A New Method to Determine Monomer Concentration in the Polymer Particles of Emulsion Polymerization Systems by Dynamic Light Scattering

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ABSTRACT: Emulsifier-free emulsion polymerization of styrene was performed in the presence of small amount of methacrylic and itaconic acids as carboxylic acid monomers and potassium persulfate as an initiator at 70°C to prepare monodisperse polymer particles. Diameter of monomer swollen polymer particles (d_{pswol}) was measured by dynamic light scattering for samples taken from the reaction mixture during the Intervals II and III of the emulsion polymerization. Graphically treatment of d_{pswol} versus conversion data allowed us for the first time to directly determine the critical monomer conversion (x_c), from which constant monomer concentration in the polymer particles (C_{MP}) dur-

ing the Interval II was then calculated. x_c and C_{MP} were obtained to be 0.379 and 5.68, respectively. C_{MP} value is in good agreement with that obtained by centrifugation method and those reported in the literature for the similar system. Attempts were also made to evaluate the average number of growing chain per particle ($\overline{n}$) during the Interval II of emulsion polymerization of styrene. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1055–1063, 2009

Key words: emulsifier-free emulsion polymerization; styrene; dynamic light scattering; critical monomer conversion; monomer concentration in the polymer particles

INTRODUCTION

The swelling of polymer particles by the monomer(s) is a key aspect in the emulsion polymerization processes. Rate of polymerization, molecular weight of the polymer, and composition of the copolymer (in the case of emulsion copolymerization) are directly related to the concentrations of monomer(s) in all the coexisting phases, i.e., the aqueous phase, the polymer particles, and the monomer (oil) droplets.[1]

Overall polymerization rate per unit volume of the continuous phase (R_p) in a batch emulsion polymerization can be determined by eq. (1).

$$R_p(t) = C_{M,0} \frac{dx_{ov}(t)}{dt} \quad (1)$$

Although the aqueous phase plays an important role in the emulsion polymerization, the particle phase is the major locus for polymerization progress. Hence, the participation of propagation in aqueous phase and its effect on R_p could be neglected.[2–4] So R_p is calculated from eq. (2).

$$R_p = \frac{\overline{k}_p \overline{n} N_p C_{MP}}{N_{av}} \quad (2)$$

Equation (2) is used to evaluate $\overline{n}$ in the Interval II of emulsion polymerization where polymerization system is in the steady state (see the next section).

It is clear from eq. (2) that the monomer concentration in the polymer particles (C_{MP}) is one of the three key factors that control the particle growth rate (R_p/N_p), and accordingly, the rate of polymerization (R_p). In emulsion polymerization, the course of emulsion polymerization is usually divided into three stages, namely, Intervals I, II and III. In the Intervals I and II of emulsion homopolymerization, C_{MP} is assumed to be approximately constant and independent of particle diameter when the polymer particles has a diameter greater than ∼ 100 nm.[5] Monomer droplets disappear in the beginning of the Interval III and the overall conversion will be also an effective parameter on the C_{MP}. So C_{MP} decreases with reaction conversion in the Interval III. It is very important to establish a precise method for determination of C_{MP} because, as mentioned earlier, C_{MP} is one of the most important parameters than governs the emulsion polymerization rate, molecular weight of the produced polymer, and composition of the copolymer (in the case of emulsion copolymerization). Two methods are now used to predict the monomer concentration in the polymer particles

(C_{MP}) in emulsion homo- and copolymerizations[6]: empirical[7–11] and thermodynamic[12–16] methods.

According to the empirical method for the emulsion homopolymerization system,[7,8] C_{MP} in the Intervals I and II can be expressed as eq. (3).

$$C_{MP} = C_{MP,C} \quad (3)$$

Critical monomer conversion (x_c) where monomer droplets disappear from the aqueous phase can be determined experimentally for the emulsion polymerization system.[5,7,8] If we assume that monomer and polymer behave ideally within the polymer particles and mutual solubility of monomer and water is low enough to be ignored, C_{MP} can then be calculated from eq. (4) by available values of x_c, M_M, ρ_M and ρ_P for the given emulsion homopolymerization system.[5]

$$C_{MP} = \frac{\frac{1-x_c}{M_M}}{\frac{1-x_c}{\rho_M} + \frac{x_c}{\rho_p}} \quad (4)$$

Interval III begins when the monomer droplets disappear from the system at x_c. The monomer concentration in the polymer particles in this interval (C'_{MP} for $x > x_c$) is approximately given by eq. (5).

$$C'_{MP} = C_{MP}\left(\frac{1-x}{1-x_c}\right) \quad (5)$$

On the other hand, several studies[12–15] have been done to thermodynamically describe the swelling behavior of polymer particles by one monomer. The thermodynamic approach now used is based on the so-called Morton equation given by eq. (6).

$$\frac{\Delta F_{ip}}{RT} = \ln(1 - \varphi_p) + \varphi_p\left(1 - \frac{1}{\overline{P}_n}\right) + \chi\varphi_p^2 + \frac{2V_m\gamma\varphi_p^{1/3}}{r_0 RT} = 0 \quad (6)$$

