Colloid Polym Sci (2007) 285:523–534
DOI 10.1007/s00396-006-1600-x

ORIGINAL CONTRIBUTION

Effect of chain transfer agents on the kinetics and mechanism of particle nucleation in the emulsion polymerization of vinyl pivalate

**Shinya Suzuki · Kenji Kikuchi · Atsushi Suzuki ·
Takuji Okaya · Mamoru Nomura**

Received: 3 August 2006 / Accepted: 1 October 2006 / Published online: 29 November 2006

Abstract We have studied the kinetics and mechanism of particle nucleation in the emulsion polymerization of vinyl pivalate (VPi) under a wide variety of conditions. Quantitative comparisons between the theoretical and experimental estimations of the average number of radicals per polymer particle, $\overline{n}$ as a function of the amounts of surfactant were performed. The relationship between $\overline{n}$ and the parameter α_w, the ratio of radical production in the aqueous phase to termination per particle, can be explained by assuming that chain-transferred monomer radicals escape from the particle. We studied the influence of the chain transfer agents (CTA), namely, *n*-dibutyl disulfide, *t*-dibutyl disulfide and L-cysteine in the emulsion polymerization. The addition of a CTA had a strong influence on the resulting degree of polymerization. The experimental results can be accounted on the basis of a kinetic analysis of the chain transfer reaction, assuming an increase of the rate of escape of chain-transferred radicals from the polymer particle.

Keywords Vinyl pivalate · Emulsion · Kinetics · Chain transfer agents · Sodium lauryl sulfate

---

S. Suzuki · K. Kikuchi · A. Suzuki (✉) · T. Okaya
Department of Materials Science, School of Engineering,
The University of Shiga Prefecture,
2500 Hassaka,
Hikone 522-8533, Japan
e-mail: suzuki@mat.usp.ac.jp

M. Nomura
Department of Materials Science and Engineering,
Faculty of Engineering, Fukui University,
3-9-1 Bunkyo,
Fukui 910-8507, Japan

Introduction

High molecular weight syndiotactic poly (vinyl alcohol) (PVA) prepared from the saponification [1] of poly (vinyl pivalate) (PVPi) has been widely used for industrial products such as clothes, films, membranes and medical drug delivery [2, 3] systems with high strength and water-resistive properties. Yamamoto et al. [1] reported that there was a highly regular ordering of acetate groups with a syndiotactic configuration in the main chain in PVA that had been converted from PVPi by complete saponification under a nitrogen atmosphere. It was demonstrated [4] that PVA derived from PVPi has a higher degree of syndiotacticity than that derived from poly (vinyl tri-fluoro acetate) (PVTFA). When used for industrial materials, the high crystallinity of ultra-high molecular weight (UHMW) syndiotactic PVA and the extensive hydrolysis of PVA produced by poly (vinyl acetate) (PVAc) affect their mechanical properties [5]. The medical properties of hydrogel material composited with high molecular weight syndiotactic PVA, in particular a high affinity for human organs, were reported [6–8]. The complete hydrolysis of PVA derived from PVPi has advantageous properties as a process for tissue engineering in many medical applications such as blood dialysis, hollow fiber filtering for artificial dialysis of microscopic blood vessels and artificial glass for the human eye [9, 10]. One of the problems found in using ultra-high molecular weight (UHMW) PVA for medical materials is the great difficulty of controlling the viscosity of the bulk polymerization process reaction mixture. Lyoo and colleagues reported the physical properties, such as the thermal behavior and the medical applications of a precursor of highly syndiotactic ultra-high molecular weight (UHMW) of PVA derived from PVPi by suspension polymerization initiated with a redox system at low temperature with a conversion of over 60% and high linearity [11–14]. To the best of our knowledge, there were few studies on the kinetics and mechanism of particle formation in emulsion polymerization of VPi varied with the amount of surfactant, initiator and chain transfer agents. This seems to be a worthwhile subject to be widely applicable for use in industrial products. Though some scientists and developers have made an attempt to industrialize the syndiotactic UHMW of PVA derived from PVPi, it was not successfully produced on a commercial basis. The basic research on the emulsion polymerization of VPi under variable conditions needs to control the molecular weight of PVA in a wide range of physical applications.

