

Electroinitiated polymerization of glycidyl methacrylate in dimethylformamide medium

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The electroinitiated polymerization of glycidyl methacrylate has been studied in dimethylformamide medium using mostly anhydrous ferric sulphate as the electrolyte. A linear structure for the electropolymer has been proposed on the basis of the results of its solubility in various organic solvents and its infra-red and nuclear magnetic resonance spectra. The thermal study of the electropolymer has also been carried out. The effects of various reaction parameters, such as duration of the electrolysis, current strength, concentrations of both monomer and electrolyte, and temperature of the reaction solution, on the yield of the electropolymer have been studied in detail. A radical mechanism has been proposed for the formation of the electropolymer.

(Keywords: electropolymerization; electroinitiated polymerization; glycidyl methacrylate; electropolymer; thermal stability; linear poly(glycidyl methacrylate))

INTRODUCTION

In recent years, the homopolymer of glycidyl methacrylate (GMA) has found much importance due to its use as a negative electron resist^{1,2}. There have been several reports on the synthesis of poly(glycidyl methacrylate) (PGMA) using radical initiators^{3,4} or γ -radiation⁵ but, except for a single study⁶ which mentions its deposition electrochemically on carbon fibres, there has hardly been any attempt to synthesize the polymer electrochemically. The present investigation deals with a detailed study of the electroinitiated polymerization of GMA in dimethylformamide (DMF) medium using mostly ferric sulphate as the electrolyte.

EXPERIMENTAL

Materials

Dimethylformamide (E. Merck, LR) was purified by following the procedure described by Nayak *et al.*⁷. GMA (Fluka AG) was distilled under reduced pressure and the middle fraction boiling at 348 K and 1.333 kPa was used. 1,4-Dioxane was dried over sodium and purified following the procedure of Kálal *et al.*⁴.

Anhydrous ferric sulphate (SBP, LR), anhydrous ferric chloride (BDH, LR), zinc acetate (E. Merck, Pro-analysis), zinc chloride (TB & Co., London), tetrabutylammonium perchlorate (TBAP) (Fluka) and tetrabutylammonium tetrafluoroborate (TBAFB) (Fluka) were used without further purification.

Cells and electrodes

The electrochemical polymerizations were carried out mostly in a single-compartment electrolysis reaction cell without any separation between the cathode and anode compartments. For reactions that required the cathode and anode sections to be analysed individually, a split cell, whose compartments were separated by a sintered

glass disc of fine porosity, was employed. One of the compartments of the cell was fitted with inlet and outlet tubes for the passage of N₂. In both cases, 1 cm² platinum foils were used as electrodes.

Polymerization procedure

All experiments were conducted at 303.15 K with stirring of the cell contents except as otherwise indicated. The temperature was maintained constant by means of a water bath and the assembly consisting of the cell and the water bath was mounted on a magnetic stirrer to provide adequate stirring of the solution whenever required during electrolysis. A variable direct-current power supply (Aplab, model 7331) with provisions for the measurement of current and voltage drop through the cell was used to provide the required direct current.

After filling the cell with the solution containing the required amount of monomer and electrolyte in pure DMF, dry nitrogen gas was bubbled through the cell for 30 min prior to electrolysis.

Analysis

Polymer yields were determined gravimetrically after precipitation with a large excess of ice-cold methanol and subsequent drying under vacuum to constant weight. The polymers were characterized from their i.r. and n.m.r. spectra. A Perkin-Elmer 578 spectrophotometer and a Varian EM 390, 90 MHz spectrophotometer were used for the i.r. and ¹H n.m.r. spectra respectively. Elemental analysis indicated the presence of only C, H and O in the polymer. The epoxide content of the polymer was determined by hydrochlorinating the polymer in dioxane medium with HCl and then back-titrating the excess acid with methanolic NaOH⁸. The viscosity-average molecular weight of the polymer samples was determined in 1,4-dioxane at 298 K using the equation⁴:

$$[\eta] = 8.32 \times 10^{-3} \bar{M}_v^{0.67} \quad (1)$$

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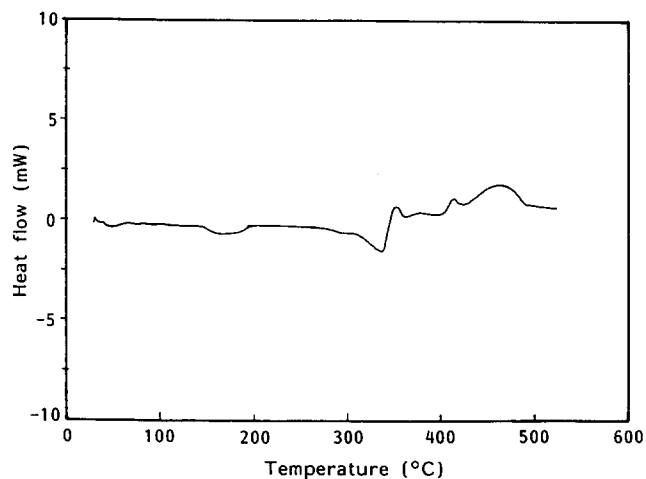


Figure 1 A differential scanning calorimetry curve of PGMA

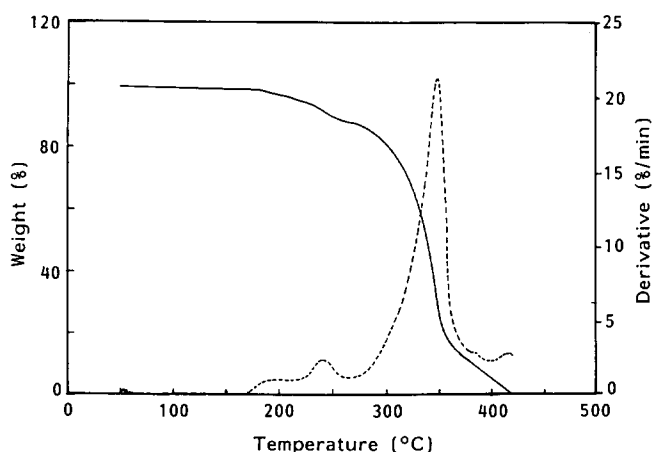


Figure 2 Thermogravimetric (—) and differential thermogravimetric (---) profiles for PGMA

Differential scanning calorimetry

Transition temperatures were determined using a Du Pont 990/910 differential scanning calorimeter at a heating rate of 10 K min^{-1} under nitrogen atmosphere (sample weight 5.0 mg).

Thermogravimetry and differential thermogravimetry

Thermal stability of the polymer samples was assessed by thermogravimetric analysis (Du Pont 990/951) carried out under nitrogen at a heating rate of 10 K min^{-1} .

X-ray diffraction

X-ray diffractograms of the powdered polymer samples were recorded with a Phillips 1316/90 diffractometer using Zr-filtered Mo K_α radiation.

Hot-stage microscopy

Optical microscopic observations were carried out with a Censico 4697 microscope equipped with a hot plate.

RESULTS

Preliminary experiments showed that a flow of electrolytic current was necessary to initiate the polymerization reaction. In the case of split-cell

experiments, polymerization occurred only in the cathode compartment.

The polymers obtained were amorphous (X-ray diffraction showed no peak), non-hygroscopic and white in colour. These were readily soluble in DMF, chloroform, acetone, tetrahydrofuran, acetonitrile and dioxane, suggesting that no crosslinking reaction occurred during polymerization.

The epoxide contents of the polymer samples obtained under certain trial experiments were found to be around 96%. This suggests that almost all the cyclic structures in the pendant groups in GMA remain unaffected during polymerization.

The PGMA obtained was confirmed from its i.r. and ^1H n.m.r. spectral data as these were identical with those reported by Iwakura *et al.*^{9,10}.

Figure 1 shows the d.s.c. curve of PGMA. The resulting curve shows three endotherms at 319 K (46°C), 441 K (168°C) and 603 K (330°C) and a number of exotherms above 616 K (343°C).

The t.g. thermogram showing the weight-loss profile of PGMA from ambient temperature to 693 K (420°C) is presented in Figure 2. The onset of the weight loss occurs at 463 K (190°C) and the maximum rate is attained at 623 K (350°C) as is shown by d.t.g. (broken curve). Virtually 100% weight loss occurs when the temperature reaches 693 K (420°C). The results obtained are in agreement with those presented in an earlier report¹¹ on the thermal stability of PGMA, prepared by thermal polymerization.

