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Synthesis and properties of functionalized β-cyclodextrin copolymer and its metal complexes

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Summary

A novel copolymer was synthesized successfully via polymerization of part (6-O-butene diacid ester)-β-cyclodextrin and styrene. Because the carboxyl groups of the new copolymer possess a strong chelating ability, the copolymer is capable of coordinating with metal ions. Utilizing this new ability, the copolymer metal complexes containing Cu(II) and Ag(I) were synthesized. The structures and properties of the copolymer and its metal complexes were characterized by IR, UV, MS, ^{13}C NMR, X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC), electron spin resonance (ESR), and cyclic voltammetry (CV). The results show that the novel copolymer metal complexes were composed of the desired metal ion, polystyrene, and the functionalized β-cyclodextrin (β-CD). Furthermore, they possess stable electrochemical activity and are paramagnetic.

Introduction

Due to their particular properties, polymer metal complexes (PMCs) are increasingly relevant to the fields of catalytic reactions, optical sensory materials, chemical sensors, magnetic materials, and other areas of biochemistry and environmental chemistry [1-4]. They have attracted much more attention in recent years and shown wide application potential. Usually, PMC ligands contain heteroatoms (N, O, P, or S) in addition to non-bonding electrons provided by pyridine, trialkylphosphines, amines, alcohols, and carboxylic acids [5]. Transition metal ions, such as Cu(II) and Ag(I), can then be introduced into the polymer [6]. Several functional materials have been synthesized rapidly using this structural motif.

Cyclodextrins are cyclic oligosaccharides composed of several glucose units joined in series by α-1,4 linkages. Cyclodextrins are classified as α-, β-, or γ-CDs based on the presence of six, seven, or eight glucose units within the ring, respectively. Each of glucose's C6 hydroxyl groups is located at the narrow side of the torus, whereas the secondary C2 and C3 glucopyranose alcohols are located at the wider side of the torus. This arrangement creates a hydrophobic cavity within the cyclodextrin ring, which in turn is surrounded by a polar hydrophilic outer shell. One of the most important features of these compounds is their capacity to host various substances, such as drugs, pesticides, perfumes, and other products, within their hydrophobic cavities to form encapsulated compounds [7]. β-CD and their derivatives are widely recognized as excellent models for understanding general enclosed phenomena and enzyme-substrate and receptor-ligand interactions, and have now become available in large quantities. Thus, this class of compounds has found extensive applications in many areas such as food, organic, and polymer chemistry, in addition to the cosmetic and pharmaceutical industries [8].

Studies [9,10] on the CD of metal complexes have been extensively carried out, but copolymer metal complexes involving β-CD are seldom reported. In this paper, we report the synthesis and characterization of a functionalized β-CD copolymer and several of its metal complexes. We believe this complex may have use as an enzyme mimetic [11].

Experimental

Materials

β-CD was purchased from Shanghai Chemical Co. and recrystallized twice from distilled water and dried under vacuum at 90 °C for 24 h. Styrene, supplied by Shenyang Chemical Co., was washed with a 5% solution of hydroxide, stirred over calcium hydroxide for 24 h, then distilled under vacuum, and stored at -15 °C until used. Dimethyl formamide (DMF) was supplied by Beijing Chemical Factory, dried over anhydrous $MgSO_4$ for 24 h and distilled under reduced pressure. 2,2-Azo-bis-isobutyronitrile (AIBN), maleic anhydride, methanol, acetone, $CuSO_4 \cdot 5H_2O$ and $AgNO_3$ (A.R.) were supplied by Beijing Chemical Factory and were used without further purification.

Instrumentation

Fourier transform infrared spectra (IR) were recorded on a Nicolet FT/IR-410 spectrophotometer. The ultraviolet (UV) spectra were recorded on a Shimadzu UV-2450 spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out with an Escalab mark II apparatus. DSC (differential scanning calorimetry) was measured on a Mettler Toledo Stare System DSC821e. The cyclic voltammograms (CV) were obtained on a HPD-1A Model bipotentiostat with a TYPE3086-23A4 X-Y recorder. The glassy carbon electrode served as the working electrode, Pt wire served as the counter electrode, and the reference electrode was Ag/Ag^+ (0.01M $AgNO_3$ in ethanol). The mass spectra were obtained on Q-star LC/quadrupole MS/MS/TOF. The ^{13}C NMR spectra were obtained on a Bruker AV300 spectrometer with deuterated dimethyl sulphoxide (d^6-DMSO) as the solvent. The electron spin resonance (ESR) was investigated using a Bruker ESR ER200D-SRC spectrometer.

