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Electroinitiated polymerization of methyl methacrylate in two phase media

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The electroinitiated polymerization of methyl methacrylate has been carried out in an intimately mixed two phase medium consisting of a polar solvent containing some added electrolytes and a non-polar phase containing the monomer. Formamide has been used as the solvent for the polar phase and methyl methacrylate either alone or in solution in benzene or toluene has been used as the non-polar phase. Ferric salts are found to catalyse the electropolymerization process; using ferric sulphate as the electrolyte, polymers having molecular weights in the range, $1–2 \times 10^6$ have been obtained, with the highest R_p of 7.3% per hour and the highest polymerization efficiency of 30.37 mol F^{-1}. A radical mechanism is suggested for the process based on the experimental results.

1. Introduction

There have been several reports [1–20] on the electroinitiated polymerization of methyl methacrylate (MMA) ever since the first such study made by Wilson *et al.* [1]. In almost all of these studies, the electrolysis has been carried out using a single homogeneous phase consisting of the monomer, solvent and added electrolyte(s). The choice of solvent is often difficult or critical since a non-polar solvent facilitates the dissolution of the polymer formed and thus keeps the electrode surface free of any polymer coating but produces solutions which are poorly conducting. On the other hand a polar liquid may be a solvent for the monomer but not for the polymer and consequently blocking of the electrodes occurs.

These difficulties could possibly be avoided if the electropolymerization was carried out in a two phase system consisting of a polar liquid containing the added electrolyte(s) and a non-polar phase which may either be the bulk monomer itself or its solution in a non-polar liquid. It was visualized that the polar phase being more conducting would allow the passage of sufficient current and serve chiefly as the medium for electrolysis, while the non-polar phase containing the bulk of the monomer will eventually trap most of the radicals and radical ions formed at the electrodes and act as the medium for polymerization. To facilitate transfer of the radicals formed in the polar phase to the non-polar phase, it was considered necessary to keep the two phases in intimate contact with each other by stirring.

Formamide, which has a high dielectric constant (109.5 at 298.15 K) [21] and has never been used as a solvent for electropolymerization studies, was thought likely to be a good solvent to use as the polar phase. Further, the solvent is known to be easily deoxygenated [22], which provides an added advantage for this type of study. With these considerations in mind, an attempt has been made to polymerize MMA following this novel two phase technique.

In this medium, the efficiency of several electrolytes including the acetates of sodium, potassium and zinc, and of various iron (III) compounds have been examined. Two insoluble iron (III) compounds, namely, ferric oxide and basic ferric acetate have also been tested for possible catalytic activities.

2. Experimental procedure

Formamide (BDH, LR) was purified by following the procedure described by Nayak *et al.* [23]. The physical constants of the final product (bp 275.55–275.65 K, specific conductance 3.2 ×

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$10^{-5}\ \Omega\ cm^{-1}$, density 1.13 gm cm^{-3} at 298.15 K) were in excellent agreement with the values reported in the literature. The solvent was made free from dissolved oxygen by passing purified and dried nitrogen gas through it for one hour and it was stored in an air-tight bottle at a temperature below 283.15 K.

Methyl methacrylate was freed from the inhibitor after washing with 10% sodium hydroxide solution several times. It was washed with distilled water until free from alkali, and then dried over fused calcium chloride (BDH). It was subsequently distilled under reduced pressure and stored below 283.15 K. Styrene was also purified by a similar procedure and stored below 283.15 K after distillation.

Anhydrous ferric sulphate (SBP, LR), anhydrous ferric chloride (BDH, LR), ferric oxide (Reachim, pure for analysis), zinc acetate (E. Merck, proanalysis), potassium acetate (BDH, AR), sodium acetate (BDH, AR), toluene (BDH, AR) and benzene (BDH, AR) were used without further purification. Basic ferric acetate was prepared by the recommended procedure [24].

