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Redox polymerization of acrylamide by polymer supported vanadium (V) ion

Sunny Skaria, C. R. Rajan and S. Ponrathnam*
Chemical Engineering Division, National Chemical Laboratory, Pune - 411 008, India
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Macroreticular glycidyl methacrylate–ethylene glycol dimethacrylate (GMA-EGDM) copolymers of controlled particle size were synthesized by suspension polymerization. The copolymer beads were derivatized to incorporate di- and tetracarboxylic acid functionalities. Vanadium (V) ion was chelated on the modified copolymers. The vanadium chelated copolymers were used in combination with cyclohexanone as redox reagent for the free radical polymerization of acrylamide at 30°C. The molecular weights of the polyacrylamide were significantly higher than that prepared by a soluble vanadium (V) ion – cyclohexanone homogeneous redox initiator pair. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

In the recent past polymer anchored ligands have triggered significant interest in applications such as separation processes, heterogeneous catalysts (polymer bound transition metal ions) and immobilization of biocatalysts[1–3]. These are generated by the suspension polymerization of functional monomers. The alternate and preferred methodology is through modification of preformed reactive polymer matrices to attach ligands suited to complexing transition metal ions and to form heterogeneous transition metal complexes[4]. Styrene–divinyl benzene copolymer beads of varying crosslinking densities have been the matrices of choice for the complexation of transition metal ions. More recently, other functional polymers such as crosslinked glycidyl methacrylate–ethylene glycol dimethacrylate (GMA–EGDM) copolymers have been evaluated. These moderately hydrophobic matrices have an oxiranoyl pendant group capable of stable covalent bond formation with a variety of reagents possessing amino, alkylamino, phenolic, carboxyl and thio groups. Thus, a rich variety of chelating ligands can be generated[5]. The beaded GMA–EGDM copolymers formed by suspension polymerization have macropores at very high relative concentration of EGDM (high crosslink density)[6]. The chelating ligands are anchored on the surface of these pores. The presence of macropores decreases the mass transfer diffusional effects[7]. If an additional positive partitioning effect could be induced then these polymeric transition metal complexes would be better reagents vis-à-vis the analogous low molecular mass homogeneous transition metal complexes. Even in the absence of a positive partitioning effect, these porous polymers are a better choice over nonporous resins used as ion exchangers.

Polymers with amino carboxylic acid moieties have been investigated in the past for chelation of multivalent metal ions[8,9]. The study of such polymeric transition metal complexes as catalyst in the organic transformations and as initiator in polymerization reactions is of some interest from environmental perspectives as well as a means to effectively recover expensive metal ions[10].

The polymerization of acrylic monomers have been initiated by redox pairs consisting of low molar mass transition metal complexes and a suitable reagent[11]. Thus, the ammonium metavanadate–cyclohexanone pair in dilute sulfuric acid media has been evaluated for the polymerization of acrylates[12]. Polymeric heterogeneous initiators are advantageous over the corresponding homogeneous pair in the recyclability of the catalyst and leads to polymers relatively free from ionic impurities or reactive end groups[13,14]. Commercially pertinent polyacrylamides of very high molecular weights are prepared either by reverse emulsion or reverse microemulsion polymerization. These methodologies have been extensively investigated by Candau *et al.*[15].

The primary objective of this study is to use a macroporous polymeric ligand–vanadium complex in combination with cyclohexanone to induce a redox reaction, particularly polymerization of water soluble monomer such as acrylamide. Thus, macroporous oxiranyl polymer beads with specific particle size distribution were synthesized and converted into di-tetra acetates. The complexation and the oxidation state of the complexed vanadium ion were examined by X-ray photoelectron spectral studies prior to the investigation of the polymer–vanadium complex as the oxidizing component in the redox pair. The molecular weight of polyacrylamide obtained was compared with that synthesized by the corresponding homogeneous pair under identical conditions.

EXPERIMENTAL

Materials

Glycidyl methacrylate and ethylene glycol dimethacrylate were obtained from Fluka AG; Switzerland.

