CHAPTER-2

EXPERIMENTAL

(RANDOM COPOLYMERS)

CHAPTER-2

Experimental (random copolymers of MMA and AN)

2.1 Introduction :

Methyl methacrylate and acrylonitrile were copolymerised to synthesise random copolymers using benzoyl peroxide as free radical initiator, toluene as solvent (reaction medium) and 75° temperature. A series of copolymers was synthesised with various compositions of methyl methacrylate and acrylonitrile. Homopolymers of methyl methacrylate and acrylonitrile were also synthesised under identical conditions.

All experimental procedures were carried out in duplicate during the course of this work to ensure reproducibility. The work is developed in a logical progression. A number of abbreviations used in this work are given below as a glossary.

2.1.1 Glossary of Abbreviations

AN - Acrylonitrile
BPO - Benzoylperoxide
DMF - N,N-dimethylformamide
DMSO- Dimethyl sulfoxide
DMA - Dimethyl acetamide
DR Differential refractometry
DSC - Differential scanning calorimetry
DTA - Differential thermal analysis
DTGA- Derivative thermogravimetric analysis
EG - Ethylene glycol
GC - Gas Chromatography
MMA - Methylmethacrylate
PAN - Polyacrylonitrile
PMMA- Poly (methylmethacrylate)
SEM - Scanning electron micrograph
THF - Tetrahydrofuran

TMS - Tetramethyl silane
TGA - Thermogravimetric analysis
η - Viscosity
$[\eta]$ - Intrinsic Viscosity
ζ - Zeta fotential
θ - Contact angle

2.1.2 Reagents and Materials

The following reagents and materials were used during the course of this work.

Acrylonitrile - Fluka, Switzerland
Acetaldehyde - Merck, India
Acetone - Merck, India
Acetic anhydride - BDH India
Absolute alcohol - Alembic Chemicals, Baroda, India.
Benzoyl peroxide - Fluka, Switzerland
Benzene - Qualigens
Chlorobenzene - Merck, India
Carbon tetrachloride - Merck, India
Cyclohexane - Merck, India
Chloroform - Merck, India
DMF - BDH, India
DMSO - BDH, India
Dimethylacetamide - Sarabhai Chemicals, Baroda, India
Dioxane - BDH, India
Ether - BDH, India
Ethanol - Alembic Chemicals, Baroda, India
Ethylene glycol - BDH, India
Glycerine - High purity chemicals (HPC), India
n - Heptane - Merck, India

Methanol - Merck, India

Methyl methacrylate - Fluka, Switzerland

Phenol - BDH, India

Propanol - Merck, India

Toluene - BDH, India

Tetrahydrofuran - BDH, India

2.1.3 Purification of monomers :

Removal of inhibitors from methyl methacrylate and acrylonitrile was done by washing them with 5% aqueous sodium hydroxide and then with distilled water until free from alkali. The monomers were then dried over anhydrous calcium chloride and distilled before use. The purity of the monomers was checked by GC analysis. All the solvents and chemicals used in this work were purified by appropriate methods before use to attain a maximum purity. Attempts were made to ensure that all the glasswares were scrupulously clean and all transfer operations were performed with uniformity at all stages. The samples given for instrumental analysis were ensured to be in the most suitable forms.

2.2 Synthesis :

Majority of the synthetic procedures for PAN, PMMA and their copolymers use DMF as reaction medium. There are almost no report except one [1] available for use of toluene as reaction medium. Hence we are reporting here the synthesis of homopolymers of MMA and AN and their copolymers in toluene, which is a relatively less expensive medium.

2.2.1 Synthesis of Poly (methyl methacrylate) [PMMA]

For synthesis of Poly(methyl methacrylate), PMMA, 40cm^3 (37.72g) of purified methylmethacrylate was taken in a three neck round bottom flask and to it was added 60cm^3 toluene as reaction medium. The reaction vessel was equipped with a thermometer and water condenser and the reaction mass was stirred magnetically. The temperature of the reaction mixture was maintained at 75° with an accuracy of ±0.5°. At 75° benzoyl peroxide initiator was added to the reaction mixture to make an initiator concentration of 5×10^{-3}M. The reaction was allowed to continue for six hours and then the reaction mixture was cooled and poured slowly into four fold excess of methanol with constant and vigorous stirring. The precipitate was allowed to settle and filtered. The polymer was washed several times with methanol. The polymer was then dried in vacuum at 60° to constant weight.

