JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 605–611 (1999)

Kinetics of electroinitiated polymerization of acrylonitrile mediated by titanium (III)–dimethylglyoxime redox system

B. S. Sherigara,[1]* M. P. Yashoda[1] and Padmalatha[2]

[1]Department of Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shimoga, 577 451, Karnataka, India
[2]Manipal Institute of Technology, Manipal 576 119, India

Received 26 October 1998; revised 12 January 1999; accepted 1 March 1999

ABSTRACT: Acrylonitrile was polymerized in an aqueous sulphuric acid–methanol medium by an electrolytically generated mediator species, titanium(III). Titanium(III)–dimethylglyoxime was used as the initiator redox system. The reaction was confined to the cathode compartment and was found to proceed via a free radical mechanism. The kinetics of polymerization were investigated for different initial monomer concentrations, acid concentrations, electric currents, dielectric constants of the solvent and electrode materials. A suitable mechanism for titanium(III)–dimethylglyoxime-mediated indirect electropolymerization of acrylonitrile is proposed. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: acrylonitrile polymerization; electroinitiated polymerization; titanium(III)–dimethylglyoxime redox system; kinetics

INTRODUCTION

The kinetics of electrochemical polymerization have received great attention by various researchers,[1–4] as they play a unique role in predicting the mechanism of polymerization. Previous studies have established that Ti(III)–NH_2OH is a potential initiator for the polymerization of vinyl monomers.[5] As a part of our mechanistic studies on redox polymerization,[6–8] we present here the results of a kinetic study of titanium(III)–dimethylglyoxime-mediated electropolymerization of acrylonitrile in aqueous sulphuric acid–methanol medium.

EXPERIMENTAL

All chemicals were of analytical grade unless indicated otherwise and doubly distilled water was used throughout. A stock solution of titanium(IV) was prepared by the gradual addition of TiO_2 (Glaxo, special quality) to hot concentrated sulphuric acid. The yellowish green solid of titanium(IV) sulphate thus produced was dissolved in distilled water, boiled well and filtered to give a clear solution.[9] The titanium(IV) concentration was determined by spectrophotometry.

Acrylonitrile (SRL) was washed with 5% sodium hydroxide followed by dilute orthophosphoric acid and finally with distilled water. It was dried over anhydrous calcium chloride and again distilled under reduced pressure in a nitrogen atmosphere. The middle fraction was collected and stored at 5 °C. A standard solution of 0.1 mol dm^{-3} dimethylglyoxime was prepared in methanol.

Polymerization method. Polymerization was carried out in a simple H-shaped cell consisting of two cylindrical glass tubes fused to two halves of square-shaped steel frames, having a circular opening at the centre. These steel frames were tightened together with the help of screws provided for this purpose by placing a cation-exchange membrane in between to act as a diaphragm. One glass tube was used as the anodic compartment and the other as the cathodic compartment.

The catholyte was an electrolytic solution containing titanium(IV) sulphate (3.0 cm^3 of 0.25 mol dm^{-3}), dimethylglyoxime (2.5 cm^3 of 0.1 mol dm^{-3}), sulphuric acid (to maintain a constant acid concentration of 0.5 mol dm^{-3}), methanol (to keep the organic substrate in a homogeneous phase), 1.21 mol dm^{-3} acrylonitrile and water (to keep the overall volume to 25.0 cm^3). The anolyte was 25.0 cm^{-3} of 0.5 mol dm^{-3} sulphuric acid. A thin, bright platinum foil was used as the anode and a rectangular copper plate (1.0×9.0 cm) as the cathode. A stream of pure nitrogen was slowly bubbled over the catholyte. The electrolytic cell was mounted on a

---

**Correspondence to:* B. S. Sherigara, Department of Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shimoga, 577 451, Karnataka, India.
Contract/grant sponsor: Department of Atomic Energy, Government of India.