Further study under the hot-stage microscope reveals that the melting of the polymer occurs over the temperature range 413 K (140°C) to 468 K (195°C).

The polymer yield obtained depended on various factors such as current strength, concentration of the electrolyte, duration of electrolysis, monomer concentration, temperature and finally whether the cell contents were stirred or not. All the electropolymerization runs were carried out under N_2 atmosphere, as air or oxygen had a strong inhibiting effect on the polymer yield. The polymerization runs were fairly reproducible, the polymer yields varying in duplicate experiments by $\pm 5\%$.

Some of the experimental results showing the inhibiting effect of air and enhancing effect of stirring on the polymer yield are shown in Table 1.

Addition of certain electrolytes to the medium not only increased the conductance of the medium but also initiated the polymerization reaction. The results with various added electrolytes are given in Table 2. Among the electrolytes, ferric sulphate is found to be the most effective in producing polymers with higher yield.

The rate of polymer formation as a function of the ferric

Table 1 Electroinitiated polymerization of GMA under various conditions^a

Nitrogen/ air	Stirred/ unstirred	Conversion (%)	R_p^b (%/h)	Polymerization efficiency (mole of GMA polymerized/faraday)
Nitrogen	Unstirred	10.48	2.10	0.42
Nitrogen	Stirred	26.43	5.29	1.07
Air	Stirred	0	—	—

^a Feed composition (mole ratio), DMF:GMA: $\text{Fe}_2(\text{SO}_4)_3$, 73:3:0.0132; current, 10 mA; time period of electrolysis, 5 h; temperature, 303.15 K

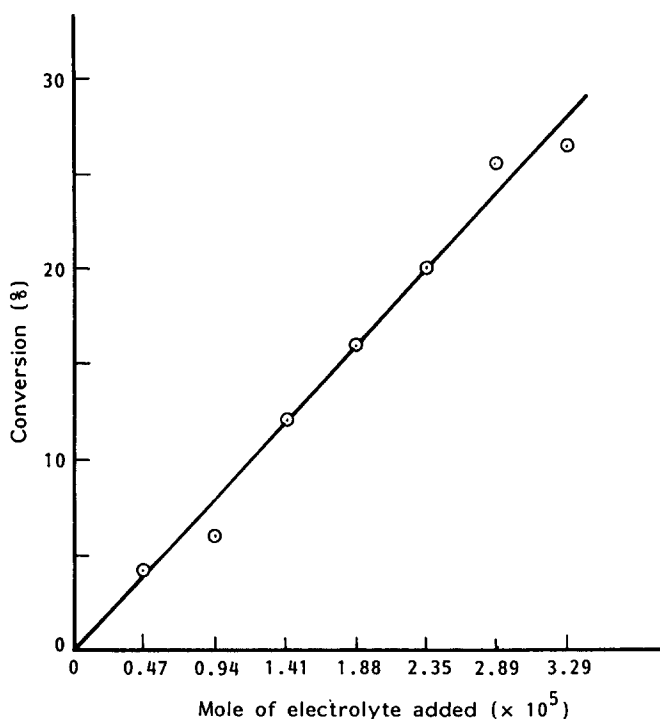
^b Rate of polymerization

Table 2 Effect of various added electrolytes on the electropolymerization of GMA in DMF medium^a

Electrolyte	Electrolyte (10 ⁻⁵ mole)	Conversion (%)	R _p ^b (%/h)	Polymerization efficiency (mole of GMA polymerized/faraday)
Zinc chloride	10.12	1.21	0.24	0.049
Zinc acetate	15.26	4.10	0.82	0.165
Ferric chloride	6.96	0.65	0.13	0.026
Ferric sulphate	3.29	26.43	5.29	1.069
TBAP	3.28	0.40	0.08	0.016
TBAFB	4.84	0.45	0.09	0.018

^a Feed composition (mole ratio), DMF:GMA, 73:3; time period of electrolysis, 5 h; current, 10 mA; temperature, 303.15 K

^b Rate of polymerization

**Figure 3** Polymer formation as a function of the quantity of electrolyte added. Feed composition (mole ratio), DMF:GMA, 73:3; time period of electrolysis, 5 h; temperature, 303.15 K; current, 10 mA

sulphate concentration is shown in *Figure 3*. It is observed that the percentage of conversion of monomer to polymer bears a linear relationship to the electrolyte concentration over the entire concentration range of the latter.

