EXPERIMENTAL
EXPERIMENTAL

III.1(i) PURIFICATION OF CHEMICALS:

(A) Purification of Solvents:

(a) Benzene:

Benzene (analytical grade, Ranbaxy) was purified [178] by shaking it with N/10 sulfuric acid until acid layer was colourless. The benzene was shaken twice with water, in order to remove acid, later on with 10% sodium bicarbonate, again with water and finally dried with anhydrous calcium chloride. It was filtered and distilled. The dried sample had B.P. 80°C. Dry sodium wires were introduced into the distilled benzene.

\[
\text{Yield} = 80\% \quad \text{B.P.} = 80^\circ\text{C}
\]

(b) Methanol/Ethanol:

The analytical reagent grade methanol/ethanol (Ranbaxy) was purified [179,180] by placing clear dry magnesium turning (2.5 gm) and sublimed iodine (2.5 gm) in a two litre double surface reflux condensor. Methanol/Ethanol (500ml) was added through the condensor and the mixture was refluxed on water bath until the iodine disappeared. The product was then distilled, the first fraction was discarded.

\[
\begin{align*}
\text{Methanol} & : \quad \text{Yield} = 90\% \quad \text{B.P.} = 65^\circ\text{C} \\
\text{Ethanol} & : \quad \text{Yield} = 81\% \quad \text{B.P.} = 78^\circ\text{C}
\end{align*}
\]
(c) **Chloroform:**

Chloroform (Ranbaxy, AR grade) was purified \[181\] by shaking it with half of its volume of distilled water for five times. The washed chloroform was dried over anhydrous calcium chloride for 24h with shaking in order to remove water and dried with anhydrous potassium carbonate.

Yield = 76%  
B.P. = 61°C

(d) **Dioxane:**

Dioxane (analytical grade, Ranbaxy) contains small quantities of acetaldehyde, glycoacetal along with water. Dioxane (500ml) \[182\] hydrochloric acid (7 ml) and water (50 ml) were refluxed for 6h under the nitrogen to remove the acetaldehyde. The water was removed by shaking it with potassium hydroxide pellets and later on keeping it over fresh potassium hydroxide pellets for 24h. This was followed by refluxing over excess sodium for 8h. Finally, the dioxane was distilled from sodium.

Yield = 80%  
B.P. = 101°C

(e) **Acetone:**

Acetone 500mg (analytical grade, Ranbaxy) containing water as impurity was purified \[183\] by refluxing successively with 2g potassium permagnate until the violet colour persisted. It was then dried with anhydrous potassium carbonate, filtered and distilled.
Yield = 90%  B.P. = 56°C

(f) Carbon tetrachloride:

Carbon tetrachloride (Ranbaxy, AR grade) was treated [184] with the solution of (potassium hydroxide dissolved in an equal weight of water) and 100ml of rectified spirit to remove carbon disulphite. The process was repeated with half the quantity of potassium hydroxide. The alcohol was then removed by shaking it with water five times, followed by small portion of concentrated sulphuric acid until there was no colouration and finally washed with distilled water. The middle fraction, boiled at 76°C was collected and dried over silica gel.

Yield = 85%  B.P. = 76°C

III.1(ii) PURIFICATION OF NITROGEN GAS:

Nitrogen gas was purified [185] by passing it through alkaline solution of pyrogallol (15 gms pyrogallol dissolved in 100 ml of 50% sodium hydroxide solution to remove traces of oxygen).

III.1(iii) PURIFICATION OF OTHER CHEMICALS:

(A) Hydroquinone:

Hydroquinone (BDH) was recrystallized twice with ethanol before use. The melting point of hydroquinone is 169°C.
(B) **α-α'-Azobisisobutyronitrile (AIBN):**

AIBN (E.Merck) was recrystallized three times from absolute ethyl alcohol by dissolving it at 30°C. The resulting white crystals, m.p. 103°C (literature 103°C) were stored in an air tight bottle in the dark in low temperature cabinet.

