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Chelating Polymers. V. Aminoacetic Acid Chelating Polymers Derived from Polyglycidyl Methacrylate*

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ABSTRACT

Prototype chelating polymeric compounds were prepared by reacting the ligands, sodium aminoacetate and disodium iminodiacetate, with low molecular weight poly(glycidyl methacrylate). These prototype compounds were characterized, and their chelating characteristics with praseodymium(III), holmium(III), and copper(II) were established by ir spectroscopy, stability constant determinations, and capacity measurements.
Cross-linked chelating copolymers were prepared by reacting the ligands, sodium aminoacetate and disodium iminodiacetate, with co-poly[glycidyl methacrylate]-[allyl methacrylate]. These copolymers were characterized, and their chelating characteristics with several rare earth ions and copper(II) were evaluated.
The results indicate that whereas some separation of the rare earths can be achieved on the copolymer containing iminodiacetic acid ligands, high separation factors are

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*Taken in part from the Ph.D. dissertation of W. F. Strazik.

not obtained because of the similarities in the stabilities of the complexes formed by the copolymer with the various rare earths.

INTRODUCTION

In a prior publication [1] the preparation and rare earth complexation characteristics of the prototype compounds, N-(2-hydroxy-2-phenylethyl)aminoacetic acid and N-(2-hydroxy-2-phenylethyl)-iminodiacetic acid were reported. It was shown that 1) sodium aminoacetate and disodium iminodiacetate could be reacted via their amine groups with monomeric α-epoxy compounds to give good yields of product; 2) the resulting compounds could form chelate structures with the rare earth ions; and 3) the alcoholic oxygen atom of the compounds could also bond to the rare earth ions to form an additional five-membered ring. These results provided the guidelines for the research reported in this publication.

The first part of this research was an investigation of linear, low molecular weight, prototype polymeric compounds related to the prototype chelating compounds reported in the prior publication [1]. The prototype polymeric compounds were poly-1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate (HAHPM) and poly-1-(N-iminodiacetic acid)-2-hydroxy-propyl methacrylate (HIHPM). These compounds were prepared by reacting sodium aminoacetic acid and disodium iminodiacetic acid, respectively, with low molecular weight, linear, poly(glycidyl methacrylate). This particular polymer was chosen to be the backbone structure for several reasons. Not only did it contain sites (epoxy rings) with which the chosen ligands could react and become attached to the polymer backbone, but it also offered the following features:

1) Ease and specific control of the polymerization reaction [2, 3].
2) Ease of controlling the degree of cross-linking by using divinyl comonomers [4].
3) Formation of hydrophilic hydroxyl groups as part of the ligand-polymer reaction.
4) Attachment of ligands to the polymer backbone through flexible oxygen linkages.

From these prototype polymeric compounds several polymeric metal chelates were prepared. These chelates were examined by ir spectroscopy, by capacity studies, and by stability constant determinations.

The second part of this research involved the preparation and characterization of two cross-linked chelating copolymers co-poly-[1-(N-aminoacetic acid-2-hydroxy-propyl methacrylate]-[allyl methacrylate] and co-poly[1-(N-iminodiacetic acid-2-hydroxy-propyl methacrylate]-[allyl methacrylate]. These two copolymers are referred to as CAHPM and CIHPM, respectively. They were prepared by postreacting sodium aminoacetate and disodium iminodiacetate, respectively, with a copolymer of glycidyl methacrylate and allyl methacrylate. These chelating copolymers were saturated with several different rare earth ions and the resulting products were analyzed by ir spectroscopy. Finally, the copolymer containing iminodiacetic acid was evaluated for its ability to separate various rare earth ions. This evaluation included the determination of batch distribution coefficients, batch selectivity coefficients, and separation factors, all as a function of pH.

EXPERIMENTAL

Analysis

Epoxy oxygen analyses were done according to the procedure of King [5]. All other remaining analyses were described in our prior publication [1].

Physical Measurements

Nonaqueous titrations were performed on the polymers containing aminoacetic acid ligands according to the procedure given by Beckett and Tinley [6] for titrating amino acids. The acetous perchloric acid and acetous sodium acetate were standardized by conventional methods. Crystal Violet B was used as an indicator.

Molecular weights were determined using the Mechrolab Model 302 Vapor Pressure Osmometer equipped with a 37° thermostat and a 37° nonaqueous probe. Reagent grade 2-butanone was used as the solvent. A calibration factor characteristic of the instrument-thermostat-probe-solvent combination was obtained using recrystallized benzil (mol wt 210.2) as a standard solute.

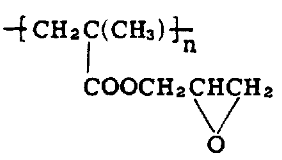
Gamma spectra of radioactive solutions were measured by using an Ortec 7 mm lithium-drifted germanium detector in conjunction with a Canberra Industries Model 1416 Linear Amplifier and a Nuclear Data Model ND3300 multichannel analyzer. The data were read out in four ways: on an oscilliscope, typewriter, plotter, and punch tape.

The intrinsic viscosities of dilute linear polymer solutions (less than 1%) were determined in 2-butanone using a semi-micro Cannon-Ubbelohde dilution viscometer. Both the solvent and the solutions were filtered prior to their use. The temperature was maintained at 20 ± 0.02°C. Reduced viscosities were calculated from the efflux times measured at no less than three solution concentrations. The intrinsic viscosities were calculated by extrapolation of the reduced viscosities to zero concentration.

All other physical measurements were described in our prior publication [1].

Synthesis

Preparation of Linear Poly(glycidyl Methacrylate)



Although several different procedures were tried, the most successful procedure found for the preparation of this polymer was that reported by Ravve and Khamis [7].

Benzoyl peroxide (0.25 g) was dissolved in glycidyl methacrylate (24.948 g), and the solution was added to 125 ml of 2-butanone. The resulting system was contained in a 250-ml three-necked flask which was covered with aluminum foil and equipped with a water condenser, thermometer, nitrogen inlet and outlet, heating mantle, and magnetic stirrer. The reaction mixture was stirred and slowly heated to 79°C in a nitrogen atmosphere. Five milliliter aliquots were removed from the reaction mixture at various times, and the polymer was precipitated and washed with 2-propanol. The per cent conversions to polymer at 30, 75, 120, 195, and 270 min. were 0.1, 24.1, 35.2, 66.9, and 87.3%, respectively. After 4.5 hr at 79°C the turbid reaction mixture was cooled to room temperature and filtered. The polymer was precipitated from the clear filtrate using 2-propanol. The white product was washed four times with approximately 30 ml portions of 2-propanol. It was then redissolved in 2-butanone, filtered, and reprecipitated with 2-propanol. The reprecipitated polymer was washed three times with methanol, and dried in vacuo at room temperature for 48 hr.

The dried polymer could be redissolved, for the most part, in solvents such as 2-butanone, acetone, dioxane, and dimethylacetamide. In all cases, however, even after vigorous and prolonged stirring, a small portion of the polymer remained insoluble in these and in all other solvents investigated.

The polymer was found to contain 10.7% epoxy oxygen and to have an intrinsic viscosity of 0.17 at 20°C in 2-butanone.

Analysis: Calculated for polymer having segmers of composition $C_7H_{10}O_3$: C, 59.15; H, 7.04; O, 33.80. Found: C, 59.10; H, 7.13; O, 33.77.

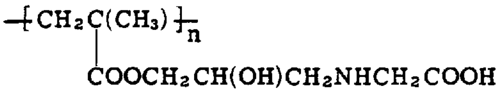
In order to prepare a linear polymer of molecular weight lower than the one described above, a corresponding procedure was followed exactly except that dodecanethiol (0.125 g, 0.5% by weight on the monomer) was added. This polymer was readily and completely redissolved in 2-butanone, in dioxane, in acetone, and in N,N-dimethylformamide. It was insoluble in water, in methanol, in 2-propanol, and in n-heptane. The polymer was found to contain 10.6% epoxy oxygen, have an intrinsic viscosity of 0.092 at 20°C in 2-butanone, and have a number-average molecular weight, as determined by vapor pressure osmometry in 2-butanone, of 7,600.

Analysis: Calculated for polymer having segmers of composition $C_7H_{10}O_3$: C, 59.15; H, 7.04. Found: C, 58.61; H, 7.06.

Preparation of Prototype Polymeric Compounds and Their Metal Complexes

These compounds were prepared according to the general procedure used by Iwakura [8] for reacting amino acids with polymers containing glycidyl methacrylate segmers. The general procedure consisted of postreacting the linear poly(glycidyl methacrylate) polymers with the sodium salts of chelating ligands.

Prototype Polymeric Compound: Poly-1-(N-aminoacetic Acid)-2-hydroxy-propyl Methacrylate



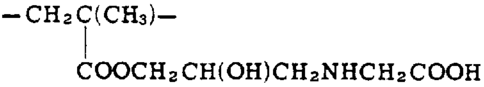
$$-\!\left[\mathrm{CH_2}\underset{\mathrm{COOCH_2CH(OH)CH_2NHCH_2COOH}}{\mathrm{C}}\mathrm{(CH_3)}\right]_n\!-$$

(HAHPM)

Linear poly(glycidyl methacrylate) (0.845 g, 5.65 mmoles of epoxy rings) was stirred in 80 ml of dimethylacetamide for 10 min at 45°C. The mixture was filtered and the clear filtrate containing the soluble linear polymer (0.832 g, 5.56 mmoles of epoxy rings) was placed in a 250-ml three-necked flask. The flask was equipped with a water condenser, thermometer, heating mantle, and magnetic stirrer. The polymer solution was heated to 85°C, and sodium aminoacetate (2.65 g, 27.80 mmoles), which was dissolved in 36 ml of deionized water, was added. After 70 min of stirring at 85°C the clear reaction mixture began to turn cloudy. Four milliliters of deionized water were added and the reaction mixture became clear once again. The reaction was continued at 85°C for a total of 17 hr. After cooling to room temperature the slightly cloudy solution (pH = 10.70) was diluted with 160 ml of water. The diluted solution was stirred for 15 min and then filtered. Upon acidification of the filtrate with 1 M hydrochloric acid a white precipitate began to form. The amount of precipitate increased as the pH was lowered to 3.9. It then slowly redissolved as the solution was made more acidic. At a pH of 2.0 all of the precipitate had redissolved. The pH was then brought back to 3.9 by the addition of 2 M sodium hydroxide. The resulting precipitate was stirred in its mother liquor for 20 min, cooled in an ice bath for 2 hr, and finally centrifuged and decanted. The residue was next dissolved in dilute sodium hydroxide and reprecipitated by adding hydrochloric acid to a pH of 3.9. The resulting precipitate was again centrifuged and decanted. It was washed five times with water and then twice with acetone. The final residue was dried in vacuo at 80°C for 24 hr. The dried product was white and did not appear to be hydroscopic. Nonaqueous titrations indicated a ligand yield of 55%.

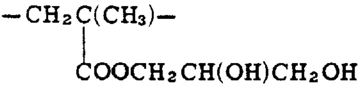
Elemental analysis indicated no chloride or residue and a ligand yield of 55%.

Analysis: Calculated for 55% Segmer A (I) and 45% Segmer B (II) (mole %): C, 50.79; H, 7.14; N, 4.02. Found: C, 50.80; H, 7.29; N,4.06.



$$\begin{array}{l} -CH_2\underset{|}{C}(CH_3)- \\ \quad COOCH_2CH(OH)CH_2NHCH_2COOH \end{array}$$

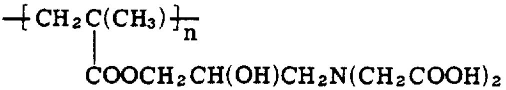
I



$$\begin{array}{l} -CH_2\underset{|}{C}(CH_3)- \\ \quad COOCH_2CH(OH)CH_2OH \end{array}$$

II

Prototype Polymeric Compound: Poly-1-(N-iminodiacetic Acid)-2-hydroxy-propyl Methacrylate



$$\begin{array}{l} -\!\left[CH_2\underset{|}{C}(CH_3)\right]_n\!- \\ \quad COOCH_2CH(OH)CH_2N(CH_2COOH)_2 \end{array}$$

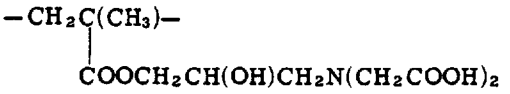
(HIHPM)

The procedure used to prepare this polymer was similar to that used in preparing poly-1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate.

