Aqueous polymerization of acrylamide initiated by cerium(IV)–nitrilotriacetic acid redox initiator

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(Received 11 February 1993; revised 1 June 1993)

Nitrilotriacetic acid (NTA) coupled with commonly used metal oxidants was used as an initiator for the aqueous polymerization of acrylamide (AM) under neutral or acidic conditions. The cerium(IV)–NTA pair under neutral conditions behaved as the most promising redox initiator. In order to find the mechanism of generation of free radicals and to determine the complex formation constant (K) and the disproportionation constant (k_d), blank tests for the reactions of Ce(IV) with NTA were conducted under conditions of neutral, 1 N HNO_3 and 1 N $NaNO_3$, respectively. The mechanism was further confirmed by ^{13}C and ^{1}H n.m.r. spectra and the kinetic parameters for the aqueous polymerization of AM were evaluated. The effects of additives on the polymerization were studied and the use of the Ce(IV)–NTA redox pair for other aqueous polymerization systems such as acrylic acid (AA), acrylonitrile (AN) and methyl methacrylate (MMA) was also studied.

(Keywords: nitrilotriacetic acid; cerium(IV) redox initiators; aqueous polymerization)

INTRODUCTION

Redox initiators have been used extensively in aqueous polymerizations[1] as well as in grafting polymerizations[2]. The reducing agents used in the redox systems are usually alcohols[3,4], aldehydes[5], acids[6,7], thiols[8], amines[9] or polymers with these functional groups, while the metal oxidants used are usually cerium(IV) (Ce(IV))[10,11], permanganate ($Mn(VII)O_4^-$)[12,13], vanadium(V) (V(V))[14,15], chromium(VI) (Cr(VI))[16,17], cobaltic ion (Co(III))[18,19] and ferric ion (Fe(III))[18–20]. The mechanism and kinetics of the polymerizations initiated by the redox systems have been well documented[1–20]. However, most redox initiators studied showed low conversions in polymerization.

Although multifunctional chelating agents were largely used as reductants for redox initiators in the past, there was some attention on the effect of the molecular structure as well as the chelating ability. Saha and Chaudhuri[9] indicated that when triethanolamine, with electron withdrawing hydroxyl and tertiary amine groups located on both sides of the methylene group, was used as a reducing agent for the ceric ion, high values of K, k_d and Rp_i for the aqueous polymerization of acrylonitrile were obtained: K, k_d and Rp_i denote the Ce(IV)–amine complex formation constant, the disproportionation constant of the complex and the initial rate of polymerization, respectively. Nitrilotriacetic acid (NTA) is one of the amino acid-type chelating agents with a structure similar to triethanolamine, i.e. with the electron withdrawing carboxyl and amine groups on both sides of the methylene group. Consequently, the Ce(IV)–NTA pair may be expected to be an effective initiator for aqueous polymerizations[11]. However, there have been only a few studies concerned with these types of redox initiators[10,11,21].

In our previous studies[11], the Ce(IV)–NTA redox pair showed the best performance in the aqueous polymerization of acrylamide. Therefore, it is valuable for us to further study the NTA–metal oxidant system. In this study, we investigated the activity of the commonly used metal oxidants reacting with NTA under conditions with or without an acid. The constants K and k_d were also evaluated under different conditions. The kinetic behaviour and polymer qualities of the polymerizations induced by the Ce(IV)–NTA redox initiator were studied. The effects of the additives on the consumption rate of Ce(IV) as well as the polymerization rate were considered. The use of this redox initiator was also extended to other aqueous polymerization systems.

EXPERIMENTAL

Reagents

Acrylamide (AM) (reagent grade, Fluka) was purified by recrystallization from methanol (two times) and dried in a vacuum oven at 45°C for 2 days. Acrylic acid (AA), acrylonitrile (AN) and methyl methacrylate (MMA) (reagent grade, Fluka) were purified by standard methods, distilled repeatedly in an atmosphere of nitrogen and stored at 5°C in the dark. The cerium(IV) ammonium nitrate (Ce(IV)) and NTA used were the products of E. Merck (G.R. grade) without further purification. The other reagents such as metal oxidants, nitric acid, sodium nitrate and sodium bromide, and other chelating agents, were all the products of Fluka or E. Merck and were used without further purification. The standards of polyethylene oxide were supplied by the Waters

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Associates Company. The nitrogen was deoxygenated by sequentially passing it through an alkaline pyrogallol solution, 98% sulfuric acid, silica gel and then an electrical furnace containing a copper gauze at 400°C. Distilled deionized water with the conductance below 3.0 μC cm^{-1} was used in all reactions.

Blank reactions of metal oxidants and NTA

The characteristic absorption wavelength of each metal oxidant was determined first, and then the decay of the u.v. absorbance intensity on reaction with NTA was monitored at this wavelength to determine whether or not the metal oxidant reacted with NTA. In this study, Ce(IV)–NTA was used as the redox initiator for the aqueous free-radical polymerization of AM. The blank tests for the reactions of Ce(IV) with NTA were studied first. They were carried out at 40 ± 0.1°C under a nitrogen atmosphere in a reactor assemblage which consisted of a 1 l pyrex reactor with a stirrer, a circulating pump and an u.v. spectrometer (JASCO, model 7850) connected to a recorder. The assemblage was described in detail in our previous paper[10]. The intensity of the absorbance at 350 nm, I_{350}, for Ce(IV) was recorded and the reaction extent of Ce(IV) could be monitored *in situ*. A calibration curve for the concentration of Ce(IV) *versus* I_{350} was prepared.

