Emulsion polymerization: determinations of the average number of free radicals per particle and kinetic parameters by use of the particle size distribution

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For emulsion polymerization of a 'zero–one' system, the method of moments is applied to the model proposed by Lichti *et al.* to describe the particle size distribution (*PSD*). Using the explicit expressions so obtained for the first four moments, the average number of free radicals par particle, $\bar{n}_{ss}$, and kinetic parameters of the system involving the rate coefficients for adsorption and desorption of free radicals, ρ and k, and the propagation rate coefficient, k_p, can be obtained easily by use of *PSD* data without involving a complicated curve fitting procedure as was required in their work. Detailed calculations on the styrene system data of Lichti *et al.* show that both ρ and k are proportional to particle surface area. The result for k is opposite to that proposed by those workers, in which k was considered to be inversely proportional to the particle surface area. After further manipulation and approximation of the expressions so obtained, explicit expressions for the number-average volume, $\bar{v}_n$, the standard deviation, σ, and the skewness, u'_3, in terms of surfactant and initiator levels, temperature and reaction time are also obtained. The effects of the variations of these variables on the three characteristic parameters of the *PSD* can be determined.

(Keywords: emulsion polymerization; particle size distribution; method of moments)

INTRODUCTION

There are three intervals in the entire process of conventional emulsion polymerization. In interval I, particle nucleation in monomer-swollen soap micelles occurs until no micelles are present, as was proposed in the Harkins–Smith–Ewart theory[1]. In interval II, the particles grow steadily until all monomer droplets disappear. In this interval, the total particle number and the monomer concentration in the particles are usually considered to be constant. In interval III, the monomer concentration in the particles starts to decrease. The whole process of emulsion polymerization involves radical adsorption by and radical desorption from the particles, and propagation and bimolecular termination of the radicals in the particles. The rate coefficients of the former two steps may depend on particle size[2-5], but the propagation rate coefficient, k_p ($dm^3 mol^{-1} s^{-1}$), is a function of temperature only and can be a function of the weight fraction of polymer below T_g. The bimolecular termination rate coefficient, c (s^{-1}), is usually considered to be so large that it can be neglected.

For interval II, which is of interest in this work, the relation between kinetic parameters and particle size is rather complicated. Lichti *et al.*[2-4] assumed that the rate coefficients for adsorption and desorption of free radicals of the particles, ρ (s^{-1}) and k (s^{-1}), respectively, are constants. These were then determined by use of polymerization rate[2,4] and particle size distribution (*PSD*) data for conventional and seeded emulsion polymerizations of styrene[3]. However, the values of k they obtained by seeded emulsion polymerization with different radii of seeded particles were found to vary with the inverse square of the swollen particle radius[4], and those of ρ not to depend on the particle size. In the subsequent paper[5], the relation $k \propto v^{-2/3}$ was used to fit the *PSD* curves, resulting in both ρ and k varying with the inverse of the particle surface area. Recently, Kao *et al.*[6] simulated the kinetics of emulsion polymerization of styrene by assuming that the desorption rate of radicals from the particles was negligible. They found that the experimental data agreed well with the collision theory[7,8] and that the rate of radical adsorption by the particles was proportional to the particle surface area. As to the desorption rate coefficient, Ugelstad *et al.*[9] considered the rate of diffusion of radicals in the interior of a particle and proposed that k varied with the inverse of the particle surface area. Nomura[10] used a deterministic approach to investigate the physical process of radical desorption and found that k also varied with the inverse of the particle surface area.

In this work, the model proposed by Lichti *et al.*[11-13] for describing the *PSD* in interval II is applied. By use of the method of moments[14], a more accurate and direct method for determining the average number of free radicals per particle, $\bar{n}_{ss}$, and the kinetic parameters, ρ, k and k_p, more accurately from the *PSD* in the emulsion polymerization system is developed. The dependences of ρ and k on particle size are also found. By use of this method, the variations of *PSD* with time, surfactant level, initiator level and polymerization temperature can be analysed.

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THEORY

In emulsion polymerization systems, each latex particle contains an integral number i of propagating free radicals. Hence, i can be considered as the 'state' of the latex particle[13]. The fraction of latex particles in state i at any time t is defined by $N_i(t)$. The unsteady-state expression for $N_i(t)$ can be described by the Smith–Ewart equations[1]. During polymerization, the total particle number is:

$$N_t(t)=\sum_{i=0}^{\infty} N_i(t) \qquad (1)$$

After the end of interval I (i.e. in intervals II or III), N_t is constant. With the normalization $N_t=1$, the average number of free radicals per particle is:

$$\bar{n}(t)=\sum_{i=0}^{\infty} iN_i(t) \qquad (2)$$

In interval II, the polymerization rate and $\bar{n}(t)$ are found to be constants and $\bar{n}(t)$ is denoted by $\bar{n}_{ss}$.

For studying the *PSD* of a growing emulsion, it is necessary to define the number density distribution of particles having volume v (swollen or unswollen) in state i at time t as $n_i(v,t)$, as first proposed by Lichti *et al.*[11] The fraction of particles with volumes in the range (a,b) can be evaluated from the integral of $n_i(v,t)$ between these limits. Thus $n_i(v,t)$ can be related to $N_i(t)$ by:

$$N_i=\int_0^{\infty} n_i(v,t)\,\mathrm{d}v \qquad (3)$$

where the dimension of $n_i(v,t)$ is $(\text{volume})^{-1}$. The observable *PSD*, $n(v,t)$, during polymerization can be calculated from $n_i(v,t)$ by summing over all states:

$$n(v,t)=\sum_{i=0}^{\infty} n_i(v,t) \qquad (4)$$

In emulsion polymerization systems, the basic theory describing the *PSD* has been established by Lichti and coworkers[3,5,11–13] as:

$$\frac{\partial n_i(v,t)}{\partial t}=\sum_{j=0}^{\infty} O_{ij}(v)n_j(v,t)-\frac{\partial(K_{ii}n_i)}{\partial v}+G_i(v,t) \qquad i\geq 0 \quad (5)$$

