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AQUEOUS POLYMERIZATION OF METHYL METHACRYLATE INITIATED BY TITANIUM(III)–SALICYLALDOXIME REDOX SYSTEM: A KINETIC STUDY

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Key Words: Aqueous Polymerization, Kinetics, Cyclic Voltammetry, Methyl Methacrylate, Titanium(III)-Salicylaldoxime Redox System

ABSTRACT

The polymerization of methyl methacrylate initiated by the titanium(III)-salicylaldoxime redox system was studied in an aqueous sulfuric acid-ethanol medium in the temperature range of 20-30°C. The rates of polymerization were investigated at various concentrations of reductant, oxidant, ethanol, sulfuric acid, and monomer. Cyclic voltammetric sensing of salicylaldoxime kinetic conditions demonstrated its reduction behavior. From the results obtained, it was inferred that the polymerization reaction was initiated by an organic free radical arising from the titanium(III)-salicylaldoxime redox system and termination took

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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 has been proposed on the basis of experimental observations.

INTRODUCTION

The use of titanium(III) ion as reductant for several classes of organic compounds has been carried out by different workers [1-4]. Davis *et al.* [5] showed that titanium(III)-hydroxylamine in aqueous hydrochloric or sulfuric acid was capable of initiating polymerization of vinyl monomers. Amino free radicals generated from titanium(III)-hydroxylamine redox systems have been studied in aqueous solution using ESR measurements with rapid-mixing flow method [6]. Kakurai *et al*. [7-8] made extensive studies on titanium(III)-hydroxylamine mediated polymerization of vinyl monomers. In all these studies, polymerization was done by slow syringe injection method, involving incremental addition of initiators to increase the yield and molecular weight of the polymer product.

Titanium(III)-potassium persulfate redox system initiated polymerizations of vinyl monomers have been reported in earlier studies [9-12]. Several workers [13- 16] have also reported utilities of titanium(III) complexes in olefin polymerization. The graft copolymerization of methyl methacrylate onto viscose fibers was studied [17] under photoactive conditions with visible light using Ce^{4+}/Ti^{3+} combination as redox initiator in a limited aqueous medium and showed polymerization conducted in the presence of light at 30°C, produced significant grafting compared with that conducted in the dark under the same condition. Further, Kumar *et al.* [18] studied the thermal behavior of methyl methacrylate-grafted viscose fibers using titanium(III) chloride-potassium persulfate redox initiators under the visible light in a limited aqueous system in the presence of various solvents. Kinetics of redox polymerization has received great attention by various researchers [19-23], as they play an unique role in predicting the mechanism of polymerization. But, there appears to be no report in the literature on the chemical polymerization involving titanium(III)-oxime redox system to induce polymerization of vinyl monomers. As a part of our polymerization studies with transition metal ion-organic component redox systems [24-29], we present here the results of this kinetic work.

EXPERIMENTAL

Reagents

Methyl methacrylate (SiscoChemical) was purified by washing successively with 10% potassium hydroxide solution and distilled water. The organic phase is dried several times over calcium chloride, then distilled over calcium hydride under reduced pressure. The purified methyl methacrylate was stored at -30°C. All other chemicals such as salicylaldoxime (S. D. Fine), sulfuric acid (S. D. Fine), N,N-dimethyl formamide, (S. D. Fine), dimethyl sulfoxide (S. D. Fine), carbon tetrachloride (Fischer), titanium dioxide (S. D. Fine), methanol (GSC), hydroquinone (GSC), sodium lauryl sulfate (Loba Chemie), triton-x-100 (S. D. Fine), benzene (S. D. Fine) were of analar grade and used without further purification.

Aqueous stock solution of titanium(III)sulfate solution was prepared by electrolytic reduction of an appropriate titanium(IV) sulfate solution and standardized against ferric ammonium sulfate using 10% ammonium thiocyanate as indicator [30]. Pure nitrogen was used for the deaeration of all experimental systems.

Kinetic Measurements

Reactions were performed under the inert atmosphere of nitrogen in pyrex glass vessels. In a typical kinetic run, a mixture of solutions containing requisite amounts of the methyl methacrylate monomer (M), salicylaldoxime (SAO), titanium(III), sulfuric acid (to maintain a known acid concentration), ethanol (to keep the organic substrate in homogeneous phase), water (to keep the total volume constant), was thermally equilibrated in a water bath at a desired temperature. A wash bottle containing an aqueous solution of methyl methacrylate whose concentration is same as in reaction vessel was interposed between the nitrogen train and the reaction vessel to avoid any loss of monomer due to deaeration. Oxygen free nitrogen was bubbled through the solution for a given period (ca. 20 min), and then the solution of the reductant , titanium(III), was added. The reaction vessel was sealed with a rubber gasket. The reaction was arrested at a desired time by adding a known amount of standard ferric ammonium sulfate or by cooling the reaction mixture to 0°Cand blowing air in. The percentage yield of polymerization was determined gravimetrically and the initial rates of polymerization were calculated by the initial slope method.

Molecular Weight Determination

The molecular weight of the purified samples of poly(methyl methacrylate) was determined by viscosity average molecular weight method using Ubblehode viscometer. The limiting viscosity values were converted into average molecular weights by the Mark-Houwink equation, $[\eta] = KM^{\alpha}$. where, M is the molecular weight of the polymer and K and (are constants, their values being $K = 0.94 \times 10^{-4}$ and $\alpha = 0.76$ for poly(methyl methacrylate) in benzene.

