Formation of polystyrene nanoparticles in ternary cationic microemulsions

L. M. Gan*, C. H. Chew and K. C. Lee
Department of Chemistry, National University of Singapore, Singapore 0511, Republic of Singapore

and S. C. Ng
Department of Physics, National University of Singapore, Singapore 0511, Republic of Singapore
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The polymerization of styrene has been studied in ternary microemulsions which were stabilized by tetradecyltrimethylammonium bromide or octadecyltrimethylammonium chloride. The initiation of polymerization occurred mainly in the styrene-swollen microemulsion droplets, and the polymeric particles grew by recruiting monomer and surfactant from uninitiated droplets. The average hydrodynamic radius (R_h) of swollen particles first increased rapidly to a maximum at ~4 or 7% conversion, and then decreased slowly to a constant value. The variation in size follows the trend as simulated by a recent thermodynamic model. Due to the continuous nucleation, the number of polymer particles and the polydispersity of particle sizes increased continuously throughout the course of the polymerization process. The low average number of free radicals per particle ($\bar{n} < 0.5$) may be responsible for polystyrene with high molecular weights ($\bar{M}_w = 6\text{–}11 \times 10^6$).

(Keywords: polystyrene; nanoparticles; microemulsion)

INTRODUCTION

Several monomers have been polymerized in oil-in-water (o/w), water-in-oil (w/o) and bicontinuous microemulsions[1–14]. Most of these microemulsions have been stabilized by a cationic or an anionic surfactant in conjunction with a cosurfactant, which is commonly a short-chain alcohol. The use of an alcohol cosurfactant in a polymerizable microemulsion may not be desirable because it may modify monomer partitioning[15] and promote chain-transfer reactions[16].

Ferrick *et al.*[17] first reported styrene polymerization in a three-component o/w microemulsion using cetyltrimethylammonium bromide (CTAB). Perez-Luna *et al.*[18] also polymerized styrene in ternary o/w microemulsions which were stabilized by dodecyltrimethylammonium bromide (DTAB). Stable microlatexes with particle diameters ranging from 40 to 60 nm were produced. Antonietti *et al.*[19,20] used cetyltrimethylammonium chloride (CTAC), DTAB or mixtures of differently charged surfactants to control the sizes of polystyrene nanoparticles (10 nm < R_h < 60 nm) by varying the weight ratio of styrene to surfactant. Larpent and Tadros[21] discussed a method for preparing polystyrene and poly(methyl methacrylate) in ternary o/w microemulsions using mainly non-ionic surfactants. It was found that the redox system produced microlatexes with the smallest sizes (18–24 nm in diameter) having a narrow size distribution. Gan *et al.*[22] also polymerized methyl methacrylate (MMA) in ternary microemulsions using octadecyltrimethylammonium chloride (OTAC), and in this case the latex particles varied slightly from 40 to 50 nm in diameter. Each of these PMMA particles contained ~2 to 3 polymer chains of high molecular weight ($5\text{–}8 \times 10^6$).

Tetrahydrofurfuryl methacrylate has also been polymerized, by Texter and coworkers[23,24], in ternary o/w microemulsions made with Aerosol-OT [sodium bis(2-ethylhexyl) sulfosuccinate] and water. Microlatex particles, ranging in diameter from 25 to 34 nm, of high-molecular-weight polymer (10^7) were obtained.

The formation of polystyrene nanoparticles in ternary microemulsions using the cationic surfactants, OTAC or tetradecyltrimethylammonium bromide (TTAB), is discussed in this paper. The growth of nanoparticles during the polymerization was closely monitored by photo-correlation spectroscopy (p.c.s.).

EXPERIMENTAL

Materials

Tetradecyltrimethylammonium bromide (TTAB) and octadecyltrimethylammonium chloride (OTAC) were obtained from Tokyo Chemical Industry, and were recrystallized from a mixture of ethanol/acetone (1/3 by volume). Styrene (Fluka) was vacuum distilled to remove the inhibitor. Potassium persulfate (KPS), obtained from Fluka, was recrystallized from doubly distilled water.

