CHAPTER-3

EXPERIMENTAL (GENERAL)

3.0 Purification of monomer-methylmethacrylate (MMA)

Stabilized monomer MMA obtained from local market was freed from inhibitors by washing with 4% aqueous NaOH solution followed by washing with distilled water. The inhibitor free monomer was then dried over fused $CaCl_2$ and distilled under reduced pressure. The middle fraction was collected for use in polymerization experiments and was preserved in well-stoppered dark glass bottles in a refrigerator at < 5°C.

3.1 Purification of Solvents

Solvents used viz., methanol, benzene, acetone, chloroform, dimethyl formamide, ethanol and acetonitrile were all A.R. quality. They were purified by distillation before polymerization and other experiments following standard procedures[205].

3.2 Purification of initiator components :

3.2.1 Benzoyl peroxide (Bz_2O_2)

Bz_2O_2 obtained from BDH was recrystallized twice from chloroform and dried in vacuo before use.

3.2.2 Dyes or dye-intermediates

Four dyes or dye-intermediates having amine moieties in the molecular structure are selected for use as initiator components in the present work viz., Rhodamine 6G, Auramine O,

Michler's ketone (MK) and crystal Violet Lactone (CVL).
Each of them was obtained from local market and treated
or purified selectively before its use as initiator in
the polymerization of MMA.

(a) The cationic dye rhodamine 6G (in the chloride salt
form) is insoluble in MMA. This dye is converted to its
anhydrobase form for use in non-aqueous polymerization
of MMA. It was dissolved in water and then made strongly
alkaline with NaOH solution (pH > 10). The dye was then
easily extracted in benzene on thorough shaking in a separating
funnel. The deep orange-yellow benzene extract is quite
stable when kept over NaOH pellets and it remains in
the anhydrobase form (Rh) in the benzene solution thus
prepared[206,207]. Concentration of the dye in benzene
was determined gravimetrically by evaporating the solvent
from a known volume of the benzene extract.

(b) The cationic dye, Auramine O is insoluble in MMA. It
is converted to its anhydrobase form (Au) which is organo-
soluble by a similar procedure adopted in case of Rhodamine
6G. The very pale yellow benzene extract is kept in benzene
solution over NaOH pellets and was used in the MMA poly-
merization experiments.

(c) Michler's ketone (MK) was recrystallized from benzene
and was dried under vacuum before use.

(d) Crystal Violet Lactone (CVL) was recrystallized from

chloroform and vacuum dried before use in the polymeriza-
tion experiments.

3.3 Purification of nitrogen gas

Nitrogen gas in pressure cylinders, obtained from
Indian Oxygen Limited, was passed through an alkaline
pyrogallol scrubber to remove trace of oxygen, if any, and
then dried by passing it through a scrubber containing
concentrated sulfuric acid.

3.4 Dilatometric technique of polymerization

The course of polymerization was followed by dilato-
metric technique, which is based on change of density/
volume during conversion of monomer to polymer during
polymerization. With the dilatometric technique conversions
of less than 1% can be accurately determined by proper
experimental set-up. Another great advantage is that polymer
density is not dependent on small differences in structure
or microstructure or to any noteworthy extent on degree
of polymerization.

3.5 Equipments and their descriptions for dilatometric measurement of polymerization

3.5.1 Dilatometer

The dilatometer was made of a cylindrical borosili-
cate glass ampoule and a capillary on the top with a volume

capacity of about 10 ml. The capillary was calibrated by the usual method. For photopolymerization in presence of visible light this borosilicate glass dilatometer was suitable because transmission through this glass was over 90% above 400 nm.

3.5.2 Thermostated bath

To carry out polymerization at a particular temperature, the dilatometer was placed in a thermostated bath. It consisted of a 10 litre borosilicate glass vessel filled with distilled water and fitted with a stirrer, a motor, an immersion heater and a temperature controlling unit consisting of an electromagnetic relay and a contact thermometer system which controlled the temperature of the bath within $\pm 0.05^\circ$C. The body of the bath was covered with black paper and there was a small (2 cm wide) vertical window in front of the bath through which light entered from the lamp used to irradiate the liquid within the dilatometer immersed in the bath. It was covered from top with a suitably designed aluminium cover.

3.5.3 Light source

For photopolymerization experiments, high pressure 125 Watt mercury vapour lamp (Philips India Ltd.) having appreciable intensities over 440 nm and 570 nm wave length region was used without any filter as the light source.

It is known from the literature of the lamp[208] that the
intensity remains more or less constant for a period of
about 100 hours. So, experiments were conducted keeping
the above limits of irradiation time in. mind. The distance
between the lamp and the dilatometer ampoule placed in the
thermostated bath was kept fixed in all the experiments in
order to avoid intensity variation.

3.6 Experimental procedure to follow the course of polymerization of MMA taken in the dilatometer

3.6.1 Procedure

The dilatometer was filled with the requisite amount
of monomer, initiator and solvent (when used), flushed with
purified nitrogen, stoppered and placed in the thermostated
bath kept at a specified temperature (40°C).

Polymerization was carried out in dark or under
photo condition in appropriate cases. When photo-polymeriza-
tion was carried out, the light source was placed in front
of the window of the thermostated bath to illuminate it
after allowing some time for the dilatometer to attain the
temperature of the bath. The volume contraction during
polymerization was measured by a cathetometer.

3.6.2 Calculation :

Rate of bulk polymerization of vinyl monomers

If ρ_m and ρ_p be the density of monomer and density of polymer respectively, the % conversion during polymerization of monomer to polymer may be calculated as follows :

Basis : 1 ml or ρ_m gm of monomer.

