

EXPERIMENTAL



## CHAPTER III

### EXPERIMENTAL

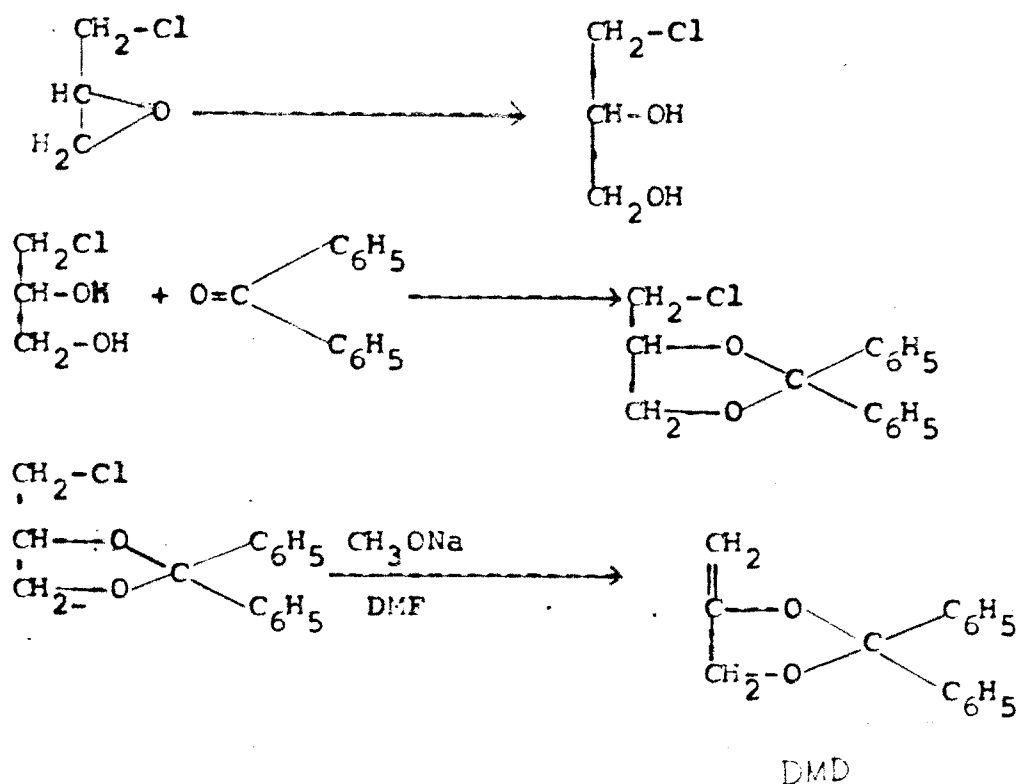
#### 3.1 MATERIALS : Following materials were used

Epichlorohydrin (AMRUT CHEMIE), Triethylamine (CP Grade), p-Toluene sulfonic acid (CP Grade), Sulfuric acid (CP Grade), N,N dimethyl formamide (BDH), Tetrahydrofuran (BDH), Petroleum ether (S.D.Fine Chem), Methylene chloride (S.D.Fine Chem), Diethyl ether (S.D.Fine Chem), Benzene (BDH), Acetone (S.D.Fine Chem).

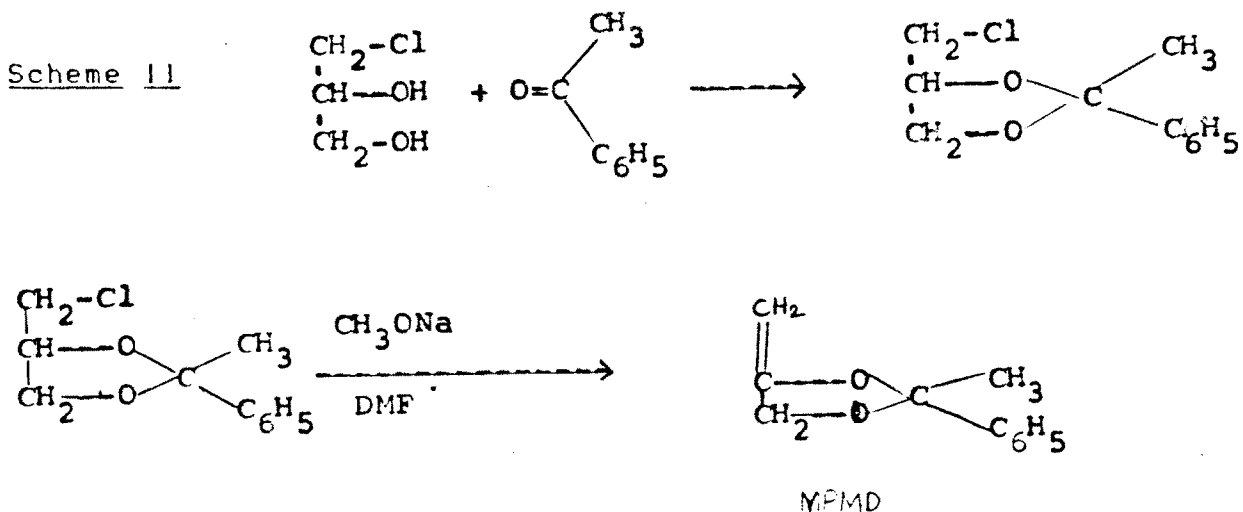
Sodium thiosulphate (BDH), Potassium Iodide (BDH), Potassium Bromide (BDH), Ammonium chloride (BDH), Ammonium nitrate (BDH), Potassium chloride (BDH). All compounds were used without further purification.