RESULTS AND DISCUSSION

Blank Experiments

Aqueous polymerization did not occur when methyl methacrylate was added separately to either of the reagents, titanium(III) or salicylaldoxime in aqueous sulfuric acid-ethanol medium. However, the addition of methyl methacrylate was found to initiate the polymerization in the presence of a mixture of titanium(III) and salicylaldoxime in aqueous sulfuric acid-ethanol medium.

Kinetics of Polymerization

Methyl methacrylate was polymerized at 26°C in an aqueous sulfuric acid-ethanol medium in the presence of titanium(III)-salicylaldoxime redox systems. Kinetics of polymerization were performed by varying the titanium (III) sulfate concentration, sulfuric acid concentration, salicylaldoxime concentration, monomer concentration, temperature, solvent medium and solvent composition and the results are computed (Table 1-4). A typical set of conversion-time curves are shown in Figures 1-4. The rate of polymerization increases linearly with time.

The effect of inhibitor and surfactants were also studied and the results were computed (Figure 5 and Table 5).

Dependence of Rate on Monomer Concentration

The rate of polymerization has been investigated by varying the concentration of monomer(M), from 0.37-1.13 mol dm^{-3}. The initial slope, as well as the maximum conversion, increases steadily with an increase of monomer concentration in the range of 0.37-0.94 mol dm^{-3}. A plot of log R_p versus log [M] was found to be linear with the slope (order), equal to 0.83 with respect to THE monomer. However, it decreases when the monomer concentration exceeds 0.94 mol dm^{-3} (Figure 1). 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), Salicylaldoxime and Sulfuric Acid Concentrations on Polymer Yield for the Redox Polymerization of Methyl Methacrylate at 299 K; [MMA]: 0.75 mol dm^{-3}; Ethanol: 44% (v/v); and Polymerization time: 90 minutes

[Ti(III)] x 10^2 (mol dm^{-3})	% Polymer	[SAO] x 10^2 (mol dm^{-3})	% Polymer	[H$_2$SO$_4$] x 10 (mol dm^{-3})	% Polymer
2.0	80.67	2.4	65.79	2.0	64.97
3.0	86.29	3.0	69.04	3.0	67.58
3.5	90.41	4.0	74.89	4.0	74.89
4.0	74.89	5.0	79.82	5.0	85.75
5.0	60.46	6.0	76.82	6.0	76.70

***[Ti(III)], 0.04 mol dm^{-3}: [H$_2$SO$_4$], 0.4 mol dm^{-3} and [SAO], 0.04 mol dm^{-3}, while varying other components.**

TABLE 2. Effect* of Monomer and Temperature on Polymer Yield for the Redox Polymerization of Methyl Methacrylate; [H$_2$SO$_4$]; 0.4 mol dm^{-3}

[MMA] x 10 (mol dm^{-3})	% Polymer	Temperature / K	% Polymer
3.7	57.40	288	38.17
5.6	64.13	293	56.58
7.5	74.89	299	74.89
9.4	85.60	306	82.55
11.3	80.19	311	66.84

***While varying the temperature, the concentration of monomer being 0.75 mol dm^{-3}**

TABLE 3. Effect of Solvent on Polymer Yield and Average Molecular Weight for the Redox Polymerization of Methyl Methacrylate at 299K; [MMA]: 0.75 mol dm^{-3}; [SAO]: 0.04 mol dm^{-3}; Ti(III): 0.04 mol dm^{-3}; [H_2SO_4]: 0.4 mol dm^{-3}; and Polymerization Time: 90 minutes

Solvent	% Polymer yield	Average molecular weight x 10^{-4}
44 % Ethanol	74.89	6.9
44 % Methanol	68.46	6.5
44 % Dimethyl formamide	79.44	6.9
44 % Dimethyl sulfoxide	35.85	0.8
Mixture of 44 % Ethanol and 3 % Carbon tetrachloride	42.62	0.9

TABLE 4. Effect of Solvent (Ethanol) Composition on Polymer Yield and Average Molecular Weight for the Redox Polymerization of Methyl Methacrylate at 299K; [MMA]: 0.75 mol dm^{-3}; [SAO]: 0.04 mol dm^{-3}; Ti(III): 0.04 mol dm^{-3}; [H_2SO_4]: 0.4 mol dm^{-3}; and Polymerization Time: 90 minutes

% Ethanol	% Polymer yield	Average molecular weight x 10^{-4}
35	88.90	7.2
40	79.25	6.9
44	74.89	6.9
50	69.79	6.3
55	44.69	5.0
60	39.98	3.6
65	23.98	1.0

