"Click" Synthesis and Redox Activity of a Water-Soluble Triazolylcobalticinium Polyelectrolyte

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Abstract Ionic macromolecules, i.e. polyelectrolytes are of academic and industrial interest due to their polycharged structures and applications. Here a polyelectrolyte containing redox-active cobalticinium groups is synthesized by Cu^I-catalyzed azide alkyne Huisgen-type regioselective 1,3-cycloaddition, which is also-called "click" synthesis between a poly(azidomethylstyrene) polymer and ethynylcobalticinium. Overall, this first triazolylcobalticinium polymer is easily prepared in only three steps, which opens the way for applications such as redox sensing in aqueous media, polymer encapsulation of hydrophobic biomedical molecules in water and stabilization of colloidal suspensions. Cyclic voltammetry shows chemically and electrochemically reversible reductions on the electrochemical time scale, to the neutral 19-electron cobaltocene polymer and to the unstable 20-electron anionic structure. Application of Bard's equation using the decamethylferrocene reference allows estimating that the number of electrons transferred in the first cyclic voltammetry wave is 29 ± 3, close to the number of cobalticinium units, 31 ± 2, determined by size exclusion chromatography.

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1 Introduction

Cobalticinium derivatives [1–5] are isoelectronic with ferrocenes, but the positive charge of the 18-electron form precludes all the electrophilic functionalization reactions related to ferrocene. Yet cobalticinium salts, as with their ferrocene analogues, have a rich electrochemistry with reversible access to neutral Co^{II}19-electron [6, 7] and anionic 20-electron metallocene species [8, 9] and this positive charge is the potential source of polyelectrolytes upon pairing with an adequate source of anions in cobalticinium polymers [10–22].

When transition metal complexes such as cobalticinium salts are linked to macromolecules, they can undergo transfer of a large number of electrons, and these multiple redox processes are useful for potential nanodevice applications. Indeed, cobalticinium polymers are known [10–22] and have been obtained either by ring-opening cobaltocenophane [10–12] or from cobalticinium carboxylic acid as a derivatizing side group [13–22].

Whereas this functionalization is tedious, ethynylcobalticinium has been known for more than 20 years and is easily synthesized [23] which provided the possibility of easy Cu^I-catalyzed "click" reactions [24–27], as demonstrated for ethynylferrocene [28–30] with a variety of alkynes. Indeed, the first "click" reaction between ethynylcobalticinium and alkynes was reported to give triazolylcobalticinium derivatives in 2010 [28], and since then this practical reaction has been systematically used in our group for cobalticinium functionalization [29, 30]. The

triazolyl derivatives are potential ligands that are useful for sensing [31–33] and catalysis [34–36], especially when they are directly linked to a redox-active metallocene unit.

Recently, triazolylcobalticinium dendrimers have been reported [30]. Here we describe the first synthesis of a triazolylcobalticinium polyelectrolyte polymer by Cu^I-catalyzed azide-alkyne "click" cycloaddition (CuAAC) of ethynylcobalticinium with an azido-functionalized polymer.

2 Experimental

2.1 Materials

Reagent-grade diethyl ether and tetrahydrofuran (THF) were predried over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. All other solvents were used as received. Ethynylcobalticinium **3** was synthesized according to [23]. p-Chloromethyl-styrene was purchased from Aldrich. Polymers **1** and **2** were synthesized according to [37] with slight modifications (vide infra).

2.2 Physical Measurements

The ^{1}H NMR spectra were recorded at 25 °C with a Bruker AVANCE II 300 MHz spectrometer. The ^{13}C NMR spectra were obtained in the pulsed FT mode at 75.0 MHz with a Bruker AVANCE 300 spectrometer. All chemical shifts are reported in parts per million (δ, ppm) with reference to Me$_4$Si (TMS). The infrared (IR) spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. UV–Vis absorption spectra were measured with a Perkin–Elmer Lambda 19 UV–Vis spectrometer. The size exclusion chromatography (SEC) measurements were carried out using the PL-GPC 50 plus Integrated GPC system from Polymer laboratories-Varian equipped with refractometric and UV detectors, column oven and integrated degasser. Columns from TOSOH: TSKgel TOSOH, HXL-L (guard column 6.0 mm ID × 4.0 cm L), G4000HXL (7.8 mm ID × 30.0 cm L), G3000HXL (7.8 mm ID × 30.0 cm L), G2000HXL (7.8 mm ID × 30.0 cm L). Flow Marker: TCB (trichlorobenzene, C$_6$H$_3$Cl$_3$), Flow: 1.0 mL/min. Solvent: THF from Aldrich, loop : 100 μL.

