CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 PURIFICATION OF SOLVENTS AND REAGENTS

2.1.1 Solvents

Benzene, chloroform, methyl ethyl ketone (MEK), dimethyl formamide (DMF), methanol, ethanol, toluene, tetrahydrofuran (THF) were purified according to the standard procedure (Vogal 1984) and distilled once before use. All the other solvents used were purified by distillation.

2.1.2 Triethylamine

Triethylamine (Fluka) was distilled and the fraction boiling at 88-89°C was collected and used.

2.1.3 Benzoyl chloride

Benzoyl chloride (BDH LR grade) was used as received for the preparation of acryloyl chloride and methacryloyl chloride.

2.1.4 Acrylic acid

Acrylic acid (Aldrich) was used as obtained for the preparation of acryloyl chloride.
2.1.5 Methacrylic acid

Methacrylic acid (Fluka) was used as obtained for the preparation of methacryloyl chloride.

2.2 PURIFICATION OF COMPOUNDS
2.2.1 Benzoyl peroxide (BPO)

Benzoyl peroxide (Fluka) was recrystallized from chloroform-methanol (1:1) mixture.

2.2.2 4-Nitrophenol

4-Nitrophenol (Aldrich) was recrystallized from ethanol for the preparation of 4-Nitrophenyl acrylate and 4-nitrophenyl methacrylate.

2.2.3 4-Hydroxyacetophenone

4-Hydroxyacetophenone (Sigma) was recrystallized from ethanol for the preparation of 4-acetylphenyl acrylate and 4-acetylphenyl methacrylate.

2.2.4 4-Phenoxyphenol

4-Phenoxyphenol, (Aldrich) was recrystallized from chloroform - benzene mixture for the preparation of 4-phenoxyphenyl acrylate and 4-phenoxyphenyl methacrylate.

2.2.5 4-Methoxyphenol

4-Methoxyphenol (Fluka) was recrystallized from ethanol for the preparation of 4-methoxyphenyl acrylate and 4-methoxyphenyl methacrylate.
2.2.6 4-Hydroxybenzophenone

4-Hydroxybenzophenone (Sigma) was recrystallized from ethanol for the preparation of 4-benzoylphenyl acrylate and 4-benzoylphenyl methacrylate.

2.2.7 Methyl methacrylate

Methyl methacrylate (MMA) (Fluka) was freed from the inhibitor by washing successively with 5% sodium hydroxide solution and distilled water, dried over anhydrous sodium sulphate and distilled under reduced pressure and used for the synthesis of copolymers.

2.2.8 Glycidyl methacrylate

Glycidyl methacrylate (GMA) (Aldrich) was purified by adopting the procedure mentioned for MMA and used for the synthesis of copolymers.

2.2.9 Butyl methacrylate

Butyl methacrylate (BMA) (Aldrich) was purified by adopting the procedure mentioned in Sec. 2.2.7 and used for the synthesis of copolymers.

2.2.10 Styrene

Styrene (STY) (Aldrich) was purified by adopting the procedure mentioned in Sec. 2.2.7 and used for the synthesis of copolymers.
2.3 PREPARATIONS

2.3.1 Preparation of acryloyl chloride

Acryloyl chloride was prepared according to (G.H. Stempel et al. 1950). A mixture of acrylic acid (23g) benzoyl chloride (134.9g) and hydroquinone (0.5g) was distilled rapidly and the fraction boiling at 90-100°C was collected. The liquid was then redistilled in the presence of hydroquinone (0.5g) and the fraction boiling at 72-74°C at 740 mm was collected (yield 72%) and used in the preparation of monomers like 4-nitrophenyl acrylate, 4-acetylphenyl acrylate etc.

\[
\text{Distillation} \quad \text{CH}_2 = \text{CH} + \text{C}_6\text{H}_5\text{COCl} \quad \xrightarrow{72-74^\circ\text{C}} \quad \text{CH}_2 = \text{CCI} + \text{C}_6\text{H}_5\text{COOH}
\]

2.3.2 Preparation of methacryloyl chloride

Methacryloyl chloride was prepared from a mixture of methacrylic acid (21.5g) and benzoyl chloride (154.9g) and the fraction boiling at 120-130°C was collected. The collected fraction was again redistilled and the fraction boiling at 95-97°C was collected (yield 65%) and used for the preparation of 4-nitrophenyl methacrylate, 4-acetylphenyl methacrylate etc.

\[
\text{Distillation} \quad \text{CH}_2 = \text{C-CH}_3 + \text{C}_6\text{H}_5\text{COCl} \quad \xrightarrow{95-97^\circ\text{C}} \quad \text{CH}_2 = \text{C-CH}_3 + \text{C}_6\text{H}_5\text{COOH}
\]

