This chapter describes the method of purification of chemicals, polymerization technique, apparatus used, the characterization of the polymer and related calculations.

3.1 Purification of chemicals
The various chemicals used in the present monograph were purified prior to use by the following method

3.1.1 Purification of monomers
The monomers are stored by adding hydroquinone, which acts as stabilizer, to prevent polymerization. It is, therefore, necessary to remove hydroquinone before polymerization. The vinyl monomers Sty (>99% stabilized by 4-tert-butylcatechol, Merck), MMA (98% Merck), AN (99% Ranbaxy) and BA (98% Merck) were of analytical grade. These were purified by standard methods as follows

Purification of BA
The monomer was washed three times with a 10% sodium hydroxide solution, washed three times with distilled water, dried over calcium chloride, and freshly distilled under vacuum. The fraction boiling at 72°C/54 mm Hg was collected [Arehart and Matyjaszewski, 1999].
Experimental

Purification of AN
AN was dried with anhydrous calcium chloride, vacuum distilled, and kept over calcium hydride. It was distilled twice before polymerization under reduced pressure in nitrogen [Capek et al, 1979].

Purification of Sty
Styrene was first triple-washed with 10% sodium hydroxide solution to remove the inhibitor and then washed with distilled water until neutral. The residual water was removed by storing over anhydrous calcium chloride for 24 h. The de-moisturized styrene was vacuum distilled, collecting the fraction boiling at 68°C / 68 mm Hg [Arehart and Matyjaszewski, 1999].

Purification of MMA
The monomer was deprived of inhibitor by gradual shaking with 10% solutions of NaOH, H$_2$SO$_4$, and Na$_2$CO$_3$ and with distilled water to neutral reaction. It was dried with calcium chloride, then over calcium hydride and vacuum distilled under reduced pressure [Capek et al, 1979].

All monomers were stored at 0°C under the inert atmosphere of nitrogen in dark and were purged with nitrogen for 10 min before use.

3.1.2 Purification of solvents
Methanol
The chief impurities in methanol (Qualikems) are water (0.1% by wt.) and acetone (0.02 % by wt.). 5 g of dry magnesium turnings and 0.5 g of
resublimed iodine were added to 100 ml methanol contained in a 2 l round bottom flask with a double surface condenser and a calcium chloride guard tube. The mixture contents were refluxed until the purple color disappeared. It was followed by further addition of 0.5 g of iodine, 900 ml of methanol and the mixture was refluxed for about an hour. Finally, the solvent was distilled and stored over Type 3A molecular sieve beads. Its boiling point is 65 °C/760 mm Hg [Vogel, 2004, 400].

**Benzene**

Benzene (Qualikems) was shaken repeatedly with 15 percent of its volume of Conc. H₂SO₄ in a separating funnel until acid layer was pale yellow on standing. It was then shaken twice with water in order to remove most of the acid, once with 10% sodium bicarbonate solution, again with water and finally dried with anhydrous calcium chloride. After filtration, the benzene was distilled through an efficient column and the fraction, b.p. 80-81 °C, collected. Dry sodium wires were introduced into distilled benzene [Vogel, 2004, 398].

**Chloroform (CHCl₃)**

The analytical reagent grade chloroform (Merck) contains up to 1% ethanol that is added as a stabilizer. It was removed by shaking three times with small volume of 5%(v/v) Conc. H₂SO₄. The acid was removed by repeatedly washing with water. The washed chloroform was dried over anhydrous calcium chloride for 24 h, distilled and stored in dark to avoid
photochemical formation of phosgene. Its b.p. is 61°C /760 mm Hg [Vogel, 2004, 399].

**Acetone**
The major impurities in the commercial grade acetone (Ranbaxy, 99%) are methanol, acetic acid and water (about one percent). It was heated under reflux with successive quantities of potassium permanganate until the violet color persisted. It was then dried over anhydrous potassium carbonate, filtered from dessicant, distilled and stored over a Type 4A molecular sieve. Its b.p. is 56°C / 760 mm Hg [Vogel, 2004, 407].

**Dimethyl sulphoxide (DMSO)**
DMSO (Rankem) was dried by standing overnight over calcium hydride. The filtered solvent was then fractionally distilled over calcium hydride under reduced pressure (12 mm Hg) and stored over a Type 4A molecular solvent. Its b.p. is 75-76°C /12 mm Hg [Vogel, 2004, 412].

