

# Electrochemical Synthesis of Poly[2-Hydroxyethylmethacrylate] Hydrogel: Kinetics and Mechanism

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**ABSTRACT:** 2-Hydroxyethylmethacrylate (HEMA) was polymerized in an aqueous sulfuric acid–*N,N*-dimethylformamide (DMF) medium in a divided cell by an electrolytically generated mediator species titanium(III). Titanium(III)–hydroxylamine sulfate 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 polymerization were investigated for variation in initial monomer concentrations, acid concentrations, electrical currents, dielectric constants of the solvent medium, and electrode materials. Chain termination of the polymer was due to coupling of growing macroradicals; also, a fraction of the termination took place by a chain transfer mechanism involving the organic solvent molecules. A suitable mechanism for titanium(III)–hydroxylamine sulfate mediated indirect electropolymerization of HEMA has been proposed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 983–992, 2002; DOI 10.1002/app.10299

**Key words:** electroinitiated polymerization; poly(2-hydroxy ethylmethacrylate) hydrogel; kinetics and mechanism

## INTRODUCTION

The kinetics of electrochemical polymerization has received great attention by various researchers<sup>1–4</sup> as they play a unique role in predicting the mechanism of polymerization. Electrochemical polymerization is a natural outgrowth of preparative electroorganic synthesis. Electroinitiated polymerization of vinyl monomers in the homogeneous system was investigated by various workers,<sup>5–8</sup> but studies in heterogeneous systems are rare. Only a few reports are available on the kinetics of free radical polymerization of 2-hydroxy-

ethylmethacrylate (HEMA).<sup>9–11</sup> During the past two decades, a large number of studies devoted to the synthetic aspects of the homopolymerization and copolymerization of HEMA has been accumulated.<sup>12–16</sup> This growing interest is largely due to different applications of the poly(2-hydroxy ethylmethacrylate) (PHEMA) and its copolymers. Their biocompatibility makes them excellent candidates for the preparation of various biomedical and pharmaceutical materials like optical lenses, implants, drug delivery devices, and support for enzyme immobilization.<sup>17–20</sup> There are no reports on electroinduced radical polymerization of HEMA. The electrochemical preparation method presents several interesting advantages—such as the initiator in the reaction system can be easily controlled by cathodic current. The reagent tita-

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**Table I** Effect of Ti(IV), and Hydroxylamine Sulfate and Sulfuric Acid Concentration, on Polymer Yield for the Cathodic Polymerization of HEMA at 300 K; Current: 250 mA; [HEMA]: 0.16 mol dm<sup>-3</sup>; DMF: 60% (v/v); Electrolysis Time: 25 min<sup>a</sup>

[Ti(IV)] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	% Polymer Yield	[NH <sub>2</sub> OH] × 10 <sup>2</sup> (mol dm <sup>-3</sup> )	% Polymer Yield	[H <sub>2</sub> SO <sub>4</sub> ] × 10 (mol dm <sup>-3</sup> )	% Polymer Yield
1.0	30.40	0.5	34.2	0.3	42.5
2.0	34.28	1.0	41.20	0.4	48.24
3.0	41.56	1.5	48.98	0.5	54.98
4.0	48.85	2.0	54.98	0.6	58.42
5.0	54.98	3.0	60.00	0.7	52.14
6.0	53.45	4.0	41.13	0.8	45.65

<sup>a</sup> [Ti(IV)]: 0.05 mol dm<sup>-3</sup>; [NH<sub>2</sub>OH]: 0.02 mol dm<sup>-3</sup>; and [H<sub>2</sub>SO<sub>4</sub>]: 0.5 mol dm<sup>-3</sup> while varying the other components.

nium sulfate is regenerated and can be reused. Reaction 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. As a part of our kinetic and mechanistic studies on redox polymerization,<sup>21–25</sup> the electroinitiated polymerization of HEMA mediated by titanium(III)–hydroxylamine sulfate in sulfuric acid–*N,N*-dimethylformamide (DMF) medium is reported in this article.

## EXPERIMENTAL

HEMA was purified by distillation under reduced vacuum, followed by extraction with hexane and subsequent distillation.<sup>26</sup> Nitrogen was bubbled through the monomer for the removal of any dissolved hexane. Hydroxylamine sulfate (s.d.fine India), DMF (GSC India), dimethyl sulfoxide (GSC India), and carbon tetrachloride (Fisher) used were of analytical grade. Doubly distilled water was used throughout.