CCC 0894–3230/99/080605–07 $17.50

Table 1. Effect of titanium (IV) and dimethylglyoxime concentration on polymer yield for the cathodic polymerization of acrylonitrile[a]

$[Ti(IV)] \times 10^2$ (mol dm^{-3})	Polymer yield (%)	$[DMG] \times 10^2$ (mol dm^{-3})	Polymer yield (%)
1.5	60.38	0.6	86.26
3.0	78.95	0.8	83.52
4.0	90.09	1.0	78.95
5.0	88.38	1.4	65.24
6.0	83.20	1.8	44.63

[a] Conditions: temperature, 300 K; current, 200 mA; [AN], 1.21 mol dm^{-3}; $[H_2SO_4]$, 0.5 mol dm^{-3}; [methanol], 18% (v/v); electrolysis time, 60 min.

Table 3. Effect of temperature on polymer yield and average molecular weight for the cathodic polymerization of acrylonitrile[a]

Temperature (K)	Polymer yield (%)	Average molecular weight
293	33.00	4.0×10^4
298	64.54	4.0×10^4
300	78.95	4.0×10^4
305	92.48	3.6×10^4

[a] Conditions: current, 200 mA; [AN], 1.21 mol dm^{-3}; $[H_2SO_4]$, 0.5 mol dm^{-3}; [DMG], 0.01 mol dm^{-3}; [methanol] 18% (v/v); electrolysis time, 60 min.

magnetic stirrer and the medium was adequately stirred. A constant current was obtained from a stabilized d.c. power supply of 0–150 V, which gave currents of 0–1000 mA.

Initially conditions were established to obtain a maximum yield of polymers. This was done by carrying out the electrolysis at a specified current for 60 min. The polymer yield was determined gravimetrically. The results are given in Tables 1 and 2.

Kinetic procedure. The kinetic measurements were performed under an inert atmosphere. In a typical kinetic run, a mixture of solutions containing the requisite amounts of the acrylonitrile monomer (M), dimethylglyoxime (DMG), titanium(IV) ions, sulphuric acid, methanol and water was thermally equilibrated in a water-bath at the desired temperature. A wash-bottle containing an aqueous solution of acrylonitrile and methanol of the same concentration as in the electrolytic cell was interposed between the nitrogen train and the electrolytic cell to avoid any loss due to deaeration. Electrolysis was carried out for a desired time. The percentage yield of polymerisation was determined gravimetrically at 300 K. The initial rate of polymerization (R_p) was determined from the initial slope of percentage conversion versus time plot by the plane mirror method, reproducible to ± 6%. The order of the reaction was found from log (rate) versus log (concentration) plots.

Table 2. Effect of sulphuric acid concentration and solvent composition on polymer yield for the cathodic polymerization of acrylonitrile[a]

$[H_2SO_4] \times 10$ (mol dm^{-3})	Polymer yield (%)	[Methanol] (mol dm^{-3})	Polymer yield (%)
3.0	56.23	15.00	82.90
4.0	67.37	18.00	78.95
5.0	78.95	25.00	73.64
6.0	86.40	30.00	65.87
7.0	79.53	35.00	59.60

[a] Conditions: temperature, 300 K; current, 200 mA; [AN], 1.214 mol dm^{-3}; [DMG], 0.01 mol dm^{-3}; [Ti(IV)], 0.03 mol dm^{-3}; electrolysis time, 60 min.

The effect of variation of the concentration of monomer, cathode current, solvent, sulphuric acid, dimethylglyoxime, titanium(IV) and cathode materials was studied. The effect of temperature on the polymer yield was also examined (Table 3) and activation parameters were calculated using Arrhenius and Eyring plots. The gravimetric determination of the polymer produced is one of the most direct ways of obtaining conversion data for polymerization. Always a constant volume of the reaction mixture was taken in the cell. In order to determine the amount of polymer formed in a known interval of time, the electrolysis was termined at the desired time and the polymer obtained was filtered through a previously weighed sintered glass crucible of the required specification, washed properly with methanol and dried in a vacuum oven at 343 K to a constant weight.

The intrinsic viscosity was measured in *N*, *N*-dimethylformamide at 300 K with an Ubbelhode viscometer. The limiting viscosity values were converted into average molecular weights by the Mark–Houwink equation, $[\eta] = KM^{\propto}$, where M is the molecular weight of the polymer and K and $\propto$ are constants, their values being $K = 2.303 \times 10^{-4}$ and $\propto = 0.75$.