**Dichloromethane (DCM)**
The commercial grade (Ranbaxy, stabilized) was purified by washing with portions of Conc. H₂SO₄ until the acid layer remained colorless, and then with water, sodium carbonate solution and water again. It was dried initially over calcium chloride and then distilled from calcium hydride, collecting the fraction boiling at 40-41°C. Finally, the solvent was stored in a dark colored bottle over Type 3A molecular sieve [Vogel, 2004, 399].
All other solvents like acetonitrile, cyclohexane, diethylether, DMF, ethanol, ethylacetate, hexane were used as received.

### 3.1.3 Purification of nitrogen gas

Compressed Nitrogen Cylinders were purchased. This gas might contain traces of oxygen, which was removed by passing it through Fieser's solution. The solution was prepared by dissolving 20g potassium hydroxide in 100ml water, then adding 2g sodium anthraquinone-β-sulphonate (Merck) and 15g commercial sodium hyposulphite to the warm solution and stirred until dissolved. A blood red solution was obtained which was cooled to room temp. The absorption of oxygen to the solution is indicated by the change in color to dull red or brown.

### 3.1.4 Purification of other chemicals

AIBN (Aldrich, 99%) was recrystallized from methanol below 40°C and stored in cold [Arehart and Matyjaszewski, 1999]. Hydroquinone [BDH, m.p. = 169°C] was recrystallized twice from ethanol before use. Pyrene [M=202.26 g/mol, m.p. = 149-151°C], 1-Acetylpyrene [M=244.3 g/mol, m.p. = 86-89°C], 1-(bromoacetyl) pyrene [M=323.2 g/mol, m.p. = 129-131°C] (Aldrich) and triphenylarsine (Merck) were used as received without purification.

Hydrochloric acid (Ranbaxy), potassium carbonate (Ranbaxy), potassium hydroxide (BDH), sodium sulphate (Ranbaxy) were used as such without any further purification.
3.2 Polymerization set-up and procedure

3.2.1 Photoreactor
A merry-go-round type photoreactor equipped with eight Philips tubes (8W each, path length=10 cm) and emitting light nominally at 253 nm at room temperature was employed to carry out the photopolymerization reactions.

3.2.2 Intensity measurements
The incident light intensity as measured by Lutron Lux Meter Model No. LX-101 was found to be $3.68 \times 10^3$ Lux.

3.2.3 Polymerization procedure
The free radical polymerization runs have been carried out by taking different combinations of vinyl monomers like styrene / methyl methacrylate / acrylonitrile / n-butylacrylate and 1-(bromoacetyl)pyrene/ 1-Acetylpyrene triphenylarsonium bromide as photoinitiator under inert atmosphere of nitrogen for a fixed duration. The required amounts of monomer, photoinitiator and additives were charged into a quartz tube. This tube was degassed and sealed off under vacuum. At the end of irradiation in the reactor, the solutions were poured into methanol. After two reprecipitations from methanol, the polymers were dried in vacuum oven at $50^\circ$C for 24 h. Copolymers were then treated with suitable solvents to remove homopolymers; cyclohexane for polystyrene and acetonitrile for poly (MMA) [Ito and Yamashita, 1965]. The copolymers were finally dried to constant weight. No significant weight loss was observed in any of the
cases. Conversions were determined gravimetrically and were independently confirmed using replicate runs.

3.3 Characterization of polymer(s)
The polymer samples were characterized by viscometric technique, elemental analysis, chromatography and spectroscopy as given below

3.3.1 Viscometric techniques

3.3.1.1 Determination of intrinsic viscosity (η) of polymer
The intrinsic viscosity of the polymer was determined with the help of Ostwald viscometer No. 1. The efflux time of pure solvent and solution of different concentrations (0.4%, 0.3%, 0.2%, 0.1%) of polymers in solvents was noted. The specific viscosity (η_sp) was calculated with the help of the following equation

\[ \eta = \frac{t - t_o}{t_o} \]

Where t_o and t are the flow times of pure solvent and solution respectively.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>K x 10^5</th>
<th>a</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>Benzene</td>
<td>6.8</td>
<td>0.76</td>
<td>30</td>
</tr>
<tr>
<td>Poly (BA)</td>
<td>Acetone</td>
<td>6.85</td>
<td>0.75</td>
<td>25</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>Benzene</td>
<td>11.5</td>
<td>0.73</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 3.3.1.2 (i) ‘K’ and ‘a’ values
Intrinsic viscosity ($\eta$) (in dl g$^{-1}$) was determined by plotting graph between $\eta_{sp}$ and concentration ($c$) (in g dl$^{-1}$) and extrapolating it to zero concentration.

$$\eta = \left( \frac{\eta_{sp}}{c} \right)_{c=0}$$

### 3.3.1.2 Determination of average viscosity molecular weight ($M_v$)

The viscosity data were used to calculate the average viscosity molecular weight of the polymers with the help of Mark-Houwink-Sakurada Eq.3.3.1.2 (i)

$$\eta = kM_v^a$$  \hspace{1cm} (Eq.3.3.1.2 (i))

Where $\eta$ is the intrinsic viscosity of the polymer, ‘$k$’ and ‘$a$’ are constants which depend on polymer, solvent and temperature. Their values for different polymers in specified solvents are given in Table 3.3.1.2 (i) [Brandrup and Immergut, 1989; Yamamoto et al 1971].

