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Intrachain Cyclization via Postmodification of the Internal Alkenes of Periodic ADMET Copolymers: The Sequence Matters

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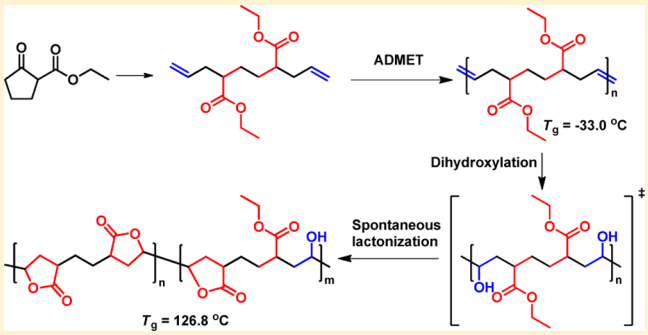
Supporting Information

ABSTRACT: We demonstrate that monomer sequence is important to regulate the vinyl copolymer thermal properties by intrachain cyclization. This is exemplified by the spontaneous intrachain cyclization with the formation of γ-butyrolactone by dihydroxylation of the internal alkenes of a designed periodic copolymer. A structurally symmetric α,ω-diene monomer **1** containing two tail-to-tail connected ethyl acrylate units was synthesized via a two-step approach. The acyclic diene metathesis (ADMET) polymerization of monomer **1** was conducted with a Hoveyda–Grubbs second generation catalyst in the presence of *p*-benzoquinone to get well-defined polymer (**P1**) with high molecular weights as revealed by GPC, NMR, and MALDI-TOF-MS characterizations. Dihydroxylation of **P1** using hydrogen peroxide as the oxidant was successfully conducted to afford **HP1**. Characterization of **HP1** by NMR and IR spectra indicated that it contained γ-butyrolactone units in the polymer main chain. Control experiments with four different polymers indicated that the formation of this ring structure was the outcome of the specific sequence of vinyl alcohol–ethyl acrylate formed by dihydroxylation of **P1**. The cyclization efficiency of **P1** was calculated to be 77%. The T_gs of all the modified polymers were increased compared to those of the unsaturated samples; significantly, the T_g of **HP1** was drastically elevated by 160 °C as compared to that of **P1**.



INTRODUCTION

Postpolymerization modification is one of the most important methods to introduce functional groups into polymers and subsequently regulate polymer properties.[1] The modification can be done in the polymer side chains, in polymer backbones, and at the polymer ends, leading to a variety of functional polymers with tunable properties from one type of polymer platform. Selective and quantitative modifications are highly desired to yield homogeneous polymers with predesigned structures. Chemical modification of polymer backbone is much more challenging than those of side chains or end groups, since the reactivity of internal functional group in the polymer backbone is significantly decreased and the steric repulsion cannot be overlooked. One important approach of post-modification of polymer backbone is the intrachain cyclization of polymers with defined microstructures, where sequence distribution plays a key role. Indeed, microstructure control including sequence regulation has attracted much attention and is definitely a significant parameter in polymer design that leads to polymers with complex structures and sophisticated functions.[2−6] For example, Grubbs et al. reported the quantitative cyclization of 1,2-polydiene via dynamic ring-closing metathesis to afford stereoregular cyclopentene–methylene alternating copolymer.[7] Recently, Kamigaito et al. developed a method to obtain thermally and optically high-performance thermoplastics via anionic random copolymerization of styrene and diene derivatives followed by intrachain Friedel–Crafts cyclization.[8−10] In these contributions, olefins are involved in cyclization processes, and successful post-modifications are guaranteed by sequence control, thus leading to property variation of the final polymers.

Olefin metathesis is one of the most powerful tools to synthesize unsaturated polyolefins. Acyclic diene metathesis (ADMET) polymerizations of structurally symmetric diene monomers have been systematically investigated to generate periodic vinyl copolymers.[11−15] Pioneered by Wagener, a series of precision polyethylenes have been synthesized by this method, and the effects of branch type, frequency, and regularity on the morphology changes of the resulting polymers have been elucidated.[16,17] Moreover, the related materials have found wide applications in energy[18,19] and biomedical[20,21] fields. Recently, our group also reported a new family of sequence-regulated vinyl copolymers via ADMET polymerization.[22−25] Generally, the internal alkenes of the ADMET polymers are exhaustively hydrogenated to obtain saturated carbon–carbon backbones. However, if the internal alkenes can

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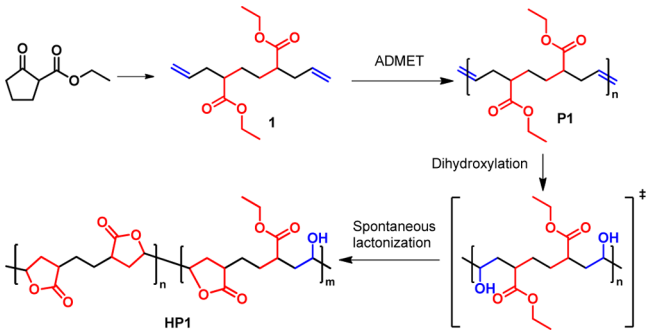
be quantitatively transformed to other entities by other efficient chemical approaches, one or two new monomer units other than ethylene will be incorporated into the repeating unit of the ADMET polymers. This strategy can thus lead to new densely functionalized periodic vinyl copolymers with defined microstructures, the property of which can be tuned due to such monomer sequence variation, thus deepening our understanding of the structure−property relationship of polymers.

Internal alkenes are functional moieties that appear in natural small molecules[26−28] (e.g., plant oil) and polymers[29] (e.g., rubber). Countless fine chemicals and valuable polymeric materials are produced through functionalization of these alkene groups. For example, vulcanization serves as an indispensable step to generate undistorted rubber. Basically, chemical transformation of internal double bonds to other functional groups that used in organic chemistry can be applied in postmodification of polymers containing these groups as well. However, polymer substrates face challenges such as incomplete modification, side reactions, and purification difficulty.[30−34] For typical polymers containing internal alkenes such as polybutadiene, chemical modifications under harsh conditions (e.g., halogenation and oxidation) were investigated decades ago, but the poor controllability (e.g., degree of functionalization) and severe side reactions (e.g., chain scission and coupling) prevented their applications in industry.[35−37] Later on, hydroboration/oxidation of the internal alkenes within the polymers by ring-opening metathesis polymerization using 9-BBN were reported, but only one hydroxyl group was incorporated with ambiguous regioselectivity for a single butadiene unit.[38−40] Very recently, a few contributions have been reported to describe the postmodification of unsaturated polymers containing butadiene units under mild conditions to generate functionalized polyolefins.[41−46] These excellent works shed light on functionalization of well-known unsaturated polymeric materials.