* To whom correspondence should be addressed

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Phase diagram of microemulsions

The clear regions of o/w microemulsions consisting of styrene, water and TTAB (or OTAC) were determined visually at room temperature (~30°C). Titrations with water of a series of mixtures of different amounts of styrene and surfactant were carried out in culture tubes. The stable microemulsion regions after polymerization were also established by polymerizing the systems with 1.0 mM KPS in a series of sealed ampoules at 60 ± 0.1°C.

Polymerization

The kinetics of polymerization were monitored by both dilatometric and gravimetric methods. Latex samples, which were withdrawn during the latter process at different time-intervals, were used for particle size determinations. Approximately 200 g of a microemulsion, contained in a 3-necked round bottom flask, were frozen by liquid nitrogen and then degassed under 1.333×10^3 Pa (10 torr) for 3 min. The flask was then charged with nitrogen. The frozen microemulsion was thawed by running tap water until it reached ambient temperature, and the flask was then placed in a thermostatted bath at 60 ± 0.1°C. A syringe was used to withdraw ~9 ml of each polymerized microemulsion at different time-intervals, via a rubber septum attached to the neck of the flask. Approximately 4 ml of each polymerized microemulsion was precipitated by adding methanol, in order to determine the polymer conversion. The remaining 5 ml were quickly chilled and then mixed with a small amount of hydroquinone to stop the polymerization; this sample was used for particle size determination.

Particle size determination

Particle sizes (hydrodynamic radii) of the microemulsion latexes were determined by p.c.s. using a Malvern 4700 light scattering spectrophotometer. Prior to the measurements, microemulsion samples were diluted with distilled water until the volume fractions of the particles were in the range 0.01–0.1. An average hydrodynamic radius of the latex particles (R_h) was calculated from the intrinsic diffusion coefficient (D_0), i.e. $R_h = RT/6\pi\eta D_0$, where η is the viscosity of the dispersion medium. The latexes were also examined by a Jeol JEM-100CX electron microscope. One drop of the latex was added to 2 ml of 0.2 wt% phosphotungstic acid (PTA) solution and mixed thoroughly. A drop of this mixture was then deposited onto a copper grid coated with a thin layer of Formvar.

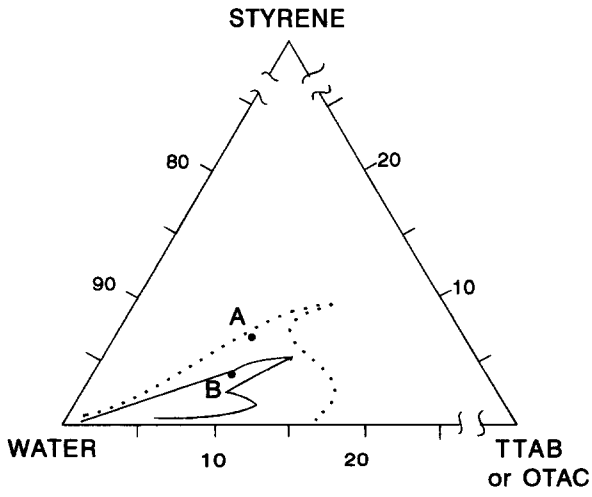

Figure 1 The partial phase diagram of the o/w microemulsion systems containing styrene, water, and OTAC or TTAB at 30°C: ——, OTAC; ···, TTAB

Molecular weight determination

Molecular weights of the polystyrene samples were determined by gel permeation chromatography (g.p.c.) using a Varian 5500 liquid chromatography system, equipped with a RI-3 detector. The columns used in this work were Varian micropak TSK 7000H and GMH 6, operating in series, with the eluent being degassed tetrahydrofuran (THF), which contained 0.025 wt% 2,6-di-tert-butyl-*p*-cresol as a stabilizer. The flow rate was maintained at 1.0 ml min^{-1}. Polystyrene standards (0.2 mg ml^{-1} in THF), from Polyscience Inc., were used for the calibration.

