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# Synthesis and characterization of 1,4,8,11-tetraazacyclotetradecane carrying poly(*p*-chloromethyl styrene-ethylene glycol dimethacrylate) microbeads and its metal ion-chelated forms

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## Abstract

Poly(*p*-chloromethyl styrene-ethylene glycol dimethacrylate) polymeric microbeads, poly(*p*-CMS-EGDMA), with an average size of 186 μm were synthesized by the suspension polymerization of *p*-CMS conducted in an aqueous medium. To increase the rigidity of the polymeric microbeads, EGDMA monomer was added to polymerization medium in the 25% for the cross-linking. 1,4,8,11-Tetraazacyclotetradecane ligand was reacted with polymer active groups that was *p*-CMS under a nitrogen atmosphere for 18 h at 65 °C. The maximum cyclam attachment was found 2.24 mmol/g polymer using an elemental analyser. Fourier transform infrared (FT-IR) spectrophotometer, thermogravimetric analyser (TGA) and differential scanning calorimeter (DSC) were used to characterize the plain, ligand modified microbeads and metal ion-chelated microbeads. TGA and DSC characterization of modified microbeads showed that stability of cyclam was increased attaching onto the polymer and metal ion-chelated form of the cyclam-modified polymer were more stable at high temperature for different applications.

*Keywords:* 1,4,8,11-Tetraazacyclotetradecane; Poly(*p*-chloromethyl styrene-ethylene glycol dimethacrylate); Metal–polymer complexes; Thermogravimetric analysis; Differential scanning calorimeter

## 1. Introduction

Removal of toxic metal ions from different water sources is very important and useful to clean water sources. Besides the toxic metal ions, separation and enrichment of precious metal ions gained a great importance to recover them selectively from the other metal ions in the recent years. Various techniques can be used for the removal of metal ions from aqueous solution, such as extraction, precipitation, dialysis, ion exchange and complexing agent modified polymers, both in microbeads and in membrane form [1–4]. In recent years, selective metal ion removal has been widely carried out using specific ligand modified polymers for the pre-concentration of some toxic metal ions and precious metal ions [5–9]. Some of these specific ligands are nitrogen containing cyclic ligands, especially for Cu(II), sulphur containing cyclic ligands for Hg(II) and Pb(II), oxygen containing cyclic ligands for Pb(II) [10–13]. Modified polymers with specific ligands are currently attracting considerable attention for a variety of applications in different

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fields [14,15]. The specific ligand bound polymers are used very conveniently for the pre-concentration or recovery of precious metal ions such as gold, platinum, palladium and silver. If the concentration of the precious metal ions are at low concentration in the aqueous sample beside the other concentrated metal ions, specific ligand bound polymer can be used very efficiently to recover the precious metal ions from the other metal ions [16,17]. Since the colour of the polymer varies with the oxidation-state of the metal ion present in the chelate, the polymer metal chelates were also found to act as electrochromic materials [18,19]. Using the metal-chelated form of ligand modified polymer, the stability of different oxidation-state of metal ion could be increased. In the chelate form of the polymer, the type and amount of the metal ion could change some different properties of the polymer [20].

A polymer–metal complex is a coordination complex resulting from the reaction of a ligand function anchored on a macromolecular matrix with a metal ion. The structural environment of the ligand function is one of the key factors determining the complexing ability of polymeric ligands with metal ions [21]. The thermal stabilities of polymer–metal complexes are modified by the polymer backbone, degree of cross-linking, the coordination geometry of the metal centres and ligand structure [22,23]. Thermogravimetric analyser (TGA) and differential scanning calorimeter (DSC) find very wide use in polymer chemistry. Therefore, a great deal of information is obtained about their thermal behaviour [24–27].

Poly(*p*-chloromethyl styrene-ethylene glycol dimethacrylate), poly(*p*-CMS-EGDMA), microbeads were first prepared by polymerization of *p*-CMS and EGDMA and then were modified with the specific 1,4,8,11-tetraazacyclotetradecane ligand. FT-IR, TGA, DSC, optical micrograph and elemental analyser were used to characterize all types of polymer. These specific microbeads were used in the adsorption of metal ions, such as Cu(II), Ni(II), Co(II) and Au(III), from aqueous solutions. Especially, the chemical structure of the modified polymer and its metal complexes were characterized by FT-IR. And also TGA and DSC were used to investigate the thermal stabilities of all types of polymer intensively.

## 2. Experimental

### 2.1. Materials

The monomer, *p*-CMS (Aldrich, Milwaukee, WI, USA) and the cross-linker EGDMA (Aldrich, Milwaukee, WI, USA) were used without further purification. Cyclohexane, CH (BDH, Poole, UK) was chosen as the diluent. Azobisisobutyronitrile (AIBN; BDH, Poole, UK) was crystallized from methanol and used as the initiator. Polyvinyl alcohol (PVA, $M_r$ 85,000–146,000, 87–89% hydrolysed; Aldrich, Buchs, Switzerland) was the stabilizer. 1,4,8,11-Tetraazacyclotetradecane was purchased from Aldrich (Buchs, Switzerland) and used as received. Sodium tetrachloro aureate ($NaAuCl_4$), nickel nitrate ($Ni(NO_3)_2$), copper nitrate ($Cu(NO_3)_2$) and cobalt nitrate ($Co(NO_3)_2$) were purchased from BDH (Poole, England). All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany).

