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Electrochemical Synthesis & Studies of Conducting Poly Quinoline

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The electrochemical polymerization of quinoline has been studied in acetonitrile medium using tetra-n-butyl ammonium perchlorate (TBAPC), tetraethylammonium perchlorate (TEAPC), tetraethylammonium fluoroborate (TEAFB) electrolytes. The polymer produced showed conductivity in the range of 10^{-6} to 10^{-1} Ω^{-1} cm^{-1} using the four probe technique. Polyquinoline was obtained in moderate yields with the highest Rp of 5.1354% per hr and polymerization efficiency of 51.698 mol/Faraday. The observations and experimental results suggested a free radical mechanism.

INTRODUCTION

The spin density and conductivity measurements show polyquinoline behave as a conducting polymer. In the electrochemical method of its preparation no blocking of electrodes occurs as the polyquinoline is a conducting polymer and obtained as a deposit on the anode surface.

EXPERIMENTAL

Acetonitrile (E. Merck), quinoline (E. Merck), tetrabutylammonium perchlorate (TBAPC) (Fluka), tetraethylammonium perchlorate (TEAPC) (Fluka) and tetraethyl ammonium fluoroborate (TEAFB) (Fluka) were used as received without any further purification.

The electro polymerization was carried out in a single compartment-cell without any separation between cathode and anode compartment with an arrangement for bubbling pure and dried N_2 gas in it. Platinum sheets working area (1.0 cm^2) were used as cathode and anode.

Electrolysis and Work up

The electrolysis was carried out by varying (i) current (ii) concentration of the monomer and concentration of the electrolytes. The electrolytic process was controlled by a regulated power supply (MPI Model MP 1016A). Nitrogen gas was bubbled for 30 minutes after filling the cell with reactants prior to electrolysis. Metallic depositions, which were found at the cathode during electrolysis, were reduced to a minimum by changing the polarity of electrodes every hour. The electrolysis was stopped at arbitrarily chosen times and the deposited polymers were separated from the electrode and dried in vacuum.

RESULTS AND DISCUSSION

Experiments show that absolutely no polymerization takes place when no current passes through the cell. The yield of the polymer depends on various factors such as current strength, concentration of electrolyte, time of electrolysis, temperature and monomer concentration. The electrochemical polymerization was carried out in the presence of nitrogen because air and oxygen have some effect on the course of polymerization. Addition of electrolyte helped in initiation of polymerization reaction in addition to considerable increase in the conductance of electrolytic medium. At 25°C the reaction was slow so that we decided to work at somewhat higher temperature at 30°C.

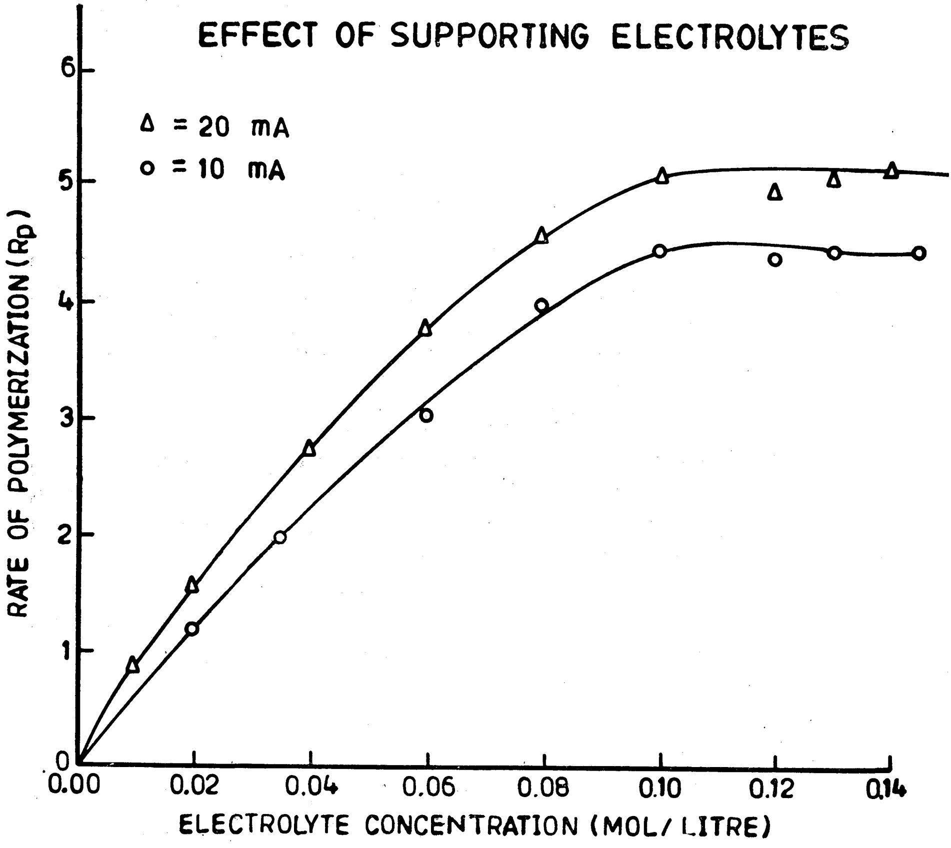


Fig. 1 Rate of polymerization against the concentration of electrolyte (30 ± 1°C quinoline 1.00 mol/litre, electrolysis time = 3 hrs, volume of acetonitrile 50 ml)