Generally a single compartment electrolysis/reaction cell was used to carry out the electrochemical polymerization. The cell was provided with arrangements for bubbling pure and dried nitrogen through the cell and for withdrawing samples from it. The platinum electrodes ($1 \times 1.5\ cm^2$) were set 2.5 cm apart in the cell.

Electrolysis was carried out at constant temperatures in a water bath and the assembly consisting of the cell and the water bath were mounted on a magnetic stirrer to provide adequate stirring of the solutions in order to bring the two phases into intimate contact during electrolysis.

The electrolyses were controlled with a variable direct current power supply unit (Aplab, model 7331) with provisions for the measurement of current and voltage drop through the cell.

After filling the cell with the polar phase ($12\ cm^3$), with or without the electrolytes or the insoluble ferric compounds which together formed the lower layer, and then the monomer or its solution ($12\ cm^3$) which formed the upper layer, nitrogen gas was bubbled through the cell for 30 min prior to electrolysis. Electrolysis was carried out in both stirred and unstirred mixtures and whenever metallic depositions were observed on the cathode, the polarity of the electrodes was reversed at intervals of one hour to minimize such deposition.

At the end of the electrolysis, the two phases were allowed to separate out by discontinuing the mechanical agitation and the upper layer in which the polymer had accumulated was examined for its polymer contents by precipitation with a large excess of acidified methanol and subsequent drying of the polymer. Viscosity-averaged molecular weights, $\bar{M}_v$ of the polymer were determined in benzene using the relation [25]

$$[\eta] = 0.94 \times 10^{-4} M_v^{0.76}$$

3. Results

When formamide and MMA are fixed in equal volumes at room temperature (304.15 K), two layers are formed of which the upper one (A) is richer in MMA (it contains 91.02% of MMA by weight) and the lower layer (B) is richer in formamide (it contains 79.6% of formamide by weight). Adequate stirring however produces a heterogeneous medium (C) where the two phases are quite intimately mixed. Under identical conditions the conductance of the stirred bisphasic system C is found to be much higher than that of the non-polar phase A and only somewhat less than that of B, which as expected, had the highest conductance. For example at 304.15 K the specific conductance of A, B and C were 1.23415×10^{-6}, 3.63389×10^{-5}, $2.53687 \times 10^{-5}\ \Omega\ cm^{-1}$ respectively.

Preliminary experiments showed that electrolysis carried out in C only without any added electrolyte produces polymerization of MMA, but only to a small extent over a period of three hours. The polymer obtained is of low molecular weight and its yield depends on various factors such as the magnitude of the current flow, temperature, presence or absence of air in the system and whether the cell contents are stirred or not. Some of the results are summarized in Table 1. It is to be noted from these results that flow of current was necessary to initiate polymerization and the polymer yield was somewhat dependent on the magnitude of the current flow. Removal of air from the system (replaced by nigrogen gas) was found to increase the polymer yield while stirring

Table 1. Exploratory studies on electroinitiated polymerization of MMA under various conditions in the absence of any added electrolytes. Feed composition (mole ratio), formamide:MMA, 13:5, time of electrolysis, 3 h

Current (mA)	*Temperature* (K)	*Gas*	*Stirred/unstirred*	*Percentage of conversion*	*Polymerization efficiency. Moles MMA polymerized per faraday*	$\bar{M}_V \times 10^{-3}$
5	318.15	Nitrogen	Stirred	Traces	–	–
15	318.15	Nitrogen	Stirred	3	1.418	49.6
15	303.15	Nitrogen	Stirred	1.5	0.709	48.75
15	318.15	Air	Stirred	Nil	–	–
15	318.15	Air	Unstirred	0.32	0.152	–
15	318.15	Nitrogen	Unstirred	6.4	3.08	142.8

tended to lower it. Increase of temperature, however, had a beneficial effect on the yield.

