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Synthesis of cationic cobaltocenophane monomers: Isomerization and ring-opening metathesis polymerization

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ABSTRACT

We report the synthesis of cyclic cobaltocenium olefins (cationic cobaltocenophane or *ansa*-cobaltocenium). This cyclic cobaltocenium is prepared by ring-closing metathesis (RCM) of diallyl cobaltocenium, which isomerizes into two different cobaltocenium dienes. The isomerization of the terminal alkene at higher temperature results in thermodynamically more stable internal alkene, which is supported by the computational calculation. RCM of these isomers produces two different cyclic cobaltocenium monomers [3]- and [4]-*ansa*-cobaltocenium, which are further evaluated as monomers for ring-opening metathesis polymerization (ROMP). The results indicate that both *ansa*-cobaltocenium monomers can be copolymerized with cyclooctene derivatives towards main-chain cobaltocenium-containing copolymers.

1. Introduction

Thirty years after the seminal work on ferrocene-containing polymers published by Manners and coworkers [1], metallopolymers containing organometallic moieties have attracted intensive interests owing to their various applications in electronics, catalyst, nanomaterial, biomedicine, hydrogel, and sensor [2–12]. Metallopolymers can be categorized based on topologies: linear, cyclic, hyperbranched, and dendritic [10,13–18]. Among metallopolymers, polymers with metallocenes placed at both side chain and main chain have been widely investigated [19–24].

In the early years, the incorporation of organometallic moieties into a polymer backbone was mostly achieved via polycondensation of difunctional metallocenes using a step-growth approach [25,26]. However, several limitations, such as high pure monomers, stoichiometry, high reaction temperature, and unexpected side reactions, make it difficult to synthesize high molecular weight polymers [27]. The discovery of ring-opening polymerization (ROP) of strained metallocenophanes by Manners and coworkers has opened up a new methodology to prepare high molecular weight main-chain metallocene polymers [1]. Since then, many research groups have intensively investigated the preparation of main-chain metallopolymers [27,28]. Ferrocene has been obviously the most focus of a variety of efforts using ring strained ferrocenophane.

However, cationic metallocenes have been substantially less investigated for the preparation of main-chain metallocene polymers [29–31]. Cobaltocenium, which is isoelectronic to 18-e ferrocene, has some unique properties [14]. In contrast to neutral ferrocene, cobaltocenium has a positive charge after the oxidation of the neutral 19-e cobaltocene. The air-stable and water-soluble cobaltocenium provides new possibilities for applications. As a class of cationic polyelectrolytes, cobaltocenium-containing polymers show potential in energy storage, self-assembly, and even antimicrobial applications [7,8,32–36]. The first main-chain cobaltocenium-containing polymers were prepared by Ito and Kenjo in 1968 as an ion-exchanger [37]. Sheats et al. reported the preparation of main-chain cobaltocenium polymers by condensation polymerization and transesterification [25,26]. However, these polymers by the aforementioned methods were actually revealed to be oligomers with very low degree of polymerization (DP = 3–6). Manners and coworkers also reported the preparation of main-chain cobaltocenium polymers by ring-opening polymerization of *ansa*-cobaltocenophane followed by oxidation [29]. They were able to achieve weight-average molecular weight of cationic polyelectrolytes as high as M_w = ~55,000 g/mol.

Main-chain cobaltocenium polymers have some of unique applications including mechanochemistry and bioconjugation. Manners et al., designed a strategy to impart main-chain cobaltocenium polymers with chirality by conjugation with DNA [30,31]. Along with others, we recently developed mechanochemistry of metallocenes by designing main-chain polymers [38–41]. Among them, <5% cobaltocenium has

