CHAPTER 3

Part A

Kinetics of Homopolymerisation

Contents

Page No.

PART A : EA / SDS / WATER SYSTEM

[3 .1] Introduction

Enormous work has been carried out on the oil-in-water emulsion and microemulsion polymerization of both hydrophobic and hydrophilic monomers [1 – 3]. Bulk of the polymer is formed in the latex particles generated by micellar, homogeneous and droplet nucleation [4]. The contribution of each however depends on the monomer polarity, surfactant concentration, rate of stirring and the level of subdivision of the monomer droplets. For styrene micellar nucleation is considered to be the primary nucleation mechanism when the surfactant concentration is above cmc [5 - 8]. However, in recent report on the emulsion polymerization of styrene Varela de la Rosa et al attributed observed particle formation after the disappearance of micelles (10-15 % conversion) to homogeneous nucleation [9]. In case of microemulsion the level of subdivision of monomers further increases and therefore the micro droplets have been recognized as the principle locus of polymerization. The classic works of Gou et al. have shown continuous nucleation in these microdroplets [10]. As the water solubility of the monomer increases the polymerization kinetics differes significantly due to

- Change in properties of the interfacial layer such as decreased interfacial energy resulting into a decrease in the adsorption of emulsifier.
- A higher rate of surface formation of the polymer phase with respect to the rate of its stabilization by adsorbed emulsifier molecules. This is responsible for a flocculation mechanism better known as homogeneous and coagulative nucleation mechanism for particle formation

Gilbert and Napper have shown that partial water solubility of the monomer and low surfactant concentration favours such mechanism [11 ,12]. The higher particle density can thus be particularly advantageous for the production of stable nanolatex at a lower surfactant and higher monomer concentration provided the surfactant provides adequate stabilization of the new particles. Therefore the present work explores the emulsion and microemulsion polymerization of ethylacrylate in order to look into the difference in the relative contribution by homogeneous and droplet nucleation and its effect on the kinetic and colloidal parameters and latex stability.

Phase Diagram:

The phase diagram was constructed in order to decide the one phase region and the composition to be selected for polymerization. The phase diagram was constructed at room temperature, [34 ^{0}C] and at the polymerization temperature, [70 ^{0}C]. At higher temperature the one phase region extended due to increase in water solubility of the monomer. The dotted region in Fig 3.1 represents ill-defined phase boundary between turbid emulsion and transparent microemulsion. The samples within one phase region were transparent and fluid except at higher SDS concentration where they were transparent gels may be due to transition of spherical micelles to rod like micelles. Polymerisation of ethyl acrylate was carried out at M / S ratios 1, 10, 40 and 54 represented by points A, B, C and D in the phase diagram. Point A corresponds to an initial microemulsion where as points B, C and D corresponds to an initial emulsion system, which transform into translucent nanolatex after polymerization. Compositions used for microemulsion and emulsion are given in Table 3.1.

[3 . 2] Kinetics

The reaction parameters for polymerisation of ethyl acrylate such as type and concentration of initiator, reaction temperature, reaction time were optimized with

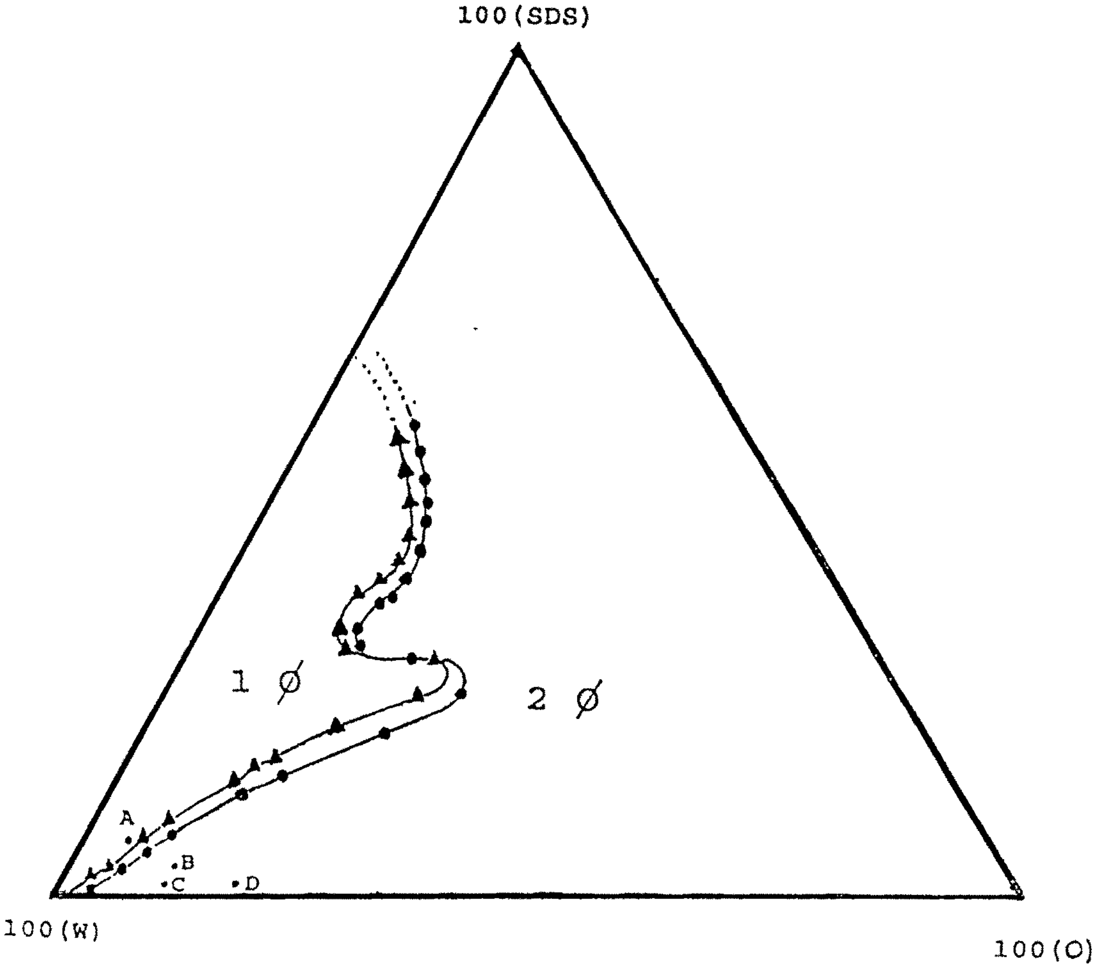

Fig 3.1 : Phase diagram of ethyl acrylate / SDS / Water system .

(▲) at 34 °C, (●) at 70 °C.

A, M / S = 1 ; B, M / S = 10 ; C, M / S = 40 and D, M / S = 54.

respect to the percentage conversion and particle size of latex using compositions given in Table 3.1.

Table 3.1 : Compositions of ternary emulsion and microemulsion system for ethylacrylate polymerization

Wt % of Components.	Microemulsion	Emulsion		
	M / S = 1	M / S = 10	M / S = 40	M / S = 54
EA	5	10	10	20
SDS	5	1	0.25	0.37
Water	90	89	89.75	89.63

M = Monomer , S = Surfactant

[3 . 2 . 1] Effect of variation in monomer / surfactant ratio and initiator type

Effect of initiator type and concentration on percentage conversion and rate of polymerization was studied by polymerizing EA / SDS / Water microemulsion at 70 °C using KPS as an initiator [Fig 3.2] AIBN initiated microemulsion system was only used for comparing the final particle size. Fig [3.3] and [3.4] show the percentage conversion vs. time and the rate of polymerization (Rp) vs. percentage conversion plots for KPS initiated emulsion polymerisation of EA studied at M / S = 10 and 40 respectively at 70 °C. Since AIBN initiated polymerizations could not produce translucent / transparent stable latexes, it was not used in further study

In the true microemulsion system with **M / S = 1** the conversion vs. time plots for the free radical polymerisation of ethyl acrylate (EA) initiated by potassium persulphate (KPS) are exhibited in Fig [3.2]. In the case of true microemulsion polymerisation the maximum conversion achieved was 80 - 85 % after 3 hr The low Tg (- 24 °C) of

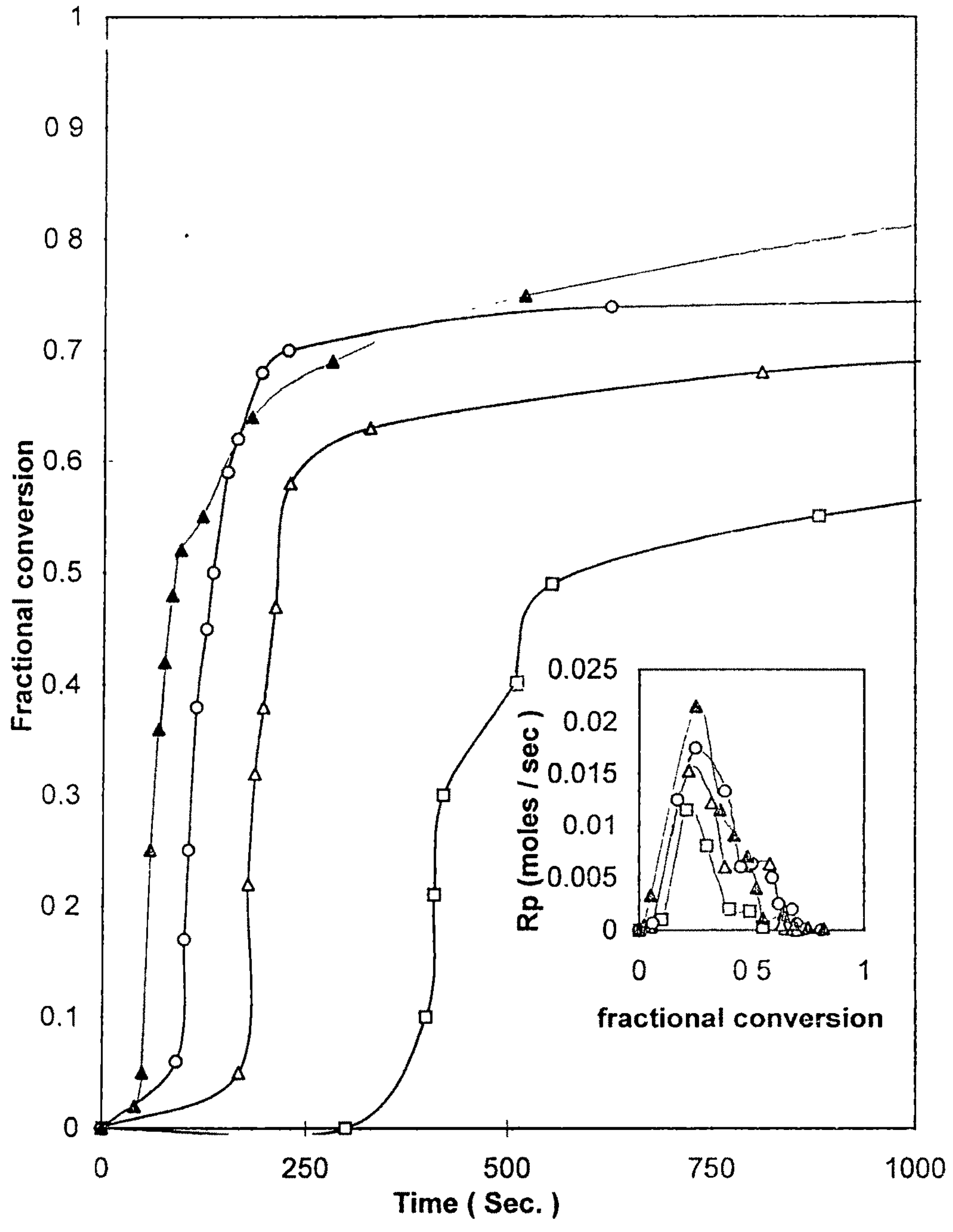

Fig 3. 2 : Effect of KPS concentration on % conversion and rate of polymerization at M / S = 1 and temperature 70 ^{0}C.

(□) 0.18 mM , (Δ) 0. 36 mM , (O) 0. 55 mM , (▲) 0.73 mM

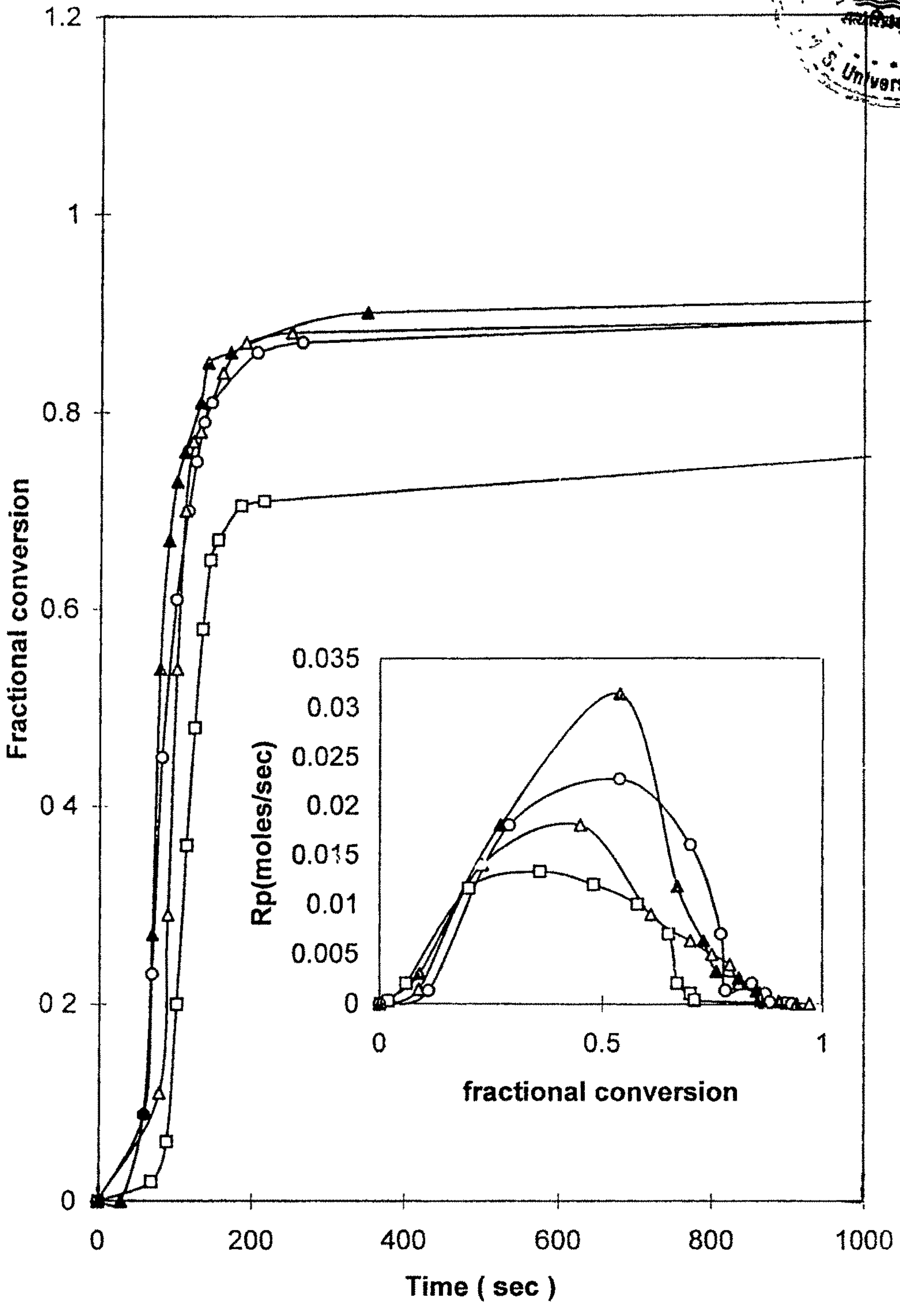

Fig 3. 3 : Effect of KPS concentration on % conversion and rate of polymerization at M / S = 10 and temperature 70 ^{0}C.

(□) 0.18 mM , (Δ) 0. 36 mM , (O) 0. 55 mM , (▲) 0.73 mM

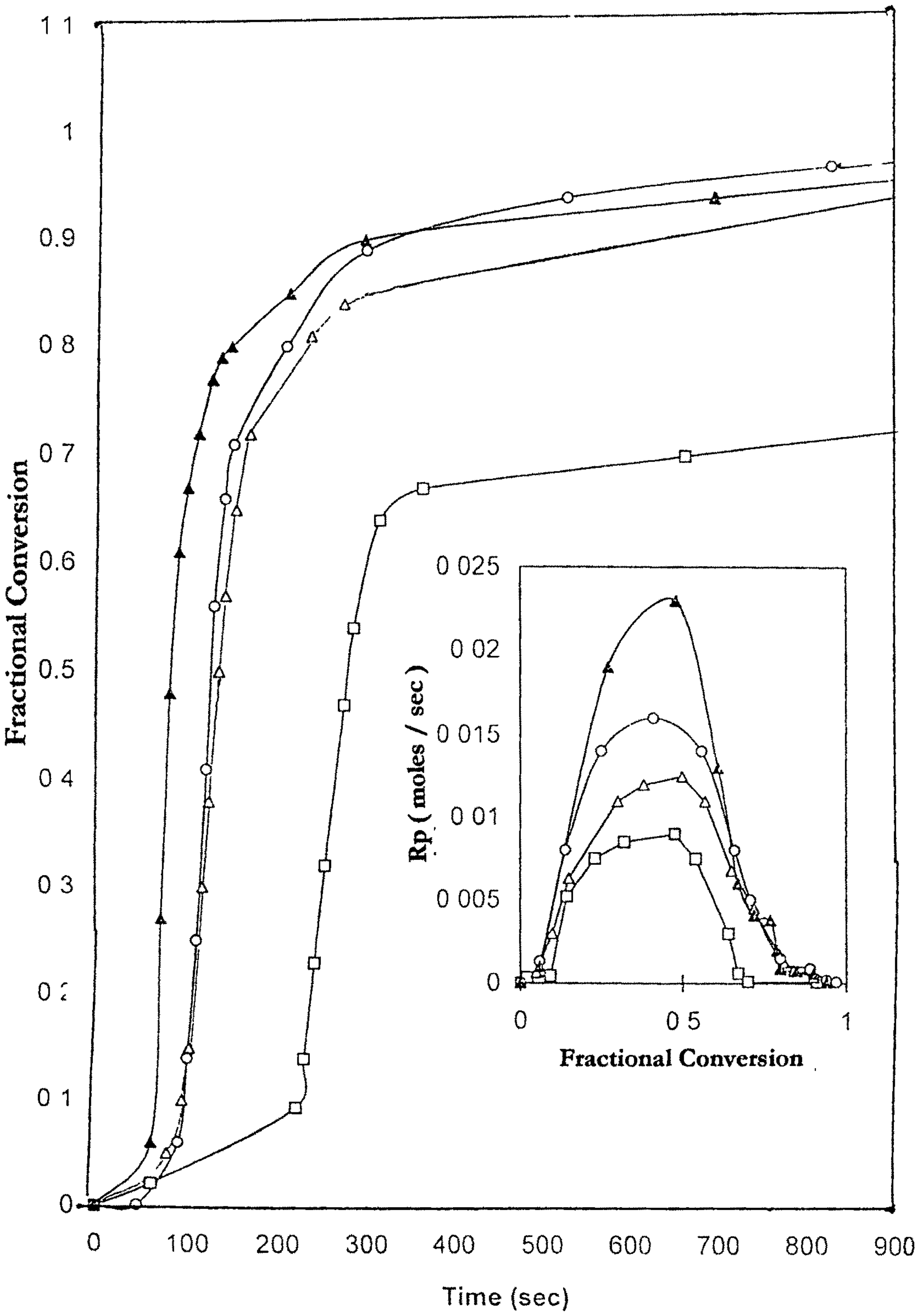

Fig 3. 4 : Effect of KPS concentration on % conversion and rate of polymerization at M / S = 40 and temperature 70 °C.

