CHAPTER 2

EXPERIMENTAL METHODS

This chapter describes the methodology for synthesizing single and di-site phase transfer catalysts as well as polymers. The determination of the rate of polymerization for monomers which have been synthesized by free radical mechanism has been explained.

2.1 PURIFICATION OF SOLVENTS AND REAGENTS

2.1.1 Solvents

Acetone, ethyl acetate, cyclohexane, cyclohexanone and all solvents were obtained from E Merck India Ltd., Mumbai and were purified by distillation prior to their use according to the standard methods (Vogel 1989). Ethanol (E Merck India Ltd) was refluxed with calcium oxide for six hours and then distilled to obtain pure alcohol.

2.1.2 Water

The double distilled water was used for polymerization reaction.

2.1.3 Monomers

The monomers namely methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA) and glycidyl methacrylate (GMA) (Merck, Mumbai, India) were distilled under reduced pressure to remove the inhibitors.
2.1.4 Other Reagents

Potassium peroxydisulphate (Merck, Mumbai, India) is used as initiator and methanol (SRL, Mumbai, India) is used as the precipitating agent for polymers respectively. H₂SO₄, HCl (AR CDH, New Delhi, India) were used as received. The other chemicals such as dimethyl hydrochloride, paraformaldehyde, acetophenone (Merck, Mumbai, India) were used as received.

2.2 EQUIPMENTS

2.2.1 Polymerization Tube

The reaction tubes used for the polymerization were long Pyrex glass tubes (4 cm × 20 cm) of 80 ml capacity with B-24 quick fit sockets fitted with B-24 concentration with a provision for inlet and outlet for nitrogen gas. The inlet tubes were extended up to the bottom of the reaction tube. An inert atmosphere was maintained inside the reaction tube by closing the inlet and outlet with rubber gaskets, after deaeration.

2.2.2 Thermostat

Polymerization reactions were carried out in a thermostat which is a rectangular glass tank of 25 litre capacity, fitted with an electrical heater and a mechanical stirrer. The temperature of the thermostat was controlled precisely to ± 0.1°C.

2.2.3 Deaeration

The nitrogen gas used for the deaeration (supplied in cylinder by the Indo Gas Limited, Chennai) was freed from traces of oxygen and other impurities by passing through Fieser’s solution (Fieser 1924), hypovanadous
chloride solution, potassium hydroxide solution and distilled water kept separately in four vertical glass tubes. The Fieser’s solution was prepared by dissolving 20 g of NaOH in 100 ml of water and adding 2 g of sodium anthra-quinone-\(\beta\)-sulfonate and 15 g of sodium dithionate (\(\text{Na}_2\text{S}_2\text{O}_4\)) in warm water. The mixture was stirred well until a clear, blood-red solution was obtained and cooled to room temperature. The sulfonate anthrahydroquinone dianion absorbs oxygen with great speed. The Fieser’s solution was covered with black cloth and whenever needed it was renewed when colour of the solution changes to dull red or brown or when precipitate appears in the solution. The gas after passing through the above solution was then allowed to pass through the hypovanadous chloride to remove the traces of oxygen. The hypovanadous chloride solution was prepared by dissolving a little ammonium-meta vanadate in concentrated hydrochloric acid and reducing it with amalgamated zinc (Vogel 1968). The above vanadium (II) was renewed frequently as and when the violet colour of the solution is changed with use. The gas was then passed through potassium hydroxide solution and then through distilled water to remove CO\(_2\) and other water soluble gaseous impurities. Finally the impurities free nitrogen gas was passed into the reaction tube containing the monomer solution. A constant deaeration time of 30 minutes was maintained for all the experiments.

2.3 SYNTHESIS OF PHASE TRANSFER CATALYSTS

2.3.1 Synthesis of Single Site Phase Transfer Catalyst: 2-Benzoylhexyldecyldimethylammonium Bromide

Single site phase transfer catalyst was prepared in two stages. In the first stage a Mannich base (dimethylaminepropiophenone hydrochloride) was prepared. In the second stage the prepared dimethylaminepropiophenone hydrochloride was quaternized by the addition of n-bromodecane in cold condition to obtain 2-benzoylhexyldecyldimethylammonium bromide.
2.3.1.1 Preparation of dimethylaminepropiophenone hydrochloride

Dimethylaminepropiophenone hydrochloride was prepared by the procedure reported in the literature (Vogel 1968). 26.5 g (0.326 mole) of dry dimethylamine hydrochloride, 10 g (0.33 mole) of powdered paraformaldehyde and 30 g (29.3 ml, 0.25 mole) of acetophenone were placed in a 250 ml round bottom flask fitted with a reflux condenser. 40 ml of 95% ethanol containing 0.5 ml of concentrated hydrochloric acid was added to it. It was then refluxed on a water bath for 2 hrs. A homogenous yellow coloured solution was obtained. It was then filtered. The filtrate was transferred to a 500 ml wide-mouthed conical flask and then 200 ml of acetone was added. The mixture was cooled to room temperature and kept in a refrigerator overnight. The crystals obtained were filtered, washed with 10 ml of acetone and dried for 6 hours at 40-50 °C. It was then recrystalised with acetone-alcohol mixture, filtered and dried at 70 °C. The melting point of the above salt is 155-156 °C.