Table 1 Polymerization of acrylamide

Polymer no.	Catalyst	[M] (mol dm^{-3})	[CH] (mol dm^{-3})	[V] × 10^4 (mol dm^{-3})	Yield (%)	$[-\eta]$ (dl g^{-1})	M_v (×10^{-5})
1	IDA	0.7	0.025	4.5	95	4.1	13.3
2	DTA	0.7	0.025	4.5	95	3.7	11.4
3	DTA	0.7	0.050	4.5	100	2.5	6.3
4	AMV*	0.7	0.025	4.5	45	1.7	3.5

All reactions were carried out at pH 2 and at 30°C for 24 h
IDA = Iminodiacetic acid–vanadium (V) complex; DTA = diamino tetraacetic acid–vanadium (V) complex; AMV* = ammonium metavanadate in homogeneous conditions; [M] = concentration of monomer, acrylamide in water; [CH] = concentration of cyclohexanol; [V] = concentration of vanadium ions

Iminodiacetic acid was obtained from Aldrich Chemical Co. (USA). Sodium hydroxide and ammonium metavanadate were obtained from Loba Chem. (India). Acrylamide and cyclohexanone were from SD Fine Chem. (India).

Macroreticular GMA–EGDM copolymer was synthesized by a reported procedure[16]. The polymer beads obtained were washed with water, methanol and dried under vacuum at 40°C. The particle size of the polymer beads was in the range of 250–420 μm.

Synthesis of chelating polymer

The GMA–EGDM copolymer beads were modified with iminodiacetic acid by refluxing 5 g polymer beads (14.68 milliequivalents of oxiranoyl units) with 100 ml aqueous solution containing 9.7 g (73.5 mmol) iminodiacetate at pH 11.5 for 24 h. The resultant iminodiacetic acid incorporated beads were washed with distilled water, and thrice with 0.2 N hydrochloric acid and 0.2 N sodium hydroxide. After a final washing with 0.2 N hydrochloric acid, the beads were dried under vacuum at 30°C. Diamino tetraacetic acid functionality was incorporated in the GMA–EGDM copolymer by a multi-step process. The capacity of the two polymeric acid (chelating) beads were estimated by chemical titration[17].

Chelation of vanadium ions

Chelating polymer beads (0.5 g) were taken in a 250 ml stoppered conical flask and shaken with 100 ml acidic solution of sodium metavanadate (1 mmol l^{-1}) for 24 h. The resultant vanadium chelated polymer beads were washed with water and dried. The amount of vanadium ion incorporated in the chelating polymer was determined by atomic adsorption spectroscopy. The result was estimated as mmol of vanadium ions adsorbed g^{-1} polymer.

Polymer characterization

The BET surface area measurements were taken on a Quantasorb unit. The pore size distribution and pore volume of the copolymer beads was estimated by mercury intrusion porosimetry in the pressure range of 0–4000 kg cm^{-2} with an Autoscan 60 mercury porosimeter, from Quantachrome (USA). I.r. spectra of copolymer beads were taken at all stages of modification in potassium bromide pellets with a Shimadzu IR-470 model spectrophotometer. The acid capacities of the chelating carboxylic acid copolymers were calculated from chemical titrations. XPS (ESCA-3 MK, VG Scientific, UK) of the vanadium chelated copolymers were taken using Mg$K\alpha$ under evacuation of the sample at 10^{-8} Torr. The scanning electron microscopy of the

base as well as the modified copolymers were taken using Stereoscan 440 scanning electron microscope unit.

Polymerization of acrylamide

The polymerizations were carried out in 50 ml stoppered flasks. Dilute sulfuric acid (20 ml) of pH 2 was taken in the flask and cyclohexanone and acrylamide were added. Then the contents were well purged with oxygen free nitrogen for 3 min. The polymeric initiator 5 wt% with respect to monomer was added. The flasks were stoppered, thermostated at 30°C and shaken for 12 h. The polymeric initiator was separated by filtration and polyacrylamide was precipitated by addition to an excess of methanol. The precipitated polyacrylamide was dissolved in distilled water, reprecipitated in methanol and dried under vacuum at 40°C. The intrinsic viscosity of polyacrylamide samples were estimated in 1 N sodium nitrate solution at 30°C with an Ubbelohde viscometer. The constants K and a were taken as 3.73 × 10^{-4} dl g^{-1} and 0.66[13]. The estimated intrinsic viscosity and the molecular weights are presented in *Table 1*.

