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Redox Aqueous Polymerization of Methacrylamide Via The Sacrificial Dissolution of Cu Anode

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ABSTRACT

The electrochemical polymerization of methacrylamide at the Cu- anode in the solution of N,N- dimethylformamide containing NH4NO3 and H2O2 has been studied. The sacrificial dissolution of the Cu- anode results in the formation of Cu (I) ions which react H2O2 to keep initiating hydroxyl radical OH the concentration of which increases with increasing current density. Under such experimental conditions, the polymers of high average molecular weights (~104) were obtained.

Keywords*: Electrochemical Polymerization, Sacrificial Dissolution of Anode, Methacrylamide*

I. INTRODUCTION

The previous papers[1,2] describe the redox polymerization of acrylamide in N,N- dimethylformamide by the sacrificial dissolution of Fe metal anodes. This paper reports on the polymerization of methacrylamide in N,N-dimethylformamide by the sacrificial dissolution of Cu-anode. However, methacrylamide is less polymerizable than acrylamide due to the presence of CH_3 group but still considerable amount of polymethacrylamide was obtained in this method. The polymer thus obtained may be used as thickening, dispersing, suspending and emulsifying agent in paints, cosmetics, and medicines[3].

II. EXPERIMENT

Materials

N,N-dimethylformamide (DMF) was purified by fractional distillation. Methacrylamide (MAA), NH_4NO_3 and H_2O_2 were of analytical grade and used without further purification.

Polymerization method

When a current of 40 mA for 120 minutes at 30°C was passed through the solution containing MAA (1.692 mol.L^{-1}) and NH_4NO_3 (0.30 mol.L^{-1}) in DMF, no polymer formation took place with Cu-electrodes. However, when H_2O_2 (4.16×10^{-3} mol.L^{-1}) was added to such a solution, a viscous solution of anolyte was obtained which precipitates in acetone to get the polymer of methacrylamide. The polymer was washed with acetone and filtered. The mass of the polymer was obtained gravimetrically.

The polymer yields at different currents for 120 minutes of electrolysis at 30°C are summarized in Table 1 which showed that the increase in current level increased the polymer yield.

Table 1. Polmer yield and Average Molecular Weights for the Anodic Polymerization of Methacrylamide (MAA) (1.692 mol L^{-1}) in Dimethylformamide (DMF) solutions of NH_4NO_3(0.30 mol L^{-1}) and H_2O_2 (4.16×10^{-3} mol L^{-1}) at Cu-electrodes. Electrolysis time =120 min; Anolyte volume =12.5 mL at 30°C.

Current (mA)	Polymer Yield (%)	Mol. Wt. ($X10^{-4}$)
5	Nil	--------
10	Nil	--------
15	5.0	18.5
20	9.0	16.5
30	30.3	12.6
40	40.0	10.8
50	45.0	0.9

The polymerization was also carried out for different electrolysis time at fixed currents levels of 25 mA and 40 mA. The results are shown in Figure1 which showed that the polymer yield increased with the increase of electrolysis time.

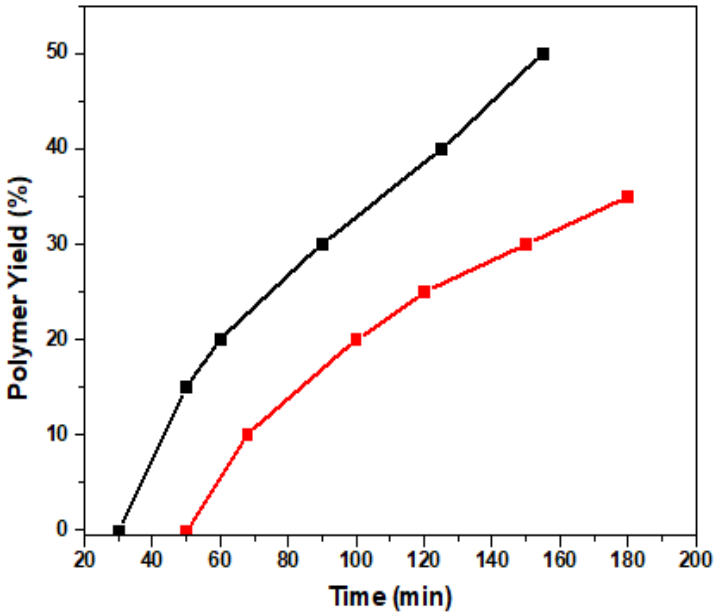

Fig 1. Time conversion curves for the anodic polymerization of MAA (1.692 mol L^{-1}) at different current levels as indicated in the curves, in DMF containing NH_4NO_3 (0.30 mol L^{-1}) at Cu-electrodes. Anolyte volume =12.5 mL at 30°C.

