Chapter - III
EXPERIMENTAL
III.1 Purification of Chemicals:

The following were the methods for purification of various chemicals used in the polymerization.

(i) Purification of solvents

The various solvents, used in polymerization were purified as follows:

(A) Methanol and Ethanol:

Methanol/Ethanol (Ranbaxy) (commercial absolute) was purified [178, 179] by keeping dry magnesium turnings (5.0 gms) and resublimed iodine (0.5 gms.) in a two litre round bottom flask, fitted with a double surface reflux condenser and the mixture was heated until colour of iodine disappeared and then a further 900 ml. of alcohol was added. Heating was continued (for one hour) until all the magnesium was dissolved to form the magnesium methanolate/magnesium ethanolate. The mixture was refluxed for one hour, followed by distillation.

Yield = 90% Methanol
B.P. = 65°C

Yield = 81% Ethanol
B.P. = 78°C
(B) Benzene

The impurity of thiophene present in benzene (Ranbaxy) was removed [180], shaking it with 15% of its volume of N/10 sulphuric acid until the thiophene gives negative test. In order to remove acid, it was shaken twice with water and then once with 10% sodium bicarbonate solution and again with water and finally dried over anhydrous calcium chloride. After filtration it was distilled. The middle fraction collected, had B.P. 81°C. Dry sodium wires were introduced into the distilled benzene.

Yield = 80%
B.P. = 81°C

(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 twenty four hours with shaking in order to remove water.

Yield = 75%
B.P. = 61°C

(D) Dioxane

Dioxane (Ranbaxy, AR grade) contains small quantities of acetaldehyde, glycol acetal together with water.
500 ml. of dioxane [182], 7.0 ml. of N/10 hydrochloric acid and 50 ml. of water were refluxed for 6 hours under the stream of nitrogen to remove the acetaldehyde. The water was removed by shaking it with potassium hydroxide pallets for 24 hours. This was followed by refluxing over excess of sodium for 8 hours. Finally, the dioxane was distilled from sodium.

Yield = 80%
B.P. = 101°C

(E) Acetone

Acetone (250 ml.) containing water as impurity was purified [180] by refluxing successively with 1 gm. of potassium permangate until the violet colour persisted. It was then dried over anhydrous potassium carbonate, filtered from desicant and distilled.

Yield = 90%
B.P. = 56°C

(ii) Purification of monomers:

Styrene and methylmethacrylate:

Styrene (Ranbaxy) and methylmethacrylate (Ranbaxy) both contains hydroquinone as main impurity. Therefore, these monomers were purified according to the method given
by Overberger [183].

The 4% aqueous solution of sodium hydroxide (400 ml.) 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 hours and then decanted onto 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 of nitrogen.

(iii) Purification of nitrogen gas:

The nitrogen gas, containing traces of oxygen was purified [184] by passing it into an alkaline solution of pyragallol (100 ml. of 5% sodium hydroxide solution containing 15 gm. of pyragallol) and then passing it into calcium chloride trap.

(iv) Purification of other chemicals

(A) \(\alpha-\alpha'\) azobisisobutyronitrile (AIBN)

The pure white crystals of AIBN were obtained after
recrystallization from ethanol. It was stored in a air tight bottle and kept in a low temperature cabinet.

\[ \text{Yield} = 85^\circ C \]
\[ \text{M.P.} = 102^\circ C \ (\text{Lit} \ 103^\circ C) \]

(B) Hydroquinone:

Hydroquinone (BDH) was recrystallized from methanol prior to use.

\[ \text{Yield} = 90\% \]
\[ \text{M.P.} = 169^\circ C \]

Other chemicals like bromine (E. Merck) dimethyl-sulphide (Merck 6230276), glacial acetic acid (Ranbaxy), acrylonitrile (Ranbaxy), chromium oxide (Ranbaxy), mercuric chloride (Fluka), sodium hydroxide (BDH), 3,2-thienylacrylic acid (Aldrich 13058.3), arsenic sulfide (Merck 819982) were used as such without further purification.

III.2 Synthesis of initiators and monomers:

(1) Phenacyl dimethyl sulphonium ylide mercuric chloride complex:

(A) Preparation of Phenacyl bromide

It was prepared according to the method given by F. Krohnke [185].
0.1 mole of acetophenone and 50 ml. solvent ether were taken in a flat bottom flask. Bromine (0.1 mole) was added into it with vigorous stirring. The mixture was then poured in the crushed ice where two layers appeared. The organic layer, kept with sodium sulphate overnight was concentrated and kept at room temperature, when phenacyl bromide separated out, which was recrystallized by ethanol.