Inspired by the previous work, in this study, we provide the first example of postmodification of the internal alkene groups of periodic ADMET polymers, with an aim to elucidate the importance of monomer sequence on regulating the polymer properties. To this end, we synthesized a new type of periodic vinyl copolymer of butadiene and ethyl acrylate with a 1:2 sequence via the ADMET polymerization of a designed structurally symmetric α,ω-diene monomer containing two tail-to-tail connected ethyl acrylate units. Upon highly efficient dihydroxylation with hydrogen peroxide, we found that spontaneous intramolecular γ-lactonization occurred due to the formation of chemically reactive vinyl alcohol−ethyl acrylate sequence (see Scheme 1). As a result, the obtained polyolefin after modification was densely functionalized with γ-butyrolactone units, which exhibited drastically elevated glass transition temperature.

Scheme 1. Postmodification of 1:2 Sequenced Butadiene and Ethyl Acrylate Copolymers Formed by the ADMET of a Structurally Symmetric α,ω-Diene Monomer



EXPERIMENTAL SECTION

Materials. The following chemicals were used as received: ethyl 2-oxocyclopentanecarboxylate (98%, Acros), ethyl 2-methyl-4-pentenoate (>98.0%, TCI), Grubbs first, second, and third generation (G-I, G-II, and G-III) catalysts (Aldrich), Hoveyda−Grubbs first and second generation (HG-I and HG-II) catalysts (Aldrich), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 98%, Aldrich), *p*-benzoquinone (BQ, ≥98.0%), trifluoroacetic acid (TFA, 99%, Acros), trifluoroacetic anhydride (TFAA, 99%, Acros), 4-methylbenzenesulfonhydrazide (TSH, 97%, Acros) ethyl vinyl ether (98%, stabilized with 0.1% *N*,*N*-diethylaniline, Alfa Aesar), and tripropylamine (TPA, 98%, Alfa Aesar). Sodium (Na, >99.5%), allyl bromide (≥97.0%), triethylamine (TEA, ≥99.0%), hydrogen peroxide (H_2O_2, 30% solution), and potassium carbonate (K_2CO_3, ≥99.0%) were purchased from Sinopharm Chem. Reagent, Co., Ltd. 1,9-Decadiene (98%, TCI) was distilled over sodium and stored at 4 °C before use. Toluene, acetone, ethanol (EtOH), chloroform ($CHCl_3$), and dichloromethane (CH_2Cl_2) were purchased from Beijing Chem. Works. CH_2Cl_2 was distilled over calcium hydride and degassed upon sonication for 2 min before use.

Synthesis of Ethyl 1-Allyl-2-Oxocyclopentanecarboxylate.[47] K_2CO_3 (33 g, 0.24 mol), acetone (75 mL), ethyl 2-oxocyclopentanecarboxylate (9.36 g, 0.06 mol), and allyl bromide (10.38 mL, 0.12 mol) were sequentially transferred into a 250 mL round-bottom flask equipped with a reflux condenser. The flask was placed in an oil bath set at 60 °C and refluxed for 20 h. After cooling to room temperature, the mixture was vacuum filtered to remove KBr and K_2CO_3. The organic filtrate was concentrated and purified by vacuum distillation to obtain the pure product as a colorless oil in 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 5.70 (ddt, J = 17.3, 10.1, 7.3 Hz, 1H), 5.08 (m, 2H), 4.15 (m, 2H), 2.19 (m, 8H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.80, 170.52, 132.99, 118.60, 61.01, 59.56, 37.69, 37.54, 31.89, 19.27, 13.81. ESI-MS: $[M + H]^+$ = $C_{11}H_{17}O_3$, calcd: 197.117 22, found: 197.117 16; $[M + Na]^+$ = $C_{11}H_{16}O_3Na$, calcd: 219.099 17, found: 219.099 00. The NMR spectra are shown in Figure S1 of the Supporting Information.

Synthesis of Monomer 1.[48] To a 100 mL round-bottom flask containing 15.6 mL of EtOH was slowly added Na (1.38 g, 0.06 mol). After the mixture was cooled to room temperature, ethyl 1-allyl-2-oxocyclopentanecarboxylate (11.76 g, 0.06 mol) was added to the solution. The reaction mixture was heated under gentle reflux with stirring for 8 h. Then, allyl bromide (5.7 mL) was dropwise added to the hot solution. The solution was heated to reflux with stirring for another 8 h, during which time NaBr precipitated out. After cooling to room temperature, dilute HCl solution was added, and the aqueous layer was separated and extracted once with ethyl acetate. The extract was combined with the organic layer, sequentially washed with dilute Na_2CO_3 solution, deionized water, and brine, and dried over anhydrous Na_2SO_4. After filtration and rotary evaporation, the dark red crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to obtain **1** as a colorless oil in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 5.72 (ddt, J = 16.8, 10.1, 6.7 Hz, 2H), 5.03 (dd, J = 20.0, 9.7 Hz, 4H), 4.13 (q, J = 7.1 Hz, 4H), 2.37 (m, 4H), 2.28−1.37 (m, 6H), 1.23 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.85 (d, J = 9.7 Hz), 135.14 (d, J = 3.8 Hz), 116.60 (d, J = 6.8 Hz), 60.00, 44.95 (dd, J = 22.4, 9.6 Hz), 36.19, 29.08 (d, J = 13.3 Hz), 14.17. ESI-MS: $[M + Na]^+$ = $C_{16}H_{26}O_4Na$, calcd: 305.172 33, found: 305.171 72.

Synthesis of Diethyl 2,7-Dimethyl-4-octenedioate (2). Ethyl 2-methyl-4-pentenoate (142 mg, 1 mmol), BQ (1.1 mg, 10 μmol), and HG-II catalyst (3.1 mg, 5 μmol) were sequentially added into a 25 mL Schlenk flask equipped with a Teflon valve. Then, 1.0 mL of CH_2Cl_2 (degassed by sonication for 2 min) was added to dissolve the mixture to obtain a homogeneous blue solution. The flask was connected to a

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reflux condenser that equipped with an anhydrous $CaCl_2$ loaded drying tube. Subsequently, the flask was placed in an oil bath at 60 °C. Nitrogen gas was continuously purged in through the Teflon valve. As the reaction proceeded, CH_2Cl_2 gradually evaporated, and the mixture became heterogeneous in that blue precipitate coexisted with a small amount of liquid. The mixture was dissolved in $CHCl_3$ (5 mL) and filtered through a pad of silica. The silica gel was washed with $CHCl_3$, and the combined organic phase was evaporated to generate pale yellow oil in 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 5.44 (m, 2H), 4.12 (q, J = 7.1 Hz, 4H), 2.28 (m, 6H), 1.25 (t, J = 7.1 Hz, 6H), 1.13 (dd, J = 11.0, 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.77 (d, J = 1.6 Hz), 129.29 (d, J = 1.9 Hz), 128.30, 59.97 (d, J = 7.3 Hz), 39.43 (d, J = 1.6 Hz), 36.45 (d, J = 4.9 Hz), 16.30 (d, J = 5.5 Hz), 14.09. ESI-MS: $[M + H]^+ = C_{14}H_{25}O_4$, calcd: 257.174 74, found: 257.174 73; $[M + Na]^+ = C_{14}H_{24}O_4Na$, calcd: 279.156 68, found: 279.156 53. The NMR spectra are shown in Figure S2.

