

Synthesis and Polymerizations of New Metal Chelating Monomers from Alkyl α -Hydroxymethacrylates

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ABSTRACT: Two new diethyl iminodiacetate-containing monomers (EBMA-ID and CMAC-ID) were synthesized through the reaction of ethyl α -bromomethacrylate (EBMA) and α -chloromethacryloylchloride (CMAC) with diethyl iminodiacetate (ID). The hydrolysis of the ethyl ester groups with potassium hydroxide gave two chelating monomers with potassium salt of iminodiacetic acid (EBMA-IDA-K⁺ and CMAC-IDA-K⁺). The homopolymerization and copolymerization with 2-hydroxyethyl methacrylate (HEMA) of EBMA-ID and CMAC-ID were investigated by photodifferential scanning calorimetry at 40°C using 2,2'-dimethoxy-2-phenyl-acetophenone (DMPA) as initiator. The monomers showed very low homopolymerization reactivity which may be attributed to the steric effect of *N,N*-disubstituted methacrylamides, the presence of allyl amine group that can undergo degradative chain transfer and the bulky ID group close to the double bond. Also, addition of these

monomers to HEMA decreased polymerization rate and conversion with fraction added. EBMA-IDA-K⁺ and CMAC-IDA-K⁺ were copolymerized with acrylamide in water using 2,2'-azobis(*N,N'*-amidinopropane) dihydrochloride (V-50) initiator. Here also, it was observed that the incorporation of the synthesized monomers into acrylamide reduced both the rate of polymerization and conversion. The copolymers were characterized by ¹H-NMR spectroscopy, thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy. The UV-visible and TGA spectra confirmed that the synthesized monomers showed chelating ability for Ni⁺² and Cr⁺³. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 459–466, 2008

Key words: alkyl α -hydroxymethacrylate; iminodiacetate; metal-polymer complexes; photopolymerization; thermogravimetric analysis

INTRODUCTION

Polymer-metal complexes have attracted considerable attention because of their potential applications in waste-water treatment, recovery of trace metal ions, nuclear chemistry, dental composites, semiconductive materials, gas-membrane separation, organic synthesis, and in many other fields.^{1,2} They are prepared by complexation between a ligand group on a polymer and a metal ion or reaction of a ligand with metal ion and polymerization of metal-containing monomers. Typical ligands are carboxylic acids, aminopolycarboxylic acids, phosphonic acids, amines, imidazoles, thiols, etc. Among these ligands iminodiacetic acid (IDA) has important complexing ability and IDA-containing polymers have been synthesized by homopolymerization or copolymerization of the chelating monomers or polymers have been modified by addition of the chelating group. Synthesis of

new chelating vinyl monomers is very effective in the design of polymeric chelating agents. For example, a chelating monomer, GMA-IDA, has been prepared from the reaction of glycidyl methacrylate (GMA) and IDA³⁻⁷; *N*-(vinylbenzyl)iminodiacetic acid was evaluated as a new dental adhesive monomer providing strong and durable adhesion for the ceramic used in dentistry⁸; new fluoride-releasing dimethacrylate monomers containing bis(aminodiacetic acid) chelating ligand and its complex with zirconium and fluoride were synthesized for use in dental composites^{9,10}; molecularly imprinted polymers for the chiral separation of underivatized amino acids were prepared from the functional monomer, Cu(II)-*N*-(4-vinylbenzyl)iminodiacetic acid¹¹; metal chelating, hydrogel polymers that have antibacterial properties and which can be used in the fabrication of soft contact lenses were prepared from aminopolycarboxylic acids such as ethylenediamine tetraacetic acid (EDTA).¹²

In this study, diethyl iminodiacetate was used as a potential chelating as well as an adhesive group, and it was attached to alkyl α -hydroxymethacrylate derivatives, ethyl α -bromomethacrylate (EBMA) and α -chloromethacryloylchloride (CMAC), via reactive secondary amine hydrogen. The homopolymerization and copolymerization reactivities and the chelat-

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ing ability of the synthesized monomers with Ni^{+2} and Cr^{+3} and the thermal properties of the polymers were investigated.

EXPERIMENTAL

Materials

EBMA and α -chloromethacryloyl chloride (CMAC) were prepared according to the literature procedures.¹³⁻¹⁵ The photoinitiator, 2,2'-dimethoxy-2-phenylacetophenone (Irgacure 651 or DMPA from Aldrich, Taufkirchen, Germany) and the thermal initiator 2,2'-azobis(*N,N'*-amidinopropane) dihydrochloride (V-50) were used as received. All other solvents and starting materials were obtained from Aldrich Chemical and used as received.

Characterization

The monomer characterization involved ^1H - and ^{13}C -NMR spectroscopy (Varian Gemini 400 MHz) and Fourier transform infrared (FTIR) spectroscopy on NaCl plates (Perkin-Elmer, Altenholz, Germany). Photo-polymerizations were carried out by TA Instruments differential photocalorimeter (DPC) (Q100) containing a high-pressure mercury lamp. The chelating ability of monomers was measured with an ultraviolet-visible spectrophotometer (UNICAM-UV2). Gel permeation chromatography (GPC) analyses were done using HP 1050 series GPC with polyethylene oxide standards and thermogravimetric analyses were done with a TA Instruments (Q50).

