M_w/M_n (Đ)[b]	yield[f] (%)	conv.[g] (%)
31	**P3(OH)$_2$**	5000	5400	5500	1.78	0					
32						30	21,300	6400	1.59	54.0	49.4
33						60	41,600	11,200	1.62	88.0	86.8
34	**P4(OH)$_2$**	13,200	13,700	13,900	1.80	0					
35						30	33,600	14,600	1.80	64.0	60.0
36						60	37,500[h]	30,800	1.69	86.0	84.0

[a]Conditions: macroinitiators (**P(OH)$_2$**), 50 mg; AlEt$_3$, 2.1 equiv (vs OH groups) in toluene; 2 h; 50 °C; ε-caprolactone (CL), 0.50 mL; 80 °C. [b]GPC (SEC) data in THF vs polystyrene standards. [c]Estimated by ^{1}H NMR spectra (integration ratios of protons between the internal olefins and the SiMe$_3$ (TMS) group in **P3(OTMS)$_2$** or **P4(OTMS)$_2$**, prepared independently) (shown in Figure S29, Supporting Information). [d]Estimated by ^{1}H NMR spectra (integration ratio of protons between the methylene proton in the HOC*H$_2$*CH═CH− end group and the internal olefins). [e]Estimated by ^{1}H NMR spectra on the basis of integration ratios between protons of internal olefins and those bound to the oxygen of poly(CL). [f]Isolated yield as the methanol insoluble fraction. [g]Conversion of CL. [h]GPC (SEC) data of the soluble fraction in THF.
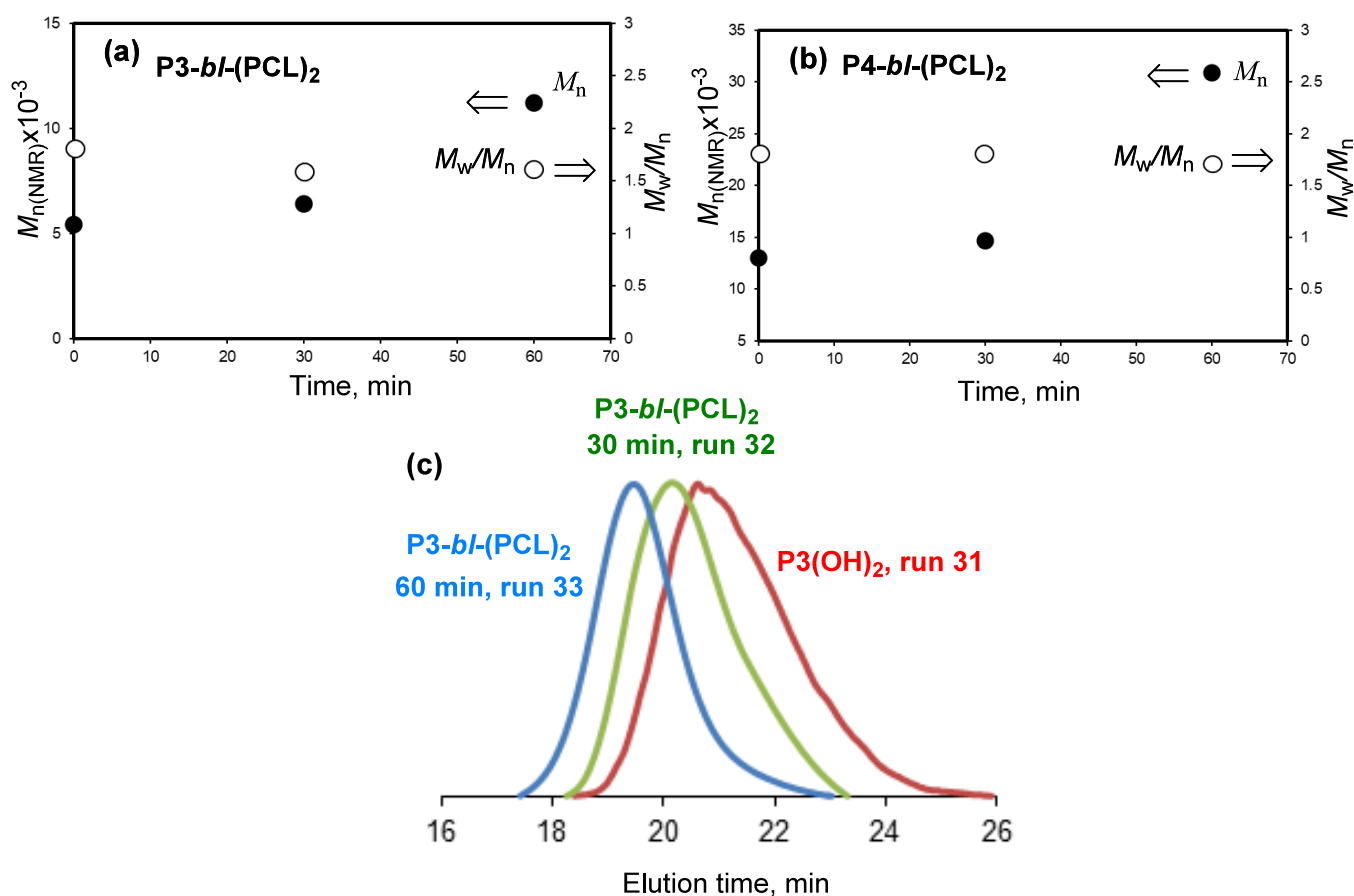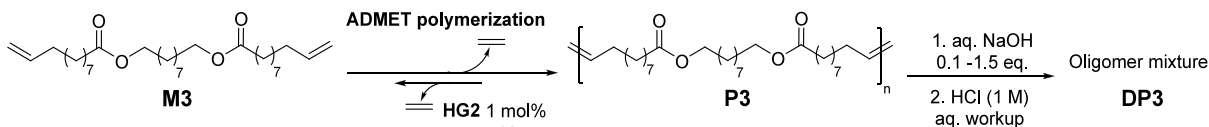

