

# Kinetics and Behavior of Copolymerization in Emulsion and Microemulsion Systems

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Copolymerization of 2-ethylhexyl acrylate and acrylonitrile in emulsions and microemulsions containing sodium dodecyl sulfate as an emulsifier was investigated, as a function of initiator concentration, temperature, monomer-feed composition, and surfactant concentration. The emulsions were observed to turn into transparent/translucent and stable latexes, mimicking the properties of true microemulsion latexes, on polymerization. The rate of emulsion polymerization was found to be faster than that of the microemulsion polymerization. The rate of polymerization, percentage conversion, and final number of latex particles were found to be a function of initiator concentration, reaction temperature, and acrylonitrile concentration in feed. The rate of polymerization showed a dependency of  $-0.05$  power of the surfactant concentration in the area covering emulsion and microemulsion regions. Intrinsic viscosity values showed that the products from true microemulsion polymerization were of higher molecular weight than those from "emulsion-to-microemulsion". The decrease in the particle size with conversion in emulsion polymerization was attributed to the role of the coemulsifier 2-ethylhexyl acrylate and engulfing of the initial polymerization system by the local heat production during polymerization.

## Introduction

Ternary emulsions and microemulsions are heterogeneous colloidal systems of oil, water, and surfactant. Emulsions, which are opaque systems with droplet size ranging from 100 to 1000 nm, are kinetically stable systems and require mechanical work against colloidal instability. On the other hand microemulsions are transparent, isotropic systems with droplet size typically below 60 nm and are thermodynamically stable.<sup>1</sup>

Both emulsion and microemulsion polymerization processes offer convenient access to the synthesis of well-defined microlatex particles with easily controlled very high molecular weights, which govern the properties of the synthesized polymers. In addition the resulting polymer latexes being water based minimize environmental and safety hazards. The only physical difference between the appearance of the resulting polymer latexes from the emulsion and microemulsion polymerization processes is that the latexes produced by the former process contain particles of bigger size, and hence look opaque, and their storage requires addition of stabilizers to prevent phase separation, whereas latexes from the later show good stability over longer periods. These processes also have inherent disadvantages such as difficulty to remove initiator decomposition products and surfactant (especially from ternary o/w microemulsions) present in the final products, which contribute to the undesirable properties when used under different conditions.

Though the emulsion (co)polymerization has been studied extensively, the first report of polymerization in microemulsions appeared only 2 decades back in 1980.<sup>2</sup> Particle nucleation in microemulsion polymerization in

oil-in-water (o/w) or water-in-oil (w/o) systems is believed to be a continuous process, and the locus of nucleation is shown to be the microemulsion droplet.<sup>3,4</sup>

To date a few reports are available on the kinetics of the copolymerization of monomer pairs of dissimilar polarity in o/w microemulsions and their comparison with emulsions. Puig et al.<sup>5</sup> reported the synthesis of monodisperse latexes of styrene–acrylic acid copolymers in o/w cationic microemulsions. However, only 60% conversion was reported with the copolymer backbone consisting of isolated acrylic acid units randomly distributed among polystyrene blocks. Roy and Devi<sup>6</sup> observed a faster copolymerization rate of butyl acrylate and methyl methacrylate copolymerization in an emulsion than in a microemulsion. Capek and Jurnicova<sup>7</sup> reported the kinetics of butyl acrylate and acrylonitrile copolymerization in o/w microemulsions using water and oil soluble initiators ammonium per sulfate and dibenzoyl peroxide. The polymerization was reported to proceed under monomer-starved conditions at medium conversions. Mendizabal et al.<sup>8</sup> studied copolymerization of styrene and acrylonitrile in cationic/anionic emulsions and microemulsions using water- or oil-soluble initiators. Zhang et al.<sup>9</sup> reported the synthesis of random copolymers of acrylamide and styrene by photopolymerization of acrylamide–styrene/dodecyl betaine/water, o/w microemulsions. The oil/water interface

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**Table 1. Compositions for Copolymerization of 2-Ethylhexyl Acrylate–Acrylonitrile (1:1, w/w)<sup>a</sup>**

system	monomers (wt %)	SDS (wt %)	water (wt %)	water/ monomer ratio	system appearance	
					BP	AP
A <sub>1</sub>	5.8	1.0	93.2	16	E	clear
A <sub>2</sub>	5.7	3.0	91.3	16	E	clear
A <sub>3</sub>	5.0	15.0	80.0	16	clear	clear

<sup>a</sup> Key: BP, before polymerization; AP, after polymerization; E, emulsion.

was reported to be the site of photoinitiation, whereas polymerization occurred in microemulsion droplets. More recently Xu et al.<sup>10</sup> have discussed the copolymerization behavior of styrene–methyl methacrylate and styrene–butyl acrylate in emulsions and microemulsions on the basis of the semiempirical equations presented by Maxwell. The report emphasizes that in such systems partitioning of the partly hydrophilic monomer in different phases governs the polymerization process. Vaskova et al.<sup>11</sup> investigated the initial stages of copolymerization of acrylamide with methyl methacrylate or styrene in w/o microemulsions initiated by radical initiators with different solubility in water. The initial rate of copolymerization was found to be dependent on the mole fraction of the acrylamide in the monomer feed but was independent of the water solubility of initiator.