Polymerization reaction of AM

The prescribed amounts of AM, chelating agent and distilled deionized water were filled into a 1 l, five-necked pyrex kettle which had been purged sufficiently with nitrogen. The kettle was immersed in a water bath which was maintained at the desired temperature. Three samples of 1 ml each were taken at suitable time intervals for determination of monomer conversion and number-average molecular weight. The concentration of the residual AM in the reaction solution was measured from the intensity at 254 nm using a Waters Associates model 510 h.p.l.c. instrument with a model 441 u.v. detector. A μBONDPAK™ C18 column was used. The mobile phase was a 5% acetonitrile aqueous solution, and the flow rate was kept at 1 ml min^{-1}. Methyl ethyl ketone was used as the internal standard. The number-average molecular weights and polydispersity indexes were measured using a gel permeation chromatograph equipped with an RI 410 detector and a model 745B data processor. Three g.p.c. columns (hydrogel) consisting of 250 and 500 Å and Linear were used. The carrier solvent was an aqueous solution of 1.36% KH_2PO_4 and 1.36% KOAc[22] and the flow rate was kept at 1 ml min^{-1} at 30°C. The calibration curve was prepared using polyethylene oxide standards ($\overline{M}_n = (1.2, 4.5, 14.5, 27.0 \text{ and } 66.0) \times 10^4$). The Benoit universal calibration[23] was used for the determination of the molecular weights of polyacrylamide. The Mark- Houwink constants K and a of polyacrylamide[24] in water at 30°C are 6.5×10^{-3} and 0.82, respectively, whereas those of polyethylene oxide[25] are 12.5×10^{-3} and 0.78.

Polymerization reactions of other vinyl monomers

The procedure for the polymerizations was the same as for the AM system, except that 20 ml samples were taken at specified intervals. The polymerization was quenched with 1 ml of 0.1 M hydroquinone and the conversion was determined gravimetrically.

RESULTS AND DISCUSSION

Reactivity of chelating agents with Ce(IV)

Table 1 shows the reactivity of Ce(IV)/chelating-type reductant pairs and their performance in the polymerization of AM. It can be seen that dibasic acid- and diamine-type chelating agent systems, except for the oxalic acid–Ce(IV) pair, show initial rates of polymerization (Rp_i) and limiting conversions (X_L) inferior to those of the amino acid systems. In general, the higher the reductive reactivity of chelating agents with Ce(IV), the faster the Rp_i and the higher the X_L, and *vice versa*. Therefore, the intensity decay of characteristic u.v. absorbance may be a criterion for the feasibility of the chelating agents. In addition, the larger the number of rings, the higher the reactivity of the chelating agents. Chelating agents forming five- or six-membered rings with a metal ion exhibit high reductive reactivity to induce the reduction of Ce(IV). Meanwhile the chelating agents with five-membered rings show higher reactivity than those with six-membered rings[11]. However, the chelating agents other than those forming five- or six-membered rings with a metal ion can hardly initiate polymerizations, because these kinds of chelating agents cannot form stable chelating structures with Ce(IV). Apparently, the amino acid-type chelating agents behave better than the dibasic acid ones. *Table 1* also shows that the diamine-type chelating agent, e.g. ethylenediamine incorporated with Ce(IV), shows no reactivity for polymerization and the redox pair containing an unchelatable reductant of monocarboxylic acid, such as acetic acid, shows no reactivity for polymerization. Therefore, the requirement for a chelating agent in coupling with Ce(IV) to be an effective redox initiator for polymerization would be composed of an amino acid group and could form more than two five- or six-membered rings where NTA was the best one among the tested chelating agents.

Activity of metal oxidants

According to the literature[1–21], we know that the free radicals for initiation could be generated by reactions of metal oxidants with reductants. In order to search for suitable oxidants, we tested the activity of the commonly used metal oxidants by reacting them with NTA.

Table 1 The effect of various chelating agent–Ce(IV) pairs on the aqueous polymerization of acrylamide at 40°C; $[M]_i = 0.2$ M, $[\text{Chelating agent}]_i = 0.0025$ M and $[Ce(IV)]_i = 0.0050$ M

Chelating agent	R_{Ce}[a]	$Rp_i \times 10^5$ (M s^{-1})	X_L (%)
None	– –	0.05	0.29
EDTA	+ +	5.05	43.99
NTA	+ +	16.93	80.97
NPA	+	2.55	78.77
IDA	+	7.07	61.72
DTPA	– –	0.25	1.82
Glycine	–	1.52	10.43
Oxalic acid	+	4.82	67.57
Malonic acid	–	1.37	44.44
Succinic acid	– –	0.25	1.45
Glutaric acid	– –	0.12	0.54
Ethylenediamine	– –	0.25	1.40
Acetic acid	– –	0.27	1.60

[a] Rate of Ce(IV) uptake: fast (+ +), medium (+), slow (–), very slow (– –)

Table 2 The decay rate of the characteristic u.v. absorbance at 40°C for the metal oxidant/NTA pairs with $[\mathrm{NTA}]_i = 0.0020$ M, $[\text{Metal oxidant}]_i = 0.0020$ M

Oxidant	Wavelength (nm)	Decay rate[a]	
		Without acid	1 M HNO_3
$(NH_4)_2[Ce(IV)(NO_3)_6]$	350	+	+ +
$Na_3[Co(III)(NO_3)_6]$	280	− −	− −
$Cr(VI)O_3$	370	− −	−
$Cu(II)(NO_3)_2$	300	− −	− −
$Fe(III)(NO_3)_3$	350	− −	− −
$KMn(VII)O_4$	550	+	+ +
$(NH_4)V(V)O_3$	350	+	−

[a] None (− −); slow (−); fast (+); very fast (+ +)

Table 3 Limiting conversions and initial rates of polymerization for aqueous polymerization of acrylamide initiated by various metal oxidant–NTA redox pairs at 40°C, $[\mathrm{M}]_i = 0.2$ M, $[\mathrm{NTA}]_i = 0.0025$ M, and $[\text{Metal oxidant}]_i = 0.0050$ M