2.3 Cyclic Voltammetry (CV) Measurements

All electrochemical measurements were recorded under nitrogen atmosphere. Conditions: solvent: dry DMF; temperature: 20 °C; supporting electrolyte: [n-Bu$_4$N][PF$_6$] 0.1 M; working and counter electrodes: Pt; reference electrode: Ag; internal reference: FeCp*$_2$ (Cp* = η^5-C$_5$Me$_5$) [38]; scan rate: 0.200 V/s^{-1}.

2.4 Synthesis of p-Polychloromethylstyrene 1

p-Chloromethylstyrene (2.17 g, 14.2 mmol) was dissolved in 5 mL dry toluene, then AIBN (0.12 g, 0.7 mmol) was added under nitrogen. The reaction mixture was allowed to stir at 80 °C for 24 h. Then, toluene was removed under vacuum, and the crude product was washed with methanol and precipitated five times in CH$_2$Cl$_2$/methanol. The p-polychloromethylstyrene 1 was obtained as a white powder in 53.9 % yield. SEC: PDI = 1.40, M$_n$ = 4,758, M$_w$ = 5,297.

2.5 Synthesis of p-Polyazidomethylstyrene 2

In a Schlenk flask, the p-polychloromethylstyrene compound **1** (2.5 g, 0.5 mmol) was dissolved in 20 mL DMF, and NaN$_3$ (1.6 g, 24.6 mmol) was added. The mixture was heated at 80 °C for 24 h, then the suspension was extracted three times with diethyl ether/H$_2$O, the organic phase was dried over Na$_2$SO$_4$, filtered and evaporated. The p-polyazidomethylstyrene compound **2** was purified by precipitation in MeOH twice. It was obtained as a white waxy product in 84.6 % yield. IR spectrum: 2,097 cm^{-1} for the azido band. SEC: PDI = 1.24, M$_n$ = 4,901, M$_w$ = 4,938.

2.6 Synthesis of Poly-triazolylcobalticinium Polymer 4

The ethynylcobalticinium compound **3** (1.5 equiv., 168.7 mg, 0.47 mmol) and the azido polymer **2** (1 equiv., 50 mg, 0.3 mmol) were dissolved in a mixture of degassed THF (15 mL), DMF (20 mL) and H$_2$O (4 mL), and the reaction mixture was cooled to 0 °C. Then, an aqueous solution of CuSO$_4$ 1 M (1.1 equiv.) was added dropwise, followed by the dropwise addition of a freshly prepared solution of sodium ascorbate (2.2 equiv.) The color of the solution changed from orange to dark red upon addition of sodium ascorbate. The reaction mixture was allowed to stir for 12 h at 50 °C under a nitrogen atmosphere. Then the mixture of solvents was removed under vacuum, and 100 mL of nitromethane was added followed by the addition of an aqueous solution of ammonia. The mixture was allowed to stir for 15 min in order to remove all the copper salt trapped inside the polymer. The organic phase was washed twice with water, dried over sodium sulfate, filtered and the solvent was removed under vacuum. Then the product was washed with THF in order to remove the excess of alkyne and precipitated from an acetone or acetonitrile solution in diethyl ether. Further washing in acetonitrile removed smaller polymer parts. The water-soluble polymer **4** was obtained as an orange-yellow sticky oil in 53 % yield.