Copolymerization of the monomers of different polarity in emulsions/microemulsions is a complex process, and the interpretation of the kinetic data is greatly affected by the partitioning of the monomers in different phases which in turn affects the actual mole ratio of the monomers in the microenvironment of the polymerization loci. As a result, reactivity of the monomers in microemulsions can differ greatly from that in other reaction media.<sup>12,13</sup> In the present work with partitioning of the monomer and effect of surfactant concentration being the prime interest, we report the copolymerization of a hydrophobic monomer 2-ethylhexyl acrylate and a partially hydrophilic monomer acrylonitrile using a water-soluble initiator potassium persulfate in anionic o/w emulsions and microemulsions containing sodium dodecyl sulfate. The emulsions which on polymerization produced transparent/translucent and stable latexes (with final latex particle size ~40 nm even smaller than the microemulsion latexes) are being termed as “emulsion-to-microemulsion”, “E→M”, systems.

### Experimental Section

**Materials.** Monomers 2-ethylhexyl acrylate (EHA) from Fluka, Switzerland, and acrylonitrile (AN) from Sisco Research Lab, Mumbai, India, were distilled under reduced pressure to remove inhibitor. Potassium persulfate (KPS) from Sisco Chemicals, Mumbai, India, and sodium dodecyl sulfate (SDS) from Qualigens, Mumbai, India, were used as received. All solvents were distilled before use, and double distilled deionized water was used throughout the work.

**Polymerization Procedure.** The single-phase microemulsion region at 30 and 70 °C was determined visually by titrating aqueous micellar solutions of SDS with monomer mixtures. Batch polymerization was carried out at different temperatures in a 250 mL five-neck reaction kettle equipped with a mechanical stirrer, nitrogen inlet, water condenser, and a thermometer. Compositions used for the polymerization are given in Table 1. Initiator concentrations used are in moles per liter of water. The

system was continuously stirred at 400 rpm and purged with nitrogen. For kinetic studies 5 mL of latex was withdrawn from the reaction kettle at regular time intervals and was added to the preweighed bottles containing methanol and hydroquinone. The conversion of monomer to polymer was determined gravimetrically.

The product was isolated by filtration after precipitation with large amount of methanol and dried under vacuum at 60 °C. Products of “emulsion-to-microemulsion” (“E→M”) microlatexes were precipitated with 1-butanol. Products were washed several times with hot water and methanol to remove surfactant and were reprecipitated from dimethyl sulfoxide using methanol to remove traces of unreacted monomers and poly(2-EHA). This product was further reprecipitated from methyl ethyl ketone using methanol to remove homopolymer poly(AN).

**Particle Size Distribution.** Latex particle size was determined by using a Brookhaven BI 90 particle size analyzer with a 500 W helium–neon laser of 623.8 nm wavelength at room temperature. Prior to the analysis the latexes were diluted with distilled deionized water to minimize the particle–particle interactions until the volume fractions of the particles were in the range of 0.01–0.1. An average hydrodynamic radius of latex particles ( $R_h$ ) was calculated from the intrinsic diffusion coefficient ( $D_0$ ) as

$$R_h = KT/6\pi\eta D_0$$

where  $\eta$  is the viscosity of the dispersion medium, i.e., water,  $K$  is the Boltzmann constant, and  $T$  is absolute temperature. The polydispersity index (PI), which is the variance of the size distribution, was obtained using the computer software provided with the instrument. Particle sizes were also checked by using a JEOL JEM 100 CX transmission electron microscope and uranyl acetate as a staining agent. At least 200 particles were counted for particle size determination. The number of the latex particles were calculated by using following equation

$$N = 6M_0X_m/\pi\rho D_n^3$$

where  $M_0$  is initial monomer concentration per mL,  $X_m$  is fractional conversion,  $\rho$  is the density of the polymer, and  $D_n$  is the diameter of the particle.

**Spectroscopic Analysis.** The IR spectrum of the purified copolymer was recorded on a Perkin-Elmer 16 PC IR spectrophotometer using solution-cast film.

**Thermal Analysis.** Glass transition temperatures of the copolymers synthesized in emulsion and microemulsion were determined at a 10 °C/min heating rate under nitrogen atmosphere on a modulated DSC 2910 T. A. instrument.