(C) **α-Picoline:**

α-picoline was purified [186] by refluxing 100ml of it with 100 gms of dry potassium hydroxide (Ranbaxy) for 10 h with a mixture of 25 gms phthalic anhydride (Ranbaxy) and 25 gms acetic anhydride to remove small amounts of N-picoline and 2:6-lutidines. The dark brown reaction mixture, after cooling was heated with a solution of 50 gms of sodium hydroxide in 150 ml of water and steam distilled until and distillate was no longer alkaline. Again 50 gms of sodium hydroxide were added to distillate in order to separate the base as an upper layer. The aqueous layer was extracted with 50ml ether. After drying with anhydrous potassium carbonate and removing ether, the residual liquid was distilled. Traces of non basic impurities (hydrocarbons etc.) were removed by keeping it under steam distillation with 100ml of hydrochloric acid until detection of hydrocarbon's odour. The middle fraction, boiling at 144°C was collected.

(D) Bromine (E.Merck), p-chloroacetophenone (SRL), imidazole (Koch-light), sodium sulphate (Ranbaxy),
hydrochloric acid (Ranbaxy), sodium hydroxide (BDH); 
potassium carbonate (Ranbaxy), triphenyl arsine (E.Merck) 
and p-methyl acetophenone (E.Merck), were used as 
received without further purification.

III.1(iv) PURIFICATION OF MONOMERS:

The vinyl monomers, generally polymerized at room 
temperature, therefore, they are stabilized with 
inhibitor like hydroquinone. In order to get accurate 
kinetic data, these impurities are removed prior to 
polymerization.

Styrene (Ranbaxy) and methylmethacrylate (Ranbaxy) 
both contained hydroquinone as impurity. Therefore, 
these monomers were purified according to the method 
given by Block et al. [187] and Overberger [188]. The 4% 
aqueous solution of sodium hydroxide (400ml) was added to 
the monomers (100 ml) in a separatory funnel with 
vigorous shaking, as a result two layers were separated in 
which the upper monomer turned slightly yellowish, the 
alkali layer containing impurity was removed. The 
remaining alkali, from monomer layer, was removed by 
shaking it with distilled water till traces of alkali 
were not present in the washings (tested with litmus 
paper). The washed monomer was dried over anhydrous 
silica gel for 24 h and then decanted into a fresh sample 
of a silica gel in a stoppered flask. The middle 
fraction was collected and stored in low temperature
cabinet under inert atmosphere in nitrogen.

III.2 SYNTHESIS OF METAL ACRYLATES:

Metal acrylates (Zn, Cu) were synthesized by the procedure given by Sayyah [189]. One mole of metal oxide (Mo, M = Zn, Cu) was added to 3 moles of acrylic acid solution in stoichiometric amount, calculated to the carboxyl group. The reaction mixture was then refluxed with continuous stirring for 22h. The excess of solvent was evaporated. The copperacrylate (CuA₂) as green solid, zincacrylate (ZnA₂) as white solid was obtained. 

The reaction scheme is as follows:—

II.2(i) Synthesis of Zinc acrylate (ZnA₂):

\[
\text{Acrylic acid} + 2\text{ZnO} \xrightarrow{\text{acetone, Reflux 22h}} \left( \begin{array}{c} O \\ \text{Zn} \end{array} \right)_2
\]

Acrylic acid
I.R.: DMF cm⁻¹ (Fig. III.2.1)
1760 cm⁻¹ (C = O)

NMR: 6 ppm, TMS (Fig. III.2.2)
7.5 (m, aromatic proton)
1-2 (S, methyl proton)

Yield = 75%
FIG. III: 2:1  IR-SPECTRUM OF ZINC ACRYLATE
FIG. III:2:2. $^1$H-NMR SPECTRUM OF ZINC ACRYLATE
III.2(ii) Synthesis of Copper acrylate (CuA₂):

\[
\text{Acrylic acid} \quad + \quad 3 \text{Cu}_2\text{O} \quad \xrightarrow{\text{acetone} \ \text{Reflux} \ 22\text{h}} \quad (\text{CuA}_2)^2
\]

NMR: \( \delta \text{ ppm, TMS (Fig. III.2.3)} \)
- 2.2-3.5 (m, CH₂)
- 7.5 (m, aromatic proton)

M.P. = 232°C
Yield = 77%

III.2(iii) Polymerization of zinc & copper acrylate:

Zinc and copper acrylate were polymerized by using styrene-arsenic sulphide complex [190, 191] as radical initiator and dimethyl formamide as inert solvent at 90±1°C for 5h under an inert atmosphere of nitrogen. The polymer was precipitated with acidified methanol and dried.