A stock solution of titanium(IV) was prepared according to the reported procedure.<sup>25</sup> Titanium(IV) concentration was determined by spectrophotometry. Hydroxylamine sulfate was recrystallized and aqueous stock solution of the same was prepared fresh each time.

### Polymerization Method

The kinetics of polymerization was followed by batch process as follows: 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 center. 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 monomer (M) HEMA, titanium(IV) sulfate (5 cm<sup>3</sup> of 0.25 mol dm<sup>-3</sup>), hydroxylamine sulfate (2.5 cm<sup>3</sup> of 0.2 mol dm<sup>-3</sup>), sulfuric acid (to maintain constant acid concentration of 0.5 mol dm<sup>-3</sup>), DMF (60%), and water (to keep the overall volume to 25 cm<sup>3</sup>).

Anolyte was 25 cm<sup>-3</sup> of 0.5 mol dm<sup>-3</sup> sulfuric 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 stabilized DC power supply of 0–150 V, which gave currents from 0 to 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 I.

### 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 HEMA monomer (M), hydroxylamine sulfate, titanium (IV) ions, sulfuric acid, DMF, and water was thermally equilibrated in a water bath

**Table II** Effect of Temperature on Polymer Yield for the Cathodic Polymerization of HEMA at 300 K; Current: 250 mA; [HEMA]: 0.16 mol dm<sup>-3</sup>; DMF: 60% (v/v); [NH<sub>2</sub>OH]: 0.02 mol dm<sup>-3</sup>; [H<sub>2</sub>SO<sub>4</sub>]: 0.5 mol dm<sup>-3</sup>; [Ti(IV)]: 0.05 mol dm<sup>-3</sup>; Electrolysis Time: 25 min

Temperature (K)	% Polymer	Degree of Polymerization (DP)
290	39.86	2242
295	47.48	2238
300	54.98	2242
305	58.42	2265
310	44.62	2198

at the desired temperature. A wash bottle containing aqueous solution of HEMA and DMF 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 polymerization was determined gravimetrically at 300 K. The initial rate of polymerization ( $R_p$ ) was determined from the initial slope of percentage vs time plot by the initial slope method. The order of the reaction was found by log[initial polymerization rate] vs log[concentration of monomer or sulfuric acid or hydroxylamine or current] (a typical plot is shown in Fig. 5).

The effect of variation in the concentration of monomer, cathode current, solvent, sulfuric acid, hydroxylamine sulfate, titanium(III), and different cathode materials on the polymerization process was studied. The effect of temperature on the polymerization yield was also examined (Table II) 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 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 terminated at the desired time and the polymer obtained was washed well with water and dried under vacuum to a constant weight.

Molecular weights were determined viscometrically. Polymer samples were purified by dissolving them in DMF followed by precipitation in water and subsequent filtration and drying in vacuum. The purified polymer samples were dis-

solved in DMF (0.1% solution) and their viscosities were determined using an Ubbelohde suspended level viscometer at 25 + 0.1°C. The intrinsic viscosity of PHEMA is related to its molecular weight as<sup>27</sup>  $[\eta] = 8.9 \times 10^{-5}[\mathbf{M}]^{0.72}$ .

## RESULTS AND DISCUSSION

### Blank Experiments

Electrochemical polymerization did not occur, when the HEMA was added separately to either of the reagents, titanium(IV), or hydroxylamine sulfate in aqueous sulfuric acid-DMF medium. However, added HEMA was found to initiate the polymerization in the presence of titanium(IV) and hydroxylamine sulfate in aqueous sulfuric acid-DMF medium only when subjected to electrolysis.

### Kinetics of Polymerization

The kinetic orders were found by varying the cathode current, concentrations of sulfuric acid, hydroxylamine sulfate, and monomer in turn, while keeping other parameters constant (Tables III-VI, and Figs. 1-4). The order with respect to cathode current was 0.68 at a lower current range of 150-300 mA.

To determine the propagation mechanism, polymerizations were conducted in the presence of free radical inhibitor, hydroquinone. It was observed that the polymer yield decrease with increase in the concentration of hydroquinone (Table VII) and the presence of hydroquinone residue in the obtained polymer has been confirmed by IR spectroscopy (Fig. 6), absorption band at 1628

**Table III** Effect of Current on Polymer Yield and Average Molecular Weight for the Cathodic Polymerization of HEMA at 300 K; [HEMA]: 0.16 mol dm<sup>-3</sup>; DMF: 60% (v/v) [NH<sub>2</sub>OH]: 0.02 mol dm<sup>-3</sup>; [H<sub>2</sub>SO<sub>4</sub>]: 0.5 mol dm<sup>-3</sup>; [Ti(IV)]: 0.05 mol dm<sup>-3</sup>; Electrolysis Time: 25 min