**Viscometric Studies.** Intrinsic viscosities of the purified copolymers were determined in dimethyl sulfoxide at 30 °C using an AVS 350 Schott Geratte auto viscometer.

### Results and Discussion

**Phase Diagram.** The phase diagrams of the three-component systems consisting of EHA-AN (1:1, w/w)/SDS/water at 30 and 70 °C exhibit relatively large o/w microemulsion regions than that of the EHA/SDS/water system due to partial solubility of AN in water (Figure 1). Samples from the one-phase region were clear and fluid, except those from very high surfactant concentrations were highly viscous (gels). A small extension arm “ABC”, very close to the water axis of one-phase region is the area from where turbid emulsion changes to a transparent microemulsion latex on polymerization. Region “ABC” exists in two phases before polymerization which can be transformed into o/w emulsions simply by agitation. Systems beyond the “ABC” region can only be polymerized to produce stable, transparent/translucent latexes by specific methods such as Winsor I like polymerization<sup>14</sup>

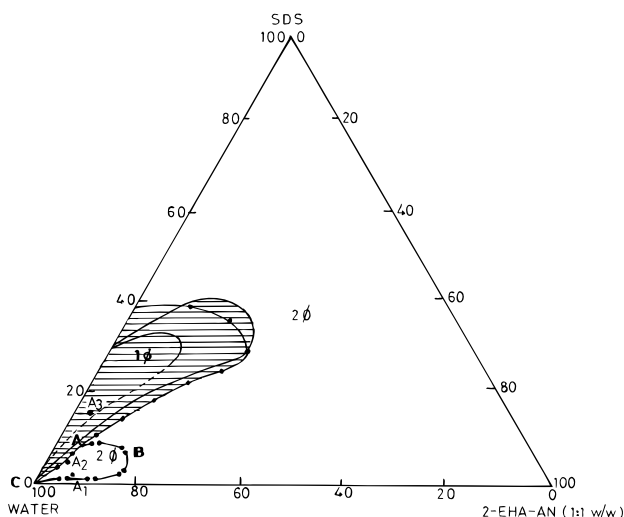
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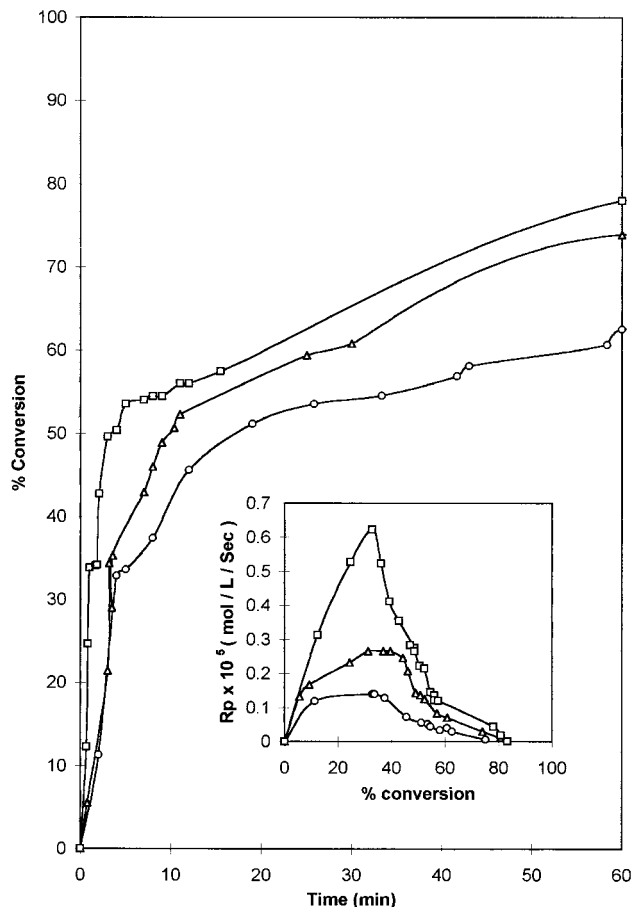
**Figure 1.** Phase diagram of ternary EHA-AN (1:1) (w/w)/SDS/water system: ●—●, at 30 °C; ○—○, at 70 °C; ●—●, after polymerization; - - -, EHA-AN (1:0) (w/w) at 30 °C. Shaded region 1 $\phi$ .

and a modified microemulsion polymerization process.<sup>15</sup> As in the present study emphasis is given on the partitioning of the monomer in different phases; in the systems used for the polymerization, the weight ratio of the water to monomer was kept constant at 16 while the surfactant concentration was increased from 1 to 15 wt % sweeping both emulsion and microemulsion regions (Table 1).