Other model metathesis reactions of ethyl 2-methyl-4-pentenoate were carried out under similar conditions with different inhibitors and catalysts and at different reaction temperatures (Scheme 4). The ^{1}H NMR spectra of the corresponding products are shown in Figures S3−S6.

Synthesis of 4,4′-Dimethyltetrahydro-[2,2′-bifuran]-5,5′(2*H*,2′*H*)-dione (3). Compound **2** (51.2 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (1.0 mL) containing TEA (20.2 mg, 0.2 mmol) and TFA (22.8 mg, 0.2 mmol) to form solution 1. H_2O_2 solution (30%, 0.5 mL) was added to CH_2Cl_2 (1.0 mL) at 0 °C, and then TFAA (84 mg, 0.4 mmol) was added dropwise to generate solution 2. Subsequently, solution 2 was slowly added to solution 1, and the resulting solution was refluxed at 45 °C for 12 h. To the reaction mixture was dropwise added 12 mol/L HCl solution (3.0 mL). The solution was heated to reflux with stirring for an additional 12 h. After cooling, the mixture was extracted three times with CH_2Cl_2. The organic layer was separated and sequentially washed with dilute Na_2CO_3 solution, deionized water, and brine and dried over anhydrous Na_2SO_4. After filtration and rotary evaporation, a white solid was obtained, which was recrystallized from ethyl acetate in 88% yield. T_m = 147.8 °C (by DSC). ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 4.53 (m, 2H), 2.77 (m, 2H), 2.09 (m, 4H), 1.30 (dd, J = 7.2, 2.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.08 (d, J = 9.9 Hz), 178.37 (d, J = 8.2 Hz), 77.66 (d, J = 7.0 Hz), 77.49 (d, J = 2.2 Hz), 34.98 (d, J = 5.8 Hz), 33.43 (d, J = 1.6 Hz), 32.70, 32.14, 31.10, 30.67, 15.96 (d, J = 9.3 Hz), 15.04 (d, J = 1.6 Hz). ESI-MS: $[M + H]^+ = C_{10}H_{15}O_4$, calcd: 199.096 49, found: 199.096 11; $[M + Na]^+ = C_{10}H_{14}O_4Na$, calcd: 221.078 43, found: 221.078 03.

ADMET Polymerization. Take the synthesis of **P1** as an example. Monomer **1** (282 mg, 1.0 mmol), BQ (1.1 mg, 10 μmol), and HG-II catalyst (3.1 mg, 5 μmol) were transferred sequentially into a 25 mL Schlenk flask that was equipped with a Teflon valve. Subsequently, CH_2Cl_2 (1.0 mL, degassed by sonication for 2 min) was added to dissolve the mixture to obtain a homogeneous blue solution. The flask was connected to a reflux condenser which was equipped with an anhydrous $CaCl_2$ loaded drying tube. Then the flask was placed in an oil bath at 60 °C. Nitrogen gas was continuously purged in through the Teflon valve during ADMET polymerization. As the reaction proceeded, the solvent CH_2Cl_2 was gradually evaporated, and the reaction mixture became highly viscous in a couple of hours as the magnetic bar was sluggish to stir. Polymerization was stopped after 120 h via adding $CHCl_3$ (5 mL) followed by a large excess of ethyl vinyl ether. The concentrated dark blue polymer solution was poured into cold petroleum ether (about 100 mL) to generate a pale blue suspension. A dark blue precipitate was obtained via storage at 4 °C overnight. After filtration and vacuum dryness, **P1** was obtained in 95% yield as a brownish semisolid.

Polymer **P2** was obtained by hydrogenation of polymer **P1**; the detailed procedure is described below. To a 100 mL round-bottom flask was sequentially added polymer **P1** (200 mg), TSH (614 mg, 3.3 mmol), TPA (572 mg, 4.0 mmol), and toluene (30 mL) to obtain a suspension. The flask was connected to a reflux condenser that equipped with an anhydrous $CaCl_2$ loaded drying tube. Under vigorous stirring, the hydrogenation proceeded at 130 °C for 12 h, and tiny bubbles were observed during that time. The reaction was then stopped upon cooling to generate an opaque solution with white precipitates. An equal supply of TSH and TPA was readded, and the reaction was allowed to proceed for another 12 h at 130 °C. The mixture was washed with water for three times, and then toluene in the organic layer was removed *in vacuo*. Chloroform (1 mL × 3) was utilized to dissolve the crude hydrogenated product. The viscous solution was poured into cold petroleum ether (100 mL) to generate a pale brown suspension, and a pale brown precipitate was formed after the suspension being stored at 4 °C overnight. **P2** was obtained in 90% yield after filtration and vacuum dryness.

Polymers **P3** and **P4** were synthesized similarly using G-I catalyst according to our previous work.[41] Polymer **P5** was synthesized by copolymerization of monomer **1** and 1,9-decadiene (1/1, molar ratio) with HG-II catalyst and BQ.

All the GPC traces and NMR spectra of **P2**, **P3**, **P4**, and **P5** are shown in Figures S7−S12.

Dihydroxylation and Cyclization. Take the synthesis of **HP1** as an example. Polymer **P1** (200 mg) was dissolved in CH_2Cl_2 (1.0 mL) containing TEA (101 mg, 1.0 mmol) and TFA (114 mg, 1.0 mmol) to form solution 1. H_2O_2 solution (30%, 2.0 mL) was added to CH_2Cl_2 (2.0 mL) at 0 °C, and then TFAA (0.42 g, 2.0 mmol) was added dropwise to generate solution 2. Subsequently, solution 2 was added to solution 1, and the resulting solution was refluxed at 45 °C for 12 h. To the reaction mixture was dropwise added 12 mol/L HCl solution (3.0 mL). The solution was heated to reflux with stirring for an additional 12 h. After cooling, an opaque suspension was generated and poured into methanol (100 mL). White precipitate was observed via storage at 4 °C for 24 h. After filtration and vacuum dryness, **HP1** was obtained in 85% yield.