Disodium iminodiacetate (0.938 g, 5.30 mmoles) was dissolved in a mixture of 40 ml of water and 80 ml of dioxane which was contained in a 250-ml three-necked flask. The flask was equipped with a water condenser, two dropping funnels, a heating mantle, and magnetic stirrer. Poly(glycidyl methacrylate) (0.800 g, 5.30 mmoles of epoxy rings) was dissolved in 20 ml of dioxane, and the solution placed in one of the dropping funnels. In the other dropping funnel was placed a solution containing disodium iminodiacetate (0.938 g, 5.30 mmoles) dissolved in a mixture of 15 ml of water and 5 ml of dioxane. The temperature in the reaction flask was raised to 80°C. The polymer feed solution and the ligand feed solution were then added, dropwise and with stirring, to the light-yellow ligand solution in the reaction flask. The feed solutions were both added at the same rate and required 7.5 hr to complete their additions. The reaction mixture became milky white with the addition of the two feed solutions. Eight hours after both feed solutions had been added the reaction mixture became a clear pale-yellow solution once again. The reaction was allowed to continue at 80°C for a total of 12 hr from the time of the last addition of the feed solutions. After cooling to room temperature a sample was removed from the reaction mixture and water was added to it. The sample became slightly cloudy at first, but then it became clear as excess water was added. The reaction mixture was concentrated to approximately 10 ml on a flash evaporator and then diluted with 30 ml of water. The slightly cloudy solution that resulted was filtered through a medium sintered glass filter. To the clear filtrate (pH of 10.5) was added 0.990 M hydrochloric acid. A precipitate began to form at a pH of 3.0, increased in size as the pH was lowered to 2.1 (18.56 ml of acid), and then slowly redissolved as the pH was lowered further. The solution was completely clear at a pH of 1.0. The product was isolated by adding 1 M sodium hydroxide to a pH of 2.1, cooling the mixture in an ice bath for 30 min, and then centrifuging and decanting. The tan gummy residue was stirred in acetone until it became a finely divided powder. The powder was next stirred in a hydrochloric acid solution of pH 2.1 for 10 min, and the resulting mixture was centrifuged and decanted. The product was washed alternately with acetone and hydrochloric acid solution (pH of 2.1) three more times. Finally it was washed in water three times. The alternate acetone washings were necessary to keep the polymer from agglomerating. The final residue was dried in vacuo over calcium chloride at room temperature for 24 hr and at 80°C for 6 hr. The dried residue was light yellow and weighed 1.1 g.

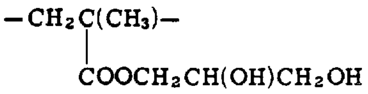
The ligand yield of the prototype polymer, as determined by aqueous potentiometric titration, was 74%. The ligand yield was also calculated from the elemental analysis according to the procedure used by Schmuckler [9]. This procedure indicated a ligand yield of 71%.

Analysis: Calculated for 71% Segmer A (III) and 29% Segmer B (IV) (mole %): C, 48.88; H, 6.44; N, 4.12. Found: C, 50.40; H, 6.48; N, 4.25.



$$\begin{array}{l} -CH_2C(CH_3)- \\ \quad\;\; | \\ \quad\;\; COOCH_2CH(OH)CH_2N(CH_2COOH)_2 \end{array}$$

III



$$\begin{array}{l} -CH_2C(CH_3)- \\ \quad\;\; | \\ \quad\;\; COOCH_2CH(OH)CH_2OH \end{array}$$

IV

The complexation behaviors of both prototype polymers toward the rare earths were studied in various ways. Besides the preparation and isolation of the metal-polymer complexes, these studies included ir analyses of these complexes, polymer capacity studies, and stability constant determinations.

The metal-polymer complexes were prepared by either of two ways:

1) Sodium hydroxide was slowly added to a mixture of the polymer in its acid form and the metal salt.

2) An aqueous solution of the sodium salt of the polymer was slowly added to a solution of the metal salt.

The preparation of the praseodymium complex of HAHPM is given as an example.

HAHPM (0.079 g, 0.200 mmole attached ligand) was added to a mixture of 25.0 ml of 0.0103 M perchloric acid solution and 55 ml of dioxane contained in a 250-ml beaker. Five milliliters of 0.0414 M praseodymium(III) chloride solution and 25 ml of 0.44 M potassium chloride solution were added to the beaker. The resulting mixture was stirred under a nitrogen atmosphere at 25°C for several minutes. Sodium hydroxide (5.5 ml of a 0.0998 M solution) was then added, slowly and with stirring, over a period of 20 hr. After all of the base had been added, the reaction mixture was centrifuged and the clear mother liquor was decanted. The light-green residue that formed was washed five times with deionized water. Each washing consisted of stirring the product in water for 10 min, centrifuging, and decanting. The final residue was dried in vacuo at 110°C for 7 hr. The dried product was a light-green, finely divided powder.

The capacity of each of the prototype polymers towards individual rare earths was determined at various pH values. Acetate buffers, made by dissolving calculated amounts of sodium acetate in measured volumes of standard acetic acid and diluting with water, were used to control the pH. The pH values of the various buffers, as measured by a pH meter, were 3.97, 4.92, 5.96, and 6.60.

The general procedure was as follows: Into each of eight 60 ml screw-cap bottles was placed sufficient prototype polymer to give 0.100 mmole of attached ligand. Buffer solution (45 ml) was added and the bottles were sealed and placed in a shaker. After shaking for 6 hr the bottles were opened. The pH values of the various solutions were checked, and 5.0 ml of a 0.04 M rare earth chloride solution were added. The bottles were then resealed and the mixtures shaken for another 12 hr. At the end of this second equilibration period, the reaction mixture of each bottle was filtered and the filtrate added to a 100-ml volumetric flask. The residues were washed several times with water. The washings of each residue were combined with the filtrate of that residue and the resulting reaction solution was diluted to 100 ml with deionized water.

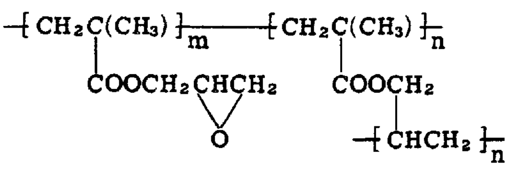
Each of the reaction solutions was spectrophotometrically analyzed for its rare earth content [10]. A 1.0-ml aliquot of the solution was diluted to approximately 40 ml with deionized water.

One milliliter of 0.01 M arsenazo solution and 16 drops of pyridine were then added to the aliquot solution. After the pH was adjusted to 8.0 by the addition of ammonium hydroxide or nitric acid, the aliquot solution was diluted to 50.0 ml with deionized water. The absorbance was measured against a reagent blank at 570 mμ. The millimoles of rare earth in the aliquot solution were obtained from a Beer's law plot and multiplied by 100 (dilution factor) to obtain the rare earth content of the original reaction solution. The rare earth content of a control solution containing no polymer was similarly determined. The millimoles of rare earth complexed by the polymer were then determined from the difference in the metal content of these two solutions.

The experimental details of this study are summarized in Table 1.

The first and second acid dissociation constants of the two prototype polymeric compounds, and the first step stability constants of these compounds with Pr(III) and Ho(III) were determined in the same manner as were the corresponding constants of the prototype monomeric compounds [1]. The only difference was that equilibration times of 2-4 hr were required after each addition of base in the titrations of the polymeric compounds. The results of these measurements are given in Table 2.

Preparation of the Cross-linked Copolymer Co-poly[glycidyl Methacrylate]-[Allyl methacrylate]



The cross-linked copolymers used in this research were prepared by free radical initiated copolymerizations of the monomers glycidyl methacrylate and allyl methacrylate. Butanone-2 and n-heptane were used as the solvents. In order to obtain cross-linked copolymers with different degrees of cross-linking, the amounts of allyl methacrylate in the monomer feeds were varied from 0.5 to 10% (mole %). The following procedure is typical of those employed.

Glycidyl methacrylate (49.989 g, 0.352 mole) and allyl methacrylate (2.229 g, 0.018 mole) were mixed together, and the mixture was added to 260 ml of 2-butanone contained in a 500-ml three-necked

TABLE 1. HAHPM Polymer Capacity Measurements

Sample	Rare earth	pH	Absorbance (control)	Absorbance (sample)	Millimoles complexed rare earth	Polymer capacity (meq/g)
Ce-A	Cerium(III)	3.97	1.08	1.08	0.000	0.00
Ce-B	Cerium(III)	4.92	1.07	1.07	0.000	0.00
Ce-C	Cerium(III)	5.96	1.02	0.93	0.020	1.50
Ce-D	Cerium(III)	6.60	0.96	0.86	0.023	1.73
Tm-A	Thulium(III)	3.97	1.07	1.07	0.000	0.00
Tm-B	Thulium(III)	4.92	1.08	1.08	0.000	0.00
Tm-C	Thulium(III)	5.96	1.02	0.90	0.027	2.03
Tm-D	Thulium(III)	6.60	0.97	0.82	0.034	2.55
HIHPM Polymer Capacity Measurements						
Tm-A	Thulium(III)	3.97	1.06	0.97	0.020	1.82
Tm-B	Thulium(III)	4.92	1.07	0.90	0.040	3.64
Tm-C	Thulium(III)	5.96	1.09	0.84	0.057	5.18
Tm-D	Thulium(III)	6.60	1.09	0.88	0.048	4.37

TABLE 2. Acid Dissociation Constants (k_n) and Step Stability Constants (K_n) in 50% v/v Dioxane-Water at 25°C and 0.1 (KCl) Ionic Strength

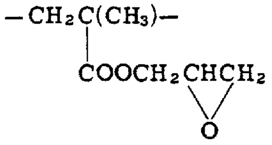
Compound	pk_1	pk_2	Praseodymium(III) log K_1	Holmium(III) log K_1
Poly-1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate	3.20	8.10	5.50	5.70
Poly-1-(N-iminodiacetic acid)-2-hydroxy-propyl methacrylate	3.70	8.80	9.00	9.30

flask. The flask was covered with aluminum foil and equipped with a water condenser, thermometer, nitrogen inlet and outlet, heating mantle, and magnetic stirrer. Benzoyl peroxide (0.527 g) was added to the monomer mixture and a nitrogen atmosphere was established in the reaction flask. The temperature was slowly raised to 79°C. After stirring at this temperature for 3 hr the reaction mixture began to turn cloudy. At the end of 6 hr the reaction mixture became a highly swollen gel. The reaction was allowed to continue at 79°C for a total of 9 hr. It was then cooled to room temperature and as much of the solvent as possible was decanted. The gel was transferred to an osterizer blender containing 250 ml of anhydrous methanol. After stirring at high speed for 5 min the methanol wash solution was decanted and fresh methanol was added. This washing procedure was repeated four additional times. The final wash mixture was filtered, and the white solid was placed in a vacuum oven. After drying in vacuo at room temperature for 48 hr, there was obtained 48.0 g (91% yield) of a finely divided, odorless, white product.

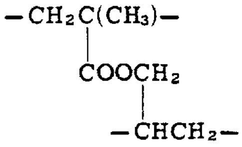
The dried copolymers were insoluble in all solvents tried. They could be swollen in such solvents as 2-butanone, acetone, tetrahydrofuran, dioxane, toluene, and dimethylacetamide.

The copolymers were analyzed by elemental analysis, infrared spectroscopy, and swelling ratio measurements. A typical elemental analysis is as follows:

Analysis: Calculated for 95% Segmer A (V) and 5% Segmer B (VI) (mole %): C, 59.49; H, 7.10; Epoxy O, 10.8. Found: C, 59.51; H, 7.20; Epoxy O, 10.9.



V



VI

The maximum swelling ratio of several cross-linked copolymers were determined by the following procedure. Each copolymer (0.200 g), after being ground to a fine powder with a mortar and pestle, was placed in a 13 × 100 mm Pyrex test tube. After each of the tubes had been rotated for 5 min in a centrifuge, the height of the solid polymer column was measured. 2-Butanone (5.00 ml) was then added to each tube. The tubes were tightly corked and allowed to stand at room temperature for 2 months. All the tubes used in this experiment were selected so that the height of a 5.00-ml volume of 2-butanone in one tube was equal to the height of that same volume of 2-butanone in every other tube. At the end of 2 months the heights of the swollen copolymers were measured and the swelling ratios were calculated. The results are summarized in Table 3.

TABLE 3. Swelling Ratios of Cross-linked Copolymers in 2-Butanone

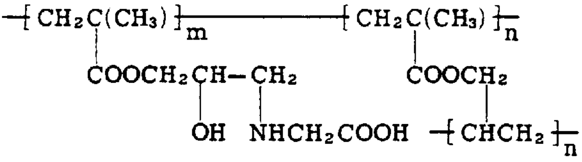
Polymer No.	Composition of monomer feed (mole %)[a]	Polymerization solvent	Swelling ratio
Q	90.0% GYMA-10.0% AMA	n-Heptane	1.4
R	95.0% GYMA- 5.0% AMA	n-Heptane	2.0
S	98.0% GYMA- 2.0% AMA	n-Heptane	2.0
T	99.5% GYMA- 0.5% AMA	n-Heptane	2.1
U	95.0% GYMA- 5.0% AMA	2-Butanone	4.6
V	99.5% GYMA- 0.5% AMA	2-Butanone	5.7

[a] GYMA = glycidyl methacrylate; AMA = allyl methacrylate.

Preparation of Cross-linked Chelating Copolymers and Their Metal Complexes

The cross-linked chelating copolymers were prepared by post-reacting the swollen cross-linked copolymers, which were made in 2-butanone according to the procedures outlined above, with the sodium salts of various chelating ligands. Various rare earth ions were complexed onto the chelating copolymers by the slow addition of base to a mixture of the rare earth chloride and the copolymer in its acid form.

As a specific example, the preparation of co-poly[1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate]-[Allyl methacrylate]



CAHPM

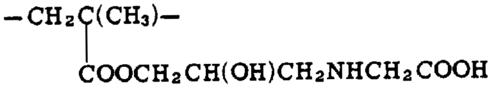
is given.