The IR spectrum of the purified copolymer exhibited sharp bands at 1720  $\text{cm}^{-1}$  for  $>\text{C}=\text{O}$  stretching, at 2876 and 2928  $\text{cm}^{-1}$  for  $-\text{C}-\text{H}$  stretching, and at 2242  $\text{cm}^{-1}$  for  $-\text{C}\equiv\text{N}$  stretching confirming copolymerization. Not much variation was observed in the glass transition temperatures of the purified copolymers synthesized in emulsion and microemulsion (9 and 12 °C, respectively) media.

**Copolymerization Kinetics.** Understanding of emulsion or microemulsion copolymerization requires considering mechanisms involving free radical formation, latex particle formation, propagation modes, and aqueous phase events which become more important if a partially water soluble monomer is used. The first reasonably accurate qualitative model of an emulsion polymerization system was given by Harkins<sup>16</sup> which was shortly thereafter quantified by Smith and Ewart.<sup>17</sup> The general kinetics of emulsion/microemulsion polymerization involves particle nucleation and its growth. The Smith–Ewart<sup>17</sup> (micellar nucleation), Roe<sup>18</sup> (homogeneous nucleation), and HUFT<sup>19</sup> (Hansen, Ugelstad, Fitch, and Tsai) theories give a general description of particle nucleation with HUFT theory recognizing three different loci for particle nucleation, i.e., micellar, homogeneous, and droplet nucleation.

**Effect of Initiator Concentration.** Kinetics of copolymerization of EHA-AN as a function of KPS concentration in the E→M system is illustrated in Figure 2. A similar trend of copolymerization was observed for true microemulsion, M, systems. Percentage conversion and rate of polymerization were found to increase with increase in initiator concentration in both systems (Table 2). This



**Figure 2.** Effect of KPS concentration on percentage conversion and rate of polymerization in E→M copolymerization of EHA-AN: EHA-AN (1:1) (w/w); temperature 80 °C; (○) 1 mM, (△) 2 mM, and (□) 4 mM.

can be readily explained from the generation of more free radicals per reaction locus per second. In all experiments the maximum % conversion (~90 to 95) was obtained within 4–5 h.

Maximum rate of polymerization,  $R_{p,\text{max}}$  for E→M polymerization occurred at 30–35% conversion (Figure 2), whereas for true microemulsion M polymerization it was located at ~40% conversion. Figure 2 indicates that the rate of polymerization abruptly increases initially and ~50% conversion is achieved during 5 min. However, after this the polymerization rate is slow and final conversion is achieved in 4 or 5 h. In principle this could be attributed to several possible factors since the rate of polymerization is given by

$$R_p = K_p [M]_p n N / N_A$$

where  $K_p$  is propagation rate constant,  $[M]_p$  is monomer concentration in particle,  $n$  is the average number of free radicals per reaction locus,  $N$  is the number of polymerization loci, and  $N_A$  is Avogadro's number. Initially the number of particles increases due to the formation of new particles via homogeneous nucleation, resulting in more polymerization loci. This could be one reason for the abrupt increase in the initial  $R_p$ . The monomer concentration in the polymer particles increases initially due to the diffusion of monomer from the large uninitiated monomer droplets leading to the increase in the rate of polymerization. However, after 50% conversion the large monomer droplets disappear and monomer concentration in the particles starts decreasing. As a result, the

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**Table 2. Variation of Kinetic and Colloidal Parameters in 2-Ethylhexyl Acrylate–Acrylonitrile Copolymerization under Different Experimental Conditions<sup>a</sup>**

parameter	$(R_p)_{\max} \times 10^5$ (mol/(L/s))		$R_h$ (nm)		PI		$(N_p) \times 10^{-16}$ per mL		$(R_{pp}) \times 10^{23}$ (mol/(particle/s))		intrinsic viscosity (g/dL)	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
KPS (mM)												
1	1.7	0.6	20	36	0.118	0.132	2.2	0.3	0.8	2.2	0.20	0.35
2	2.8	1.3	18	33	0.123	0.147	2.9	0.4	1.0	3.3	0.22	0.39
4	6.2	5.4	17	32	0.129	0.165	3.6	0.5	1.7	10.7	0.24	0.44
reaction temperature (°C)												
70	1.2	0.7	20	40	0.123	0.09	2.1	0.2	0.6	3.5	0.18	0.11
75	3.3	2.5	19	36	0.140	0.118	2.5	0.3	1.3	8.3	0.19	0.20
80	6.2	5.4	17	32	0.129	0.165	3.6	0.5	1.7	10.7	0.24	0.44
monomer-feed, EHA-AN (w/w)												
1:0	10.6	8.6	21	33	0.187	0.119	0.9	0.2	11.7	43.2		
3:1	9.8	6.3	15	31	0.166	0.137	3.1	0.3	3.1	20.9	0.18	0.34
2:1	8.4	5.8	22	40	0.144	0.149	1.3	0.2	6.4	28.9	0.20	0.37
1:1	6.2	5.4	17	32	0.129	0.165	3.6	0.5	1.7	10.7	0.24	0.44
[SDS] (mol/L)												
0.04	6.2		17		0.129		3.6		1.7		0.24	
0.13	5.7		19.5		0.142		2.4		2.4		0.26	
0.65		5.4		32		0.165		0.5		10.7		0.44