### 2.2. Preparation of poly(*p*-CMS-EGDMA) microbeads

A modified version of suspension polymerization method proposed by Nonaka et al. [28] was used for the preparation of spherical poly(*p*-CMS-EGDMA) beads. A typical preparation procedure was exemplified below. Continuous medium was prepared by dissolving PVA (100 mg) in the distilled-deionized water (50 ml). For the preparation of dispersed phase, *p*-CMS (2.5 ml), EGDMA (0.75 ml) and CH (3.6 ml) were mixed and AIBN (60 mg) was dissolved in the homogeneous organic phase. The organic phase was dispersed in the aqueous medium by stirring the mixture magnetically (300 rpm) in a sealed cylindrical pyrex polymerization reactor. The reactor content was heated to polymerization temperature (i.e., 78 °C) within 40 min and the polymerization was conducted for 8 h with a 300 rpm stirring rate at 78 °C. Finally, the beads were washed with ethanol and water several times to remove any unreacted monomer or diluent and then stored in distilled water at +4 °C until use.

### 2.3. Cyclam attachment onto poly(*p*-CMS-EGDMA) microbeads

About 5.00 g of poly(*p*-CMS-EGDMA) polymer was placed in a 200 ml round-bottomed flask with

60 ml of $CHCl_3$ and left for 42 h at room temperature. Then 40 ml of $CHCl_3$ containing 2.50 g of cyclam was slowly added by a dripping funnel and the mixture was heated in a water bath with reflux condenser for 18 h under nitrogen atmosphere. The resin was filtered off and washed with chloroform, ethanol and water several times to remove any unreacted cyclam ligand, solvent and the other side products and then stored in distilled water at +4 °C until use. A part of the polymeric microbeads was dried at 60 °C in vacuum oven for the characterization of all polymeric microbeads.

### 2.4. *Characterization of poly(p-CMS-EGDMA) microbeads and their metal ion complexes*

FT-IR spectra of the cyclam, poly(*p*-CMS-EGDMA) microbeads, cyclam-modified poly(*p*-CMS-EGDMA) and modified polymer–metal ion complexes were obtained using FT-IR spectrophotometer (Nicolet 520 Model FT-IR Spectrophotometer, USA). About 0.02 g of each sample was thoroughly mixed with 0.1 g of KBr (IR Grade, Merck, Germany), and pressed into pellet form. The spectrum was then recorded.

TGA curves of cyclam, poly(*p*-CMS-EGDMA), modified polymer and modified polymer–metal ion complexes were obtained using a Du Pont model 951 TGA. The mass of the samples was generally in the range 5–7 mg. The sample pan was placed onto the balance and the temperature raised from 30 to 900 °C at a heating rate of 10 °C/min under nitrogen atmosphere at 25 ml/min. The mass of the sample pan was continuously recorded as a function of temperature.

Differential scanning calorimetry curves were obtained using a Du Pont models 910 DSC. About 5–7 mg samples of these hydrogels were analysed at a 10 °C/min heating rate under nitrogen atmosphere. DSC was used to obtain thermal stabilities of cyclam, plain microbeads, modified microbeads and polymer–metal ion complexes. The extent of cyclam attachment was determined by elemental analysis data of the dried samples obtained using an elemental analysis device (Leco, CHNS-932, USA).

### 2.5. *Metal ion adsorption to the cyclam-modified poly(p-CMS-EGDMA) microbeads*

Metal ion adsorption from single metal ion (nitrate salts of metal ions were used) aqueous solutions was investigated in batch adsorption experiments. The effects of the initial concentration of metal ions and the pH of the medium on the adsorption rate and capacity was studied. Aqueous metal ion solutions of 50 ml with different concentrations (in the range 0.01–10 mmol) was treated with the cyclam attached microbeads at different pH values (in the range 1.0–6.5, adjusted with NaOH and $HNO_3$) at room temperature, in flasks magnetically agitated at 500 rpm. The microbeads were separated from the adsorption medium at the end of the each adsorption experiment, and the remaining concentration of the metal ions in the aqueous phase was measured by an inductively coupled sequential plasma spectrometer (ICP, SHCMADZU, 1000 II Series, JAPAN). The adsorbed metal ion amount was calculated using the initial and final metal ion concentrations in the supernatant after the adsorption experiment.