RESULTS AND DISCUSSION

Blank experiments

Electrochemical polymerization did not occur when acrylonitrile was added separately to either of the reagents, titanium(IV) or dimethylglyoxime, in aqueous sulphuric acid–methanol medium. However, the addition of acrylonitrile was found to initiate the polymerization in the presence of a mixture of titanium(IV) and dimethylglyoxime in aqueous sulphuric acid–methanol medium only when subjected to electrolysis.

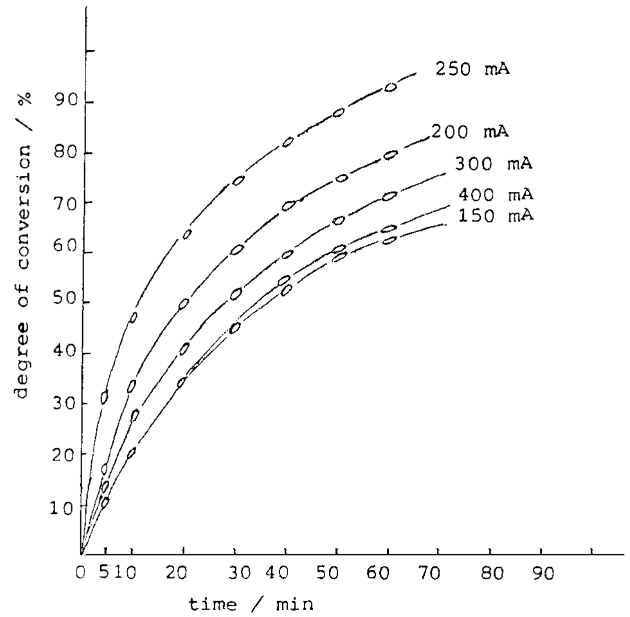


Figure 1. Time–conversion curves for the cathodic polymerization of acrylonitrile (1.21 mol dm^{-3}) at different current levels in aqueous sulphuric acid–methanol medium at 300 K

Kinetics of polymerization

The polymerization kinetic studies were carried out with different currents, monomer concentrations and solvents at 300 K and the results are presented in Figs 1–3 and Tables 4–6.

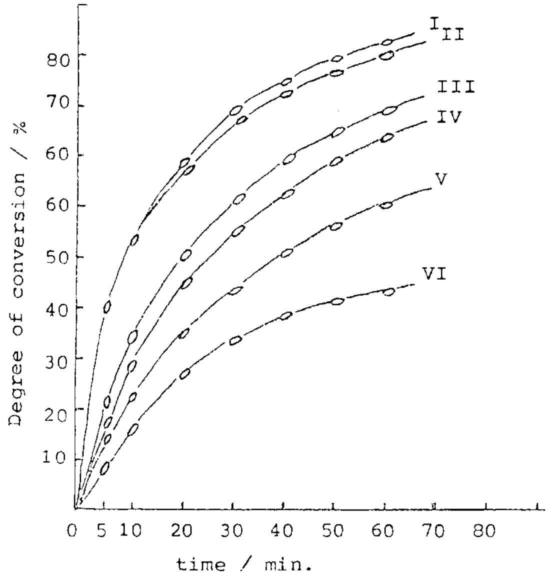


Figure 2. Time–conversion curves for the cathodic polymerization of acrylonitrile at a fixed current of 200 mA in aqueous sulphuric acid–methanol medium at 300 K. Acrylonitrile concentration: (I) 1.82; (II) 1.52; (III) 1.21; (IV) 2.12; (V) 2.42; (VI) 0.91 mol dm^{-3}

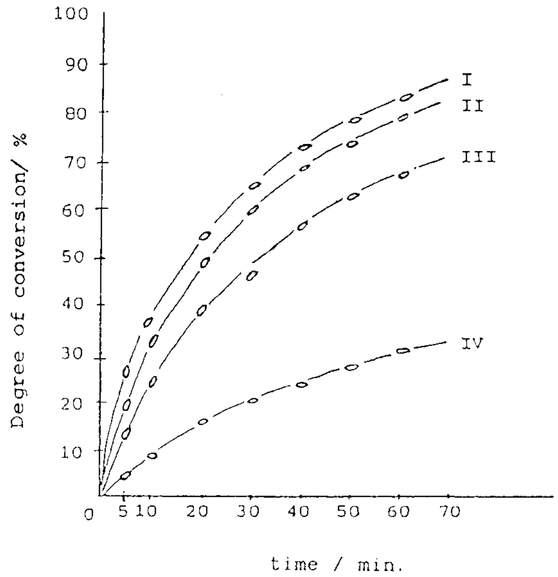


Figure 3. Effect of various solvents on the yield of the cathodic polymerization of acrylonitrile at a fixed current of 200 mA and 300 K: (I) in aqueous sulphuric acid–dimethylformamide medium; (II) in aqueous sulphuric acid–methanol medium; (III) in aqueous sulphuric acid–dimethyl sulphoxide medium; (IV) in aqueous sulphuric acid–methanol–carbon tetrachloride medium