### 3.3.2 Elemental analysis

**Model Make: Vario EL III (Germany)**

**Principle and operation**

The vario EL operates on the oxidative digestion method and employs thermal conductivity detector (TCD).
3.3.2.1 Substance Digestion

The substance to be analyzed is digested through oxidative combustion. The quantitative substance digestion is based on the principle of the explosive combustion in a highly oxygenated helium-atmosphere in an empty combustion tube at a temperature of approx. 1100°C. The oxidative combustion of the elements C, H, N and S produces, apart from molecular nitrogen, the oxidation products CO₂, H₂O, NO, NO₂, SO₂, SO₃, as well as volatile halogen compounds, if the sample contains halogens. A copper contact (reduction tube), switched in sequence, quantitatively reduces the nitrogen oxides and sulphur oxides at 850°C to molecular nitrogen, SO₂ and binds excess oxygen. The volatile halogen compounds are chemically bound by suitable absorbents (e.g. silver wool) and thus removed from the gas flow. The remaining gas mixture of helium, CO₂, H₂O, N₂, and SO₂ components is subsequently guided to a separation and measuring system.

3.3.2.2 Separation of reaction gases

The components are separated in U-shaped separation columns in accordance with gas-chromatographic principles. First, the gas mixture, consisting of CO₂, H₂O, N₂, SO₂ and helium flows through an adsorption column at 50°C. In this column, water is quantitatively removed. The remaining gas flows through a second adsorption column. With this column the SO₂ is quantitatively removed from the gas flow. Finally, the gas mixture consisting of CO₂, N₂ and helium flows through a third adsorption column. With this column the CO₂ is quantitatively removed from the gas flow.
Nitrogen, which is unaffected by the adsorption columns enters the thermal conductivity detector with the helium carrier gas as first component. When the measuring of the nitrogen content is completed, the adsorption column charged with CO₂ is heated to approx. 130°C, causing the CO₂ to be rapidly desorbed and then flushed with helium into the TCD. After measuring of the CO₂ content is concluded, the SO₂ adsorption column is heated to 140°C. When SO₂ desorption is over; the H₂O column, now only charged with water, is heated up to approx. 280°C, causing the water to be desorbed. The water is flushed as vapor by the carrier gas, helium, into the measuring module.

3.3.2.3 Detection
A thermal conductivity detector (TCD), with a dynamic range, and improved sensitivity to the carrier gas helium, serves as a detector module. TCD consists of two chambers, each equipped with a thermistor. Helium passes through one chamber at a constant rate of flow (reference flow) while helium and the foreign gas component due to be measured pass through the other chamber (measure flow).

3.3.3 Fourier Transform- Infrared (FT-IR) Spectroscopy
Model Make: Bruker, Vector 22
Infrared radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions. The ordinary infrared region extends from 2.5 µ to 15 µ or 4000 cm⁻¹ to 667 cm⁻¹. IR
absorption spectroscopy is most widely used for the identification of the organic compounds.

Absorption in IR region occurs due to the changes in the vibrational and rotational levels. When radiations with frequency range less than 100 cm\(^{-1}\) are absorbed, molecular rotation takes place in the substance. Molecular vibrations are set in, when more energetic radiation in the region \(10^4\) to \(10^2\) cm\(^{-1}\) is passed. A single vibrational energy change is accompanied by a large number of rotational energy changes. In IR Spectroscopy, the absorbed energy brings about predominant changes in the vibrational energy that depends upon

i. Masses of the atoms present in a molecule,

ii. Strength of the bonds, and

iii. The arrangement of the atoms within the molecule.

When IR light is passed through the sample, the vibrational and the rotational energies of the molecules are increased. The two kind of fundamental vibrations are: stretching and bending. A stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. This includes symmetric and asymmetric stretchings. A bending vibration may consist of a change in bond angle between bonds with a common atom or the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another.
Experimental

Bending vibrations are of four types: Scissoring, rocking, wagging and twisting. Stretching modes have higher energies than bending modes for the same atoms.

Only those vibrations that result in a rhythmical change in the dipole moment of the molecule are observed in the infrared. The alternating electric field, produced by the changing charge distribution accompanying a vibration, couples the molecular vibration with the oscillating electric field of the electromagnetic radiation.