<sup>a</sup> Key: (a) E→M polymerization, A<sub>1</sub> composition. (b) M polymerization, A<sub>3</sub> composition.

polymerization rate falls.  $R_{p\max}$  was observed to be proportional to the 0.68 and 0.76 powers of [KPS] in M and E→M polymerization, respectively, indicating that unimolecular termination mechanism is operative in these reactions. This may be due to the incompatibility of the polymer and monomer which can shift the locus of polymerization from particle core to the particle/continuous phase interfacial region.<sup>20</sup> In microemulsion systems, with increase in the initiator concentration more particles are formed due to increased flux of the primary free radicals into large number of the microemulsion droplets. Due to more number of the particles, the exit rate of the growing radicals from the particles also increases. Though desorbed radicals can reenter into particles or microemulsion droplets, the reaction order >0.5 indicates that a first-order radical loss process is operative.

The  $R_p$  was faster for the E→M polymerization than for the M polymerization. Roy and Devi<sup>6</sup> have observed a similar trend in the copolymerization of methyl methacrylate and butyl acrylate. A faster rate of emulsion polymerization of methyl methacrylate than microemulsion polymerization is also reported by Gan et al.<sup>21</sup> The high concentration of surfactant used for the stabilization of microemulsion droplet results in the formation of a charged layer around it, retarding the entry of charged oligomeric radicals in microemulsion droplets. As a result the radical capture efficiency decreases. However, in emulsion polymerization the probability of reaction between the oligomeric radicals and monomer molecules in the aqueous phase and between the oligomeric radicals and monomer in the newly formed particles via homogeneous nucleation is very high. This can be the main reason for the higher emulsion polymerization rates.

The rate of polymerization per particle,  $R_{pp}$ , can be considered as a semiquantitative equivalent of the average number of the radicals per reaction locus and was calculated according to the approach suggested by Capek et al.<sup>7</sup> From Table 2 it is evident that increase in initiator concentration results in increase in radical concentration (or  $R_{pp}$ ) at reaction locus, due to more free radicals generated per second per unit volume of the aqueous phase.

**Table 3. Variation in Particle Size ( $R_h$ ) with Percentage Conversion in EHA-AN (1:1, w/w) E→M Copolymerization with 4 mM KPS, at 70 °C**

