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Electrosynthesis of Electrically Conducting Polynaphthalene

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ABSTRACT

The electrochemical polymerization of naphthalene was carried out in acetone with $HClO_4$ as a supporting electrolyte in an undivided cell. The polymer was deposited as a dark brown brittle crust on the surface of anode. The conductivity of the polymer was of the order 10^{-2}

$\Omega^{-1}m^{-1}$. However, the conductivity and yield of the polymer varied with the variation of impressed current. The cyclic voltammetry of the obtained polymer was investigated. The mechanism of polymerization has been elucidated.

Key Words: *Electro Chemical Polymerization, Naphthalene, Cyclic Voltammetry, Conductivity.*

Introduction

Several methods may be used to polymerize naphthalene such as thermal polymerization, photochemical technique using gaseous initiator and catalyst, etc. But electrochemical method is an elegant way because the process of polymerization and doping in polymers may be controlled at will [1]. However, in comparision to the other methods, the reports on the electrochemical methods for the polymerization of naphthalene is scanty [2].

Polynapthalene as an electrically conducting polymer may be used in the fabrication of sensor, preparation of batteries and in the stealth technology in fighter aircraft, etc. In this paper, the electrochemical technique was used to prepare polynapthalene using $HClO_4$ as a supporting electrolyte in acetone.

Experimental Methods

Blank Experiment

5 g of naphthalene was added to 30 ml acetone and stirred well. On addition of $HClO_4$, the solution remained transparent. Now, two tin electrodes [dimensions: 2.5 X 3.5 cm^2] was introduced and the temperature of 25°C was maintained using thermostat. The solution was left for 6 hours without supplying current but no polymer was found to be formed. The color change was also not observed.

Polymerization

$HClO_4$ was added to the solution of 5 g naphthalene in 30ml of acetone and stirred well. Electrolysis was started in the undivided cell of diameter 1 inch fitted with tin electrodes. On electrolysis, a rapid polymerization was observed and dark brown deposition of polymer occurred at anode. The obtained polymer was rough and highly brittle and found attached to the substrate. The polymer film was removed from the electrode. The mass of the polymer was determined gravimetrically where as the conductivity by four probe method.

Cyclic Voltammetry

The cyclic voltammograms for polynaphthalene were obtained using the cyclic voltammeter (model: Palm Sens) using the platinum working electrode and Ag/Ag^+ reference electrode. The voltammograms have been depicted in fig.5.

FTIR Study

The FTIR spectra for raw naphthalene (dry form) and naphthalene in $HClO_4$ (solution) have been recorded using the FTIR spectrophotometer using ATR (attenuated total reflection) technique. The FTIR curves have been represented in fig. 6(a) and 6(b).

Results and Discussions

When the electrolysis was carried out at different current levels with constant $HClO_4$ concentration (1.5 mol litre^{-1}) and constant mass of naphthalene (5g) in 30ml of electrolytic solution, then the polymer yield and electrical conductivity of polymer was found to increase as shown in Table 1.

Table 1. Yield and electrical conductivity of semiconducting polynaphthalene in acetone, containing [$HClO_4$] = (1.5 mol/L) [acetone] = 0.5 mol/L. Volume of acetone = 30ml. Mass of naphthalene = 5gm, $HClO_4$ = 5 drops. Temp. of electrolyte = 25°C. Electric current = variable. Time of electrolysis = variable.

Electric Current (mA)	Time (h)	Polymer Deposited X 10^{-1} gm	Electrical Conductivity X 10^{2} $\Omega^{-1}m^{-1}$
25	1	0.4	5.5
	2	0.8	
	3	1.2	
	4	1.45	
	5	1.6	
50	1	0.6	7.0
	2	1.2	
	3	1.7	
	4	2.08	
	5	2.37	
100	1	0.9	9.0
	2	1.7	
	3	2.4	
	4	3.0	
	5	3.5	

Similarly, the yield of polynaphthalene with time of polymerization at different current levels also increased at constant temperature of 25 °C which is shown in figure 1. The variation of conductivity of polynaphthalene at different current levels has been depicted in figure 2. The maximum polymer yield was found to be 35 mg and conductivity was found to be 9.0 X $10^{-2}\ \Omega^{-1}m^{-1}$.