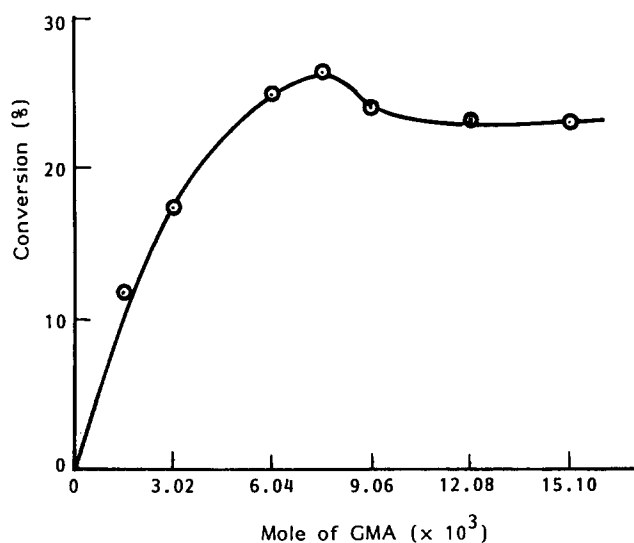
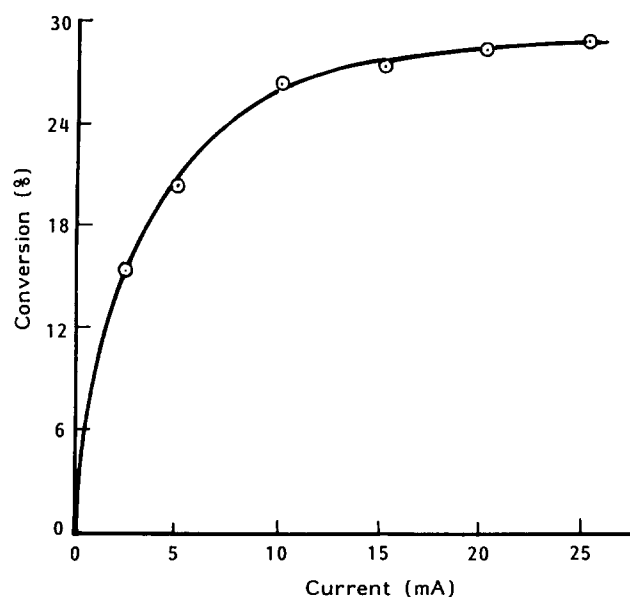
The polymer yield as a function of monomer concentration is shown in *Figure 4*. It is found that at a lower concentration of monomer, the rate of polymerization increases at first, reaches a maximum and then decreases gradually more or less to a constant value. This observation is similar to that found in the case of electropolymerization of acrylamide in the acetonitrile medium as has been reported earlier⁷.

The effect of the magnitude of electrolytic current on polymer formation as observed over a fixed period of electrolysis is shown in *Figure 5*. It is to be noted that, at the lower current range, the polymer yield is proportional to the current, but at higher currents, it is insensitive to the current. This observation is similar to that observed by earlier workers¹².

The dependence of the polymer yield on the time period of electrolysis, at three different current values, is shown in *Figure 6*. There is a general increase of polymer yield with the time period of electrolysis but at the lower value of the current, i.e. 2.5 mA, an initial induction period is noticed.

Table 3 shows the effect of current and time period of electrolysis on the intrinsic viscosity as well as molecular weight of the polymer. It is found that the molecular weight of the polymer decreases with increasing value of the electrolytic current as well as the time period of electrolysis.