2.2.2 Synthesis of polyacrylonitrile (PAN)

Polyacrylonitrile was synthesised at the same experimental conditions as mentioned earlier for PMMA. The amount of monomer used for the synthesis was 40cm^3 (32.20g) in 60cm^3 toluene. The product was separated, washed, and dried following the procedure described earlier for PMMA.

2.2.3 Synthesis of random copolymers

Copolymerisation reaction was carried out in a three neck round bottom flask. Precise predetermined amounts of monomers MMA and AN were taken in 60cm^3 toluene in the reaction vessel. The reaction vessel was equipped with a thermometer and a water condenser and was heated in an oil-bath with constant stirring. The reaction temperature was maintained at 75° with an accuracy of ±0.5°. A requisite quantity of benzoyl peroxide was added to the reaction mixture to ensure 5×10^{-3}M concentration of benzoyl peroxide. The reaction was continued for a predetermined time (6 hours) with uniform stirring and then the cooled contents were poured into four fold excess of methanol with vigorous stirring. For complete precipitation the container along with precipitate was kept undisturbed for 24 hours. The isolated precipitate was then washed several times with methanol and then dried in vacuum at 60° to constant weight.

2.3 Optimisation of Reaction Conditions for Random Copolymers :

The reaction conditions for random copolymerisation of MMA and AN have been optimised by varying the composition of the monomers in the feed and by varying reaction time, temperature and initiator concentration.

2.3.1. Monomer : Monomer ratio :

A series of copolymers with different feed compositions of MMA and AN was synthesised by keeping the initiator concentration, reaction time, temperature and reaction volume constant and varying the monomer feed ratios. As mentioned in section (2.2.2), the reaction was carried out in three neck round bottom flask. The total volume of the reaction mixture was maintained at 100 cm^3 and the reaction time six hours. Initiator concentration was maintained at 5×10^{-3}M (0.121g in 100 cm^3), while the ratio of the two monomers was varied. The total monomer concentration (volume) was maintained at 40 cm^3 (in 100 cm^3 reaction mixture). 60 cm^3 toluene was used as reaction medium. Seven copolymers with different feed ratios were synthesised and Table 3.1. shows the feed compositions of the monomers in terms of volume ratio, mole fraction and mole ratio. The copolymers were precipitated by pouring the reaction mixture into four fold excess of methanol and keeping for 48 hours for complete precipitation. The copolymers were washed several times with methanol to remove traces of solvent and then dried in vacuum at 60° to constant weight.

2.3.2 Reaction time

To study the effect of reaction time on the copolymerisation of MMA and

AN, the copolymerisation was carried out by keeping monomer feed composition constant at 2:1 (v/v), MMA:AN and 3×10^{-4}M initiator concentration. In all these reactions 26.5 cm^3 (24.99g) of MMA and 13.5 cm^3 (10.87g) of AN were taken in the feed mixture in 60 cm^3 of toluene to make the total volume to 100 cm^3. The reaction was carried out at 75° by varying the reaction time in the range of 1 hour to 12 hours. Precipitation and further treatment of the precipitate was similar to that mentioned earlier in section 2.3.1.

2.3.3 **Initiator Concentration :**

The influence of initiator concentration on the copolymerisation of MMA and AN was studied by carrying out the reaction at a fixed monomer feed composition of 2:1 (v/v) of MMA:AN at 75° in toluene for six hours and by varying the initiator concentration in the range of 2.3×10^{-3} - 9.0×10^{-3}M. In all these reactions 26.5 cm^3 of MMA and 13.5 cm^3 of AN were taken in the feed mixture in 60 cm^3 of toluene to make the total volme of the reaction mixture to 100 cm^3. Precipitation and method of drying of precipitate was same as mentioned earlier in section 2.3.1.

