

# Functionalized regio-regular linear polyethylenes from the ROMP of 3-substituted cyclooctenes

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**Abstract** We demonstrated that the ring-opening metathesis polymerization (ROMP) of 3-substituted cyclooctenes bearing polar substituents allows the synthesis of highly regio- and stereo-regular polymers. A series of polyalkenamers with 90–99 % head-to-tail/*trans* configuration were synthesized in good yields (33–87 % yield). Upon saturation of the backbone using diimide, these polymers represent a class of linear polyethylene derivatives where the polar side chain is located on every eighth carbon. The thermal properties of both the saturated and unsaturated polymers depend strongly on the size and polarity of the functional side groups. The results presented here demonstrate that the 3-substituted cyclooctenes can be used not only for the synthesis of precisely functionalized polyethylene derivatives, but also to participate in the ring-opening metathesis copolymerization with unfunctionalized cyclic olefins to generate copolymers with tunable properties.

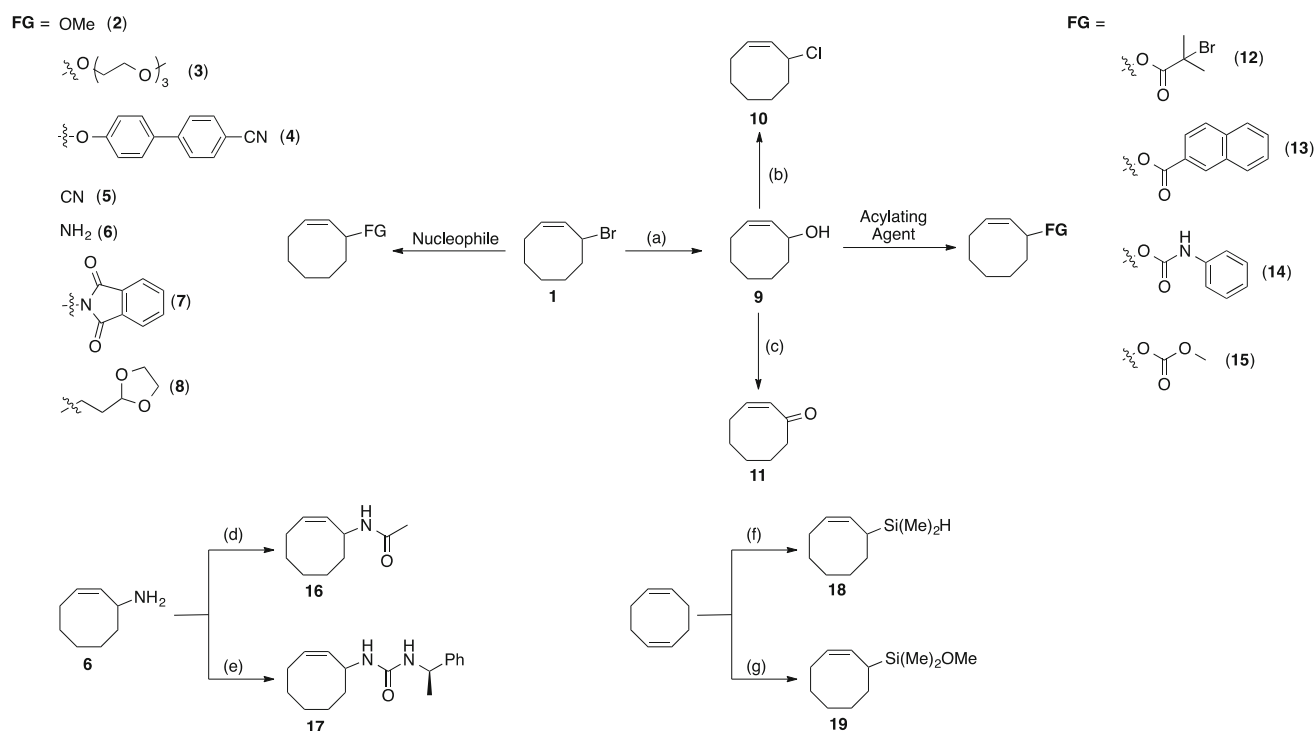
**Keywords** ROMP · Polyethylene · Substituted polyolefin · Metathesis

