CHAPTER - III

EXPERIMENTAL

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3.1 Materials

Cellulose acetate (CA) (LOBA Chemie) D.S = 2.5 was used after Soxhlet extraction with ethanol/benzene mixture and drying. Ethyl cellulose (EC) from (s.d.Fine Chem.Ltd.) D.S = 2.5, ethoxy content 48.2% was used. Chloromethylated polystyrene (PS) (2%DVB) was received as a gift sample from M/S. Thermax Ltd, Pune. Hexamethylene diisocynate (HMDI) (Fluka) was used as received. Tolylene 2-4, diisocynate (TDI) (Aldrich) was distilled over phosphorous pentoxide under vacuum in nitrogen atmosphere before use.

2-Hydroxy 1-naphthaldehyde (Fluka) and diacetylmonoxime (DAMO) (John Baker) were used after recrystallisation from ethanol.

Dichloromethane (DCM) (s.d.Fine Chem Ltd.) was purified by drying over anhydrous calcium chloride overnight then refluxed over calcium hydride and distilled before use. Benzene (Qualigens Fine Chemicals) ,toluene (s.d.Fine Chem Ltd),and hexane (s.d. Fine Chem. Ltd.) were purified by drying over anhydrous calcium chloride and refluxed over sodium metal (s.d.Fine Chem Ltd.) and distilled before use.

Dimethyl acetamide (DMAc) (Qualigens Fine Chem .) was used as received.

Manganese acetate $(CH_3COO)_2$ Mn.H_2O (BDH), zinc sulfate $ZnSO_4.7H_2O$(MERCK), cobaltous chloride $CoCl_2.6H_2O$ (BDH), cupric acetate $(CH_3COO)_2$ Cu.H_2O (BDH), nickel ammonium-sulphate $(NH_4)_2SO_4.NiSO_4.6H_2O$ (LOBA Chemie.),and ethylenediaminetetraacetic acid (EDTA)(BDH) were used as received.

All the glasswares were thoroughly cleaned, rinsed with deionized water and dried in an oven at 120°c.

3.2 Methods

3.2.1. Isocynato - Acetyl Cellulose (IAC - H)

(Reaction of Cellulose Acetate with HMDI)

A one litre three necked round bottomed flask was fitted with a magnetic stirrer , a Subaseal septum ,a nitrogen inlet and a water condenser . The whole assembly was flame dried under nitrogen atmosphere . After cooling the reaction flask to room temperature, 10 g cellulose acetate and 500 ml dichloromethane were placed in it and stirred. When dissolution was complete, 6 to 7 drops of dibutyltindilaurate (DBTDL) were added and stirring was continued. About 10 min. later 10 ml HMDI was added dropwise, the flask was then stoppered, and the reaction mixture was refluxed for 1-6 h.

After the end of stipulated reaction time, the reaction mixture was cooled to room temperature . About 200-300 ml of dry hexane was forced into the reaction flask through a

stainless steel cannula under nitrogen atmosphere . The contents were stirred for 30 min., then allowed to settle down and the supernatant liquid was siphoned off, using a stainless steel cannula under nitrogen atmosphere.

This process was repeated 4-5 times . After the washing was completed, the remaining solvent was removed and the product was dried under vacuum at room temperature.

3.2.2 Amino-Acetyl Cellulose (AAC-H)

The dried (IAC-H) was wetted with dry acetone and then acetone/water (1:1) mixture was added. The contents were stirred overnight and then filtered, washed successively with water, ethanol and finally with acetone. The product was dried under vacuum at 80 °C.

3.2.3 Amino-Acetyl-Cellulose (AAC-T)

The same procedures as described in Section 3.2.1 and 3.2.2 were followed for the preparation of amino acetyl cellulose (AAC-T) except that tolylene 2-4-diisocynate (TDI) was used in place of HMDI, and the reaction time was 6 h

3.2.4 Amino Ethyl Cellulose (AEC-H)

Amino ethyl cellulose was prepared by following the same procedures as described in Sections 3.2.1 and 3.2.2 except that ethyl cellulose (DS = 2.47) was used in place of acetyl cellulose, and the reaction time was 6 h

3.2.5 Polystyrene with Pendant Amino Groups (A - PS)

About 5 g chloromethylated polystyrene was weighed and suspended in 25 ml dimethyl formamide (DMF) in 250 ml round bottomed flask. A solution of 7.5 g hexamine in 25 ml acetic acid /water (1:1) was added to above suspension. The reaction mixture was heated at 120 °C for 12 h

The product obtained was then cooled to room temperature filtered and washed successively with DMF, water, methanol and acetone. For each washing about 10 ml of above solvents were used for three times except DMF. The product obtained was dried under vacuum.

Yield 4.274 g.

3.3 Polymer Supported Schiff Bases

General Procedure

In a 100 ml round bottomed flask equipped with a magnetic stirrer bar, and water condenser, 1 to 4 g desired polymer with pendant amino group such as AAC-H, AAC-T, AEC-H or A-PS, and 10 ml DMAc were placed. To it excess of the desired aldehyde or ketone compound dissolved in 5 ml DMAc, was added slowly and the reaction mixture was refluxed in an oil bath for 6 h. The flask was then cooled to room temperature. 20 ml ethanol was added and the reaction mixture was stirred for few min. and then allowed to settle down. The supernatant liquid was decanted off. Again 20 ml.

The various polymer anchored Schiff bases synthesized are listed in Table 3.1.

Table 3.1 POLYMER SUPPORTED SCHIFF BASES.