Emulsion polymerization was well-known to control the kinetics, particle formation and the degree of polymerization of the resulting polymer, which makes it possible to apply in a variety of industrial products such as medical applications of PVA with high strength. Emulsion polymerizations are commonly studied both to understand the physical basis of the kinetic behavior of radicals in polymer particles and to control emulsion particle sizes and the number average degree of polymerization ($\overline{P_n}$) of the resulting polymers. The kinetics and mechanisms of the role of surfactants on particle nucleation in emulsion polymerizations have been investigated to clarify the phenomenon of radicals escaping from a polymer particle. Studies were pursued to determine the average number of radicals per particle, $\overline{n}$, for styrene [15–17] by solving the theoretical steady state equation proposed by Smith and Ewart [15–17] and for of vinyl acetate (VAc) and vinyl chloride (VCl) [19, 20] using a rigorous estimation by O'Toole [18] that considers the radical balance equation in the aqueous phase.

Nomura and Ugelstad showed a log–log plot of the calculated value of $\overline{n}$ against the parameter α_w as the ratio of radical termination per particle, which has become known as the Ugelstad plot [19, 20]. Nomura made a qualitative comparison between experimental and theoretical results with an approximate equation in terms of $\overline{n}$ against the parameter α_ω in the emulsion polymerization of methyl methacrylate (MMA) and vinyl chloride (VCl) vs the amounts of sodium lauryl sulfate (SLS) used [21]. This type of quantitative comparison between experimental variables with respect to the average number of radicals per particle, $\overline{n}$, assuming that chain-transferred monomer radical can escape from the particle, suggests that this approach to the kinetics and mechanism of particle formation may be useful.

Reactive chain transfer agents (CTA) are increasingly popular agents for controlling the number average molecular weight ($\overline{M_n}$) of the resulting polymer. Recently, several authors have studied the influence of CTAs on the kinetics and mechanism of particle formation in emulsion polymerizations. Nomura has investigated the influence of CTAs in the emulsion polymerization of styrene [22]. For example, mercaptans with the thiol-end groups as chain transfer agents have high transfer constant coefficients. An ideal chain transfer agent should not affect the kinetics, but only the average molecular weight of the polymer. In fact, it is well-known that the addition of chain transfer agents does affect the rate of polymerization. The present authors pointed out that the presence of chain transfer agents enhanced radical desorption and proposed a theoretical rate coefficient of radical desorption from the particles, which included their contribution [23]. Although the role of chain transfer agents in the emulsion polymerization is not completely understood, some reasons for radical desorption increasing the rate of particle formation were suggested [23, 24]: (1) a decrease in the growth rate of particle during polymerization and (2) a decrease of the consumption rate of micelles in the system attributed to the desorption of chain-transferred radical from the particle. Nomura reported that there was a strong influence of carbon tetrachloride, carbon tetrabromide and four primary mercaptans (C_2, n-C_4, n-C_7 and n-C_{12}) as model chain transfer agents on the kinetics and mechanism of particle formation and on the number average degree of polymerization of resulting polymers in the emulsion polymerization of styrene [22]. The effect of chain transfer agents can be explained on the basis of an increase of desorption of chain-transferred radicals from the polymer particles assisted by the chain transfer agent.

We have studied the kinetics and mechanism of particle formation in the emulsion polymerization of vinyl pivalate (VPi) using varying amounts of sodium lauryl sulfate (SLS), potassium persulfate (KPS) and a water-soluble azo compound, such as 2, 2′-azobis (2-amidinopropane) dihydrochloride (V-50), as initiators. The kinetic results over a wide variety of conditions allowed a quantitative comparison between theory and experiment for the ratio of radical termination, that is, the average number of radicals, $\overline{n}$, divided by the parameter α_ω. In particular, we have investigated the influence of chain transfer agents (CTA) on the initial rate of polymerization, the mechanism of the particle nucleation and number average molecular weight of the resulting polymer obtained from the emulsion polymerization.

Experiments

Materials

Commercially available vinyl pivalate monomer (VPi: Nihon vinyl poval, Japan) was purified by distillation under a nitrogen atmosphere. Sodium lauryl sulfate (SLS: Nacalai tesque, Japan) as a protective colloid, potassium peroxodisulfate (KPS) (Wakenyaku, Japan) and 2, 2′-azobis (2-methylpropionamidine) dihydrochloride (V-50) (Wako, Japan) as water-soluble initiators and sodium sulfate (Na_2SO_4, Wakenyaku, Japan) as a pH regulator. Chain transfer agents such as *n*-dibutyl disulfide, *t*-dibutyl disulfide (Aldrich, Japan), and L-cysteine (Wako, Japan) of guaranteed reagent grades were used as received without further purification.