IR: DMF, cm⁻¹
- 1660 cm⁻¹ (\(>\text{C=O}\)) (Fig. III.2.4)

Reaction:

\[
(\text{Zinc acrylate}) \quad \xrightarrow{\text{Polymerization}} \quad \left[ (\text{Poly zinc acrylate}) \right]_n
\]
FIG.III:2:3 $^1$H-NMR SPECTRUM OF COPPER ACRYLATE
FIG. III:2:4 IR-SPECTRUM OF COPPER ACRYLATE
III.3 SYNTHESIS OF 1,2-DIPOLAR COMPOUNDS:

III.3(i) Synthesis of \( \alpha \)-picolinium-p. bromophenacyl- bromide (\( \alpha \)-PBPY):

\( \alpha \)-PBPY was prepared according to the method of Krohnke [192,193] and Lumb [194]. The reaction scheme is as follows:

\[
\begin{align*}
\text{Br} & \quad \text{COCH}_2\text{Br}^+ & \quad \text{N} & \quad + \\
\text{Br} & \quad \text{COCH}_2\text{Br}^+ & \quad \text{N} & \quad \text{CH}_3
\end{align*}
\]

(p.bromophenacyl- (\( \alpha \)-picolene) (p.bromophenacyl picolinium bromide)

\[
\begin{align*}
\text{Br} & \quad \text{COCH} & \quad \text{N} & \quad \text{CH}_3
\end{align*}
\]

(\( \alpha \)-picolinium p.bromophenacylide)

(a) Preparation of p. bromophenacylbromide:

0.1 ml of p. bromoacetophenone (1) and 50ml solvent ether were taken in a flat bottom flask. Bromine (0.1 mole) was added into it with vigourous stirring.
The mixture was then poured into crushed ice where two layers appeared. The organic layer was kept with sodium sulphate overnight, was concentrated and kept at room temperature when p. bromophenacylbromide (2) was separated out, which was recrystallized by ethanol.

M.P. : 85°C

Elemental analysis: Found C, 41.10 H, 2.57

(40.00) (3.00)%

(b) Preparation of p. bromophenacyl picolinium bromide:

0.1 mole of (2) were digested in 20 ml. of anhydrous benzene and 0.1 mole of β-picolene were added dropwise with constant stirring when the addition of picolene was completed, the reaction mixture was refluxed for 1 h, the excess of solvent was evaporated and petroleum ether (60-80°C) was added to it which caused the precipitation of crude product. The resulting product on recrystallization from ethanol gave cream coloured crystals of p. bromophenacyl picolinium bromide.

M.P. : 210-211°C

Elemental analysis:

Found C, 51.45 H, 3.98, N, 4.29

(51.31) (4.00) (4.35)%
(c) **Generation of \( \alpha \cdot \text{PBPY} \):**

0.019 moles of (4) were dissolved in 30 ml of water and then treated with concentrated aqueous solution of potassium carbonate. The solution was stirred and extracted with chloroform. The chloroform extract was dried and evaporated to obtain the \( \alpha \) or \( \beta \) PBPY.

**M.P.:** 240°C

**Yield:** 85%

**NMR:** \( ^1H\text{-NMR (acetones } d_6), \) ppm (Fig.III.3.1)

- 7.13 (Singlet, 3H, methyl group)
- 6.7 (Singlet, 2H, N-CH\(_2\))
- 1.2-2.6 (multiplet; 8H, aromatic)

**IR:** cm\(^{-1}\) (Fig.III 3.2)

- 3030 cm\(^{-1}\) (C-H aromatic)
- 1640 cm\(^{-1}\) (\( \geq \)C=O)
- 820 cm\(^{-1}\) (C-H aromatic)
- 1290 cm\(^{-1}\) (C-N)

**Elemental analysis:** Found C, 50.09 H 3.61 N, 4.40

(49.92) (3.52) (4.48)%

**III.3(ii) Synthesis of Imidazolium p-chlorophenacyllylde (ICPY):**

The p-chlorophenacylbromide & p-chlorophenacyl imidazolium bromide & generation of ylide were carried out by the same procedure as mentioned in section(III.3.1) with
FIG. III:3:1 $^1$H-NMR SPECTRUM OF α-PICOLINIUM p-BROMOPHENACYLIDE
FIG. III:3:2 IR SPECTRUM OF $\alpha$-PICOLINIUM p-BROMOPHENACYLIDE
the change of chemicals needed i.e. imidazolium in place of picolinium

Imidazolium p.chlorophenacylride (ICPY) was prepared by the method of Boeklheide and Fedoruk [195].