Current (mA)	% Polymer	Degree of Polymerization (DP)
150	43.33	2209
200	50.00	2324
250	54.98	2242
300	58.22	2265
350	51.52	2275

**Table IV** Effect of HEMA on Polymer Yield and Degree of Polymerization for the Cathodic Polymerization of HEMA at 300 K; Current: 250 mA; DMF: 60% (v/v); [NH<sub>2</sub>OH]: 0.02 mol dm<sup>-3</sup>; [H<sub>2</sub>SO<sub>4</sub>]: 0.5 mol dm<sup>-3</sup>; [Ti(IV)]: 0.05 mol dm<sup>-3</sup>; Electrolysis Time: 25 min

[HEMA] × 10 mol dm <sup>-3</sup>	% Polymer	Degree of Polymerization (Dp)
1.0	39.86	2130
1.3	47.48	2142
1.6	54.98	2234
1.9	58.42	2398
2.3	44.62	2202

cm<sup>-1</sup> was observed, indicating the presence of aromatic hydroquinone ring. The results indicated that the polymerization reaction occurred primarily by a free radical mechanism.

### Factors Influencing Polymer Yield

#### *Effect of Cathode Current.*

The effect of variation in titanium(IV) sulfate concentration, electrical current, temperature, and sulfuric acid concentration on the current efficiency for the generation of titanium(III) was studied by Udupa and co-workers.<sup>28</sup> The current efficiency was found to decrease with an increase in current density or concentration of titanium(IV) sulfate. In addition the current efficiency was found to increase with increase in sulfuric acid concentration or temperature.

It was found that the polymer yield increases with 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 and Table III). This can be explained as follows: as already stated, the current efficiency for the generation of titanium(III) decreases with

**Table VI** Effect of Solvent on Polymer Yield for the Cathodic Polymerization HEMA at 300 K; [HEMA]: 0.16 mol dm<sup>-3</sup>; Current: 250 mA; [NH<sub>2</sub>OH]: 0.02 mol dm<sup>-3</sup>; [H<sub>2</sub>SO<sub>4</sub>]: 0.5 mol dm<sup>-3</sup>; [Ti(IV)]: 0.05 mol dm<sup>-3</sup>; Electrolysis Time: 25 min

Solvent (%)	% Polymer
60% Dimethylformamide	54.98
60% Methanol	25.26
60% Dimethylsulfoxide	17.5
Mixture of 60% dimethylformamide and 2% carbon tetrachloride	8.0

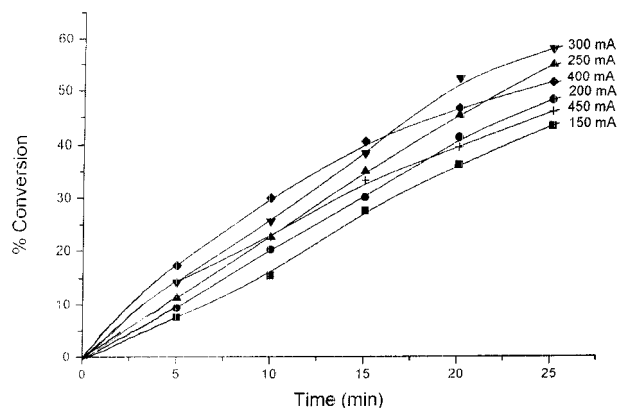
increase in current.<sup>28</sup> Consequently, reduction of hydroxylamine becomes slower and there will be slow and steady generation of free radicals. Hence, the polymer yield increases. However, at high current levels (above 300 mA) the apparent decrease in current efficiency can be due to the depletion of the monomer at the cathode–catholyte interface and also due to hydrogen production or reduction of the free radicals itself, as shown in some early studies.<sup>29,30</sup>

#### *Effect of Titanium(IV) Concentration.*

The polymer yield increases with increase in the titanium(IV) sulfate in the concentration range of 0.1 to 0.5 mol dm<sup>-3</sup> (Table I). This may be due to the steady generation of free radicals in the range 0.1–0.5 mol dm<sup>-3</sup>. This situation favors chain propagation and hence polymer yield gradually increases. However, beyond a certain optimum concentration of titanium(IV)sulfate (>0.5 mol dm<sup>-3</sup>) the titanium(III) generated will be of low concentration<sup>28</sup> and the free radicals generated by the reduction of hydroxyl amine will be of lower concentration. Consequently, the polymer yield gradually decreases.