Table 4. Effect of current on polymer yield and average molecular weight for the cathodic polymerization of acrylonitrile[a]

Current (mA)	Polymer yield (%)	Average molecular weight
150	61.95	4.0×10^4
200	78.95	4.0×10^4
250	91.86	3.8×10^4
300	71.46	3.2×10^4
400	63.95	2.5×10^4

[a] Conditions: temperature, 300 K; [AN], 1.21 mol dm^{-3}; [H_2SO_4], 0.5 mol dm^{-3}; [DMG], 0.01 mol dm^{-3}; [Ti(IV)], 0.03 mol dm^{-3}; [methanol], 18% (v/v); electrolysis time, 60 min.

Table 5. Effect of acrylonitrile concentration on polymer yield and average molecular weight for the cathodic polymerization of acrylonitrile[a]

[AN] (mol dm^{-3})	Polymer yield (%)	Average molecular weight
0.91	43.46	4.0×10^4
1.21	78.95	4.0×10^4
1.52	89.05	4.0×10^4
1.82	92.28	4.0×10^4
2.12	74.82	3.8×10^4
2.42	59.89	3.7×10^4

[a] Conditions: temperature, 300 K; current, 200 mA; [H_2SO_4], 0.5 mol dm^{-3}; [DMG], 0.01 mol dm^{-3}; [Ti(IV)], 0.03 mol dm^{-3}; [methanol], 18% (v/v); electrolysis time, 60 min.

Table 6. Effect of solvent on polymer yield and average molecular weight for the cathodic polymerization of acrylonitrile[a]

Solvent	Polymer yield (%)	Average molecular weight
Methanol	78.95	4.0×10^4
Dimethyl sulphoxide	68.30	3.6×10^4
Dimethyl formamide	83.21	4.7×10^4
Mixture of methanol and carbon tetrachloride	30.30	2.0×10^4

[a] Conditions: temperature, 300 K; current, 200mA; [H_2SO_4], 0.5 mol dm^{-3}; [Ti(IV)], 0.03 mol dm^{-3}; [DMG], 0.01 mol dm^{-3}; [methanol], 18% (v/v); electrolysis time, 60 min.

Factors influencing polymer yield

Effect of cathode current. The effect of variations in titanium(IV) sulphate concentration, electric current, temperature and sulphuric acid concentration on the current efficiency for the generation of titanium(III) was studied by Narasimhan *et al.*[10] The current efficiency was found to decrease with increase in current or concentration of titanium(IV) sulphate. Also, the current efficiency was found to increase with increase in sulphuric acid concentration or temperature.

It was found that the polymer yield increases with increase in cathode current in the range 150–250 mA. However, when the cathode current exceeds 250 mA, the polymer yield decreases (Fig. 1). This can be explained as follows. As already stated, the current efficiency for the generation of titanium(III) decreases with increase in current. Consequently, the reduction of dimethylglyoxime becomes slower and there will be a slow and steady generation of free radicals. Hence the polymer yield increases.

However, at higher current levels (250–400 mA), the apparent decrease in current efficiency can be due to the depletion of the monomer at the cathode–catholyte interface, and also due to hydrogen production, as shown in some early studies.[11,12]

Effect of monomer concentration. The polymer yield increases with increase in monomer concentration in the range 0.91–1.82 mol dm^{-3}. However, it decreases when the monomer concentration exceeds 1.82 mol dm^{-3}. This deviation may be due to an increase in the viscosity of the medium and a consequent decrease in the mobility of the propagating species.

