

Synthesis and Characterization of Novel Star Polymer with β -Cyclodextrin Core and Its Metal Complexes

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ABSTRACT: A novel star polymer with β -cyclodextrin (β -CD) core and polyacrylonitrile arms and its metal complexes (Cu^{2+} , Zn^{2+} , and Ag^{+}) were synthesized and characterized by means of infrared spectra, ultraviolet, GPC, X-ray photoelectron spectroscopy, differential scanning calorimetry, cyclic voltammetry, and electron spin resonance. The results indicate that the monomers of acrylonitrile were initiated by functionalized β -CD. The thermal properties of star polymer

were improved greatly after transitional metal ions were introduced into it. The novel star polymer metal complexes possess properties of metal ions, polymer, and β -CD. Furthermore, it shows stable electrochemical activity. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 28–33, 2007

Key words: β -cyclodextrin; star polymer; polymer metal complex; electrochemical activity

INTRODUCTION

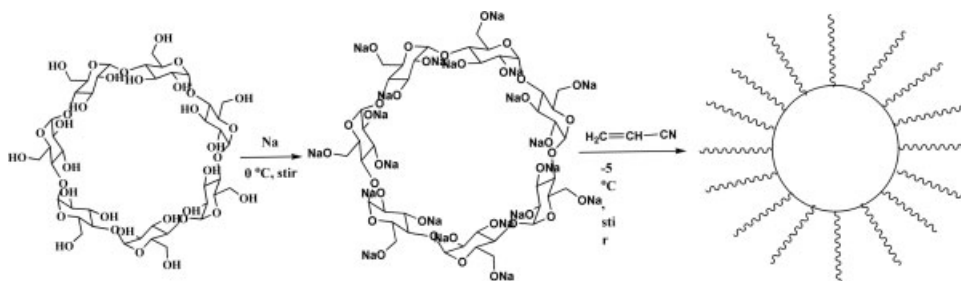
Star-shaped polymers are characterized as structures in which all the chains of a molecule are linked together to a small-molar-mass core. The interest in star polymers arises not only from the fact that they are models for branched polymers but also from their enhanced segment densities.¹ More recently, star polymers see increasingly widespread application as, for example, rheology control agents, dispersants, toughening agents, thermoplastic elastomers, membranes, and drug delivery systems.² As a consequence, efficient methods of construction of these multi-armed polymers and their precursors are highly sought after. Because cyclodextrin (CD) possesses many hydroxyl groups, it should be used for conforming star polymers. But at present, the star polymers containing CDs are seldom reported.

CDs are a series of cyclic oligosaccharides composed of six, seven, and eight glucose units linked by α -1,4 linkage, which are called α -, β -, and γ -CDs, respectively. The primary hydroxyl groups at C6 are located at the narrow side of the torus, whereas the secondary glucose hydroxyl groups are located at the wider side of the torus. Owing to their polar hydrophilic outer shells and hydrophobic cavities, one of the most important features of CDs and their

derivatives is their capacity to host various substances (drugs, pesticides, perfumes, and other products) in their hydrophobic inner cavities, thus forming encapsulated compounds.³ Because β -CD and their derivatives are widely recognized as excellent models for understanding general enclosed phenomena, enzyme–substrate and receptor–ligand interactions, etc.,^{4–7} and they have become available in high quantities; this kind of compounds has found extensive application in many areas such as food chemistry, cosmetic, and pharmaceutical industries. Furthermore, they can be used in organic chemistry or in polymer chemistry as well.⁸ Much attention has been paid to CDs and their derivatives and will last for a long term.

Polymer metal complexes (PMCs) have been the subjects with an increased interest in the fields of catalytic reactions, optical sensory materials, chemical sensors, magnetic materials and those in connection with biochemistry and environmental chemistry due to their particular properties. So they have aroused much more attention of some scientists in recent years and have shown widely applied prospects and values.⁹ Usually the ligands are composed of N, P, O, S with lone-pair of electrons such as pyridine, PPh_3 , $-\text{NH}_2$, $-\text{OH}$, $-\text{SH}$, carboxylic acid, etc.¹⁰ Then the transitional metal ions such as Fe^{3+} and Co^{2+} can be introduced into the polymer.¹¹ It is believed that the redox potential of an organic macromolecule is the same as or below that of the metal center. The design of new conducting macromolecular architectures containing transition metals in well-defined coordination

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Scheme 1 The synthetic process of star polymer.

environments has attracted much attention of some scientists.¹² The researches on the CD of complexes with metal ions have been extensively carried out but star polymers with β -CD metal complexes are seldom reported. For those, novel star polymers with β -CD core and polyacrylonitrile arms have been synthesized by classical anionic polymerization. The star polymer Cu^{2+} , Zn^{2+} , and Ag^+ metal complexes were also synthesized. The star polymer metal complex owns some particular properties such as electrochemical activity.

