

## ELECTROPOLYMERIZATION OF VINYL ACETATE

M CHANDRASEKARAN S PITCHUMANI and V KRISHNAN

Central Electrochemical Research Institute, Karaikudi-623006

## ABSTRACT

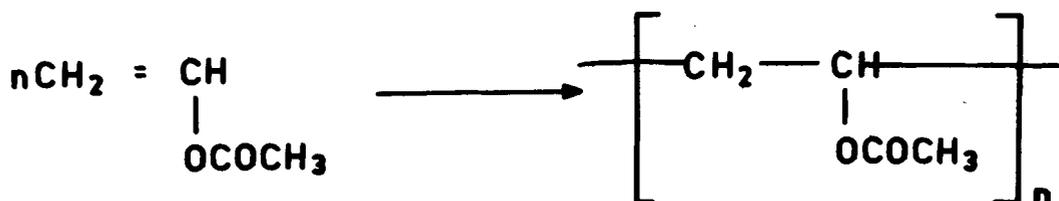
Electropolymerization of vinyl acetate has been investigated in an aqueous tetraethyl ammonium p-toluene sulphonate medium employing aluminium cathode. These experiments have yielded a straw coloured, tough, horny polyvinyl acetate having a high molecular weight.

**Key Words:** Electropolymerization, Vinyl acetate

## INTRODUCTION

Vinyl polymers are of prime importance as they have been widely used as precursor material for many of the industrial applications such as surface coating [1] adhesives [2] and binders [3]. These polymers have hitherto been prepared through chemical methods [4]. It has been achieved by activating the double bond which yields the polymerizing species such as free radical, anion, cation etc. The advantage of electroinitiation offers an early method of activating the double bond by careful selection of voltage and current which helps to generate the desired species for a selective reaction to occur.

Kolbe electrolysis has since been considered as source for free radical generation [5] which, in turn, propagates the polymerization of the given monomer. Such study has been extended [6] to the polymerization of vinyl acetate using potassium acetate as electrolyte where the polymer was isolated at the Pt anode. The use of tetra alkyl salts can also serve as source for the generation of the initiating species and the polymerization of vinyl acetate has been examined through this method, the process being represented as:



## EXPERIMENTAL PROCEDURE

Electropolymerization was carried out at  $30^\circ \pm 5^\circ\text{C}$  in an undivided electrochemical cell wherein graphite was used as an anode and aluminium as cathode. Calculated quantities of vinyl acetate monomer was dissolved in the electrolyte solution of tetraethyl ammonium p-toluene sulphonate (TEATS) and fed into electrolytic cell. A fixed current density was impressed on the system and the potential was measured with respect to SCE. The

product was isolated from the electrolytic cell directly and washed with suitable solvent to remove the occluded monomer. The product was dried in an oven and subjected to IR spectral analysis. The cell voltage for the polymerisation varied from 8V to 11V.

## RESULTS AND DISCUSSION

Electropolymerization of vinyl acetate has been found to proceed cathodically and the polymer settles down around the cathode. The polymer can conveniently be isolated from the electrolytic cell just by decanting and filtering. The resultant polymer is found to be straw-coloured, tasteless, odourless, tough, horny and insoluble in common organic solvents. The total yield of the polymer that can be obtainable in this polymerization is 60%. The IR spectral data of monomer (A) and polymer (B) are given in Fig.1. As can be seen, the characteristic band at  $1650\text{ cm}^{-1}$  for -C=C- is absent in the product confirming that the polymerization has proceeded through electrochemical activation of the double bond of vinyl acetate monomer. The determination of softening point of the product obtained has been very difficult, indicating that the polymer obtained is of high molecular weight. This is in accordance with the fact that the softening

point of polyvinyl acetate increases with molecular weight and is difficult to be determined at higher ranges of molecular weight, as reported earlier [7]. This is further supported by the straw coloured, hard and horny nature of product which is usually associated with higher molecular weight of polyvinyl acetate in the range of 1,500,000 (Mw). Thus we find that the high molecular weight polyvinyl acetate can easily be prepared through electrochemical route.

