Synthesis of Ethylene/Vinyl Ester Copolymers with Pendent Linear Branches via Ring-Opening Metathesis Polymerization of Fatty Acid-Derived Cyclooctenes

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Received 10 January 2017; accepted 24 March 2017; published online 00 Month 2017 DOI: 10.1002/pola.28606

ABSTRACT: Fatty acid-derived cyclooctenes, including *n*-hexanoic acid (M1), *n*-octanoic acid (M2), lauric acid (M3), and palmitic acid (M4), were prepared as monomers and polymerized by ring-opening metathesis polymerization (ROMP) using Grubbs second-generation catalyst (G2). In all the cases, the regio-irregular unsaturated polymers with pendent linear branches were obtained, which could be saturated by chemical hydrogenation with TSH/TPA in high conversion, yielding ethylene/vinyl ester copolymers with pendent linear branches on precisely every eighth backbone carbon. Both unsaturated and saturated polymers were amorphous, and their structures were

INTRODUCTION Polyethylene (PE) is widely used in our daily life as one of the most chemically stable and most important commercial polymers.¹ However, its fully saturated hydrocarbon skeleton and the absence of polar functional groups usually lead to its poor adhesion and incompatibility with other materials. The introduction of polar functionalities into PE has a tremendous effect on its properties, and the functionalization of PE has been extensively studied for the purpose of expanding its application fields.^{2-ô10} Based on their different structures, the functionalized PEs mainly include the following categories: (a) randomly functionalized copolymers with either branched or linear structures, (b) end-functionalized polymers, (c) block copolymers, (d) graft copolymers.^{2-ô10}

Due to the random distribution of monomers along the backbone, randomly functionalized PEs exhibit completely different properties, depending on the different type and amount of functional groups or different microstructures. The functionalized PEs with linear structures are very interesting because they can be regarded as a functionalized form of high-density polyethylene (HDPE).^{2,10} In general, the random PE copolymers could be achieved in a variety of ways, such as postfunctionalization of preformed PE,^{3,11} direct copolymerization of ethylene with polar vinyl monomers,^{11- δ 15} and

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Materials

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characterized by FTIR, ¹H and ¹³C NMR spectra, and elemental analysis. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to study their thermal properties. The chain length of branches greatly affected the thermal properties of polymers. After hydrogenation, the thermal degradation stability of polymers was relatively improved. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

KEYWORDS: branches; ethylene/vinyl ester copolymers; hydrogenation; ROMP

ring-opening metathesis polymerization $(\text{ROMP})^{16,17}$ or acyclic diene metathesis polymerization $(\text{ADMET})^{18-\hat{o}20}$ followed by hydrogenation. Without any reactive groups in the nonfunctionalized PEs, the chemical modifications of inert C—H bonds generally require harsh conditions. This may also cause the occurrence of many undesirable side reactions, such as crosslinking or chain scission, which thus severely alter the properties of polymers. In addition, the postfunctionalization is often hindered by the poor solubility of PE, multisteps, and low functionality. The direct copolymerization always suffers from a special catalytic system with good tolerance to polar monomers and the largely different reactivity between ethylene and polar vinyl monomers.

The preparation of linear functionalized polyolefins by ROMP of functionalized cyclooctenes and subsequent hydrogenation is of particular interest.^{16–621} Although the presence of functional groups in cyclooctenes may slow down the polymerization rate in some extent,^{22–625} the field is rapidly growing because of the breakthrough of more efficient and tolerant catalysts.^{26,27} In this way, the functionalized polyolefins bearing various functional groups in a precise sequence distribution have been prepared, theoretically containing 25 mol % of polar vinyl monomers.^{16,17,25} For example, the linear VAE

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copolymers of vinyl acetate/ethylene have been achieved by the combination of ROMP of acetoxy-substituted at the 3or 5-position of cyclooctene using Grubbs catalysts and hydrogenation.^{28- δ 32} The 3-acetoxycyclooctene (3AcCOE) with a sufficiently bulky functional group afforded regioregular and isotactic VAE copolymers, whereas the VAE analogues from 5-acetoxycyclooctene (5AcCOE) were regioirregular and atactic.

Recently, the interest in synthesizing and utilizing biomassderived polymers is growing significantly, and fatty acidderived monomers have been broadly used in the synthesis of renewable materials using various polymerization methods.^{33–} ^{642} In this study, a series of 5-substituted fatty acid-derived cyclooctenes and their corresponding polymers via ROMP with Grubbs second-generation catalyst (**G2**) were synthesized. The resulting polymers were converted to the hydrogenated polymers by chemical hydrogenation, which represent a class of precision ethylene/vinyl ester copolymers with pendent linear branches on precisely every eighth backbone carbon. The structures of polymers were characterized by FTIR, ¹H and ¹³C NMR spectra, and elemental analysis and the thermal properties were investigated by DSC and TGA.