Emulsion polymerization

Prescribed amounts of SLS were added to a 50-ml flask equipped with an argon inlet tube, a vacuum and sampling connections and argon introduced and evacuated three times to remove oxygen in the system. We carried out the emulsion polymerizations of VPi under several sets of conditions. The basic recipe was VPi: 4.3 g, water: 45 g, Na_2SO_4: 0.07 g, KPS: 0.0125 g, SLS: 0.018–6.129 g at 50 °C under an Ar atmosphere. In the case of seed emulsion polymerization, the polymer seed latex was prepared by emulsion polymerization under the same conditions but using 4.315 g VPi per 45 g water and SLS (0.06 g), initiated by KPS (0.0125 g). In the feed stage of emulsion polymerization, the seed emulsion polymerization was performed in the seed-particle solution (1.118 g PVPi per 10 ml water) using SLS (0.00612 g), Na_2SO_4 (0.070 g), initiated by KPS (0.0125 g) at 50 °C under an Ar atmosphere for 4 h. We investigated the influence of chain-transferred agents (CTA) with addition of sodium sulfate (Wakenyaku, Japan) with pH controlled at 3.5. Table 3 lists a typical recipe varied with a mole ratio of CTA to VPi in the range of 1.0×10^{-5}–1.0×10^{-2}.

Measurements

The particle sizes of the emulsion polymers were measured by dynamic light scattering (Parl III, Otsuka, Japan). The number average degrees of polymerization ($\overline{P_n}$) of PVPi were measured by GPC (TSKgel GMH_{HR}-M, Tosho, Japan). The degree of polymerization of a standard sample of PVPi was determined by a viscosity measurement.

Results and discussion

Emulsion polymerizations

Figure 1 shows the time–conversions curves in the emulsion polymerization of VPi as a function of time for various amounts of SLS. In the cases where the SLS concentration exceeded the critical micelle concentration (CMC=7.07×10^{-3} mol L^{-1}), more than 90% polymerizations was achieved in 2 h. The initial rate of polymerization, R_p, measured from the slopes of the initial linear portion of the curves was found to be 8.03×10^{-4} mol L^{-1} s^{-1}. The initial rate of polymerization increased with increasing the initial amounts of SLS. In the initial stages, there was a short induction period before the polymerization started. The behavior is thought to arise from a small amount of dissolved oxygen remaining in the aqueous phase. After freeze-evaporation was performed several times with a rotary pump to remove this oxygen, a new set of polymerization data, shown in Fig. 2a and b, confirmed that there was no induction period in the absence of oxygen dissolved in the aqueous phase. We obtained evidence that the initial rate of polymerization (R_p) increased with the amount of SLS and with that of the KPS initiator, as shown in Figs. 1 and 2b. The dependence of R_p on the [SLS] and that on [KPS] was to the 0.16 and 0.32 power, the relationship, which differed slightly from that found in Smith–Ewart's theory [15–17]. This variation can be attributed to the kinetic effect of the escape of chain-transferred monomer radicals from the polymer particle.

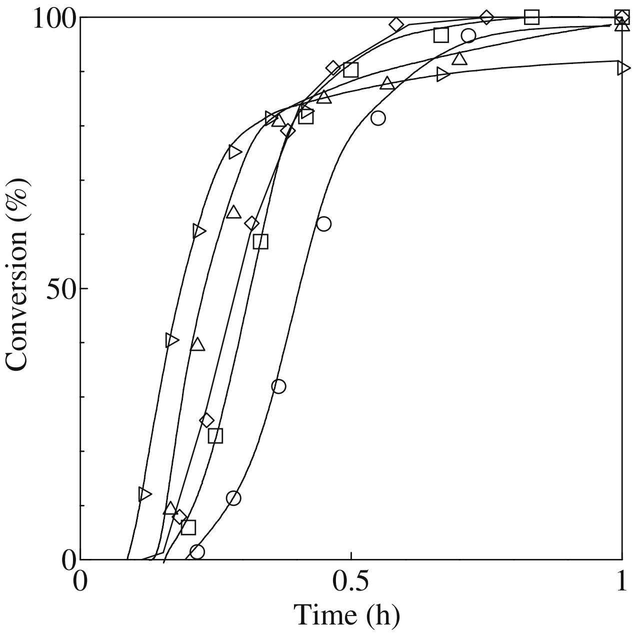

Fig. 1 Time–conversion curves in the emulsion polymerization of vinyl pivalate (VPi) vs the amount of SLS using KPS at 50 °C. Recipe: VPi 4.32 g, water 45 g, Na_2SO_4 0.07 g, KPS 0.01 g. The value of [SLS] is expressed as a multiplier relative to $[SLS]_0$ at 4.5×10^{-4} mol L^{-1}: *open circles*, 2.0; *open squares*, 4.0; *open diamonds*, 6.6; *open triangles*, 20; *open inverse triangles*, 66; Ar atmosphere, 50 °C