The reaction scheme is as follows:

\[
\text{Cl-COCH}_3 + \text{Br}_2 \rightarrow \text{Cl-COCH}_2\text{Br}
\]

(p.chloroacetophenone)  (p.chlorophenacyl bromide)

\[
\text{Cl-COCH}_3^+ \quad \text{N} \quad \text{H}
\]

(Imidazolium p.chlorophenacylride)

\[
\text{Br}^- \quad \text{N} \quad \text{H}
\]

(p.chlorophenacylimidazolium bromide)

\[\text{^1H-NMR: (DMSO d}_6) \gamma \text{ ppm (Fig.III.3.3)}\]

6.80 γ ppm (Singlet 2H, N-CH₂)

2.0-2.86 γ ppm (Multiplet 8H, aromatic)

\[\text{IR: cm}^{-1} \quad \text{(Fig.III.3.4)}\]

3030 cm\(^{-1}\) (C-H aromatic)

1640 cm\(^{-1}\) (>C=O)

1390 cm\(^{-1}\) (C-H)

1290 cm\(^{-1}\) (C-N)

820 cm\(^{-1}\) (C-H aromatic)
FIG. III:3:3 $^1$H-NMR SPECTRUM OF IMIDAZOLIUM p.CHLOROPHENACYLIDE
FIG. III:3:4 IR SPECTRUM OF IMIDAZOLIUM p-CHLOROPHENACYLIDE
III.3(iii) Synthesis of p-acetylbenzylidene triphenyl arsoniumylide (p.ABTAY):

p.ABTAY was prepared by the method of Tiwari et al. [196].

\[
\begin{align*}
\text{(p. bromomethyl acetophenone)} & \quad \text{(Triphenylarsine)} & \quad \text{(p. acetylbenzylidene triphenylarsonium bromide)} \\
\text{(p. acetylbenzylidene triphenylarsonium ylide)} & \quad \text{NaOCH}_3 & \quad \text{CH}_3\text{OH}
\end{align*}
\]
(a) Preparation of bromomethyl acetophenone:

So in ice cold solution of p.methylacetophenone (6.7 ml dissolved in 13 ml dioxane & 13.0 ml dimethyl ether) 3.0 ml bromine was added dropwise & after complete addition, the mixture was stirred for 3h. Therefore, the stirred mixture was decomposed by pouring it into ice cold water. The white precipitate of p.methyl acetophenone was separated by filtration.

(b) Preparation of p.acetyl benzylidine triphenylarsine:

A solution of 0.04 mole of triphenyl arsenion and 0.04 mole of p.bromomethyl acetophenone in 12.0 ml benzene was refluxed for 72 h & excess of solvent was evaporated. 12.0 ml ethyl acetate was added to the residue. The precipitate salt was isolated by filtration & recrystallized twice from chloroform: benzene mixture (v/v) to get white microcrystals.

M.P: 250°C

$^1$H-NMR: \( \gamma \) ppm (Fig.III.3 5)

6.53 (Singlet, 2H As-CH$_2$)

7.34 (Singlet, 3H, -C-CH$_3$)

1.0-2.0 (Multiplet, 19H)

IR: cm$^{-1}$ (Fig.III.3.6)

2853 (C-H), 1370, 1450 (-CH$_2$-), 1730 (>C=O)

680, 760 (C-H aromatic), 1520 (C=C, aromatic)
FIG. III:3:5 $^1$H-NMR SPECTRUM OF p.ACETYL BENZYLIDENE TRIPHENYL ARSONIUMYLIDE
FIG. III:3:6 IR-SPECTRUM OF p.ACETYL BENZYLIDENE TRIPHENYL ARSONIUM YLIDE
Elemental analysis: C, 62.67 %
H: 4.46 %

(c) Generation of p-acetyl benzylidene triphenyl arsoniumylide

2 gm of 4 acetylbenzylidene triphenyl arsonium bromide in 100 ml of benzene was treated with sodium ethoxide in methanol. When yellow suspension of ylide was obtained.

III.4 POLYMERIZATION PROCEDURE:

III.4(i) Polymerization apparatus:

Modified dilatometric apparatus:

The polymerization reactions were carried out in modified dilatometric apparatus [197] (Fig.III.4.1) which consists of three parts.