EXPERIMENTAL

Methods and Materials

The molecular weight and molecular weight distribution of polymers were measured by gel permeation chromatography (GPC) using Waters 2414 series system in THF at 25 °C calibrated with polystyrene standards. FTIR spectra were recorded on a Perkin-Elmer FTIR 2000 spectrometer by using liquid films. The ¹H and ¹³C NMR spectra were recorded on a Bruker DMX-400 instrument in CDCl₃ with TMS as the internal standard at room temperature. Thermogravimetric analysis (TGA) was carried out in nitrogen atmosphere on a TA Q500 TGA analyzer. The differential scanning calorimetry (DSC) analysis was recorded on a TA Q200 thermal analyzer under N₂ atmosphere. The samples were first cooled from ambient temperature to -100 °C at 50 °C/min and then heated to 120 °C at 10 °C/min to remove the thermal history. After isotherm at 120 °C for 3 min, the samples were subsequently cooled to -100 °C at 10 °C/min and reheated to 120 °C at 10 °C/min.

All the chemical reagents were obtained commercially and used without further purification unless otherwise stated, including 1,5-cyclooctadiene (COD, 99.5%), LiAlH₄ (1 mol/L solution in THF), and *p*-toluenesulfonyl hydrazide (TSH, 98%) from J&K Scientific, 3-chloroperbenzoic acid (*m*CPBA, 75%), dicyclohexyl-carboimide (DCC, 99%), dimethylaminopyridine (DMAP, 99%), *n*-hexanoic acid (AR), and *n*-octanoic acid (AR) from Aladdin chemistry, lauric acid (AR), palmitic acid (AR), chloroform (AR), petroleum ether (AR), ethyl acetate (AR), and diethyl ether (AR) from Sinopharm Chemical Reagent. Tri-*n*-propylamine (TPA, 99%, Aladdin chemistry) was purified by CaH₂ and distilled under vacuum at 65–70 °C. *o*-Xylene (98%, Aladdin Chemistry) was immersed with activated 4Å molecular sieves for 24 h prior

to use. Tetrahydrofuran (THF) and dichloromethane were purified by passing through solvent purification systems (MB-SPS, MBRAUN). Grubbs second-generation catalyst {**G2**: [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro (phenylmethylene)(tricyclohexylphosphine)ruthenium(II)} and Grubbs third-generation catalyst {**G3**: dichloro[1,3-bis(2,4,6trimethylphenyl)-2-imidazolidinylidene]-(benzylidene)bis(3bromopyridine)ruthenium(II)} were purchased from Shanghai Coachchem and used directly. Cyclooctadiene monoepoxide and cyclooct-4-enol were prepared according to the literature.^{28,43}

Synthesis of Monomers (M1–M4)

Cyclooct-4-enyl Hexanoate (M1)

Monomer **M1** was prepared via the esterification reaction between cyclooct-4-enol and *n*-hexanoic acid according to the literature method as a clear liquid in 98% yield.⁴⁴

¹H NMR (400 MHz, CDCl₃), δ (ppm): 5.71–5.57 (m, 2 H, –CH=), 4.85–4.79 (m, 1 H, –CH0–), 2.36–2.31 (m, 1 H, –CH₂CH=), 2.24 (t, J = 7.6 Hz, 2 H, –CH₂C(0)–), 2.18–2.13 (m, 2 H, –CH₂CH₂C(0)–), 2.11–2.03 (m, 1 H, –CH₂CH=), 1.90–1.79 (m, 2 H, –CH₂CH=), 1.71–1.54 (brm, 6 H, –CH₂– in cyclooctene), 1.33–1.25 (m, 4 H, –CH₂– in side chain), 0.88 (t, J = 6.8 Hz, 3 H, –CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 173.25 (C=0), 129.73 (–CH=), 129.58 (–CH=), 75.30 (–CH0–), 34.67, 33.73, 33.59, 31.27, 27.98, 25.50, 24.78, 24.70, and 22.29 (–CH₂–), 13.88 (–CH₃). ELEM. ANAL. calcd (%) for C₁₄H₂₄O₂ (224.34): C 74.95, H 10.78; found: C 75.02, H 10.48.

Cyclooct-4-enyl Octanoate (M2)

Cyclooct-4-enol (4.74 g, 36.60 mmol) was combined with 1.2 equiv. of *n*-octanoic acid (6.33 g, 43.92 mmol), dicyclohexylcarboimide (DCC, 9.30 g, 45.07 mmol), and dimethylaminopyridine (DMAP, 0.56 g, 4.58 mmol) in 100 mL of dichloromethane in a 250-mL round-bottom flask. The reaction mixture was stirred at ambient temperature for 24 h. The solvent was removed by rotate evaporation under reduced pressure, and the residual crude product was purified by column chromatography (silica, petroleum ether/ethyl acetate 3:1). The desired product was obtained as a clear liquid in 99% yield (9.20 g).