Addition of certain electrolytes into the medium not only increased the conductance of the medium, but also increased the polymer yield over the same electrolysis period. Table 2 gives the results found with several electrolytes of which ferric salts were found to be the most effective in producing polymers not only in higher yield but also of high molecular weights. Insoluble ferric compounds like ferric oxide or basic ferric acetate had no significant catalytic effect on the polymerization process. Consequently in subsequent experiments one of the soluble ferric salts, namely, ferric sulphate was used as the electrolyte. Ferric chloride produced slight thermal polymerization under some experimental conditions. For a similar reason a lower temperature around 318.15 K was fixed for most of the experimental runs under electropolymerization conditions.

The polymer yield, as a function of the ferric sulphate concentration is shown in Fig. 1. It is found that the polymer yield increases with the concentration of the electrolyte up to a limiting concentration. The effect of current flow on the polymer yield at a fixed electrolyte concentration is shown in Fig. 2. Here also it is found that for a lower current range the polymer yield is proportional to current but at higher current it is insensitive to current density. Reversal of polarity of the electrodes to minimize the deposition of metallic iron had little effect on the polymer yield.

The effect of the duration of the current flow on the polymer yield obtained (a) up to the termination of the current flow and (b) over a total period of 3 h from the initiation of current flow is shown in Table 3. The results clearly show the dependence of yield on the charge passed and also a post electrolysis polymerization effect. Increasing the temperature of the reaction medium, increases the polymer yield as expected (Table 4), but the effect is small.

Substitution of formamide by water as the

Table 2. Effects of various added electrolytes on the electropolymerization of MMA. Feed composition (mole ratio), formamide:MMA, 13:5; temperature, 318.15 K; time of electrolysis, 3 h

Electrolyte	*Mole of the electrolyte used*	*Percentage of conversion*	*Polymerization efficiency. Moles MMA polymerized per faraday*	$\bar{M}_V \times 10^{-3}$
Zinc acetate	4.2×10^{-3}	0.9	0.4	61.9
Potassium acetate	5.1×10^{-3}	1.9	0.9	69.1
Sodium acetate	5.5×10^{-3}	2.2	1.06	69.9
Ferric chloride	1.7×10^{-4}	16.6	7.9	184.3
Ferric sulphate	1.7×10^{-4}	17.6	8.4	178.6
Ferrous sulphate	1.5×10^{-4}	2.8	1.3	71.3
Basic ferric acetate	1.6×10^{-4}	3.1	1.5	–
Ferric oxide	1.6×10^{-4}	1.7	0.8	–

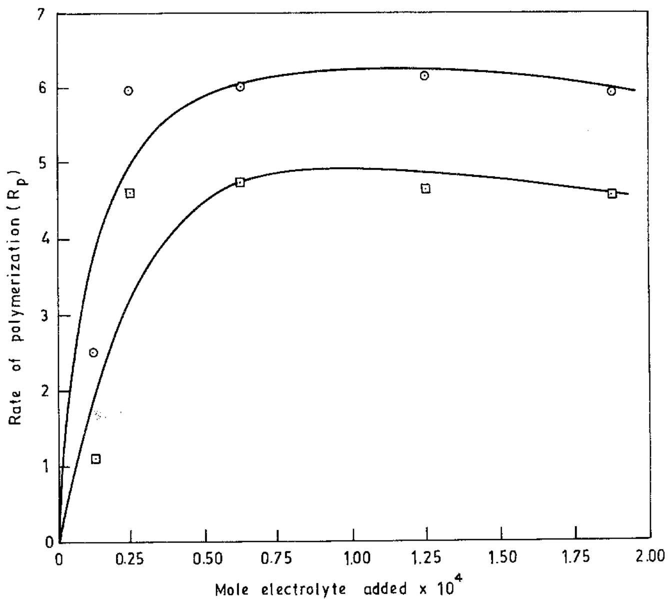

Fig. 1. Rate of polymerization as a function of the quantity of electrolyte added and current in the electroinitiation reaction. Feed composition (Molar ratio), Formamide : MMA, 13 : 5; Time of electrolysis, 3 h; Temperature, 318.15 K; ⊡, 5 mA; ⊙, 15 mA.

polar phase produced the unexpected effect of inhibiting the polymerization process whereas substitution of the MMA by a solution of the same either in benzene or toluene as the non-polar phase allowed the polymerization to occur but with lower rates, the rate with toluene however being more than that with benzene. Dilution of the non-polar phase consisting of a solution of the monomer in toluene with more toluene always led to a further decrease of the polymerization rate. These results are summarized in Table 5.