RESULTS AND DISCUSSION

Figure 1 shows the partial phase diagrams (at 30°C) of ternary o/w microemulsions which are composed of styrene, water, and TTAB or OTAC. The microemulsion regions are those enclosed by the solid and dotted lines. Due to a higher TTAB solubility in water, this microemulsion region is larger than that of the OTAC. Two sets of microemulsions were chosen for the kinetic study of the polymerization. The compositions (in wt%) were based on point A for the TTAB system and on point B for the OTAC system, as shown in *Figure 1*. System A consisted of 7% styrene, 9% TTAB and 84% water, while system B contained 4% styrene, 9% OTAC and 87% water. *Table 1* summarizes the information concerning the polystyrene nanoparticles prepared from these microemulsions.

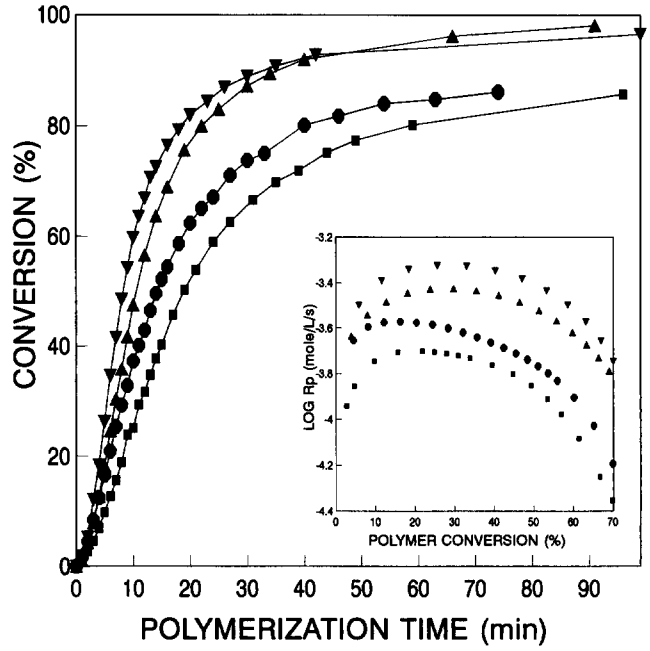

Figure 2 The styrene polymerization curves (conversion *versus* time) for microemulsions stabilized by TTAB and OTAC at 60°C, with different KPS concentrations (shown in brackets): ●, TTAB (0.15 mM); ■, OTAC (0.15 mM); ▲, OTAC (0.45 mM); ▼, OTAC (0.75 mM). Inset shows variation of polymerization rate with conversion for the same set of samples

Table 1 Information concerning the polystyrene nanoparticles prepared from the two microemulsion systems examined in this study

System	Conversion (%)	R_h[a] (nm)	N_p[b] (10^{15} ml^{-1})	n_p[c]	$\bar{n}$[d]	$\bar{M}_w$ (10^6)	$\bar{M}_w/\bar{M}_n$
A[e]	0	16.2	8.01	–	–	–	–
	3.46	33.9	0.87	0.92	0.18	7.9	6.7
	4.62	30.2	1.23	1.01	0.18	8.5	6.9
	11.9	28.6	1.46	1.12	0.17	11.5	5.8
	35.7	28.4	1.48	1.24	0.16	11.3	6.1
	49.2	27.9	1.54	1.49	0.13	11.9	6.2
	68.1	27.2	1.69	1.65	0.10	10.5	6.3
B[f]	0	14.6	9.10	–	–	–	–
	6.27	23.6	1.60	0.91	0.33	8.3	4.3
	9.55	23.5	2.29	1.02	0.32	8.0	4.3
	13.2	22.6	2.59	1.05	0.33	7.9	4.4
	29.9	21.3	3.09	1.12	0.32	0.74	4.4
	49.6	20.6	3.44	1.15	0.31	6.2	4.6
	67.8	20.1	3.60	1.20	0.30	5.6	4.7
	73.5	20.2	3.63	1.25	0.26	5.5	5.7
	84.5	20.2	3.65	–	0.19	–	–