(□) 0.18 mM , (Δ) 0. 36 mM , (O) 0. 55 mM , (▲) 0.73 mM poly (ethyl acrylate) [13] and high amount of free monomer left in the polymer latex would not favour glassy state approach for limiting conversion. Hence, the limiting conversion at 80 - 85 % can be attributed to the decrease in the pH to 3.8 at the end of the polymerization from initial pH of 7.1. The decrease in pH may be due to the generation of bisulfate ions in addition to the free radicals produced from KPS decomposition. This results in decreased flux of the generated free radicals as the decomposition rate constant k_d has been reported to depend on the pH [14]. Hence there is a possibility of initiator autoinhibition in persulphate initiated polymerization. This effect is reported to be significant at pH below 3 for KPS by Kolthoff and Miller [15]. Though the observed pH of 3.8 for the system under study was higher than pH 3, it is possible that the pH at the interface of the micelles which are the initiating sites, may be different than the measured pH due to enhanced or reduced concentration of hydronium ion at the charged surface [16]. In addition to it, at lower pH the ionic dissociation of SDS is reduced, which might affect the mass transfer of the monomer as well as free radicals across the interface, which happens to be the initiating sites in the present case. This emphasises the importance of pH in the microemulsion polymerisation Infact, Morgan et al. [17] have demonstrated for the microemulsion polymerisation of hexylmethacrylate initiated with KPS, that conversion can reach upto 100% by controlling the pH. The rate of polymerisation (Rp) vs. conversion plots illustrated in Fig 3 . 2 show two intervals. The number of particles [Table 3.2] show a steady increase upto 70% conversion and thereafter remains almost constant.

Table 3.2 : Variation in kinetic and colloidal parameters for polymerization of EA initiated with 0.73 mM KPS at 70 ^{0}C.

Fractional conv.	Rp in (moles/sec)	Np/ cm^3	Rpp, Rate per particle (moles/particle.sec)	Diameter (Dn) in nm	Average Radical per particle $(\bar{n})$
M / S = 1					
0.06	0.006	1.1X10^{14}	5.45 X10^{-18}	36	0.320
0.39	0.0175	6.6X10^{14}	2.6X10^{-17}	37	1.570
0.70	0.0006	1.1X10^{15}	5.04X10^{-19}	37	-
0.74	0.00012	1.1X10^{15}	1.01X10^{-19}	38	-
0.82	0.00005	1.2X10^{15}	4.16X10^{-20}	38	-
For M / S = 10					
0.11	0.0015	3.4X10^{14}	4.41 X10^{-18}	38	0.26
0.29	0.018	1.1X10^{15}	1.55X10^{-17}	35	0.92
0.54	0.023	2.1X10^{15}	1.10X10^{-17}	35	0.63
0.84	0.0022	3.3X10^{15}	6.52X10^{-19}	35	-
0.93	0.00025	3.4X10^{15}	7.35X10^{-20}	36	-
0.95	0.00011	3.5X10^{15}	2.85X10^{-20}	36	-
For M / S = 40					
0.17	0.0092	6.8X10^{14}	1.3 X10^{-17}	35	0.80
0.24	0.012	7.5X10^{14}	1.6X10^{-17}	38	0.95
0.40	0.015	9.3X10^{14}	1.61X10^{-17}	42	0.96
0.72	0.0052	1.0X10^{15}	5.2X10^{-18}	49	-
0.97	0.0001	1.2X10^{15}	7.8X10^{-20}	51	-

This shows an exsistance of continuous nucleation process. The maximum rate (Rp max) was observed to be in the range of 20 - 25 % conversion. Thereafter, decrease in the monomer concentration in the particle causes a decrease in the polymerization rate. However, a small shoulder appearing around 40 - 60 % conversion in Rp vs. conversion plots [Fig 3.2] can be attributed to gel effect caused by an increase in the microviscosity. Increase in microviscosity around 40 -60 % conversion can be attributed to the solubility of the polymer in the monomer, high kp~ 1680 $dm^3 mol^{-1} sec^{-1}$ [18] and high monomer concentration at the micellar core [19] which explains the observed gel effect. Capek et al. [19] have also reported increase in microviscosity around 40% conversion for the microemulsion polymerisation of ethylacrylate. This results into an increase in the propagation rate due to decrease in the rate of termination. Termination being diffusion-controlled, process is affected by the increase in local viscosity making termination process relatively slower to propagation. Once the monomer in the immediate vicinity is exhausted, the rate finally decreases due to the non-availability of monomer. With AIBN the final particle size was only marginally smaller than KPS initiated system at 70 ^{0}C and M / S ratio one and is given in Table 3.3.

Table 3.3 : Effect of initiator type and concentration on particle size of a microemulsion system at 70 ^{0}C.

Initiator	Concentration in mM	Particle Size [Dn nm]
KPS	0 18	46
AIBN	0.18	42
KPS	0.36	39
AIBN	0.36	35
KPS	0 73	35
AIBN	0.73	32

In the system with **M / S ratio 10,** batch polymerisation of ethyl acrylate in two phase region , [**point B** of phase diagram] was carried out as described earlier for microemulsion with M / S ratio one. The conversion vs. time plots are shown in [Fig 3.3]. These emulsions turned into translucent nanosize latexes (36 - 44 nm), when potassium persulphate was used but such transition was not observed with AIBN at the same monomer / surfactant ratio and temperature. AIBN initiated system containing similar concentration of initiator showed separation of two phases at ~ 50 % conversion. This can be explained by considering the fact that the small proportion of the initiator dissolved in the water is reported to be significantly influencing the initiation of the emulsion polymerisation [20]. In addition, the smaller decomposition rate constant (k_d) of AIBN [21] at 70 ^{0}C [1.27×10^{-4}] compared to KPS at 70 ^{0}C [5.01×10^{-2}] [13] leads to the smaller fraction of active radicals initiating polymerization and resulting in the generation of lesser number of polymerization sites. Diffusion of monomer from monomer droplets and uninitiated micelles results in particle growth. Also the rate of coagulation is expected to be higher compared to KPS initiated system due to the absence of surface charge on the initiator head group. The combination of these facts renders the available surfactant insufficient, resulting into phase separation.

The Rp vs. conversion plots [Fig 3. 3] show that particle nucleation stage is prolonged upto 55 % conversion and also shows the absence of constant rate region as in conventional emulsion polymerisation. A similar observation was reported by Gan et al. [22], where they have discussed the effect of surfactant concentration on the emulsion and microemulsion polymerization of MMA and styrene. A possibility of miniemulsion polymerisation mechanism in the present system can be ruled out as it requires vigrous stirring [23] whereas, we have observed even the conversion of unstirred system containing ethylacrylate into transparent / translucent latex after polymerisation.

The solubility of ethyl acrylate in water is reported to be about 2.5 % [24] hence, when water soluble initiator KPS is employed, the sulphate radicals propagate with the monomer dissolved in aqueous phase to produce oligomeric radicals that are relatively soluble in water [25]. These oligomeric radicals during propagation in the aqueous phase, may also undergo termination with another radical. Formation of such species due to aqueous phase termination in the case of KPS has been confirmed by isotachophoresis by Morrison et al. [26]. Subsequent aqueous phase propagation of oligomers , which escape termination enables them to attain a degree of polymerisation at which the species is now surface active [25] This degree of polymerisation is reported to be about 3 for styrene and 4 - 5 for MMA [27]. As far as our knowledge, for ethylacrylate this value is not reported. If these oligomeric species grow further, they precipitate in aqueous phase (homogenous nucleation). Once the critical chain length for surface activity is attained the oligomeric radical attains sufficient hydrophobicity to enter the monomer swollen micelles. This results in the generation of newer active sites along with the active sites created via homogenous nucleation. Simultaneous diffusion of monomer to these active particles leads to the disappearance of monomer as a separate phase at an early conversion, turning the system translucent / transparent. This corresponds to the rate maxima (Rp max) in these relatively low monomer content emulsion systems. Thereafter the rate falls due to the decrease in the monomer concentration at the polymerization loci.

The only difference between microemulsion [M / S = 1] and emulsion [M / S = 10] system lies in the level of subdivision of the monomer droplets. M / S = 1 system has larger subdivision of the monomer droplets due to higher surfactant concentration and therefore expected to have larger number of potential initiating sites. It is reported that decrease in droplet size increases their probability of getting nucleated [2 8]. Therefore, under identical reaction conditions microemulsion system is expected to produce higher number of particles with smaller particle size compared to emulsion system. Whereas experimental results show a reverse trend. The Np obtained for M / S = 10 was higher than M / S = 1[Table 3.2]. Also the R_p max was found to shift to higher % conversion for M / S =10 , which can be explained on the basis of particle generation through homogeneous nucleation in addition to micellar nucleation. The evidence for homogeneous nucleation becomes more clear in the study of copolymerisation. In contrast, microemulsion polymerisation initiated with KPS, results into lower fraction of effective radicals initiating polymerisation due to insitu decrease in pH [disscussed earlier]. This results in some particle growth in microemulsion polymeristion. The final particle size then depends on the amount of monomer. The difference becomes more apparent in the study of copolymerisation kinetics due to higher monomer content.

Microemulsion showed an monomodal particle size distribution , whereas emulsion system showed a bimodal nature [Fig 3. 5 and 3. 6]. The nature of rate curves and particle size show similarities with microemulsion polymerisation. However, the underlying mechanism is quiet different for microemulsion polymerisation. A similar observation has been reported by Pokhriyal and Devi for the microemulsion copolymerisation of 2 - ethylhexylacrylate / acrylonitrile system [29]. Particle stability in these systems is provided by the products of aqueous phase termination events

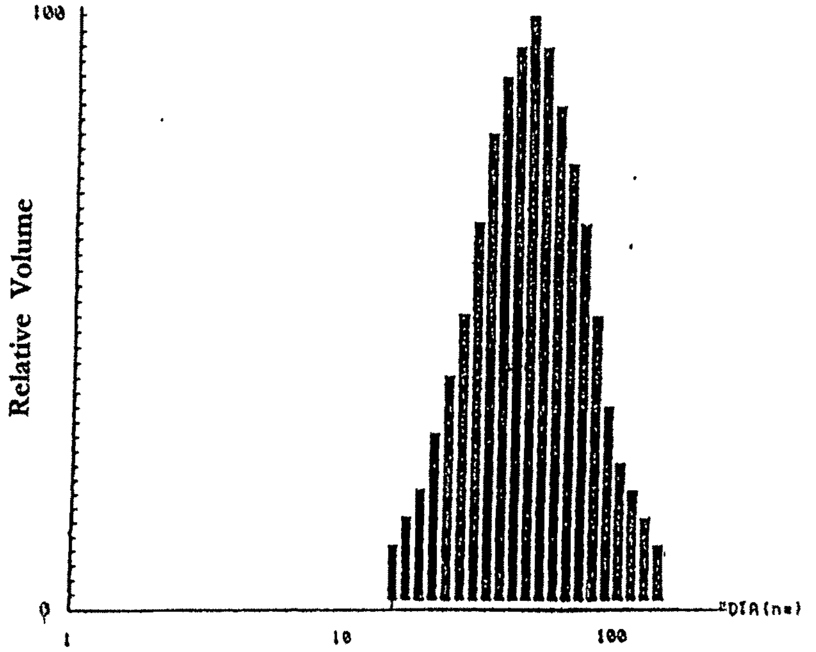

Fig 3. 5 : Particle size distribution at M / S = 1 at 85 % conversion.

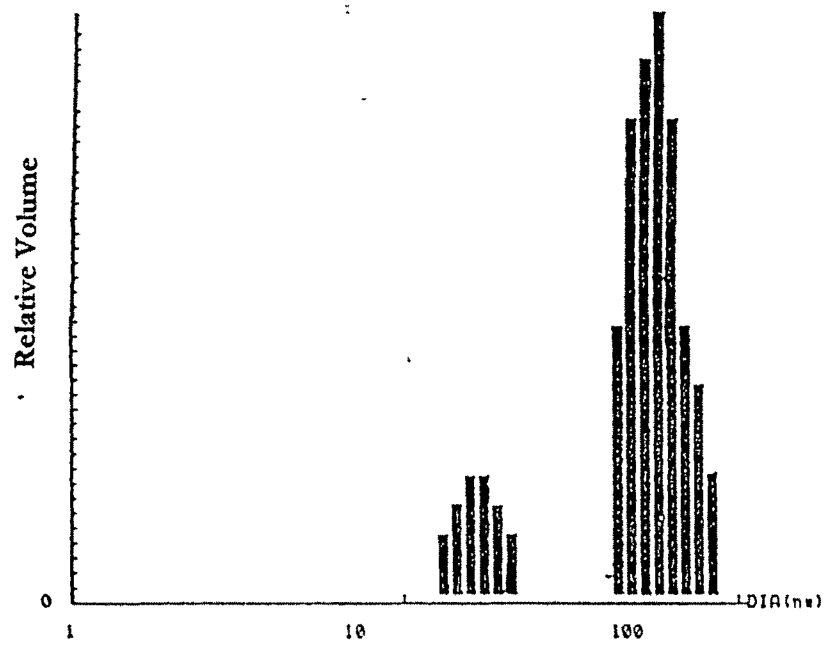

Fig 3 . 6 : Particle size distribution at M / S = 10 at 95 % conversion.

and the available surfactant molecules. For a given surface area, polar polymer like poly - (ethyl acrylate) requires lesser amount of emulsifier compared to a hydrophobic polymer like polystyrene [24]. Therefore a greater number of particles can be stabilised with the same amount of surfactant.

Polymerisation of ethyl acrylate in two phase region at **point C** of the phase diagram with **M / S ratio 40** was carried out as described earlier. The two phase system was turbid before polymerisation and turned translucent after polymerisation. The conversion vs. time plots are shown in Fig 3. 3. The Rp vs. % conversion plots [Fig 3.4] show a slow increase in rate rather than a constant rate period observed in classical emulsion polymerisation. At M/S = 40 the concentration of the surfactant is just above CMC. This leads to relatively smaller number of micelles compared to M / S = 10. Hence rate of nucleation in this system will be slower than in the system M / S = 10. Also the rate of particle growth will be higher than the rate of nucleation. This results into smaller number of particles of larger size. On the other hand for M / S = 10 a higher concentration of surfactant generates more number of micelles which are initiated and converted into particles. The rate of nucleation was observed to be higher than the rate of particle growth. This results into larger number of particles with relatively smaller particle size. When the monomer / surfactant ratio was increased to 54, a slow increase in rate was observed in the range of 15 - 62 % conversion as illustrated in Fig 3. 7. The very slow increase in rate after the disappearence of micelles indicates the simultaneous operation of another nucleation mechanism.

[3 . 2 . 2] Effect of initiator concentration

Increase in the initiator concentration increases the free radical flux, as a result the fraction of micelles that capture the free radicals to become active particles

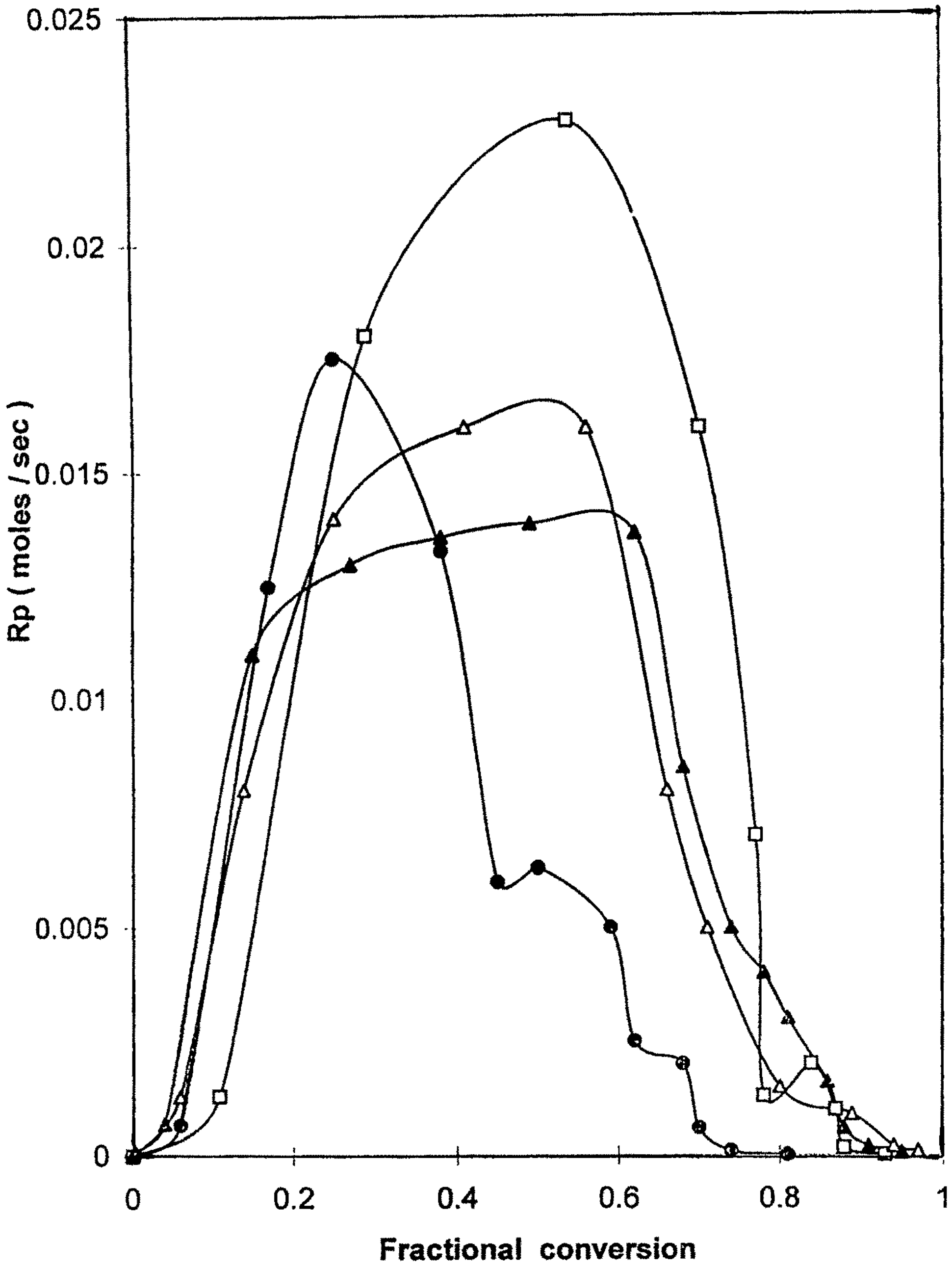

Fig 3.7 : Effect of Monomer / Surfactant ratio on the rate of polymerisation at KPS concentration 0.55 mM and temperature 70 ^{0}C.

