CHAPTER 2
MATERIALS AND METHODS

2.0 Introduction

In this chapter, all the materials and methods used for the studies covered in this thesis has been compiled. All aspects of the experimental work have been described here.

The experimental work involving polythiol and polythiourethane involved the following major aspects, which has been covered by detailed experimental plans:

- Synthesis
- Polymerization
- Characterization

2.1 Raw materials

Chemicals like epichlorohydrin, trialkylamine, sodium sulfide flakes, conc. HCl, thiourea, toluene and ammonia solution used in the synthesis of polythiol were procured from s. d. fine Chem. Ltd., Mumbai, India. Tricresyl phosphate used in the polymerization process was procured from CDH chemicals, Mumbai, India. Toluene diisocyanate (98% purity) and dibutyl tin dilaurate of 95% purity was procured from ALDRICH, USA. Thio alcohol was procured from CDH chemicals, Mumbai, India. The diol formed during step one was used as the raw material for the formation of the second intermediate i.e. tetrol which was further used for the synthesis of isothiouronium salt. Isothiouuronium salt was used for polythiol formation. Polythiols as synthesized by the four-step reaction was used for polymerization of thiol to polythiourethane.

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2.2 Apparatus

A five necked round bottom (RB) flask fitted with (i) thermometer pocket, (ii) nitrogen inlet, (iii) dropping funnel (iv) stirrer and (v) glass condenser was used for the synthesis of polythiol. This glass apparatus was used for the preparation of all four intermediates. A schematic diagram of the apparatus is presented in Fig. 2.1.

Fig. 2.1: Schematic diagram of reaction assembly showing, 1) Stirrer, 2) Water condenser, 3) Thermometer, 4) Dropping funnel, 5) Nitrogen inlet, 6) Five necked R.B. flask, 7) Heating Bath, 8) Stand.
2.3 Synthesis

Synthesis of polythiol was carried out in four steps involving the formation of three intermediates. The intermediates were analyzed after each step for product formation, unreacted materials, functional groups such as chlorine, mercaptan and yield by analytical techniques as described under the section, characterization. The flow diagram of the synthesis work involving the three intermediates has been shown in Fig. 2.2. Here, it may be noted that each process step has been duly optimized for the purpose of scale-up. The details of each step are described in the following sections.

2.3.1 Synthesis of intermediate I: Diol

Raw materials: The raw materials used in the synthesis of Diol are thioalcohol, chloro epoxyalkane and trialkylamine.

Method: The procedure for the synthesis of diol involved the following steps:

(i) Preparation of reaction set-up: The reaction set up as shown in Fig. 2.1 was used for carrying out the synthesis of first intermediate.

(ii) Synthesis: Thioalcohol and trialkylamine were taken in the RB flask. Chloro epoxyalkane was added drop wise from a dropping funnel to the reactants in the flask.

(iii) Cooking: After completion of addition, the reaction mixture was kept under stirring for the reaction to take place.

(iv) Completion of reaction: The completion of the reaction and the formation of diol were analyzed at frequent intervals by
analyzing the diol for various parameters. Diol was characterized with respect to specific gravity, refractive index, acid value etc.

**Reaction parameters:** During the addition of chloro-epoxy alkane to thioalcohol, parameters such as time of addition were studied. After addition, the effect of parameters such as catalyst, reaction temperature and reaction time were studied.

**(a) Effect of catalyst**

Tertiary amine was used as a catalyst for the formation of the first intermediate. Reactions were carried out in the absence and presence of catalyst. Reactions were carried out with 0.5% - 1.0% catalyst and the effect of catalyst on diol formation was studied.

**(b) Effect of reaction temperature**

The effect of temperature on diol formation was studied by carrying out reactions at temperature ranges of 25-30°C, 30-35°C, 35-40°C and 40-45°C. Reactions were also carried out without control of temperature.