In the preparation of CAHPM, co-poly[glycidyl methacrylate]-allyl methacrylate] (0.200 g, 1.15 mmoles of epoxy rings) was stirred in 30 ml of dimethylacetamide at room temperature for 24 hr. The temperature was then raised to 80°C and 0.558 g (5.75 mmoles) of sodium aminoacetate, which had been dissolved in 10 ml of deionized water, was added to the highly swollen copolymer. The copolymer contracted slightly upon addition of the aqueous solution, and the reaction mixture became cloudy. The reaction mixture was stirred at 80°C in a 100-ml three-necked flask equipped with a water condenser, thermometer, heating mantle, and magnetic stirrer. After 27 hr at 80°C the mixture was cooled to room temperature and the copolymer was allowed to settle to the bottom of the flask. The supernatant liquid was then decanted. The copolymer was placed in a 40-ml centrifuge tube and washed nine times with water and five times with acetone. Each washing consisted of stirring the copolymer, by means of a magnetic stirrer, for 5-10 min in the wash solution, centrifuging, and decanting. The copolymer swelled to a high degree in water and contracted as the water was displaced by the acetone. The residue from the last acetone washing was a white powder. After drying in vacuo at 80°C for 24 hr there was obtained 0.24 g of a finely divided, hydroscopic, white powder (W).

Copolymer W was dispersed in water and slowly titrated with 0.010 M hydrochloric acid. As the pH of the solution was lowered, W began to coalesce. The equivalence point of the acid form of the product occurred at a pH of 5.0. The copolymer was isolated at this pH and washed six times with water and two times with acetone as in the previous washings. The acid form of the product was dried in vacuo over phosphorus pentoxide for 24 hr at room temperature and for 6 hr at 80°C.

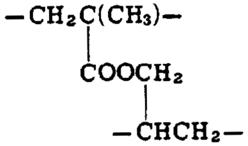
The cross-linked chelating copolymers were analyzed by potentiometric titrations, ir spectroscopy, thermogravimetric analysis, and elemental analysis of the acid forms. The potentiometric titrations were based on the procedure used by Mathieson and Shet [11].

Analysis of CAHPM: Calculated for 42% Segmer A (VII); 5% Segmer B (VIII); 41% Segmer C (IX); 6% Segmer D (X); 6% Segmer E (XI); plus 3.7% H_2O (mole %): C, 49.9%; H, 7.3%; N, 3.5%; H_2O, 3.5%. Found: C, 49.30%; H, 7.58%; N, 3.76%; H_2O, 3.5%.



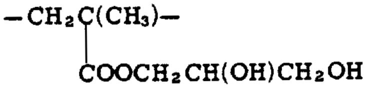
$$\begin{array}{l} -\mathrm{CH_2C(CH_3)}- \\ \qquad | \\ \qquad \mathrm{COOCH_2CH(OH)CH_2NHCH_2COOH} \end{array}$$

VII



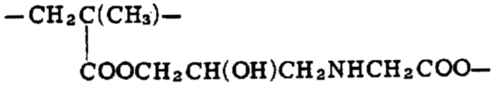
$$\begin{array}{l} -\mathrm{CH_2C(CH_3)}- \\ \qquad | \\ \qquad \mathrm{COOCH_2} \\ \qquad\qquad | \\ \qquad -\mathrm{CHCH_2}- \end{array}$$

VIII



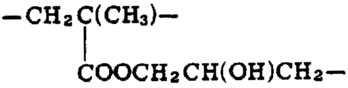
$$\begin{array}{l} -\mathrm{CH_2C(CH_3)}- \\ \qquad | \\ \qquad \mathrm{COOCH_2CH(OH)CH_2OH} \end{array}$$

IX



$$\begin{array}{l} -\mathrm{CH_2C(CH_3)}- \\ \qquad | \\ \qquad \mathrm{COOCH_2CH(OH)CH_2NHCH_2COO}- \end{array}$$

X

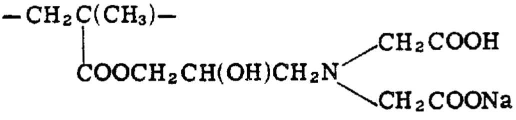


$$\begin{array}{l} -\mathrm{CH_2C(CH_3)}- \\ \qquad | \\ \qquad \mathrm{COOCH_2CH(OH)CH_2}- \end{array}$$

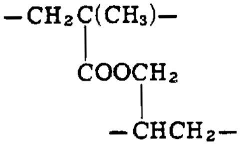
XI

Co-poly[1-N-iminodiacetic acid)-2-hydroxy-propyl methacrylate]-allyl methacrylate], CIHPM, was made similarly using disodium iminodiacetate with dioxane as the solvent and a pH of 2.0 to isolate the acid form of the product (V).

Analysis of CIHPM: Calculated for 55% Segmer A (XII); 5% Segmer B (XIII); 24% Segmer C (XIV); 8% Segmer D (XV); and 8% Segmer E (XVI) (mole %): C, 47.4%; H, 6.0%; N, 3.7%. Found: C, 47.65%; H, 6.36%; N, 3.74%.

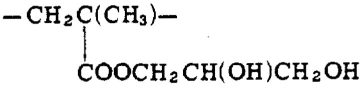


XII



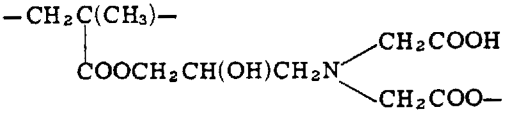
$$\begin{array}{l} -CH_2C(CH_3)- \\ \quad\ | \\ \quad COOCH_2 \\ \qquad\quad | \\ \qquad -CHCH_2- \end{array}$$

XIII

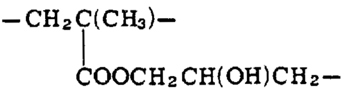


$$\begin{array}{l} -CH_2C(CH_3)- \\ \quad\ | \\ \quad COOCH_2CH(OH)CH_2OH \end{array}$$

XIV



XV



$$\begin{array}{l} -CH_2C(CH_3)- \\ \quad\ | \\ \quad COOCH_2CH(OH)CH_2- \end{array}$$

XVI

The following general procedure was used to prepare metal saturated cross-linked copolymers. The copolymer (0.20 M moles of attached ligand) was placed in a 50-ml centrifuge tube containing

5.0 ml of 0.096 M hydrochloric acid solution. After the copolymer had been stirred for several minutes, 25.0 ml of 0.04 M metal chloride solution were added. Ten milliliters of 0.048 M sodium hydroxide were then added over a period of 8 hr. The resulting reaction mixture (pH of approximately 6.5) was stirred for an additional 4 hr at room temperature before it was centrifuged and the mother liquor decanted. The residue was washed four times with deionized water. The last decantate was colorless. The final residue was dried in vacuo for 11 hr at 70°C and at 110°C for 8 hr.

The colors of the dried metal saturated CAHPM and CIHPM copolymers were as given in Table 4. These colors could not be washed from the copolymers by additional washings with water. The colors were readily removed, however, by one washing with dilute hydrochloric acid.

TABLE 4

Copolymer containing	Color
Cerium(III)	Yellow
Evropium(III)	White
Samarium(III)	White
Holmium(III)	Pale pink
Thulium(III)	Cream
Copper(II)	Light blue

Distribution Studies. Following general procedures that Tompkins and Mayer used with ion exchange resins [12], and that Leyden and Underwood used with the chelating resin Dowex A-1 [13], the bath distribution coefficients of various rare earth ions with co-poly[1-(N-iminodiacetic acid)-2-hydroxy-propyl methacrylate]-[allyl methacrylate] were determined at various pH values. The batch selectivity coefficients were also determined for the same systems as a function of pH. Radiochemical techniques were used in both of the above measurements. The radioactive rare earth isotopes used were chosen such that a strong gamma radiation peak (reference peak) of one of the rare earth isotopes was separated from the gamma radiation peaks of the other rare earth isotopes. In this way the concentration of each rare earth in a mixture could be determined by gamma spectroscopy without prior separation from the other rare earths.

Batch Distribution Coefficient Determinations. If the quantity of metal ions absorbed by the chelating copolymer and that remaining in solution of an equilibrated system are known, the batch distribution coefficient, K_d, can be calculated. When radioactive metal isotopes are used, K_d is defined [14] as

$$K_d = \frac{\text{activity in copolymer phase per gram of dry copolymer}}{\text{activity in solution phase per ml of solution}}$$

The separation factor, α_B^A, for two ions, A and B, relative to each other is given by $\alpha_B^A = K_{dA}/K_{dB}$. The following procedure was used to determine K_d for cerium(III), europium(III), and thulium(III) with co-poly[1-(N-iminodiacetic acid)-2-hydroxy-propyl methacrylate]-[allyl methacrylate]. In the procedure the total equivalents of rare earth ions present were less than 8% of the equivalents of iminodiacetic acid groups present in the copolymer.

Fifteen milliliters of a rare earth stock solution containing tracer amounts of ^{141}Ce, ^{152}Eu, and ^{170}Tm along with 0.15 meq of each of the respective inactive species was prepared. The radioactive isotopes were added in such a way that the radioactivity of each, as determined by its reference gamma peak, was approximately equal to the activity of the others.

The co-poly[1-(N-iminodiacetic acid)-2-hydroxy-propyl methacrylate]-[allyl methacrylate] was prebuffered at pH values of 1.5, 2.8, 3.3, 3.9, 4.4, 5.1, and 6.5. This was done by stirring 0.15 g portions of the copolymer into 25 ml samples of buffer solutions each at one of the pH values listed. The systems were stirred for 3 hr at room temperature, and the supernatant liquids decanted. Each residue, after being washed rapidly two times with deionized water, was dried in vacuo at 70°C for 21 hr and at room temperature for 48 hr.

The actual distribution mixtures were then prepared. Into each of seven 15 ml screw cap bottles was placed the following:

1) 0.100 g (approximately 0.4 meq of attached ligand) of a prebuffered copolymer.

2) 1.00 ml of the rare earth stock solution (0.01 meq of each rare earth plus its radioactive tracer.
3) 1.00 ml of an acetate or hydrochloric acid-sodium chloride buffer of the same pH as the prebuffered copolymer used.
4) 6.00 ml of deionized water.
5) Solid KCl to make the ionic strength of the solution equal to 0.1 M.

Two reference solutions were prepared in the same way, using buffer solutions whose pH values were 3.3 and 5.1, except that no copolymer was added.

The jars containing the seven distribution mixtures and the two reference solutions were sealed with parafilm and screw caps. They were then shaken for 36 hr at 30°C. The mixtures were then allowed to stand at 30°C for an additional 24 hr. Each solution, in turn, was then removed from the oven and approximately 4 ml of the supernatant liquid was removed. The 4-ml samples were centrifuged and 1.00 ml aliquots of the resulting supernatant liquid were pipetted into 13 × 100 mm Pyrex test tubes for radioactivity counting.

The radioactivity of each rare earth in each of the samples was determined by gamma spectroscopy using the counting equipment described in the Physical Measurements portion of the Experimental section. Each sample was counted for at least 64 min. The reference peaks used for the ^{141}Ce, ^{152}Eu, and ^{170}Tm were at 145, 122, and 84 keV, respectively. The actual radioactivity of each rare earth in the sample was obtained by adding the counts in each channel under the respective peak of that isotope and subtracting from this the background counts in the same channels. All activities were normalized to a 64-min counting time.

Using the average of the radioactivities of each isotope found in the two reference solutions as the initial activity of that isotope (I) and the radioactivity of each isotope found in the aliquots of the distribution mixtures as the final activity of that isotope (F) in the given mixture, the batch distribution coefficients were determined from Eq. (1).

$$K_d = \frac{I - F}{F} \quad \frac{8 \text{ ml}}{\text{wt of dry copolymer (g)}} \tag{1}$$

The results are summarized in Table 5. A plot of log K_d vs pH for each of the rare earth ions is shown in Fig. 1.

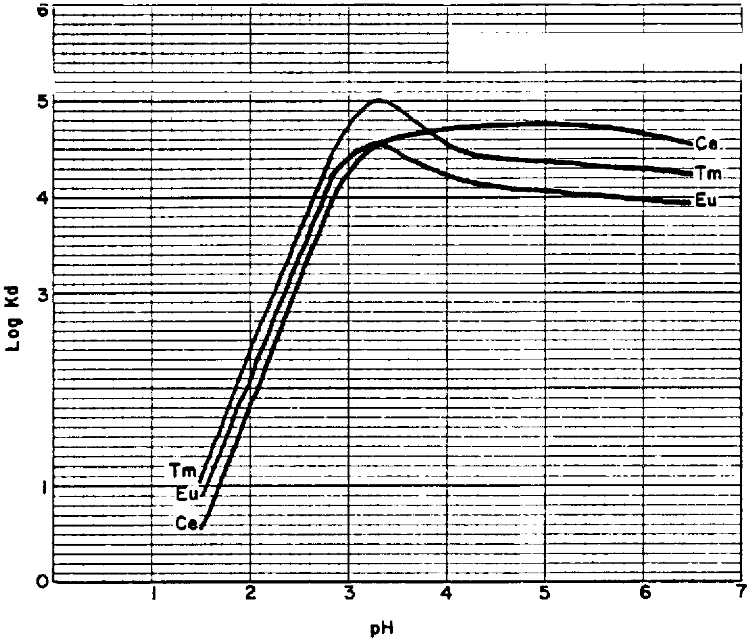


FIG. 1. Batch distribution coefficients of various rare earth ions with co-poly [1-N-iminodiacetic acid)-2-hydroxy-propyl methacrylate]-[allyl methacrylate].

