Polyaminocarboxylic Acids–Ce(IV) Redox Systems as an Initiator in Acrylamide Polymerization

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SYNOPSIS

Acrylamide polymerization by Ce(IV)-polyaminocarboxylic acids, i.e., EDTA, DTPA, EGTA, and NTA, which have strong chelating properties, have been studied at different $[H^+]$, initiator concentration, and reaction time. Initiation of polymerization proceeds through the formation of the free radical after decarboxylation of the carboxyl group of polyaminocarboxylic acid. Results also indicate that the termination of the polymerization reaction is mainly mutual termination. Decrease of the rate of disappearance of the cerium(IV) is in the order of DTPA $\geq$ EDTA > NTA > EGTA. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyaminocarboxylic acids, commonly used as chelating agents, in the decontamination of living organisms, and, recently, as possible substitutes for phosphates in detergents, are known to form complexes with trivalent lanthanides.[1-3] Hafez and Guillaumont referred briefly to the reduction of Ce(IV) by DTPA and the formation of a Ce(IV)-DTPA complex.[4] Hanna et al. studied the oxidation of EDTA, CDTA, DTPA, and NTA with Ce(IV) in sulfuric acid and perchloric acid solutions and found that the rates of reduction of Ce(IV) by the four chelating agents decreased in the order of CDTA > EDTA > DTPA > NTA.[5-9]

The most important feature of oxidation with the ceric ion is that it proceeds via a single-electron transfer with the formation of free radicals on the reducing agent. Thus, if the reducing agent is a polymeric resin, and the oxidation is carried out in the presence of a vinyl monomer, the free radical produced on the polymeric backbone initiates polymerization to produce a graft copolymer.[10,11] *N*-benzyliminodiacetic acid (BIDA), which is a chelating agent and is used frequently, particularly in cross-linked polymer forms, and the polymeric resins exhibit similar complexation behavior. They are capable of forming transition–metal complexes of BIDA and EDTA with Ce(IV) and the polymerization of acrylamide with these systems has been studied before.[12,13] The reducing agent may also be carboxylic acid.[14,15]

In a previous paper, the polymerization of acrylamide initiated with the Ce(IV)–EDTA redox system was shown to produce polyacrylamide-containing carboxyl endgroups and the electrolytic method had an advantage over the nonelectrolytic method at a very low concentration of cerium(IV) when Ce(III) formed in the reaction media was oxidized to Ce(IV).[13] The present paper reports the results of investigations of polymerizations of acrylamide initiated by NTA, EDTA, DTPA, and EGTA in the presence of Ce(IV). These polymerizations were conducted in acidic sulfate media. The influence of varying the acidity of the medium and the Ce^{4+} concentration on the polymerization yield and molecular weight were studied.

EXPERIMENTAL

Materials

Ceric sulfate $Ce(SO_4)_2 \cdot 4H_2O$, the disodium salt of (ethylenedinitrilo)tetraacetic acid dihydrate, H_2EDTA(Titriplex III); nitrilotriacetic acid, NTA

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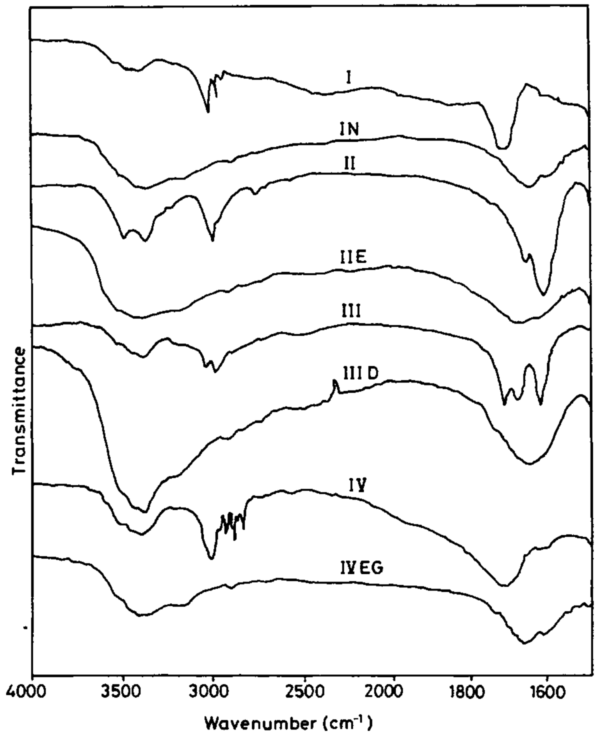


Figure 1 IR spectra of polyaminocarboxylic acids and polymers prepared by using the following reducing agents: (1) NTA (I) and PAAm-NTA (IN); (2) EDTA (II) and PAAm-EDTA (IIE); (3) DTPA (III) and PAAm-DTPA (IIID); (4) EGTA (IV) and PAAm-EGTA (IVEG).