Figure 3 shows the development of the particle diameters (a) and the number of particles (b) during the course of the emulsion polymerization. When the amounts of SLS exceeded the CMC more than two times, we observed the particle size to be about 90 nm and the number of particles to be approximately 1.9×10^{14}/ml water. As Table 2

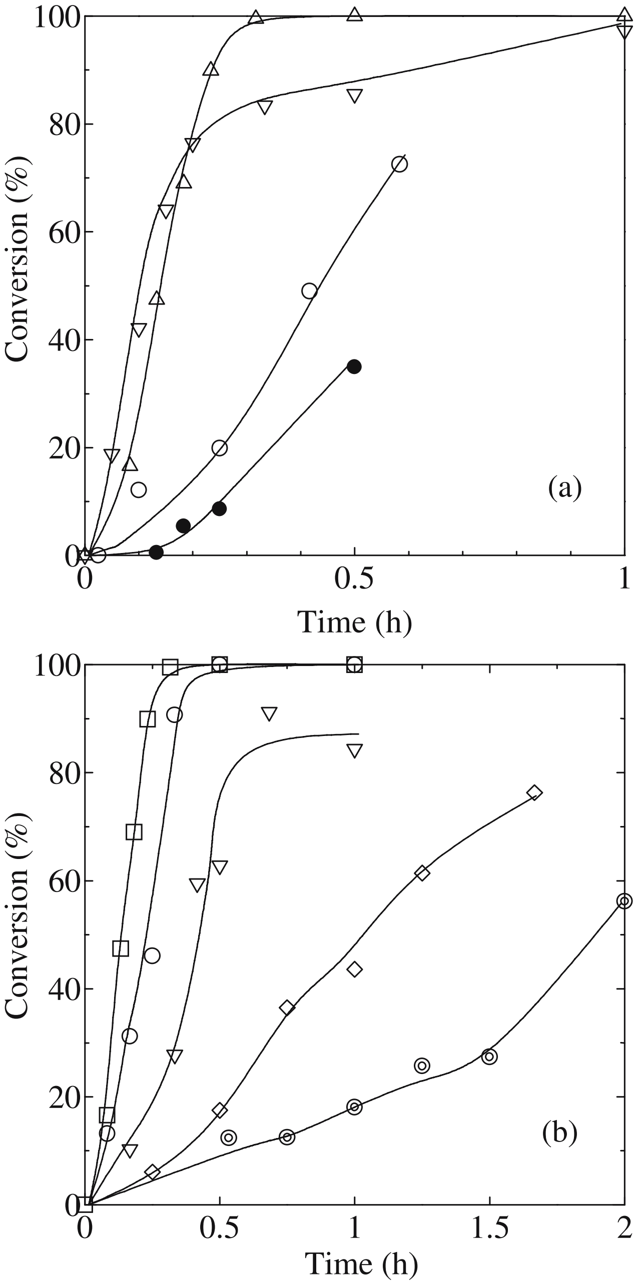

Fig. 2 Time–conversion curves in the emulsion polymerization of VPi vs the amounts of SLS (**a**) and KPS (**b**) after freeze-evaporation treatment. Recipe for **a**, the same as in Fig. 1. The value of [SLS] is expressed as a multiplier relative to $[SLS]_0$ at 4.5×10^{-4} mol L^{-1}: symbols for **a**: *closed circles*, 0.2; *open circles*, 2.0; *open triangles*, 20; *open inverse triangles*, 66; symbols for **b**: variable weight of KPS: *double open circles*, 0.0001 g; *open diamonds*, 0.0004 g; *open reverse triangles*, 0.0013 g; *open circles*, 0.0063 g; *open squares*, 0.0125 g; SLS 1.83 g