2.3.4 **Reaction temperature**

The effect of reaction temperature on the copolymerisation of MMA and AN was studied by synthesising a series of copolymers at a fixed composition of MMA:AN (2:1, v/v). The reaction was carried out for six hours with a reaction mixture of 100 cm^3 containing 60 cm^3 toluene, 26.5 cm^3 of MMA and 13.5 cm^3 of AN. The concentration of benzoyl peroxide was 5×10^{-3}M in the total solution mixture. Copolymerisation was carried out at 70°, 75°, 80°, 85° and 90° temperatures. After the completion of the reaction the precipitation and further treatment of the precipitate was done as described earlier in section 2.3.1.

2.4 Characterisation :

Products synthesised by the copolymerisation of MMA and AN were thoroughly characterised by the following methods. Here the characterisation is reported for copolymers synthesised by keeping 6 hours reaction time except for the composition study, for which the copolymerisation was carried out for 45 minutes to ensure lower conversion ($<5\%$).

2.4.1 Infra-red Analysis :

IR spectroscopic analysis of the random copolymers was done on a Shimadzu IR - 408 (4000-650 cm^{-1}) spectrophotometer using KBr pallets.

2.4.2 NMR Analysis :

NMR spectra of the copolymers were recorded on a Perkin Elmer spectrophotometer at 90 MHz using deuterated DMSO and $CDCl_3$ as solvents and tetra methyl silane (TMS) as internal reference.

2.4.3 Thermal Analysis :

2.4.3a Differential Scanning Calorimetry (DSC)

The DSC analysis of the copolymers was carried out on a DuPont 2000 Thermal analyser located in the Wolfson Laboratory of the Department of Colour Chemistry at the University of Leeds, U.K. Measurements were based on the temperature differences between a reference and a sample, being heated in identical heat flux environments. Samples were weighed into 5 mm diameter aluminum pans, covered and sealed. The samples and reference pans were placed on their respective platforms and the apparatus purged with nitrogen (0.2 dm^3 $min.^{-1}$). Heating was carried out at 10° /min. in the range 25° to 500°.

2.4.3b Thermogravimetric Analysis (TGA)

This technique involves measuring the extent and rate of change of mass of a sample continuously either as a function of increasing temperature (dynamic study) or preheated temperature over a period of time (isothermal study) in a controlled atmosphere. The thermogravimetric analysis of all the copolymers was carried out on the DuPont 2000 model with 951 TGA model, located in the University of Leeds, U.K. The samples were weighted into platinum sample pans and heated in the range 25° to 500° at a heating rate of 10° /min. All the measurements were made under nitrogen at a flow rate of 50 cm^3/min. The thermograms of the copolymers were analysed to obtain information about the percentage weight loss at different temperatures. Various methods are available for the analysis of TGA data [2-18]. We have analysed the thermograms of the copolymers by the method proposed by Broido [19] with a view to estimate the kinetic parameters of their degradation reaction.

2.4.3.c. Broido's method for analysis of TGA

When a polymeric substance is heated it undergoes pyrolysis. It is assumed that the pyrolysed products are volatile. The progress of the reaction can be determined by continuous weighing of the sample. The weight (Wt) of the material at any given time (t) is relatd to fraction (Y) of the number of initial molecules not yet decomposed, by equation (2.1)

$$Y = \frac{N}{N_0} = \frac{Wt - W\alpha}{Wo - W\alpha} \tag{2.1}$$

Where $W\alpha$ is the weight when the reaction is completed and Wo is the initial weight. If the pyrolysis is carried out isothermally, the reaction rate is given by,

$$dy/dt = - KY^n \tag{2.2}$$

Where n is the order of the pyrolysis reaction. The rate constant K changes with absolute temperature according to Arrhenious equation.

$$K = A.\ e^{-E/RT} \qquad (2.3)$$

From equation (2.2) and (2.3) it follows,

$$\frac{dy}{Y^n} = -\ kdt = -\ A\ e^{-E/RT}\ dt \qquad (2.4).$$

If instead of operating the reaction isothermally, the reaction is operated at increasing temperature and the temperature T is a linear function of t, i.e.