## Introduction

Polyethylene (PE) is one of the most common plastics, the derivatives of which have found themselves useful in a variety of applications [1–3]. Incorporation of side chains, especially polar functional side chains, is desirable and often necessary to give the polymer desired properties and better performance. Due to the physical and chemical stability of PE, direct functionalization of PE is challenging [4]. Therefore, PE derivatives bearing functional side chains are typically produced by radical or coordination copolymerization of ethylene and functionalized olefin(s). These polymerizations, however, frequently suffer from dramatically different comonomer reaction rates, intolerance of catalyst to polar functional groups and lack of control of polymer microstructure. As a consequence, controlling the scope, content and distribution of functional side chains in the polymer is undermined. A number of methods have been developed to overcome these problems, and notable examples include development of compatible catalysts [5, 6] and metathesis polymerization of functionalized monomers. The latter method is interesting because of catalyst compatibility to polar functional groups and, more attractively, potential to precisely control the polymer structure. Wagener and coworkers have utilized acyclic diene metathesis polymerization (ADMET) [7] of functionalized  $\alpha,\omega$ -dienes to prepare linear PE derivatives bearing a broad range of polar functional groups [8–29]. Many of the ADMET-derived polymers feature precisely placed polar side chains when a symmetric monomer is used. As opposed to the condensation polymerization nature of ADMET, ring-opening metathesis polymerization (ROMP) is an addition polymerization which requires less demanding conditions and allows better control of the polymer molar mass [30]. The use of functionalized cyclic

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**Scheme 1** Synthesis of various 3-substituted COEs. (a) Acetone/water, NaHCO<sub>3</sub>, reflux 1 h. (b) SOCl<sub>2</sub>, Py. (c) Pyridinium chlorochromate, CH<sub>2</sub>Cl<sub>2</sub>. (d) Et<sub>3</sub>N/AcCOCl, CH<sub>2</sub>Cl<sub>2</sub>. (e) DMAP,

isocyanate. (f) 1. H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, ClSiMe<sub>2</sub>H, Cy, 2. LAH, THF. (g) 1. H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, ClSiMe<sub>2</sub>H, Cy, 2. MeOH, Py

olefins in ROMP has also been explored by many research groups to access to linear PE derivatives with diverse polar side chains, including boranes, thioethers, halides, nitrile, hydroxyl, carbonyl, esters, amides, urethanes and liquid crystal moieties [31–54]. However, excluding those in which the monomer is symmetrically substituted, only few examples resulted in regio-regular products [46, 48].

We recently published a series of reports [55–59] demonstrating that single substitution at the 3-position (i.e., the allylic position) of *cis*-cyclooctene (COE) was an effective way to synthesize regio- and stereo-regular polyalkenamers by ROMP using the well-defined Grubbs second (G2) or third (G3) generation catalysts. Such substituents we have explored included hydrocarbon groups (3RCOE, R = methyl, ethyl, hexyl or phenyl) [55, 56] and the acetoxy group [57–59]. All the reported polyalkenamers possess high levels (>95 %) of head-to-tail (HT) repeating unit connectivity and *E* double bond configuration. Hydrogenation of these polymers afforded PE derivatives with precisely positioned branches, which exhibit distinct physical properties compared to their random counterparts. More importantly, these reports suggest that ROMP of any COE substituted with a sufficiently bulky group at the 3-position could proceed in a regio- and stereo-selective manner, which in combination with the exceptional functional group tolerance of Ru-based

catalysts allows us to conveniently synthesize diversely functionalized precision PE derivatives.

In the present study, we explore the scope of polar functional groups that, when placed at the 3-position (3FGCOE, Scheme 1), are amenable to controlled ROMP with Ru-based catalysts. The polymer regio-regularity [head-to-tail (HT), head-to-head (HH) and tail-to-tail (TT)] and stereo-regularity (*cis* and *trans*) were analyzed in this study. These polymers, after the backbone is saturated, represent a class of linear PE derivatives where the polar side chain is located on every eighth carbon. The precision microstructure further enables investigation of the effect of side chain size and polarity on the polymer properties.