HP3, **HP4**, and **HP5** were synthesized similarly. **HP3** was precipitated in cold ethyl ether. **HP4** was obtained as follows: The reaction mixture was extracted with CH_2Cl_2. Then, the organic layer was washed with deionized water for three times and concentrated through rotary evaporation, and the viscous solution was poured into cold petroleum ether (100 mL) and stored at 4 °C for 24 h. After filtration and vacuum dryness, **HP4** was obtained in 70% yield.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded in either $CDCl_3$ or DMSO-d_6 on a Bruker ARX-400 spectrometer with tetramethylsilane (TMS) as the internal reference for chemical shifts. Number-average molecular weights (M_n) and polydispersity indices (PDI = M_w/M_n) of the polymers were determined by gel permeation chromatograph (GPC). The measurements were conducted with DMF (containing 0.02 mol/L LiBr, flow rate: 1 mL/min) as the eluent at 50 °C with a Waters 1515 isocratic HPLC pump connected to a Waters 2414 refractive index detector. A family of narrowly dispersed polystyrenes was utilized as the standards, and Breeze 2 software was used for data acquisition and spectra manipulation. Infrared (IR) spectra were recorded on a Bruker Vector-22 Fourier transform infrared spectrometer. All the samples were dispersed in potassium bromide (KBr) by grinding, and OPUS/IR software was used to manipulate the spectra. Electrospray ionization mass spectroscopy (ESI-MS) characterizations were conducted on a Bruker APEX-IV Fourier transform mass spectrometer in a positive ion mode. A Bruker BIFLEX-III MALDI-TOF mass spectrometer was utilized to perform the matrix-assisted laser desorption/ionization time-of-fight mass spectroscopy (MALDI-TOF-MS) measurement in a linear mode. Thermal gravimetric analysis (TGA) was carried out by using Q600-SDT thermogravimetric analyzer (TA Co., Ltd.) with nitrogen purging rate set at 100 mL/min. All the measurements were conducted from 50 to 600 °C at a heating rate of 10 °C/min. Calorimetric measurements were performed using a Q100 differential scanning calorimeter (TA Co., Ltd.) with nitrogen purging rate set at 50 mL/min. The program was set to finish two cycles in the temperature range from −80 to 100 °C for unsaturated polymers and from −20 to 160 °C for modified polymers. The heating/cooling rate was set to 10 °C/min. Data of the endothermic curve were acquired from the second scan and analyzed with TA Universal Analysis software.

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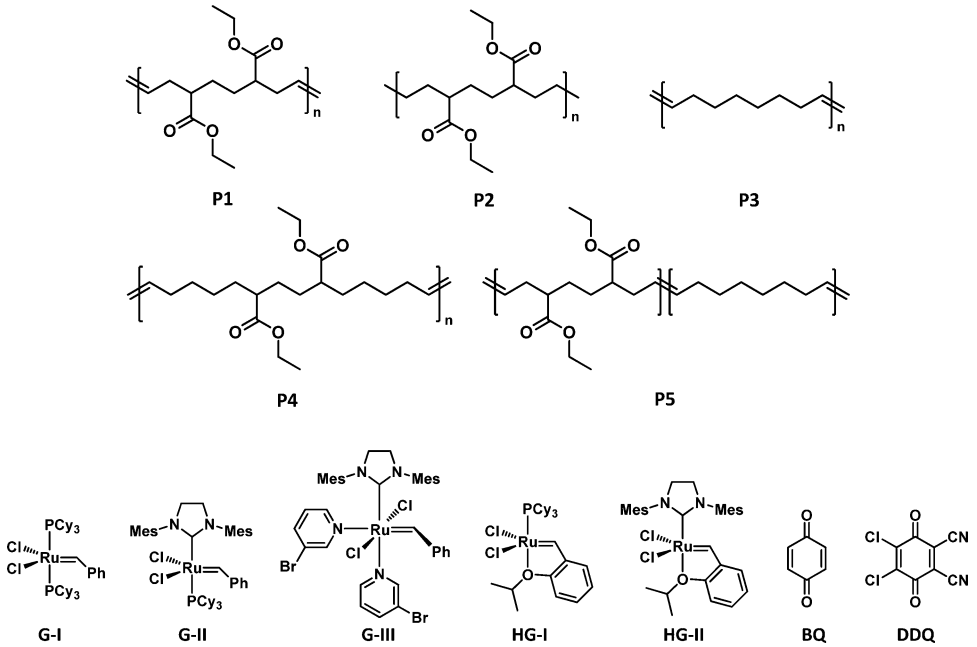
Scheme 2. Polymers, Metathesis Catalysts, and Olefin Isomerization Inhibitors in This Work

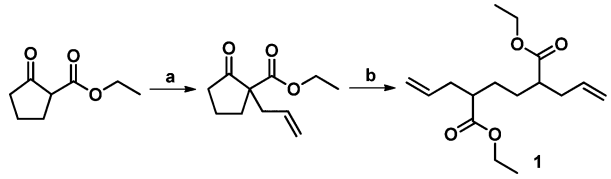


RESULTS AND DISCUSSION

To investigate the effects of microstructure on the alkene hydroxylation and intrachain cyclization of the ADMET polymers, we designed and synthesized five types of polymer samples (**P1**−**P5**) as shown in Scheme 2. Polymer **P1** was the primary polymer used to reveal the concept of postmodification and sequential intramolecular cyclization. Polymers **P2**−**P5** are control polymer samples to demonstrate the importance of internal alkene, pendant ester group, and the methylene spacer length between those two moieties for spontaneous γ-lactonization after dihydroxylation, respectively.

Monomer Synthesis. Monomer **1** is a structurally symmetric diene monomer containing two tail-to-tail connected ethyl acrylate units. The two terminal alkenes are separated by a carbon chain which is long enough to guarantee the ADMET polymerization instead of ring-closing metathesis (RCM) reaction of this monomer.[50] After ADMET polymerization of this monomer, followed by dihydroxylation, a vinyl alcohol−ethyl acrylate microstructure would be generated in the polymer main chain. This sequence would potentially undergo γ-lactonization. We first tried to synthesize this monomer by direct α-allylation of diethyl adipate using butyllithium;[49] however, multiple allylation caused purification difficulty. We then tried radical allylation of diethyl *meso*-2,5-dibromoadipate with AIBN as an initiator in benzene at 80 °C for 8 h. Unfortunately, a complex product mixture was generated as reflected by TLC. Distillation under reduced pressure was unsuccessful to get the desired monomer. Finally, we selected a two-step approach as shown in Scheme 3. In the first step, allylation of ethyl 2-oxocyclopentanecarboxylate with allyl bromide in the presence of K_2CO_3 in acetone at 60 °C for 20 h afforded ethyl 1-allyl-2-oxocyclopentane carboxylate in almost quantitative yield. This compound was then sequentially treated with sodium ethoxide and allyl bromide to obtain the targeted monomer **1** in 76% yield. Chemical structure and purity of **1** were confirmed by ESI-MS, ^{1}H NMR, and ^{13}C NMR spectra (Figure 1).

Scheme 3. Monomer Synthesis[a]



[a]Reagents and conditions: (a) 2.0 equiv of allyl bromide, 4.0 equiv of K_2CO_3, acetone, 60 °C, 20 h; (b) 1.0 equiv of EtONa, EtOH, 80 °C, 8 h; 1.1 equiv of allyl bromide, 80 °C, 8 h.

