ELSEVIER

Polymer 41 (2000) 7381–7389

polymer

Electroinitiated polymerisation of methyl methacrylate mediated by titanium(III)–hydroxylamine redox system: a kinetic study

M.P. Yashoda[a], B.S. Sherigara[a,*], G. Venkateswaran[b]

[a]Department of Studies in Industrial Chemistry, Kuvempu University, Jnana Sahyadri, 577451 Shimoga, Karnataka, India
[b]Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

Received 3 August 1999; received in revised form 17 September 1999; accepted 7 January 2000

Abstract

Methyl methacrylate was polymerised in an aqueous sulphuric acid–methanol medium in a divided cell by an electrolytically generated mediator species titanium(III). Titanium(III)–hydroxylamine sulphate 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. Kinetics of polymerisation were investigated for different initial monomer concentrations, acid concentrations, electrical currents, dielectric constants of the solvent and electrode materials. Chain termination of the polymer was due to coupling of growing macroradicals, also a fraction of the termination took place by chain transfer mechanism involving the organic solvent molecules. A suitable mechanism for titanium(III)–hydroxylamine sulphate mediated indirect electropolymerisation of methyl methacrylate has been proposed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Electroinitiated polymerisation; Kinetic and mechanistic studies; Spectrophotometry

1. Introduction

Davis et al. [1] showed that titanium(III)–hydroxylamine in aqueous hydrochloric or sulphuric acid was capable of initiating polymerisation of vinyl monomers. Amino free radicals generated from titanium(III)–hydroxylamine redox systems have been studied in aqueous solution using ESR measurements with the rapid-mixing flow method [2]. Kakurai et al. [3,4] made extensive studies on titanium(III)–hydroxylamine mediated polymerisation of vinyl monomers. Utility of this redox pair in the emulsion polymerisation of various vinyl monomers have been examined [5]. In all these studies, polymerisation was carried out by the slow syringe injection method, involving incremental addition of initiators to increase the yield and molecular weight of the polymer product. All these studies centred on the chemical polymerisation. But there appears to be no report in the literature on the electrochemical polymerisation involving titanium(III)–hydroxylamine redox system.

Electrochemical polymerisation is a natural out growth of preparative electroorganic synthesis. Various useful reviews on electroinitiated polymerisation are available [6–10]. Electroinitiated polymerisation of vinyl monomers in the homogeneous system was investigated by several workers [11–16], but studies in heterogeneous systems (polymer insoluble [17,18] and copolymerisation [19]) are rare. Kinetics of electrochemical polymerisation have received great attention by various researchers [20–23], as they play an unique role in predicting the mechanism of polymerisation. As a part of our kinetic and mechanistic studies on redox polymerisation [24–27], electroinitiated polymerisation of methyl methacrylate initiated by titanium(III)–hydroxylamine sulphate in sulphuric acid–methanol medium is reported in this communication.

2. Experimental

2.1. Materials and method

Methyl methacrylate (Sisco. Chem. India), hydroxylamine sulphate (CDH), methanol (s.d.fine), dimethyl formamide (GSC), dimethyl sulphoxide (GSC), benzene (s.d.fine), carbon tetrachloride (Fisher), and titanium dioxide (s.d.fine) used were of analytical grade. Doubly distilled water was used through out.

A stock solution of titanium(IV) was prepared by the gradual addition of titanium dioxide to hot concentrated sulphuric acid. The yellowish green solid of titanic sulphate thus produced was dissolved in distilled water, boiled well

---

[*] Corresponding author.
E-mail address: root@shikuv.kar.nic.in (B.S. Sherigara).

PII: S0032-3861(00)00101-4

Table 1
Effect ([Ti(IV)], 0.05 mol dm^{-3}: [H_2SO_4], 0.5 mol dm^{-3}: [NH_2OH], 0.01 mol dm^{-3}, while varying other components) of titanium(IV), hydroxylamine and sulphuric acid concentration on polymer yield for the cathodic polymerisation of methyl methacrylate at 295 K; current: 200 mA; [MMA]: 0.75 mol dm^{-3}; methanol: 40% (v/v); and electrolysis time: 25 min

Ti(IV) × 10^2 (mol dm^{-3})	% Polymer yield	[NH_2OH] × 10^2 (mol dm^{-3})	% Polymer yield	[H_2SO_4] × 10 (mol dm^{-3})	% Polymer yield
1.0	14.58	0.2	41.45	0.5	41.59
1.5	22.14	0.4	47.95	1.5	49.08
2.0	28.67	0.6	50.27	2.0	54.16
3.0	39.82	0.8	62.81	3.0	63.29
4.0	44.06	1.0	53.30	4.0	59.23
5.0	53.30	1.4	41.30	5.0	53.30
6.0	62.32	1.8	28.49	6.0	45.25

and filtered to get a clear solution [28]. Titanium(IV) concentration was determined by spectrophotometry.

Methyl methacrylate was successively washed with a 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.

Hydroxylamine sulphate was recrystallised and aqueous stock solution of the same was freshly prepared each time.

2.2. Polymerisation method

Polymerisation 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 anodic compartment and the other as cathodic compartment.