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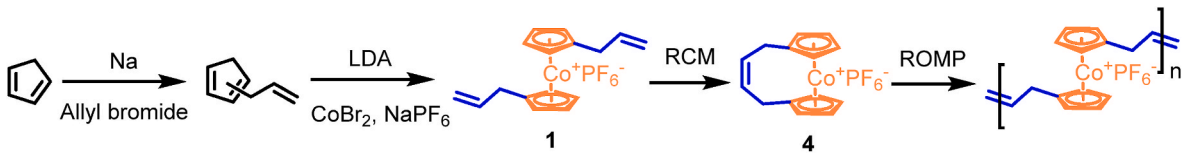
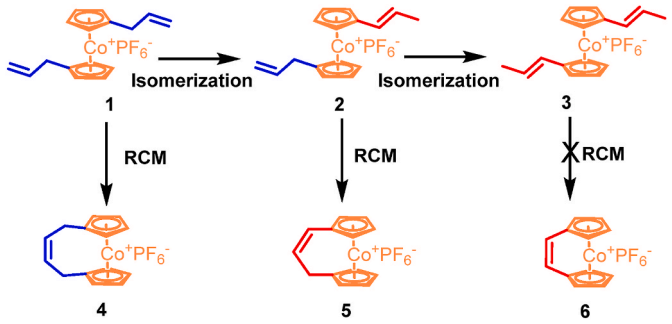


Scheme 1. Synthesis of diallyl cobaltocenium hexafluorophosphate, cyclic cobaltocenium monomer ([4]-*ansa* cobaltocenium) via RCM, and main-chain cobaltocenium-containing polymers via ROMP.



Scheme 2. Isomerization of diallyl cobaltocenium hexafluorophosphate and respective synthesis of cyclic cobaltocenium hexafluorophosphate via RCM.

been successfully integrated into the main chain of a polymer as an active mechanophore [42]. Beyond this very recent work, however, there have been no studies on the synthesis of cobaltocenium monomers and their integration into main-chain polymers.

Herein we report the synthesis of cationic cobaltocenophane [3]-*ansa* cobaltocenium and [4]-*ansa* cobaltocenium, and evaluation of their suitability as monomers for homopolymerization and copolymerization. The results are, in many aspects, surprisingly different from ferrocenophane. For the first time, isomerization of cobaltocenium dienes was observed, which led to different ring-closing products correlated with computational calculations.

2. Results and discussion

2.1. Synthesis of diallyl cobaltocenium

Although a few literatures reported the synthesis of cyclic cobaltocenophane or their salts [43–48], neither of the early work explored polymerization of these compounds as monomers until the work reported by Manners et al., in 2009 [29]. We sought to prepare monomers that could be in the scope for ring-opening metathesis polymerization (ROMP), which has risen as an attractive alternative to prepare metallopolymers [40,49–51]. For ROMP, an unsaturated alkene bridge is a key functional linkage for the design of cyclic metallocene monomers. To introduce an unsaturated bridge onto cobaltocenium, the substitution of cobaltocenium is a key hurdle to overcome. Synthesis of substituted cobaltocenium can be performed mainly in three ways: "flytrap" reactions between the bridged dicyclopentadienide and cobalt (II) dihalide [45], direct substitution of cobaltocenium [52,53], and modification of cyclopentadiene (Cp) ligand. Modification of Cp has advantages over the former methods due to the scalability and selectivity.

