CHAPTER 2

Experimental

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EXPERIMENTAL

[2.0] Introduction

The primary aim of the work was to generate stable, translucent nanolatex with high solid content. One of the ways this can be achieved is by choosing an appropriate system having a higher rate of particle nucleation and at the same time requiring lower concentration of surfactant to stabilize the newly formed particles [1 – 3]. Higher particle nucleation is expected for polar monomers since it involves particle generation in both aqueous phase and micelles [4 – 5]. Therefore polymerisation of partially water soluble monomers ethyl acrylate [EA], methylmethacrylate [MMA] was studied both in emulsion and microemulsion.

For the formulation of microemulsion the monomers were taken as oil and aqueous micellar solutions of all the three types of surfactants viz. anionic (sodium dodecyl sulphate, dodecyl benzene sulphonic acid and AOT) cationic (DTAB, DDAB,CPC) and non ionic (SPAN 20 , TWEEN 20, TRITON X 100) and their combinations were tried. Monomer solubilisation capacity was in the following order anionic > cationic > non-ionic. Non – ionic surfactants were not used as at the polymerization temperature 70 - 90 ^{0}C the dehydration of polyoxyethylene chains results in destabilization of the latex system. Though monomer solubilisation capacity of cationic surfactants was equivalent to that of anionics, they were not used for polymerisation, as KPS was used as a free-radical initiator, which reacts with cationic surfactants reducing its activity. Among the anionic surfactants studied, SDS gave the best results in terms of its solubilisation, latex particle stabilization and lower kraft temperature.

[2 . 1] Reagents and Materials

Monomers

Ethylacrylate from BDH England, methymethacrylate from Sisco Research Lab., Mumbai,India and hydroxyethylmethacrylate from Fluka, Switzerland were distilled under vacuum and were stored at 4 ^{0}C till further use.

Surfactant

Sodium dodecyl sulphate (SDS) from SDFine Chemicals, Baroda, India was used without further purification

Initiators

Potassium persulphate (KPS) from Sisco Chemicals, Mumbai, India was recrystallised from water. AIBN from Sulab Chemicals, Baroda , India was recrystallised from a (1:1) mixture of chloroform methanol.

Miscellaneous

AR grade methanol, acetone, chloroform, sodium hydroxide, from Qualigens, Mumbai, India and hydroquinone from Merck, Mumbai, India were used as received

[2 . 2] Construction of Phase Diagram

The single phase o / w microemulsion region at 25 and 70 ^{0}C was determined visually by titrating clear aqueous micellar solutions of sodium dodecylsulphate with monomer or monomer mixtures, in ground glass stoppered graduated test tubes, until slight turbidity was observed. Phase boundaries were checked by preparing samples with weight compositions below and above the boundaries determined by titration. Since even a small amount of polymer formed can substantially reduce the size of one phase microemulsion region due to the very high interfacial tension between continuous phase and the polymer a few ppm of hydroquinone was added to the monomers, prior to titration, to inhibit thermal polymerization. Difficulty was observed in determination of one phase boundary at higher sodium dodecyl sulphate concentrations, due to the high viscosity of the samples.

[2 . 3] Synthesis of Polymers

Poly (ethyl acrylate) , poly (ethyl acrylate – co – methylmethacrylate) and poly (HEMA – co – MMA) were synthesized by batch process in emulsion and microemulsion media. For the synthesis of polymers receipes given in Table 2.1 were charged in a five-neck reaction kettle, equipped with mechanical stirrer, water condenser, thermometer and nitrogen inlet. All reactions were carried out under nitrogen atmosphere. At desired temperature initiator solution was added to the reaction mixture. The reaction temperature was maintained with an accuracy of + 0.5 ^{0}C. The reaction was continued for 4 - 6 hours and after that polymer from the latexes was precipitated out using four – -fold excess of methanol. Polymers were thoroughly washed several times with hot water to remove surfactant. The polymers were then reprecipitated from their respective solvents using methanol. The polymers were finally dried under vacuum at 70 ^{0}C to constant weight.

Table 2.1: Microemulsion and Emulsion compositions in weight % used for Polymerisaton.

System	**Microemulsion**			**Emulsion**		
	Monomer	Surfactant	Water	Monomer	Surfactant	Water
EA	5	5	90	10	1	89
				10	0 25	89.75
EA – MMA	10	15	75	10	1	89
				25	0.5	74.5
MMA-HEMA	-	-	-	10	1	89

[2 . 4] Kinetic Studies

Kinetic studies were carried out to understand the polymerization behaviour of the systems under study. Kinetics of the homopolymerisation of ethyl acrylate and its copolymerisation with methylmethacrylate was studied in emulsion and microemulsion. For kinetic studies 5 cm^3 latex was withdrawn periodically from the reaction kettle and was added to the preweighed glass tubes containing 40 ppm hydrquinone dissolved in methanol. The conversion of monomer to polymer was determined gravimetrically.

[2 .4 .1] Homopolymerisation of ethylacrylate

[i] Effect of initiator concentration

Production of polymers with desired properties such as high molecular weight, complete conversion and reasonable rate of polymerization requires the use of optimum level of initiator concentration. Hence water soluble initiator potassium per sulphate (KPS) concentration was varied from 0.18 – 0.73 mM. Oil-soluble initiator 2,2 – azo – bis – iso- butyronitrile (AIBN) was used for comparison at 0.73 mM.

[ii] Effect of variation in Monomer / Surfactant ratio

M / S ratio was varied from 1 to 54 in order to investigate the contribution of different nucleation mechanism on changing the surfactant concentration. This can have important implications pertaining to particle size and latex stability.

