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Kinetics of Polymerization of 2-Hydroxyethylmethacrylate Initiated by a Titanium(III)-Dimethylglyoxime Redox System

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The polymerization of 2-hydroxyethylmethacrylate (HEMA) initiated by the redox system titanium(III)-dimethyl glyoxime (DMG) was studied in dimethyl formamide (DMF)-water (80:20 v/v) medium in the temperature range 290-310 K. The rate of polymerization (R_p) was investigated at various concentrations of reductant, oxidant, sulfuric acid, and monomer. Cyclic voltametric sensing of dimethylglyoxime under the kinetic conditions demonstrated its reduction behavior. From the obtained results, it was inferred that the polymerization reaction was initiated by an organic free radical arising from the titanium(III)-dimethylglyoxime redox system. Chain termination of the polymer took place predominantly by mutual coupling and small fraction by chain transfer mechanism involving solvent molecules. The effects of some water miscible organic solvents and surfactants on the rate of polymerization were investigated. The temperature dependence of the rate was studied and the activation parameters were computed using Arrhenius and Eyring plots. A suitable kinetic scheme is proposed on the basis of experimental observations.

Key Words: Poly[2-hydroxyethylmethacrylate], Cyclic Voltammetry and Titanium(III)-Dimethylglyoxime

Introduction

The utility of the titanium(III) ion as a reductant for several classes of organic compounds has been examined by different researchers¹⁻³. However, not much attention has been paid to the use of this metal ion in redox polymerization. Previous research by our group established the kinetics of reduction of certain oximes by titanium(III) in the absence as well as in the presence of various vinyl monomers⁴⁻⁷. A number of workers have previously studied the copolymerization of HEMA, the bulk copolymerization of HEMA with a number of alkyl acrylates and N-vinyl-2-pyrrolidone⁸⁻⁹. Hill et al. extensively studied the copolymerization of HEMA with various monomers¹⁰⁻¹³. Recently Buback and Kurz investigated the free radical propagation

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coefficient for poly(2-hydroxyethylmethacrylate)[PHEMA]¹⁴. In spite of extensive literature on the application of PHEMA especially in the biomedical field, the number of basic studies on the kinetics and mechanism of the polymerization of HEMA is limited^{15–16}. The kinetics of redox polymerization have received great attention from various researchers^{17–20}. However, there appears to be no report in the literature on the chemical polymerization of HEMA involving a titanium(III)-dimethylglyoxime redox system. As a part of our polymerization studies with transition metal ion-organic component redox systems^{21–23}, we herewith present the result of kinetics of polymerization of HEMA initiated by a titanium(III)-dimethylglyoxime redox system.

Experimental Section

Materials

2-Hydroxyethylmethacrylate from Merck, Germany, was purified by distillation under vacuum followed by extraction with hexane and subsequent distillation¹⁶. The dimethylglyoxime (GSC, India), dimethylformamide (s.d. fine, India), methanol (s.d. fine, India) dimethylsulfoxide (s.d. fine, India) Triton X-100 and sodium lauryl sulfate (Fischer, India), and titanium dioxide (s.d. fine, India) used were of analytical grade. Doubly distilled water was used throughout. A stock solution of titanium(III)sulfate solution was prepared by electrolytic reduction of an appropriate titanium(IV)sulfate solution⁸ and was standardized against ferric ammonium sulfate²⁴. Pure nitrogen was used for the deaeration of all experimental systems.

Kinetic measurements

The kinetics of polymerization were followed by a batch process as follows: the required amount of monomer HEMA, DMG and solvent were taken in a tubular reaction vessel fitted with inlet and outlet tubes for the passage of nitrogen. The total volume of the reaction mixture was adjusted to 25 cm³. The reaction mixture was thermostated to attain the desired temperature and deaerated by bubbling nitrogen. Polymerization was initiated by adding deaerated solution of DMG. Reactions were homogeneous at all conversions. Ice-cold water was added to arrest the polymerization. Excess water was added to precipitate the arrested reaction mixture. The precipitated polymer was isolated, washed well with water and dried under vacuum to constant weight. The percentage yield of polymerization was determined gravimetrically and the rate of polymerization was determined by the initial slope method.