## 3. Results and discussion

### 3.1. *Characterization of poly(p-CMS-EGDMA) and metal ion-chelated forms of modified poly(p-CMS-EGDMA) microbeads*

#### 3.1.1. *Characterization by optical micrograph*

In this study, the suspension polymerization procedure provided cross-linked poly(*p*-CMS-EGDMA) microbeads in a spherical form. From BET measurements, the specific surface area of poly(*p*-CMS-EGDMA) beads was found to be 14.1 $m^2$/g polymer [29]. Also optical photographs of poly(*p*-CMS-EGDMA), its modified form and metal ion-chelated forms are obtained (data not shown). The wet forms of poly(*p*-CMS-EGDMA) microbeads are opaque, which is an indication of the porosity in the matrix. However, the colour of the microbeads significantly changed and the colour of the microbeads became dark brown, dark blue, green and purple for the Au(III), Cu(II), Ni(II) and Co(II) complexes formed, which are a clear indication of the complexation of the metal ions to the surface structure of the poly(*p*-CMS-EGDMA) microbeads.

Elemental analysis of cyclam attached microbeads was carried out, the attachment of cyclam was found as 2.24 mmol/g polymer from nitrogen stoichiometry. This was the maximum attachment value achieved.

About 1 g of polymer was treated with 1.2 g of cyclam to obtain this value.

Metal ion adsorption capacity of the cyclam-modified poly(*p*-CMS-EGDMA) microbeads used in this study for the characterization of metal ion-chelated microbeads were found as 6.1, 3.7, 2.4 and 1.8 mmol/g polymer for Au(III), Cu(II), Ni(II) and Co(II), respectively. For all metal ions, adsorption pH was 5.0 and adsorption time was 24 h. These conditions were found to give maximum metal ion adsorption onto poly(*p*-CMS-EGDMA) microbeads following preliminary experiments and all of the parameters were obtained using single aqueous metal ion solutions. The selectivity of the cyclam-modified poly(*p*-CMS-EGDMA) microbeads for different metal ions in the competitive adsorption is under our investigation.

### 3.1.2. Characterization by FT-IR

For the characterization of poly(*p*-CMS-EGDMA), modified poly(*p*-CMS-EGDMA) with cyclam and metal ion complexes of the modified polymer, FT-IR spectra were recorded and are presented in Fig. 1. In Fig. 1, FT-IR spectra of cyclam, poly(*p*-CMS-EGDMA) and cyclam-modified poly(*p*-CMS-EGDMA) microbeads were carried out in order to clarify the possible structure of all beads. The bands at 3070 and 3250 cm$^{-1}$ in Fig. 1A were assigned to *cis* and *trans* stretching of N–H, as also pointed out by the chemical structure of the cyclam ligand. These two adsorption bands disappeared and a new broad band appeared when the poly(*p*-CMS-EGDMA) beads were modified with cyclam, as shown in Fig. 1C. The new broad adsorption band in this region was because of the symmetry change of four N–H functional groups on the cyclam ligand and the hydrogen bonding between the other N–H groups on cyclam and C=O groups on the cross-linker of EGDMA in the polymeric structure. The main change in the FT-IR spectrum of poly(*p*-CMS-EGDMA) was the disappearance of C–Cl stretching at 670 cm$^{-1}$ wavenumber (Fig. 1B). Intensity decreasing of two bands at 1265 cm$^{-1}$ (bending of Ar–CH$_2$–Cl) and 670 cm$^{-1}$ (stretching of Ar–CH$_2$–Cl) responsible for the chloromethyl group on poly(*p*-CMS-EGDMA) confirms the formation of a new C–N bond. This result indicates that the cyclam moieties are attached to the poly(*p*-CMS-EGDMA) microbeads through covalent C–N linkage.

The FT-IR spectrum of gold and copper complexes of the modified polymer is given in Fig. 2A and D. As shown in Fig. 2A and D, the N–H stretching adsorption band intensity in the range of 3200–3600 cm$^{-1}$ was decreased dramatically compared to the FT-IR spectrum of cyclam-modified poly(*p*-CMS-EGDMA)

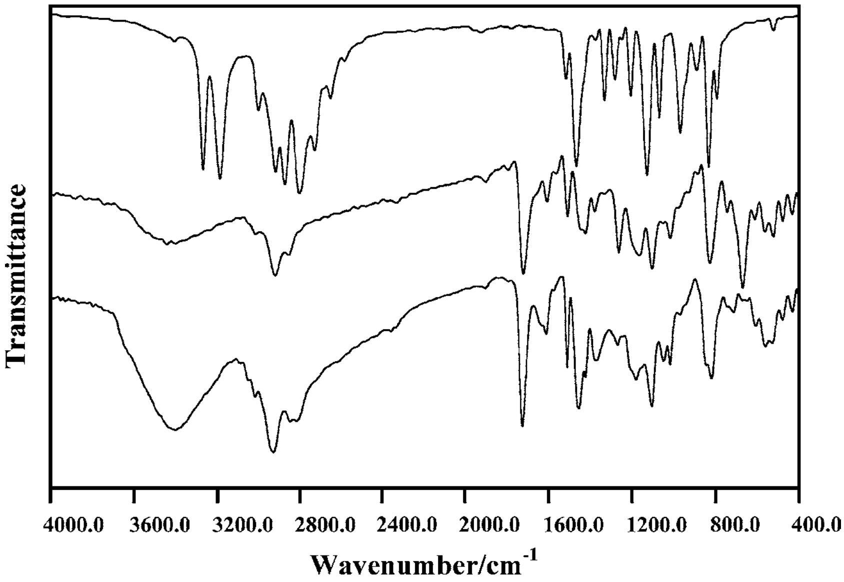

Fig. 1. FT-IR spectra: (A) cyclam ligand, (B) poly(*p*-CMS-EGDMA), and (C) cyclam-modified poly(*p*-CMS-EGDMA).