Here O_{ij} is composed of the rate coefficients (i.e. ρ, k and c) for describing how latex particles change state as a consequence of adsorption (entry), desorption (exit) and bimolecular termination of free radicals, and can be derived from the Smith–Ewart equations[1]. K_{ii} is the volume growth rate of a particle containing i free radicals and can be represented as:

$$K_{ii}=iK \qquad (6)$$

$$K=10^{21}k_pC_MM_0/(dN_A) \qquad (7)$$

Here 10^{21} is to force the two sides of (7) to have the same dimensions, K ($\text{nm}^3\ \text{s}^{-1}$) is the volume growth rate of a particle containing one free radical, C_M (mol dm^{-3}) the monomer concentration in the particles, M_0 (g mol^{-1}) the molecular weight of monomer and N_A (mol^{-1}) Avogadro's constant. Also d (g cm^{-3}) is the density of polymer (being a constant) if v is the unswollen particle volume, but d is the weight of polymer per unit swollen volume of the polymer particle (being a function of C_M) if v is the swollen particle volume. The relationship between d and C_M for the swollen particle, as derived in our previous paper[15], is:

$$d=1/v_s=d_P(1-10^{-3}C_MM_0d_M^{-1}) \qquad (8)$$

where d_P and d_M are densities of polymer and monomer respectively, and v_s the swollen particle volume. In (5), $G_i(v,t)$ is a nucleation source term and is non-zero only during interval I. In this work, only the *PSD* in interval II is of interest, and thus $G_i(v,t)$ is taken as zero; C_M is essentially independent of time for the monomer in particles being replenished by diffusion from the monomer droplets, and then both d (see (8)) and K (see (7)) are also constants.

Usually, during emulsion polymerization, the rate of bimolecular termination is comparatively more rapid than either of the rates of adsorption or desorption (i.e. $c \gg \rho$ and k)[4]. Thus, the average number of free radicals per particle is small compared with unity (i.e. $\bar{n}_{ss} \ll 1$) as in cases 1 and 2 in the Smith–Ewart theory[1]. The systems are called 'zero–one' systems in which each particle contains at most one free radical during polymerization. In (5), only ρ and k need to be considered, and we have[3,5]:

$$\partial n_0/\partial t=-\rho(v)n_0+[\rho(v)+k(v)]n_1 \qquad (9)$$

$$\partial n_1/\partial t=\rho(v)n_0-[\rho(v)+k(v)]n_1-K\partial n_1/\partial v \qquad (10)$$

If the time interval is not long or the variation in volume of the particles is not large, $\rho(v)$ and $k(v)$ can be assumed to be constants. Take Laplace transforms of (9) and (10) with respect to v, and get:

$$\mathrm{d}N_0^*/\mathrm{d}t=-\rho N_0^*+(\rho+k)N_1^* \qquad (11)$$

$$\mathrm{d}N_1^*/\mathrm{d}t=\rho N_0^*-(\rho+k)N_1^*-sKN_1^* \qquad (12)$$

where

$$N_0^*(s,t)=\int_0^{\infty} \mathrm{e}^{-sv}n_0(v,t)\,\mathrm{d}v \qquad (13)$$

$$N_1^*(s,t)=\int_0^{\infty} \mathrm{e}^{-sv}n_1(v,t)\,\mathrm{d}v \qquad (14)$$

Solving (11) and (12), we have:

$$N_1^*(s,t)=C_1\mathrm{e}^{A(s)t}+C_2\mathrm{e}^{B(s)t} \qquad (15)$$

$$N^*(s,t)=N_0^*+N_1^*$$

$$=\int_0^{\infty} \mathrm{e}^{-sv}n(v,t)\,\mathrm{d}v=\frac{C_1}{\rho}[2\rho+A(s)+k+sK]\mathrm{e}^{A(s)t}+$$

$$\frac{C_2}{\rho}[2\rho+B(s)+k+sK]\mathrm{e}^{B(s)t} \qquad (16)$$

Here C_1 and C_2 are constants and

$$A(s)=0.5\{-(2\rho+k+sK)+[(2\rho+k+sK)^2-4\rho sk]^{1/2}\} \tag{17}$$

$$B(s)=0.5\{-(2\rho+k+sK)-[(2\rho+k+sK)^2-4\rho sk]^{1/2}\} \tag{18}$$

According to the method of moments[14], the kth moment about the origin of the arbitrary volume distribution function $g(v)$, u_k, is:

$$u_k=\int_0^\infty v^k g(v)\,\mathrm{d}v \tag{19}$$

The Laplace transform of $g(v)$ is

$$G(s)=\int_0^\infty \mathrm{e}^{-sv}g(v)\,\mathrm{d}v \tag{20}$$

and the relationship between $G(s)$ and u_k is

$$u_k=(-1)^k\left.\frac{\mathrm{d}^kG(s)}{\mathrm{d}s^k}\right|_{s=0} \tag{21}$$

Therefore, the zero moments of N_1^* and N^* are:

$$N_1^*(0,t)=N_1(t)=\int_0^\infty n_1(v,t)\,\mathrm{d}v \tag{22}$$

$$N^*(0,t)=N_t(t)=\int_0^\infty n(v,t)\,\mathrm{d}v \tag{23}$$

which denote respectively the number of particles containing one free radical and the total particle number in the system. For 'zero–one' systems, assuming that $\rho(v)$ and $k(v)$ are constants for simplicity according to Lichti *et al.*[4], we have:

$$\bar{n}_{ss}=\rho/(2\rho+k) \tag{24}$$

With normalization, $N^*(0,t)=N_t=1$ and $N_1^*(0,t)=N_1=\bar{n}_{ss}N_t=\bar{n}_{ss}=\rho/(2\rho+k)$. Substituting these conditions into (15) and (16), we have $C_1=\bar{n}_{ss}$, $C_2=0$ and

$$N^*(s,t)=\frac{\bar{n}_{ss}}{\rho}[2\rho+A(s)+k+sK]\mathrm{e}^{A(s)t} \tag{25}$$