Molecular weights were determined viscometrically. Polymer samples were purified by dissolving them in DMF followed by precipitation in water and subsequent filtration and drying under vacuum. The purified polymer samples were dissolved in DMF (0.1% w/v) and their viscosity determined using a Ubbelohde suspended level viscometer at 25°C. The intrinsic viscosity of PHEMA is related to its molecular weight as²⁵ $[\eta] = 8.9 \times 10^{-5}[M]^{0.7}$.

Results and Discussion

Blank experiments

Polymerization did not occur when 2-hydroxyethylmethacrylate was added separately to either of the reagents, titanium(III) or dimethylglyoxime in DMF-water medium. However, added monomer was found

to initiate polymerization in the presence of the mixture of titanium(III)-dimethylglyoxime in DMF-water medium.

Kinetics of polymerization

HEMA was polymerized at 27°C in DMF-water (80:20% v/v) in the presence of titanium(III)-DMG redox systems. The kinetics of polymerization were performed by varying the concentration of titanium(III)sulfate, sulfuric acid, dimethylglyoxime, monomer and temperature and the results were computed. The effect of the inhibitor and surfactants were also studied and the results were computed. A typical set of conversion-time curves is shown in Figure 1. The rate of polymerization increases linearly with time.

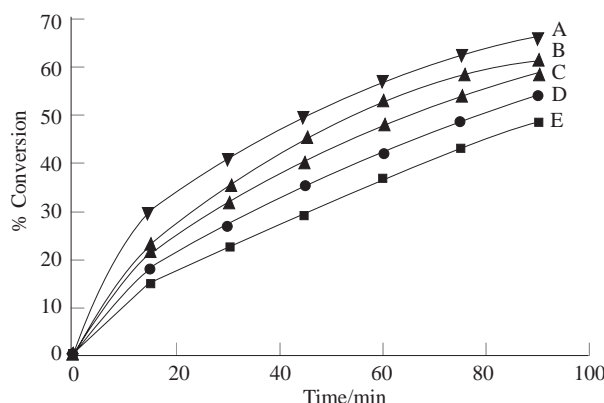


Figure 1. Time - Conversion curves for the redox polymerization of HEMA at 300 K: [Ti(III)]; 0.03 mol dm⁻³; [H₂SO₄]; 0.4 mol dm⁻³; [DMG]; 0.02 mol dm⁻³; Polymerization time: 90 min. HEMA concentration (mol dm⁻³) (A) 0.49 (B) 0.57 (C) 0.33 (D) 0.24 (E) 0.16.

Dependence of rate on monomer concentration

The rate of polymerization was investigated by varying the concentration of monomer (M) from 0.16 to 0.57 mol dm⁻³. The initial slope as well as the maximum conversion increases steadily with an increase of monomer concentration in the range 0.16-0.49 mol dm⁻³ (Table 1). A plot of log R_p versus log [M] was found to be linear with the slope (order) equal to unity with respect to the monomer (Figure 2A). However, it increases when the monomer concentration exceeds 0.57 mol dm⁻³. This deviation may be due to the increase in the viscosity of the medium and a consequent decrease in the mobility of the propagating species.

Table 1. Effect* of titanium(III), dimethylglyoxime and HEMA concentration on polymer yield for the redox polymerization of HEMA at 300K; [H₂SO₄]: 0.4 mol dm⁻³; DMF: 80% v/v; Polymerization time: 90 minutes.