^{1}H NMR (1D 1H), (D$_2$O, 300 MHz): δ_{ppm}: 8.35 (C*H* of trz), 7.0 (C*H* arom.), 6.03 (C*H* of Cp sub.), 5.73 (C*H* of Cp sub.), 5.44 (C*H* of Cp free and C*H$_2$* -trz), 1.56, 1.40 (C*H$_2$* and C*H* of polymeric chain). ^{13}C NMR (D$_2$O, 75 MHz): 140.43 (*C*q of Ar), 138.68 (*C*q of trz), 128.75 (C*H* of Ar polymer chain), 125.24 (C*H* of trz), 93.22 (*C*q of Cp sub.), 85.83 (C*H* of Cp), 86.74, 85.72, 84.59, 80.55 (C*H* of Cp sub.), 55.34 (C*H$_2$*-trz), 53.72 (C*H*, C*H$_2$* of polymeric chain).

3 Results and Discussion

3.1 Synthesis and SEC Characterization of Polymers 1 and 2

The polychloromethylstyrene polymer **1** was prepared by free-radical polymerization of commercial chloromethyl-styrene using AIBN as the initiator (Scheme 1). The reaction took place in toluene, at 80 °C under nitrogen. Azidation reaction gave the azido-polymer **2** in 85 % yield.

SEC (reference: polystyrene) shows the molecular weight distribution curve of **1** with polydispersity index (PDI) = 1.4 and **2** with PDI = 1.2. The polydispersity improved from **1** to **2**, because after the azidation reaction the product was further purified by precipitation in MeOH twice. Molecular weight data using polystyrene as the standard reference show that polymer **2** consists of 31 units (Fig. 1).