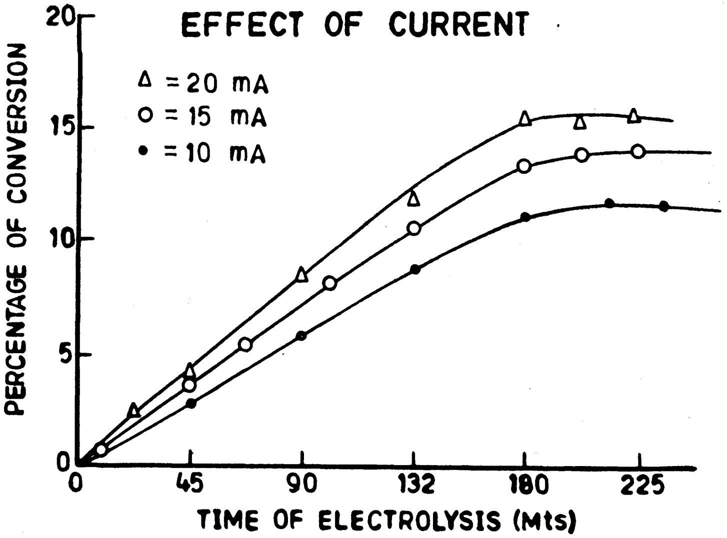


Fig. 2 Percentage of conversion of monomer with time of electrolysis at 3 different currents (30 ± 1°C quinoline 1.00 mol/litre) electrolyte 0.1 mol/litre volume of acetonitrile 50 ml)

TABLE 1

ELECTROPOLYMERIZATION OF QUINOLINE AT 30 ± 1°C WITH DIFFERENT ELECTROLYTES; CURRENT 20 mA; CONCENTRATION OF QUINOLINE 1.00 MOL/LITRE; TIME 3 HOURS; ACETONITRILE 50 ML, ELECTROLYTES CONCENTRATION = 0.1 MOL/LITRE

S. No.	Electrolyte	Conversion	R_p	Polymerization efficiency mol/faraday
1.	TEAPC	15.40	5.13	51.69
2.	TBAPC	15.29	5.09	51.26
3.	TEAFB	14.96	4.98	50.16

TEAPC was found to be most suitable in producing polymers of higher yield. The course of reaction was studied by changing the concentrations of electrolyte at two different current strengths; 10 mA, 20 mA. In both cases, the rate of polymerization increased with increase in concentration of electrolyte but finally attained a constant value (Fig. 1).

The percentage of conversion as a function of time of electrolysis was plotted (Fig. 2), the conversion varied linearly with time as shown in the figure. The yields were low at initial stages. Fig. 3 shows the polymer formation as a function of monomer concentration. Examining the figure,

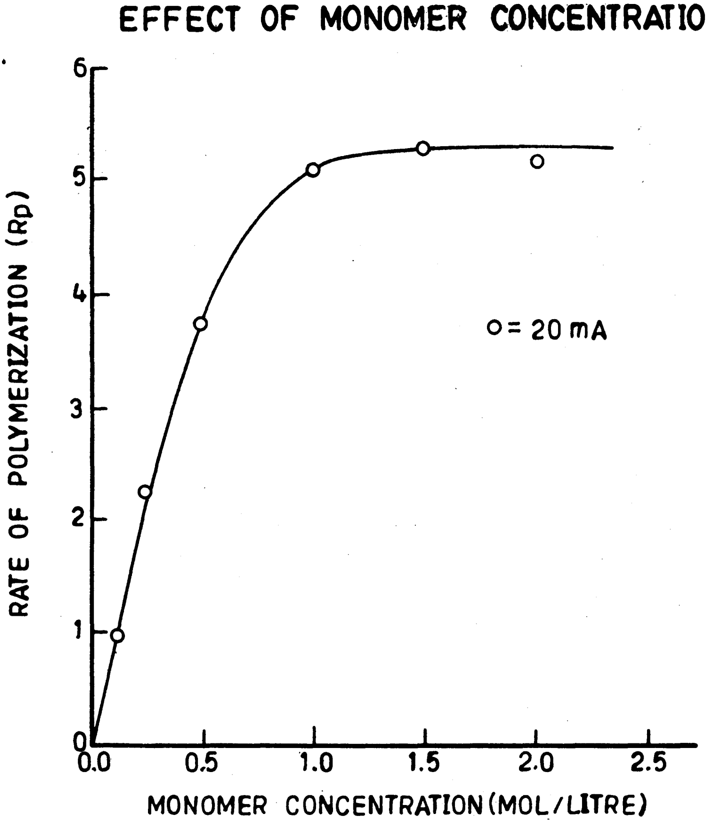


Fig. 3 Rate of polymerization as a function of concentration of monomer (30 ± 1°C; electrolysis time = 3 hrs; current 20 mA; volume of acetonitrile 50 ml; electrolyte used 0.1 mol/litre)