Synthesis of functionalized β-CD monomer of part (6-O-butene diacid ester)-β-CD [12]

A mixture of β-CD (17.0 g) and maleic anhydride (22.5 g) were ground using a mortar and pestle. Then, the mixture was transferred to a conical flask and heated to 80 °C for 8 h while being stirred every 15 minutes using a vitreous rod. The reaction became very stringy, and eventually turned into a solid. The crude solid was crushed and poured into acetone. After filtration, the product was washed with acetone and methanol several times. The resulting solid was dried under vacuum at 70 °C for 12 h.

Synthesis of copolymer of styrene and functionalized β-CD monomer

A round-bottom flask was charged with styrene (8 ml), part (6-O-butene diacid ester)-β-CD (2 g), DMF (10 ml), and AIBN (0.05 g). The flask was sealed and removed of oxygen using a vacuum- and-argon-flush cycle that was repeated thrice. Then, the flask was immersed in a 80 °C oil bath. After 6 hours, the reaction was cooled to room temperature to terminate polymerization. The product was precipitated from methanol and dried under vacuum at 60 °C for 24 hours.

Synthesis of functionalized β-CD copolymer metal complexes

The copolymer (0.5 g) was added into a solution of DMF (10 ml) and $CuSO_4$ (2 g) with stirring. The reaction was stirred for 6 h at room temperature. Afterwards, the reaction mixture was poured into methanol, and the resulting solid was collected by filtration and washed by methanol twice. The product was dried under vacuum at 60 °C for 12 h. The functionalized β-CD copolymer Ag^+ complex was synthesized using this procedure as well.

Results and Discussion

Characterization of functionalized β-CD

Figure 1 shows the IR spectra of (A) β-CD and (B) part (6-O-butene diacid ester)-β-CD. Compared with the IR spectrum of β-CD, the partially substituted β-CD displayed a new intense absorption peak at 1727 cm^{-1} that is attributed to the unsaturated ester and unsaturated carboxyl groups. In addition, the absorption peaks at 581 cm^{-1} and 946 cm^{-1} of β-CD are still preserved, suggesting that the ringed structure of β-CD was not destroyed after the maleic anhydride linked with β-CD [13].

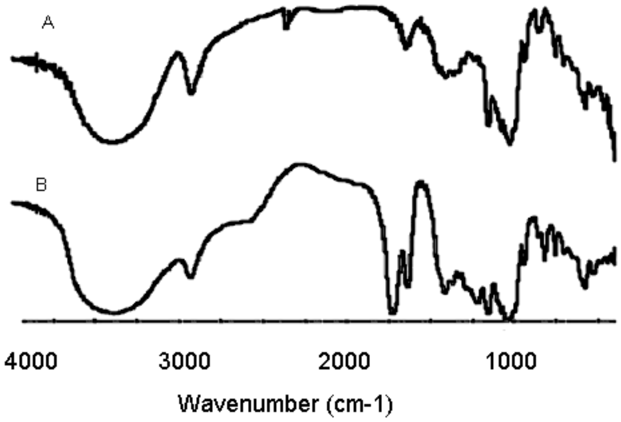

Fig. 1 The IR spectra of (A) β-CD; (B) part (6-O-butene diacid ester)-β-CD

The UV spectra of (A) part (6-O-butene diacid ester)-β-CD, (B) copolymer, (C) copolymer Ag^+ complex and (D) copolymer Cu^{2+} complex are shown in figure 2. The UV spectrum of the functionalized monomer (part (6-O-butene diacid ester)-β-CD) shows evidence that a broadened absorption peak of partly substituted β-CD exists from 200 nm to 225 nm, which is attributed to the $n \rightarrow \pi^*$ transition of the –CH=CHCOO- group. When compared with UV spectra of β-CD, the absence of peaks between 200 nm to 400 nm indicates maleic anhydride had been introduced into β-CD. This data supports the addition of maleic anhydride to the hydroxyl group of the anhydroglucose unit of β-CD. After the polymerization of part (6-O-butene diacid ester)-β-CD and styrene, the absorption peaks of the functionalized β-CD copolymer is now broader than that of the functionalized monomer because the copolymer now includes polystyrene, which has an inherent absorption from 210 nm to 230 nm. From this data, we believe that the radical polymerization was successful and that the desired functionalized copolymer was synthesized.

