Some Observations on the Emulsion Polymerization of Styrene in the Aqueous Phase at 50° & Low Monomer Concentration

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The kinetics of emulsion polymerization of styrene in the aqueous phase at 50° with $K_2S_2O_8$ as initiator and sodium lauryl sulphate as emulsifier and at low concentration of the monomer (below 10% v/v) has been investigated. It has been found that some of the kinetic parameters in the steady state rate period, viz. order of the initiator (0.35), order of the emulsifier (0.67), etc., are apparently consistent with the theory of Smith and Ewart for the emulsion polymerization of styrene at high monomer concentration in the aqueous media. The number of latex particles (N) per ml of the aqueous phase and the viscosity average molecular weight ($\bar{M}_v$) of the polymers are not constant in the steady state rate period, i.e. from 15 to 60% conversion approximately, as required by the Smith and Ewart theory. It has been observed that the number of latex particles per ml of the aqueous phase at low monomer concentration (5% by volume) increases continuously up to 35% conversion and thereafter remains approximately constant within experimental error. The viscosity average molecular weight, on the other hand, increases with conversion, attains a maximum at about 30 to 40% conversion, and then decreases with the further increase of conversion. Initiator injection and soap injection late in a run in the constant rate period are found to increase the rate of polymerization, contrary to the theories of Smith and Ewart, and of Gardon. N in the steady state rate period increases whereas $\bar{M}_v$ decreases in the initiator perturbation experiment, but increases in the soap injection experiment. It has been suggested that the existence of a constant rate in the yield-time curve does not give guarantee for the occurrence of the steady state rate in the system. It may well be that the emulsion polymerization of styrene under the experimental conditions is a case of non-steady state kinetics from the start to finish, and the Smith and Ewart theory gives only a qualitative description of a very complex process of emulsion polymerization of vinyl monomers.

THE emulsion polymerization of styrene in the aqueous phase has been described by Harkins[1], Smith and Ewart[2-4], and others[5-12]. The kinetic model of Smith and Ewart is based on the following assumptions:

(i) No initiation occurs in the oil phase (i.e. in the monomer droplets) when the initiator is water soluble. Initiation occurs only inside the soap micelles loaded with monomer.

(ii) Termination is always due to the primary radicals, and is instantaneous as soon as an oligomeric radical enters a growing polymer particle, and the rate of termination is independent of particle size, volume or viscosity of the monomer swollen polymer particles.

(iii) Sustained coexistence of radicals in a particle is not allowed.

(iv) Once a constant number of latex particle is produced at the end of the first phase of polymerization when micelles disappear, no new latex particles are allowed to form.

(v) A steady state rate is then assumed to prevail in the system up to about 50 to 60% conversion, i.e. in the second phase of polymerization.

(vi) The rate of generation of primary radicals in the aqueous medium is equal to the rate of capture of the primary radicals by the latex particles,

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i.e. the rate of entry of primary radicals into the latex particles, and this is independent of the viscosity of the medium during the course of polymerization. The side reactions of the primary radicals in the aqueous media are ignored.

Some of these assumptions were tested experimentally by Smith and Ewart and also by others[4-12], but the reports are conflicting and sometimes misleading due to large experimental errors. Besides, the emulsion polymerization of styrene had been carried out by the previous workers using higher concentration of monomer (i.e. 35 to 50% styrene). We therefore undertook this work to reinvestigate the emulsion polymerization of styrene at low monomer concentration (5 to 10%, v/v), and to test the quantitative validity of the Smith and Ewart theory (case II). In this paper we report the results of the emulsion polymerization of styrene obtained in some 500 experiments in the aqueous media at 50°C in nitrogen atmosphere, using sodium lauryl sulphate as the emulsifier and potasium persulphate as the initiator.

Materials and Methods

All the reagents were of BDH (Analar) grade. Monomer was purified, dried and fractionated under reduced pressure as described by Robb[11]. For every run, freshly distilled monomer was used.