The polymer yields obtained with different initial monomer concentration at a fixed current of 40 mA for NH_4NO_3 (0.30 mol. L^{-1}) and H_2O_2 (4.16 $\times 10^{-3}$ mol. L^{-1}) in DMF are shown in Figure 2. The data showed that polymer yield increased with an increase of monomer concentration, when the concentrations of NH_4NO_3 and H_2O_2 were fixed.

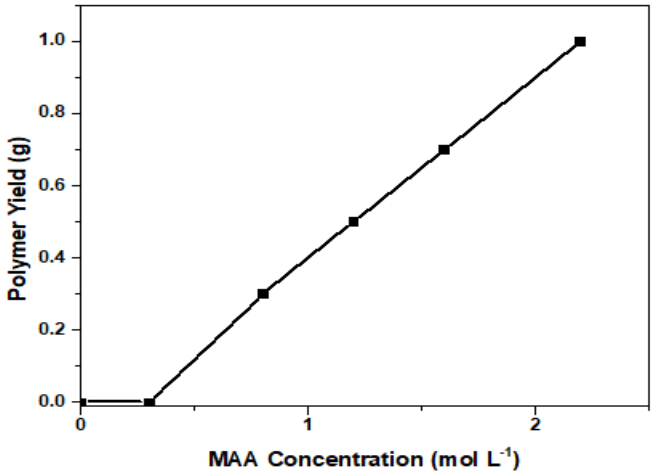

Fig 2. Plot of Polymer yield versus MAA Concentration in anodic compartment in DMF solution of NH_4NO_3 (0.30 mol. L^{-1}) and H_2O_2 (4.16×10^{-3} mol. L^{-1}) at Cu-electrodes. Current = 40 mA; Electrolysis time=120 min; Anolyte volume =12.5 mL at 30°C. In presence of 2,2-diphenyl-1-picrylhydrazyl, the polymerization of MAA was completely inhibited as shown in Table 2, indicating the likelihood of free radical mechanism.

TABLE 2. The effect of 2,2-diphenyl-1-picrylhydrazyl on anodic polymerization of methacrylamide (MAA) (1.692 mol L^{-1}) in Dimethylformamide (DMF) solutions of NH_4NO_3(0.30 mol L^{-1}) and H_2O_2 (4.16×10^{-3} mol L^{-1}) at Cu-electrodes. Current=40 mA; Electrolysis time=120 min; Anolyte vol=12.5 mL at 30°C.

Concentration of 2,2-diphenyl-1-picryl (mol.L^{-1})	Polymer Yield (%)
0.0	40.0
(0.75×10^{-3})	0.0
(1.00×10^{-3})	0.0

The effect of H_2O_2 concentration on the polymer formation was examined and found that the polymer yields initially increased and then decreased with H_2O_2 concentration, as illustrated in Figure3.