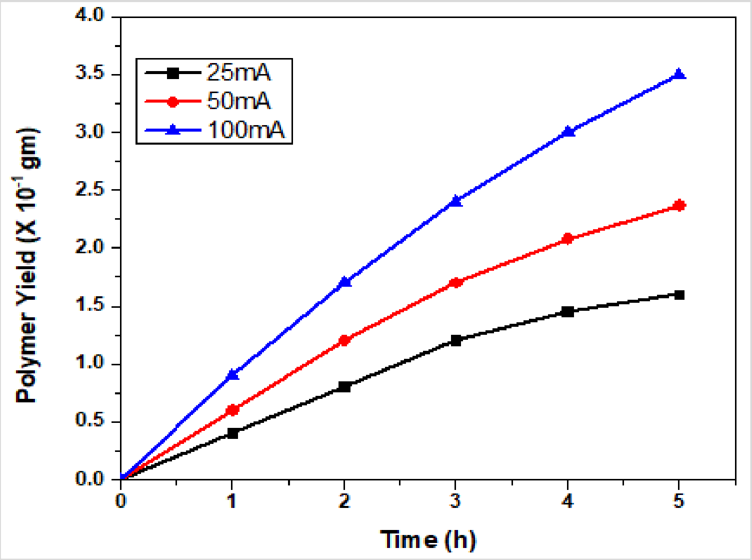

Fig.1. Variation of polymer (polynaphthalene) yield with time of polymerization on Sn electrodes. Volume of Acetone = 30ml, mass of naphthalene = 5gm, $HClO_4$ = 5 drops. Temp. of electrolyte = 25 °C, Electric current = variable.

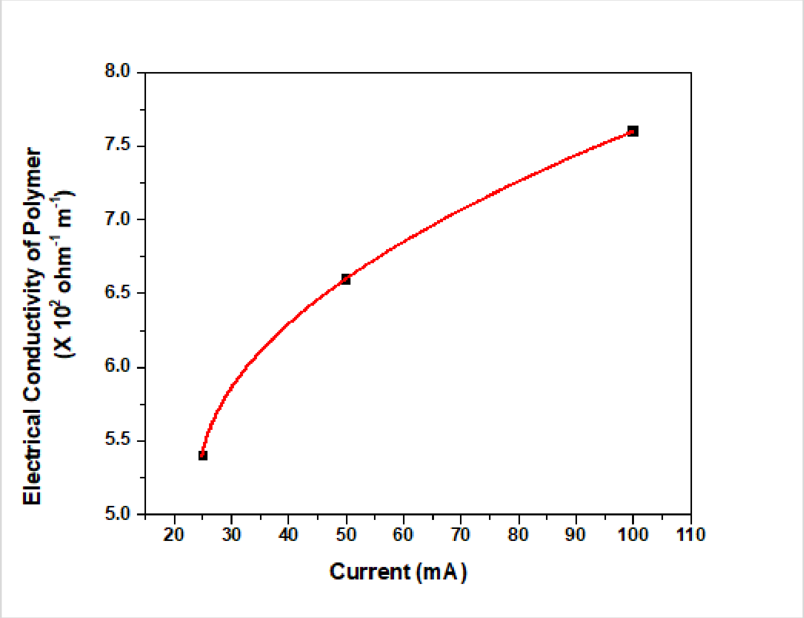

Fig.2. Electrical conductivity of polymer (polynaphthalene) yield with time of polymerization on Sn electrodes. Volume of Acetone = 30ml, mass of naphthalene = 5gm, $HClO_4$ = 5 drops. Temp. of electrolyte = 25 °C, Electric current = variable.

The decrease in electric current in the power supply during electrolysis with the time of polymerization has been shown in figure 3 which also indicated that the resistivity of polymer increased with duration of electrolysis. This substantiate that the polymer deposited is a semiconductor in nature.