¹H NMR (400 MHz, CDCl₃), δ (ppm): 5.72–5.58 (m, 2 H, –CH=), 4.85–4.80 (m, 1 H, –CHO–), 2.37–2.28 (m, 1 H, –CH₂CH=), 2.24 (t, J = 7.6 Hz, 2 H, –CH₂C(O)–), 2.19–2.14 (m, 2 H, –CH₂CH₂C(O)–), 2.12–2.05 (m, 1 H, –CH₂CH=), 1.90–1.80 (m, 2 H, –CH₂CH=), 1.71–1.54 (brm, 6 H, –CH₂– in cyclooctene), 1.31–1.27 (m, 8 H, –CH₂– in side chain), 0.87 (t, J = 6.8 Hz, 3 H, –CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 172.94 (C=O), 129.48 (–CH=), 129.36 (–CH=), 75.08 (–CHO–), 34.46, 33.56, 33.39, 31.47, 28.89, 28.75, 25.33, 24.83, 24.61, 22.39, and 22.11 (–CH₂–), 13.81 (–CH₃). ELEM. ANAL. calcd (%) for C₁₆H₂₈O₂ (252.40): C 76.14, H 11.18; found: C 76.15, H 10.95.

Cyclooct-4-enyl Dodecanoate (M3)

Monomer **M3** was synthesized by using a similar procedure as described for the preparation of **M2** starting with cyclooct-4-enol

and lauric acid. The desired product was collected as a clear liquid in 99% yield.

¹H NMR (400 MHz, CDCl₃), δ (ppm): 5.71–5.57 (m, 2 H, –CH=), 4.85–4.79 (m, 1 H, –CHO–), 2.36–2.28 (m, 1 H, –CH₂CH=), 2.23 (t, *J* = 7.6 Hz, 2 H, –CH₂C(O)–), 2.18–2.13 (m, 2 H, –CH₂CH₂C(O)–), 2.12–2.03 (m, 1 H, –CH₂CH=), 1.90–1.80 (m, 2 H, –CH₂CH=), 1.72–1.54 (brm, 6 H, –CH₂– in cyclooctene), 1.30–1.24 (m, 16 H, –CH₂– in side chain), 0.87 (t, *J* = 6.8 Hz, 3 H, –CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 173.08 (*C*=O), 129.66 (–*C*H=), 129.53 (–*C*H=), 75.19 (–*C*HO–), 34.65, 33.71, 33.55, 31.84, 29.53, 29.39, 29.27, 29.21, 29.07, 25.47, 24.98, 24.75, 22.62, and 22.26 (–*C*H₂–), 14.03 (–*C*H₃). ELEM. ANAL. calcd (%) for C₂₀H₃₆O₂ (308.51): C 77.87, H 11.76; found: C 77.20, H 11.94.

Cyclooct-4-enyl Palmitate (M4)

Monomer M4 was synthesized by using a similar procedure as described for the preparation of M2 starting with cyclooct-4-enol and palmitic acid. The desired product was collected as a clear liquid in 98% yield.

¹H NMR (400 MHz, CDCl₃), δ (ppm): 5.71–5.57 (m, 2 H, –CH=), 4.84–4.79 (m, 1 H, –CHO–), 2.35–2.27 (m, 1 H, –CH₂CH=), 2.23 (t, J = 7.6 Hz, 2 H, –CH₂C(O)–), 2.18–2.12 (m, 2 H, –CH₂CH₂C(O)–), 2.11–2.02 (m, 1 H, –CH₂CH=), 1.90–1.79 (m, 2 H, –CH₂CH=), 1.71–1.53 (brm, 6 H, –CH₂– in cyclooctene), 1.30–1.24 (m, 24 H, –CH₂– in side chain), 0.86 (t, J = 6.8 Hz, 3 H, –CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 173.07 (C=O), 129.66 (–CH=), 129.52 (–CH=), 75.19 (–CHO–), 34.64, 33.71, 33.56, 31.87, 29.63, 29.60, 29.59, 29.54, 29.41, 29.22, 29.08, 25.48, 24.99, 24.75, 22.63, and 22.27 (–CH₂–), 14.04 (–CH₃). ELEM. ANAL. calcd (%) for C₂₄H₄₄O₂ (364.61): C 79.06, H 12.16; found: C 78.67, H 11.95.

General Procedure of Ring-Opening Metathesis Polymerization

A typical procedure of ring-opening metathesis polymerization was as follows: To a three-necked round-bottom flask with a magnetic stir bar which was predried under vacuum, the monomer cyclooct-4-enyl hexanoate (M1, 1.24 g, 5.5 mmol) was added. The flask was purged three times with nitrogen through the vacuum-nitrogen system and then placed into a water bath set at 30 °C. An aliquot of a solution containing Grubbs second-generation catalyst (G2) (9.3 mg, 11.0 μ mol, $[M]_0/[G2] = 500$) in CH₂Cl₂ was rapidly and completely added via syringe into the flask. After the reaction solution was stirred at 30 °C for 30 h, an excess of ethyl vinyl ether was added and the solution was stirred for another 30 min and was then poured into a large amount of ethanol to precipitate the desired polymers. The polymers were collected by filtration, washed multiple times with ethanol, and dried overnight under vacuum. The following spectral properties were observed for each polymer.