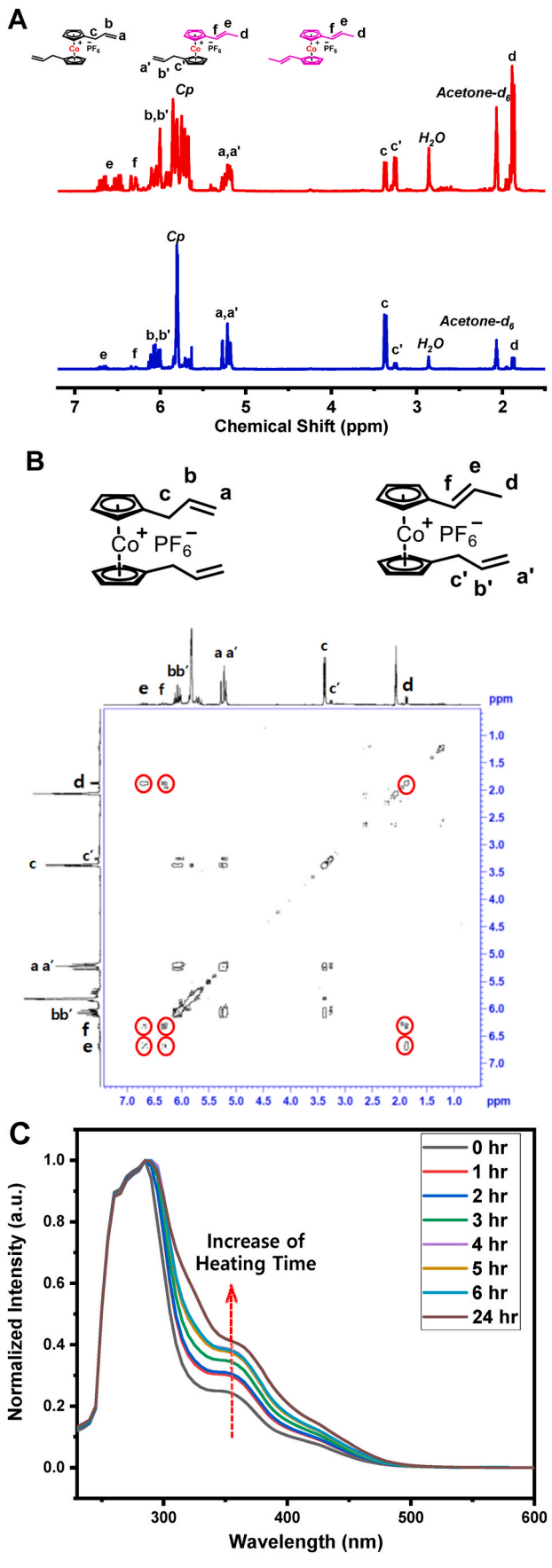
Modification of Cp was chosen as an approach to installing an olefin group onto Cp followed by constructing a sandwich structure, leading to disubstituted cobaltocenium (Scheme 1). The diallyl substituted cobaltocenium is an effective precursor for the preparation of 1,1′-bridged cobaltocenium, inspired by an early study reported by Hayashi and coworkers who demonstrated the synthesis of bridged metallocenes with Fe(II), Ru(II), Zr(IV), or Hf(IV) as metal centers [54]. We previously reported the synthesis of multi-substituted cobaltocenium derivatives from substituted Cp derivatives [32,36]. Building on the prior research, we introduced an allyl group onto Cp by nucleophilic addition. The allyl cyclopentadiene was treated with lithium diisopropylamide (LDA) to make allylcyclopentadienyl anion followed by the addition of $CoBr_2$, oxidation with sodium hexafluorophosphate, resulting in 1,1′-diallyl cobaltocenium hexafluorophosphate.

However, it was surprising to observe that the reaction between allyl Cp and $CoBr_2$ afforded two inseparable isomers: 1,1′-diallyl cobaltocenium **1** and 1-allyl-1'-(1-propenyl) cobaltocenium **2** with a molar ratio of 6.4:3.6 based on ^{1}H NMR (Figure S2). The ratio was calculated based on the integration of 3.25 and 3.37 ppm, which correspond to *–CH$_2$-* of allyl moiety of each isomer, respectively. It is noted that ~1.8 ppm is assigned to a terminal *–CH$_3$* of the isomerized allyl group in cobaltocenium. The mass spectrum analysis showed that only one corresponding mass value, 269 for $C_{16}H_{18}Co^+$, was observed (Figure S20-S21). We ascribed the cause of this isomerization to the heat during the work-up step of the reaction (Scheme 2). After the reaction between allyl Cp and $CoBr_2$, the reaction residue was dissolved in hot water and followed by oxidation. The isomerization of terminal alkenes to internal alkenes is thermodynamically favorable. Thus, applied heat would facilitate the formation of a more stable internal alkene.

