Kinetic and Mechanistic Studies on the Block Copolymerization of Methyl Methacrylate Initiated by Ce^{4+}-Poly(ethylene glycol) Redox System

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SYNOPSIS

The kinetic and mechanistic features of tetravalent cerium-poly(ethylene glycol)(PEG, molecular weight 6000) redox couple initiated block copolymerization of methyl methacrylate (MMA) have been investigated in aqueous acidic medium in the temperature range 30–50°C. The block copolymerization behavior as a function of $[Ce^{4+}]$, $[PEG]$, $[MMA]$, $[H^+]$, $[NO_3^-]$, as well as temperature, have been studied. The overall rate of polymerization (R_p), the rate of disappearance of Ce^{4+} (R_{Ce}), and the number average molecular weight $(\bar{M}_n)$ have been determined from gravimetry, cerimetry, and gel permeation chromatography, respectively. R_p has been found to bear a square dependence on $[MMA]$ and independent of both $[Ce^{4+}]$ and $[H^+]$. R_{Ce} has been found to be directly proportional to $[Ce^{4+}]$ and $[H^+]$, and independent of $[MMA]$. Both R_p and R_{Ce} have been found to be retarded on adding nitrate ions, while increase of temperature accelerated the rates. The $\bar{M}_n$ of the block copolymer has been found to depend on $[Ce^{4+}]$, $[PEG]$, $[MMA]$, and $[H^+]$ as well as on temperature. A plausible reaction scheme has been derived and suitable kinetic expressions have been evaluated based on these observations. It has been concluded that by varying the temperature and concentration of the components of the redox system, it is possible to control the rate of polymerization and the molecular weight of the resulting block copolymer. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene glycol) (PEG) is commercially potential in a variety of fields[1] such as biology, biomedical science, surface chemistry, and electrochemistry, owing to its unique properties such as solubility and flexibility of the chains, basicity of the ether oxygen in the main chain, etc. It is used as a carrier polymer because of its biocompatibility, solubility in water and in organic solvents, and its availability in a wide range of molecular weights. The block copolymers of hydrophilic PEG with hydrophobic vinyl monomers may represent useful characteristics,[2] e.g., surface active agents, high-impact plastics, etc.

The essence of redox initiation is a reduction–oxidation reaction. In this process, free radicals are produced by the oxidation of the substrate, which in turn initiate the polymerization. Commonly employed oxidants are $Ce(IV)$,[3] $Mn(III)$,[4] $V(V)$,[5] $Cr(VI)$,[6] $Co(III)$,[7] $Fe(III)$,[8] $Cu(II)$,[9] etc. These oxidants form potential redox systems with various reducing agents[10] like alcohols, aldehydes, ketones, acids, amines, amides, thiols, etc. for the aqueous polymerization of vinyl monomers. The use of reducing agents is limited to simple organic substrates in the literature. We have envisaged and established that the use of a polymer as a reducing agent leads to the formation of a block copolymer.[11]

As a part of our research work on redox initiators, we have earlier investigated and reported the kinetic behavior of the systems, Ce^{4+}-PEG-acrylonitrile (AN)[11] and Mn^{3+}-PEG-AN.[4] Also, a series of block copolymers with varying molecular

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weights of PEG have been prepared with AN,[12,13] MMA,[14] acrylamide,[15] and methacrylic acid[15] using these redox systems. The purpose of the present article is to investigate the kinetic and mechanistic aspects of the block copolymerization of MMA using the redox system, Ce^{4+}-PEG, in aqueous acidic medium.

EXPERIMENTAL

Materials

Ceric ammonium nitrate (AR, S. D. Fine Chem., India) was oven dried at 105°C for 1 h and then in a desiccator over phosphorous pentoxide prior to use. Stock solution of Ce^{4+} was prepared by dissolving weighed ceric salt in standard nitric acid. This solution was then titrated against standard ammonium ferrous sulfate for its Ce^{4+} content and was double checked spectrophotometrically. PEG (LR, S. D. Fine Chem., India) was purified as reported in our earlier article.[11] It was then lyophilized and characterized for molecular weight homogeneity ($\bar{M}_w/\bar{M}_n = 1.1$). The monomer, MMA (Sisco-Chem.) was purified by the standard procedure,[16] distilled repeatedly in nitrogen atmosphere, and stored in dark brown bottles at 5°C. All the other reagents used were either AR grade or BDH samples and used as received.