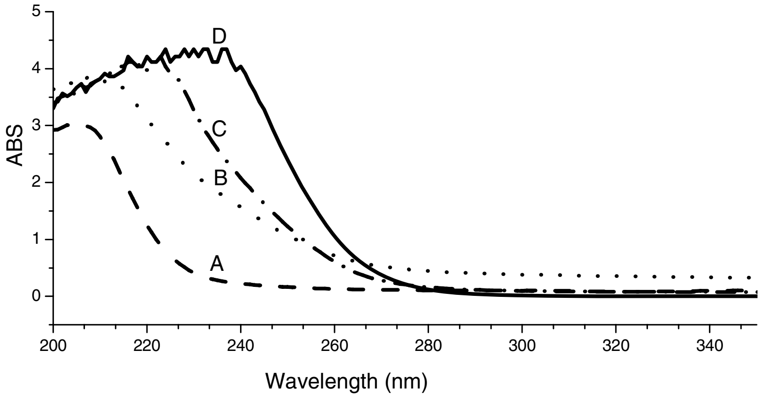

Fig. 2 The UV spectra of (A) functionalized β-CD; (B) copolymer; (C) copolymer Ag^+ complex; (D) copolymer Cu^{2+} complex

In the mass spectrum of part (6-O-butene diacid ester)-β-CD, the peaks at m/z of 1452, 1550 and 1648 correspond to the expected ions of functionalized β-CD coupled with three, four, and five maleic anhydrides, respectively. These values are in agreement with the calculated molecular weights of each variant. Overall, the mass spectrum confirms that maleic anhydride was bonded with the free hydroxyl groups of β-CD.

Figure 3 shows the ^{13}C NMR spectrum of the functionalized monomer. After the β-CD was modified by maleic anhydride, new carbon resonances were detected via ^{13}C NMR. The peak at 168 ppm is assigned to the carbon in the maleic anhydride (-CH=CH*C*OOH) which was linked with β-CD. The resonance at 165 ppm is assigned to the -CH=CH*C*OOCH$_2$- carbon of the functionalized monomer. The resonances at 131 ppm and 128 ppm are assigned to the -CH=*C*HCOOCH$_2$- and -CH=*C*HCOOH carbons, respectively, which further supports the conclusion that the maleic anhydride was introduced into β-CD successfully. Compared with the ^{13}C NMR spectrum of β-CD, the appearance of new peaks between 50 ppm to 75 ppm indicates the maleic anhydride was bonded with hydroxyl group of C6 of anhydroglucose unit of β-CD.

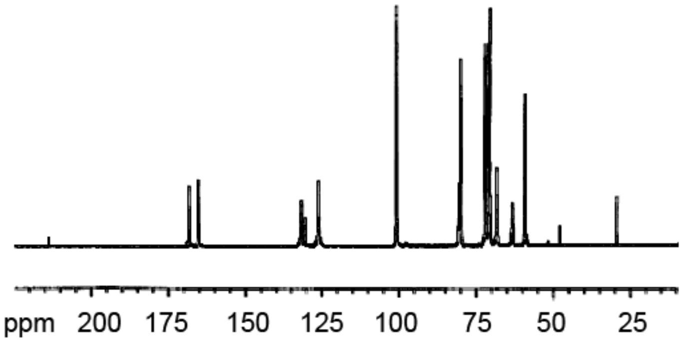

Fig. 3 The ^{13}C NMR spectra of functionalized monomer

Characterization of functionalized β-CD copolymer and its metal complexes

Figure 4 shows the IR spectra of functionalized β-CD, functionalized β-CD copolymer and its metal complexes. In spectrum B, the absorption at 1650 cm^{-1} was increased after the functionalized β-CD was polymerized with styrene. The new absorption at 700 cm^{-1} is attributed to the appended phenyl group. This data suggests that the styrene and part (6-O-butene diacid ester)-β-CD were indeed polymerized. After the metal ions were introduced into the copolymer, the intense absorption peak of the carboxyl-salt at 1420 cm^{-1} was further increased, indicating the metal ions had been coordinated with the copolymer's carboxyl groups. The functional β-CD copolymer metal complex was synthesized. In addition, we can confirm that the ringed structure of β-CD was not destroyed after the metal ions were introduced into the copolymer.

