ROMP Synthesis of Cobalticenium−Enamine Polyelectrolytes

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S *Supporting Information*

ABSTRACT: The synthesis of redox-robust polyelectrolyte polymers has long been investigated. Two simple methods of synthesis of well-defined cobalticenium-containing polymers are presented using both the norbornene ring-opening-metathesis polymerization (ROMP) method initiated by a third-generation Grubbs catalyst and the mild uncatalyzed hydroamination of the easily available ethynyl cobalticenium hexafluorophosphate salt. In the first strategy, a norbornene monomer functionalized with an enamine-cobalticenium group is polymerized by ROMP, whereas in the second one a norbornene derivative functionalized with a secondary amine group is polymerized by ROMP using the same catalyst followed by hydroamination of ethynyl cobalticenium. The structures of the polymers have been established by ^1H, ^{13}C NMR, and DOSY NMR, IR, UV−vis spectroscopy, mass spectrometry, elemental analysis, and cyclic voltammetry. The number of units in the polymers have been determined for various polymer lengths using end-group analysis by ^1H NMR using the diffusion coefficient determined by DOSY NMR and by cyclic voltammetry upon comparing the relative intensities of a monomer reference and the cobalticenium polymers.
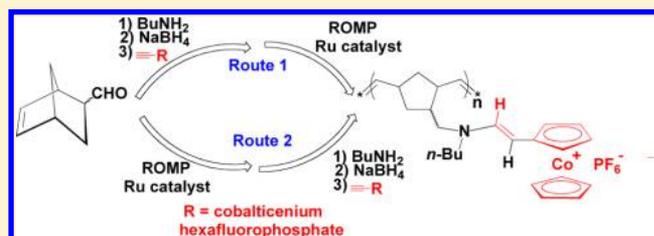
INTRODUCTION

Metallocene polymers[1] have been largely developed as a privileged area of metal-containing polymers,[2] in particular due to their robustness and redox properties.[3] Although by far the most extensively investigated metallocene polymers are ferrocene-containing polymers,[4] cobalticenium containing polymers[5−8] and dendrimers[9,10] have attracted attention for a long time. Cobalticenium salts are monocationic in the robust 18-electron configuration.[11] Cobalticenium polymers and dendrimers are polyelectrolytes, a field of interest in materials chemistry because of specific solubilities, physical properties, and applications, for instance, in batteries.[12]

The most common cobalticenium starting materials for the synthesis of cobalticenium polymers are cobalticenium carboxylic acids that are subjected to amide coupling upon reaction with polymeric[5,6] and dendritic amines.[9] Tang's group has also recently reported several articles on cobalticenium polymers based on such useful coupling reactions.[6] Manners' group[7] very recently published the remarkable, facile, and efficient ring-opening polymerization reaction of a cobaltocenophane monomer as an extension of the rich ferrocenophane ring-opening polymerization chemistry.[13] Another useful starting material is ethynylcobalticenium hexafluorophosphate, **1**,[14] that readily undergoes click reactions with terminal azides yielding 1,2,3-triazolyl cobalticenium derivatives (Scheme 1).[15] This click reaction has indeed been used to synthesize cobalticenium polyelectrolytes[8] and dendritic cobalticenium complexes.[10] Ethynyl cobalticenium hexafluorophosphate has also been reported to react with primary and secondary amines according to a facile uncatalyzed hydroamination reaction yielding *trans*-enamines under ambient or nearly ambient conditions (Scheme 1).[16]

Scheme 1. Two Useful Reactions of Ethynylcobalticenium Hexafluorophosphate, **1**[15,16]
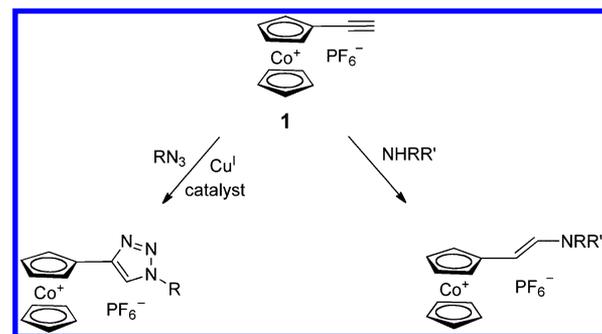
We now report two new mild and efficient routes to cobalticenium polymers using ethynylcobalticenium hydroamination reactions: (i) the functionalization of an amino derivative of a norbornene polymer (obtained by ROMP) with ethynyl cobalticenium and (ii) the ROMP polymerization of a cobalticenium derivative of a norbornene monomer bearing an amino group to which ethynyl cobalticenium has been connected using this hydroamination reaction.

RESULTS AND DISCUSSION

For the preparation of the organic and organometallic polymers, the ring-opening-metathesis polymerization (ROMP) reaction of norbornene derivatives has been selected.[17] This reaction is

known to be very efficient using the third-generation Grubbs catalyst **3** that is easily prepared using the commercial second-generation Grubbs catalyst **2** (eq 1).[18]
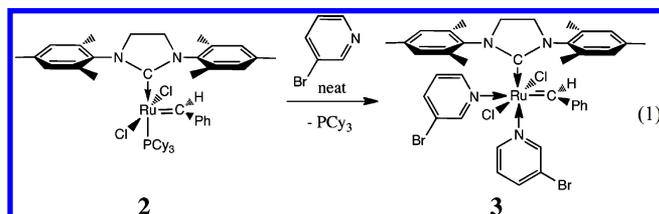
1. Hydroamination of 1 by a Norbornene-Functionalized Secondary Amine. Commercial 5-norbornene-2-carboxaldehyde (endo + exo) monomer was treated with excess butylamine at room temperature under N_2 for 16 h to give the imine product as a light yellow oil quantitatively. The reduction reaction of the imine was carried out in dry THF/CH_3OH (1:1) at 0 °C (Scheme 2) using the mixed powder $NaBH_4/PhCOOH$[19] to give the norbornene-substituted secondary amine as a light yellow oil in 99% yield. This secondary amine reacted stoichiometrically with **1** in CH_3CN at 35 °C for 16h under N_2 to give the cobalticenium−enamine monomer **4** as a deep red solid in 98% yield. This monomer has been fully characterized by ^1H, ^{13}C, ^{31}P NMR, IR, UV−vis, cyclic voltammogram, mass, and elemental analysis (Figures S1−S5, Supporting Information).