Synthesis of the monomers

EBMA-ID

To a solution of EBMA (0.52 g, 2.69 mmol) in diethyl ether (3.5 mL) in an ice bath, triethylamine (0.28 g, 2.79 mmol) was added dropwise followed by diethyl iminodiacetate (0.51 g, 2.71 mmol). After stirring at room temperature for 1 day, the mixture was extracted with 1 wt % of HCl (3×10 mL), and the aqueous layer was back-extracted with dichloromethane. The organic layers were combined and dried with CaCl_2 . The evaporation of dichloromethane gave the product as light yellow oil in a 90.8% yield.

^{13}C -NMR (CDCl_3): $\delta = 14.21$ (CH_3), 54.82 ($\text{CH}_2\text{-N}$), 60.30 ($\text{O-CH}_2\text{CH}_3$), 126.52 (C=CH_2), 137.53 (C=CH_2), 166.19 (C=O), 170.84 ($\text{CH}_2\text{-C=O}$) ppm.

^1H -NMR (CDCl_3): $\delta = 1.18$ (m, 9H, CH_3), 3.48 (s, 4H, $\text{N-CH}_2\text{-C=O}$), 3.54 (s, 2H, $\text{CH}_2\text{-N}$), 4.07 (m, 6H, $\text{O-CH}_2\text{CH}_3$), 5.74 (s, 1H, $\text{CH}_2\text{=C}$), 6.15 (s, 1H, $\text{CH}_2\text{=C}$) ppm.

FTIR (neat): 2981 (C-H), 1740 (C=O, ester), 1632 (C=C), 1190 (C-O) cm^{-1} .

EBMA-IDA- K^+

To monomer EBMA-ID (0.57 g 1.89 mmol), equimolar amount of KOH (3.0 mL, 5.66 mmol) was added in an ice bath. The solution was stirred at room temperature for 12 h. After removal of water, the solid product was purified by dissolving in warm methanol and precipitating into acetone. Yield: 76.6%.

^{13}C -NMR (D_2O): $\delta = 56.11$ ($\text{CH}_2\text{-N}$), 58.08 ($\text{CH}_2\text{-C=O}$), 122.47 (C=CH_2), 143.30 (C=CH_2), 176.84 (C=O), 179.78 ($\text{CH}_2\text{-C=O}$) ppm.

^1H -NMR (D_2O): $\delta = 3.10$ (s, 4H, $\text{N-CH}_2\text{-C=O}$), 3.34 (s, 2H, $\text{CH}_2\text{-N}$), 5.39 (s, 1H, $\text{CH}_2\text{=C}$), 5.73 (s, 1H, $\text{CH}_2\text{=C}$) ppm.

FTIR (neat): 1577 (asymmetrical stretching of carboxylate anion), 1408 (symmetrical stretching of carboxylate anion) cm^{-1} .

CMAC-ID

To a mixture of CMAC (1.66 g, 11.9 mmol) and triethylamine (2.42 g, 23.9 mmol) in 16 mL of THF, diethyl iminodiacetate (4.53 g, 23.9 mmol) was added dropwise in an ice bath under nitrogen. The mixture was stirred at room temperature for 1 day. The formed precipitate was filtered off and the solvent was evaporated. The residue was dissolved in 10 mL of dichloromethane and washed twice with 10 mL of water. After the organic phase was dried with CaCl_2 , the solvent was removed to obtain the product as yellow oil in 91.1% yield.

^{13}C -NMR (CDCl_3): $\delta = 14.22$ (CH_3), 47.21, 51.10 ($\text{CH}_2\text{-N-C=O}$), 54.68 (N-CH_2), 56.97 ($\text{CH}_2\text{-N}$), 60.31, 61.05, 61.36 ($\text{O-CH}_2\text{CH}_3$), 116.78 (C=CH_2), 140.71 (C=CH_2), 168.37, 168.95, 170.64 (C=O), 171.62 (N-C=O) ppm.

^1H -NMR (CDCl_3): $\delta = 1.28$ (m, 12H, CH_3), 3.56 (s, 4H, $\text{N-CH}_2\text{-C=O}$), 3.59 (s, 2H, $\text{CH}_2\text{-N}$), 4.18 (m, 12H, $\text{O-CH}_2\text{CH}_3$ and N-CH_2), 5.28 (s, 1H, $\text{CH}_2\text{=C}$), 5.51 (s, 1H, $\text{CH}_2\text{=C}$) ppm.

FTIR (neat): 2983 (C-H), 1742 (C=O, ester), 1655 (C=O, amide), 1623 (C=C), 1448 (C-N), 1186 (C-O) cm^{-1} .

CMAC-IDA- K^+

To monomer CMAC-ID (0.75 g, 1.68 mmol), equimolar amount of KOH (3.6 mL, 6.73 mmol) was added in an ice bath and the reaction mixture was stirred at room temperature for 12 h. After removal of water, the solid product was purified by dissolving in warm methanol and precipitating into acetone. Yield: 58.5%.

