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ARTICLE

Unsymmetrical Difunctionalization of Cyclooctadiene under Continuous Flow Conditions: Expanding the Scope of Ring Opening Metathesis Polymerization

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Xianwang Shen, [a,b] Honghong Gong,[a] Yang Zhou,[a] Yucheng Zhao,[a,b] Jun Lin,[*b] Mao Chen[*a]

Functionalized cyclooctenes (FCOEs) are important monomers in ring-opening metathesis polymerization (ROMP). Herein, a new library of disubstituted FCOEs bearing adjacent heteroatoms were synthesized and applied in ROMP. To address issues associated with the handling of reactive thienyl chloride intermediate, a two-step continuous flow method has been developed to prepare 5-thio-6-chlorocyclooctene compounds from abundant cyclooctadiene starting materials. These newly synthesized FCOE monomers were subsequently polymerized through ROMP, giving rise to a range of functionalized polymers with high molecular weights. Furthermore, we demonstrated that the thermal properties of these polymers could be fine-tuned by changing the functional groups in the FCOE monomers. We expect that this functionalization-polymerization strategy will enable the preparation of a range of polymeric materials with complex structures.

Introduction

The development of synthetic methods to access functionalized polymers is of considerable interest due to the interesting physical and chemical properties associated with these materials. As a result, extensive efforts have been made to accomplish this task by designing well-tailored monomers for different synthetic methods such as controlled radical polymerization[1] and ring-opening metathesis polymerization (ROMP).[2] Alternatively, a number of methods for the postsynthetic modification of polymers have also been developed.[3] Due to the robustness and functional group tolerance of ROMP, it has become one of the most powerful methods for accessing polymers bearing a wide range of functionalities,[4] thus enabling the development of materials for drug delivery,[5] liquids manipulation,[6] ion exchange[7] and others.[8] While this method is widely utilized, norbornene, cyclobutene and cyclooctadiene are most frequently used monomers.[4] A simple method that could provide cyclic olefins with various substituents is important for expanding the scope of functionalized polymers.

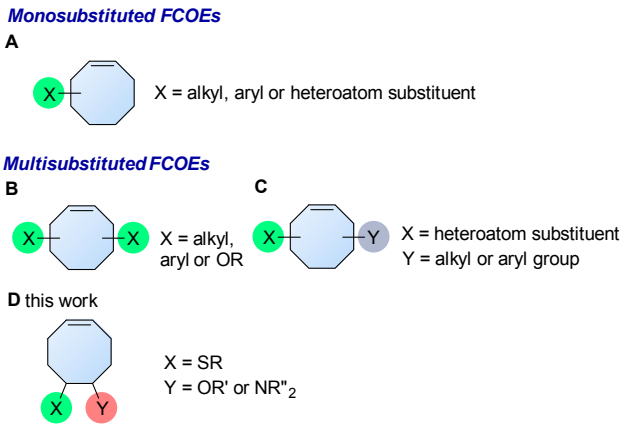


Fig. 1 The FCOE toolbox scope for the ROMP study.

FCOE derivatives are a class of the most widely used monomers for ROMP.[6, 8a-e, 9] Among many applications of poly(FCOE)s, [6, 8a-e, 9a-k] ROMP of FCOEs followed by hydrogenation yields linear polyolefins with well-defined chemical structures possessing a wide range of side chains.[9a-k] It represents an useful approach to high-precision functionalized polyolefins,[9a-k] which are otherwise difficult to synthesize.[10] To further explore the utility of ROMP, it is necessary to expand the scope of FCOEs. Thanks to the efforts devoted to catalyst development and monomer scope exploration, a variety of FCOEs have shown high reactivity in ROMP.[4, 7-8, 9a-k, 11] Among them, most examples are mono-

[a] X. Shen, Dr. H. Gong, Y. Zhao, Prof. Dr. M. Chen
State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science
Fudan University
Shanghai 200433, China
Email: chenmao@fudan.edu.cn
Homepage: http://chenmaofudan.wixsite.com/polymao
[b] X. Shen, Y. Zhao, Prof. Dr. J. Lin
Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry Education, School of Chemical Science and Technology
Yunnan University
Kunming, 650091, China