2. Ring-Opening-Metathesis Polymerization (ROMP) of Norbornene Functionalized with trans-Enamine Cobalticenium Hexafluorophosphate Using Grubbs' Third-Generation Catalyst. The cobalticenium−enamine-substituted norbornene monomer **4** has been polymerized in distilled CH_2Cl_2 in the presence of the catalyst **3** at room temperature in 30 min. Then excess ethyl vinyl ether was added to quench the reaction. After the solvent was removed under vacuum, the remaining deep red solid was washed with THF (3 × 10 mL) to remove the catalyst and the short-chain polymers. The use of different ratio of catalyst (0.01, 0.05, and 0.10 equiv) gives the polymers **5** in 90% yield, **9** in 98% yield, and **10** in 99% yield respectively as deep-red solids, characterized by ^1H, ^{13}C, and DOSY NMR, IR, UV−vis spectroscopy, MALDI−TOF mass spectrometry, cyclic voltammetry (CV), and elemental analysis (Figures S6−S8 and S14−S19).

3. ROMP of Norbornene Functionalized with a Secondary Amine. The cobalticenium−enamine polymer **8** was obtained by the uncatalyzed hydroamination reaction of **1** with the secondary amine-functionalized polymer **7** (Scheme 3). First 5-norbornene-2-carboxaldehyde (endo + exo) was polymerized in CH_2Cl_2 in the presence of catalyst **3** (0.03 equiv) at room temperature for 30 min. Then excess of ethyl vinyl ether was added to quench the reaction. The mixture was concentrated to 1 mL under vacuum, then excess of MeOH was added to precipitate the polymer **6** as a white solid that was characterized by ^1H and ^{13}C NMR, SEC (size exclusion chromatographie) and elemental analysis (Figures S9 and S10). The SEC of **6** shows a broad-ranged, ill-defined bimodal polymer due to the probably fast aggregation during the measurement (Figure S11). Polymer **6** was treated with excess butylamine at 35 °C to give the imine polymer as a light-yellow oil quantitatively. Then this imine polymer was reduced in THF/CH_3OH (1:1) at 0 °C in the presence of a $NaBH_4/PhCOOH$ powdery mixture to give after work-up the secondary amine-substituted polymer **7** as a light yellow oil in 95% yield.[19] Polymer **7** was characterized by ^1H and ^{13}C NMR and elemental analysis (Figures S12 and S13).

4. Hydroamination of 1 with the Secondary Amine-Functionalized Polynorbornene Polymer 7. The secondary amine-functionalized polymer **7** was treated with a slight excess of **1** in $CH_2Cl_2:CH_3CN$ (1:1) providing the cobalticenium−enamine polymer **8** in 2 days in 97% yield, and **8** was fully characterized.

5. Characterization. *^1H NMR Spectra of the Monomer 4 and Polymer 5.* Figure 1 shows the compared ^1H NMR spectra of the cobalticenium−enamine monomer **4** (Figure 1A) and polymer **5** (Figure 1B) in CD_3COCD_3. For the monomer **4**, the typical two protons on the C=C bond on the norbornene were found in the area of 6.08−6.28 ppm. The splitting of all the peaks is caused by the mixture of endo and exo structures. The two protons of the C=C bond between the amino and the cobalticenium were found in the area of 4.72−4.78 and 7.16−7.28 ppm, respectively showing the trans-enamine−cobalticenium structure. After polymerization in the presence of catalyst **3**, these two protons of the C=C bond on the norbornene structure appeared in the region of 5.37 ppm that was merged with that of the substituted Cp ligand of cobalticenium. All the peaks are broad as reported in the literature for the ROMP polymers and each peak was well assigned for the polymer. The