**(c) Effect of reaction time**

The effect of reaction time on diol formation was studied by carrying out the reaction for a period of 30 min, 45 min, 1 hr, 1.5 hrs and 2hrs.
Fig. 2.2: Steps and process involved in the synthesis of polythiol: This is a four step reaction involving the conversion of basic components i.e. thioalcohol and chloroepoxy alkane into a high refractive index monomer polythiol
2.3.2 Synthesis of intermediate II: Tetröl

**Raw materials:** The raw materials used in the synthesis of tetröl are diol (intermediate I) and sodium sulfide.

**Method:** The procedure involved in the synthesis of tetröl involved the following steps:

(i) *Preparation of reaction set-up:* The reaction set up as shown in Fig. 2.1 was used for carrying out the synthesis of the second intermediate.

(ii) *Synthesis:* Sodium sulfide solution was prepared by dissolving sodium sulfide flakes in water. Diol was taken in the RB flask to which sodium sulfide solution was added drop wise from a dropping funnel.

(iii) *Cooking:* After completion of addition, the reaction mixture was stirred continuously for the reaction to take place.

(iv) *Completion of reaction:* The formation of tetröl and complete consumption of diol and sodium sulfide was evaluated at frequent intervals for analyzing the completion of reaction. The completion of the reaction was analyzed by HPLC and TLC.

**Reaction parameters:** The effect of reaction parameters like reaction time, reaction temperature and molar ratio of sodium sulfide involved in the formation of tetröl were studied.

(a) *Effect of reaction time:* The effect of reaction time was studied by carrying out reactions for a time period of 1hr, 2hrs and 3hrs.
(b) **Effect of temperature:** The effect of temperature on polythiol formation was studied by carrying out reactions at 25-30°C, 30-35°C, 35-40°C, 40-45°C, 45-50°C, 50-55°C and 55-60°C.

(c) **Effect of molar ratio of sodium sulfide:** The effect of molar ratio of sodium sulfide on the yield of polythiols was studied by carrying out reactions with 0.5 M, 0.7 M, 0.8 M, 0.9 M and 1.0 M of sodium sulfide.

**2.3.3 Synthesis of intermediate III: Isothiouuronium salt**

**Raw materials:** The raw materials used in the synthesis of isothiouuronium salt were tetrol (intermediate II), concentrated hydrochloric acid and thiourea.

**Method:** Procedure for the formation of isothiouuronium salt involved the following steps:

(i) **Preparation of reaction set-up:** The reaction set up as shown in Fig. 2.1 was used for carrying out the synthesis of IIIrd intermediate.

(ii) **Synthesis:** Tetrol was taken in the RB flask to which conc. HCl and thiourea were added.

(iii) **Cooking:** After completion of addition, the reaction mixture was stirred at 100-110°C for the reaction to take place.

(iv) **Completion of reaction:** The completion of reaction was determined by HPLC and TLC.

**Reaction parameters:** The reaction parameters such as reaction temperature, reaction time and molar ratio of reagents involved in the third step were studied.
(a) **Reaction temperature:** The effect of temperature was studied by carrying out reactions at temperatures of 90-100°C, 100-110°C, and 110-120°C.

(b) **Reaction time:** The effect of reaction time was studied by carrying out the reaction for a period of 3 hrs, 6 hrs, 9 hrs and 12 hrs.

(c) **Molar ratio of the reagents:** The effect of molar ratio of conc. HCl: thiourea of 2:2, 2:2.5 and 3:2.5 were studied on the yield of polythiol.

The effect of the various parameters on the yield of polythiols was studied. The isothiouronium salt was analyzed by HPLC and TLC.

**2.3.4 Synthesis of intermediate IV: Polythiol**

**Raw materials:** The raw materials used in the synthesis of polythiol are isothiouronium salt (intermediate III), ammonia solution and toluene.

**Method:** Procedure for the synthesis of polythiols involved the following steps:

i) **Preparation of reaction set-up:** The reaction set up as shown in Fig. 2.1 was used for carrying out the synthesis of polythiol.

ii) **Synthesis:** To the isothiouronium salt, ammonia solution was added drop wise from a dropping funnel.

iii) **Cooking:** After completion of addition, the reaction mixture was stirred for three hours for cooking of the reaction mixture.

iv) **Purification:** The reaction product was washed, distilled and filtered.
(a) **Washing of polythiol**

Since the reagents used during the synthesis of polythiols involve acids and bases, various impurities formed during the reaction, needs to be removed. Polythiols are washed thoroughly to remove acidic and basic impurities.