EXPERIMENTAL

Materials

Na (analytical grade) was purchased from Shanghai Chemical Co. (Shanghai, China) Methanol, acrylonitrile, acetone, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, ZnCl_2 , and AgNO_3 (analytical grade) were supplied by Beijing Chemical Factory (Beijing, China). All those reagents were used directly without further purification. β -CD was purchased from Shanghai Chemical Co. and recrystallized twice from water and dried under vacuum at 90 °C for 24 h. Dimethyl formamide (DMF) was supplied by Beijing Chemical Factory, dried by anhydrous MgSO_4 for 36 h and distilled under reduced pressure.

Instrumentation

Fourier transform infrared spectra (IR) were recorded on a Nicolet FT/IR-410 spectrophotometer. The samples used included solid powder. The ultraviolet (UV) spectrum was recorded on a Shimadzu UV-2450 spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out with an Escalab mark II spectrometer. Molecular weights and molecular weight distributions were measured on a Shimadzu CTO-10A VP GPC system using DMF as eluent. DSC (differential scanning calorimetry) was measured on the Mettler Toledo Stare System DSC821e. The cyclic voltammogram (CV) was obtained on a HPD-1A Model bipotentiostat with a type 3086-23A₄ 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 electron spin resonance (ESR) was investigated by means of Bruker (German) ESR ER200D-SRC.

Synthesis of star initiator

β -CD (0.2 g, 1.76×10^{-4} mol) and Na (0.086 g, 3.7×10^{-3} mol) was added in anhydrous DMF (8 mL) and stirred for 3 h at 20 °C.

Synthesis of star polymer

Acrylonitrile (3 mL, 83 mmol) was dissolved in DMF (7 mL) and stirred for 20 min under 0 °C. The 1 mL star initiators were introduced into the system at -5 °C and stirred for 30 min. The mixture was immediately poured into ice water with furious stirring after the polymerization was terminated by diluted hydrochloric acid. The target deposition was filtrated and washed thrice with water and methanol. The product was dried under vacuum overnight at room temperature. Other two kinds of star polymers with different ratio of acrylonitrile and star initiators (6/1 and 9/1, v/v) were synthesized by adjusting the quantity of initiator and monomer with same reactive condition.

Synthesis of star polymer metal complexes

Star polymer metal complexes were prepared only from matrix containing ratio 1/6 (v/v) of initiator/monomer. The 10 mL DMF solution of star polymer (0.5 g) was dropped slowly into the tree neck flask that included 15 mL DMF and excess of metal ions with stirring at 80 °C for 12 h. After the precipitate was filtrated and washed by water, the product was dried under vacuum at 40 °C for 24 h. In addition, the synthesis of star polymer Ag^+ complex was performed in aphotic flask under argon to prevent Ag^+ from being oxidized.

RESULTS AND DISCUSSION

Characterization of star polymer

The synthesis of star polymer is depicted in the Scheme 1. The solution of β -CD became very slabby after Na had been added in this system. When the star initiators were introduced into the solution of acrylonitrile the reaction was exothermic at once.

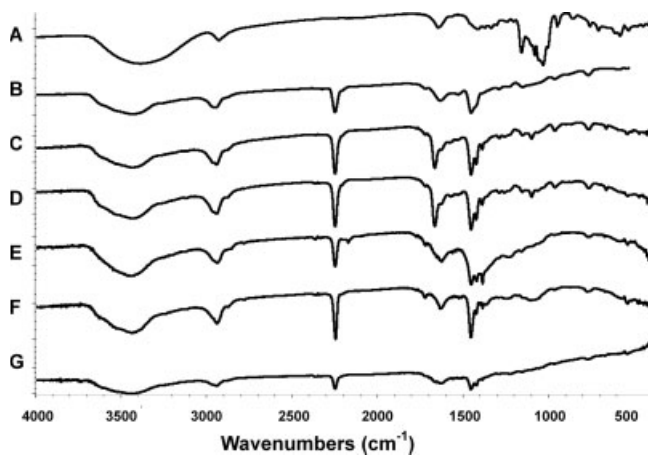


Figure 1 The IR spectra of (A) β -CD; (B) star polymer (1 : 3); (C) star polymer (1 : 6); (D) star polymer (1 : 9); (E) star polymer Ag^+ metal complex; (F) star polymer Cu^{2+} metal complex; and (G) star polymer Zn^{2+} metal complex.