[Ti ³⁺ × 10 ² mol dm ⁻³	% Polymer yield	[DMG] × 10 ² mol dm ⁻³	% Polymer yield	[HEMA] × 10 mol dm ⁻³	% Polymer yield
2.0	37.32	1.0	52.44	1.6	46.20
2.5	48.40	2.0	57.08	2.4	50.24
3.0	57.08	3.0	62.05	3.3	57.08
3.5	64.44	4.0	55.20	4.9	62.42
4.0	52.50	5.0	47.62	5.7	49.60

* [Ti³⁺], 0.03 mol dm⁻³; [DMG], 0.02 mol dm⁻³; [HEMA]; 0.33 mol dm⁻³ while varying other components.

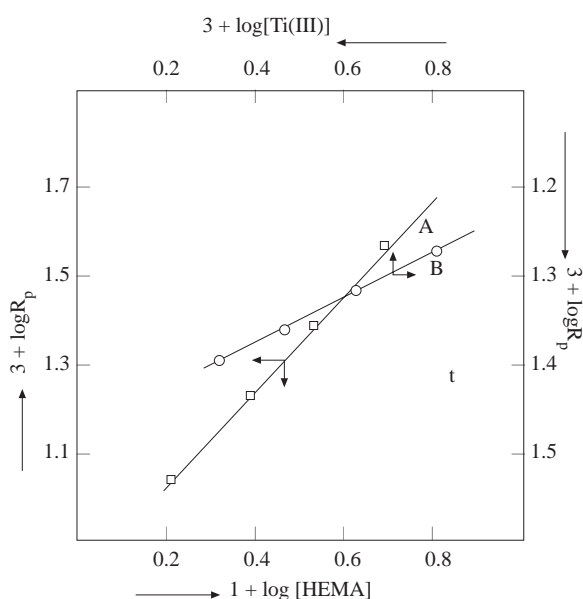


Figure 2. Plots of \log (initial rate, R_p) versus \log (concentration).

(A) Plot of $3 + \log R_p$ versus $1 + \log [M]$ at 300 K; [DMG]: 0.02 mol dm^{-3} ; $[\text{H}_2\text{SO}_4]$: 0.4 mol dm^{-3} ; $[\text{Ti(III)}]$: 0.4 mol dm^{-3} , DMF: 80% $[M] = 0.16, 0.24, 0.33,$ and 0.49 mol dm^{-3} .

(B) Plot of $3 + \log R_p$ versus $3 + \log [\text{Ti(III)}]$ at 300 K; [DMG]: 0.02 mol dm^{-3} ; [HEMA]: 0.13 mol dm^{-3} ; $[\text{H}_2\text{SO}_4]$: 0.4 mol dm^{-3} ; $[\text{Ti(III)}]$: $2 \times 10^{-2}, 2.5 \times 10^{-2}, 3.0 \times 10^{-2}$ and $3.5 \times 10^{-2} \text{ mol dm}^{-3}$ DMF: 80% (v/v).

Dependence of rate on titanium(III)sulfate concentration

The influence of activator titanium(III)sulfate on R_p was studied in the concentration range (2.0×10^{-2} to $4.0 \times 10^{-2} \text{ mol dm}^{-3}$). The initial rate as well as the maximum conversion steadily increases with an increase of titanium(III)sulfate in the range of 2.0×10^{-2} to $3.5 \times 10^{-2} \text{ mol dm}^{-3}$ (Table 1) and the plot of $\log R_p$ versus $\log [\text{Ti(III)}]$ was linear indicating 0.5 order with respect to titanium (III) sulfate (Figure 2B). However, the decrease in polymer yield beyond $3.5 \times 10^{-2} \text{ mol dm}^{-3}$ may be due to the local overconcentration of free radicals produced during the reduction of dimethylglyoxime, which enhances the termination process.

Dependence of rate on dimethylglyoxime concentration

The influence of initiator dimethylglyoxime concentration on the rate of polymerization was studied by varying its concentration from 1.0×10^{-2} to $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ (Table 1). The rate of polymerization was found to increase linearly with increases in dimethylglyoxime concentration within the range 1.0×10^{-2} to $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ yielding the order of 0.5 with respect to dimethylglyoxime concentration. However, when its concentration exceeds $3.0 \times 10^{-2} \text{ mol dm}^{-3}$, the polymer yield decreases. This is because an increase in dimethylglyoxime concentration results in an increase in the rate of its reduction⁶ and there will be a local overconcentration of the free radicals. Consequently, the polymer yield decreases.