The value of the stretching vibrational frequency of a bond can be calculated fairly accurately by the application of Hooke’s Law that may be represented as

\[
\frac{\nu}{c} = \frac{1}{2\pi c} \left( \frac{k}{m_1 m_2} \right)^{1/2} = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2}
\]

Where \( \mu \) is the reduced mass; \( m_1 \) and \( m_2 \) are the masses of the atoms concerned in grams in a particular bond; \( k \) is the force constant of the bond and relates to the strength of the bond; \( c \) is the velocity of the radiation i.e. \( 2.998 \times 10^{10} \) cm sec\(^{-1}\).
3.3.4 Ultraviolet and Visible Spectroscopy

Model Make: Perkin Elmer, Lambda 40

Ultraviolet or electronic spectroscopy involves the promotion of electrons (σ, π, n* electrons) from the ground state to the higher energy state. It is very useful to distinguish between conjugated and non-conjugated systems; α, β unsaturated carbonyl compounds from β, γ analogues; homoannular and heteroannular conjugated dienes etc.

Since the energy levels of a molecule are quantized, electromagnetic radiation with only a particular value of frequency will be able to cause excitation. Thus light radiation, on leaving the sample, after absorption will be either less or its intensity may be completely lost. A record of the amount of light absorbed by the sample as a function of the wavelength of light is called absorption spectrum. The absorption of light is governed by a photophysical law; Lambert-Beer law.

Lambert-Beer Law

When a beam of monochromatic radiation is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the intensity of incident radiation as well as the concentration of the solution. Mathematically, this law is expressed as

\[- \frac{dI}{dx} = k I c\]
Where,
\( c = \) concentration of the solution in mol/l;
\( k = \) proportionality constant.
If \( I_0 \) be the intensity of the radiation before entering the absorbing solution, the intensity of radiation, \( I \) after passing through the thickness \( x \), of the medium can be calculated as

\[
\int_{I_0}^{I} \frac{dI}{I} = - \int_{0}^{x} kcdx
\]

Or

\[
\ln \left( \frac{I}{I_0} \right) = 2.303 \log \left( \frac{I}{I_0} \right) = -kcx
\]

Or

\[
I = I_0 e^{-kcx}
\]

Putting \( k / 2.303 = \varepsilon \) and defining \( \log \left( \frac{I}{I_0} \right) \) as the absorbance \( A \) of the solution, gives

\[
A = \log \left( \frac{I_0}{I} \right) = \varepsilon \ c \ x
\]

where, \( \varepsilon \) is the absorption coefficient or extinction coefficient of the absorbing substance. It is characteristic of the solute and depends on the nature of the solvent, temperature and the wavelength of the radiation absorbed. Transmittance \( T \) is defined as

\[
T = \frac{I}{I_0}
\]

Evidently, absorbance \( A \) and transmittance \( T \) are related as

\[
A = - \log T
\]

Or

\[
T = 10^{-A} = 10^{-EcX}
\]
As can be seen from the above formulas, transmittance is not proportional to sample concentration. However, absorbance is proportional to sample concentration. In addition, when the optical path is 1 cm and the concentration of the target component is 1 mol/ml, the proportionality constant is called the molar absorption coefficient.

3.3.5 Nuclear Magnetic Resonance Analysis (\(^1\)H and \(^{13}\)C NMR)

Model Make: Jeol JNM LA 400 Lambda NMR spectrophotometer

Samples of polymer were measured in deuterated chloroform (Aldrich) with tetramethylsilane as an internal reference standard.

Principle

NMR involves the interaction between an oscillating magnetic field of electromagnetic radiation and the magnetic energy of the hydrogen nucleus or some other type of nuclei when these are placed in an external static magnetic field. All nuclei carry a charge. In some nuclei this charge "spins" on the nuclear axis, and this circulation of nuclear charge generates a magnetic dipole along the axis. The angular momentum of the spinning charge can be described in terms of spin numbers \(I\); Each proton and neutron has its own spin, and \(I\) is a resultant of these spins. In quantum mechanical terms, the spin number \(I\) determines the number of orientations a nucleus may assume in an external uniform magnetic field in accordance with the formula \(2I + 1\). For a proton \(I = 1/2\); when it is placed in an external magnetic field, it will be capable of taking one of the two orientations with respect to the axis of the external field.
i. Alignment with the field (low energy).

ii. Alignment against the field (high energy).