3.2 Synthesis of the Cobalticinium Polymer 4

The polymer **4** was synthesized by CuAAC "click" reaction between ethynylcobalticinium **3** and the azido polymer **2**. Previous studies concerning the click cobalticinium dendrimers showed that as the number of the triazolyl (trz) cobalticinium groups increases in a molecule, its polarity also increases due to charge clustering. Charge clustering favors solubilization in more polar solvents such as water, which is a polyelectrolyte property. Assuming that the polymer **2** consists of a large number of units, a mixture of THF/DMF/H$_2$O as solvent was chosen for the click reaction in order to achieve the solubility of the final product **4**.
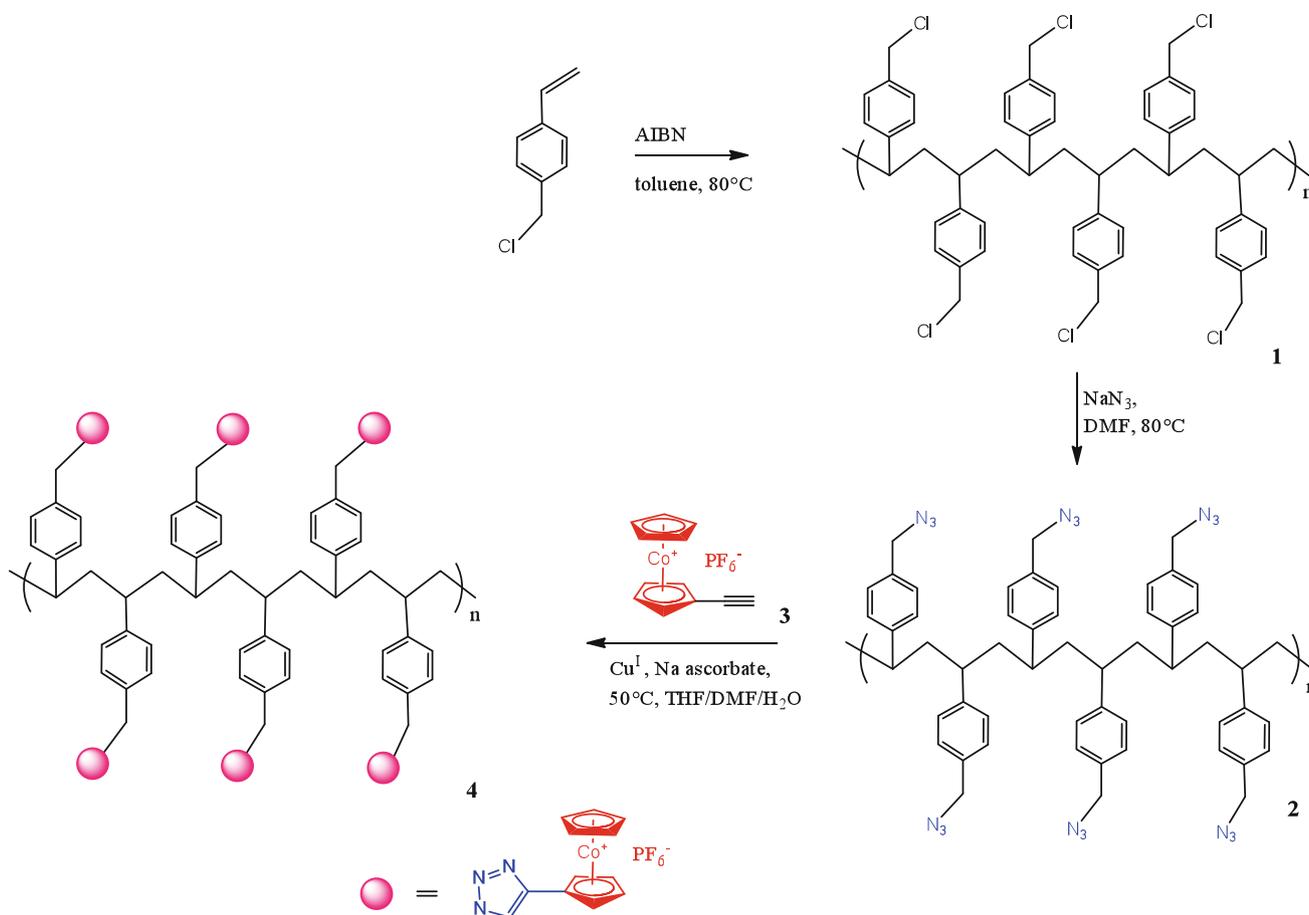
Scheme 1 Synthesis of the water-soluble triazolylcobalticinium polyelectrolyte
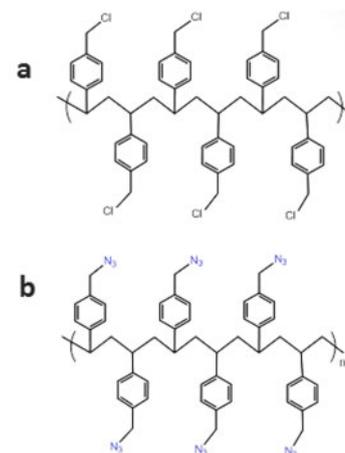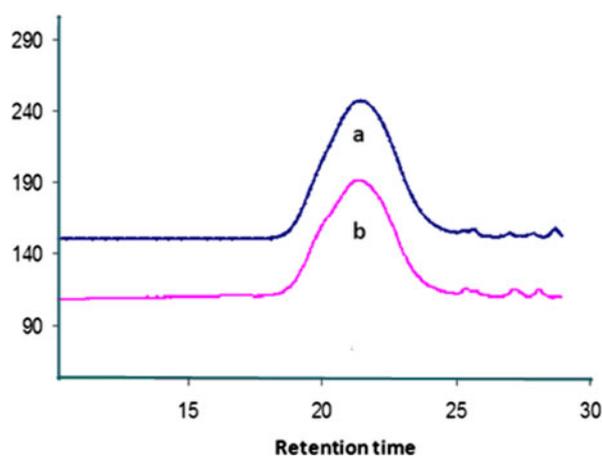
The reaction lasted 12 h at 50 °C. The copper salt was removed as [Cu(NH₃)₂(H₂O)₂] [SO₄] after adding an aqueous solution of NH₃ to the mixture. The polymer was purified by precipitation in diethyl ether and washed with acetonitrile in order to remove smaller polymeric units that might have formed. The final yellow product was soluble only in very polar solvents such as water (Fig. 2), DMF and DMSO.

