Summary and Conclusion

Polymerization in microemulsion has achieved wide spread attention in recent years. It provides a novel technique for the production of microlatexes in the nanometer range and polymers with specific properties. Microemulsion differs completely from macroemulsion or miniemulsion in respect to their thermodynamic stability. Macroemulsions conventionally known as emulsions are opaque, milky and thermodynamically unstable mixtures of immiscible liquids having droplet size more than 100 nm. Microemulsions on the other hand are isotropic, transparent or translucent and thermodynamically stable systems with droplet size ranging from 10-40 nm. However, a bicontinuous lamellar structure has also been postulated which is consistent with their transparency.

Polymerization in microemulsions, can be carried out by adding monomers to the oil or water phase or replacing either of them by monomer. Due to the difference in the polymerization mechanism in emulsion and microemulsion medium products obtained from these processes are expected to give distinctly different properties:

The main advantages of the process are :

- Low viscosity, optical transparency and high stability of the microlatex.
- No coagulum formation.
- Low dimensions and relatively narrow particle size distribution.
- High molecular weight polymers.
- More homogeneous compositions of polymers than those prepared in solution.
- Easier storage and handling.

The microemulsion polymerization can lead to the development of novel materials useful in separation science, medical technology, enhanced oil recovery and surface coatings.

Polymerization medium influences the properties of the polymers synthesized, as well as its mechanism of formation. Hence co-polymerization of MMA and BA was carried out in microemulsion media using free radical initiation. Various conditions such as initiator type and concentration, temperature, effect of cosurfactant pentanol, monomer concentration and time were optimized at batch levels to get translucent polymerized latexes.

Kinetics of the polymerization of MMA, BA and MMA-BA was studied at various temperatures, potassium persulphate concentrations and monomer concentrations.

The products formed were characterized for their particle size in latex form and for their thermal and spectral properties and for molecular weights. Particle size measurement was done through transmission electron microscopy and particle size analyzer. Molecular weights were determined by gel permeation chromatography. Spectral characterization was done through high resolution ^1H and ^{13}C NMR and UV-Vis transmission spectroscopy. Thermal analysis was done through TG and DSC. Activation energy for the degradation was calculated through Broido's equation using TGA results.

Selected experiments for the copolymerization of MMA and BA were carried out in a semicontinuous process using Dowfax 2A-1 and SDS surfactants. The effect of surfactant concentration, monomer concentration, cosurfactant type, initiator type and concentration and temperature was studied using Dowfax 2A-1. Viscosities were measured using Brookfield synchroelectric viscometer. The products were characterized by TEM, GPC, TGA, particle size analyzer and viscometry.

Representative microemulsion systems were tested for mechanical stability, electrolytic stability, freeze-thaw stability and film forming properties. The latexes were used to prepare microemulsion based paints containing TiO_2 pigment and, china clay and steatite as extenders. Paint properties such as scrub resistance, stain resistance and colour intensity were examined and compared with the paints based on standard emulsions from Asian Paints (India) Ltd.

From the above studies following conclusions are drawn,

(i) The rate of polymerization is lower for microemulsion systems than for emulsion systems.

(ii) Two stages in rate of polymerization in microemulsion and three stages in emulsion polymerization were found from the log Rp vs % conversion plots for the polymerization of MMA, BA and copolymerization of MMA and BA.

(iii) Higher percentage of isotacticity was found for PMMA synthesized in microemulsion medium compared to that synthesized in emulsion medium from ^1H and ^{13}C NMR studies.

(iv) Average particle size of the microlatexes was within and around 40 nm. Bimodal distribution of particle size was identified in one particular case.

(v) High molecular weights were found for all the polymers synthesized in microemulsion system and emulsion system. Polydispersity was lower for polymers synthesized in microemulsion system than from emulsion system.

Broad polydispersity was found in semicontinuous process and bimodal distribution in one particular case.

(vi) Activation energy of polymerization from Arrhenius equation shows higher values for microemulsion systems than emulsion systems.

(vii) Activation energy of degradation from TGA shows lower value for polymers synthesized from microemulsion system than emulsion system.

(viii) No short chain alcohols were used as cosurfactant in the batch process of polymerization and has been shown as not to favour microemulsion polymerization for the studied monomer.

(ix) Microemulsion latex serves as an excellent binder in surface coatings.

It can be concluded that in microemulsion, polymerization is taking place in microdroplets predominantly and at times, other processes such as polymerization in monomer swollen micelles in semicontinuous polymerization and homogeneous polymerization (in PMMA synthesis) become significant.