Figure 4. Plots of M_n and M_w/M_n values vs time in ring-opening polymerization of ε-caprolactone to prepare block copolymers (a) (**P3-*bl*-(PCL)$_2$**) and (b) (**P4-*bl*-(PCL)$_2$**). (c) GPC (SEC) traces of the time course for the synthesis of triblock copolymers (**P3-*bl*-(PCL)$_2$**) (runs 31−33, Table 3).

Scheme 5. Depolymerization of the Resultant Polyester (P3) under Basic Conditions

tion of the block copolymers with the efficient initiation (Figure S45, Supporting Information).

2.4. Depolymerization (Hydrolysis) of Polyesters under Basic Conditions. Efficient depolymerization (hydrolysis) of **P3** occurred by treating with aqueous solution of

NaOH (Scheme 5 and Scheme S2, Supporting Information).[31,76,77] Various parameters such as time, temperature, and the NaOH concentration were studied, and the depolymerization gave a mixture of monomer units (1,9-nonanediol and icos-10-enedioic acid) and oligomers (expressed as **DP3**) that were evaluated using ^{1}H NMR spectra and GPC traces (Figures S46–S51, Supporting Information). The prepared polyesters [(**P3**, run S3, Table S1, Supporting Information), M_n = 16,800 g/mol; M_w/M_n = 1.57] were thus depolymerized under mild basic conditions [0.1 M NaOH (0.1 equiv to the monomeric units) at 50 °C for 20 min to yield oligomers (M_n = 4100; M_w/M_n = 2.09, Figures S46 and S49, Supporting Information)]. Further efficient depolymerization was thus achieved by treatment with 1.5 M NaOH (1.5 equiv to the monomeric units) aqueous solution at 50 °C for 2 min to yield a mixture of low-molecular-weight oligomers (M_n = 600, M_w/M_n = 2.80, Figures S47, S48, and S51, Supporting Information).

3. CONCLUDING REMARKS

We have shown that the synthesis of high-molecular-weight polyesters (expressed as **P1–P5**, M_n = 35,700–61,600 g/mol, M_w/M_n = 1.50–1.97) has been achieved by ADMET polymerization of α,ω-diene monomers prepared from biobased bis(undec-10-enoate) and a series of diols [ethylene glycol (**M1**), propylene glycol (**M2**), 1,9-nonanediol (**M3**), 1,4-benzenedimethanol (**M4**), and hydroquinone (**M5**)] using ruthenium-carbene catalysts (**G2** and **HG2**). The solvent replacement during the polymerization runs was quite effective for obtainment of the high-molecular-weight polymers, and the method could be used in the laboratory-scale synthesis. The resultant polymers (**P3**) were depolymerized (hydrolyzed) by treating with aqueous solution of NaOH; the treatment with 1.5 M NaOH solution at 50 °C seemed to be the optimized conditions.