Scheme 2. ROMP Reaction of the Enamine−Cobalticenium Norbornene Yielding the Homopolymer 5
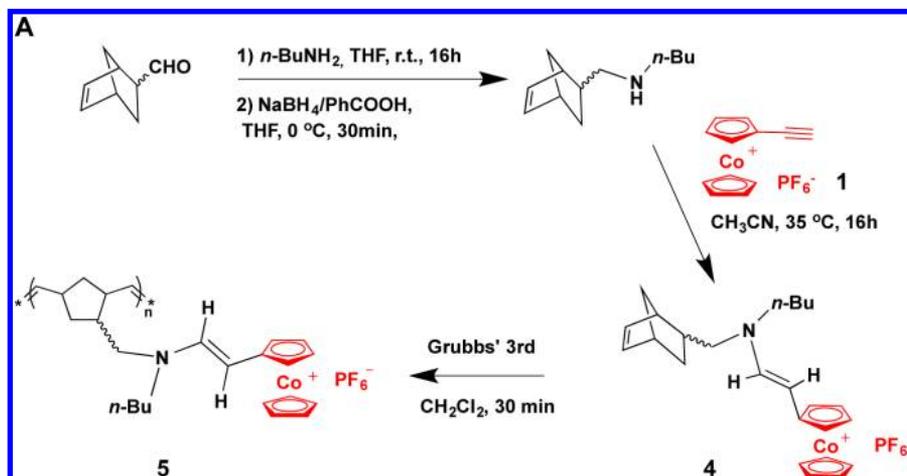
Scheme 3. Hydroamination of 1 by the Secondary Amine-Functionalized Norbornene Polymer 7, Yielding the Cobalticenium−Enamine-Functionalized Norbornene Polymer 8
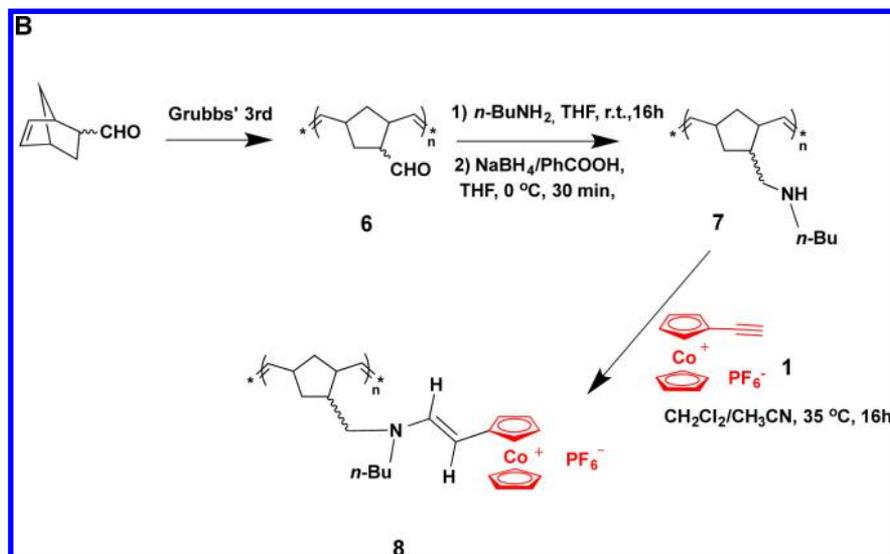
phenyl group of the catalyst is located at the end of the polymer chain after polymerization. This phenyl group in the polymer was found in the area of 7.20−7.40 ppm, which is convenient for the rough estimation of the molecular weight of the polycationic polymers by the end-group analysis (*vide infra*).

MALDI−TOF Mass Spectrometry. The ESI mass spectrum of the cationic monomer **4** ($C_{24}H_{31}CoN^+$) was simulated as 392.44 and found at 392.18 indicating the presence of the molecular ion. The MALDI−TOF spectrum of the polycationic cobalticenium polymer **5** showed well-defined individual peaks for polymer fragments that are separated by exactly 537.1 g/mol corresponding to the mass of one norbornene enamine-cobalticenium hexafluorophosphate unit **4** (Figure 2). The highest molecular peak observed was located at 10303.5 g/mol corresponding to a polymer fraction of 19 monomer units with terminal groups. Several other fragments are also observed due to the additions or losses of PF_6 anions and end groups. Thus, it was not possible to obtain the true molecular weight for the polymer **5** due to the limit of the MALDI−TOF technique, but the MALDI−TOF spectrum clearly shows the structure and motifs of **5**. For the polymers **8**, **9**, and **10**, the MALDI−TOF mass spectra also showed the splitting of each unit in the same area in accord with their structures.

UV−Vis Spectroscopy. The solution of **1** in acetone is yellow (Figure 3, left). On the other hand, all the cobalticenium enamine monomers and polymers are deep red in acetone (Figure 3, right). As shown in Figure 3, compound **1** (blue line) showed adsorptions at 350 and 420 nm in the UV−vis spectrum. The weak peak around 420 nm is assigned to the d−d* transition of cobalticenium.[20] The new absorption around 500 nm seems to be due to d−d* transition mixed with charge transfer from the ligand to the metal in the cobalticenium−enamine monomers and polymers **4**, **5**, and **8**.[16] The weak peak around 420 nm caused by the d−d* transition of cobalticenium is still on the shoulder of the main absorptions around 500 nm for all the cobalticenium−enamine monomers and polymers. The polymers **9** and **10** showed identical adsorptions under the UV−vis with the polymer **5** as expected.

Cyclic Voltammetry (CV) and Multielectron-Transfer Process in the Polymers. The redox processes of cobalticenium salts have been thoroughly studied by cyclic voltammetry and

other electrochemical techniques, in particular by Geiger's group.[21] It is well-known that the single-electron reduction of cobalticenium salts gives stable cobaltocene and the second single-electron reduction gives unstable cobaltocene anion. Such studies have been extended to polymers and the cyclic voltammograms have been recorded in this work for all the cobalticenium−enamine monomer and polymers. For example, the cyclic voltammogram of polymer **5** has been recorded at 20 °C with decamethylferrocene, $[Fe(\eta^5\text{-}C_5Me_5)_2]$, $\{(\eta^5\text{-}C_5Me_5) = Cp^*)\}$ as the internal reference in DMF in order to cover the largest possible electroactivity.[22] It shows two redox waves coresponding to the two redox states of the cobalt center. The redox process of cobalticenium does not clearly appear as fully chemically and electrochemically reversible, because it is marred by some adsorption (*vide infra*), but some data have been extracted and gathered in Table 1. For the $Co^{III/II}$ wave $E_{1/2} = -1.04$ V, and for the $Co^{II/I}$ wave $E_{1/2} = -2.02$ V vs $FeCp^*_2$ (Figure 4). For the polymer **5**, the first redox wave ($Co^{III/II}$) is slightly broadened compared to a standard single-electron wave. It is probable that some adsorption and electrostatic interactions slightly differentiate the multiple single electron-transfer steps corresponding to the $Co^{III/II}$ redox, whereas in the second electron-transfer ($Co^{II/I}$) for which the starting polymer does not contain cationic species this phenomenon does not appear. The CV of the monomer **4** includes a partly chemically reversible oxidation of the amine group to somewhat unstable aminium at 1.04 V and two reversible waves for the two redox states of cobalt under identical electrode potentials with the polymer **5**. On the other hand, both the monomer **4** and polymer **5** show large differences in electrode potentials compared to the starting complex **1** under identical conditions ($Co^{III/II}$ wave, $E_{1/2} = -0.70$ V; $Co^{II/I}$ wave, $E_{1/2} = -1.63$ V vs $FeCp^*_2$) (Table 1).