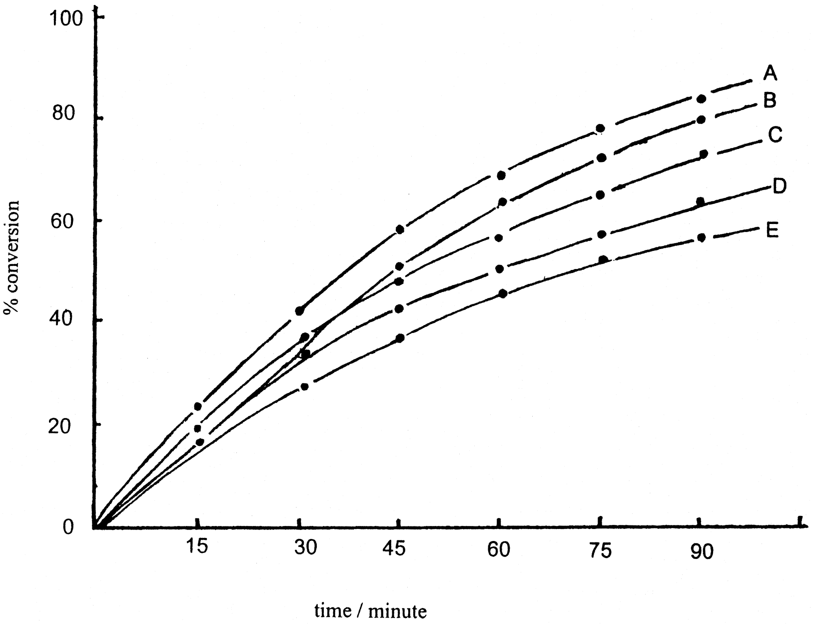


Figure 1. Time-conversion curves for the redox polymerization of methylmethacrylate in aqueous sulfuric acid-ethanol medium at 299 K ; [Ti(lll)] : 0.04 mol dm^{-3}; [SAO] : 0.04 mol dm^{-3}; [H_2SO_4] : 0.4 mol dm^{-3} ; ethanol : 44% (v/v) ; polymerization time : 90 minutes. Methyl methacrylate(MMA) concentrations (mol dm^{-3}) : (A) 0.94 (b) 1.13 (C) 0.75 (D) 0.56 and (E) 0.37

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 5.0×10^{-2} 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 3.5×10^{-2} mol dm^{-3} and the plot of R_p versus [Ti(III)] is linear, indicating 0.66 order with respect to titanium(III) sulfate. However, the decrease in polymer yield beyond 3.5×10^{-2} mol dm^{-3} may be due to the local over concentration of free radicals produced during the reduction of salicylaldoxime, which enhances the termination process.

Dependence of Rate on Sulfuric Acid Concentration

The kinetics of polymerization were performed at a different sulfuric acid concentration in the range of 0.2 to 0.6 mol dm^{-3}. It was found that the R_p increased steadily with an increase in [H^+] up to 0.5 mol dm^{-3}. A linear plot of log

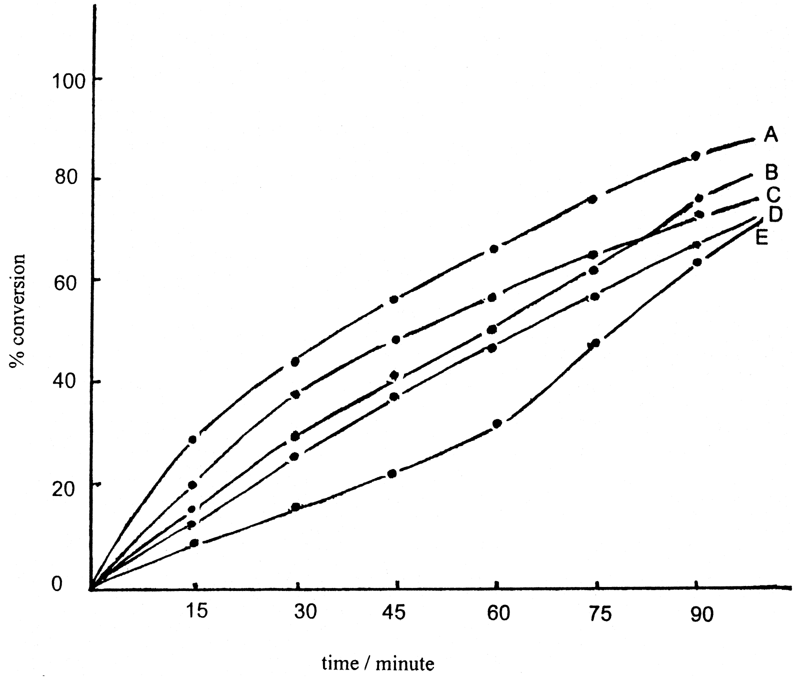


Figure 2. Time-conversion curves for the redox polymerization of methylmethacrylate in aqueous sulfuric acid-ethanol medium at 299 K ; [Ti(lll)] : 0.04 mol dm^{-3}; [SAO] : 0.04 mol dm^{-3}; [MMA] : 0.75 mol dm^{-3} ; ethanol : 44% (v/v) ; polymerization time : 90 minutes. Sulfuric acid concentrations (mol dm^{-3}) : (A) 0.05 (b) 0.6 (C) 0.4 (D) 0.3 and (E) 0.2

R_p versus log [H$^+$] shows dependence of an order 0.7 with respect to sulfuric acid concentration. However, beyond 0.5 mol dm^{-3} sulfuric acid, the rate of polymerization, as well as maximum conversion, decreases. This is due to the increase in reduction reaction rate. This situation favors chain initiation and chain termination against chain propagation. Hence, the polymer yield decreases at higher concentration.

Dependence of Rate on Salicylaldoxime Concentration

The influence of initiator, salicylaldoxime concentration on the rate of polymerization has been studied by varying its concentration from 2.4 × 10^{-2} to 6.0 × 10^{-2} mol dm^{-3}. The rate of polymerization was found to increase linearly with an increase of salicylaldoxime concentrations within the range of 2.4 × 10^{-2} to 5.0 × 10^{-2} mol dm^{-3}, yielding an order of 0.62 with respect to salicylaldoxime.