Dependence of rate with temperature

The reactions were carried out at various temperatures within the range 17-35°C (Table 2). The rate of polymerization increases with an increase in temperature from 17 to 32°C. This is because as the reaction rate of titanium(III) reduction of dimethylglyoxime increases with temperature, there will be slow and steady generation of free radicals, and hence the polymer yield increases gradually in the temperature range 17-32°C. However, above 32°C reduction becomes very fast, resulting in a local overconcentration of free radicals. This situation favors chain initiation and chain termination at the expense of chain propagation. Hence the polymer yield decreases. The activation energy (E_a) calculated from the Arrhenius plot $\log(\text{rate})$ versus $1/T$ in the temperature range 17-32°C was $27.5 \pm 2.5 \text{ kJ mol}^{-1}$. The other activation parameters calculated from the Eyring plot are ΔH : $25.2 \pm 2.5 \text{ kJ mol}^{-1}$; ΔG : $64.5 \pm 1.5 \text{ kJ mol}^{-1}$ and ΔS : $-138 \pm 8.5 \text{ JK}^{-1} \text{ mol}^{-1}$. The relative low energy of activation or enthalpy of activation and high negative entropy of activation observed are characteristic of a free radical polymerization process.

Table 2. Effect of sulfuric acid and temperature on polymerization yield for the redox polymerization of HEMA at 300 K; [Ti(III)]: 0.03 mol dm^{-3} ; [DMG]: 0.02 mol dm^{-3} ; DMF: 80% v/v; Polymerization time: 90 minutes.

$\text{H}_2\text{SO}_4 \times 10^2$ mol dm^{-3}	% Polymer yield	Temperature/K	% Polymer yield
2.0	46.20	290	36.00
3.0	50.24	295	48.20
4.0	57.08	300	57.08
5.0	62.42	305	65.58
6.0	49.60	310	60.46

*While varying the temperature sulfuric acid being 0.4 mol dm^{-3}

Dependence of rate on sulfuric acid concentration

The kinetics of polymerization were performed at different sulfuric acid concentrations in the range 2.0×10^{-2} to $6.0 \times 10^{-2} \text{ mol dm}^{-3}$. The initial rate as well as the maximum conversion steadily increases with an increase of 2.0×10^{-2} to $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ (Table 2) and the plot of $\log R_p$ versus $\log[\text{H}^+]$ shows dependence of an order of 0.6 with respect to sulfuric acid concentration. However, beyond 0.5 mol dm^{-3} sulfuric acid the rate of polymerization as well as the maximum conversion decreases. This is because of an increase in reduction rate. Hence the polymer yield decreases at higher concentrations.

Polymer characterization

Molecular Weight

The viscosity-average molecular weight of the polymer product in a typical run was found to be 3.4×10^4 .

Spectral Analysis

The infrared spectrum of the polymer product (Figure 3) revealed absorption frequencies at 3447 cm^{-1} (O-H and N-H stretching), 2952 cm^{-1} (C-H stretching), 1720 cm^{-1} (-COO- stretching), and 1642 cm^{-1}

(-C=N-stretching); this indicates the dimethylglyoxime moiety as an end group of the poly(2-hydroxyethyl methacrylate).

Polymerization in a different solvent medium

Solvent plays an important role in the rate of polymerization. The effect of the solvent on the rate of polymerization as well as on the polymer yield were studied using a number of polar solvents such as dimethyl sulfoxide (DMSO), ethyl alcohol (EtOH), methanol (MeOH), (maintaining 80% v/v) and nonpolar solvent like carbon tetrachloride (3% in 80% dimethylformamide). The rate of polymerization and the polymer yield were different in different solvent media (Table 3 and Figure 4). However, the kinetic behavior in different media is expected to be similar.