Because the value of $\overline{P}_n$ is usually very large, the term $1/\overline{P}_n$ can be neglected. Given the values of χ and r_0, eq. (6) can be solved iteratively to yield φ_p. Then, by introducing the value of φ_p into the following equation [eq. (7)], one can get the C_{MP} value.

$$C_{MP} = \frac{1 - \varphi_p}{V_m} \quad (7)$$

x_c and C_{MP} values for the seeded or unseeded emulsion polymerization of styrene has been reported in the literature[5,7,8,17,18] to be in the range of 0.40–0.43 and 5.48–6.28 mol.dm^{-3}, respectively. It has been reported that x_c and thereby C_{MP} is independent of the initial emulsifier concentration.[7] When the polymer particles are small ($d_p < 100$ nm), C_{MP} is only weakly dependent on x (or equivalently on d_p) dur-

ing the Interval II of emulsion polymerization.[5,19] This dependence arises, e.g., from changes in the surface free energy of the small particles with size. However, results show that C_{MP} can be considered to be almost constant and equal to ~ 5.5 mol.dm^{-3} during the Interval II of styrene emulsion polymerization when d_p is larger than ~ 100 nm.[5,7] In the recent years, C_{MP} value of 5.5 mol.dm^{-3} reported in the original works has been used to investigate the kinetics of particle growth stage (i.e., Interval II) in the emulsion polymerization of styrene.[2–4,20–23]

In the classical emulsion polymerization systems, d_p increases continuously with conversion in the Intervals II and III of emulsion polymerization (see the "Results and Discussion" section for more details). On the other hand, d_{pswol} increases with conversion only in the Interval II of emulsion polymerization and then slightly decreases with conversion in the Interval III (see the next section for more details). Moreover, C_{MP} is approximately constant in the Interval II of classical emulsion polymerization and then decreases with conversion in the Interval III, reaching zero when the monomer is fully converted to polymer at the end of Interval III of emulsion polymerization.

It has been well known that compared with conventional emulsion polymerization, monodisperse polymer particles can be obtained through emulsifier-free emulsion polymerization.[24,25] d_{pswol} will change only with conversion when polymer particles are monodisperse and N_p is constant during the Intervals II and III of emulsion polymerization. Hence, emulsifier-free emulsion polymerization of styrene in the presence of small amount of unsaturated carboxylic acid monomers is performed in this study to obtain monodisperse polymer particles. A new method is developed for the first time (to the best of our knowledge) on the basis of volume average diameter of (nearly monodisperse) monomer swollen polymer particles (d_{pswol}) data obtained from dynamic light scattering (DLS) to determine x_c and C_{MP}. First, x_c is determined directly by graphically treating d_{pswol} of the samples withdrawn at the various time intervals. The directly obtained x_c from DLS is then used to calculate C_{MP} in the Interval II of the above mentioned emulsion polymerization system. It is believed that the new method can be used with accuracy for any emulsion polymerization with nearly monodisperse polymer particles and slightly water-soluble liquid monomer(s), where the mutual solubility of monomer and water is low enough to be ignored, to evaluate x_c and then C_{MP}. It should also be mentioned that for the emulsion copolymerization systems, although x_c can be directly obtained from DLS analysis, however, determining the mole fraction of comonomers in the copolymer chains or in the unreacted comonomer mixture at x_c is necessary to calculate C_{MP}.

EXPERIMENTAL

Materials and equipments

Styrene (St) monomer from Merck Chemical Co. (Darmstadt, Germany)was washed three times with a 5% aqueous solution of sodium hydroxide followed by three times washing with distilled water and then dried over anhydrous calcium chloride. To remove the inhibitor completely, St was passed through activated basic aluminum oxide (Brockmann I standard grade, basic, $\sim$ 150 mesh, 58 Å, 155 m^2/g surface area, Aldrich, Tehran, Iran) column. The purified St monomer was stored in a refrigerator until use. Methacrylic acid (MAA) from Merck was distilled under vacuum to remove the inhibitor. The purified MAA were stored at about 14°C under running tap water. Potassium persulfate (KPS) as initiator and itaconic acid (IA) monomer both from Merck Chemical Co. were used without further purification. Double distilled water was used in the polymerization recipe.

Emulsion polymerization of St was carried out in a stainless steel Buchi reactor equipped with mechanical stirrer and heating system with silicon oil circulation. In addition to withdrawing the samples for conversion analysis, a separate sampling for DLS analysis and SEM observations was carried out at the various time intervals. Then, suitable samples for particle size analysis by DLS and SEM were selected according to the conversion-time data, so that the conversion of sample falls in the Intervals II and III of emulsion polymerization. Volume average diameter of the monomer swollen polymer particles (d_{pswol}) was measured by a D5000 SIEMENS DLS (using a He-Ne laser as light source with wavelength of 632.8 nm under scattering angle of 90°) at ambient temperature) (20°C) immediately after diluting the latexes up to $\sim$ 0.01% solid content (SC) with double distilled water saturated with St monomer. The dilute latexes were also filtered using Millipore filter to remove dust from the latexes, which is necessary to avoid the heterodyne scattering. Direct inversion technique (cumulants analysis) was used for obtaining the average diameter and polydispersity. In the cumulants method, the logarithm of autocorrelation function is expanded in a Taylor series $[Ln(G_1(\tau)) \underset{\tau \to 0}{\approx} K_0 - K_1\tau + K_2(\tau^2/2) - \ldots]$ to obtain average diameter of the polymer particles. Coefficients in this series are called the cumulants. For polydisperse particles, the first cumulant (K_1) is related to the diffusion coefficient of particles and gives the average value of the particles size ($\bar{d}_p$) and the second cumulant (K_2) gives the standard deviation of the particle size distribution (PSD). The polydispersity is then defined as the standard deviation of the PSD divided by the average value of the par-