% conversion	$R_h$ (nm)	% conversion	$R_h$ (nm)
0		60	20
20	216	90	20
45	38		

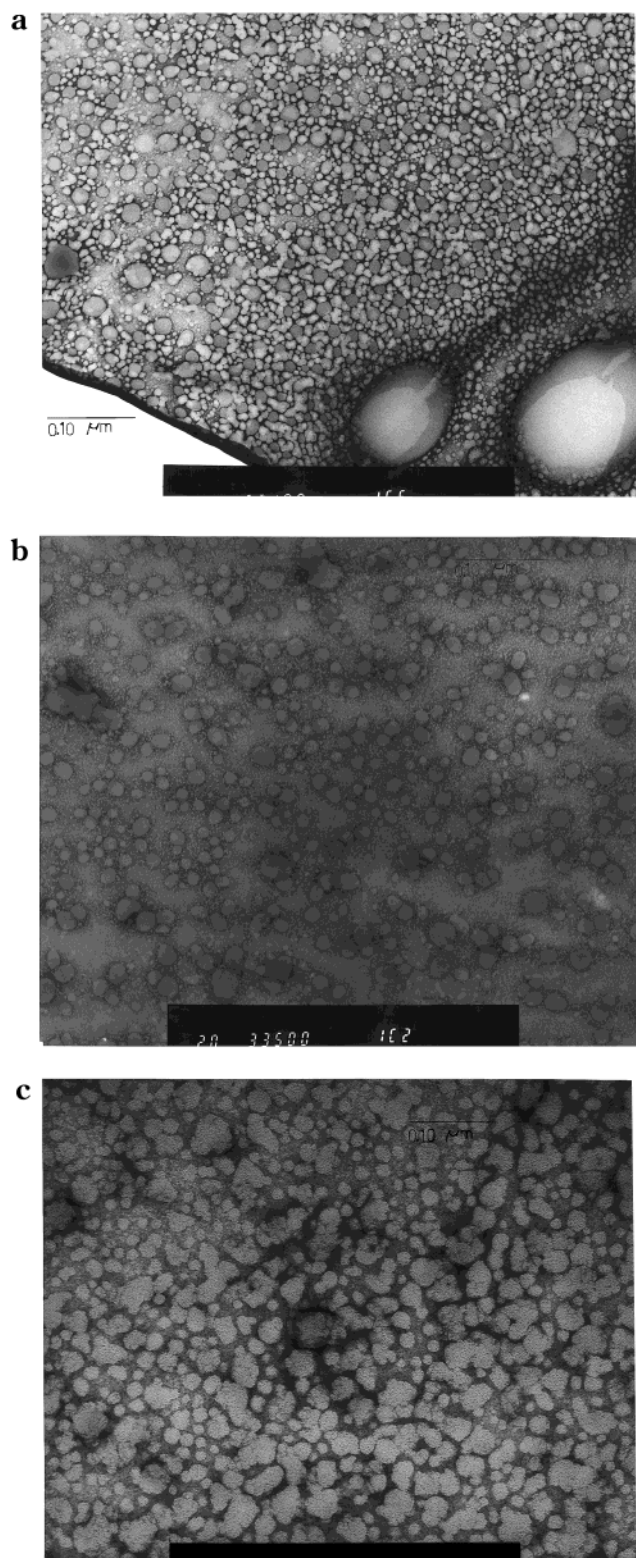
Particle size was found to decrease with increase in initiator concentration in both the systems (Table 2). In emulsion polymerization, after the nucleation stage (interval I) all monomer swollen micelles disappear and in interval II particles continue to grow in size due to the diffusion of monomer from the monomer droplets through aqueous phase. However, in E→M systems particle size was found to decrease with increase in percentage conversion. Results given in Table 3 show a drastic decrease in particle size at around 30% conversion, when emulsion turns into translucent latex. Two different types of particles formed from either micellar or homogeneous nucleation with very broad particle size distribution are clearly seen in the transmission electron micrograph (Figure 3a) of the E→M system (A<sub>1</sub>) at around ~25% conversion just before the sample turned translucent. However, after transition (Figure 3b) or in a true M (A<sub>3</sub>) system (Figure 3c) the particle size distribution was observed to be narrower. The following four phenomena are assumed to be responsible for the observed decrease in particle size: (i) the density difference between the copolymer (1.121 g/mL) and monomers 2-ethylhexyl acrylate (0.886 g/mL) and acrylonitrile (0.806 g/mL); (ii) consumption of interfacial monomer 2-ethylhexyl acrylate and faster diffusion of monomer from reservoirs; (iii) engulfing of the points A<sub>2</sub> and A<sub>3</sub> by the local heat production at the locus of polymerization at initial stages of polymerization as suggested by Hernandez-Barajas and Hunkeler<sup>22</sup> for the nonisothermal polymerizations in hybrid inverse emulsion/inverse microemulsion; (iv) monomer droplet nucleation at lower conversions.

We feel the first two factors contribute more significantly: because the higher density of the copolymer corresponds to lower specific volume and can partly explain the continuous shrinking of the droplets, though it is not sufficient to explain the very steep decrease observed at

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**Figure 3.** Transmission electron micrographs of poly(EHA-co-AN) copolymer latexes: EHA-AN (1:1) (w/w), temperature 80 °C, KPS concentration 4 mM; (a) E→M system at ~25% conversion just before turning transparent; (b) E→M system at ~90% conversion; (c) M system at ~90% conversion.

low conversions. The coemulsifier role of 2-ethylhexyl acrylate proposed by Capek and Juranicova<sup>23</sup> can also be used to explain shrinking of polymer particles at lower conversions. The hydrophobic chains of SDS make an

appreciable volume of the micelles<sup>7</sup> and most of the monomer 2-ethylhexyl acrylate resides at the droplet–water interface. As a water-soluble initiator is employed, the interfacial monomer is rapidly consumed at lower conversions by the diffusing oligomers from the aqueous phase. The absence of the monomer at the interface lowers the optimal HLB required for the stabilization of the particle;<sup>24</sup> hence monomer from the stabilized monomer droplets diffuses at a faster rate to the growing particles to compensate for the used coemulsifier 2-ethylhexyl acrylate. This hypothesis is further supported by the failure to obtain transparent/translucent latex by using an oil-soluble initiator 2,2-azobis(isobutyronitrile). In the case of 2,2-azobis(isobutyronitrile), the interface as a locus of polymerization is less likely. Furthermore phase separation above 50 wt % of acrylonitrile in monomer feed indicates that a homogeneous nucleation mechanism dominates at higher acrylonitrile concentration, with more oligomers rather than diffusing to the interface, precipitate in aqueous phase and form bigger particles which are barely protected by the small amount of surfactant available. An important corollary of the proposed explanation is that in such systems the locus of propagation is the **particle/water interface**. However, on the basis of the arguments presented, the mechanism of the polymerization in E→M systems can be assumed similar to the classical emulsion polymerization.<sup>16</sup>