**Table V** Effect of Electrode Material on Polymer Yield and Degree of Polymerization for the Cathodic Polymerization HEMA at 300 K; [HEMA]: 0.16 mol dm<sup>-3</sup>; Current: 250 mA; DMF: 60% (v/v); [NH<sub>2</sub>OH]: 0.02 mol dm<sup>-3</sup>; [H<sub>2</sub>SO<sub>4</sub>]: 0.5 mol dm<sup>-3</sup>; [Ti(IV)]: 0.05 mol dm<sup>-3</sup>; Electrolysis Time: 25 min

Electrode Material	% Polymer	Degree of Polymerization (Dp)
Copper	54.98	2234
Lead	25.2	1208
Graphite	17.5	912
Platinum	No polymer detected	



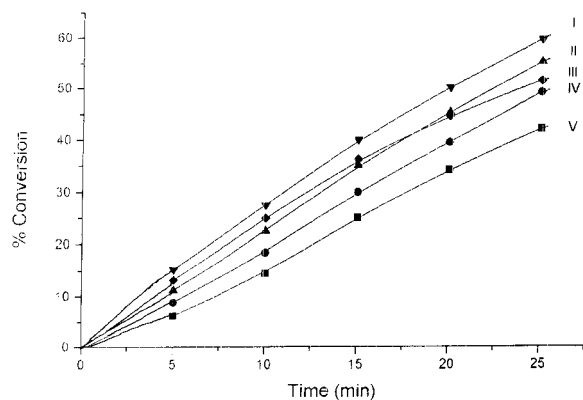
**Figure 1** Conversion-time curves for the cathodic polymerization of HEMA at different current levels in aqueous sulfuric acid-DMF at 300 K.

#### Effect of Monomer Concentration.

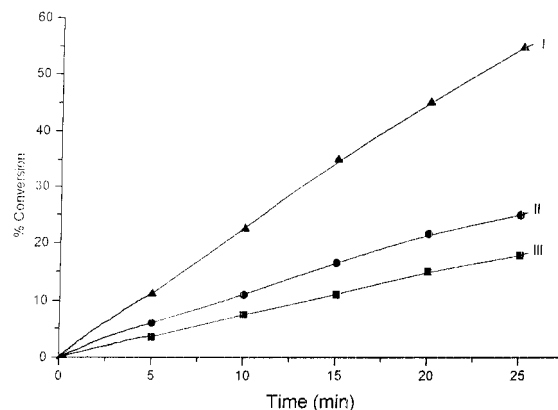
The polymer yield increases with increase in monomer concentration  $[M]$  in the lower concentration range of  $0.10\text{--}0.19\text{ mol dm}^{-3}$  (Table IV). A plot of  $\log R_p$  vs  $\log [M]$  was found to be linear with the slope (order) equal to 1.43 with respect to the monomer (Fig. 5). However, the product yield decreases when the monomer concentration exceeds  $0.19\text{ mol dm}^{-3}$ . 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 as observed in our previous work.<sup>25</sup>

#### Effect of Hydroxylamine Sulfate Concentration.

The polymer yield increases with an increase in concentration of hydroxylamine sulfate in the



**Figure 2** Conversion-time curves for the cathodic polymerization of HEMA at a fixed current of 250 mA in aqueous sulfuric acid-DMF medium at 300 K. The concentration of HEMA is (I) 0.19, (II) 0.16, (III) 0.23, (IV) 0.13, and (V)  $1.0\text{ mol dm}^{-3}$ .

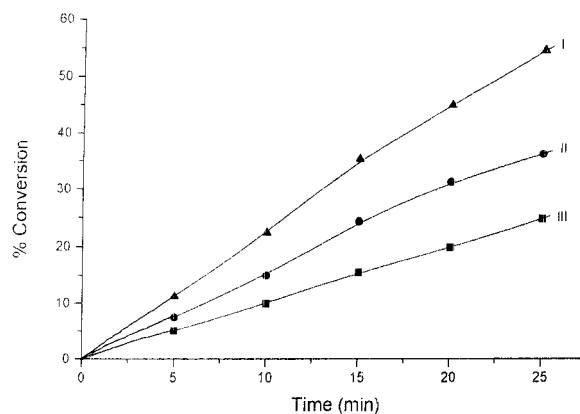


**Figure 3** Effect of various electrode materials on yield of PHEMA at a fixed current of 250 mA and 300 K: (I) copper, (II) lead, and (III) graphite.

range of  $0.5 \times 10^{-2}$  to  $3 \times 10^{-2}\text{ mol dm}^{-3}$ , yielding the order of 0.56 with respect to hydroxylamine sulfate concentration (Fig. 5). However beyond  $3 \times 10^{-2}\text{ mol dm}^{-3}$ , the polymer yield decreases (Table I). This is because of the fact that, an increase in hydroxylamine sulfate concentration beyond a certain value would increase in the rate of its reduction as shown in our previous study.<sup>24</sup> Hence, there will be local over concentration of the free radicals in the immediate vicinity of the electrode surface. This situation favors chain initiation and chain termination. Consequently, the polymer yields gradually decreases.