Catholyte was an electrolytic solution containing titanium(IV) sulphate (5.0 cm^3 of 0.25 mol dm^{-3}), hydroxylamine sulphate (2.5 cm ^{3} of 0.1 mol dm^{-3}), sulphuric acid (to maintain constant acid concentration of 0.5 mol dm^{-3}), methanol (40% to keep the monomer in homogeneous phase), 0.75 mol dm^{-3} methyl methacrylate and water (to keep the overall volume to 25.0 cm^3). Anolyte was 25.0 cm^3 of 0.5 mol dm^{-3} sulphuric acid. A thin and bright platinum foil was used as anode and the cathode was rectangular copper plate (6 × 8 cm). A stream of pure nitrogen was bubbled over the catholyte. The electrolytic cell was mounted on a magnetic stirrer and the medium was adequately stirred. A constant current was obtained from an electrolytically stabilised dc power supply of 0–150 V, which gave currents from 0–1000 mA.

Initially, conditions were established to get a maximum yield of polymers. This was done by carrying out the electrolysis at a specified current for 25 min. The polymer yield was determined gravimetrically. The results have been tabulated in Table 1.

2.3. Kinetic procedure

The kinetic measurements were performed under the inert atmosphere. In a typical kinetic run, a mixture of solutions containing requisite amounts of the methyl methacrylate monomer (M), hydroxylamine sulphate, titanium(IV) ions, sulphuric acid, methanol and water was thermally equilibrated in a water bath at the desired temperature. A wash bottle containing aqueous solution of methyl methacrylate 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 295 K. The initial rate of polymerisation (R_p) was determined from the initial slope of percentage versus time plot by the initial slope method [29], reproducible to ±6%. The order of the reaction was found by log [initial polymerisation rate] versus log [concentration of monomer or sulphuric acid or hydroxylamine or titanium(IV)] plots (a typical plot is shown in Fig. 5).

The effect of variation in the concentration of monomer, cathode current, solvent, sulphuric acid, hydroxylamine sulphate, titanium(III) and cathode materials on the polymerisation process were studied. The effect of temperature on the polymer yield was also examined (Table 2) and activation parameters were computed using Arrhenius and Eyring plots. The gravimetric determination of the polymer produced is one of the most direct ways of obtaining conversion data for polymerisation. Always a constant volume of the reaction mixture was taken in the cell. In order to determine the amount of the polymer formed in a known interval of time, the electrolysis was terminated 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 value was measured in benzene at 295 K by an Ubblehode viscometer. The limiting viscosity numbers were converted into average molecular weights by the Mark–Houwink equation, $[\eta] = KM^{\alpha}$, where M is the molecular weight of the polymer, K and α are the constants, their values being, $K = 0.94 \times 10^{-4}$ and $\alpha = 0.76$.

Table 2
Effect of temperature on polymer yield and average molecular weight for the cathodic polymerisation of methyl methacrylate at current: 200 mA; [MMA]: 0.75 mol dm^{-3}; [NH_2OH]: 0.01 mol dm^{-3}; [H_2SO_4]: 0.5 mol dm^{-3}; [Ti(IV)]: 0.05 mol dm^{-3}; methanol: 40%(v/v) and electrolysis time: 25 min

Temperature/K	% Polymer yield	Average molecular weight × 10^{-4}
285	39.19	2.4
290	50.05	2.8
295	53.30	2.8
300	59.89	2.8
305	71.17	2.8

3. Results and discussion

3.1. Blank experiments

Electrochemical polymerisation did not occur, when methyl methacrylate was added separately to either of the reagents, titanium(IV) or hydroxylamine sulphate in aqueous sulphuric acid–methanol medium. However, added methyl methacrylate was found to initiate the polymerisation in the presence of the mixture of titanium(IV) and hydroxylamine sulphate in aqueous sulphuric acid–methanol medium only when subjected to electrolysis. Polymer product formed was amorphous in nature and therefore no coating of the cathode by the polymer was observed in the polymerisation experiments.

3.2. Stoichiometry

The stoichiometry for the reduction of hydroxylamine by titanium(III) was established by back titration method. To a known volume (v_1) of substrate in aqueous medium (5 cm^3 of 0.001 mol dm^{-3}), titanium(III) sulphate (5.0 cm^3 of 0.01 mol dm^{-3}) solution (v_2) was added under deaerated condition. To this, ammonium iron(III) sulphate solution (5 cm^3 of 0.025 mol dm^{-3}) was added. The resulting solution was back-titrated against standard titanium(III) sulphate (0.05 mol dm^{-3}) stored under nitrogen atmosphere using 10% ammonium thiocyanate indicator (v_3). A blank titration was carried out by taking same amount of titanium(III) sulphate and ammonium iron(III)sulphate solutions. The titration volume was v_4. The number of electrons (n) is given by Eq. (1)

$$n = [v_2 - (v_4 - v_3) \times M_2]/v_1 \times M_1 \qquad (1)$$

Here M_1 and M_2 are the molarities of sample solution and titanium(III) sulphate solution, respectively. The stoichiometry of reduction of hydroxylamine by titanium(III) was