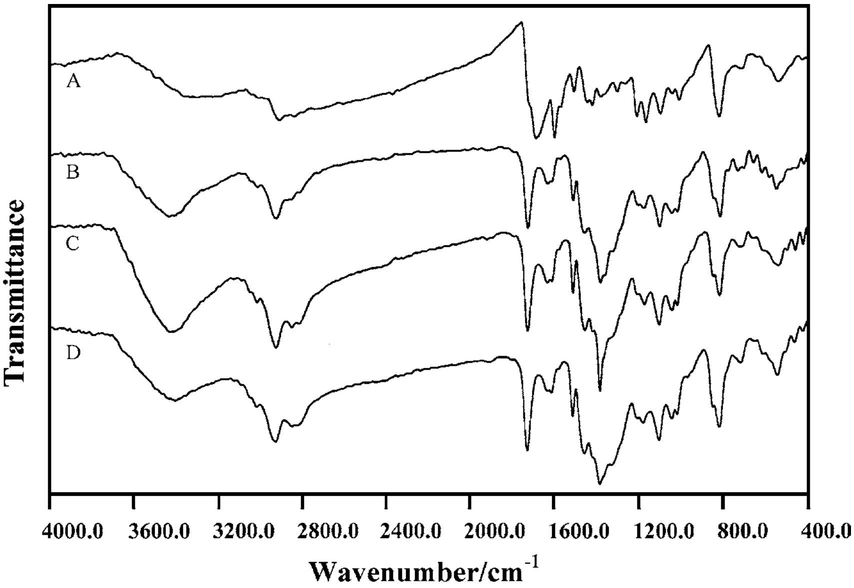

Fig. 2. FT-IR spectra: (A) poly(*p*-CMS-EGDMA)–Cu(II) complex, (B) poly(*p*-CMS-EGDMA)–Ni(II) complex, (C) poly(*p*-CMS-EGDMA)–Co(II) complex, and (D) poly(*p*-CMS-EGDMA)–Au(III) complex.

polymer. This is the case of complexation of gold and copper with N–H groups on the modified polymer. Also, new adsorption bands at 1595, 1530 and 1180 cm$^{-1}$ were characterized for the gold–polymer complex. In the case of complexes of the other metal ions (i.e., Cu(II), Ni(II) and Co(II)) with the polymer, all of the complex structures are similar each other, but those have a broad band in the range 1230–1550 cm$^{-1}$ that is related to polymer–metal complexes. When the cyclam monomer attached to poly(*p*-CMS-EGDMA), the FT-IR absorption bands of the polymeric structure were limited compared to the cyclam ligand absorption bands. This is due to a more rigid structure of the polymer compared to that of the cyclam ligand.

### 3.1.3. Characterization by TGA

For the thermogravimetric analysis of ligand and different types of microbeads in this study, cyclam,

Table 1
Phenomenological data of the thermal decomposition of cyclam, poly(*p*-CMS-EGDMA), modified poly(*p*-CMS-EGDMA) and metal complexes of cyclam-modified poly(*p*-CMS-EGDMA)

| Polymer/complex | Initial decomposition temperature in TGA, $T_i$ (°C) | Final decomposition temperature in TGA, $T_f$ (°C) | Peak temperature in DTG, *T* (°C) | | Mass loss up to 600 °C (%) |
|---|---|---|---|---|---|
| | | | First | Second | |
| Cyclam | 142 | 235 | 209 | – | 98 |
| Poly(*p*-CMS-EGDMA) | 215 | 620 | 392 | 454 | 83 |
| Cyclam-modified poly(*p*-CMS-EGDMA) | 235 | 555 | 328 | 442 | 87 |
| Cyclam-modified poly(*p*-CMS-EGDMA)–Cu(II) complex | 180 | 580 | 281 | 437 | 66 |
| Cyclam-modified poly(*p*-CMS-EGDMA)–Ni(II) complex | 190 | 520 | 298 | 441 | 80 |
| Cyclam-modified poly(*p*-CMS-EGDMA)–Co(II) complex | 210 | 550 | 302 | 449 | 78 |
| Cyclam-modified poly(*p*-CMS-EGDMA)–Au(III) complex | 340 | 525 | – | 447 | 35 |

