CHAPTER - 5

SUMMARY AND CONCLUSION

Acrylonitrile homopolymer and its copolymers have always been an interesting field of research. Difficulty in molding and processing of polyacrylonitrile has restricted its applications in the homopolymeric form particularly because of its high glass transition temperature. Improvements in these properties can be achieved by copolymerising acrylonotrile with other suitable monomers. Acrylates have comparatively lower glass transition temperature and their copolymers are expected to show better processibility. Poly(methyl methacrylate) is a good plastic material. It is widely used as a molded and fabricated plastics. The crystal clarity, light weight, outstanding weather resistance, and strength of poly(methylmethacrylate) have resulted in extensive use of this polymer in aircraft glazing, in signs, in lighting in the architectural, transportation and home appliances. The monomer methylmethacrylate has the ability to copolymerise with practically all types of monomers. Therefore methyl methacrylate - acrylonitrile copolymers study was undertaken.

Literature survery reveals that MMA-AN system has been studied extensively using various initiation systems. Most of the synthesis has been carried out in DMF medium. In the present work the synthesis of random copolymers of MMA and AN has been carried out in comparatively less expensive solvent toluene

The arrangment of monomeric segments in the copolymers strongly influences the physico-chemical properties of the copolymers. Therefore attempts are made to see the effect of morphology of the copolymers on their properties by synthesising two types of copolymers.

a) random copolymers of MMA-and AN, and

b) graft copolymers, (PAN-g-MMA),

The random copolymers of methylmethacrylate and acrylonitrile were synthesised by solution polymerisation process using benzoyl peroxide as free radical initiator and toluene as reaction medium. A series of copolymers was synthesised and throughly characterised by IR, NMR, elemental analysis, thermal analysis, X-ray diffraction, viscosity studies, contact angle measurement, swelling studies etc. Hydrolysis of the copolymers by KOH was carried out and the amount of potassium in the copolymers was determined by flame photometric technique. Reaction conditions for random copolymerisation were studied and optimised. Composition of the copolymers was determined by nitrogen analysis by Dumas method. Viscosity study of the copolymers was done extensively in different solvents (acetone, DMF, DMSO) at different temperatures. From the intrinsic viscosity data, solubility behaviour of the copolymers in DMF and DMSO as well as polymer-solvent interactions were predicted. Instrinsic viscosity data was also used to calculate the thermodynamic activation parameters such as over all activation energy, the activation enthalpy and entropy changes ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) due to polymer-solvent interactions. Equivalent hydrodynamic volume (Ve), a measure of shape of the polymer molecule at infinite dilution was also calculated from viscosity data. The Simha shape factor was determined. Thermal analysis was carried out by thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetric (DSC) methods. Zeta potential of the random copolymers and their adiabatic compressibility was calculated. The copolymer has been fractionated and the intrinsic viscosity of each fraction has been determined in different solvents and the solubility parameter of the copolymer was determined. A summary of the results obtained for MMA-AN random copolymers is given here.

1. From the study of different parameters on percentage yield it has been observed that maximum percentage yield (80%) was obtained for 6.8×10^{-3} M

concentration of benzoyl peroxide at 75°C and 6 hours reaction time using 2:1 MMA: AN (v/v) concentration.

2. Reactivity ratios of the monomers MMA and AN determined by Fineman Ross (r_1=1.20, r_2 = 0.15) and Kelen-Tudos method (r_1=1.20, r_2=0.16) are in agreement with the literature values.

3. From viscosity study of the copolymer in DMF and DMSO at different temperature, it was observed that intrinsic viscosity decreases with increased temperature giving good linear relationship. The decrease in value is more pronounced in DMF than in DMSO. From the comparison of intrinsic viscosity in DMF and DMSO it was observed that, at 30° the intrinsic viscosities of the copolymers and of PAN show overall lower values in DMSO than in DMF which indicates the poor solvent nature of DMSO at lower temperature. However, at higher temperature intrinsic viscosity values for PAN and copolymers are higher in DMSO indicating that at higher temperature, DMSO acts as a better solvent. At higher temperature conformational changes take place in the polymer-solvent system and hence a changed intrinsic viscosity trend is observed. It was also observed that the thermodynamic properties of the copolymers are governed by the both monomeric segments.
The entropy values of copolymers suggest that the copolymer systems were assumed to be poorly ordered. The Simha shape factor for all the copolymers at all temperatures was observed to be 2.5 which indicates that the copolymer molecules are spherical in shape.

4. From X-ray diffraction study it was observed that the copolymers have intermolecular spacing values in between that of PAN and PMMA (i.e between 5.27 - 6.27 Å) and with the increase of MMA concentration in the feed intermolecular spacing increases.

5. Differential scanning calorimetric results reveal that the glass transition temperatures of the copolymers are much lower than those of homopolymers.

the grafted chain with main chain polymer.

4. Viscosity study of graft copolymers reveal that intrinsic viscosity of the graft copolymers are lower than that of parent homopolymer PAN. It is also observed that $\Delta S^{\ddagger}$ values in DMF are all negative and in DMSO are positive. indicating more ordered system in DMF than in DMSO. The Simha shape factor for all graft copolymers was found to be 2.44, indicating a spherical nature for polymer molecules.

5. Swelling behaviour of graft copolymers reveal that the extent of swelling in a given solvent decreases with the increase in percentage grafting and the extent of swelling increases with the polarity of the solvent for a given graft copolymers sample.