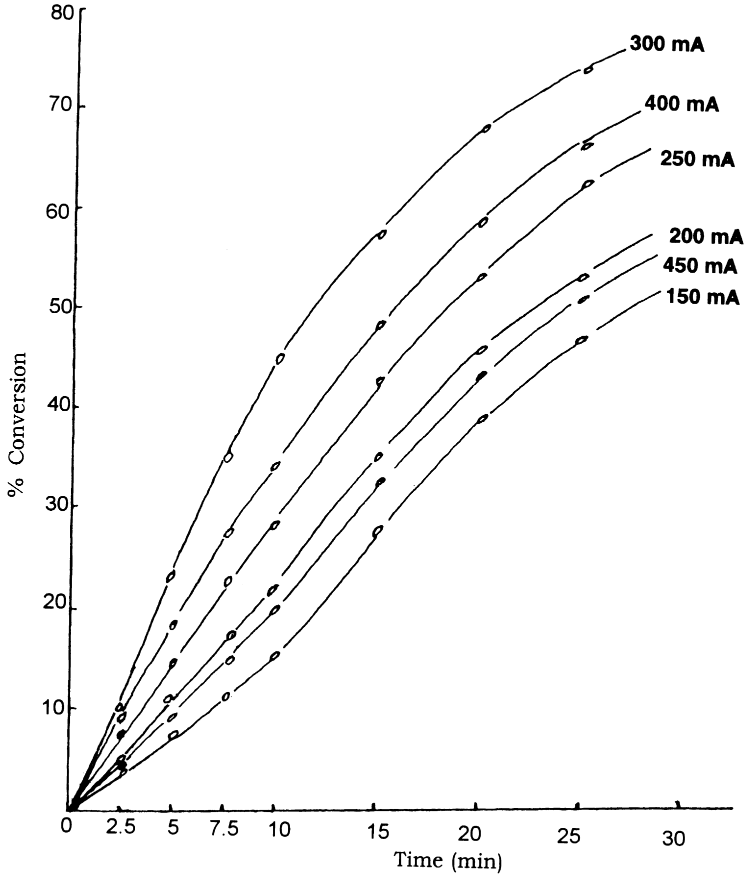

Fig. 1. Conversion-time curves for the cathodic polymerisation of MMA at different current levels in aqueous sulphuric acid–methanol medium at 295 K.

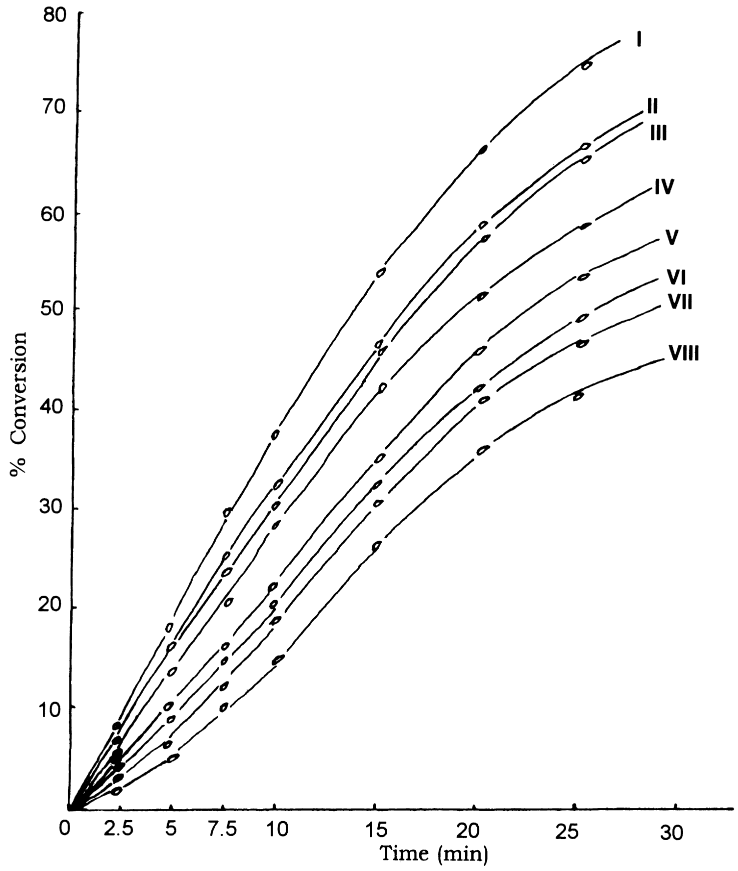

Fig. 2. Conversion–time curves for the cathodic polymerisation of MMA at fixed current of 200 mA in aqueous sulphuric acid–methanol medium at 295 K. The concentration of MMA being: (I) 0.37 mol dm^{-3}; (II) 0.34 mol dm^{-3}; (III) 0.56 mol dm^{-3}; (IV) 0.28 mol dm^{-3}; (V) 0.75 mol dm^{-3}; (VI) 0.19 mol dm^{-3}; (VII) 0.94 mol dm^{-3}; and (VIII) 1.13 mol dm^{-3}.

found to be 1:2 as shown below

$$^{+}NH_3OH + 2Ti^{3+} + 2H^{+} \rightarrow NH_4^{+} + 2Ti^{4+} + H_2O \qquad (2)$$

The product NH_4^+ in the reaction mixture was confirmed by Nessler's test after rendering the solution alkaline. The quantitative estimation of NH_4^+ by the colorimetric method [30] concurred with the above stoichiometry.