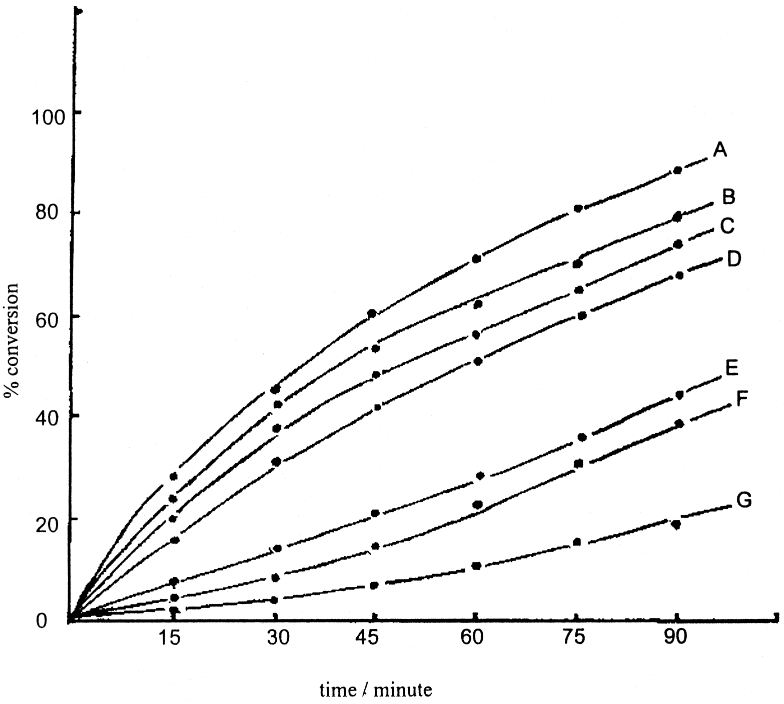


Figure 3. Effect of solvent, ethanol composition on the polymer yield of redox polymerization of methyl methacrylate at 299 K ; [Ti(lll)] : 0.04 mol dm^{-3}; [SAO] : 0.04 mol dm^{-3}; [H_2SO_4] : 0.4 mol dm^{-3} [MMA] : 0.75 mol dm^{-3} ; polymerization time : 90 minutes. Ethanol compositions (%) : (A) 35 (b) 40 (C) 44 (D) 50 (E) 55 (F) 60 and (G) 65

However, when its concentration exceeds 5.0×10^{-2} mol dm^{-3}, the polymer yield decreases. This is because an increase in salicylaldoxime concentration results in an increase in the rate of its reduction [31], and there will be a local over concentration 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 of 20-40°C. The rate of polymerization increases with an increase of temperature from 20-33°C. This is becausethe reaction rate of titanium(III) reduction of salicylaldoxime increases with temperature, there will be a slow and steady generation of free radicals, hence the polymer yield increases gradually in the temperature range of 20-33°C . However, above, 33°C, the reduction reaction becomes very fast, resulting in a local over concentration of free radicals. This situation

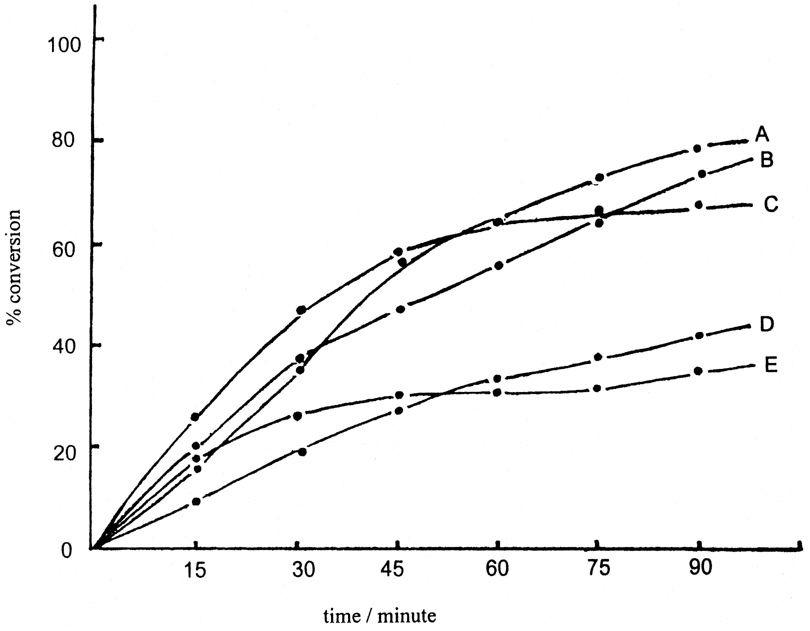


Figure 4. Effect of various solvents on the polymer yield of redox polymerization of methyl methacrylate at 299 K ; [Ti(lll)] : 0.04 mol dm^{-3}; [SAO] : 0.04 mol dm^{-3}; [H_2SO_4] : 0.4 mol dm^{-3}; [MMA] : 0.75 mol dm^{-3} ; polymerization time : 90 minutes. (A) in aqueous sulfuric acid-dimethyl formamide medium (B) in aqueous sulfuric acid-ethanol medium (C) in aqueous sulfuric acid-methanol medium (D) in aqueous sulfuric acid-ethanol-carbon tetrachloride medium and (E) in aqueous sulfuric acid-dimethyl sulfoxide medium.