^{13}C -NMR (D_2O): $\delta = 50.77$, 54.29 ($\text{CH}_2\text{-N-C=O}$), 56.58 ($\text{CH}_2\text{-N}$), 58.08 (N-CH_2), 119.15 (C=CH_2), 140.45 (C=CH_2), 173.85 (N-C=O), 175.85, 176.40, 179.46 (C=O) ppm.

$^1\text{H-NMR}$ (D_2O): $\delta = 3.26$ (s, 4H, $\text{N-CH}_2\text{-C=O}$), 3.45 (s, 2H, $\text{CH}_2\text{-N}$), 3.98, 4.07 (d, 4H, $\text{CH}_2\text{-N-C=O}$), 5.44 (s, 1H, $\text{CH}_2=\text{C}$), 5.63 (s, 1H, $\text{CH}_2=\text{C}$) ppm.

FTIR (neat): 1594 (asymmetrical stretching of carboxylate anion), 1397 (symmetrical stretching of carboxylate anion) cm^{-1} .

Thermal-polymerization procedure

The copolymerization of EBMA-IDA- K^+ and CMAC-IDA- K^+ with acrylamide (5 : 95 and 10 : 90) was carried out in water in sealed glass tubes containing the initiator (V-50) and the monomer. The tubes were degassed by freeze-evacuate-thaw procedures and placed in a constant temperature bath at 65–67°C. After a selected period of time, the polymer solutions were precipitated into acetone. Purification of the polymers was performed by dissolution in water and dialysis against water with tubing with a molecular cutoff of 6000–8000. The polymers were recovered by freeze drying.

Photo-polymerization procedure

EBMA-IDA and CMAC-IDA were homopolymerized at 40°C using 2.0 mol % Irgacure 651 as initiator. Also, EBMA-IDA (20 and 50 mol %) was copolymerized with 2-hydroxyethyl methacrylate (HEMA). Typically, 4 mg of sample was placed in an aluminum DSC pan and irradiated for 10 min with an incident light intensity of 15 mW/cm^2 . The DSC chamber was purged with nitrogen before and during polymerization. The heat flux as a function of time was monitored using DSC under isothermal conditions and both the rates of polymerization (R_p) and conversions were calculated as a function of time. The heat of reaction values, $\Delta H_p = 57.5$, 50.0 and 54.5 kJ/mol were used as the theoretical heat evolved for ethyl ester and 2-hydroxyethyl ester of methacrylic acid and methacrylamide double bonds respectively.^{16,17} The rates of polymerizations were calculated according to the following formula:

$$R_p = \frac{(Q/s)M}{n\Delta H_p m}$$

where Q/s is the heat flow per second during reaction, M is the molar mass of the monomer, n is the number of double bonds per monomer molecule, ΔH_p is the heat released per mole of double bonds reacted and m is the mass of the monomer in the sample.

Spectrophotometric measurements

The chelating abilities of EBBR-IDA- K^+ and CMAC-IDA- K^+ were investigated using UV-visible spectro-

scopy at 500–900 nm. First equimolar amount of metal and EBBR-IDA- K^+ stock solutions were prepared and maximum absorption value for the metal solution was obtained. Then, EBBR-IDA- K^+ solution was diluted and mixed with the metal solution in a 1 : 1 ratio. The same procedure was used for CMAC-IDA- K^+ also. As EBBR-IDA- K^+ or CMAC-IDA- K^+ was added to the metal solution, the maximum absorption values and the corresponding wavelengths were recorded. NiCl_2 and CrCl_3 were used as the salts of the metal solutions.

RESULTS AND DISCUSSION

Synthesis of monomers

The monomer EBMA-ID was prepared by the reaction of EBMA with diethyl iminodiacetate in the presence of TEA. It was obtained as a light-yellow oil with a yield of 90.8%. The hydrolysis of the ethyl ester groups with equimolar amount of KOH to the corresponding carboxylic acid salt gave a chelating monomer EBMA-IDA- K^+ as a white solid in 76.6% yield (Fig. 1). This monomer was soluble in water, whereas EBMA-ID was soluble in methanol, THF, diethyl ether, chloroform, and hexane. The complexing properties of EBMA-IDA- K^+ are expected to be higher than mono-IDA-containing monomers because the additional $-\text{COOK}^+$ group may pro-

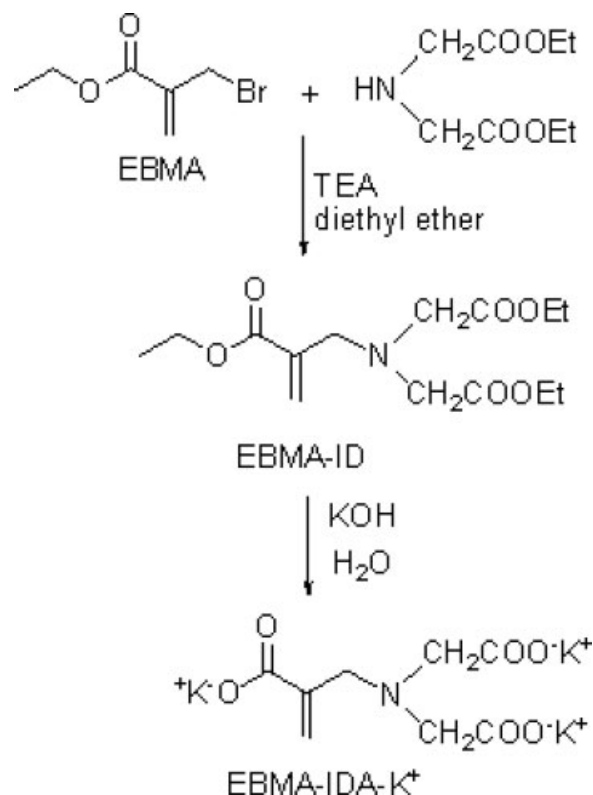


Figure 1 Synthesis of EBMA-ID and EBMA-IDA- K^+ .