3.3 Characterization of the Cobalticinium Polymer 4

"Click" reactions are easily monitored by infrared spectroscopy (neat), because the azido groups have a characteristic peak at 2,094 cm^{-1} that disappears at the end of the reaction confirming that all the azido groups are replaced by trz groups. A strong band at 838 cm^{-1} is due to the absorption of the PF₆ anion, and the band at 3,118 cm^{-1} is due to the = C–H stretching of the trz and the Cp groups of the cobalticinium units. NMR spectroscopy in D₂O confirms the structure of the water-soluble polymer 4. ^{1}H NMR shows the disappearance of the –CH₂N₃ peak at 4.25 ppm, the appearance of the trz-C*H* peak at 8.35 ppm
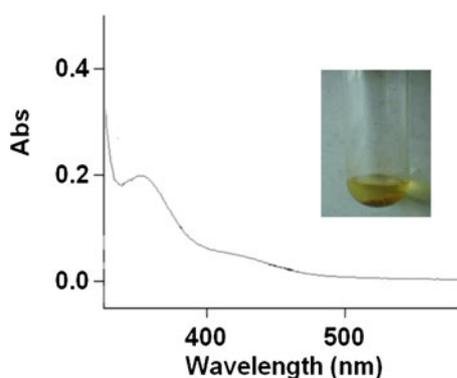

Fig. 2 UV–Vis spectroscopy of the cobalticinium polymer 4 in water (Color figure online)

as well as the other characteristic peaks of the polymer. The presence of trz group is also confirmed by the appearance of the characteristic peaks of *C*q and *C*H of trz in the ^{13}C NMR spectra. UV–Vis spectroscopy recorded in water shows a strong absorption at 347 nm due to d–d* transitions of cobalticinium and an absorption shoulder at 425 nm (Fig. 2).

The MALDI-TOF mass spectrum of the polycationic cobalticinium polymer 4 showed well-defined individual peaks for polymer fragments that are separated by 517 Da, which exactly corresponds to the mass of one methylenestyryltriazolylcobalticinium hexafluorophosphate unit (Fig. 3). The highest molecular peak that could be obtained was that of 5,796 Da corresponding to a polymer fraction of 11 trz-cobalticinium units. Several other fragments are also observed probably due to additions or losses of some PF₆ anions. The intensities of the peaks separated by 517 Da progressively decrease and vanish towards high molecular masses. Thus the molecular peak and higher masses cannot be observed. While this MALDI TOF mass spectrum clearly shows the structure and motifs of the polymer 4, the SEC analysis of the precursor polymer 2 is a more viable method to determine the total number of units. SEC analysis of the final polycationic cobalticinium itself, polyelectrolyte 4, is difficult due to the strong electrostatic interactions between the cobalticinium moieties. Therefore CV studies were conducted in order to examine the thermodynamics and kinetics of the heterogeneous electron-transfer processes, the stability of the reduced states and finally to confirm the number of units in the cobalticinium polymer 4.