(▲) M / S = 54, (△) M / S = 40, (□) M / S = 10, (●) M / S = 1 increases leading to increased rate of polymerization and decreased particle size Table3. 4.

Table 3.4 : Effect of initiator concentration on particle size for emulsion and microemulsion polymerisation of EA at 70 ° C.

	0.18 mM KPS		0.36 mM KPS		0.55 mM KPS	
System	Dn nm	Rpmax moles / sec	Dn nm	Rp max moles / sec	Dn nm	Rp max moles/ sec
M / S = 1	46	0.011	39	0.015	38	0.018
M / S = 10	45	0.013	40	0.018	36	0.022
M / S = 40	57	0.0075	54	0.011	52	0.016

The dependency of R_p and N_p on initiator concentration was found to be **0.5th** and **0.47th** for M / S = 1, **0.75th** and **0.77th** for M / S = 10, and **0.82th** and **0.77th** for M / S = 40. The above values indicate that both polymerisation rate and number of particles formed show practically the same initiator dependency within experimental error. This indicates that the polymerisation rate was directly proportional to the number of latex particles generated. However, systems with M / S = 10 and 40 show a greater dependency of R_p on KPS concentration in comparison to the systems with M / S = 1. This greater dependency on initiator concentration becomes obvious if we assume the aqueous phase growth of primary free radicals to a certain chain length as the rate determining step. Once the critical chain length is attained, the surface active oligomers can contribute to particle nucleation through the entry into micelle, or by forming micelles by aggregating with the surfactant molecules or else precipitating as primary particle in aqueous phase (homogenous nucleation)[25]. All the above mentioned processes will make the rate more sensitive to initiator concentration for M / S = 10 and 40 in comparison with M / S = 1. In the case of microemulsion polymerisation (M/ S = 1) a fast radical capture by monomer droplets is expected because of larger surface area of the microemulsion droplets. This implies less degree of homogenous nucleation and can explain less dependency on initiator concentration. One also observes that the constant rate period characteristic of emulsion polymerization becomes less prominent, especially for the higher initiator concentration in the case of system with M/ S = 40. At higher initiator concentration the monomer diffuses to a greater number of polymerization sites with the early disappearance of monomer as a separate phase in these low monomer content emulsion systems. At lower initiator concentration the same amount of monomer diffuses to lesser number of polymerization sites. Hence the fraction of larger monomer droplets remains higher, which contributes to particle growth and is characterized by a slower increase in rate of polymerisation [Fig 3.4]. Also the rate maxima shifts towards higher % conversion with the increase in initiator concentration especially for M / S = 10. Since the conversion of micelles into polymer particle is achieved at an early conversion, the observed extended nucleation thus can be attributed to the polymerisation in the additional sites created by homogeneous nucleation, the extent of which, then depends on the initiator concentration for a given monomer concentration. Such a shift has not been observed for system with M / S = 1.

Probable Termination Events : The average number of radicals per particle ($\bar{n}$) were calculated using the following equation and experimentally determined rate of polymerisation (Rp) and number of particles (Np) determined from the dynamic light scattering data given in Table 3.2..

$$R_p = k_p [M]_{eq} \bar{n} N_p / N_A$$

where kp is the propagation rate constant for ethylacrylate and has been reported to be 1680 $dm^3 mol^{-1} sec^{-1}$ [20] , $[M]_{eq}$ is the equilibrium monomer concentration taken as 6 mole / dm^3 as reported by Capek et al. [30] for ethylacrylate. Since this concentration of 6 mole / dm^3 in the particle cannot be maintained during microemulsion polymerisation, $\bar{n}$ was calculated only at lower conversions below 40%. While for emulsion polymerisation, monomer diffusion can maintain the equilibrium monomer concentration at relatively higher conversion [20]. Therefore n values upto 60% conversion have been calculated for M/S 10 and 40. N_A is the Avagadro number. The results in Table 3.2 indicate that $\bar{n}$ assumes the highest value near the rate maxima (Rp max) and then it decrease with conversion. Near the rate maxima, n is close to 1 for M / S ratio 1, indicating that each particle has at least one radical. In the case of microemulsion system (M / S ratio 1) , $N_{micelles} >> N_{particles}$, hence the rate of entry of a second radical into a particle is low and therefore the particle undergoes chain transfer reaction to the monomer before a second radical enters. Termination is largely unimolecular for M / S= 1 system. However, in the systems with M / S = 10 and 40 the flocculation of the primary particles formed by homogeneous nucleation, prior to equilibrium adsorption by emulsifier results in some interparticle termination. This leads to a low value of n. Similar observations are reported earlier in the emulsion polymerisation of ethylacrylate [24]. In none of the systems the value of n exceeds two indicating that the possibility of bimolecular termination within the same particle is less. In addition, the smaller particle size and partial water solubility of the monomer can facilitate faster radical exit. Subsequently, bimolecular termination of the desorbed radical can take place either in aqueous phase or by re-entry into another growing radical. Nevertheless, this does not completely exclude the possibility of bimolecular termination within the particle; especially at higher conversion, since $\bar{n}$ is a time average value for $\bar{n}$. For microemulsion system (M / S = 1), each latex particle was observed to consist of only single chain which is calculated from the weight of polymer in each milliliter of microemulsion / emulsion as reported by Gan et al. [31]. In conformity with this, the viscosity average molecular weight was observed to be of the order of 10^7 and for systems with M / S ratio 10 and 40 the number of chains per particle were observed to be 3 to 4 and the viscosity average molecular weights were of the 10^6 order High molecular weights observed for the emulsion polymerisation , have been explained by Lovell et al. [32] on the basis of cross linking due to chain transfer to polymer at the latter stages of emulsion polymerisation of butylacrylate. However, a lesser number of radicals per particle observed in the present system make this possibility less likely to happen.

[3 . 2 . 3] Effect of temperature

Fig 3.8 , 3.9 and 3.10 exhibit the effect of temperature studied at 65 °C , 70 °C and 75 °C respectively for the M / S ratios 1, 10 and 40. As expected the polymerisation rate increases with increasing temperature. From the results of particle size measurement Table 3 .5 it is observed that the particle size decreases and the number of particles increase with increasing temperature.

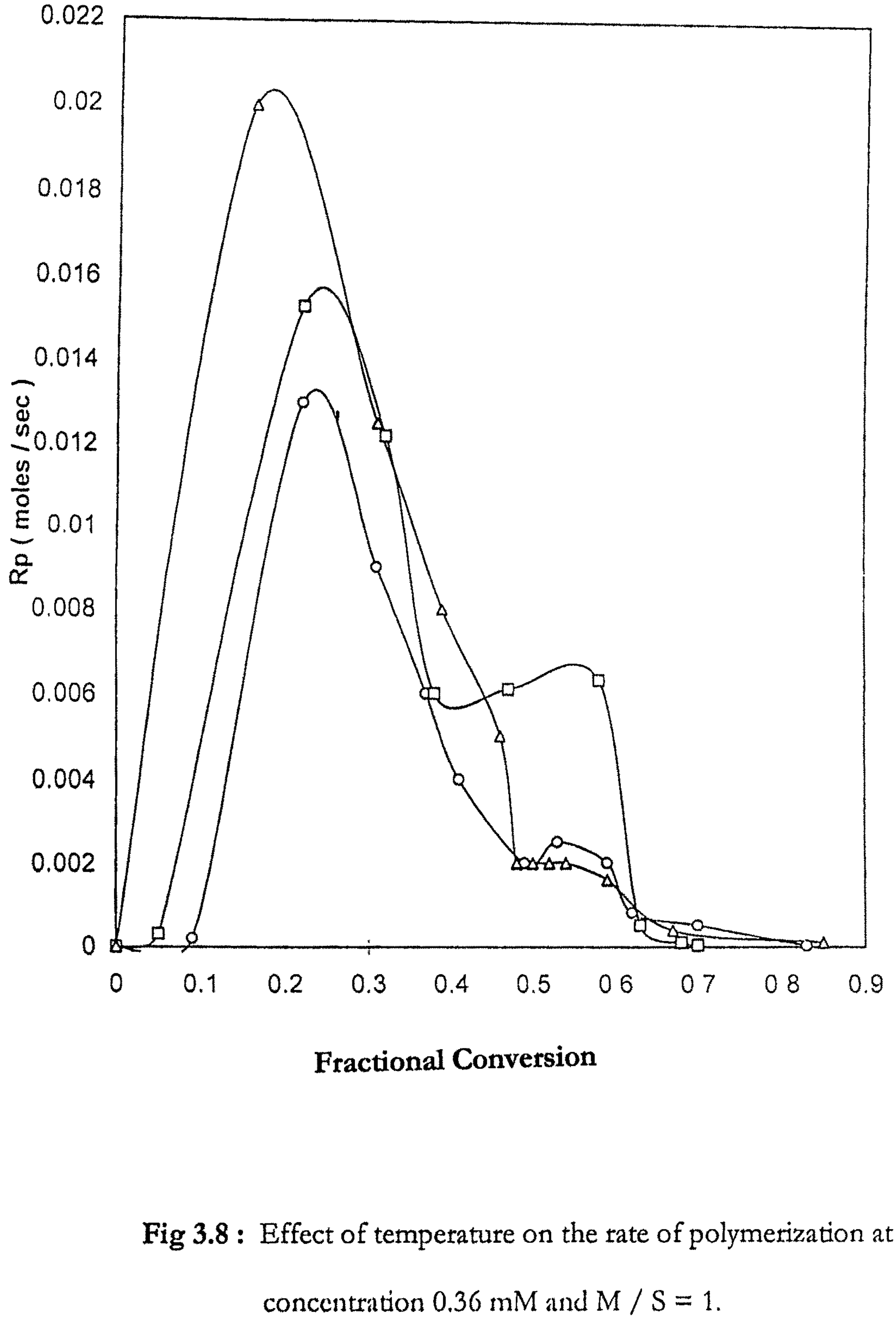

Fig 3.8 : Effect of temperature on the rate of polymerization at KPS concentration 0.36 mM and M / S = 1.

(O) 65 °C , (□) 70 °C , (Δ) 75 °C .

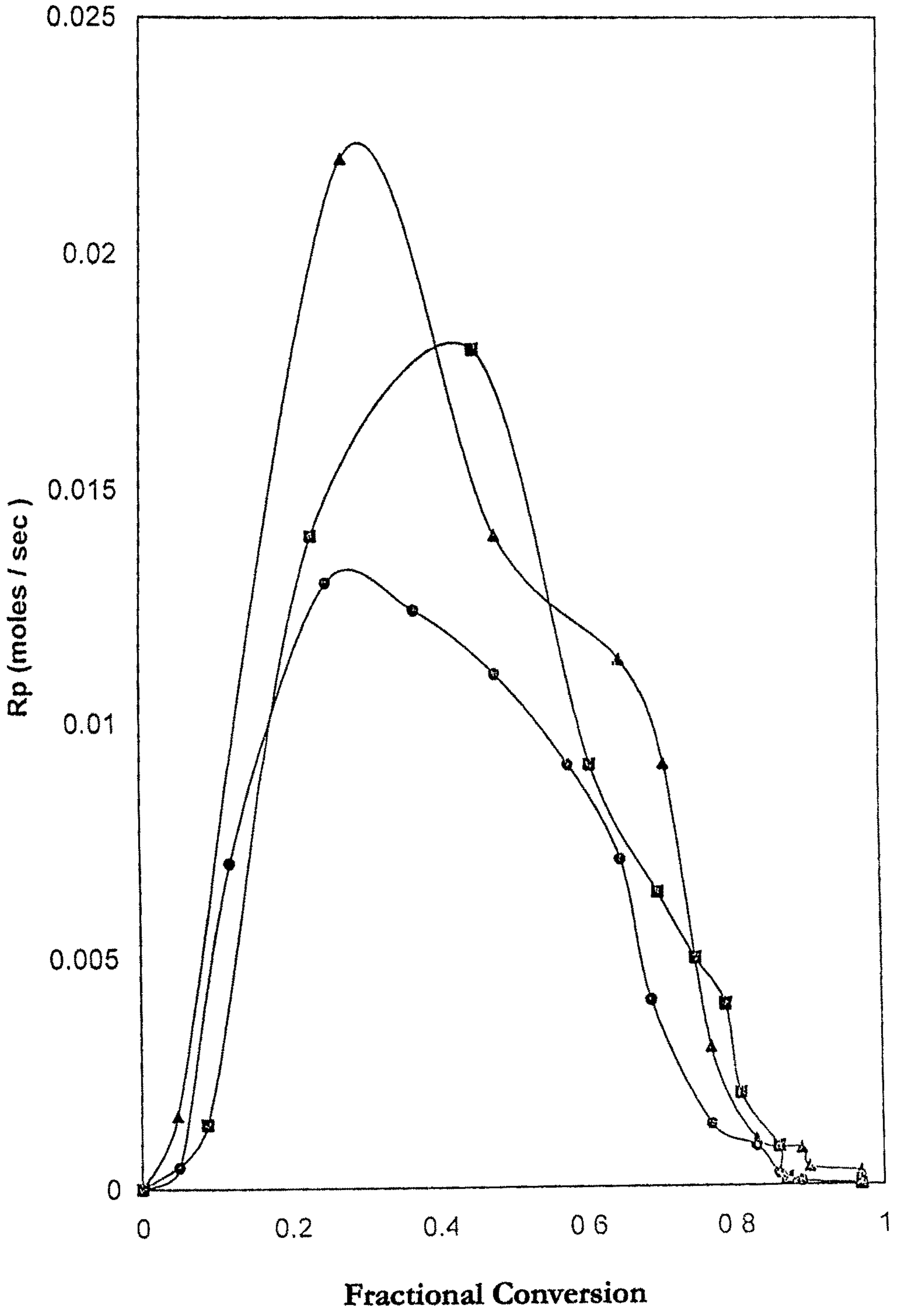

Fig 3. 9: Effect of temperature on the rate of polymerisation

KPS concentration 0. 36 mM and M/S = 10.

(●) 65° C, (■) 70° C, (▲) 75° C.

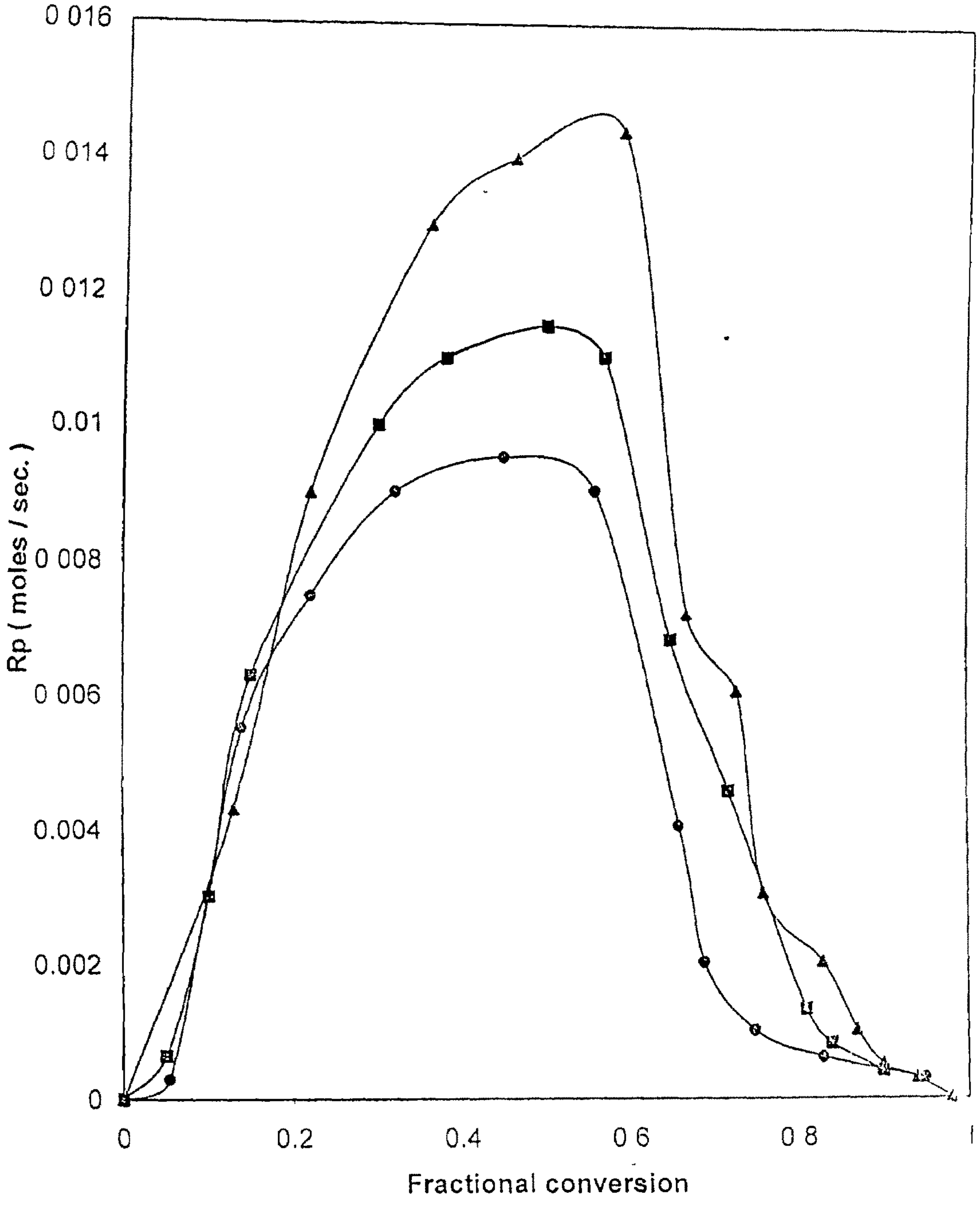

Fig 3.10 : Effect of temperature on the rate of polymerisation

KPS concentration 0. 36 mM M/S = 40.