Table I Variation of the Polymerization Yield with [H_2SO_4] at 55°C

	[H_2SO_4] (mol dm^{-3})			
	0.40	0.50	0.75	100
% Conversion				
With NTA	82.95	59.74	71.72	41.77
With EDTA	76.76	63.04	61.60	48.43
With DTPA	80.64	73.87	60.23	49.80
With EGTA	61.11	57.06	51.01	47.30

[AAm] = 0.60 mol dm^{-3}; [polyaminocarboxylic acids] = 0.020 mol dm^{-3}; [Ce(IV)] = 0.030 mol dm^{-3}. % Conversion = g polymer × 100/(g ceric sulfate + g polyaminocarboxylic acid + g AAm + g H_2SO_4).

(Titriplex I); diethylenetriamine pentaacetic acid, DTPA(Titriplex V); (ethylenedioxybis)ethylenenitrilotetraacetic acid, EGTA(Titriplex VI); acrylamide, and sulfuric acid were all Merck reagent-grade chemicals and were used without further purification.

Apparatus and Procedure

Polymerizations were carried out at 55°C (water bath) in a two-necked round-bottomed flask equipped with a stirrer. Chelating agents and monomer were dissolved in the water. The initial concentrations in the reaction mixture were 0.60*M* acrylamide (AAm) and 0.020*M* chelating agent for most of the studies. The acidity of the medium (H_2SO_4) was varied from 0.40 to 1.00*M* for each polyaminocarboxylic acid. Then, the calculated amount of Ce(IV) salt solution was added dropwise under stir-

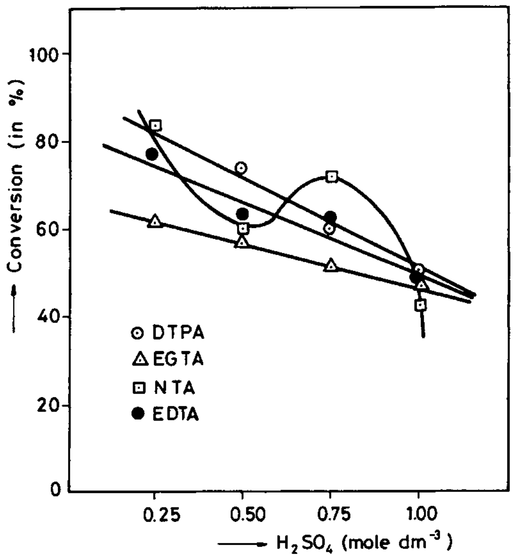


Figure 2 The effect of H_2SO_4 concentration on the conversion: [AAm] = 0.60 mol dm^{-3}; [polyaminocarboxylic acids] = 0.020 mol dm^{-3}; [Ce(IV)] = 0.030 mol dm^{-3}; T = 55°C; t = 60 min.

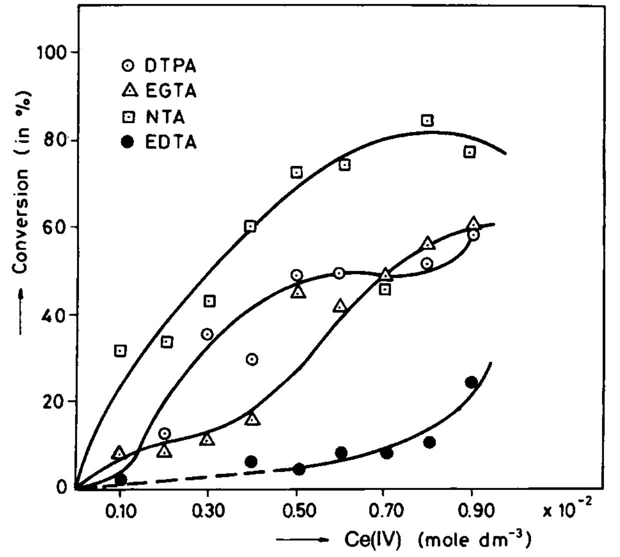


Figure 3 The effect of Ce(IV) concentration on the conversion: [AAm] = 0.60 mol dm^{-3}; [NTA] = [EDTA] = [DTPA] = [EGTA] = 0.020 mol dm^{-3}; [H_2SO_4] = 0.50 mol dm^{-3}; T = 55°C; t = 60 min.