#### Effect of Temperature.

Current efficiency for the generation of titanium(III) increases with temperature. There will be



**Figure 4** Effects of various solvents on yield of cathodic polymerization of HEMA at a fixed current of 250 mA and 300 K: (I) aqueous sulfuric acid-DMF medium, (II) aqueous sulfuric acid-dimethyl sulfoxide medium, and (III) aqueous sulfuric acid-methanol medium.

**Table VII Effect of Inhibitor on Polymer Yield for the Cathodic Polymerization HEMA at 300 K; [HEMA]: 0.16 mol dm<sup>-3</sup>; Current: 250 mA; DMF: 60% (v/v); [NH<sub>2</sub>OH]: 0.02 mol dm<sup>-3</sup>; [H<sub>2</sub>SO<sub>4</sub>]: 0.5 mol dm<sup>-3</sup>; [Ti(IV)]: 0.05 mol dm<sup>-3</sup>; Electrolysis Time: 25 min**

% Concentration of Inhibitor	% Polymer
0.00	54.98
0.25	28.22
0.50	17.56
1.00	10.42

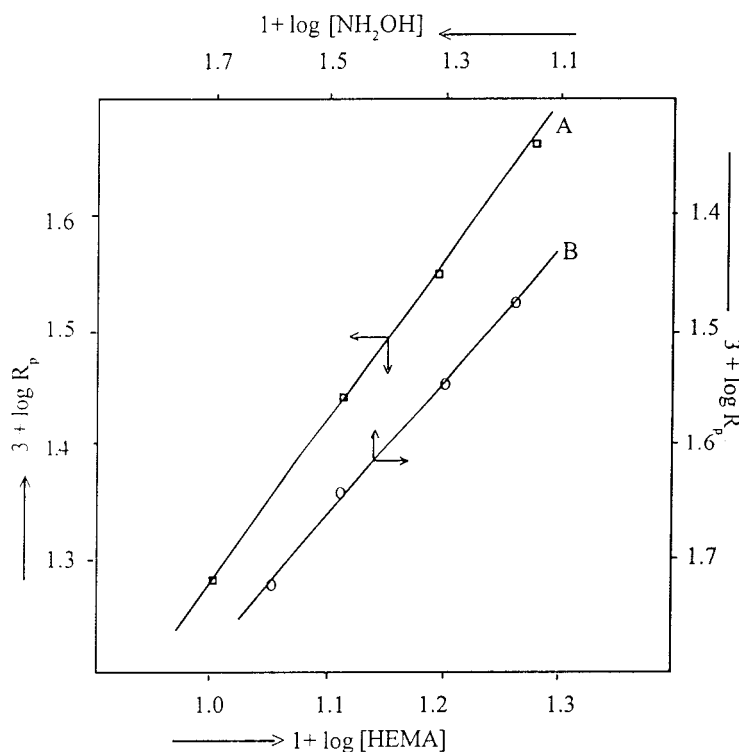
slow and steady generation of free radicals<sup>31</sup>; hence polymer yield gradually increases in the temperature range of 290–305 K (Table II). However above 305 K, the reduction rate becomes very fast, resulting in a local overconcentration of free radicals near the electrode surface. This situation favors chain initiation and chain termination at

the expense of propagation, thereby decreasing the polymer yield.

The activation energy ( $E_a$ ) calculated from the Arrhenius plot of  $\log(\text{rate})$  vs  $1/T$ , in the temperature range of 290–305 K, was  $26.21 + 1.5 \text{ kJ mol}^{-1}$ . The other activation parameters calculated from the Eyring plot are  $\Delta H^\ddagger = 30.14 \pm 2 \text{ kJ mol}^{-1}$ ,  $\Delta G^\ddagger = 79.54 \pm 2.2 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -127.18 \pm 5 \text{ JK}^{-1} \text{ mol}^{-1}$ . The relatively low energy of activation or enthalpy of activation and high negative entropy of activation observed is characteristic of a free radical polymerization process.