$$T = To + ut \qquad (2.5)$$

$$dT = udt \qquad (2.6)$$

From equation (2.4) and (2.6), it follows

$$\frac{dY}{Y^n} = -\ \frac{A}{u}\ e^{-E/RT}\ dT \qquad (2.7)$$

The TGA curve of such a relation represents this last equation integrated from a temperature (To) at which Y = 1, Thus,

$$\int_{Y}^{1} \frac{dY}{Y^n} = \frac{A}{\mu} \int_{T_0}^{T} e^{-E/RA}\ dT \qquad (2.8)$$

A large number of pyrolysis processes are known to be first order (n=1) reactions. So,

$$\int_{Y}^{1} \frac{dY}{Y^n} = \int_{Y}^{1} dy = -\ln Y = \ln\left(\frac{1}{Y}\right) \qquad (2.9)$$

Conversely ; the integration of the right hand part of the equation (2.8) is anything but simple. However, Vallet, in a trilingual monograph reported, in 1961 [12] values of integration of terms like those involved in equation (2.8). From these data, the value of interactionof the left hand-side, term was obtained by Broido. Van Krevelen and co-workers [13] noticed that almost the entire measurable reaction usually occurs with ±10% of T_m, the temperature of maximum reaction velocity, applied to a certain approximations and obtained the following relation.

$$\ln[\ln(1/Y)] = (E/R.T_m + 1)\ln T + \text{Const.} \qquad (2.10)$$

According to this relation (2.10), a plot of ln [ln (1/Y)] versus ln T yields a straight line whose slope is related to the energy of activation.

Horowitz and Metzger [14,15] introduced two alternate approximations and developed relation (2.11) and (2.12).

$$\ln[\ln(1/Y)] = (E/R.\,T_m)\,T + \text{Const.} \qquad (2.11)$$

$$\ln[\ln(1/Y)] = -(E/R)(1/T) + \text{constant} \qquad (2.12)$$

The expression (2.12) has been found to be the most accurate of the three equations, (2.10), (2.11) and (2.12). Broido method is simple and readily produces a linear plot from which an activation energy can be found. We have followed Broido's method for the interpretation of thermogravimetric data.

2.4.3.d. Differential Thermal Analysis (DTA)

Differential thermal analysis of the copolymers was carried out with a Shimadzu Thermal analyser DT-30 equipped with R-123T recorder. In this experiment, the temperature at the center of the sample is compared with a reference material (powdered alumina) as both are heated at a uniform rate. Any change in the sample's specific heat as at Tg, any structural change which is endothermic or exothermic as at Tm, or chemical reactions will show as changes in the temperature difference between sample Ts and reference Tr. The sample and the reference material are held in a heated metal block at a controlled temperature To. As To is raised (a rate of 10° /minute), Ts and Tr follow perhaps by as little as 0.1°. . If an endothermic reaction takes place, Ts will lag behind Tr temporarily. If an exothermic reaction takes place, Ts will exceed

Tr temporarily. It means a difference in specific heats between sample and reference Ts-Tr will not be zero even when no thermal changes are occuring. However, when the specific heat of the sample changes, Ts-Tr will change with a shift in the base line.

2.4.4 Viscometry :

The study of conformational changes in dilute solution has drawn the attention of researchers [20-30]. Hence viscosity measurement, a relatively simple technique, is used for the study of conformational changes [26,28,31]. Viscometric studies were carried out for random copolymers and homopolymers of MMA and An using an Ubbelohde viscometers at different temperatures using different solvents such as acetone, DMF and DMSO. The viscometer was fitted with a sintered glass filter in order to prevent any undissolved polymer or dust agglomerates from entering the capillary. The viscometer was clamped in an upright position in a large thermostated water bath maintained at a desired temperature with an accurary of ± 0.05°. The solvent flow times were measured. Approximately 15 cm^3 of the solvent was used for the measurement of flow-time. The time required (t_o) for the meniscus to fall between the two etched marks was recorded. Measurements were repeated until the readings were constant to within 0·1 seconds. Similar procedure was used to measure the flow time (t), of accurately assembled polymer solutions. The design of the viscometer permits successive dilution to be made in-situ, hence several flow times can be obtained for any particular polymer sample. The solution was also given time to equilibrate to the required temperature. The flow time of each solution was readily calculated.