Yield = 92%
M.P. = 85°C

Elemental analysis:

Calculated: C = 4.10%, H = 2.57%
Found: C = 4.00%, H = 2.87%

(B) Preparation of phenacyl dimethyl sulfonium bromide

A solution of 0.1 mole of phenacyl bromide and 3.0 ml. of dimethyl sulphide (Merck 6230276) was refluxed and stirred for 3 hours. The sulfonium bromide was washed with ether and recrystallized twice from ether-ethanol mixture (1:1 v/v) as a colourless solid [186].

Yield = 81%
M.P. = 132°C

Elemental analysis:

Calculated: C = 35.29%, H = 3.53%
Found: C = 35.09%, H = 3.60%
Fig. III.21 IR Spectrum of phenacyl dimethyl sulfonium bromide
Fig. III.2-2 NMR Spectrum of Phenacyl dimethyl sulfonium bromide
IR(Film); cm$^{-1}$ (Fig. III. 2.1)

1730 cm$^{-1}$ ( $\geq$C=O)  
1310 cm$^{-1}$ ( C-H)  
1420 cm$^{-1}$ (CH$_3$)  
780 cm$^{-1}$ (C-H aromatic)  
510 cm$^{-1}$ (C-Br)  
1140 cm$^{-1}$ (C-S)

NMR: $^{1}$HNMR (DMSO D$_6$) $\delta$ ppm (Fig. III. 2.2)

3.6 (S, 2H, S-CH$_2$)  
1.6 (S, 6H, S<CH$_3$)

(C) Preparation of phenacyl dimethyl sulfonium ylide

Phenacyl dimethyl sulfonium bromide was dissolved in 30 ml. of water. The coloured suspension was filtered and the clear filtrate was treated with 10% sodium hydroxide. The solution was stirred and extracted several times with chloroform. The chloroform extract was dried and evaporated to give an orange oil which upon cooling solidified to orange solid. It was recrystallized from chloroform and used to generate the ylide [187].

Yield = 96%  
M. P. = 75°C
(D) Preparation of phenacyl dimethyl sulfonium ylide mercuric chloride complex

A methanolic solution (25 ml.) of mercuric chloride (1.0 m. mole) was treated drop wise to a solution of sulfrane (2.0 m. mol) in methanol (20 ml.) stirred for 2 hours at room temperature and then isolated by suction filtration. It was then washed with methanol followed by diethyl ether.

Yield = 93%
M.P. = 195°C

Elemental analysis:

Calculated: C = 26.81%, H = 2.81%, Cl = 5.99%
Found: C = 26.84%, H = 2.79%, Cl = 5.98%

IR: (Film); cm\(^{-1}\) (Fig. III. 2.3)
1580-1600 cm\(^{-1}\) (\(\geq\)C=0)
1310 cm\(^{-1}\) (C-H)
780 cm\(^{-1}\) (C-H aromatic)
1140 cm\(^{-1}\) (C-S)

\(^1\)HNMR (TMS d\(_6\)) \(\delta\)= ppm (Fig. III. 2.4)
3.7 (S, 2H, S)\(_\text{CH}_2\)
7.6 (S, 6H, S)\(_\text{CH}_3\)
7.4 (S, 2H)
Fig. III.2.3  IR Spectrum of phenacyl dimethyl sulfonium ylide mercuric chloride complex
Fig. III.2.4  NMR Spectrum of phenacyl dimethyl sulfonium ylide mercuric chloride complex
The reaction scheme is as follows

(A) \[
\text{Phenacyl bromide}
\]

(B) \[
\text{Phenacyl dimethyl sulfonium bromide}
\]

(C) \[
\text{Phenacyl dimethyl sulfonium ylide}
\]

(ii) **Styrene–arsenic sulfide complex:**

It was prepared according to the method reported in literature [25-27] from this laboratory. A solution containing arsenic sulfide \((\text{As}_2\text{S}_3)\) (1 to 10 wt%) in styrene was stirred for 2.5 hours when the complex was obtained as transparent and viscous liquid.