Table 3. Effect of solvent on the polymer yields and average molecular weight for the redox polymerization of HEMA at 300K.

[HEMA]: 0.33 mol dm⁻³; [Ti(III)]; 0.03 mol dm⁻³; [H₂SO₄]; 0.4 mol dm⁻³; [DMG]; 0.02 mol dm⁻³; Polymerization time: 90 min.

Solvent	% Polymer yield	Average molecular weight
80% Ethanol	32.6	2.6×10^4
80% Methanol	44.26	2.1×10^4
80% DMF	57.08	3.4×10^4
80% DMSO	35.8	2.2×10^4
3% CCl ₄ in 80% DMF	24.6	0.6×10^4

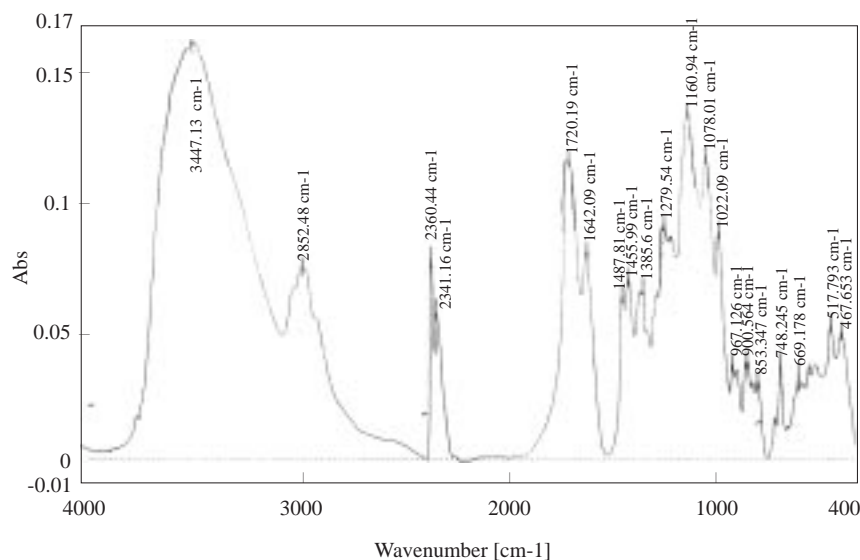


Figure 3. IR spectrum of Poly[2-hydroxyethylmethacrylate].

We wanted to know whether the chain transfer mechanism operates in the termination step. Carbon tetrachloride is known to be an efficient chain transfer agent. The formulation containing a solvent mixture of 3% carbon tetrachloride in 80% DMF resulted in a 60% decrease in the polymer yield and a consequent lowering of molecular weight. This is due to enhanced termination by the chain transfer mode.

Dependence of rate on inhibitor concentration

In the present work we observed inhibition of the rate in polymerization initiated by titanium(III)-dimethylglyoxime redox pair using hydroquinone as the potential inhibitor. The rate of polymerization dramatically decreases with an increase in the concentration of the inhibitor (Figure 5). It was concluded that the polymerization reaction proceeds through a free radical mechanism.

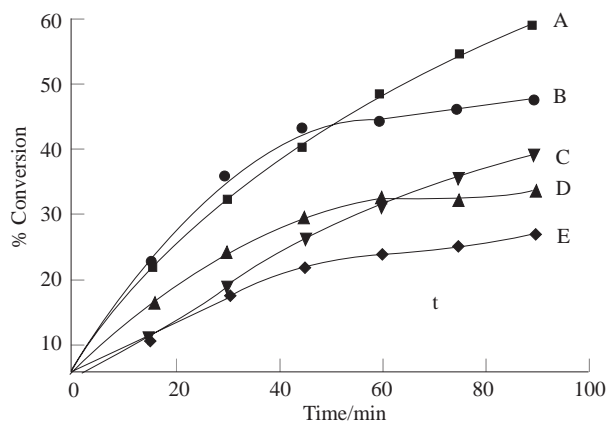


Figure 4. Effect of various solvents on polymer yield of redox polymerization of HEMA at 300 K; [Ti(III)]: 0.03 mol dm⁻³; [H₂SO₄]: 0.4 mol dm⁻³; [DMG]: 0.02 mol dm⁻³; [HEMA]: 0.33 mol dm⁻³; Polymerization time: 90 min.