The polymerization in the presence of 1,4-cis-diacetoxy-2-butene (DAB) afforded the end-functionalized polyesters containing acetoxy groups [**P3(OAc)₂** and **P4(OAc)₂**]. The acetoxy end group could be then converted to the hydroxy group [expressed as **P3(OH)₂** and **P4(OH)₂**] exclusively by treatment with CF₃CO₂H/H₂O mixed solution; the OH end groups were treated with Me₃SiCl to afford **P3(OTMS)₂** and **P4(OTMS)₂**. The ABA-type triblock copolymers have been prepared by treating the OH end groups with AlEt₃ in toluene followed by addition of ε-caprolactone (CL) through Al-alkoxide-initiated ring-opening polymerization (ROP). The ROP proceeded in a living manner, and the approach shall pave the way to the synthesis of various block copolymers by the grafting-from (or grafting-to) method.

We believe that the method shall provide a possibility of synthesis of high-molecular-weight recyclable polymers,[40] which should have enough mechanical properties as films. Moreover, the results also provide a new possibility of synthesis of end-modified polyesters including synthesis of block copolymers[5] through the postmodification. We believe that the approach should be helpful for further studies for development of recyclable biobased polyesters, which should contribute to the circular economy.

4. EXPERIMENTAL SECTION

4.1. General Procedure. Polymerization and syntheses experiments were conducted under an inert (N₂) atmosphere in a drybox or using standard Schlenk techniques. Anhydrous-grade solvents such as dichloromethane, chloroform, hexane, and toluene (>99.5%, Kanto Chemical Co., Inc.) were kept in the drybox in bottles containing a mixture of molecular sieves (3A 1/16, 4A 1/8, and 13X 1/16). Ruthenium-carbene catalysts RuCl₂(PCy₃)(H₂IMes)(CHPh) [called the second-generation Grubbs catalyst (**G2**); IMesH₂ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene] and RuCl₂(IMesH₂)-(CH-2-O^{i}Pr-C₆H₄) [called the second-generation Hoveyda–Grubbs catalyst (**HG2**)] and anhydrous methanol were obtained from Aldrich Chemical Co. Reagent-grade chemicals (>99.0%, GC) such as 10-undecenoyl chloride, ethylene glycol, propylene glycol, 1,9-nonanediol, hydroquinone, 1,4-benzene-dimethanol, benzoquinone, and trimethylamine were purchased from Tokyo Chemical Industry (TCI), Co., Ltd. Ethyl vinyl ether (EVE), >98% (GC), activated alumina, and Celite were obtained from Fujifilm Wako Pure Chemical Industries, Ltd. The chemicals were used as received.

A Bruker AV500 spectrometer (500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C) was used to record NMR spectra (^{1}H and ^{13}C{^{1}H}). Molecular weights (M_w and M_n) of the prepared polymers and their distributions (M_w/M_n, Đ) were obtained by gel permeation chromatography (GPC). GPC measurements were conducted at 40 °C with a flow rate of 1.0 mL/min on a Shimadzu SCL-10A using an RID-10A detector (Shimadzu Co., Ltd.) in HPLC-grade THF stabilized with 0.03 wt % 2,6-di-tert-butyl-p-cresol (BHT). GPC columns (ShimPAC GPC-806, 804, and 802, 30 cm × 8.0 mm ϕ) were calibrated versus standard samples of polystyrene (in g/mol). Melting temperature (T_m) values were determined by differential scanning calorimetric (DSC) thermograms using a Hitachi DSC 7020 analyzer using nitrogen as the purging gas. Polymer samples, 4–5 mg in standard aluminum pans, were first heated from 30 to 150 °C and then cooled to −100 °C. The second heating cycle was used to obtain T_m. All measurements were conducted at a rate of 10 °C/min. Atmospheric-pressure chemical ionization (APCI) mass spectrometry was conducted on Bruker MicroTOF IISDT1.