3.3. Kinetics of polymerisation

The polymerisation kinetic studies were carried out with different currents, monomer concentrations, different electrode materials and solvents at 295 K and the results are presented (Figs. 1–4) and computed (Tables 3–6). The initial rates of polymerisation were obtained from the slopes of percentage yield versus time plots excluding the slope values at higher concentrations of monomer or hydroxylamine (as shown in Fig. 1). The orders were found by varying the cathode current, concentrations of sulphuric acid, hydroxylamine sulphate monomer in turn, while keeping concentration of others constant. The order with respect to cathode current was 0.88 at a lower current range of 150–300 mA, order with respect to sulphuric acid was 0.58 in the range of 0.05–0.3 mol dm^{-3}, order with respect to hydroxylamine was 0.65 at lower concentration range of 0.002–0.008 mol dm^{-3} and order with respect to monomer was 1.6 at lower concentration range of 0.19–0.37 mol dm^{-3}.

To determine the propagation mechanism, polymerisations were conducted in the presence of a free radical inhibitor, hydroquinone. It was observed that the polymer yield decreases with increase in the concentration of hydroquinone (Table 7). The results indicated that the polymerisation reaction occurred primarily by a free radical mechanism.

Table 3
Effect of current on polymer yield and average molecular weight for the cathodic polymerisation of methyl methacrylate at 295 K; [MMA]: 0.75 mol dm^{-3}; [NH_2OH]: 0.01 mol dm^{-3}; [H_2SO_4]: 0.5 mol dm^{-3}; [Ti(IV)]: 0.05 mol dm^{-3}; methanol: 40%(v/v) and electrolysis time: 25 min

Current/mA	% Polymer	Average molecular weight × 10^{-4}
150	47.08	2.8
200	53.30	2.8
250	63.36	2.8
300	74.35	2.5
400	66.34	1.7
450	51.08	1.6

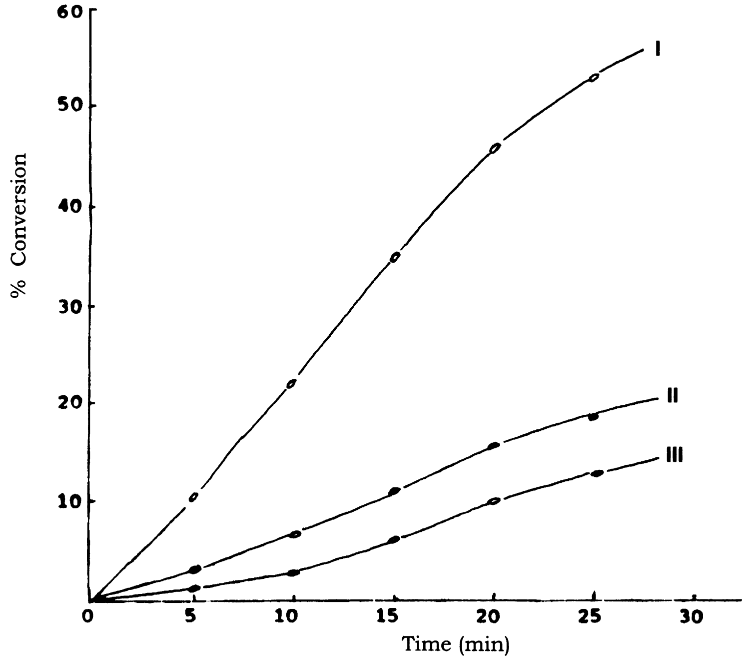

Fig. 3. Effect of various electrode materials on yield of MMA at fixed current of 200 mA and 295 K: (I) copper; (II) lead; and (III) graphite.

Table 4
Effect of methyl methacrylate on polymer yield and average molecular weight for the cathodic polymerisation of methyl methacrylate at 295 K; [NH_2OH]: 0.01 mol dm^{-3}; [H_2SO_4]: 0.5 mol dm^{-3}; [Ti(IV)]: 0.05 mol dm^{-3}; methanol: 40%(v/v) and electrolysis time: 25 min

[MMA] × 10 (mol dm^{-3})	% Polymer	Average molecular weight × 10^{-4}
1.9	49.21	2.8
2.8	58.11	2.8
3.4	65.92	2.8
3.7	74.28	2.8
5.6	65.27	2.8
7.5	53.30	2.8
9.4	46.86	2.2
11.3	41.56	1.6

Table 5
Effect of electrode material on polymer yield and average molecular weight for the cathodic polymerisation of methyl methacrylate at 295 K; Current: 200 mA;[MMA]: 0.75 mol dm^{-3}; [NH_2OH]: 0.01 mol dm^{-3}; [H_2SO_4]: 0.5 mol dm^{-3}; [Ti(IV)]: 0.05 mol dm^{-3}; methanol: 40%(v/v) and electrolysis time: 25 min

Electrode material	% Polymer	Average molecular weight × 10^{-4}
Copper	53.30	2.8
Lead	18.60	1.1
Graphite	12.65	0.3
Platinum	No polymer is detected	

3.4. Factors influencing polymer yield

3.4.1. Effect of cathode current

The effect of variation in titanium(IV) sulphate concentration, electrical current, temperature and sulphuric acid concentration on the current efficiency for the generation of titanium(III) was studied by Udupa and coworkers [31]. The current efficiency was found to decrease with increase in, current or concentration of titanium(IV) sulphate. In addition, the current efficiency was found to increase with increase in, sulphuric acid concentration or temperature.