(iii) **Synthesis of chromium thiophene carboxylate:**

It consist of following steps:
(A) Preparation of 2-acetyl thiophene:

It was prepared according to the method of D. Hartough [188].

The thiophene (3 moles) and acetic anhydride (1 mole) and orthophosphoric acid were refluxed for two hours. The content was then cooled to 50°C followed by addition of distilled water (200 ml.). The organic layer, further washed with 200 ml. of 10% sodium carbonate solution, was subjected to vacuum distillation to remove excess of thiophene.

Yield = 81%
B.P. = 77°C

(B) Preparation of 2-thiophene carboxylic acid:

2-acetyl thiophene (1 mole) was added slowly to 1 M sodium hydroxide solution containing sodium hypobromide at 60±1°C. The content was refluxed for 2 hours followed by addition of sodium bisulphite to remove excess of sodium hypobromide. The product was recrystallized from distilled water.

Yield = 90%
M.P. = 128°C
Fig. III.25 IR Spectrum of chromium thiophene carboxylate
Fig. III.2.6  NMR Spectrum of chromium thiophene carboxylate
(C) **Synthesis of chromium thiophene carboxylate**

Solution of calcinated chromium trioxide (1 mole) and 2-thiophene carboxylic acid (3 moles) in acetone was refluxed with continuous stirring for 22 hours. The excess solvent was subsequently evaporated when chromium thiophene carboxylate was obtained as greenish solid.

**Yield = 88%**

**IR: (Film) cm\(^{-1}\)** (Fig. III.2.5)

- 1310 cm\(^{-1}\) (C-H)
- 1760 cm\(^{-1}\) (C=O)
- 1200 cm\(^{-1}\) (C-S)
- 780 cm\(^{-1}\) (C-H aromatic)

**\(^1\)HNMR (TMS d\(_6\)) \(\delta\) ppm (Fig. III.2.6)**

- 2-3 (S, -CH\(_2\))
- 7-8 (S, 4H, aromatic)

The reaction scheme is as follows:

\[
\begin{align*}
\text{(1) } \text{CrO}_3, \text{ acetone} & \xrightarrow{22 \text{ hr. refluxing}} [\text{S-COO}]_3 \text{Cr} \\
\text{(ii) excess of solvent evaporated} & \\
\end{align*}
\]

(iv) **Chromium acrylate**:

It was prepared according to the method of Sayyah et al. [156].
Fig. III.27 IR Spectrum of chromium acrylate
Fig. III.2·8  NMR Spectrum of chromium acrylate
Calcinated chromium oxide (1 mole) was added to 3 moles of acrylic acid followed by 22 hours refluxing with continuous stirring. The excess solvent was subsequently evaporated and residue was dried to constant weight.

IR: (Film): cm$^{-1}$ (Fig.III.2.7)

1760-1735 cm$^{-1}$ (>$\text{C=O}$)

1340 cm$^{-1}$ (C-H)

3000 cm$^{-1}$ (C-H stretching)

$^1$HNMR: (TMS$\delta$) $\delta$=ppm (Fig.III.2.8)

2-3 (S, 12H, $-\text{CH}_2$)

(v) Poly vinyl acetate template (PVAc)

Atactic polyvinyl acetate (at-PVAc) was obtained by the polymerization of vinyl acetate (3.6 mol l$^{-1}$) in benzene at 60±0.1°C in an inert atmosphere of nitrogen using AIBN (4.12x10$^{-2}$mol l$^{-1}$) as an initiator for 4 hours. The polymer, precipitated with distilled water, was dissolved in acetone and reprecipitated in n-hexane. Finally, it was dried to constant weight. When benzene was replaced by chain promoting solvent viz toluene (.5 ml., 1.0 ml., 1.5 ml., 2.0 ml.) atactic polyvinyl acetate of different molecular weight were obtained.
Fig. III.2.9 IR Spectrum of polyvinyl acetate template
Fig. III.2·10 NMR Spectrum of template (PVAc)
Characterization:

IR: (Film); cm$^{-1}$ (Fig. III.2.9)
- $1760-1600$ (C=O)
- $1000$ (C-H bending)
- $3000$ (C-H stretching)

NMR: $^1$HNMR; (CDCl$_3$); $\delta$ ppm (Fig. III.2.10)
- 4.1 (S, 3H, methoxy protons)
- 2.5, 1.8, 1.6 (T, 2H, methylene)
- 1.5, 1.3, 1.1 (T, 3H, methyl)