4.2. General Procedure for ADMET Polymerization. ADMET polymerizations for the prepared monomers (**M1**–**M5**) were conducted by the analogous procedure reported by us.[32,34] In the drybox, the monomers (**M1**–**M5**), solvent, and ruthenium catalyst were charged with the prescribed amounts in Table 1 and Table S1 (SI) into a sealed 25 mL Schlenk-type tube. The reaction mixture was stirred for a specific time at 50 °C in an oil bath. The formed ethylene gas was removed continuously by freezing the reaction medium using liquid nitrogen, and the tube was shortly connected to the vacuum line with a certain time interval (first h every 15 min, second h every 30 min, and then every 1 h). The solvent exchange technique was conducted by solvent replacement[37] with a fresh solvent two or three times in the first 2 h under a N₂ atmosphere. The tube was then kept under reduced pressure by freezing the reaction medium using liquid nitrogen and connecting shortly to the vacuum line every 1 h. Two drops of EVE were used to quench the ADMET polymerization with stirring for 1 h. The reaction mixture was diluted using 4 mL of chloroform and precipitated in 100 mL of cold methanol. The resultant polymers were collected via filtration and dried in vacuo and were characterized using ^{1}H (500.13 MHz) and ^{13}C{^{1}H} (125.77 MHz) NMR spectra in CDCl₃ at 25 °C, GPC (SEC), and DSC.

P1 [run 1, Table 1; M_n = 11,700, M_w/M_n = 1.52]. ^{1}H NMR: δ (ppm) = 5.8 (ddt, J = 17, 10.3, 6.6 Hz, −CH=CH$_2$), 5.37 (−CH=CH−), 4.98 (dd, J = 17.1, 1.9 Hz, −CH=CH_2), 4.92 (dt, J = 10.1, 1.8 Hz, −CH=CH_2), 4.26 (s, −COO−CH_2−CH$_2$−OCO−) 2.31 (t, J = 7.5 Hz, CH$_2$CH_2COO), 1.97 (−CH_2CH=CH−), 1.61 (t, J = 7.1 Hz, −CH$_2$CH_2COO−), 1.21−1.42 (m, −CH$_2$−). ^{13}C{^{1}H}: δ (ppm) = 173.7 (−COO−), 130.4 (−CH=CH−), 62.1, 34.2, 32.7, 29.9, 29.7, 29.6, 29.5, 29.4, 29.2, 29.1, 27.3, 25.0. Yield 93.0%, white solid.

P2 [run 6, Table 1; M_n = 11,600, M_w/M_n = 1.67]. ^{1}H NMR: δ (ppm) = 5.82 (ddt, J = 17, 10.3, 6.6 Hz, −CH=CH$_2$), 5.39 (−CH=CH−), 5.0 (dd, J = 17.1, 1.9 Hz, −CH=CH_2), 4.94 (dt, J = 10.1, 1.8 Hz, −CH=CH_2), 4.16 (t, J = 6.35 Hz, −COO−CH_2−CH$_2$−CH_2−OCO−), 2.31 (t, J = 7.5 Hz, CH$_2$CH_2COO), 1.99 (−CH_2CH=CH−), 1.63 (t, J = 7.1 Hz, −CH$_2$CH_2COO−), 1.23−1.42 (m, −CH$_2$−). ^{13}C{^{1}H} NMR: δ (ppm) = 173.8 (−COO−), 130.4 (−CH=CH−), 60.9, 34.3, 32.7, 32.6, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 28.1, 27.3, 25.0. Yield 90.0%, white solid.

P3 [run 14, Table 1; M_n = 60,000, M_w/M_n = 2.00]. ^{1}H NMR: δ (ppm) = 5.40 (−CH=CH−), 4.16 (t, J = 6.70 Hz, −COO−CH_2−(CH$_2$)$_5$−CH_2−OCO−), 2.31 (t, J = 7.5 Hz, CH$_2$CH_2COO), 1.97 (−CH_2CH=CH−), 1.63 (t, J = 7.1 Hz, −CH$_2$CH_2COO−), 1.21−1.42 (m, −CH$_2$−). ^{13}C{^{1}H} NMR: δ (ppm) = 174.1 (−COO−), 130.5 (−CH=CH−), 64.5, 34.5, 32.7, 29.9, 29.8, 29.7, 29.5, 29.4, 29.3, 29.1, 28.8, 27.4, 26.1, 25.2, 18.1. Yield 93.0%, white solid.