Comparing with β -CD, the IR spectra (Fig. 1) of star polymers (B, C, and D) show a new intensive absorption peak at 2245 cm^{-1} attributed to stretching vibration of $-\text{CN}$ group. The absorption peaks at 1450 and 1422 cm^{-1} assigned to group of $-\text{CH}_2-$, and the peak at 1230 cm^{-1} attributed to stretching vibration of $-\text{CH}_2-$ and $-\text{CN}$. When the content of polyacrylonitrile increased, the intensity of absorption peaks at 2245 , 1450 , and 1422 cm^{-1} were enhanced. In addition, the absorption peak of star polymers at 1230 cm^{-1} is bigger than the peak at 1250 cm^{-1} , which suggest that the arms of star polymers possessed isotactic structure acting as the reference reports.¹³ The absorption peak at 2930 cm^{-1} of star polymer is reduced, which reveals that the ringed hydrogen bond formed by hydroxyls of the anhydroglucose unit in β -CD has disappeared. Furthermore, because the absorption peaks at 580 and 948 cm^{-1} assigned to the vibration of the ring and the skeleton including α -1,4 linkage of β -CD still remain, the orbicular structure of β -CD is not destroyed after monomers have been initiated and polymerized. All data of IR show that the production was composed of β -CD core and polyacrylonitrile arms.

Figure 2 is the UV spectra of the star polymers and polyacrylonitrile. It shows that the evidence absorption peak of star polymers appear at 306 nm compared with absorption peak of polyacrylonitrile at 308 nm , which are due to the $n \rightarrow \pi^*$ transitions of $-\text{CN}$ group. Compared with the UV absorption spectrum of β -CD in which no peaks appeared from 200 to 400 nm indicates that acrylonitrile has been initiated by functionalized β -CD. Star polymers with different ratio of β -CD and polyacrylonitrile were synthesized.

Table I shows the data of T_g and molecular weights tested by DSC and GPC. It shows that the

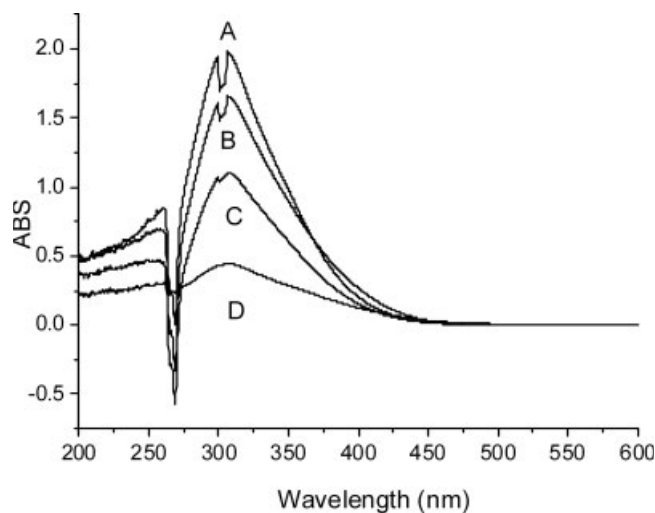


Figure 2 The UV spectra of star polymers with different rate of β -CD and polyacrylonitrile (V : V) (A) 1 : 3; (B) 1 : 6; (C) 1 : 9; and (D) polyacrylonitrile.