Effect of dimethylglyoxime concentration. The polymer yield decreases with an increase in the concentration of dimethylglyoxime. This is because an increase in dimethylglyoxime concentration results in an increase in the rate of its reduction[13] and there will be a local over-concentration of the free radicals in the vicinity of the eletrode surface. This situation favours chain initiation and chain termination. Consequently, the polymer yield decreases.

Effect of titanium(IV) sulphate concentration. The polymer yield increases with increase in titanium(IV) sulphate concentration in the range 0.015–0.04 mol dm^{-3}. However, the yield decreases if the titanium(IV)sulphate concentration exceeds 0.04 mol dm^{-3}. This may be due to the steady generation of free radicals in the range 0.015–0.04 mol dm^{-3}. This situation favours chain propagation and hence the polymer yield gradually increases. However, beyond a certain optimum concentration of titanium(IV) sulphate ($>$0.04 mol dm^{-3}) the titanium(III) generated will be of low concentration and the free radicals generated by the reduction of dimethylglyoxime will also be of lower concentration. Consequently, the polymer yield gradually decreases.

Effect of temperature. The current efficiency for the generation of titanium(III) increases with increase in temperature. Also, the reaction rate of titanium(III) reduction of dimethylglyoxime has been shown to be temperature dependent.[13] There will be slow and steady generation of free radicals, hence the polymer yield gradually increases in the temperature range 293–305 K. However, above 305 K, the reduction reaction becomes very fast, resulting in a local over-concentration of free radicals near the electrode surface. This situation favours 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 293–305 K was 36.35 ± 2 kJ mol^{-1}. The other activation parameters calculated from the Eyring plot are $\Delta H^{\ddagger} = 33.86 \pm 2$ kJ mol^{-1}, $\Delta G^{\ddagger} = 71.31 \pm 0.6$ kJ mol^{-1} and $\Delta S^{\ddagger} = -125.18 \pm 6$ J K^{-1} mol^{-1}. The relatively low energy of activation or enthalpy of activation and high negative entropy of activation observed are characteristic of a free radical polymerization process.

Effect of sulphuric acid concentration. The current efficiency for the generation of titanium(III) sulphate and also the rate of titanium(III) reduction of dimethylglyoxime increase with increase in sulphuric acid concentration.[13] This situation favours chain propagation. Hence the polymer yield increases in the range 0.3–0.6 mol dm^{-3} sulphuric acid. However, when the sulphuric acid concentration exceeds 0.6 mol dm^{-3}, the reduction reaction becomes so fast as to increase the production of free radicals to favour chain initiation and chain termination against chain propagation. Hence the polymer yield decreases at higher acid concentrations.

Effect of solvent composition. It was found that the polymer yield decreases when the percentage of methanol increases. This is due to retardation of the

Table 7. Effect of electrode material on polymer yield and average molecular weight for the cathodic polymerization of acrylonitrile[a]

Electrode	Polymer yield (%)	Average molecular weight
Copper	78.95	4.0×10^4
Lead	70.38	3.8×10^4
Graphite	62.06	3.6×10^4
Platinum	59.29	3.3×10^4

[a] Conditions: temperature, 300 K; current, 200 mA; [H_2SO_4], 0.5 mol dm^{-3}; [Ti(IV)], 0.03 mol dm^{-3}; [DMG], 0.01 mol dm^{-3}; [methanol], 18% (v/v); electrolysis time, 60 min.

titanium(III) reduction reaction of dimethylglyoxime with decrease in dielectric constant of the medium brought about by the increase in methanol concentration.[13]

Polymer characterization

Molecular weight. The viscosity-average molecular weight of the polymer product in a typical standard run was found to be 4.00×10^4.

Spectral analysis. The IR spectrum of the polymer product revealed absorption frequencies at 3468 cm^{-1} (N—H and O—H stretching), 2939 cm^{-1} (C—H stretching), 2250 cm^{-1} (C≡N stretching) and 1650 cm^{-1} (N—H bending and C═N stretching), indicating that the dimethylglyoxime moiety is an end group of the polyacrylonitrile macromolecule.

Influence of electrode material. Apart from copper, several other electrode materials, such as platinum, lead and graphite, were also tried for the polymerization process. Although the yields were different for different electrode materials, the molecular weights of the polymer products were nearly the same (Table 7). Work relating to the kinetic behaviour pattern with different cathode materials (platinum, lead and graphite) is in progress.