2.3.3 Preparation of 4-Nitrophenyl acrylate (NPA) and 4-Nitrophenyl methacrylate (NPMA)

A three necked round bottomed flask fitted with thermometer, stirrer, dropping funnel containing 20g of 4-nitrophenol, 20.1 ml of triethylamine and 200 ml of 2-butanone was cooled at -5°C to 0°C. Acryloyl chloride (11.69ml) dissolved in 50 ml of chloroform was added slowly with stirring and the temperature was maintained at -5°C to 0°C. The stirring was continued for another 2 hrs. Then that the reaction mixture was transferred
to a separating funnel and extracted with water. The unreacted 4-nitrophenol was removed by extracting with sodium hydroxide solution and finally the solvent was evaporated and the residual product was recrystallized from petroleum ether which resulted in a light yellow crystalline product. Yield 58%; m.p. 74-76°C.

NPMA was prepared from 4-nitrophenol (20 g) and Methacryloyl chloride (14.05 ml) in the presence of triethylamine (20.01 ml) in 200 ml of 2-butanone solution as described earlier for NPA. The crude product on recrystallization from petroleum ether gave pale yellow crystals. Yield 62%; m.p. 80-82°C.

\[
\begin{align*}
\text{OH} & + \text{CH}_2 = \text{C-R} \xrightarrow{\text{MEK, Et}_3\text{N}} \text{CH}_2 = \text{C-R} \\
\text{N}_2 \quad \text{C} = \text{O} & \quad \text{O} \\
\end{align*}
\]

where \( R = \text{H} \) for NPA

\( R = \text{CH}_3 \) for NPMA

2.3.4 Preparation of 4-Acetylphenyl acrylate (APA) and 4-Acetylphenyl methacrylate (APMA)

APA was prepared as described in Sec. 2.3.3 above from equimolar mixture of 4-hydroxyacetophenone (20 g), triethylamine (20.43 ml) and acryloyl chloride (11.93 ml) in 200 ml 2-butanone solution. The crude product on recrystallization with diethyl ether gave pale yellow crystals. Yield 53%; m.p. 66-68°C.

APMA was obtained as described in Sec.2.3.3 from equimolar mixture of 4-hydroxyacetophenone (20 g), triethylamine (20.43 ml) and
methacryloyl chloride (14.35 ml). The crude product was recrystallized from diethyl ether. Yield 56%; m.p. 70-72°C.

\[
\text{OH} \quad + \quad \text{CH}_2 = \text{C-R} \quad \xrightarrow{\text{MEK, Et}_3\text{N}} \quad \text{CH}_2 = \quad \text{C-R} \\
\text{O} \quad \text{COC}_3 \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ quart 2.3.5 Preparation of 4-Benzoylphenyl acrylate (BPA) and 4-Benzoylphenyl methacrylate (BPMA)

BPA was prepared by reacting equimolar mixture 4-hydroxy benzophenone (20 g) and acryloyl chloride (8.2 ml) in the presence of triethylamine (14.03 ml) as described in Sec.2.3.3. By evaporating the solvent crystals of 4-benzoylphenyl acrylate were obtained and recrystallized from diethyl ether. Yield 52%; m.p. 56-58°C.

BPMA was prepared as described in sec 2.3.3 from equimolar mixture of 4-hydroxy benzophenone (20 g) and methacryloyl chloride (9.85 ml) in the presence of triethylamine (14.03 ml). The crude product was recrystallized from diethyl ether. Yield 55%; m.p. 60-62°C.
2.3.6 Preparation of 4-Methoxyphenyl acrylate (MOPA) and 4-methoxyphenyl methacrylate (MOPMA)

MOPA was obtained by the reaction of equimolar mixture of 4-methoxyphenol (20 g) and acryloyl chloride (13.9 ml) in the presence of triethylamine (22.41 ml) by adopting the procedure mentioned in Sec.2.3.3. The solvent was evaporated to leave a liquid. Yield 54%.

MOPMA was obtained by the reaction of equimolar mixture of 4-methoxyphenol (20 g), methacryloyl chloride (15.74 ml) in the presence of triethylamine (22.41 ml), by adopting the procedure mentioned in Sec.2.3.3. The solvent was evaporated to leave a liquid. Yield 62%.

\[
\text{OH} \quad \text{+ CH}_2 = \text{C-R} \quad \text{MEK, Et}_3\text{N} \quad \text{CH}_2 = \text{C-R}
\]
\[
\text{OCH}_3 \quad \text{C=O} \quad -5 \text{ to } 0^\circ\text{C} \quad \text{OCH}_3
\]

where R = H for MOPA

R = CH₃ for MOPMA

2.3.7 Preparation of 4-Phenoxyphenyl acrylate (POPA) and 4-Phenoxyphenyl methacrylate (POPMA)

POPA was prepared by reacting 4-phenoxyphenol (20 g) and acryloyl chloride (9.5 ml) in the presence of triethylamine (16.36 ml) by adopting the procedure mentioned in Sec.2.3.3. The solvent was evaporated and recrystallized from diethyl ether. Yield 58%; m.p.48-50°C.