vide additional interaction with metals and improve binding as observed in GMA-IDA.

The expected structures of the monomers were confirmed by NMR and FTIR spectroscopy. For example, the ^{13}C -NMR spectrum of EBMA-ID is characterized by methyl carbons at 14.21 ppm, methylene carbons attached to the nitrogen atom at 54.82 ppm, methylene carbon attached to the oxygen atom at 60.3 ppm, double-bond carbons at 126.52 and 137.53 ppm and carbonyl carbons at 166.19 and 170.84 ppm (Fig. 2). The FTIR spectrum of this monomer showed the characteristic absorptions of $\text{C}=\text{O}$ and $\text{C}=\text{C}$ at 1740 and 1632 cm^{-1} (Fig. 3). After hydrolysis both ^{13}C -NMR (Fig. 2) and ^1H -NMR spectra showed a complete disappearance of the ethyl groups of EBMA-ID. Also, in the ^{13}C -NMR there were significant shifts of the carbonyl carbons to 176.84 and 179.78 ppm. In the FTIR spectrum of EBMA-IDA- K^+ , a strong asymmetrical stretching band of carboxylate anion at 1577 cm^{-1} and a weaker, symmetrical stretching band of carboxylate anion at 1408 cm^{-1} were observed.

As an extension of this work, a new diethyl iminodiacetate-containing monomer (CMAC-ID) with identical amide and amine groups was synthesized by the reaction of CMAC with diethyl iminodiacetate in the presence of TEA as an acid scavenger and catalyst in THF (Fig. 4). CMAC-ID was also hydrolyzed by equimolar amount of KOH at room temperature to give monomer CMAC-IDA- K^+ . CMAC-ID was a yellow oil and soluble in methanol, CH_2Cl_2 , acetone, and ether but insoluble in hexane whereas CMAC-IDA- K^+ was a white solid soluble in water and methanol but insoluble in acetone. CMAC-IDA- K^+ has two of the IDA groups which are expected to increase the binding of metals.

The spectral data of these monomers were in agreement with the expected structures. The ^{13}C -

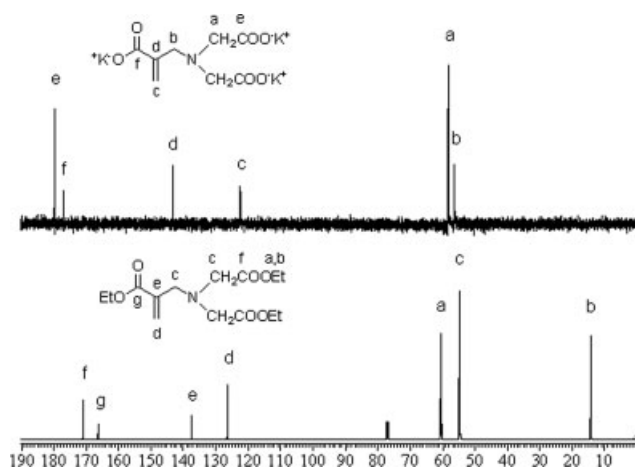


Figure 2 ^{13}C -NMR spectra of EBMA-ID and EBMA-IDA- K^+ .

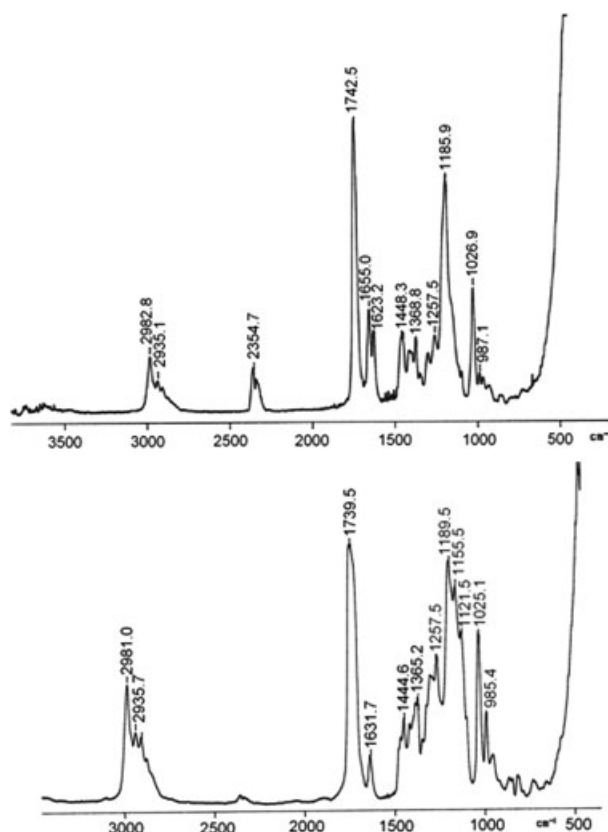


Figure 3 FTIR spectra of CMAC-ID (top) and EBMA-ID (bottom).