From the plots in *Figure 6*, the initial rate of polymerization (R_p) can be calculated in principle. However, because of the occurrence of an induction period in the initial stage of polymerization under certain conditions, R_p values so obtained would not truly reflect

**Figure 4** Polymer formation as a function of the quantity of monomer added. Feed composition (mole ratio), DMF:Fe₂(SO₄)₃, 73:0.0132; time period of electrolysis, 5 h; temperature, 303.15 K; current, 10 mA**Figure 5** Polymer formation as a function of current flow. Feed composition (mole ratio), DMF:GMA:Fe₂(SO₄)₃, 73:3:0.0132; time period of electrolysis, 5 h; temperature, 303.15 K

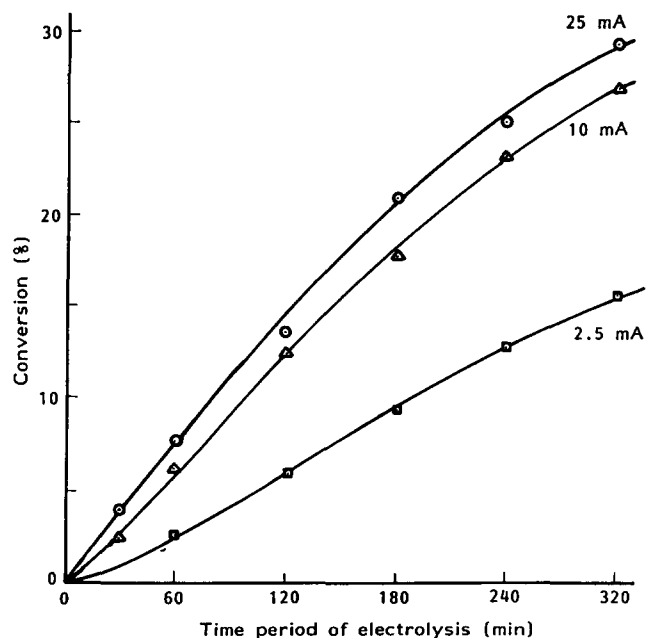


Figure 6 Polymer formation as a function of time period of electrolysis at different current flows. Feed composition (mole ratio), DMF:GMA:Fe₂(SO₄)₃, 73:3:0.0132; temperature, 303.15 K

Table 3 Effect of current and time period of electrolysis on intrinsic viscosity^a

Current, I_e (mA)	Time period of electrolysis (h)	Intrinsic viscosity, $[\eta]$ (dl g ⁻¹)	Approximate molecular weight
2.5	5	1.81	3100
10.0	5	1.58	2500
10.0	3	1.65	2700
10.0	2	1.73	2900
15.0	5	1.34	2000
15.0	3	1.40	2100
25.0	5	1.14	1600

^a Feed composition (mole ratio), DMF:GMA:Fe₂(SO₄)₃, 73:3:0.0132; temperature, 303.15 K

the uninhibited initial rate of polymerization. To minimize the error on this account, an overall R_p corresponding to a 5 h reaction period was calculated at different current values in milliamperes (I_e) and another set of R_p values were also calculated from Figure 5 based on the yield over 5 h reaction period at different values of the current. Both sets of R_p values are found to satisfy the general equation¹³:

$$R_p = k(I_e)^n + C \quad (2)$$

as shown by the linearity of the plot of $\log R_p$ vs. $\log I_e$ in Figure 7. In the present case, C may be assumed to be zero as there was no polymerization in the absence of the current. This enables the evaluation of k from the intercept of the plot $\log R_p$ vs. $\log I_e$ and the current exponent from the slope of the same plot. The values found for k and n are 2.59%/h and 0.27 respectively.

The dependence of the percentage of conversion of the monomer to the polymer on the total charge transferred through the solution based on two different sets of experiments described earlier, i.e. (a) by varying the current while fixing the time period of electrolysis constant and (b) by varying the duration of electrolysis at

fixed values of the current, is shown in Figure 8. Although the points in Figure 8 show some scatter, there is still a distinct trend, which is more or less similar to the one observed in Figure 5.

As expected, the increase of temperature produces an enhancing effect on the yield of the electropolymer. From the Arrhenius plot, the activation energy for the electropolymerization is determined to be 29.89 kJ mol⁻¹.

The electropolymerization process is accompanied by a post-electrolysis polymerization effect, which is shown in Table 4.