Nitrogen (Indian Oxygen Co., India) used to deaerate the experimental system was freed from oxygen by passing through Fieser's solution, and then through saturated lead acetate solution, and finally through distilled water. Double distilled water was used throughout the kinetic studies.

Polymerization Procedure

All the polymerization experiments were carried out in Pyrex glass tubes of 6″ length provided with an inlet and outlet for flushing nitrogen. The reaction tubes were covered completely with a black cloth to ensure that the kinetic studies were done in the absence of light. The polymerizations were always carried out within the solubility range of MMA in water. All the solutions, except the Ce^{4+} solution, were taken in the reaction tube, deaerated, and the reaction system was maintained at a temperature of 35 ± 0.1°C in a thermostatic reservoir. Then the Ce^{4+} solution, previously deaerated and temperature-equilibrated, was added instantaneously. In all cases, no induction period (as seen from the appearance of turbidity) was

observed. The reaction was arrested by adding a known excess of ferrous ammonium sulfate solution when all the unreacted ceric ions were reduced to cerous ions. The precipitated polymer was filtered using sintered glass crucible, washed well with water to remove unreacted PEG, Ce^{4+}, MMA as well as Ce^{3+}, and any other oxidation products of PEG, then dried under vacuum and weighed. From the weight of the polymer, the rate of monomer disappearance (or the rate of polymerization, R_p) was calculated using the relation,

$$R_p(\text{mol/L}\cdot\text{s}) = \frac{1000\ W}{VtM}$$

where W = weight of the polymer, V = total volume of the reaction mixture, t = reaction time in seconds, M = average of molecular weights of ethylene oxide and MMA.

The filtrate with excess ferrous ions was back titrated with standard Ce^{4+} solution to determine the rate of ceric ion disappearance (R_{Ce}). The ferrous solution was standardized before each run against potassium dichromate in the presence of diphenylamine indicator. Duplicate runs were carried out for the determination of the rate of monomer disappearance as well as the rate of ceric ion disappearance.
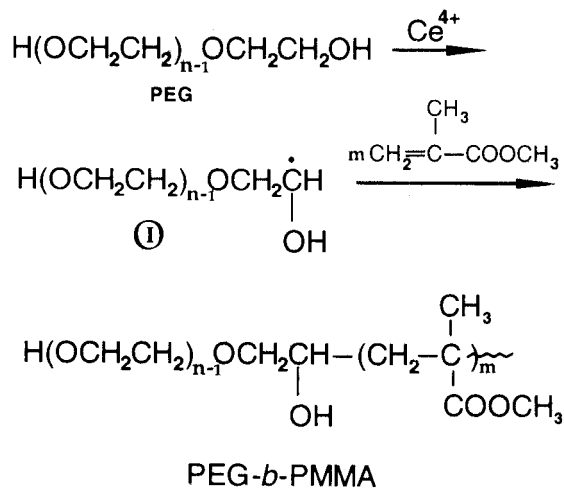
Characterization

FT-IR spectra of the block copolymers were recorded using Nicolet Impact 400 Fourier-Transform Infrared spectrometer. The $\bar{M}_n$ of the block copolymers were determined by gel permeation chromatography (GPC) using a Waters unit interfaced with an NEC (IBM AT compatible) computer. A Waters 510 HPLC pump with high resolution columns (Ultrastyragel 10^3 Å, 10^4 Å, and 10^5 Å in series) coupled with a Waters 410 differential refractometer was used with HPLC grade THF at a flow rate of 1 mL/min. The instrument was set at 40°C before starting the analysis. Molecular weight calibration curve was obtained with six polystyrene standards in the molecular weight range 2.3×10^3 to 3.1×10^6 (Polymer Laboratories, Church Stretton, Shropshire, UK).