Poly(cyclooct-4-enyl hexanoate) (**P1**): ¹H NMR (400 MHz, CDCl₃), *δ* (ppm): 5.36–5.31 (m, 2 H, –C*H*=), 4.87–4.85 (m, 1 H, –C*H*O–), 2.26 (t, *J* = 7.4 Hz, 2 H, –C*H*₂C(O)–), 1.99–1.95 (m,

4 H, $-CH_2CH=$), 1.64–1.47 (m, 6 H, $-CH_2-$ in main chain), 1.34–1.24 (m, 6 H, $-CH_2-$ in side chain), 0.88 (t, J = 6.8 Hz, 3 H, $-CH_3$). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 173.53 (*C*=0), 130.23 (*-C*H=), 129.68 (*-C*H=), 73.35 (*-C*H0–), 34.59, 34.02, 33.64, 32.37, 31.31, 28.41, 25.16, 24.78, and 22.30 (*-C*H₂-), 13.91 (*-C*H₃). ELEM. ANAL. calcd (%) for ($C_{14}H_{24}O_2$)_n: C 74.95, H 10.78; found: C 74.34, H 10.89.

Poly(cyclooct-4-enyl octanoate) (P2): ¹H NMR (400 MHz, CDCl₃), δ (ppm): 5.37–5.32 (m, 2 H, –C*H*=), 4.88–4.85 (m, 1 H, –C*H*O–), 2.27 (t, *J* = 7.4 Hz, 2 H, –C*H*₂C(O)–), 2.00–1.96 (m, 4 H, –C*H*₂CH=), 1.63–1.47 (m, 6 H, –C*H*₂– in main chain), 1.35–1.27 (m, 10 H, –C*H*₂– in side chain), 0.87 (t, *J* = 6.8 Hz, 3 H, –C*H*₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 173.57 (*C*=O), 130.25 (–*C*H=), 129.69 (–*C*H=), 73.37 (–*C*HO–), 34.65, 34.05, 33.68, 32.41, 31.67, 29.12, 28.93, 28.43, 25.20, 25.12, and 22.58 (–*C*H₂–), 14.06 (–*C*H₃). ELEM. ANAL. calcd (%) for (C₁₆H₂₈O₂)_n: C 76.14, H 11.18; found: C 76.20, H 10.98.

Poly(cyclooct-4-enyl dodecanoate) (**P3**): ¹H NMR (400 MHz, CDCl₃), δ (ppm): 5.37–5.32 (m, 2 H, –C*H*=), 4.88–4.85 (m, 1 H, –C*H*O–), 2.26 (t, *J* = 7.6 Hz, 2 H, –C*H*₂C(O)–), 2.00–1.95 (m, 4 H, –C*H*₂CH=), 1.67–1.49 (m, 6 H, –C*H*₂– in main chain), 1.34–1.25 (m, 18 H, –C*H*₂– in side chain), 0.87 (t, *J* = 6.8 Hz, 3 H, –C*H*₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 173.53 (*C*=O), 130.24 (–*C*H=), 129.69 (–*C*H=), 73.36 (–*C*HO–), 34.64, 34.05, 33.69, 32.41, 31.89, 29.59, 29.48, 29.32, 29.28, 29.18, 28.44, 25.22, 25.12, and 22.67 (–*C*H₂–), 14.10 (–*C*H₃). ELEM. ANAL. calcd (%) for (C₂₀H₃₆O₂)_n: C 77.87, H 11.76; found: C 77.57, H 11.85.

Poly(cyclooct-4-enyl palmitate) (P4): ¹H NMR (400 MHz, CDCl₃), δ (ppm): 5.37–5.32 (m, 2 H, --C*H*=), 4.88–4.85 (m, 1 H, --C*H*O--), 2.27 (t, *J* = 7.4 Hz, 2 H, --C*H*₂C(O)--), 2.00–1.95 (m, 4 H, --C*H*₂CH=), 1.62–1.49 (m, 6 H, --C*H*₂-- in main chain), 1.33–1.25 (m, 26 H, --C*H*₂-- in side chain), 0.87 (t, *J* = 6.8 Hz, 3 H, --C*H*₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 173.53 (*C*=-0), 130.24 (--*C*H=-), 129.69 (--*C*H=-), 73.36 (--*C*HO--), 34.65, 34.07, 33.71, 32.42, 31.91, 29.69, 29.66, 29.62, 29.50, 29.36, 29.30, 29.20, 28.45, 25.21, 25.13, and 22.68 (--*C*H₂--), 14.11 (--*C*H₃). ELEM. ANAL. calcd (%) for (C₂₄H₄₄O₂)_n: C 79.06, H 12.16; found: C 78.65, H 11.95.