(A) 20% water and 80% DMF, (B) 20% water and 80% methanol

(A) 20% water and 80% DMSO (D) 20% water and 80% ethanol

(E) 20% water and 3% CCl₄ in 80% DMF

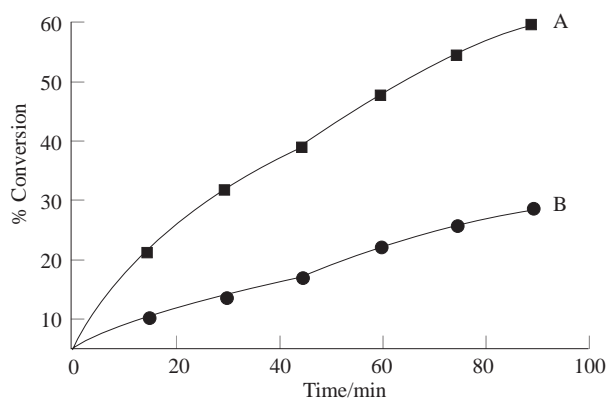


Figure 5. Effect of inhibitor, hydroquinone on the polymer yield of redox polymerization of HEMA at 300 K: Ti(III); 0.03 mol dm⁻³; [H₂SO₄]; 0.4 mol dm⁻³; [DMG]: 0.02 mol dm⁻³; [HEMA]: 0.33 mol dm⁻³; Polymerization time: 90 min HEMA concentration (mol dm⁻³).

(A) In absence of hydroquinone, (B) In presence of 2.0% hydroquinone

Effects of surfactants on the rate

The rate of polymerization was studied in the presence of certain surfactants such as sodium lauryl sulfate and Triton X-100 above and below the critical micelle concentration (CMC) value (Table 4). It was found

that polymer yield increases gradually with increases in the concentration of sodium lauryl sulfate above the CMC value. The enhancement or retardation of the rate of polymerization may be due to electrostatic attractions²⁶.

Table 4. Effect of surfactants on polymer yield for the redox Polymerization of HEMA at 300K

[HEMA]: 0.33 mol dm⁻³; [Ti(III)]; 0.03 mol dm⁻³; [H₂SO₄]; 0.4 mol dm⁻³; [DMG]: 0.02 mol dm⁻³; Polymerization time: 90 min.

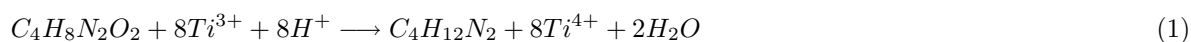
[Sodium lauryl sulfate] × 10 ³	% Polymer	[Triton-X100] × 10 ² mol dm ⁻³	% Polymer
0.30	36.6	0.8	42.2
0.60	47.42	1.6	48.5
0.87*	54.5	2.4*	57.8
1.40	60.28	60.0	52.5
1.60	36.6	10.0	46.6