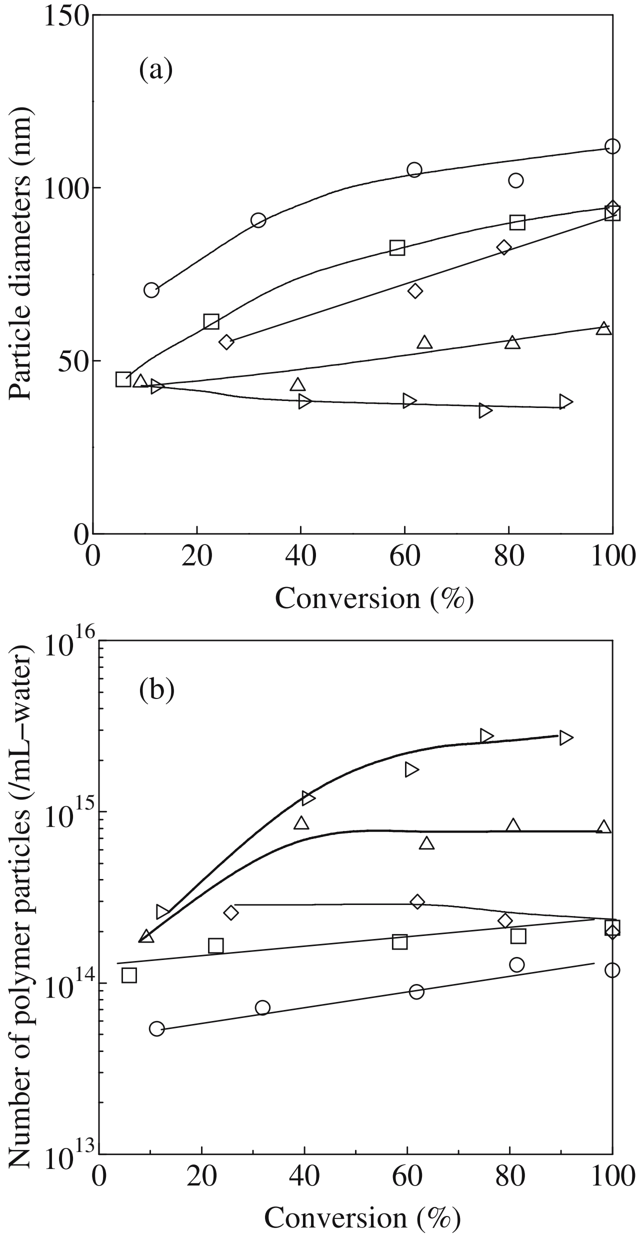

Fig. 3 Effect of the amounts of SLS on the particle diameters (**a**) and the number of particles (**b**) during the emulsion polymerization. Recipe and symbols: the same as in Fig. 1

indicates, the particle size (d_p) decreased to less than 40 nm with increasing amounts of SLS, while the total number of particles (N_p) increased considerably to 24.0×10^{14} ml^{-1}. Further insight into the relationship between R_p and N_p and the amounts of SLS and KPS was achieved by constructing a log–log plot of R_p and N_p with [SLS] or [KPS] obtained in Figs. 1 and 3b. As shown in Fig. 4a, the relationship of R_p and N_p with the amounts of SLS was estimated to be $R_p\propto[SLS]^{0.16}$ and $N_p\propto[SLS]^{0.77}$, respectively. However, these relationships do not correspond to those in Smith–Ewart's theory ($R_p\propto[SLS]^{0.6}$, $N_p\propto[SLS]^{0.6}$). The log–log plot in Fig. 4b shows that the initial amount of KPS initiator has a great influence on R_p and N_p ($R_p\propto[KPS]_0^{0.32}$ and $N_p\propto[KPS]_0^{0.46}$). The relationship between R_p, N_p and