It was found that the polymer yield increases with an increase in the cathode current in the range of 150–300 mA. However, when the cathode current exceeds 300 mA, the polymer yield decreases (Fig. 1). This can be explained as follows: as already stated, current efficiency for the generation of titanium(III) decreases with increase of current.

Table 6
Effect of solvent on polymer yield and average molecular weight for the cathodic polymerisation of methyl methacrylate at 295 K; Current: 200 mA;[MMA]: 0.75 mol dm^{-3}; [NH_2OH]: 0.01 mol dm^{-3}; [H_2SO_4]: 0.5 mol dm^{-3}; [Ti(IV)]: 0.05 mol dm^{-3}; and electrolysis time: 25 min

Solvent (%)	Polymer	Average molecular weight × 10^{-4}
40% Methanol	53.30	2.8
40% Dimethyl formamide	36.02	1.7
40% Dimethyl sulphoxide	20.64	1.1
Mixture of 40% methanol and 3% carbon tetrachloride	No polymer is detected	

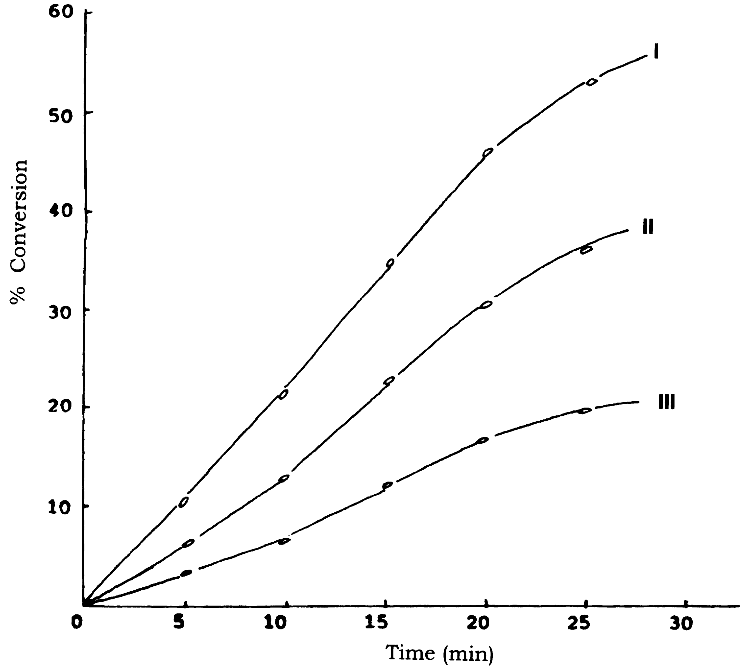

Fig. 4. Effect of various solvents on yield of cathodic polymerisation of MMA at fixed current of 200 mA and 295 K: (I) aqueous sulphuric acid–methanol medium; (II) aqueous sulphuric acid–dimethyl formamide medium; and (III) aqueous sulphuric acid–demethylsulphoxide medium.

Consequently, the reduction of hydroxylamine sulphate becomes slower and there will be slow and steady generation of free radicals. Hence, the polymer yield increases. However, at higher current levels (above 300 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 or reduction of the free radical itself, as shown in some early studies [32,33].

3.4.2. *Effect of monomer concentration*

The polymer yield increases with increase in monomer concentration in the lower concentration range of 0.19–0.37 mol dm^{-3}. However, the polymer yield decreases, when the monomer concentration exceeds 0.37 mol dm^{-3}. This may be due to the heterogeneous situation, wherein occlusion of the macroradical ends in the polymer coils, which effects termination to a considerable degree.

Table 7

Effect of inhibitor on polymer yield for the cathodic polymerisation of methyl methacrylate at 295 K; Current: 200 mA; [MMA]: 0.75 mol dm^{-3}; [NH_2OH]: 0.01 mol dm^{-3}; [H_2SO_4]: 0.5 mol dm^{-3}; [Ti(IV)]: 0.05 mol dm^{-3}; Methanol: 40% (v/v) and electrolysis time: 25 min

% Concentration	% Polymer yield
0.00	53.30
0.25	39.58
0.50	33.92
1.00	25.85
2.00	13.07

3.4.3. *Effect of hydroxylamine concentration*

The polymer yield increases with an increase in concentration of hydroxylamine sulphate in the range of $2.0 \times 10^{-3} - 8.0 \times 10^{-3}$ mol dm^{-3}. However, beyond 8.0×10^{-3} mol dm^{-3}, the polymer yield decreases, this is because of the fact that, an increase in hydroxylamine sulphate concentration results in increase in the rate of its reduction and there will be local over concentration of the free radicals in the vicinity of the electrode surface. This situation favours chain initiation and chain termination. Consequently polymer yield decreases.

3.4.4. *Effect of titanium(IV) sulphate concentration*

The polymer yield increases with increase in the titanium(IV) sulphate concentration in the range of 0.02–0.06 mol dm^{-3}. There will be steady generation of free radicals. This is because the current efficiency for the generation of titanium(III) decreases with increase in concentration of titanium(IV) sulphate. This situation favours the chain propagation and hence the polymer yield gradually increases.