Polymerization was studied by a dilatometer as used by Robb[11] and also by the gravimetric methods due to Palit and coworkers[13,14]. The polymerization was carried out at $50° \pm 0.1°C$. Intrinsic viscosity (η) of polymers was determined at $30°$, and the viscosity average molecular weights of polymers were determined from Eq. (1)

$$\eta = K.\bar{M}_v^\alpha \qquad \qquad \ldots (1)$$

using toluene as solvent and taking $K = 1.60 \times 10^{-4}$, and $\alpha = 0.69$ as suggested by Mark *et al.*[15].

Number of latex particles per unit volume of the aqueous phase was determined by the soap titration method[16-18]. The shape and size of the latex particles were determined by taking their electron micrograph in an electron microscope (Hitachi HS/7S-medium resolution type, 90,000 magnification).

The variation of pH of the media during polymerization was recorded using a Beckman pH meter. The variation of viscosity of the media was recorded with a modified Ostwald viscometer.

Results

To check the reproducibility of the results, a polymerization experiment [recipe: $K_2S_2O_8$ (0.1%) + styrene (5%, v/v) + soap (0.6%) + water (95%, v/v) doubly distilled] was repeated 10 times. In Fig. 1, per cent yield versus time is shown with the standard error. It has been found that the results are 100% reproducible if the induction period is exactly identical from run to run. The standard error shown in Fig. 1 is mainly due to the non-reproducibility of the induction period although each and e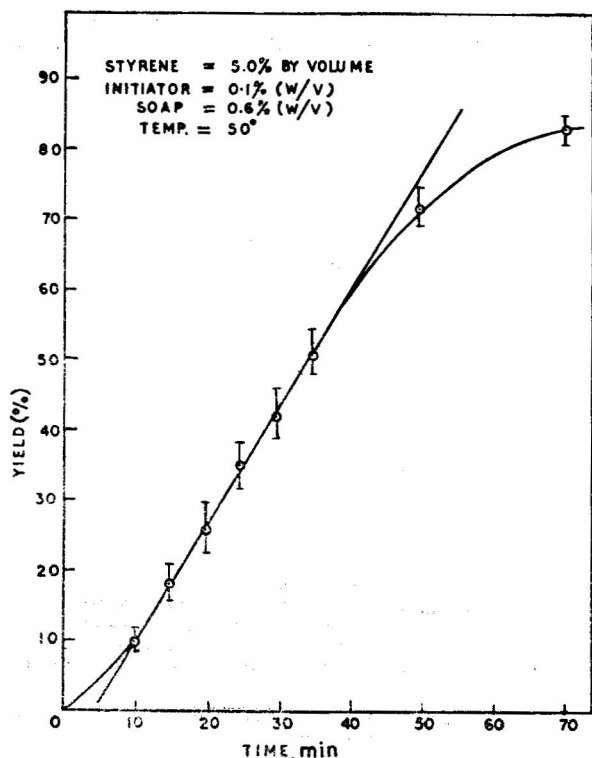very run was carried out under exactly identical conditions. Fig. 2 shows the variation of number of particles per ml of the aqueous phase with conversion or time. Fig. 2 shows also the variation of particle size with conversion.

The reaction orders with respect to initiator and the soap were determined from the constant rate period data. The results are summarized in Table 1, and some typical order plots are shown in Fig. 3. The kinetic parameters are in fair agreement with those of Smith and Ewart.
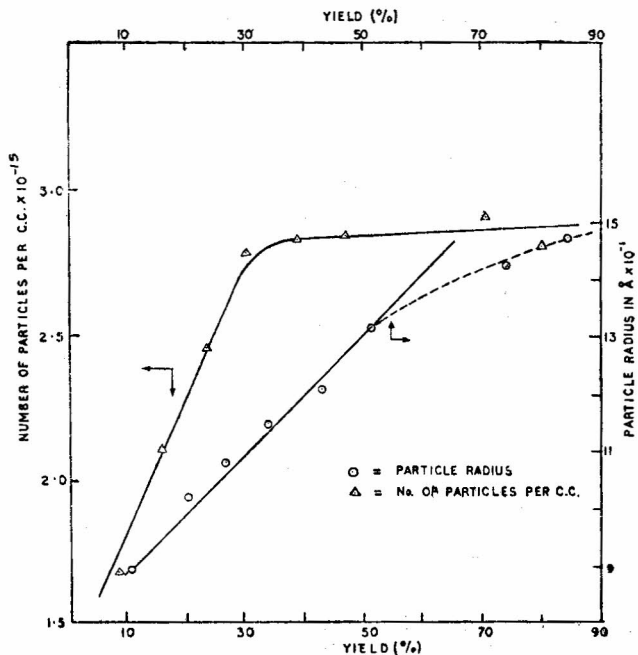