By using the definition of u_k in (21), the first, second and third moments of $N^*(s,t)$ about the origin are:

$$\begin{aligned}u_1&=\int_0^\infty vn(v,t)\,\mathrm{d}v\\&=\sum_{j=0}^\infty v_jn(v_j,t)\\&=\bar{v}_n\\&=\bar{n}_{ss}Kt-(1-\bar{n}_{ss})\bar{n}_{ss}K/\rho\end{aligned} \tag{26}$$

$$\begin{aligned}u_2&=\int_0^\infty v^2n(v,t)\,\mathrm{d}v\\&=\sum_{j=0}^\infty v_j^2n(v_j,t)\\&=(\bar{n}_{ss}Kt)^2+2(1-\bar{n}_{ss})\bar{n}_{ss}^3K^2/\rho^2\end{aligned} \tag{27}$$

$$\begin{aligned}u_3&=\int_0^\infty v^3n(v,t)\,\mathrm{d}v\\&=\sum_{j=0}^\infty v_j^3n(v_j,t)\\&=(\bar{n}_{ss}Kt)^3+\frac{3(1-\bar{n}_{ss})\bar{n}_{ss}{}^3K^3t^2}{\rho}+\frac{6(1-\bar{n}_{ss})(1-2\bar{n}_{ss})\bar{n}_{ss}{}^4K^3}{\rho^3}\end{aligned} \tag{28}$$

where $\bar{v}_n=u_1/N_t$ is the number-average volume of the particles and $\bar{v}_n=u_1$ for $N_t=1$. The detailed derivations are shown in Appendix 1. Note that in solving C_1 and C_2 of (15) and (16), the conditions used, $N^*(0,t)=1$ and $N_1^*(0,t)=\bar{n}_{ss}$, are independent of time. So the time t in (26)–(28) is not the reaction time or the sampling time. It merely represents the time 't' at which the *PSD* has the values of u_1, u_2 and u_3. But the time interval in this timescale is the same as that of the reaction time. Note, also, that the value of the time 't' is larger than that of $1/\rho$. For example, from *Table 2*, in the time interval 30 to 35 min, $\bar{n}_{ss}=0.315$, $\bar{n}_{ss}K=55.71\ \mathrm{nm}^3\,\mathrm{s}^{-1}$ and $1/\rho=124\,\mathrm{s}$; substituting these values into (26), we get $t=1426\,\mathrm{s}$. Thus, it can be seen in (26)–(28) that the order of the terms having the time t is larger than the other terms. If we use these equations directly to estimate $\bar{n}_{ss}$, ρ and K, serious errors will result, because these terms are not of the same order of magnitude. To resolve this problem, we use the kth moment about the mean, u_k', in statistics[16]. Its definition is:

$$u_k'=\int_0^\infty (v-u_1)^kn(v,t)\,\mathrm{d}v \tag{29}$$

For $k=1$, 2 and 3, we have

$$u_1'=0 \tag{30}$$

$$u_2'=u_2-u_1^2=\sigma^2 \tag{31}$$

$$u_3'=u_3-3u_1u_2+2u_1^3 \tag{32}$$

where σ is the standard deviation and u_3' describes the skewness (non-symmetry) of the *PSD*. Substituting (26)–(28) into (31) and (32), we have:

$$u_2'=\sigma^2=\frac{2(1-\bar{n}_{ss})\bar{n}_{ss}^2K^2}{\rho}t+\frac{(1-\bar{n}_{ss})(3\bar{n}_{ss}-1)\bar{n}_{ss}^2K^2}{\rho^2} \tag{33}$$

$$u_3'=\frac{6(1-\bar{n}_{ss})(1-2\bar{n}_{ss})\bar{n}_{ss}^3K^3}{\rho^2}t-\frac{2(10\bar{n}_{ss}^2-8\bar{n}_{ss}+1)(1-\bar{n}_{ss})\bar{n}_{ss}^3K^3}{\rho^3} \tag{34}$$

Table 1 Calculation of u_1 $(=\bar{v}_n)$, u_2, u_3, u'_2 $(=\sigma^2)$ and u'_3 from the experimental *PSD*s of Lichti *et al.*[5] at $t=20$, 25, 30 and 35 min

Time (min)	$u_1(=\bar{v}_n)$ (10^{-4} nm^3)	u_2 (10^{-8} nm^6)	u_3 (10^{-12} nm^9)	u'_2 $(=\sigma^2)$ (10^{-8} nm^6)	u'_3 (10^{-12} nm^9)
20	1.530	3.663	11.181	1.322	1.531
25	3.362	15.756	91.876	4.450	8.972
30	5.102	32.587	243.742	6.552	10.604
35	6.774	54.019	488.331	8.136	12.202