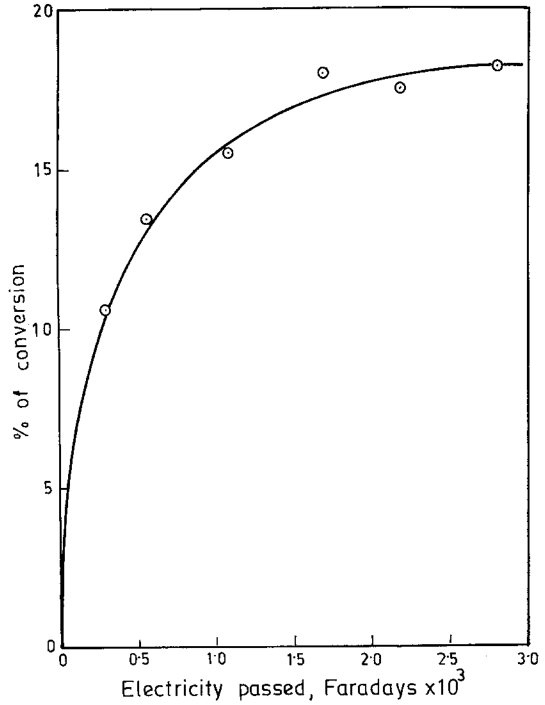

Fig. 2. Polymer formation as a function of the charge passed. Feed composition (Molar ratio), Formamide : MMA : $Fe_2(SO_4)_3$, 13 : 5 : 0.0028; Temperature, 318.15 K; Time of electrolysis, 3 h.

Replacement of MMA by styrene in the system did not lead to any polymer formation by styrene. However a mixture of styrene and MMA taken as the non-polar phase led to the formation of a copolymer in low yield. Introduction of hydroquinone, a radical quencher into the system had a drastic inhibiting effect on the polymer formation.

One significant aspect of the foregoing studies was that when the two phases were allowed to separate after the electrolysis, the non-polar phase

Table 3. Post electrolysis polymerization effect in formamide + MMA mixed biphasic medium. Feed composition (mole ratio), formamide : MMA : $Fe_2(SO_4)_3$, 13 : 5 : 0.0028; temperature, 318.15 K; current, 15 mA

Time of the current flow (min)	*Time allowed for polymerization* (min)	*Percentage of conversion*
30	30	1.9
30	180	12.3
60	60	4.5
60	180	14.7

Table 4. Effect of temperature on the electro polymerization of MMA. Mole ratio, formamide:MMA:$Fe_2(SO_4)_3$, 13:5:0.0028; time, 3 h; current, 5 mA

Temperature (K)	*Percentage of conversion*	*Polymerization efficiency*
293.15	4.89	6.98
303.15	10	14.27
308.15	11.9	17.01
313.15	13.62	19.44
318.15	14.04	20.05
323.15	15.5	22.17
328.15	15.95	22.78

carried almost the whole of the polymer with it while the polar phase, the whole of the electrolyte.

4. Discussion

From the foregoing results it appears that two phase systems of the type used here are more suitable for electroinitiated polymerization studies of MMA than monophasic systems. The presence of the non-polar phase helps the propagation of the polymerization steps as well as the dissolution of the polymer thus keeping the electrodes free of any polymer coating. The presence of the polar phase together with the dissolved electrolyte increases the conductance of the medium significantly.