3.4 Cyclic Voltammetry Studies and Multi-Electron-Transfer Process

The trz-cobalticinium polymer 4 was studied by cyclic voltammetry using decamethylferrocene as the internal reference [38]. DMF was used as a solvent (Fig. 4). The
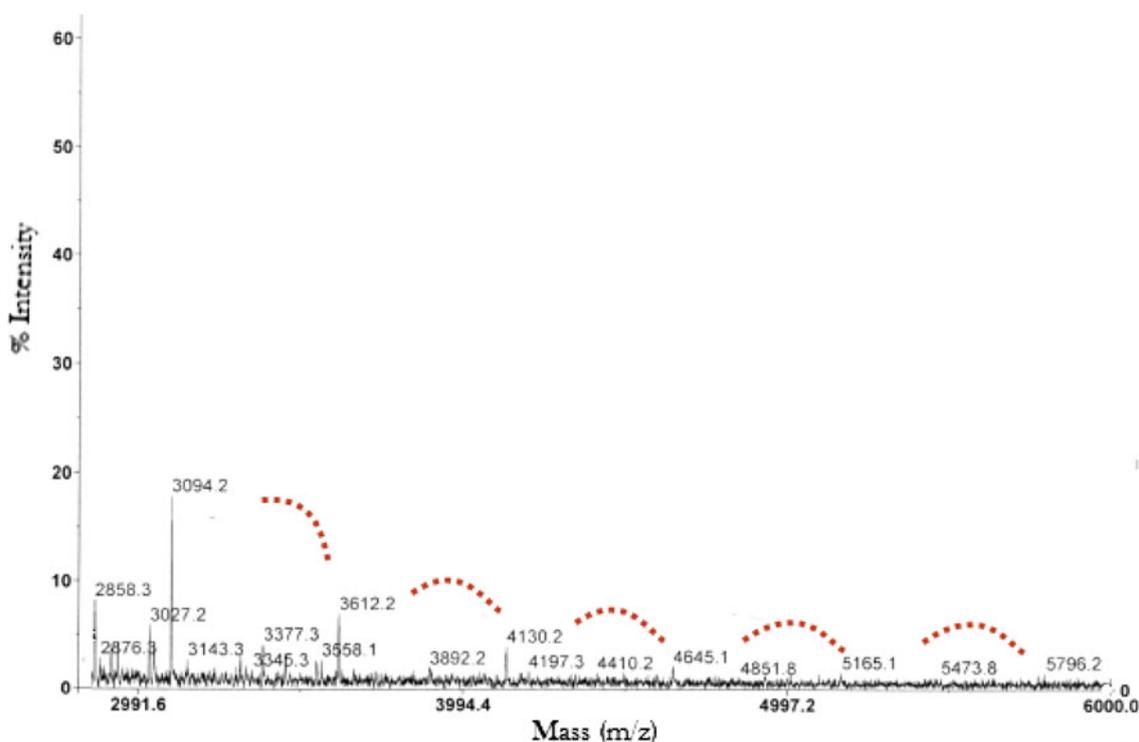
Fig. 3 MALDI-TOF mass spectrum of polymer **4**

first reduction wave corresponding to the reduction of cobalticinium to the 19-electron cobaltocene (Co$^{III/II}$) takes place at −0.8 V [6, 7]. The second wave corresponding to the reduction of cobaltocene to the 20-electron cobaltocenyl anion (Co$^{II/I}$) appears at −1.73 V [8, 9] (Table 1). Although heterogeneous electron transfers from the electrode to the metallocene polymer proceed one by one [39], both waves are single. This can be explained by the weakness of the electrostatic factor between the redox sites which are separated by several bonds [40–43]. Additionally both waves appear to be electrochemically reversible. The electrochemical reversibility is due to very fast rotation within the electrochemical time scale, where all the redox groups come close to the electrode provoking fast electron transfer between all the redox groups and the electrode, [44] and/or the electron-hopping mechanism [45].

Supporting electrolyte: [n-Bu$_4$N][PF$_6$] 0.1 M; working and counter electrodes: Pt; reference electrode: Ag; internal reference: FeCp*$_2$ (Cp* = η^5-C$_5$Me$_5$); scan rate: 0.200 V/s^{-1}. The ΔE value of 0.045 V obtained for the Co$^{III/II}$ wave, slightly lower than the standard 0.059 V value at 25 °C [39], is probably due to partial adsorption of **4** onto the electrode.

The envelope of the first redox wave (Co$^{III/II}$) is slightly broadened compared to a standard single-electron wave shape which is most probably due to electrostatic interactions slightly differentiating the multiple single electron-
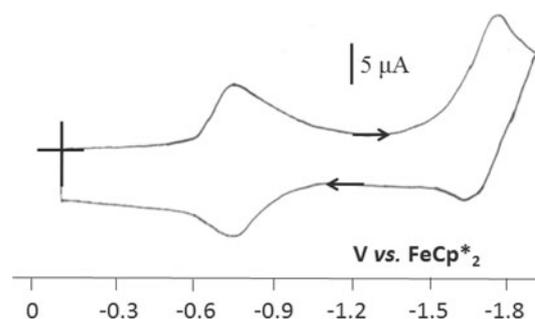
Fig. 4 CV of **4**. Internal reference: FeCp*$_2$. Solvent: DMF; 298 K; reference electrode: Ag; working and counter electrodes: Pt; scan rate: 0.2 V/s^{-1}; supporting electrolyte: [n-Bu$_4$N][PF$_6$]

