Experimental Methods
EXPERIMENTAL METHODS

I. EQUIPMENT

1. Thermostat

The preparation of polymers and the kinetic experiments were conducted in a thermostat of 20 litre capacity consisted of a cylindrical glass tank of 30 cm diameter equipped with an electrical heater and a mechanical stirrer to maintain uniform temperature with an accuracy of ± 0.1°C.

2. Gas Chromatograph

GLC analyses were preformed on a Varian model 3700 flame ionization instrument with varian Vista CDS 401 data system. 10% SE-30 on 80/100 Chrom WHP, 3 m x 1/8" stainless steel column and 5 ft x 0.25 inch carbovax 20 m-3% in DMCS 100-125 mesh column were used.

3. RPM Control Mechanical Stirrer

Reaction mixtures were stirred by a mechanical stirrer (Tullu. F.H.P. Motor, U.P.National Manufacturers Pvt. Ltd., Varanasi). Stirring speed was measured by a tachometer (Teclock, Japan).

4. Polymerization Flask

The polymerization flask used for the suspension polymerization was a three-necked flask (made of pyrex glass) of capacity 2 litres. It was fitted
with B-32 socket carrying an air-tight stirrer with teflon or steel blade at the centre. A double-walled condenser with calcium chloride guard tube and an inlet tube for nitrogen were fitted on either side to ensure air tightness.

For kinetic experiments, a 100 mL three-necked round-bottomed flask (pyrex glass) equipped with stirring bar, adaptor fitted with septum and stopcock was used.

II. DEAERATION TECHNIQUE

Oxygen-free Nitrogen gas was obtained by passing it through Fieser's solution\(^1\) prepared by dissolving 20 g of NaOH in 100 mL of water and adding to the warm solution 15 g of sodium dithionitrite followed by 2 g of sodium salt of anthraquinone-2-sulfonic acid. The contents were stirred well to get a blood-red coloured solution. The solution was renewed frequently. The oxygen-free \(N_2\) gas was then freed from sulfur containing gases like SO\(_2\) by passing it through saturated lead acetate solution. It was then passed through distilled water to remove any water-soluble impurities.

III. REAGENTS

1. Water

The distilled water obtained from a water still was redistilled over alkaline KMnO\(_4\) in an all glass quickfit setup and used for the preparation of solutions.
2. **Monomers**

Styrene (Fluka) and divinyl benzene (DVB) (Poly Sciences, Inc., P.A.) were used as such in the preparation of polymer beads. 4-vinylpridine (Fluka) was distilled under reduced pressure and used for the preparation of polymer beads.

3. **Other reagents**

AIBN (Koch-light, USA), a free radical initiator, was recrystallized from ethanol. Poly(vinyl alcohol) (Fluka), Gelatin (AR, BDH), Boric acid (AR, SD's), sodium hydroxide (SD's), ZrCl₄ (Fluka) and SnCl₄ (SD's) were used as such and chloroform, methanol, acetone, and other organic solvents were purified according to the standard procedures².

Nitrogen gas (supplied by Asiatic Oxygen Ltd., Madras) used for the purpose of deaeration in the preparation of polymers and catalysts was freed from traces of oxygen by passing through vertical glass tubes containing Fieser's solution.

**Synthesis of pyridine stannic chloride complex (soluble complex)**

This complex was prepared by the following method³:

0.2 mol (16.2 mL) of pyridine was dissolved in 100 mL of chloroform and to the homogenous solution, 0.2 mol (23.5 mL) of stannic chloride was added. The mixture was stirred for 1 hr at room temperature. The pyridine-
stannic chloride (Py-SnCl₄) complex was filtered under vacuum and repeatedly washed with chloroform (3x100 mL). The complex (hygroscopic), containing 21.75% of chloride ion, was stored in a vacuum desiccator (scheme-1). The scheme-1 is given in the discussion part (Page 138).

Synthesis of pyridine-zirconium tetrachloride complex (soluble complex)

The same experimental procedure described above is used for the preparation of pyridine-zirconium tetrachloride (Py-ZrCl₄) complex catalyst. The complex (hygroscopic), containing 21.17% of chloride ion, was stored in a vacuum desiccator (scheme-2). The scheme-2 is given in the discussion part (Page 138).