## Results and discussion

### Monomer synthesis

3-bromocyclooctene (**1**) was chosen as the principal starting material because of its scalable and highly efficient preparation. Several synthetic pathways were explored as shown in Scheme 1. The bromo group exhibited a wide range of reactivity towards the hydroxyl group in alcohols and phenol derivatives (compounds 2–4). Stirring compound **1** in anhydrous methanol at room temperature

afforded 3-methoxy-COE (**2**) in 24 h; and elevated temperature and extended reaction time was required to obtain compound **3** from its respective alcohol. However, no reaction of **1** with more hindered alcohols (e.g., secondary alcohols) or their deprotonated forms was observed, even after months. The phenoxide anion derived from phenol 4'-hydroxy-4-biphenylcarbonitrile, which is a liquid crystal building block, reacts readily with **1** in DMF to give 3-substituted COE with an aryl ether group (compound **4**). Other types of nucleophiles, including cyanide, ammonia, phthalimide and a Grignard reagent, reacted with **1** to generate the corresponding 3FGCOEs (compounds **5–7**). 3-amino-COE (**6**) was used to synthesize 3FGCOE having amide (**16**) or urea (**17**) groups substituted at the 3-position (Scheme 1).

Treatment of 3-hydroxy-COE (**9**) [59] with thionyl chloride in the presence of pyridine gave 3-chloro-COE (**10**). The hydroxyl group in **9** was also oxidized to give 2-cyclooctenone (**11**). Furthermore, a variety of ester or urethane groups were introduced through the hydroxyl group by acylation or reaction with isocyanate (3FGCOE **12–15**).

Two silicon-containing monomers (**18** and **19**) were synthesized from hydrosilylation of *cis*-1,5-cyclooctadiene followed by nucleophilic attack of hydride or methanol to replace the chloride atom. The hydrosilylation at the 3 position was expected if taken into account that the isomerization of cyclic dienes from non-conjugated to conjugated dienes has been previously reported using  $H_2PtCl_6$  [60]. Based on NMR <5 % of 5-substituted COE monomer was obtained using this method.

### Polymer synthesis and characterization

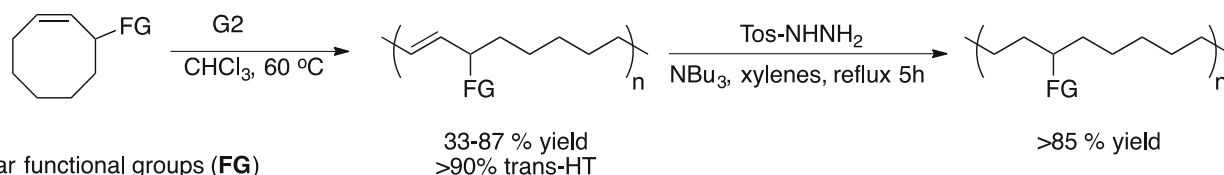
The compatibility of these 3FGCOEs with **G2** and the capability of these functional groups to give regio- and stereo-selective polymerizations were tested in ROMP under various conditions (Scheme 2) and the results are summarized in Table 1. To have a fair basis to compare the reactivity of these monomers, all polymerizations were carried out at the same temperature (60 °C) with comparable initial monomer concentration (1–2 M). Some 3FGCOEs with highly polar functional groups (**4**, **7**, **16** and **17**) were essentially insoluble in  $CHCl_3$  at the prescribed concentration; a co-solvent was employed in these

cases to give a homogeneous solution. We attempted to use *cis*-4-octene as a chain transfer agent (CTA) to regulate the polymer molar mass as demonstrated in previous studies [55]. However, this effort only succeeded with some monomers while the others required higher catalyst loading to give polymers, suggesting these particular polar functional groups may inhibit the activity of **G2**.

Polymerization of ether-functionalized monomers **2** and **3** and carbonate monomer **15** under standard conditions resulted in polyalkenamers with the highest yields (87, 85 and 88 %, respectively) among all the monomers in this study. Polymerization and isolation of these polymers were straightforward. In contrast, polymerization of monomers **8** and **13** under standard conditions resulted in reaction mixtures containing considerable quantities of residual monomer, even after 24 h of reaction, suggesting a lower reactivity of such monomers under the chosen conditions. Initial attempts to polymerize monomer **11** yielded insoluble gels upon precipitation in methanol. However, the polymerization proceeded successfully in the presence of butylated hydroxytoluene (BHT). Additional BHT was added to a solution of the dissolved polymer immediately after precipitation to avoid subsequent cross-linking. Monomers bearing a cyclic imide (**7**), urethane (**14**) or aryl-cyanide group (**4**) were successfully polymerized, but required a relatively high catalyst loading.