Batch Selectivity Coefficient Determinations. The batch selectivity coefficient, K_s, is defined as

$$K_s = \frac{\text{activity in copolymer phase per gram of dry copolymer}}{\text{activity in solution phase per ml of solution}}$$

when radioactive metals are distributed between the copolymer and the solution. While K_s is identical in form to K_d, a distinction is made because of the difference in experimental conditions used to obtain these two parameters. When determining K_s, the ratio of the equivalents of each rare earth ion to the equivalents of ligand attached to the polymer is 1:1. Because three metals were used in

TABLE 5. Batch Distribution Coefficients of Rare Earth Ions with Co-poly[1-(N-iminodiacetic acid)-2-hydroxy propyl methacrylate]-[allyl methacrylate] at 30°C and 0.1 Ionic Strength

Rare earth ion	pH	I	F	Wt of copolymer (g)	K_d	α^{Ln}_{Eu}
Thulium(III)	1.5	216,818	189,983	0.1003	11.3	1.40
Europium(III)	1.5	358,256	325,687	0.1003	8.0	1.00
Cerium(III)	1.5	197,647	188,993	0.1003	3.6	0.45
Thulium(III)	2.8	197,244	666	0.0915	25,807	1.42
Europium(III)	2.8	112,305	539	0.0915	18,130	1.00
Cerium(III)	2.8	202,902	2,073	0.0915	8,470	0.47
Thulium(III)	3.3	197,244	152	0.0985	105,312	2.84
Europium(III)	3.3	112,305	245	0.0985	37,148	1.00
Cerium(III)	3.3	202,902	447	0.0985	36,785	0.99
Thulium(III)	3.9	197,244	420	0.1004	37,341	1.98
Europium(III)	3.9	112,305	473	0.1004	18,839	1.00
Cerium(III)	3.9	202,902	336	0.1004	48,038	2.55

Thulium(III)	4.4	197,244	838	0.1005	18,657	1.95
Europium(III)	4.4	112,305	926	0.1005	9,575	1.00
Cerium(III)	4.4	202,902	455	0.1005	35,418	3.70
Thulium(III)	5.1	197,244	566	0.1004	23,915	2.07
Europium(III)	5.1	112,305	770	0.1004	11,542	1.00
Cerium(III)	5.1	202,902	288	0.1004	56,057	4.85
Thulium(III)	6.5	197,244	1,021	0.0930	16,532	1.73
Europium(III)	6.5	112,305	1,001	0.0930	9,565	1.00
Cerium(III)	6.5	202,902	438	0.0930	39,763	4.15

each distribution mixture in this study, the total equivalents of rare earth ions present was the three times the equivalents of iminodiacetic acid groups present in the copolymer.

The procedure used for determining K_s was identical to the one used for K_d except that the compositions of the distribution mixtures were appropriately altered. Each distribution mixture contained the following:

1) 0.30 g (approximately 0.12 meq of attached ligand) of a prebuffered copolymer.
2) 1.00 ml of the rare earth stock solution (containing 0.005 meq of each rare earth plus the radioactive tracers).
3) 1.00 ml of 0.12 N rare earth chloride solution of each of the rare earths used.
4) 1.00 ml of an acetate buffer of the same pH as the prebuffered copolymer used.
5) 3.00 ml of deionized water.
6) Solid KCl to make the ionic strength of the solution equal to 0.1 M. Two reference solutions were prepared in exactly the same way, using buffer solutions whose pH values were 3.3 and 5.1, except that no copolymer was added.

The distribution mixtures and the reference solutions were shaken for 36 hr at 30°C. They were then allowed to stand at 30°C for an additional 24 hr before being prepared for radioactivity counting. A 1.00-ml aliquot of the supernatant liquid of each sample was used in the K_d determinations. The gamma spectrum of each aliquot was then determined. Each aliquot was counted for at least 32 min. The radioactivity in each aliquot was normalized to a 32-min counting time.

The value of K_s at various pH values was calculated from Eq. (2),

$$K_s = \frac{I - F}{F} \quad \frac{8 \text{ ml}}{\text{wt of dry copolymer (g)}} \qquad (2)$$

where I and F are as defined in the equation for K_d. The results are summarized in Table 6. A plot of the per cent rare earth extracted by the resin vs pH for each of the rare earth ions is shown in Fig. 2.

TABLE 6. Batch Selectivity Coefficients of Rare Earth Ions with Co-poly[1-(N-iminodiacetic acid)-2-hydroxy-propyl methacrylate]-[allyl methacrylate] at 30°C and 0.1 Ionic Strength

Rare earth ion	pH	I	F	Wt of copolymer (g)	K_s	% Rare earth ion extracted
Thulium(III)	2.8	216,818	203,884	0.0305	16.63	5.96
Europium(III)	2.8	358,256	311,457	0.0305	39.41	13.06
Cerium(III)	2.8	197,647	179,566	0.0305	26.41	9.14
Thulium(III)	3.3	216,818	198,212	0.0306	24.64	8.58
Europium(III)	3.3	358,256	309,789	0.0306	40.90	13.52
Cerium(III)	3.3	197,647	178,440	0.0306	28.14	9.71
Thulium(III)	3.9	216,818	171,324	0.0305	69.65	20.98
Europium(III)	3.9	358,256	261,273	0.0305	97.36	27.07
Cerium(III)	3.9	197,647	166,711	0.0305	48.67	15.65
Thulium(III)	4.4	216,818	158,246	0.0308	96.13	27.01
Europium(III)	4.4	358,256	241,959	0.0308	124.83	32.46
Cerium(III)	4.4	197,647	169,408	0.0308	43.27	14.28
Thulium(III)	5.1	216,818	130,088	0.0300	177.79	40.00
Europium(III)	5.1	358,256	212,876	0.0300	182.11	40.57
Cerium(III)	5.1	197,647	170,557	0.0300	42.35	13.70
Thulium(III)	6.5	216,818	105,229	0.0300	282.77	51.46
Europium(III)	6.5	358,256	208,408	0.0300	191.73	41.82
Cerium(III)	6.5	197,647	164,523	0.0300	53.68	16.75

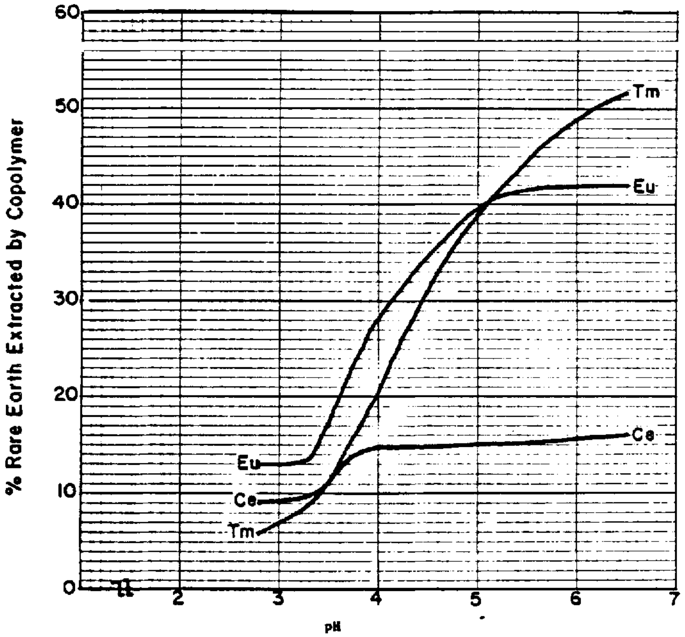


FIG. 2. Batch selectivity coefficients of various rare earth ions with co-poly[1-(N-iminodiacetic acid)-2-hydroxy-propyl methacrylate]-[allyl methacrylate].

Knowing the per cent of each rare earth ion extracted by the copolymer and the total equivalents of each rare earth ion initially present, the capacity of the capacity of the copolymer at various pH values was determined. These capacities are given in Table 7.

DISCUSSION

It was decided that the linear poly(glycidyl methacrylate) to be used in preparing the prototype polymeric compounds should be made by a homopolymerization of glycidyl methacrylate in 2-butanone solvent. Because of the high chain transfer properties of this solvent, the polymer so obtained not only would be free of cross-linking, but it would also be of the desired lower molecular weight. The procedure used is given in the Experimental section.

TABLE 7. Copolymer Capacity

pH	Capacity (meq/g)
2.8	1.15
3.3	1.30
3.9	2.60
4.4	2.98
5.1	3.90
6.5	4.55

The linear polymer isolated was analyzed by ir spectroscopy. The spectrum of the polymer (Fig. 3) was identical to that of poly(glycidyl methacrylate) [15]. As expected, the C=C vinyl absorption that occurs at 1643 cm^{-1} in the spectrum of the monomer was absent from the polymer spectrum. The intensity of the peak at 3000 cm^{-1}, which has been assigned to the CH stretching vibration of the epoxy ring [15], and the intensities of the peaks at 1250, 900, and 840 cm^{-1}, which have been assigned to the epoxy ring vibrations, were equal to the intensities found for the same peaks in the monomer spectrum. This indicates that the epoxy rings were not affected by the polymerization reaction. The ester peak at 1725 cm^{-1} was the strongest peak in the polymer spectrum.

The results of the epoxy oxygen analysis and the elemental analysis were in excellent agreement with those calculated for a polymer containing only glycidyl methacrylate segmers.

Using the measured value of the intrinsic viscosity of this polymer (0.17) along with the value of K (7.22×10^{-5}) and the accepted value of a (0.8) for acrylate and methacrylate polymers, the approximate molecular weight (M_η) of the polymer may be calculated from Eq. (3).

$$[\eta] = KM^a \tag{3}$$

This calculated molecular weight is 16,500.

In order to prepare a linear poly(glycidyl methacrylate) polymer of still lower molecular weight, the same homopolymerization procedure

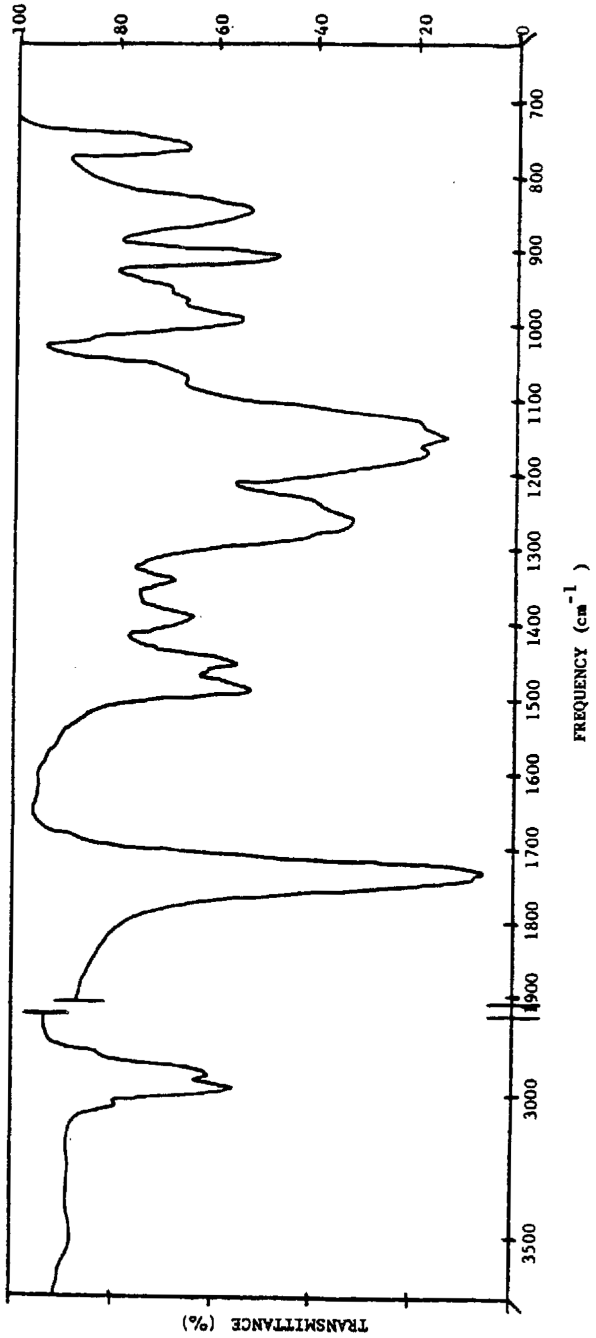


FIG. 3. Infrared spectrum of poly(glycidyl methacrylate) (KBr disk).

as used above was repeated with the modification that dodecanethiol (0.05% by weight on the monomer) was added to the reaction mixture. The linear polymer obtained was analyzed in the same way as the first poly(glycidyl methacrylate) polymer. Its ir spectrum, epoxy oxygen analysis, and elemental analysis were identical to those of the first polymer.

That the molecular weight of the poly(glycidyl methacrylate) prepared in the presence of the mercaptan was lower than the molecular weight of the polymer prepared in the absence of the chain transfer agent is readily demonstrated by a comparison of their respective intrinsic viscosities. The intrinsic viscosity of the mercaptan-modified polymer was measured to be 0.092 in 2-butanone at 20°C. This is about half the value obtained for the polymer prepared in the absence of the mercaptan.

The number-average molecular weight of the modified polymer was obtained by vapor pressure osmometry. The measured value was 7,600. This low molecular weight again reflects the chain transfer actions of the mercaptan.