The main part of apparatus, which contained lower glass bulb of 9 ml capacity attached to 10 cm long capillary of 2.0 mm diameter. The upper end of capillary was fused with B-14 female standard joint.

The second part of apparatus contained two single way stopcocks a and b, the former was used for passing nitrogen gas into dilatometer and was fused with a B-14 male joint through which it was connected to main part.

The third part contained a trap having bulb of capacity 8 ml, filled with glycol (BDH). The bulb was
FIG. III:4:1 MODIFIED DILATOMETRIC APPARATUS
fused with a glass tube at right angle with B-14 female joint.

III.4(ii) **Polymerization reaction:**

The conversion of monomer to polymer is accompanied by a contraction in the volume of solution since the monomer has larger molal volume than the corresponding monomer unit in the polymeric chain. The volume contraction \( V_C \) was measured in terms of the meniscus movement (in cms.) per unit volume per unit time and the progress of reaction was monitored with the help of a cathetometer. The dilatometric content was precipitated into acidified methanol and the copolymers were dried to a constant weight.

III.4(iii) **Fractionation of copolymer:**

The copolymers were refluxed with non-solvents of corresponding homopolymers for about 60 minutes. The copolymer was dried to a constant weight.

III.4(iv) **Viscometric technique:**

(a) **Determination of average degree of polymerization \( [\eta] \):**

The intrinsic viscosities were used to calculate the average degree of polymerization of the copolymers as given below for MMA-Co-Sty. [198].

\[
[\eta] = 5.76 \times 10^{-3} \times \bar{P}_n^{-0.746} \quad \ldots\ldots\ldots\ldots\ldots(1)
\]
for AN-Co-Sty [199].

\[
[\eta] = 3.6 \times 10^{-2} \bar{M}_w^{0.62} \\
\ldots\ldots(2)
\]

(b) Determination of intrinsic viscosity [200] \([\eta]\):

The reflux time (seconds) of pure solvent \((t_o)\) and solution \((t)\) of different concentrations \((0.4, 0.3, 0.2 \& 0.1\%)\) of copolymers in solvent were determined with the help of Ubbelohde viscometer.

\[
\eta_{sp} = \frac{t - t_o}{t_o} \\
\ldots\ldots(3)
\]

Intrinsic viscosity \([\eta]\) was computed by extrapolating a plot of \(\eta_{sp}\) vs. concentration to zero concentration:

\[
[\eta] = (d1 \text{ gm}^{-1}) = (\eta_{sp}/\text{conc.}) \text{ conc.} = 0 \ldots(4)
\]

III.4(v) Determination of \%conversion and rate of polymerization \((R_p)\):

The volume contraction data for the copolymerization of MMA with Sty. was converted to percentage conversion \((U)\) with the help of master graph (within the error of 0.004\%). The \(R_p\) was calculated by the following equation:

\[
R_p \text{ (mol l}^{-1} \text{s}^{-1}) = 0.75150 \times 10^{-3} \times \frac{U}{t} \\
\ldots\ldots(1)
\]

where \(t\) is polymerization time in minutes.

The weight of AN-Sty copolymer was used to evaluate the conversion.
The conversion(%) was elucidated with the help of following equation:

\[
\text{Conversion (\%) } = \frac{W_1 \times 100}{W_2} \quad \ldots \ldots (2)
\]

where \( W_1 \) and \( W_2 \) are weight of polymer and monomer (gms) respectively. For conversion (mol l\(^{-1}\)) was calculated with the help of following equation:

\[
\text{Conversion (mol l}\^{-1}\text{)} = \frac{W \times 100}{V} \quad \ldots \ldots (3)
\]

where \( V \) is total volume (ml) of reactants. Finally, \( R_p \) was determined from the slope value of time-conversion plots.

III.4(vi) Determination of \( \frac{k_p^2}{k_t} \):

The \( \frac{k_p^2}{k_t} \) (1 mol\(^{-1}\) s\(^{-1}\)) volume [201] was determined using Mayo equation:

\[
\frac{1}{P_n} = X \frac{k_t}{k_p^2} \cdot \frac{R_p}{[M]^2} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]} \quad \ldots \ldots (1)
\]

or

\[
\frac{1}{P_n} = X \frac{k_t}{k_p} \cdot \frac{R_p}{[M]^2} \leq \frac{R_{tr}}{R_p} \quad \ldots \ldots (2)
\]

where \([I], [M], [S]\) denote the concentration of initiator monomer & solvent, respectively, and other terms have their usual meaning. The second term in right hand side of equation (2) represents side effects owing to chain
transfer reactions. It has been assumed that this would not affect the slope of plot of $1/P_n$ versus $R_p$, which was used to evaluate the volume of $k_d^2/k_t$.