ticles sizes (see the equation of "footnote e" in Table III). It should be noted that the software of DLS equipment gives directly both average value of the particles size and polydispersity. As polymer particles contain carboxyl and sulfate groups covalently bonded onto the surface of particles, it is expected that polymer particles keep their colloidal stability during the dilution with water. Moreover, narrow PSD measured by DLS indicates that polymer particles maintain their stability during the dilution with water.

In particle size measurements by scanning electron microscopy (SEM) (Model Stereoscan 360, Cambridge Instrument Co.), one drop of diluted latex was placed on the sample holder and then freeze dried under vacuum for removing the water and unreacted monomers (which swell the particles). Typically 500–1000 particles were measured on the micrographs. The volume average diameter of polymer particles (d_p) and polydispersity was determined from these measurements, which was then used to calculate N_p. It should be mentioned that the ratio of weight average to number average diameter of polymer particles (i.e., polydispersity index) at the various conversions was calculated from SEM micrographs to be always below 1.020, indicating that polymer particles are monodisperse.

To further verify the accuracy of the new approach introduced in this study, C_{MP} was also determined by the following method. Emulsifier-free emulsion polymerization of St in the presence of carboxylic acid monomers was performed according to a recipe given in Table I. Four samples were withdrawn at the various conversions corresponding to the Interval II of emulsion polymerization. Monomer droplets remained in the samples were separated by a high-speed centrifuge.[7] Monomer concentration in the polymer particles was then measured by weighing the polymer before and after polymerizing the residual monomer in the polymer particles. C_{MP} was obtained by this method to be 5.54 $\pm$ 0.03 mol.dm^{-3}.

TABLE I
Recipe for the Emulsifier- Free Batch Emulsion Polymerization of Styrene in the Presence of Carboxylic Acid Monomers[a]

Ingredients	Amount (g)
Distilled water	525.000
Styrene	125.000
Methacrylic acid	3.000
Itaconic acid	2.000
Potassium persulfate[b]	0.910

[a] Total SC is $\sim$ 20%. pH of the reaction mixture was $\sim$ 2.5 due to the presence of carboxylic acid monomers. Polymerization was performed at 70°C. Reaction time was about 6 h (see Fig. 6)
[b] Initiator concentration is 6.4 $\times$ 10^{-3} mol.dm^{-3}.

Emulsion polymerization procedure

Emulsifier-free batch emulsion polymerizations were carried out in a Buchi reactor equipped with a six-bladed turbine impeller, which was set at 300 rpm. Reaction was performed at 70°C under N$_2$ atmosphere. The amounts of monomers and initiator in the experiment have been mentioned in Table I. The reactor was charged under nitrogen at room temperature with all ingredients except the initiator. Nitrogen flow-pump cycle was repeated three times to remove oxygen from the reaction mixture as far as possible. The reaction mixture was equilibrated for $\sim$ 30 min at reaction conditions (temperature of 70°C and stirring speed of 300 rpm). Emulsion polymerization was initiated by adding the initiator under N$_2$ atmosphere to the reaction mixture. Mixture of IA and MAA was selected as the carboxylic acid monomers to obtain a polymerization system with the complete monomer conversion[21] and stable polymer particles,[26] which are necessary for the full investigation of d_{pswol} during the Intervals II and III of emulsion polymerization.

In most of the studies, it has been reported that stirring speed of $\sim$ 300 rpm is enough to obtain homogeneous emulsions.[27,28] Also, in the previous studies,[20–22] we observed that at the stirring speed of 300 rpm, emulsions are homogeneous. To check the homogeneity of emulsions, samples were withdrawn from the various points of reactor at the various time intervals of emulsion polymerization. It was observed that difference in the conversions obtained from the various points of reactor was always below $\pm$0.1% relative to the average value, indicating that stirring rate of 300 rpm is enough to prepare homogeneous emulsions.

Determination of conversion and polymerization rate

SC of latex during the progress of reaction was measured gravimetrically according to ASTM D1417 (method B). A sample $\sim$ 5–6 g was withdrawn from the bottom of reactor. After weighing, each sample was quenched immediately by addition of 1 mL of 1% (w/v) hydroquinone solution in methanol. Then, samples were dried at 80°C under reduced pressure until the weight of dried samples become constant. SC at time t (SC(t)) was calculated by dividing the weight of dried sample to that of initial sample. It should be mentioned that the weight of dried samples was corrected by considering the amount of hydroquinone added to the each sample (0.01 g). Overall mass conversion ($x_{ov}(t)$) was calculated according to the following equation [eq. (8)] for each sample. All the obtained data have been figured out in the next section.

$$x_{ov}(t) = \frac{SC(t) - SC(initial)}{SC(final) - SC(initial)} \quad (8)$$

R_p in a batch emulsion polymerization can be determined from eq. (1) by known values of $C_{M,0}$ and $dx_{ov}(t)/dt$. It should be noted that the effect of carboxylic acid monomer amount on R_p could be neglected relative to the St monomer due to its low amount in the emulsion polymerization recipe and its low solubility in the particle phase (see the partition coefficients of carboxylic acid monomers in Table II).