Metal oxidant	X_L (%)		$Rp_i \times 10^5$ (mol dm^{-3} s^{-1})	
	Without acid	1 M HNO_3	Without acid	1 M HNO_3
$Ce(III)(NO_3)_3$	3.41	2.52		
$(NH_4)_2Ce(IV)(NO_3)_6$[a]	0.29	1.20		
$(NH_4)_2Ce(IV)(NO_3)_6$	80.97	19.11	16.93	4.20
$Co(II)(CH_3COO)_2$	1.75	1.25		
$Na_3[Co(III)(NO_3)_6]$	1.89	2.01		
$[Co(III)(NH_3)_6]Cl_3$	1.92	2.12		
$K_2Cr(VI)_2O_7$	2.80	3.05		
$Cr(VI)O_3$	2.53	3.12		
$Cu(II)Cl_2$	0.60	0.92		
$Fe(II)SO_4$	1.49	1.24		
$Fe(III)Cl_3$	4.38	3.56		
$Mn(II)SO_4$	0.29	0.45		
$KMn(VII)O_4$[a]	2.74	3.25		
$KMn(VII)O_4$	12.75	26.42	2.04	7.35
$Ni(II)(NO_3)_2$	0.97	0.88		
$(NH_4)V(V)O_3$	2.35	3.05		

[a] Without NTA

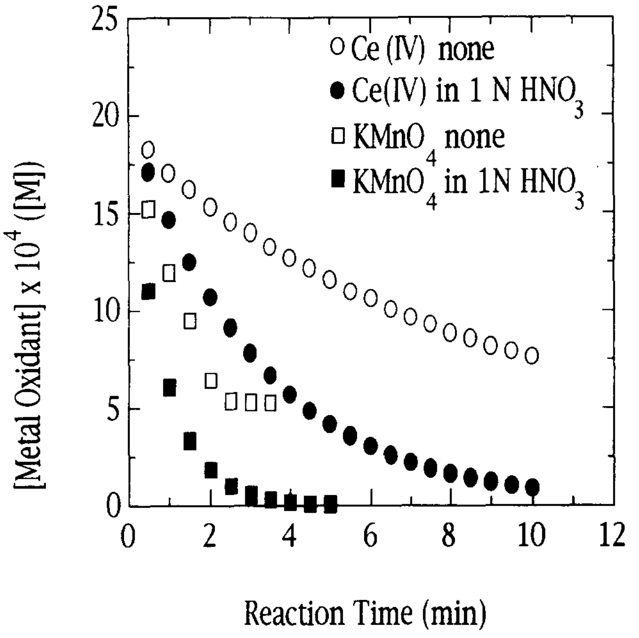


Figure 1 Plots of [Ce(IV)] and $[KMn(VII)O_4]$ *versus* reaction time at 40°C: $[\mathrm{NTA}]_i = 0.0020$ M; $[\text{Metal oxidant}]_i = 0.0020$ M

Table 2 shows their activity with or without acid. Among the oxidants tested, only Ce(IV) and $Mn(VII)O_4^-$ showed effective activity in reacting with NTA. In addition, Ce(IV) and Mn(VII) showed a higher activity in the acidic condition as indicated by their rapid decay compared with those in the neutral condition (*Figure 1*). *Table 3* displays X_L and Rp_i when the metal oxidants coupled with NTA were used as the initiators for the aqueous polymerization of AM with or without acid. In the same way, only Ce(IV) and Mn(VII) could significantly initiate the polymerization, while Ce(IV) and $Mn(VII)O_4^-$ alone could not effectively initiate the polymerization. Although Ce(IV) showed a higher activity in the acidic condition (*Figure 1*), premature termination of the primary free radicals by Ce(IV) resulted in lower Rp_i and X_L. $Mn(VII)O_4^-$ in the neutral condition would be reduced to $Mn(IV)O_2$ which was suspended in the solution as black particles. It could, however, transform into a lower valence state, i.e. Mn(II), in the acidic condition[26]. Thus, Mn(VII) could oxidize more NTA into primary free radicals in the acidic condition and higher limiting conversions would result.

From the above results, the major premise for a useful redox pair is that the metal oxidant has oxidative activity with NTA, and Ce(IV)/NTA in neutral conditions is the most promising redox pair.

Generation of primary free radicals

Figure 1 shows an exponential decay of Ce(IV) concentration. The figure suggests that Ce(IV) follows a first-order reaction in the neutral or acidic condition. *Table 4* shows the effect of initial monomer concentration ($[M]_i$) on the Ce(IV) consumption rate. Clearly, the consumption rates of Ce(IV) were independent of the monomer concentration. *Figure 2* shows the ^{13}C n.m.r. spectra of NTA alone and NTA-terminated polyacrylamide. It can be seen that the methylene group of NTA was split into two peaks after reacting with Ce(IV), with one peak representing the reacted methylene and the other representing the unreacted methylene. Therefore, the mechanism may be depicted as:

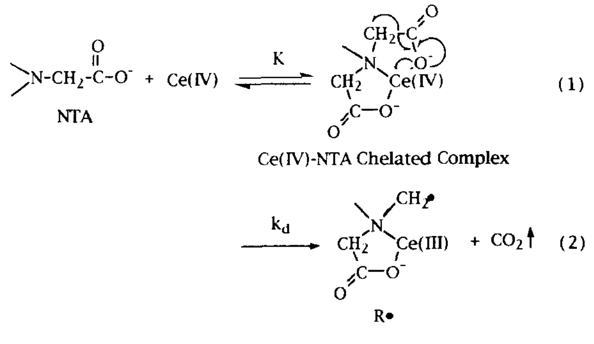


Table 4 The effect of additives on the complex formation constant and the disproportionation constant, and the dependence of ceric ion consumption rate on monomer concentration at 40°C

	K (M^{-1})	$k_d \times 10^3$ (s^{-1})	$(-d[Ce(IV)]/dt)_i \times 10^6$ (M s^{-1})			
$[M]_i$ (M)			0.05	0.10	0.20	0.30
Without acid	740	1.62	2.97	2.96	2.97	2.98
HNO_3 (1 M)	1252	7.28	10.40	10.42	10.38	10.41
$NaNO_3$ (1 M)	415	1.70	2.76	2.82	2.74	2.70