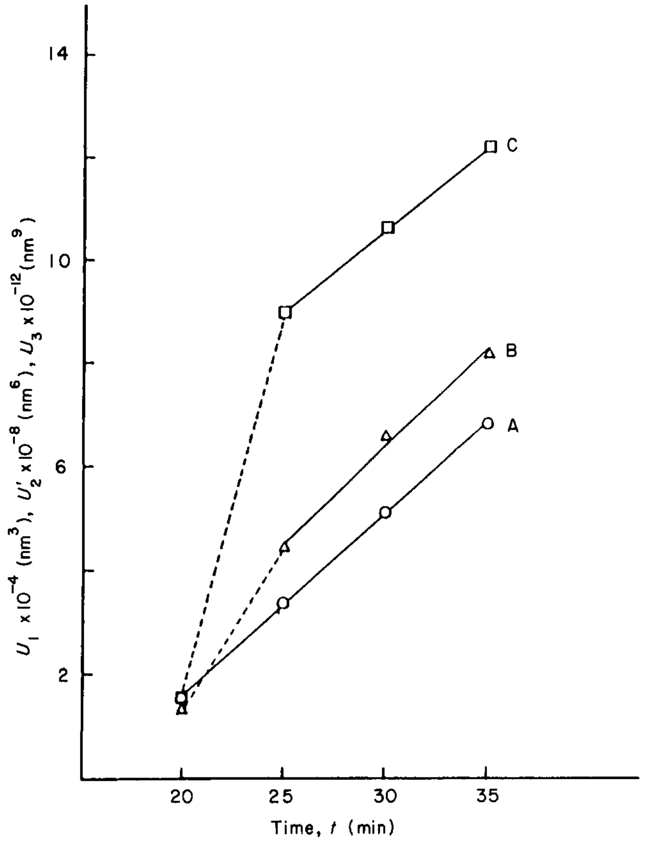

Figure 1 Plots of u_1 $(=\bar{v}_n)$, u'_2 $(=\sigma^2)$ and u'_3 *versus* time: curve A, u_1 vs. time (○), slope$=5.824\times10^{-3}$; curve B, u'_2 vs. time (△), slope$=6.222\times10^{-3}$; curve C, u'_3 vs. time (□), slope$=5.383\times10^{-3}$

From (26), (33) and (34), as can be seen, u_1, u'_2 and u'_3 are all proportional to time t. Plots of u_1, u'_2 and u'_3 *versus* time would yield three straight lines. By use of the slopes of these lines, the three parameters $\bar{n}_{ss}$, ρ and K can be determined without involving the difference in order of magnitude among the terms of each of (26)–(28). Then k can be obtained from (24) and k_p from (7). Hence, by use of this proposed method, a direct determination of $\bar{n}_{ss}$ and the kinetic parameters (i.e. ρ, k and k_p) from the *PSD* becomes possible.

EXAMPLE: CALCULATION OF EMULSION POLYMERIZATION OF STYRENE

To illustrate how the *PSD* data can be used to calculate the average number of free radicals per particle and kinetic parameters, the experimental data for the emulsion polymerization of styrene at 50°C obtained by Lichti *et al.*[5] are used. The experiment used *ab initio* (i.e. unseeded) systems with potassium persulphate as initiator and sodium dodecyl sulphate as surfactant. The *PSD* data with unswollen volume v were measured at 20, 25, 30 and 35 min.

First, from the observed *PSD*s, successive pairs of $(n(v,t), v)$ from $v_{\min}$ to $v_{\max}$ with an appropirate volume interval (in this work, $\Delta v=0.1216\times10^4$ nm^3) can be taken. Substituting the values of these pairs into (26)–(28) to calculate u_1 $(=\bar{v}_n)$, u_2 and u_3, which are then substituted into (33) and (34), the values of u'_2 $(=\sigma^2)$ and u'_3 are obtained. The results are shown in *Table 1*.

Next, plot u_1 $(=\bar{v}_n)$, u'_2 $(=\sigma^2)$ and u'_3 *versus* time (*Figure 1*); their slopes obtained by use of the least-squares method are respectively:

$$\bar{n}_{ss}K=58.24 \tag{35}$$

$$2(1-\bar{n}_{ss})\bar{n}_{ss}^2K^2/\rho=6.222\times10^5 \tag{36}$$

$$6(1-2\bar{n}_{ss})(1-\bar{n}_{ss})\bar{n}_{ss}^3K^3/\rho^2=5.383\times10^9 \tag{37}$$

As shown in *Figure 1*, u'_2 and u'_3 at $t=20$ min deviate from straight lines. This is due to the fact that, at that moment, nucleation has just ended and the system may not be in a steady state (i.e. $\bar{n}(t)$ is not equal to $\bar{n}_{ss}$). Solving (35)–(37) simultaneously, we have:

$$\bar{n}_{ss}=0.315 \qquad K=184.9\ \text{nm}^3\,\text{s}^{-1} \tag{38}$$

$$\rho=7.47\times10^{-3}\,\text{s}^{-1} \qquad k=1.175\rho=8.78\times10^{-3}\,\text{s}^{-1} \tag{39}$$

where $k=1.175\rho$ is obtained by use of (24); the value $\bar{n}_{ss}=0.315$ is close to 0.3 of Lichti *et al.*[5] obtained by use of polymerization rate data; and $K=184.9$ nm^3 s^{-1} is also close to 170 nm^3 s^{-1} used by them[5] to fit the curves of the *PSD*s. Then, substituting $C_M=4.6$ and 5.6 mol dm^{-3} (used by Lichti *et al.*[5]), $d=0.906$ g cm^{-3} (ref. 17) and $M_0=104.15$ g mol^{-1} into (7), we get $k_p=173.2$ and 210.8 dm^3 mol^{-1} s^{-1}, respectively, which are close to 206 dm^3 mol^{-1} s^{-1} obtained by Gerrens[18].

For the variation of ρ and k with particle volume, Lichti *et al.*[5] first tried $\rho=3.9\times10^{-6}v^{2/3}$, $1.3\times10^{-4}v^{1/3}$ s^{-1} and $k=7.6v^{-2/3}$ s^{-1} to calculate the *PSD*s. However, significant deviations from the experimental *PSD*s were obtained. Then they used $\rho=0.9k=7.1v^{-2/3}$ s^{-1} to recalculate the *PSD*s and found agreement with the experimental *PSD*s. Thus they concluded that $\rho(v)$ was proportional to the inverse square of the swollen particle radius. This conclusion is contrary to the collision theory[6–8]. In the following, the method derived in this work is applied to find the relation between ρ (or k) and the particle volume.