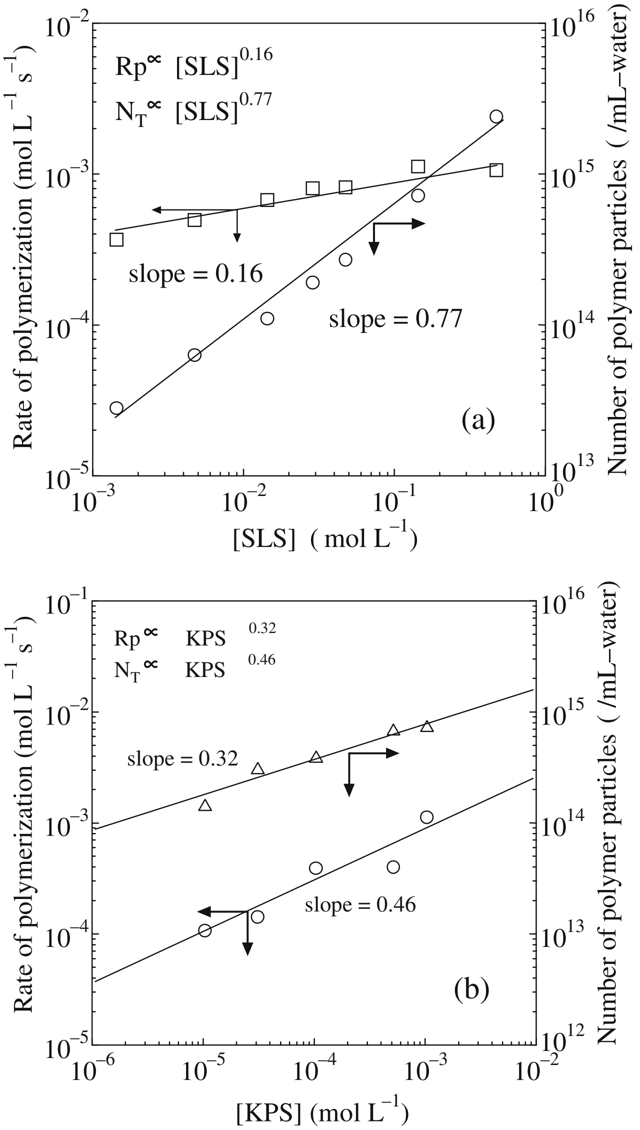

Fig. 4 Relationship of R_p and N_p as a function of the amounts of SLS (**a**) and KPS (**b**) in the emulsion polymerization. Recipe: the same as in Fig. 1

$[KPS]_0$ were a little at variance with those predicted by the Smith–Ewart theory ($R_p \propto [KPS]_0^{0.4}$, $N_p \propto [KPS]_0^{0.4}$). The slight differences indicate the effect of the escape of some chain-transferred radicals from the particle, rather than the initiation reaction of the primary radicals with the monomer in the aqueous phase.

Theoretical kinetics and mechanism of particle nucleation

Smith–Ewart's theory suggested the following relationship between R_p, N_p and the number average radicals per particle, $\overline{n}$, assuming that polymerization occurs inside the polymer particles, but not in the aqueous phase:

$$R_p = -d[M]_0/d\,t = \overline{n} k_p [M]_p N_p \left(M_g/N_A\right) \tag{1}$$

Here, $[M]_0$ is the initial monomer concentration, k_p is the propagation rate constant, $[M]_p$ is the monomer concentration in the polymer particles, N_p is the total number of polymer particles and N_A is Avogadro's number. The observed number average radicals per particle, $\overline{n}_{obs}$, are derived using the following equation.

$$\overline{n_{obs}} = \frac{R_p N_A}{k_p [M]_p N_p} \tag{2}$$

where k_p=3,153 L mol^{-1} s^{-1} is the propagation rate constant in the VPi system, which can be estimated from $k_p/k_{tw}{}^{1/2} = 274\ \exp\left(-2214/T\right) = 1.57 \times 10^{-5}$ [26] $k_{tw} = 9.99 \times 10^8\ exp(-9.4\omega)$ (L mol^{-1} s^{-1}) and ω is percent ratio of polymers in solution and is assumed to the same as those in the VAc system at 50 °C.

Ugelstad et al. [19, 20] has suggested that a general solution for $\overline{n}$ derived by Stockmayer [27] and O'Toole [18] should be solved simultaneously with the steady state radical balance equation in the aqueous phase. Nomura and Fujita [25, 28, 29] considered the overall radical balance in the system (i.e. Y=0), that is, the adsorption of chain-transferred monomer radical from a polymer particle and the entry of a radical into a particle, assuming radical termination in the aqueous phase to be insignificant, are balanced. They proposed a semi-empirical expression for $\overline{n}$ that gives a maximum error of only 4% error compared to the exact values given as the solutions to the simultaneous equation by Ugelstad. The expression provides an approximate relationship between $\overline{n}$ and the rate constant for radical desorption from the polymer particles (k_f) using a parameter α_w that is the ratio of the rate of radical production to that of radical termination:

$$\overline{n} = \frac{1}{2}\left\{\left[\left(\alpha_w + \frac{\alpha_w}{m}\right)^2 + \left(\alpha_w + \frac{\alpha_w}{m}\right)\right]^{1/2} - \left(\alpha_w + \frac{\alpha_w}{m}\right)\right\} + \left(\frac{1}{4} + \frac{\alpha_w}{2}\right)^{1/2} - \frac{1}{2} \tag{3}$$

$$\alpha_w = \frac{\rho_w v_p}{k_{tp} N_p} \qquad m = \frac{k_f v_p}{k_{tp}} \tag{4}$$

$$k_f = K_0 \frac{K_{mf}[M]_p}{K_0\ \overline{n} + k_p [M]_p} = \frac{12 D_w \delta \cdot}{m_d D_p^2}\left(\frac{k_{mf}}{k_p}\right) = K_0 C_{mf} \tag{5}$$

$$K_0 = \frac{12 D_w \delta}{m_d D_p^2} \qquad C_{mf} = \frac{\cdot\ k_{mf}}{k_p} \tag{6}$$

Table 1 Numerical values of constants used in the emulsion polymerization of vinyl pivalate (VPi) vs the amounts of SLS at 50 °C