Table II Variation of the Polymerization Yield with Ceric Ion Concentration at 55°C

	$10^2 \times$ [Ce(IV)] mol dm^{-3}								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
% Conversion									
With NTA	32.49	34.32	43.18	60.58	72.42	74.66	46.21	83.80	77.04
With EDTA	—	—	—	5.96	4.51	8.04	8.24	10.86	24.30
With DTPA	2.40	13.25	35.61	29.89	49.28	49.75	49.95	51.53	58.38
With EGTA	8.04	9.59	11.76	16.31	46.03	41.49	49.39	55.59	59.72

[AAm] = 0.60 mol dm^{-3}; [NTA] = [EDTA] = [DTPA] = [EGTA] = 0.020 mol dm^{-3}; [H_2SO_4] = 0.50 mol dm^{-3}.

ring in 5 min. After 1 h, the polymers were precipitated in about 10 vol of acetone to free them from any residual monomer and then dried in air. The polymer yield was determined by direct weighing of the polyacrylamide produced. The molecular weights of the polymers were determined by viscosity measurements in water at 30°C, the relationship of eq. (1) being used[16]:

$$[\eta] = 6.80 \times 10^{-4} \bar{M}_v^{0.66} \qquad (1)$$

Tests for Free Radicals

A series of reactions between Ce(IV) and each of EDTA, NTA, DTPA, and EGTA was carried out in the presence of acrylamide, and gel formation was observed after 1 h. Blank experiments from which either Ce(IV) or polyaminocarboxylic acids were excluded gave no detectable polymerization during this time. The experiments indicate that the reaction between Ce(IV) and the chelating agents produce species that are capable of the initiation of acrylamide polymerization.

RESULTS

IR Spectra of Polymers

IR spectra of DTPA, EDTA, NTA, and EGTA and polyacrylamides prepared by using these polyaminocarboxylic acids with Ce(IV) as initiators are shown in Figure 1. The IR spectrum of the polymer shows characteristic peaks of both polyaminocarboxylic acid and polyacrylamide. The strong and broad peaks due to C=O, OH, and NH_2 stretching are seen at around 1700, 3000, and 3400 cm^{-1}, respectively. The IR absorption spectra of all these samples were determined by preparing the KBr disk of the polymer.

Table III Variation of the Molecular Weight and Conversion (in %) with Ceric Ion Concentration at 55°C

	$10^2 \times$ [Ce(IV)] (mol dm^{-3})	
	0.20	0.90
Conversion (in %) with EGTA	9.59	59.72
$10^{-4} \times$ molecular weight	0.89	1.45

[AAm] = 0.60 mol dm^{-3}; [EGTA] = 0.020 mol dm^{-3}; [H_2SO_4] = 0.50 mol dm^{-3}.

Relation between Conversion and Concentration of Hydrogen Ion

Inspection of the curves in Figure 2 reveals that the yield is decreased with increasing [H^+]. The inhibition effect of H^+ in complex and radical formation may be due to the coordination of the SO_4^{2-} to form