General Procedure for the Hydrogenation of Unsaturated Polymers

The sealed flask loaded with the unsaturated polymers (0.16 g) was purged three times with nitrogen through a nitrogen system. The solvent *o*-xylene was added into the flask to dissolve the polymers. Upon the complete dissolution of polymers, *p*-toluenesulfonyl hydrazide (TSH) and tri-*n*-propyl amine (TPA) were added and the 2/2/1 molar ratio of TSH/ TPA/C=C double bonds was used in the hydrogenation reaction. The reaction mixture was refluxed at 135–140 °C for 4 h. The color of reaction solution changed from colorless to deep orange in the end. Finally, the cooled solution was poured into cold ethanol to precipitate the product. The hydrogenated polymers were filtered, washed several times with ethanol,





SCHEME 1 Synthesis of monomers and the corresponding polymers via ROMP, followed by hydrogenation. Reagents and conditions: (i) Epoxidation: *m*CPBA, CHCl₃, 0 °C \rightarrow r.t., 12 h; (ii) Reduction: LiAlH₄, THF, 0 °C \rightarrow r.t., 12 h; (iii) Esterification: DCC, DMAP, CH₂Cl₂, r.t., 24 h; (iv) Polymerization: **G2** catalyst, CH₂Cl₂, 30 h; (v) Hydrogenation: TSH/TPA, *o*-xylene, 135–140 °C, 4 h.

and dried overnight under vacuum. The following spectral properties were observed for each polymer.

HP1: ¹H NMR (400 MHz, CDCl₃), δ (ppm): 4.85 (m, J = 6.0Hz, 1 H, -CHO--), 2.27 (t, J = 7.4 Hz, 2 H, -CH₂C(O)--), 1.61 (m, J = 7.4 Hz, 2 H, -CH₂CH₂C(O)--), 1.49-1.48 (m, 4 H, -CH₂-- next to side chain), 1.31-1.24 (m, 14 H, -CH₂-- in main chain and side chain), 0.89 (t, J = 6.8 Hz, 3 H, -CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 173.66 (C=O), 73.98 (-CHO--), 34.65, 34.17, 31.31, 29.48, 25.32, 24.81, and 22.31 (-CH₂--), 13.91 (-CH₃). ELEM. ANAL. calcd (%) for (C₁₄H₂₆O₂)_n: C 74.29, H 11.58; found: C 74.02, H 11.75.

HP2: ¹H NMR (400 MHz, CDCl₃), δ (ppm): 4.85 (m, J = 6.0 Hz, 1 H, -CHO-), 2.27 (t, J = 7.4 Hz, 2 H, -CH₂C(O)-), 1.61 (m, J = 7.4 Hz, 2 H, -CH₂CH₂C(O)-), 1.49-1.48 (m, 4 H, -CH₂- next to side chain), 1.30-1.24 (m, 18 H, -CH₂- in main chain and side chain), 0.87 (t, J = 6.8 Hz, 3 H, -CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 173.66 (*C*=O), 73.98 (-*C*HO-), 34.69, 34.19, 31.67, 29.51, 29.11, 28.93, 25.36, 25.14, and 22.57 (-*C*H₂-), 14.05 (-*C*H₃). ELEM. ANAL. calcd (%) for (C₁₆H₃₀O₂)_n: C 75.54, H 11.89; found: C 75.34, H 11.92.

HP3: ¹H NMR (400 MHz, CDCl₃), δ (ppm): 4.85 (m, J = 6.0 Hz, 1 H, -CHO-), 2.27 (t, J = 7.8 Hz, 2 H, -CH₂C(O)-), 1.61 (m, J = 7.4 Hz, 2 H, -CH₂CH₂C(O)-), 1.49-1.48 (m, 4 H, -CH₂- next to side chain), 1.30-1.25 (m, 26 H, -CH₂- in main chain and side chain), 0.88 (t, J = 6.8 Hz, 3 H, -CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 173.65 (**C**=0), 73.98 (-**C**HO-), 34.70, 34.22, 31.90, 29.60, 29.54, 29.49, 29.33, 29.29, 29.18, 25.35, 25.15, and 22.67 (**-***C*H₂**-**), 14.10 (**-***C*H₃). ELEM. ANAL. calcd (%) for (C₂₀H₃₈O₂)_n: C 77.36, H 12.34; found: C 77.59, H 12.18.

HP4: ¹H NMR (400 MHz, CDCl₃), δ (ppm): 4.85 (m, J = 6.0 Hz, 1 H, -CHO--), 2.27 (t, J = 7.8 Hz, 2 H, -CH₂C(O)--), 1.61 (m, J = 7.4 Hz, 2 H, -CH₂CH₂C(O)--), 1.49-1.48 (m, 4 H, -CH₂-- next to side chain), 1.30-1.25 (m, 34 H, -CH₂-- in main chain and side chain), 0.88 (t, J = 6.8 Hz, 3 H, -CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 173.65 (*C*=O), 73.98 (-*C*HO--), 34.70, 34.23, 31.92, 29.69, 29.66, 29.62, 29.55, 29.51, 29.36, 29.30, 29.19, 25.37, 25.16, and 22.68 (-*C*H₂--), 14.11 (-*C*H₃). ELEM. ANAL. calcd (%) for (C₂₄H₄₆O₂)_n: C 78.63, H 12.65; found: C 78.54, H 12.69.