(●) 65° C, (■) 70° C, (▲) 75° C.

TABLE 3.5: Effect of temperature on particle size for emulsion and microemulsion polymerization of EA at fixed initiator concentration of 0.36 mM KPS.

Temp ^{0}C	M / S = 1		M / S = 10		M / S = 40	
	Diameter Dn (nm)	Np /cm^3	Diameter Dn (nm)	Np / cm^3	Diameter Dn(nm)	Np/ cm^3
65	43	9.5x10^{14}	43	1 95x10 ^{15}	63	6.6 x 10 ^{14}
70	39	1.0x10 ^{15}	40	2.6 x 10 ^{15}	52	1 1 x 10 ^{15}
75	33	2.0x10 ^{15}	37	3.2x 10 ^{15}	49	1.4 x 10 ^{15}

Nevertheless, the shape of particle size distribution plot remains unchanged [3.11].

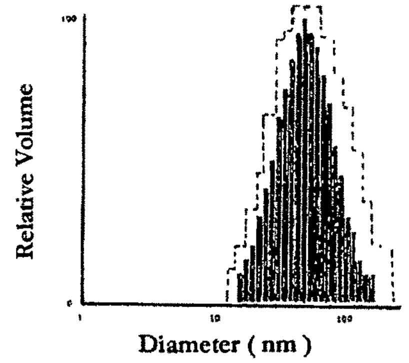

Fig 3.11: Effect of temperature on particle size distribution at [M / S = 1].
Dotted background is at 65 ^{0}C , Dark background is at 75 ^{0}C.

The overall activation energies calculated from the Arrhenius equation for the systems with M / S ratios 1 , 10 and 40 were 28.7 kJ / mole , 27 kJ /mole and 14.3 kJ /mole respectively. Both M / S = 1 and 10 showed similar energies of activation.

[3. 3] Characterization

[3.3.1] IR analysis

The copolymers precipitated from the latex were found to be soluble in chloroform and acetone. IR spectra of the solution casted film of Poly-(EA) exhibited a strong band at 1720 cm^{-1} for $>$C=O stretching and at 2870 cm^{-1} and 2928 cm^{-1} for $\geq$ CH stretching confirming polymerisation.

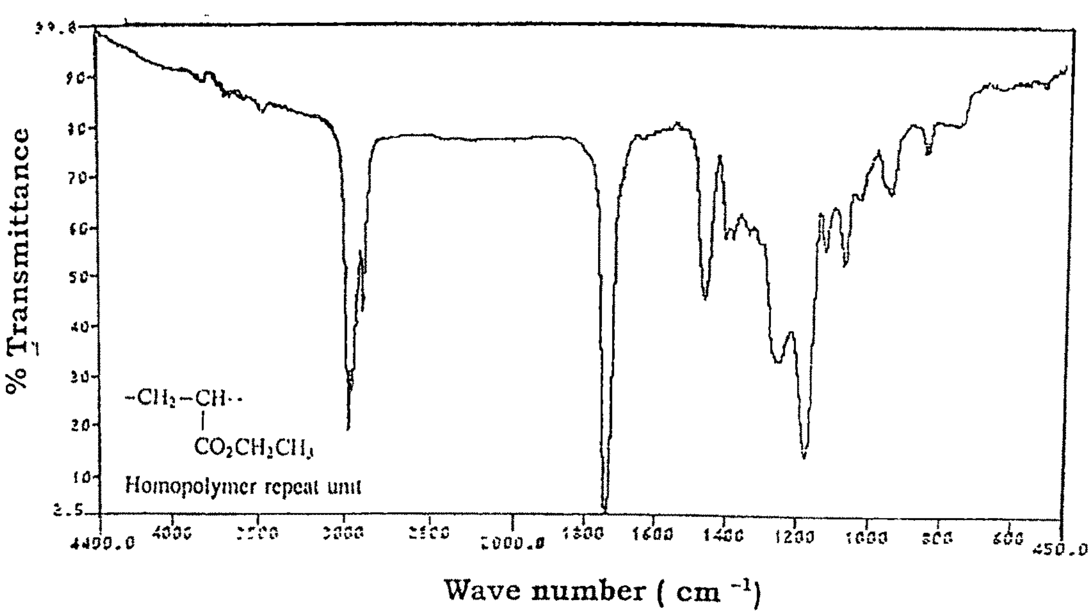

Fig 3 . 11 ' : IR spectra of poly-(ethyl acrylate).

[3 . 3. 2] Particle size analysis

Particle size of the resulting microemulsion and emulsion latexes was found to be in the range of 30 – 115 nm. The particle size obtained in the present study are discussed at the relevant places in the text [Section 3 . 2. 1 – 3 . 2 . 3].

[3 . 3 . 3] Molecular weight by viscometry

Viscosity average molecular weight of Poly - (EA) synthesized through microemulsion was in the order of (10^7) with number of polymer chains per particle close to unity. Whereas polymers synthesized through emulsion polymerisation resulted into slightly lower molecular weight ($\sim10^5$) and number of polymer chain per particle ranged between 3 and 4.

CHAPTER 3

Part B

Kinetics of Copolymerisation

Contents

PART B : EA – MMA / SDS / WATER SYSTEM

[3 . 4] Introduction

Earlier work on kinetics of ethylacrylate indicated higher rate of particle nucleation for emulsion system compared to microemulsion due to the contribution of both homogeneous and micellar nucleation to the overall process of particle formation and also stabilisaton of the newly formed particles by the available surfactant. In order to confirm this hypothesis copolymerisation of partially water soluble monomers ethylacrylate [EA] – methylmethacrylate [MMA] was studied since it will allow a more quantitative interpretation of the results in terms of its properties and composition. Microemulsion polymerisation of EA – MMA system was used for comparison. The emulsion copolymerisation of EA – MMA has been reported by Capek et al., [33] where initiation was reported to take place both in the aqueous phase and micelles.

Phase Diagram

In order to determine the one phase micromicroemulsion region the phase diagram was constructed at 30 ^{0} [room temperature] and 70 ^{0} C [polymerization temperature] The three component phase diagram included EA – MMA [1 : 1] / SDS / water and is illustrated in Fig 3.12. The dotted region represents ill-defined phase boundary between turbid emulsions and transparent microemulsions. The samples within one phase region were transparent and fluid except at high SDS concentrations where they were transparent gels , which may be due to the transition of spherical to rod like micelles. On increasing the temperature the one phase region extended due to increase in solubility of monomer in water. The composition selected for microemulsion polymerization has been represented by point A [M / S = 0.66] while B , C refer to the

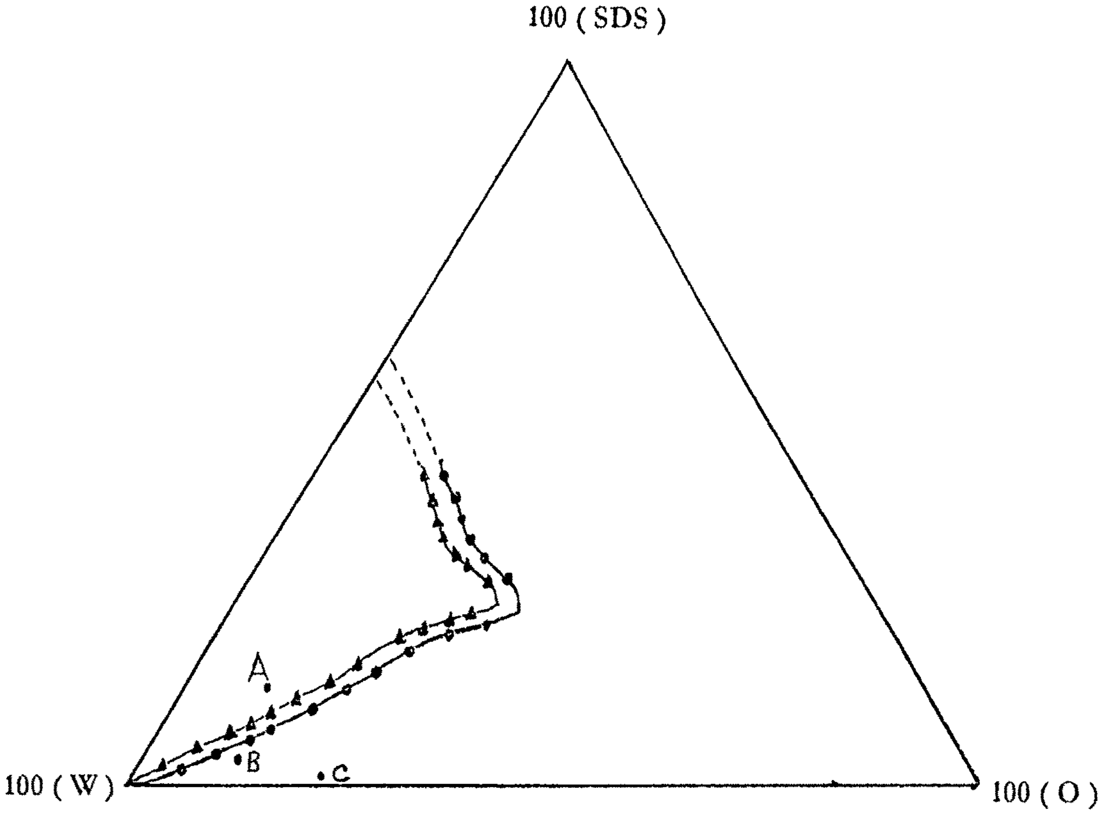

Fig 3.12 : Phase diagram of EA [0.5] – MMA [0.5] / SDS / Water system.

(▲) at 34 ^{0}C and (●) at 70 ^{0}C compositions selected for emulsion polymerization at M / S = 10 and 50 to produce stable translucent nanolatexes. Compositions used for the microemulsion and emulsion polymerisation are given in Table 3.6.

Table 3.6 : Composition selected for the copolymerisation of EA – MMA in emulsion and microemulsion.

System	Monomer Wt % EA (0.5) – MMA (0 5)	SDS Wt %	Water Wt %	System Appearence	
				BP	AP
M [M / S= 0.66]	10	15	75	Clear	Turbid
E [M / S = 10]	10	1	89	Turbid	TP/TS
E [M / S = 50]	25	0 5	74.5	Turbid	TS

BP = Before Polymerisation, AP = After Polymerisation, TP = Transparent, TS = Translucent, E = Emulsion, M = Microemulsion, M / S = Monomer / Surfactant

[3.5] Kinetics of Copolymerisation

An initially turbid emulsion system turned translucent after polymerisation to generate a stable nanolatex. Whereas an initially clear microemulsion turned turbid after polymerisation. This observation warrants understanding of the basic mechanistic difference between emulsion and microemulsion polymerisation. Also the results involving oil soluble initiator AIBN and water soluble initiator KPS are quiet contradicting for these two systems. In order to understand the mechanistic aspects complete conversion at an optimal rate of polymerisation is desirable. Hence the kinetics was studied by varying the initiator concentration for both KPS and AIBN. The reaction parameters such as type and concentration of initiator, monomer feed concentration and reaction time were optimized with respect to percentage conversion and particle size of latex.

[3.5.1] Effect of initiator type, concentration and its relation to particle nucleation in microemulsion and emulsion.

In systems represented as 'M' the transparent microemulsions became increasingly turbid as the reaction proceeds due to particle growth and increased difference between refractive index between the polymer particles and the suspending medium. Increasing initiator concentration yields faster polymerisation rates and higher conversions regardless of the type of initiator employed. The increasing polymerisation rate is a consequence of increasing flux of the free radicals, which increases the probability of radical capture by droplets [heterogeneous nucleation] or by monomer in the aqueous phase to induce formation of oligomers [homogeneous nucleation] to produce active particles. The dependency of KPS in microemulsion and emulsion was observed to be 0.5 and 0.86 respectively. The higher dependency for emulsion system [compared to microemulsion] can be explained on the basis of a greater sensitivity of polymerization rate on KPS concentration. The greater sensitivity is an artifact of higher rate of particle nucleation for emulsion system than in microemulsion.

The kinetic study for the microemulsion system was carried out with 10 % of the monomer and 15 % surfactant. The conversion vs time plots for both KPS and AIBN initiated systems showed the presence of gel effect between 60 – 70 % conversion [Fig 3.13 and 3.14]. The final particle size obtained for KPS initiated system was 130 nm [Fig 3.15] while those initiated with same molar concentration of AIBN at same temperature and M / S ratio resulted into particles with 79 nm [Fig 3.16]. The particle

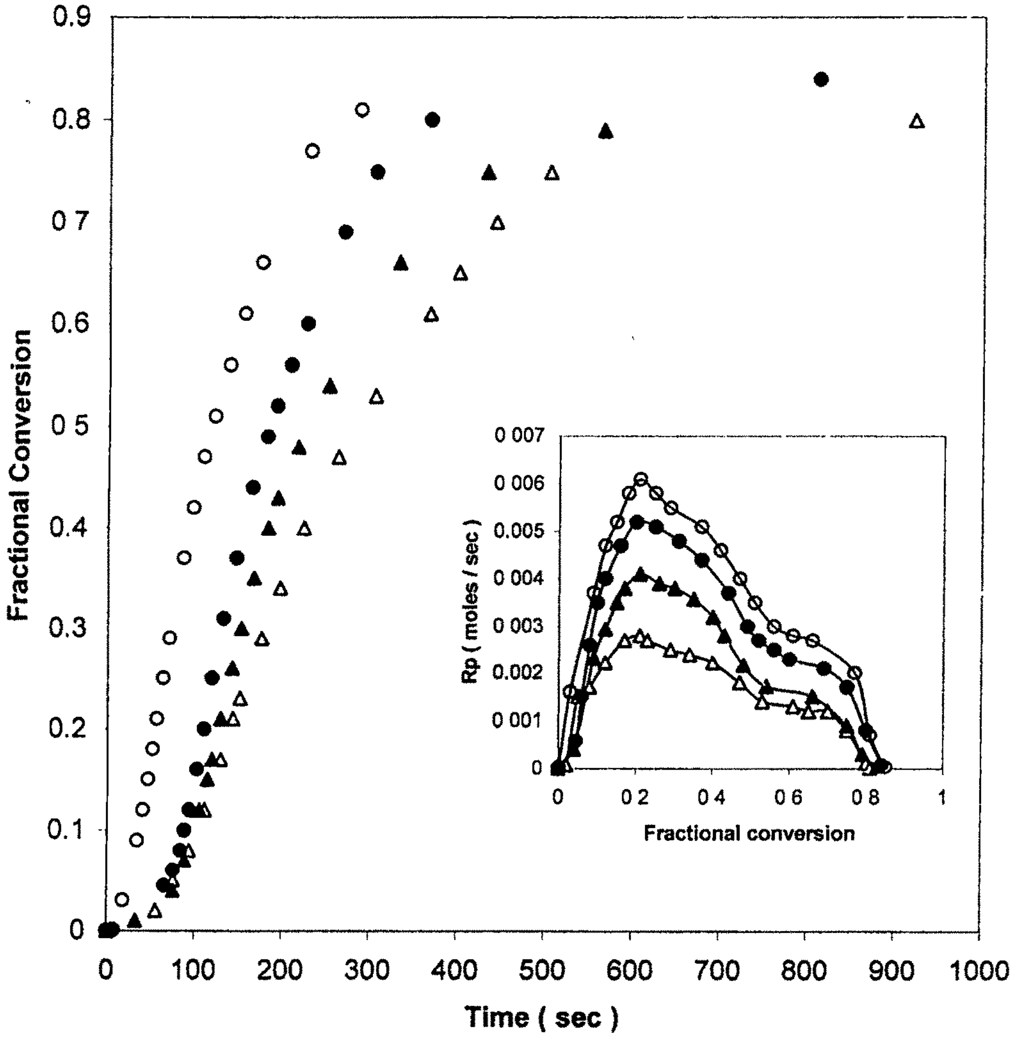

Fig 3. 13 : Effect of KPS concentration on % conversion and rate of polymerization at M /S = 0.66, temperature 70 °C and EA (0.5) – MMA (0.5).