Polymerization in a different solvent medium. The percentage yields were different in dimethylformamide, dimethyl sulphoxide and methanol. This is in accordance with the findings of previous workers.[14,15] However, the molecular weights of the products were more or less the same. The kinetic behaviour 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 most efficient chain transfer agent. The kinetic study with a solvent mixture containing 18% methanol + 3% carbon tetrachloride resulted in a 50% decrease in polymer yield (Fig. 3) and a consequent lowering of molecular weight from 4.0×10^4 to 2.0×10^4. This is due to the enhanced termination by the chain transfer mode. It can be concluded that chain transfer to initiator molecules, monomer molecules or solvent molecules is not significant in the absence of chain transfer agents such as carbon tetrachloride. Therefore, in all probability under the conditions employed for the polymerization in this investigation, the termination occurs mostly by coupling.

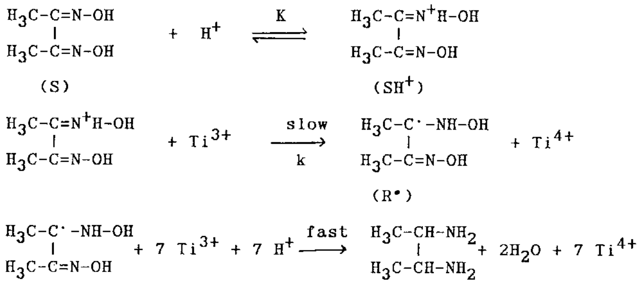
Kinetic scheme

The kinetics of the reduction of dimethylglyoxime by titanium(III) in aqueous sulphuric acid medium has recently been studied.[13] The stoichiometry of the reduction of dimethylglyoxime by titanium(III) was found to be 1:8 according to

$$C_4H_8N_2O_2 + 8Ti^{3+} + 8H^+ \longrightarrow C_4H_{12}N_2 + 8Ti^{4+} + 2H_2O \quad (1)$$
$$(\text{butane} - 2,3 - \text{diamine})$$

The kinetic orders of the reactants were found from log (rate) versus log (concentration) plots. The order was found by varying the concentrations of dimethylglyoxime, titanium(III), sulphuric acid in turn while keeping the others constant. The kinetic orders with respect to dimethylglyoxime and titanium(III) was nearly unity and the order with respect to sulphuric 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 protonated substrate SH$^+$ reacts with Ti^{3+} in the slow step to give a free radical, R$^\cdot$. This free radical further reacts with additional Ti^{3+} ions in a fast step to give the product. By applying the steady-state approximation to the intermediate SH$^+$, the rate law was derived:

$$\text{rate} = \frac{Kk[\mathrm{S}]_0[\mathrm{Ti}^{3+}][\mathrm{H}^+]}{1 + K[\mathrm{H}^+]} \quad (2)$$

where the resultant substrate concentration, [S], is the difference between the initial, $[S]_0$, and protonated, $[SH^+]$, substrate concentration values, K is the equilibrium constant for the protonation step and k is the rate constant for the rate-determining step.

The kinetic scheme which accounts for the results obtained in the electroinitiated polymerization system can be described by Scheme 2.

In Scheme 2, M is the monomer, acrylonitrile, k_e, k_d, k_i, k_p, k_t, k_{tr} are the rate constants for the electrolysis, decomposition, initiation, propagation, termination and chain transfer steps, respectively, and XH is the chain-transfer agent.

$$Ti^{4+} + H \xrightarrow{k_e} Ti^{3+}H^+$$

(at the cathode)

$$Ti^{3+} + SH^+ \xrightarrow{k_d} Ti^{4+}R^\bullet$$

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

$$RM^\bullet_{(m-1)} + M \xrightarrow{k_p} RM^\bullet_m$$

$$RM^\bullet_m + RM^\bullet_n \xrightarrow{k_t} RM_{m+n}R$$

$$RM^\bullet_m + H \xrightarrow{k_{tr}} RM_mH$$

$$RM^\bullet_m + XH \xrightarrow{k_{tr}} RM_mH + X^\bullet$$

Scheme 2

The rate of initiation is

$$R_i = fk_d[Ti^{3+}][SH^+] \qquad (3)$$

Substituting for $[Ti^{3+}]$ with the product, k_e [I], leads to

$$R_i = fk_dk_e[I][SH^+] \qquad (4)$$

where [I] is the current in farady per unit volume and f is the factor representing the fraction of the current which initiate chains.