P4 [run 19, Table 1; M_n = 59,500, M_w/M_n = 1.97]. ^{1}H NMR: δ (ppm) = 7.37 (s, −COO−CH_2−Ar(CH_2)$_4$−CH$_2$−OCO−), 5.39 (−CH=CH−), 5.12 (s, −COO−CH_2−Ar-(CH$_2$)$_4$−CH$_2$−OCO−), 2.36 (t, J = 7.5 Hz, CH$_2$CH_2COO), 2.01 (−CH_2CH=CH−), 1.65 (t, J = 7.1 Hz, −CH$_2$CH_2COO−), 1.21−1.42 (m, −CH$_2$−). ^{13}C{^{1}H} NMR: δ (ppm) = 173.6 (−COO−), 136.1 (−COO−CH$_2$−Ar-(CH$_2$)$_4$−CH$_2$−OCO−), 128.3 (−CH=CH−), 65.7, 34.5, 32.6, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 24.9. Yield 93.0%, white solid.

P5 [run 23, Table 1; M_n = 39,000, M_w/M_n = 1.69]. ^{1}H NMR: δ (ppm) = 7.28 (s, −COO−Ar(CH_2)$_4$−OCO−), 5.83 (ddt, J = 23.7, 10.3, 6.6 Hz, −CH=CH$_2$), 5.42 (−CH=CH−), 5.02 (dd, J = 17.1, 1.9 Hz, −CH=CH_2), 4.96 (dt, J = 10.1, 1.8 Hz, −CH=CH_2), 2.56 (t, J = 7.5 Hz, CH$_2$CH_2COO), 2.01 (−CH_2CH=CH−), 1.75 (t, J = 7.1 Hz, −CH$_2$CH_2COO−), 1.23−1.47 (m, −CH$_2$−). ^{13}C{^{1}H} NMR: δ (ppm) = 172.2 (−COO−), 148.1 (−COO−Ar(CH$_2$)$_4$−OCO−), 130.3 (−CH=CH−), 34.4, 32.6, 29.6, 29.4, 29.3, 29.2, 29.1, 27.2, 24.9. Yield 95.0%, white solid.

4.3. Synthesis of P(OAc)$_2$ Using Ruthenium-Carbene Catalysts in the Presence of 1,4-cis-Diacetoxy-2-butene.

The acetoxy end-functionalized unsaturated polyesters (**P3-(OAc)$_2$**) and (**P4(OAc)$_2$**) were prepared as reported previously.[63] In the drybox, the initial ADMET polymerization was conducted as follows: the monomer (**M3** or **M4**), chloroform, ruthenium catalyst (**HG2** or **G2**, 1 mol %), and 1 mol % benzoquinone were charged with the prescribed amounts in Table 2 and Table S2 (SI) into a sealed 25 mL Schlenk-type tube. The reaction mixture was stirred for the prescribed time (2 or 24 h) at 50 °C in an oil bath with the removal of the formed ethylene through two or three times solvent exchanges at 30, 60, and 120 min. For 24 h reactions, the vacuum line was connected to the frozen reaction mixture every 1 h. 1,4-cis-Diacetoxy-2-butene (DAB) was added in two

consequent reactions. The first reaction was performed by the addition of DAB under nitrogen with different molar ratios [DAB]/[M3] = 0.01−0.1 and stirred for 2 h at 50 °C under reduced pressure. The formed ethylene gas was eliminated by placing the reaction tube in liquid nitrogen and connecting it to a vacuum line at different time intervals of 20, 50, and 110 min. The second reaction was conducted by further addition of DAB and stirred for 1.5 h at room temperature with the removal of the formed ethylene as demonstrated before at 20 and 90 min. The reaction mixture was diluted with 2 mL of chloroform and precipitated in cold methanol. The resultant end-functionalized polymers were collected by filtration and dried under *vacuo*. The end functionalization was confirmed by ^{1}H (500.13 MHz) and ^{13}C{^{1}H} (125.77 MHz) NMR spectra in CDCl$_3$ at 25 °C and GPC (SEC), and the thermal behavior was studied using DSC.