The polythiol is taken in a separating funnel to separate the organic layer from the aqueous layer. The aqueous layer is discarded and the organic layer is washed sequentially with:

- Water
- Concentrated hydrochloric acid
- Water
- Ammonium hydroxide
- Water

Washing with water is done till the aqueous layer becomes neutral to litmus thereby indicating that the polythiol was free of acidic and basic impurities.

(b) **Distillation**

After washing, the organic layer was distilled to remove toluene. Distillation was carried out under atmospheric pressure. Toluene distills out at 110 °C leaving behind the polythiol as the residue.

The polythiol was then characterized by FTIR, TGA-DTA, $^{13}$C- NMR, Mass spectroscopy etc.

**Reaction parameters:** The reaction parameters such as reaction time and reaction temperature involved in the synthesis of polythiols was studied.
(a) **Reaction temperature:** The effect of temperature on polythiol synthesis was studied by carrying out reactions at 35-40°C, 50-55°C and 60-65°C.

(b) **Reaction time:** The effect of reaction time on polythiol synthesis was studied by carrying out reactions for 1hr, 2 hrs, 3 hrs, 4 hrs and 6 hrs.

2.4 **Preparation of final product: Polythiourethane**

The polythiol that were synthesized were co-polymerized and were cast into lenses. Various parameters such as polymerization time and polymerization temperatures were studied to select an optimum polymerization cycle. The polythiols synthesized in the present study were used for the preparation of polythiourethanes.

2.4.1 **Raw materials:** The raw materials used in the polymerization of polythiourethanes are polythiol, toluene diisocyanate, tricresyl phosphate and dibutyl tindilaurate.

2.4.2 **Method:** The synthesized polythiol was used for the preparation of polythiourethane. Polythiourethane was cast and polymerized into lenses involving the steps as described below:

i) Preparation of gasket

ii) Fitting of molds

iii) Preparation of polymer mixture

iv) Cast molding of polymer mixture

v) Curing of polymers

(i) **Preparation of gasket:** A suitable gasket consisting of grooves of 2mm thickness into which the lens blanks were fitted was
prepared from plastisol. For the preparation of plastisol, PVC powder (grade - SR 10A) was homogeneously mixed with plasticizer, poured into a stainless steel mold and kept in the oven at 180°C for 30 minutes. The mold was cooled and the gasket was removed from the mold.

(ii) **Fitting of molds**: Clean and polished glass molds were fitted into the grooves of the gasket and held by a clamp.

(iii) **Preparation of polymer mixture**: Synthesized polythiol was mixed with additives and degassed for an hour. It was cooled to room temperature, mixed with polyisocyanate, degassed and injected.

(iv) **Injection of polymer mixture**: The degassed mixture was injected into the glass mold using the filling machine. During injection, care was taken so that no bubbles were entrapped inside the mold. The unit used for the casting and filling of lenses is shown in **Fig. 2.3**.
(v) **Curing of polymers:** Glass mold filled with the polymer mixture was kept in the circulating hot air oven. After curing, the lenses were demolded from the gasket. The lenses were evaluated for parameters such as hardness, scratch resistance, yellowness index, heat resistance, glass transition temperature, refractive index and Abbe number based on which optimization of parameters was carried out.

**2.4.3 Polymerization parameters:** For the polymerization of polythiol into polythioureas, the effects of various parameters such as effect of time, effect of temperature, and effect of molar ratio of TDI:polythiol was studied.

**(a) Effect of molar ratio:** Polythiol: toluene di-isocyanate ratios of 1.0:1.0, 1.0:2.0, 1.0:3.0 and 1.0:4.0 were studied to find out the effect on polymerization.

**(b) Effect of temperature:** Effect of temperature on polymerization and curing was studied by carrying out reactions at 30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 120°C and 150°C.