#### Effect of Sulfuric Acid Concentration.

Current efficiency for the generation of titanium(III) and also the rate of titanium(III) reduction of hydroxylamine sulfate increases with an increase in sulfuric acid concentration.<sup>31</sup> This situation favors chain propagation. Hence the yield of polymer increases with increase in the sulfuric



**Figure 5** Plots of  $\log$  (initial rate,  $R_p$ ) vs  $\log$  (concentration). (A) Plot of  $3 + \log R_p$  vs  $1 + \log [\text{HEMA}]$  at 300 K. Current: 250 mA; DMF: 60% (v/v);  $[\text{NH}_2\text{OH}]$ : 0.02 mol dm<sup>-3</sup>;  $[\text{H}_2\text{SO}_4]$ : 0.5 mol dm<sup>-3</sup>;  $[\text{Ti(IV)}]$ : 0.05 mol dm<sup>-3</sup>; electrolysis time: 25 min. (B) Plot of  $3 + \log R_p$  vs  $1 + \log [\text{NH}_2\text{OH}]$  at 300 K. Current: 250 mA; DMF: 60% (v/v);  $[\text{HEMA}]$ : 0.16 mol dm<sup>-3</sup>;  $[\text{H}_2\text{SO}_4]$ : 0.5 mol dm<sup>-3</sup>;  $[\text{Ti(IV)}]$ : 0.05 mol dm<sup>-3</sup>; electrolysis time: 25 min.  $[\text{NH}_2\text{OH}] = 1.5, 2.0, 3.0, \text{ and } 4.0 \text{ mol dm}^{-3}$ .

acid concentration range of 0.3–0.6 mol dm<sup>-3</sup>, yielding the order of 0.6 with respect to sulfuric acid concentration. However, the yield decreases when the sulfuric acid concentration exceeds 0.6 mol dm<sup>-3</sup>, the reduction reaction becomes so fast as to increase the production of free radicals to favor chain initiation and chain termination against chain propagation. Hence the polymer yield decreases at higher acid concentrations.

## Polymer Characterization

### Molecular Weight.

Viscosity average molecular weight of the polymer product in a typical standard kinetic run was found to be  $2.9 \times 10^4$ .

### Spectral Analysis.

The infrared spectrum of the polymer (Fig. 6) product revealed the absorption frequencies at 3430 cm<sup>-1</sup> (N—H and O—H stretching), 2930 cm<sup>-1</sup> (CH stretching), 1716 cm<sup>-1</sup> (C=O stretching), and 1651 cm<sup>-1</sup> (N—H bending), indicating the —NH<sub>2</sub> as end group of the PHEMA macromolecule.

### Influence of Electrode Materials

Other than copper, experiments with several electrode materials like platinum, lead and graphite were tried at constant current density (Table V and Fig. 3). It was found that copper was superior to both lead and graphite. Platinum was found to be unsuited for electropolymerization of HEMA under the set conditions, because of the formation of coating of polymer product on the surface of the electrode materials.

### Polymerization in Different Solvent Medium

Percentage yields were different in DMF, dimethylsulfoxide, methanol, and ethanol. This is in accordance with the findings of previous workers.<sup>32,33</sup> But the molecular weight of the polymer products obtained in different solvent media were more or less the same (Table VI and 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. Electrolysis of the formulation containing a solvent mixture of 60% DMF and 2% carbon tetrachloride gave the polymer product with considerably smaller yield and low molecular weight, probably due to enhanced ter-