† Electronic Supplementary Information (ESI) available: General information concerning experimental procedures, characterization data including NMR, IR of isolated monomers and NMR, IR, GPC, DSC, TGA spectra of isolated polymers are available. See DOI: 10.1039/x0xx00000x

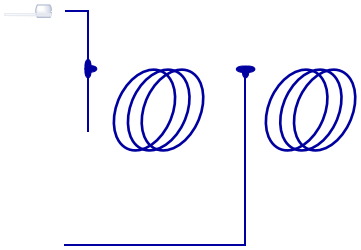
substituted compounds (Fig. 1A) prepared via C=C bond addition of cyclooctadienes (CODs),[7-8, 9a-e, 11] allyl C-H bond functionalization of cyclooctenes (COEs),[9f-j] or other methods.[9k]

In contrast to monosubstituted FCOEs, polysubstituted FCOEs are much less investigated for ROMP reactions.[9e, 12] Grubbs and coworkers reported the synthesis and ROMP of symmetrically disubstituted COEs connected with two adjacent hydroxyl groups and their derivatives (Fig. 1B).[12a, 12b] Hillmyer and coworkers reported the preparation and ROMP of an ester and a methyl/phenyl disubstituted COEs (Fig. 1C).[12c] Nuyken found that the polymerization of dicyano COEs is sluggish, while the monocyano COE polymerizes efficiently.[12d] However, the ROMP of FCOEs possessing different vicinal heteroatoms (Fig. 1D) has not been reported so far. The incorporation of these functional side chains could not only allow for the fine tuning of polymer properties, but also open up new opportunities to bring in orthogonal reactive sites, and is thus highly desirable.

In this regard, we have designed a two-step sequence of thienyl chloride formation/C=C bond addition to prepare FCOEs from *cis*,*cis*-1,5-COD (Fig. 1D: X = SR, Y = Cl). Since the chloride group is easily cleavable through the assistance of the adjacent thioether via neighboring group participation,[13] we envisioned that the 5-Cl,6-SR-COE would be a versatile intermediate to prepare FCOEs with different functionalities (Fig. 1D: X = SR^1, Y = OR^2/NR_2). Although the thienyl chloride (RSCl) species has been known for over half a century, the explosive nature[14] and unpleasant smell of these compounds somewhat limits their application. Flow processes are useful alternatives to traditional batch procedures.[15] Many examples have shown the possibility to safely handle hazardous intermediates under flow conditions.[16] Given our experience with this technique,[17] we anticipated that a flow approach would significantly enhance the practicality of olefin chlorothiolation processes using thienyl chloride by allowing for a safe and convenient handling of these reactive intermediates.

Results and discussion

We began our studies on the thienyl chloride intermediate formation/difunctionalization sequence with a setup depicted in Scheme 1A with *p*-toluenethiol **1a** as the model substrate. In the flow setup, a solution of **1a** in anhydrous dichloromethane (DCM) was mixed with SO_2Cl_2 in anhydrous DCM and introduced into a tubing reactor (R1) immersed in a cooling bath. After the arylthiol was completely converted as monitored with thin layer chromatography (TLC) analysis, R1 was assembled with the following setup of step II via a T-mixer, allowing the solution from R1 to combine with the COD (**3**) solution in-line. The resulted mixture was further delivered into the second tubing reactor (R2) submerged in another cooling bath to perform the direct difunctionalization of the C=C double bond. After reaction, the mixture was collected and directly analyzed without isolation of **4a**. Upon investigating a variety of reaction parameters, we determined that the synthesis of **4a** proceeded in a good yield with a 1/1.05/4 ratio of **1a**/**2**/**3**, and two reactors cooled at 0 °C and -20 °C respectively (Scheme 1B, entry 1). Notably, this two-step flow method only needed a residence time (t_R) of less than 4 min.[18] As shown in entries 2 to 7, changing the temperature of either reactors, or the molar ratio of three components resulted in lower yields of the target product **4a** (see Section II in the supporting information). In contrast, when this reaction sequence was performed under batch conditions, only 50% yield of **4a** was obtained in 2.5 h reaction time as detected by ^{1}H NMR analysis.