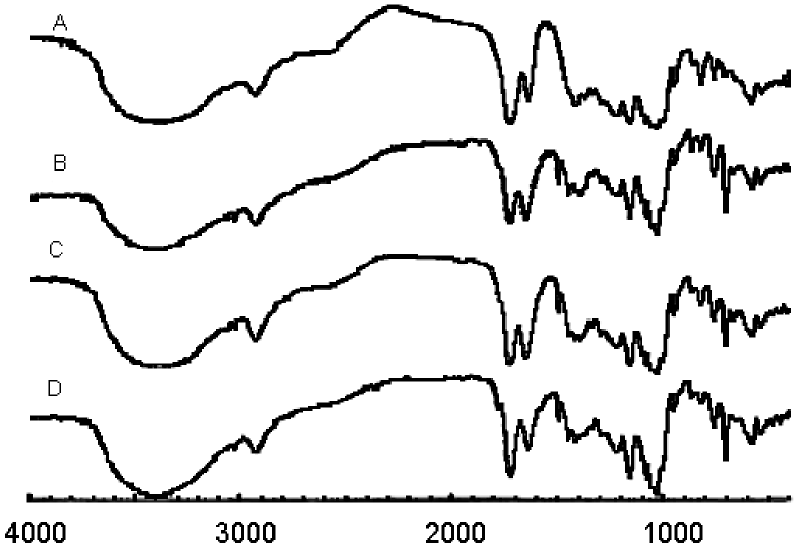

Fig. 4 The IR spectra of (A) functionalized β-CD; (B) copolymer; (C) copolymer Cu^{2+} complex; (D) copolymer Ag^{+} complex

The interactions of the metal ions with the copolymer exhibit not only the electrovalent bond character but also the covalent bond character. In figure 2, the UV absorptions of the copolymer metal complexes are different from the original copolymer, illustrating the carboxyl groups' chelation of the metal ions. Broad absorption peaks from 200 nm to 230 nm (Ag^+ complex, Curve C) and from 200 nm to 250 nm (Cu^{2+} complex, Curve D) appeared. After the metal-oxygen bond formed, the absorption of the carboxyl groups was reduced. Thus, the absorption peaks of copolymer metal complexes show an Einstein shift when compared with those of the uncoordinated copolymer. From this we conclude that coordination of the metal ions by the carboxyl groups of the partially substituted β-CD occurred.

Figure 5 is a typical polymer ^{13}C NMR spectrum, showing broadened peaks. After the polymerization of styrene and the functionalized monomer, the methylene group at 40 ppm and aromatic carbons at 126, 128, and 145 ppm appeared in the ^{13}C NMR spectrum of the copolymer. As a result, we confirmed that the monomers of styrene and part (6-O-butene diacid ester)-β-CD had indeed been polymerized.