Table 1 Redox potentials, chemical (i_a/i_c) and electrochemical (Ep$_a$-Ep$_c$ = ΔE) reversibility data for compound **4**

Compound	Solvent	Co$^{III/II}$ [V]			Co$^{II/I}$ [V]		
		$E_{1/2}$	ΔE	i_a/i_c	$E_{1/2}$	ΔE	i_a/i_c
4	DMF	−0.80	0.045	0.8	−1.73	0.060	0.6

transfer steps corresponding to the Co$^{III/II}$ redox change. In the second electron-transfer (Co$^{II/I}$) for which the starting polymer does not contain cationic species, this phenomenon does not appear, because it is weaker. The electrostatic interaction for the first electron transfers involve all the cationic charges whereas the last ones involve a neutral or

anionic polymer. Interactions between the cationic centers, the counter anions and the solvent molecules are responsible for the variation of the electrostatic energy engaged in the heterogeneous electron transfers [43–47].

The second wave ($Co^{II/I}$) is electrochemically reversible, indicating that the 20-electron fully sandwich structure is retained on the electrochemical time scale without significant structural change [8, 9] (only a small increase of the Co–Cp bonds is expected due to the presence of two electrons in slightly anti-bonding e^*_1 orbitals [48, 49]). On the other hand, the chemical reversibility is weaker than that of the first wave (Table 1), signifying that on a longer timescale the anionic metallopolymer structure collapses. Lastly, the number of electrons involved in the first redox change ($Co^{III/II}$) was calculated by cyclic voltammetry analysis in order to confirm the number of trz-cobalticinium units, 31, determined from SEC analysis of the precursor **2**. The total number of electrons transferred in the oxidation wave for the polymer (n_p) can be estimated from the limiting currents and approximate relative values of the diffusion coefficients of the monomer (D_m) and the polymer (D_p):

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

Assuming that the reduction of each redox moiety is an one-electron reaction (Co^{III} Co^{II}), the value of n_p can be estimated by employing Bard's equation previously derived for conventional polarography [39, 40]:

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

Consequently comparison with the internal reference $[Fe(\eta^5-C_5Me_5)_2]$ provides a good estimation of the number of electrons n_p involved in the $Co^{III/II}$ redox process as a function of the monomer and polymer intensities (i), concentrations (C) and molecular weights (M) [40]. Measurement of the respective intensities for the decamethylferrocene reference and the first wave led to the data of $n_p = 29 \pm 3$ electrons for the polyelectrolyte **4**, which is in good agreement with the experimental values of 31 ± 2 derived by SEC of the polyazido polystyrene polymer precursor, **2**. The value of 29 is lower than 31, probably due to the lowering of the wave due to the electrostatic factor (vide supra). This factor should indeed result in a lower value than the actual one as found, but the decrease is only modest judging from the comparison with the SEC data.

4 Concluding Remarks

The first triazolylcobalticinium polymer has been synthesized by facile Cu^I-catalyzed azide-alkyne "click" CuAAC of ethynylcobalticinium with an azido-functionalized polymer. The three-step synthesis represents a very practical synthetic method from commercial *p*-chloromethylstyrene. The number of triazolylcobalticinium units in this polymer **4** has been estimated to be 31 using the SEC data of the polyazido polymer and was confirmed (29 ± 3) using Bard's equation by cyclic voltammetry using decamethylferrocene as the internal reference. Remarkably, this polymer is water soluble, which can lead to significant applications in redox sensing in water or polymer encapsulation in aqueous media of hydrophobic biomedical molecules and drugs. Cyclic voltammetry studies showed two reversible electron-transfer processes which make this polymer a very good candidate as a molecular–battery material. Such studies are currently underway in our laboratory.

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