RESULTS AND DISCUSSION

The macroreticular GMA–EGDM beads was prepared from a GMA–EGDM feed mole ratio of 50:50. The concentration of oxiranoyl group present was 2.94 mmol g^{-1} of polymer. The crosslinking density of the copolymer beads were calculated from the mole percent of the divinyl monomer (ethylene glycol dimethacrylate) relative to the functional monovinyl monomer (glycidyl methacrylate). The surface area of the copolymer beads was estimated to be 108 m^2 g^{-1}. The pore volume was determined by mercury porosimetry as 0.50 cm^3 g^{-1}. The mercury porosimetry data implied a bimodal distribution of pore sizes in the copolymer (*Figure 1*). The i.r. spectra of the base copolymer showed characteristic peak of oxiranoyl group at 908.2 cm^{-1}.

The iminodiacetic acid copolymer (I) was synthesized by a one step process as presented earlier. The mole ratio of iminodiacetate to oxiranoyl group was kept at 5:1. Various methodologies (changing the solvents, aqueous environment, pH) were tested with a high loading of iminodiacetic acid ligand. An aqueous environment and a pH of 11.5 was the most suitable one for the reaction. The acid capacity was estimated to be 1.19 mmol of univalent sodium ions g^{-1} copolymer while the elemental nitrogen analysis showed 1.81 wt% nitrogen g^{-1} copolymer (I). This indicates a 45% modification of the oxiranoyl groups (ligand loading) on the copolymer. The GMA–EGDM copolymer is nonswelling in water. Hence this 45% modification points to a large concentration of
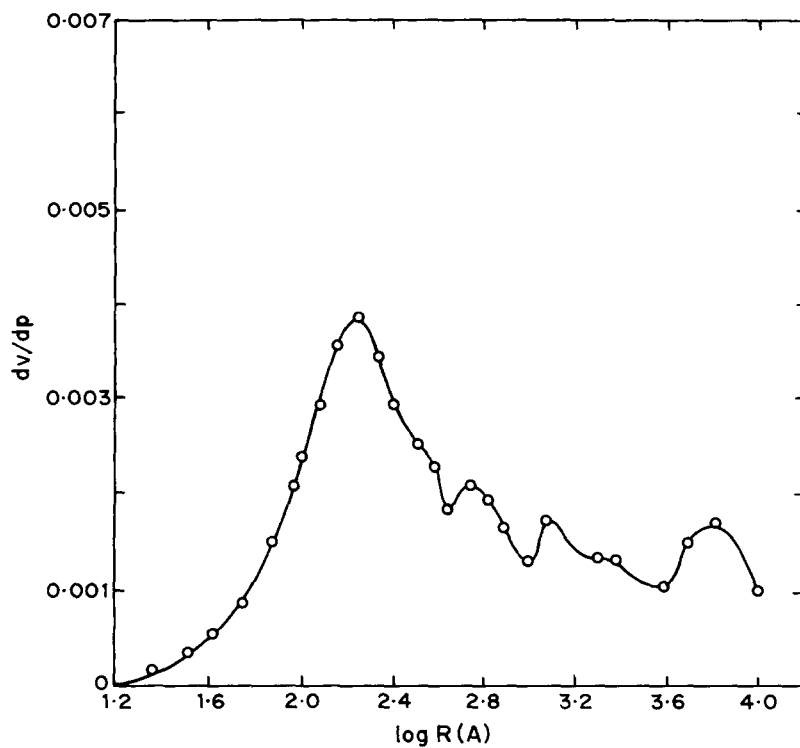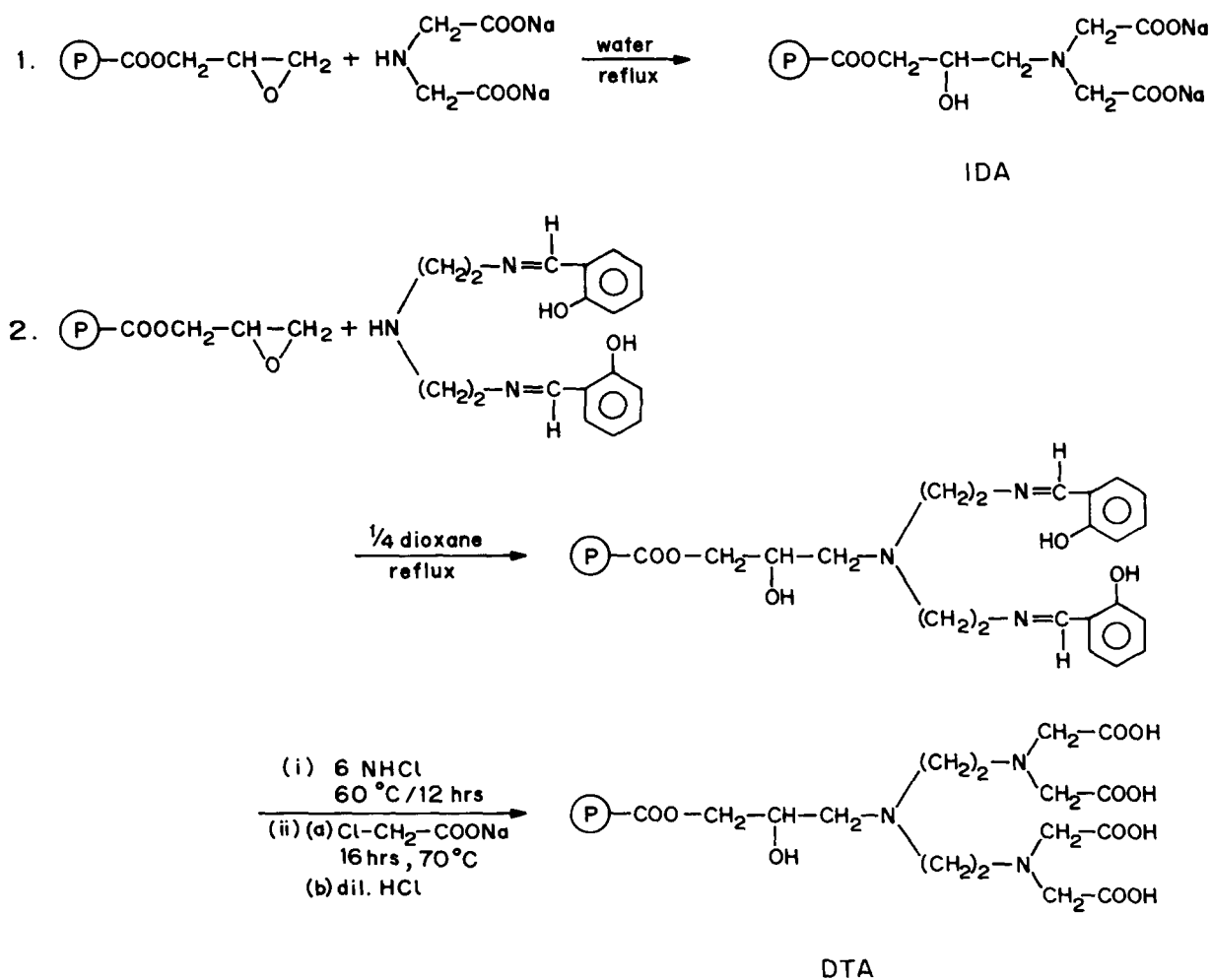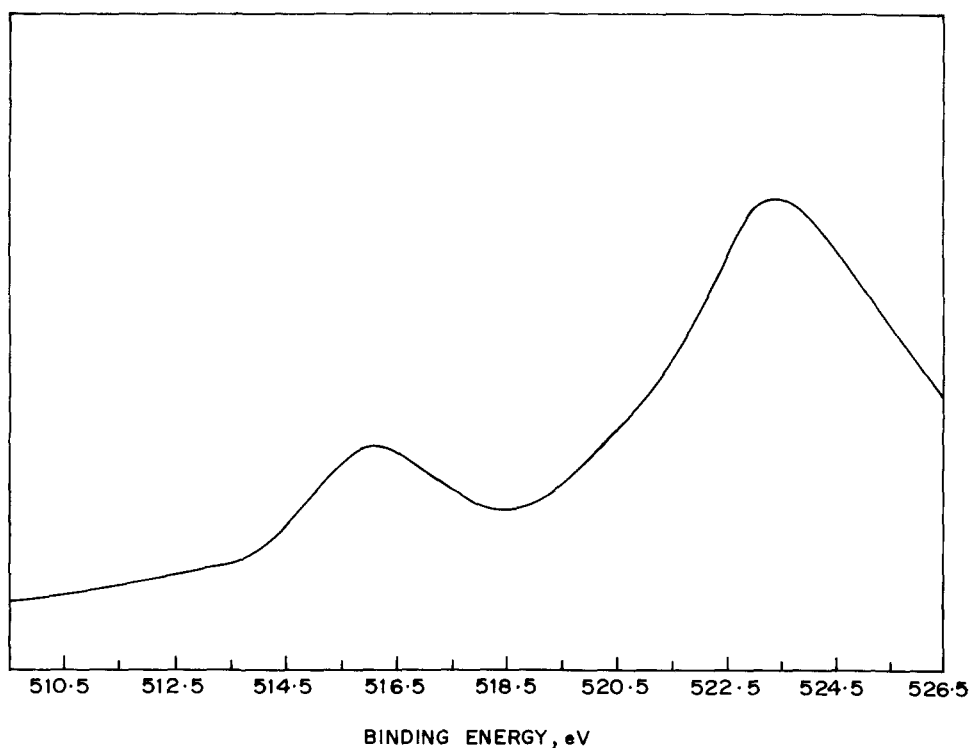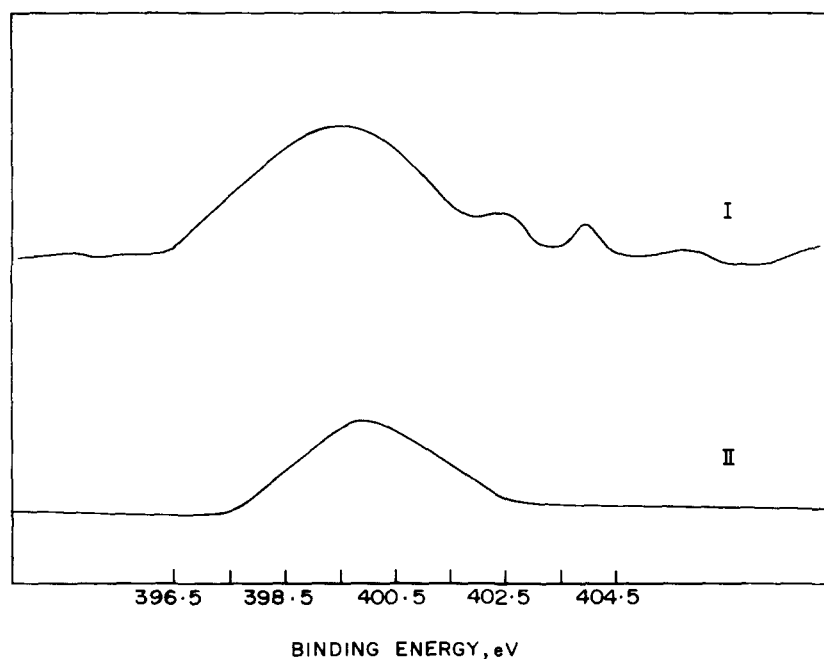
Figure 1 Mercury porosimetry graph of the copolymer