Metathesis of Model Compound Ethyl 2-Methyl-4-pentenoate. To obtain high molecular weight polymers with minimal structural defects, we carried out the metathesis of ethyl 2-methyl-4-pentenoate to optimize the appropriate catalytic system for the following ADMET polymerization (Scheme 4). In general, for monomers with long methylene spacers, the G-I catalyst is preferentially chosen for ADMET polymerization since olefin isomerization can be effectively suppressed. However, this catalyst exhibits limited catalytic activity for bulky substituted α-olefins.[51] Highly active catalysts have proved to be powerful for metathesis reaction of multisubstituted alkenes, but olefin isomerization cannot be avoided.[52−57] Therefore, in this study, we investigated the dimerization of ethyl 2-methyl-4-pentenoate using five commercially available metathesis catalysts (see Scheme 2). The products of the dimerizations were characterized by NMR. The results revealed that 100% conversion of ethyl 2-methyl-4-pentenoate was achieved using the HG-II catalyst, and the dimerized product **2** was obtained in high purity and quantitative yield by adding benzoquinone. The other four catalysts showed moderate catalytic activity and high tendency to cause olefin isomerization even if BQ or DDQ was added (Figures S3−S6). Hence, the HG-II catalyst was selected for the following ADMET polymerization of monomer **1**.

Dihydroxylation of compound **2** was performed according to the previously reported procedure.[58] Environmentally benign

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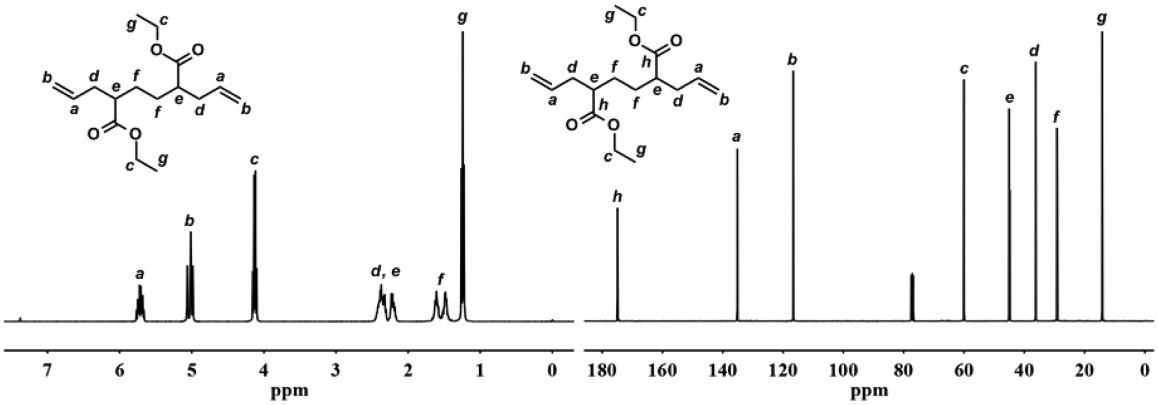
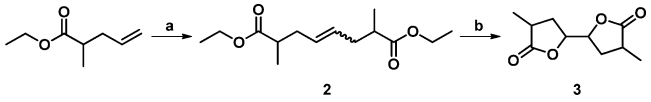


Figure 1. ^{1}H and ^{13}C NMR spectra of monomer **1** in $CDCl_3$.

Scheme 4. Metathesis of Ethyl 2-Methyl-4-pentenoate[a]



[a]Reagents and conditions: (a) 0.5 mol % HG-II catalyst, 1.0 mol % BQ, CH_2Cl_2, 40 °C, 24 h; (b) H_2O_2 in excess, 1.0 equiv of TEA, 1.0 equiv of TFA, 2.0 equiv of TFAA, CH_2Cl_2, 45 °C, 24 h.

oxidant H_2O_2 was used for dihydroxylation of **2** with the assistance of TFAA, TFA, TEA, and HCl in CH_2Cl_2 at 45 °C to obtain compound **3**. It is impossible to isolate the dihydroxyl-modified intermediate since the formed γ-hydroxyl ester possesses a high tendency to form a thermodynamically stable γ-butyrolactone unit.[59−62] Compound **3** was obtained as an amorphous solid in quantitative yield, and it was recrystallized from ethyl acetate in 88% yield (see Figure 2 for NMR spectra). These results suggest that complete dihydroxylation and highly efficient intramolecular γ-lactonization of ADMET polymers can also be realized to afford vinyl copolymers that densely functionalized with γ-butyrolactone units.

ADMET Polymerization and Polymer Synthesis. **P1** was synthesized in 95% yield by the ADMET of monomer **1** using HG-II catalyst in the presence of BQ. **P2** was obtained through exhaustive hydrogenation of **P1** based on the method reported by Hahn et al.[63] **P3** and **P4** were synthesized using G-I catalyst according to the previously reported synthetic procedures.[24] **P5** was obtained via random copolymerization of 1,9-decadiene and monomer **1** at a feed molar ratio of 1:1. Molecular weights of polymers **P1**−**P5** were characterized by GPC in DMF except **P3** due to its insolubility. All the GPC traces are unimodal (see Figure S7), and the M_n values are summarized in Table 1. All these polymers show M_n values exceeding 30 000, suggesting the efficient polymerization. The high PDI values are in accordance with the step-growth mechanism. The slightly increased M_n of **P2** compared with that of **P1** was attributed to the inherent elevated molecular weight and repetitive selective precipitation.

Table 1. Molecular Weight and Thermal Data of Polymer Samples

entry	M_n[a]	M_w/M_n[a]	T_g[b] (°C)	T_d[c] (°C)
P1	44 700	1.59	−33.0	360
P2	49 100	1.56	−36.8	371
P3			n.d.	409
P4	34 900	1.49	−50.4	362
P5	32 600	1.53	−51.3	360
HP1	30 200	1.50	126.8	243
HP3	33 200	1.45	12.1	244
HP4	42 800	1.60	29.3	249
HP5	25 100	1.46	57.2	233

[a]Determined by GPC (1 mL/min in DMF, 50 °C) using polystyrene calibration. [b]Determined by DSC, 10 °C/min scan rate. Values were recorded from second scan data. [c]Determined by TGA, 10 °C/min scan rate. T_d was defined as the temperature at 5% weight loss.