* CMC value of the corresponding surfactant

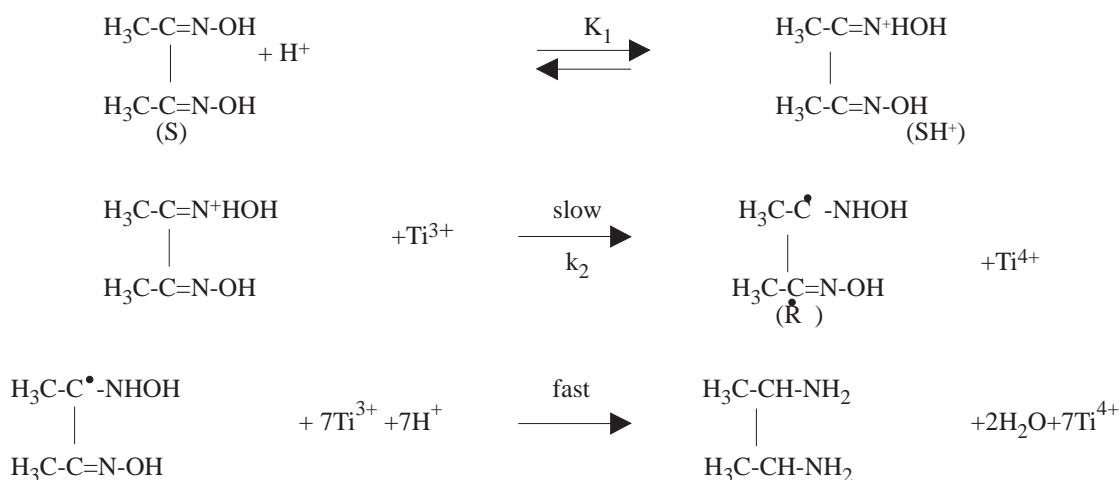
In contrast, the polymer yield increases with gradual increases in the concentration of Triton X-100. However, above the CMC value polymer yield decreases. This is because in the region near CMC the formation of a large number of new micelles occurs and hence polymer yield increases. However, above CMC separation of a new phase occurs in surfactant solutions and an aggregation of surfactant molecules is formed. Due to the decrease in concentration of new micelles, polymer yield decreases.

Kinetic scheme

The kinetics of reduction of dimethylglyoxime by titanium(III)-dimethylglyoxime in aqueous sulfuric acid medium has recently been studied⁶. The stoichiometry of the reduction of dimethylglyoxime by titanium(III) was found to be 1:8 according to



The kinetic orders of the reactions were found from log(rate) versus log(concentration) plots. The order was found by varying the concentration of dimethylglyoxime, titanium(III), sulfuric acid in turn while keeping the others constant. The kinetic orders with respect to dimethylglyoxime and titanium(III) were nearly unity and the order with respect to sulfuric acid was about 0.5. In the absence of a free radical scavenger in the system, the titanium(III) reduction of dimethylglyoxime has been shown to follow Scheme 1.


Scheme 1

The eight electron reduction of dimethylglyoxime was further supported by an irreversible cyclic voltammogram with a well defined cathodic peak (Figure 6) decreasing from -817mV to -494mV as the concentration of sulfuric acid varied from 4.0 to 72.0 mM, due to the involvement of H^+ in the reaction²⁷.

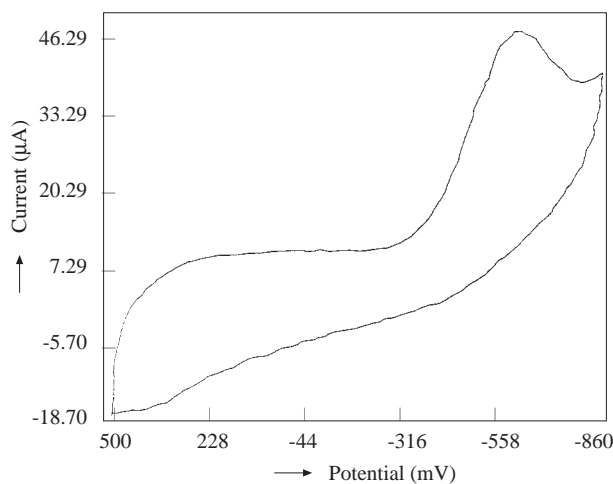
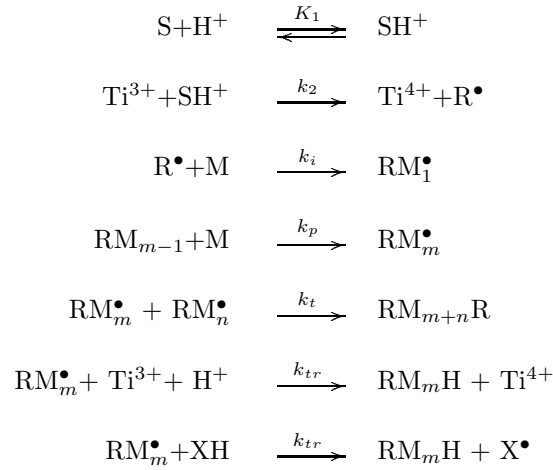