[iii] Effect of temperature

The variation of temperature greatly affects the polymerization rate. Therefore the reaction temperature was varied from 65 – 75 ^{0}C to determine the activation energy for the polymerization.

[2 . 4 . 2] Copolymerisation of ethyl acrylate - methylmethacrylate

Kinetics of copolymerisation of ethyl acrylate – methylmethacrylate in emulsion and microemulsion was studied with respect to the effects of initiator concentration and type.

[i] Initiator concentration and type:

Water-soluble initiator KPS is partitioned only in aqueous phase while the oil soluble initiator AIBN is distributed mainly in the oil droplets. Their preferential distribution in aqueous phase and oil phase therefore gives an idea about the relative influence of different nucleation mechanisms for emulsion and microemulsion system in terms of its effect on particle size, its distribution, molecular weight and latex stability followed under identical reaction conditions with the initiator concentration ranging from 0.18 – 0.73 mM for both KPS and AIBN. Neutral redox initiating system ascorbic acid - hydrogen peroxide (1 : 1 mole) was also studied to see the effect of initiator charge.

[ii] Monomer feed composition

The copolymer properties are dependent on the composition and sequence of the components in the copolymer chain. Moreover in case of partially hydrophilic monomers, partitioning affects the kinetics. Hence the effect of monomer feed composition were studied at 0.25 / 0. 75 , 0.5 / 0.5 and 0.75 / 0.25 concentrations of EA - MMA. In addition the copolymer composition and thermal properties were correlated to the way particles evolve in emulsion and microemulsion polymerization.

[2 . 4 . 3] Reactivity ratios of ethylacrylate – methylmethacrylate

Correct estimation of monomer reactivity is an important parameter in the study of copolymerisaton as it allows the freedom to tailor copolymer properties. For polar monomers, the effect of monomer partitioning between aqueous and organic phases leads to drift in copolymer composition. Therefore reactivity ratio was recalculated including the effect of monomer partitioning in emulsion and microemulsion medium. The details of the determination of monomer reactivities are given in section 4. 3.

[2 . 5] Characterization of the Products

(i) Spectral analysis

IR spectra of the purified products were recorded on a Perkin Elmer 16 PC IR spectrophotometer using 1 cm diameter KBr pellets. ^{1}H NMR spectra of the products were recorded on a Varian XL – 300 NMR spectrophotometer at room temperature using $CDCl_3$ as solvent at 300 MHz . All chemical shifts were referenced to TMS. The spectral width was 2000 Hz , pulse delay was 5 sec and 20 pulses were accumulated.

(ii) Thermal analysis

Glass transition temperature of the products synthesized in emulsion and microemulsions were determined at 10 ^{0}C/ min heating rate under nitrogen atmosphere on a modulated DSC 2910 T.A. instrument.

(iii) Particle size measurements

A Malvern Photon Correlation spectrophotometer, model 4700, equipped with a vertically polarized argon ion laser source operating at 488 nm., was used to measure the particle size of the polymerized emulsion latexes in dynamic mode. The scattering intensities from the sample were measured at 90^0 with the help of a photomultiplier tube. Intensity correlation data were analysed by the method of cumulants to provide the average decay rate, $< \Gamma^2 > = q^2 D$, where $q = (4 \Pi n / \lambda) \sin \theta / 2$ is the scattering vector, n the index of refraction, D the diffusion coefficient and the variance, $v = < \Gamma^2 > - < \Gamma >^2 / < \Gamma >^2$, which is a measure of the width of the distribution of the decay rate. The measured diffusion coefficients were represented in terms of apparent radii by means of Stokes law. Latexes were diluted up to 100 times and filtered through 0.2 μm Millipore filters before measurements to minimize particle – particle interaction and remove dust particles. The number of particles were, calculated using the following equation,

$$N_p = 6\, M_o\, X_m \,/\, \pi\, \rho\, D_n^3$$

where D_n is a number average diameter of the polymer particles obtained from dynamic light scattering, X_m is fractional conversion, Mo is amount of monomer initially charged in g / cm^3, ρ is density of polymer in g / cm^3 and N_p is number of particles / cm^3.

Particle sizes of the polymer latexes at 97 % conversion were also determined using a Philips Technai – 20 transmission electron microscope operated at 200 kv accelerating voltage. The polymerized latexes were diluted 100 times with deionised distilled water and one drop of the diluted dispersion was placed on 200-mesh carbon coated copper grid. Uranyl acetate (2% w / v) was used as a staining agent. Diameters of at least 60 randomly chosen particles were measured directly from the micrograph. The number and weight average diameters were calculated using the following equations, where Di is the diameter of the particle and **n** is the number of particles measured.

$$D_n = \Sigma\, n_i D_i \,/\, n$$

$$D_w = \Sigma\, n_i D_i^4 \,/\, \Sigma n_i D_i^3$$

(iv) Molecular weight measurements

A Thermo – Quest GPC equipped with Spectra system RI 150 refractive index detector, As-300 auto sampler and Spectra system P100 pump was used along with PSS – GPC software for molecular weight determinations. HPLC grade THF from S.D.Fine

Chemicals was used as a mobile phase at room temperature. The stationary phase consisted of two PL Gel SDV 5µ linear and 100 ^{0}A (8 x 600 mm) columns. 20µL of 0.1% polymer solutions were injected to get a neat chromatogram. Narrow molecular weight distribution PMMA samples (molecular weight range, 1.4 x 10^6 to 3.06 x 10^2) were used as calibrating standards.

(v) Viscometric studies

Intrinsic viscosities of the purified products were determined in acetone at 30 ^{0}C using AVS 350 Schott Geratte auto viscometer.

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