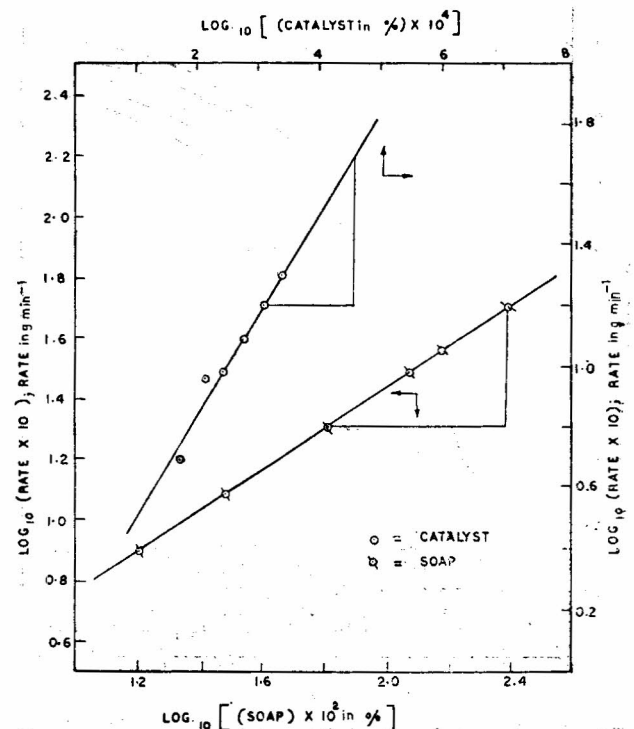Fig. 2 — Variation of particle size and of number of particles with conversion

Fig. 1 — Per cent yield versus time curve

Fig. 3 — Order plots with respect to (i) initiator and (ii) soap

TABLE 1 — REACTION ORDER WITH RESPECT TO
INITIATOR AND SOAP

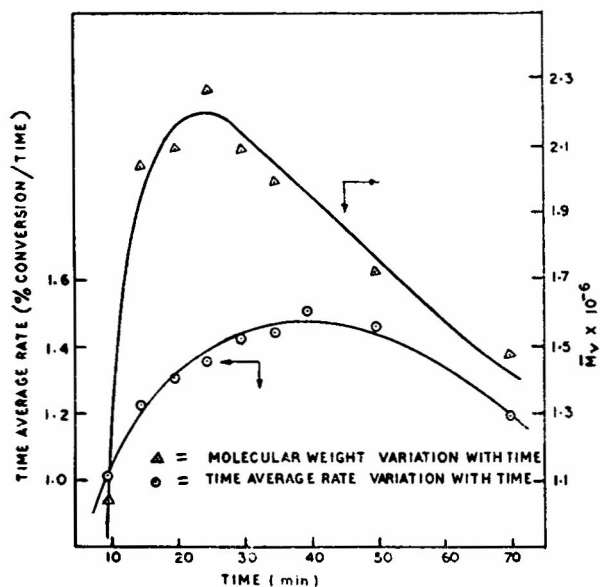|	Order of soap	Order of initiator
	(by least square method)	
Rate determined dilatometrically	0·73±0·02	0·35±0·03
Rate determined gravimetrically	0·67±0·02	0·35±0·05