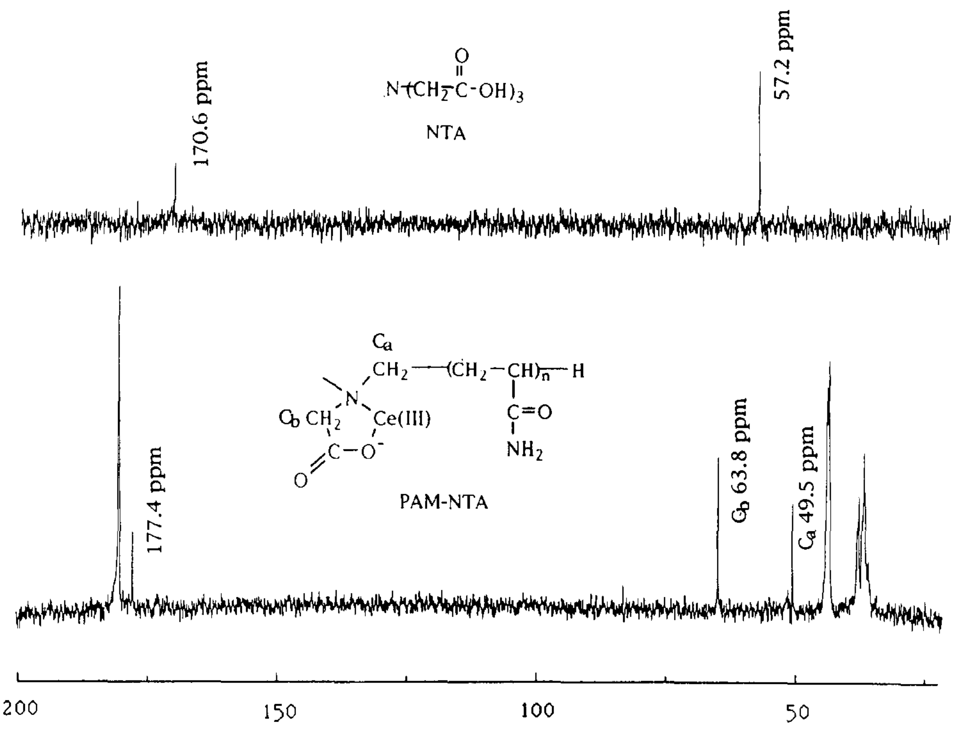


Figure 2 ^{13}C n.m.r. spectra of NTA and NTA-terminated polyacrylamide

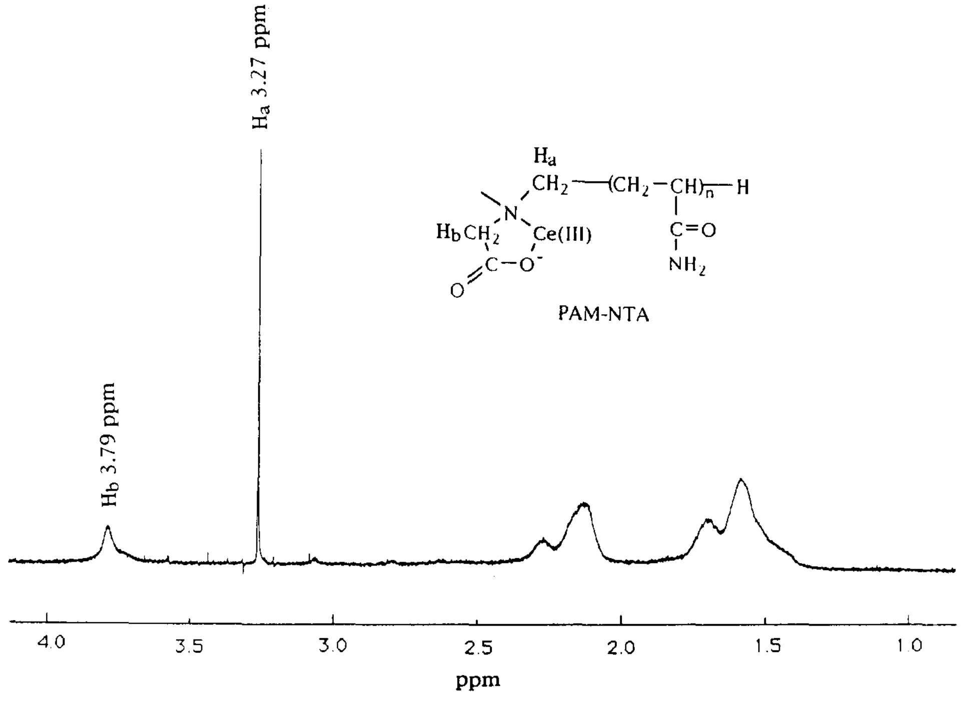
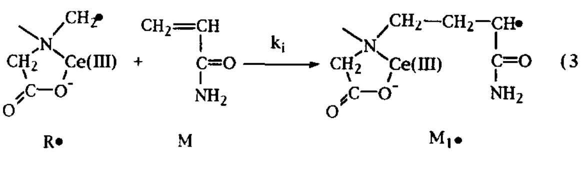


Figure 3 ^1H n.m.r. spectrum of NTA-terminated polyacrylamide



(3)

If the proposed mechanism is correct, the ^1H n.m.r. spectrum of the NTA-terminated polyacrylamide would have two different chemical shifts. As shown in *Figure 3*, the chemical shifts of 3.27 and 3.79 ppm represent the hydrogens of the reacted and unreacted methylene, respectively. The liberation of carbon dioxide (CO_2) was verified by the formation of white precipitated calcium carbonate ($CaCO_3$) by passing the off-gas through a calcium hydroxide aqueous solution. Thus, the suggested mechanism could satisfactorily explain the experimental results. The following rate expression is proposed:

$$\frac{-d[Ce(IV)]}{dt}=\frac{k_d K[NTA][Ce(IV)]}{1+K[NTA]} \qquad (4)$$

where [Ce(IV)], [NTA], K and k_d represent the concentration of ceric ion, the concentration of NTA, the complex formation constant, and the disproportionation constant, respectively. Rearranging equation (4)

$$\frac{[\mathrm{Ce(IV)}]}{\dfrac{-\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t}}=\frac{1}{k_dK}\frac{1}{[\mathrm{NTA}]}+\frac{1}{k_d} \tag{5}$$

As shown in *Figure 4*, the plots of $[\mathrm{Ce(IV)}]_i/(-\mathrm{d}[\mathrm{Ce(IV)}]/\mathrm{d}t)_i$ *versus* $1/[\mathrm{NTA}]_i$ were linear. Hence, k_d and K could be obtained from the intercepts and slopes (*Table 4*). The constants K and k_d in the acidic condition were both larger than those in the neutral condition. The rapid exhaustion of Ce(IV) in acidic conditions was mainly due to the larger disproportionation rate which might be due to the higher oxidative potential of Ce(IV) in the presence of acid[27]. The addition of $\mathrm{NaNO_3}$ had little effect on k_d, but it decreased the value of K because of the competition between $\mathrm{NO_3^-}$ and NTA for coordinating with Ce(IV).