**(c) Effect of time:** The effect of time on polymerization and curing for 3hrs, 5hrs, 10 hrs, 12 hrs, 14 hrs, and 16 hrs. was studied.

**2.5 Modification of low refractive index materials using polythiol**

The polythiols that were synthesized for the development of high refractive index materials was used as an additive to improve the optical properties of low refractive index materials such as diethylene glycol bis (allyl carbonate).
2.5.1 Raw material: The raw material used for the modification of the existing low refractive index materials are diethylene glycol bis (allyl carbonate) and polythiol.

2.5.2 Method: The method adopted for the casting of lenses with modified refractive index is similar to the method discussed in 2.2.2.

2.5.3 Polymerization parameters: The effect of blending various percentages of polythiol on the optical properties of diethylene glycol bis (allyl carbonate) such as refractive index, transmittance and impact resistance were studied. The percentage ratios of polythiol: diethylene glycol bis (allyl carbonate) that were studied were 87:13, 78:22, 70:30, 63:37, 58:42, 54:46, 50:50, 47:53 and 44:56.

2.6 Characterization

Polythiol which were synthesized by a four step method was analyzed for various parameters such as refractive index, viscosity, mercaptan content (%), acid number, elemental analysis, hydroxyl content (%) and chloride content (%).

Instruments such as DSC and TGA were used for thermal analysis; High Performance Liquid Chromatography (HPLC) and Thin Layer Chromatography (TLC) were used for analyzing the effect of various reaction parameters; refractometer was used for refractive index; viscometer was used for determining the viscosity; impact tester was used for determining the impact resistance of the polymer. Polythiourethane was characterized for properties such as impact strength, scratch resistance, color, %SH, yellowness index, etc.
2.6.1 Thermal analysis

In thermal analysis, Differential Scanning Calorimetry (DSC), Thermo-Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were used to characterize different aspects of polymer systems. For DSC studies, model 2910 of TA Instruments, USA (Fig. 2.4) was used. The rise in temperature was kept at 10°C/min. The studies were carried out in the presence of nitrogen gas. DSC is a widely used calorimetric method because it is rapid, easy to operate and a reliable technique.

Fig. 2.4: DSC instrument (TA-2910) and sample chamber

TGA (Fig 2.5) was used to measure the thermal stability of polythiol and polythiourethane. It was also used to follow the change in the mass of sample as it was heated or held isothermally at a specific temperature. The TGA studies were carried out in nitrogen atmosphere with the operating temperature ranging from room temperature to 1500°C.
2.6.2 High Performance Liquid Chromatography (HPLC)

HPLC analysis was used to detect the presence of unreacted materials and the formation of final products. Components of HPLC system are shown in Fig. 2.6.

HPLC analysis was carried out using Waters High Performance Liquid Chromatographic system consisting of 515 Modular pump, 486 UV-Visible detector & equipped with Waters Millenium Software under the following conditions:
Column : Phenomenex C18
Mobile phase : Water:Acetonitrile(95:5)
Flow rate : 1ml/min
Detector : UV-Visible
Temperature : 30°C
Injection volume : 1ml

2.6.3 Thin Layer Chromatography (TLC)

Thin Layer Chromatography (TLC) was carried out using aluminium sheets (20cm x 20cm) coated with silica gel 60. Methanol, water, acetic acid, toluene and acetonitrile was used as the mobile phase. The systematic representation of TLC has been depicted in Fig. 2.7.

![TLC Plate and Developing Chamber Diagrams](image)

**Fig. 2.7:** (a) TLC plate, and (b) developing chamber

2.6.4 Refractive index

Refractive index was determined by using Abbe refractometer depicted in Fig. 2.8. Refractive index (n) was calculated using the following formula:

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Where, "n" is refractive index, "i" is angle of incidence and "r" is angle of refraction.

Fig. 2.8: Abbe refractometer

2.6.5 Viscosity

The viscosity measurements were carried out using an Ostwald viscometer immersed in a constant temperature bath as illustrated in Fig. 2.9. The viscosity was calculated using the following formula:

\[ \eta = F \times A \frac{d_u}{d_\Delta} \]

Where \( d_u \) = velocity in the direction of flow (min.)