Three N-containing monomers, **6**, **16** and **17**, as well as nitrile monomer **5**, did not generate any polymer using **G2** or the more reactive **G3**. In all cases, the reaction mixture turned a brown color within a few minutes, suggesting deactivation of the Ru catalyst. The failure of **5** or **6** was not surprising, as compounds containing nitrile groups or primary amines are known to deactivate the Ru catalysts [33, 36, 37, 61, 62]. However, the monomers bearing acetamide (**16**) and urea (**17**) functional groups did not polymerize either. Some studies suggested that amides and ureas were compatible with the Ru catalysts in both polymerizations [49–51] and small molecule reactions [63]. The reason for the inactivity in our trials is unknown.

The two Si-containing monomers, **18** and **19**, did not polymerize even at high catalyst loading. In both cases, the reaction mixture remained a yellow color even after 24 h, suggesting that the catalyst was active. Addition of COE after 24 h to both reaction mixtures yielded poly(COE) only in the solution that contained monomer **19**, which not



**Scheme 2** Synthesis of linear polyethylene derivatives via ROMP followed by hydrogenation

**Table 1** Polymers from ROMP of various 3FGCOEs bearing polar functional groups using G2<sup>a</sup>

3FGCOE	[G2] <sup>a</sup> (mol %)	[CTA] <sup>a</sup> (mol %)	Conv. <sup>b</sup> (%)	Yield <sup>c</sup> (%)	$M_n$ (kg/mol)		$\bar{D}$ <sup>e</sup>	$E$ -HT <sup>f</sup> (%)	$T_g^g$ (°C)
					Cal. <sup>d</sup>	SEC <sup>e</sup>			
<b>1</b> <sup>h</sup>	0.20	N/A	–	69	–	–	–	–	–
<b>2</b>	0.04	1.0	>99	87	13.5	29.0	1.8	95	–54
<b>3</b>	0.10	1.0	>99	85	21.0	33.6	2.5	90	–69
<b>4</b> <sup>i</sup>	0.10	N/A	89	33	270	258	2.0	96	32
<b>7</b> <sup>j</sup>	0.10	N/A	98	71	250	240	1.4	>99	58
<b>8</b>	0.025	1.0	91	64	18.7	26.0	1.5	98	–34
<b>10</b> <sup>h</sup>	0.2	N/A	–	81	–	–	–	–	–
<b>11</b> <sup>k</sup>	0.025	1.0	92	73	12.1	27.6	1.7	>99	–26
<b>13</b>	0.025	1.0	66	42	18.1	15.3	2.0	>99	2
<b>14</b>	0.2	N/A	82	66	101	121	1.7	92	37
<b>15</b>	0.025	1.0	>99	88	18.0	38.3	1.9	97	–28

All polymerizations conducted at 60 °C with initial monomer concentration of 1–2 M in CHCl<sub>3</sub> if not otherwise stated

<sup>a</sup> Relative to monomer concentration, CTA = *cis*-4-octene

<sup>b</sup> Determined by <sup>1</sup>H NMR analysis of the reaction mixture

<sup>c</sup> Isolated yield

<sup>d</sup>  $M_n$  (cal) = MW (monomer) × Conv. ×  $[M]_0/([G2] + [CTA])$

<sup>e</sup> Determined by SEC in CHCl<sub>3</sub> at 30 °C versus polystyrene standards

<sup>f</sup> Estimated by <sup>1</sup>H NMR of the isolated polymer in CDCl<sub>3</sub>

<sup>g</sup> Determined by DSC (2nd heating cycle) at 10 °C min<sup>–1</sup>

<sup>h</sup> At room temperature

<sup>i</sup> 1:1 (v/v) CHCl<sub>3</sub>:toluene

<sup>j</sup> 3:1 (v/v) CHCl<sub>3</sub>:THF

<sup>k</sup> This polymer showed a  $T_m$  at 106 °C ( $\Delta H = 64$  J g<sup>–1</sup>)

only suggested that the catalyst was active, but also that the SiMe<sub>2</sub>OMe group in position 3 of the COE is bulky enough to inhibit the catalyst approach to the double bond. The fact that COE did not polymerize in the solution that contained monomer **18** might be due to oxidative addition of the Si–H group to the Ru center. Similar reactions have been used to perform hydrosilylation on terminal alkynes using Grubbs' first generation catalyst (**G1**) or **G2** catalyst [64, 65].