[a] R_h, hydrodynamic radius
[b] N_p, number of monomer-swollen polymer particles
[c] n_p, number of polymer chains per polymer particle
[d] $\bar{n}$, number of radicals per polymer particle
[e] System A consists of 7 wt% styrene, 9 wt% TTAB and 84 wt% H_2O, plus 0.15 mM KPS, at 60°C
[f] System B consists of 4 wt% styrene, 9 wt% OTAC and 87 wt% H_2O, plus 0.75 mM KPS, at 60°C

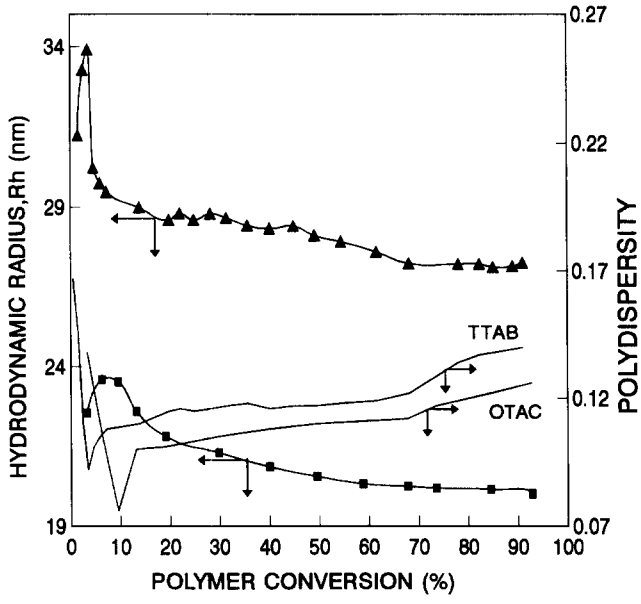

Figure 3 Microemulsion particle sizes and the corresponding polydispersities as a function of polymer conversion for the different systems: ▲, TTAB; ■, OTAC

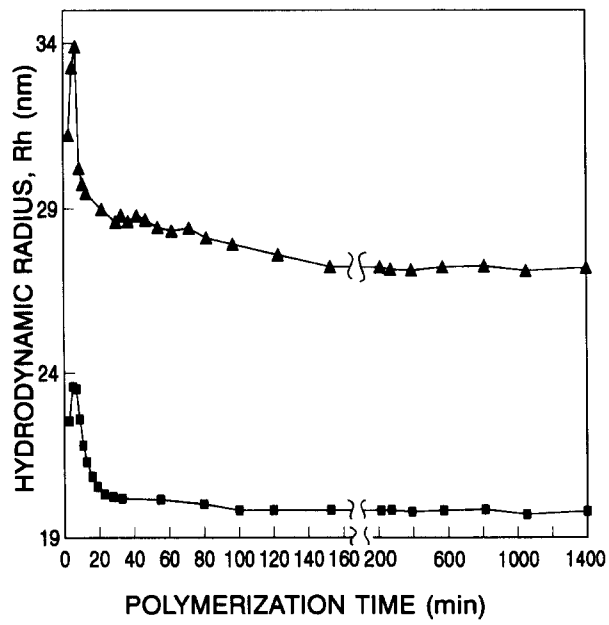

Figure 4 Microemulsion particle sizes as a function of polymerization time for the different systems: ▲, TTAB; ■, OTAC

Polymerization

The polymerization time *versus* conversion curves for systems A and B with different KPS concentrations are shown in *Figure 2*. (These plots do not include the induction periods of polymerization.) The rate of polymerization (R_p) increased with the initiator concentration, as expected. However, R_p increased with polymer conversion up to a maximum of ~20%, and then decreased with further polymer conversion, as shown by the inset of *Figure 2*. A similar trend has also been observed for styrene polymerization in microemulsions containing a cosurfactant[9,25,26]. The increasing rate of polymerization in the early stages is attributed to the increasing number of polymerization loci which are nucleated by free radicals. The decreasing rate in the later stages of polymerization is due to a diminishing monomer concentration in the growing particles.

Since most of the styrene monomer was solubilized in a very large number of microemulsion droplets ($8–9 \times 10^{15}$ ml), the monomer-swollen droplets could

compete very effectively with the dissolved monomer (0.031 wt%) in the aqueous phase as potential loci for radical initiation. Therefore, the polymer initiation process for styrene might occur in the monomer-swollen microemulsion droplets. Polymeric particles grew by recruiting monomer and surfactant from uninitiated droplets.