Constant	Unit	Vinyl pivalate (VPi)
k_p	mol^{-1} L s^{-1}	k_p=3153[a]
k_t	mol^{-1} L s^{-1}	$k_t = 1.19 \times 10^{8}$[b]
δ	–	$\delta = (1 + D_w/m_d D_p)^{-1}$[c]
C_m[d]	–	0.0237 exp (−224/T)=1.57×10^{-5}
D_w[e]	cm^2 s^{-1}	1.50×10^{-5}
m_d[f]	–	1,300

[a] Estimated with equation, $k_p/k_t^{1/2} = 274\ \exp(-2214/T) = 0.289$ at 50 °C in Ref. 26

[b] Assuming termination reaction constant of VPi to be equal to that of VAc

[c] Diffusion coefficient of radical in the aqueous phase, D_p=$k_B T/3\pi\eta_0 r_o$ where k_B is Boltzmann constant, T (K) is the temperature, η_0 is the ratio of viscosity in water (0.7795) and r_o is the particle diameter

[d] C_m: chain transfer coefficient to monomer

[e] D_w: diffusion coefficient of the radical in the aqueous phase

[f] m_d: partition coefficient of the radical capable of escaping from the polymer particle to the water phase

Here, K_0 is the mass transfer parameter, C_m is rate of chain transfer reaction to the monomer estimated from the equation C_m=0.0237 exp (−2364/T)=1.57×10^{-5} (50 °C for VPi) reported by Kuraray, v_p is the volume of a polymer particle, k_{tp} is the termination rate constant for radical desorption from the polymer particles, k_{tp}=9.99×10^{8} exp (−9.4ω) [L mol^{-1} s^{-1}] where ω is ratio of distribution of the polymer in the aqueous phase, which was assumed to be the same as in the case of VAc. Other parameters in these formulae are: k_{tw} is the termination rate constant in the aqueous phase, k_a is the rate coefficient for radical entry into the polymer particles and m_d is the partition coefficient for a radical capable of escaping from polymer particle to water phase.

The expression for the number average of radicals (3) involves the parameters α_w and m, which themselves (4) contain several rate constants. The rate of radical production in the aqueous phase is given by

$$\rho_w = 2\, k_d f [I_0] \tag{7}$$

where k_d is the thermal decomposition rate constant, f is the initiator efficiency, which has a value of 0.6 and $[I_0]$ is the initiator concentration. There might be difficulties in predicting the exact real value of ρ_w because the decomposition rate constant for KPS is affected by ion strength and the nature of the chemical species in the reaction system. To determine $\overline{n}$ using the parameter α_w, m and k_f, we estimated ρ_w=5.89×10^{17} (molecules cm^{-3} s^{-1}) by (Eq. 7) using a value of the thermal decomposition rate constant, k_d of 1.1×10^{-6} (s^{-1}) and the initiator efficiency f= 0.6 at 50 °C.

The parameter δ, the ratio of the water side mass transfer resistance to the overall mass transfer resistance for a radical desorbed from the polymer particles that demonstrated in (Eq. 5) can be estimated with the following equation.

$$\delta = \left(1 + \frac{D_w}{m_d D_p}\right)^{-1} \tag{8}$$

$$D_p = k_B T/3\pi\eta_0 r \tag{9}$$

where D_w and D_p are the diffusion coefficients of the radical in a polymer particle and in the aqueous phase, respectively. The latter diffusion coefficient is given by $D_p = k_B T/3\pi\eta_0 r$ where k_B is Boltzmann's constant, T is the temperature, η_0 is the solvent viscosity and r is the particle radii. Table 1 lists the numerical values of the constants used in the analysis of the emulsion polymerization of VPi initiated by KPS at 50 °C vs the amounts of SLS.

Table 2 Values of polymer particle properties from emulsion polymerization using various amounts of SLS

[SLS] (X CMC*)	R_p (10^{-4} mol L^{-1} s^{-1})	d_p (nm)	$[M]_p$ (mol L^{-1})	N_p (10^{14} ml^{-1})	$\overline{n}_{ex}$	$\overline{n}_{th}$	t (10^{-4} s)	τ (10^{-4} s)	θ (10^{-4} s)
0.2	3.66	142	2.7	0.28	0.92	0.43	1.16	2.95	0.40
0.7	4.92	134	2.1	0.63	0.60	0.37	1.17	2.39	0.19
2.0	6.73	91	2.3	1.1	0.60	0.30	1.37	0.77	0.20
4.0	8.03	90	2.0	1.9	0.37	0.24	1.19	0.75	0.095
6.6	8.17	70	2.3	2.9	0.16	0.17	1.16	0.36	0.076
20	11.2	55	2.7	7.2	0.14	0.10	1.17	0.17	0.045
66	10.6	39	2.9	24.0	0.04	0.04	1.10	0.06	0.023