Molecular Weights. It was challenging to observe a GPC signal for the cobalticenium-containing polymers due to the strong electrostatic interaction between the cationic cobalticenium moieties and the stationary phase of microstyragel columns. It was not possible to determine the precise molecular weight by MALDI−TOF spectrometry due to the limit of this technique, although the splitting of each unit was found for all the cobalticenium polymers in this work (Scheme 1). The end-group analysis by ^{1}H NMR allows the approximate determination of the
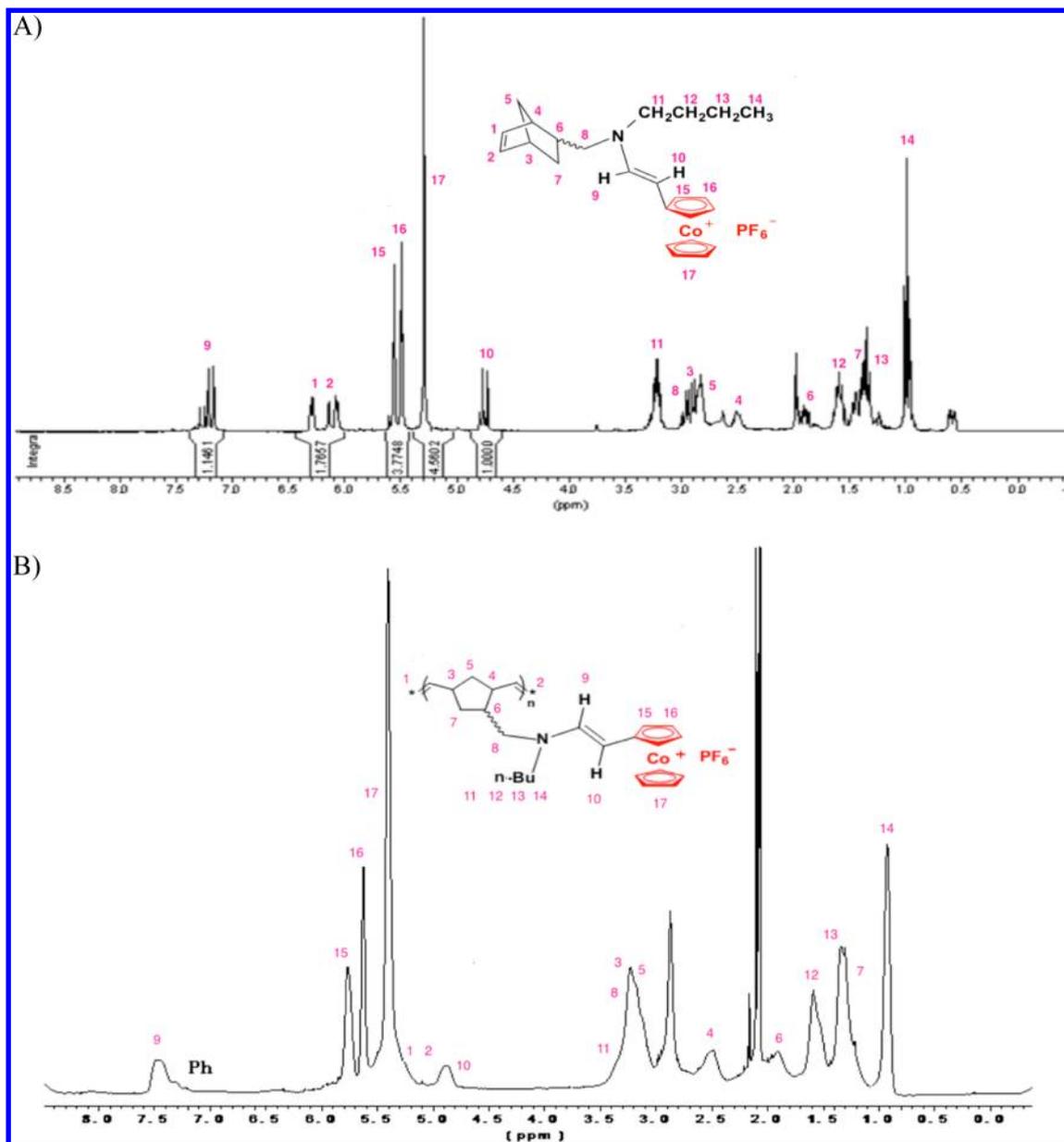
Figure 1. ^{1}H NMR spectra of the cobalticenium−enamine monomer **4** (A) and homopolymer **5** in CD$_3$COCD$_3$ (B).

molecular weight of the polymers obtained by ROMP. For example, the molecular weight of polymer **5** determined from end-group analysis is $M_n = 44750$ g/mol which corresponds to 83 units (Table 2). The objective of DOSY (diffusion-ordered spectroscopy) NMR experiments was thus double: measuring the diffusion coefficients of the molecules in solution and obtaining a DOSY spectrum that reflects the purity of the polymer. The DOSY NMR of the homopolymer **5** obtained in CD$_3$COCD$_3$ gives the diffusion coefficient as 9.1×10^{-11} m^2/s using eq 2:

$$D_p/D_m = (M_m/M_p)^{0.55} \qquad (2)$$

using the known diffusion coefficients of the monomer (D_m) and the polymer (D_p). The molecular weight of **5** is $M_n = 47783$ g/mol which corresponds to a number of monomer units n_p in the polymer approximatively equal to 89, i.e., slightly higher than the result obtained by end-group analysis using the ^{1}H NMR spectrum. Since the reduction of each redox moiety corresponds