III.3 Polymerization Procedure:

(i) Polymerization apparatus:

(A) Modified dilatometric apparatus:

The modified dilatometer [190,191] was used in order to carry out the reactions in an inert atmosphere. The modified dilatometer consist of three parts A, B and C (Fig. III.3.1) Part "A" is the corning glass dilatometer having 3 ml. capacity, attached to a 10.0 Cm. long capillary of 2.0 mm diameter and is attached to "B" which has two high vacuum stop cocks, one connected with nitrogen cylinder and other part "C" which consist of trap having 8.0 ml. capacity bulb containing ethylene glycol. The bulb was fused with a glass tube at right angle having female
Fig. III.3-1 Modified dilatometric apparatus
(B) Cathetometer (ELFO UV 111):

The cathetometer, by which the progress of the reaction was monitored as meniscus movement (per unit volume per unit time) during the polymerization, consists of a vertical scale of 10 Cm. length on which the telescope with vernier scale slides and can be fixed on the vertical scale with the help of attached screw.

(C) Photopolymerization apparatus:

The polymerization reactions (chapter IV.8) were illuminated with monochromatic light of 440 nm wavelength obtained by placing a corning filter in front of a 125-w high pressure mercury vapour lamp (Phillips) with fluorescent coating.

(ii) Operation of dilatometer:

The reaction mixture was injected into the part "A" of the modified dilatometric apparatus under the stream of nitrogen gas. The part "B" and "C" were attached to the part "A" and nitrogen gas was bubbled, then the cock 'b' was closed and connection of nitrogen gas was cut off. A thin layer of silicon grease was applied on all the joints of
apparatus. The polymerization runs were carried out at required temperature.

(iii) Progress of reaction:

When monomer is polymerized, there are gradual changes in most of its specific properties in which specific volume is perhaps more significantly affected than any other properties. The conversion of monomer to polymer is accompanied by the contraction. Since the monomer has larger molal volume than the corresponding monomer units in the polymer chain. This arises from the loss on the polymerization of the electron bond, perpendicular to the double bond, which results decrease in the level's of dilatometer's capillary. The progress of the reaction was monitored as volume contraction in centimeters (meniscus movement) and was converted into percentage conversion by means of master graphs (Fig. III.3.2 to III.3.6).

(iv) Determination of rate of polymerization:

Rate of polymerization was calculated from the slopes of linear conversion vs. time plots in all cases.

(v) Determination of activation energy:

The activation energy [192] of the system was computed with the help of Arrhenius plot, using following
Fig. III.3.2 Master graph showing relationship between volume contraction and percentage conversion of chromium acrylate (Capillary dia=1.2mm)
Fig. III.33 Master graph showing relationship between percentage conversion and volume contraction of chromium acrylate (Capillary dia = 12 mm)
Fig. III.3-4 Master graph showing relationship between percentage conversion and volume contraction of styrene with chromium acrylate (Capillary dia = 1.2 mm)
Fig. III.35 Master graph showing relationship between percentage conversion and volume contraction of 3,2 thienyl chromium acrylate (Capillary dia=1.2mm)
Fig. III.3.6 Master graph showing relationship between percentage conversion of acrylonitrile and volume contraction with chromium acrylate.

(Capillary dia = 1.2 mm)
equation

\[ E_{\text{rate}} = -2.303 \frac{R_d (\text{rate})}{d(I/T)} \]

(vi) Separation of daughter polymers:

Daughter polymers were separated by refluxing the polymers with suitable solvent for template. The percent separation varied from 25-75\%. The particular system and inspite by best of efforts separation was not complete.

III.4 Characterization of polymers:

The polymer samples were characterized by viscometric and spectroscopic (IR, NMR & ESR) techniques and elemental analysis as given below:

(i) Viscometric technique

The intrinsic viscosity \( [\eta_{\text{int}}] \) of the polymers were determined in suitable solvent of appropriate temperature using an Ubbelohde viscometer.