NMR spectrum of CMAC-ID showed methyl carbons at 14.22 ppm, methylene carbons attached to the amide nitrogen at 47.21 and 51.10 ppm (doublet), methylene carbons attached to the nitrogen atom at 54.68 ppm, methylene carbon attached to double bond carbon at 56.97 ppm, methylene carbons attached to oxygen atoms at 60.31, 61.05, 61.36 ppm, the double-bond peaks at 116.78 and 140.71 ppm, amide

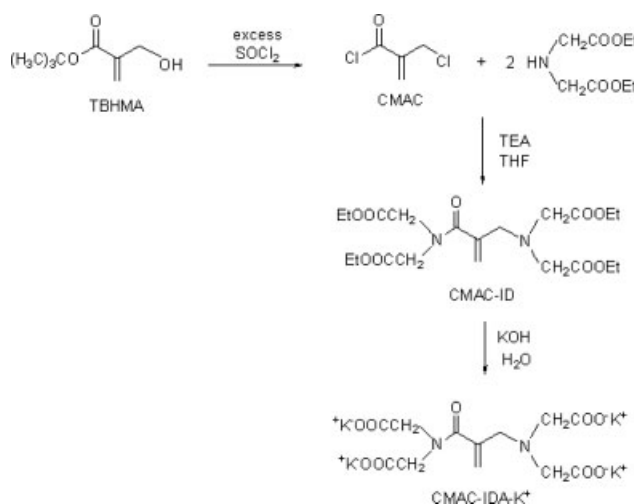


Figure 4 Synthesis of CMAC-ID and CMAC-IDA- K^+ .

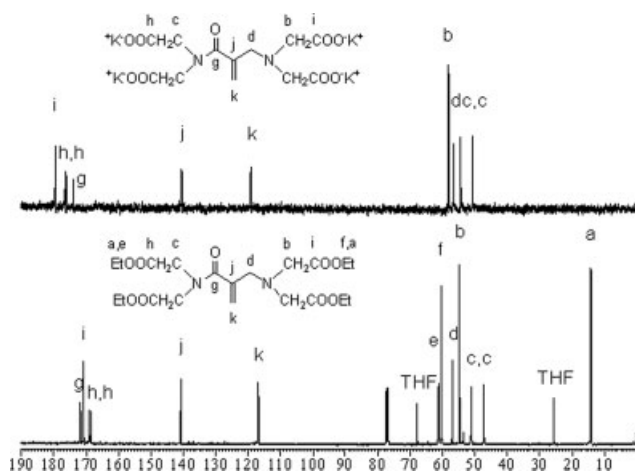


Figure 5 ^{13}C -NMR spectra of CMAC-ID and CMAC-IDA- K^+ .

carbonyl carbon at 168.37, 168.95 ppm and ester carbonyl carbons at 170.64 ppm and 171.62 ppm (Fig. 5). The FTIR spectrum of this monomer showed characteristic peaks for $\text{C}=\text{O}$ (ester), $\text{C}=\text{O}$ (amide), $\text{C}=\text{C}$ and $\text{C}-\text{O}$ at 1742, 1655, 1623 and 1186 cm^{-1} , respectively, (Fig. 3). The ^{13}C -NMR spectrum of CMAC-IDA- K^+ showed a complete disappearance of ethyl ester groups (Fig. 5). In the FTIR spectrum, a strong asymmetrical stretching band of carboxylate anion is at 1594 cm^{-1} and a weaker, symmetrical stretching band of carboxylate anion is at 1397 cm^{-1} .

Polymerizations

The homopolymerization reactivities of EBMA-ID and CMAC-ID in photo-polymerization were investigated with photo-DSC. All the polymerizations were performed under identical conditions of initiator concentration (2.0 mol %), UV light intensity (15 mW/ cm^2) and temperature (40°C). Photo-polymerizations of solid monomers EBMA-IDA- K^+ and CMAC-IDA- K^+ were not possible at this temperature. The maximum rate of polymerizations of monomer EBMA-ID and CMAC-ID were found to be 0.00057 and 0.00028 s^{-1} (Table I). The conversions were 9.4 and 6.5%. In these monomers, the steric effect of *N,N*-disubstituted methacrylamides reduce the conjugation between $\text{C}=\text{C}$ and $\text{C}=\text{O}$ double bonds; the presence of allyl amine group that can undergo degradative chain transfer and the bulky iminodiacetate group close to the double bond are the three factors decreasing the reactivity.^{18,19} CMAC-ID with all these three properties, is less reactive than EBMA-ID, which has the last two of them. To check the copolymerizability of the monomers, EBMA-ID was added at a concentration of 20 and 50 mol % to HEMA. The incorporation of EBMA-ID resulted in a decrease of polymerization rate and conversion of

HEMA (0.036 s^{-1} , 93.4%). The maximum rate of polymerizations and conversions were 0.0033 s^{-1} , 65.3% and 0.0016 s^{-1} , 33.4% for mixtures containing 20 and 50 mol % of monomer EBMA-ID.