poly($p$-CMS-EGDMA), cyclam-modified microbeads and polymer–metal complexes were used. In order to investigate the stability of the ligand and polymer and the interaction nature of metal ions onto the modified polymeric microbeads, dynamic and derivative thermogravimetric results were obtained for ligand and all types of polymer. TGA and DTG curves of ligand, plain and cyclam-modified polymeric microbeads are shown in Fig. 3. Also initial, final and peak temperatures with mass losses up to 600 °C are given in Table 1 for all species. Decomposition peak temperatures of cyclam, plain and cyclam-modified polymeric microbeads are 209, 392/454 and 328/442 °C. Decomposition of cyclam is in single step (Fig. 3A), but the decomposition of plain and cyclam-modified polymeric beads occur in two steps (Fig. 3B and C). In this case, there are two monomers: $p$-CMS and EGDMA in the polymeric structure. Because of two different monomers in the polymeric structure, decomposition is taking place in two steps. In the plain polymeric structure, the decomposition temperatures are about 392 and 454 °C. If cyclam is attached covalently to the polymeric structure, in this case the degradation temperatures are shifted to 328 and 442 °C. This shows that stability of the polymer is decreased, but this is not a dramatic decrease. However, first degradation temperature of modified polymer is 119 °C higher than the degradation temperature of cyclam. In this way, cyclam was stabilized in the polymeric structure after the modification. TGA curves of the modified polymer–metal ion complexes are given in Fig. 4 in order to examine the thermal stability of the species. The thermal stability order of modified polymer–metal ion complexes are Cu(II) < Ni(II) < Co(II) < Au(III) complexes, which have 281, 298, 302 and 447 °C for the first degradation temperatures. Polymer–Au(III) complex showed a single degradation temperature in contrast to the other three metal ion–polymer complexes. This is due to the nature of the complex structure of the polymer–Au(III) complex. In the polymer–Au(III) complex, Au(III) ion is staying on the exterior surface of cyclam ligand and making an extra interaction with the other functional groups in the polymer–Au(III) complex [30]. But all of the other metal ions, namely Cu(II), Ni(II) and Co(II), are in the interior cavity of cyclam ligand because the suitable their ionic radius fits inside the ring of cyclam ligand. Nevertheless, polymer–metal ion complexes are rather stable compared to the cyclam ligand stability in all cases. In the case of Cu(II), the initial decomposition temperature decrease is very high and is about 47 °C. This difference is because of the reactivity of Cu(II) with N–H groups on the cyclam and the low redox potential of Cu(II). If the amount of metal ion loaded onto the poly($p$-CMS-EGDMA) was increased with increasing

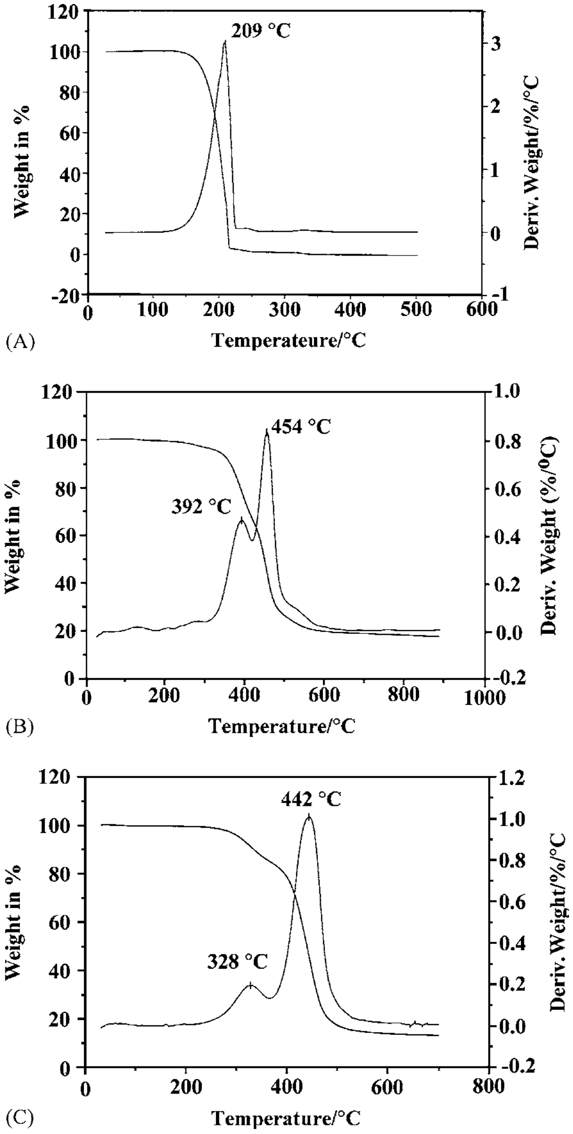

Fig. 3. TGA curves of: (A) cyclam ligand, (B) poly($p$-CMS-EGDMA), and (C) cyclam-modified poly($p$-CMS-EGDMA).