The transition between the two states, called flipping, can be brought about by the absorption of a quantum of electromagnetic radiation in the radiowave region with energy $\hbar \nu$ ($\hbar$ is the Planck’s constant; $\nu$ is the frequency of electromagnetic radiation) in a magnetic field of given strength $H_0$. The fundamental equation correlating electromagnetic frequency with magnetic field strength is

$$\nu = \frac{\gamma H_0}{2\pi} \quad \text{(Eq. 3.3.5(i))}$$

Where $\gamma$ is the gyromagnetic ratio and is a fundamental constant.

In classical mechanical terms proton is visualized as a spinning magnet in an external magnetic field: the magnetic axis of the proton will precess about the axis of the external magnetic field in the same manner in which a spinning gyroscope precesses under the influence of gravity. The precessional angular velocity $\omega_0$ is equal to the product of the gyromagnetic ratio and the external magnetic field $H_0$.

$$\omega_0 = \gamma H_0 \quad \text{(Eq.3.3.5 (ii))}$$

Comparing with the fundamental NMR equation (3.3.5 (i)),
Thus the precessional frequency of the spinning nucleus is equal to the frequency of electromagnetic radiations in megacycles per second necessary to induce a transition from one spin state to another.

Absorption by a proton depends upon the magnetic field that a particular proton feels i.e. the effective field strength, which is different for different set of protons. Thus at a given radio frequency, different protons (different sets of equivalent protons) will require slightly different applied field strengths to produce the same effective field strength which causes absorption. In NMR spectrum, this applied field strength for each set of protons and the absorption peaks are plotted.

3.3.6 Electron Spin Resonance Spectroscopy (ESR)

Model Make: X-band Bruker EMX-EPR Spectrometer (Model 1444)

The ESR. Spectra were recorded at liquid N\textsubscript{2} temperature (Center Field: 3300 G, sweep width: 1000G, Mod. Amplitude: 10G, Sweep time: 167.77s, Microwave power 0.201 mW).

ESR is observed in microwave region of the electromagnetic spectrum. ESR has limited applications because it is primarily observed in systems containing unpaired electrons. Thus, the systems, which can be investigated by ESR spectroscopy, are inorganic or organic free radicals and ions of
transition metals, which contain unpaired \( d \) or \( f \)-electrons. The \( g \)-factor and the hyperfine coupling constant are the most important quantities determined from the ESR spectra of odd-electron systems. The gyromagnetic ratio \( (g) \) [Pryor, 1966] was calculated with the help of the following relationship:

\[
\nu = \frac{g \beta H}{h}
\]

Or

\[
g = \frac{\nu h}{\beta H}
\]

where
\( \nu = \) frequency
\( h = \) planck's constant
\( \beta = \) conversion factor called Bohr Magneton
\( H = \) external field strength

### 3.3.7 Chromatographic Technique

**Thin Layer Chromatography (TLC)**

TLC was carried out by coating a glass slide by a thin layer of adsorbent, silica gel. The slide was spotted with the solution of the mixture at its one end and placed in a closed compartment containing solvent of appropriate polarity, which helps as a capillary for the mixture to move
along the slide. As a result, the components are separated to produce colored spots.

3.4 Determination of kinetic parameters

3.4.1 Determination of Rate of Polymerization ($R_p$)

Rate of polymerization and percent conversion was calculated as

$$R_p \text{ (mol l}^{-1} \text{s}^{-1}) = \frac{w \times 10^3}{t \times 60 \times M} \quad \text{(Eq.3.4.1 (i))}$$


$$w = \text{weight of polymer from 1 ml of monomer(s)}$$

$$t = \text{time in minutes}$$

$$M = \text{molecular weight of monomer(s)}$$

$$C = \text{percent conversion}$$

$$d = \text{density of monomer(s)}$$

$$C = \frac{w \times 100}{d} \quad \text{(Eq.3.4.1 (ii))}$$
\[
R_p (\text{mol l}^{-1} \text{s}^{-1}) = \frac{C \times d \times 10^3}{t \times 60 \times M \times 100} \quad \text{(Eq.3.4.1 (iii))}
\]

\[
R_p (\text{mol l}^{-1} \text{s}^{-1}) = \frac{\text{Constant} \times C \times 10^{-3}}{t} \quad \text{(Eq.3.4.1 (iv))}
\]

<table>
<thead>
<tr>
<th>Homo/Copolymer</th>
<th>Value of Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>1.451</td>
</tr>
<tr>
<td>Polymethylmethacrylate</td>
<td>1.498</td>
</tr>
<tr>
<td>Poly (n-butylacrylate)</td>
<td>1.165</td>
</tr>
<tr>
<td>Poly (Sty-co-MMA)</td>
<td>0.7515</td>
</tr>
<tr>
<td>Poly (nBA-co-MMA)</td>
<td>6.703</td>
</tr>
<tr>
<td>Poly (Sty-co-BA)</td>
<td>6.476</td>
</tr>
<tr>
<td>Poly (Sty-co-AN)</td>
<td>0.909</td>
</tr>
</tbody>
</table>