The radical solution polymerization of EBMA-IDA- K^+ with HEMA (5 : 95) was run in water in the presence of V-50 at 65–67°C. However, a crosslinked polymer was obtained in less than 10 min. Then, polymerizations of EBMA-IDA- K^+ and CMAC-IDA- K^+ were carried out with acrylamide (AAm) (5 : 95 and 10 : 90) in water (Table II). The polymers were soluble in water and methanol, but insoluble in acetone and ether. Therefore, they were isolated by precipitation into acetone and purified by dialysis against water. Polymer yields after dialysis with 6000–8000 molecular weight cut off dialysis tubing were low and decreased with increasing EBMA-IDA- K^+ or CMAC-IDA- K^+ in the feed. This observation implies that polymers contained high fractions of short chains, probably because of chain transfer. ^1H -NMR spectra of the polymers showed no residual double bonds (Fig. 6). The copolymer compositions were determined from the integrated ^1H -NMR spectra with the ratio of peak areas of backbone protons of the copolymer around 1.0–2.7 to the peak areas of methylene protons of EBMA-IDA- K^+ or CMAC-IDA- K^+ around 2.7–4.2 ppm. The amounts of EBMA-IDA- K^+ and CMAC-IDA- K^+ units in the copolymers were lower than in the feed compositions, indicating lower copolymerization reactivity of these monomers. Also, the molar fractions of CMAC-IDA- K^+ units in the copolymers were much lower than those of EBMA-IDA- K^+ units. EBMA-IDA- K^+ is clearly more reactive than CMAC-IDA- K^+ .

Gel permeation chromatography analysis

The number average molecular weights (M_n) and the weight average molecular weights (M_w) for the copolymers of AAm : EBMA-IDA- K^+ and AAm : CMAC-IDA- K^+ [(95 : 5) and (90 : 10) mixtures] were estimated by GPC. Each chromatogram showed bimodal molecular weight distributions that were sufficiently different to be distinguished. 90 : 10 mixtures of AAm : EBMA-IDA- K^+ and AAm : CMAC-

TABLE I
Photo-Polymerization Results of EBMA-ID and CMAC-ID

Composition	R_p (s^{-1})	Conversion (%)
HEMA	0.03598	93.4
HEMA : EBMA-ID (80 : 20)	0.00333	65.3
HEMA : EBMA-ID (50 : 50)	0.00157	33.4
EBMA-ID	0.00057	9.4
CMAC-ID	0.00028	6.5

TABLE II
Copolymerization Results of EBMA-IDA-K⁺ and CMAC-IDA-K⁺ with AAm

Monomer	M	V-50	AAm in feed	AAm in copolymer	Time (min)	Yield (%)
AAm only	4.73	0.042	100	–	2	99.1 ^a
AAm : EBMA-IDA-K ⁺	8.33	0.042	95	98.80	210	75.4 ^b , 30.9 ^c
AAm : EBMA-IDA-K ⁺	8.33	0.042	90	93.76	390	65.8 ^b , 23.2 ^c
AAm : CMAC-IDA-K ⁺	8.33	0.042	95	99.75	70	66.9 ^b , 17.6 ^c
AAm : CMAC-IDA-K ⁺	8.33	0.042	90	99.48	160	68.8 ^b , 11.3 ^c

Temperature = 65–67°C.

^a After second precipitation.

^b After first precipitation.

^c After dialysis.

IDA-K⁺ had high-molecular weight fractions with M_n values of 1,190,000 and 527,600 and low-molecular weight fractions of 63,451 and 117,670 whereas 95 : 5 mixtures of AAm : EBMA-IDA-K⁺ and AAm : CMAC-IDA-K⁺ had high-molecular weight fractions with M_n values of 1,549,300 and 1,569,900 and low-molecular weight fractions of 113,190 and 122,910, respectively. Higher-molecular weights were probably the homopolymer of acrylamide and lower-molecular weights were due to EBMA-IDA-K⁺ or CMAC-IDA-K⁺ incorporated fractions.

Thermal gravimetric analysis

The thermal stabilities of EBMA-IDA-K⁺ and CMAC-IDA-K⁺ and their copolymers were investigated by TGA under nitrogen at a heating rate of 10°C/min (Figs. 7 and 8). The monomers showed two-stage decomposition. The first is due to dehydration and the second is the decomposition of the monomer. However, the copolymers degraded by a three-stage process. First stage is dehydration, secondary stage is probably decomposition due to acrylamide (imidization), and third stage is the random scission of the copolymer chain.²⁰ The char residues increased on the incorporation of EBMA-IDA-K⁺ and CMAC-IDA-

K⁺ in the copolymers. Polyacrylamide had a char residue of 18.3% at 550°C. The copolymers AAm : EBMA-IDA-K⁺ (95 : 5) and (90 : 10) gave char residues of 28.4% and 34.3%, whereas the char residues for the copolymers AAm:CMAC-IDA-K⁺ (95 : 5) and (90 : 10) were 23.3% and 26.3%, respectively.