RESULTS AND DISCUSSION

Synthesis of Monomers M1-M4

The monomers, fatty acid derived cyclooctenes (**M1–M4**), were prepared from the starting material 1,5-cyclooctadiene (COD). One of the C=C double bonds in 1,5-cyclooctadiene was first transformed into epoxy group by using 3-chloroperbenzoic acid (*m*CPBA) as an epoxidation reagent, yielding cyclooctadiene monoepoxide, which was then reduced into cyclooct-4-enol by LiAlH₄.^{28,43} The esterification reaction of cyclooct-4-enol with fatty acids, including *n*-hexanoic acid, ⁴⁴ *n*-octanoic acid, lauric acid and palmitic acid, generated the corresponding fatty acid derived cyclooctenes (**M1–M4**) in the presence of DCC and DMAP (Scheme 1). The structure and purity of monomers were determined by FTIR, ¹H and ¹³C NMR spectra, and elemental analysis.



FIGURE 1 ¹H NMR (a) and ¹³C NMR (b) spectra of **M3**, **P3**, and **HP3**. *Impurity. [Color figure can be viewed at wileyonlinelibrary. com]

In the ¹H NMR spectra of monomers [Fig. 1(a)], the multiple peaks at 5.71–5.57 ppm corresponded to the protons in the C=C double bonds of cyclooctenes and the multiple peaks at 4.85–4.79 ppm were assigned to the -CH- proton connected to the side chain. The signals of methylene protons next to the carbonyl group and methyl protons in the side chain appeared at 2.24 and 0.87 ppm as the triplet peaks, respectively. Besides, the signals of residual methylene protons could be also clearly found in the spectra. The ¹³C NMR spectra also confirmed the structure of monomers [Fig. 1(b)]. The signal of carbonyl-C atom showed up around 173.0 ppm and the two carbon atoms in the C=C double

bonds had a little different chemical shifts (129.7 and 129.5 ppm) due to the presence of side chain at the 5-position of cyclooctene. The signal of -CH- carbon atom connected to the side chain located at 75.2 ppm. The signals of saturated carbon atoms in the methylene groups appeared in the range of 35.0–22.0 ppm and the peak of methyl groups located around 14.0 ppm.

Polymerization of Monomers M1-M4

The Grubbs second-generation catalyst (G2) was chosen for all the polymerization reactions because no large influence on the polymerization between catalysts G2 and G3 was

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TABLE 1 The ROMP of Monomers M1-M4 Using Catalyst G2^a

Entry	Monomer	[M] ₀ /[G2]	Yield ^ь (%)	<i>M</i> n ^c (kg⋅mol ^{−1})	$M_{ m w}/M_{ m n}^{ m c}$
1	M1	500	37	22.8	2.00
2	M1	750	58	43.7	1.89
3	M1	1000	64	70.2	1.94
4	M2	500	59	83.2	1.89
5	M2	750	65	139.8	1.71
6	M2	1000	73	138.8	2.34
7	M3	500	68	80.6	1.80
8	M3	750	73	116.9	1.69
9	M3	1000	75	166.5	2.03
10	M4	500	67	93.7	1.92
11	M4	750	76	124.3	2.10
12	M4	1000	82	126.7	2.05

^a Polymerization conditions: **G2**: 9.3 mg, 11.0 μ mol; CH₂Cl₂: 15 mL; reaction temperature: 30 °C; reaction time: 30 h. Ethyl vinyl ether was used as the polymerization terminator.

^b Isolated yield.

 $^{\rm c}$ Determined by GPC using polystyrene standards in THF at 25 $^{\circ}{\rm C}$ and reported without calibration.

found. The ROMP of monomers was carried out in dichloromethane with **G2** at 30 °C for 30 h and the results were summarized in Table 1. In all the cases, the polymerization reactions were homogeneous and the reaction mixtures turned to be deep purple during the polymerization. The polymerization was finally quenched by adding an excess of ethyl vinyl ether and being stirred for another 30 min. All the polymers were isolated by precipitation in ethanol as extremely viscous semisolids. (**P4** became wax-like solid when ambient temperature was below 10 °C.) All the monomers were polymerized under the similar conditions at a molar ratio of $[M]_0/[G2] = 500$, 750, and 1000. For each monomer, the isolated yield and molecular weight of resulted polymers increased gradually as the increase in the



FIGURE 2 GPC traces of P3 polymers.



FIGURE 3 The olefinic region of ¹³C NMR spectra of polymers **P1–P4**. [Color figure can be viewed at wileyonlinelibrary.com]

monomer concentration. The GPC traces exhibited a unimodal, and the molecular weight distribution ranged from 1.69 to 2.34 (Fig. 2). In addition, the higher isolated yield was obtained for the monomer with longer side chains.