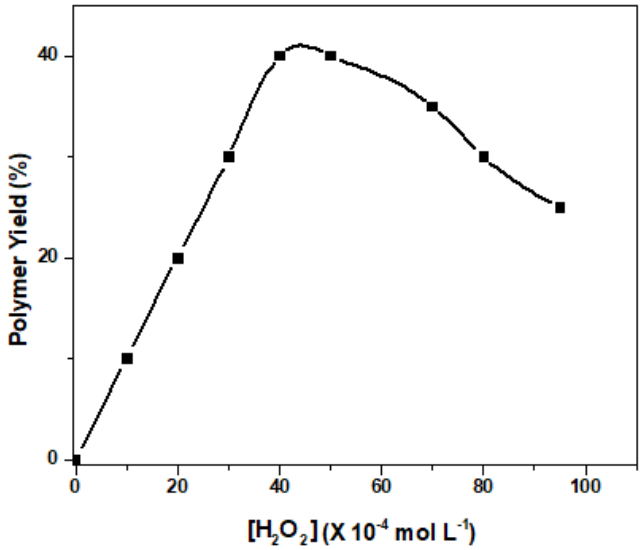

Fig 3. Plot of polymer yield versus H_2O_2 Concentration in anodic compartment in DMF solution of MAA (1.692 mol L^{-1}) and NH_4NO_3 (0.30 mol. L^{-1}) at Cu-electrodes. Current=40 mA, Electrolysis time=120 min, Anolyte volume =12.5 mL at 30°C.

It was percieved that H_2O_2 act as a retarder at a high concentration. Indeed, the complete inhibition of polymerization was observed when the concentration of H_2O_2 exceeded (4.16×10^{-3} mol. L^{-1}). H_2O_2 has propensity to give up oxygen that acts as an inhibitor when it is present in excess. The slow decomposition of H_2O_2 was brought about even by the traces of alkali released by glass[2,4].

The mechanism of electrochemical polymerization is based on the generation of Cu(I) ions by sacrificial dissolution of Cu- anode, as in case of Fe[2]. The Cu(I) ions generated in site, reacts with H_2O_2 present in the solution to yield $OH^{\bullet}$ radical which initiated the polymerization. The following reaction schemes are suggested for the polymerization process

$$Cu \longrightarrow Cu(I) + e^-$$

$$Cu(I) + H_2O_2 \longrightarrow Cu(II) + OH^- + OH^{\bullet}$$

$$OH^{\bullet} + M \xrightarrow{k_i} OHM^{\bullet}$$

$$OHM^{\bullet} + M \xrightarrow{K_p} OHMM^{\bullet}$$

Where k_i and k_p are the rate constants of the respective steps.
The final step in polymerization is termination. If termination occurs by the combination of two growing chains, i.e; coupling then it can be represented as

$$OHM_{n1}M^{\bullet} + OHM_{n2}M^{\bullet} \xrightarrow{K_t} OHM_{n1+n2+2}\ OH\ (polymer)$$

Where k_t is the rate constant for termination step.
The initiation rate is proportional to the quantity of the current in faraday per unit volume available in the electrode process i.e., $\frac{I}{FV}$ where I= constant current in ampere, V= volume of anolyte and F= faraday [6]. Therefore, the rate of initiation may be given as

$$R_i = K_i [OH^{\bullet}] [M] = K_i \frac{I}{FV} \quad -(1)$$

Similarly, the rate of propagation is given as

$$R_p = K_p [OHM^{\bullet}] [M] \quad -(2)$$

The rate of termination is given as

$$R_t = 2K_t [OHM^{\bullet}]^2 \quad -(3)$$

When steady state prevails

$$R_i = R_t$$

$$K_i \frac{I}{FV} = 2K_t [OHM^{\bullet}]^2$$

$$\therefore [OHM^{\bullet}]^2 = \left(\frac{K_i}{2Kt} \frac{I}{FV}\right)$$

$$\therefore [OHM^{\bullet}] = \left(\frac{K_i}{2Kt} \frac{I}{FV}\right)^{1/2} \quad -(4)$$

From equation (2)

$$[OHM^{\bullet}] = \frac{Rp}{Kp[M]} \quad -(5)$$

From equation (4) and (5), we can write:

$$\frac{Rp}{Kp[M]} = \left(\frac{K_i}{2Kt} \frac{I}{FV}\right)^{1/2}$$

$$\therefore R_p = K_p\left(\frac{K_i}{2Kt}\right)^{1/2}\left(\frac{I}{FV}\right)^{1/2} [M]$$

Hence, the rate of polymer formation was proportional to the square root of the impressed current in ampere and first power of the monomer concentration.

Polymethacrylamide has a wide range of applications due to its unique properties such as water solubility and high molecular weight. It is used as flocculation and coagulation agent[6]. It is also in soil erosion control[7], orthopedics[8] ophthalmology[9].

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