The intrinsic viscosity $[\eta]$ and the molecular weight (M) of a polymer are related by Eq. (3). The value of a in this equation has been found to be close to 0.8 for many acrylate and methacrylate polymers [17]. Since the intrinsic viscosity and the molecular weight of the modified poly(glycidyl methacrylate) were measured, the equation can be used to calculate an approximate value of K for poly(glycidyl methacrylate) in 2-butanone at 20°C. The calculated value is 7.2×10^{-5}. This value is consistent with the K values that have been found for other similar types of polymers under similar conditions. Some of these K values are [18]: poly(methyl methacrylate) = 7.1×10^{-5}, poly(n-butyl methacrylate) = 9.7×10^{-5}, poly(cyclohexyl methacrylate) = 7.0×10^{-5}, and poly(n-butyl acrylate) = 7.15×10^{-5}.

Knowing the number-average molecular weight of the poly(glycidyl methacrylate) made in the presence of and in the absence of the dodecanethiol, the transfer constant, C_t, to the mercaptan can be calculated from Eq. (4),

$$\frac{1}{\overline{M}_n} = \frac{1}{\overline{M}_{n,o}} + C_t \frac{(t)}{(m)} \tag{4}$$

where $\overline{M}_n$ = number-average molecular weight obtained in the presence of transfer agent t, $\overline{M}_{n,o}$ = number-average molecular weight obtained in the absence of transfer agent t, C_t = transfer constant to transfer agent t, (t) = transfer agent concentration, and (m) = monomer concentration. The calculated transfer constant is 0.02.

Prototype Polymeric Compounds and Their Metal Complexes. Prototype polymeric compounds were prepared by reacting sodium aminoacetic and disodium iminodiacetate with linear poly(glycidyl methacrylate). The preparations involved attaching the ligands to the polymeric backbone through reaction with the epoxy rings of the polymer. Further, the ligands were attached in such a way that they were able to form chelate rings with metal ions. Two problems were encountered in the preparation of these prototype polymeric compounds: 1) preventing the products from cross-linking, and 2) obtaining high ligand yields. These problems were solved by using a large excess of the sodium salt form of the ligand in the postreaction and by the proper choice of a solvent system. The detailed preparation and characterization of each of these prototypes are given in the Experimental section.

The poly-1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate (HAHPM) was analyzed by ir spectroscopy. The spectrum, Fig. 4, indicates that the aminoacetic acid ligands became attached to the polymer backbone via reaction with the epoxy rings. The evidence for this interpretation is the absence of the absorption peaks associated with the epoxy ring at 3000, 900, and 840 cm^{-1} and the presence of peaks associated with the carboxylate group at 1635 and 1385 cm^{-1} and the presence of the peaks associated with the OH—NH groups at 3400 cm^{-1}. Further, the absorption frequencies of the carboxylate groups suggest that the attached ligands of the isolated polymer are in their zwitterion form [20]. This is not unexpected because it is well known that aminoacetic acid itself occurs in the zwitterion form in the pH region from which the polymeric prototype was isolated. In agreement with this interpretation is the behavior of the chelating polymer, Dowex A-1, as reported by Schmuckler [21]. The iminodiacetic acid ligands which are contained in this polymer progress through the same zwitterion forms as the free ligand and at about the same pH values.

In view of the spectral data, the pH characteristics of the HAHPM polymer are readily understood. When the attached ligands are in their sodium salt forms or their acid salt forms, the chelating polymer is water soluble; however, when the attached ligands are in their zwitterion acid forms, the polymer is water insoluble.

The prototype HIHPM polymer was isolated at pH value of 2.1 and 10.2. The spectra of the two products were very similar to that of the prototype polymer HAHPM. That the desired product was obtained was again shown by the absence of the peaks associated with the epoxy ring and the presence of peaks associated with the carboxylate and hydroxyl groups. The peaks associated with the antisymmetric and symmetric carboxylate stretching vibrations, which are at 1623 and 1382 cm^{-1}, respectively, in the spectrum of the HIHPM isolated at pH = 2.1, indicate that the attached ligands are in their zwitterion acid forms. In the disodium salt spectrum, the antisymmetric carboxylate stretching peak is at 585 cm^{-1} and is more intense than the ester peak at 1723 cm^{-1}. It is seen that the antisymmetric carboxylate peak is more intense and at a lower frequency in the disodium salt form whereas the symmetric carboxylate peak is at a higher frequency in the disodium salt form. These findings are in agreement with those of Nakamoto et al [22] and Malinovskii [23] and serve to substantiate that the desired product has been isolated.

The HIHPM polymer is thus water soluble in its disodium monosodium, and acid salt forms, but insoluble in its acid form.

The number of moles of ligand attached to a given weight of prototype polymer was determined by potentiometric titrations. This number was compared to the number of moles of ligand that would have become attached had each segmer of the polymer reacted with a ligand molecule. The ligand yield was then calculated as a ratio of these two numbers (Eq. 5).

$$\text{ligand yield} = \frac{\text{moles ligand present}}{\text{maximum possible moles ligand present}} \times 100 \qquad (5)$$

The ligand yield for this HAHPM polymer, as determined by monaqueous titrations, was 55%. The ligand yield of the isolated HIHPM polymer was determined by an aqueous potentiometric titration. The titration curve, although somewhat skewed at the monopolymer, contained iminodiacetic acid groups.

An elemental analysis was performed on the linear HAHPM polymer isolated at pH of 3.9. The measured nitrogen content indicated a ligand yield of 55%. The carbon and hydrogen analysis were also in good agreement with a polymer in which 55% of the segmers were

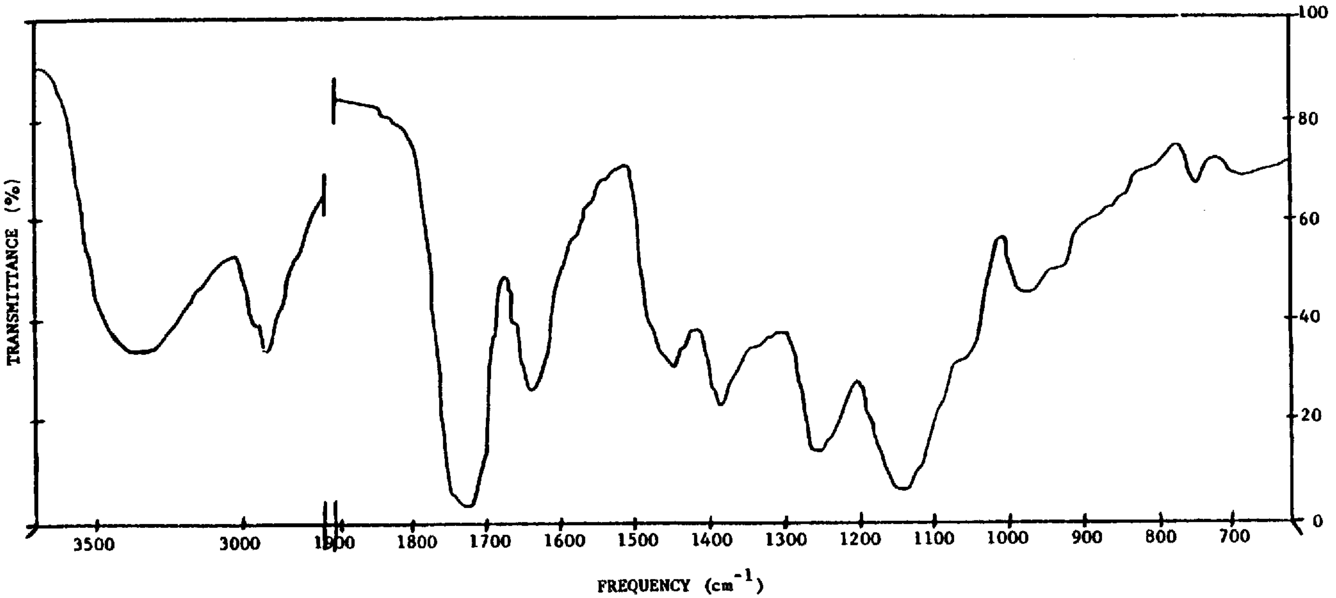
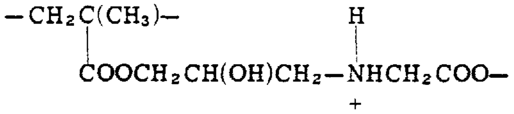
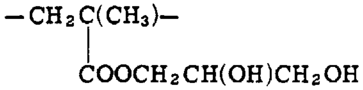


FIG. 4. Infrared spectrum of poly-1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate (KBr disk).



$$\begin{array}{l} -CH_2\underset{|}{C}(CH_3)- \\ \qquad COOCH_2CH(OH)CH_2-\overset{H}{\underset{+}{N}}HCH_2COO- \end{array}$$

and 45% of the segmers were



$$\begin{array}{l} -CH_2\underset{|}{C}(CH_3)- \\ \qquad COOCH_2CH(OH)CH_2OH \end{array}$$

The former structure is consistent with the ir spectral data which indicated that the attached ligands were in the zwitterion form. That the segmers which did not react with the ligand molecules reacted with water to form a glycol structure is consistent with the fact that a glycol structure (phenyl 1,2-ethanediol) is the main by-product in the preparations of the prototype monomeric compounds [1]. This by-product segmer would also be expected from the known tendency of epoxides to react with water in basic solutions. Furthermore, it is a desirable by-product because the hydrophilic nature of the hydroxyl groups should aid in the wetting of the polymer [24].

An elemental analysis was performed on the acid form of the HIHPM prototype polymer. Based on the nitrogen content, the ligand yield was calculated to be 71%. This is in good agreement with the titration data, especially in view of the skewed titration curve. The hydrogen content is also in excellent agreement with that calculated for a polymer in which 71% of the segmers have the desired ligand structure and 29% of the segmers have a glycol structure like that found in HAHPM. However, the carbon analysis is higher than predicted by theory. Assuming that these results are accurate, they indicate that either impurities are present or that segmers other than those of the ligand or glycol type, and which have a higher carbon content than either of these, may be present in the isolated HIHPM. A possible example of such a segmer would be unreacted glycidyl methacrylate segmer.

The prototype polymers were also characterized by potentiometric titrations. These titrations were carried out in 50% v/v dioxane-water at 25°C. The ionic strength was maintained constant by making the solution 0.1 M in potassium chloride. These conditions, which are the same as those used in measuring the acid dissociation constants of the prototype monomeric compounds, were used so that a comparison between the acid dissociation constants of the two types of prototypes could be made. The general procedure consisted of stirring the polymer in a dioxane-water solution of perchloric acid and then back-titrating with sodium hydroxide.

The measured acid dissociation constants of the polymeric prototype poly-1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate are shown in Table 2. A comparison of the pk_1 values of HAHPM and its monomeric analog N-(2-hydroxy-2-phenylethyl) (aminoacetic acid) indicates that the basicity of the amine group in the polymer is lower than it is in the monomeric ligand. The reason for this lowering is not readily apparent. It could be speculated, however, that it is due to increased hydrogen bonding between the amine nitrogen and the higher concentration of alcoholic OH groups which is found in the polymer. This explanation is consistent with the observed lowering of the amine basicity on going from iminodiacetic acid to N-2-hydroxyethyl aminoacetic acid [25] to N,N-bis(2-hydroxyethyl)aminoacetic acid [26].

The measured acid dissociation constants of the polymeric prototype poly-1-(N-iminodiacetic acid)-2-hydroxy-propyl methacrylate are also shown in Table 2. These dissociation constants are within experimental error, the same as those of its monomeric analog N-(2-hydroxy-2-phenylethyl)iminodiacetic acid [1]. This indicates that the acidity of the carboxylate group and the basicity of the amine group in the prototype polymer are the same as they are in the prototype monomeric analog. Several investigators [13, 21, 27] have found a similar resemblance between the acid dissociation constants of the iminodiacetic acid groups in the Dowex A-1 polymer and the acid dissociation constants of iminodiacetic acid monomeric analogs.

The prototype polymers were also examined for their complexing abilities with Pr(III), Ho(III), and Cu(II). This examination included the preparation, isolation, and ir spectral analysis of the various metal-polymer complexes, the determination of the polymer capacities as a function of metal ion and pH, and stability constant determinations.

The general preparation in each case consisted of slowly adding sodium hydroxide to a solution containing excess perchloric acid, prototype polymer, and the rare earth chloride. The rare earth ions and the attached ligands were in a 1:1 molar ratio in all of the preparations. To enable a comparison with the rare earth-polymer complexes, the analogous copper complexes were prepared in a similar fashion.

The ir spectra of the metal-polymer complexes were measured from 3900 to 600 cm^{-1}. They are all very similar to that of the praseodymium(III) complex shown in Fig. 5.

Unfortunately, only limited information concerning the nature of the metal-polymer complexes can be obtained from the recorded spectra. This is due partly to the broadness of the peaks and partly to the presence of groups other than the pertinent groups which absorb strongly in the regions of correlative interest. One conclusion that can be drawn from a comparison of the spectra is the interaction of the metal ions with the carboxylate groups of the attached ligands. This is shown more clearly in Tables 8 and 9. In these tables the carboxylate stretching frequencies are taken to be the midpoints of the respective peaks at maximum absorption.

Based on the splittings of the carboxylate stretching peaks, the degree of covalent bonding in the metal-carboxylate bonds appears to increase in the order Pr < Na < Ho < Cu < H. This is the same order that was found with the corresponding monomeric prototype compounds. The order is consistent with that expected on the basis of the relative basicities of the metals involved. Also, the frequencies of the carboxylate stretching vibrations in the spectra of the various metal complexes indicates that the bonding between the carboxylate groups of the polymer and the metal ions is highly ionic in nature.