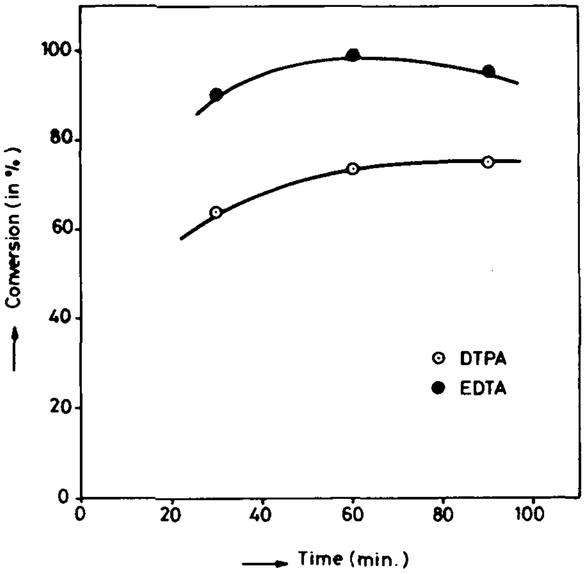
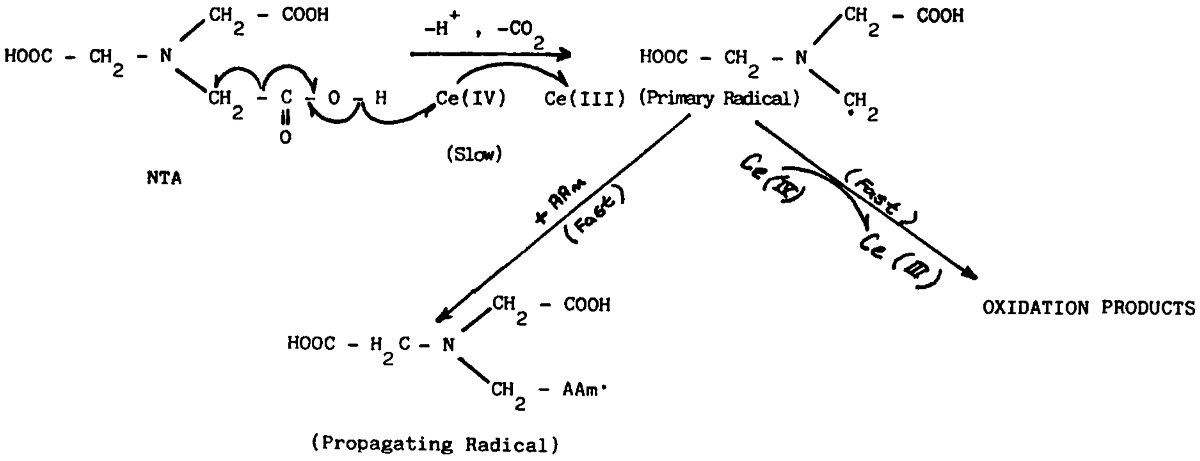


Figure 4 Plot of conversion vs. reaction time: [AAm] = 0.60 mol dm^{-3}; T = 55°C; [Ce(IV)] = 0.030 mol dm^{-3}; [EDTA] = [DTPA] = 0.020 mol dm^{-3}; (●) for EDTA, H_2SO_4 = 0.050 mol dm^{-3} (○) for DTPA, H_2SO_4 = 0.50 mol dm^{-3}.



Scheme I

relatively stable Ce(IV)—SO_4^{2-} species and the protonation of the amino nitrogens (Table I).

Relation between Conversion and Initiator Concentration

The relation between polymerization yield after 60 min and Ce(IV) concentration is shown in Figure 3. The data of Table II show that at about $0.5M$ H_2SO_4 the conversion is dependent on the initial concentration of total ceric ion and the yield increases when Ce(IV) concentration is increased. At such a low concentration of initiator as 0.20×10^{-2} to 0.9×10^{-2} mol dm^{-3}, the conversion and molecular weight is found to increase in proportion to the Ce(IV) concentration (Table III). This probably indicates that at low catalyst [Ce(IV)] concentration, termination is due to the usual bimolecular collision between two chain radicals. This finding eliminates the linear termination by Ce(IV) and emphasizes the mutual termination as a major process.

Relation between Conversion and Reaction Time

By considering the effect of the polymerization time and concentration of H^+ on the yield, the polymerization was carried out at three different times and two different pH's and polyaminocarboxylic acid (Fig. 4). The results clearly show that the considerable conversion increase was achieved in about 60 min of polymerization time.

DISCUSSION

Free-radical Formation of Polyaminocarboxylic Acids

Electron transfer from the carboxyl group of NTA, EDTA, DTPA, and EGTA to Ce(IV) initiates decarboxylation and leads to the formation of a free radical. The presence of free radical is supported by the formation of a polymer, when acrylamide was introduced into a reaction mixture of polyaminocarboxylic acid and Ce(IV).

Table IV Variation of the Yield with the Rate of Disappearance of Total Ceric Ion

	Disappearance in			
	DTPA	EDTA	NTA	EGTA
Time of the yellow color of ceric salt (min)	7	~ 6	15	Light yellow
Conversion [in (%)]	73.87	63.04	59.74	57.06

[AAm] = 0.60 mol dm^{-3}; [polyaminocarboxylic acid] = 0.030 mol dm^{-3}; [Ce(IV)] = 0.020 mol dm^{-3}; [H_2SO_4] = 0.50 mol dm^{-3} and T = 55°C.