We measured the NMR spectra of all the polymer samples to confirm their chemical structures (Figure 3 and Figures S8−

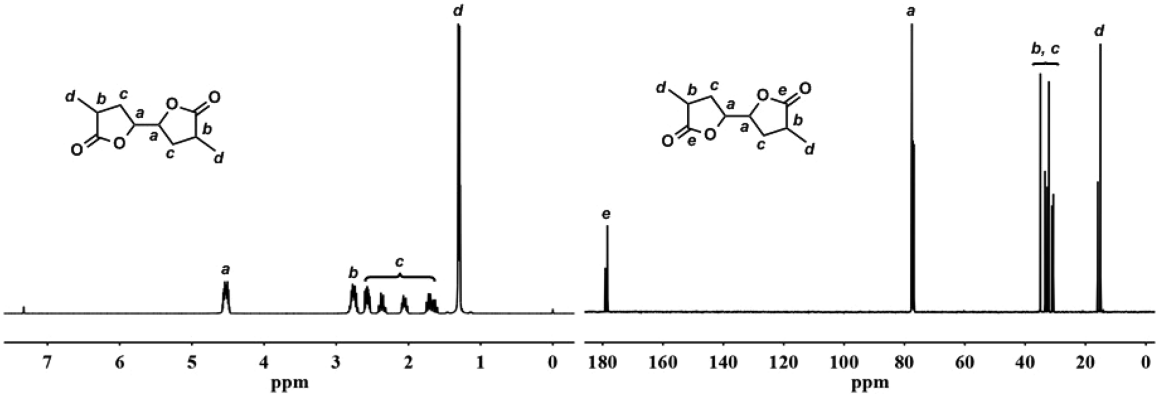


Figure 2. ^{1}H and ^{13}C NMR spectra of compound **3** in $CDCl_3$.

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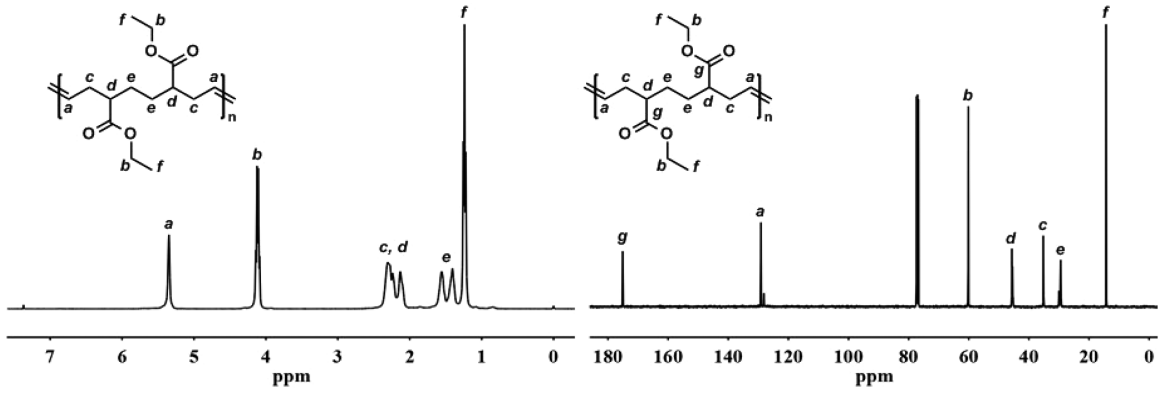

Figure 3. ^{1}H and ^{13}C NMR spectra of **P1** in $CDCl_3$.

S11). In all these spectra, signals of the internal alkenes were clearly observed while those of the terminal olefins could not be clearly detected, indicating that high molecular weight polymers were generated. We noticed that the olefinic proton signals of **P5** were more complex than those of the others, reflecting that irregular monomer sequence existed. Chemical composition of **P5** was calculated based on the peak area integration ratio of the methylene protons of ester groups (4.0−4.1 ppm) to those of the internal alkenes (5.2−5.5 ppm). The result showed that the molar ratio of monomer **1** to 1,9-decadiene in **P5** was 49/51, indicating the random nature of ADMET copolymerization. In addition, **P5** showed four groups of olefinic signals (regardless of the *cis* and *trans* conformation) in the ^{13}C NMR spectrum (Figure S12), again confirming the microstructure randomness.

To confirm the fine chemical structures of **P1**, a low molecular weight sample was further characterized by MALDI-TOF-MS (Figure 4). A series of peaks with regular interval that equals to the theoretical repeating unit mass were observed. Importantly, a minor series of peaks due to possible olefin isomerization could not be detected, indicating the integrity of the periodic microstructures of these samples.

Dihydroxylation and Cyclization. A collective research effort has been dedicated to chemical transformation of internal alkenes to other functional moieties in organic chemistry. Among all the reported reactions, dihydroxylation with hydrogen peroxide is an interesting reaction to introduce two adjacent hydroxyl groups with high efficiency and in an osmium-free manner.[64] Grinstaff et al. performed dihydroxylation of ROMP polymer to functionalize the internal alkenes for gelation and further modification.[58] A quantitative conversion of double bonds was achieved using this method. Inspired by this work, we conducted dihydroxylation of the four ADMET polymers containing internal alkenes (**P1**, **P3**, **P4**, and **P5**) under the same reaction condition as that applied to compound **2**.

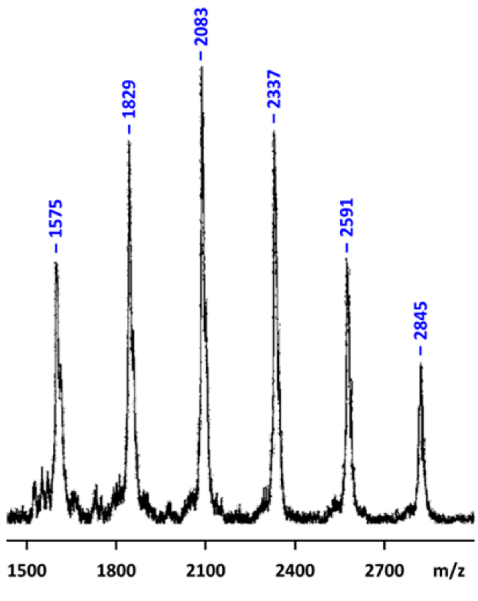

Figure 4. MALDI-TOF-MS spectrum of **P1**.

In this study, the dihydroxylation and γ-lactonization of the ADMET polymers occurred in a sequential order so that the modification efficiency was governed by the key step of intrachain cyclization. The four modified ADMET polymers were denoted as **HP1**, **HP3**, **HP4**, and **HP5**. These polymers could not dissolve in many organic solvents; fortunately, they exhibited limited solubility in DMF and DMSO (Figure 5). This phenomenon could be ascribed to the high polarity and rigidity of the formed γ-butyrolactone units on the polymer backbones.[60−62]

The molecular weights of **HP1**, **HP3**, **HP4**, and **HP5** were measured by GPC (Figure S7), and the data are summarized in Table 1. After hydroxylation and subsequent γ-lactonization, the M_n values of these four polymers were varied, but the PDI values were almost the same. Among them, **HP4** had higher molecular weight than that of **P4**, while **HP1** and **HP5** exhibited smaller molecular weights than those of **P1** and **P5**. The ^{1}H NMR spectra of **HP1**, **HP3**, **HP4**, and **HP5** were measured and are shown in Figure 5; the ^{1}H NMR spectra of **3** and **P2** were inserted for comparison. Signals of the internal alkenes in the polymer precursors could not be detected, indicating complete hydroxylation.