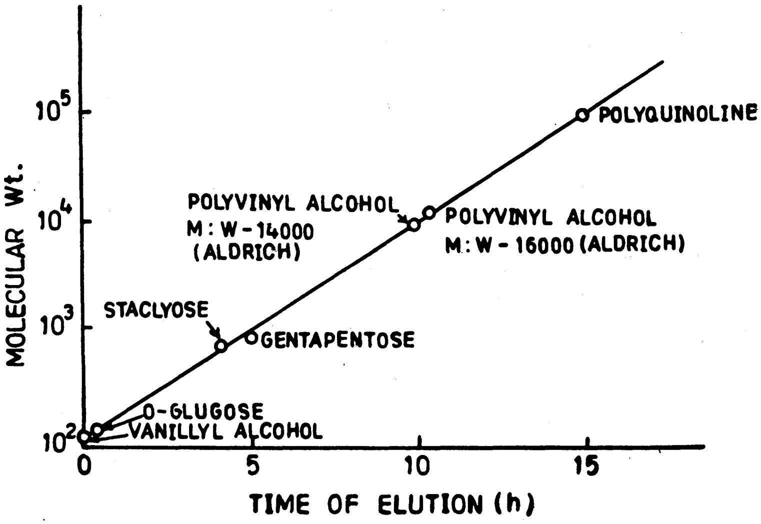


Fig. 4 Comparison of elution time for polyquinoline and other molecules of known molecular weight on the same column in DMF to compute the molecular weight

it it evident that the polymer formation is insensitive beyond a certain monomer concentration and at lower concentrations, the yield is proportional to the monomer concentration.

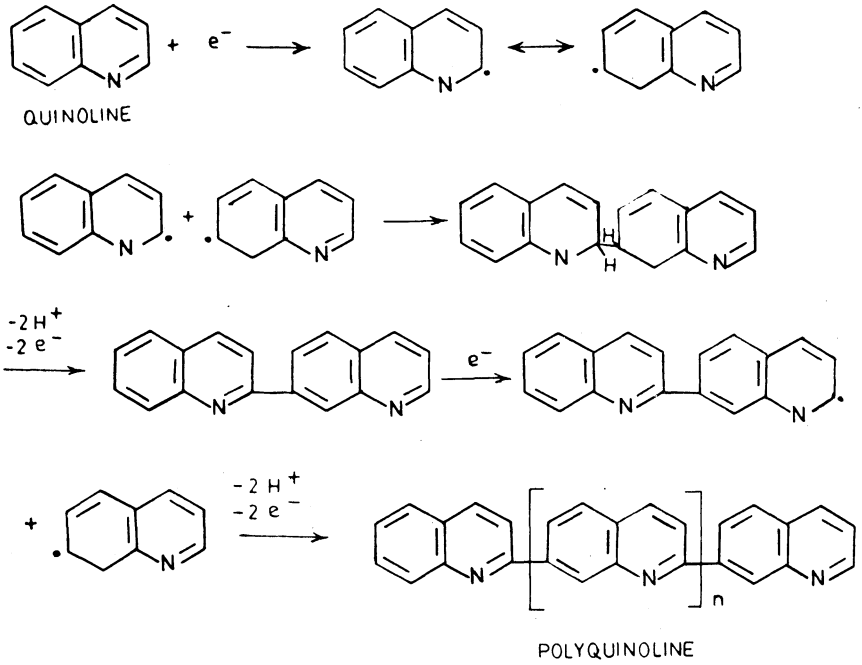
Polyquinoline was soluble in dimethyl formamide (DMF). The gel permeation chromatography of polyquinoline in DMF + sephadex column and the comparison of elution time for polyquinoline and some other molecules showed that the soluble part of polyquinoline had an average molecular weight of 50,000 (Fig. 4).

After, the electrolysis was stopped, solvent was evaporated under vaccum as the yield of polymerization was affected by presence of air or oxygen. As no polymerization took place in the absence of electrolytes and current the following free radical mechanism suggested.

In the bulk of the solvent

$$(C_2H_5)_4N(ClO_4) \rightleftarrows (C_2H_5)_4N^+ + ClO_4^-$$

$$ClO_4^- \xrightarrow{-e^-} ClO_4^\circ + e$$



The monomer acts as e⁻ acceptor. The electron given by (ClO_4^-) is taken by the monomer to give radical anion. The polymerization step may be written as shown below.

This mechanism is fairly convincing because the reaction goes till all the quinoline is consumed.

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