Table V Variation of the Yield and Molecular Weight with H_2SO_4 Concentration in the System at 55°C

$[H_2SO_4]$ (mol dm^{-3})	Yield with EDTA (mol AAm/L)	Molecular Weight ($\times 10^{-4}$)	Yield with DTPA (mol AAm/L)
0.05	0.781	3.40	—
0.50	0.980	Swelling	1.160
0.75	1.170	Swelling	1.154

[AAm] = 0.60 mol dm^{-3}; [chelating agent] = 0.020 mol dm^{-3}; [Ce(IV)] = 0.030 mol dm^{-3}; mol AAm/L = g polymer/71.08 $\times 10^3$.

This free radical loses an electron rapidly to another Ce(IV) and gives the organic products if a vinyl monomer is absent in the medium (Scheme I). This duality of decarboxylation pathways is also observed in the Ce(IV)-EDTA,[13] Ce(IV)-BIDA,[12] and Ce(IV)-NTA[17] reactions and may prove to be generally true for Ce(IV) oxidations of polyaminocarboxylic acids.

Acidity Dependence and Relative Reactivities

The polymerization yields of polyacrylamide prepared by using chelating agents–Ce(IV) redox systems in H_2SO_4 media are shown collectively in Figure 2. In H_2SO_4 solution, extensive protonation of the amino acid and progressive sulfato complexation of Ce(IV) with increasing acidity is probably the main reason behind the observed decreased reactivity, and, as a result, conversions reach a limiting value of less than 100%.

The relationship between the conversions of polymers and the concentrations of H_2SO_4 and Ce(IV) in the system are shown in Figure 2–4. At high concentrations of H_2SO_4 and low concentrations of Ce(IV), conversions fall probably due to the acidity of the medium acting as an inhibiting agent for the polymer. At lower acid concentration, the cerium ion complex governs the generation of primary radicals and leads to the increase in the conversion (Fig. 4).

Hanna et al. observed a maximum for NTA at about $0.8M$ and for EDTA between 1.0 and $1.5M$ H_2SO_4.[6] We have also made similar observations with acrylamide polymerizations initiated by the Ce(IV)-NTA and Ce(IV)-EDTA systems.

Cerium ions are known to form a complex with polyaminocarboxylic acids, and this complex acts essentially as a slower but steadier source of free radicals. Our experimental results indicate that at low and high H_2SO_4 concentrations, the various complexes of ceric sulfate in solution [Ce(IV)-NTA, Ce(IV)-EDTA, Ce(IV)-SO_4^-, protonated complex species] react with the polyacrylamide radicals and acrylamide at different rates. The relative concentration of each species is not known. The minimum and maximum conversions in the NTA and EDTA plots are probably due to the effect of these different complexes. In our polymerization conditions, the inflexion points in the conversion vs. $[H^+]$ plots were not observed in the case of DTPA[6] and EGTA.

The reactivities of the four polyaminocarboxylic acids as reducing agents toward Ce(IV) in perchloric acid and sulfuric acid media decrease in the order CDTA* > EDTA > DTPA > NTA.[6]

In this work, at $0.5M$ H_2SO_4 and in the presence of 3.0×10^{-2} M chelating agent, the rate of disappearance of the total ceric ion (practically colorless solution) decreased about in the order DTPA ≥ EDTA > NTA > EGTA (Table IV). In the EGTA case, the solution at the end of the polymerization time was light yellow. This is similar to the reactivity order observed by Hanna et al.[6,9]

Effect of Sulfuric Acid

As stated already, ceric salts are capable of initiating polymerization in the presence of reducing agents. However, even if a reducing agent is not present, Ce(IV) and MnO_2 acts as an initiator in presence of inorganic acids, viz., sulfuric acid.[18,19] As advanced by Palit and Konar,[19] these polymers contain strong acid endgroups, possibly the sulfate endgroup. This group, which is being oxidized by the oxidizing agent, produces a sulfate ion radical. The molecular weights of these polymers are very high.

The relationship between the yield of polymer and the concentration of sulfuric acid in the system is given in Table V. The data available in this table (the yields are higher than 0.60 mol AAm/L and the polymers are insoluble in water but swell) indicates that at high $[H_2SO_4]$ the polymers contain sulfate groups.

[†] CDTA: *trans*-1,2-diaminocyclohexane tetraacetic acid.

In view of these facts, it seemed reasonable to assume that the produced polymers at high H_2SO_4 concentrations are mixture of polymers containing both carboxyl and strong acid endgroups.

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