In each case, the ratio of (t_1/t_o) was a measure of relative viscosity (η_r). The specific viscosity (η_{sp}) was calculated as ($\eta_r - 1$). The limiting viscosity number i.e. intrinsic viscosity was obtained from the combined plots of (η_{sp}/c) and ($\ln \eta_r/c$) versus concentration according to the relations,

$$\eta_{sp}/C = [\eta] + K[\eta]^2 C \qquad \text{Huggins}$$

$$\ln \eta_r/C = [\eta] - \beta[\eta]^2 C \qquad \text{Kraemer.}$$

Where concentrations were expressed in g/dl.

The intrinsic viscosity $[\eta]$ was determined in each case from the best pair of the curves having the same intercepts and value of K and β such that,

$$K + \beta = 0.5$$

Measurements were also done in θ-solvent (mixture of DMF and methanol, solvent and non-solvent for the copolymers) system to find out the intermolecular expansion factor (α) which determines the flexibility of the polymer chains. Densities of the polymer solutions (dilute) at different temperatures were assumed to be those of solvent at that temperature. No kinetic energy corrections were made because the flow times of the solvents were quite high. Since intrinsic viscosities of the copolymers are below 2.0 dl/g, the effect of shear rate was negligible [32]. Extensive viscosity measurements were carried out to determine the intrinsic viscosity of the copolymers having different compositions of MMA and AN in the copolymer. Measurements in different solvents were carried out to predict the polymer solvent interactions. To determine the viscosity activation parameters, the hydrodynamic volume and Simha shape factor of the polymer molecules, viscosities were measured at different temperatures.

2.4.5 X-ray analysis

The X-ray study of materials is useful for the determination of detailed information on the state of order or dis-order of the system. For crystalline polymers, the X-ray analysis, at various levels of sophistication, may give data concerning (1) the identification of the material; (2) its crystallinity, (3) the relative disposition and geometry of the crystallites and (4) the relative disposition of atoms in the atoms in the crystallites. The crystallinity and texture of the crystals in the polymeric material may be studied as functions of the preparative procedure and of the thermal and mechanical treatment that the material has undergone.

From the X-ray spectrum of unoriented polymer, it is possible to determine the degree of crystallinity. It is also possible to distinguish in the X-ray spectrum of a polymer differences between the X-ray intensity diffracted from amorphous regions and that diffracted from crystalline regions. This is the basis of the most widely used method of crystallinity determination.

X-ray diffraction study was done using a Siemens crystalloflex 4 model, X-ray generator, coupled with a Hiltonbrooks/phillips diffractrometer located in the Department of colour chemistry, in the University of Leeds, U.K. The copolymers were finely ground and placed in 2mm diameter sample tubes. The sample tubes were then mounted and centered on a standard goniometer stage. The generated X-rays were Cu_{α} rays at 40 Kv and 20 mA.

The d-spacing corresponding to each peak (θ_1 and θ_2) was calculated according to the Bragg's formula

$$n \lambda = 2d \sin \theta$$

Where

n = diffraction order = 1

λ = Wavelength

θ = Bragg's angle

2.4.6 Microscopy :

Scanning electron microscopic study was carried out using (SEM) (JEOL-15) operated at 15-25 Kv. To avoid any charging under an electron beam, the samples were mounted on a SEM stub using a double sided tape. The samples were then coated using a polaroin S-5000 diode sputtering coater, with 200°A gold coating. Magnification was used as discussed in the results section.