The fact that polymerizations occurred preferentially in the vicinity of the cathode rather than the anode as was confirmed in divided cell experiments, and experiments with unstirred solutions, is suggestive of an anionic mechanism [17]. However such a mechanism cannot explain the inhibiting effect of hydroquinone or that resulting from the presence of air in the system. Moreover at higher currents, the polymer yield was not found to be proportional to the current flow. It is therefore likely that some radical mechanism was operating in the system rather than an anionic mechanism.

The radical formation may occur through the following mechanism,

$$2HCONH_2 \rightleftharpoons HCONH_3^+ + HCONH^-$$

$$HCONH_3^+ + e\ (\text{at cathode}) \rightarrow HCONH_2 + H^{\cdot}(\text{ad})$$

$$M + H^{\cdot} \rightarrow M^{\cdot}(\text{monomer radical})$$

The monomer radical thus formed diffuses to the non-polar phase to initiate the polymerization. One piece of experimental evidence in favour of this suggestion is that a small amount of hydrogen is actually evolved at the cathode during the electrolysis and the mechanism is also supported by the earlier work by G. Paravano *et al.* [2], on electroinitiated polymerization of MMA in acid aqueous medium.

The role of Fe^{+3} seems to be to stabilize the radical formed in the polar phase through a mechanism similar to that postulated by Yoshizawa *et al.* [26] for the polymerization of acrylamide by Kolbe's electrolysis. This prevents the recombination of the radicals prior to their diffusion into the non-polar phase which is the seat of polymerizations. This also explains why, in the

Table 5. Effect of various biphasic systems on the electropolymerization of MMA. Mole of $Fe_2(SO_4)_3$, 6.3×10^{-5}; time of electrolysis, 3 h

Biphasic system	*Mole ratio of polar solvent:Monomer: non-polar solvent*	*Temperature* (K)	*Charge passed* (F)	*Rate of polymerization,* R_p *(percentage of conversion per hour)*	*Polymerization efficiency*
Formamide + MMA	13:5:0	303.15	5.6×10^{-4}	3.33	14.27
Water + MMA	29:5:0	318.15	5.6×10^{-4}	–	–
	29:5:0	318.15	2.8×10^{-3}	–	–
Formamide + solution of MMA in benzene	13:4.4:0.52	303.15	5.6×10^{-4}	0.76	4.3
Formamide + solution of MMA in toluene	13:4.4:0.39	303.15	5.6×10^{-4}	1.7	9.44
	13:3.6:1.2	303.15	5.6×10^{-4}	1.13	5.15
	13:2.5:2.5	303.15	5.6×10^{-4}	0.56	1.72
	13:1.2:3.6	303.15	5.6×10^{-4}	0.53	0.79

absence of the electrolyte, some polymerization occurs. Although Fe^{+3} also undergoes a parallel reduction reaction at the cathode giving rise to deposition of Fe, the reaction has no bearing on the polymerization reaction.

The mechanism postulated above is compatiable with the experimental findings such as the post electrolysis polymerization and insensitivity of polymer yield to current at higher values of the current. In the latter case, diffusion of the radicals into the non-polar phase is slower than their formation rate in the polar phase and this leads to the accumulation of the radicals in the polar phase and their consequent recombination. The increase of polymer yield with temperature which tends to taper off at higher temperatures can also be explained as being due to the promotion of termination steps, in general, due to the lowering of the viscosity of the medium. The mechanism also allows the explanation of the inhibiting effect produced by water when it is used as the polar phase in the place of formamide. In the presence of water, oxygen is produced at the anode and this has its usual inhibiting effect on the polymerization reaction proceding through a radical mechanism. The lowering of the polymerization rate in the benzene or toluene solutions of MMA, when these were used as the non-polar phase, is mostly due to the dilution of the monomer. However there is no ready explanation for the fact that the polymerization rate is significantly higher in toluene solution than in benzene solutions.

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