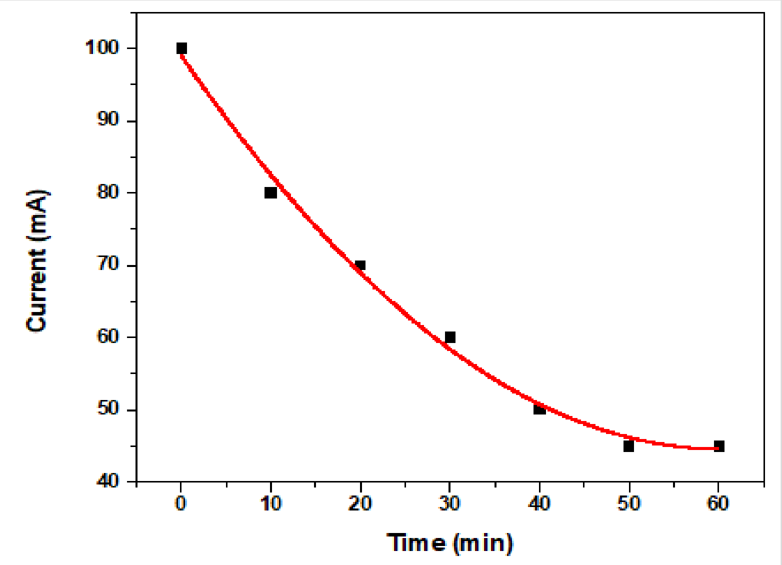

Fig.3. Electric current vs time during polymerization of naphthalene on Sn electrode when voltage is kept constant. Volume of Acetone = 30ml, mass of naphthalene = 5gm, $HClO_4$ = 5 drops. Temp. of electrolyte = 25 °C, Voltage = 10.4 volt. Time of electrolysis = variable.

Mechanism of Polymerization

Perchloric acid, $HClO_4$ may exist in acetone as polar molecule H^+ and ClO_4^- which causes electrolysis. The anion goes under the electrochemical reaction initiation by direct anodic oxidation of naphthalene at the anode. It was perceived that the polymerization was initiated either by ClO_4^-, or other reactive species which might have been generated electrochemically in situ.

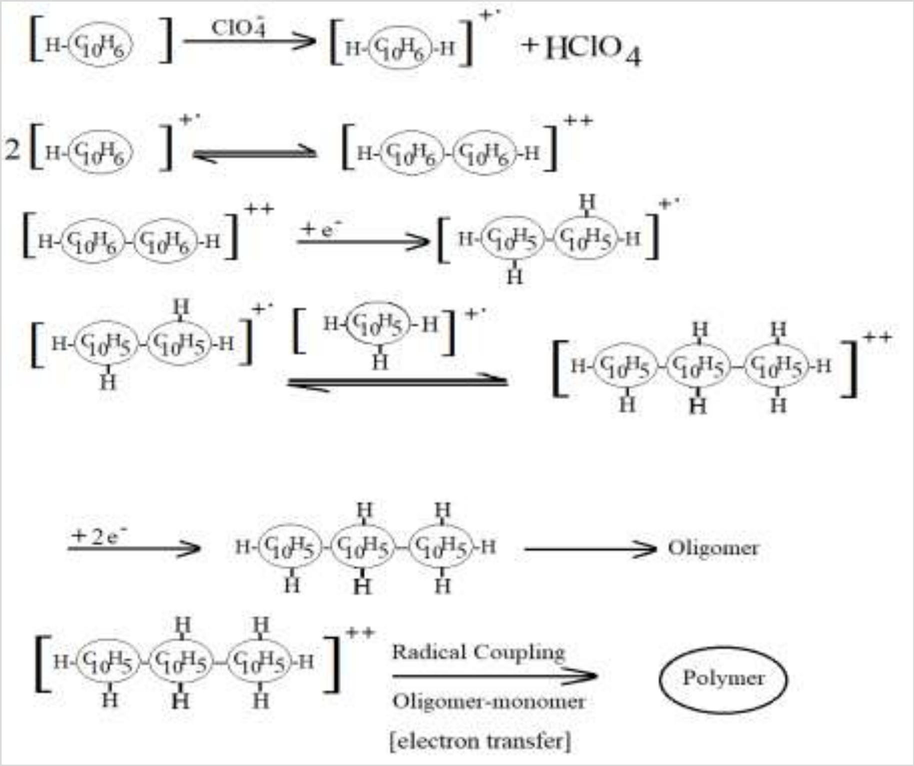

Fig.4. Mechanism of Polymerization

Conductance in polynapthalene occured via the hoping mechanism. The band gap in polynaphthalene was very large in comparision to that of polyacetylene [3]. Hence, Conductivity was very low in comparision to polyacetylene. The relative permittivity of the so obtained polynapthalene was 2.2. Polynaphthalene films with electrical conductivity of 10^{-3} Ω^{-1} cm^{-1} were successfully electrosynthesized[4] i.e., the electrical conductivity of polynaphthalene was in the range of semiconductor[5,6].