Droplet nucleation is reported in miniemulsion systems<sup>25</sup> which requires intensive mechanization or ultrasound treatment to achieve fine droplets of 1 or 2 orders of magnitude larger than microemulsion droplets. As we have carried out the experiments at 400 rpm the presence of such fine droplets is less likely. Hence, we rule out this possibility of nucleation in the systems under study.

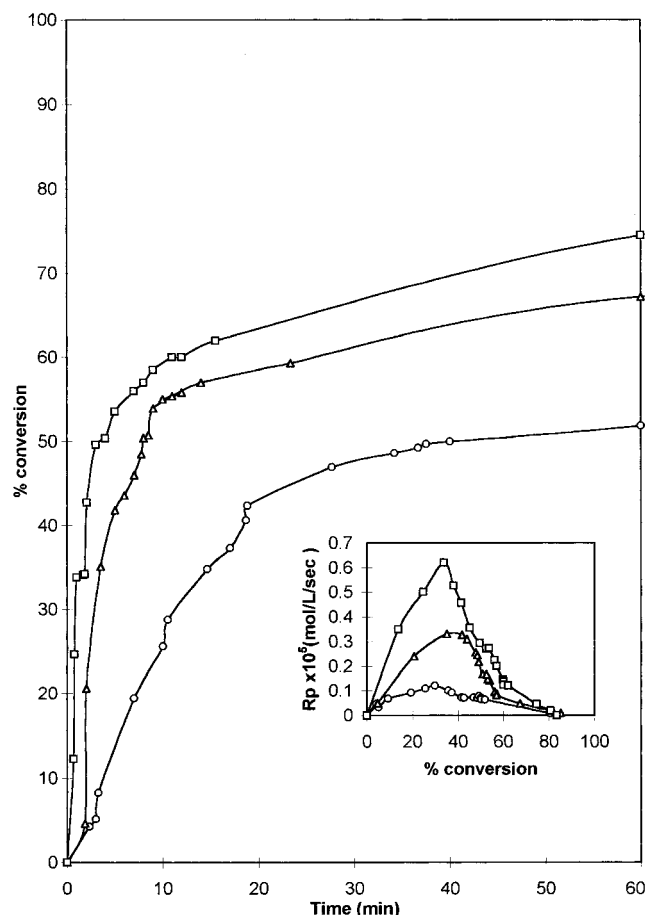
From phase diagram Figure 1 it is clear that the extension of a one-phase o/w microemulsion region to engulf the experimental point A<sub>3</sub> by local heat production at polymerization loci is improbable because this point is far away from the one-phase microemulsion region at 30 as well as 70 °C. However, for the point A<sub>2</sub>, which lies near/on the microemulsion/emulsion phase boundary, the engulfing of this point by the local heat production at polymerization locus can be expected.

**Effect of Reaction Temperature.** The effect of temperature on the copolymerization kinetics was studied by using 4 mM potassium persulfate. The variation in percentage conversion and rate of polymerization with reaction temperature in the E→M system is shown in Figure 4. From Table 2 it can be observed that  $R_p$  was higher for the E→M system than for the M polymerization. Both percentage conversion and rate of polymerization were found to increase with increase in the reaction temperature. With increase in the reaction temperature the number of free radicals generated per second in aqueous phase will increase leading to high polymerization rates, rate of polymerization per particle ( $R_{pp}$ ), and the final number of latex particles ( $N_p$ ) irrespective of the type of the polymerization. The overall energy of activation  $\Delta E$  was calculated using the Arrhenius equation and was found to be 32 kJ/mol for E→M and 46 kJ/mol for M polymerization, respectively. Smaller values of activation energy for the E→M system also favors faster rate of polymerization in these systems. The observed small  $\Delta E$  value for the E→M polymerization can be explained on the basis of the lower energy barrier for the entry of

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**Figure 4.** Effect of temperature on percentage conversion and rate of polymerization in E→M copolymerization of EHA-AN: EHA-AN (1:1) (w/w); KPS concentration 4 mM; (○) 70 °C, (△) 75 °C, and (□) 80 °C.

radicals into monomer swollen micelles. Moreover, the high probability of reaction of oligomeric radicals with the new particles (which are stabilized with few surfactant molecules) formed via homogeneous nucleation favors growth events, whereas due to the high concentration of surfactant used, the entry of the primary radicals in the microemulsion droplets is somewhat restricted due to high  $\xi$ -potential of the condensed interfacial layer of the droplets.<sup>26</sup> A small increase in the polydispersity index was observed with increase in reaction temperature (Table 2).