#### 3.2 SYNTHESIS OF MONOMERS :

Scheme 1



Scheme 11



### 3.3 SYNTHESIS OF 2,2-DIPHENYL-4-METHYLENE-1,3-DIOXOLANE

#### 3.3.1 Synthesis of 3-chloro-1,2-propanediol :

In a 500 ml round bottom flask, was taken 78.0 ml of Epichlorohydrin, 18.0 ml of water and 0.5 ml of conc. sulfuric acid. This mixture was stirred for about 6 hours and was subsequently neutralized by sodium bicarbonate. The residue was distilled under reduced pressure to give 69.5 ml of 3-chloro-1,2-propanediol bp. 121° C / 5mm Hg.

#### 3.3.2 Synthesis of 2,2-diphenyl-4-chloromethyl-1,3-dioxolane :

In a 500 ml three necked round bottom flask equipped with a Dean-Stark apparatus and thermovel, were placed 3-chloro-1,2-propanediol (22.1 g, 0.2 mol) and benzophenone (36.4 g, 0.2 mol) in 170 ml of dried benzene and (0.3 g) p-toluenesulfonic acid (pTsOH). This mixture was refluxed for about 7 hours with azeotropic removal of water. Then TsOH was destroyed by addition of triethylamine. Benzene was removed by distillation. The

residue was distilled under reduced pressure to give 2-2 diphenyl 4-chloromethyl-1,3-dioxolane bp = 132°C/5 mm Hg. Yield = 35.0 g (63%).

### 3.3.3 Dehydrochlorination of 2,2-diphenyl-4-chloromethyl-1,3-dioxolane :

In a 500 ml three necked round bottom flask equipped with condenser and thermovel, were placed 2-2 diphenyl 4-chloromethyl 1,3 dioxolane (30.0 g, 0.11 mol), sodium methoxide (12.0 g, 0.22 mol), N,N dimethylformamide (150ml) and stirred for 6 hours at 50°C in an oil bath. This mixture was poured into water followed by extraction with five portions of ether. The organic layer was removed, and was distilled under reduced pressure to obtain 14.3 g of DMD bp. = 82° C / 2mm Hg. Yield = 54.4 %

### 3.4 SYNTHESIS OF 2-METHYL-2-PHENYL-4-METHYLENE-1,3-DIOXOLANE :

#### 3.4.1 Synthesis of 2-methyl-2-phenyl-4-chloromethyl-1,3-dioxolane

In a 500 ml three necked round bottom flask equipped with a Dean-Stark apparatus and thermovel, were placed 3-chloro-1,2-propane diol (22.1 g, 0.2 mol) and acetophenone (24.0 g, 0.2 mol) in 170 ml of dried benzene and (0.3 g) p-toluenesulfonic acid (pTsOH). This mixture was refluxed for about 7 hours with azeotropic removal of water. Then TsOH was destroyed by addition of triethylamine. Benzene was removed by distillation. The residue was distilled under reduced pressure to give 2-methyl-2-phenyl 4-chloromethyl-1,3-dioxolane bp = 118.5°C/5 mm Hg. Yield = 33.5 g.

### 3.4.2 Synthesis of 2-methyl-2-phenyl-4-methylene-1,3-dioxolane

In a 500 ml three necked round bottom flask equipped with condenser and thermometer, were placed 2-methyl-2-phenyl-4-chloromethyl-1,3 dioxolane (21.6g, 0.11 mol), sodium methoxide (12.0 g, 0.22 mol), N,N dimethyl formamide (150ml) and stirred for 6 hours at 50° C in an oil bath. This mixture was poured into water followed by extraction with five portions of ether. The organic layer was removed, and was distilled under reduced pressure to obtain 13.5 g MPMD bp. = 115° C / 10mm Hg.

### 3.5 ELECTROLYTIC CELL :

An 'H' shaped corning glass cell shown in the figure was used for carrying out the electropolymerization. It consisted of three parts A, B and C. The glass frit fitted in the adaptor (figure 1) served to divide the electrolyte into anolyte and catholyte. Part A and B were provided each with suitable inlets for passing the nitrogen gas and collecting the generated gases during the course of electropolymerization.

### 3.6 POLYMERIZATION OF DMD

A solution of DMD of required concentration was saturated with ammonium chloride. This solution was taken (50ml. each) in the anode and the cathode compartments of the electrolytic cell respectively. Oxygen was flushed out by purging with oxygen free nitrogen, for about twenty minutes prior to electrolysis. The electrolysis was conducted for the desired duration with required current density.

In gas collection studies, hydrogen generated at the cathode was collected in an eudiometer tube, and the volume of gas collected was measured at regular intervals of time.

For kinetic studies aliquots were withdrawn from anolyte and catholyte solution at regular intervals.

After electrolysis, the anolyte and catholyte were treated with methylene chloride when the polymer precipitated out. The polymer was redissolved in DMF and was reprecipitated using methylene chloride. The solid polymer was dried under reduced pressure for 10 hours.

### 3.7 POLYMERIZATION OF MPMD :

Monomer solution of MPMD in DMF of required concentration was saturated with ammonium nitrate. This solution (50ml) was placed in the electrolytical polymerization set up. Oxygen was flushed out by purging with oxygen free nitrogen, for about twenty minutes prior to electrolysis. The electrolysis was conducted for the desired duration with required current density.

For kinetic studies aliquots were withdrawn from anolyte and catholyte at regular intervals and iodometrically was performed.

After the electrolysis, the electrolyte solutions were treated with water when the polymer precipitated out. The precipitated polymer was separated and dissolved in THF and reprecipitated with distilled water. The solid polymer was dried under reduced pressure for 12 hours.