Theoretical treatment of DLS data

Generally, polymer particles diameter (d_p) and PSD can be measured by SEM and TEM techniques. These methods can be applied with accuracy when there are dried latexes. Number of latex particles per unit volume of the aqueous phase can then be calculated from the following eq. (9).

$$N_P = \frac{6P/W}{\frac{\rho_P}{\rho_W} \pi d_P^3} \quad (9)$$

P/W is a function of monomer to water ratio and conversion. So P/W in emulsion polymerization systems can be calculated as below [eq. (10)].

$$\frac{P}{W} = \frac{M}{W} x_{ov} \quad (10)$$

Diameter of the monomer swollen polymer particles in the batch emulsion polymerization can be calculated by eq. (11).[4,21,23]

TABLE II
Some Useful Parameters Used in the Calculations

Parameter	Monomer	Amount	Reference
M_M (g mol^{-1})	St	104.15	Chemical catalogue
ρ_M (kg dm^{-3})	St	0.9050 (20°C)	29
ρ_P (kg dm^{-3})	St	1.044 (50°C)	2,3,5
C_{MP} (mol dm^{-3})	St	5.5	2,3,5,21
k_p(dm^3 mol^{-1} s^{-1}) at 70°C	St	480	30
k_p(dm^3 mol^{-1} s^{-1}) at 70°C	MAA	1208	31
k_p(dm^3 mol^{-1} s^{-1}) at 70°C	IA	35.6[a]	32
α_{MAA}[b]	MAA	1.01 (25°C)	33
α_{IA}[b]	IA	0.01 (50°C)	34

[a] Value reported for dimethyl itaconate. It is very likely that IA has a k_p value similar to that of dimethyl ester, although no study on this matter currently exists.
[b] α_i is the partition coefficient of carboxylic acid monomer i between styrene and water.

$$d_{\text{pswol}}^3 = d_p^3 \left[1 - \frac{M_M C_{\text{MP}}}{\rho_M} \right]^{-1} \quad (11)$$

In Intervals I and II of emulsion polymerization model introduced by Harkins,[35] the monomer still exists as a separate phase and C_{MP} depends only on the particle diameter. It should be noted that for polymer particles greater than ~ 100 nm in diameter, C_{MP} is almost independent of particle diameter.[5,13] Monomer droplets disappear in Interval III, and the overall conversion will be also an effective parameter on the C_{MP} value.

Two situations can be considered in determination of the polymer particles diameter by using DLS technique: (i) when the conversion is near 100%. Then, the measured particle sizes are almost equal to those obtained from SEM and TEM techniques. It should be mentioned that the hydrodynamic diameter of latex particles measured by DLS is slightly larger than those measured by SEM and TEM at the dry state. (ii) When the conversion is low. In this case, DLS analysis gives d_{pswol} (diameter of polymer particles swelled with the monomers under the polymerization conditions) whereas SEM and TEM give d_P (diameter of dried polymer particles).

Because N_p and C_{MP} are considered to be almost constant in the Interval II of emulsion polymerization ($\sim 0.1 < x < 0.4$ in the case of St[2,3,7,21,23]), d_{pswol} will grow by increasing monomer conversion in this interval up to x_c where monomer droplets disappear from the aqueous phase (see Fig. 1). By further progress of the reaction in the absence of monomer droplets (i.e., Interval III of emulsion polymerization), monomers inside the polymer particles consume and convert to the polymer chains. Because ρ_P is generally greater than ρ_M, d_{pswol} will, thus, decrease as a function of monomer conversion in the
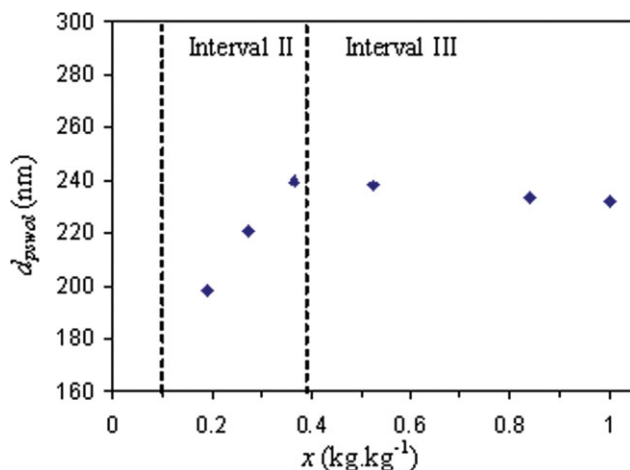

Figure 1 Dependence of d_{pswol} on the x in the emulsifier-free batch emulsion polymerization of styrene in the presence of carboxylic acid monomers (MAA + IA).

Interval III of emulsion polymerization ($\sim x_c > 0.40$ in the case of St emulsion polymerization system[2,3,7,21,23]) (see Fig. 1). Therefore, determination of x_c by treating d_{pswol} versus conversion data seems to be possible, which will be discussed in detail in the next section.