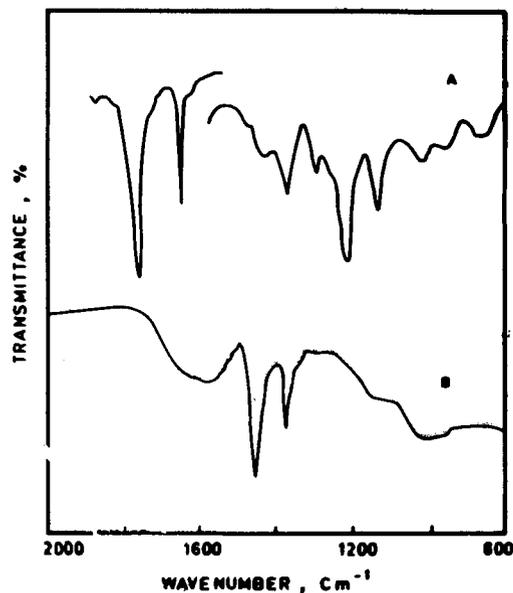
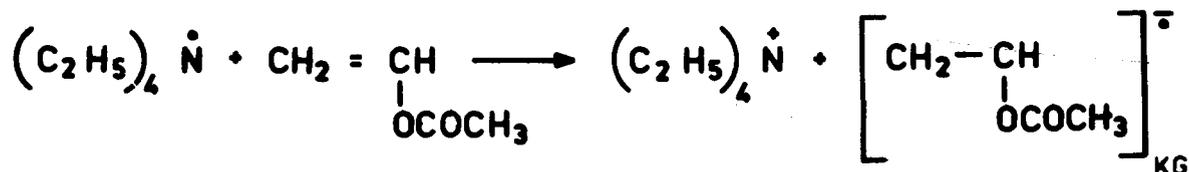


Fig.1. IR Spectral data of monomer (A) and polymer (B)



## REFERENCES

1. Paint Handbook, *Airco Chemical and Plastic Division of Air Reduction Co. Inc.* New York, (1969)
2. R A Weidner in R L Patrick, ed. *Treatise on Adhesion and Adhesives*, Vol.2, Marcel Dekker Inc. New York, (1969) Chapt. 10, pp.432-477, 467-471
3. W E Daniels and W H Pippen *U S Pat* 4,228,047, (1981)
4. H Bartl in E Muller, Ed. *Methods of Organic Chemistry (Houben-Wayl) Macromolecular Materials*; Georg Thieme Verlag, Stuttgart, FRG, 1961. Part I, pp 905-918
5. R V Lindsey, Jr and M L Peterson, *J Amer Chem Soc* 81 (1959) 2073
6. N B Smith and H G Gilde, *J Amer Chem Soc*, 82 (1960) 659
7. H Fikentscher, *Cellul Chem*, 13 (1932) 71
8. E O Kraemer, *Ind Eng Chem* 30 (1938) 1200
9. M J Allen, *Organic Electrode Processes*, Reinhold, New York, (1958)
10. M Chandrasekaran, S Pitchumani and V Krishnan (Under publication)

The cathodic polymerization of vinyl acetate has been found to occur around—1.8V vs SCE. Such a high cathodic potential is possible when tetraalkyl salts are used as electrolytes. The hydrophobic character of tetraalkyl cations offer an easy method of generating a stable radical anion [9], thus avoiding the protonation of the radical anion. This can give rise to an abundant availability of radical anions which can help to propagate the macro molecular chain to a greater extent, leading to high molecular weight of the product. This is indeed true with the product as described earlier. A probable mechanism of electroinitiation can be proposed for the polymerization as follows: (SEE EQUATION BELOW)

After this effective initiation, the polymerization can be expected to proceed smoothly to a greater extent with the abundant availability of the radical anions.

Thus it can be concluded that the electrochemical method can be sought to prepare polyvinyl acetate in desired form. Besides, it also helps to prepare polyvinylacetate which can readily be hydrolysed into polyvinyl alcohol in situ, when  $\text{H}_2\text{SO}_4$  is used as electrolyte [10].