2.4.7 Contact angle measurements :

Contact angle measurements were carried out using a contact-θ-meter developed at the University of Leeds. It is a versatile instrument which has been designed to allow effective and reproducible measurements of the surface wetting characteristics of a variety of surfaces and as such it is of value to all concerned with assessment of planar solid surfaces. For measurement of contact angle, polymer films were prepared by solution casting over mercury pool. Care was taken to make the film free of solvent. The polymer film was cut into the size of 40 mm x 75 mm and was placed on the upper surface of a plate. Then carefully a sessile droplet of liquid from a syringe was applied to the film. The droplet was then positioned so that its leading edge was in the centre of the area covered by viewing tube. When observed through the viewing tube, the reflection of the incident beam of light emitted from a narrow filament source, was seen as a bright star on the surface of the droplet. Then the viewing tube was moved keeping the image in the centre of the tubes, until the reflection was just disappeared. The point at which the reflection just disappears was the contact angle (θ). The procedure was repeated for other areas of the film. Critical wetting tension of the copolymer was determined by plotting cos θ values against the surface tension of contacting liquids. Recently contact angle measurement for surface characterisation has drawn the attention of investigators[33-45]

2.4.8 Elemental analysis : Copolymer composition :

The composition of the copolymers of methyl methacrylate and acrylonitrile was determined from acrylonitrile content [46-48] through nitrogen analysis by Dumas method. Copolymers synthesised at $\angle$5% conversion were used for this study. From the composition data of the copolymer, the monomer reactivity ratios of MMA and AN were determined by both Fineman-Ross [49] and Kelen-

Tudos [50] methods. Fineman - Ross (F.R.) method is based on the differential version of the copolymer composition equation proposed by Mayo and Lewis for "Terminal Model" (section 1.3.1). The modified form of this equation is as follows.

$$\frac{F}{f}(f-1) = r_1 F^2/f - r_2 \qquad (2.13)$$

Where F represents the molar ratio of MMA to AN in the feed and f represents the molar ratio in the resulting copolymer. Thus a plot of F (f-1)/f against F^2/f yields a straight line of slope r_1 and intecepts - r_2.

Kelen-Tudos method uses the equation -

$$\eta = r_1\xi - r_2 (1-\xi)/\alpha \qquad (2.14)$$

Where

$\eta = G/(\alpha+H)$ and $\xi = H/(\alpha+H)$

and $G = F(f-1)/f$ and $H = F^2/f$

A plot of η values calculated from experimental data as a function of ξ yields a straight line which can be extrapolated to $\xi=0$ and $\xi=1$ to give $-r_2/\alpha$ and r_1 both as intercepts. Here α is an arbitrary constant.

2.4.9 Determination of Solubility parameters of the Copolymers.

The solubility parameter [51-53] of the copolymers of MMA and AN were determined by measuring the intrinsic viscosity of the copolymer in different solvents. The intrinsic viscosity is determined in different solvents using the following relationship [54-55].

$$[\eta] = [2\{t/t_o - \ln(t/t_o) - 1\}]^{1/2}\ 1/C \qquad 2.15$$

Where C is the concentration in g/dl and t_0 and t are flow-times of pure solvent and solution respectively. Liquids with similar solubility parameters are apt to dissolve the same solutes and to be mutually compatible. This leads to an indirect method of measuring the solubility parameter (δ) for a polymer. The dissolving of a polymer in a low molecular weight liquid causes the random coil to expand and occupy a greater volume than it would in the dry, amorphous state. If the polymer is composed of single molecules viscous flow can occur, and the viscosity will be increased as the polymer expands. It is expected that when the polymer and the solvent have the same solubility parameter, the maximum expansion will occur and therefore the highest viscosity (for a given concentration) will be obtained. By measuring the viscosity of solutions of the same polymer at the same concentration (usually dilute) in variety of solvents, it is possible to deduce a consistent value of solubility parameter of the polymer. In the present work the solvents benzene, chlorobenzene, 1,4-dioxane, acetic anhydride, diethylformamide, and dimethyl acetamide are used. Six different fractions of 2:3 (MMA:AN) polymer A_5 were collected by successive addition of methanol to 2% solution of A_5 polymer in DMF. The polymers collected were washed and dried. The fractions are expected to have different molecular weights. The concentration of the copolymer solution used for viscosity measurements was 0.3 g/dl at 30°.