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 of log (rate) vs. 1/T in the temperature range 20 –33°C was 25.23 (3.4 kJ mol^{-1}. The other activation parameters calculated from the Eyring plot are $\Delta H = 22.75 \pm 3.4$ kJ mol^{-1}; $\Delta G = 72.68 \pm 1.5$ kJ mol $^{-1}$ and $\Delta S = -166.81 \pm 11$ JK^{-1} 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.

Dependence of Rate on Solvent Composition

It was found that the polymer yield decreases, when the percentage of ethanol increases. This may be due to retardation of the reduction reaction

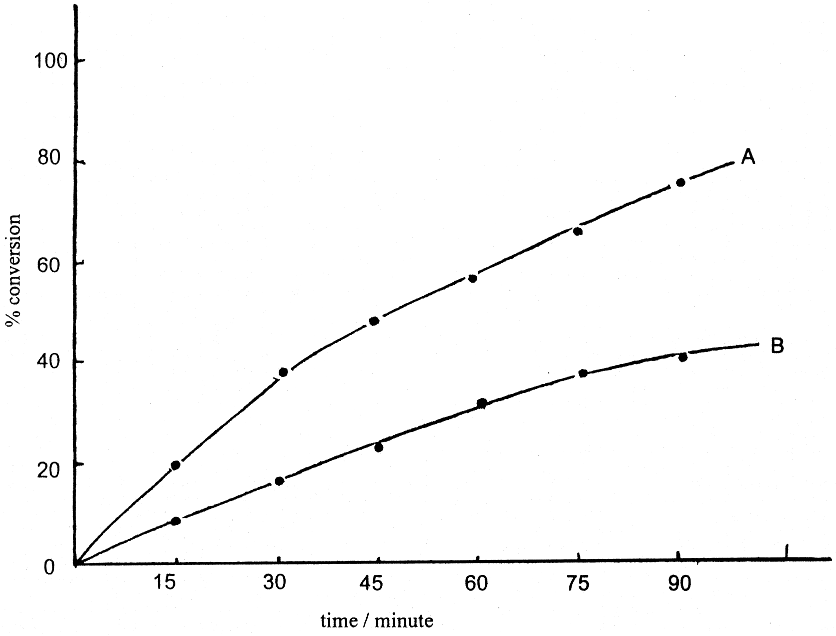


Figure 5. Effect of inhibitor, hydroquinone on the polymer yield of redox redox polymerization of methyl methacrylate in aqueous sulfuric acid-ethanol medium at 299 K ; [Ti(lll)] : 0.04 mol dm^{-3}; [SAO] : 0.04 mol dm^{-3}; [H_2SO_4] : 0.4 mol dm^{-3} [MMA] : 0.75 mol dm^{-3} ; polymerization time : 90 minutes. (A) in absence of hydroquinone and (B) in presence of 2.0% hydroquinone.

between titanium(III) and salicylaldoxime [31] with a decrease in the dielectric constant of the medium brought about by the increase in ethanol concentration and also, due to a small fraction of chain transfer by solvent molecules.

Polymer Characterization

Molecular Weight

The viscosity-average molecular weight of the polymer product in a typical standard run was found to be 6.9×10^{-4}.

Spectral Analysis

The infrared spectrum of the polymer product revealed the absorption frequencies at 3443 cm^{-1} (O-H stretching and N-H stretching), 2997 cm^{-1} (C-H stretching), 1730 cm^{-1} (-C=O stretching), 1624 cm^{-1} -N-H bending), and 754 cm^{-1}

TABLE 5. Effect of Surfactants on Polymer Yield for the Redox Polymerization of Methyl Methacrylate at 299K; [MMA]: 0.75 mol dm^{-3}; [SAO]: 0.04 mol dm^{-3}; Ti(III): 0.04 mol dm^{-3}; [H_2SO_4]: 0.4 mol dm^{-3}; and Polymerization Time: 90 minutes

[Sodium lauryl sulfate] x 10^3 (mol dm^{-3})	% Polymer	[Triton-X-100] x 10^4 (mol dm^{-3})	% Polymer
0.30	69.87	0.8	74.23
0.60	71.03	1.6	76.85
0.87*	86.40	2.4*	78.37
1.40	90.09	6.0	75.07
1.60	93.48	10.0	63.67

*** CMC value of the corresponding surfactant.**

(aromatic hydrogen bending) indicating the salicylaldoxime moiety as an end group of the poly(methyl methacrylate). Also, a significant absorption frequencies at about 1150 cm^{-1} and 1270 cm^{-1} reveals the aliphatic ether linkage (-CH_2-O-C_2H_5) at the methyl methacrylate macromolecule.

Polymerization in a Different Solvent Medium

Solvent plays an important role on the rate of polymerization. The effect of solvent on rate of polymerization, as well as polymer yield were studied using a number of polar solvents such as Dimethyl formamide (DMF), Dimethyl sulfoxide (DMSO), Ethyl alcohol (EtOH), Methanol (MeOH) (maintaining 44% (v/v) and non polar solvent like carbon tetrachloride (3% in 44% ethanol). The rate and polymer yield were different in different solvent media. This observation is agreed with the findings of previous workers [32-33]. However, the kinetic behavior in different media is expected to be similar.

