CHAPTER - II

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2.1 Dry and Oxygen-free Environments

Atmospheric oxygen and traces of moisture have very adverse effect on transition metal halides, organometallic compounds and their reaction products. Therefore all the experiments were carried out under extremely dry and inert atmosphere. The preparation of catalyst solutions and their mixing were also carried out inside a dry glove box made of wood. A glass frame on the top and two rubber gloves by the side were fitted for manipulations inside the box. The box had an opening on one side to an antechamber through a sliding door. All materials to be taken in or out of the box were first kept in this chamber before transporting across the sliding door, so that the dry box was never open directly to the outside atmosphere. The box was constantly flushed with dry and oxygen free nitrogen introduced through an inlet and the outlet for outgoing gas was guarded by silica gel tower.

2.2 Purification of Nitrogen Gas

The nitrogen gas was made oxygen-free by successively passing through four columns of 8" of Fieser's solution (see 2.3.1). It was then passed through a bubbler containing aqueous saturated lead acetate solution to remove sulphurous gases. After bubbling through distilled water, it was successively dried over calcium chloride, sulphuric acid,
phosphorous pentoxide, potassium hydroxide pellets, silica gel and drierite in the given order before passing into the dry box. In addition to this, few more dessicants such as silica gel and activated drierite, potassium hydroxide pellets and phosphorous pentoxide were kept in the dry box. Every day silica gel was freshly reactivated and replaced. Indicator type blue silica gel was used to determine the dryness inside the box.

2.3 Reagents and Solvents

All reagents and solvents used in experiments were pure, dry and were preserved over nitrogen atmosphere.

2.3.1 Reagents

**Fieser's Solution**

Sodium hydrosulphite \((\text{Na}_2\text{S}_2\text{O}_4)\) (15 gms) was dissolved in 100 ml. of water containing 12 gms. of sodium hydroxide \((\text{NaOH})\) and 2 gms. of anthraquinone-\(\beta\)-sulphonic acid-sodium salt (B.D.H.). The solution is blood red initially and becomes dull brown with the formation of white scum on the absorption of oxygen. At this stage, the solution was discarded.

Triethyl amine\(^{127}\) was freed from traces of primary and secondary amines by distilling from acetic anhydride. It was further dried with activated alumina and fractionally distilled three times under reduced pressure. The 1 M solution of triethyl amine was prepared in n-hexane prior to use.

C.P. grade (B.D.H.) hydroquinone was recrystallised
twice from benzene before use.

2.3.2 Solvents

Commercial grade n-hexane$^{128}$ was washed by shaking repeatedly with concentrated sulphuric acid (C.P) (100 ml. for each litre solvent) till the acid layer became colourless. Then it was washed free of acid with distilled water, dried over anhydrous calcium chloride, distilled and kept over sodium wire. The pure solvent was refluxed overnight over sodium under pure dry nitrogen atmosphere and fractionally distilled before use in polymerization experiments. Commercial methanol was fractionally distilled before use.

Carbon tetrachloride$^{128}$ was washed successively in three portions of alcoholic sodium hydroxide. The carbon disulphide free solvent was then washed several times with water, dried over anhydrous calcium chloride and then refluxed over 5% NaOH for about 1-2 hrs. and then distilled in nitrogen atmosphere at 74°C. The distilled solvent was stored in nitrogen atmosphere.

Commercial grade chloroform$^{128}$ was washed several times by shaking with concentrated sulphuric acid for removing alcohol, then washed with dilute sodium hydroxide and with water. The solvent was dried over potassium carbonate and stored in completely filled brown flask and distilled shortly before use.

2.4 Catalysts

2.4.1 Aluminium Diethyl Chloride

It was obtained from M/s. Polyeleins, Bombay, and was
distilled under nitrogen and reduced pressure. A middle cut was used to prepare 2 M solution in n-hexane.

2.4.2 Diethyl Aluminium Bromide

It was prepared by reaction of ethyl bromide with an aluminium-magnesium alloy containing aluminium 69\% and magnesium 33\% corresponding to \( \text{Al}_2\text{Mg}_{12} \), supplied by the courtesy of National Metallurgical Laboratory, Jamshedpur, and analysed as given below:

\[
\text{Al}_2\text{Mg} + 4 \text{C}_2\text{H}_5\text{Br} \rightarrow 2 \text{Al}(\text{C}_2\text{H}_5)_2\text{Br} + \text{MgBr}_2
\]

The alloy was chipped to small pieces and in a typical reaction 55 gms. of it were taken in a three necked 250 ml. flask fitted with nitrogen inlet, dropping funnel, reflux condenser and mercury sealed stirrer. A slight excess over the stoichiometric quantity of ethyl bromide (viz. 204 gms.) which was dried over phosphorous pentoxide, distilled (35\°/710 mm.) and preserved over anhydrous calcium sulphate, was added drop-wise and the reaction initiated with a crystal of iodine. The exothermic reaction resulted in vigorous refluxing of ethyl bromide. Heat of reaction was removed by surrounding the reaction flask with oil bath and the evaporation loss minimised by circulating chilled water in the condenser. The reaction was allowed to proceed under continuous stirring for about 2–3 hours till the refluxing of ethyl bromide had stopped, and taken to completion by raising the temperature to 160\°C.

The alkyl was soaked up in the even mass of magnesium
bromide and removed by distillation under vacuum. The bromide content of the alkyl was estimated by hydrolysis and application of World's method. It was then redistilled under vacuum (b.p. 70°/1 mm.) and stock solution was prepared in n-hexane (0.5 M).