Scheme 1 Synthesis of IDA and DTA catalyst

(a)

510·5 512·5 514·5 516·5 518·5 520·5 522·5 524·5 526·5

BINDING ENERGY, eV

(b)

I

II

396·5 398·5 400·5 402·5 404·5

BINDING ENERGY, eV

Figure 2 (a) X.p.s. spectrum on V_{2p} in DTA catalyst; (b) X.p.s. spectra of N_{1s} in DTA (I) and IDA (II) catalyst

oxiranoyl groups on the surface of the pores in the copolymer.

The copolymer (II) carrying a diamino tetraacetic acid ligand was synthesized by a multi-step process, as presented in *Scheme 1*. Diethylene triamine was incorporated in the base copolymer in this manner to generate a diamine moiety. A homogeneous substitution was obtained by this process. This indirect mode of derivatization was worked out to avoid additional crosslinking of copolymer by the reaction of primary

amino groups with the oxiranoyl group in the copolymer which would result in a decreased capacity[18]. Further reaction of this copolymer with sodium monochloro acetate resulted in a polymer with diamino tetraacetic acid functionality, and generated the tetraacetic acid copolymer (DTA). The nitrogen analysis indicated a 24% modification with the tetraacetic acid functionality in copolymer (DTA). The stiff pore present in nonswelling copolymer which would have interdicted the diffusion of the bulky pentadentate Schiff base towards the oxiranoyl

Table 2 X.p.s. studies on complexes

Complex	Binding energy (eV)			
	C_{1s}	N_{1s}	O_{1s}	V_{2p}
IDA	285	398, 401.1	532	517
DTA	285	398, 399, 402.5	532.2	515.5, 523.5

group as well as the steric difficulty of the secondary amino group in reacting with the oxiranoyl group would both lead to a decrease in the extent of ligand binding in the first step.

