

ELECTROPOLYMERIZATION OF ACRYLAMIDE*M VIJAYAN and V KRISHNAN*

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Acrylamide was polymerized by electrochemical oxidation in glacial acetic acid medium containing sodium acetate. The influence of monomer concentration and current density on polymerization were examined. The polymerization is possibly initiated by the species produced by the anodic reaction of the supporting electrolyte. Introduction of hydroquinone into the system prevents the formation of polymer, indicating a free radical mechanism. Influence on the addition of ferric salt on polymerization was also examined. Molecular weight of the polymer has been examined by viscometry method. The chain structure of the polymer has been identified by IR spectrum of the polymer.

Key words: Electropolymerization, polyacrylamide, platinum anode

INTRODUCTION

Polyacrylamides are readily soluble in water making them adaptable to many processes, viz. as a flocculant in liquid-solid separation, as a chemical additive in paper-board industries, and in oil fields. Evidence from the literature [1,2] suggested the Kolbe electrolysis as a useful source of free radicals for the initiation of vinyl polymerization. It has been reported that the electrolysis of sodium acetate in acetic acid solutions of styrene produced a low molecular weight polystyrene oil [2]. However, attempts to polymerize acrylonitrile during the electrolysis of potassium laurate [3] has failed. Electroinitiated polymerization of vinyl monomers at a platinum anode has been studied using acetate as an electrolyte [4,5]. The present investigation deals with the electroinitiated polymerization of acrylamide at Pt anode using an electrolyte of sodium acetate.

EXPERIMENTAL

Anhydrous sodium acetate and acrylamides were used without further purification. Acetic acid was vacuum distilled and then used as such.

Electrolysis was carried out in a 500 ml beaker covered with a PVC cover having the provisions for the placement of electrodes, stirrer and glass tube to flush N₂ gas. Anodes and cathodes were separated by a porous diaphragm. Platinum anode having an area of 27.2 cm² and lead cathode were used. Electrolytic cell was continuously flushed with nitrogen gas throughout the duration of electrolysis. After completion of the electrolysis the polyacrylamide was isolated as white solid, by the addition of excess methanol to the electrolytic bath. To remove the solvent and the unreacted monomer, repeated washings were given with methanol and dried.

Viscosity of the polymer was determined in water by an Ubbelohde viscometer immersed in a constant temperature bath held at 303 ± 0.1K. Intrinsic viscosity was determined by the usual graphical plots. From the intrinsic viscosity the molecular weight of the polymers were determined using the relationship,

$$|\eta| = K [M]^\alpha$$

where K, and α are constants. The IR spectrum of the polymer samples were also taken.

RESULTS AND DISCUSSION

The molecular weight of the polymers obtained by the electrolysis of the solution containing sodium acetate was found to have low mol. wt. (10³) while in MeOH - sodium acetate it resulted in very high mol.wt (10⁵).

Effect of monomer concentration

At a current density of 0.2kA.m⁻², it is noted that as the monomer concentration increases, the yield of polymer also increases (Table I) due to increase in the availability of number of monomer radicals.

TABLE-I: Effect of monomer concentration on the yield of polymer
Electrolyte: 1M sodium acetate in glacial acetic acid; Current density: 0.2kA. m⁻²

Concentration of acrylamide (M)	Yield of polyacrylamide (%)
0.2	54
0.3	57
0.5	66

Effect of current density

The yield of polymer on the variation of current density at a monomer concentration of 0.2M in acetic acid is shown in Table II.

As the current density is increased, the temperature of the reaction mixture increases leading to the degradation of the polymer and hence the reduction in the yield of the polymer.

TABLE-II: Effect of current density on the yield of polyacrylamide
Electrolyte: 1M sodium acetate in glacial acetic acid; Monomer concentration: 0.2M in acetic acid

Current density KA. m ⁻²	Yield of polyacrylamide (%)
0.10	59
0.15	57
0.20	54

Influence of the solvent

Electropolymerization of acrylamide is very much influenced by the solvents. At the monomer concentration of 0.2M and current density (0.2 kA. m⁻²), the influence of solvents on the electropolymerization of acrylamide is shown in Table III.