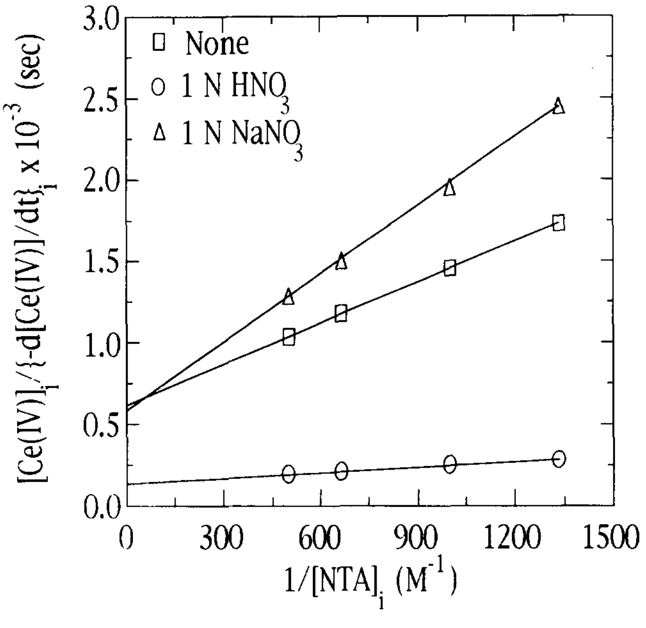


Figure 4 Plots of $[\mathrm{Ce(IV)}]_i/(-\mathrm{d}[\mathrm{Ce(IV)}]/\mathrm{d}t)_i$ *versus* $1/[\mathrm{NTA}]_i$ at $[\mathrm{Ce(IV)}]_i = 0.0020$ M and 40°C for the determination of K and k_d for the Ce(IV)–NTA complex

Kinetics of the Ce(IV)–NTA initiation system

The results suggested that Ce(IV)–NTA without acid showed the best performance for polymerization, so we focused our attention on the kinetics of polymerization of the Ce(IV)–NTA system in conditions without acid. *Table 5* shows the effects of initial monomer concentration ($[\mathrm{M}]_i$), initial chelating agent concentration ($[\mathrm{NTA}]_i$), initial ceric ion concentration ($[\mathrm{Ce(IV)}]_i$) and temperature on the aqueous polymerization of AM. *Table 5* shows that Rp_i and X_n increased significantly as $[\mathrm{M}]_i$ and $[\mathrm{NTA}]_i$ increased when the ratio of $[\mathrm{NTA}]_i/[\mathrm{Ce(IV)}]_i \leqslant 1$, but decreased as $[\mathrm{Ce(IV)}]_i$ increased. However, as the ratio $[\mathrm{NTA}]_i/[\mathrm{Ce(IV)}]_i \geqslant 1$, Rp_i and X_L became almost independent of $[\mathrm{NTA}]_i$. According to equation (1), generation of the free radicals occurred through formation of a chelated complex of Ce(IV)–NTA, which sequentially followed the redox reaction. Therefore, the excess chelating agent did not contribute anything else to the polymerization. The polydispersity index (PDI) of polymers for the Ce(IV)–NTA redox system fell in the range 1.7 to 2.1, which narrowed as $[\mathrm{Ce(IV)}]_i$ increased. From the above discussion, it is clear that free Ce(IV) played an important role in the termination of the propagation radicals[10,11,28]. Accordingly, the mechanism of the polymerization may be depicted as follows[2,10,11,29–31]:

Generation of initiator fragment

$$\mathrm{Ce(IV)+NTA}\overset{K}{\rightleftharpoons}\underset{\text{Complex C}}{(\mathrm{Ce(IV)}\text{—}\mathrm{NTA})}\xrightarrow{k_d}\mathrm{NTA^{\bullet}+Ce(III)+H^+} \tag{6}$$

$$\mathrm{NTA^{\bullet}+M}\xrightarrow{k_i}\mathrm{M_1^{\bullet}} \tag{7}$$

Propagation

$$\mathrm{M_1^{\bullet}+M}\xrightarrow{k_p}\mathrm{M_2^{\bullet}}$$

$$\mathrm{M_{n-1}^{\bullet}+M}\xrightarrow{k_p}\mathrm{M_n^{\bullet}}\ \text{etc.} \tag{8}$$

Table 5 The initial rates of polymerization, limiting conversions, degrees of polymerization and polydispersity indexes of the Ce(IV)–NTA system at various conditions

$[\mathrm{M}]_i$ (M)	$[\mathrm{NTA}]_i$ (M)	$[\mathrm{Ce(IV)}]_i$ (M)	Temp (°C)	$Rp_i \times 10^3$ ($\mathrm{M\,min^{-1}}$)	X_L (%)	$X_n{}^a \times 10^{-2}$	PDI
0.1	0.0025	0.0050	40	4.46	69.44	2.7	1.75
0.2	0.0025	0.0050	40	10.16	80.97	4.3	1.79
0.3	0.0025	0.0050	40	37.07	80.62	5.7	1.84
0.4	0.0025	0.0050	40	69.82	85.31	7.3	1.81
0.2	0.0020	0.0050	40	7.00	79.51	4.5	1.77
0.2	0.0050	0.0050	40	31.31	81.79	4.7	1.75
0.2	0.0075	0.0050	40	31.38	82.22	5.0	1.76
0.2	0.0025	0.00125	40	5.39	80.61	15.9	2.07
0.2	0.0025	0.0025	40	28.57	81.75	7.3	1.90
0.2	0.0025	0.0075	40	7.87	80.98	3.7	1.74
0.2	0.0025	0.0050	25	8.31	59.68	4.8	1.81
0.2	0.0025	0.0050	30	8.90	80.98	4.7	1.76
0.2	0.0025	0.0050	50	11.50	86.45	4.1	1.73