Table 3.4.1 (i) Value of constant for various homo-/copolymers

The value used for the constant has been calculated by substituting the values for \(M\) and \(d\) and simplifying the equation. The value of constant [Mishra and Mathur, 1990; Srivastava and Mathur, 1981] for various homo-/copolymers are given in Table 3.4.1 (i)
3.4.2 Determination of order of the reaction

The rate of polymerization (free-radical, chain) is given by the equation

\[ R_p = k_p \left[ M \right] \left( \frac{f k_d [I]}{k_i} \right)^{1/2} \]  

(Eq.3.4.2 (i))

The order of reaction was calculated from the slope of the linear plot of log \( R_p \) Vs log \([I]\) for fixed \([M]\) and log \( R_p \) Vs log \([M]\) at fixed \([I]\) which gave the values of initiator and monomer exponents respectively.

Kinetics of free-radical photopolymerization

Although the kinetic treatment of photopolymer systems is similar to that in thermal systems, significant differences arise in the description of the initiation step, which in turn affect the description of the rate of polymerization. The decomposition rate \( (k_d) \) of thermal initiators strongly depends on temperature. In contrast, for photopolymerization, the rate at which photons are absorbed at a specific wavelength will determine the decomposition rate of photoinitiators. This process is not temperature dependent.

The rate of initiation \( (R_i) \), using a photoinitator, \( I \), is, therefore, expressed as the rate of formation of PI*, i.e.
\[ R_i = 2 \phi I_a [I] \]

Where \( I_a \) corresponds to the intensity of active radiation absorbed i.e. the number of photons absorbed by \( I \) per unit time per unit volume, \( \phi \) the quantum yield for chain initiation or radical generation which actually stands for the number of pairs of chain radicals generated per quantum of light absorbed. Assuming, for simplicity, that the incident light intensity does not measurably vary with thickness of the reaction mass, \( I_a \) will be proportional to the product of the intensity of incident light, \( I_0 \) i.e. the number of photons incident to the system per unit time per unit area; and the monomer concentration, i.e.,

\[ I_a = \varepsilon I_0 [M] \]

\[ \therefore R_i = 2 \phi \varepsilon I_0 [I] \]

where \( \varepsilon \) is the molar absorptivity of the photoinitiator. A higher coefficient matching the spectral output of the energy source indicates more efficient energy absorption at that wavelength. For highly absorbing species such as certain dyes, \( \varepsilon \) may be of the order of \( 10^5 \), the highest value theoretically achievable.

Hence under steady-state and assuming bimolecular termination, \([M]^+\) in case of thermal polymerization given by Eq. 3.4.2 (ii)


\[ [M'] = \left( \frac{f k_d[I]}{k_t} \right)^{1/2} \]  
\text{(Eq.3.4.2 (ii))}

Where \( f \) is the initiator efficiency; takes the form:

\[ [M'] = \left( \frac{\phi I_0}{k_t} \right)^{1/2} \]  
\text{(Eq.3.4.2 (iii))}

and, the rate of related photopolymerization is given by:

\[ R_p = \frac{k_p}{k_t^{1/2}} \left( \frac{\phi I_0}{k_t} \right)^{1/2} \left[ I \right]^{1/2} \left[ M \right] \]  
\text{(Eq.3.4.2 (iv))}

### 3.4.3 Determination of Degree of polymerization (\( P_n \))

The kinetic chain length \( \nu \) of a radical chain polymerization is defined as the average number of monomer molecules consumed per each radical, which initiates a polymer chain i.e.

\[ \nu = \frac{R_p}{R_t} \quad \text{or} \quad \frac{R_p}{R_t} \]

Hence,

\[ \nu = \frac{k_p [M] [M']}{2 k_t [M'] [M']} = \frac{k_p [M]}{2 k_t [M']} \]

Substituting \([M']\) from Eq.3.4.2 (iii),

\[ \nu = \frac{k_p [M]}{2 \left( f k_d k_t [I] \right)^{1/2}} \]  
\text{(Eq.3.4.3 (i))}
The number average degree of polymerization $P_n$, defined as the average number of monomer molecules contained in a polymer molecule, is related to the kinetic chain length. If the propagating radicals terminate by coupling, then

$$\bar{P}_n = 2v$$

For termination by disproportionation,

$$\bar{P}_n = v$$

The number average degree of polymerization ($\bar{P}_n$) of the polymer samples were calculated from the following relationships which relate intrinsic viscosity ($\eta$) to degree of polymerization ($\bar{P}_n$) [Mishra and Mathur, 1990 (poly-MMA); Odell et al, 1997 (poly-Sty); Bajpai and Srivastava, 2001 (poly-(Sty-co-MMA))].