Determination of \( \frac{k_p^2}{k_t} \)

The corresponding values of \( R_p \) and \( \Phi_n \) or \( \eta_{\text{int}} \) were used to calculate the value of \( \frac{k_p^2}{k_t} \) using Mayo equation [193].
\[
\frac{1}{P_n} = X \left( \frac{k_t}{k_p} \right) \frac{R_p}{[M]^2} + C_M + C_s \frac{[S]}{[M]} + C_1 \frac{[I]}{[M]}
\]

or

\[
\frac{1}{P_n} = X \left( \frac{k_t}{k_p} \right) \frac{R_p}{[M]^2} + \frac{R_{tr}}{R_p}
\]

where

\[
[I] = \text{concentration of initiator}
\]
\[
[M] = \text{concentration of monomer}
\]
\[
[S] = \text{concentration of solvent}
\]

Other terms have their usual meanings. The second term in the right hand side of the equation represents the side effect owing to chain transfer reactions.

(ii) Spectroscopy:

The IR, NMR and ESR spectroscopy techniques were applied for characterization of initiators and monomers.

(A) Infrared (IR) spectroscopy:

The IR spectrum was recorded on Perkin-Elmer 599B spectrometer using appropriate solvent.

(B) Nuclear magnetic resonance (NMR) spectroscopy:

The \(^1\)HNMR spectrum was recorded on Varian 100HA spectrometer using acetone (D\(_6\)) and CDCl\(_3\) as solvent and
tetramethyl silane (TMS) as internal reference.

(C) Electron spin resonance (ESR) spectroscopy:

The ESR of the polymerization content was recorded on X-Band EPR-109 E-line century series spectrometer. The gyrometric ratio \( \gamma \) [194] was calculated with the help of following relationships

\[
g = \frac{\gamma \cdot B \cdot H}{h}
\]

or

\[
g = \frac{\gamma \cdot h}{B \cdot H}
\]

where

\( \gamma \) = frequency

\( h \) = plank's constant

\( B \) = conversion factor called the Bohr Magneton

\( H \) = strength of external field

(iii) Reactivity Ratios:

(A) The monomer reactivity ratios \( r_1, r_2 \) were evaluated in some of the systems by Fineman & Ross[195] method with the help of monomer composition as given below:

\[
\begin{align*}
\frac{dM_1}{dM_2} &= \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{r_2 M_2 + M_2} = \frac{m_1}{m_2}
\end{align*}
\]

(III. 4. 1)

where \( M_1 \) and \( M_2 \) refer to monomer composition and \( m_1 \) and \( m_2 \) to the copolymer composition [196-198].
The value of monomer reactivity ratios $r_1$ & $r_2$ in eq.III.4.1 have been determined by the 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 equation (III.4.1) can be written as

$$f = F, \frac{r_1F + 1}{r_2 + F} \quad \ldots (III.4.2)$$

By managing terms one obtains

$$\frac{F}{f} (f - 1) = r_1 \frac{F^2}{f} - r_2 \quad (III.4.3)$$

A plot of $(F/f) (f-1)$ as ordinate and $F^2/f$ as abscissa is a straight line whose slope is $r_1$ and intercept is minus $r_2$. Equation III.4.3 can also be rearranged to

$$\frac{f - 1}{F} = - r_1 \frac{f}{F^2} + r_2 \quad (III.4.4)$$

(B) The reactivity ratios $(r_1,r_2)$ were also determined by Kelen-Tudos[199] method. By introducing

$$\eta = \frac{G}{\alpha + F} \quad \text{and} \quad \xi_1 = \frac{F}{\alpha + F} \quad (III.4.5)$$

where denotes and arbitrary constant ($\alpha > 0$)

$$\eta = (r_1 + \frac{r_2}{\alpha}) \xi_1 - \frac{r_2}{\alpha} \quad (III.4.6)$$
and/or

\[ \eta = r_1 \xi_1 - \frac{r_2}{\alpha} (1 - \xi_1) \]  

(III. 4. 7)

Thus plotting the \( \eta \) values calculated from the experimental data in the function of \( \xi_1 \), we obtain a straight line which when extrapolated to \( \xi_1 = 0 \) and \( \xi_1 = 1 \) gives \(-\frac{r_2}{\alpha}\) and \( r_1 \) (both as intercepts).

(iv) Thermal characterization

(A) Thermogravimetric analysis (TGA) of the polymer was carried using a V2.2A DuPont 9900 analyser.

(B) Differential scanning calorimeter (DSC) of the polymer were carried out using a DuPont 910 analyser.

(v) Elemental analysis

The elemental analysis of the synthetic organic compound were carried out in Perkin Elmer 240'C' elemental analyser.