Both 3-hydroxy-COE (**9**) and 3- $\alpha$ -bromoisobutyrate-COE (**12**) [66] monomers quickly gave insoluble gels, indicating the formation of physically cross-linked networks possibly through strong hydrogen bonding (**9**) or covalent bonds (**12**) among polymer chains.

Polymers obtained from the halide-containing monomers (**1** and **10**) decomposed easily during the polymerization, generating dark insoluble rubbery materials. This result was not observed during the ROMP of 5-chloro or 5-bromo substituted COE [33–35], which suggests polymers of **1** and **10** are prone to halide elimination to generate conjugated dienes, possibly facilitated by the Ru catalyst.

Qualitatively, different rates of polymerization were observed with these 3FGCOEs, most of which gave polymers in high or quantitative conversion. However, significantly lower conversions were obtained with

3FGCOEs bearing aryl groups (**4** and **13**). This result is consistent with that reported on 3-phenyl COE, suggesting that bulky and rigid substituents result in lower polymerization rate. The polymer number average molar mass ( $M_n$ ) determined by size exclusion chromatography (SEC) compared with polystyrene standards and the corresponding theoretical value were only in good agreement for the polymers containing aryl groups. This phenomenon can be attributed to the systematic difference of hydrodynamic radius between the polymer and the polystyrene standard, which is likely smaller in structurally similar polymers. The molar mass dispersity ( $\bar{D}$ ) ranged from 1.4 to 2.5, in accordance with the typical values for products from ROMP with extensive cross-metathesis.

The regio- and stereo-regularity of poly(3FGCOE) samples was characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (see spectra in SI). Results comparable to those reported for our original poly(3RCOE) [55, 59] samples were observed for every poly(3FGCOE), namely high content of head-to-tail (HT) structure and *E* double bond configuration (Table 1). This result confirms our hypothesis that sufficiently bulky substituent at the 3-position gives rise to regio- and stereo-selective polymerization [55–59]. Thermal characterization using differential scanning calorimetry

**Table 2** Characterization of hydrogenated polymers

	Yield <sup>a</sup> (%)	$M_n^b$ (kg mol <sup>-1</sup> )	$D^b$	$T_g^c$ (°C)	$T_m^c$ (°C)	$\Delta H_m^c$ (J g <sup>-1</sup> )
PH2	80	36.8	1.6	-70	15 <sup>d</sup>	25
PH3	85	34.1	1.9	-74	-5	25
PH7	90	38.3	4.1	37	-	-
PH8	92	24.9	1.6	-49	-	-
PH13	60	17.0	1.8	18	-	-
PH14	77	57.6	3.4	51	-	-
PH15	83	49.4	2.1	-32	49	0.4

<sup>a</sup> Isolated yield<sup>b</sup> Determined by SEC in CHCl<sub>3</sub> at 30 °C versus polystyrene standards<sup>c</sup> Determined by DSC (2nd heating cycle) at 10 °C min<sup>-1</sup><sup>d</sup> Cold crystallization at -38 °C ( $\Delta H = 25 \text{ J g}^{-1}$ )

(DSC) suggested nearly all poly(3FGCOE) are amorphous with glass transition temperatures ( $T_g$ ) in the range of -69 to 58 °C (Table 1). The  $T_g$  of these polyalkenamers vary substantially (from -69 to 58 °C) and are clearly dependent on the functional group identity. Poly(3FGCOE) with relatively small and less polar functional groups (e.g., P2) consistently exhibit lower  $T_g$  than those with relatively bulky and more polar functional groups (e.g., P7). Interestingly, P11 showed a  $T_m$  at 106 °C ( $\Delta H = 64 \text{ J g}^{-1}$ ). When compared with the regio-irregular poly(cyclooct-4-enone) reported by Hillmyer et al. [33] in 1995 via ROMP using a Ru-based catalyst, P11 has a higher  $T_g$  (-58 vs. -26 °C) and  $T_m$  (34 vs. 106 °C). This is consistent with the fact that at higher regio- and stereo-regularity both  $T_g$  and  $T_m$  increases [55, 59]. Similarly, the polymer microstructure has been shown to have profound influence on the thermal properties in precision polyethylenes prepared by ADMET [67].