For PMMA at 30 °C in benzene

$$\log (\bar{P}_n) = 3.342 + 1.13 \log \eta$$

For Polystyrene at 30 °C in benzene

$$\bar{P}_n = 1770 (\eta)^{1.4}$$

For Sty-co-MMA at 30 °C in benzene

$$[\eta] = 5.76 \times 10^{-3} \bar{P}_n^{0.746}$$
3.4.4 Determination of non-ideal kinetics

A given polymerization conforming strictly to Eq.3.4.2 (i) is commonly termed ideal. The ideal behavior prescribes constancy of the term \( \frac{R_p^2}{[I][M]^2} \) expressed as

\[
\frac{R_p^2}{[I][M]^2} = \frac{k_p^2}{k_t} f k_d \quad \text{ (Eq.3.4.4 (i))}
\]

Any system deviating from this pattern of reaction is to be considered as a case of non-ideal polymerization [Ghosh, 1998]. A number of side effects or additional reactions, not taken into consideration in the normal polymerization scheme, that are put forward to explain the observed kinetic deviations are

i. Complex formation between monomer and initiator, and monomer dependent initiation.

ii. Cage effect

iii. Initiator dependent termination: Primary radical termination and Degradative initiator transfer

iv. Retardation by solvents

v. Enhancement of the rate of initiation by solvents or additives

vi. Solvent/additive influencing the propagation rate constant

vii. Retarded termination and dependence of termination rate on medium viscosity
Chain Transfer

Chain transfer is the premature termination of a growing polymer chain and the initiation of another polymer chain by the transfer of a hydrogen, or other atom or species, to the growing polymer chain from some compound present in the system, which could be the monomer, initiator, solvent, or polymer.

\[ M_n^* + XA \xrightarrow{k_{tr}} M_n-X + A^* \]

( Growing (Transfer agent) (Stabilized (Free-radical) Polymer Chain)

It is a chain breaking reaction, which leads to a decrease in the length of the polymer chains. The number of propagating chain ends remains constant, however. When reinitiation is rapid, with no change in the polymerization rate, in other words, the chain reinitiation rate constant \( k_a \) is approximately equal to the propagation rate constant \( k_p \), then two different scenarios can occur. In the first case, when the chain transfer rate constant is much slower than the propagation rate constant \( (k_p >> k_{tr}) \), this is considered the normal mode of chain transfer, where the molecular weight of the polymer chains is decreased. In the second case, when the chain transfer rate constant is much larger than the propagation rate constant \( (k_p << k_{tr}) \), the molecular weight is drastically reduced, and the resulting polymers are referred to as telomers. In both cases, the overall rate of polymerization remains constant.
When reinitiation is slow compared to propagation \( (k_a < k_p) \), there is a decrease in both the molecular weight and the rate of polymerization. When the chain transfer rate constant is much slower than the propagation rate constant \( (k_p \gg k_{tr}) \), then this effect is called retardation. When the chain transfer rate constant is much larger than the propagation rate constant \( (k_p \ll k_{tr}) \), then there is a large decrease in the molecular weight and this effect is known as degradative chain transfer [Bevington, 1961; Ghosh and Mitra, 1977; Ghosh and Maity, 1979; Ghosh and Mukherjee, 1982; Sengupta and Mukopadhyay, 1982; Ghosh and Ghosh, 1984; Odian, 2002, 243].

Transfer reactions

\[
\begin{align*}
M_n^- + M & \rightarrow M_n + M^- \quad \text{(Monomer transfer } k_{tr}, M) \\
M_n^- + S & \rightarrow M_n + S^- \quad \text{(Solvent transfer } k_{tr}, S) \\
M_n^- + I & \rightarrow M_n + I^- \quad \text{(Initiator transfer } k_{tr}, I)
\end{align*}
\]

where transfer constants are defined as,

\[
C_M = \frac{k_{tr}, M}{k_p}, \quad C_S = \frac{k_{tr}, S}{k_p}, \quad \text{and} \quad C_I = \frac{k_{tr}, I}{k_p}
\]

The degree of polymerization is now redefined as the polymerization rate divided by the sum of the rates of all chain breaking reactions. For the general case of a polymerization initiated by the thermal homolysis of a
catalyst and involving termination by coupling and chain transfer to monomer, initiator, solvent (or chain transfer agent), $P_n$ follows

\[ P_n = \frac{R_p}{(R_t/2) + k_{tr,M} [M']M + k_{tr,S} [M']S + k_{tr,I} [M'][I]} \]