RESULTS AND DISCUSSION

Generation of PEG Macroradical

The redox reaction between Ce^{4+} and PEG has been proposed to proceed via the formation of an

$$H(OCH_2CH_2)_{n-1}OCH_2CH_2OH \xrightarrow{\;Ce^{4+}\;}$$

PEG

$$H(OCH_2CH_2)_{n-1}OCH_2\overset{\displaystyle\cdot}{C}H \xrightarrow{\;m\,CH_2\!=\!\overset{\displaystyle CH_3}{\underset{\displaystyle}{C}}\!-\!COOCH_3\;}$$

(I)   OH

$$H(OCH_2CH_2)_{n-1}OCH_2\underset{\displaystyle OH}{\overset{\displaystyle}{C}}H\!-\!(CH_2\!-\!\underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{C}})_m\!\sim$$

PEG-*b*-PMMA

Scheme 1

intermediate PEG macroradical which initiates the polymerization of MMA, resulting in the formation of a block copolymer of PEG and MMA as depicted in Scheme 1.

The PEG macroradical in the absence of any vinyl monomer is subsequently oxidized to yield a long chain aldehyde.[17] On adding Ce^{4+} solution to MMA monomer in the range of concentrations used for the kinetic studies in dark, no polymer was formed within 3 h at 35°C, indicating the absence of homopolymerization of MMA by Ce^{4+}. The polymerization in the presence of PEG was inhibited by atmospheric oxygen, indicating the free radical nature of the redox reaction. The rates were enhanced markedly when the system was exposed to diffused day light. Also, the rates in unstirred conditions were found to be greater than those in stirred conditions. The decreased rate in the stirred conditions might be attributed to the greater probability of encounters between the propagating radicals and the terminating agent. The results are analogous to the system, Ce^{4+}-PEG-AN.[11]

Initially, the polymerization is a homogeneous process as all the components of the redox system are water soluble. Initial growth of the polymeric chain takes place in the aqueous phase. They grow until they reach a critical size and then they separate out as primary particles dispersed in the aqueous phase.

The FT-IR spectrum of the block copolymer shows peaks (ν in cm^{-1}) corresponding to both PEG and MMA components [1115 (C—O—C$_{str}$), 1280, 1350, and 1465 (CH$_2$ bending), 3236 (—O—H$_{str}$) and 1734 (C=O$_{str}$)].

Rate of Monomer Disappearance/Rate of Polymerization (R_p)

The effects of several parameters were studied by varying their concentrations and keeping all the other kinetic factors constant. The rate is found to be dependent on [MMA]^2 [Fig. 1(A)] and on [PEG] [Fig. 1(B)] as indicated from their log-log plots which are linear with slopes of two and one respectively, indicating the second and first order dependencies of the rate on [MMA] and [PEG], respectively. The second order dependence of the rate on MMA concentration is of greater significance, as it completely rules out the possibility of mutual termination which requires an order of 3/2 for [MMA]. If the initiation and termination processes are effected by ceric ions, the second order dependence is easily reconciled. The $\bar{M}_n$ of the block copolymer increases with an increase in [MMA] (Table I), which is in line with the observations made earlier.[18] On the other hand, $\bar{M}_n$ decreases on increasing [PEG] (Table I). This might be attributed to the generation of an excess of primary radicals, which leads to the premature termination of the growing chains, resulting in a drop in molecular weight.

The [Ce^{4+}] was varied from 2×10^{-3} to 7×10^{-3} mol/L. The rate decreases linearly with