III.4(vii) Reactivity ratios:

The monomer reactivity ratios ($r_1$ & $r_2$) were evaluated by Fineman and Ross method [202] with the help of monomer composition, as given below:

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \quad \frac{r_1 M_1 + M_2}{r_2 M_2 + M_2} = \frac{m_1}{m_2} \quad \ldots(1)$$

where $M_1$ & $M_2$ refer to the monomer composition and $m_1$ & $m_2$ to the polymer composition [203, 204].

The value of monomer reactivity ratios, $r_1$ and $r_2$ have been determined by the elegant but laborious graphical method of Mayo and Lewis using integrated form. A simpler method involved by carrying out if $f = (m_1/m_2)$ and $F = (M_1/M_2)$, then above equation can be written as:

$$f = F \frac{r_1 F + 1}{r_2 + F} \quad \ldots\ldots(2)$$

By rearranging terms one obtains:

$$\frac{F}{f} \cdot (f-1) = r_1 \frac{F^2}{f} - r_2 \quad \ldots\ldots(3)$$

A plot of $(F/f) \cdot (f-1)$ as ordinate and $(F^2/f)$ as abscissa is a straight line whose slope is $r_1$ and intercept to
minus $r_2$. Equation (2) can also be rearranged to:

$$\frac{f-1}{F} = -r_2 \frac{f}{F^2} + r_2 \quad \ldots \ldots (4)$$

III.4(viii) **Copolymer Composition**:

The copolymer composition of MMA-Sty copolymer was calculated with the help of respective peak area of aliphatic and aromatic protons in NMR spectra by the method of Srivastava & Mathur [205]. In case of Sty-AN copolymer, AN content was calculated from percentage of nitrogen (elemental analysis) and Sty. content was determined by phenyl protons (NMR spectra).

III.4(ix) **Determination of activation energy** ($\Delta E$):

The energy of activation [206] of the system was evaluated with the help of Arrhenius plot $\log R_p$ Vs $1/T$, according to the following equation:

$$E_{rate} = -2.303 \, R \, d \log \frac{(rate)}{d(1/T)}$$

III.5 **CHARACTERIZATION OF THE POLYMER SPECTROSCOPY**:

The IR, $^1H$-NMR spectroscopic techniques were applied for characterization of polymer and metal acrylates.
III.5(i) **Infrared spectroscopy (IR):**

The infrared spectra were recorded on Perkin Elmer-397 spectrometer.

III.5(ii) $^{1}H$-**Nuclear Magnetic Resonance Spectroscopy:** ($^{1}H$-NMR)

The $^{1}H$-NMR spectra were recorded on Varian EM-390, 90 Mz spectrometer, using CdCl$_3$ as solvent and tetramethyl silane (TMS) as internal reference.

III.5(iii) **Elemental Analysis:**

Elemental analysis of the polymer and metal acrylates were carried out in Perkin Elmer 240°C elemental analyser.

III.5(vi) **Differential Scanning Calorimetry (DSC):**

The Differential scanning calorimetry (DSC) was recorded at a DuPont (99xR) thermal analyser with a 910 DSC cell under dynamic condition with a programming rate of 10°C min$^{-1}$ from 50°C to temperature at which the exothermic rate have been completed.

III.5(v) **Thermogravimetric (T.G.A.):**

Thermogravimetric analysis (TGA) was recorded on TG-750 thermogravimetric analyser (Stanton Redcraft, U.K.). Dynamic thermogram were obtained using a programming rate of 15°C min$^{-1}$ under nitrogen atmosphere.
III.6 SYNTHESIS OF EPOXY RESINS:

Epoxy resins (DGEBA) were prepared by the method of Lee and Naville [207]. DGEBA (Diglycidyl ether of bisphenol-A), having an average molecular weight of approximately 380, is synthesized as follows:

The reaction vessel (Fig.III.6.1) was charged with epichlorohydrin (10 moles) and bisphenol-A (1 mole) and refluxed. Aqueous sodium hydroxide (3 moles) solution was added over a period of 3h to the boiling reaction mixture. The salt was separated from the crude product by adding toluene followed by filtration. The reaction scheme is as follows:

\[
\begin{align*}
\text{Bisphenol-A} & \quad \text{(1 mole)} \\
\text{NaOH} & \quad \text{(aq.)} \\
\text{EPICHLOOROHYDRIN} & \quad \text{(10 moles)}
\end{align*}
\]
FIG. III:6:1  APPARATUS FOR THE SYNTHESIS OF EPOXY RESINS
Characterization of Epoxy Resins:

III.6(i) Epoxide equivalent:

Epoxide equivalent weight (E.E.W.) was determined by the pyridinium chloride method, pyridinium chloride was continuously stirred and refluxed for 25 min. followed by addition of 50 ml methanol. This blank was then titrated against standardised methanolic NaOH (0.5N). Similarly, 0.5 gms of epoxy resin in 25 ml of pyridinium chloride solution was stirred and refluxed for 25 min followed by addition of 50 ml of methanol and titrated against methanolic NaOH (0.5N). Epoxide equivalent was calculated using the following equation [208]:

$$\text{Epoxide equivalent} = \frac{(16) \times (\text{Sample weight, gms})}{\text{gms of oxirane oxygen in sample}}$$

where,

$$\text{gms of oxirane oxygen in sample} = (A-B)(N)(0.016)$$

A = millilitres of NaOH for blank
B = millilitres of NaOH for sample
N = normality of methanolic NaOH

III.6(ii) Hydrolyzable chlorine content:

15 ml of toluene was added to epoxy resin (2 gm) sample and dissolved in 50 ml of 0.1M alcoholic KOH and the content was refluxed for 15 min. It was titrated against 0.1 M HCl. The titre value was used to calculate the chlorine content of sample with the help of following formula derived by Srivastava & Anand [209]:
Hydrolyzable chlorine content = \[ \frac{355 \times 10^{-4} \times \text{Normality of KOH} \times \text{volume of KOH neutralised by epoxy}}{\text{Weight of Sample}} \]

III.6(iii) **Hydroxyl equivalent:**

Hydroxyl equivalent is the weight of the resin containing one equivalent weight of hydroxyl group. Hydroxyl equivalent was determined by acetyl chloride method [210].

10 ml of acetyl chloride (Ranbaxy) (1.5N) solution in toluene was added to cooled 10% (by weight) solution of epoxy resin in dioxane. This was followed by addition of 2 ml pyridine (Ranbaxy) and the contents were heated for 1h then cooled 25 ml chilled acetone was added to solution to check emulsification. This solution was titrated against 0.5M methanolic NaOH solution.

The titre value was used to calculate hydroxyl content using following formula:

\[
\text{Hydroxyl content} = \frac{\text{Weight of sample}}{\text{Normality of KOH} \times (V_1 - V_2) \times 170}
\]

\[ V_1 = \text{Volume of KOH used for blank.} \]
\[ V_2 = \text{Volume of KOH used for sample} \]

III.6(iv) **Viscometric technique:**

A solution of epoxy resin in the suitable solvent (i.e. dioxane and dimethylformamide) was prepared and the
specific viscosity $\eta_{sp}$ was determined by using Ubbelohde viscometer at different temperature (30°, 50°, 70° and 90°C).

III.6(v) Specific gravity and refractive index:

Refractive index was determined by the SIPCON Refractometer Model No. AR-22 S.No. 5668.

III.7 CHARACTERISTIC VALUES OF BLANK EPOXY RESINS:

The epoxy resins were characterized by infrared spectroscopy, nuclear magnetic spectroscopy and elemental analysis.

III.7(i) Physical properties:

The values of viscosity, refractive index, epoxide equivalent, chlorine content, hydroxyl content, specific gravity of diglycidyl ether of bisphenol-A (DGEBA) are summarised in Table III.7.1.