[a] X_n = number average molecular chain length

Linear termination by Ce(IV)

$$M_n^{\bullet} + \mathrm{Ce(IV)} \xrightarrow{k_t} \mathrm{Product} + \mathrm{Ce(III)} + \mathrm{H}^+ \qquad (9)$$

Oxidative termination

$$\mathrm{NTA}^{\bullet} + \mathrm{Ce(IV)} \xrightarrow{k_o} \mathrm{Oxidative\ Product} + \mathrm{Ce(III)} + \mathrm{H}^+ \qquad (10)$$

Accordingly, the primary radical of NTA would have the chelating ability in nature. Therefore, it would preferably react with Ce(IV) to induce polymerization[10,11,31], i.e.

$$[\mathrm{M}]_i \ll \left\{ \frac{k_o}{k_i} \frac{[\mathrm{Ce(IV)}]}{\{1+K[\mathrm{R}]\}} \right\}$$

Using the above scheme and the pseudo-steady-state assumption, we derived the rate expressions as follows:

$$\frac{-\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t} = \frac{2k_d K[\mathrm{NTA}][\mathrm{Ce(IV)}]}{1+K[\mathrm{NTA}]} \qquad (11)$$

$$R_p = \frac{k_p}{k_t} \frac{k_i}{k_o} \frac{k_d K[\mathrm{M}]^2[\mathrm{NTA}]\{1+K[\mathrm{NTA}]\}}{[\mathrm{Ce(IV)}]} \qquad (12)$$

$$\overline{X}_n = \frac{k_p}{k_t}\{1+K[\mathrm{NTA}]\} \frac{[\mathrm{M}]}{[\mathrm{Ce(IV)}]} \qquad (13)$$

Figures 5 and *6* imply that Rp_i had a second-order relation to $[\mathrm{M}]_i$ and was inversely proportional to $[\mathrm{Ce(IV)}]_i$ when $[\mathrm{NTA}]_i/[\mathrm{Ce(IV)}]_i \leqslant 1$. In the same way, $Rp_i/[\mathrm{NTA}]_i$ had a linear relation with respect to $[\mathrm{NTA}]_i$ as $[\mathrm{NTA}]_i/[\mathrm{Ce(IV)}]_i \leqslant 1$ (*Figure 7*). By examining those experimental results mentioned above, the dependence of $(-\mathrm{d}[\mathrm{Ce(IV)}]/\mathrm{d}t)_i$, Rp_i and $\overline{X}_n$ on $[\mathrm{M}]_i$, $[\mathrm{NTA}]_i$ and $[\mathrm{Ce(IV)}]_i$ obeyed the above equations. The kinetic parameters k_o/k_i and k_p/k_t evaluated from the above results were 111 and 2.66, respectively.

Figure 8 indicates that the temperature dependence of Rp_i followed the Arrhenius relations and the apparent activation energy estimated from the slope of the plot was 10.42 kJ mol^{-1} which fell in the range of common redox initiator systems[7,31].

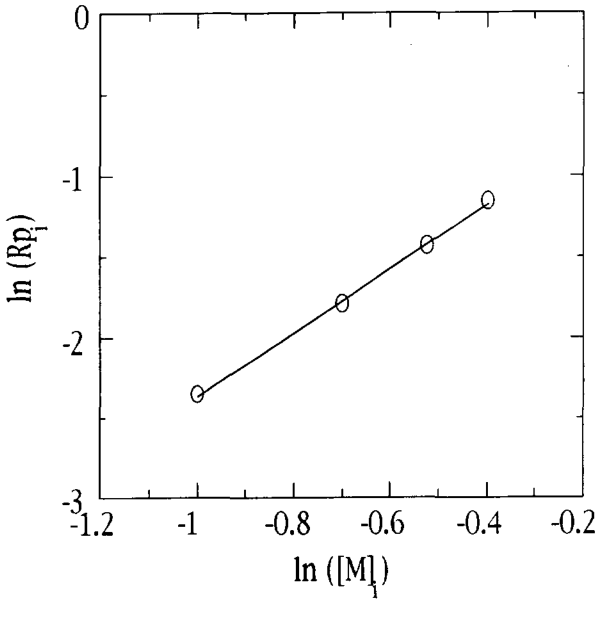


Figure 5 Logarithm plot of Rp_i *versus* $[\mathrm{M}]_i$ at 40°C: $[\mathrm{NTA}]_i = 0.0025$ M; $[\mathrm{Ce(IV)}]_i = 0.0050$ M

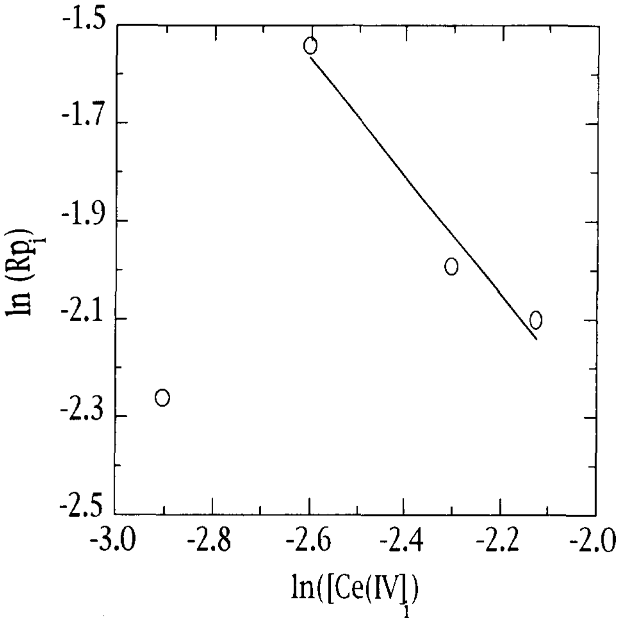


Figure 6 Logarithm plot of Rp_i *versus* $[\mathrm{Ce(IV)}]_i$ at 40°C: $[\mathrm{M}]_i = 0.2$ M; $[\mathrm{NTA}]_i = 0.0025$ M