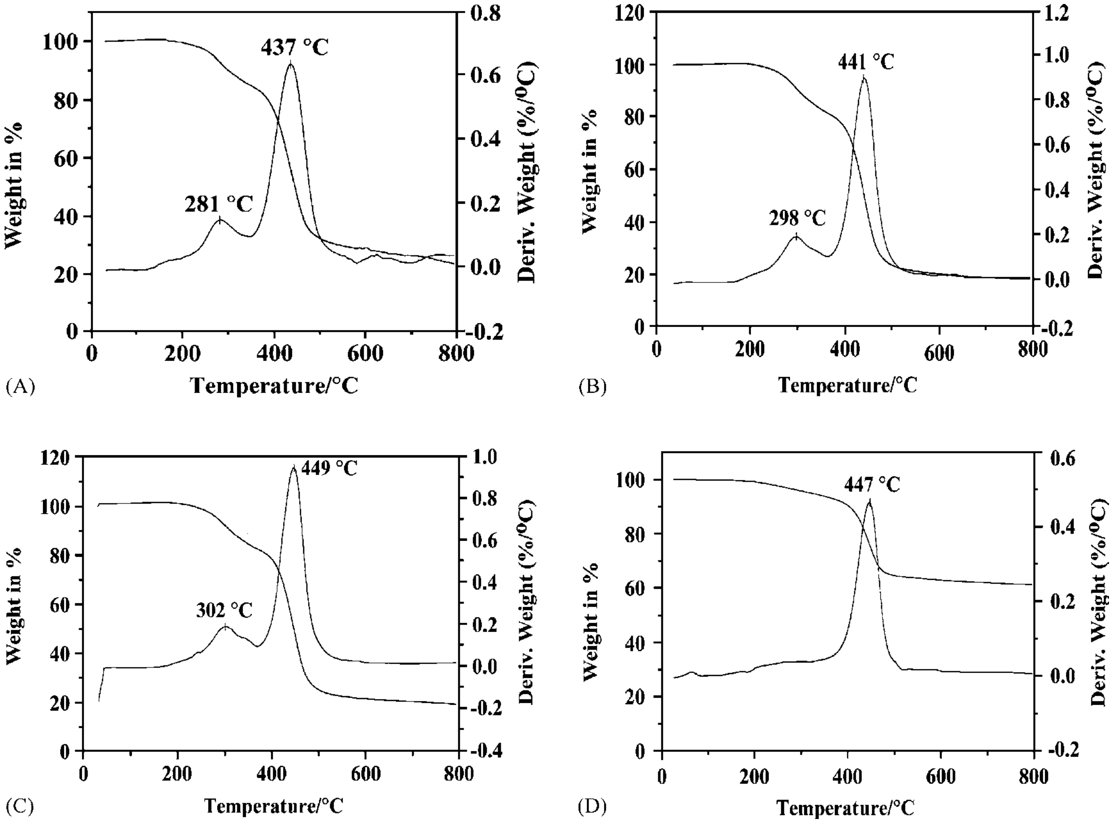

Fig. 4. TGA curves of: (A) poly(*p*-CMS-EGDMA)–Cu(II) complex, (B) poly(*p*-CMS-EGDMA)–Ni(II) complex, (C) poly(*p*-CMS-EGDMA)–Co(II) complex, and (D) poly(*p*-CMS-EGDMA)–Au(III) complex.

metal ion concentration in the adsorption medium, the first degradation temperature of the polymer–metal complexes could be increased. In this case, many degradation and transition temperatures are observed in TGA curves of polymer–metal complexes (data not shown). This type of study is under our investigation.

### *3.1.4. Characterization by DSC*

DSC was also used as a thermal analysis method for the characterization of polymer and its metal ion complexes. Fig. 5A shows the DSC curve for cyclam thermal degradation. The melting point of the cyclam was not observed in our case because of the amorphous structure of this ligand. The degradation of the cyclam leads to an increase of the heat capacity. In this case, the maximum limit is reached at about 193 °C, while the final temperature of chemical decomposition occurs around 221 °C, with some loss of heat capacity. When the cyclam-modified polymer was used, the stability of the modified cyclam was increased because of hydrogen bonding in the modified polymer (Fig. 5C). The decomposition enthalpy of the cyclam-modified polymer is higher than that enthalpy of plain polymeric microbeads. The higher decomposition enthalpy of cyclam-modified polymer is because of the re-organization after the modification and the inter hydrogen bonding capacity of ligand modified polymer. The hydrogen bonding capacity of cyclam-modified polymer is really high because of the existing of N–H groups on the cyclam and C=O groups on the EGDMA. That is why the decomposition enthalpy of plain polymer (17 and 28 J/g) is very low compared to the cyclam-modified polymer (76 and 104 J/g). In the DSC curves of metal ion-chelated forms of polymer, a transition peak was observed except for Au(III)–polymer complex (Fig. 6). Ionic