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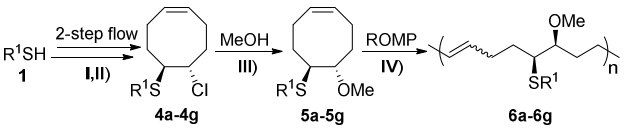
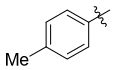
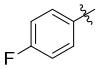
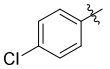
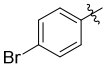
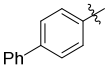
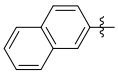
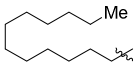
supporting our hypothesis of an vicinal SR group assisted substitution process.[13]

Table 1 Synthesis and ROMP of **5a**-**5g** [a]



entry	R^1	**5** yield (%) [b]	$[5]_0/[G2]$	**5** conv (%) [c]	**6** yield (%) [d]	$M_{n,calc}$ (kg/mol) [e]	$M_{n,GPC}$ (kg/mol) [f]	$Đ$ [f]
1		64 (**5a**)	500/1	>99	96 (**6a**)	131	148	1.71
2		68 (**5b**)	1000/1	>99	95 (**6b**)	266	291	1.49
3		55 (**5c**)	500/1	>99	93 (**6c**)	142	159	1.68
4		56 (**5d**)	400/1	>99	90 (**6d**)	131	106	1.68
5		64 (**5e**)	500/1	>99	91 (**6e**)	163	226	1.69
6		63 (**5f**)	500/1	>99	93 (**6f**)	149	201	1.73
7		70 (**5g**)	1000/1	36	31 (**6g**)	127	311	1.67

[a] Reaction conditions for I) to IV): I,II) **4** were synthesized using conditions as shown in Scheme 1B, entry 1; III) rt, 4 hours, anhydrous MeOH (10 eq. to **4**); IV) G2 carbene complex was used to initiate the ROMP, DCM, rt. [b] Isolated yields of three steps, calculated based on R^1SH. [c] Calculated based on the amount of recovered monomer by column chromatography. [d] Isolated yields were calculated based on monomers added in the ROMP. [e] Calculated based on conversions of FCOEs **5**. [f] Analyzed with GPC.

With the established methods for the preparation of **5a**, we turned our attention to synthesize FCOEs with different SR^1 substituents. To our delight, all R^1SH substrates (**1**) investigated in Table 1 underwent complete conversion into **5b**-**5g** in about 4 h reaction time (Table 1, step I to III). After three-step consecutive transformations, the resulting mixture was purified by silica gel column chromatography to afford FCOEs **5b**-**5g** in satisfactory yields (55-70%). Notably, since aryl halides (e.g. Cl, Br) are versatile functional groups in metal-catalysed cross-coupling reactions, the incorporation of such groups (**5c**, **5d**) would bring in reactivities orthogonal to the substituent on the COE backbone.[20] All FCOE monomers were characterized with nuclear magnetic resonance (NMR), infrared radiation (IR), and high-resolution mass spectroscopy (HRMS) analysis (Section III and Figure S3-S23), demonstrating the successful introduction of two adjacent heteroatom substituents of SR^1 and OMe into COE.

Moreover, to streamline the synthesis of FCOEs **5**, a three-step continuous-flow setup has been developed (Figure S2) using a pressurised heating system at 80 °C for step III. As exemplified with **5a**, facilitated by the efficient heat transfer under flow conditions, reaction time was reduced to 20 min, affording **5a** in 66% isolated yield.