to a one-electron process (Co$^{III/II}$), the value of n_p is then estimated by employing the Bard−Anson equation, 3,[23] previously derived for conventional polarography:

$$n_p = (i_{dp}/C_p)/(i_{dm}/C_m)(M_p/M_m)^{0.275} \qquad (3)$$

Using this eq 3, comparison between the intensities (i) of the CV wave of the internal reference [FeCp*$_2$] and the polymer provides a good estimation of the number of electrons n_p involved in the Co$^{III/II}$ redox process of the polymer using the known concentrations (c) and molecular weights (M) obtained from eq 2. Measurement of the ratio between the intensities of the decamethylferrocene reference wave and the first wave of the polymer led to the result $n_p = 99$ electrons for the polyelectrolyte **5**, which is slightly higher than the experimental values of 83 and 89 derived by the end-group analysis and the DOSY measurements, respectively. It is assumed that some adsorption is responsible for enhancing the n_p value determined with eq 3, thus the actual value is better represented by the average of the two
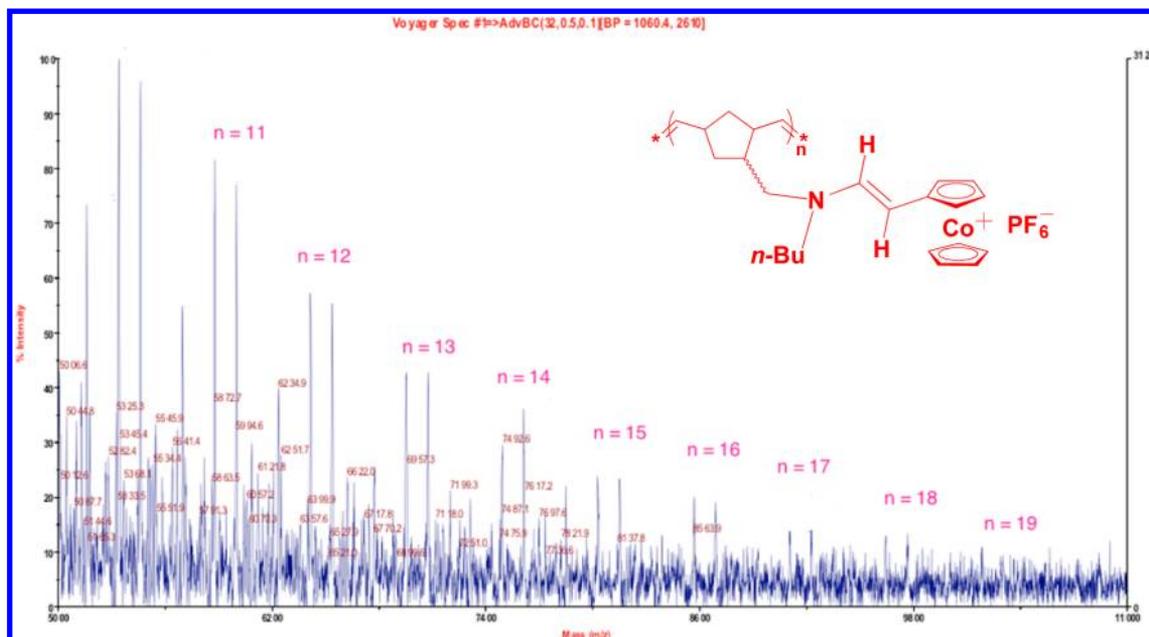
Figure 2. MALDI−TOF spectrum of polymer **5**.
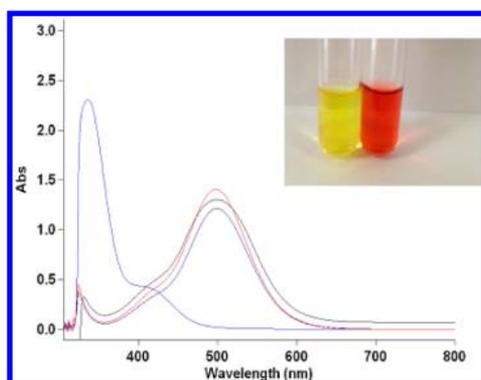
Figure 3. Compared UV−vis spectra of **1** (blue line), cobalticenium−enamine monomer **4** (red line), cobalticenium−enamine polymer **5** (black line) and cobalticenium−enamine polymer **8** (violet line) in acetone. The inset photograph shows the color of **1** (left) and the cobalticenium−enamine norbornene polymers **5** (right) in acetone.

Figure 4. CV of polymer **5** (2 mM) obtained at a Pt electrode at 20 °C in DMF. Supporting electrolyte: $[n\text{-Bu}_4\text{N}][\text{PF}_6]$. Scan rate: 0.2 V/s. Top: Reference and Co$^{\text{III/II}}$ wave, $E_{1/2} = -1.04$ V ($\Delta E_p = 40$ mV) vs $[\text{FeCp*}_2]^{0/+}$ (Cp* = η^5-C$_5$Me$_5$). Bottom: Co$^{\text{III/II}}$ wave, $E_{1/2} = -1.04$ V ($\Delta E_p = 40$ mV); Co$^{\text{II/I}}$ wave, $E_{1/2} = -2.02$ V ($\Delta E_p = 40$ mV).

Table 1. Compared $E_{1/2}$ Values for the Cyclic Voltammograms of 1, Monomer 4, and Polymer 5[a]

compound	$E'_{1/2}$ (V)	$\Delta E'$ (mV) $(E'_{\text{pa}} - E'_{\text{pc}})$	$E''_{1/2}$ (V)	$\Delta E''$ (mV) $(E''_{\text{pa}} - E''_{\text{pc}})$
1	−0.70	70	−1.63	80
4	−1.04	40	−2.02	70
5	−1.04	40	−2.02	40

[a]Cyclic voltammograms (2 mM) were obtained at a Pt electrode at 20 °C in DMF; scan rate = 0.2 V/s; supporting electrolyte = [n-Bu$_4$N][PF$_6$]; internal reference = $[\text{FeCp*}_2]^{0/+}$ (Cp* = η^5-C$_5$Me$_5$). The redox potential values for the polymer **8**, **9**, and **10** are identical to those of the polymer **5** under identical conditions.