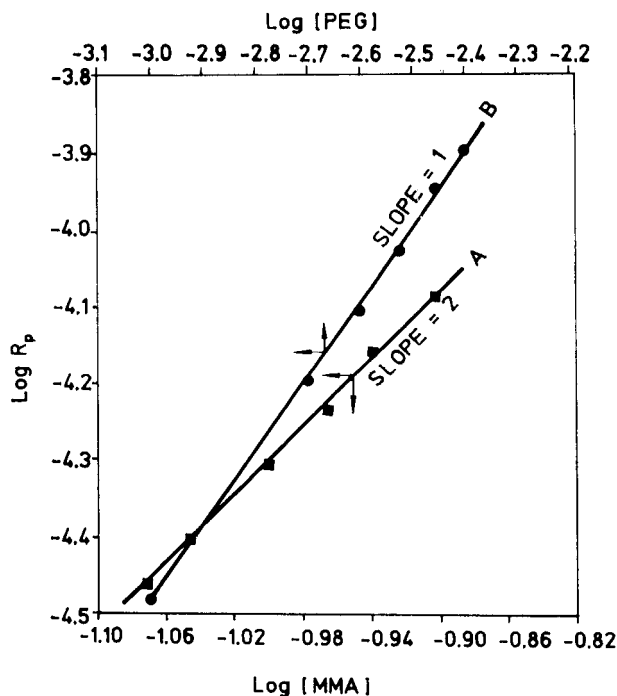**Figure 1** Plots of log R_p against log [MMA] (A) and log [PEG] (B).

Table I   Effect of [MMA]^a and [PEG]^b on $\bar{M}_n$ of the Block Copolymer

[MMA] (mol/L)	$\bar{M}_n \times 10^{-4}$	[PEG] $\times 10^3$ (mol/L)	$\bar{M}_n \times 10^{-4}$
0.085	1.35	1.0	4.51
0.090	1.84	2.0	3.64
0.010	2.55	2.5	3.59
0.110	3.49	3.0	3.21
0.115	4.95	3.5	3.13
0.125	6.47	4.0	2.98

^{a}1[Ce^{4+}] = 3 × 10^{-3} mol/L, [PEG] = 1.1 × 10^{-3} mol/L, [H$^+$] = 0.1 mol/L, μ = 1.0 mol/L, T = 35°C, Time = 30 min.
^{b} [Ce^{4+}] = 3 × 10^{-3} mol/L, [MMA] = 0.1 mol/L, [H$^+$] = 0.1 mol/L, μ = 1.0 mol/L, T = 35°C, Time = 30 min.

an increase in [Ce^{4+}] (Table II). This observation excludes the participation of Ce^{4+} ion directly in the initiation process. $\bar{M}_n$ values decrease on increasing [Ce^{4+}] (Table II), which provides a support to our earlier assumption that the termination of the growing radicals is only by ceric ion. The rate is unaffected by changes in [H$^+$] (0.06–0.25 mol/L) at constant ionic strength (Table III). Also, it is evident from the table that the $\bar{M}_n$ values decrease with an increase in [H$^+$], possibly due to the generation of an excess of radicals.

If the termination of the growing radicals is effected by the Ce^{4+}OH$^-$ species, R_p should increase with an increase in [H$^+$] and should be independent of the latter when Ce^{4+} ion acts as the terminating agent. Our experimental observations thus support the termination by Ce^{4+} ion. The termination by metal ions is very common in several redox polymerizations.

Rate of Ceric Ion Disappearance (R_{Ce})

The rate is found to be directly proportional to [Ce^{4+}] and a plot of R_{Ce} versus [Ce^{4+}] [Fig. 2(A)]

Table II   Effect of [Ce^{4+}] on R_p and $\bar{M}_n$

[Ce^{4+}] $\times 10^3$ (mol/L)	$R_p \times 10^5$ (mol/L·s)	$\bar{M}_n \times 10^{-4}$
2	7.197	5.26
3	6.954	4.20
4	5.863	4.03
5	4.961	3.92
6	4.116	3.16
7	3.836	2.85

[PEG] = 1.1 × 10^{-3} mol/L, [MMA] = 0.1 mol/L, [H$^+$] = 0.1 mol/L, μ = 1.0 mol/L, T = 35°C, Time = 30 min.