Sr. No.	Polymer Support (g)	Carbonyl Comp in excess (g)	Polymer Supported Schiff Base code	Yield (g)
1.	AAC-H 1.83	salicylaldehyde 4.00	AAC-H-1	2.20
2.	AAC-H 4.0	2-hydroxyl-1-naphthaldehyde 6.0	AAC-H-2	5.22
3.	AAC-H 2.5	DAMO 3.48	AAC-H-3	2.4
4.	AAC-T 1.50	salicylaldehyde 1.0	AAC-T-1	1.22
5.	AAC-T 1.25	2-hydroxy-1-naphthaldehyde 1.576	AAC-T-2	1.23
6.	AAC-T 1.25	DAMO 0.739	AAC-T-3	1.31
7.	AEC-H 2.5	salicylaldehyde 2.3	AEC-H-1	2.99
8.	AEC-H 2.5	2-hydroxy-1-naphthaldehyde 2.67	AEC-H-2	2.6
9.	AEC-H 2.5	DAMO 1.5	AEC-H-3	2.37
10.	A-PS 4.0	salicylaldehyde 7.0	APS-1	4.12
11.	A-PS 4.0	2-hydroxyl-1-naphthaldehyde 6.0	APS-2	4.16
12.	A-PS 4.0	DAMO 5.0	APS-3	3.95

ethanol was added and the process was repeated 3 to 4 times. Finally the residue was filtered, washed with ethanol and then with acetone and vacuum dried. The dried product was further purified by soxhlet extraction with acetone.

Polystyrene supported Schiff bases were prepared in the same manner except that the reaction was carried out in ethanol instead of DMAc (68).

3.4 Chemical Methods

3.4.1 Determination of Acetyl Content and Degree of Substitution of Cellulose Acetate

Acetyl content of cellulose acetate was determined by saponification under mild condition followed by back titration with standard acid according to the procedure of (74). This method is applicable to a wide range of cellulose acetate including partially insoluble acetates.

About 1 g of exactly weighed powdered cellulose acetate was taken in 250 ml Erlenmeyer flask and 40 ml of 75% ethanol was added to the flask. The flask was loosely stoppered and kept at 50°to 60°C for 30 min. To the same flask 40 ml of 0.5 N sodium hydroxide solution was added and the contents were again heated to 50°to 60°C for 15 to 20 min. Then the flask was stoppered tightly and allowed to stand at room temperature for about 48 h .After 48 h the

unreacted (excess) alkali was titrated with 0.5 N HCl solution using phenolphthalein as an indicator. Duplicate runs were made for each sample.

A blank titration reading without using cellulose acetate sample was taken in the same manner.

Calculations

$$\% \text{ Acetyl group.} = \frac{[(A-B)\ Nb - (C-D)\ Na] \times 4.3}{W}$$

where,

A = ml of NaOH added to sample.

B = ml of NaOH added to blank.

C = ml of HCl added to sample.

D = ml of HCl added to blank.

Nb = normality of NaOH solution.

Na = normality of HCl solution.

W = weight of the sample.

4.3 is a factor to calculate % acetyl equivalent weight 43, degree of substitution (D.S) is given by

$$D.S = \frac{3.86 \times \text{acetyl content}}{102.4 - \text{acetyl content.}}$$

3.4.2 Estimation of Amino Group Capacity.

Acetylating mixture was prepared by mixing 2.4 ml acetic anhydride with 35 ml pyridine and diluting the mixture to 100 ml with toluene.

Polymer with pendant amino groups AAC-H, AAC-T, AEC-H

or A-PS was accurately weighed (0.2 g) and placed in a 100 ml Erlenmeyer flask. Acetylating mixture (10 ml) was added to the sample and refluxed for 1 h .The flask was then cooled and 5 ml of water was added and refluxed for 5 min. The flask was finally cooled to room temperature, and the condenser was rinsed with 10 ml of methanol. The contents were titrated against standard potassium hydroxide (0.2 N) using phenolphthalein as an indicator. A blank titration was run in the same manner except without using the polymer sample.

$$\text{Amino gr.capacity} = \frac{(B - A)\ N}{W} \quad \text{m mol /g}$$

where,

A = burette reading for sample titration.

B = burette reading for Blank titration.

N = normality of KOH solution.

W = wt. of sample.

3.4.3 Adsorption of Metal Ions

Standard solutions of ethylenediaminetetraacetic acid (EDTA) (0.1 M), zinc sulphate (0.1 M) and buffer solutions of pH 10 and pH 5.4 were prepared according to the standard text (72).

Manganese acetate $Mn(CH_3COO)_2.4H_2O$,

Cobaltous chloride $CoCl_2.6H_2O$,

Zinc sulphate $ZnSO_4.7H_2O$,

Nickel Ammonium Sulphate $(NH_4)_2SO_4.NiSO_4.6H_2O$,

Cupric acetate $(CH_3COO)_2Cu.H_2O$, were used to prepare the respective metal ion solutions. Solutions were made using pH 5.4 buffer solution and the concentration in each case was 400 μg/ml.

The polymer supported Schiff base resin (100 mg) was swelled in dimethylacetamide, excess of the solvent was wiped off by lightly pressing with filter paper, and placed in a Erlenmeyer flask. Metal ion solution (400 μg/ml,20 ml) was added and allowed to equilibriate at room temperature for 20 min. Aliquots of the solution were withdrawn and the residual concentration of the metal ions determined by titrating against standard EDTA solution (.0025 M) (72).

3.5 Instrumental Methods

Infrared spectra were recorded on a Perkin Elmer 883 IR spectrophotometer.

About 1 to 1.5 mg of the sample was dispersed in 80 mg of dry KBr and KBr pellets were prepared using the standard procedure. The spectra were scanned in 4000 to 600 cm^{-1} region except for resin metal-complex where the range was 2000 to 200 cm^{-1}.In all the cases a KBr pellet containing no sample was used as a reference.

Microanalyses were performed at National Chemical Laboratory,Pune.