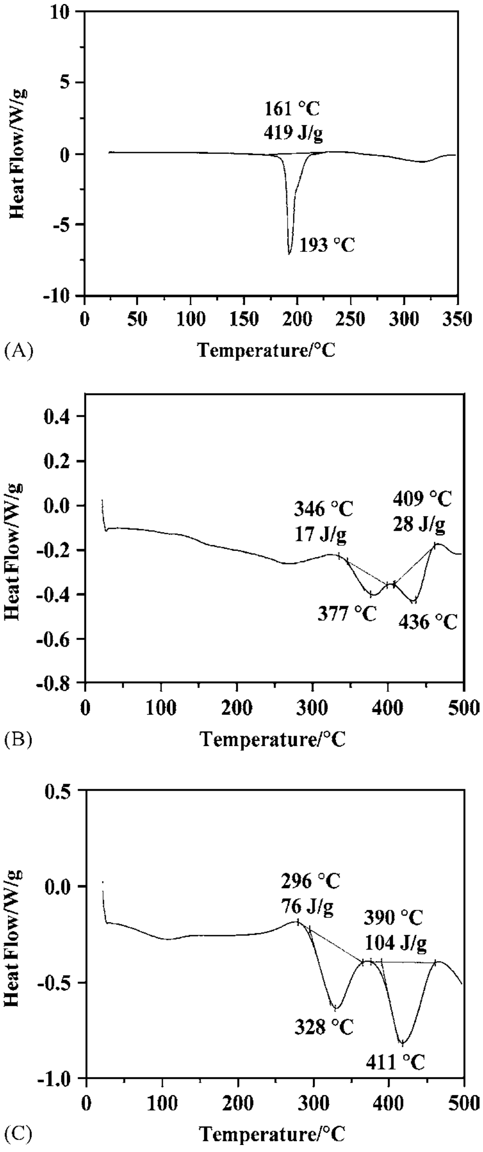

Fig. 5. DSC curves of: (A) cyclam ligand, (B) poly(*p*-CMS-EGDMA), and (C) cyclam-modified poly(*p*-CMS-EGDMA).

radii of Cu(II), Ni(II) and Co(II) fit the cavity of the cyclam ligand. In the complex, these metal ions are getting inside the cyclam cavity to form a complex. But the ionic radius of Au(III) is much high to fit in the cyclam cavity. In this case, Au(III) is complexing with cyclam ligand sticking on the exterior rim of cyclam. Because of this reason Cu(II), Ni(II) and Co(II)–polymer complexes are re-organizing at high temperatures and shifted from blue to yellow [30]. But the same situation is not valid for Au(III). That is why a transition peak before degradation was observed in the case of Cu(II), Ni(II) and Co(II) ion complexes. When Cu(II), Ni(II), Co(II) and Au(III) are incorporated into the modified polymer, the decomposition enthalpies of metal ion-chelated polymeric forms are changing (Fig. 6). In the case of Co(II) and Cu(II), decomposition enthalpies are increased comparing to the cyclam-modified polymer. After Co(II) and Cu(II) were incorporated to cyclam-modified polymer, addition of the inter hydrogen bonds in the modified polymer structure would be more stable. However, Co(II) and Cu(II) could be completed the interaction in the cavity of cyclam on the modified polymer and re-organized the metal ion–polymer structure. In this way, Co(II)– and Cu(II)–polymer complexes need more heat to degrade. As can be seen from Table 2, decomposition enthalpies of Co(II)– and Cu(II)–polymer complexes are higher than for the cyclam-modified polymer because of the explanation above. The maximum degradation enthalpy was observed for Co(II)–polymer complex. This is because the coordination number of six for Co(II) was completed with four nitrogen atoms in the cyclam and two C=O groups on EGDMA in the polymer structure. In the case of Ni(II), the degradation enthalpy value is very small compared to Cu(II) and Co(II)–polymer complexes. The reason is the low complex stability of Ni(II) with cyclam-modified polymer. It is also seen from the DSC curves that the stability of Au(III)-chelated form of polymer is less stable than the other metal ion–polymer complexes. Au(III) is staying on the exterior surface of the cyclam ligand onto the polymer and all of the hydrogen bonding in the cyclam-modified polymer was broken down. Thus, Au(III)–polymer complex would be thermally less stable than all the other type polymers. Table 2 summarizes glass transition ($T_g$) and enthalpy changes for the dissociation ($\Delta H_d$) values, which were obtained from DSC curves of all systems investigated. As can be seen from this table, $T_g$ value is available only for Au(III)–polymer complex. In addition, after metal ion chelation, the stability of the polymer increases and reaches to 411, 419, 427 and 433 °C for Ni(II), Co(II), Au(III) and Cu(II) complexes, respectively. These results are in conformity with $\Delta H_d$ values obtained from DSC curves.