P3(OAc)$_2$ [Table 2, run 26; M_n = 10,400, M_w/M_n = 1.80]. ^{1}H NMR: δ (ppm) = 5.78 (ddt, −CH=CH−, DAB), 5.57 (ddt, −CH=CH−, DAB), 5.40 (internal −CH=CH−), 4.63 (d, J = 6.8 Hz, CH$_2$, DAB), 4.52 (d, J = 6.3 Hz, CH$_2$, DAB), 4.16 (t, J = 6.70 Hz, −COO−CH_2−(CH$_2$)$_5$−CH_2−OCO−), 2.31 (t, J = 7.5 Hz, CH$_2$CH_2COO), 2.08 (s, CH$_3$, DAB), 1.97 (−CH_2CH=CH−), 1.63 (t, J = 7.1 Hz, −CH$_2$CH_2COO−), 1.21−1.42 (m, −CH$_2$−). ^{13}C{^{1}H} NMR: δ (ppm) = 173.9 (−COO−), 136.6, 130.3, 129.9, 123.7, 65.3, 64.3, 34.4, 32.2, 29.7, 29.6, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 28.7, 27.2, 25.9, 25.0. Yield 92.0%, white solid.

P4(OAc)$_2$ [Table 2, run 29; M_n = 12,900, M_w/M_n = 1.80]. ^{1}H NMR: δ (ppm) = 7.37 (s, −COO−CH_2−Ar(CH_2)$_4$−CH$_2$−OCO−), 5.78 (ddt, −CH=CH−, DAB), 5.57 (ddt, −CH=CH−, DAB), 5.40 (internal −CH=CH−), 5.13 (s, −COO−CH_2−Ar(CH$_2$)$_4$−CH$_2$−OCO−), 4.63 (d, J = 6.8 Hz, CH$_2$, DAB), 4.52 (d, J = 6.3 Hz, CH$_2$, DAB), 4.16 (t, J = 6.70 Hz, −COO−CH_2−(CH$_2$)$_5$−CH_2−OCO−), 2.37 (t, J = 7.5 Hz, CH$_2$CH_2COO), 2.08 (s, CH$_3$, DAB), 2.00 (m, −CH_2CH=CH−), 1.66 (t, J = 7.1 Hz, −CH$_2$CH_2COO−), 1.21−1.40 (m, −CH$_2$−). ^{13}C{^{1}H} NMR: δ (ppm) = 173.6 (−COO−), 136.2, 130.4, 130.3, 129.9, 65.7, 64.3, 34.3, 32.6, 29.7, 29.6, 29.4, 29.3, 29.2, 29.1, 29.0, 27.2, 24.9. Yield 92.0%, white solid.

4.4. Synthesis of Telechelic Polyester Diols P(OH)$_2$.

(a) For acetoxy deprotection using trifluoroacetic acid/water (9/1 v/v, 1.5 g), the respective polymer (**P3(OAc)$_2$** or **P4(OAc)$_2$**) (100 mg) was added to a cold solution of trifluoroacetic acid/water (9/1 v/v, 1.5 g). The mixture was stirred at room temperature for 10 h, and the solution was then poured into cold methanol. The resultant telechelic polyester diols were collected by filtration and dried under *vacuo*. The acetoxy deprotection was confirmed by ^{1}H and ^{13}C NMR spectra, and the thermal behavior was studied using DSC. (b) For acetoxy deprotection using 0.01 M NaOH, three drops of 0.01 M methanolic solution of NaOH (*ca.* 0.033 mL) were added to a solution of acetoxy end-functionalized unsaturated polyesters (**P3(OAc)$_2$** or **P4(OAc)$_2$**) (100 mg) in 3 mL of chloroform. The reaction mixture was stirred at room temperature for 60 min. The reaction mixture was diluted with 5 mL of chloroform and washed with acidified water (3 drops of 1.0 M HCl in 20 mL of water). The resultant organic phase was dried over anhydrous MgSO$_4$. The volatile was removed by a rotary evaporator. The resulting white solid was dried under *vacuo*. The acetoxy deprotection was confirmed by ^{1}H (500.13 MHz) and ^{13}C{^{1}H} (125.77 MHz) NMR spectra

in CDCl$_3$ at 25 °C and GPC (SEC), and the thermal behavior was studied using DSC.