DISCUSSION

The foregoing results show that it is possible to electropolymerize PGMA under certain experimental

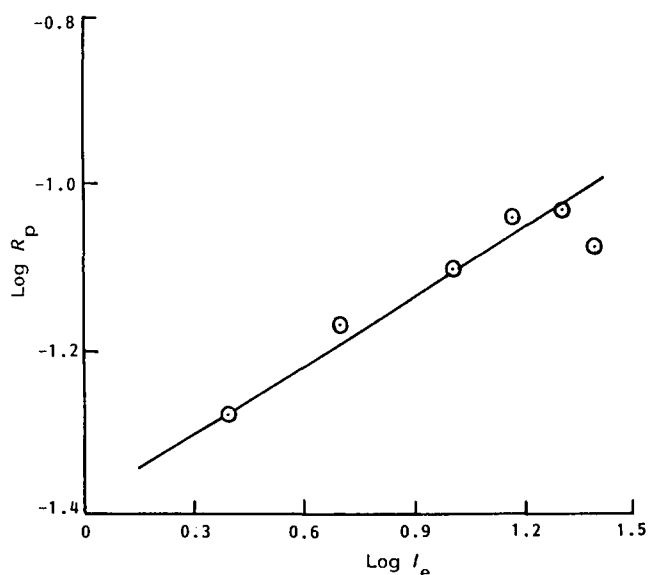


Figure 7 Determination of the current exponent in the rate equation, $R_p = k(I_e)^n + C$

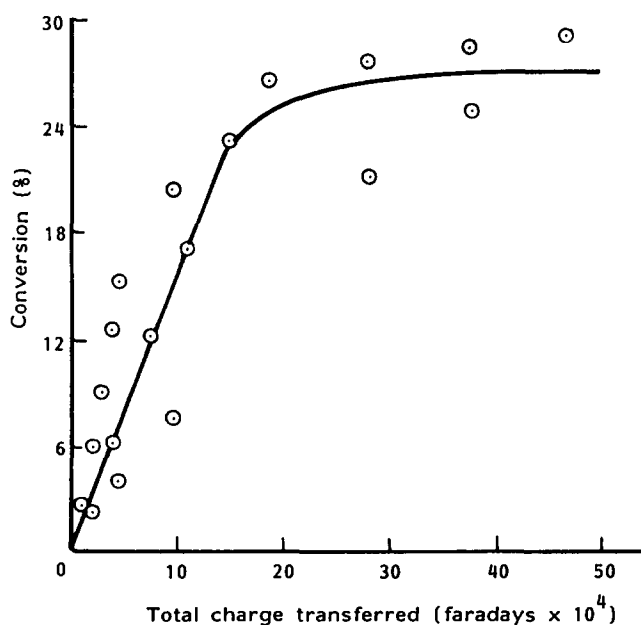


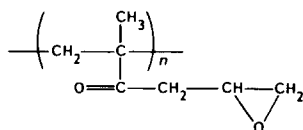
Figure 8 Polymer formation as a function of the total charge transferred into the system. Feed composition (mole ratio), DMF:GMA:Fe₂(SO₄)₃, 73:3:0.0132; temperature, 303.15 K

Table 4 Post-electrolysis polymerization effect on the electro-polymerization of GMA^a

Time of current flow (h)	Time allowed for polymerization in absence of current flow (h)	Conversion (%)
0.5	0.0	4.13
0.5	4.0	7.20
1.0	0.0	7.55
1.0	2.0	13.22
1.0	4.0	12.75
1.0	10.0	13.33

^a Feed composition (mole ratio), DMF:GMA:Fe₂(SO₄)₃, 73:3:0.0132; current, 25 mA; temperature, 303.15 K

conditions. The i.r. and ¹H n.m.r. spectra of the polymer along with quantitative determination of the epoxy content in the polymer clearly suggest a linear structure with the pendant epoxy group all along the polymer chain, i.e.:

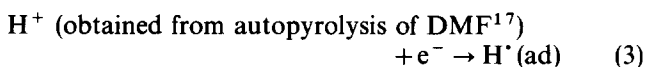


The solubility behaviour of the polymer also confirms a linear structure.