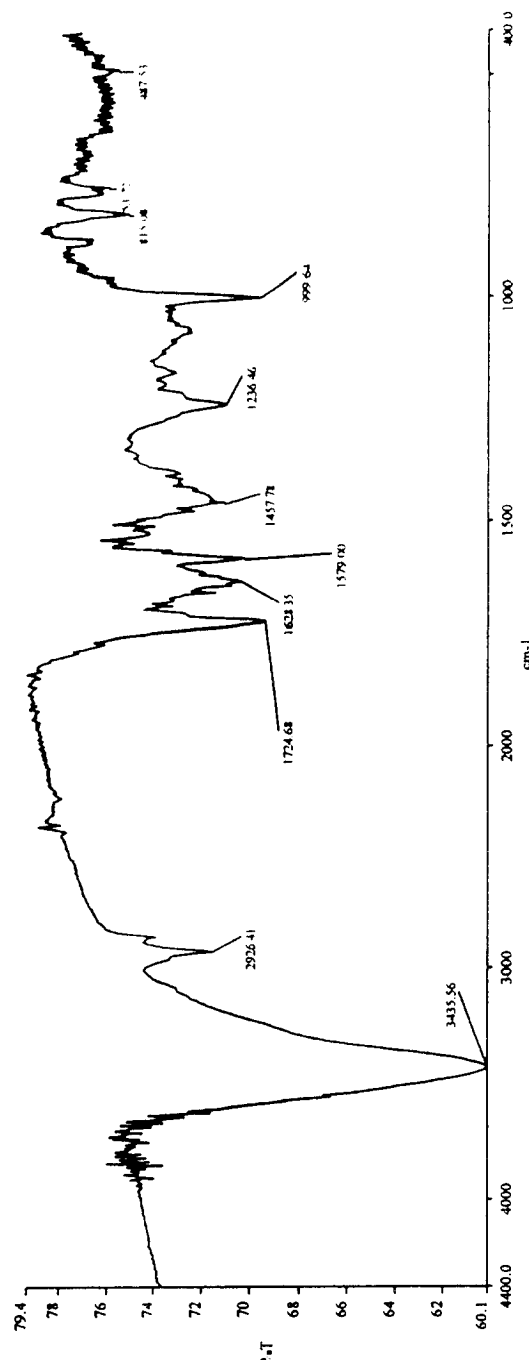
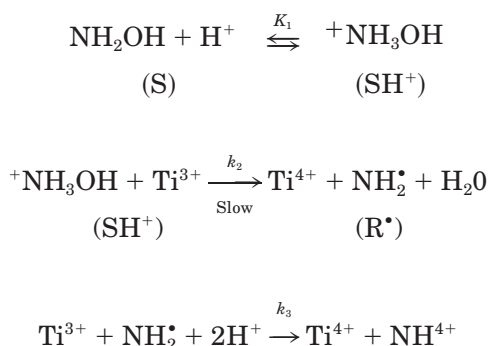


Figure 6 Infrared spectrum of the polymer product.

mination by chain transfer mode. The presence of chloride residue in the polymer product was confirmed by the elemental analysis using concentrated solution of the sodium fusion extracts of the sample.

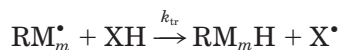
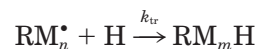
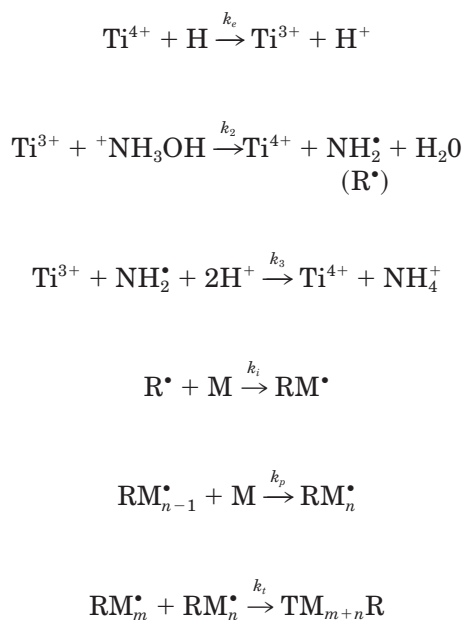
### Kinetic Scheme

In the absence of any monomer in the system, the titanium(III) reduction of hydroxylamine sulfate follows the scheme



where  $K_1$ ,  $k_2$ , and  $k_3$  are the equilibrium and rate constants, respectively.

The polymerization kinetic scheme, which accounts for the observed fractional order dependence each on  $[\text{NH}_2\text{OH}]$ , current, and  $[\text{H}^+]$  and 1.43 order dependence on monomer  $[\text{M}]$  in this electropolymerization can be represented as follows:



Here "M" is the monomer, HEMA;  $k_e$ ,  $k_i$ ,  $k_p$ ,  $k_t$ , and  $k_{tr}$  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:

$$R_i = k_i[\text{R}^\bullet][\text{M}] \quad (1)$$

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

$$\begin{aligned} d[\text{R}^\bullet]/dt &= k_2[\text{Ti}^{3+}][\text{SH}^+] - k_3[\text{R}][\text{Ti}^{3+}][\text{H}^+] \\ &\quad - k_i[\text{R}^\bullet][\text{M}] = 0 \quad (2) \end{aligned}$$

Then, based on the above equations, the rate of polymerization when the termination takes place by coupling mode can be given by

$$R_p = k_p \left[ \frac{fk_2k_e k_i[\text{I}][\text{SH}^+][\text{M}]}{k_i\{fk_3k_e[\text{I}][\text{H}^+] + k_i[\text{M}]\}} \right]^{1/2} [\text{M}]^{3/2} \quad (3)$$

where  $[\text{I}]$  is the current in farady per unit volume and  $f$  is the factor representing the fraction of the current that initiates chains.