Macroinitiator (**P3(OH)$_2$**) [run S13, Table S3 (SI); M_n = 10,100, M_w/M_n = 1.82]. ^{1}H NMR: δ (ppm) = 5.78 (ddt, −CH=CH−), 5.57 (ddt, −CH=CH−), 5.40 (internal −CH=CH−), 4.73 (d, J = 6.8 Hz, CH_2, DAB), 4.16 (t, J = 6.70 Hz, −COO−CH_2−(CH$_2$)$_5$−CH_2−OCO−), 3.78 (s, CH_2OH), 2.31 (t, J = 7.5 Hz, CH$_2$CH_2COO), 1.97 (−CH_2CH=CH−), 1.63 (t, J = 7.1 Hz, −CH_2CH$_2$COO−), 1.21−1.42 (m, −CH_2−). ^{13}C{^{1}H} NMR: δ (ppm) = 174.0 (−COO−), 130.3, 64.3, 34.4, 32.6, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.6, 27.2, 25.9, 25.0. Yield 93.0%, white solid.

Macroinitiator (**P4(OH)$_2$**) [run S15, Table S3 (SI), M_n = 13,000, M_w/M_n = 1.80]. ^{1}H NMR: δ (ppm) = 7.37 (s, −COO−CH_2−Ar(CH_2)$_4$−CH_2−OCO−), 5.78 (ddt, −CH=CH−), 5.57 (ddt, −CH=CH−), 5.40 (internal −CH=CH−), 5.13 (s, −COO−CH_2−Ar(CH$_2$)$_4$−CH_2−OCO−), 4.16 (t, J = 6.70 Hz, −COO−CH_2−(CH$_2$)$_5$−CH_2−OCO−), 3.78 (s, CH_2OH), 2.37 (t, J = 7.5 Hz, CH$_2$CH_2COO), 2.00 (m, −CH_2CH=CH−), 1.66 (t, J = 7.1 Hz, −CH_2CH$_2$COO−), 1.21−1.40 (m, −CH_2−). ^{13}C{^{1}H} NMR: δ (ppm) = 173.6 (−COO−), 136.2, 130.3, 128.3, 65.7, 34.3, 32.6, 29.7, 29.6, 29.3, 29.2, 29.1, 29.0, 27.2, 24.9. Yield 95.0%, white solid.

4.5. Synthesis of Trimethylsilane End-Functionalized Unsaturated Polyesters P4(OTMS)$_2$.

In the drybox, trimethylsilyl chloride (2.5 mg, 3.0 equiv) was added to a solution of (50 mg, 7.6 μmol) telechelic polyester diols (**P4(OH)$_2$**) [M_n = 13,200, M_w/M_n = 1.80] in 3 mL of toluene and (1.4 mg, 3.0 equiv) trimethylamine. The reaction mixture was then stirred for 6 h at room temperature. The resulting solution was precipitated in cold methanol and separated by filtration. The protected diols were characterized by ^{1}H NMR and GPC (SEC). ^{1}H NMR (500.13 MHz, CDCl$_3$ at 25 °C): δ (ppm) = 7.37 (s, −COO−CH_2−Ar(CH_2)$_4$), 5.40 (−CH=CH−), 5.13 (s, −COO−CH_2−Ar(CH$_2$)$_4$), 4.16 (t, J = 6.70 Hz, −COO−CH_2−(CH$_2$)$_5$−), 2.37 (t, J = 7.5 Hz, CH$_2$CH_2COO), 2.00 (m, −CH_2CH=CH−), 1.66 (t, J = 7.1 Hz, −CH_2CH$_2$COO−), 1.21−1.40 (m, −CH_2−), 0.3 (s, CH$_3$, TMS).

4.6. Synthesis of the ABA-Triblock Copolymers (P-bl-(PCL)$_2$) by Combination with Ring-Opening Polymerization (ROP) of ε-Caprolactone.