\( d_\Delta \) = difference in position between two fluid layer (m)

A = Area of contact (m²)
2.6.6 Determination of impact strength

Impact strength was determined using impact tester (Fig 2.10) fabricated as per FDA 21 CFR 801.410\[98\], where a steel ball weighing 16.2 g was dropped from a height of 127 cm upon the horizontal upper surface of the lens. Lenses which did not crack or break were taken to be impact resistant.

Fig. 2.10: Impact tester
2.6.7 Determination of scratch resistance

Scratch resistance was determined as per ASTM D3363-92[99]. Pencils of different hardness were used to scratch the surface of the lens/sheet. This process was started with the hardest pencil and continued down. The scale of hardness where it left no scratch mark on the tested specimen was noted down as scratch hardness.

2.6.8 Determination of color

Color CIE system was used to determine the color as per ASTM E-308[100]. UV-Vis spectroscopy was used for transmittance determination in the entire uv-visible range. The three parameters that represent color are the lightness of the color (L* = 0 indicates black and L* =100 indicates white), its position between magenta and green (negative values of a, indicate green while positive values indicates magenta) and its position between yellow and blue (negative value of b indicates blue and positive value indicates yellow).

CIE Lab is the most complete color model used conventionally to describe all the colors visible to the human eye. Lab model is a three-dimensional model, which can only be represented properly in a three dimensional space. The non-linear relations for L, a & b are the logarithmic response of the eye. The model of different types of color indices is presented in Fig 2.11.
Fig. 2.11: Model of different types of color indices

2.6.9 Determination of SH content (%) 

The thiol content of polythiols was determined by iodometry. It was conducted by titration of thiol functional group with iodine solution and is based on following oxidation-reduction process:

\[ 2 \text{RSH} + I_2 \rightarrow \text{RSSR} + 2 \text{HI} \]
\[ I_2 + \text{HI} \rightarrow H^+ + I_3^- \]

A sample weighing approximately 0.1 g was dissolved in 50-ml mixture of chloroform and methanol (50: 50 ratio). 25-ml iodine solution was added and stirred continuously for 15 min. The solution was titrated by sodium thiosulphate. Starch solution was used as an indicator. Disappearance of yellow color and appearance of white color was taken as the end point. Titration of the blank was carried out simultaneously by the same procedure except that the sample was not added in the titration mixture.

% SH content was calculated using the following formula:
\[
\% \text{SH} = \frac{(B-S) \times N \times M \times 100}{W \times 1000}
\]

Where,

- B = Sodium thiosulphate required for the titration of blank (ml)
- S = Sodium thiosulphate required for the titration of sample (ml)
- N = Normality of thiosulphate solution
- W = Sample weight (g)
- M = Molecular mass of sulfur

2.6.10 Determination of yellowness index

Yellowness Index was determined as per BS: 872: Part-5[101] by observing percent transmittance at 700 nm, 560 nm and 420 nm on UV spectrophotometer. Yellowness index was calculated according to the following formula:

\[
\text{Yellowness Index} = \frac{T_{700} - T_{420}}{T_{560}}
\]

Where, \(T_{700}\) is transmittance at a wavelength of 700nm (red)

\(T_{560}\) is transmittance at a wavelength of 560nm (green)

\(T_{420}\) is transmittance at a wavelength of 420nm (violet)

2.6.11 Machinability

Machinability i.e. ability to cut and grind, of lens blanks and sheet of polythiourethane was carried out on a lathe cutting machine. Polishing of lens blanks was carried out by rubbing the surface of polythiourethane materials on emery paper of various grades.
Polishing was carried out on a rotating wheel fitted with a velvet cloth in the presence of micropolished alumina powder (0.3 micron) procured from Buehler (USA). After polishing, clear and transparent plastics were obtained.

2.6.12 X-ray diffraction (XRD)

X-ray diffraction of the samples was carried out using X-ray diffractometer at IIT Delhi, India. It is a versatile, non-destructive analytical technique for identification and quantitative determination of the various crystalline forms, known as ‘phases’ of the compounds present in the powdered and the solid samples. Identification was achieved by comparing the X-ray diffraction pattern, or ‘dиффрактограм’, obtained from the unknown sample with an internationally recognized database containing reference patterns for more than 70,000 phases.