As it was stated in the literature, decomposition activation energies for the metal complexes are higher than that of the functionalized sodium salt, indicating the thermal stability gained on complexation with metal ions.⁵ The extra stability of the polymer–metal complexes arises from the formation of stable ring structures of the metal complexes. We investigated the thermal decompositions of AAm : EBMA-IDA-K⁺ (90 : 10) copolymer and its Ni²⁺ and Cr³⁺ complexes by plotting the derivative of weight with respect to temperature for each complex. We observed that the major decomposition for the AAm : EBMA-IDA-K⁺ (90 : 10) copolymer was at around 340°C with a mass loss of 31.4%. For the Ni²⁺ and Cr³⁺ complexes, the major decompositions were around 360 and 366°C with mass losses of 35.4 and 39.5%, respectively. This indicates the thermal

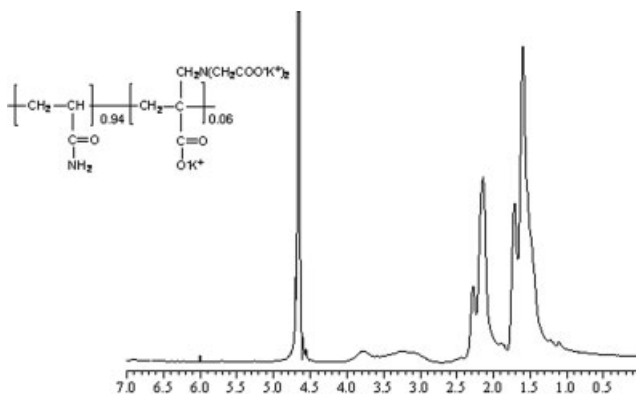


Figure 6 ¹H-NMR spectrum of poly(AAm : EBMA-IDA-K⁺).

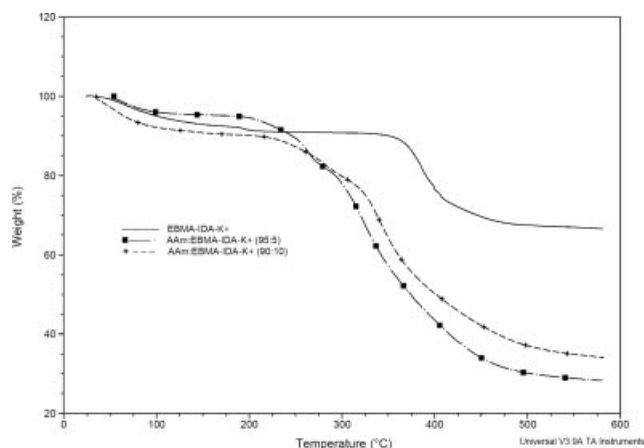


Figure 7 TGA curves of EBMA-IDA-K⁺ and copolymers of AAm : EBMA-IDA-K⁺ (95 : 5), AAm : EBMA-IDA-K⁺ (90 : 10).

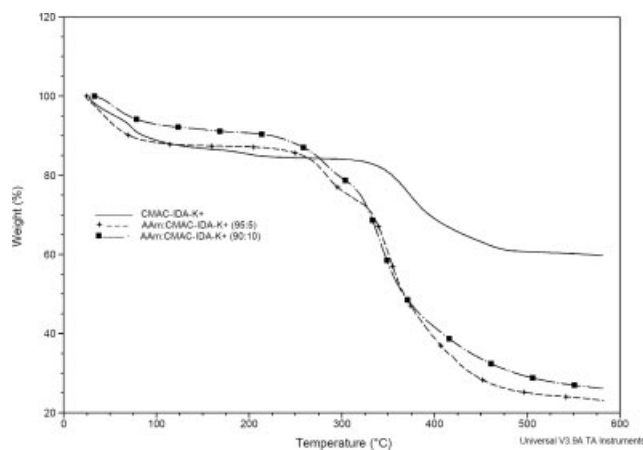


Figure 8 TGA curves of CMAC-IDA-K⁺ and copolymers of AAm : CMAC-IDA-K⁺ (95 : 5), AAm : CMAC-IDA-K⁺ (90 : 10).

stability of AAm : EBMA-IDA-K⁺ (90 : 10) copolymer increases on complexation with Ni⁺² and Cr⁺³ ions as expected (Fig. 9).