Chemical hydrogenation of polyalkenamers using diimide has shown to be an effective way to generate saturated backbone [68]. We applied this method to hydrogenate poly(3FGCOE), which resulted in a polymer equivalent to a copolymer of one part functionalized alpha olefin and three parts ethylene. With the exception of P4 and P11, the corresponding hydrogenated polymers were obtained in decent yields (Table 2). P4 has poor solubility in xylenes, while P11 cross-linked while heating the solution of xylenes (even in the presence of large amounts of BHT) resulting in an insoluble gel. NMR analysis revealed the presence of the expected functional group in the expected content in the hydrogenated polymers (see SI), suggesting the reaction conditions are compatible with these functional groups. The clean and well-defined <sup>13</sup>C NMR spectra further support the regio-regular structure in the hydrogenated polymers as well as in their unsaturated precursors. With the exception of P7 and P14, SEC in

CHCl<sub>3</sub> versus polystyrene standard showed slight increase of molar mass and comparable dispersity for all hydrogenated polymers. Hydrogenated polymers of P7 and P14 (PH7 and PH14, respectively) exhibited a large decrease in apparent molar mass and much broader dispersity compared to the unsaturated precursors. Considering that no noticeable change of functional group was observed in NMR spectra, we assume that the change of molar mass and dispersity may be due solely to conformational changes (i.e., hydrodynamic radius) of the hydrogenated polymers in CHCl<sub>3</sub>. However, we cannot rule out some level of chain scission.

Table 2 summarizes the thermal characterization using DSC of the hydrogenated polymers. PH7, PH8, PH13 and PH14, where the functional group is bulky, remained amorphous. The  $T_g$  of the saturated polymers range from -74 to 51 °C, and dependent on the functional group. Similarly to the unsaturated polymers, small substituents exhibit a much lower  $T_g$  than those with relatively bulky substituents. In addition to a glass transition, both PH2 and PH3 displayed well-defined melting transition transitions and PH15 showed a small but unambiguous melting peak, indicating that these polymers are semi-crystalline. PH3 with the larger substituent (PEG) showed a lower melting point than that in PH2 or PH15 with the smaller substituents (OMe and OCOMe, respectively). The only report of a 5-methoxy-COE polymerized via ROMP with a Ru-based catalyst does not report thermal properties for such polymer [69]. We previously reported that the saturated polymer of 3-methyl-COE (poly(3MeCOE)) exhibited a  $T_g$  at -59 °C, a  $T_m = 2 \text{ °C}$  and  $\Delta H_m = 30 \text{ J g}^{-1}$  [55]. When the  $T_m$  of poly(3MeCOE) is compared with that of PH2 and PH15, the more polar polymers (PH2 and PH15) show a higher  $T_m$  despite being larger groups; however, the  $\Delta H_m$  was lower in both cases. The more polar PH3, despite having the largest of all substituents, shows a  $T_m$  with equal enthalpy of melting to that of PH2. These results indicate that the polarity of the substituent and that of the polymer has a strong influence in the final thermal properties of the polymer. The polarity appears to have greater effect on crystallization than does the size; this could possibly be due to the polar functional group strengthening inter-chain interaction and thus favoring crystallization.

## Conclusions

In summary, we demonstrated an efficient pathway to rapidly expand the scope of 3-substituted COE bearing diverse polar functional groups (3FGCOEs). Many of these 3FGCOEs allow ROMP using the Grubbs Ru-based catalyst (G2) to afford functionalized polyalkenamers, which possess HT regio-regularity and *E*-stereo-regularity. Both



poly(3FGCOE) and the saturated poly(3FGCOE) exhibit thermal properties dependent on the size and polarity of the functional groups. This methodology, complementary to the ADMET approach, can be utilized to prepare PE derivatives with diverse polar side chains, including but not limited to those described in this study, which are difficult to be synthesized through radical or coordination copolymerization. Some examples demonstrated here further enable the incorporation of functional groups that are problematic with typical ROMP catalysts and conditions. For instance, PH7 can be properly treated to release free amine side or PH8 can be used to generate free aldehyde groups. It is envisioned that 3FGCOEs would be used not only to synthesize precision functionalized PE derivatives but also to participate in the ring-opening metathesis copolymerization with unfunctionalized cyclic olefins. These advances are a step forward to new graft copolymers [66, 70] and complex supramolecular structures with PE backbone.

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