Interactions between the metal ions and the nitrogen atoms of the attached ligands cannot be proven from the ir spectra of the metal-polymer complexes. The C—N—C stretching vibration, which was used for this purpose in the prototype monomeric complexes, cannot be used here because of the strong, broad ester band present at 1140 cm^{-1}. Likewise, the presence of the glycol segmers in the polymer makes it impossible to prove interaction between the metal ions and the alcoholic groups of the ligand segmers.

Because of these shortcomings in the ir spectral analysis, it was decided that the praseodymium(III) and holmium(III) complexes of HIHPM and HAHPM should be investigated potentiometrially. Thus the prototype polymer was potentiometrically titrated with standard sodium hydroxide in the presence of rare earth ions. So that the results could be more accurately compared to those of the prototype monomeric compounds, the experimental conditions employed were the same as those used in the potentiometric studies of the monomeric compounds. The derived stability constants are given in Table 2.

Complexation in the metal-polymeric prototype compounds is

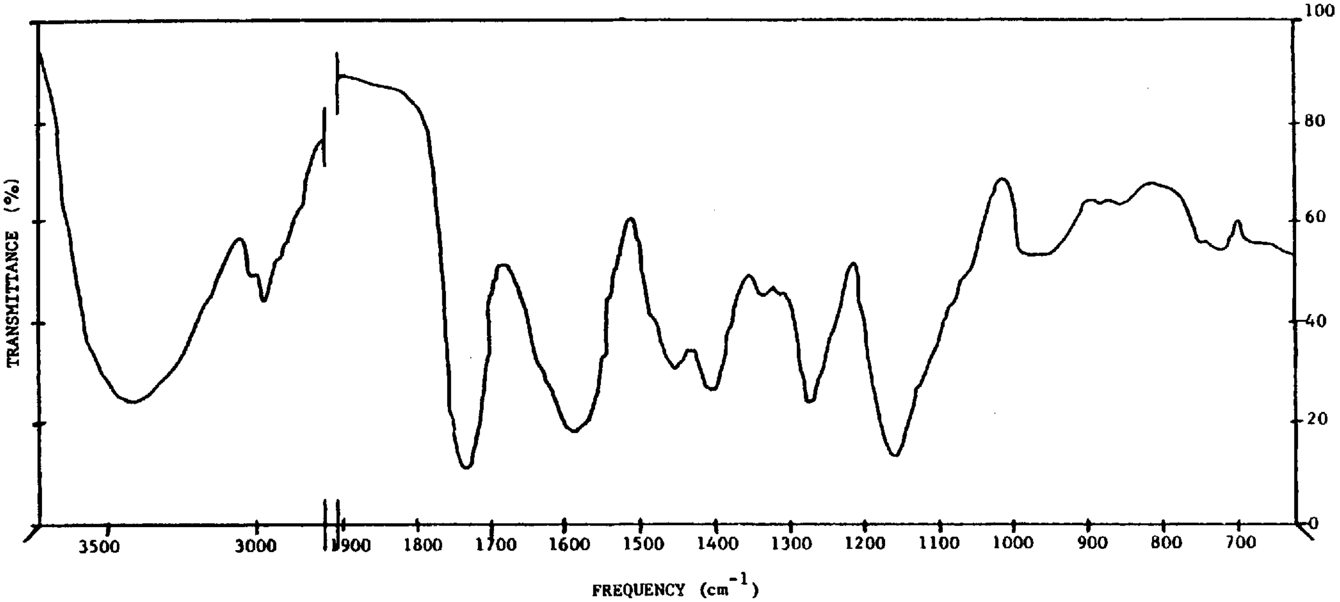


FIG. 5. Infrared spectrum of praseodymium(III) complex of poly-1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate (KBr disk).

TABLE 8. Carboxylate Stretching Frequencies of Metal-HAHPM Complexes

Metal	Antisymmetric frequency (cm^{-1})	Symmetric frequency (cm^{-1})	Frequency difference (cm^{-1})
Sodium	1585	1395	190
Praseodymium(III)	1580	1400	180
Holmium(III)	1600	1394	206
Copper(II)	1620	1380	240
Hydrogen	1635	1385	250

TABLE 9. Carboxylate Stretching Frequencies of Metal-HIHPM Complexes

Metal	Antisymmetric frequency (cm^{-1})	Symmetric frequency (cm^{-1})	Frequency difference (cm^{-1})
Sodium	1585	1400	185
Praseodymium(III)	1580	1400	180
Holmium(III)	1595	1395	200
Copper(II)	1618	1380	238
Hydrogen	1623	1382	241

shown by the magnitudes of the derived first stability constants. The log K_1 values for the metal-HAHPM complexes are the same, well within experimental error, as their corresponding values in the N-(2-hydroxy-2-phenylethyl)aminoacetic acid monomeric complexes. This strongly suggests that the complexing in the polymer is the same as it is in the monomeric prototype. This same result has been found for most monomer-polymer systems which have been studied [27-29]. It implies that the ligand segmers of the HAHPM polymer are acting as tridentate chelating ligands which are bonding to the rare earth ions through their carboxylate oxygen atoms, their amine nitrogen atoms, and their alcoholic oxygen atoms.

Likewise, the similarities between the magnitudes of the measured stability constants of the rare earth-HIHPM complexes and those of the rare earth-N-(2-hydroxy-2-phenylethyl)iminodiacetic acid chelates strongly suggest that the nature of the rare earth complexes in this polymer is the same as that in the monomeric analog. The implication is that the ligand segmers are acting as quadridentate chelating ligands toward the trivalent rare earth ions. By analogy to the prototype monomer, the donor atoms involved are the oxygen atoms of the two carboxylate groups, the nitrogen atom of the amine group, and the oxygen atom of the alcoholic group.

A comparison of the difference in the stability constants for the Pr(II) and Ho(II) complexes of each prototype polymer with the difference in the stability constants for the complexes of the same metals with aminoacetic acid and with iminodiacetic acid again shows a leveling effect in the prototype compounds. Whereas there is a difference of about 0.7 log unit between the log K_1 values of the praseodymium and holmium complexes of the iminodiacetic acid, these same metals with HIHPM have log K_1 values that are separated by only 0.3 log unit. Similarly, the difference between the log K_1 values of the praseodymium and holmium complexes of HAHPM is only 0.2 log unit whereas the difference between the log K_1 values of the aminoacetic acid complexes with these same metals is 0.4 log unit. Since the same trend was found in both the monomeric and polymeric prototypes, it is expected to occur also in the cross-linked chelating polymer to be used for the rare earth separations. This condition is not desireable because the separation of metals on a chelating polymer, measured as a function of pH, demonstrates the complexing behavior of that polymer. The capacities of HAHPM and HIHPM for trivalent rare earth ions were determined as a function of pH. A detailed description of the experimental procedure used in these measurements was given in the Experimental section. The results are tabulated in Table 1.

The results shown in Table 1 are interpretable in terms of the complexing behaviors of the ligands attached to the polymer. A case in point is that of the HAHPM polymer. The attached aminoacetic acid ligands in solutions below a pH of 5 are almost entirely present in their acid forms. Because the rare earth complexes of this ligand, both attached and unattached to the polymer, are relatively weak, the metal ions cannot favorably compete with the protons for the coordination sites. At higher pH values, however, the concentration of unprotonated ligands increases and hence metal coordination also increases. Further, at any given pH, the metal which forms the strongest complex with the attached ligand is expected to compete with the protons for the coordination sites more favorably than a metal which forms weaker complexes. Since it has been shown that the stability constants of the rare earth-HAHPM complexes increase when going from low to high atomic numbered metals, the observed greater complexing of thulium over cerium at pH values above 5 is understandable. Furthermore, whereas the attached ligands in HAHPM are essentially in their acid forms in the pH range 4-5, it is in this pH range that the first ionization of the ligands occurs, and it is expected that the HIHPM polymer should complex at lower pH values than the HAHPM polymer. This, together with the observed greater stability of the metal-HIHPM complexes over the metal-HAHPM complexes, would also account for the greater complexing ability of the HIHPM polymer at any given pH.

Cross-linked Copolymer Co-poly[glycidyl Methacrylate]-[Allyl Methacrylate]

As described in the Experimental section, this copolymer was made by a free radical polymerization in both 2-butanone and in n-heptane. The copolymer compositions were varied from 0.5% AMA/99.5% GYMA to 10.0% AMA/90.0% GYMA.

The ir spectrum of the copolymers were very similar to that of linear poly(glycidyl methacrylate). This similarity is not unexpected in view of the low concentration of allyl methacrylate segmers in the copolymer and of the very similar structures of the glycidyl methacrylate and allyl methacrylate segmers.

The epoxy oxygen analysis of the copolymer containing 95% glycidyl methacrylate segmers, and 5% methacrylate segmers is in excellent agreement with the calculated values.

The copolymer (R) prepared in n-heptane exhibited essentially the same properties as the co-poly[glycidyl methacrylate]-[allyl methacrylate] (U) made in 2-butanone. There was, however, one important difference the two copolymers. In any given solvent, Copolymer R would swell only to about half the volume of copolymer U. This is an important difference because successful postreactions of a cross-linked polymer are dependent upon the extent to which the polymer can be swollen. In order to investigate this problem in a more quantitative way, the swelling ratios of all of the copolymers were determined. The swelling ratio of a cross-linked polymer, as defined by Flory [30], is equal to the ratio of the volumes of the swollen and unswollen structures. If the swollen volume of the polymer is determined at maximum swelling, the swelling ratio is dependent upon the degree of crosslinking in the polymer; thus, the higher the maximum swelling ratio, the lower the degree of cross-linking in the polymer. The swelling ratios are listed in Table 3.

An examination of the results clearly shows that a copolymer made in n-heptance from a given comonomer composition has a swelling ratio of about one-half the value for the copolymer prepared in 2-butanone from the same comonomer composition. Further, it appears that the degree of swelling of the copolymers made in n-heptane is independent of the amount of allyl methacrylate in the comonomer mixture, at least until very high concentrations of allyl methacrylate are used. These results indicate that cross-linkages other than those attributed to allyl methacrylate are being formed in the copolymerizations in n-heptane. This cross-linking could be due to radical abstraction reactions. This type of reaction was suggested by others as the case of cross-linking in the preparation of poly(glycidyl methacrylate) in benzene [2]. In a solvent such as n-heptance, which is expected to have poor chain transfer properties, radical abstraction reactions allow the formation of the noted additional cross-links. However, in 2-butanone, which has been shown to have high chain transfer properties with polymers closely related to poly(glycidyl methacrylate) [31-33], additional cross-linking is inhibited.

Cross-linked Chelating Copolymers. These compounds were prepared by postreacting the 95/5 copolymer of glycidyl methacrylate and allyl methacrylate with sodium aminoacetate and with disodium iminodiacetate. Because of its higher swelling ratio, the copolymer that was prepared in 2-butanone was used.

The (W) co-poly[1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate]-[allyl methacrylate] (CAHPM) was isolated directly from the reaction mixture (WA) and also from an aqueous medium at a pH of 5.0 (WB). The ir spectrum of each of the isolated CAHPM copolymers was recorded. The spectra are almost identical as shown in Fig. 6. The only apparent difference between them is that in the spectrum of WA, the carboxylate

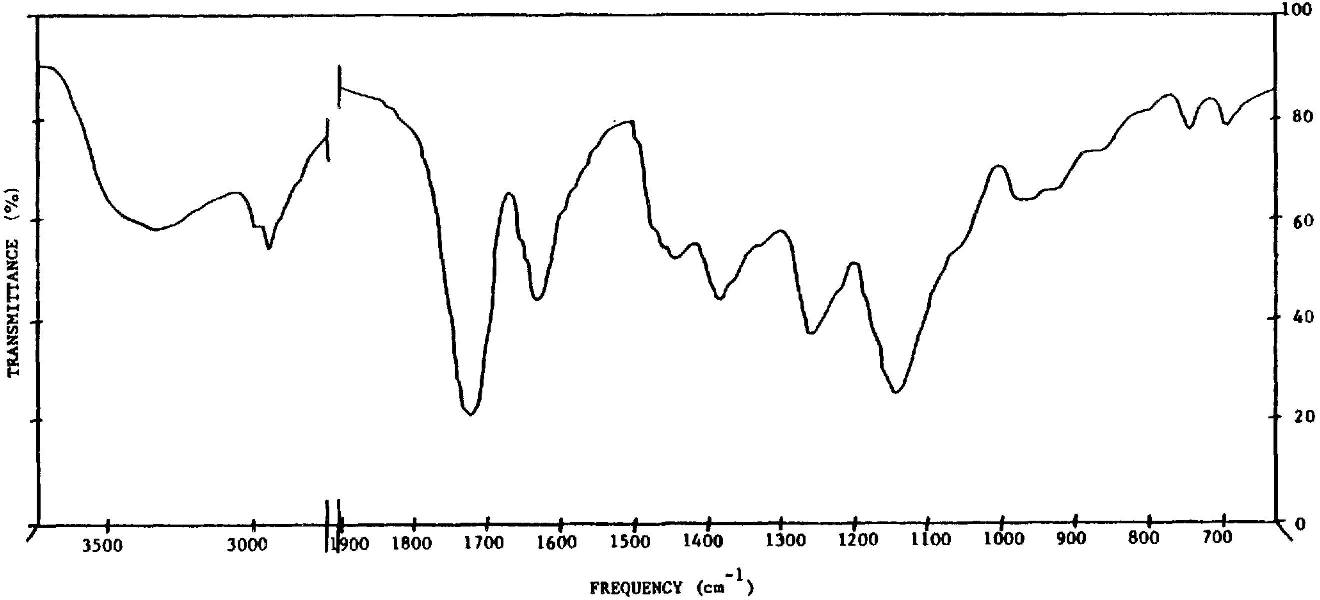


FIG. 6. Infrared spectrum of co-poly[1-(N-aminoacetic acid)-2-hydroxy-propyl methacrylate acrylate]-[allyl methacrylate] (KBr disk).

antisymmetric and symmetric stretching vibrations absorb at 1580 and 1390 cm $^{-1}$, respectively, whereas in the spectrum of WB these same absorptions occur at 1630 and 1383 cm^{-1}, respectively. Both spectra are similar to that of co-poly[glycidyl methacrylate]-[allyl methacrylate] except that they have no epoxy ring peaks at 900 or 840 cm^{-1} and they have strong absorptions in the OH—NH region (3300 cm^{-1}) and in the carboxylate region. These are precisely the spectral changes that would be expected from the structures of the starting copolymer and the CAHPM product. Also, the spectrum of WA is essentially identical to that of HAHPM in its sodium salt form, and the spectrum of WB is identical to that of HAHPM in its acid form. These similarities may be taken as indications that WA and WB are the sodium salt form and the acid form of CAHPM, respectively. This conclusion is also consistent with the potentiometric titration data of CAHPM which shows that the isoelectric point of the compound occurs at a pH of 5.0.