III.7(ii) Spectral analysis for blank epoxy resin:

<table>
<thead>
<tr>
<th>IR</th>
<th>cm$^{-1}$</th>
<th>(Fig.III.7.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>cm$^{-1}$</td>
<td>(epoxy ring)</td>
</tr>
<tr>
<td>920</td>
<td>cm$^{-1}$</td>
<td>(C-O-C-)</td>
</tr>
<tr>
<td>1060</td>
<td>cm$^{-1}$</td>
<td>(ArH)</td>
</tr>
<tr>
<td>1160</td>
<td>cm$^{-1}$</td>
<td>(Ar-O-R)</td>
</tr>
<tr>
<td>1430</td>
<td>cm$^{-1}$</td>
<td>(Phenylene)</td>
</tr>
<tr>
<td>1520</td>
<td>cm$^{-1}$</td>
<td>(Aromatic)</td>
</tr>
<tr>
<td>3020</td>
<td>cm$^{-1}$</td>
<td>(-OH)</td>
</tr>
</tbody>
</table>
FIG. III: 7:1 IR SPECTRUM OF BLANK EPOXY RESINS
<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Properties</th>
<th>Blank epoxy resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Colour</td>
<td>Amber</td>
</tr>
<tr>
<td>2.</td>
<td>Viscosity ($\eta_{sp}$) 30°C</td>
<td>1.58</td>
</tr>
<tr>
<td>3.</td>
<td>Refractive Index (30°C)</td>
<td>1.5695</td>
</tr>
<tr>
<td>4.</td>
<td>Epoxide equivalent (eq/100gm)</td>
<td>195</td>
</tr>
<tr>
<td>5.</td>
<td>Chlorine content (%)</td>
<td>0.50</td>
</tr>
<tr>
<td>6.</td>
<td>Hydroxyl content</td>
<td>0.12</td>
</tr>
<tr>
<td>7.</td>
<td>Specific gravity (30°C)</td>
<td>1.173</td>
</tr>
<tr>
<td>8.</td>
<td>Molecular weight</td>
<td>390</td>
</tr>
</tbody>
</table>
$^1H$-NMR: CDCl$_3$, $\delta$ ppm (Fig.III.72)

- 1.5-2.3 (m, methyl proton)
- 3.5-4.5 (m, CH$_2$ proton)
- 7.0-8.0 (m, aromatic)

III.8 SYNTHESIS OF INTERPENETRATING POLYMER NETWORK (IPN)

Monomer, initiator and crosslinking agent were added to a solution of polymer in appropriate solvent. The solution mixture was polymerized under blanket of nitrogen to obtain IPN. The reaction yielded IPN which was dried under vacuum at 60±1°C.

III.8(i) Interpenetrating Polymer Network Characterization:

The crosslinked density of polymer network is primarily controlled by the amount of chemical crosslinking agent added or method of crosslinking. The two parameters namely $M_c$ (average molecular weight of network between crosslinks) and the percent extractable material removed while approaching equilibrium swelling.

III.8(ii) Estimation of crosslinked density by swelling measurement swelling property:

Swelling measurements were made by soaking the samples in solvents (DMF, Dioxane and Toluene) until an equilibrium weight was achieved (approx. 24h). Weight measurements were made by blotting the sample dry and immediately weighing them. The swelling solvent was then removed by heating the sample to 60°C under vacuum until equilibrium weight was achieved. The swelling percentage was determined from the equilibrium swollen
FIG. III: 7:2 $^1$H-NMR SPECTRUM OF BLANK EPOXY RESINS
weight and the final equivalent dried weight to account for solvent extraction of low molecular components. The relationship used to calculate percentage swelling is as follows [211]

$$\% \text{Swelling} = \frac{W_s - W_d}{W_d} \times 100$$

$W_s$ = weight of swollen IPN
$W_d$ = weight of dry IPN

The crosslinked density of the network was determined by using swelling data of IPN in dioxane with the help of Flory-Rehner equation [212]

$$\frac{1}{\bar{M}_c} = \frac{1}{n} \frac{(1-V_p) + V_p + X_{1,2} V_p^2}{p V_1 \left(V_p^{1/3} - V_p/2\right)}$$

where,

$\bar{M}_c$ = average molecular weight of network between crosslinks
$p$ = density of network
$V_1$ = molar volume of solvent
$V_p$ = volume fraction of polymer in swollen gel
$X_{1,2}$ = Polymer solvent interaction parameter, as calculated by the following expression

$$X_{1,2} = B + \frac{V_1}{RT} \left( \delta_p - \delta_s \right)$$

where,

$\delta_p$ and $\delta_s$ are solubility parameters [213] of polymer and swelling solvent respectively, $B$ = lattice content, the value of which is taken as 0.34.