3.4.5. *Effect of the temperature*

Current efficiency for the generation of titanium(III) increases with temperature. There will be slow and steady generation of free radicals, hence polymer yield gradually increases in the temperature range of 285–305 K.

The activation energy (E_a) calculated from the Arrhenius plot of log (rate) vs. $1/T$, in the temperature range of 295–305 K, was 24.21 ± 1.9 kJ mol^{-1}. The other activation parameters calculated from the Eyring plot of log (rate)

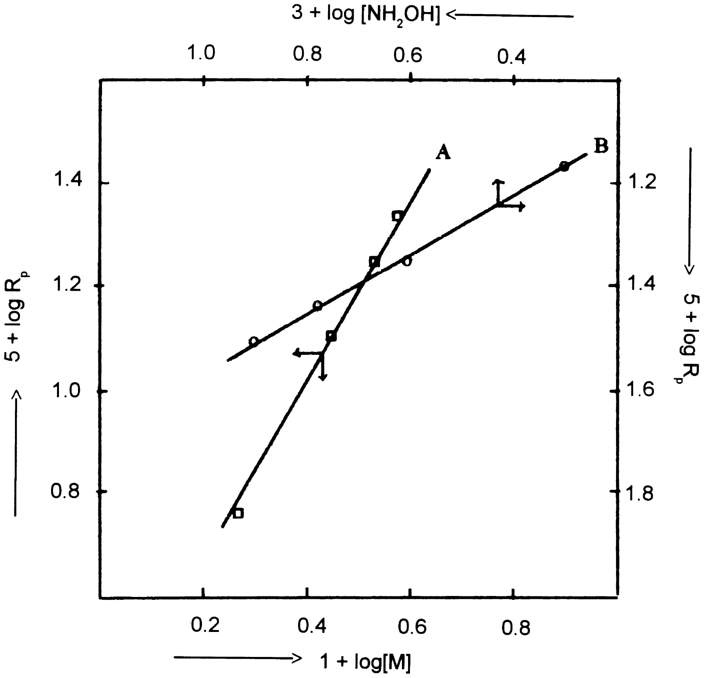

Fig. 5. Plots of log (initial rate, R_p) versus log (concentrations). (A) Plot of 5 + log R_p versus 1 + log(monomer concentration, [M]) at 295 K; current = 200 Ma; [Ti(IV)] = 0.05 mol dm^{-3}; [NH_2OH] = 0.01 mol dm^{-3}; [H_2SO_4] = 0.5 mol dm^{-3}; Methanol = 40%(v/v); electrolysis time = 25 min and [MMA] = 0.19, 0.28, 0.34 and 0. 37 mol dm^{-3}. (B) Plot of 5 + log R_p versus 3 + log[NH_2OH] at 295 K; current = 200 mA; [Ti(IV)] = 0.05 mol dm^{-3}; [AN] = 0.75 mol dm^{-3}; [H_2SO_4] = 0.5 mol dm^{-3}; Methanol = 40%(v/v); electrolysis time = 25 min and [NH_2OH] = 0.002, 0.004, 0.006 and 0.008 mol dm^{-3}.

vs. (k/*T*) are $\Delta H = 21.72 \pm 2$ kJ mol^{-1}; $\Delta G = 70.57 \pm 4$ kJ mol^{-1}; and $\Delta S = -162.80 \pm 6$ J K^{-1} mol^{-1}. The relatively low energy of activation or enthalpy of activation and high negative entropy of activation observed is characteristic of a free radical polymerisation process.

3.4.6. Effect of sulphuric acid concentration

It has been found that the yield of polymer increases with increase in sulphuric acid concentration in the concentration range of 0.05–0.3 mol dm^{-3}. However, it decreases when the sulphuric acid concentration exceeds 0.3 mol dm^{-3}. It can be explained as follows: Current efficiency for the generation of titanium(III) and also the rate of titanium(III) reduction of hydroxylamine sulphate becomes fast, resulting in the local over concentration of amino free radicals. This situation favours chain initiation and chain termination at the expense of chain propagation.

3.5. Polymer characterisation

3.5.1. Molecular weight

Viscosity average molecular weight of the polymer product in a typical standard run was found to be 2.8×10^4.

3.5.2. Spectral analysis

The infrared spectrum of the polymer product revealed the absorption frequencies at 3441 cm^{-1} (N–H stretching), 2990 cm^{-1} (C–H stretching), 1731 cm^{-1} (C–O stretching) and 1632 cm^{-1}(N–H bending), indicating the $-NH_2$ as end group of the poly(methyl methacrylate) macromolecule. Also, significant absorption frequencies at about 1150 and 1350 cm^{-1} reveals the aliphatic ether linkage ($-CH_2-O-CH_3$) moiety at the methyl methacrylate macromolecule originating most likely from the organic solvent, methanol.

3.6. Influence of electrode materials

Apart from copper, tests with several other electrode materials like platinum, lead and graphite were tried at constant current density (Fig. 3). It was found that copper was superior to both lead and graphite. Platinum was found to be unsuited for electropolymerisation of methyl methacrylate under the said conditions, because of coating of polymer product on the surface of the electrode materials.

3.7. Polymerisation in different solvent medium

Percentage yields were different in dimethyl formamide, dimethyl sulphoxide and in methanol. This is in accordance with the findings of previous workers [34,35]. But the molecular weight of the product were more or less the same (Fig. 4).