As the isomerization of terminal alkenes to internal alkenes can be facilitated by heat [55], we tested the effect of temperature on 1, 1′-diallyl cobaltocenium hexafluorophosphate in aqueous solution at 4, 25, and 50 °C. When the solution was stirred at 4 °C, the isomerization was significantly suppressed, showing a decreased portion of internal alkene (Figure S3). The isomer ratio was changed from 6.4:3.6 to 8.0:2.0. On the other hand, the increase of temperature to 50 °C facilitated further isomerization into 1,1'-(di-(1-propenyl)) cobaltocenium **3** (Scheme 2). The solution has three isomers: **1**, **2**, and **3** with a molar ratio of 1.7:5.0:3.3 (Fig. 1A, Figure S5). We attributed the observed isomerization to the effect of π-conjugation through Cp and alkenes, which further stabilizes the internal alkene. When heating from 4 °C to 50 °C, the portion of more thermodynamically stable isomers increased from 20% to 70%. For better confirmation, a mixture of **1** and **2** isomers at 8.0:2.0 was characterized by 2D COSY ^{1}H NMR. As shown in Fig. 1B, the isomerized allyl-cobaltocenium shows a different correlation of the double bond. The protons of internal alkene (marked as **e** and **f**) show distinct interactions with the proton of the terminal methyl group. UV spectroscopy further confirmed that heating resulted in the increase of absorption intensity at the higher wavelength (Fig. 1C), indicating the formation of more internal double bonds. The internal double bonds (in isomers **2** and **3**) facilitate the formation of larger conjugated systems with Cp rings, which would reduce the energy gap of π-π*, thereby resulting in stronger absorption at the longer wavelength.

2.2. Synthesis of cationic cobaltocenophane

As previously stated, we expected that cationic cobaltocenophane with an alkene bridge could be utilized as a potential building block for ROMP. The above cobaltocenium diene mixtures were subject to ring-closing metathesis (RCM) with the aid of Grubbs catalysts. The RCM products further verified the isomerization. When a mixture of compounds **1** and **2** (8.0:2.0) was subjected to RCM, it was found that the resulting cyclic cationic cobaltocenophane olefins have two different *ansa*-cobaltocenium hexafluorophosphate: 1,1'-(2-buten-1,4-diyl)



(caption on next column)

Fig. 1. (A) ^{1}H NMR spectra of a mixture of compounds **1** and **2** at a molar ratio of 8.0:2.0 (bottom blue) and a mixture of compounds **1**, **2,** and **3** at a molar ratio of 1.7:5.0:3.3 (top red); **(B)** 2D COSY ^{1}H NMR spectrum of a mixture of compounds **1** and **2** at a molar ratio of 8.0:2.0; **(C)** UV–vis absorption spectra of the isomerized cobaltocenium at 50 °C. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

cobaltocenium **4** and 1,1'-(1-propen-1,3-diyl) cobaltocenium **5**. The mass-spectroscopic analysis confirmed the existence of two different molecular masses, 241 and 227 (Figure S22), corresponding perfectly to cyclic monomers **4** and **5**.^{1}H NMR revealed that the resulting cyclic cobaltocenium has a 7.0:3.0 ratio (Fig. 2), originating from the 8.0:2.0 ratio of **1** and **2**. The small discrepancy could be explained by that isomer **1** may be rearranged to isomer **2** before it forms the cycloalkene during RCM at 50 °C. The increased portion of compound **5** might be directly attributed to the increased portion of **2**. Next, the mixture of cobaltocenium isomers that contain compounds **1**, **2**, and **3** with a molar ratio of 1.7:5.0:3.3 was subject to RCM. All isomers were expected to form cyclic monomers with different lengths of alkene bridges. Interestingly, the result showed that only **4** and **5** were obtained, but not **6** (Fig. 2). It was ascribed to the very high strain of ring and the tilted structure of hypothetical **6**. The smaller ring size induces a highly tilted structure of cobaltocenium with high ring strain, leading to the unsuccessful synthesis of monomer **6**.

We further carried out atomistic computational analysis to compare the ring strain of three cyclic cobaltocenium monomers. The ring strain can be assessed by calculating their ring-opening energy (negative value of ring strain) using the density functional theory (DFT) [56,57]. As shown in Fig. 3A, compound **3** has the lowest energy, 11.2 kcal/mol lower than **1**. The ring strains of cyclic monomers were calculated based the reaction between cyclic cobaltocenium olefins and an ethylene molecule, producing corresponding ring-opened structures (Scheme S1). It was shown that the ring strain of monomer **6** is three times of monomer **4** (Fig. 3B). The difference of ring strains between seven-membered (**4**) and six-membered (**5**) cyclic cobaltocenium olefins is much smaller. It should be noted that this estimation is semi-quantitative. The high ring strain makes the synthesis of monomer **6** very challenging, explaining well the observed results. It should be mentioned that previously the ring strain of cyclic ferrocene olefins was also evaluated using a similar method [57].