(Δ) 0.18 mM , (▲) 0. 36 mM , (●) 0. 55 mM , (O) 0.73 mM

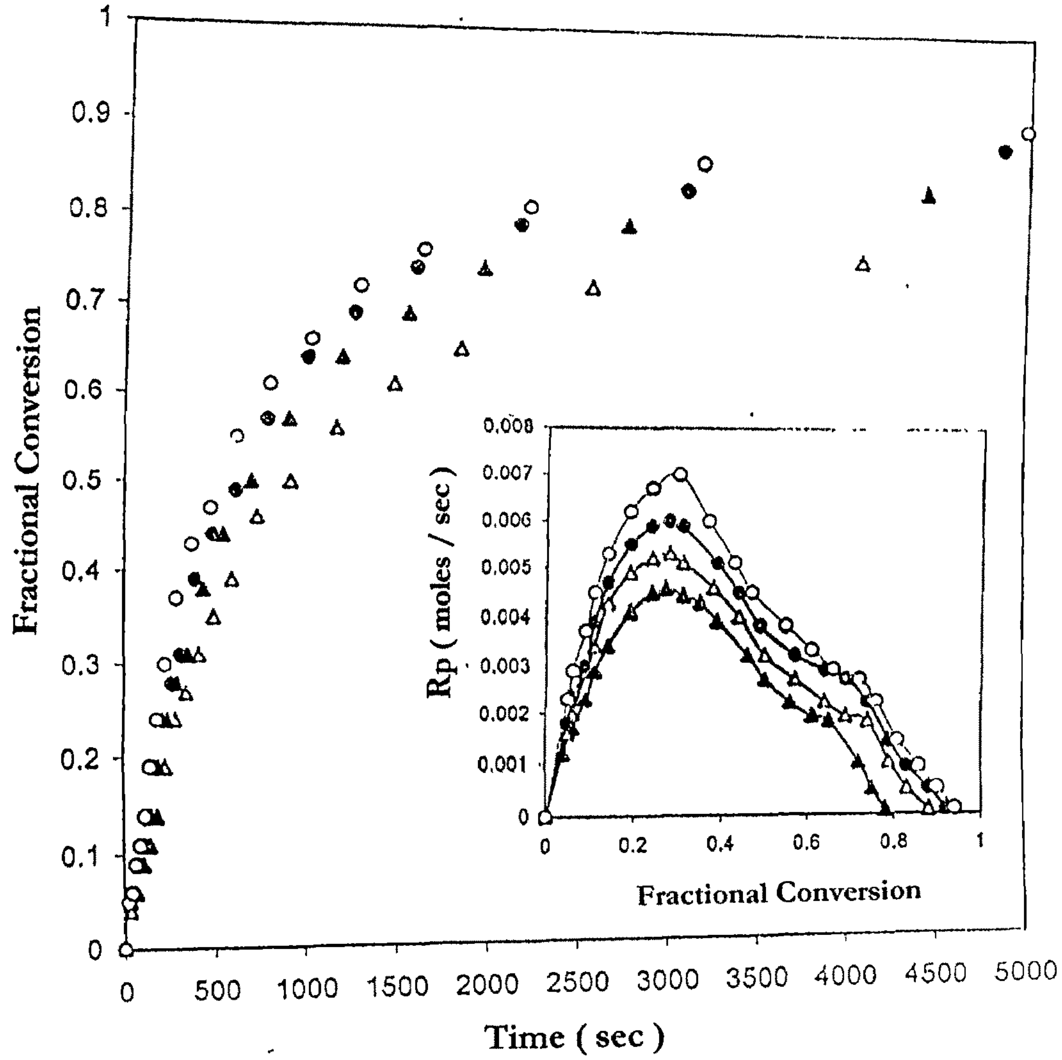

Fig 3. 14 : Effect of AIBN concentration on % conversion and rate of polymerization at M /S = 0.66, temperature 70 ^{0}C and EA (0.5) – MMA (0.5).

(Δ) 0.18 mM , (▲) 0. 36 mM , (●) 0. 55 mM , (O) 0.73 mM

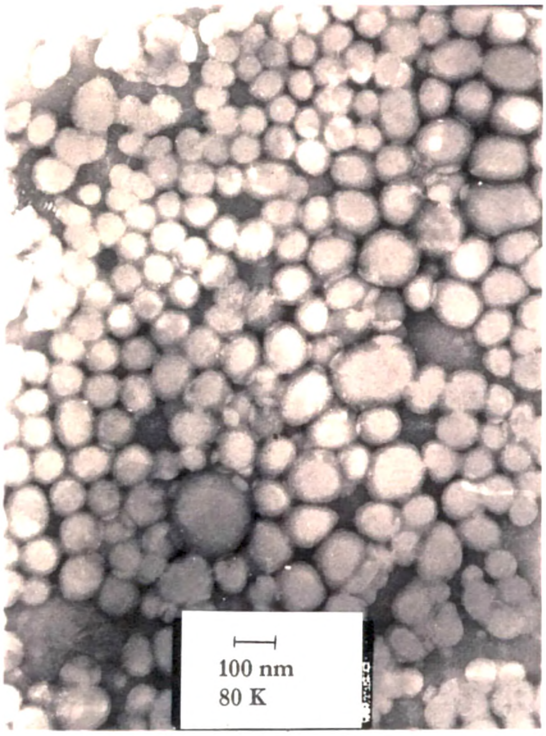

Fig 3.15 : TEM of 85 % conversion sample synthesized through microemulsion polymerisation of EA [0.5] – MMA [0.5] initiated with 0.73 mM KPS at 80 K magnification.

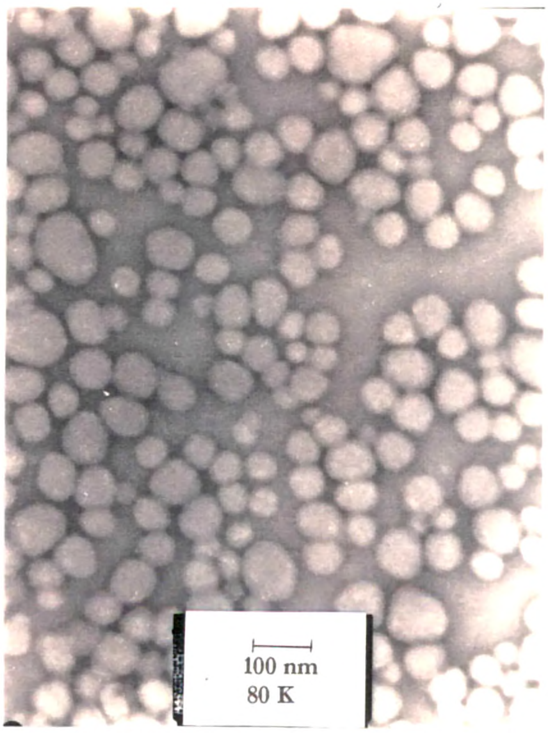

Fig 3.16 : TEM of 95 % conversion sample synthesized through microemulsion polymerisation of EA [0.5] – MMA [0.5] initiated with 0.73 mM AIBN at 80 K magnification.

size distribution showed considerable broadening at higher conversion for KPS initiated system [Fig 3.17 c] while AIBN initiated system resulted into lesser broadening in particle size distribution at higher conversions [Fig 3.18].

KPS initiated emulsion polymerisation of EA – MMA, containing 10 and 25 wt % of monomer with a corresponding M / S ratio 10 and 50, resulted in the production of stable translucent nanolatex with final particle size of 37 nm [Table 3.7] and 64 nm [Fig 3.19] respectively.

Table 3.7 : Kinetic and colloidal parameters for the emulsion copolymerisation of EA – MMA studied at 70 ^{0} C with 0. 73 mM KPS.

Fractional conversion	Rate moles/sec	Dn in nm	Np/cm^3	n	PI
M : S = 10,					
0.18	0.0038	28	1.35X10^{15}	4.66	0.13
0.41	0.0056	33	1.88X10^{15}	4.13	0.11
0.76	0.0025	36	2.7X10^{15}	1.38	0.10
0.89	0.0009	38	2.7X10^{15}	-	0.11
0.95	0.0001	37	3.06X10^{15}	-	0.11
M : S = 50,					
0.05	0.0011	30	7.58X10^{14}	-	0.39
0.17	0.0041	35	1.62X10^{15}	2.79	0.08
0.56	0.0065	46	2.3X10^{15}	3.73	0.08
0.70	0.0049	50	2.3X10^{15}	2.81	0.05
0.86	0.0007	54	2.3X10^{15}	-	0.08
0.92	0.0001	57	2.03X10^{15}	-	0.11
0.97	0.00002	59	1.99X10^{15}	-	0.10

n is average number of radical per particle and **PI** is the polydispersity index.

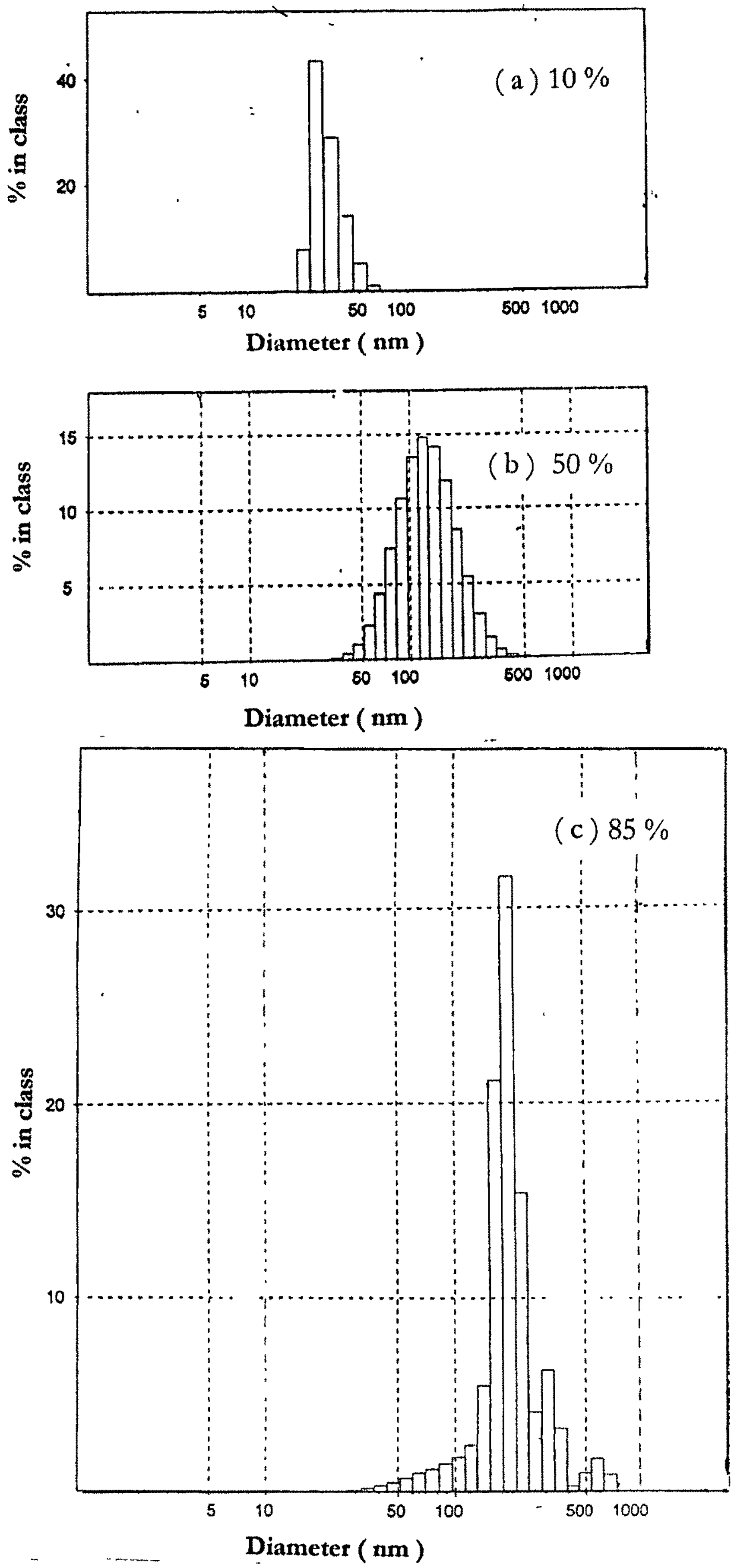

Fig 3.17 : Particle size distribution for KPS initiated system at three different stages of microemulsion polymerization.

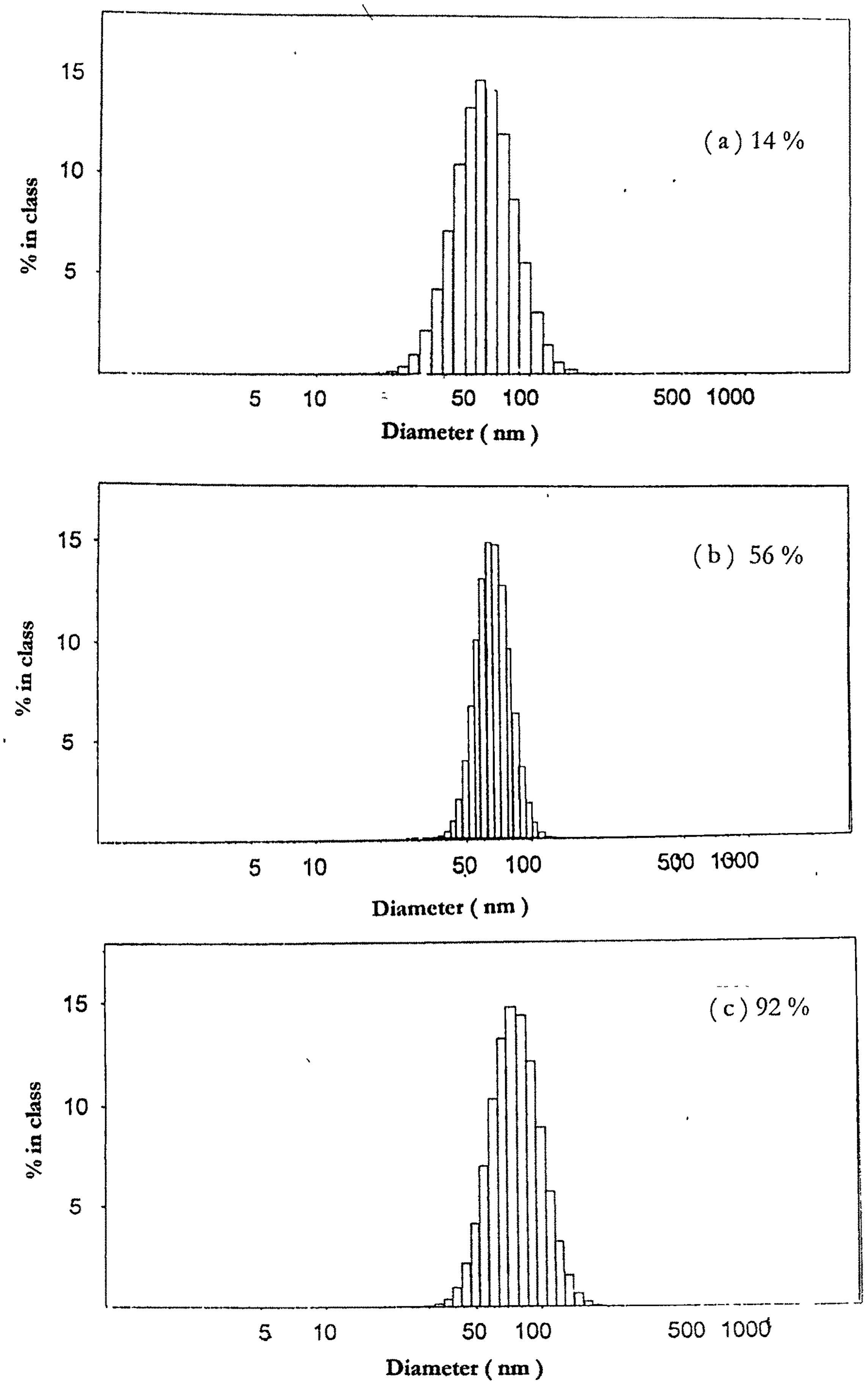

Fig 3.18 : Particle size distribution for AIBN initiated system at three different stages of microemulsion polymerization.

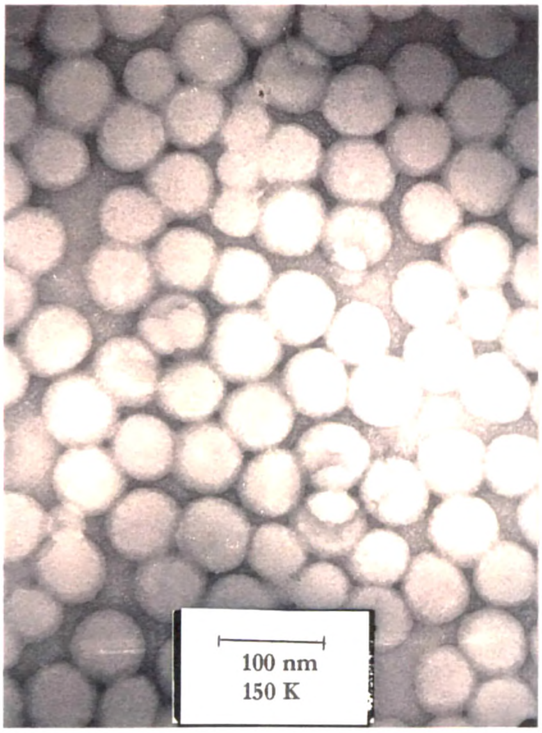

Fig 3.19 : TEM of 97 % conversion sample synthesized through emulsion polymerisation of EA [0.5] – MMA [0.5] initiated with 0.73 mM KPS at M / S = 50 , at 150 K magnification.

AIBN initiated system resulted into phase separation at identical reaction conditions. However, stable latexes were generated at AIBN concentration as high as 12 mM with a final particle size of 85 nm. The particle size distribution for KPS initiated system showed a bimodal nature during the nucleation stage while at higher conversion the particles were more monodispersed especially at M / S ratio 50 [Fig 3. 20].