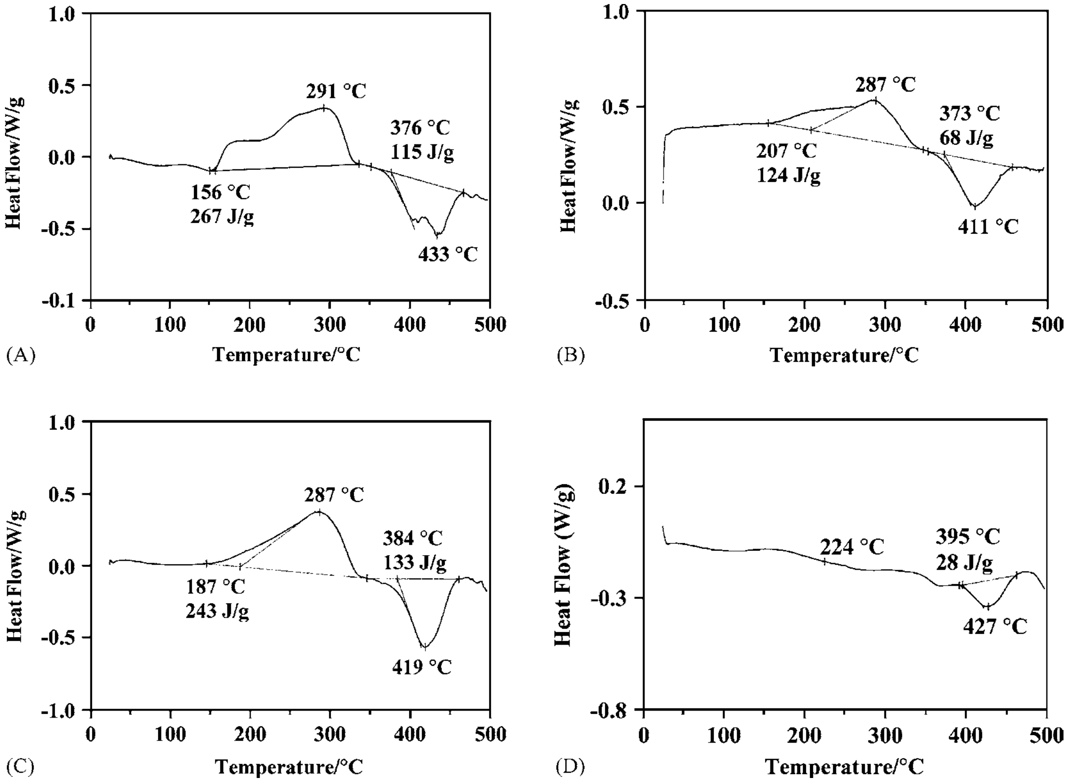

Fig. 6. DSC curves of: (A) poly(*p*-CMS-EGDMA)–Cu(II) complex, (B) poly(*p*-CMS-EGDMA)–Ni(II) complex, (C) poly(*p*-CMS-EGDMA)–Co(II) complex, and (D) poly(*p*-CMS-EGDMA)–Au(III) complex.

Table 2
$T_g$ and $\Delta H_d$ values obtained from DSC curves for all investigated systems

| Resin/complex | Glass transition temperature in DSC, $T_g$ (°C) | Decomposition enthalpy in DSC, $\Delta H_d$ (J/g) |
|---|---|---|
| Cyclam | – | 419 |
| Poly(*p*-CMS-EGDMA) | – | 17/28 |
| Cyclam-modified poly(*p*-CMS-EGDMA) | – | 76/104 |
| Cyclam-modified poly(*p*-CMS-EGDMA)–Cu(II) complex | – | 267/115 |
| Cyclam-modified poly(*p*-CMS-EGDMA)–Ni(II) complex | – | 124/68 |
| Cyclam-modified poly(*p*-CMS-EGDMA)–Co(II) complex | – | 243/133 |
| Cyclam-modified poly(*p*-CMS-EGDMA)–Au(III) complex | 224 | 28 |

From our thermal analysis studies, we can conclude that the thermal stability of cyclam-modified polymer increases after the adsorption of metal ions because of the strong interactions between modified polymer and metal ions. In addition, we observed that the thermal stability of cyclam on the polymer increases with different metal ion. These results show that the metal ion-chelated form of cyclam-modified polymer could be used efficiently for the some different applications at high temperature.

## 4. Conclusion

Cross-linked poly(*p*-CMS-EGDMA) was synthesized by the suspension polymerization of *p*-CMS conducted in an aqueous medium. 1,4,8,11-Tetraazacyclotetradecane was reacted with polymer. The FT-IR spectra for all different type polymers showed that modification and the metal complexes of the cyclam-modified polymer could be characterized by FT-IR spectroscopy. The maximum cyclam attachment was found to be 2.24 mmol/g polymer and adsorption capacities of the metal ions were very high. TGA and DSC characterization of modified microbeads showed that stability cyclam was increased by attaching cyclam onto the polymer and the metal ion-chelated forms of the cyclam-modified polymer were more stable at high temperature for different applications. Enthalpy values of the metal ion-modified polymer complexes show the complex stability of the species and transition of the complexes could be determined by DSC experiments.

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