Particle sizes

The hydrodynamic radii (R_h) of the styrene-swollen microemulsion droplets, as determined by p.c.s., were 14.6 and 16.2 nm for the OTAC and TTAB systems, respectively. *Figure 3* shows the variation of R_h and its polydispersity during the polymerization process. R_h reached a maximum at approximately 4 or 7% conversion, for systems A and B, respectively, in a matter of ~5 min, and then decreased continuously towards a constant size. On the other hand, the polydispersity of the particle sizes decreased to a minimum at ~4 or 7% conversion, and then increased on further polymerization. This shows that the monomer-swollen polymer particles were relatively monodispersed at their maximum swelling levels.

These results are in contrast with those reported by Perez-Luna *et al.*[18] for styrene microemulsions which were stabilized by DTAB. These authors found that the apparent particle size decreased first and then increased steadily during the polymerization. On the other hand, Antonietti *et al.*[19] concluded that R_h did not depend on

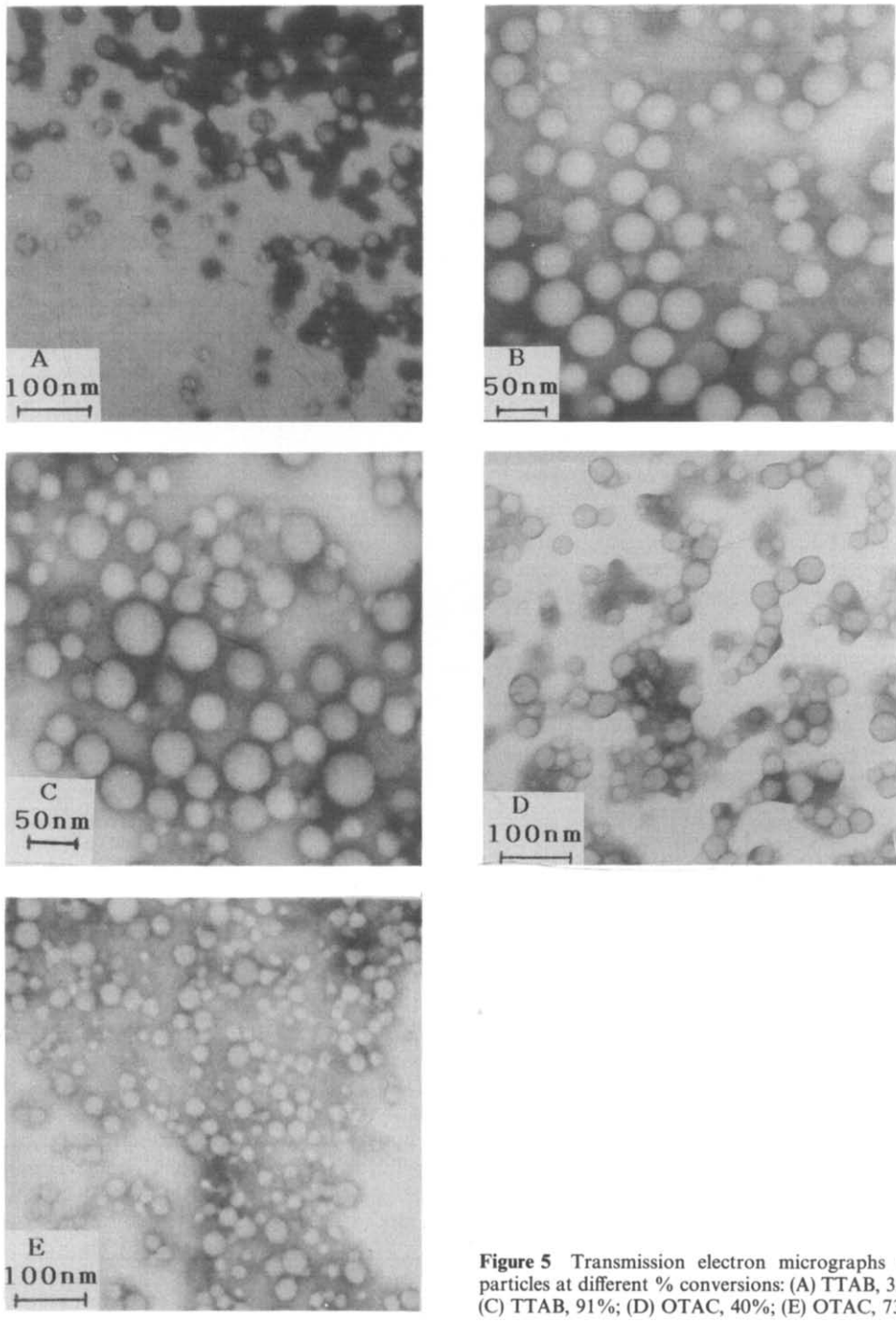

Figure 5 Transmission electron micrographs of polystyrene latex particles at different % conversions: (A) TTAB, 3.5%; (B) TTAB, 49%; (C) TTAB, 91%; (D) OTAC, 40%; (E) OTAC, 73%

the polymerization time or the extent of styrene polymerization in microemulsions which were also stabilized by DTAB. Their conclusion was based only on the R_h values obtained from microemulsion systems with more than three hours of polymerization time. We would have drawn a similar conclusion if this was also only based on R_h values obtained from microemulsions with more than three hours of polymerization time (as shown in *Figure 4*).

The trend shown by our R_h values agrees very well with that simulated by a thermodynamic model developed by Guo *et al.*[25,26]. The maximum particle sizes, from the TTAB (R_h = 33.9 nm) and OTAC systems (R_h = 23.6 nm) were obtained at 4 and 7% conversions, respectively. This is, perhaps, the first set of experimental results which is able to substantiate the thermodynamic model, where the latter can successfully simulate the partitioning behaviour of a monomer in the different phases during the microemulsion polymerization process.