Microemulsion copolymerisation of EA – MMA [1 : 1 mole ratio] was carried out at M / S ratio 0.66. The composition selected for polymerisaton is represented by **point A** in the phase diagram [Fig 3.12]. The conversion vs time plot is shown in Fig 3.13. The maximum conversion achieved with KPS as initiator was around 80 – 85 % after 3 hrs. The limiting conversion at 80 – 85 % conversion can be attributed to the decrease in pH to 3.6 at the end of polymerisation from an initial pH of 7.2. The decrease in pH may be due to the generation of bisulphate ions in addition to the free radicals produced from KPS decomposition. This results in decreased flux of the generated free radicals since the decomposition rate constant is reported to depend on the pH[14]. Hence there is a possibility of initiator auto inhibition in persulphate-initiated polymerisation. The effect is reported to be significant at pH below 3 for KPS [15]. The observed pH at the interface of the micelles, [which are the initiating sites] may be different than the measured pH due to enhanced or reduced concentration of hydrogen ion at the charged interface [16]. When the reaction was performed under buffered conditions in the presence of 3 mM $NaHCO_3$ at a controlled pH of 8.4, the final conversion increased to 96 % and particle size decreased to 80 nm from 130 nm observed for an unbuffered system. Similar observation has also been reported by Morgan et al.[17] where it was demonstrated that conversion can reach nearly 100 % by controlling the pH for the microemulsion polymerisation of hexylmethacrylate initiated with KPS. However,

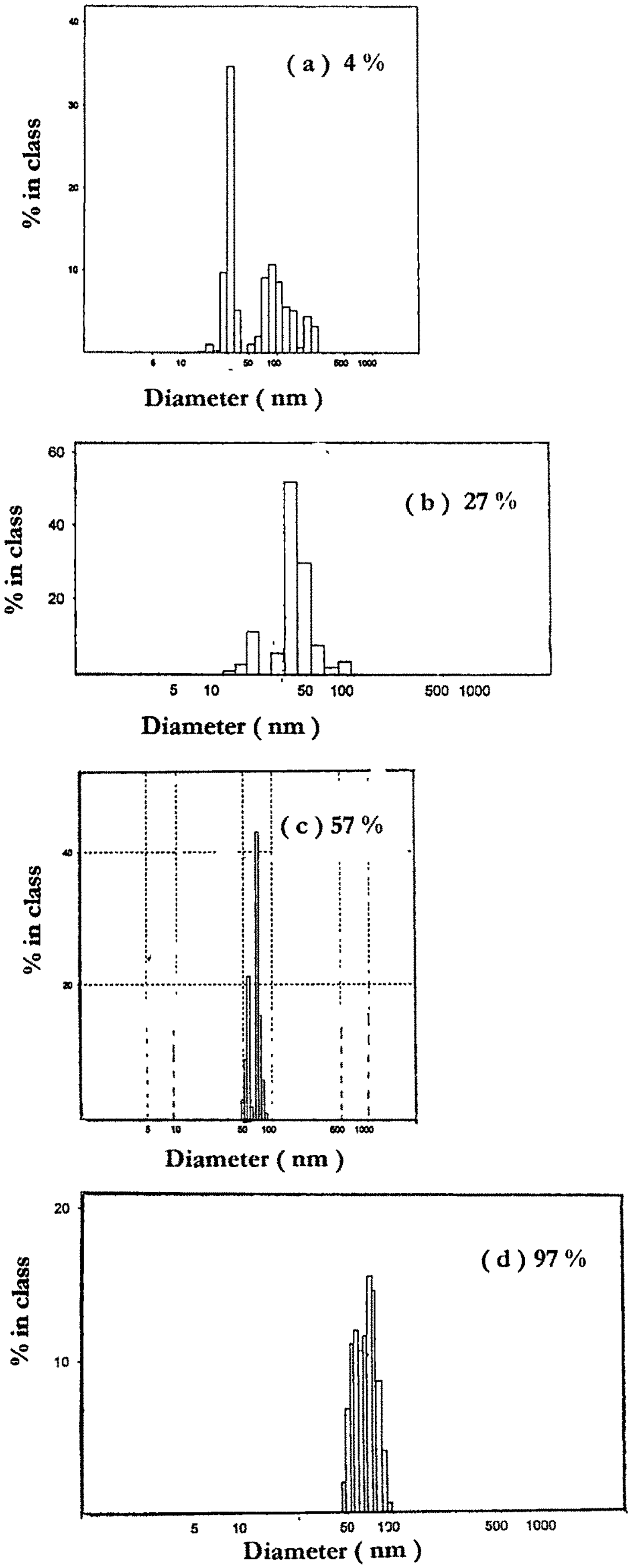

Fig 3.20 : Particle size distribution of EA [0.5] – MMA [0.5] copolymer synthesized through emulsion polymerization at M / S = 50 at various conversions initiated with 0.73 mM KPS.

AIBN initiated system resulted in lower particle size [compared to KPS initiated system] at the same M / S ratio, temperature and molar concentration of intiator [Fig 3.16]. This is surprising because the decomposition rate constant k_d of AIBN at 70 °C is 1.27 x 10^{-4} [21], which is lower than KPS [5.01x 10^{-2}] [13] at the same temperature. Hence lesser number of polymer particles having larger particle size are expected for AIBN initiation. A lower particle size for AIBN indicates greater number of effective radicals initiating polymerisation and hence the higher rate of polymerisation and Np / ml . [Table 3.8].

Table3.8: Kinetic and colloidal parameters for microemulsion copolymerisation of EA – MMA at 70 °C using 0.73 mM KPS and AIBN.

Fractional conversion	Rate, moles/sec	Dn in nm	Np/cm^3	$\bar{n}$	PI
M : S = 0.66 [KPS]					
0.11	0.0046	56	9.8x10^{13}		0.07
0.37	0.0051	31	1.94x10^{15}	4.19	0.064
0.50	0.0034	36	1.84x10^{15}	4.81	0.060
0.67	0.0026	47	1.01x10^{15}	5.73	0.069
0.75	0.002	57	6.18x10^{14}		0.077
0.84	0.00003	124	1.1x10^{14}		0.18
M / S = 0.66 [AIBN]					
0.42	0.006	27	3.2X10^{15}	1.0	0.09
0.50	0.0045	33	2.13X10^{15}	1.4	0.10
0.85	0.0014	48	1.2X10^{15}		0.10
0.90	0.00007	55	8.45X10^{14}		0.04
M / S = 0.66 , HP / AA [1:1]					
0.98	-	27	5.6 x10^{15}	-	0.1

$\bar{n}$ is average number of radical per particle and **PI** is the polydispersity index.

Radical generation for AIBN is generally explained on the basis of single radical produced either from the very small portion of the initiator dissolved in aqueous phase or radical desorption from the microdroplets or monomer swollen micelles unless they recombine within the droplet [34 , 35]. It seems that smaller size of the microdroplet [leading to an increased surface area] favours single radical formation by radical desorption. However, more work is necessary to arrive at a definite conclusion. Microemulsion polymerisation studied at 40 ^{0} C with redox initiator hydrogen peroxide [HP] / ascorbic acid [AA] produced larger number of particles with low particle size [Table 3.8]. Whereas KPS initiated microemulsion system showed a decrease in Np at higher conversions [Table 3 8] due to particle agglomeration as seen in TEM [Fig 3.15]. This also leads to a broad particle size distribution [PSD] for a 85 % conversion sample [Fig 3.17 c]. Fig 3.17 and 3.18 show the variation in PSD with conversion for microemulsion system initiated with both KPS and AIBN. A monomodal distribution for lower conversion samples irrespective of initiator type indicates predominantly single nucleation mechanism which is widely accepted to be the microemulsified droplets [36, 37]. This however doesn't rule out the possibility of homogeneous nucleation particularly for polar monomers. Infact, Kim and Napper [38] have shown that a more sensitive technique like fluorescence can distinguish between the competitive nucleation mechanisms. Whereas the contribution of homogeneous nucleation in an emulsion system can be traced using the conventional techniques.

Emulsion copolymerisation of EA – MMA (1: 1 mole ratio) was carried out at M / S ratios 10 and 50. Fig 3.21 and 3.22 show the conversion vs time and Rp vs conversion plots for M/S=10 and 50 respectively. These emulsions turned into stable, translucent nanosized latexes, when 0.73 mM KPS was used at 70^{0}C. Such a transition was not

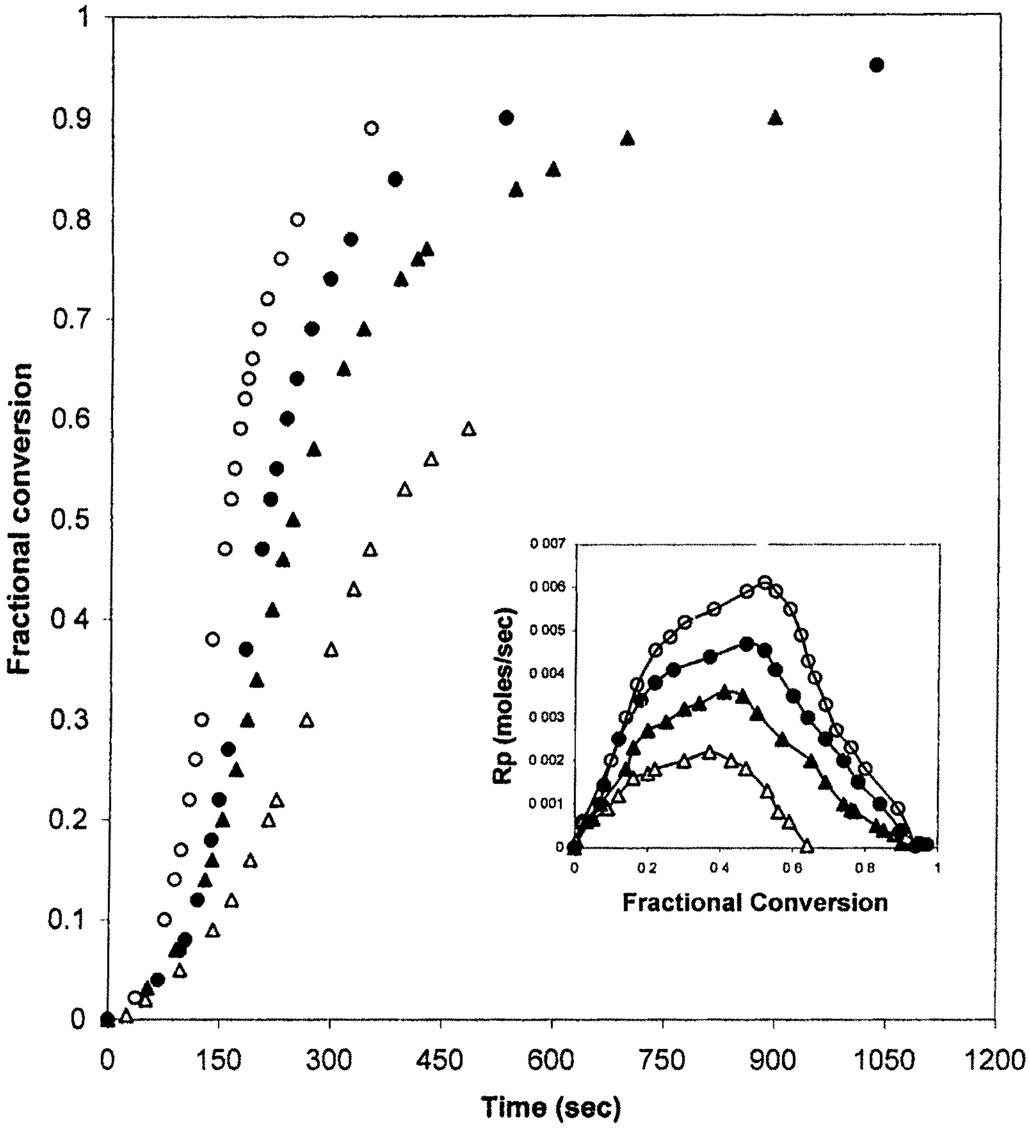

Fig 3. 21 : Effect of KPS concentration on % conversion and rate of polymerization at M /S = 10, temperature 70 ^{0}C and EA (0.5) – MMA (0.5).

(△) 0.18 mM , (▲) 0. 36 mM , (●) 0. 55 mM , (O) 0.73 mM

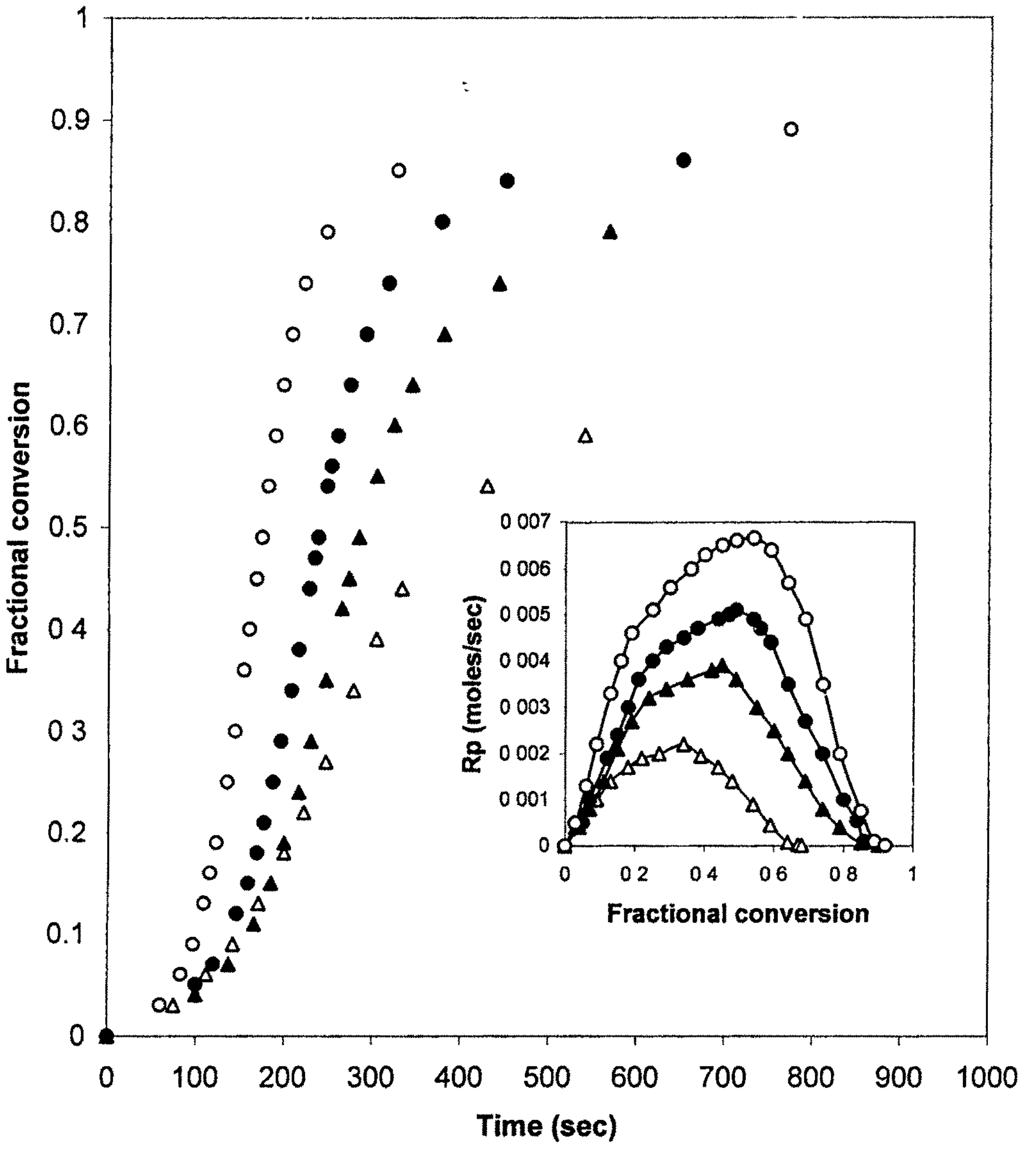

Fig 3. 22 : Effect of KPS concentration on % conversion and rate of polymerization at M /S = 50, temperature 70 °C and EA (0.5) – MMA (0.5)

(Δ) 0.18 mM , (▲) 0. 36 mM , (●) 0. 55 mM , (O) 0.73 mM

observed with AIBN at the same M/ S ratio, AIBN concentration and temperature. Instead, the system showed phase separation at around 70 % conversion. This can be attributed to the lower decomposition rate constant (k_d) of AIBN at 70 ^{0}C compared to KPS at the same temperature [21 , 13] and availability of lower concentration of AIBN dissolved in water in the initiation of emulsion polymerisation [39]. This leads to the lesser number of active radicals initiating polymerization resulting in the generation of lesser number of polymerization sites. Diffusion of monomer from monomer droplets and uninitiated micelles results in the particle growth. The rate of coagulation is also expected to be higher compared to KPS initiated system due to the absence of surface charge on the initiator head group. The combination of these facts renders the available surfactant insufficient, resulting into phase separation.

It has been reported for water soluble initiators such as KPS that the oligomeric radical formed in aqueous phase can make an entry into the monomer swollen micelle only after the attainment of a critical chain length or hydrophobicity at which it becomes surface active [25]. This can increase its residence time at the micelle water interface and hence the probability of radical entry. For the present system, the critical chain length for entry was calculated from hydrophobic free energy consideration using Maxwell's model [27]

$$z = 1 - 23\ \mathrm{kJ\ mol^{-1}} \,/\, RT \ln C_w^{sat}$$

where, z is the average degree of polymerization for entry , C_w^{sat} is the saturated aqueous phase concentration of the monomer in mol dm^{-3}. The saturated water solubility reported for EA and MMA is 1.8 % and 1.5% respectively [20]. The average value of C_w^{sat} was used for calculation, since 0.5 mole fraction of each monomer was taken for kinetic studies. The value of **z** was observed to be 6. Further addition of monomer units in aqueous phase results in the increase in hydrophobic free energy of the surfactant making it hydrophobic enough not to form a micelle but to precipitate out to generate new particle in aqueous phase leading to homogeneous nucleation. It has been reported [25] that the critical degree of polymerization for homogeneous nucleation, j_{crit}, can be calculated from the consideration of hydrophobic free energy of the surfactant having a Kraft temperature same as the temperature of the emulsion polymerization under study. This leads to

$$j_{crit} = 1 - 55 \text{ kJ mol}^{-1} / RT \ln C_w^{sat}$$

The value of j_{crit} for the present system was observed to be 12 at 70 °C. The fact that polymer particles are generated by both micellar and homogeneous nucleation is evident from the following studies.