The two overlapping sets of peaks centered at 5.32 and 5.37 ppm in the olefinic region of the ¹H NMR spectra were observed and assigned to the protons in the C=C double bonds in the main chains of polymers for cis and trans repeat units, respectively [Fig. 1(a)]. The cis/trans ratio was calculated to be approximately 20/80, which was close to the ratio observed in the poly(5AcCOE).³¹ In comparison with the corresponding monomer, the multiple peaks assigned to the -CH- proton connected to the side chain appeared with the similar chemical shift in the ¹H NMR spectra. The chemical shifts of the methylene protons next to the C=C double bonds were found at 2.00-1.95 ppm. The triplet peaks of methylene protons next to the carbonyl group and methyl protons in the branch ends also showed up at 2.26 and 0.87 ppm, respectively. The chemical shifts of the other methylene protons were found in the range of 1.67-1.25 ppm.

Homopolymerization of 5-subsituted cyclooctenes have been reported to generate polymers theoretically containing 25 mol % of polar vinyl monomers, in which polar groups were separated by either 6 (tail-to-tail, TT), 7 (head-to-tail, HT), or 8 (head-to-head, HH) methylene units depending on the different regio-addition of monomers.^{28,29,45} For each polymer synthesized in this work, eight resonances were observed in the olefinic region of the ¹³C NMR spectra (Fig. 3), which was in accordance with the presence of the three possible regio-isomers (HH, HT, and TT) as well as the concurrence of *cis* and *trans* C=C double bonds in the main chain. These results revealed that the resulted polymers were completely regio-irregular. The lack of regiospecificity



FIGURE 4 FTIR spectra of M3, P3, and HP3. [Color figure can be viewed at wileyonlinelibrary.com]

could be ascribed that the substituent at the 5-position of cyclooctene was probably too far away from the double bond to affect the catalyst orientation during the propagation step. In the ¹³C NMR spectra of polymers [Fig. 1(b)], the signal of carbonyl-C atom kept around 173.0 ppm. The signal of --CH-- carbon atom connected to the side chain shifted a little to 73.4 ppm. The signals of the saturated carbon atoms in the methylene groups appeared in the range of 34.6-22.7 ppm and the peak of methyl group in the branch ends still located around 14.0 ppm. The characteristic C--H out-of-plane bending absorptions in the double bonds at 967 (*trans*, mainly) and 722 cm⁻¹ (*cis*) were observed in the IR spectra of polymers, respectively (Fig. 4).

Hydrogenation of the Unsaturated Polymers

The unsaturated polymers via ROMP could be successfully saturated by the chemical hydrogenation reaction using *p*-toluenesulfonyl hydrazide (TSH) as a hydrogenation regent (Scheme 1), as previously reported.^{17,46} In all the cases, the saturated polymers were obtained in high conversion (>99%, Table 2) and the branches were not influenced as indicated by NMR spectroscopy. After hydrogenation, the saturated polymers were still viscous semisolids but a little less sticky than the corresponding unsaturated precursors.

The FTIR spectra confirmed that the C=C double bonds were hydrogenated with the evidence of disappeared C-H stretching vibration bands and C-H out-of-plane bending vibration at 967 cm⁻¹ in the double bonds (Fig. 4). In addition, the stretching vibration of carbonyl group kept at 1733 cm⁻¹ whether for the monomers or corresponding polymers.

In the ¹H NMR spectra [Fig. 1(a)], the various peaks related to the protons in the C=C double bonds at 5.37-5.32 ppm and in the methylene groups next to the C=C double bonds at 2.00-1.95 ppm disappeared completely after hydrogenation. The resonances of saturated methylene protons merged into an intensive peak at 1.28 ppm. The multiple peaks of the triplet peaks of methylene protons next to the carbonyl group (2.27 ppm) and methyl protons in the branch ends (0.87 ppm) kept almost unchanged. In the ¹³C NMR spectra [Fig. 1(b)], all the resonances of C=C carbon atoms entirely disappeared and turned into methylene carbon atoms, showing up around 30.00 ppm, which also confirmed the complete hydrogenation of unsaturated polymers. The similar signals of carbonyl-C atom at 173.0 ppm and -CH- carbon atom connected to the branches at 74.0 ppm also indicated that the hydrogenation reaction had almost no influence on the branches. Because all the monomers are racemic, both unsaturated and saturated polymers obtained are expected to be atactic. The ¹³C NMR spectra of hydrogenated polymers HP1-HP4 gave the multiple signals at 74.0 ppm for the methine carbon atoms, indicating their regio-irregularity (Fig. 5). The hydrogenated polymers are the equivalents of a series of ethylene/vinyl ester copolymers with pendent linear branches on precisely every eighth backbone carbon.