The drastic increase in sizes of the monomer-swollen polymer particles of the TTAB (R_h, 16.2–33.9 nm) and OTAC (R_h, 14.6–23.6 nm) systems, at 4 and 7% conversions, respectively, is attributed to the rapid transport of monomer into the highly swelling polymer/monomer particles. Once polystyrene was formed inside the microemulsion droplets, the components in the system would rapidly redistribute to maintain the equilibrium. The newly formed polymer particles grew via the supply of monomer from both the microemulsion droplets and the inactive polymer particles, either by diffusion or collision. On the other hand, the decrease in size from its maximum R_h value was mainly due to a redistribution of styrene monomer to the newly formed polymer particles.

Some transmission electron micrographs of the polystyrene particles are shown in *Figure 5*. For the TTAB system at 3.5% conversion, the particle sizes were not uniform (see *Figure 5a*) and the average radius (R = 11.3 nm) was much smaller than the corresponding R_h value (33.9 nm). This supports the view that polymer particles were highly swollen by styrene monomer in the early stages of polymerization. The particles continued to grow bigger at increasing conversions, and appeared to be somewhat uniform at 49% conversion (see *Figure 5b*). However, the polymer particles became polydispersed again at 91% conversion (*Figure 5c*). This is explained by the continuous nucleation of polymer particles during the whole course of the o/w microemulsion polymerization process, as previously observed by Candau *et al.*[4] in w/o microemulsion polymerization studies. *Figures 5d* and *5e* also show similar variations in the particle sizes during polymerization in the OTAC system.