The CIHPM copolymer was isolated at three different pH values. It was isolated directly from the reaction mixture (pH = 10.7) and from aqueous dispersions which were at pH values of 6.5, the pH value at which the inflection point of its potentiometric titration curve occurred, and 2.0, the pH value at which its linear polymeric analog (HIHPM) was found to be in its acid form.

The ir spectrum of each of the three isolated CIHPM copolymers was measured from 3900 to 600 cm^{-1}. These spectra, shown in Fig. 7, were all very similar to that of CAHPM. The main differences between the three CIHPM spectra were in the 1650 to 1350 cm^{-1} region. Two important features that appear in this spectral regions region are: 1) With increasing pH, the carboxylate antisymmetric stretching peak increases in intensity with respect to the ester peak at 1720 cm^{-1}; and 2) the antisymmetric carboxylate stretching peak is centered at 1625 cm^{-1} in the spectra of the CIHPM copolymers isolated at pH values of 2.0 and 6.5 whereas it is at 1585 cm^{-1} in the spectrum of the CIHPM copolymer isolated at a pH of 10.7. These two observations are the same as those noted by Nakamoto [22] in the spectra of the various forms of iminodiacetic acid and N-hydroxyethyliminodiacetic acid. The similarities between the CIHPM spectra and the spectra of monomeric ligands can be used to identify the various forms of the CIHPM copolymer. Accordingly, CIHPM is predominantly in its acid form at a pH of 2.0, in its monsodium salt form at a pH of 6.5, and in its disodium salt form at a pH of 10.7. These pH values are very close

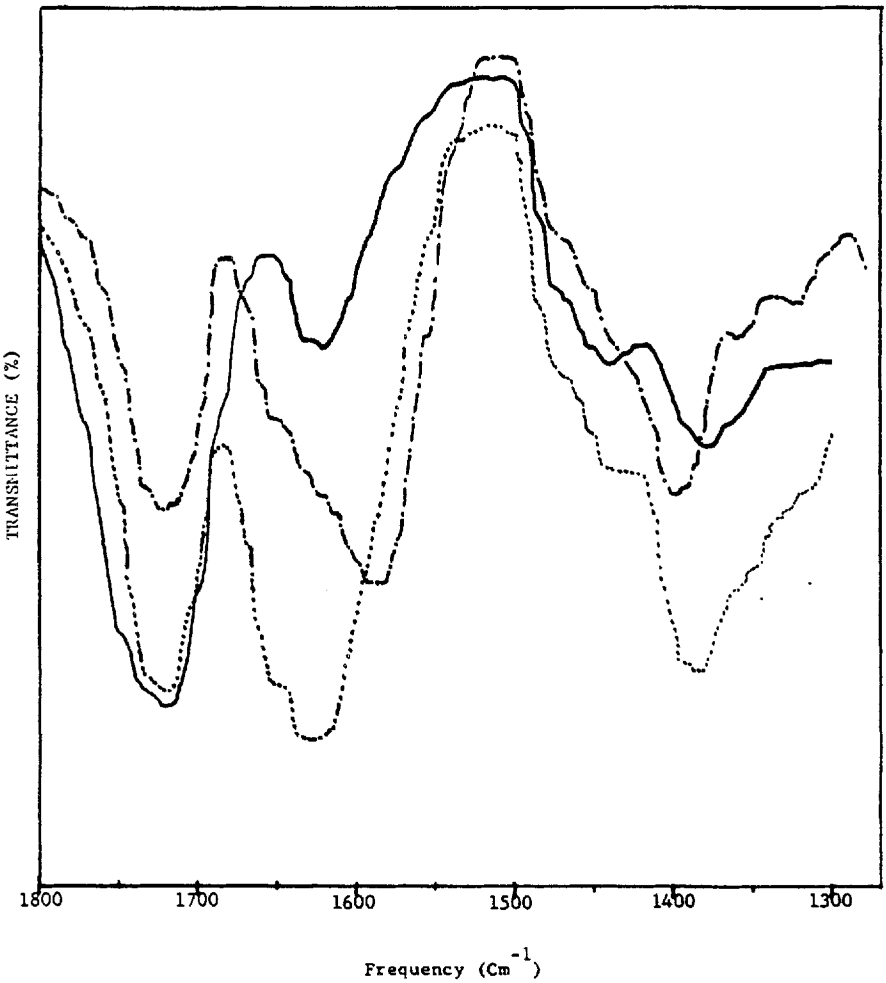


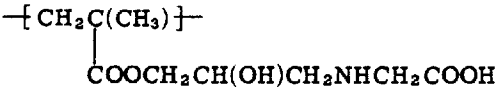
FIG. 7. Portion of ir spectra of co-poly[1-(N-iminodiacetic acid)-2-hydroxy-propyl methacrylate]-[allyl methacrylate]. (——) Copolymer isolated at pH 2.0. (· · ·) Copolymer isolated at pH 6.5. (- · -) Copolymer isolated at pH 10.7.

to those that were found by Nakamoto [22] for the corresponding structures of the free iminodiacetic acid.

Aqueous potentiometric titrations of CAHPM indicated that the apparent pk_1 and pk_2 values of this copolymer were 2.5 and 7.5, respectively. A comparison of these values with those of aminoacetic acid (pk_1 = 2.43 and pk_2 = 9.62 at 25°C in water [34], shows the same trends observed for the prototype compounds: the acidity of the carboxylate group in the copolymer is about the same as it is in free aminoacetic acid, and the basicity of the amine nitrogen in the copolymer is appreciably lower than it is in free aminoacetic acid.

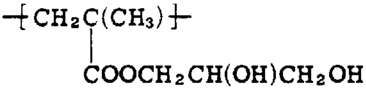
The potentiometric titrations of CIHPM gave a titration curve with definite inflection points at pH values of 10.4 (disodium salt form) and 6.8 (monosodium salt form). In agreement with the proposed structure of CIHPM, the apparent pk_1 and pk_2 values of 3.2 and 9.0, respectively, are close to those found by Leyden and Underwood [13] for the iminodiacetic acid ligands in Dowex A-1 chelating resin (pk_1 = 2.97 and pk_2 = 8.55). They are also comparable to the acid dissociation constants of iminodiacetic acid [35] (pk_1 = 2.54 and pk_2 = 9.12) and of N-hydroxyethyliminoacetic acid [25] (pk_1 = 1.96 and pk_2 = 8.78).

Additional information concerning the structures of the cross-linked chelating copolymers were obtained from their elemental analysis. The integration of the data on CAHPM is described here to illustrate how this was accomplished. Assuming that the 5% allyl methacrylate segmers present in the co-poly[glycidylmethacrylate]-[allyl methacrylate] starting material were unaltered by the reaction with sodium aminoacetate, the CAHPM copolymer should contain 5% allyl methacrylate cross-linking segmers. According to the potentiometric titration data, another 42% of the segmers are ligand segmers of the type



$$-\!\left[\mathrm{CH_2}\underset{\mathrm{COOCH_2CH(OH)CH_2NHCH_2COOH}}{\underset{|}{\mathrm{C}}}\mathrm{(CH_3)}\right]\!-$$

According to values obtained from a thermogravimetric analysis of a sample of CAHPM dried in the same manner as the sample used for the elemental analysis, the CAHPM contains approximately 3.5% by weight of water. Also, since the main by-product of the HAHPM prototype polymer was a glycol segmer of the type

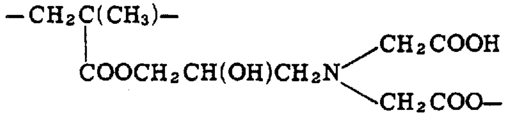


$$\begin{array}{l}-\!\!\left[\mathrm{CH_2\underset{|}{C}(CH_3)}\right]\!\!-\\ \qquad\quad \mathrm{COOCH_2CH(OH)CH_2OH}\end{array}$$

this same segmer should account for the remaining 53% of the segmers in the CAHPM copolymer.

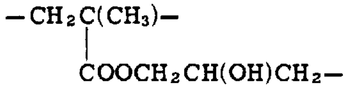
The elemental analysis of CAHPM, however, did not agree with this predicted structural composition. The nitrogen content indicated that 48% of the segmers in the copolymer contained attached ligands. This apparent discrepancy is explained reasonably if one considers that the carboxylate groups can also react with the epoxy rings in the desired manner (i.e., via the amine nitrogen) in 48% of the segmers; a certain amount of the ligand segmers formed reacted further through their carboxylate groups with other epoxy rings. The amount of segmers taking part in this secondary reaction is 6%; this value represents the difference between the percentage of ligand segmers calculated from the potentiometric titration and the percentage calculated from the elemental analysis. When this additional reaction is taken into consideration, the determined elemental analysis is in much better agreement with theory and the titration data is then consistent with the elemental analysis.

Using the same approach for integrating the data on CIHPM, it can be shown that the polymer contains 55% ligand segmers, 5% cross-linking segmers, 24% glycol segmers, 8% segmers of the type



$$\begin{array}{l}-\mathrm{CH_2\underset{|}{C}(CH_3)}-\\ \qquad \mathrm{COOCH_2CH(OH)CH_2N}\begin{array}{l}\diagup \mathrm{CH_2COOH}\\ \diagdown \mathrm{CH_2COO}-\end{array}\end{array}$$

and 8% segmers of the type



$$\begin{array}{l}-\mathrm{CH_2\underset{|}{C}(CH_3)}-\\ \qquad \mathrm{COOCH_2CH(OH)CH_2}-\end{array}$$

The latter two segmers are the results of secondary reactions of the attached ligands.

The metal complexation behaviors of the CAHPM and the CIHPM copolymers were studied by reacting each copolymer with several trivalent rare earths and with divalent copper. The procedure employed was described in the Experimental section. That the metal ions were absorbed by the cross-linked chelating copolymers was shown by the colors of the isolated products. In each case, the color of the product was the characteristic of the compounds of the metals. Furthermore, that the metal ions were complexed by the copolymers and not merely entrapped by the copolymer matrix was shown by the stability of these colors toward water washings.

Complexation of the metals by CAHPM and CIHPM was shown in a more quantitative fashion by ir spectroscopy. Because of the broadness of the peaks in all of these spectra, as shown by that for the samarium(III) complex in Fig. 8, their usefulness for structural determinations is quite limited. Besides their noted similarities, the only information that can be discerned from the spectra is the shifting of the peaks associated with the carboxylate stretching vibrations. The frequencies of these vibrations for the metal saturated copolymers are given in Table 10. It may be recalled that the antisymmetric and symmetric carboxylate peaks occurred at 1630 and 1383 cm^{-1}, respectively, in the acid form of CAHPM, and at 1580 and 1390 cm^{-1}, respectively, in the sodium salt form of CAHPM. Comparing the carboxylate frequencies in the spectra of these two forms of the CAHPM copolymer with the carboxylate frequencies in the spectra of the metal-CAHPM products, the complexation of the metal ions by the carboxylate groups is evident. A similar conclusion is reached by comparing these same peaks in the spectra of the metal saturated CIHPM copolymers with those of the disodium salt form of CIHPM (antisymmetric = 1585 cm^{-1}; symmetric = 1400 cm^{-1}) and the acid form of CIHPM (antisymmetric = 1625 cm^{-1}; symmetric = 1380 cm^{-1}). Also, as in the rare earth complexes of the prototype polymers, the frequencies and frequency differences between the antisymmetric and symmetric carboxylate stretching peaks found in the CAHPM and CIHPM-metal complex spectra indicate that 1) the carboxylate-rare earth bonds are all highly ionic, and 2) the degree of covalent bonding increases with increasing atomic number of the rare earth.