Fig. 4 — Variation of viscosity-average molecular weight and time-average rate with time in a given run
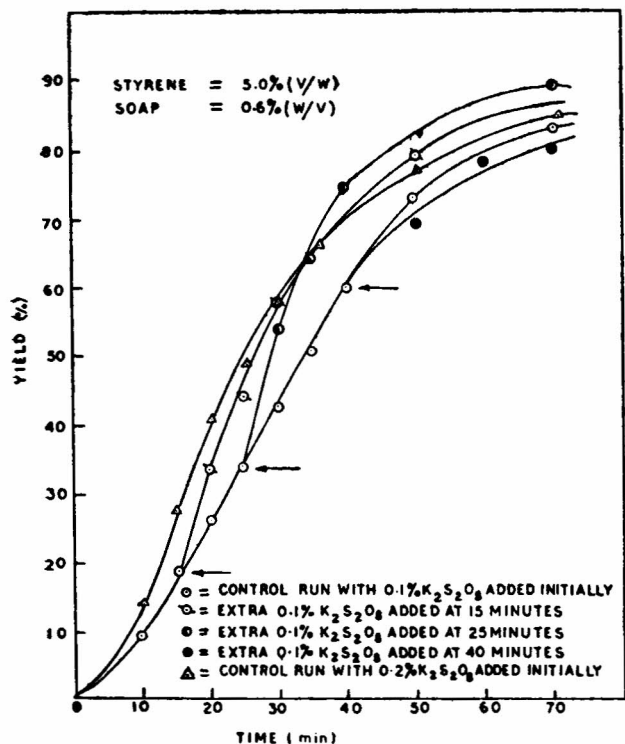

Fig. 5 — Initiator perturbation experiment [Yield-time curves when different amounts of initiator were injected late in a run]

Fig. 4 shows the variation of $\bar{M}_v$ with time or conversion. Fig. 5 shows the results when the initiator was injected late in a run. The variation of molecular weight of polymers in the initiator perturbation experiment is shown in Table 2. Fig. 6 shows the effect of soap when injected in the steady state rate period, and the variation of molecular weight of polymers with soap concentration is shown in Table 3. When the rate of polymerization increases due to the injection of extra soap or initiator in a given run, the number of latex particles per ml of the aqueous phase was also found to increase[37].

Discussion

From Fig. 1 it is evident that polymerization occurs (i) at an accelerated rate initially (<10% conversion), (ii) at a constant rate from 10 to 60% conversion and (iii) at a decelerated rate from 60 to 100% conversion approximately. Smith and Ewart assumed that this constant rate was the steady state rate, and deduced that the rate of polymerization (R_p) in the steady state could be written as[5]

$$R_p = (\tfrac{1}{2})k_p[M]N$$

where k_p is the propagation rate constant, $[M]$ is the monomer concentration in the latex particles, and N is the number of latex particles per ml of aqueous phase. It was assumed that at any instant during the second phase of polymerization, the average number of radicals per particle was 0·5. The above Smith-Ewart equation predicts a constant value of N in the second phase of polymerization. The analytical data presented here, however, show that N increases in a given run up to about 35% conversion and then remains constant within experimental error (Fig. 2), although the polymerization occurs at a constant rate. It
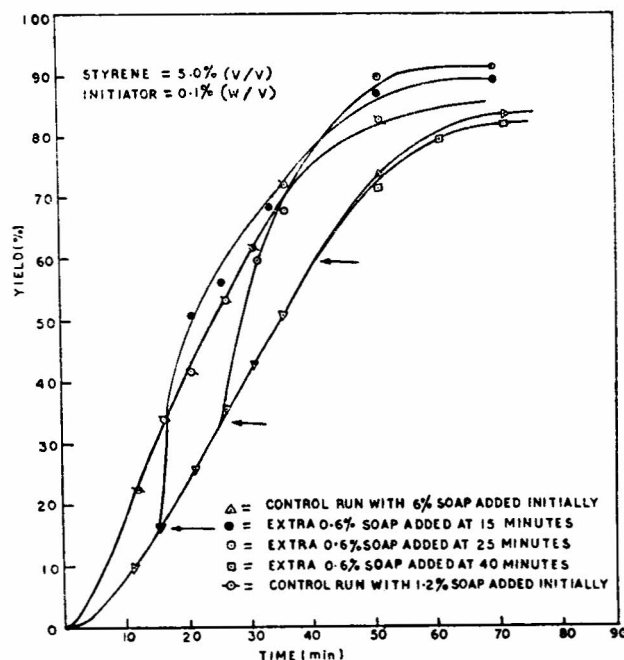