Table 2. Sizes of the Polymers (Number of Molecular Units n_p) Obtained from the End-Group Analysis, DOSY NMR Data, and CV Experiments, Respectively

compound	D^a (diffusion coefficient) (± 0.1) m^2/s	n_p (from end group ^{1}H NMR analysis)[b]	n_p (from eq 2)[c] (DOSY NMR)	n_p (from eq 3)[d] (CV)
5	0.91×10^{-10}	83 ± 10	89 ± 10	99 ± 10
8	1.06×10^{-10}	60 ± 5	67 ± 5	72 ± 5
9	1.28×10^{-10}	44 ± 5	48 ± 5	50 ± 5
10	1.98×10^{-10}	18 ± 3	22 ± 3	25 ± 3

[a]DOSY NMR were measured in CD$_3$COCD$_3$ at 25 °C. [b]Values obtained by ^{1}H NMR in CD$_3$COCD$_3$ at 25 °C. [c]Values obtained using eq 2 with the diffusion coefficient obtained from DOSY experiments. [d]Values obtained from eq 3.

other methods for the determination of n_p. Identical measurements including the end-group analysis, DOSY NMR for the diffusion coefficient determination and the calculations of the number of electrons heterogeneously transferred in the CV process were also carried out for the polymer **8**, **9** and **10**, and the values obtained are gathered in Table 2.

■ **CONCLUDING REMARKS**

The facile, mild hydroamination of ethynylcobalticenium was shown to easily apply to the syntheses of cobalticenium polymers. It can be used either in the metalation of

polynorbornene polymers containing a secondary amine group and synthesized by ROMP using Grubb's third-generation ROMP catalyst or alternatively in the hydroamination using a secondary amine-functionalized norbornene derivative followed by ROMP using the same ruthenium catalyst. Both methods proceed easily in high yields with various polymer lengths and form facile and readily available routes to redox-robust polycobalticenium polyelectrolytes. It is remarkable that the three methods, end-group analysis, DOSY NMR and cyclic voltammetry give comparable results for the determination of the number of monomeric units in the polymers, although adsorption onto the Pt electrode becomes more significant as the polymer is larger, which provides data in slight excess by the cyclic-voltammetry method for large polymers. This study thus shows the compared reliability of these three methods at least for redox-active metallopolymers of such sizes.

■ EXPERIMENTAL SECTION

General Information. Reagent-grade THF, diethyl ether, and pentane were dried over Na foil and distilled from sodium benzophenone under nitrogen immediately prior to use. DCM was dried over calcium hydride and distilled under nitrogen prior to use. CH_3CN was dried over P_2O_5 and distilled under nitrogen prior to use. All other solvents and chemicals were used as received. ^1H NMR spectra were recorded at 25 °C with a Bruker AC (200, 300, or 600 MHz) spectrometer. The ^{13}C NMR spectra were obtained in the pulsed FT mode at 75 or 150 MHz with a Bruker AC 300 or 600 spectrometer. All the chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si for the ^1H and ^{13}C NMR spectra. ^{31}P stands for ^{31}P (^1H) in the data, with chemical shifts referenced to external H_3PO_4. The mass spectra were recorded using an Applied Biosystems Voyager-DE STR-MALDI−TOF spectrometer. The infrared spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. UV−vis spectra were measured with PerkinElmer Lambda 19 UV−vis spectrometer. Electrochemical measurements (CV) were recorded on a PAR 273 potentiostat under nitrogen atmosphere. Cyclic voltammo-grams were obtained at a Pt electrode at 20 °C in DMF; supporting electrolyte, $[n\text{-}Bu_4N][PF_6]$; reference, $[FeCp*_2]^{0/+}$ ($Cp* = \eta^5\text{-}C_5Me_5$). The elemental analyses were performed at the Center of Microanalyses of CNRS at Lyon Solaize (France). DOSY NMR measurements were performed at 25 °C with a Bruker AVANCE II 600 MHz spectrometer. They were performed using ^1H NMR pulsed-gradient experiment: the simulated spin−echo sequence which led to the measurement of the diffusion coefficient D. D is the slope of the straight line obtained when $\ln(I)$ is displayed against the gradient-pulse power's square according to the following equation: $\ln(I) = -\gamma^2 G^2 D\delta^2(\Delta - \delta/3)$, I is the relative intensity of a chosen resonance, γ is the proton gyromagnetic ratio, Δ is the intergradient delay (150 ms), δ is the gradient pulse duration (5 ms), and G is the gradient intensity. The diffusion constant of water (2.3×10^{-9} m^2/s) was used to calibrate the instrument. Size exclusion chromatography (SEC) of polymers were performed using a Malvern Viscotek TDA max at 30 °C with THF as eluent and PS standards were used for calibration.