2.6.13 UV-Visible spectroscopy

The transmittance of the cast lenses in the uv-visible region of 200nm – 800 nm was determined (Fig. 2.12) on the UV-Visible spectrophotometer (Model no. UV-1700) procured from Shimadzu.

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2.6.14 FTIR spectroscopy

IR analysis was carried out using Impact 410 spectrophotometer using. Liquid cell was used for the IR analysis of polythiols while for the solid samples potassium bromide pellets were used. IR was used to identify and confirm the presence of the various intermediates involved in polythiol synthesis. The collection of absorption bands was used to confirm the identity of a pure compound or to detect the presence of specific impurities.

2.6.15 NMR and Mass spectroscopy

Structural elucidation of polythiol and intermediates was done by NMR spectroscopy and mass spectroscopy. $^{13}$C NMR was done at CDRI, Lucknow and mass spectroscopy was done at IOC, Faradized.

2.6.16 Elemental analysis

The amount (%) of carbon and hydrogen, nitrogen, sulfur and oxygen contained in the intermediates and the polymer materials was determined on the CHN analyzer (model no. Vario EL-III) (Fig. 2.13) at SRI.

![Fig. 2.13: CHN analyzer](image)
2.6.17 Determination of Sulfur content

The presence of sulfur was estimated by bomb calorimeter as per IS 1448:1991\textsuperscript{102}. The sample was oxidized by combustion in bomb calorimeter. The sulfur compounds liberated were absorbed in sodium carbonate solution and precipitated by barium chloride solution. The amount of sulfur (%) was determined by ash content by ignition of precipitate and is calculated using the following formula:

\[
\%S = \frac{(W_2 - W_1) \times 32 \times 100}{Wt. \text{ of samples} \times 233}
\]

Where, \(W_2\) = Weight of ash with crucible (g)

\(W_1\) = Weight of empty crucible (g)

2.6.18 Determination of chloride content

The presence of chloride content was estimated as per ASTM-D808 (1991)\textsuperscript{103}. The chlorine that is liberated is absorbed in sodium carbonate solution. Amount of chloride (%) present was determined gravimetrically by precipitation as silver chloride and calculated as follows:

\[
\text{Chloride, mass } \% = \frac{[(P-B) \times 24.74]}{W}
\]

\(P\) = AgCl obtained from the sample (g)

\(B\) = AgCl obtained from the blank (g), and

\(W\) = Weight of samples (g)
2.6.19 Determination of hydroxyl value

The hydroxyl value was determined as per method described in Anal. Chem., 31, 1808 (1959)[104]. For this method, primary and secondary alcohols were determined by acetylation in ethyl acetate or pyridine solution using perchloric acid to catalyze the reaction. Soluble alcohols in ethyl acetate are completely acetylated within five minutes at room temperature. In pyridine, a somewhat longer reaction time is required for secondary and hindered alcohols. The amount of hydroxyl groups present is calculated from the difference between the blank and sample titration with sodium hydroxide.

\[
\% \text{ OH} = \frac{(B-S) \times N \times \text{OH} \times 100}{W \times 1000}
\]

Where,  
B = Alcoholic KOH required for the titration of blank (ml)  
S = Alcoholic KOH required for the titration of sample (ml)  
N = Normality KOH  
W = Sample weight (g).

The results and discussion of the experimental part is described in Chapter 3.

2.7 Conclusion

From the above discussion, following conclusion can be drawn
a) The process development scheme as mentioned below would be taken as the basis for the synthetic work presented here:
Fig. 2.14: Reaction scheme for synthesis of polythiourethane
b) The basic parameters such as change in pH, acid value, viscosity, hydroxyl value, thiol content etc. would be used for the process control as well as for understanding of the completion of the reaction.

c) Analysis techniques such as TLC, HPLC, FTIR, NMR etc. would be used for identification and confirmation of the products formed at each step of the reaction.

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