The 5-SR^1,6-OMe-COE monomers **5a**-**5g** were polymerized with the second-generation Grubbs carbene complex (G2) in DCM at room temperature (step IV).[21] As illustrated in Table 1, when the arylthio group was substituted with an electron-donating group (Me, entry 1, **5a**), an electron-withdrawing group (F, entry 2，**5b**; Cl, entry 3, **5c**; Br, entry 4, **5d**), or a phenyl group (entry 5, **5e**), all monomers achieved full conversions upon G2-catalyzed ROMP, affording a variety of functionalized polymers in high yields (**6a**-**6f**: 90-96% yields) via isolation by a three-time precipitation from methanol. Similar to Ru-promoted ROMP of alkylthio mono-substituted COEs reported by Noels and coworkers,[11d] when the 5-$n$$C_{12}H_{25}$S,6-MeO-COE (**5g**, entry 7) was used, a decreased polymerizing reactivity was observed, providing **6g** ($M_{n,GPC}$ = 311 kg/mol, M_w/M_n = 1.67) with 36% monomer conversion in 48 h reaction time, which is probably due to the increased coordinating effect of an alkylthio group to the metal center compared with an arylthiol group. For all examples (**5a**-**5g**) investigated in Table 1, high molecular weight polymers ($M_{n,GPC}$ = 106-311 kg/mol, $Đ$ = 1.49-1.73) were obtained, further confirming the reliability of the ROMP of these new FCOEs (Section IV and Figure S24-S58). Notably, polymers **6a**-**6g** have the same chemical component with butadiene/vinyl ether/vinyl thioether terpolymers possessing a 1/1/1 molar ratio for each monomer, representing a novel group of functionalized polyolefins.

While substituting a chloro group on substrates **4** with a methoxy group is efficient, and FCOEs **5** were successfully polymerized. We further focused on expanding the ROMP substrate scope by replacing the Cl group with other functionalities.

A solution containing COE **4** freshly prepared via a flow process was concentrated and treated with silica gel chromatography using 0-2% (v/v) EtOAc in petroleum ether as an eluent. During the column chromatography process, **4a** underwent a full hydrolysis within 30 min, resulting in a cyclic olefin **7a** with a hydroxy handle. Upon reacting with different electrophiles (step IV), the hydroxy handle was readily connected to a *t*-butyldimethylsilane (TBS, **7b**, **7c**), a benzyl (Bn, **7d**), or an acetyl (MeCO, **7e**) group. Additionally, the chloro group was also converted to *N*-heteroatom containing substituents by simply reacting with nucleophiles (step V, eg. morpholine, **7f**). Although 3-4 steps were employed, compounds **7a** to **7f** were isolated in good overall yields, and these compounds were characterized with NMR, IR and HRMS analysis (Section V and Figure S59-S82). To further identify the FCOE structure, **7f** was assigned by X-ray crystallography (Table 2, bottom left). While the C=C double bond keeps *cis* configuration, the SAr group and the morpholine group are

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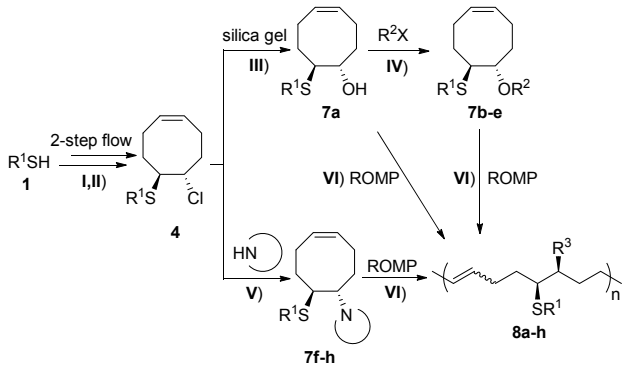
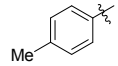
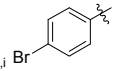
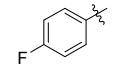
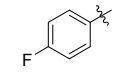
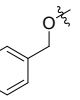
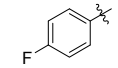
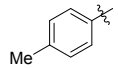
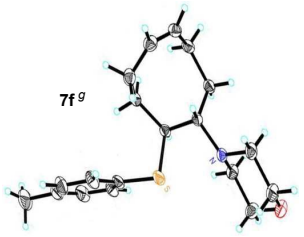
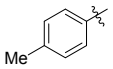
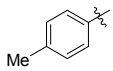
trans to each other. It is consistent with the vicinal SR group assisted substitution process, which could experience a thiiranium ion intermediate.[13a-d]