Rate of polymerization when the termination takes place by chain transfer mode would be

$$R_p = \frac{k_p}{k_{tr}} \frac{fK_1k_2k_e k_i[\text{I}][\text{S}][\text{H}^+][\text{M}]^2}{[\text{XH}]\{fk_3k_e[\text{I}][\text{H}^+] + k_i[\text{M}]\}} \quad (4)$$

(The details of the derivation is depicted in the Appendix).

The dependence of the initial rate of polymerization  $R_p$  on  $[\text{I}]^{0.68}$ ,  $[\text{NH}_2\text{OH}]^{0.57}$ ,  $[\text{H}^+]^{0.6}$ , and  $[\text{M}]^{1.43}$ , which were experimentally observed, are consistent with the combined form of rate eqs. (3) and (4).

### CONCLUSION

Electrolytically generated reactive species  $\text{Ti}^{3+}$  reacts with the chemical initiator, hydroxylamine, present in the bulk of the solution to produce free radicals. Chain termination of the poly-



mer 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 chemical method. Thus titanium(III)-mediated electropolymerization offers a safe and simple technique for the synthesis of high molecular weight polymers in higher yield. Moreover, the 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.

One of the authors (KP) thanks the Kuvempu University authorities for awarding a fellowship.

## APPENDIX

The rate of initiation:

$$R_i = k_i[R^*][M] \quad (5)$$

Applying steady state approximation for the concentration of intermediate radical  $R^*$ ,

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

$$[R^*] = \frac{k_2[Ti^{3+}][SH^+]}{\{k_3[Ti^{3+}][H^+] + k_i[M]\}} \quad (6)$$

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

$$[R^*] = \frac{f k_e k_1 k_2 [I][SH^+]}{\{f k_3 k_e [I][H^+] + k_i[M]\}} \quad (7)$$

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

Substituting for  $[R^*]$  in eq. (5) leads to

$$R_i = \frac{f k_2 k_e k_i [I][SH^+][M]}{f k_3 k_e [I][H^+] + k_i[M]} \quad (8)$$

The rate of polymerization when the termination takes place by coupling mode can be given by

$$R_t = k_t[RM^*]^2 \quad (9)$$

Under steady state condition,

$$R_i = R_t \quad (10)$$

Substituting the value of  $R_i$  and  $R_t$  in eq. (12) and rearranging,

$$[M^*] = \left[ \frac{f k_2 k_e k_i [I][SH^+][M]}{k_t \{f k_3 k_e [I][H^+] + k_i[M]\}} \right]^{1/2} \quad (11)$$

The rate of polymerization is given by

$$R_p = k_p[M^*][M] \quad (12)$$

Substituting for  $[M^*]$  and writing  $[SH^+]$  equals  $K_1 [S] [H^+]$ :

$$R_p = k_p \left[ \frac{f k_2 k_e k_i [I][SH^+][M]}{k_t \{f k_3 k_e [I][H^+] + k_i[M]\}} \right]^{1/2} [M]^{3/2} \quad (13)$$

The rate of polymerization when the termination takes place by chain transfer mode would be given by

$$R_i = R_{tr} \quad (14)$$

Substituting the value of  $R_i$  and  $R_{tr}$  in eq. (14), we get

$$\frac{f k_2 k_e k_i [I][SH^+][M]}{k_t \{f k_3 k_e [I][H^+] + k_i[M]\}} = k_{tr}[M^*][XH] \quad (15)$$

Rearranging:

$$[M^*] = \frac{f k_2 k_e k_i [I][SH^+][M]}{k_{tr} \{f k_3 k_e [I][H^+] + k_i[M]\} [XH]} \quad (16)$$

Now the rate of polymerization by substituting the value of  $[M^*]$  in eq. (12):

$$R_p = \frac{k_p}{k_{tr}} \frac{f K_1 k_2 k_e k_i [I][S][H^+][M]^2}{[XH] \{f k_3 k_e [I][H^+] + k_i[M]\}} \quad (17)$$

The dependence of the initial rate of polymerization  $R_p$  on  $[I]$ ,  $[NH_2OH]$ ,  $[H^+]$ , and  $[M]$  were experimentally observed, and are consistent with the combined form of rate equations (13) and (16).

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