POPMA was prepared by reacting 4-phenoxyphenol (20 g), and methacryloyl chloride (11.49 ml) in the presence of triethylamine (16.36 ml)
as described in Sec.2.3.3. The product was recrystallized from diethyl ether. Yield 64%; m.p. 54-56°C.

\[
\begin{align*}
\text{OH} & \quad + \quad \text{CH}_2 = \text{C}-\text{R} \\
\text{OC}_6\text{H}_5 & \quad \xrightarrow{\text{MEK, Et}_3\text{N}, -5 \text{ to } 0^\circ\text{C}} \\
\text{COCl} & \quad \xrightarrow{\text{CH}_2 = \text{C}-\text{R}} \\
& \quad \xrightarrow{\text{C}=\text{O}} \\
& \quad \text{OC}_6\text{H}_5
\end{align*}
\]

where $R = H$ for POPA

$R = \text{CH}_3$ for POPMA

### 2.4 HOMOPOLYMERIZATION

Free radical solution polymerization was carried out in pyrex tubes containing an inlet and outlet for the nitrogen passage. All the synthesized monomers were polymerized as 4 M solution in methylethylketone using benzoyl peroxide (BPO) (0.5 to 1% of monomer) as the initiator. Monomer, BPO and solvent were taken in a polymerization tube and flushed with nitrogen gas for 20 min. and the tube was sealed to ensure inert atmosphere. The sealed tube was kept in a thermostat maintained at 70°C. When the polymerization was complete the contents were poured into nonsolvent (methanol/petroleum ether) to precipitate the polymer. The polymer was purified by repeated reprecipitation by methanol/petroleum ether from a solution of chloroform and finally dried in vacuum at ambient temperature for constant weight.

#### 2.4.1 Polymerization of Para substituted phenyl acrylates

The synthesized monomers NPA, APA, BPA, POPA and MOPA were polymerized in 2-butane solution using BPO as initiator at 70°C in an inert nitrogen atmosphere. By adopting the procedure mentioned in Sec.2.4. The following substituted phenyl acrylate polymers were prepared.
1. poly (4-nitrophenyl acrylate) poly(NPA)
2. poly (4-acetylphenyl acrylate) poly(APA)
3. poly (4-benzoylphenyl acrylate) poly(BPA)
4. poly (4-methoxyphenyl acrylate) poly(MOPA)
5. poly (4-phenoxyphenyl acrylate) poly(POPA)

\[ \text{CH}_2 = \text{CH} \quad \text{C} = 0 \quad \text{CH}_2 - \quad \text{C} = 0 \]
\[ \text{O} \quad \text{O} \quad \text{BPO/MEK} \quad 65^\circ\text{C} \quad \text{O} \quad \text{O} \]

\( R \) = NO\(_2\) => poly (NPA)
\( R \) = COCH\(_3\) => poly (APA)
\( R \) = COC\(_6\)H\(_5\) => poly (BPA)
\( R \) = OCH\(_3\) => poly (MOPA)
\( R \) = OC\(_6\)H\(_5\) => poly (POPA)

2.4.2 Polymerization of para substituted phenyl methacrylates

The synthesized monomers NPMA, APMA, BPMA, MOPMA, POPMA were polymerized in 2-butanone solution using BPO as initiator at 70°C in an inert nitrogen atmosphere. By adopting the procedure mentioned in Sec.2.4, the following substituted phenyl methacrylate polymers were prepared.

1. poly(4-nitrophenyl methacrylate) poly(NPMA)
2. poly(4-acetylphenyl methacrylate) poly(APMA)
3. poly(4-benzoylphenyl methacrylate) poly(BPMA)
4. poly(4-methoxyphenyl methacrylate) poly(MOPMA)
5. poly(4-phenoxyphenyl methacrylate) poly(POPA)
2.5 COPOLYMERIZATION

2.5.1 Copolymers of substituted phenyl acrylates

Free radical solution polymerization method was adopted for synthesizing the copolymers. In a representative experiment, various compositions of synthesized phenyl acrylate and alkyl methacrylates (MMA, BMA, GMA) and styrene in 2-butane with BPO as initiator were placed in the reaction tubes and the reaction mixtures were flushed with a slow stream of oxygen-free nitrogen for 30 min. The tubes were tightly sealed and immersed in a thermostat for a suitable period at 65 ± 0.5°C. The copolymers formed were separated by precipitation of the reaction mixture with excess non-solvent (methanol/petroleum ether) dissolved again in chloroform and reprecipitated with excess non-solvent (methanol/petroleum ether). The solvent was filtered and the copolymers were dried in vacuum at 40°C for 16 hrs.