2.3. *Synthesis of main-chain cobaltocenium polymers by ROMP*

Cyclic olefins of neutral metallocenes especially ferrocene have been widely reported as precursors for preparing main-chain polymers [35, 57–60]. We first attempted the synthesis of main-chain cobaltocenium-containing homopolymers by ROMP using the isomer mixtures of **4** and **5** (7.0:3.0 ratio). However, copolymerization of cyclic cobaltocenium olefin monomers was unsuccessful. No copolymers were recovered by precipitation, the solution mostly comprised of monomers (Figure S13). This was not entirely surprising. Previously, the work on ROMP of ferrocenophane indicated the balance of ring strain and monomer solubility [57]. Manners' unsuccessful anionic ring-opening polymerization of strained cobaltocenophane toward high molecular weight polymers indicated the complicated thermodynamics and possible kinetics of these cyclic cobaltocenium monomers [29]. Moreover, Kennemur and Moore reported reversible ROMP of cyclopentene and its derivatives due to its low ring strain [61,62].

We then sought to copolymerize the cyclic cobaltocenium olefin isomer mixtures of **4** and **5** (7.0:3.0 ratio) with cyclooctene derivatives by ROMP. Copolymers **P1**, **P2**, **P3** were prepared in a similar approach to previous reports [39,40,42]. Cyclooctene derivatives have comparable ring strain to that of compound **4** and are versatile to further functionalization [63]. In these studies, 1,2-epoxy-5-cyclooctene, 5-hydroxy-1-cyclooctene, and 5-methoxy-1-cyclooctene were employed

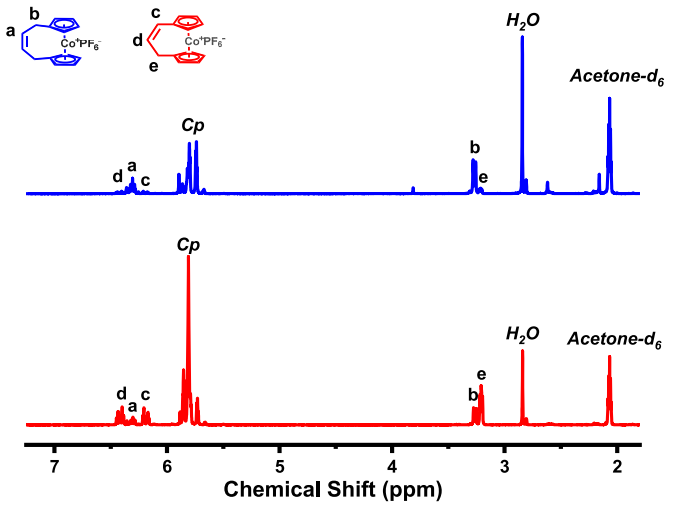


Fig. 2. ^{1}H NMR spectra of a mixture of compounds 4 and 5 at a molar ratio of 7.0:3.0 (top blue) and 2.2:7.8 (bottom red). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(Fig. 4A). It was revealed that cyclic cobaltocenium monomers were successfully incorporated in the main-chain copolymers. The incorporation of cobaltocenium into the polymer backbone was confirmed by ^{1}H NMR and ^{19}F NMR (Fig. 5). The labeling ratio, representing the inserted portion, was calculated by comparison of the characteristic cobaltocenium peaks (5.4–5.7 ppm for Cp, ~3.2 ppm for –CH_2–) and other characteristic peaks from the cyclooctene derivatives. The results are summarized in Table 1. Molecular weight was determined by Gel Permeation Chromatography (GPC) with tetrahydrofuran as an eluent (Fig. 4B). As shown in Table 1, the molecular weight (M_n) of **P3** with the highest fraction of cobaltocenium was relatively lower than **P1** and **P2**. Likely due to the electrostatic binding between the cobaltocenium moieties and GPC column, it is challenging to calibrate the peak signal from more cobaltocenium-labeled polymer **P3**. The incorporation of cobaltocenium in the main chain shows different efficiency. In the case of 1,2-epoxy-5-cyclooctene and 5-hydroxy-1-cyclooctene, the labeling ratio was lower than 5-methoxy-1-cyclooctene.