Spectrophotometric measurements

Because of the low copolymerization yields metal binding ability of the copolymers could not be investigated. Only the chelating abilities of the monomers EBMA-IDA-K⁺ and CMAC-IDA-K⁺ were studied using UV-visible spectroscopy at 500–900 nm where the monomer has no absorption. Maximum absorption values for Ni⁺² and Cr⁺³ were obtained at 717 and 588 nm, respectively. As EBMA-IDA-K⁺ or CMAC-IDA-K⁺ was added to the Ni⁺² (or Cr⁺³) solution, the maximum value shifted to shorter wavelengths (624 nm for Ni⁺² and 556 nm for Cr⁺³) with an increase in absorbance. This result confirms the

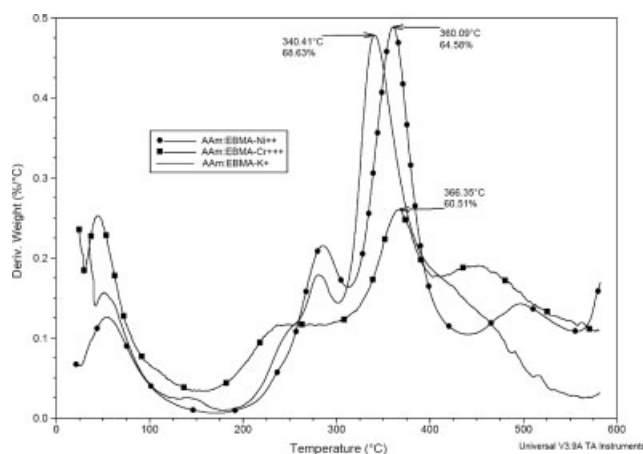


Figure 9 Derivative of the weight loss with respect to temperature curves of AAm : EBMA-IDA-K⁺ (90 : 10) and its complexes with Ni⁺² and Cr⁺³.

Ni⁺² and Cr⁺³ chelating ability of EBMA-IDA-K⁺ and CMAC-IDA-K⁺. Maximum absorption values and the corresponding wavelengths for different concentrations of EBMA-IDA-K⁺ and CMAC-IDA-K⁺ were given in Table III. Both crystal and Ligand Field Theories invoke a parameter, the ligand-field splitting parameter (Δ), to correlate spectroscopic properties.²¹ The ligand-field splitting parameter varies with the identity of the ligand and the oxidation number of the metal ion. For M⁺² ions the size of Δ is much less than for M⁺³ ions. The absorption maxima of the Cr⁺³ + EBMA-IDA-K⁺ (or CMAC-IDA-K⁺) complexes were at shorter wavelengths than the absorption maxima of the Ni⁺² complexes as expected. Also, when EBMA-IDA-K⁺ complexes were compared with CMAC-IDA-K⁺ complexes for the same metal ion and the same metal ion to ligand ratio, it was observed that values for the λ_{\max} were similar meaning that these two ligands showed nearly the same ligand-field strengths.

CONCLUSION

New monomers with increased coordinating sites were synthesized from derivatives of alkyl α -hydroxy-methacrylates successfully. EBMA-IDA-K⁺ can act as a metal chelate through iminodiacetate group and a metal binder through carboxylate group whereas CMAC-IDA-K⁺ contains two metal chelating functionality. However, the results of the homopolymerization and copolymerization studies of these monomers with HEMA and acrylamide were not that promising when compared with the currently used

TABLE III
Results of UV-Visible Spectrophotometer Studies

Concentrations ($\times 10^{-3}$ M)	Absorbance	λ_{\max} (nm)
Ni ⁺² [4.8]	0.013	717
Ni ⁺² [4.8] + EBMA-IDA-K ⁺ [1.2]	0.013	654
Ni ⁺² [4.8] + EBMA-IDA-K ⁺ [2.4]	0.025	639
Ni ⁺² [4.8] + EBMA-IDA-K ⁺ [3.6]	0.028	630
Ni ⁺² [4.8] + EBMA-IDA-K ⁺ [4.8]	0.053	624
Ni ⁺² [3.08]	0.008	717
Ni ⁺² [3.08] + CMAC-IDA-K ⁺ [0.77]	0.011	651
Ni ⁺² [3.08] + CMAC-IDA-K ⁺ [1.54]	0.014	639
Ni ⁺² [3.08] + CMAC-IDA-K ⁺ [2.31]	0.017	630
Ni ⁺² [3.08] + CMAC-IDA-K ⁺ [3.08]	0.025	624
Cr ⁺³ [4.8]	0.141	588
Cr ⁺³ [4.8] + EBMA-IDA-K ⁺ [1.2]	0.109	565
Cr ⁺³ [4.8] + EBMA-IDA-K ⁺ [2.4]	0.202	558
Cr ⁺³ [4.8] + EBMA-IDA-K ⁺ [3.6]	0.251	557
Cr ⁺³ [4.8] + EBMA-IDA-K ⁺ [4.8]	0.326	556
Cr ⁺³ [3.08]	0.096	588
Cr ⁺³ [3.08] + CMAC-IDA-K ⁺ [0.77]	0.057	576
Cr ⁺³ [3.08] + CMAC-IDA-K ⁺ [1.54]	0.090	567
Cr ⁺³ [3.08] + CMAC-IDA-K ⁺ [2.31]	0.130	560
Cr ⁺³ [3.08] + CMAC-IDA-K ⁺ [3.08]	0.157	556

chelating monomer, GMA-IDA.²² Rate of copolymerizations and conversions decreased upon increasing the amount of the synthesized monomers due to steric effects. The thermogravimetric weight loss of the copolymers decreased with increasing IDA-K⁺ fraction and thermal stability increased when K⁺ was replaced by Ni²⁺ or Cr⁺³. The UV-visible spectroscopy indicated that IDA-K⁺ containing monomers can be used for metal binding, suggesting that its polymers may be used for the same purpose too.

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