To validate the new approach introduced here for calculation of C_{MP}, it is necessary to confirm the accuracy of d_{pswol} values obtained by DLS (see the following section). There are still issues regarding accurate determination of offline particle size and its distribution of polymer particles, even though recent advances have been made. However, it has been reported that for monodisperse polymer particles (as be the case in this study), DLS technique gives accurate average particle size and its distribution.[36,37] In the present approach, volume average diameter of (nearly monodisperse) monomer swollen polymer particles (d_{pswol}) is measured with accuracy by off-line DLS at the various conversions. d_{pswol} is then treated graphically to obtain x_c, from which C_{MP} is then calculated by eq. (4). Hence, even though we accept a minor error in the d_{pswol} measurements, it will not affect graphically obtained x_c value, because error percentage for all d_{pswol} values measured at the various conversions will be almost the same. Therefore, it is believed that the present method can be used accurately to obtain precise x_c especially for nearly the monodisperse polymer particles.

Relationship between d_{pswol} and x in the Interval II of emulsion polymerization

Substituting eq. (11) in eq. (9) results in eq. (12).

$$\frac{6\frac{M}{W}x_{ov}}{\frac{\rho_P}{\rho_W}\pi N_p} = d_{\text{pswol}}^3 \left[1 - \frac{M_M C_{\text{MP}}}{\rho_M} \right] \quad (12)$$

As already mentioned, N_p and C_{MP} are almost constant in the Interval II of emulsion polymerization. Consequently, eq. (12) can be simplified to eq. (13).

$$d_{\text{pswol}}^3 = \frac{k}{1 - k'} x \quad (13)$$

$$\text{where } k = \frac{6\frac{M}{W}}{\frac{\rho_P}{\rho_W}\pi N_p} \text{ and } k' = \frac{M_M C_{\text{MP}}}{\rho_M} \quad (14)$$

Equation (13) can be rewritten as eq. (15).

$$\frac{1}{d_{\text{pswol}}} = \left(\frac{1 - k'}{k} \right)^{1/3} \left(\frac{1}{x} \right)^{1/3} \quad (15)$$

This equation [eq. (15)]) can be used to plot $1/d_{\text{pswol}}$ versus $(1/x)^{1/3}$ for d_{pswol} data obtained from DLS analysis in the Interval II of emulsion polymerization ($0.1 < x < 0.4$ in the case of St[2,3,7,21,23]).

Relationship between d_{pswol} and x in the Interval III of emulsion polymerization

Interval III begins when the monomer droplets disappear from the system at x_c. Same as Interval II, N_p is assumed to be constant during the Interval III of emulsion polymerization. However, monomer concentration in the polymer particles in this interval (C'_{MP}) decreases with conversion according to eq. (5). Substituting eq. (5) in eq. (11) results in eq. (16). This equation [eq. (16)] can be used for evaluating the variations in d_{pswol} with conversion during the Interval III of emulsion polymerization.

$$d_{\mathrm{pswol}}^3 = d_p^3 \left[1 - k' \left(\frac{1-x}{1-x_c} \right) \right]^{-1} \qquad (16)$$

For simplicity, eq. (16) can be rewritten as eq. (17).

$$d_p^3 = d_{\mathrm{pswol}}^3 [1 - k'' + k''x] \qquad (17)$$

$$\text{where } k'' = \frac{k'}{1-x_c} \text{ and } k' = \frac{M_M C_{\mathrm{MP}}}{\rho_M} \qquad (18)$$

As N_p is constant in the Interval III, substituting eq. (17) in eq. (9) and some manipulation results in eq. (19).

$$\frac{1}{d_{\mathrm{pswol}}} = \left(\frac{1-k''}{k} \right)^{1/3} \left(\frac{1}{x} \right)^{1/3} + \left(\frac{k''}{k} \right)^{1/3} \qquad (19)$$

It is clear from eqs. (15) and (19) that plotting $1/d_{\mathrm{pswol}}$ versus $1/x^{1/3}$ for d_{pswol} data obtained from DLS analysis in the Intervals II and III will result in two straight lines with different slopes and intercepts. Therefore, monomer conversion at which two straight lines meet each other will be equal to x_c (see the next section).

RESULTS AND DISCUSSION

As mentioned earlier, eqs. (15) and (19) were derived by assuming the constant value of N_p in both the Intervals II and III as well as the constant value of C_{MP} in the Interval II of emulsion polymerization. Thus, it will be proper to check the variations in N_p (see the following section) and C_{MP} (see the next section) with conversion to confirm the above-mentioned assumptions. It has been reported for the emulsifier-free emulsion polymerization of St-carboxylic acid monomer that homogeneous-coagulative particle nucleation is occurred in the conversions below $\sim 10\%$ and then N_p become almost constant in the particle growth stage (i.e., Interval II) and Interval III of emulsifier-free emulsion polymerization of St in the presence of small amount of carboxylic acid monomer.[21] Constant N_p in the Intervals II and III not only allow us to evaluate the steady state $\bar{n}$ in the Interval II of emulsion polymeriza-