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 formulation containing a solvent mixture of 40% methanol and 3% carbon tetrachloride yielded no polymer at all probably due to enhanced termination by chain transfer mode. There is also the possibility of the molecular weight of resulting polymer is too low to be detected. Further, it was observed that the percentage yield decreases from 55–46% on increasing the alcohol concentration in the range of 30–60%. Therefore, it is inferred that, chain termination of the polymer is due to coupling, also a fraction of the termination takes place by chain transfer mechanism involving solvent molecules, which is supported by the IR spectrum, indicating the $-CH_2-O-CH_3$ as end group of the methyl methacrylate macromolecule.

4. Kinetic scheme

In the absence of free radicals scavenger in the system, the titanium(III) reduction of hydroxylamine sulphate follows the scheme

$$NH_2OH + H^+ \overset{K_1}{\rightleftharpoons} {}^+NH_3OH$$

$${}^+NH_3OH + Ti^{3+} \underset{k_2}{\overset{\text{slow}}{\longrightarrow}} Ti^{4+} + NH_2^{\cdot} + H_2O$$

$$Ti^{3+} + NH_2^{\cdot} + H^+ \xrightarrow{k_3} Ti^{4+} + NH_3 (NH_3 + H^+ \longrightarrow NH_4^+)$$

Where K_1, k_2 and k_3 are the equilibrium and rate constants, respectively. The kinetic scheme, which accounts for the observed fractional order dependence each on $[NH_2OH]$, current, and $[H^+]$ and 1.6 order dependence on monomer, [M] in this electropolymerisation can be accounted by the kinetic scheme detailed as follows:

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

$$Ti^{3+} + {}^+NH_3OH \xrightarrow{k_2} Ti^{4+} + \underset{(R^{\cdot})}{NH_2^{\cdot}} + H_2O$$

$$Ti^{3+} + \underset{(R^{\cdot})}{NH_2^{\cdot}} + H^+ \xrightarrow{k_3} Ti^{4+} + NH_3 (NH_3 + H^+ \longrightarrow NH_4^+)$$

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

$$RM_{n-1}^{\cdot} + M \xrightarrow{k_p} RM_n^{\cdot}$$

$$RM_m^{\cdot} + RM_n^{\cdot} \xrightarrow{k_t} RM_{m+n}R$$

$$RM_n^{\cdot} + H \xrightarrow{k_{tr}} RM_mH$$

$$RM_m^{\cdot} + XH \xrightarrow{k_{tr}} RM_mH + X^{\cdot}$$

Here 'M' is the monomer, methyl methacrylate, k_e, 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.

The rate of initiation

$$R_i = k_i[R^{\cdot}][M] \tag{3}$$

Applying steady state approximation for the concentration of intermediate radical $R^{\cdot}$

$$d[R^{\cdot}]/dt = k_2[Ti^{3+}][SH^+] - k_3[R^{\cdot}][Ti^{3+}][H^+] - k_i[R^{\cdot}][M] = 0$$

$$[R^{\cdot}] = \frac{k_2[Ti^{3+}][SH^+]}{\{k_3[Ti^{3+}][H^+] + k_i[M]\}} \tag{4}$$

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

$$[R^{\cdot}] = \frac{fk_e k_2[I][SH^+]}{\{k_3 fk_e[I][H^+] + k_i[M]\}} \tag{5}$$

where, [I] is the current in faraday per unit volume, f is the factor representing the fraction of the current which initiate chains

Substituting for $[R^{\cdot}]$, in Eq. (3) leads to

$$R_i = \frac{\{fk_2k_ek_i[I][SH^+][M]\}}{\{fk_3k_e[I][H^+] + k_i[M]\}} \tag{6}$$

4.1. Termination by coupling mode

$$R_t = k_t[RM^{\cdot}]^2 \tag{7}$$

Under steady state condition

$$R_i = R_t \tag{8}$$

Substituting the value of R_i and R_t in Eq. (8) and rearranging

$$[M^{\cdot}] = \left[\frac{fk_2k_ek_i[I][SH^+][M]}{k_t\{fk_3k_e[I][H^+] + k_i[M]\}}\right]^{1/2} \tag{9}$$

The rate of polymerisation is given by

$$R_p = k_p[M^{\cdot}][M] \tag{10}$$

Substituting for $[M^{\cdot}]$ and writing $[SH^+]$ equals K_1 [S] $[H^+]$

$$R_p = k_p\left[\frac{fK_1k_2k_ek_i[I][S][H^+]}{k_t\{fk_3k_e[I][H^+] + k_i[M]\}}\right]^{1/2}[M]^{3/2} \tag{11}$$

4.2. Termination by chain transfer mode

$$\frac{fk_2k_ek_i[I][SH^+][M]}{k_t\{fk_3k_e[I][H^+] + k_i[M]\}} = k_{tr}[M^{\cdot}][XH] \tag{12}$$

Rearranging

$$[M^{\cdot}] = \frac{fk_2k_ek_i[I][SH^+][M]}{k_{tr}\{fk_3k_e[I][H^+] + k_i[M]\}[XH]} \tag{13}$$

Now the rate of polymerisation by substituting the value of $[M^{\cdot}]$ in Eq. (10) and writing $[SH^+]$ equal to K_1 [S] $[H^+]$, is

$$R_p = \frac{k_p}{k_{tr}}\,\frac{fK_1k_2k_ek_i[I][S][H^+][M]^2}{[XH]\{fk_3k_e[I][H^+] + k_i[M]\}} \tag{14}$$

The dependence of the initial rate of polymerisation R_p on $[I]^{0.88}$, $[NH_2OH]^{0.65}$, $[H^+]^{0.58}$ and $[M]^{1.6}$, which were experimentally observed, is consistent with the combined form of rate Eqs. (11) and (14).