3. Conclusions

In summary, we synthesized 1,1′-dially cobaltocenium, which isomerizes to two notable isomers. Increasing isomerization at higher temperature revealed thermodynamically favored isomers with more stable internal alkene partially due to the effect of π-conjugation with Cp. These isomers afford cationic cobaltocenophane with different ring sizes by RCM. Together with thermodynamics, the ring strain energy dictates the formation of cyclic cobaltocenium. Although these cyclic cobaltocenium olefins were not able to homopolymerize, they were utilized for making main-chain cobaltocenium-containing copolymers with cyclooctene derivatives via ROMP. This study reveals the limitation and opportunities of ring-strained *ansa*-cobaltocenium monomers in organometallic chemistry and metallopolymers.

CRediT authorship contribution statement

Yujin Cha: Conceptualization, Methodology, Investigation, Writing – original draft. **JiHyeon Hwang:** Formal analysis, Visualization. **Luis Ramos:** Formal analysis. **Huina Lin:** Formal analysis. **Tianyu Zhu:** Investigation. **Chuanbing Tang:** Conceptualization, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

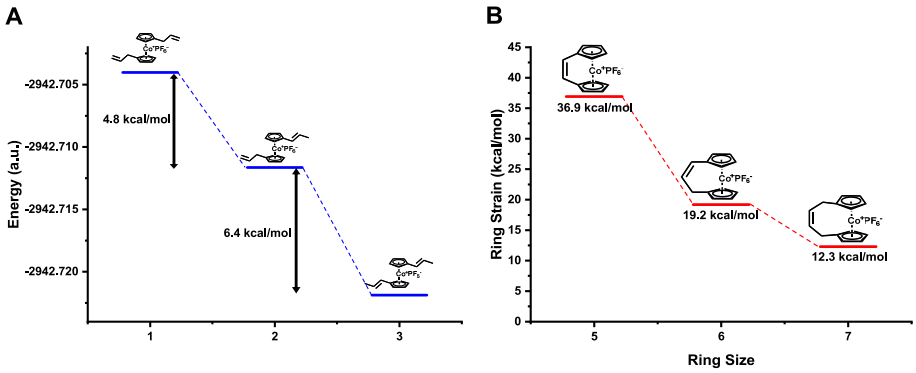


Fig. 3. (A) Optimized energy of cobaltocenium dienes 1, 2, and 3; (B) Ring strain energy of cationic cobaltocenophane 4, 5, and 6.

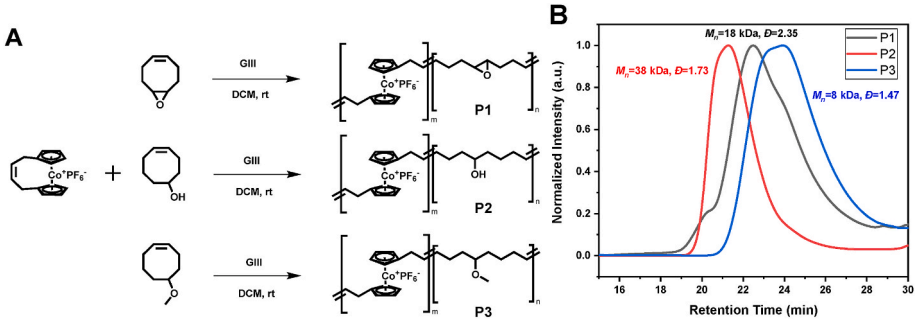


Fig. 4. (A) Synthesis of main-chain cobaltocenium-containing copolymers via ROMP; (B) GPC traces of copolymers.