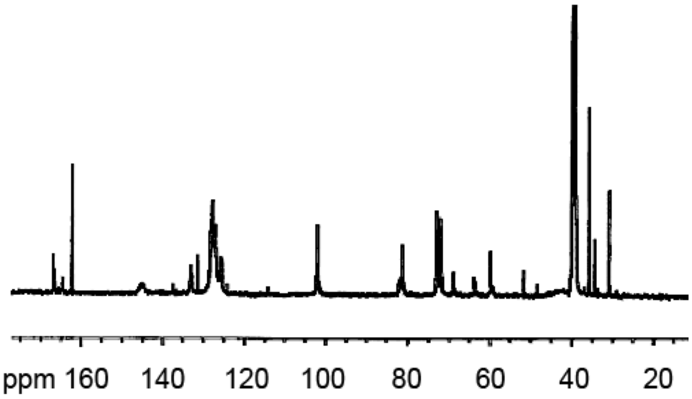

Fig. 5 The ^{13}C NMR spectra of copolymer

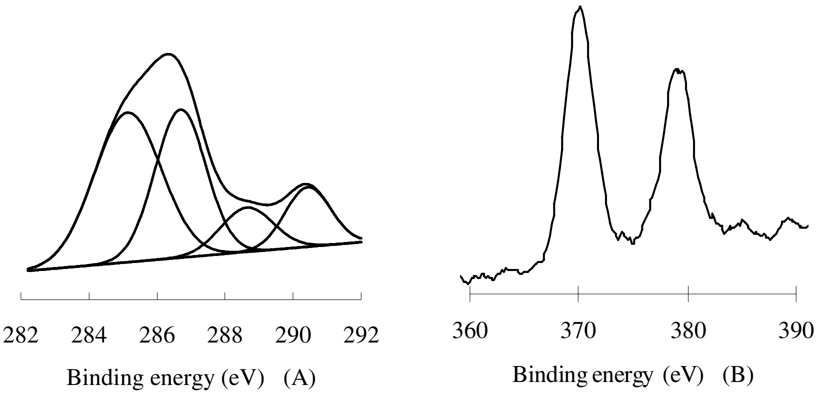

Fig. 6 The XPS spectra of copolymer metal (Ag^+) complex: (A) the peaks of C 1s; (B) the peaks of Ag 3d

XPS was used to confirm the formation of the copolymer Ag^+ complex. Figure 6 (A) is the C 1s of the copolymer Ag^+ complex. The C 1s spectrum appears around 285 eV with a broad shoulder at the higher binding energy and can be curve-fitted with four peaks of binding energy at approximately 285.0, 286.5, 288.8, and 290.2 eV. They are assigned to the (1) aliphatic hydrocarbon (C-C/C-H), (2) an ester-induced, α-shifted carbon (C-COO), (3) the methyl ester (C-O), and (4) the carbonyl carbon (C=O) respectively [14]. The fitted peaks are in accordance with the theoretical structures of the copolymer metal complex. The peaks in figure 6 (B) are of the Ag^+ 3d, which are observed at 369.3 and 376.0 eV. The peaks of Cu^{2+} 2p of the copolymer metal complex are seen at 961.8, 954.4, 942.2, and 934.4 eV. The above results are robust proof of the formation of functionalized β-CD copolymer metal complexes.

The DSC data displayed in figure 7 indicate that the thermal property of the copolymer was improved greatly after metal ions are introduced into copolymer. Compared with the Tg of the uncomplexed copolymer (181 °C) the Tg of the Ag^+ complex is 185 °C, an increase of 4 °C. However, no Tg value of the copolymer Cu^{2+} complex was obtained from 100 to 200 °C. Because the functionalized monomer contains multiple unsaturated bonds, the copolymer could potentially form cross-linked structures, which would be considerably more heat-resistant. The degree of cross-linkage is increased after metals were introduced into copolymer. Because metal ions can coordinate with the multiple carboxyl groups of multiple copolymer units, the net effect is similar to that obtained with a traditional cross-linking agent; intermolecular friction increased and the movement of the copolymer's macromolecular chains was restricted [15]. We also noticed that the Tg's of the copolymer and its metal complexes are different. This is because each specific metal ion possesses particular complex conditions, i.e. the intensity of the complex's bond and degree of coordination around the central cations are different, giving rise to different degrees of cross-linked copolymer structures. The copolymer Cu^{2+} complex displays a high degree of cross-linkage.

The cyclic voltammogram (figure 8) of the copolymer Cu^{2+} complex shows that the reduction potentials are -0.79 V and -0.32 V, and that the corresponding oxidation potentials are -0.53 V and -0.23 V respectively, demonstrating that the Cu^{2+} complex

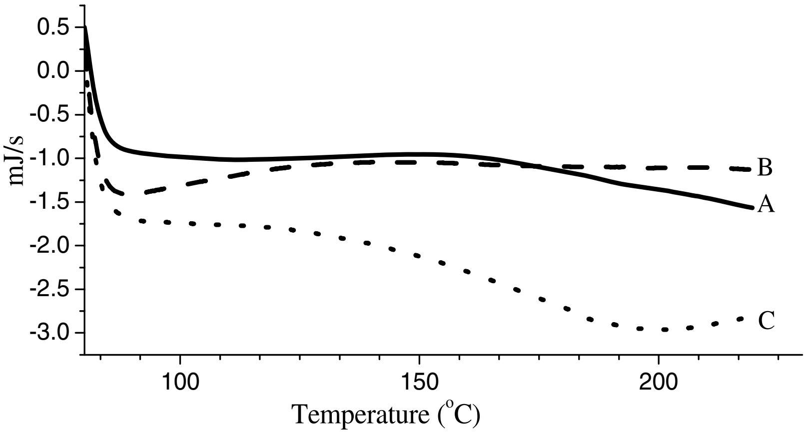

Fig. 7 The DSC Spectra of (A) copolymer; (B) copolymer Cu^{2+} complex; (C) copolymer Ag^+ complex