Table 2 Synthesis and ROMP of **7a**-**7h** [a]



entry	R^1	R^3	**7** yield (%) [b]	**7** conv (%) [c]	**8** yield (%) [d]	$M_{n,calc}$ (kg/mol) [e]	$M_{n,GPC}$ (kg/mol) [f]	$Đ$ [f]
1			67 (**7a**)	41	20 (**8a**)	51	80	1.66
2[g]				>99	90 (**8a'**)	6.2	6.8	1.65
3[h]			63 (**7b**)	>99	81 (**8b**)	85	109	1.71
4[h,i]			(**7b**)	>99	82 (**8b'**)	85	106	1.62
5			65 (**7c**)	>99	78 (**8c**)	183	160	1.76
6			62 (**7d**)	65	45 (**8d**)	111	71	1.57
7			54 (**7e**)	90	77 (**8e**)	125	104	1.58
8			59 (**7f**)	92	82 (**8f**)	146	193	1.78



R^1	R^3		
	N_3	(**7g**)	<5 % conv
		(**7h**)	<5 % conv

[a] Reaction conditions for I) to IV): I,II) **4** were synthesized using the optimized conditions as shown in Scheme 1B, entry 1; III) silica gel; IV) **7b** and **7c**: TBSCl, imidazole, DMAP, DCM, 0 °C to rt; **7d**: BnBr, NaH, 0 °C to rt; **7e**: AcOH, DCC, DMAP, DCM, 0 °C to rt; V) **7f**: morpholine, rt; **7g** $N(n\text{Bu})_4N_3$, rt; **7h**: imidazole, rt; VI) G2 was used to initiate the ROMP, [M]/[G2] = 500/1, room temperature. [b] Isolated yields of three steps (**7a**, **7f**) or four steps (**7b**-**7e**), calculated based on R^1SH. [c] Calculated based on the amount of recovered monomer by column chromatography. [d] Isolated yields were calculated based on monomers added in the ROMP. [e] Calculated based on conversions of **7**. [f] Analyzed with GPC. [g] X-ray structure of **7f**. [g] [M]/[G2] = 20/1. [h] [M]/[G2] = 200/1. [i] reaction temperature = 45 °C.

The new synthesized FCOE monomers (**7a**-**7h**) were next polymerized in the presence of G2 at room temperature (Table 2, step VI).[22] When FCOE **7a** with an unprotected hydroxy group was employed in a [**7a**]/[G2] ratio of 500/1, less than 50% conversion was achieved in 48 h reaction time, providing **8a** in 20% isolated yield ($M_{n,GPC}$ = 80 kDa/mol, entry 1). Although decreasing the monomer/G2 ratio to 20/1 led to a complete monomer conversion within 24 h, **8a'** with a much lower $M_{n,GPC}$ of 6.8 kDa was provided (entry 2) with a $Đ$ value similar to **8a** (for **8a**, $Đ$ = 1.66, for **8a'**, $Đ$ = 1.65). We hypothesized that the improved monomer conversion was due to less transition-metal was poisoned by increasing the G2/monomer ratio. When the reaction temperature was increased from room temperature to 45 °C, poly(FCOE)s was generated with similar M_n and slightly improved control over the molecular weight distributions (entry 3, M_n = 109 kDa, $Đ$ = 1.71 *vs* entry 4, M_n = 106 kDa, $Đ$ = 1.62). When the third-generation of Grubbs carbene complex (G3) was used to initiate the ROMP of **7b** ([**7b**]/[G3] = 200/1) at room temperature, the corresponding polymer was produced with $Đ$ = 1.65, M_n = 94 kDa at >99% conversion.

To produce poly(FOE)s with high molecular weights, a monomer/G2 ratio of 500/1 was used during the ROMP reaction of other FOCEs. When **7c**-**7e** were applied in the ROMP for 24 h, 45-78% isolated yields were obtained for polymers **8c**-**8e** with $M_{n,GPC}$ of 71-160 kDa (entries 5-7). When the SR^1 group is adjacent to a morpholine group instead, polymer **8f** was isolated in 82% yield ($M_{n,GPC}$ = 193 kg/mol, entry 8). Both NMR and IR analysis clearly demonstrate that both types of functional groups have been successfully incorporated of into polymers **8a**-**8f** (Section VI and Figure S83-S112). Replacing the morpholine group with an azide, or an imidazole group provided less than 5% monomer conversion, which is probably caused by the irreversible coordination of the functional group to the Ru-center as observed by Noels and coworkers.[11d] Notably, it represents the first ROMP of FCOEs possessing adjacent substituents of SR^1 and OR^2/NR_2 functionalities.