We wanted to know whether the chain transfer mechanism operates in the termination step. Carbon tetrachloride is known to be the efficient chain transfer agent. The formulation containing a solvent mixture of 44% ethanol and 3% carbon tetrachloride resulted in a 50% decrease in polymer yield (Figure 2) and a consequent lowering of molecular weight from 69,000 to 9,600. This is due to the enhanced termination by the chain transfer mode. Further, it was observed that not only the percentage yield decreases gradually on increasing the alcohol concentration from 35-65% but also there was a drastic reduction in the molecular weight of the polymer product from 69,000 to 10,000 (Table 4). Therefore, it is inferred that, although the predominant mode of termination is by coupling, a small fraction of the termination takes place by chain transfer mechanism involving solvent ethanol molecules which is supported by the IR spectrum, indicating the -CH_2-O-C_2H_5 moiety as end group of the poly(methyl methacrylate).

Dependence of Rate on Inhibitor Concentration

The effects of hydroquinone and aromatic nitro compounds as inhibitors of polymerization were investigated more extensively by Foord [34] and later by Schulz [35]. It was stated that the retarding effect is enhanced by increasing the number of nitro groups. Various inhibition mechanisms have been suggested by Tidos and co-workers [36-37] .

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

Effect of Surfactants on the Rate

The rate of polymerization has been investigated involving certain surfactants such as sodium lauryl sulfate and Triton-X-100 above and below the critical micelle concentration (CMC) value. It was found that the polymer yield increases gradually with increasing the concentration of sodium lauryl sulfate above the CMC value. However, it decreases below the CMC value. This may probably be due to hydrophobic interactions and electrostatic attractions for the enhancement or inhibition of the rate of polymerization [38].

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

Kinetic Scheme

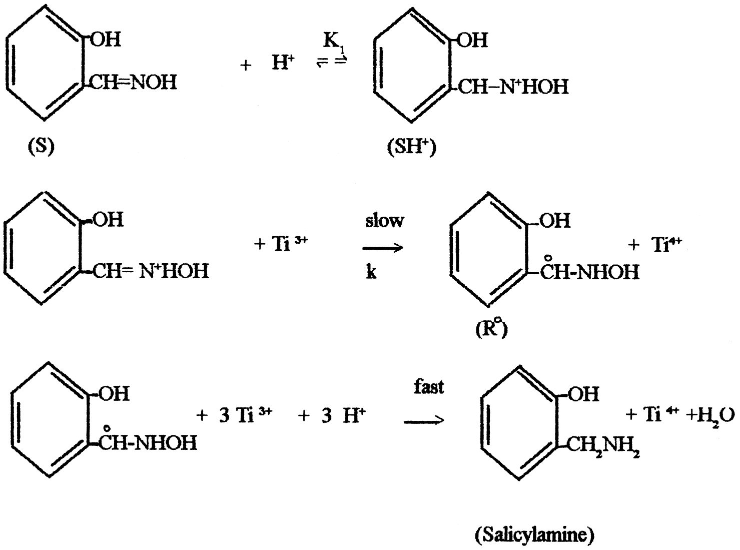
The stoichiometry of the reduction of salicylaldoxime by titanium(III) has been shown to be 1:4 in our earlier work [2].

The electrochemical reduction of salicylaldoxime in sulfuric acid medium was found to give irreversible cyclic voltammogram with a well defined cathodic peak (as shown in Figure 6). The cathodic peak potential was found to decrease from –572 to –430 mV as the concentration of the sulfuric acid varied from 4 to 72 mM, thereby showing the involvement of H+ion (proton) in the reduction process.

In the absence of a free radical scavanger, the titanium(III) reduction of salicylaldoxime follows Scheme 1.

The protonated substrate SH^+ reacts with Ti^{3+} in the slow step to give a free radical, R°. This free radical further reacts with Ti^{3+} in the slow step to give an intermediate, which further reacts with additional Ti^{3+} ions in a fast step to give the product, salicylamine. However, in the presence of vinyl monomers, these free radicals initiate the polymerization reaction. In this investigation, we used methyl methacrylate as a free radical scavenger.

The observed dependence of the rate of polymerization on initiator, activator, sulfuric acid, and monomer concentrations could be expressed by Scheme 2.



Scheme 1.