I.r. spectra of copolymer samples were recorded after each modification reaction. The presence of oxiranoyl group in the base oxiranoyl-ester copolymer is indicated by the absorption at $1730 \, cm^{-1}$ ($C = O$) and at $908 \, cm^{-1}$ (oxiranoyl group). The acetic acid copolymers absorb at $3440 \, cm^{-1}$ and show a doublet at 1730 and $1726 \, cm^{-1}$ while the intensity of the oxiranoyl group diminishes. The capacity of the polymers were estimated by chemical titration, as 1.19 and 1.92 mmol of univalent ions g^{-1} copolymer for diacetic and tetraacetic acid copolymers, respectively.

In acidic solutions, vanadium ions exist as VO_2^+. The coordination of VO_2^+ to amino acids is through the oxygen atom of the carboxylate ion and N atom of the amino group[19,20]. The complexation of vanadium ions was effected by contacting an acidic solution of meta-vanadate ion of pH 2 and 3 with the acetic acid copolymers. There was only a marginal difference in the adsorption of vanadium ions at the two pHs. The coordination of vanadium ions on the copolymeric ligands was estimated by atomic absorption spectroscopy as 0.120 and 0.176 mmol vanadium ions incorporated g^{-1} copolymers I and II, respectively at pH 2.

X.p.s. analysis of the copolymer II–vanadium complex (DTA catalyst) shows that the oxidation state of the coordinated vanadium ions was $+5$. The measured binding energies were 515.5 and 523.5 eV which correspond to the $2p$ electron of the vanadium atom[21]. Two different microenvironments are noted for the nitrogen atoms in the modified copolymer with binding energy values of 398/399, 401 and 402.5 eV which correspond to N_{1s} electrons of the nitrogen atom. The former correlates well with non-coordinated nitrogen. Metal coordination shifts the binding energy to $402.5 \, eV^{22}$. A similar trend was noted for the copolymer I–vanadate complex as well. The binding energy of all other elements are presented in *Table 2*. Thus, all nitrogen atoms of the ligand are not coordinated to metal ions. The e.s.r. spectra of the vanadium coordinated copolymers were inactive. This indicates a $5+$ oxidation state which does not possess unpaired electrons. The surface morphology of the base and the DTA copolymer were studied by SEM. The SEM photographs reveal beads of similar particle size which indicates the absence of attrition during the modification reactions.

The coordinated vanadium ion hydrates in acidic aqueous medium and complexes with cyclohexanone. This complex reacts with the monomer yielding the primary radical, which initiates the polymerization. Propagation is followed by termination either by combination of two growing radicals or through chain transfer to metal ions[23]. The relative efficiencies of the

homogeneous metavanadate ion–cyclohexanone and the heterogeneous copolymer coordinated vanadium ion–cyclohexanone as initiators systems for the polymerization of acrylamide were examined under identical conditions. The molecular weights of polyacrylamide obtained are presented in *Table 1*. The molecular weight of polyacrylamide obtained under heterogeneous conditions is four-fold higher than that obtained with homogeneous catalyst system. The yield of the polyacrylamide formed by homogeneous catalyst system was low, probably due to the disappearance of the quinquivalent vanadium ions in the solution as the reaction proceeds. The polymerization of vinyl monomers are influenced by the cyclohexanone concentration and the acidic strength of the reaction medium[24]. Polymerization does not proceed when pH exceeds 2.25 and/or cyclohexanone concentration is below 5 wt%. In the heterogeneous system at higher volumes of cyclohexanone, the polyacrylamide yield was quantitative, however, the molecular weight was low. This indicates an increase in the concentration of initiator species with the volume of cyclohexanone. The recyclability of the catalyst, DTA was checked for three cycles and there was no change either in the molecular weight or yield of polyacrylamide formed.

CONCLUSION

The polymer bound catalysts prepared having amino acid functionalities, were synthesized from hydrophilic glycidyl methacrylate copolymer. These show promise for the chelation of vanadium ions from aqueous solutions and to act as a heterogeneous catalytic system. In the presence of cyclohexanone the polymeric vanadium complex initiates the polymerization of acrylamide. The heterogeneous catalyst does not leach out metal ion. This results in metal free polyacrylamide of higher molecular weight and is recyclable.

ACKNOWLEDGEMENTS

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