Fig. 6 — Soap perturbation experiment [Yield-time curves when different amounts of soap were injected late in a run]

TABLE 2 — VARIATION OF MOLECULAR WEIGHT IN THE INITIATOR PERTURBATION EXPERIMENT

[Recipe = styrene 5% (v/v) and soap 0.6% (w/v)]

Time (min)	Control run with 0.1% initiator		Extra initiator added at 18.2% conversion		Extra initiator added at 33.5% conversion		Initiator injected at 60% conversion		Control run with 0.2% initiator added initially	
	X	$\bar{M}_v \times 10^{-6}$	X	$\bar{M}_v \times 10^{-6}$	X	$\bar{M}_v \times 10^{-6}$	X	$\bar{M}_v \times 10^{-6}$	X	$\bar{M}_v \times 10^{-6}$
10.0	9.83	1.13	—	—	—	—	—	—	14.50	—
15.0	18.20	2.14	18.20	*	—	—	—	—	27.50	—
20.0	25.97	2.19	33.24	1.75	—	—	—	—	40.50	1.63
25.0	33.50	2.37	43.78	1.81	33.50	*	—	—	49.00	—
30.0	42.36	2.19	57.63	1.60	53.77	2.20	—	—	57.00	1.58
35.0	60.25	2.09	60.37	1.37	63.30	1.59	—	—	65.00	1.48
40.0	60.00	—	—	—	74.81	1.50	60.00	*	—	—
50.0	73.40	1.83	76.80	—	—	—	67.00	1.50	77.00	1.11
70.0	83.50	1.57	89.63	1.21	88.00	1.42	80.00	1.20	85.00	—

X = % conversion at that time.
*Initiator (0.1%) injected here.

TABLE 3 — VARIATION OF MOLECULAR WEIGHT IN THE SOAP PERTURBATION EXPERIMENT

[Recipe = styrene 5% (v/v) and initiator 0.1% (w/v)]

Time (min)	Control run with 0.6% soap		Soap injected at 18.2% conversion		Soap injected at 33.5% conversion		Soap injected at 60.0% conversion		Control run with 1.2% soap added initially	
	X	$\bar{M}_v \times 10^{-6}$	X	$\bar{M}_v \times 10^{-6}$	X	$\bar{M}_v \times 10^{-6}$	X	$\bar{M}_v \times 10^{-6}$	X	$\bar{M}_v \times 10^{-6}$
10.0	9.83	1.13	—	—	—	—	—	—	21.06	3.30
15.0	18.20	2.14	18.20	*	—	—	—	—	33.13	3.80
20.0	25.97	2.19	49.70	2.42	—	—	—	—	40.39	3.90
25.0	33.50	2.37	55.35	2.85	33.50	*	—	—	55.05	2.52
30.0	42.36	2.19	58.29	3.78	59.30	3.43	—	—	58.20	2.70
35.0	50.25	2.09	68.31	3.58	67.42	3.33	—	—	72.64	2.07
40.0	60.00	—	—	—	—	—	60.00	*	—	—
50.0	73.40	1.83	—	—	89.68	2.79	70.43	4.32	75.00	2.04
70.0	83.50	1.57	—	—	90.68	2.88	81.41	3.92	90.00	0.88

X = % conversion at that time.
*Soap (0.6%) injected here.

is evident that R_p will remain constant as long as k_p, $[M]$ and N remain constant. The constant value of R_p will also be maintained if N increases and $[M]$ decreases with time or conversion. Smith and Ewart assumed a thermodynamic equilibrium between the monomer swollen polymer particles and the emulsified monomer droplets, so that $[M]$ would remain constant during polymerization. Some experimental supports were provided for this assumption by carrying out experiments in the static condition[5,20-26], but the work of William *et al.*[9] showed that $[M]$ decreased continuously even in the constant rate period of polymerization.