Table III   Effect of [H$^+$] on R_p and $\bar{M}_n$

[H$^+$] (mol/L)	$R_p \times 10^5$ (mol/L·s)	$\bar{M}_n \times 10^{-4}$
0.06	5.299	5.28
0.07	5.234	4.84
0.08	5.263	4.15
0.15	5.061	3.05
0.20	5.300	2.50
0.25	5.220	1.67

[Ce^{4+}] = 3 × 10^{-3} mol/L, [PEG] = 1.1 × 10^{-3} mol/L, [MMA] = 0.1 mol/L, μ = 1.0 mol/L, T = 35°C, Time = 30 min.

results in a straight line passing through the origin. The rate is observed to be independent of [MMA] (Table IV), which confirms that ceric ions are not directly involved in the initiation reaction of the type M + Ce^{4+} which could lead to a homopolymer. The rate increases with increase in [PEG] (Table IV). The straight line plot of the rate against [PEG] passing through the origin [Figure 2(B)] substantiates the absence of complex formation between the ceric ion and PEG. Furthermore, from the absorption spectra of Ce^{4+} and Ce^{4+}-PEG mixture,[17] it could be seen that after the addition of PEG, there was no shift in the absorption maxima of Ce^{4+}, confirming the absence of complex formation in the redox process. The rate is found to increase with increasing [H$^+$] at constant ionic strength, whereas it de-
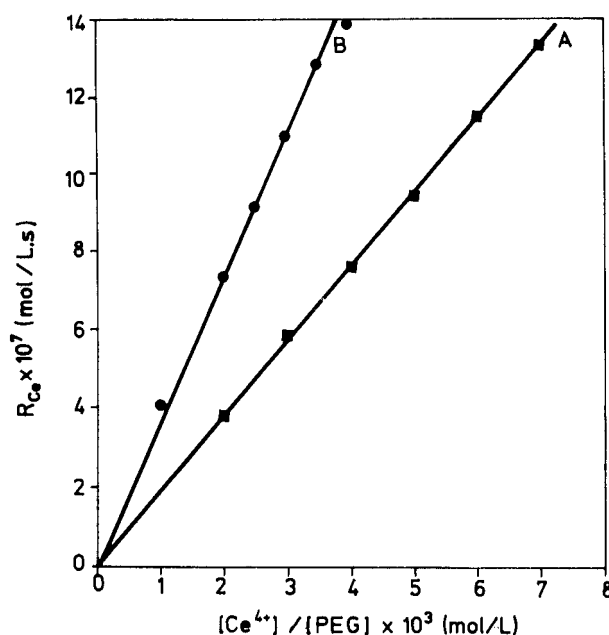

**Figure 2**   Effect of [Ce^{4+}] (A) and [PEG] (B) on R_{Ce}.

Table IV   Effect of [MMA] and [PEG] on R_{Ce}[a]

[MMA] (mol/L)	$R_{Ce} \times 10^7$ (mol/L·s)	[PEG] $\times 10^3$ (mol/L)	$R_{Ce} \times 10^7$ (mol/L·s)
0.085	10.995	1.0	4.042
0.090	11.130	2.0	7.301
0.010	12.136	2.5	9.103
0.110	11.269	3.0	10.915
0.115	11.315	3.5	12.763
0.125	11.640	4.0	13.901

[a] Experimental conditions same as in Table I.

creases with increasing $[H^+]$ when ionic strength is not a constant. $NaNO_3$ was used for adjustments of ionic strength. This could be explained as follows.

Ceric ions in aqueous acidic solution consist of different species such as Ce^{4+}, $Ce(OH)^{3+}$, and $(Ce-O-Ce)^{6+}$, whose relative amounts depend on the acid concentration according to the following equilibria:

$$Ce^{4+} + H_2O \rightleftharpoons (CeOH)^{3+} + H^+ \qquad (1)$$

$$2(CeOH)^{3+} \rightleftharpoons (Ce-O-Ce)^{6+} + H_2O \quad (2)$$
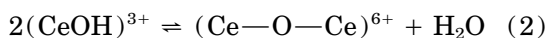
On increasing the acid concentration both the equilibria shift to the left, and therefore, the higher the acid concentration, the higher the concentration of Ce^{4+} species, and hence higher the rate. However, when the ionic strength is not maintained constant, nitrate ion concentration also increases on increasing the acid concentration, which results in the decreased rate as evidenced from the following studies.