2.4.10 Swelling

Swelling behaviour of the copolymers of MMA and AN with different monomer contents was studied on powered samples (approximately uniform particle size) in solvents like water, methanol, absolute alcohol, 1-propanol, cyclohexane and n-heptane. The copolymers were first dried to constant weight and 0.5 g. of each copolymer sample was taken in tubes, bottom of which were made of perforated sintered glass for easy passage of liquid to the tube when placed in liquids. After predetermined time when equilibrium swelling was obtained, the tubes were removed from the liquid container and were drained in a centrifuge machine for 2-3 minutes and then immediately the weight of the swollen polymers was recorded. The percent swelling was calculated from the expression,

$$\text{Percent swelling} \quad \frac{Ws - Wd}{Wd} \times 100 \tag{2.16}$$

Where Ws is the weight of the swollen polymer and Wd is the weight of the dry polymer before swelling. The measurement of swelling was carried out in triplicate.

2.4.11 Differential Refractometry

Differential refractive index measurements have significance in polymer characterisation because of its wide use in the light scattering studies for molecular weight determination. This property not only depends upon the molecular weight but also on the configuration, i.e. the arrangement of the monomer units in the copolymer and the solvents used for the preparation of the polymer solutions. A Brice - Phoenix Differential Refractometer with 632.8 nm filter was used for the measurement. The measurements were made according to the method recommanded in the maker's manual. The direction of the beam was measured using a micrometer screw gauge attached to a telescope for an obliquely divided glass cell containing solvent on one side and polymer solution on the other. The cell has been arranged in such a way that when a pure liquid is used in both compartments, there will be no displacement and the 0° and 180° readings would be identical. In practice, a solvent reading must be taken to account for slight deviations from the ideal solution. The instrument also has a variable slit, semialuminised and inclined at 45° to the light path; an adjustible shutter and provision for thermosetting the cell. The measurement was carried out at 25°c by using a thermostated fast circulating water heater. Accurate monitoring of temperature was achieved by having thermometers located at about 3 cm either side of the cell house.

The difference in refractive index between a solution and its solvent was determined for five different concentrations of solute. The solutions were made up by the accurate weighing of vacuum dried samples into volumetric flasks, followed by dissolution in the required solvent. A suitable range of concentrations was achieved from further dilutions. From the results obtained the difference in displacements Δd was calculated as

$$\Delta d = (d_2 - d_1)_{\text{solution}} - (d_2 - d_1)_{\text{solvent}} \qquad (2.17)$$

Where d_2 and d_1 refer to the measurements of displacement at 0° and 180° respectively.

The difference in refractive index is given by

$$\Delta n = \Delta d \; Kc$$

Where Kc is a calibration constant for the instrument. The calibration constant was determined by using aqueous potassium chloride solutions on solution side and distilled deionised wate on the solvent side of the split cell. The data pertaining to the known difference in refractive index between salt solution and pure water at 25° and at 632.8 nm was obtained from Hu'ds [56] and was also confirmed experimentally. A plot of $\Delta n/c$ versus concentration in g/cm^3 is used to yield the specific refractive index increment of a polymer solution by extrapolation to zero concentration.

2.4.12 Measurement of adiabatic compressibility :

Adiabatic compressibility of the copolymers and homopolymers of MMA and AN was measured using a Multifrequency Ultrasonic Interferrometer". The Measurement is based on the determination of the ultrasonic velocity in polymer solution. The principle of the measurement of velocity (v) is based on the accurate determination of the wavelenth (λ) in the medium. Ultrasonic waves of known frequency (f) are produced by a quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separattion between these two plates is exactly a whole multiple of the sound wavelength, standing wavelengths are formed in the medium. This accoustic resonance gives rise to an electrical reaction of the generator driving the quartz crystal and the anode current of the generator becomes maximum. If the distance is increased or decreased and the variation is exactly one half wavelength ($\lambda/2$) or multiple of it, anode current becomes maximum From the knowledge of wavelengths (λ), the velocity (V) can be obtained by the relation :

Velocity = wave length x frequency

$$V = \lambda \cdot f \qquad (2.18)$$

Measurements :

The ultrasonic interferrometer consists of a) the high frequency generator and b) the measuring cell. During measurements the measuring cell is connected to the output terminal of the high frequency generator through a shielded cable. The cell is filled with copolymer solution in DMF before switching on the generator. The Ultrasonic waves move normal from the quartz crystal till they are reflected back from the movable plate and the standing waves are formed in the solution in between the reflector plate and the quartz crystal.