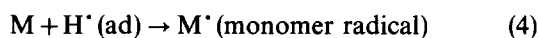
The thermal behaviour of the polymer as revealed from both d.s.c. and t.g. may be explained as follows. In the d.s.c. curve (Figure 1) the first endotherm at 319 K (46°C) corresponds to its glass transition temperature, which is in good agreement with the reported value¹⁴. The second endotherm over the temperature range 416 K (143°C) to 463 K (190°C) is clearly due to melting as it is confirmed by hot-stage optical microscopic study. The third wide endotherm, with its minimum at 603 K (303°C) and also coinciding with the major weight loss in the t.g. curve, is believed to be associated with the decomposition of the polymer into monomer units and other products similar to methacrylate polymers^{15,16}. The exothermic peaks beyond 616 K (343°C) may be attributed to the oxidation of the decomposition products of the polymer.

From the results of the split-cell experiments, the locus of the polymerization was found to be the cathode compartment, which is suggestive of an anionic or radical mechanism. The fact that the presence of hydroquinone as well as air exhibits a drastic inhibiting effect points to the operation of a radical mechanism rather than an anionic mechanism.

Considering all these aspects, the following mechanism may be suggested for the electropolymerization reaction. The main cathodic reaction may be visualized as follows:



where H[·](ad) is an adsorbed H atom (radical) on the cathode surface:



The monomer radical thus formed migrates from the electrode surface into the bulk solution and takes part in the further propagation steps. One experimental piece of evidence in favour of this suggestion is that a small amount of hydrogen is actually evolved at the cathode during the electropolymerization reaction and the mechanism is also supported by the earlier work by Parravano¹⁸ on electroinitiated polymerization of methyl methacrylate in acid aqueous solution.

The role of Fe³⁺ seems to be to stabilize the radical formed at the electrode surface through a mechanism similar to that postulated by Yoshizawa *et al.*¹⁹ for the polymerization of acrylamide by Kolbe's electrolysis. This prevents the recombination of the radicals formed at the electrode and helps them to diffuse from the reaction area just next to the electrode surface into the bulk, where the propagation reaction continues.

The mechanism postulated above can satisfactorily explain most of the experimental findings such as the post-electrolysis polymerization effect and the insensitivity of the polymer yield to current at higher values of the latter. In this case, with the increase of current, the concentration of H[·] formed due to the cathodic reaction (3), as expected, will increase, and this will facilitate the formation of M[·] and subsequent polymerization. However, at still higher currents, the H[·] concentration becomes sufficient to make the termination step more predominant. This is further supported by the results of the molecular-weight data (Table 3), which show that, with increase of current, the molecular weight decreases.

The mechanism also explains the increase in the polymer yield with the increase in ferric sulphate concentration at a fixed value of the current. With the rise in Fe³⁺ concentration, the increase in polymer yield is due to the increase in the number of stabilized initiating species in the medium.

The increase in the polymer yield with the increase in the monomer concentration at lower values of the latter is due to the increase in the number of initiating species in the reaction medium. But at higher concentration of the monomer, the stability of M[·] gets partially affected as free monomer molecules also compete with M[·] to form charge transfer complexes with Fe³⁺ ions. This leads to the lowering of the concentration of M[·] on account of their increased recombination.

The increase in the polymer yield with the time period of electrolysis can be attributed to the increase in the concentration of growing radicals with continued electrolysis. This is further reflected in the decrease of the molecular weight of the polymer with the time period of electrolysis. However, a small induction period noticed at lower current, i.e. 2.5 mA, may be due to the presence of adventitious moisture which has a deleterious effect on the polymerization process proceeding through a radical mechanism on account of electrochemical generation of oxygen at the anode.

The enhancement in the polymer yield due to stirring may be due to the rapid diffusion of the M[·] into the bulk of the solution and quick diffusion of Fe³⁺ ions from the bulk solution to the electrode surface to stabilize the monomer radicals formed by reaction (3).

The lower value of the current exponent, i.e. 0.27, clearly shows that the current efficiency of the process is rather low. This may be due to the partial recombination of H atoms as well as some free radicals giving rise to either molecular hydrogen or oligomers. Other parallel electrode reactions such as the reduction of Fe³⁺ to Fe, for which there is experimental evidence, may also partly account for the current flow.

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