If growing time is long, ρ and k may vary with the particle size. Now let us calculate ρ by use of the values of $\bar{n}_{ss}K$ and $2(1-\bar{n}_{ss})\bar{n}_{ss}^2K^2/\rho$ for each successive time interval, and plot ln ρ *versus* ln $\bar{v}_n$. The relation between ρ

Table 2 Calculation of the values of ρ and k at different time intervals[a,b]

Time interval (min)	$\frac{\Delta u_1}{\Delta t} = \bar{n}_{ss}K$ (nm^3 s^{-1})	$\frac{\Delta u_2'}{\Delta t} = \frac{2(1-\bar{n}_{ss})\bar{n}_{ss}^2K^2}{\rho}$ (10^{-5} nm^6 s^{-1})	$\frac{(1-\bar{n}_{ss})}{\rho}$ (s)	$\rho \times 10^3$ (s^{-2})	$k \times 10^3$ (s^{-1})	$\ln(\rho \times 10^3)$ (nm^3)	$\bar{v}_n \times 10^{-4}$	$\ln(\bar{v}_n \times 10^{-4})$
20–25	61.08	10.426	139.732	4.90	5.76	1.590	3.362	1.213
25–30	58.00	7.007	104.105	6.58	7.73	1.885	5.102	1.630
30–35	55.71	5.280	85.053	8.06	9.47	2.087	6.774	1.913

[a] In the calculation of $(1-\bar{n}_{ss})/\rho$, $\bar{n}_{ss}K$ obtained at each time interval is used
[b] In the calculation of ρ, $\bar{n}_{ss} = 0.315$ is used

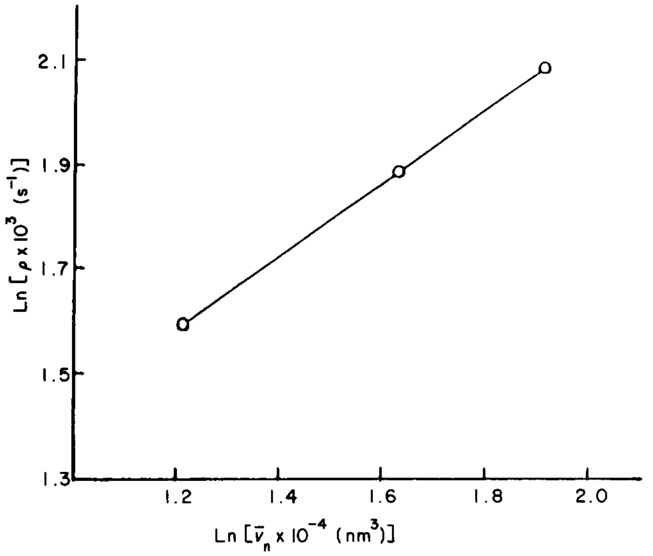

Figure 2 Plot of $\ln(\rho \times 10^3)$ *versus* $\ln(\bar{v}_n \times 10^{-4})$, slope = 0.708 (close to 2/3)

and $\bar{v}_n$ can be obtained from the slope of the straight line. The results are shown in *Table 2*, and the plot of $\ln(\rho \times 10^3)$ *versus* $\ln(\bar{v}_n \times 10^{-4})$ is in *Figure 2*. The slope of the straight line is 0.708, close to 2/3, indicating that ρ is proportional to the particle surface area. This is similar to the result used in deriving the total particle number in the Smith–Ewart theory[1] and the collision theory proposed by Gardon[6-8], but is different from the result of Lichti *et al.*[5] in which ρ is considered to vary with the inverse of the particle surface area.

From (24), $k = \rho(1-2\bar{n}_{ss})/\bar{n}_{ss}$ for 'zero–one' systems in interval II. At steady state $\bar{n}_{ss}$ is constant; thus k increases with ρ and is also proportional to the particle surface area. This is different from the result of Lichti *et al.*[5], Ugelstad *et al.*[9] and Nomura[10], in which k is considered to vary with the inverse of the particle surface area. As the conventional emulsion polymerization system (small particle size with the use of surfactant) is at steady state, $\bar{n}(t)$ and C_M are found to be constants. The adsorption rate of free radicals by the particles is found to be proportional to the particle surface area[1,5-8]. If the desorption rate of free radicals from the particles varies with the inverse of the particle surface area, then according to (24), $\bar{n}(t)$ will increase with time and there will be no steady state in interval II. This is contradictory to the existence of a zero-order region found experimentally. Thus in conventional emulsion polymerization systems, k is proportional to ρ and varies with the particle surface area, which seems to be more physically reasonable.

The values of $\bar{n}_{ss}$, K, ρ and k shown in (38) and (39) and *Table 2* were used to calculate the *PSD* at $t = 25$, 30 and 35 min by solving (9) and (10) and using the forward–backward difference method with the *PSD* data of Lichti *et al.*[5] at 20 min as the initial conditions (see Appendix 2). Comparisons of the calculated results with the experimental curves and those calculated by Lichti *et al.*[5] are shown in *Figure 3*. Obviously, our calculated curves are closer to the experimental curves than those of Lichti *et al.*[5] The value of u_1, u_2' and u_3' of each *PSD* curve in *Figure 3* are listed in *Table 3*, also indicating that our values are closer to the experimental values than those of Lichti et al.[5] Therefore, the proposed method provides a simpler and more accurate way to calculate $\bar{n}_{ss}$ and the kinetic parameters. Note that in *Figure 3* the curves calculated using different values of $\rho(v)$ and $k(v)$ at different time intervals are more accurate than those calculated using constant values of ρ and k for the entire period. This result indicates that $\rho(v)$ and $k(v)$ are in proportion and both vary with the particle surface area.