Preparation of the polymer-supports

The polymer beads were prepared by the suspension polymerization technique using a modified procedure. Typical polymerization experiment for the preparation of 2% crosslinked copolymer with 25% (4-vinylpyridine), styrene is described below:

A. Aqueous phases (450 mL) containing gelatin, poly(vinylalcohol) (PVA) and Boric acid were prepared as given below:

1. At 50°C, 2.7 g of gelatin was dissolved in 60 mL of water and temperature was not allowed to exceed 60°C to avoid gelatin getting denatured. The hot solution was added to the aqueous phase in step 5.
2. Boric acid (5.11 g) was dissolved in the remaining water (390 mL).

3. Poly(vinylalcohol) (PVA, 4.5 g) was dissolved in the above solution to maintain the viscosity of the medium.

4. The pH of the boric acid solution was adjusted to 10.0 with a digital pH meter (model: H-120, Elico) by the addition of 25% aqueous NaOH solution to maintain the conformation of gelatin.

5. The gelatin solution was mixed with remainder of the aqueous solution and mixed thoroughly.

6. Before the addition of organic phase, the aqueous solution was added to a three-necked 2-litre flask.

B. Organic phase consisting of appropriate quantities of styrene, DVB, and 4-vinylpyridine (total: 165 g) and AIBN was prepared: 117.75 g of styrene, 41.25 g of 4-VP, 6.0 g of DVB and 0.82 g of AIBN were taken to get 2% crosslinking and 25% active site, after thorough mixing the monomer(s) solution was added to the flask containing aqueous phase.
C. Polymerization

\( \text{N}_2 \) gas was passed through the flask to remove atmospheric oxygen for about 45 minutes at room temperature. The blade level of stirrer was adjusted so that the tips were in organic phase and most of the blade in aqueous phase. The \( \text{N}_2 \) sweep in the flask was stopped but slight positive pressure of nitrogen was maintained throughout the course of polymerization. Then the formation of the polymer beads was frequently checked with the help of microscope and the size of the droplets was controlled by varying stirring speed. With 400 rpm, the mixture of organic and aqueous layer was heated to 70°C over a period of 30 minutes and the same temperature was maintained throughout the polymerization time (36 h). Polymers with different percentage of crosslinking 2-8% by weight of DVB, and different percent active sites, viz, 25, 50 and 70% by weight of 4-vinylpyridine, were prepared. The scheme for the preparation of polymer-supported 4-vinylpyridine (PVP) (Scheme-3), is given in the discussion part (Page 139).

D. Polymer Isolation

Polymer beads were transferred from three-necked flask to the beaker and washed with hot water repeatedly till all the PVA got removed. It was then filtered through buchner funnel and washed with hot water, acetone and methanol. It was dried at 60°C in vacuum oven.
Synthesis of polymer-supported (4-vinylpyridine)-stannic chloride complex (PVP-SnCl$_4$) [insoluble]

This insoluble complex was synthesized by the following method.$^{3,4}$

The insoluble, microporous 4-vinylpyridine anchored polymer beads (10 g) were swelled in chloroform (100 mL), and 11.10 g (5 mL) of stannic chloride was added. The mixture was stirred for 7 hours at room temperature and then cooled (0-10°C). The beads were filtered and then washed with chloroform and acetone. The polymer-supported catalyst was further dried under vacuum at 50°C for 24 h. The steps involved in the preparation of poly (4-vinylpyridine)-stannic chloride complex (scheme-4) are given in the discussion part (Page 140).

Synthesis of polymer-supported (4-vinylpyridine)-zirconium tetrachloride complex (PVP-ZrCl$_4$) [insoluble]

The same experimental procedure (scheme-4) was used for the synthesis of PVP-ZrCl$_4$ complex catalyst using poly(4-vinylpyridine-co-styrene) (PVP) supports (scheme-5) is given in the discussion part (Page 140).