Distribution Studies of Rare Earth Ions with Co-poly[1-(N-iminodiacetic Acid)-2-hydroxypropyl Methacrylate]-[Allyl Methacrylate]. The final phase of this research was an investigation into the possibility

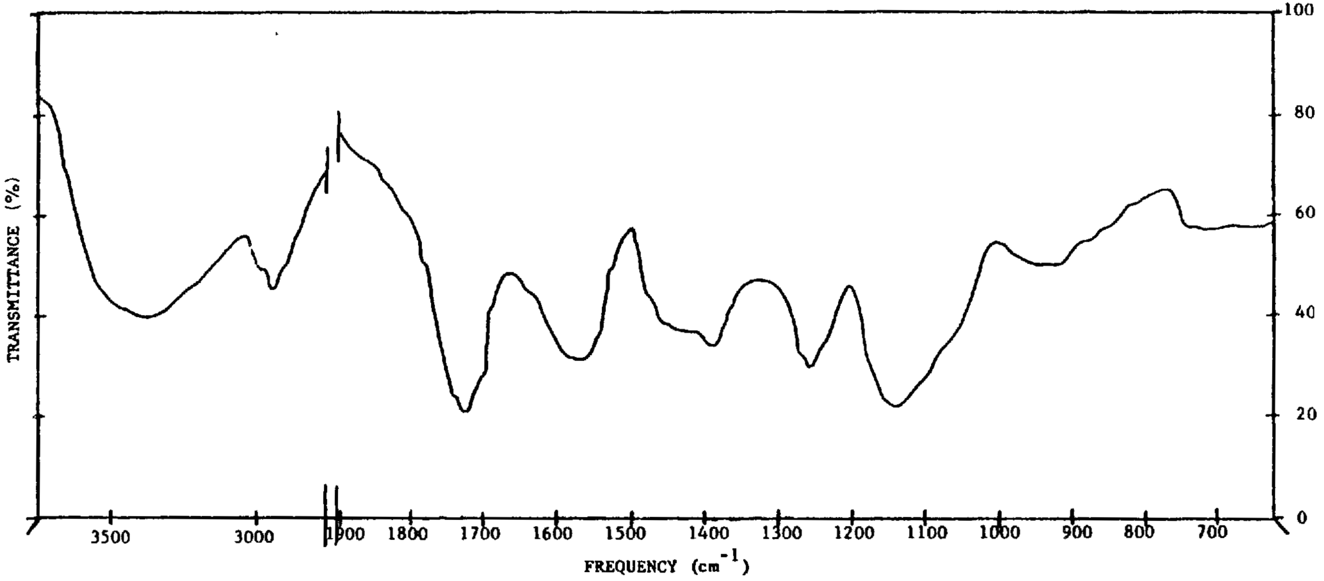


FIG. 8. Infrared spectrum of samarium(III) saturated co-poly[1-(N-aminoacetic acid)-2-hydroxypropyl methacrylate]-[allyl methacrylate] (KBr disk).

TABLE 10. Carboxylate Stretching Frequencies of Metal Saturated Cross-linked Copolymers

Copolymer	Metal	Antisymmetric frequency (cm^{-1})	Symmetric frequency (cm^{-1})	Frequency difference (cm^{-1})
CAHPM	Cerium(III)	1570	1390	180
CAHPM	Samarium(III)	1570	1390	180
CAHPM	Holmium(III)	1585	1385	200
CAHPM	Copper(II)	1625	1380	245
CIHPM	Cerium(III)	1570	1395	175
CIHPM	Europium(III)	1580	1390	190
CIHPM	Thulium(III)	1585	1390	195
CIHPM	Copper(II)	1620	1370	250

of separating the rare earths with the CIHPM chelating copolymer. A brief review of the literature [12, 28, 36-39] suggests that there are many factors that can effect such separations. However, one of the primary factors involved in metal separations on chelating resins is pH. At a given pH, a metal that forms a weak complex with the resin is more apt to be displaced from the resin than one that forms a stronger complex. The present investigation was designed to study the effect of pH on the ability of the CIHPM copolymer to separate the rare earths.

The distribution studies involved the determinations, at various pH values, of the batch distribution coefficients (K_d) and the batch selectivity coefficients (K_s) of several rare earth ions with the chelating copolymer CIHPM. This particular copolymer was chosen for the following reasons:

1) The stabilities of the rare earth complexes with the prototype polymer HIHPM showed the greatest variation from one end of the rare earth series to the other end of the series.
2) Because of the high ligand yield that was obtained in the preparation of CIHPM, that copolymer has the highest capacity for metal ions.
3) As shown in the capacity studies with HIHPM, the copolymer containing iminodiacetic acid ligands can complex the rare earth ions at lower pH values than can the other copolymers that were investigated.

The particular radioactive isotopes used were ^{141}Ce, ^{152}Eu, and ^{170}Tm. A portion of the gamma spectrum of a mixture of these isotopes is shown in Fig. 9. The separations of the reference gamma peaks are clearly shown. The radioactive tracers were used with their inactive isotopes in order to avoid the problems that are normally encountered in using carrier-free tracers in experiments of this type [40].

The results of the batch distribution coefficient study are given in Table 5. A plot of log K_d vs pH for each of the rare earth ions is shown in Fig. 1. It is seen that between a pH of 1.5 and 3.3, the affinity of the resin for the three rare earths is in the same order as the chelate stabilities of these metals with the attached ligands of the resin. However, at a pH value above 3.8 cerium is extracted by the CIHPM copolymer to a greater extent than either europium or thulium. This is not understandable in view of the relative

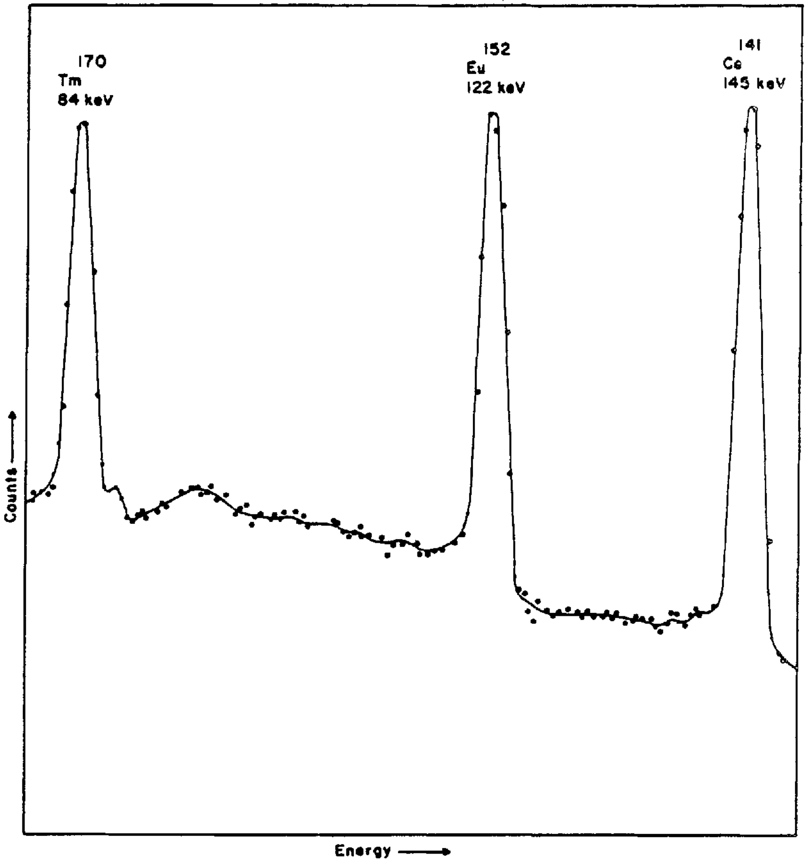


FIG. 9. Gamma spectrum of a mixture of ^{170}Tm, ^{152}Eu, and ^{141} Ce.

stabilities that would be expected for these metals with CIHPM. Strangely enough, however, it would explain the seemingly contradictory results obtained by Hering [38] and by Christell [41]. Hering reports that in the pH range 3-4, a chelating resin containing iminodiacetic acid ligands prefers the high atomic numbered ytterbium over the lower atomic numbered lanthanum. Christell, on the other hand, reports that the high atomic numbered lutetium is eluted before the lower atomic numbered lanthanum from a column of Dowex A-1 at a pH of 4.6. Both of these results are seen to be consistent with the results found in the distribution coefficient study of this research.

The data obtained in this study are consistent with those obtained by others. For example, Leyden and Underwood [13], and also Szidon and Fritz [42], found trends in K_d values of several metals with Dowex A-1 chelating resin that were similar to the trends reported in this study. The shapes of the log K_d vs pH curves found in this study are also the same as those found by Gregor [43] for the pretransition metals with an m-phenylene diglycine resin; they are distinctly different from the shapes of the curves that Gregor found for the transition and posttransition metals. This is in keeping with the observation that the complexing behavior of the trivalent rare earths is more like that of the alkaline earths than like that with the d-type transition elements.

The separation factors of the rare earths relative to europium were calculated from the K_d values obtained from the batch equilibration experiments. These values are listed in the last column of Table 5. A comparison of these values indicates that the most successful separations of the rare earths on a column of CIHPM should occur at a pH of about 5. This applies only to separations that are attempted under the same conditions as those that were used in the batch equilibrations.

It is interesting to compare the separation factors found in this study with those found under similar conditions on other resins. Surls and Choppin [44] found that in the absence of any complexing ligands, sulfonated styrene-divinylbenzene ion exchange resins gave separation factors for the various trivalent rare earth ions that were not very different from unity. They found, for example, that the separation factor for cerium and europium was 1.42 and that for thulium and europium was 1.38. These values are considerably lower than those found with the CIHPM copolymer at pH values between 4.5 and 6.5. Stewart [45], however, working with the same type of sulfonic acid resin, reported much higher separation factors when glycolic or lactic acid was present in the system. He found, for example, that in the presence of glycolic acid at a pH of 4.0, the separation factor for cerium and europium is 7.9 whereas that for thulium and europium is 2.5. Even larger separation factors were found by Cornish [46] when ethylenediaminetetraacetic acid was used as an elutrient in the column separation of the rare earths. He found separation factors as high as 5.0 for adjacent rare earth ions. These values are much higher than those found for the CIHPM copolymer. It appears, therefore, that better separations of the rare earths can be effected by using complexing elutrients in conjunction with a sulfonic acid type ion exchange resin rather than by using the chelating copolymer CIHPM.

A final comparison can be made between the separation factors found with the CIHPM copolymer and those reported for a weakly acidic ion exchange resin. Arnold and Son Hing [47] investigated the ability of a carboxylic acid resin to separate the trivalent rare earth ions. Their data indicate a separation factor of 2.6 for cerium and europium and 1.7 for thulium and europium. These values are seen to be lower than those found for these same metal ions with the CIHPM copolymer, and thus it should be able to separate the rare earths more efficiently than should a weakly acidic ion exchange resin.

The batch selectivity coefficients (K_s) that were determined in this study are listed in Table 6. A plot of the per cent rare earth extracted by the resin vs pH for each of the rare earth ions that was investigated is shown in Fig. 2. It is seen that except at the lowest pH values studied, cerium is not able to complete with the other two metals for the ligand sites of the copolymer. This is expected since cerium should form the least stable complex with CIHPM. However, it is also noted that, over most of the pH range investigated in this study, the affinity of the resin for thulium is about the same as it is for europium. Only as the pH is raised above 5.1 does the copolymer clearly show a preference for the thulium(III) ions over the europium(III) ions. Apparently the stabilities of the complexes which these two metals form with CIHPM are not sufficiently different to permit the resin to be highly selective for either of the metals. The reason for the greater selectivity at pH values above 5.1 is not now understood.

The rare earth capacity of the CIHPM copolymer as a function of pH was also determined from the batch selectivity coefficient study. These capacities are shown in the Experimental section. These capacities are very close to those found for the prototype polymer HIHPM. A comparison can also be made to the capacity of the commercial chelating resin Dowex A-1. This resin, in the ammonium form, has a capacity of 5 meq of Cu(II) per gram of dry resin [48]. This is seen to be very close to the value found for CIHPM in its sodium form.

CONCLUSIONS

The results of this research suggest that some separation of the rare earths can be achieved with the chelating copolymer co-poly-[1(N-iminoiacetic acid)-2-hydroxy-propyl methacrylate]-[allyl methacrylate]. A comparison of the separation factors of the rare earths shows that the CIHPM copolymer should yield better separations of these elements than the sulfonic acid resins or the carboxylic acid resins alone. However, these same factors indicate that separations on a column of CIHPM under the same conditions that were used in this study would probably not compare with those obtained when complexing agents are used in conjunction with the sulfonic acid ion exchange resins. Further work on the CIHPM system should be directed towards finding conditions which would improve the separation ability of this resin. This work might include a study of the effects of temperature, solvent composition, ionic strength, and counterions on the rare earth separations.

It might prove more helpful, however, to use a modified form of the CIHPM copolymer for separating the rare earth ions. Such a form would be one in which the hydroxy groups that are attached to the ligand nitrogen atoms would be eliminated. A possible way of doing this would be to convert them to methoxy groups or to some other groups that would not interact with the rare earth ions. Based on the findings of the prototype studies, it is felt that the elimination of these hydroxy groups would result in a greater difference in the stabilities of the rare earth-CIHPM complexes. This greater difference in stabilities would, in turn, be expected to considerably enhance the ability of the copolymer to separate the rare earth ions from one another.

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