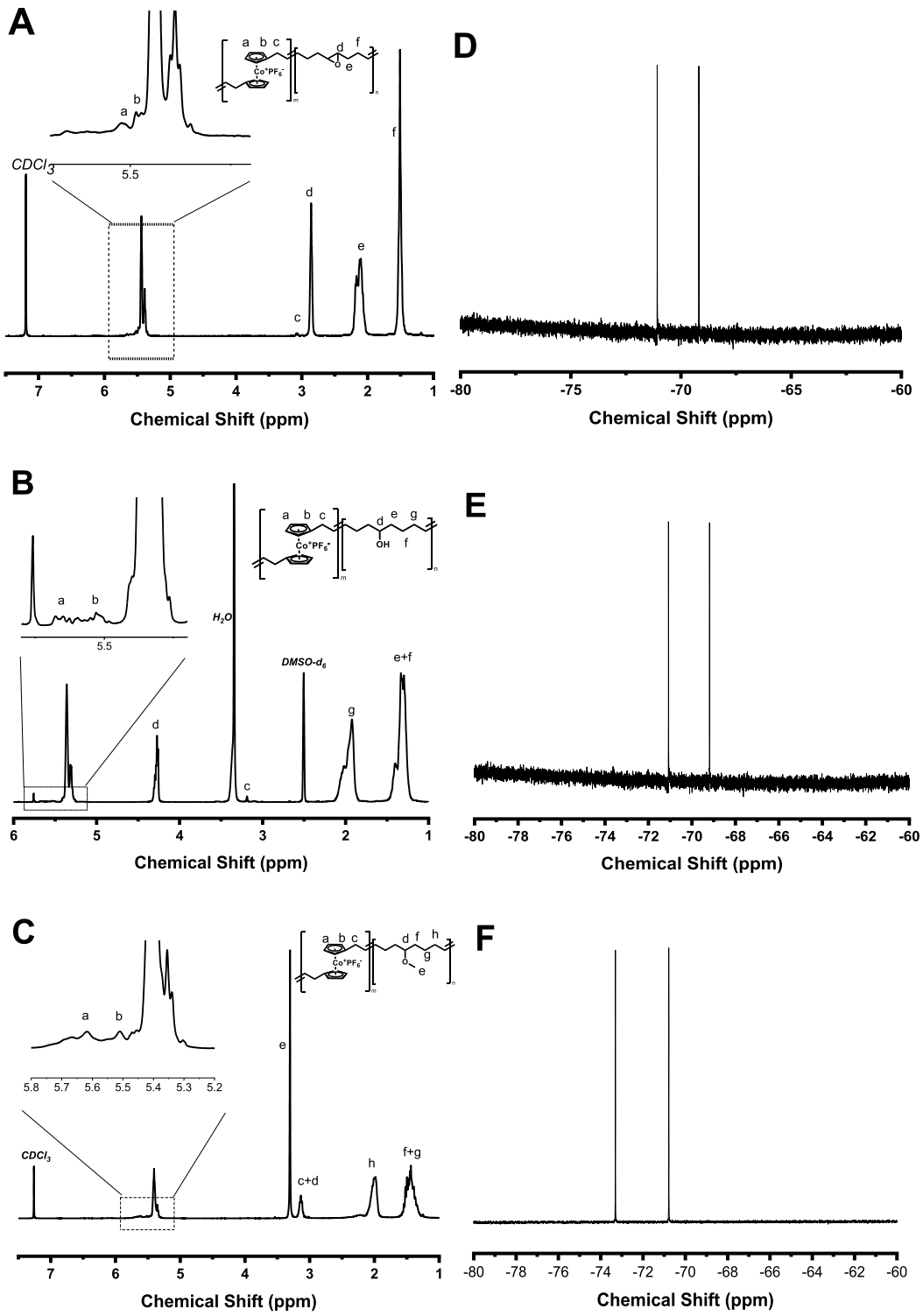


Fig. 5. ^{1}H NMR spectra of (A) **P1**, (B) **P2**, and (C) **P3**; ^{19}F NMR spectra of (D) **P1**, (E) **P2**, and (F) **P3**.

Table 1
Characterization of main-chain cobaltocenium-containing copolymers obtained by ROMP.

Polymers	Feed ratio	Labeling ratio	M_n	$Đ$
P1	5.9%	1.9%	17,600	2.35
P2	4.4%	1.3%	38,300	1.73
P3	5.9%	5.2%	8700	1.47

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.

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