tions[2–4,20–23] (see the next section) but also make possible to use eqs. (15) and (19) to determine x_c and C_{MP} from DLS data. Figure 2 shows the SEM micrograph of polymer particles obtained at the final conversion (see sample XPS6 in Table III) for the emulsifier-free emulsion polymerization of St in the presence of small amount of carboxylic acid monomers (MAA + IA). Full results of d_p and polydispersity of polymer particles obtained from SEM micrographs for all samples are given in Table III. It is clear from Figure 2 and Table III that polydispersity of polymer particles is in general low (below $\sim 5\%$ in the all cases) and also decreases by increasing the monomer conversion. This is reasonable because the polymer particles nucleate during the time period of the Interval I of emulsion polymerization ($\sim x < 0.1$ in the case of St[21,38]). As a result, it is expected that the polydispersity of polymer particles decreases further by increasing the monomer conversion in the Intervals II and III of emulsion polymerization.

In the Intervals II and III where N_p is constant, it is expected according to the eqs. (9) and (10) that d_p is proportional with $x^{1/3}$. d_p as a function of $x^{1/3}$ for the latex samples taken at the various time intervals during the Intervals II and III of St emulsion polymerization has been plotted in Figure 3. It is clear from Figure 3 that the relationship between d_p and $x^{1/3}$ is linear, indicating that N_p in the Intervals II and III of the emulsifier-free emulsion polymerization of St in the presence of small amount of MAA and IA is constant. N_p was calculated from eq. (9) by d_p data of SEM and other available data given in Tables II and III. Results of N_p values as a function of x in the Intervals II and III (Fig. 4) confirm this assumption that N_p is constant in the Intervals II and III of emulsion polymerization. Assumption of
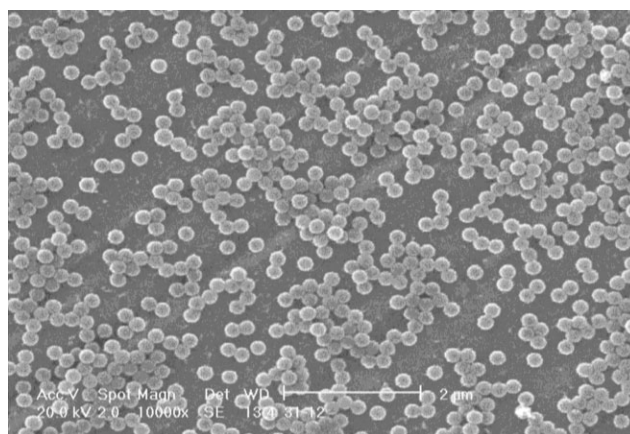

Figure 2 SEM micrographs of polymer particles obtained at the conversion of 99.95% (see sample XPS6 in Table III) for the emulsifier-free batch emulsion polymerization of styrene in the presence of carboxylic acid monomers (MAA + IA).

Parameter	XPS1	XPS2	XPS3	XPS4	XPS5	XPS6
x_{ov} (kg kg^{-1})[a]	0.1888	0.2715	0.3644	0.5227	0.8392	0.9995
P/W (kg kg^{-1})[b]	0.04675	0.06723	0.09023	0.1294	0.2078	0.2475
d_{pswol} (nm)[c]	198.6 (5.0)[e]	220.7 (4.5)	239.4 (3.7)	238.4 (3.2)	233.3 (3.0)	232.2 (2.8)
d_p (nm)[d]	132.2 (4.6)[e]	149.6 (4.2)	165.7 (3.5)	186.1 (3.1)	216.5 (2.7)	229.8 (2.5)
$N_p \times 10^{-16}$(dm^{-3})[f]	3.70	3.67	3.63	3.67	3.75	3.73[g]

[a] Conversions corresponding to the samples used for DLS and SEM.
[b] $P/W = M/W \times x$ where M/W is equal to 0.248 according to the emulsion polymerization recipe (Table I).
[c] d_{pswol} and its polydispersity were obtained from DLS measurements.
[d] These data were obtained from SEM micrographs.
[e] Values presented inside the parentheses indicate polydispersity (C_v, %) of particles size defined as
$C_v = \frac{S}{\bar{d}_p} = \left\{ \sum_i [d_i - (\sum_i n_i d_i / \sum_i n_i)]^2 / \sum_i n_i \right\}^{1/2} / \sum_i n_i d_i / \sum_i n_i$.
[f] N_p was calculated from eq. (9) by available data given in Tables II and III and $\rho_w = 1.000$ kg.dm^{-3}.
[g] This value of N_p was used to evaluate steady state $\bar{n}$ during the Interval II.

constant C_{MP} value during the Interval II can be confirmed via investigating the dependence of d_p/d_{pswol} on conversion by coupling of data obtained from DLS and SEM. d_p/d_{pswol} ratio will be independent of x when the value of C_{MP} is constant [see eq. (11)]. On the other hand, in the Interval III where C_{MP} is dependent on x, it is expected from eq. (17) that d_p/d_{pswol} ratio will be dependent on the x. $(d_p/d_{pswol})^3$ as a function of x is shown in Figure 5, indicating that $(d_p/d_{pswol})^3$ in the Interval II ($0.1 < x < 0.4$) is almost independent of x. It means that C_{MP} can be considered to be almost constant in the Interval II of the present system.