TABLE-III: Effect of solvent on the yield of polyacrylamide

Solvent	Yield of polyacrylamide (%)	Molecular wt.
Acetic acid	54	1.3 x 10 ³
Ethylene glycol	58	—
Methanol	75	4.8 x 10 ⁵

Effect of Fe³⁺ ion

Addition of ferric sulphate into the system increases the yield of polyacrylamide. The role of Fe³⁺ ions in the polymerization reaction is to prevent the recombination of free radicals [6].

Differential thermal analysis (DTA)

The DTA curve obtained for the electrochemically prepared polyacrylamide is shown in Fig.1. From this the glass transition

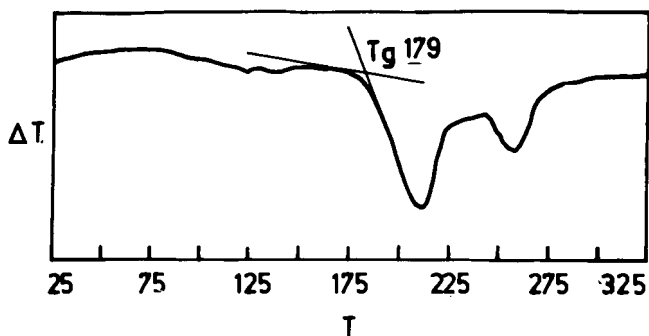


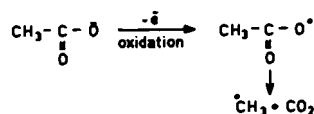
Fig.1: Differential thermal analysis of polyacrylamide

temperature (Tg) is found to be 452K, which is higher than the chemically prepared one (Tg = 426K).

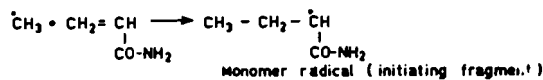
Mechanism

Free radical mechanism is supported by the fact that the addition of hydroquinone into the system inhibits the polymerization of acrylamide. Further it was reported [7] that the methyl radical is the initiating radical in the electroinitiated polymerization of acrylamide. Thus the possible mechanism can be written as follows:

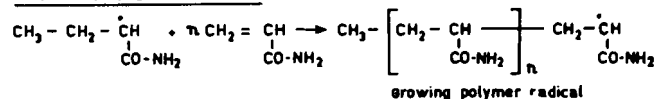
a. Electrolytic step, Kolbe electrolysis



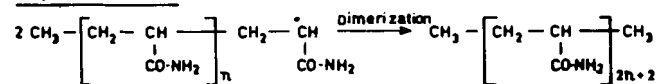
b. Initiation of monomer by methyl radical



c. Polymer propagation reaction



d. Polymer termination



The IR spectra of the synthesised polyacrylamide agreed well with that of the reported sample [8] obtained by anodic polymerisation. This IR resemblance confirms that the polymerisation is by anodic mechanism only.

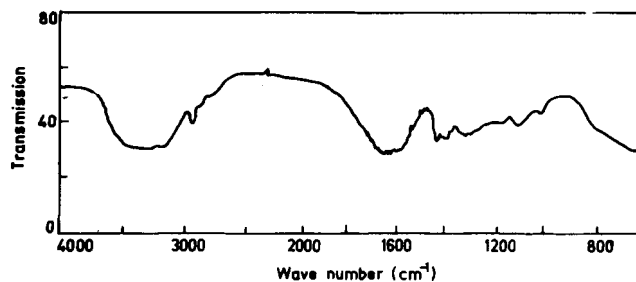


Fig.2: IR spectrum of electrochemically prepared polyacrylamide

CONCLUSION

An electrochemical synthetic route has been worked out for preparing polyacrylamide having a molecular weight of the order of 10³ in acetic acid medium and 10⁵ in methanol medium.

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