The simplified equation is

\[ \frac{1}{P_n} = \frac{R_i}{2R_p} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]} \]  

(Eq. 3.4.4(ii))

OR

\[ \frac{1}{P_n} = \frac{k_i R_p}{k_p^2 [M]^2} + C_M + C_S \frac{[S]}{[M]} + \frac{C_I \frac{k_i R_p^2}{k_p^2 f k_d [M]^3}}{[M]} \]  

(Eq. 3.4.4(iii))

Eq. 3.4.4 (ii) or (iii) is referred to as Mayo equation [Mayo, 1943].

Hence, according to Mayo equation, an intercept in the plot of $1/ P_n$ Vs. $R_p/[M]^2$ is evidence of chain transfer. Non-ideality with respect to monomer and/or initiator in different homo/co polymerization systems is confirmed through various plots, which are discussed in the corresponding sub-chapters of Result and Discussion.
3.4.5 Determination of $k_p^2 / k_t$

The determination of corresponding value of rate of polymerization ($R_p$) and average degree of polymerization ($\bar{P}_n$) permits the evaluation of another kinetic parameter, $k_p^2 / k_t$ using Mayo equation (Eq.3.4.4 (iii)) which is rewritten as

$$\frac{1}{\bar{P}_n} = X \cdot \frac{k_t R_p}{k_p^2 [M]^2} + \frac{\Sigma R'tr}{R_p} \quad \text{(Eq.3.4.5(i))}$$

The factor $X$ depends on the overall nature of bimolecular termination, in case of MMA and Sty, the value of $X$ approximates to 1.85 and 2.0 respectively. The second term in the right hand side of equation 3.4.5 (i) represents side effects owing to chain transfer reactions. It has been assumed that this would not effect the slope of the plot of $1 / \bar{P}_n$ Vs. $R_p / [M]^2$ to evaluate the value of $k_p^2 / k_t$.

3.5 Computation of copolymer composition and Determination of monomer reactivity ratios (MRRs)

MRRs have been determined by performing a series of polymerizations under identical experimental conditions, but beginning each polymerization at different concentrations of the two monomers. The polymerizations were terminated at low conversion (<10%), and the resulting polymer was characterized to determine the levels of incorporation of the two monomers.
(\(F_1\) and \(F_2\)). The copolymer microstructure was determined from a high-resolution NMR study. The relative peak area of resonance peaks in NMR spectra or nitrogen percentage was used to calculate the copolymer composition.

A variety of methods have been devised for extracting \(r_1\) and \(r_2\) from copolymer feed \((f_n)\) and composition \((F_n)\) data [Odian, 2002, 467]. The monomer reactivity ratios were calculated by Finemann-Ross [Finemann and Ross, 1950] and Kelen-Tudos method [Kelen and Tudos, 1975].

The Finemann-Ross equation is one of the earliest attempts to linearize the copolymer composition equation

\[
G = r_1 F - r_2
\]

Eq.3.5 (i)

where,

- \(r_1\) = reactivity ratio of monomer 1
- \(r_2\) = reactivity ratio of monomer 2
- \(G = X (Y-1)/Y\) and \(F = X^2/Y\)
- \(X=\frac{M_1}{M_2}\) and \(Y=\frac{m_1}{m_2}\)
- \(M_1, M_2\) are the monomer molar compositions in the feed
- \(m_1, m_2\) are the copolymer molar compositions

A plot of \(G\) as ordinate and \(F\) as abscissa is a straight line whose slope gives \(r_1\) and intercept gives \(r_2\). However, this linearization method
unequally weights the experimental composition data; if the notation of the two monomers is switched (i.e., \( f_1 \) becomes \( f_2 \) and vice versa), different answers for \( r_1 \) and \( r_2 \) can be obtained.

Kelen and Tudos refined this method by introducing new parameters into the linearized copolymerization equation, such as \( \eta \), \( \xi \) and \( \alpha \)

\[
\eta = \left[ r_1 + \frac{r_2}{\alpha} \right] \xi - \frac{r_2}{\alpha} \tag{Eq. 3.5 (ii)}
\]

where,

\( \eta = G (\alpha + F) \), \( \xi = F (\alpha + F) \) and \( \alpha = (F_{\text{min}} \times F_{\text{max}})^{1/2} \)

The intercepts at \( \xi = 0 \) and \( \xi = 1 \) of the \( \eta \) vs. \( \xi \) plot gives \(- r_2 / \alpha \) and \( r_1 \) respectively.