Monomer 4. 5-Norbornene-2-carboxaldehyde (1.22 g, 10 mmol, 1 equiv) was dissolved in 10 mL of butylamine. The mixture was stirred at room temperature under N_2 for 16 h, the solvent was removed *in vacuo* to give the imine derivative as a light-yellow oil, dry THF/CH_3OH (1:1), 30 mL, was added, and the solution was stirred at 0 °C for 10 min. A mixed powder of $NaBH_4$ (1.89 g, 50 mmol, 5 equiv) and PhCOOH (6.10 g, 50 mmol, 5 equiv) was added portionwise into the solution at 0 °C, the mixture was stirred for another 30 min at 0 °C, the solvent was removed *in vacuo*, 30 mL of dry CH_2Cl_2 and 50 mL of saturated $NaHCO_3$ solution were added to the remaining white solid, and the mixture was stirred for 30 min. After separation, the organic phase was washed three times with distilled H_2O and dried with anhydrous Na_2SO_4, and the solvent was removed *in vacuo* to yield the secondary amine-substituted norbornene as a light-yellow oil (1.78 g, 99% yield). Then the norbornene-substituted secondary amine (35.8 mg, 0.2 mmol,

1 equiv) and **1** (71.6 mg, 0.2 mmol, 1 equiv) were dissolved in 10 mL of CH_3CN, the mixture was stirred at 35 °C for 16 h under N_2, the color changed from orange to deep red, and the solvent was removed *in vacuo* to give the enamine monomer **4** as a deep red solid (105.2 mg, yield = 98%). ^1H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 0.78 (m, 1H), 0.88 (t, 3H, CH_3/Bu), 1.34 (m, 5H), 1.61 (m, 2H), 1.88 (m, 1H), 2.66 (m, 1H), 2.90 (m, 2H), 3.01 (m, 1H), 3.35 (m, 2H, CH_2), 4.91−4.95 (d, 1H), 5.46 (5H/Cp), 5.68 (t, 2H, Cp/sub.), 5.82 (t, 2H, Cp/sub.), 6.08−6.28 (m, 2H/CH=CH), 7.46−7.51 (d, 1H), 2.05 (s, $(CD_3)_2CO$). ^{13}C NMR ($(CD_3)_2CO$, 75 MHz): 147.57 (CH=CH), 137.90 (CH=CH), 131.95 (CH=CH), 117.66 (CH=CH), 84.26 (Cp), 84.35 (C/norbornene), 82.67 (sub. Cp), 81.37 (sub. Cp), 73.13 (sub. Cp), 49.33,44.26, 42.25 (C/norbornene), 19.78 (CH_2/Bu), 13.20 (CH_3/Bu), 29.84, 206.26 $(CD_3)_2CO$. ^{31}P NMR (121 MHz, CD_3COCD_3), δ_{ppm}: −144.11 (m, PF_6). UV−vis: λ_{max1} = 320 nm; λ_{max2} = 420 nm; λ_{max3} = 500 nm ($\varepsilon = 1.15 \times 10^4$ L mol^{-1} cm^{-1}). Cyclic voltammogram was obtained at a Pt electrode at 20 °C in DMF: supporting electrolyte, $[n\text{-}Bu_4N][PF_6]$. ($i\text{-}Pr)_2NR$ wave: $E_{1/2}$ = 1.04 V (ΔE_p = 80 mV). $Co^{III/II}$ wave: $E_{1/2}$ = −1.04 V (ΔE_p = 40 mV). $Co^{II/I}$ wave: $E_{1/2}$ = −2.02 V (ΔE_p = 70 mV) vs $[FeCp*_2]^{0/+}$ ($Cp* = \eta^5\text{-}C_5Me_5$). ESI: calcd m/z for ($C_{24}H_{31}CoN^+$), 392.44; found, 392.18. Anal. Calcd for $C_{24}H_{31}CoNPF_6$: C, 53.64; H, 5.81; N, 2.61. Found: C, 53.76; H, 5.98; N, 2.44.

Polymer 5. The cobalticenium enamine-substituted norbornene monomer **4** (40 mg, 0.0745 mmol, 1 equiv) was dissolved in 4 mL of dry CH_2Cl_2, a solution of **3** (0.63 mg, 0.000745 mmol, 0.01 equiv) in 1 mL of CH_2Cl_2 was added to the mixture at room temperature under N_2, and the mixture was stirred at this temperature for 30 min. Then 2 mL of ethyl vinyl ether was added to quench the reaction, the solvent was removed *in vacuo*, and the remaining solid was washed three times with distilled THF. After filtration, the polymer was obtained as a deep red solid. ^1H NMR (300 MHz, $(CD_3)_2CO$), δ_{ppm}: 0.88 (m, 3H, CH_3/Bu), 1.34 (m, 5H), 1.61 (m, 1H), 1.88 (m, 1H), 2.45 (m, 1H), 2.66 (m, 1H), 2.90 (m, 2H), 3.35 (m, 2H, CH_2), 3.61 (m, 1H), 4.89 (m, 1H), 5.38 (5H/Cp), 5.38 (m, 2H/CH=CH), 5.60 (m, 2H, Cp/sub.), 5.73 (m, 2H, Cp/sub.), 7.40 (m, 1H), 2.05 (s, $(CD_3)_2CO$). ^{13}C NMR ($(CD_3)_2CO$, 150 MHz): 147.99 (CH=CH), 130.09−134.99 (CH=CH), 117.71 (CH=CH), 84.32 (Cp), 84.31 (sub. Cp), 81.34 (sub. Cp), 73.12 (sub. Cp), 41.13−37.09 (C/norbornene), 19.80 (CH_2/Bu), 13.36 (CH_3/Bu), 29.84, 206.26 $(CD_3)_2CO$. DOSY (CD_3COCD_3, 600 Hz): the coefficient diffusion $D = 9.1 \times 10^{-11}$ m^2/s. IR (KBr): 1606 cm^{-1} ($\nu_{C=C}$), 835 cm^{-1} (ν_{PF6}). UV−vis: λ_{max1} = 320 nm; λ_{max2} = 420 nm; λ_{max3} = 500 nm (for each nuit, $\varepsilon = 1.15 \times 10^4$ L mol^{-1} cm^{-1}). CV of **5** (2 mM) obtained at a Pt electrode at 20 °C in DMF; supporting electrolyte, $[n\text{-}Bu_4N][PF_6]$. $Co^{III/II}$ wave: $E_{1/2}$ = −1.04 V (ΔE_p = 40 mV), $Co^{II/I}$ wave: $E_{1/2}$ = −2.02 V (ΔE_p = 40 mV) vs $[FeCp*_2]^{0/+}$ ($Cp* = \eta^5\text{-}C_5Me_5$). Anal. Calcd for $(C_{24}H_{31}CoNPF_6)_n$: C, 53.64; H, 5.81; N, 2.61. Found: C, 53.77; H, 5.67; N, 2.49.