The apparently constant value of R_p can also be explained by considering the increase of viscosity of the medium during polymerization (after 80% conversion, it increased by 27%). If it is assumed that as long as emulsified oil droplets exist in the system (i.e. up to 30% conversion according to William *et al.*[9], and up to the end of the second phase of polymerization, i.e. 50 to 60% conversion according to Gardon[26] and Billmeyer[27]), there exists thermodynamic equilibrium between the latex particles and the emulsified oil droplets, so that

$[M]$ will remain constant. Since the viscosity of the media increases gradually during polymerization, it may well be that the rate of entry (ρ) of a primary radical from the aqueous phase into the latex particle is gradually slowed down with conversion. This will not lead to the decrease of the polymerization rate with conversion according to the theory of Smith and Ewart, but will lead to the increase of molecular weight and of degree of polymerization, because the average lifetime of a growing macroradical in the latex particle will be increased with the decrease of ρ. If, however, the entry of a primary radical into a growing latex particle does not terminate the growing macroradical, but initiate a new chain[31], the rate of polymerization should increase continuously with time because the average number of radicals per particle (Q) will increase with time or conversion or particle size, if $[M]$ does not alter. This is evident from Gardon's equation[12], i.e.

$$(dP/dt) = (k_p/N_A)(d_m/d_p)\phi_m N Q$$

where P = volume of polymer formed per unit volume water in time t, N_A = Avogadro number, d_m = den-

sity of monomer, d_p=density of polymer, and ϕ_m=monomer volume fraction in the latex particle.

Thus the increase of viscosity will affect P, which in turn will affect Q. If Q decreases, rate will decrease provided all other parameters do not alter. If however, Q decreases and N (number of latex particle per ml of aq. phase) increases, the overall rate of polymerization may, however, remain constant within experimental error. It should be remembered that when more than one radical propagates in a latex particle, the thermodynamic equilibrium between the emulsified monomer droplets and the latex particles may be disturbed and so ϕ_m or $[M]$ will not remain constant during polymerization. In any case the system is very complicated and cannot be explained quantitatively by the model of Smith and Ewart.

The number average degree of polymerization ($\bar{X}_n$) is given by $\bar{X}_n=(2R_p/R_i)$ or $(2R_p/P)$, where R_i is the rate of initiation, and $P=2k_d$ $[I]$, is the rate of generation of primary radicals in the aqueous phase. The amount of initiator decomposed after 70 min under the experimental conditions was estimated[28] to be only 4% and so $[I]$ will remain essentially constant during the period of polymerization. Thus $\bar{X}_n$ and hence the molecular weight should remain constant in the constant rate period. Since the molecular weight increases with conversion (Fig. 4) (attaining a maximum value at 30-40% conversion) or with the increase of particle size or volume, it seems that the termination reaction is not instantaneous as pictured by Smith and Ewart (Case II). If the entry of a primary radical into a growing latex particle does not stop the growing chain instantaneously, then sustained coexistence of radicals in a particle will be possible. This will increase the polymerization rate and the average lifetime of a macroradical, and decrease the termination rate. Therefore, as the particle size or volume increases, the termination inside the particles may be of two types: (i) between two growing macroradicals, and (ii) between a macroradical and a primary radical. If the termination rate decreases, obviously molecular weight will increase with conversion. The fall of average molecular weight at high conversion (>35-40%) is presumably due to the formation of short chain polymers, since the concentration of monomer at the reaction site decreases steadily after 60% conversion.