Thermal Properties

Differential scanning calorimetry (DSC) was applied to analyze the thermal properties of unsaturated and hydrogenated polymers. The DSC curves of polymers were shown in Figure 6, and the results were summarized in Table 2. Both glass transition temperature (T_g) and melting point (T_m) values were determined on the heating scan and crystallization temperature (T_c) values were determined on the cooling scan. The results indicated that the chain length of branches had great influence on the thermal properties of obtained polymers. Both unsaturated polymers (**P1**, **P2**) and hydrogenated polymers (**HP1**, **HP2**)

TABLE 2 Characterization of Hydrogenated Polymers and Their Precursors

	Hydrogenated Polymers					Unsaturated Precursors ^c			
	Conv.ª (%)	Yield ^b (%)	T _g ^d (°C)	T _m ^d (°C)	T _c ^d (°C)		τ _g ^d (°C)	T _m ^d (°C)	<i>T</i> _c ^d (°C)
HP1	>99	53	-58.6	-	-	P1 (1)	-61.4	-	-
HP2	>99	98	-62.9	-	-	P2 (4)	-66.0	-	-
HP3	>99	98	-62.5	-32.8, -4.9	-45.8	P3 (7)	-56.8	-30.6	-42.9
HP4	>99	73	-	7.9	-3.1	P4 (10)	-	10.6	0.8

^a Determined by ¹H NMR spectroscopy from the ratio of integral areas between the remaining and original double bond. ^b Isolated yield.

^c The numbers in brackets are the entries in Table 1.

 $^{\rm d}$ Determined by DSC on the second heating/cooling cycle at 10 °C/min.





FIGURE 5 ¹³C NMR spectra of saturated polymers HP1–HP4. [Color figure can be viewed at wileyonlinelibrary.com]

with shorter branches were completely amorphous materials with $T_{\rm g}$ values below -55 °C. A slightly decreased $T_{\rm g}$ with the increase in the chain length of branches was observed and this tendency was consistent with the other poly(vinyl ester)s containing fatty acid side chains.^{47,48} By comparing the $T_{\rm g}$ values of unsaturated polymers to those of saturated polymers, the hydrogenation of polymers led to slightly higher $T_{\rm g}$ values. However, because of the presence of longer linear alkyl side chains, the polymers with the branches of 12 or 16 carbon atoms started to crystallize with the lower $T_{\rm m}$ values, which was in good agreement with other polymers bearing the saturated fatty acid-derived side chains.^{37– δ 39,49} As a result, the $T_{\rm m}$ values at -30.6 and 10.6 °C were observed for the unsaturated polymers **P3** and **P4**, respectively. As the chain length of pendant linear branches increased, the crystallization of side chains might be enhanced, leading to the higher $T_{\rm m}$ values and crystallinity of polymers.^{37– δ 39,49} After the saturation of the backbone, the $T_{\rm m}$ values for the saturated polymers **HP3** and **HP4** increased slightly, and there were two endothermic peaks observed for **HP3** (-32.8 and -4.9 °C) and a shoulder peak



FIGURE 6 DSC curves of obtained polymers. (a) Unsaturated polymers P1-P4; (b) saturated polymers HP1-HP4. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 7 TGA curves of representative polymers **P3** and **HP3**. [Color figure can be viewed at wileyonlinelibrary.com]

alongside for **HP4**. Due to the disturbance of crystallization of long alkyl side chains, no significant T_g was found for both **P4** and **HP4**.

In order to determine the thermal stability of obtained polymers, the thermo-gravimetric analysis (TGA) of unsaturated polymer **P3** and corresponding hydrogenated polymer **HP3** was carried out in nitrogen atmosphere as the representative samples (Fig. 7). About 3% weight loss was observed between 130 and 220 °C probably because of the presence of traces of residual solvents or impurity. There were two thermal degradation stages observed for both samples. The real initial degradation happened around 220 °C and a similar complete degradation temperature was found at about 480 °C. In both stages, the hydrogenated polymer had relatively better thermal stability than the unsaturated one because the C==C double bonds were hydrogenated into the saturated methylene groups although they had the same branches.

CONCLUSIONS

A series of cyclooct-4-enyl esters of fatty acid (M1–M4), as the vinyl ester-functionalized cyclooctenes with long linear side chains, were synthesized and polymerized via ROMP with **G2** catalyst. The NMR analysis determined that the functionalized monomers underwent ROMP in regioirregular manners to produce the unsaturated polymers. The resulting polymers were successfully hydrogenated by chemical hydrogenation with TSH/TPA, generating the saturated polymers with precisely long linear branches on every eighth backbone carbon. All the polymers obtained were amorphous at room temperature, but the unsaturated polymers were much more viscous than the saturated ones. The thermal properties of obtained polymers were analyzed by DSC and TGA. The T_g values of both unsaturated polymers (**P1**, **P2**) and hydrogenated polymers (**HP1**, **HP2**) with short branches were below -55 °C, whereas no significant $T_{\rm g}$ was observed for the polymers with longer linear alkyl branches (**P4** and **HP4**), indicating that the length of branches had great influence on the thermal properties. The hydrogenated polymers had relatively better thermal degradation stability than the unsaturated polymers.

ACKNOWLEDGEMENTS

The work was supported by the Zhejiang Provincial Natural Science Foundation (No. LY16B040001) and the National Natural Science Foundation of China (No. 21536011).

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