Under steady-state conditions,

$$R_i = R_t \qquad (5)$$

If termination takes place by coupling,

$$fk_dk_e[I][SH^+] = k_t[M^\cdot]^2 \qquad (6)$$

Rearrangement of Eqn. (6) gives

$$[M^\cdot] = \frac{(fk_dk_e[I][SH^+])^{1/2}}{k_t} \qquad (7)$$

The rate of polymerization is given by

$$R_p = k_p[M^\cdot][M] \qquad (8)$$

Substituting for $[M^\cdot]$ in Eqn. (8) gives

$$R_p = k_p(fk_dk_e/k_t)^{1/2}[I]^{1/2}[SH^+]^{1/2}[M] \qquad (9)$$

Replacing $[SH^+]$ by K[S] $[H^+]$ leads to

$$R_p = K^{1/2}k_p(fk_dk_e/k_t)^{1/2}[I]^{1/2}[S]^{1/2}[H^+]^{1/2}[M] \qquad (10)$$

The dependence of the initial rate of polymerization R_p on $[I]^{1/2}$, $[S]^{1/2}$, $[H^+]^{1/2}$ and [M], which was experimentally observed, is consistent with Scheme 2.

The kinetic chain length, ν, has the following dependence on the current and monomer concentration:

$$\nu = R_p/R_t = k_p[M^\bullet][M]/k_t[M^\bullet]^2 \qquad (11)$$

Substituting for R_p and R_t and on simplification, Eqn. (11) gives

$$\nu = k_p[M]k_t/(fk_dk_e)^{1/2}[I]^{1/2}[SH^+]^{1/2} \qquad (12)$$

CONCLUSIONS

This is a clear case of indirect electrochemical polymerization. It involves the electrolytic generation of a reactive species, Ti^{3+}, which in turn reacts with a chemical initiator, dimethylglyoxime, present in the bulk of the solution to produce free radicals. Chain termination of the polymer is essentially by coupling. This provides an excellent means for the controlled initiation of polymerization reactions.

Acknowledgements

The authors thank the Department of Atomic Energy, Government of India, for the financial assistance.

REFERENCES

1. B. L. Funt and F. D. Williams, *J. Polym. Sci., Part A-2,* 865 (1964).
2. S. N. Badani and P. P. Barnawal, *Trans. Soc. Adv. Electrochem. Sci. Technol.* **11**, 273 (1976).
3. S. N. Badani, Q. Ansari and S. K. Sen Gupta, *J. Appl. Polym. Sci.* **44**, 121 (1992).
4. G. Parravano, *J. Am. Chem. Soc.* **73**, 628 (1951).
5. T. Kakurai, S. Iwal and T. Noguchi, *Kobunshi Kagaku*, **25**, 274 (1968).
6. Padmalatha, B. S. Sherigara and H. V. K. Udupa, *Indian J. Chem.* **36A**, 722 (1997).
7. K. S. Rai, B. S. Sherigara and N. M. Made Gowda, *Eur. Polym. J.* in press.
8. K. S. Rai and B. S. Sherigara. *Transition Met. Chem.* **20**, 630 (1995).
9. A. I. Vogel. *Textbook of Quantitative Inorganic Analysis*. Longman, Harlow (1989).

10. K. C. Narasimhan, S. Vasundara and H. V. K. Udupa, *Trans Soc. Adv. Electrochem. Sci. Technol.* **15**, 147 (1980).
11. M. Albeck and J. Relis, *J. Polym. Sci., Part A-1,* **9**, 2963 (1971).
12. M. Albeck, M. Konigsbuch and J. Relis. *J. Polym. Sci., Part A-1*, **9**, 1375 (1971).
13. M. P. Yashoda, Padmalatha, B. S. Sherigara and P. V. Nayak, *Indian J. Chem.* in press.
14. B. M. Tidswell and A. G. Doughty, *Polymer* **12**, 431 (1971).
15. G. Pistoia, *J. Polym. Sci., Polym. Lett. Ed.* **10**, 787 (1972).