T_g 's of star polymers are 87.6°C (1 : 3), 73.1°C (1 : 6), and 70.8°C (1 : 9), respectively. Clearly, as polyacrylonitrile increased the T_g of star polymer decreased. Two factors are important to this. First, the rigidity and heat-resistant property of β -CD is higher than polyacrylonitrile. Thereby, star polymer (1/3) with the highest content of β -CD possesses the highest T_g (87.6°C). Second, as the length of flexible polyacrylonitrile is increased the T_g of star polymer also decreased. The data of GPC show that all the polydispersities (M_w/M_n) of star polymers were low by about 1.1, which suggest that the method of synthesis is anion polymerization. But we notice that the designed molecular weights (M_{th}) and tested molecular weights of star polymers are greatly different. This is because, first, the star polymers are composed of polyacrylonitrile and β -CD, which bring error of test with standard sample (polystyrene) of GPC. Second, the spatial structures of star polymer are complex and the star polymer possesses many branches that affect fixed phase of GPC. The star polymer will spend more reserved time in GPC, which lead tested molecular weights less than designed molecular weights.

XPS analyses were carried out to determine composition of the star polymer. In these experiments, all of the C 1s signals are due to the polymer chains of polyacrylonitrile and β -CD. In the XPS spectra of

TABLE I
The Data of Star Polymers and Its Metal Complexes

Sample	T_g ($^\circ\text{C}$)	M_n	M_w	M_w/M_n	M_{th}
Star polymer (1 : 3, v/v)	87.66	16,328	17,993	1.10	28,237
Star polymer (1 : 6, v/v)	73.15	17,028	19,007	1.11	55,339
Star polymer (1 : 9, v/v)	70.88	18,073	19,698	1.08	82,441

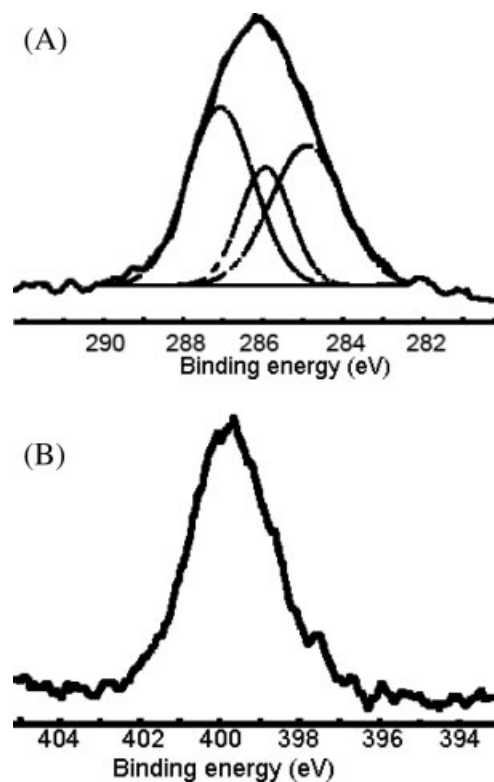


Figure 3 The XPS spectra of star polymer (1 : 6): (A) the peaks of C 1s; (B) the peak of N 1s.

star polymer, the broad C 1s peaks appeared around 285.0 eV. According to Ref. 14, careful peak fitting on the C 1s peaks resolves three peaks representing different carbons in star polymer¹: aliphatic hydrocarbon (C—C/C—H, at a binding energy of 284.9 eV),² the nitrile group (C—N at 286.1 eV), and³ ether or hydroxy carbon (C—O at 287.3 eV) [Fig. 3(A)]. On the basis of the aforementioned results, the C 1s peaks of the star polymer were fitted. N can be used as unambiguous elemental markers for the star polymer component for the acrylonitrile monomer, which showed N 1s peak at 400.0 eV in Figure 3(B), indicating the formation of the polyacrylonitrile arms from the β -CD core. Therefore, the star polymer was composed of polyacrylonitrile and β -CD. This result was consistent with the infrared results.

Characterization of star polymer metal complexes

The IR spectra of star polymer metal (Cu^{2+} , Zn^{2+} , and Ag^+) complexes [Fig. 1(E–G)] show that the intensive absorption peaks at 2245 and 1634 cm^{-1} shifted to low wave numbers because of the formation of new bond of complex. At the same time, those absorptions of star polymer metal complexes were feebler than that of star polymer, which indicate that the reaction of complex occurred between the —CN and cations. Obviously, the absorption peak at 1420 cm^{-1} of the star polymer Ag^+ complex

split and broaden, and the peaks of the star polymer Cu^{2+} and Zn^{2+} complexes at 1420 cm^{-1} also broaden. All those also reveal that the bonds of complex are formed between polyacrylonitrile and metal ions. This viewpoint has been proved also by the UV spectra. On the other hand, the isotactic structure of polyacrylonitrile (arms) and orbicular structure of β -CD (core) in star polymer metal complex still existed after metal ions were introduced into the star polymer because the absorption of 1230, 580, and 948 cm^{-1} did not changed.