When ρ_m gm (or 1 ml) of monomer is converted to ρ_m gm of polymer, resultant volume contraction will be

$$1 - \frac{\rho_m}{\rho_p} \quad ml \qquad or \qquad \frac{\rho_p - \rho_m}{\rho_p} \quad ml$$

i.e., ρ_m gm polymer is formed when volume contraction is

$$\frac{\rho_p - \rho_m}{\rho_p} \quad ml.$$

So, for a volume contraction of hα ml, weight of polymer formed is $\dfrac{\rho_m \, \rho_p}{(\rho_p - \rho_m)}$ .hα gm

where 'h' is the fall in height (cm) of liquid meniscus in the dilatometer capillary in time 't' (min) and α is the area of cross-section of the capillary (sq.cm).

If V ml is the total volume of monomer taken, then

$$\% \ conversion \ (W/V) = \frac{\rho_m \, \rho_p \, h\alpha}{(\rho_p - \rho_m)V} \times 100 \qquad (23)$$

With the knowledge of % conversion in time 't', rate of polymerization of monomer may then be obtained from the following equation

$$R_p = \frac{\rho_m \times \rho_p}{(\rho_p - \rho_m)} \frac{h\alpha}{6Vt} \ mol.L^{-1} \ s^{-1} \qquad (24)$$

The values of ρ_m and ρ_p for MMA was obtained from literature[209].

3.6.3 Rate of polymerization of MMA in diluted system

When polymerization of MMA was done in diluted systems for a particular monomer-solvent ratio, corresponding to an observed fall in height of liquid meniscus in the capillary, weight of polymer formed was obtained by carefully isolating the polymer from the solution by complete precipitation and then by successive drying and weighing. The capillary of the dilatometer was then calibrated for weight of polymer formed per unit fall in height (h). The total volume of monomer being known, R_p was then easily calculated.

3.7 Isolation and purification of polymer

Polymers formed at low conversions (< 10%) in the dilatometer was taken out and were isolated from the solution by precipitation with non-solvent petroleum ether. The precipitated polymer was collected, washed repeatedly with non-solvent and dried under vacuum.

3.8 Determination of polymer molecular weight from intrinsic viscosity

Number average molecular weight ($\overline{M}_n$) and hence degree of polymerization ($\overline{P}_n$) of polymers (polymethyl

methacrylate, PMMA) were determined viscometrically by using an Ubbelohde viscometer.

The molecular weight, $\overline{M}_n$, of a polymer sample is related to its intrinsic viscosity, $[\eta]$ of its solution in a given solvent by the Mark-Houwink equation :

$$[\eta] = K \overline{M}_n^{\alpha} \qquad (25)$$

where K and α are constants for a particular solvent system at a given temperature.

If the polymer solution is very dilute and consequently the density change of the solvent is negligible due to the dissolved polymer, then the viscosities of the solvent and the solution would be proportional to their flow times in a capillary viscometer. If η be the viscosity of the solution and η_0 is the same for the solvent at a given temperature, and t and t_0 are the respective flow times in a capillary viscometer, then the specific viscosity, η_{sp} is expressed as $(\eta-\eta_0)/\eta_0$, which is equal to $(t-t_0)/t_0$. The reduced viscosity, $\eta_{sp}/C = (t-t_0)/t_0 C$ (where C is the concentration usually expressed in $g.dl^{-1}$) is related to the intrinsic viscosity, $[\eta]$ by the following expression[210],

$$\eta_{sp}/C = [\eta] + K_1 [\eta]^2.C \qquad (26)$$

Thus, a plot of η_{sp}/C values at various concentrations against the respective C values would give a straight line.

Extrapolation of this linear plot to zero concentration would give an intercept on the η_{sp}/C axis, and the intercept gives the value of the intrinsic viscosity, $[\eta]$ expressed in $dl.g^{-1}$. All the viscometric measurements were (measurement of flow times of polymer solutions in benzene of different concentrations) made in a thermostatic bath maintained at $30\pm0.05^{\circ}C$. On determination of the intrinsic viscosity, the molecular weight of the polymer was calculated using equation (26) and taking K and α values as 8.69×10^{-5} and 0.76 respectively from the literature[8].

3.9 Spectrophotometric studies of initiator systems

Combinations of Bz_2O_2 with the dye or dye intermediates were used as the initiating systems for the polymerization of MMA. Therefore, to study whether any interaction takes place between the two components of the initiator combinations to yield a separate chemical entity in the form of a complex and to study whether the monomer MMA is also taking part in any complexation reactions with the initiating components, spectral studies of dilute solutions of the components of the initiators, their mixtures and the mixtures of the initiator components and MMA in acetonitrile or benzene in appropriate cases, were carried out. A CARY-17D UV-VIS Spectrophotometer was used for this purpose. Quartz cells of 1 cm path length were used. The spectral data are given in the respective sections

of the results and discussions.

3.10 Spectrophotometric analysis of polymers obtained

With a view to understanding the mechanism of radical generation and of the initiation of polymerization, selected polymers initiated by each dye system under otherwise comparable conditions were purified by repeated precipitation (using benzene as solvent and petroleum ether as non-solvent), dissolved in pure acetonitrile or benzene to give 1% solutions and then studied spectrophotometrically in the UV-VIS region. In each case, in the spectrums of the dye-sensitized polymer, appreciable absorption was shown in the specific wave length regions where the corresponding pure dye solutions showed absorption peaks in contrast with the spectrum of a pure PMMA prepared by using only Bz_2O_2 as the photoinitiator.