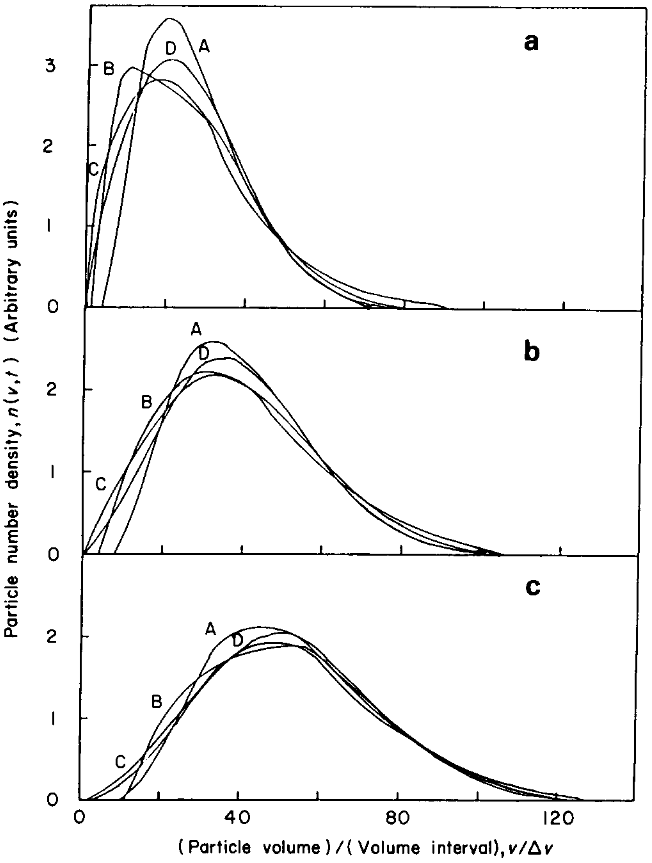

Figure 3 Plots of theoretical and experimental *PSDs* at (a) 25 min, (b) 30 min and (c) 35 min: curve A, the *PSDs* calculated by Lichti *et al.*[5]; curve B, the experimental *PSDs*; curves C and D, the *PSDs* obtained in this work, using the kinetic parameters in *Table 3*

Table 3 Calculation of u_1 $(=\bar{v}_n)$, u_2' $(=\sigma^2)$ *and* u_3' from each *PSD* of *Figure 3* at $t=25$, 30 and 35 min; curve A is the *PSD* fitted by Lichti *et al.*[5], curve B the experimental *PSD* and curves C and D[a] the *PSD*s obtained in this work

Time (min)	Curve	u_1 $(=\bar{v}_n)$ (10^{-4} nm^3)	u_2' $(=\sigma^2)$ (10^{-8} nm^6)	u_3' (10^{-12} nm^9)
25	A	3.443	2.615	3.170
	B	3.362	4.450	8.972
	C	3.276	3.784	4.597
	D	3.277	3.169	3.298
30	A	5.169	4.513	5.986
	B	5.102	6.552	10.604
	C	5.023	6.226	7.763
	D	5.027	5.228	5.483
35	A	6.873	7.394	11.362
	B	6.774	8.136	12.202
	C	6.769	8.225	9.897
	D	6.767	7.313	7.811

[a] For both curves $K=184.9\,\text{nm}^3\,\text{s}^{-1}$ and $\bar{n}_{ss}=0.315$ were used. For curve D, $\rho=7.47\times10^{-3}\,\text{s}^{-1}$ and $k=8.78\times10^{-3}\,\text{s}^{-1}$ for the entire period were used. Fur curve C, a different set of ρ and k at each time interval was used:
at $t=25$ min, $\rho=4.90\times10^{-3}\,\text{s}^{-1}$, $k=5.76\times10^{-3}\,\text{s}^{-1}$;
at $t=30$ min, $\rho=6.58\times10^{-3}\,\text{s}^{-1}$, $k=7.73\times10^{-3}\,\text{s}^{-1}$;
at $t=35$ min, $\rho=8.06\times10^{-3}\,\text{s}^{-1}$, $k=9.47\times10^{-3}\,\text{s}^{-1}$

QUALITATIVE AND QUANTITATIVE ANALYSIS OF THE PARTICLE SIZE DISTRIBUTION

For characterizing the *PSD*, it is necessary to use the mean, u_1 (or $\bar{v}_n$), the standard deviation, u_2' (or σ^2), and the skewness, u_3'. Qualitative analysis on the effects of reaction time (or conversion), initiator, surfactant and temperature levels on the *PSD* can be made by use of the relations of these variables with these three characteristic parameters. In (26), (33) and (34), the terms containing time are much larger than the other terms in the same equation, as shown in the theory section, and therefore only need to be considered. Since the 'zero–one' limit for free radicals is considered, so the average number of free radicals per particle, $\bar{n}_{ss}$, is considered to be less than 0.5.

According to the extension of the Smith–Ewart theory[1], Gardon[7] proposed that:

$$N_t \propto (k_d[\mathrm{I}]/k_p)^{0.4}[\mathrm{S}]^{0.6} \qquad (40)$$

where k_d (s^{-1}) is the rate constant for initiator decomposition. From the Smith–Ewart equations[1], $\rho=\rho_i/N_t$ and $\rho_i=2fk_d[\mathrm{I}]$ (ref. 19), where f and ρ_i are initiator efficiency and the rate of free-radical generation from decomposition of the initiator. From (40) and the definition of ρ, we have:

$$\rho \propto k_d^{0.6}k_p^{0.4}[\mathrm{I}]^{0.6}[\mathrm{S}]^{-0.6} \qquad (41)$$

Based on the mass balance, the mass of monomer reacted, ΔM, must be equal to the mass of polymer in the particles, that is, $\Delta M = dN_t\bar{v}_n$, where the definition of d is the same as that of (7). Thus, at the same conversion (i.e. at the same ΔM), $\bar{v}_n$ varies with the inverse of N_t. From (40), we have

$$\bar{v}_n \propto N_t^{-1} \propto k_d^{-0.4}k_p^{0.4}[\mathrm{I}]^{-0.4}[\mathrm{S}]^{-0.6} \qquad (42)$$

