ROMP Synthesis of Cobalticenium−Enamine Polyelectrolytes

Yanlan Wang, Amalia Rapakousiou, and Didier Astruc*

ISM, UMR CNRS No. 5255, Université de Bordeaux, 33405 Talence Cedex, France

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, 13C 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 polymers1 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 polymers5−8 and dendrimers9,10 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 polymeric5,6 and dendritic amines.9 Tang’s group has also recently reported several articles on cobalticenium polymers based on such useful coupling reactions.6 Manners’ group7 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 polyelectrolytes8 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

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 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).

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 N₂ 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/CH₃OH (1:1) at 0 °C (Scheme 2) using the mixed powder NaBH₄/PhCOOH to give the norbornene-substituted secondary amine as a light yellow oil in 99% yield. This secondary amine reacted stoichiometrically with 1 in CH₃CN at 35 °C for 16 h under N₂ to give the cobalticenium–enamine monomer 4 as a deep red solid in 98% yield. This monomer has been fully characterized by ¹H, ¹³C, ³¹P NMR, IR, UV-vis spectroscopy, 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 CH₂Cl₂ 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, ¹³C, 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 CH₂Cl₂ 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 ¹³C NMR, SEC (size exclusion chromatography) 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/CH₃OH (1:1) at 0 °C in the presence of a NaBH₄/PhCOOH powdery mixture to give after work-up the secondary amine-substituted polymer 7 as a light yellow oil in 95% yield. Polymer 7 was characterized by ¹H and ¹³C 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 CH₂Cl₂:CH₃CN (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 CD₃COCD₃. For the monomer 4, the typical two protons on the C≡C bond of 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 3. Hydroamination of 1 by the Secondary Amine-Functionalized Norbornene Polymer 7, Yielding the Cobalticenium—Enamine-Functionalized Norbornene Polymer 8

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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 (C24H31CoN+) 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 PF6 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 absorptions 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. 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. 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 absorptions 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. 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(η5-C5Me5)2], {[(η5-C5Me5) = Cp*]) as the internal reference in DMF in order to cover the largest possible electroactivity.22 It shows two redox waves corresponding 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 CoIII/II wave E1/2 = −1.04 V, and for the CoII/I wave E1/2 = −2.02 V vs FeCp*2 (Figure 4). For the polymer 5, the first redox wave (CoIII/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 CoIII/II redox, whereas in the second electron-transfer (CoII/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 (CoIII/II wave, E1/2 = −0.70 V; CoII/I wave, E1/2 = −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 1H NMR allows the approximate determination of the

Enamine-Functionalized Norbornene Polymer 8
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 $9.1 \times 10^{-11}$ m$^2$/s using eq 2:

$$
\frac{D_p}{D_m} = \left( \frac{M_m}{M_p} \right)^{0.55}
$$

(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:

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

(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

Figures 1. $^1$H NMR spectra of the cobalticenium–enameine monomer 4 (A) and homopolymer 5 in CD$_3$COCD$_3$ (B).
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 metatation of...

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**Table 1.** Compared \( E_{1/2} \) Values for the Cyclic Voltammograms of 1, Monomer 4, and Polymer 5

<table>
<thead>
<tr>
<th>compound</th>
<th>( E_{1/2} ) (V)</th>
<th>( \Delta E^p ) (mV)</th>
<th>( E^p - E^pc ) (V)</th>
<th>( \Delta E^p ) (mV)</th>
<th>( E^p - E^pc ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−0.70</td>
<td>70</td>
<td>−1.63</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>−1.04</td>
<td>40</td>
<td>−2.02</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>−0.04</td>
<td>40</td>
<td>−2.02</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \)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_4N][PF_6]; internal reference = [FeCp^*2]^0/+ (Cp^* = η^5-C_5Me_5). The redox potential values for the polymer 8, 9, and 10 are identical to those of the polymer 5 under identical conditions.

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**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

<table>
<thead>
<tr>
<th>compound</th>
<th>( D^p ) (diffusion coefficient) (±0.1) m^2/s</th>
<th>( n_p ) (from end group ( ^1H ) NMR analysis)</th>
<th>( n_p ) (from eq 2)</th>
<th>( n_p ) (from eq 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.91 × 10^{-10}</td>
<td>83 ± 10</td>
<td>89 ± 10</td>
<td>99 ± 10</td>
</tr>
<tr>
<td>8</td>
<td>1.06 × 10^{-10}</td>
<td>60 ± 5</td>
<td>67 ± 5</td>
<td>72 ± 5</td>
</tr>
<tr>
<td>9</td>
<td>1.28 × 10^{-10}</td>
<td>44 ± 5</td>
<td>48 ± 5</td>
<td>50 ± 5</td>
</tr>
<tr>
<td>10</td>
<td>1.98 × 10^{-10}</td>
<td>18 ± 3</td>
<td>22 ± 3</td>
<td>25 ± 3</td>
</tr>
</tbody>
</table>

\( ^a \)DOSY NMR were measured in CD_3COCD_3 at 25 °C. \( ^b \)Values obtained by \( ^1H \) NMR in CD_3COCD_3, at 25 °C. \( ^c \)Values obtained using eq 2 with the diffusion coefficient obtained from DOSY experiments. \( ^d \)Values obtained from eq 3.
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 polycobaltocene 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 on 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 and distilled from sodium benzophenone under nitrogen immediately prior to use. DCM was dried over calcium hydride and distilled under nitrogen prior to use. A mixed powder of NaBH₄ (1.89 g, 50 mmol, 5 equiv) and Ph₂COOH under nitrogen immediately prior to use. DCM was distilled over calcium hydride and distilled under nitrogen prior to use. Reagent-grade THF, diethyl ether, and general information.

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at 0 °C for 10 min. A mixed powder of NaBH₄ (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 CH₂Cl₂, and 50 mL of saturated NaHCO₃ solution were added to the remaining white solid. After stirring and separation, the organic phase was washed three times with distilled H₂O and dried over anhydrous Na₂SO₄. The solvent was removed under evaporation to give the polymeric amine as a light-yellow oil in 95% yield. ¹H NMR (300 MHz, CDCl₃), δ ppm: 1.20 (broad, 2H), 2.41 (broad, 2H), 2.88 (broad, 2H), 3.68 (broad, 1H), 3.79 (broad, 1H), 4.28 (broad, 2H), 4.31 (broad, 2H), 5.45 (m, 2H/CH₂=CH=), 7.26 (s, CDCl₃), 2.79, 2.89, 7.95 (DMF). ¹³C NMR (50 MHz, CDCl₃), δ ppm: 14.01, 22.18, 25.60, 27.74, 29.28, 31.40, 37.54, 38.62, 42.35, 49.80, 134.72 (C/polymer), 77.16 (CDCl₃). Anal. Calcd for (C₁₂H₂₁N)₃P: C, 80.38; H, 11.81; N, 7.83. Found: C, 80.77; H, 11.60; N, 7.85.

Polymers 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 (CH₂Cl₂/CH₂CN = 1/1). The mixture was stirred for 16th at 35 °C under N₂, 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. Calcld for (C₂₁H₄₁N)₃P: 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, ¹³C NMR, ³¹P NMR, and cyclic voltammetry) 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, ¹³C 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, ¹³C NMR, ³¹P 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.

AUTHOR INFORMATION

Corresponding Author

* (D.A) E-mail: d.astruc@ism.u-bordeaux1.fr.

Notes

The authors declare no competing financial interest.

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REFERENCES

5. (b) S Supporting Information