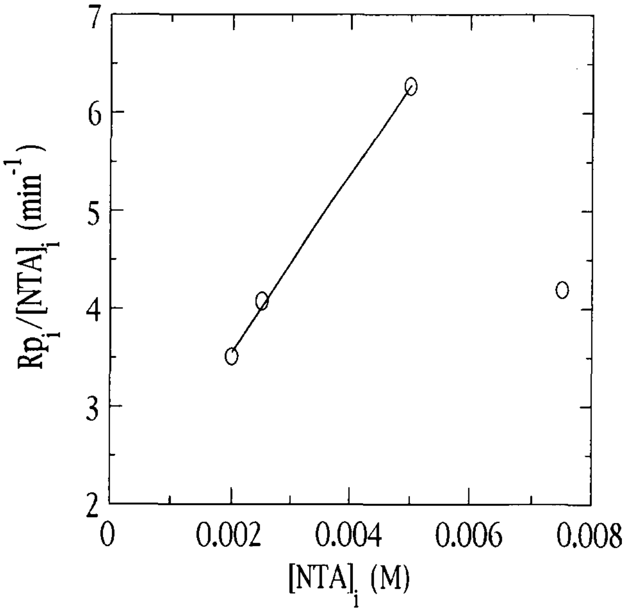


Figure 7 Plot of $Rp_i/[\mathrm{NTA}]_i$ *versus* $[\mathrm{NTA}]_i$ at 40°C: $[\mathrm{M}]_i = 0.2$ M; $[\mathrm{Ce(IV)}]_i = 0.0050$ M

Effects of the additives on Ce(IV)-NTA redox system

In order to investigate the effect of acid concentration on polymerization rate, we followed the polymerization behaviour by varying the acid concentrations while keeping the concentration of the nitrate anion ($[\mathrm{NO_3^-}]$) constant. As depicted in *Figure 9* at constant $[\mathrm{NO_3^-}]$, both Rp_i and X_L decreased significantly upon the addition of nitric acid. *Figure 10* shows the effect of $[\mathrm{NO_3^-}]$ on polymerization at constant concentration of $\mathrm{HNO_3}$. Variation of $[\mathrm{NO_3^-}]$ had almost no effect on Rp_i and had only a small effect on X_L. As described in *Figure 1* and *Table 4*, the decrease in Rp_i and X_L at the acidic

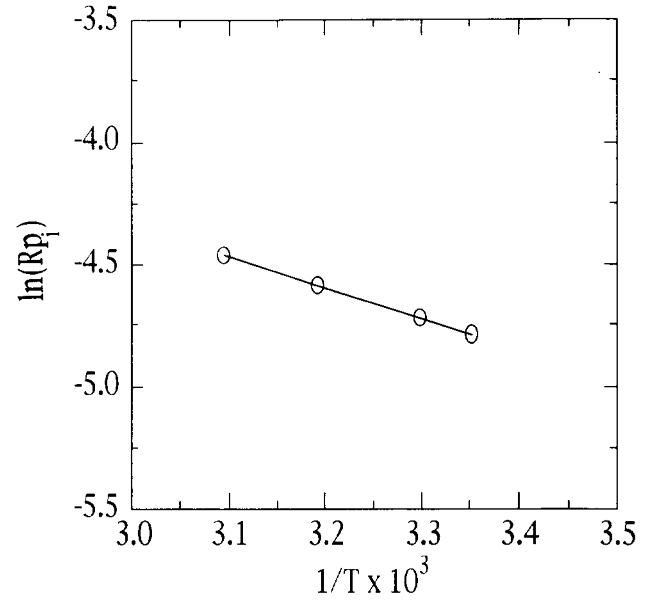


Figure 8 The Arrhenius plot of the Ce(IV)–NTA system with $[M]_i = 0.2$ M, $[NTA]_i = 0.0025$ M and $[Ce(IV)]_i = 0.0050$ M

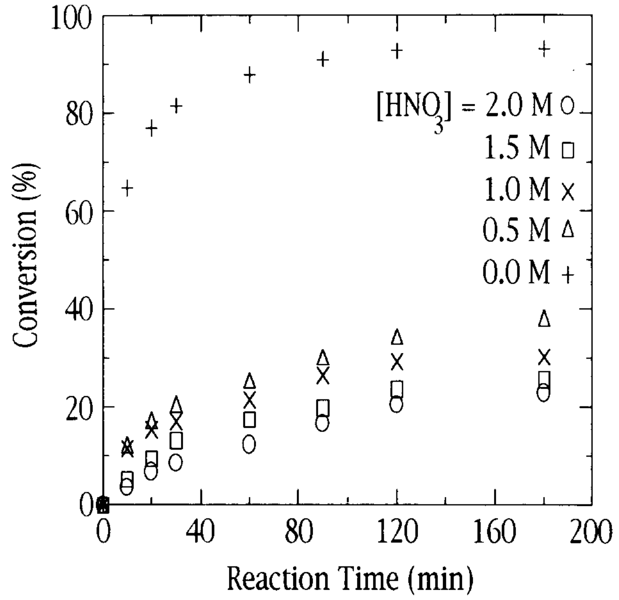


Figure 9 The effect of acid concentration on the course of polymerization at 40°C with $[NO_3^-] = 2.0$ M, $[M]_i = 0.2$ M, $[NTA]_i = 0.0025$ M and $[Ce(IV)]_i = 0.0020$ M

Table 6 The effects of additives on the consumption rate of Ce(IV), initial rate of polymerization, limiting conversion and degree of polymerization at 40°C with $[M]_i = 0.2$ M, $[NTA]_i = 0.0025$ M and $[Ce(IV)]_i = 0.0050$ M