The Rp vs. Conversion plots [Fig 3.21and 3.22] show a prolonged nucleation period and the absence of a constant rate period. Since the conversion of micelles into polymer particles takes place at lower conversion, the further slower increase in the rate of polymerization can be attributed to particle nucleation in aqueous phase [homoeneous nucleation]. TEM [Fig 3 .23] for a 50 % conversion sample [soon after the system turned translucent] shows a large number of smaller particles most likely to be generated by homogeneous nucleation for M / S = 50 system The slower increase in rate due to particles generated through homogeneous nucleation has been attributed [40] to reduced swelling of the particles by monomer due to their hydrophilic character and rapid exit of free radicals due to their small size. Simultaneous diffusion of monomer into the particles generated via micellar and homogeneous nucleation results in the disappearance of monomer as a separate phase by the time the rate maxima is achieved. Due to higher rate of particle nucleation, particle growth kinetics becomes less

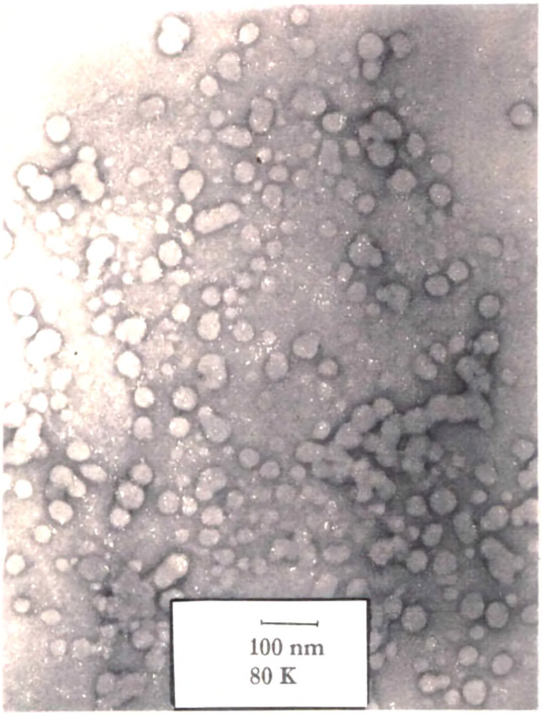

Fig 3.23 : TEM of 50 % conversion sample synthesized through emulsion polymerisation of EA (0.5) – MMA (0.5) initiated with 0.73 mM KPS at M / S = 50 and 80 K magnification.

important in these emulsion systems involving both partially water soluble monomers. Two-stage kinetics in emulsion polymerization has been reported even in the case of styrene and SDS as a surfactant by Varela de la Rosa et al. [7] where the conversion was monitored by a microcalorimeter. Gan et al. also have reported two stage kinetics in the emulsion polymerisation of styrene and MMA [22]. To the best of our knowledge, no reports have tried to explain such an observation.

The particle size distribution at 4 % , 27 % and 57 % conversion for M / S = 50 clearly shows a bimodal nature [Fig 3.20 a ,b, c] indicating particle generation through two nucleation mechanisms. Table 3 .7 shows the final number of particles (Np/ml) for the system with M / S ratio 10 and 50. Number of particles were observed to increase initially and thereafter remained nearly constant. The particles generated by homogeneous nucleation are relatively unstable in a colloidal state, which is reported [40] to arise as a consequence of their small size and extreme curvature of electrical double layer. Therefore, the particles are prone to coagulative events resulting into a slight decrease in the Np/ cm^3 , [Table3 .7] and a slight increase in particle size and increase in monodispersity as seen in TEM [Fig 3.19]and particle size distribution [Fig 3.20 d].

Therefore the role of KPS and AIBN varies in emulsion and microemulsion system depending upon their preferential distribution in aqueous or organic phase as well as on the relative importance of droplet and homogeneous nucleation to the overall particle nucleation for both the systems. Kinetic details implicated that homogeneous nucleation has a greater contribution to latex particle formation in emulsion system compared to microemulsion. The above point is substantiated more quantitatively by ^1H NMR and DSC measurements

[3 .5 .2] Copolymer composition through ^{1}H NMR

Even the small difference in solubility of EA [1.8%] and MMA [1.5%] has shown considerable influence in the copolymer composition as seen from NMR studies and thermal properties. The copolymer composition data for emulsion polymerisation obtained by ^{1}H NMR at various feed compositions and below 10 % conversion is given in [Table 3.9]. The copolymers synthesized through emulsion polymerisation showed greater fraction of the more water-soluble monomer EA in comparison to the copolymer synthesized by bulk polymerisation of EA-MMA [41] for identical feed concentration and below 10 % conversion. This indicates that composition drift in emulsion polymerisation, arises due to the initiation of polymerisation in both aqueous phase and micelles. In addition, the contribution of homogeneous nucleation to the overall particle nucleation increases with decrease in the surfactant concentration. Therefore copolymer composition studied at M / S = 10 for conversion below 10% and at various compositions shows lesser drift in copolymer composition from bulk copolymerisation as compared to M / S = 50 [Table 3.9]. On increasing the surfactant concentration further for microemulsion polymerisation at M / S = 0.66, negligible drift in copolymer composition was observed when the results were compared to bulk polymerisation at identical feed concentration and below 10 % conversion [Table 3.10]. A drift in copolymer composition for a microemulsion system could not be traced as the effect has been subdued by little difference in the relative solubility of the comonomers and lesser degree of homogeneous nucleation compared to an emulsion system. A representative ^{1}H NMR for EA - MMA copolymer is given in [Fig 3.24].

Table 3.9: Comparison of Copolymer composition below 10 % conversion for emulsion and bulk copolymerisation of EA – MMA .

Feed concentration		Emulsion , M / S = 50		Emulsion , M / S = 10		Bulk [41]	
f_{EA}	f_{MMA}	F_{EA}	F_{MMA}	F_{EA}	F_{MMA}	F_{EA}	F_{MMA}
0.90	0.10	0.81	0.19	0.76	0.24	0.72	0.27
0.75	0.25	0.58	0.42	0.54	0.46	0.51	0.49
0.66	0.33	0.48	0.52	0.43	0.57	0.42	0.57
0.50	0.50	0.35	0.65	0.32	0.68	0.30	0.70
0.25	0.75	0.19	0.81	0.14	0.86	0.13	0.86
0.10	0.90	0.10	0.90	0.06	0.94	0.05	0.94

f_{EA} , f_{MMA} : Feed concentrations of ethylacrylate and methylmethacrylate.

F_{EA} , F_{MMA} . Ethylacrylate and methylmethacrylate fraction in copolymer

Table 3.10 : Comparison of Copolymer composition below 10 % conversion for microemulsion and bulk copolymerisation of EA – MMA.

Feed concentration		Microemulsion, M/ S = 0.66		Bulk [41]	
f_{EA}	f_{MMA}	F_{EA}	F_{MMA}	F_{EA}	F_{MMA}
0.9	0.1	0.73	0.27	0.72	0.28
0.75	0.25	0.52	0.48	0.51	0.49
0.66	0.33	0.39	0.61	0.42	0.58
0.50	0.50	0.30	0.70	0.30	0.70
0.25	0.75	0.13	0.87	0.13	0.87
0.1	0.90	0.05	0.95	0.05	0.95

f_{EA} , f_{MMA} : Feed concentrations of ethylacrylate and methylmethacrylate.

F_{EA} , F_{MMA} : Ethylacrylate and methylmethacrylate fraction in copolymer

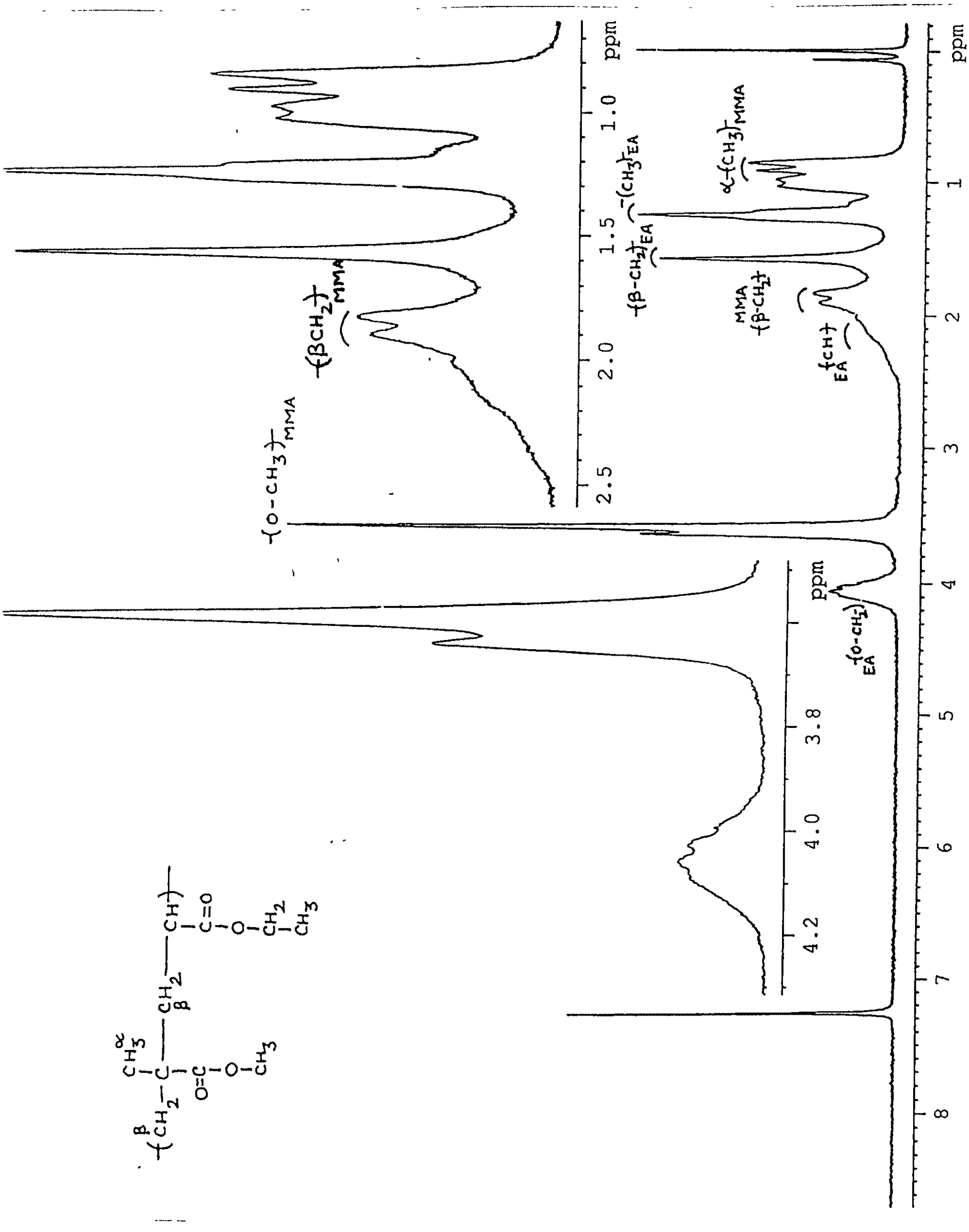

Fig 3.24 : ^1H NMR spectra of EA – MMA copolymers synthesized through emulsion polymerisation. MMA in feed 0.5 and in copolymer 0.651.

[3.5.3] Thermal properties by DSC

The copolymers synthesized through emulsion polymerization show two Tg's [Fig 3 .25 and Table 3.11]. Appearance of two Tg 's can be attributed to the formation of a diblock copolymer due to large difference in their monomer reactivities [$r_{MMA} = 1.44$, $r_{EA} = 0.25$] which is further discussed in chapter 4. However, such a possibility can be denied as the polymer characterization is done below 10 % conversion and copolymer synthesized in microemulsion showed single Tg [Fig 3.25]. Hence the appearance of two Tg's confirms the formation of two types of copolymer chains with different composition arising from micellar and homogeneous nucleation. The polymer generated via micellar polymerization is expected to have a greater fraction of the less water soluble monomer, MMA and corresponds to the higher Tg. Whereas, homogeneous nucleation generates polymer chains with higher fraction of the more water soluble monomer, EA resulting into the lower Tg. The difference in observed Tg's is significant due to the large difference in the Tg's of the homopolymers. Whereas copolymers synthesized through microemulsion polymerization show single Tg indicating a predominance of single copolymerisation locus [Fig 3.25].

Table 3.11: Glass transition temperature for copolymers below 10 % conversion through emulsion polymerization of EA – MMA.

Feed Composition		at M / S = 10		at M / S = 50	
EA	MMA	Tg_1 ° C	Tg_2 ° C	Tg_1 ° C	Tg_2 ° C
0.25	0.75	72	100	68	102
0.50	0.50	69	91	62	86
0.75	0.25	28	66	23	71
0.90	0.10	0.30	50	-1.0	68

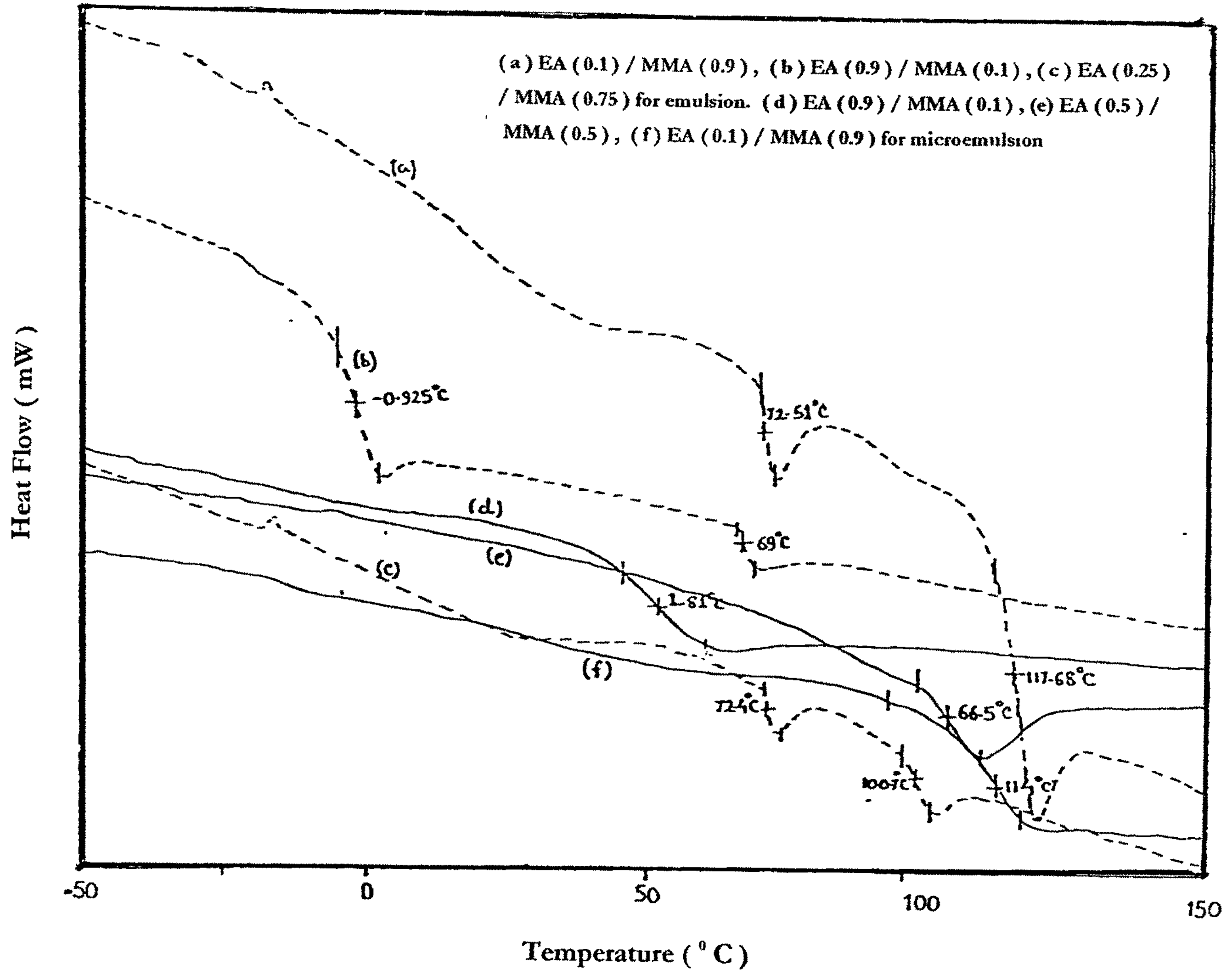

Fig 3.25 : DSC thermograms of EA / MMA copolymer synthesised through emulsion and microemulsion for three different compositions (. ..) Emulsion , (———) Microemulsion

[3.5.4] Effect of monomer feed concentration

Emulsion copolymerisation of EA – MMA at M / S = 50 was carried out at three different monomer feed concentrations to check the nature of rate curve. The Rp vs. conversion plots [Fig 3.26] showed similar nature for all the three different feed ratios. Increasing the concentration of MMA in feed resulted into higher rate of polymerisation due to higher reactivity of MMA in the presence of EA. The reactivity ratio values were observed to be 2. 1 for MMA and 0.25 for EA and the necessary details are discussed in the next chapter.

[3.5.5] Probable termination events

The number of radicals per particle [$\bar{n}$] for the system under study was calculated using the following equation, and the results are given in [Table 3 . 7].

$$\bar{n} \approx \frac{Rp(c) \times N_0 \times (kp_{EA} \times r_{MMA} + kp_{MMA} \times r_{EA} \times L) \times (1 + L)}{[M]eq \times kp_{MMA} \times kp_{EA} \times Nc \times (r_{MMA} + 2L + r_{EA} \times L^2)}$$

where [M]eq is the equilibrium monomer concentration, taken as 6. 0 mol / dm^3 as reported by Capek et al. [33] from the swelling studies of the final MMA – EA copolymer latexes. The reported [33] propagation rate constant [kp] values of 1500 and 686 dm^3 mol^{-1} sec^{-1} , for EA and MMA have been used for the calculation of n. The monomer ratio [EA] / [MMA], is represented as L. Reactivities of EA and MMA used for calculation in emulsion medium are reported to be 0.25 and 1.44[42] respectively by us and are discussed in chapter 4. N $_p$ / cm^3 is the number of particles calculated from equation 1 using dynamic light scattering data.