The observed percentages of the elements present in the (2% DVB, 25% 4VP) PVP-SnCl$_4$ and PVP-ZrCl$_4$ (2% DVB, 25% 4VP) complex were calculated and presented in Table - I and is given in the discussion part (Page 135). The chloride ion concentrations were estimated according to the oxygen flask method$^{5,6}$ and were found to be 1.64, 3.28, 4.94 and 1.05, 2.15, 3.22 mequi of chloride per/g for PVP-SnCl$_4$ and PVP-ZrCl$_4$ for 25%, 50% and 75% active site (with respect to pyridine group of the polymer), respectively.
Esterification of acetic acid with 1-hexanol

Typical kinetic experiments

The catalytic efficacy of these catalysts such as Py-SnCl₄, Py-ZrCl₄ and PVP-SnCl₄ (2% DVB, 25% VP, -60 + 100 mesh), PVP-ZrCl₄ (2% DVB, 25% VP, -60 + 100 mesh) complex catalysts was tested by carrying out the esterification reaction of acetic acid with 1-hexanol under identical conditions. To a 150 mL three-necked round bottomed flask fitted with double walled condenser containing 25 mL (435.14 mmol) of acetic acid and 3 mL (24.02 mmol) of 1-hexanol. The reaction was performed in a thermostat maintained at 50 ± 0.1°C and stirred mechanically with a 45 x 18 mm curved Teflon blade at 500 rpm for 10 minutes to condition the substrate after a sample was drawn at zero time. 0.6 g of Py-SnCl₄ complex was added to the reaction mixture. At regular intervals, the samples were collected from the organic layer and analyzed using GC. The kinetics was followed by the disappearance of 1-hexanol. The pseudo-first order rate constants were evaluated from the plots of log (a-x) versus time, where, (a-x) is the concentrations of 1-hexanol at a given time t. The rate constant was evaluated for the kinetics of esterification of acetic acid with 1-hexanol.

The above experimental procedure was used to follow the esterification of acetic acid with cyclohexanol and phenethyl alcohol in the presence of pyridine-zirconium tetrachloride (homogeneous) complex catalyst and polymer-supported 4-vinylpyridine-zirconium tetrachloride (2% DVB, 25% VP, -60 + 100 mesh) complex catalyst.
Part-A

\[ \text{CH}_3\text{COOH} + \text{HO-CH}_2\text{(CH}_2)_4\text{-CH}_3 \rightarrow \text{CH}_3\text{C-O-CH}_2\text{(CH}_2)_4\text{-CH}_3 + \text{H}_2\text{O} \]

\[ \text{Py-SnCl}_4 \quad \text{Py-ZrCl}_4 \]

\[ 50^\circ\text{C}, 500 \text{ rpm} \]

Part-B

\[ \text{CH}_3\text{COOH} + \text{HO-CH}_2\text{(CH}_2)_4\text{-CH}_3 \rightarrow \text{CH}_3\text{C-O-CH}_2\text{(CH}_2)_4\text{-CH}_3 + \text{H}_2\text{O} \]

\[ \text{PVP-SnCl}_4 \quad \text{PVP-ZrCl}_4 \]

\[ 50^\circ\text{C}, 500 \text{ rpm} \]
Part - C

\[
\begin{align*}
&\text{CH}_3\text{CO}_2\text{H} + \\
&\text{Py-ZrCl}_4 \\
&\quad 50^\circ\text{C}, 500\text{ rpm} \\
&\rightarrow \\
&\text{OH} \\
&\text{CH}_2\text{C}_2\text{OH} \\
&\quad 50^\circ\text{C}, 500\text{ rpm} \\
&\rightarrow \\
&\text{H}_3\text{C} \text{O} \text{C} \text{O} \text{C}_2\text{H}_5 + \text{H}_2\text{O} \\
&\text{Py-ZrCl}_4 \\
&\quad 50^\circ\text{C}, 600\text{ rpm} \\
&\rightarrow \\
&\text{OH} \\
&\quad 50^\circ\text{C}, 600\text{ rpm} \\
&\rightarrow \\
&\text{H}_3\text{C} \text{O} \text{C} \text{O} \text{C}_2\text{H}_5 + \text{H}_2\text{O} \\
&\text{Py-ZrCl}_4 \\
&\quad 50^\circ\text{C}, 500\text{ rpm} \\
&\rightarrow \\
&\text{H}_3\text{C} \text{O} \text{C} \text{O} \text{C}_2\text{H}_5 + \text{H}_2\text{O}
\end{align*}
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REFERENCES