$[NaNO_3]$ (M)	[NaBr] (M)	$R_{Cei} \times 10^7$ ($M s^{-1}$)	$Rp_i \times 10^5$ ($M s^{-1}$)	X_L (%)	$X_n \times 10^{-2}$
0.00	0.00	29.71	16.93	80.97	4.34
1.00	0.00	27.41	17.02	87.52	4.66
2.00	0.00	26.39	17.10	93.16	4.84
0.00	2.00	29.48	16.95	83.02	4.31

condition may be due to the rapid exhaustion of Ce(IV) because of the larger K and k_d. Although NO_3^- would compete with NTA for coordinating with Ce(IV), it exhibited little effect on $(-d[Ce(IV)]/dt)_i$ and had almost no effect on polymerization (*Table 5*), which was due to its lower coordinating ability compared to that of NTA. As shown in *Table 6*, NO_3^- would retard the exhaustion rate of Ce(IV) and had almost no effect on Rp_i. Therefore, the increase of X_L as a function of $[NO_3^-]$ might be caused by the lower generation rate of the primary free radicals as indicated by slower $(-d[Ce(IV)]/dt)_i$ and lower termination rates. The addition of NaBr had no effect on polymerization (*Table 5*), so the retardation by $NaNO_3$ must have been caused by the effect of NO_3^-, but not Na^+.

The use of the Ce(IV)–NTA redox pair in aqueous polymerization systems

Figure 11 shows the aqueous polymerizations of AM, AA, MMA and AN initiated by the Ce(IV)–NTA

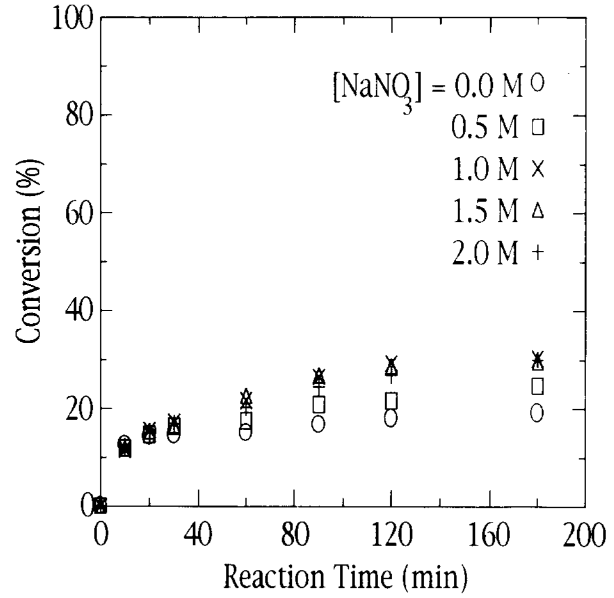


Figure 10 The effect of nitrate ion concentration on the course of polymerization at 40°C with $[HNO_3] = 1.0$ M, $[M]_i = 0.2$ M, $[NTA]_i = 0.0025$ M and $[Ce(IV)]_i = 0.0020$ M

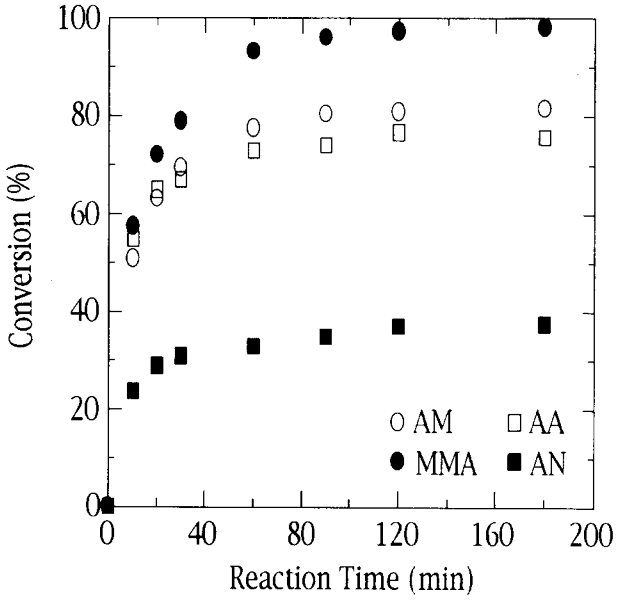


Figure 11 The polymerization courses of different vinyl monomer systems at 40°C with $[AM]_i = 0.2$ M, $[AA]_i = [AN]_i = [MMA]_i = 0.5$ M, $[NTA]_i = 0.0025$ M and $[Ce(IV)]_i = 0.0020$ M

redox pair. The aqueous polymerization systems of AM and AA were inherently homogeneous and their behaviour was almost the same. On the other hand, the aqueous polymerization systems of MMA and AN were heterogeneous but their behaviour was very different. The polymer of MMA could dissolve in its own monomer, i.e. MMA, and NTA has the characteristics of a surfactant, so the aqueous polymerization of MMA was somewhat like the soap-free emulsion system. On the other hand, the polymer of AN could not dissolve in its own monomer, i.e. AN, in the aqueous polymerization of AN, and AN has a larger solubility in water than MMA, which would disperse the monomer into the bulk solution. Thus its Rp_i and X_L were much lower than those of the MMA system.

SUMMARY

Ce(IV)–NTA is a promising redox initiator for aqueous polymerizations. It exhibited higher Rp_i and X_L than other redox initiators, although its kinetic behaviour is the same as that reported in the literature[5,29,30]. It also showed high efficiency on polymerization at room temperature without acid, and addition of salts had little effect on polymerization. Such behaviour might be due to the characteristics of the chelating agent. Besides these, NTA also showed selectivity for the metal oxidants. In summary, the Ce(IV)–NTA redox pair exhibited an excellent performance in the polymerizations of water-soluble monomers as well as water-insoluble monomers.

ACKNOWLEDGEMENT

The authors wish to express their thanks to the National Science Council of the Republic of China for its support of this work (NSC79-0405-E-006-26).

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