Effect of Nitrate Ions

A set of experiments was carried out by varying $[NO_3^-]$ in the range 0.12–0.24 mol/L using sodium nitrate at 35°C. Concentrations of Ce^{4+}, PEG, MMA, and H^+ were set constant at 3×10^{-3} mol/L, 1.1×10^{-3} mol/L, 0.09 mol/L, and 0.1 mol/L, respectively. The results are reported in Table V. The rate of polymerization decreases steadily on increasing $[NO_3^-]$. This can be explained taking into account the dissociation of the salt as well as on the conversion of $Ce(OH)^{3+}$ species into $[Ce(OH)NO_3]^{2+}$, which is less reactive.

Effect of Temperature

The effect of temperature on the rate of polymerization and ceric ion consumption was investi-

Table V   Effect of $[NO_3^-]$ on R_{Ce}

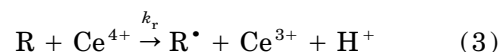| $[NO_3^-]$ (mol/L)	$R_{Ce} \times 10^7$ (mol/L·s)
0.12	11.365
0.14	11.273
0.16	11.230
0.18	11.175
0.20	11.130
0.24	11.100

$[Ce^{4+}] = 3 \times 10^{-3}$ mol/L, [PEG] = 1.1×10^{-3} mol/L, [MMA] = 0.09 mol/L, $\mu = 1.0$ mol/L, $[H^+] = 0.1$ mol/L, $T = 35°C$, Time = 30 min.

gated in the temperature range 30–50°C. Both the rate of polymerization and that of the ceric ion consumption increase on increasing the temperature (Table VI). The overall activation energy of polymerization as calculated from the Arrhenius plot (Fig. 3) is found to be 16.8 kJ/mol. The $\bar{M}_n$ of the block copolymer decreases on increasing the temperature (Table VI), which could be due to the fact that higher temperatures favor the termination step.

Kinetic Scheme and Rate Law

Based on the experimental results, the following reaction scheme is proposed:
Ia. Reaction of the reducing agent with ceric ion:

$$R + Ce^{4+} \xrightarrow{k_r} R^{\bullet} + Ce^{3+} + H^+ \qquad (3)$$

where R is the reducing agent (PEG) and $R^{\bullet}$ is the macroradical formed from PEG.
Ib. Reaction of the macroradical with Ce^{4+} to give the oxidation product:

Table VI   Effect of Temperature on R_p, R_{Ce} and $\bar{M}_n$

T (°C)	$R_p \times 10^5$ (mol/L·s)	$R_{Ce} \times 10^7$ (mol/L·s)	$\bar{M}_n \times 10^{-4}$
30.0	4.421	1.118	4.42
37.5	5.173	3.247	4.25
40.0	5.426	3.896	4.11
42.5	5.710	4.563	4.04
45.0	5.975	5.353	3.96
50.0	6.465	6.753	3.80

$[Ce^{4+}] = 3 \times 10^{-3}$ mol/L, [PEG] = 1.1×10^{-3} mol/L, [MMA] = 0.1 mol/L, $\mu = 1.0$ mol/L, $[H^+] = 0.1$ mol/L, Time = 30 min.
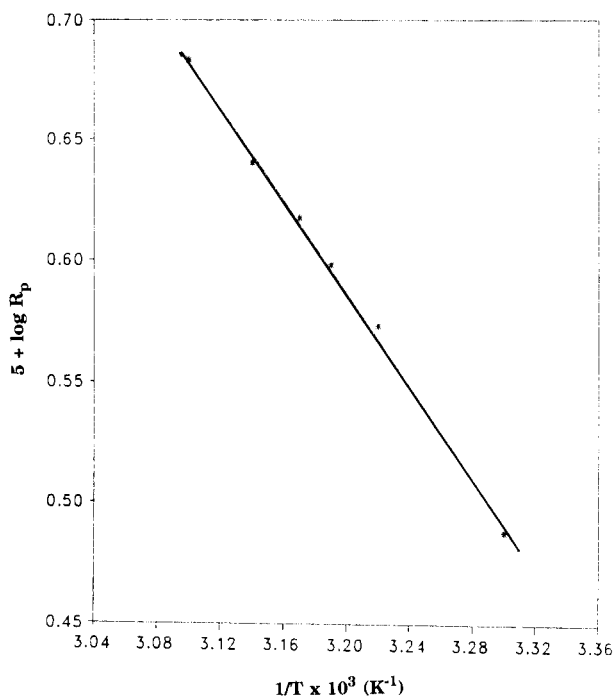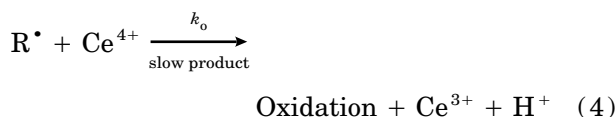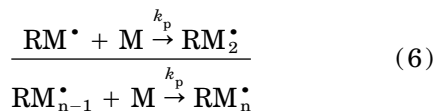
Figure 3 Arrhenius plot.

