ELECTROCHEMICAL PREPARATION OF IMMOBILISED SUPPORT FOR TRIPHASE CATALYSIS

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Polymers such as poly(p-phenylene) and poly(p-phenylene sulphide) consisting of a sequence of aromatic rings are excellent insulators and can be transformed into cation exchange resins of low capacity to serve as polymeric support for triphase catalysis. In this communication an electrochemical method for the synthesis of poly(p-phenylene) has been described and also the method to sulphonate it to a cation exchange resin.

Heterogeneous catalysts are preferred in industry and industrial research because of the ease in separation of the catalyst from the reaction product. Trivedi [1] reported the use of CTAC as a phase transfer catalyst in a two phase system. It is but logical to think of immoblized phase transfer catalyst, that is, the heterogenized analogue of phase transfer catalyst known to catalyse reactions that occur in two phase liquid system.

In 1975, Regen [2] reported the polystyrene bound onium ion and crown ether as catalysts which were more hydrophobic and less crosslinked than conventional ion exchange resins and that were active in the aqueous-organic solvent mixture normally used for phase transfer catalysis. Regen described the reaction as "triphase catalysis". This is the logical extension of Merrifield's technique [3] of solid phase synthesis of peptides. The advantage of using lightly crosslinked polymers over common heterogeneous catalysts like alumina or silica support are many. The main advantage is that the active sites in polymer are distributed throughout the surface of the polymer and secondly due to hydrophobic nature, the organic-aqueous solvent mixture can diffuse through the solvent swollen polymer matrix to reach the active sites. These polymeric support catalysts are of much importance for alkaline medium, where silica gel or alumina are not very stable.

EXPERIMENTAL

The chemical synthesis of Poly (p-Phenylene) (PPP) was first reported by Kovacic [4], using anhydrous $AlCl_3/CuCl_2$ (2:1 molar ratio) as a catalyst for the polymerization of benzene. We have found that other aromatic hydrocarbon can be polymerised by this method. In principle, any Friedel-Craft catalyst can be used for the chemical synthesis of ppp from benzene. This method has one drawback that all used chemicals in the reaction should be anhydrous and during the course of reaction a copious evolution of HCl gas occurs which poses serious problem in maintaining laboratory or industrial atmosphere.

Poly-(p-phenylene) films were deposited galvanostatically at $1mA/cm^2$ on platinum (apparent area 1 cm^2), anode from a homogeneous solution of 1 m tetrabutyl ammonium flurobo-rate in benzene and acetonitrile mixed solvent in the ratio of 3:1 with a current efficiency of 88.13 percent. Benzene is oxidized at $\sim$ 1.1 V vs SCE. As soon as current is impressed, a brown colour film starts forming at the anode surface. After growth of sufficient thickness, this film can be readily peeled off from the electrode, surface. To get the thick deposit of the film a high current density at the anode is required to create pin holes in the film, so that electrical conduction can be maintained. A thin film of PPP is formed by electrolysis at $1 \cdot mA/cm^2$ for two hours. However a thick film (0.1 to 1 mm thick) is obtained at higher current density (20-100 mA/cm^2 after a prolonged electrolysis of 5-7 hours.

This PPP thus formed and the anode surface is eletroactive in presence of BF_4^- due to the formation of charge transfer complex. It was observed that there is a thick growth of PPP on anode, which indicates that BF_4^- ion gets entrapped in the polymer which makes it conducting (S 10^{-4} cm), otherwise PPP in native state has the conductivity of S 10^{-9} cm.

The chemical analysis and I.R. spectrum clearly indicates that the PPP formed at low c.d. as well as at high c.d. are essentially the same. The only difference observed was that PPP

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synthesised at low c.d. has a smooth surface whereas pinholes are created at high current density. These pin holes act as window for the electrolyte which maintains the electrical conduction. The SEM photographs show chemially synthesised PPP and Electrochemically synthesised PPP.

Sulphonation of Poly(para-phenylene) (PPP)

The sulphonated product was obtained by reaction of PPP with conc. H_2SO_4/Oleum and sulphonyl chloride ($SOCl_2$) mixture at 80-100 °C. The reaction mixture was heated till the gas evolution ceases. At the end of the reaction a



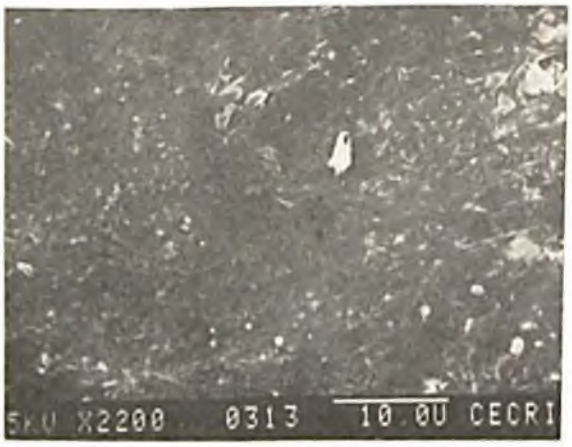


Fig.1 & 2 0390 and 0313 SEM Photographs of Chemically Prepared Poly-p-phenylene

brown colour was obtained. Under these conditions only 5 to 10% polymer gets disintegrated to give brown solution, containing mostly quinone. The reaction mixture after cooling was filtered through a G4 crucible and was