The following substituted phenyl acrylate copolymers were prepared,

- poly(4-nitrophenyl acrylate-co-methyl methacrylate) Poly(NPA-co-MMA)
- poly(4-nitrophenyl acrylate-co-glycidyl methacrylate) Poly(NPA-co-GMA)
poly(4-nitrophenyl acrylate-co-butyl methacrylate) Poly(NPA-co-BMA)
poly(4-nitrophenyl acrylate-co-styrene) Poly(NPA-co-STY)
poly(4-acetylphenyl acrylate-co-methyl methacrylate) Poly(APA-co-MMA)
poly(4-acetylphenyl acrylate-co-glycidyl methacrylate) Poly(APA-co-GMA)
poly(4-acetylphenyl acrylate-co-butyl methacrylate) Poly(APA-co-BMA)

2.5.2 Copolymers of substituted phenyl methacrylates

By adopting the procedure mentioned in Sec.2.51 above copolymers of substituted phenyl methacrylates were copolymerized with alkyl methacrylates (MMA, GMA, BMA) and Styrene in MEK using BPO as initiator.

The following copolymers were prepared:

poly(4-nitrophenyl methacrylate-co-methyl methacrylate) poly(NPMA-co-MMA)
poly(4-nitrophenyl methacrylate-co-butyl methacrylate) poly(NPMA-co-BMA)
poly(4-nitrophenyl methacrylate-co-glycidyl methacrylate) poly(NPMA-co-GMA)
poly(4-nitrophenyl methacrylate-co-styrene) poly(NPMA-co-STY)
poly(4-acetylphenyl methacrylate-co-methyl methacrylate) poly(APMA-co-MMA)
poly(4-acetylphenyl methacrylate-co-butyl methacrylate) poly(APMA-co-BMA)
poly(4-acetylphenyl methacrylate-co-glycidyl methacrylate) poly(APMA-co-GMA)

Totally seven copolymer systems of phenyl methacrylates were prepared.

2.6 ANALYTICAL TECHNIQUES
2.6.1 IR Spectroscopy

IR spectra of the monomers, polymers and copolymers were recorded on Hitachi 270-50 spectrometer as potassium bromide pellets.
2.6.2 $^1$H NMR Spectroscopy

$^1$H NMR spectra of the samples were run on Joel 400 spectrometer. Spectra were recorded at room temperature as 15-20% (W/V) solutions of CDCl$_3$ with TMS as internal standard.

2.6.3 $^{13}$C NMR Spectroscopy

$^{13}$C NMR spectra of the samples were recorded on Bruker 270 MHz NMR spectrometer, in CDCl$_3$ with TMS as internal standard. Protons were decoupled from $^{13}$C nuclei by broad band irradiation.

2.6.4 Gel permeation chromatography

The number-average and weight-average molecular weights of the polymers were determined by gel permeation chromatography (Waters 501) equipped with a differential refractometer index detector. The columns used were ultra styragel and tetrahydrofuran was used as a mobile phase at 10ml/min flow rate. Polystyrene samples from multipore were used for calibration.

2.6.5 Thermogravimetric analysis

TGA and DTG thermograms of the polymer & copolymers were recorded on Mettler TA 3000. Thermogravimetric system in nitrogen atmosphere/air at a heating rate of 20°C/min with a time constant of 1 sec. The kinetics of degradation were followed by measuring the rate of change of weight over a series of temperatures.
2.6.6 Differential scanning calorimetry

DSC curves of the polymers and copolymers were recorded on Dupont 3700. \( T_g \) of the polymers and copolymers were determined 5-10 mg of the samples were sealed in aluminium pan and a sealed empty pan was used for reference. The rate of heating was 10°C/min in nitrogen atmosphere.

2.6.7 Elemental analysis

Molecular composition of the monomers and polymers were determined in Perkin Elmer 2400 elemental analyses.

2.6.8 Solubility

Solubilities of all the polymers were determined in the solvents like tetrahydrofuran, ethanol, methanol, acetone, dimethylformamide, chloroform, Dimethyl sulfoxide, benzene, toluene and xylene. These solvents (3 ml) were taken in a test tube and the polymers were added to them. The solutes were shaken well and were allowed to stand for 12 hrs at ambient temperature. A qualitative result of solubility was recorded.