$$R^{\bullet} + Ce^{4+} \xrightarrow[\text{slow product}]{k_o}$$

$$\text{Oxidation} + Ce^{3+} + H^+ \quad (4)$$

II. Initiation of polymerization by the reaction of the macroradical with the monomer (M):

$$R^{\bullet} + M \xrightarrow{k_i} RM^{\bullet} \quad (5)$$

III. Propagation:

$$\frac{RM^{\bullet} + M \xrightarrow{k_p} RM_2^{\bullet}}{RM_{n-1}^{\bullet} + M \xrightarrow{k_p} RM_n^{\bullet}} \quad (6)$$

IV. Termination:
a. Mutual termination:

$$2RM_n^{\bullet} \xrightarrow{k_{t1}} \begin{array}{l} \text{Block} \\ \text{copolymer} \end{array} \quad (7)$$

b. Linear termination by Ce^{4+}:

$$RM_n^{\bullet} + Ce^{4+} \xrightarrow{k_{t2}} \begin{array}{l} \text{Block} \\ \text{copolymer} \end{array} + Ce^{3+} + H^+ \quad (8)$$

With the usual assumptions for the steady-state concentrations of free radicals and the rate constants being independent of chain length, and considering only the linear type of termination by Ce^{4+} as the effective process under our experimental conditions, the following equations are derived for the rate of monomer disappearance, $-d[M]/dt$ and the rate of ceric ion disappearance, $-d[Ce^{4+}]/dt$.

$$R_p = -d[M]/dt = \frac{k_r k_p [M]^2 [R]}{k_{t2}\{[M] + (k_o/k_i)[Ce^{4+}]\}} \quad (9)$$

$$R_{Ce} = -d[Ce^{4+}]/dt = 2k_r[Ce^{4+}][R] \quad (10)$$

Considering the equilibrium:

$$Ce^{4+} + H_2O \overset{k_h}{\rightleftharpoons} (Ce^{4+}OH^-) + H^+ \quad (11)$$
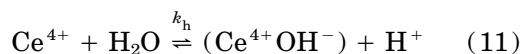
and with the assumption that Ce^{4+} and $(Ce^{4+}OH^-)$ are the only cerium containing species present,

$$[Ce^{4+}]_T = [Ce^{4+}] + [Ce^{4+}OH^-] \quad (12)$$

where $[Ce^{4+}]_T$ is the total concentration of the ceric ions present, $[Ce^{4+}]$ and $[Ce^{4+}OH^-]$ are the concentrations of equilibrium unhydrolyzed ceric ion and the ion pair respectively:

$$[Ce^{4+}] = \frac{[Ce^{4+}]_T[H^+]}{k_h + [H^+]} \quad (13)$$

Substituting this in eq. (10), we get

$$R_{Ce} = -d[Ce^{4+}]/dt = \frac{2k_r[Ce^{4+}]_T[H^+][R]}{k_h + [H^+]} \quad (14)$$

The rate expressions in eqs. (9) and (14) clearly explain the dependence of R_p and R_{Ce} on the various kinetic parameters studied.

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