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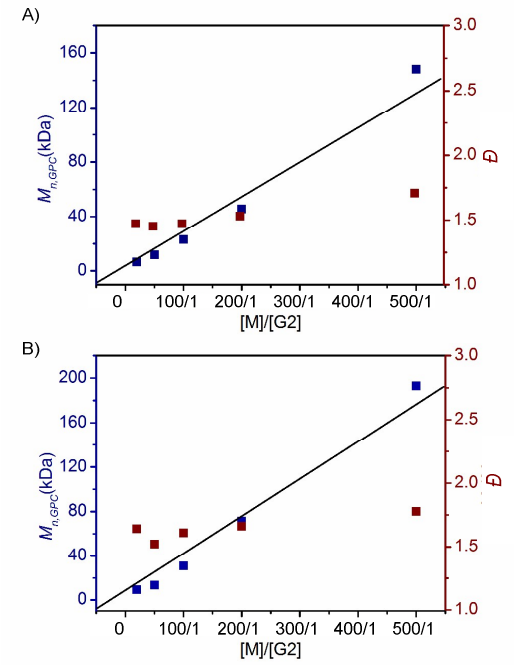

Fig. 2 ROMP of the FCOEs at different [M]/[G2] ratios (20/1, 50/1, 100/1, 200/1, 500/1) for 24 h in DCM. $M_{n,GPC}$ and $Đ$ values are analysed with GPC instrument. A) **5a** was used. B) **7f** was used.

To investigate the ROMP of difunctionalized FCOEs at different monomer/G2 ratios, **5a** and **7f** were employed. As shown in Fig. 2, for both monomers, when the [M]/[G2] ratios were increased from 20/1 to 500/1, poly(FCOE)s were produced with different $M_{n,GPC}$, while keeping $Đ$ values at a similar level ($Đ$ = 1.47-1.71 in Fig. 2A, $Đ$ = 1.52-1.78 in Fig. 2B). Notably, a linear increase of $M_{n,GPC}$ *vs* [M]/[G2] was observed for both examples, which demonstrated that these poly(FCOE)s can be generated at the desired M_n by choosing a proper [M]/[G2] ratio within the investigate range.[22]

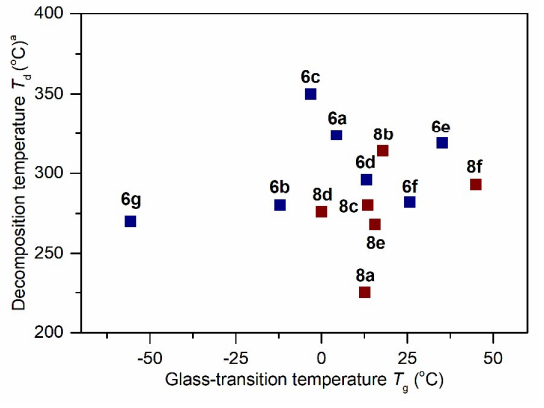

Fig. 3 Thermal properties of polymers. T_g and T_d were determined by DSC and TGA measurement respectively. All values were obtained under a nitrogen atmosphere at a scan rate of 10 °C/min. DSC experiments were conducted between -80 to 200 °C. Temperatures at 5% weight loss (T_d) are given.

Thermal properties for polymers **6a**-**6g** and **8a**-**8f** were analyzed with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Their summarized results of glass-transition temperature (T_g) and decomposition temperature (T_d) are shown in Fig. 3[23,24] (for DSC and TGA profiles, see Section IV and VI). From **6a** to **6g**, while keeping the same MeO group, changing alkylthio side chains to arylthio chains resulted in polymers possessing increased T_g values (**6g**: -56 °C *vs* **6a**-**6f**: -12 °C to 35 °C). Among **6b**-**6g**, increasing the functional group size on the aryl ring (from **6b** to **6e**: -12 °C, -3 °C, 13 °C, 35 °C respectively) or increasing the degree of conjugation (e.g., **6f**: 26 °C *vs* **6a**: 4 °C) leads to increased T_g values. These results are in an agreement with the sidechain influence on the glass transition temperature as observed by others.[9g, 24a, 24b] For polymers **8b**-**8e**, when the hydroxy side groups are protected with groups larger than methyl, the resulted T_g values are higher than **6b** (**8b**-**8e**: 0-18 °C *vs* **6b**: -12 °C). Replacing the MeO group with a morpholine group also leads to an increased glass-transition temperature (**8f**: 45 °C *vs* **6a**: 4 °C). The thermogravimetric analysis in Fig. 3 has shown that the thermal stabilities of these polymers are also dictated by connecting with different functional groups. Polymers **6a**-**6g** and **8a**-**8f** possess T_d values ranging from 225 °C to 350 °C at 5% weight loss.