The bonds of the metal ions with polyacrylonitrile exhibit not only the electrovalent bond character but also the covalent bond character. From Figure 4, it can be seen that the absorptions of star polymer metal complexes are different from star polymer, which shows that the —CN has participated in the complex bond with metal ions. Because Ag^+ and Zn^{2+} own d^{10} structure of outer electron, their polymer metal complexes can produce transition of charge-transfer. A new broad absorption peak at 385 nm appears in the UV spectrum of the star polymer Ag^+ complex that is due to the transition of charge-transfer (Ag^+). But the peaks of the $d \rightarrow d$ transition (Cu^{2+}) and transition of charge-transfer (Zn^{2+}) polymer metal complexes have been superposed by the absorption (306 nm) of star polymer, which show the broad absorption peak.

Data of DSC in Table I and Figure 5 indicate that thermal property of star polymer was improved greatly after metal ions were introduced into matrix. T_g 's of the three kinds of star polymer metal complexes are given in Figure 5. The T_g 's of star polymer Zn^{2+} , Cu^{2+} , and Ag^+ complexes are 91.56, 95.91, and 98.00°C, respectively. It is increased about 20°C

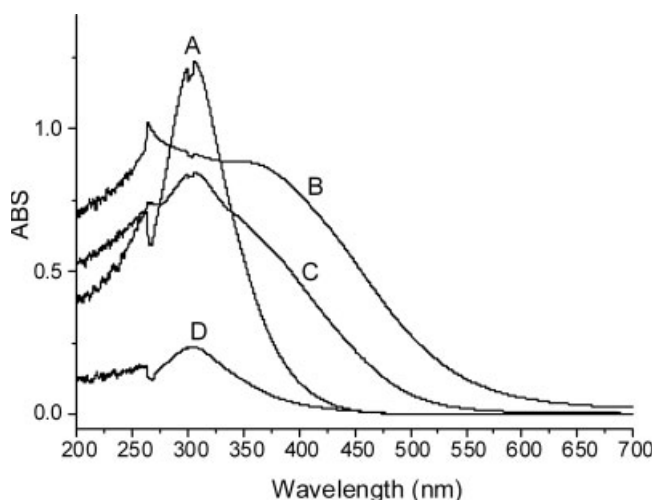


Figure 4 The UV spectra of star polymer and its metal complexes (A) star polymer (1 : 6); (B) star polymer Ag^+ complex; (C) star polymer Zn^{2+} complex; and (D) star polymer Cu^{2+} complex.

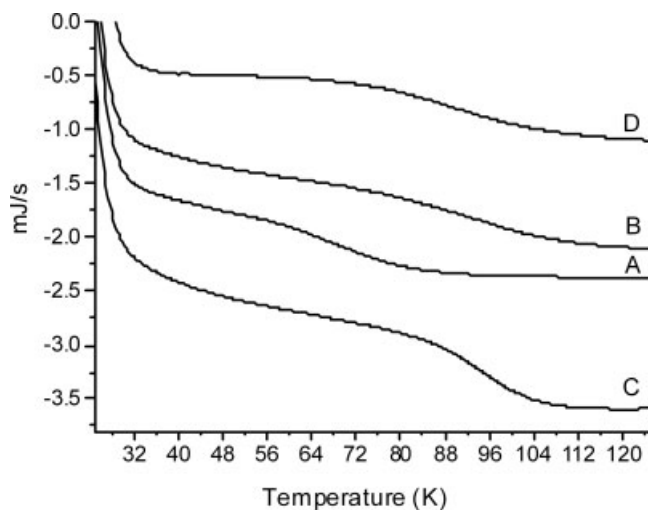


Figure 5 The DSC spectra of (A) star polymer (1 : 6); (B) star polymer Ag^+ complex; (C) star polymer Cu^{2+} complex; and (D) star polymer Zn^{2+} complex.

compared with T_g of matrix, 73.15°C . This is because metal ions can combine with ligands of star polymer. Thus, networks structures with crosslinked bonds between intrachain or interchain of polyacrylonitrile (arms) are formed. The use of metal ions is similar in effect to a crosslinked agent: intermolecular friction increased and the movement of macromolecular chains of star polymer was restricted.¹⁵ On the other hand, we notice that the T_g 's of the three kinds of star polymer metal complexes are different. This is because each kind of metal ions owns particular complex conditions, i.e., the complex bond intensity and number of ligand around the central cations are different, which aroused different degree of cross-linked networks structures of star polymer metal complexes.