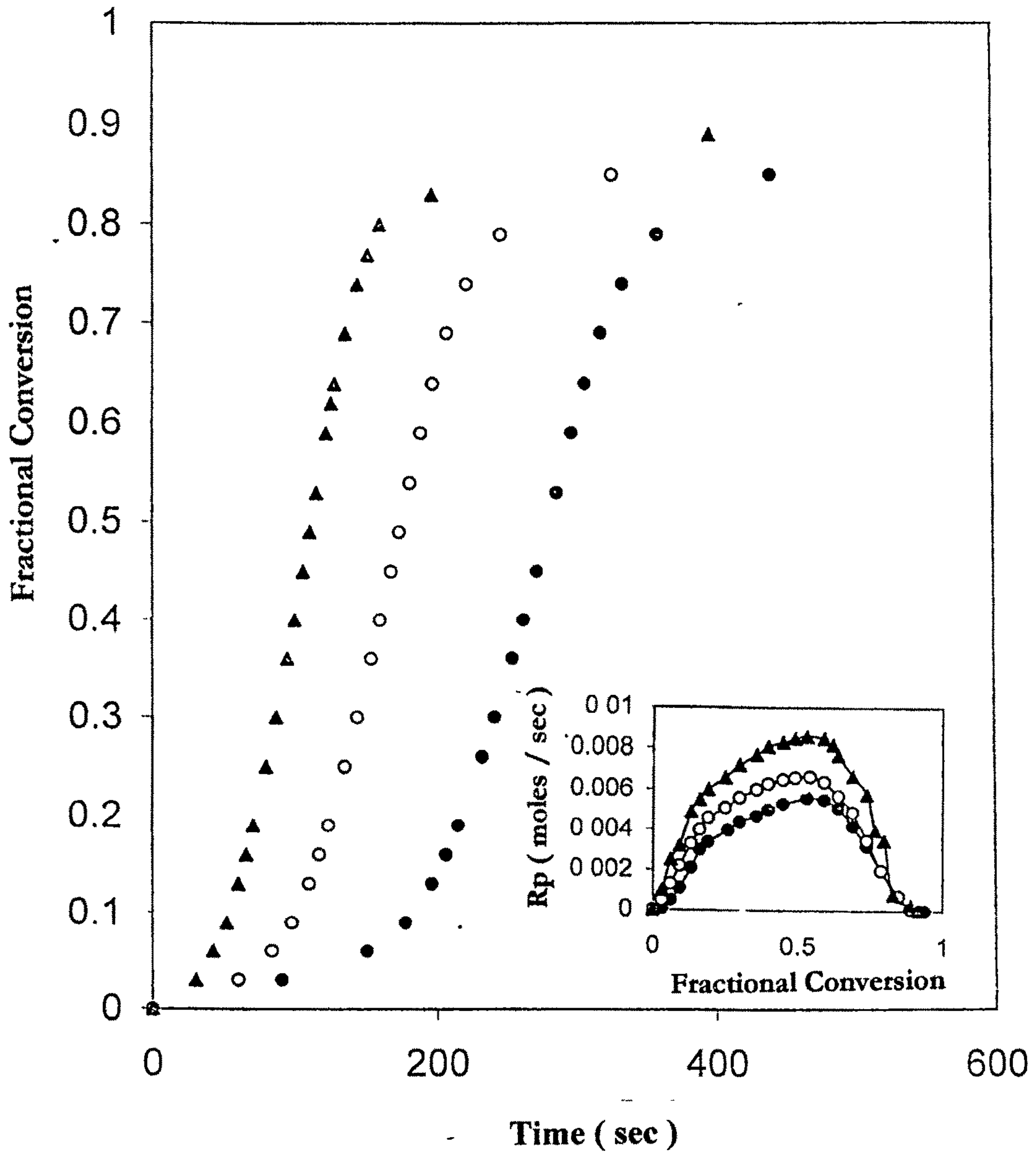

Fig 3.26 : Effect of monomer feed ratio on the rate of the copolymerisation of EA – MMA initiated with 0.73 mM KPS at M / S = 50.

(●) MMA (0.25) – EA (0.75) , (O) MMA (0.5) – EA (0.5) ,

(▲) MMA (0.75) – EA (0.25).

Table 3.8 shows a relatively high value of $\bar{n}$ in the microemulsion polymerisation initiated with KPS. Gardon [43] reported as high as five radicals per particle in the emulsion polymerisation of MMA. Fig 3. 27 and Table 3.12 give the molecular weight distribution and molecular weights for emulsion and microemulsion system.

Table 3.12 : Molecular weights for emulsion and microemulsion based copolymers.

Molecular Weight	Microemulsion		Emulsion	
	M S= 0.66 [KPS]	M/S = 0.66 [AIBN]	M / S = 10 [KPS]	M/ S = 50 [KPS]
Mn	9.1×10^4	5.6×10^5	5.19×10^5	1.34×10^6
Mw	2.4×10^5	1.0×10^6	1.63×10^5	5.09×10^5
Mw / Mn	2.6	1.9	3.17	2.64

The polymer synthesised through microemulsion polymerisation has larger fraction of low molecular weight polymer chains which is in contrast to what is generally reported in case of microemulsion polymerisation where molecular weight can reach as high as $10^6 - 10^7$. The number of polymer chains per particle [n p] calculated from the weight of the polymer in each millilitre of microemulsion was also found to be 1279. Similar results were reported by Pilcher and Ford [44] for the microemulsion polymerisation of MMA [n p = 1034]. The higher value of np can arise due to the combined effect of coagulation and radical accumulation [also suggested by a higher value of $\bar{n}$, Table 3.8] at higher conversion. Radical accumulation is due to the inability of the radicals to terminate [which is diffusion controlled] due to the combined effect of closeness of Tg and reaction temperature, larger particle size and increased microviscosity due to solubility of polymer in the monomer. The above condition might lead to unimolecular

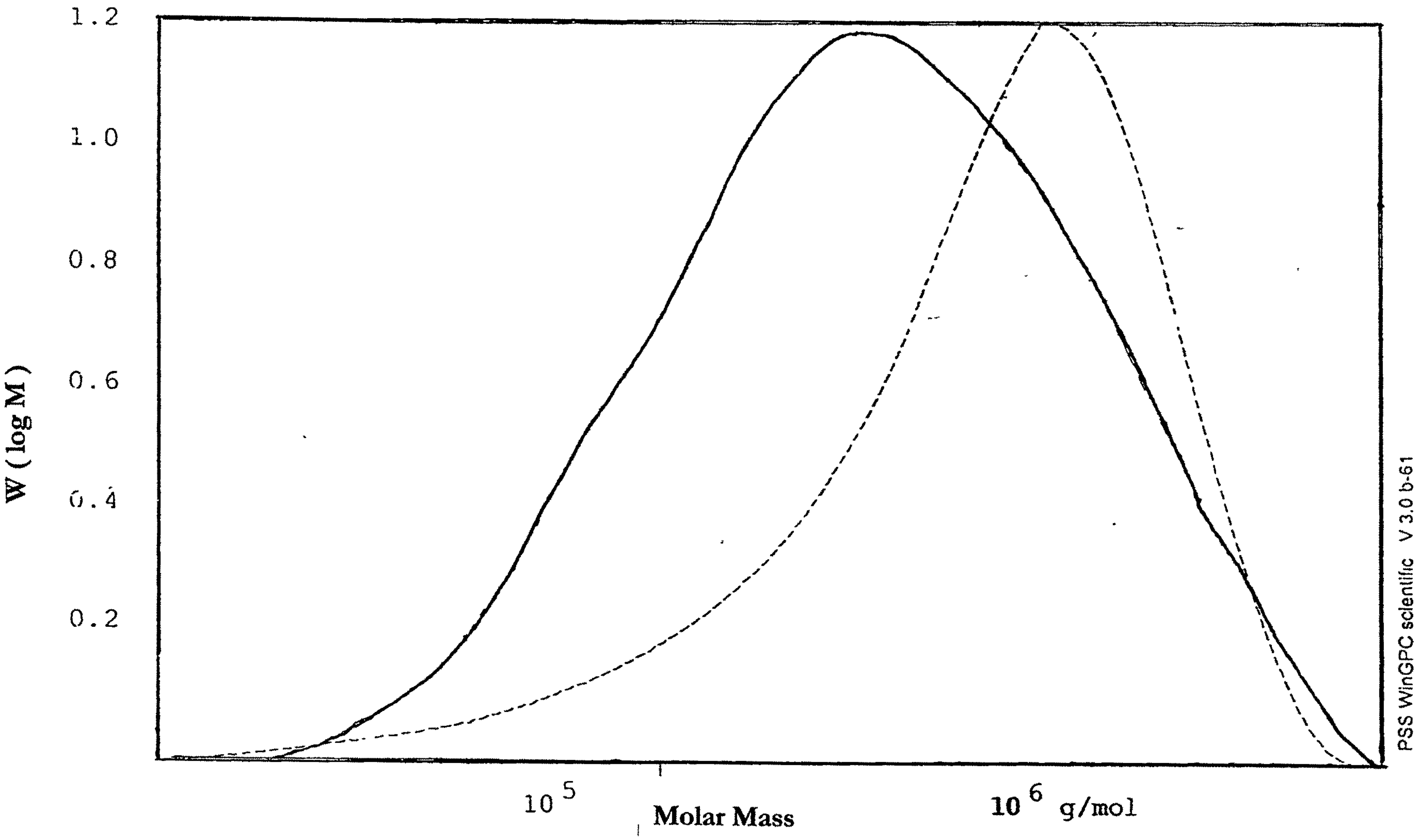

Fig 3.27 : Molecular weight distribution of copolymers synthesized through microemulsion (———) and emulsion (-------) .

termination through chain transfer to the monomer and surfactant as the operative termination mechanism for microemulsion polymerisation initiated with KPS. AIBN initiated microemulsion system gives value of np equal to 540 which is due to the smaller particle size [Table 3. 8] and higher molecular weight [Table 3.12] compared to KPS initiated system.

In comparison to microemulsion, emulsion systems with M / S ratio 10 and 50, show much lower value of np and lower fraction of low molecular weight fractions. The np values are 35 and 135 respectively. The lower particle size and higher number of particles can make radical exit more facile. Subsequently bimolecular termination and chain transfer to the desorbed radical can take place either in aqueous phase or by re – entry into the growing radical.

[3 . 6] Characterisation

[3 . 6 . 1] NMR analysis

The composition of the copolymer was determined from ^{1}H NMR recorded on 200 MHz Bruker DPX 200 instrument using TMS as an internal reference and 2 % w / v sample solution in $CDCl_3$. Fig 3.24 shows the NMR spectrum of EA - MMA copolymer. The signal for the methyl protons of O - CH_3 group from MMA appeared around 3.6 ppm and that for protons from O - CH_2 group of ethylacrylate appeared around 4.07 ppm. The MMA mole fraction F_{MMA} in the copolymer was calculated from the area under peak for the O-CH_3 protons from MMA and the peak area for O-CH_2 protons from ethylacrylate.

[3 . 6 . 2] Thermal analysis

The Tg's of the purified Poly-[EA - co – MMA] synthesised from emulsion and microemulsion and having different copolymer compositions were found to be in the range of – 2 to 117 °C. Emulsion copolymers showed two Tg's whereas microemulsion based copolymers exhibited single Tg. Necessary explanations related to this observation have been discussed in section 3.5.3.

[3 . 6 . 3] Particle size analysis

Particle size of the resulting microemulsion and emulsion latexes were found to be in the range of 27 – 160 nm. Necessary explanations related to variation in particle size have been given in section 3.5.1.

[3 .6 . 4] Molecular weight

The molecular weight of the copolymers synthesised in emulsion and microemulsion were determined by GPC method. They were observed to be in the range of $10^4 - 10^6$. The polydispersity was in the range of 1.9 – 3.17. Higher polydispersity might be due the partial water solubility of both the monomers resulting into both micellar as well homogeneous nucleation mechanism. The details are discussed in section 3.5.5

[3 . 7] Conclusion

1. The kinetics of emulsion system at [M / S = 10 , 40 and 54] was studied with respect to microemulsion at M / S =1 for ethylacrylate. While the copolymerisation of ethylacrylate – methylmethacrylate in emulsion was carried out at M / S = 10 and 50 with respect to microemulsion system at M / S = 0.66. Transition of the emulsion system into transparent / translucent nanolatexs is attributed to the simultaneous distribution of monomer into the sites created by homogeneous and micellar nucleation resulting into early disappearance of monomer as a separate phase. The rate of particle nucleation was observed to be higher than the rate of particle growth resulting into a larger number of smaller particles stabilized by the available surfactant for KPS initiated systems. Breaking of the same emulsion system with AIBN also supports this observation. AIBN generates lesser number of effective radicals initiating polymerisation, resulting in lower rate of nucleation and higher rate of particle growth. This results into lesser number of larger size particles, which are not stabilised with the available surfactant, resulting into phase separation. Gel effect dominance was observed in the case of microemulsion polymerisation.
2. The fact that polymer particles are indeed generated by both micellar and homogeneous nucleation in the emulsion polymerisation of polar monomers was confirmed by the study of copolymerisation.

   [a] ^{1}H NMR studies showed a drift in composition. Such a drift was more evident for M / S = 50 having the lowest surfactant concentration.

   [b] DSC study showed the appearance of two Tg' s for emulsion based samples indicating mainly two different compositions of the polymer chain. Particle size distribution showed a bimodal nature during the nucleation stage. Whereas no such drift

in composition was observed for microemulsion based copolymers studied below 10 % conversion. Copolymers also showed a single Tg.

3. The contribution of homogeneous nucleation to the overall process of particle nucleation was observed to be higher for emulsion system compared to microemulsion.
4. In contrast, microemulsion polymerisation studied at lower monomer and higher surfactant concentration resulted into much larger particles, showing effects of coagulation.
5. The role of KPS and AIBN was found to be opposite for emulsion and microemulsion. AIBN initiated system generated larger number of smaller particles compared to KPS in case of microemulsion polymerisation under identical reaction conditions. Whereas emulsion system initiated with KPS produced a stable latex system with low particle size. AIBN initiated emulsion system showed phase separation under identical reaction conditions.
6. pH seems to influence the decomposition rate constant of KPS at higher emulsifier concentration thus lowering the fraction of effective radicals initiating polymerisation.

References

1. Carver MT , Hirsch E , Wittmann JC , Fitch RM and Candau F , *J . Phys . Chem* , **93** , 4867 (1989).
2. Penboss IA , Napper DH and Gilbert RG , *J .Chem . Soc . Faraday Trans . I* , **79**, 1257 (1983).
3. Sudol ED ,El – Aasser MS and Vanderhoff JW , *J .Polym . Sci .* , *Polym .Chem .Ed .*, **24** , 3515 (1986)
4. Gilbert RG , Emulsion Polymerisation : A Mechanistic Approach , Academic Press , London (1995).
5. Roe CP, *Ind . Eng . Chem .*, **60** , 20 (1968).
6. Hansen FK , *Chem . Eng . Sci .* , **48** , 437 (1993).
7. Zhu WZ, Li GZ, Zheng GZ, Liu SJ, Shui LL, Liang HJ and Wu Q , *Acta Chimica Sinica* , **59** , 1 (2001).
8. Chern CS and Wu LJ, *Journal of Polymer Science Part A – Polymer Chemistry* , **39**, 898(2001).
9. Varela de La Rosa L , Sudol ED , El – Aasser MS and Klein A , *J. Polym . Sci .* , *Part A : Polym . Chem .* , **34** , 461 (1996).
10. Gou JS , Sudol ED , Vanderhoff JW and El – Aasser MS , *J. Polym .Sci . Part A : Polym Chem .* , **30** , 691(1992).
11. Giannetti E , *A.I.Ch .E. Journal*, **39** , 1210 (1993).
12. Feeney PJ , Geissler E , Gilbert RG , Napper DH , *J.Colloid Interface Sci* ,**121**, 508 (1988).
13. Bandrup J, Immergut ED , editor , Polymer Handbook , 3 rd ed., New York , Wiley (1989).
14. Behrman EJ, Edwards JO , *Rev Inorg Chem* , **2** 179 (1980).
15. Kolthoff IM, Bovey FA , Medalia AI, Meehan EJ, Emulsion Polymerisation , New York : Interscience Publishers , 68 (Chapter 3) , 1955.

16. Bunton CA, *Acc Chem Res* **24**, 357 (1991).

17. Morgan JD, Lusvardi KM and Kaler EW , *Macromolecules* , **30** ,1897 (1997).

18. Kamachi M, Fuji M, Ninomiya SI, Katsuki SN, Oyakura SI, *J. Polym.Chem*, **20**, 1482 (1982).

19. Capek I, Juranicova V, Barton J , Asua JM , Ito K , *Polym Int* , **43** , 1 (1997).

20. Lovell PA, El-Aasser MS, Emulsion Polymerisation and emulsion Polymers, New York, Wiley , 15 , 145 , Chapter 4 (1997).

21. Bamford CH, Denyer R, Hobbs J , *Polymer* , **8** , 493 (1967).

22. Gan LM, Chew CH, Ng SC, Loh SE, *Langmuir* , **9** , 2799 (1993).

23. Choi YT, El – Aasser MS, Sudol ED, Vanderhoff JW, *J.Polym. Chem Ed.* **23**, 2973 (1985).

24. Yeliseyeva VI, In Pirma I , editor , Emulsion Polymerisation , New York , Academic Press , 256 , 258 (1982).

25. Gilbert RG, Emulsion Polymerisation : A Mechanistic Approach, New York , Academic Press, 15,16,309 (1995).

26. Morrison BR, Maxwell IA , Napper DH, Gilbert RG, Ammerdorffer JL, German AL *J.Polym.Sci.Polym.Chem Ed* , **31**, 467 (1993).

27. Maxwell IA , Morrison BR , Napper DH, Gilbert RG , *Macromolecules* , **24** , 1629 (1991).

28. Kuo PL, Turro NJ , Tseng CM , El – Aasser MS and Vanderhoff JW, *Macromolecules,* **20** , 1216 (1987).

29. Pokhriyal NK , Devi S , *Eur Polym J* , **37** , 1695 (2001).

30. Capek I, Barton J, Orolinova E, *Chem Zvesti* , **38** , 803 (1984).

31. Gan LM , Chew CH , Lee KC , Ng SC, *Polymer* , **34** , 3064 (1993).

32. Lovell PA , Shah TH , Heatley F, *Polym Commun* , **32** , 98 (1991).

33. Capek , I. and Tuan , L . Q ., *Macromol. Chem* , **187**, 2063 (1986).

34. Nomura M , Fujita K , *Makromol. Chem., Rapid Commun.* **10** , 581 (1989).

35. Sudol ED, El - Aasser MS, Vanderhoff JW , *J.Polym .Sci. Polym. Chem .Ed.*, **24**, 3515 (1986).

36. Gou JS , Sudol ED , Vanderhoff JW and El – Aasser, *J . Polym . Sci . Part A : Polym Chem.*, **30** , 691 (1992).

37. Bleger F, Murthy AK , Pla F and Kaler EW , *Macromolecules* , **27** , 2559 (1994).

38. Kim DR and Napper DH , *Macromol. Rapid Commun* , **17** , 845 (1996).

39. Barton J, Karpatyova A , *Makromol. Chem* , **138** , 623 (1987).

40. Feeney, P. J.; Napper, D. H. ; Gilbert, R. G.,*Macromolecules*, **17**, 2520 (1984).

41. Gressie,N; .Torrance,B.J.D; Fortune, J.D. , *Polymer*, **6** , 653 (1965).

42. Bhawal S and Devi S , *J. Appl . Polym . Sci* . Accepted (2002).

43. Gardon JL , *J.Polym.Sci ., A –1* , **6** , 628 (1968).

44. Pilcher SC and Ford WT , *Macromolecules* , **31** , 3454 (1998).