Four possible microstructures existed in these polymers: γ-butyrolactone unit, two adjacent hydroxyl groups, γ-hydroxyl ester moiety, and pendant ester group. Among them, the γ-hydroxyl ester microstructure was derived from the specific sequence of vinyl alcohol−ethyl acrylate that failed to undergo γ-lactonization. These four microstructures could be assigned unambiguously and were used to estimate the extent of γ-lactonization formation. The NMR spectra of **HP1** and **HP5** both showed the same characteristic peaks of γ-butyrolactone units as that of **3**. By comparing the NMR spectra of **HP3**, **P2**, and **HP4**, we could conveniently distinguish the characteristic signals of methine protons connected with hydroxyl (4.4−4.5 ppm) and pendant ester moieties (2.2−2.4 ppm) as well as

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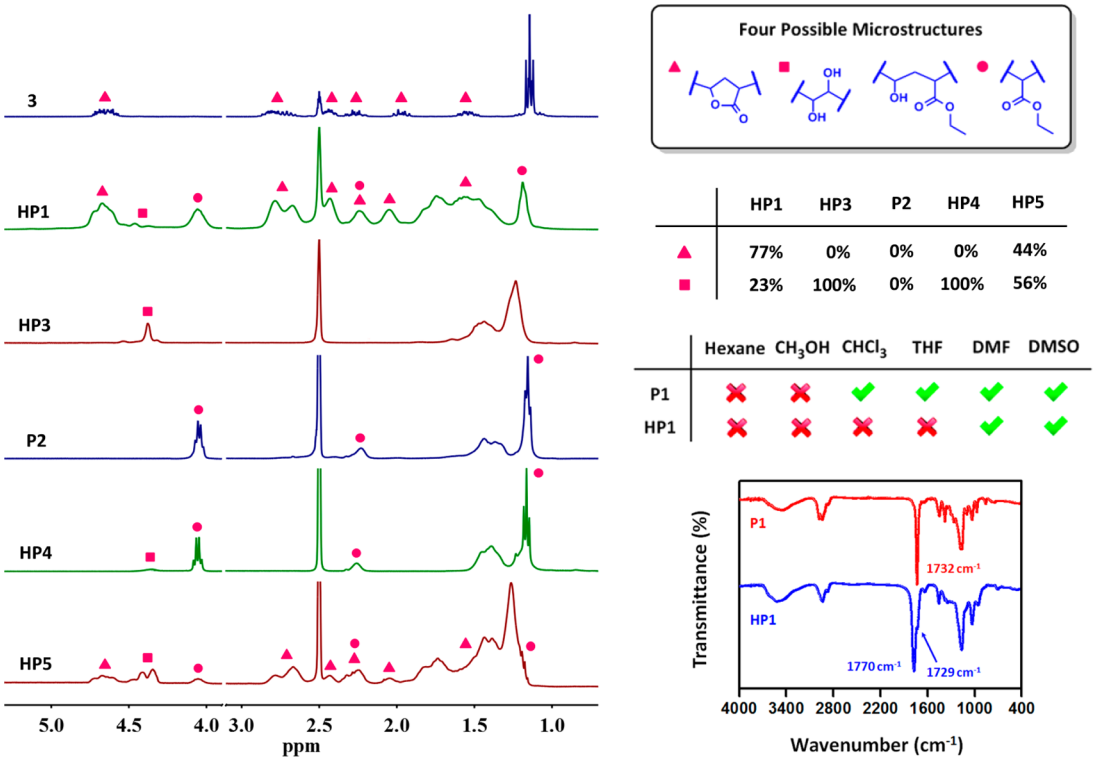

Figure 5. ^{1}H NMR spectra of compounds **3**, **P2**, and **HP1**−**HP4** in DMSO-d_6. The four possible microstructures were assigned in the NMR spectra, and the molar content of each microstructure was calculated based on the integration ratio of the corresponding characteristic peaks. The result of solubility test of **P1** and **HP1** in representative organic solvents was presented. The IR spectra of **P1** and **HP1** were exhibited in the bottom right, and the peaks corresponding to γ-butyrolactone units and pendant ester groups were designated.

methylene (4.0−4.1 ppm) and methyl protons (1.1−1.2 ppm) of the pendant ester groups. In this way, peaks other than γ-butyrolactone signals could be assigned for NMR spectra of **HP1** and **HP5** (see Figure 5). The molar percentage of the γ-butyrolactone groups and the pendant hydroxyl moieties was calculated based on the peak area integration ratio of the corresponding signals, and the results are summarized in Figure 5. Moreover, the peak area integration ratio of the pendant hydroxyl moieties and the residual ester groups coincided well with the calculated results. High γ-lactonization efficiencies of 77% and 44% were achieved for **HP1** and **HP5**, respectively. It is worth mentioning that the postmodification-induced γ-lactonization of specific sequence of acrylate−vinyl ether has been reported, and the cyclization efficiencies were comparable to our results.[59−62] As expected, for polymers **P2**, **HP3**, and **HP4**, no any lactone formation was observed as evidenced by NMR spectra.

Formation of γ-butyrolactone units after modification was further confirmed by the FT-IR measurements. The sharp peak at 1764 cm^{-1} in the IR spectrum of **3** (see Figure S13) was unambiguously assigned to the C═O stretching vibration of γ-butyrolactone units, while the characteristic peak at 1732 cm^{-1} in the IR spectrum of **P1** was assigned to the C═O stretching vibration of the pendant ester group. On the other hand, the IR spectrum of **HP1** exhibited a clearly distinguishable peak at 1770 cm^{-1} with a shoulder peak appearing at 1729 cm^{-1}, indicating the coexistence of two types of ester C═O bonds (see Figure 5). The IR spectrum of **HP5** showed a comparatively broad peak at this region, suggesting the coexistence of two types of C═O bonds (see Figure S13). Obvious decrease in relative transmittance in the region of O−H stretching vibration was observed for **HP3** and **HP4** compared with those of **P3** and **P4**, respectively. Collectively, the above results demonstrated that γ-butyrolactone formation was only possible for those polymers with defined periodic microstructure.

Thermal Properties of the Polymers. The thermal stabilities of all the polymers were examined by TGA. Polymers **P1**−**P5** were thermally stable up to 320 °C before catastrophic decomposition due to the pyrolysis of the polymer backbones was observed (see Figure S14). On the other hand, as shown in Figure 6, the TGA curves of polymer **HP1**, **HP3**, **HP4**, and

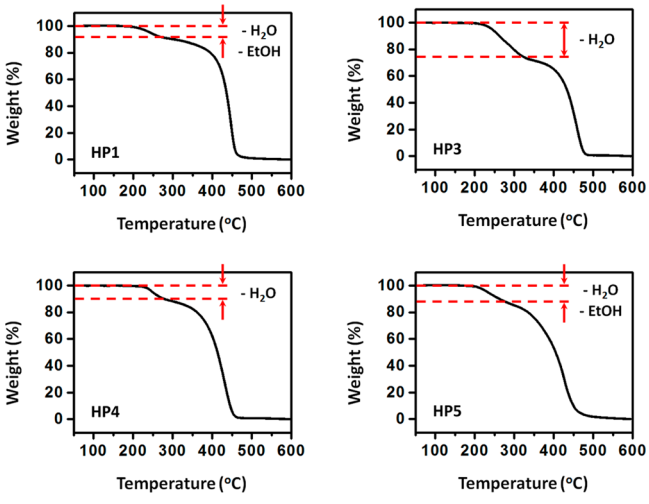

Figure 6. TGA curves of **HP1**, **HP3**, **HP4**, and **HP5**. The first stage weight loss of each sample was marked and tagged by the types of released small molecules.