5. Conclusion

Electrolytically generated reactive species Ti^{3+} reacts with the chemical initiator, hydroxylamine present in the bulk of the solution to produce free radicals. Chain termination of the polymer is due to coupling, also a fraction of the termination takes place by chain transfer mode involving solvent molecules. In situ generation of titanium(III) enables us to overcome the difficulties involved in the chemical method. The concentration of the initiator in the reaction system can be easily controlled by careful control of cathodic current. The electrolyte titanium sulphate is regenerated and can be reused. Reactions can be terminated at will by stopping the cathodic current. It is pollution free, as it does not produce any harmful gas either in the anodic compartment or in the cathodic compartment of the cell. Thus titanium(III) mediated electropolymerisation offers a safe and simple technique for the synthesis of high molecular weight polymers in higher yield. Moreover titanium(III)–hydroxylamine redox system results in polymers with amine end groups. These telechelic polymers play a decisive role in the tailor making of advanced polymeric materials.

Acknowledgements

The authors thank the Department of Atomic Energy (DAE), Government of India, for the financial assistance through, Board of Research in Nuclear Sciences (BRNS), as a Research Project Grant No. 36/11/96-R & D-II /878.

References

[1] Davis P, Evans M, Higginson WCE. J Chem Soc 1951:2563.
[2] Izumi Z, Ranby B. Macromolecules 1975;8(2):151.
[3] Kakurai T, Iwal S, Noguchi T. Kobunshi Kagaku 1966;23:279.
[4] Kakurai T, Sugata T, Noguchi T. Kobunshi Kagaku 1968;25:120.
[5] Patsiga RA, Lerdhusnu W, Marawl I. Ind Engng Chem Prod Res Rev 1984;23:238.
[6] Friedlander HZ. In: Mark HF, editor. Encyclopedia of polymer science and technology, vol. 5. New York: Interscience, 1966.
[7] Funt BL. Macromolecular reviews, vol 2. New York: Interscience, 1966.
[8] Wilson CL. Encyclopedia of electrochemistry. New York: Reinhold, 1964.
[9] Breitenbach JW, Srna Ch. Pure Appl Chem 1962;4:245.
[10] Guerra GD. Comprehensive Polym Sci 1992:4.
[11] Funt BL, Yu KC. J Polym Sci 1962;62:359.
[12] Funt BL, Williams FD. J Polym Sci 1963;B-1:181.
[13] Bhadani SN, Qayumuddin, Ansari, Sen Gupta SK. J Appl Polym Sci 1992;44:121.
[14] Davis M, Venkataraman B, Krishnamoorthy J. J Electrochem Soc India 1990:107.
[15] Funt BL, Bhadani SN. Can J Chem 1964;43:2733.
[16] Funt BL, Bhadani SN. J Polym Sci 1965;A-3:4191.
[17] Smith WB, Glide HC. J Am Chem Soc 1960;82:659.
[18] Smith WB, Glide HC. J Am Chem Soc 1961:355.
[19] Toppare BL, Even S, Tunker L, Akbulul U. Polymer 1984;25:1955.
[20] Bhadani SN, Barnawal Tr. Soc Adv Electrochem Sci Technol 1976;11:73.
[21] Parravano H. J Am Chem Soc 1951;73:628.
[22] Sezai Sarac A, Ozlem Yavuz, Esma Sezer. J Appl Polym Sci 1999;72:861.
[23] Sarac AS, Soydan AB, Coka V. J Appl Polym Sci 1996;62:111.
[24] Rai SK, Sheigara BS. Transition Met Chem 1995;20:630.
[25] Sherigara BS, Yashoda MP. Padmalatha. J Phys Org Chem 1999;12:605.
[26] Rai SK, Sherigara BS, Made Gowda NM. Eur Polym J 1998;34:1031.
[27] Rai SK, Shivakumar K, Sherigara BS. Eur Polym J 1999;35 (in press).
[28] Yashoda MP, Padmalatha, Sherigara BS, Nayak PV. Indian J Chem 1999;38A:176.
[29] Laidler KJ. Chemical kinetics. New York: Harper & Row, 1987.
[30] Vogel's text book of quantitative chemical analysis, 1989.
[31] Narasimhan KC, Vasundara, Udupa HVK. Trans Soc Adv Electrochem Sci Technol 1980;15:147.
[32] Albeck M, Konigsbuch M, Relis J. J Polym Sci Part A-1 1971;9:1375.
[33] Albeck M, Relis J. J Polym Sci Part A-1 1971;9:2963.
[34] Tidwell BM, Doughty AG. Polymer 1971;12:431.
[35] Pistoia. J Polym Sci Polym Lett Ed 1972;10:787.