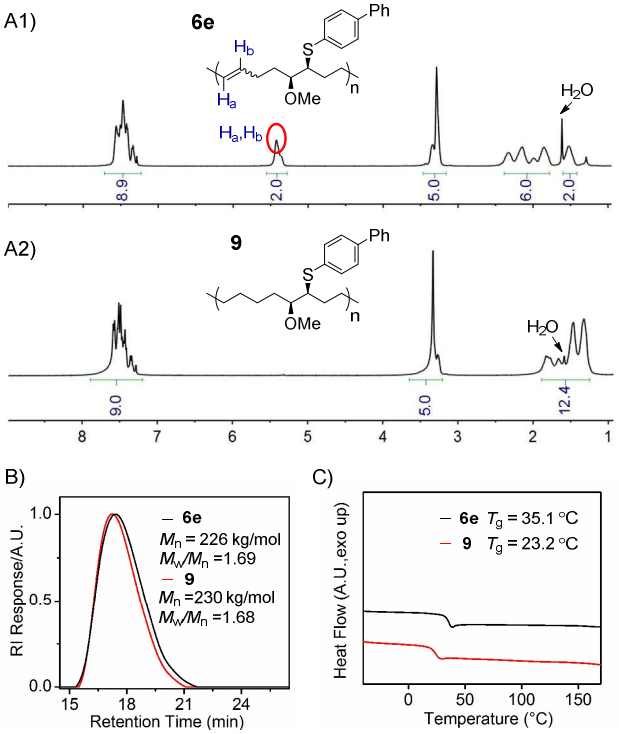

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Fig. 4 Characterization of polymers **6e** and **9**. A1) and A2) ^{1}H NMR; B) GPC traces, M_n and M_w/M_n values are analysed with GPC; C) DSC profiles obtained at a heating rate of 10 °C/min.

Finally, the hydrogenation of polymer **6e** was conducted to demonstrate the preparation of linear polyolefins possessing two different side chains on every seventh and eighth backbone carbons, from corresponding poly(FCOE)s. The hydrogenation reaction was performed using *p*-toluenesulfonylhydrazide as reductant and tri-*n*-hexylamine as base with catalytic amount of 2,6-di-*t*-butyl-4-methylphenol (BHT) in *o*-xylene solvent.[9c-k, 25] The reduced product **9** was obtained in 88% isolated yield via precipitation from methanol. As shown in the ^{1}H NMR spectra (Fig. 3A1 and 3A2; Section VIII and Figure S104-S108), during the hydrogenation process, signals at 5.5-5.3 ppm corresponding to H_a and H_b in polymer **6e** are completely disappeared in polymer **9**. As a result, an increase in the signal region corresponding to alkyl protons is clearly observed for polymer **9** (Fig. 4A1 *vs* 4A2, at 1.0-2.5 ppm region), indicating the successful hydrogenation transformation. GPC analysis of **6e** and **9** (Fig. 4B) have shown 1) similar $M_{n,GPC}$ and M_w/M_n values, 2) no new shoulder peak in the GPC traces, suggesting the polymer backbone remains intact during the reduction process. Moreover, hydrogenated polymer **9** has a lower T_g value than **6e** (Fig. 4C), indicating the formation of saturated backbone results in higher molecular mobility. Hillmyer[9f] and Tanaka[9g, 9h] have also reported the decrease in T_g values upon hydrogenating corresponding poly(FCOE)s.