2.3.1.2 Synthesis of 2-benzoylethyldecyldimethylammonium bromide

63.18 g (0.32mole) of dimethylaminepropiophenone hydrochloride was added to 300 ml of water in a 500 ml beaker. It was stirred well for complete dissolution. A 5% solution of sodium bicarbonate was added slowly to the solution with vigorous stirring until effervescence ceased. The liberated amine was extracted with ether (50 ml) three times. The ether extract was transferred to a 250 ml separating funnel. It was washed three times with distilled water and the ether layer after separation was evaporated over water bath. To the resulting tertiary amine, n-bromodecane was added under cold condition. 2-Benzoylethyldecyldimethylammonium bromide thus obtained was purified by recrystalization with alcohol-acetone mixture. The melting point of the catalyst is 165-166°C. The steps involved in both the stages of preparation are shown in the Scheme 2.1.
Scheme 2.1 Synthesis of single site phase transfer catalyst
2.3.2 Synthesis of Di-Site Phase Transfer Catalyst: 1,1,4,4-
Tetramethyl-1,4-Dioctyl Ethylene Diammonium Bromide

A solution of 0.01 mole of N,N,N',N'-tetramethylethlenediamine
and 0.02 mole of 1-bromoocctane were introduced into a 250 ml flask. The
mixture was gently refluxed for 2 hrs at 60 °C. The white precipitate of
1,1,4,4- tetramethyl-1,4-dioctyl ethylene diammonium bromide was formed.
It was filtered and dried. Then it was purified by dissolving in minimum
amount of acetone-alcohol mixture. The melting point of the catalyst is
173 °C. The synthesis of di-site phase transfer catalyst is shown in the
Scheme 2.2.

\[
\text{H}_3\text{C} \cdots \text{N} \cdots \text{CH}_2 \cdots \text{CH}_2 \cdots \text{N} \cdots \text{CH}_3 + 2 \text{ Br(CH}_2)_7\text{CH}_3
\]

\[
\text{CH}_3 \hspace{1cm} \text{CH}_3
\]

\[
60 \, ^\circ C, \, 2 \, \text{hrs}
\]

\[
\text{H}_3\text{C(H}_2\text{C})_7\text{N} \cdots \text{CH}_2 \cdots \text{CH}_2 \cdots \text{N} \cdots (\text{CH}_2)_7\text{CH}_3
\]

\[
\text{Br} \hspace{1cm} \text{Br}
\]

\[
\text{CH}_3 \hspace{1cm} \text{CH}_3
\]

1,1,4,4-Tetramethyl-1, 4-dioctyl ethylene diammonium bromide

Scheme 2.2 Synthesis of di-site phase transfer catalyst

2.4 POLYMERIZATION TECHNIQUE

Polymerization was carried out using a long closed Pyrex tube
under unstirred, inert atmospheric condition at 60 ±1 °C. The reaction mixture
consists of 10 ml aqueous phase and 10 ml organic phase. The monomer in ethyl acetate was the organic phase. The aqueous phase contained phase transfer catalyst, sodium bisulphate (for adjusting the ionic strength) and sulphuric acid (for maintaining the H⁺). Prior to polymerization the nitrogen gas was sent in to the tubes to conduct the reaction in an inert atmosphere. To ensure an inert atmosphere throughout, the reaction tubes are carefully sealed.

Polymerization reaction was initiated by the addition of calculated amount of potassium peroxydisulphate to the reaction mixture. The precipitation of polymer was observed as the reaction was proceeding. After stipulated time, the reaction was arrested by pouring the reaction mixture into ice cold methanol. The polymer formed was filtered through a G-4 sintered glass crucible, washed with double distilled water followed by anhydrous methanol. Then it was dried in vacuum oven at 50 °C until constant weight was obtained.

The rate of polymerization (Rp) was calculated using the following formula:

\[ Rp = \frac{1000 \times W}{V \times t \times M} \]  \hspace{1cm} (2.1)

where

- \( W \) = Weight of polymer formed in grams
- \( V \) = Volume of reaction mixture
- \( t \) = Reaction time in seconds
- \( M \) = Molecular weight of the monomer.

In the same way polymerization reactions were carried out by changing the concentration of the monomer, initiator, catalyst, temperature and volume of aqueous phase as said by the above procedure.
2.5  ANALYTICAL TECHNIQUES

2.5.1  Elemental Analysis

Micro elemental analysis was performed with Perkin-Elmer 240C-CHN elemental analyzer.

2.5.2  Infrared Spectra

IR spectra of the solid samples were recorded in Perkin Elmer RXI FT-IR spectrophotometer using potassium bromide (KBr) pellets and the liquid samples in solution.

2.5.3  $^1$H-NMR Spectra

High resolution $^1$H-NMR spectra were recorded on a Bruker 500 MHz FT-NMR spectrometer at room temperature using D$_2$O solvent.

2.5.4  $^{13}$C-NMR spectra

$^{13}$C-NMR spectra were recorded on Bruker DRX 125.77 MHz, FT-NMR spectrometer at room temperature using D$_2$O solvent.

2.5.5  Gel Permeation Chromatography

The number ($M_n$) and weight ($M_w$) average molecular weight and polydispersity indices of the polymers were determined with Waters 501 gel permeation chromatography equipped with three ultra styrigel columns and a differential refractive index ($R_I-401$) detector. The molecular weights were calibrated against polystyrene standards using dimethylformamide as mobile phase.
2.5.6 Differential Scanning Calorimetry (DSC)

The glass transition temperatures (Tg °C) of the polymers were determined with NETZSCH-Geratebau GmbH DSC 204 thermal analyzer. Polymer samples of 10 mg were used at a temperature rise of 10 °C/min in N₂ atmosphere.

2.5.7 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using Mettler TA 3000 thermal analyzer. TGA traces were recorded on 10 mg samples in air atmosphere at a heating rate of 20 °C/min.