Polymer 6. 5-Norbornene-2-carboxaldehyde (179 mg, 1.47 mmol, 1 equiv) was dissolved in 7.5 mL of dry CH_2Cl_2, a green solution of **3** (12.5 mg, 0.0147 mmol, 0.01 equiv) in 2.5 mL of CH_2Cl_2 was added to the mixture at room temperature under N_2, and the color of the solution instantaneously changed from green to brown, indicating initiation of the polymerization. The mixture was stirred at room temperature for 30 min, 2 mL of ethyl vinyl ether was added to quench the reaction, the solvent was removed *in vacuo* until 0.5 mL of CH_2Cl_2 was left, and 50 mL of MeOH was added to the remaining mixture. The polymer was precipitated as a white solid and washed three times with MeOH. After filtration, the remaining white solid was dried *in vacuo* to give the polymer as a white solid. ^1H NMR (300 MHz, $CDCl_3$), δ_{ppm}: 1.18 (m, 3H, CH_3/Bu), 1.33−1.47 (m, 9H), 1.89 (m, 1H), 2.26−2.34 (m, 2H), 2.58 (m, 3H), 2.81−2.88 (m, 2H), 5.35−5.48 (m, 2H/CH=CH), 9.67 (m, 1H/CHO), 7.26 (s, $CDCl_3$). ^{13}C NMR (150 MHz, $CDCl_3$), δ_{ppm}: 32.36, 37.64, 42.33, 45.52, 54.96 (C/norbornene), 128.53−134.95 (m, CH=CH), 204.02 (broad, CHO), 77.16 ($CDCl_3$). Anal. Calcd for $(C_8H_{10}O)_n$: C, 78.65; H, 8.25. Found: C, 78.77; H, 8.27.

Polymer 7. The polymeric aldehyde **6** (122.2 mg, 1 mmol, 1 equiv) was dissolved in 10 mL of a mixed solvent (THF/butylamine: 1/1). The mixture was stirred at room temperature under N_2 overnight, the solvent was removed *in vacuo* to give the polymeric imine as an light-yellow oil, dry THF/CH_3OH (1:1), 30 mL, was added, and the solution was stirred

at 0 °C for 10 min. A mixed powder of $NaBH_4$ (189 mg, 5 mmol, 5 equiv) and $PhCOOH$ (610 mg, 5 mmol, 5 equiv) was added portionwise into the solution under 0 °C, the mixture was stirred for another 30 min at 0 °C, the solvent was removed *in vacuo*, 30 mL of dry CH_2Cl_2, and 50 mL of saturated $NaHCO_3$ solution were added to the remaining white solid. After stirring and separation, the organic phase was washed three times with distilled H_2O and dried over anhydrous Na_2SO_4. The solvent was removed under evaporation to give the polymeric amine as a light-yellow oil in 95% yield. ^1H NMR (300 MHz, $CDCl_3$), δ_{ppm}: 1.20 (broad, 3H, CH_3/Bu), 1.85 (broad, 2H), 2.22 (m, 2H), 2.41 (broad, 2H), 2.88 (broad, 2H), 3.68 (broad, 1H), 3.79 (broad, 1H), 3.99 (broad, 1H), 4.28 (broad, 1H), 4.31 (broad, 2H), 5.45 (m, 2H/CH=CH), 7.26 (s, $CDCl_3$), 2.79, 2.89, 7.95 (DMF). ^{13}C NMR (50 MHz, $CDCl_3$), δ_{ppm}: 14.01, 22.18, 25.60, 27.77, 29.28, 31.40, 37.54, 38.62, 42.35, 49.80, 130.21−134.72 (C/polymer), 77.16 ($CDCl_3$). Anal. Calcd for $(C_{12}H_{21}N)_n$: C, 80.38; H, 11.81; N, 7.81. Found: C, 80.77; H, 11.60; N, 7.83.

Polymer 8. The norbornene amine polymer **7** (35.8 mg, 0.2 mmol, 1 equiv) and **1** (71.6 mg, 0.2 mmol, 1 equiv) were dissolved in 10 mL of a mixed solvent ($CH_2Cl_2/CH_3CN = 1/1$). The mixture was stirred for 16h at 35 °C under N_2, the color of the solution changed from orange to deep red, the solvent was removed *in vacuo*, and the remaining solid was washed three times with distilled THF to give the polymeric enamine **8** as a deep red solid (104.2 mg, 90% yield). Anal. Calcd for $(C_{24}H_{31}CoNPF_6)_n$: C, 53.64; H, 5.81; N, 2.61. Found: C, 53.70; H, 5.77; N, 2.60. The characterizations (IR, UV−vis, ^1H NMR, ^{13}C NMR, ^{31}P NMR, and cyclic voltammogram) of polymer **8** were identical with those of polymer **5**: except for the diffusion coefficient by DOSY ^1H NMR.

Polymers 9 and 10. The use of the ratios of catalyst 0.05 and 0.10 equiv leads to the polymer **9** in 98% yield and polymer **10** in 99% yield, respectively, as deep red solids, giving the same ^1H, ^{13}C, NMR, IR, UV−vis spectroscopies, MALDI−TOF mass spectrometry, cyclic voltammetry (CV), and elemental analysis as polymer **5** except for the diffusion coefficient by DOSY ^1H NMR.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H NMR, ^{13}C NMR, ^{31}P NMR, IR, UV−vis, and mass spectra, SEC, and CV of monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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