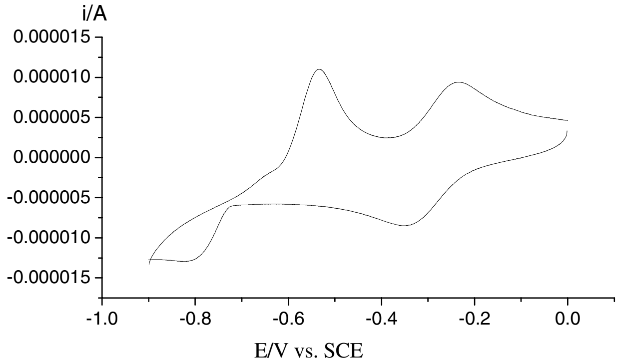

Fig. 8 The CV spectrum of copolymer Cu^{2+} metal complex

has undergone a gradual oxidation process. It suggests that a redox process between the ligands and Cu^{2+} has taken place. Furthermore, on continuous rescanning within this range of potentials, the Ip and Ep showed negligible change. This indicates that the complex possesses stable redox properties. Because the copolymer Cu^{2+} complex possesses quasi-reversible redox potentials of -0.32 V (reduction potential) and -0.23 V (oxidation potential), the transfer of electrons between the central metal ions and the ligand must be fast [16,17]. Thus, the metal complexes can be used as prospective electrode materials and in electrocatalytic chemistry.

As seen in figure 9, the reduction potential of the copolymer Ag^{+} complex is -0.29 V, with an oxidation potential of 0.30 V. This negative reversible redox potential indicates that the transfer of the electrons between the metal ion and its ligands is difficult for this system. However, the data does show that the introduction of metal ions improved the properties of copolymer. These results are consistent with those results of UV and ESR also. The pointed peak at 0.11 V is given by the Ag/Ag^{+} electrode.

The paramagnetic nature of the copolymer Ag^{+} and Cu^{2+} complexes can be derived from the results of ESR. The factors of g's are as follows: Cu^{2+} $g_{//}$=2.3501, $g_{\perp}$=2.0447; Ag^{+} g_1=2.1556, g_2=2.0492, g_3=1.9932. At room temperature, the curve of the Ag^{+} complex is multithreading and broad; in addition, the superfine structure did not

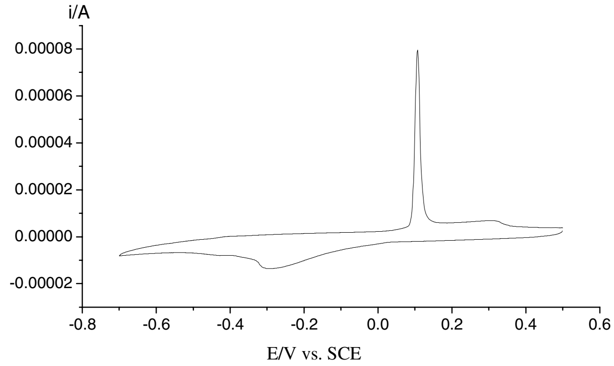

Fig. 9 The CV spectrum of copolymer Ag^{+} metal complex

appear, indicating the materials are combined and that the ions display intense reciprocity with each other. The $A_{//}$=2.4606 of Cu^{2+} complex shows the reciprocity between Cu^{2+} ions is feeble. From this, we conclude that the environment around the central metal ions is different for the two copolymer metal complexes [18]. However, the cross-linking action of metal ion is similar to that described above. The ESR data suggests that the copolymer metal complexes formed different degrees of cross-linked structures dependent upon which metal was used, Cu^{2+} or Ag^{+}.

Conclusions

A novel functionalized β-CD copolymer and its metal complexes have been synthesized and characterized by means of IR, UV, MS, NMR, XPS, DSC, CV and ESR. The functionalized copolymer possesses a strong ability to coordinate ions via its multiple carboxyl groups and Ag(I) and Cu(II) complexes derived from this copolymer possess electrochemical activity and magnetic properties. That the formation of the metal complex is quick suggests this functionalized β-CD copolymer may have applications as an excellent metal scavenger. In addition, the copolymer metal complex is composed of β-CD, polystyrene, and common metal ions making it suitable for use as an electrochemical catalyst material or even artificial enzymes.

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