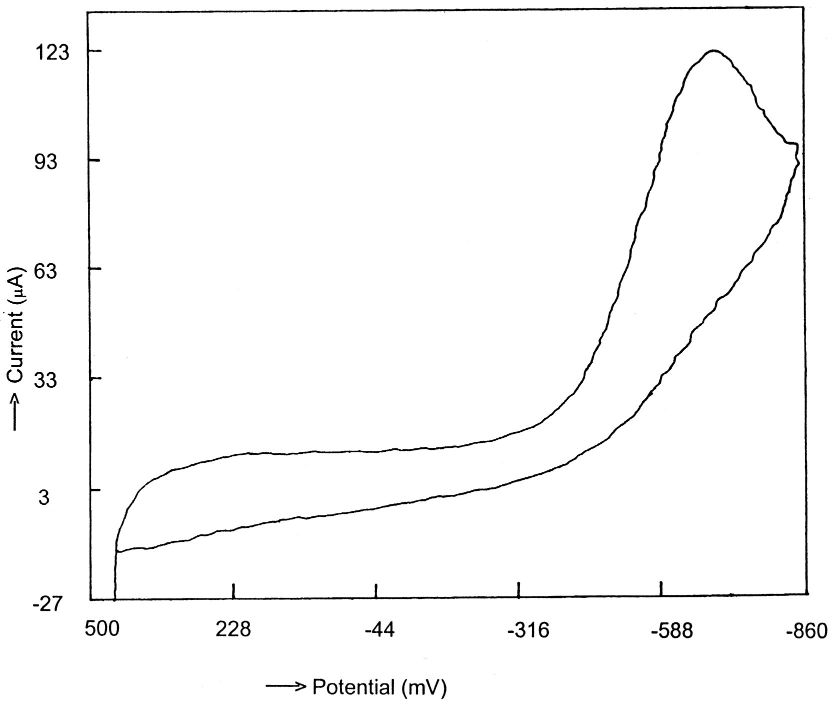
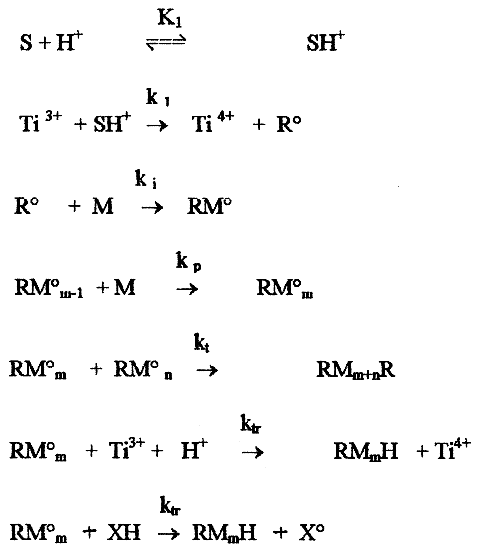


Figure 6. Typical cyclic volammogram of salicylaldoxime (10 mM) at glassy carbon electrode surface ; Sweep rate : -50mV/sec ; electrolyte : mixture of 20 mM sulfuric acid and 12% (v/v) ethanol; and temperature : 295 K.



$$S + H^+ \overset{K_1}{\rightleftharpoons} SH^+$$

$$Ti^{3+} + SH^+ \xrightarrow{k_1} Ti^{4+} + R^\circ$$

$$R^\circ + M \xrightarrow{k_i} RM^\circ$$

$$RM^\circ_{m-1} + M \xrightarrow{k_p} RM^\circ_m$$

$$RM^\circ_m + RM^\circ_n \xrightarrow{k_t} RM_{m+n}R$$

$$RM^\circ_m + Ti^{3+} + H^+ \xrightarrow{k_{tr}} RM_mH + Ti^{4+}$$

$$RM^\circ_m + XH \xrightarrow{k_{tr}} RM_mH + X^\circ$$

Scheme 2.

Application of a steady state concept to the primary radical R° and growing radical $RM°_m$.

$$d[R°]/dt = k_1[Ti^{3+}][SH^+] - k_i [R°][M] = 0$$

$$[R°] = k_1[Ti^{3+}][SII^+] / k_i[M]$$

Based on the usual assumption that the radical reactivity is independent of the radical chain length 'ν' the rate of polymerization,

$$R_p = k_p [RM°_m][M]$$

In the overall polymerization, the rate of initiation and rate of termination become equal, resulting in a steady state concentration of the free radicals.

If termination takes place by coupling

$$k_i [R°] [M] = k_t [RM°]^2$$
$$[RM°] = (k_i /k_t)^{1/2} [R°]^{1/2} [M]^{1/2}$$

Substituting for [R°]

$$[RM°] = (k_1/k_t)^{1/2} [Ti^{3+}]^{1/2} [SH^+]^{1/2}$$

So that the rate of polymerization takes the form:

$$R_p = k_p (k_1/k_t)^{1/2} [Ti^{3+}]^{1/2} [S]^{1/2} [H^+]^{1/2} [M] \qquad (1)$$

If the termination takes place by chain transfer to a solvent molecule, it takes the form:

$$R_p = (k_1/k_{tr}) k_p \{[Ti^{3+}] [SH^+] [M]/[XH]\} \qquad (2)$$

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

$$k_i [R°] [M] = k_{tr} [RM°_m] [Ti^{3+}] [H^+] \text{ and}$$
$$[RM°] = k_i [R°] [M]/k_{tr} [Ti^{3+}] [H^+]$$

Substituting for R°,

$[RM°] = k_i k_1 [Ti^{3+}] [SH^+] [M]/k_{tr}\, k_I [M] [Ti^{3+]} [H^+]$ or

$[RM°] = k_1 [SH^+]/k_{tr} [H^+]$ so that,

$$R_p = k_p\, k_1 [S] [M]/k_{tr} \quad (3)$$

The dependence of initial rate of polymerization Rp on $[Ti^{3+}]$ 0.6, [M] 1.0, [H2SO4] 0.7 [S] 0.7 which were actually determined by experiment is consistent with the combined form of rate Equations 1 and 2.

Termination involving $[Ti^{3+}]$ would have yielded the rate expression (3), which is not showing independence on $[Ti^{3+}]$ and $[H^+]$ which is not in accordance with the experimental data. Therefore, termination by process (3) is ruled out.

CONCLUSION

Oxime in combination with Ti(III) is introduced as redox initiator for free radical polymerization. Salicylaldoxime with electron releasing hydroxyl(-OH) group undergoes reduction by titanium(III) at the oxime group in a controlled manner and induces free radical. Similar work of redox polymerization involving other initiator systems like ketoximes/aldoximes in conjunction with titanium (III), are in progress.