According to the above results, eqs. (15) and (19) can now be used with accuracy to investigate $1/d_{pswol}$ as a function of $1/x^{1/3}$ in the Intervals II and III. Corresponding results are shown in Figure 6. It is clear from Figure 6 that two straight lines with different slopes and intercepts obtain individually

for the Intervals II and III according to the eqs. (15) and (19). As already mentioned, conversion at which two straight lines meet each other is equal to x_c. Hence, x_c was obtained directly from Figure 6 to be 0.379, which is in good agreement with x_c value reported in the literature for the styrene emulsion polymerization.[5,7] It has been reported that the monomer partitioning between the various (aqueous and polymer particle) phases under the partial swelling of polymer particles (i.e., Interval III of emulsion polymerization and $x \geq x_c$) is insensitive to the temperature.[14] As a result, it is expected that there is no significant difference between x_c at the various temperatures. x_c obtained from DLS analysis can be used in eq. (4) to calculate C_{MP} by available values of ρ_P and ρ_M. C_{MP} at 20°C (temperature at which DLS analysis was carried out) was calculated to be 5.68 mol.dm^{-3}. There is a good agreement between the C_{MP} value obtained in this study with that
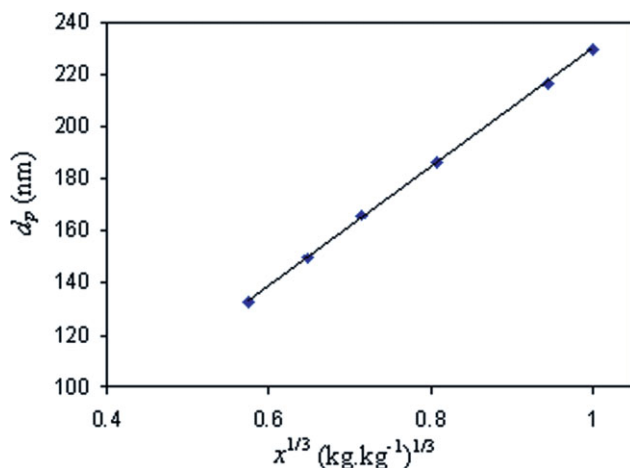

Figure 3 d_p as a function of $x^{1/3}$ for the emulsifier-free batch emulsion polymerization of styrene in the presence of carboxylic acid monomers (MAA + IA).
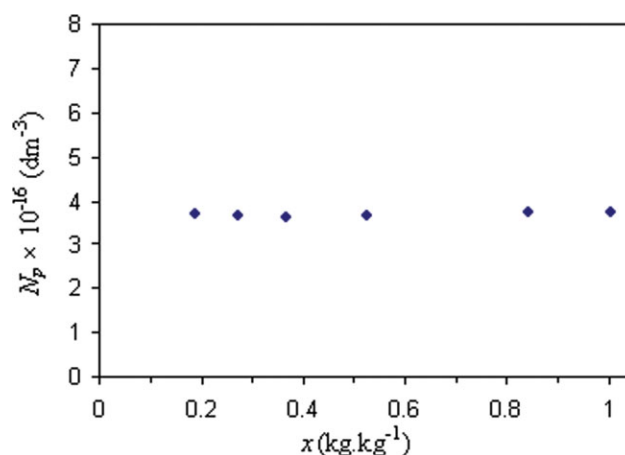

Figure 4 N_p versus x in the Intervals II and III of emulsifier-free batch emulsion polymerization of styrene in the presence of carboxylic acid monomers (MAA + IA).
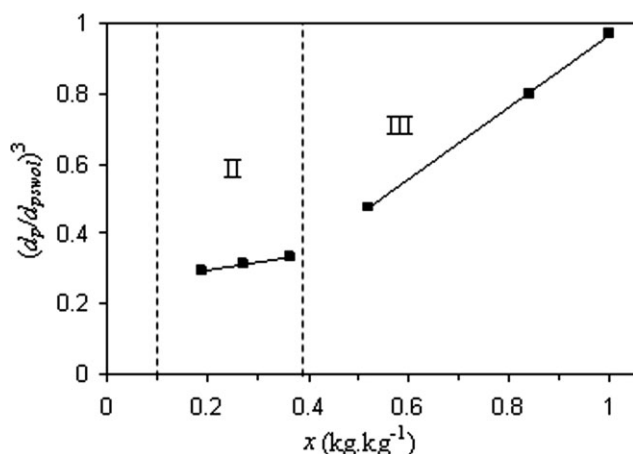
Figure 5 Variations in $(d_p/d_{\mathrm{pswol}})^3$ as a function of x in the Intervals II and III of emulsifier-free batch emulsion polymerization of styrene in the presence of carboxylic acid monomers (MAA + IA).

obtained by centrifugation method in this study (5.54 ± 0.03 mol.dm^{-3}) and those reported in the literature.[5,7,17] Therefore, measuring d_{pswol} as a function of the monomer conversion by DLS technique allow us to directly determine x_c and then calculate C_{MP} with accuracy for any emulsion polymerization system with nearly monodisperse polymer particles and slightly water-soluble liquid monomer(s). It should also be mentioned that for emulsion copolymerization systems, x_c can be directly obtained from DLS analysis, however, determining the mole fraction of comonomers in the copolymer chains or in the unreacted comonomer mixture at x_c is necessary to calculate individual or overall C_{MP}.