Figure 6. Typical cyclic voltammogram of dimethylglyoxime (4 mM) at 300 K; Electrode: glassy carbon; sweep rate: 50mV/s; electrolyte: mixture of 20 mM sulfuric acid and 80(%) DMF.

In the presence of vinyl monomers the free radical initiates polymerization. The observed dependence of the polymerization rate on initiator, activator, sulfuric acid and monomer concentration could be explained by Scheme 2.

In Scheme 2, M is the monomer, HEMA, k_i , k_p , k_t and k_{tr} are the rate constants for the initiation, propagation, termination and chain transfer steps respectively and XH is the chain transfer agent, and K_1 and k_2 are the equilibrium constant and the rate constant respectively.



Scheme 2

Applying the steady state approximation to R^\bullet and the growing radical RM^\bullet

$$\frac{d[R]}{dt} = k_2[Ti(III)][SH^+] - k_i[R^\bullet][M] \quad (2)$$

$$[R^\bullet] = \frac{k_2[Ti(III)][SH^+]}{k_i[M]} \quad (3)$$

Further assuming that the radical reactivity is independent of the radical chain length, the rate of polymerization may given by

$$R_p = k_p[RM^\bullet][M] \quad (4)$$

If the termination takes place by coupling

$$k_i[R^\bullet][M] = k_t[RM^\bullet]^2$$

$$[RM^\bullet] = (k_i/k_t)^{1/2}[R^\bullet]^{1/2}[M]^{1/2} \quad (5)$$

substituting for $[R^\bullet]$

$$[RM^\bullet] = (k_2/k_t)^{1/2}[Ti^{3+}]^{1/2}[SH^+]^{1/2} \quad (6)$$

so that the rate of polymerization takes the form

$$R_p = k_p(K_1)^{1/2}(k_2/k_t)^{1/2}[Ti^{3+}]^{1/2}[S]^{1/2}[H^+]^{1/2}[M] \quad (7)$$

Further, if the chain transfer takes place by $(Ti^{3+}+H^+)$

$$k_i[R^\bullet][M] = k_{tr}[RM^\bullet][Ti^{3+}][H^+]$$

Substituting for $[R^\bullet]$

$$[RM^\bullet] = k_i k_2 [Ti^{3+}] [SH^+] [R^\bullet] [M] / k_{tr} k_i [M] [Ti^{3+}] [H^+] \text{ or}$$

$$[RM^\bullet] = k_2 [SH^+] / k_{tr} [H^+] \quad (8)$$

Hence,

$$R_p = K_1 k_2 k_p [S][M]/k_{tr} \quad (9)$$

The dependence of the initial rate of polymerization R_p on $[\text{Ti}^{3+}]^{0.5}$, $[\text{M}]^{1.0}$, $[\text{H}_2\text{SO}_4]^{0.6}$, $[\text{S}]^{0.5}$, which are actually determined by the experiment, is consistent with rate equation (7). Termination involving $[\text{Ti}^{3+}]$ would have yielded the rate expression (9), which is showing independence on $[\text{Ti}^{3+}]$ and $[\text{H}^+]$ is not in accordance with the experimental data. Therefore, termination by (9) is ruled out.

Conclusions

In this work oxime in combination with titanium(III) is introduced as a redox initiator for free radical polymerization. Dimethylglyoxime with an electron releasing hydroxyl group undergoes reduction by titanium(III) at the oxime group in a controlled manner and induces free radicals. Further work on the kinetics of the electroinitiated polymerization of HEMA mediated by titanium(III) in conjugation with suitable substrate is in progress.

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