In the drybox, a solution of telechelic polyester diols (**P(OH)$_2$**) (50 mg) and toluene containing AlEt$_3$ (2.1 equiv of the OH group in 5 mL of toluene) was charged to the Schlenk tube. The reaction mixture was stirred for 2 h at 50 °C. ε-Caprolactone (0.5 mL) was then added under nitrogen, and the stirring was continued for 30 or 60 min at 80 °C. The resulting solution was then poured into cold methanol. The resultant copolymers were collected by filtration and dried under *vacuo*. The successful initiation of ROP was confirmed by ^{1}H (500.13 MHz) and ^{13}C{^{1}H} (125.77 MHz) NMR spectra in CDCl$_3$ at 25 °C and GPC (SEC), and the thermal behavior was studied using DSC.

P3-bl-(**PCL**)$_2$ [Table 3, run 32; M_n = 21,300, M_w/M_n = 1.59]. ^{1}H NMR: δ (ppm) = 5.40 (−CH=CH−, **P3**), 4.16 (t, J = 6.70 Hz, −COO−CH_2−, **P3** and PCL), 3.76 (s, CH_2O), 2.32 (t, J = 7.6 Hz, CH$_2$CH_2COO, **P3** and PCL), 1.97 (−CH_2CH=CH−), 1.67 (dt, J = 7.1 Hz, −CH_2CH$_2$COO−, **P3** and PCL), 1.24−1.48 (m, −CH_2−). ^{13}C{^{1}H} NMR: δ (ppm) = 173.5 (−COO−), 64.2, 34.1, 28.4, 25.5, 24.6. Yield 54.0%, white solid.

P4-bl-(**PCL**)$_2$ [Table 3, run 35, M_n = 33,600, M_w/M_n = 1.80]. ^{1}H NMR: δ (ppm) = 7.37 (s, −COO−CH_2−Ar(CH_2)$_4$, **P4**), 5.39 (−CH=CH−, **P4**), 5.13 (s, −COO−CH_2−Ar-(CH$_2$)$_4$, **P4**), 4.16 (t, J = 6.70 Hz, −COO−CH_2−, **P4** and PCL), 3.67 (s, CH_2O), 2.33 (t, J = 7.5 Hz, CH$_2$COO, **P4** and PCL), 2.00 (m, −CH_2CH=CH−), 1.67 (dt, −CH_2CH$_2$COO−, **P4** and PCL), 1.23−1.48 (m, −CH_2−). ^{13}C{^{1}H} NMR: δ (ppm) = 173.5 (−COO−), 64.2, 34.1, 28.4, 25.5, 24.6. Yield 95.0%, white solid.

4.7. Depolymerization (Hydrolysis) of Polyesters under Basic Conditions.

Four drops of 0.1−1.5 M NaOH aqueous solution (*ca.* 0.044 mL) were added to a solution of 20 mg of unsaturated polyester (**P3**, run S3, Table S1, Supporting Information) [M_n = 16,800, M_w/M_n = 1.57] in 0.3 mL of chloroform. The reaction mixture was stirred at the prescribed temperature (room temperature or 50 °C) for 2 min to study the effect of NaOH concentration or 2−25 min to study the effect of the reaction time. The reaction mixture was diluted with 5 mL of chloroform and washed with acidified water (3 drops of 1.0 M HCl in 20 mL of water). The resultant organic phase was dried over anhydrous MgSO$_4$. The volatile was removed by a rotary evaporator. The resulting white solid was dried under *vacuo*. The depolymerization of polyesters was confirmed by ^{1}H NMR and GPC (SEC).

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c07858.

(i) Synthesis of nonconjugated α,ω-diene monomers (**M1−M5**), (ii) additional results for ADMET polymerization of α,ω-diene monomers (**M1−M5**) using ruthenium-carbene catalysts (**G2** and **HG2**), (iii) additional results for synthesis of end-functionalized polymers [**P3(OAc)$_2$**, **P4(OAc)$_2$**, **P3(OH)$_2$**, and **P4-(OH)$_2$**], (iv) selected NMR spectra of the prepared monomers and polymers, (v) DSC thermograms of the prepared polymers, (vi) selected GPC (SEC) traces of the prepared polymers, (vii) additional results for synthesis of ABA-type block copolymers, and (viii) depolymerization (hydrolysis) of polyesters by NaOH aqueous solution (PDF)

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Notes

The authors declare no competing financial interest.

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