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HP5 all exhibited a typical two-stage decomposition profile. Water was initially released when the temperature was above 200 °C probably due to the intra- and/or interchain etherification and thermal-induced olefination.[65−68] Periodic ethylene−vinyl alcohol copolymers showed similar TGA curves.[25] However, it is impossible to predict weight loss percentage of these polymers according to their repeating unit structures due to the different amounts of water elimination caused by two mechanisms (see below). Moreover, thermal-induced γ-lactonization should be considered for polymers containing the microstructure of vinyl alcohol−ethyl acrylate so that the elimination of ethanol would play a role in theoretical value prediction. For instance, according to the molar contents of various microstructures within **HP1**, the theoretical percentage of the first-stage weight loss is between 1.9% (etherification) and 9.7% (γ-lactonization), and the actual value is 8.3%. This result also indicates that increasing the efficiency of γ-lactonization cannot be accomplished by thermal treatment due to the occurrence of water elimination as a side reaction. Likewise, the percentage of the first-stage weight loss of **HP3** was 22.8%, between the theoretical values of 12.5% (etherification) and 25.0% (olefination). Polymers **HP4** and **HP5** behaved similarly. All these results demonstrated that the thermal stability of ADMET polymer was decreased after dihydroxylation owing to the incorporation of pendant hydroxyl moieties.

Finally, we conducted DSC measurements to investigate the glass transition and melting behavior of these polymers (see Figure 7). Polymer **P3** was the only sample that shows a sharp

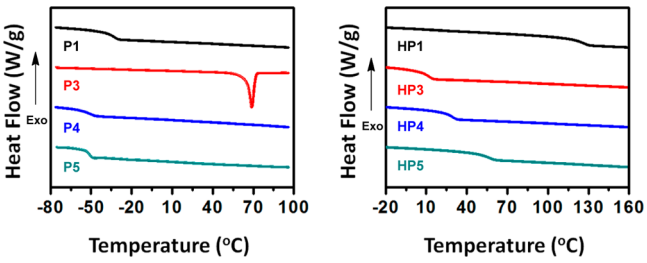

Figure 7. DSC thermograms of eight polymer samples.

melting peak due to the regular periodic microstructure and the absence of pendant groups.[69] However, the T_m value of **P3** (67.8 °C) was much lower than that of high-density polyethylene[70] (134 °C), since internal alkene moieties would disturb the crystallization of polymer backbone. The T_g value of **P1** was −33.0 °C, between the T_gs of poly(ethyl acrylate)[71] (−24 °C) and polyethylene[72] (−125 °C). Much to our interest, the corresponding **HP1** exhibited a T_g of 126.8 °C, about 160 °C higher than that of **P1**. This drastic increase was mainly attributed to the high content and rigidity of the formed five-membered γ-butyrolactone ring structure. It is also worth mentioning that the T_g of **HP1** was even higher than those of previously reported ADMET polymers containing γ-butyrolactone units.[22] The reason was also ascribed to the much higher content of this functional moiety within the polymer backbone. On the other hand, the T_gs of **HP3** (12.1 °C) and **HP4** (29.3 °C) were both higher than those of **P3** (T_g < −80 °C) and **P4** (−50.4 °C). This elevation was owing to the hydrogen bonding between the hydroxyl groups which restricts the polymer chain segment motion.[73] Polymer **P5** showed a lower T_g value (−51.3 °C) than that of **P1** owing to the lower content of ethyl acrylate units and the random microstructure. Likewise, a drastic increase of T_g was also observed for **HP5** (57.2 °C) as compared to that of **P5**. However, this elevation could not be solely attributed to the γ-butyrolactone units since hydrogen bonding between the pendant hydroxyl groups also played a key role in enhancing T_g.

Equally interesting is the absence of melting peaks of polymers possessing periodic microstructures (**HP3** and **HP4**). We speculated that chain segment consisting of identical monomer structure possesses a high tendency of crystallization. For example, ADMET polymers with long methylene spacers tend to crystallize due to the minor disturbance caused by pendant functional groups. However, in this study, polyethylene main chain was densely modified with functional groups so that it is difficult for polymer chains to pack regularly. Densely functionalized vinyl copolymers in this study differ from crystalline homopolymers in monomer structure diversity, uncertain stereospecificity, and defect of microstructure periodicity (**HP1** and **HP5**). These three factors prevented crystallization of polymer chains so that only glass transitions were observed except for **P3**. It can be anticipated that polymers with even higher glass transition and melting temperatures would be generated if quantitative γ-lactonization and control over stereoregularity are realized.

Overall, the thermal stabilities of polymers are diminished after dihydroxylation due to the chemical reactivity of pendant groups and/or specific sequence upon heating. Besides hydrogen bonding between the pendant hydroxyl groups, formation of γ-butyrolactone ring structure by the spontaneous intrachain cyclization of the specific sequence of vinyl alcohol−ethyl acrylate renders rigidity to polymer chains and thus drastically elevates the T_g. However, microstructure defects within this family of densely functionalized polyolefins prevent the formation of crystalline regions.

■ CONCLUSIONS

We have demonstrated the importance of sequence regulation for intrachain cyclization of periodic ADMET copolymers initiated by postmodification of the internal alkenes with dihydroxylation. The periodic copolymer of butadiene and ethyl acrylate with a 1:2 sequence was obtained by the ADMET of a designed structurally symmetric α,ω-diene monomer containing two tail-to-tail connected ethyl acrylate units. Dihydroxylation of this unsaturated polymer using hydrogen peroxide as the oxidant leads to the formation of a vinyl alcohol−ethyl acrylate sequence, which undergoes spontaneous intramolecular cyclization to form γ-butyrolactone units. This intramolecular cyclization was closely related to the copolymer microstructure, and the efficiency of γ-lactonization can reach 77% for the designed polymer. The thermal stability of polymers was decreased after dihydroxylation due to the thermal-induced release of water and/or ethanol followed by catastrophic decomposition. However, drastic increase of T_g after dihydroxylation was observed and was explained as the synergistic outcome of cyclic microstructure formation and hydrogen bonding. The present work not only provides an example of highly efficient modification of internal alkenes but also shows the importance of monomer sequence to determine and regulate chemical reaction and polymer properties.

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■ ASSOCIATED CONTENT

Supporting Information

NMR and IR spectra, GPC traces, and TGA curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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