Substituting (7) for K into (26) and then combining with (42) to eliminate $\bar{v}_n$, we have:

$$t \propto N_t^{-1}K^{-1} \propto k_d^{-0.4}k_p^{-0.6}[\mathrm{I}]^{-0.4}[\mathrm{S}]^{-0.6} \qquad (43)$$

Substituting (7) for K, (41) for ρ and (43) for t into (33) and (34), we have:

$$\sigma \propto (1-\bar{n}_{ss})^{0.5}\bar{n}_{ss}k_d^{-0.5}k_p^{0.5}[\mathrm{I}]^{-0.5} \qquad (44)$$

$$u_3' \propto (1-\bar{n}_{ss})(1-2\bar{n}_{ss})\bar{n}_{ss}^3k_d^{-1.6}k_p^{1.6}[\mathrm{I}]^{-1.6}[\mathrm{S}]^{0.6} \qquad (45)$$

For the effects of reaction time (or conversion), (26) shows $\bar{v}_n$ increasing with reaction time. $\rho(v)$ also increases, but has negligibly small effect on the *PSD* in comparison with the reaction time. Hence, from (33) and (34), both σ and u_3' would also increase with reaction time, respectively indicating that the *PSD* is broadened and has increased positive skewness. These effects are in agreement with the experimental data of Lichti *et al.*[5] (*Table 1*).

For the effects of initiator level, from (42), (44) and (45), as [I] increases, $\bar{v}_n$, σ and u_3' all decrease.

For the effects of surfactant level, as [S] increases, from (42) and (45), $\bar{v}_n$ decreases but u_3' increases; from (41), (24) and (44), σ is decreasing.

For the effects of temperature level, in general, the activation energies for initiator decomposition ($\sim 10^2\,\text{kcal mol}^{-1}$) are greater than that of polymer propagation ($\sim 10\,\text{kcal mol}^{-1}$)[17]. Thus, as temperature increases, the effect of k_d is greater than that of k_p. From (42), (44) and (45), $\bar{v}_n$, σ and u_3' would all decrease with reaction temperature.

Now, let us compare this work quantitatively with the experimental results of Gerrens[20], and assign the initial values of the levels of surfactant and initiator as $1x$ to give the corresponding initial values of mean volume ($1y$), standard deviation ($1z$) and skewness ($1s$), in the same way as was done by Sundberg[21], where x, y, z and s can be any reasonable values. As the levels of surfactant, initiator and temperature increase several fold over the initial values, the corresponding variations of $\bar{v}_n$, σ and u_3' can be calculated easily by use of (42), (44) and (45) by assuming $\bar{n}_{ss}$ to be constant. The results are shown in *Table 4* and found to be in good agreement with the experimental results, except for the σ variation as [S] increases. This discrepancy is due to the fact that the effects of nucleation on the *PSD* and the variation of $\bar{n}_{ss}$ are omitted. Sundberg[21] also performed the same calculation by use of a set of simultaneous partial differential equations to describe the *PSD* for a 'zero–one' system. His results are also in agreement with the experimental data (*Table 4*), but the calculation procedure used is much more complicated.

CONCLUSIONS

By use of the method of moments[14] on the model proposed by Lichti *et al.* to describe the *PSD* of 'zero–one' systems in interval II, a simple method is developed for determining the average number of free radicals per particle and kinetic parameters.

Both the adsorption and desorption rate constants of free radicals are found to be proportional to the particle surface area.

For 'zero–one' systems, as the reaction time (or

Table 4 Comparisons of the calculated characteristic parameters of *PSD* with the experimental data of Gerrens[20,a,b]

This work[c]				
Surfactant level	$1x$	$1.87x$	$3.75x$	$7.52x$
mean volume	$1y$	$0.687y$	$0.452y$	$0.298y$
standard deviation	$1z$	$1z$	$1z$	$1z$
skewness	$1s$	$1.456s$	$2.210s$	$3.355s$
Initiator level	$1x$	$2x$	$5.3x$	$10x$
mean volume	$1y$	$0.758y$	$0.513y$	$0.398y$
standard deviation	$1z$	$0.707z$	$0.434z$	$0.316z$
skewness	$1s$	$0.330s$	$0.069s$	$0.025s$
Temperature (°C)[d]	40	50	60	
mean volume	$1y$	$0.655y$	$0.404y$	
standard deviation	$1z$	$0.589z$	$0.323z$	
skewness	$1s$	$0.184s$	$0.027s$	
Gerrens' data				
Surfactant level	$1x$	$1.87x$	$3.75x$	$7.52x$
mean volume	$1y$	$0.688y$	$0.443y$	$0.241y$
standard deviation	$1z$	$0.745z$	$0.555z$	$0.348z$
Initiator level	$1x$	$2x$	$5.3x$	$10x$
mean volume	$1y$	$0.790y$	$0.567y$	$0.471y$
standard deviation	$1z$	$0.730z$	$0.510z$	$0.369z$
Temperature (°C)	40	50	60	
mean volume	$1y$	$0.900y$	$0.624y$	
standard deviation	$1z$	$0.676z$	$0.414z$	
Sundberg's model				
Surfactant level	$1x$	$2x$	$4x$	$8x$
mean volume	$1y$	$0.653y$	$0.398y$	$0.300y$
standard deviation	$1z$	$0.873z$	$0.677z$	$0.545z$
Initiator level	$1x$	$2x$	$5x$	$10x$
mean volume	$1y$	$0.775y$	$0.542y$	$0.412y$
standard deviation	$1z$	$0.770z$	$0.532z$	$0.403z$
Temperature (°C)	40	50	60	
mean volume	$1y$	$0.565y$	$0.352y$	
standard deviation	$1z$	$0.562z$	$0.346z$	

[a] The skewness was not determined in Gerren's work[20]
[b] x = initial level of surfactant or initiator
[c] y = average particle volume at the level of $1x$
z = standard deviation at the level of $1x$
s = skewness at the level of $1x$
[d] The activation energies were taken as 33.5 and 7.78 kcal mol^{-1} for the same initiator decomposition[22] and polymer propagation rate constants as those used by Sundberg[21]

conversion) increases, the number-average volume of the particles would be increased and the *PSD* broadened with increased positive skewness. At the same conversion, as the surfactant, initiator or temperature level increases, the total particle number would increase and $\bar{v}_n$ decrease, and the *PSD* becomes narrower. For the effect of skewness of the *PSD*, it decreases with initiator or temperature level but increases with surfactant level.