Figure 6 shows XPS afford surface composition of star polymer metal complex. The content of metal ions in star polymer metal complex is very low. For example, binding energy peaks of Ag 3d appeared at 368.6 and 375.0 eV, which suggest that the content of Ag^+ on the surface of star polymer metal complex is 1.0%. From those we know the ability of combination between ligand ($-\text{CN}$) and cations is very feeble. At same time, the binding energy of carbon and oxygen has not changed, which indicates that the coordinates occurred between $-\text{CN}$ and metal ions and it did not affect $\beta\text{-CD}$. There are two peaks at 397.7 and 400.2 eV, which suggest that partial nitrile groups take part in the bonds of complex.

Figure 7 is the CV of Cu^{2+} complex, with the reduction potential at -0.35 V and the oxidation potentials at -0.22 and 0.02 V, respectively, which shows that the Cu^{2+} complex has undergone a gradual oxidation process. It suggests that a redox process between the ligands and Cu^{2+} has taken place.

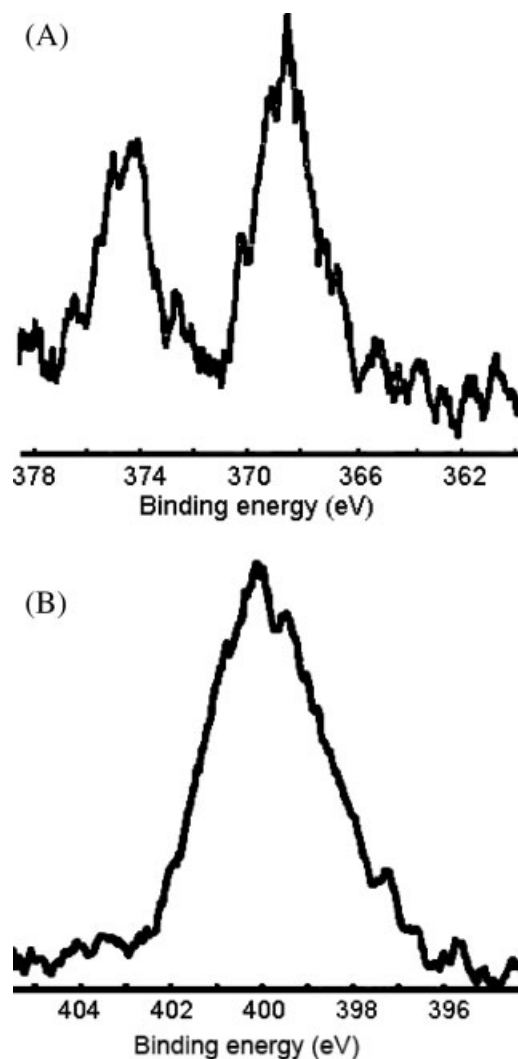


Figure 6 The XPS spectra of star polymer metal (Ag^+) complex (A) the peaks of Ag 3d; (B) the peak of N 1s.

Furthermore, on continuous rescanning in this range of potentials, the I_p and E_p almost did not change. This indicates that the complex owns stable redox property. Because the star polymer Cu^{2+} complex possesses quasi-reversible redox electric potential at -0.35 V (reduction potentials) and -0.22 V (oxidation potential), the transfer of electrons between the

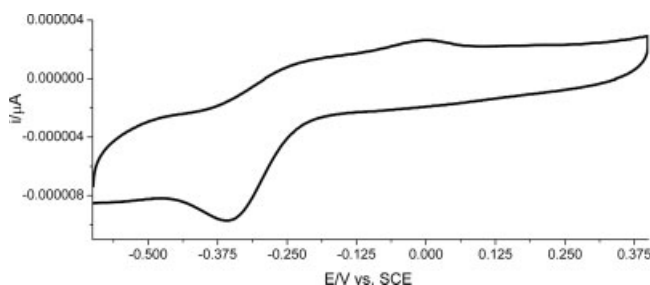


Figure 7 The CV spectrum of star polymer Cu^{2+} metal complex.