2.4.3 Vanadium Tetrachloride

It was obtained by the courtesy of M/s. Stauffer Chemical Co. U.S.A. It was distilled under inert conditions at 148.5°/760 mm. and its stock solution (0.5 M) was made in n-hexane. A fresh solution was made after every 4-5 days from freshly distilled VCl₄.

2.4.4 Vanadium Oxychloride

It was prepared by reacting vanadium pentoxide with aluminium chloride:

\[ \text{V}_2\text{O}_5 + 2 \text{AlCl}_3 \rightarrow 2 \text{VCl}_3 + \text{Al}_2\text{O}_3 \]

Vanadium pentoxide (Riedel) (35 g) was dried at 110°C, cooled in dry box and mixed thoroughly with 50 gms. of anhydrous aluminium chloride (E. Merck) powder in 250 ml. round bottom flask. This flask was attached to an all-glass distillation unit with ground glass joints, greased with syrupy phosphoric acid. It was heated on a sand bath upto 400°C, when vanadium oxychloride distilled over. The brown liquid thus obtained was redistilled under inert conditions. The pure product obtained was a pale yellow liquid. Stock solution was prepared in n-hexane (0.5 M) and preserved inside the dry box.
2.4.5 Estimation of Vanadium Oxychloride

2 ml. of vanadium oxychloride solution was taken and 25 ml. of sulphuric acid (4 N) was added to it. The vanadium was reduced to tetravalent state by addition of 0.1 N ferrous ammonium sulphate and evaporating to dryness. A further quantity (5 ml.) of ferrous ammonium sulphate solution was added to ensure completion of reduction to tetravalent state.

The ferrous ammonium sulphate was destroyed with 10 ml. of 10% ammonium persulphate. This was titrated against standard potassium permanganate solution (0.1 N) potentiometrically using standard calomel and platinum indicator electrode.

2.5 Purification of Monomers

2.5.1 Methyl Methacrylate

Methyl methacrylate (Rohm and Hass) monomer was washed with 5% alkali till it was free from the inhibitor tert-butyl catachol. It was then washed with distilled water, dried over anhydrous sodium carbonate overnight at low temperature and distilled under vacuum (28 mm Hg) at 25°C under dry nitrogen.

2.5.2 Isoprene

Isoprene (Phillips) was freed from tert butyl catachol by washing with 10% alkali solution followed by washing with a large quantity of distilled water. It was distilled and later stored over anhydrous magnesium sulphate. The required amount of monomer was redistilled over sodium under nitrogen prior to use.
2.6 Polymerization and Isolation of Polymers

The catalyst system under investigation consists of the metal alkyls and transition metal halides. Both are very sensitive to moisture and air. The reaction vessels and dispensers were thoroughly dried and kept under nitrogen. All the reaction flasks and magnetic stirrers (enclosed in glass) were thoroughly cleaned with chromic acid, washed with distilled water and dried overnight at 160° in an oven. They were first transferred inside the dry box when hot and cooled under the atmosphere of nitrogen. Similarly, all glass hypodermic syringes with stainless steel needles were cleaned with chromic acid, washed with distilled water, dried at 110° and transferred into dry box while hot.

Stock solutions of catalysts, dry solvents and monomers were preserved inside dry box and required amount of reagents were added with syringes (1-20 ml.) in the predetermined order. Conical flasks (50 ml.) with B13 (male) cone joint and with B19 (female) stoppers were used for all the systems. Temperature of the thermostat was controlled to ±0.05°C by a toluene-mercury regulator connected to an electronic relay. The stirring element inside the reaction flask was moved by a rotating horse-shoe magnet kept under it, enclosed in a water-proof brass case and carried on ball bearings. The magnet was connected by a flexible speedometer shaft cable to a stirring motor and the speed of its rotation adjusted.

After allowing the polymerization to proceed to the
required time, it was quenched by addition of acidified methanol and polymer precipitated by further addition of large excess of methanol. The mother liquor was treated with excess of methanol to make sure that the entire polymer precipitated. The polymers were settled in the container after keeping overnight in refrigerator. The polymers filtered through weighed sintered crusible, dried to constant weight and weighed.

2.7 Molecular Weights

Polymers of methyl methacrylate prepared with VOCl₃-AlEt₂Cl and VOCl₃-AlEt₂Br catalyst systems were purified by reprecipitation from chloroform solutions using methanol as precipitant. Stock solutions were prepared in chloroform.

Molecular weights were determined viscometrically in an Ostwald viscometer. The following relationship of intrinsic viscosity with molecular weight was used to calculate molecular weight of polymethyl methacrylate.

\[ \eta = 4.3 \times 10^{-5} M^{0.8} \] (in chloroform at 30°)

2.8 Analysis of Polymers by NMR & IR Spectra

NMR spectra were recorded on a Varian T-60 mc/s spectrophotometer. The samples of polymethyl methacrylate were dissolved in purified chloroform (3-10% solution) and NMR spectra were recorded at 25° in chloroform.

The NMR spectra of polymethyl methacrylate were examined for the tacticity of the polymers. This was done by calculating areas under the respective α-methyl
triad units with a planimeter. The stereoregular sequence distribution in the polymers was then computed.

The IR spectra of complexes of methyl methacrylate were recorded with Perkin Elmer Infracord 137B spectro­photometer.

The IR absorption spectra of polyisoprene on KBr pellet (3.5 mgm/0.5 gm, 13 mm disc) were recorded on Perkin Elmer Infracord 137B Spectrophotometer.