APPENDIX I

Derivations of equations (26)–(28)

By use of the method of moments[14], expressions for the kth moment about the origin, u_k, can be obtained as follows from (21):

$$u_k = \left.\frac{\partial^k N^*(s,t)}{\partial s^k}\right|_{s=0} \tag{A1}$$

Differentiating (25) with respect to s, we have:

$$\frac{\partial^2 N^*}{\partial s} = \frac{\bar{n}_{ss}}{\rho}\left(\frac{\mathrm{d}A}{\mathrm{d}s}+K\right)\mathrm{e}^{At} + N^* t\frac{\mathrm{d}A}{\mathrm{d}s} \tag{A2}$$

$$\frac{\partial^2 N^*}{\partial s^2} = \frac{\bar{n}_{ss}}{\rho}\mathrm{e}^{At}\frac{\mathrm{d}^2A}{\mathrm{d}s^2} + \frac{\bar{n}_{ss}}{\rho}\mathrm{e}^{At}t\left(\frac{\mathrm{d}A}{\mathrm{d}s}+K\right)\frac{\mathrm{d}A}{\mathrm{d}s} + t\frac{\partial N^*}{\partial s}\frac{\mathrm{d}A}{\mathrm{d}s} + N^* t\frac{\mathrm{d}^2A}{\mathrm{d}s^2} \tag{A3}$$

$$\frac{\partial^3 N^*}{\partial s^3} = \frac{\bar{n}_{ss}}{\rho}\mathrm{e}^{At}\frac{\mathrm{d}^3A}{\mathrm{d}s^3} + \frac{\bar{n}_{ss}}{\rho}\mathrm{e}^{At}\left(\frac{\mathrm{d}A}{\mathrm{d}s}+K\right)\left[t^2\left(\frac{\mathrm{d}A}{\mathrm{d}s}\right)^2 + t\frac{\mathrm{d}^2A}{\mathrm{d}s^2}\right] + \frac{2\bar{n}_{ss}}{\rho}\mathrm{e}^{At}t\frac{\mathrm{d}^2A}{\mathrm{d}s^2}\frac{\mathrm{d}A}{\mathrm{d}s} + t\frac{\partial^2 N^*}{\partial s^2}\frac{\mathrm{d}A}{\mathrm{d}s} + 2t\frac{\partial N^*}{\partial s}\frac{\mathrm{d}^2A}{\mathrm{d}s^2} + N^* t\frac{\mathrm{d}^3A}{\mathrm{d}s^3} \tag{A4}$$

Differentiating (17) with respect to s, we have:

$$\frac{\mathrm{d}A}{\mathrm{d}s} = 0.5\{-K + 0.5[(2\rho+k+sK)^2 - 4\rho sK]^{-1/2}(2kK+2sK^2)\} \tag{A5}$$

$$\frac{\mathrm{d}^2A}{\mathrm{d}s^2} = 0.5\{-0.25[(2\rho+k+sK)^2-4\rho sK]^{-3/2}(2kK+2sK^2)^2 + 0.5[(2\rho+k+sK)^2-4\rho sK]^{-1/2}2K^2\} \tag{A6}$$

$$\frac{\mathrm{d}^3A}{\mathrm{d}s^3} = 0.5\{0.375[(2\rho+k+sK)^2-4\rho sK]^{-5/2}(2kK+2sK^2)^3 - 0.75[(2\rho+k+sK)^2-4\rho sK]^{-3/2}(2kK+2sK^2)2K^2\} \tag{A7}$$

Let $s=0$ in (A5)–(A7) and we get:

$$\left.\frac{\mathrm{d}A}{\mathrm{d}s}\right|_{s=0} = -\bar{n}_{ss}K \tag{A8}$$

$$\left.\frac{\mathrm{d}^2A}{\mathrm{d}s^2}\right|_{s=0} = 2\bar{n}_{ss}^2(1-\bar{n}_{ss})K^2/\rho \tag{A9}$$

$$\left.\frac{\mathrm{d}^3A}{\mathrm{d}s^3}\right|_{s=0} = -6\bar{n}_{ss}^3(1-\bar{n}_{ss})(1-2\bar{n}_{ss})K^3/\rho^2 \tag{A10}$$

where $\bar{n}_{ss} = \rho/(2\rho+k)$. Substituting (A8)–(A10) into (A2)–(A4) and letting $s=0$, we have ((26)–(28).

APPENDIX 2

Explanation of the initial conditions for solving equations (9) and (10)

To solve (9) and (10) requires a set of initial conditions, that is, the *PSD* at a particular time t_0, and values of the kinetic parameters, ρ, k, c and K. The kinetic parameters have been determined and the initial conditions are to be determined below.

The system in interval II is at steady state, so for a 'zero–one' system, $N_0 = 1 - \bar{n}_{ss}$ and $N_1 = \bar{n}_{ss}$ with the normalization conditions, $N_t = 1$. Lichti *et al.*[5] took the initial conditions as:

$$n_0(v,t_0) = (1 - \bar{n}_{ss})n(v,t_0) \tag{A11}$$

and

$$n_1(v,t_0) = \bar{n}_{ss}n(v,t_0) \tag{A12}$$

which are also used for (9) and (10). Here $\bar{n}_{ss} = \rho/(2\rho + k)$ (ref. 4), by which $n_0(v,t_0)$ and $n_1(v,t_0)$ can be determined.

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