The micro meter is slowly moved till the anode current on the high frequency generator meter shows a maximum. A number of maximum readings of anode current are passed and their number 'n' is counted. The total distance 'd' passed by the micrometer gives the value of wavelength (λ) with the help of the following relation.

$$d = n\lambda/2 \qquad 2.19$$

Once the wavelength (λ) is known the velocity (v) in the solution (or liquid) can be calculated by the equation (2.18). The adiabatic compressibility can be calculated by the relation.

adiabatic compressibility = $1/V^2 D$ (2.20)

Where D is the density of the solution (or liquid). In this experiment 1% solutions of PMMA, PAN and copolymers in DMF were used.

2.4.13 Measurement of Zeta potential :

Zeta potential measurement of the copolymers was carried out with a Zeta potential meter in association with a digital multimeter. Before the measurements the copolymer was kept in 10^{-4}M KCl solution for 24 hours. Then the copolymer was kept in a cylindrical tube fitted with two electrode plates placed at two ends of the tube. The sample (copolymer) placed in between two electrodes was in a form of good compact column to avoid voids leading to erroneous results. Then 10^{-4}M KCl solution was passed through the whole assembly including sample column. The pressure of KCl solution was recorded from the movement of mercury column in the barometer. Care was taken to ensure that no air bubbles remained in KCl solution passing through the instrument. The multimeter reading was recorded for each change in pressure. A graph of change in e.m.f against change in pressure was drawn and its slope was determined. Both conductance and resistance were measured using 10^{-4}M KCl solution and resistance was also measured for 0.1M KCl solution in the presence of the copolymer. Zeta potential (ζ) of the copolymer was measured from the relation

$$\zeta = (4\pi\eta / D).(E/P).K_s.A \qquad (2.21)$$

Where η = Viscosity of the solution at room temerature (30°C)

D = Dielectric constant.

E/P = Slope of e.m.f. versus pressure curve.

Ks = Cell constant.

$$= \frac{\text{Specific conductance using 0.1M KCl solution}}{\text{Conductance using 0.1M KCl solution}}$$

$$= 0.01437 \times \text{Resistance using 0.1M KCl solution}$$

$$A = \text{Conductance using } 10^{-4}\text{M KCl solution}$$

$$\frac{1}{\text{Resistance using } 10^{-4}\text{M KCl solution.}}$$

2.4.14 Hydrolysis of Copolymers :

Hydrolysis of copolymers having high acrylonitrile content was carried out using KOH (20%). The copolymer (0.5 g/25 cm^3) was dissolved in DMF and was refluxed at 40°. KOH solution (20%) 10 cm^3) was added to achieve predetermined degree of hydrolysis and stirring was continued for 1 hour. The solution was then poured into four times its volume of methanol and THF mixture (1:1 v/v) and the precipitate obtained was filtered and dried to constant weight. The hydrolysed products were water soluble. The amounts of potassium ion K$^+$ (i.e. the extent of hydrolysis) in the hydrolysed product was determined by flame emission technique using Systronics, India flame photometer.

2.4.15 Determination of rate of Copolymerisation :

For the determination of rate of copolymerisation of MMA and AN, 50 cm^3 of total solution containing 30 cm^3 of toluene and 20 cm^3 of monomers of known composition was polymerised at 75°c for 45 minutes to achieve low conversion. The same products were used for the determination of reactivity ratios as discussed in section 2.4.8. Since rate measurements in copolymerisation require the rate of homopolymerisation of individual monomers, the homopolymerisation of MMA and AN were carried out under identical reaction conditions in toluene at 75°. A plot of percentage yield and reaction time was drawn and the rate of polymerisation was measured from the slope of the linear graph. The ratio of termination rate constant (Φ), necessary for the measurement of rate of copolymerisation according to equation 1.21 as discussed in section 1.4, was taken from literature [57].

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