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REFERENCES

[1] S. A. A. Newton, E. J. Stubbes, and C. Hinshelwood, *Can. J. Chem. Soc., 91*, 3384 (1953).

[2] Padmalatha, B. S. Sherigara, and H. V. K. Udupa, *J. Electrochem. Soc. India, 44-4*, 197 (1995).

[3] J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *J. Org. Chem.*, *43*, 3255 (1978).

[4] J. E. McMurry and J. Melton, *J. Org. Chem., 38*, 4367 (1973).

[5] P. Davis, M. G. Evans, and W. C. E. Higginson, *J. Chem. Soc.*, 2563 (1951).

[6] Z. Izumi and B. Ranby, *Macromolecules.*, *8(2),* 151 (1975).

[7] T. Kakurai, S. Iwal, and T. Noguchi, *Kobunshi. Kagaku.*, *23*, 279 (1966).

[8] T. Kakurai, T. Sugata, and T. Noguchi, *Kobunshi. Kagaku.*, *25*, 120 (1968).

[9] R. G. R. Bacon, *Trans. Faraday Soc., 42*, 140 (1946).

[10] W. Kern, R. C. Schulz, and H. Cherdron*, Makromol. Chem., 24*, 141 (1957).

[11] N. Moszner and M. Hartmann, *Makromol, Chem., 180*, 97 (1979).

[12] C. Pinazzi, J. C. Lenain, J. C. Broose, and G. Ligay, *Makro. Chem., 177*, 3139 (1976).

[13] N. Yu. Kovaleva, Yu. A. Gavrilov, and L. A. Novokshonova, *Polimery* (Warsaw), *42* (10), 616 (1997).

[14] Eiichi Kaji, Toshiya Uozumi, Jizhu Jin, Tsuneji Sano, and Kazuo Soga, *J. Polym. Sci., Part A : Polym. Chem.*, 36 (15), 2735 (1998).

[15] Sean W. Ewart, Mark J. Sarsfield, Dusan Jeremic, Tracey L. Tremblay, Edan F. Williams, and Michael C. Baird, *Organometallics, 17(8),* 1502 (1998).

[16] T. H. Newman and M.T. Malanga, *Polym. Prepr.,* (Am. Chem. Soc., Div. Polym. Chem.), *37(2),* 534 (1996).

[17] Ranjit Kumar Das, Diya Basu, and Amarnath Banerjee, *J. Appl. Polym. Sci.*, 72(1), 135 (1999).

[18] Tarun Kumar Maji, Ashis Kumar Khan, and Amarnath Banerjee, *Indian J. Fibre Text. Res., 21(4),* 280 (1996).

[19] Subasini Lenka and Sudhansu B. Dash, *J. Macromol. Sci. Chem,* A, *20(3),* 397 (1983).

[20] Jainamma Mathew and Venkatanarayana Mahadevan, *Macromol. Chem. Phys., 197*, 367 (1996).

[21] Manabendra Patra and Bijoy K. Sinha, *J. Appl. Polym. Sci., 64* (1997).

[22] Claudio Pellecchia and Alfonso Grassi, *Top. Catal.*, 7(1-4), 125 (1999).

[23] Thomas E. Ready, Ronald Gurge, C. W. Chien, C. W. James, and Marvin D. Rausch, *Organometallics*, 17(24), 5236 (1998).

[24] K. S. Rai and B. S.Sherigara, *Transition Met. Chem.*, *20*, 630 (1995).

[25] K. S. Rai, B. S. Sherigara, and N. M. Made Gowda*, Eur. Polym. J.*, *34*, 1031 (1998).

[26] B. S. Sherigara, K. Shivakumar, and K. S. Rai, *J. T. R. Chem., 6(1),* 55 (1999).

[27] B. S. Sherigara, M. P. Yashoda, and Padmalatha, *J. Phy. Org. Chem*., *12*, 605 (1999).

[28] K. Shivakumar, K. S. Rai, and B. S. Sherigara, *J. T. R. Chem., 5(2),* 1 (1999).

[29] K. S. Rai, K. Shivakumar, and B. S. Sherigara, *Eur. Polym. J*., in press (1999).

[30] A. I. Vogel, *Textbook of Quantitative Chemical Analysis,* ELBS, Longman, London, 5th Ed., Chapt. XVII, 1989, p. 690.

[31] M. P. Yashoda, Padmalatha, B. S. Sherigara, and P. V. Nayak, *Indian J. Chem*., *38A*, 176 (1999).

[32] B. M. Tidwell and A. G. Doughty, *Polym*., *12*, 431 (1971).

[33] G. Pistoia*, J. Polym. Sci. Polym. Lett. Ed., 10*, 787 (1972).

[34] S. G. Foord, *J. Chem. Soc., 48* (1940).

[35] G. V. Schulz, *Makromol. Chem., 1*, 94 (1947).

[36] F. Tudos, I. Kende, and M. Azori, *J. Polym. Sci., A-1*, 1369 (1963).

[37] F. Tudos, I. Kende and M. Azori, *J. Polym. Sci., A-1*, 1353 (1963).

[38] V. R. Gowariker, N. V. Viswanathan and Jayadev Sreedhar, *A Textbook of Polymer Science,* Wiley Eastern Limited, New Delhi, 1996, p. 73.

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