It is also expected that when the Norrish-Smith[24] and the Trommsdroff effect[29] will be operating inside the latex particles, termination will be diffusion-controlled. As the concentration of polymer inside the latex increases with conversion (particularly in the stage III of Smith and Ewart), the viscosity inside the latex particles will also increase, and this will decrease the termination rate (and hence k_t), and so the molecular weight is expected to increase with conversion, provided k_p does not decrease[9,10,30,31] The ratio (k_t/k_p) will actually control the molecular weight. Thus when termination will be diffusion-controlled, termination rate will decrease which will favour formation of polymers of high molecular weight, but the propagation

rate (and hence k_p) falls so rapidly due to the rapid fall of [monomer] at the reaction site that the molecular weight of polymers actually decreases in spite of gel effect (Fig. 4). The rise and fall of the molecular weight of polymers in a given run have been found to run parallel approximately with those of the time average rate of polymerization in the same run.

Number of latex particles (N) — It has been found that N increases approximately linearly up to 35 to 40% conversion in a given run, and thereafter remains constant within the experimental error, and this observation is in agreement with the findings of Robb[11]. A latex sample was prepared by using the recipe of Robb[11]. N was determined and compared with that of Robb under identical experimental conditions. If all soap molecules (or soap ions) above c.m.c. form micelles, and each micelle contains 50 soap molecules[12,30], then there should be 2.64×10^{17} micelles per ml of the aqueous phase when the initial soap concentration is 2.19×10^{-2} (mole/litre). C.m.c. value of NaLS under the experimental conditions was found to be very small by the conductivity method. If every micelle gives birth to a latex particle during polymerization, the maximum number of latex particles per ml of the aqueous phase would be 2.64×10^{17}. By the soap titration technique[16-18], the value of N was found to be 6.29×10^{15}, on the assumption that all the soap was absorbed by the latex particles and surface area (SA) of NaLS molecule was the same as that of sodium laurate[16], i.e. 42 Å^2, and $N = 1.81 \times 10^{16}$ if SA is 60 Å^2 as used by Gardon. The surface area of NaLS is not precisely known and the literature results are conflicting[5,31-34]. Since there is considerable uncertainty in both of these assumptions, the value of N found in this work is only approximate. This value ($N = 6.29 \times 10^{15}$ per ml) is however in fair agreement with that of Gardon (1.02×10^{15}/ml in the steady state)* but not with that of Robb (1.08×10^{14}/ml at 30% conversion). The results of this work show that N increases even in the steady state rate period, and this observation is in agreement with the findings of Robb[11]. It may be mentioned here that the theoretical value of N is always greater than the experimental value[32] by a factor of 2-5.

Since the number of latex particles increases as long as the emulsified oil droplets exist in the system, it is suggested that new micelles are formed during polymerization in the steady state period by the combination of free soap molecules in the aqueous phase and the water soluble oligomers formed in the system[25], and these new mixed micelles produce new latex particles as long as there are oil droplets. If there is no oil droplet, no new particles will be formed. This is demonstrated by the initiator injection experiment (Fig. 5). The polymerization rate did not increase if extra amount of initiator was added after 50 to 60% conversion. However when initiator was injected at about 18 and 35·5% conversion the rate in either case was found to

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*Gardon[32] observed that N determined by the soap titration method was much higher than that found electron microscopically.

increase in agreement with Gerrens and Kohnlein[19,20] and contrary to Smith and Ewart. The same result was also obtained when extra soap was injected after 50 to 60% conversion (Fig. 6). The results show clearly that new latex particles will be formed only when both the emulsified monomer droplets and micelles or mixed micelles are present in the system. This also explains the findings of Robb[11] and of Kolthoff *et al.*[5], who reported that the rate of polymerization of styrene in the aqueous media was increased even when the soap was present below c.m.c. Formation of new particles by chain transfer is ruled out because of very low chain transfer constant of styrene[35]. Some new particles may well also be formed from the dead water insoluble oligomeric particles[36]. As expected from the theory, particle radius (volume/surface area) increases continuously with conversion (Fig. 3). The theoretical particle size at 100% conversion is estimated to be 221 Å from the equation of Gardon[12], and this is root-mean-cubic radius.

Acknowledgement

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