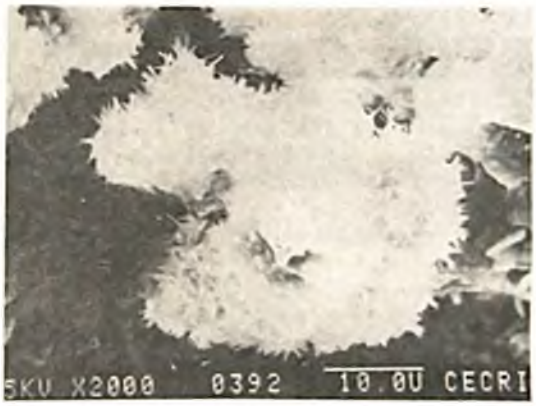


Fig. 3 & 4 0391 and 0392 SEM Photograph of Electrochemically Synthesised Poly-p-phenylene

repeatedly washed with double distilled water till it became neutral to indicator paper. This resin was dried at 110°C for two days and was titrated against previously standardised sodium hydroxide solution. This acid-alkali titration showed that the sulphonated product (cation exchange resin) has the capacity of 0.49 m eq of sulphonates per gram. The cation exchange resin synthesised did not show any disintegration or shrinkage in pure organic solvents containing alkali metal ions and is capable of fixing these cations under drastic reaction conditions.

It was also observed that if boiling $SOCl_2$ is used for sulphonation, then a gel is obtained which is difficult to filter. $SOCl_2$ was removed completely under vacuum and the gel was treated with NaOH (16N) which yielded a very stable alkaline gel of very high conductivity.

DISCUSSION

The polymerization reaction at an anode surface is initiated by the adsorption of benzene-BF_4^- adduct.

Under the influence of anodic current, the benzene molecule loses first one hydrogen thereby generating an activated complex. The formation of activated complex initiates the oxidative polymerization of benzene.

It has been reported [5] that due to π electrons, the aromatic nuclei possess the basic properties. This basicity leads to the formation of π complex. Based on these findings, it is but logical to think that BF_4^- salts containing borofluoride group like tetraethyl ammonium borofluoride would also form π complex with aromatic nucleus under properly controlled conditions like solvents, temperature and concentration of supporting electrolyte. Hence, instead of HF, the BF_4^- ion has been used.

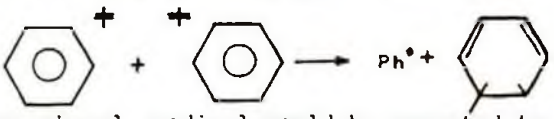
The PPP can be deposited only on platinum electrode. Other electrode materials like nickel get dissolved in presence of BF_4^- ion and go into the electrolyte. Benzene molecule gets oxidized on Pt electrode to give biphenyl which can further get oxidised to terphenyl under anhydrous conditions. The reaction conditions are almost identical with Friedel-Craft reaction.

The PPP synthesised by Kovacic method [4] and present method gave identical infrared characteristic bands at 810 cm^{-1} (S) 1005 cm^{-1} (W) and 1485 cm^{-1} (M) indicating that the structure of polymer is identical in both cases. However, scanning electron micrography studies showed that the polymer obtained by chemical method gets disintegrated under the impact of powerful eletron beam. The electrochemically prepared PPP does not get disintegrated under the impact of electron beam: a layer structure is also indicated in SEM.

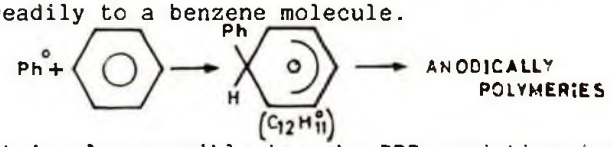
The second observation which is worth reporting is that PPP prepared by chemical method when cold pressed to make a pellet, changes from the light brown colour to pink colour, probably due to surface oxidation. This aspet needs further study. The electrochemically prepared PPP does not change its colour on cold pressing. The inference which one can draw from these observations is that polymer chain in the case of eletrochemically prepared PPP is larger than in chemically prepared PPP. Since the PPP obtained by either method was found to be insoluble in any known organic solvent, the polymer molecular weight could not be determined by cnventional methods. We tried to determine the length of chain of polymer by indirect method. On sulphonation under mild condition with concentrated H_2SO_4 the chemically prepared PPP showed increase in weight which shows that every 17th molecule gets sulphonated indicating that the polymer is composed of 17-benzene rings, whereas electrochemically prepared PPP showed that every 29th molecule is getting sulphonated under identical conditions and hence should have 29 benzene rings in a polymer.

Based on our observations and experimental results the following reaction mechanism is suggested:

The initial ionization and excitation at the anode surface probably gives radicals.



The phenyl radical would be expected to add readily to a benzene molecule.



It is also possible to make PPP conduting just by doping with Iodine or suitable oxidants like AsF_5.

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