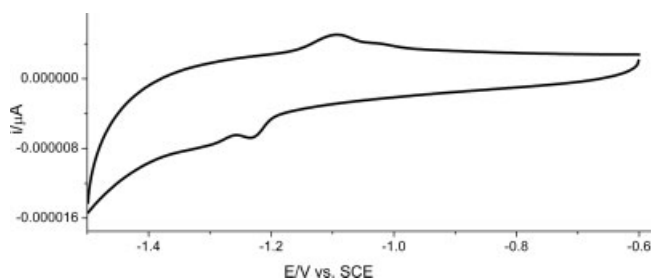


Figure 8 The CV spectrum of star polymer Zn^{2+} metal complex.

central metal ions and the ligands is fast and easy. Thus the metal complex can be used as electrode material and in electric catalytic chemistry.

Figures 8 and 9 are the CVs of the star polymer Zn^{2+} and Ag^+ complexes. Compared with those of the star polymer Cu^{2+} complex, the reduction potentials of the star polymer Zn^{2+} and Ag^+ complexes are at -1.23 V (Zn) and -0.37 V (Ag^+), the oxidation potentials are at -1.09 V (Zn^{2+}), -0.23 V (Ag^+), and 0.17 V (Ag^+), respectively, and they are all negative reversible redox electric potential, which suggest that the transfer of the electrons between the metal ions and the ligands of the complexes is difficult.

From ESR (Fig. 10), we can know that the star polymer (Cu^{2+}) complex is paramagnetic. And the factor g is given as follows: $g = 2.052$. At room temperature, the superfine structure did not appear, which indicates the materials are complicated and the particle display intense reciprocity with each other; furthermore, the circumstance central metal ions are different.¹⁶ Same results are obtained from those data, that in star polymer metal complex the metal ions are similar in effect to a crosslinked agent with bonding between ligands and metal ions. ESR data suggest that the star polymer metal (Cu^{2+}) complex is formed at different degree of crosslinked networks structures.

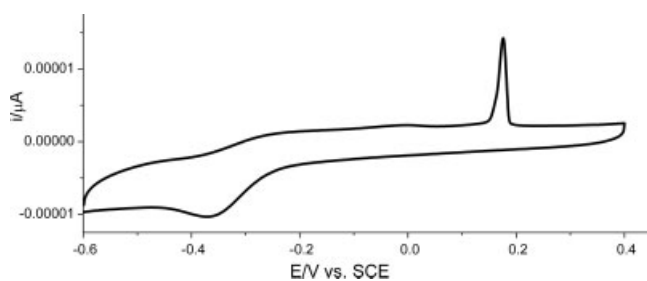


Figure 9 The CV spectrum of star polymer Ag^+ metal complex.

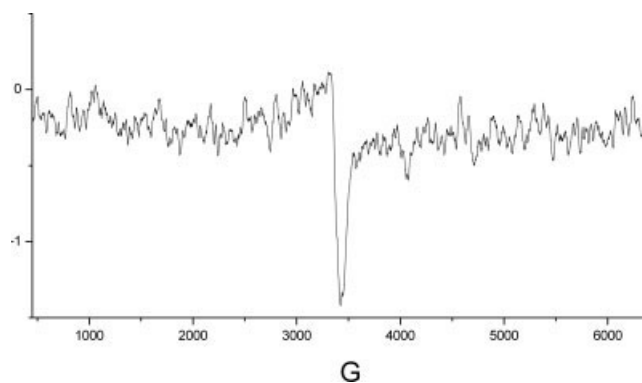


Figure 10 The ESR spectra of star polymer Cu^{2+} metal complex.

CONCLUSIONS

A novel star polymer with β -CD core and polyacrylonitrile arms and its metal complexes have been synthesized and characterized by means of IR, UV, XPS, GPC, DSC, CV, and ESR. The functional star polymer possesses coordination ability and its metal complexes present particular properties such as electrochemical activity and magnetic properties. Considered that star polymers possess the properties of β -CD, polymer, and metal ions, the novel functional materials may be used as catalyst electrochemical materials, artificial enzyme, etc.

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