Cyclic Voltammetry

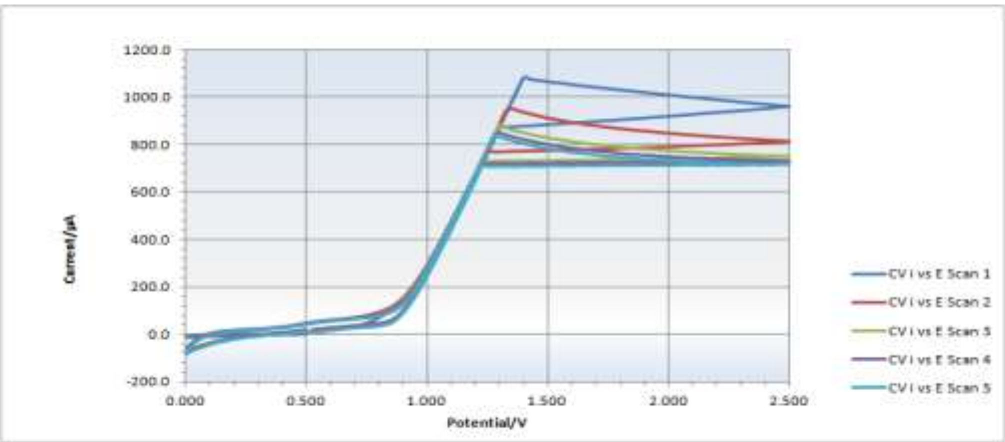

Fig. 5. CV of Naphthalene in $HClO_4$

From the Cyclic voltammetric investigation, it is clear that the oxidation potential of naphthalene was 0.82 volt which is at par with the oxidation potential of pyrrole [7]. The reduction of polynaphthalene therefore began at 0.82 volt by the doping of ClO_4^- ion and thereby at this stage, conductivity began to increase. It continuously increased upto 1.4V, as the peak was maximum at this stage and as a result, the doping processs was also maximum. Thereafter, the oxidation began upto 2.5 volt by undoping the ClO_4^- ion. This cycle was repeated again and again along with the increase and decrease of conductivity.

FTIR Study

From the FTIR analysis, it was found that no changes occurred in the spectra of raw naphthalene and naphthalene in $HClO_4$ used for electrolysis. This was expected as in polynaphthalene, the naphthalene units are basically repeated. The FTIR curves have been represented in fig.6(a) and 6(b) respectively.

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Fig.6(a) FTIR of Raw Naphthalene

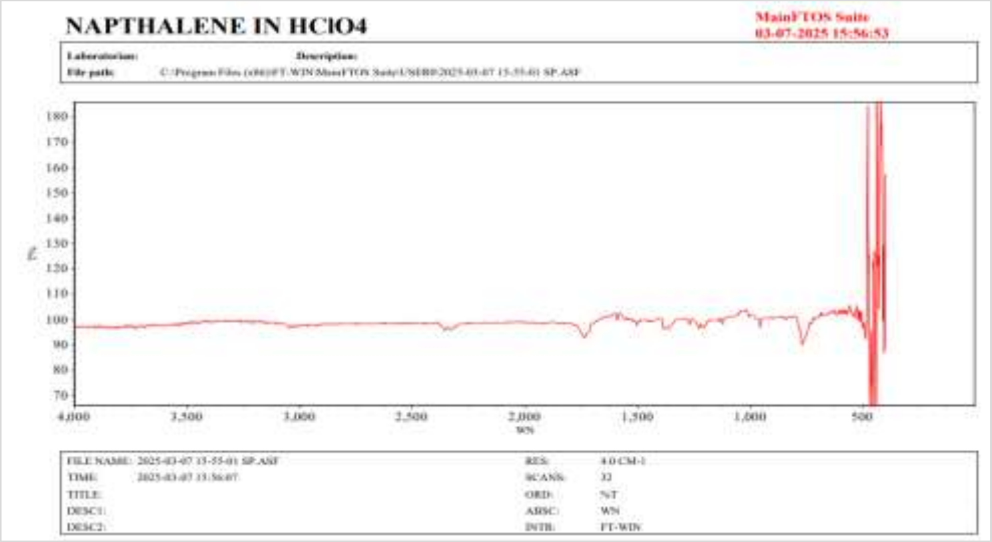

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Fig.6(b) FTIR of naphthalene in $HClO_4$

Conclusion

The electrochemical technique is an elegant way to prepare a conducting polymer which can be controlled at will. The process of doping and undoping ClO_4^- ion may also be varied easily to change the conductivity of the polymer. The polymer revealed a promising future in fields of electrode material for rechargeable battery, polymer LED and high temperature resistant materials, stealth technology in fighter aircraft, and many similar applications.

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