**Effect of Acrylonitrile Concentration.** With increase in the acrylonitrile concentration in the monomer feed, percentage conversion, rate of polymerization, and final number of latex particles were found to decrease in both E→M and M types of polymerizations (Table 2). Marginal increase in the polydispersity index was observed with increase in the acrylonitrile concentration in the monomer-feed in M type of polymerization whereas the opposite trend was observed in the E→M type polymerization. Acrylonitrile concentration above 50 wt % in monomer-feed resulted in complete phase separation during either type of polymerization.  $R_{pp}$  was found to decrease with increase in AN concentration in monomer-feed in both types of polymerizations, whereas the opposite trend was observed for intrinsic viscosities (Table 2).

In the microemulsion copolymerization of styrene–acrylonitrile, the distribution coefficient of acrylonitrile between aqueous phase and microemulsion was observed to be 1.81, assuming that the water solubility of styrene is negligible. We have further observed that 56% acrylonitrile of initial monomer feed [styrene/acrylonitrile (1/1, mole)] resides in microemulsion droplets whereas 44% resides in aqueous phase.<sup>13</sup> As the water solubility of 2-ethylhexyl acrylate and that of styrene are comparable, partitioning behavior of acrylonitrile in the present study was assumed to be similar to that in the styrene–acrylonitrile microemulsion copolymerization. In the absence of acrylonitrile, the micellar nucleation mechanism is predominant irrespective of the type of polymerization due to low solubility of 2-EHA (0.02 wt % at 25 °C) in water.<sup>23,27</sup> As acrylonitrile (water solubility 7.5 wt % at 25 °C) partitions between micelles and aqueous phase, a little addition of acrylonitrile results initially in a large number of particles formed due to homogeneous nucleation resulting in smaller particle size but higher polydispersity index (Table 2). Significant decrease in the  $R_{pp}$  after addition of acrylonitrile in monomer feed (Table 2) supports our hypothesis of predominance of micellar nucleation mechanism in the M type of polymerization. Similar results have been reported for microemulsion polymerization of butylacrylate–acrylonitrile.<sup>7,28</sup> With further increase in the acrylonitrile concentration in monomer feed, the homogeneous nucleation mechanism prevails even in the M polymerization irrespective of the large number of micelles present, leading to more polydisperse latexes. Hence aqueous phase events dominate the polymerization process in either type of system.

**Effect of Surfactant Concentration.** To understand the transition behavior in E→M systems during polymerization, another composition, A<sub>2</sub> (Figure 1), just on the one-phase region boundary line was selected for polymerization. With increase in the SDS concentration, decrease in percentage conversion, rate of polymerization, final number of latex particles, and increase in particle size were observed (Figure 4, Table 2). Though this is unusual, similar results have been reported by Gan et al.<sup>21</sup> for the polymerization of methyl methacrylate in emulsion and microemulsion media. When  $\log R_{pmax}$  from three different systems covering emulsion to microemulsion was plotted against  $\log [SDS]$  mol/L, it was found to follow  $-0.05$  power of the surfactant concentration.  $R_{pp}$  and intrinsic viscosity values were found to increase with increase in [SDS] irrespective of polymerization type (Table 2). The intrinsic viscosity values suggest that the copolymers from the M polymerization were of higher molecular weights than those from the E→M polymerization as the number of polymer chains per particle in microemulsion polymerization is reported to be less, i.e., 1–5 compared to those in emulsion polymerization. In microemulsions, during polymerization small microemulsion droplets of uniform size are always in excess, due to the augmented level of emulsifier and lower monomer concentration with respect to emulsions. These microemulsion droplets preferentially capture the primary free radicals formed in the continuous phase, due their high interfacial area compared to nucleated particles. This leads to the process of continuous nucleation with each particle formed in single step and, hence, a low number of polymer chains per particle, whereas in the emulsion polymerization the number of polymer chains per particle can go up to hundreds.

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### Conclusion

Transparent/translucent latexes of poly(2-EHA-*co*-AN) can be prepared with high weight ratio of polymer to surfactant (~5.8:1) by E→M polymerization. Droplet nucleation along with micellar and homogeneous nucleation is expected in E→M systems. A unimolecular termination mechanism was found operative in these systems. With increase in SDS concentration, the decrease in the rate of polymerization and increase in the particle size were observed. Acrylonitrile solubility in

water was found to play an important role in copolymerization.

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