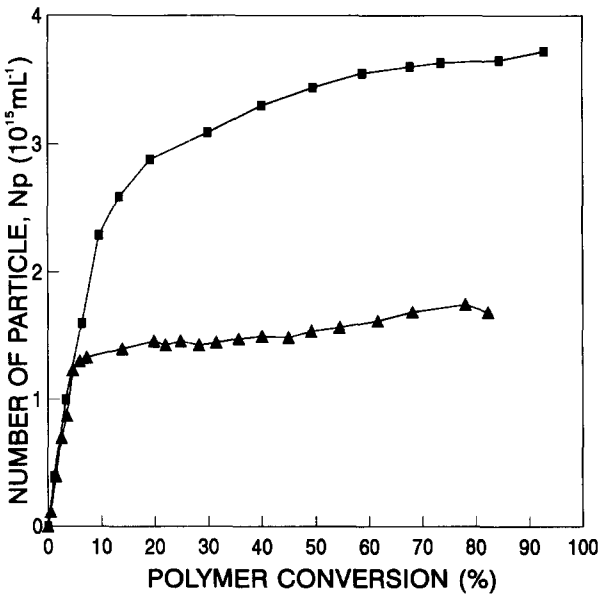

Figure 6 Number of polymer particles (N_p) as a function of styrene conversion at 60°C: ▲, TTAB with 0.15 mM KPS; ■, OTAC with 0.75 mM KPS

Number of polymer particles

Figure 6 shows that the number of polymer particles per ml (N_p) increased continuously throughout the course of polymerization. A larger N_p obtained for the OTAC system was due to the much higher concentration of KPS that was used. N_p increased extremely fast up to ~4 and 7% conversion for the TTAB and OTAC systems, respectively. At these levels of polymer conversion, the oil cores of uninitiated microemulsion droplets could have just disappeared. Thereafter, N_p only increased very slowly and almost levelled off at higher polymer conversions. This trend of a continuous formation of N_p is, in fact, a novel feature of microemulsion polymerization[27].

It is estimated that the number of 'mixed micelles' which contained only a small amount of styrene monomer[28] were still four and two times larger than those of the monomer-swollen polymer particles (even at 50% conversion) for the TTAB and OTAC systems, respectively. This leads to a continuous slow generation of new particles through the capture of some radicals by the vast number of mixed micelles. The number and total area of these species became smaller, while the surface area of polymer particles increased with increasing conversion. Therefore, the polymer particles could increasingly compete with these mixed micelles in capturing radicals. This is evidenced from the increase in the number of polymer chains per particle (n_p) at higher polymer conversions, as shown in *Table 1*.

Average number of free radicals per particle ($\bar{n}$)

The rate of polymerization (R_p, in mol dm^{-3} s^{-1}) in conventional emulsion polymerization can be expressed as follows[29]:

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

where k_p is the propagation rate constant (376 dm^3 mol^{-1} s^{-1} at 60°C)[30], $[M]_p$ is the concentration of monomer in the polymer particle (mol dm^{-3}), N_p is the particle number per dm^3, $\bar{n}$ is the average number of free radicals per particle, and N_A is the Avogadro constant. $[M]_p$ can be obtained from the material balance of styrene monomer, based on the assumption that the unreacted styrene monomer is only present in monomer-swollen polymer particles after the disappearance of the oil cores of the microemulsion droplets. This assumption may lead to a slightly lower value of $\bar{n}$, because a small amount of styrene monomer may still be present in the mixed micelles, according to the simulation by the thermodynamic model[25,26].

It can be seen from *Table 1* that $\bar{n}$ decreased from about 0.20 to 0.10 with increasing conversions (up to 68%) for

the TTAB system. However, it remained rather constant (at ~0.32), up to ~30% conversion in the OTAC system, and then decreased to ~0.19 at 85% conversion. A higher value of $\bar{n}$ for the OTAC system was due to a higher initiator concentration being used. The decrease in $\bar{n}$ with increasing conversions might be due to the continuous formation of polymer particles. The $\bar{n}$ values for both the TTAB and OTAC systems were always less than 0.5. This is attributed to chain transfer of growing polymer radicals to the styrene monomer, with the subsequent desorption[25,26,31] of the newly formed monomer radicals. It has also been shown[32] that the 'removal' rate of monomer radicals which are generated by a chain transfer process increases with decreasing particle size.

These low values of $\bar{n}$ might be responsible for the obtaining of very high molecular weights ($\sim 8 \times 10^6$) for polystyrene. The molecular weight distributions ($\bar{M}_w/\bar{M}_n$) for both the TTAB and OTAC systems were rather broad (see *Table 1*). This could be due to the effect of radical chain transfer to the monomer.

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