Conclusions

In conclusion, the synthesis and ROMP of FCOEs bearing adjacent heteroatom groups have been successfully realized. Notably, the unstable thienyl chloride species has been generated and used under flow conditions for the first time, allowing for an efficient synthesis of 5-SR,6-Cl-COE compounds, which were employed as versatile intermediates for the preparation of a library of FCOEs. Moreover, ROMP of these new cyclic monomers has produced a library of polyolefins with different substituents connected with S, O or N heteroatoms in high molecular weights. It represents a useful avenue to synthesize polymers with high level of complexity. The investigation of thermal properties of these functionalized polymers has shown the effect of side chains on their glass-transition temperatures and thermal stabilities. Finally, this approach complements the useful strategy of producing high precision model polyolefins via ROMP, allowing the preparation of terpolymers of ethylene, vinyl thioether, and a variety of polar olefins including vinyl ethers, vinyl esters and vinyl amines, which are inaccessible via other methods

Experimental

Experimental procedure for the preparation of **5a** with the optimized reaction conditions: A Syringe was loaded with the solution of *p*-toluenethiol **1a** (1.0 M, flow rate = 250 μL/min) in anhydrous DCM, and fitted to a syringe pump. Another Syringe was loaded with the solution of **2** (1.05 M, flow rate = 250 μL/min) in anhydrous DCM, and fitted to a same syringe pump. The third syringe was loaded with the solution of COD (0.5 M, flow rate = 2.0 mL/min) in anhydrous DCM, and fitted to the second syringe pump. Following the setup as shown in Scheme 1, solutions of **1a** and **2** were mixed and reacted in tubing reactor R1 (volume = 1.0 mL, t_{R1} = 2.0 min) submerged in a cooling bath. When the reaction was complete, the resulting solution was mixed with the solution of COD and reacted in tubing reactor R2 (volume = 5 mL, t_{R2} = 2.0 min) submerged in another cooling bath. After reaction, the resulting mixture was passed through a back-pressure regulator (BPR, 20psi) before collection. After reaching steady state (waiting for 12 min), 1.0 mmol samples (10 mL reaction solution) were collected into an oven-dried vial equipped with a stir bar.

Anhydrous MeOH (10 mmol) were added into the vial via a syringe at room temperature. When the reaction was completed as monitored by TLC analysis, the mixture was treated with DCM (150 mL) and $NaHCO_3$ (20 mL) saturated aqueous solution. The separated organic layer was washed brine for two times (2×10 mL), dried over Na_2SO_4, concentrated under vacuum. The residue was purified by column chromatography (eluting with 0-2% EtOAc in petroleum ether) to afford **5a** in 64% isolated yields.

An oven-dried vial equipped a stir bar was charged with 1.0 mL solution of **5a** (0.5 M) in anhydrous DCM under N_2. The G2 compound solution (100μL, 8.5 mg/mL in degassed DCM) was added via a micro syringe into the vial at room temperature. After stirring for 24 h, the mixture was concentrated and was dropwisely added into MeOH with vigorously stirring. Solid compound was collected and re-dissolved in minimal amount of DCM. The precipitation procedure was repeated for three times in total to afford target product. The produced polymer was characterized with ^{1}H NMR, ^{13}C NMR, FT-IR, GPC, DSC and TGA analysis.

Conflicts of interest

There are no conflicts to declare.

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18. When the reaction time was extended, oligomerization of COD was observed.

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21. The asymmetry of the substituted FCOEs allowed for yielding polymers with regiorandom placement of the functional groups.
22. Increasing the [M]/[G2] ratio to 1000/1 (e.g., M = 7e) led to 52% conversion (Mn = 208 kDa, Đ = 1.79).
23. Although the molar mass of a polymer influences its glass-transition temperature, it only undergoes very slightly change on the Tg value when a high molecular weight range is reached as illustrated by the Flory-Fox equation.
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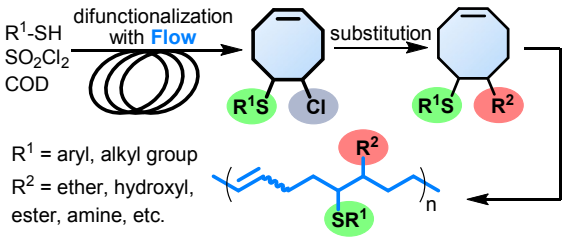

New cyclooctenes have been synthesized under continuous-flow conditions and applied in ring opening metathesis polymerization, providing highly functionalized materials.