C_{MP} value calculated in this study along with data reported in the literature was used to evaluate the average number of growing chain per particle ($\bar{n}$) during the Interval II of emulsion polymerization of
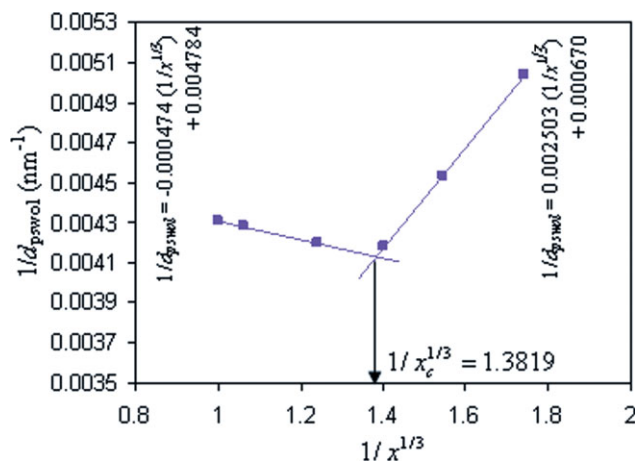
Figure 6 Dependence of $1/d_{\mathrm{pswol}}$ on the $1/x^{1/3}$ in the Intervals II and III of emulsifier-free batch emulsion polymerization of styrene in the presence of carboxylic acid monomers (MAA + IA).

St (see supporting information). It was observed that emulsion polymerization of St in the presence of carboxylic acid monomers (IA and MAA) obeys Case 3 ($\bar{n} > 0.5$) of Smith- Ewart theory.

CONCLUSIONS

Emulsifier-free emulsion polymerization of St was performed in the presence of small amounts of methacrylic acid and IA as carboxylic acid monomers and KPS as an initiator at 70°C to obtain monodisperse polymer particles. DLS technique was used to determine d_{pswol} for the samples taken at the various time intervals from the reaction mixture during the Intervals II and III of the emulsion polymerization. Theoretical treatment of d_{pswol} versus conversion data showed for the first time that it is possible to directly determine x_c from graphically treating d_{pswol} data obtained by DLS. The experimentally obtained x_c was then used to calculate C_{MP} during the Interval II. x_c and C_{MP} for the present system were obtained to be 0.379 and 5.68, respectively. C_{MP} value obtained by the new approach is in good agreement with that obtained by centrifugation method and those reported in the literature for the similar system. It is believed that the new method can be used with accuracy for any emulsion polymerization with nearly monodisperse polymer particles and slightly water soluble liquid monomer(s) to evaluate x_c and then C_{MP}. It should also be mentioned that for emulsion copolymerization systems, x_c can be directly obtained from DLS analysis; however, determining the mole fraction of comonomers in the copolymer chains or in the unreacted comonomer mixture at x_c is necessary to calculate individual or overall C_{MP}. Finally, attempts were also made to evaluate the average number of growing chain per particle ($\bar{n}$) during the Interval II of emulsion polymerization of St. It was observed that emulsion polymerization of St in the presence of carboxylic acid monomers (IA and MAA) obeys Case 3 ($\bar{n} > 0.5$) of Smith- Ewart theory.

NOMENCLATURE

$x_{\mathrm{ov}}(t)$	Overall mass conversion at time t
x_c	Critical monomer conversion where monomer droplets disappear from the aqueous phase
$SC(t)$	Solid content at time t
SC(initial)	Solid content at the beginning of reaction
SC(final)	Solid content at the end of reaction
R_p	Polymerization rate per unit volume of the continuous phase
$C_{M,0}$	Initial monomer concentration (moles per unit volume of the continuous phase)

$\bar{n}$	Average number of growing chains per particle
N_p	Number of latex particles per unit volume of the aqueous phase
C_{MP}	Overall monomer concentration in the monomer swollen polymer particles at interval II
$C_{MP,C}(=C_{MP})$	Saturation monomer concentration in the monomer swollen polymer particles
C'_{MP}	Monomer concentration in the polymer particles at interval III
N_{av}	Avogadro's number
P/W	Weight ratio of polymer to water
M/W	Weight ratio of monomer(s) to water
ρ_P	Average density of the polymer
ρ_W	Density of water
ρ_M	Density of the swelling monomer
d_p	Volume average diameter of polymer particles
d_{pswol}	Volume average diameter of monomer swollen polymer particles
M_M	Molecular weight of the swelling monomer
$\bar{k}_p$	Average propagation rates constant in the particle phase
$k_{p,ii}$	Propagation rate coefficient in homopolymerization of monomer i
α_i	Partition coefficient of carboxylic acid monomer i between styrene and water
M_i	Molecular weight of monomer i
ΔF_{ip}	Partial molar free energy of the monomer in the polymer particles
φ_p	Volume fraction of polymer in the polymer particles
$\bar{P}_n$	Number average degree of polymerization
χ	Flory- Huggins interaction parameter
r_0	Unswollen radius of the particles
R	Gas constant
T	Temperature in Kelvin
V_m	Partial molar volume of the monomer
γ	Interfacial tension between the particles and the aqueous phase

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