

CHAPTER - III

EXPERIMENTAL

IIIA. Materials and Purification

i) Bentonite (Evans Medical Co., England) : An aqueous suspension of 25 lit. was prepared by stirring continuously 100 gms of bentonite in distilled water. The suspension was maintained at pH ~ 8 with NaOH solution. After every 24 hours, 10 cm layer of the suspension (from the top) was siphoned out and each time the original volume was restored by adding water. This process resulted in particle size less than $2\mu^1$. The clay collected, on acidification with HCl to pH ~ 4, settled at the bottom of the container by coagulation. This coagulated portion was stirred continuously with 30% (v/v) H_2O_2 (2 ml per 3 lit. suspension) in a large beaker followed by heating on a water bath for a long time with occasional stirring to ensure complete removal of H_2O_2 . On cooling, the suspension was passed successively through columns packed with Amberlite IR-120 and Amberlite IRA-400. The hydrogen bentonite HB suspension, thus obtained, was stored at 5-10°C.

ii) Monomers: Methylmethacrylate MMA (BDH) was washed repeatedly with 2% NaOH solution, water to remove NaOH, dried over fused $CaCl_2$ at 0°C. It was distilled before use under reduced pressure (~ 2 mm) and the middle fraction was collected (35°C).

Acrylonitrile ACN (BDH) was washed with 5% Na_2CO_3 solution followed by acidifying with dilute H_2SO_4 . The monomer was acid freed

by repeated washing with water. It was dried over fused CaCl_2 for 24 hours at 0°C and pure ACN was obtained by distillation just before use.

Methacrylonitrile MACN (Gift Sample) was washed and dried following similar method as for ACN. It was distilled fractionally under reduced pressure (~ 1 mm) before use and the middle fraction (30°C) was collected.

iii) Solvents: Benzene (C.P) was thiophene freed with conc. H_2SO_4 , neutralised with aqueous KHCO_3 , washed several times with water, and finally dried over P_2O_5 . It was filtered and distilled into a brown bottle.

Rectified Spirit (C.P) was treated with proportional amount of freshly burnt quicklime and kept overnight. Absolute ethanol was obtained on distillation and the middle fraction (78°C) was stored in a sealed brown bottle.

n-propanol, n-butanol, isobutanol and tert-butanol were dried over anhydrous K_2CO_3 , filtered and fractionally distilled.

N,N' -dimethylformamide DMF (B.D.H) was stored over P_2O_5 for nearly 10 hours and distilled.

Methanol (E. Merck, Analytical Reagent), tetrahydrofuran THF (Fluka, AG), diphenyl-picryl hydrazyl DPPH (Sigma), petroleum ether (C.P) and sodium hexametaphosphate (obtained from Prof. B.K. Theng, New Zealand) were used as received.

Water was distilled with alkaline KMnO_4 .

iv) Nitrogen: The commercial grade (Indian Oxygen Ltd) was passed through a series of bubblers containing Fieser's solution². The oxygen free nitrogen was dried by passing through 2 bubblers containing conc. H_2SO_4 .

IIIB. Polymerizations

i) Homopolymerization: The polymerization of MMA was carried out in 100 ml ground joint pyrex bottled (outside painted black). Measured amount of alcohol was added, under N_2 , to known volume of HB suspension in the bottles, stoppered, shaken vigorously and allowed to equilibrate at the polymerization temperature. The polymerization was started by adding MMA under N_2 and shaking well. Control runs were carried out side by side without alcohol. The bottles were withdrawn from time to time and the reaction was arrested with alcoholic solution of DPPH followed by chilling. The solid mass was separated by centrifugation ($16-17 \times 10^3$ r.p.m), dried in a vacuum oven at 40°C and weighed.

ii) Copolymerizations:

The copolymerization was carried out in 100 ml standard joint stoppered bottles with different monomer compositions. The process was similar for reactions with both the monomers (MMA and MACN). The copolymers separated out when the reaction were carried out at the same time intervals but different monomer compositions and were separated by centrifugation (~ 16000 r.p.m).

dried in vacuum oven at the room temperature. The purification was made from dimethyl formamide in which the copolymer was soluble. The pptn. of the copolymer was made from petroleum ether. Such a purification of the copolymer is carried out three to four times and then dried in the vacuum oven at the room temperature. The infrared spectroscopy reading of the copolymer and its glass transition temperature confirmed the formation of the copolymer.

III C. Polymer Separation

i) Polymethylmethacrylates

Non-extractable (polymer bonded to bentonite) and extractable polymethylmethacrylates PMMA's were separated by repeated extraction (Soxhlet) of the whole mass with benzene followed by centrifugation. Benzene extracted PMMA was purified by repeated precipitation into a mixture of methanol and petroleum ether followed by drying under vacuum at 40°C .

ii) Copolymers:

The copolymers of MMA - MACN and MMA - ACN are very hard and sticky due to characteristic nature of the nitrile polymers. The copolymers are found to be hardly soluble in DMF and THF and almost insoluble in benzene. Moreover, the copolymers are degraded at the higher temperature (at 40°C and above) to a significant extent. Such a property makes the separation of the copolymer a formidable task. Of the solvents used, THF has been found to be suitable one for the separation of the copolymer at or below 35°C . Still there remains a large amount of the copolymer intimately adhered to the mineral

particles. Repeated extraction with the solvent produces about 80% of the total copolymer formed. The copolymer is precipitated from petroleum ether. The pure copolymer is obtained by dissolving it in THF and then precipitating from petroleum ether for three to four times.

III D. Fractionation:

The polymer, PMMA, is made free from the extraneous admixtures like, clay mineral, unreacted monomer etc. before going for fractionation. Extraction, washing with Benzene or DMF, reprecipitation from Petroleum ether/methanol mixture are carried out for this purpose. After the above treatments the sample is dried to constant weight by putting the sample in vacuo at room temperatures. The fractional precipitation is then carried out by the procedure given as follows. The polymer solution in benzene is placed in a constant temperature water bath in a beaker at 30°C . When the solution has attained the temperature of the bath, Methanol as used for the precipitation of the lower molecular weight fraction is gradually added from a burette and the solution is stirred thoroughly but gently until the faint turbidity redissolves. The stirring with high speed is avoided to prohibit the degradation of the polymer. The degree of turbidity of the solution serves as an indicator of the amount of the precipitant required to redissolve the precipitate a given fraction. The solution with the precipitant (methanol) is gently warmed to

redissolve the precipitate, and then gradually cooled in the thermostat. Phase separation occurs after a while, and the phases are isolated from each other by filtration. The first two fractions are isolated in the same way by further successive addition of methanol to the solution. The last fraction is isolated by addition of large volume of petroleum ether (B.P. 60° - 80°C). Sometimes each fraction is refractioned to get more narrow range of molecular weight fragments.

R E F E R E N C E S

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