Initial polymerization rate (R_p), particle diameter (d_p), the concentration of the monomer in the polymer particle ($[M]_p$), number of polymer particles (N_p) and the experimental and theoretical number average of radicals in a particle ($\overline{n}_{ex}$ and $\overline{n}_{th}$), respectively

The table also compares the times of desorption of chain-transferred radical from the particle (τ), that of the entry of the oligomers radical into a particle (θ) and that of the propagation radical to the monomer in the particle (t)

Recipe: VPi 4.3 g, water 45 g, Na_2SO_4 0.07 g, KPS 0.0125 g, several moles of SLS, Ar atmosphere 50 °C

*CMC=7.20×10^{-3} mol L^{-1}

Theory–experiment comparisons

Using Eqs. (2) and (3), we performed a quantitative comparison between the theoretical and experimental number average radical per particle, $\overline{n}$. As listed in Table 2, an increase of the amount of SLS caused a decrease of the number average of radicals per particle $\overline{n}$ to less than 0.1. We can interpret this result as resulting from an increase of the rate of escape of chain-transferred monomer radical from the particle (k_f) relative to the rate of the monomer propagation reaction (k_p), producing a low value of α_w. Figure 5 shows the "Ugelstad-plots" that compare the theoretical and experimental values of $\overline{n}$ vs α_w in the emulsion polymerizations of VPi initiated with KPS at 50 °C and refers to the theoretical lines in the system of styrene (St), methyl methacrylate (MMA) and vinyl acetate (VCl). In the case of the VPi system, the experimental values of $\overline{n}$ (open circles) were in good agreement with the values estimated with the theoretical calculations (closed circles). The theoretical value of $\overline{n}$ decreased to less than 0.5 with decreasing values of α_w. This theoretical behavior of $\overline{n}$ vs α_w in the emulsion polymerizations of VPi was close to the experimental results observed in the emulsion polymerization of styrene. This behavior might be ascribed to several reasons: a high rate constant of the propagation reaction of the polymer radicals to the monomer, a high rate constant of the chain transfer reaction from the propagation radical to the monomer or the low solubility of VPi, being only 0.09 vol.% in water.

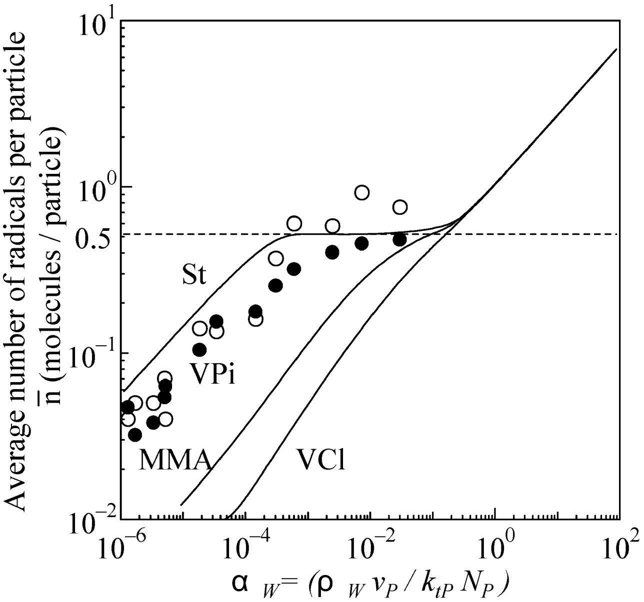

Fig. 5 Relationship of number average radicals in a particle $\overline{n}$ as a function of α_ω, assuming that the termination reaction in the aqueous phase can be ignored. *Solid lines*: theoretical results of $\overline{n}$ in the case of styrene (St), methyl methacrylate (MMA) and vinyl chloride (VCl) on the basis of equations reported by Nomura and colleagues [25, 28, 29]. The experimental results in the VPi system, *open circles*; the theoretical results, *closed circles*

To consider the kinetics and mechanism of the particle nucleation in more detail, we will compare the times of the chemical reactions such as the initiation reaction, propagation reaction, the chain transfer reaction of propagating radical to monomer and those of the entry/escape of the chain transfer monomer radical into/from the polymer particle. The time of escaping of the chain-transferred monomer radical (τ) from the particle, the time of entry of the oligomer radicals with a sulfate end group into the particle (θ) and the time needed for a propagation radical to locate in the polymer particle (t) can be formulated by the following equations.

$$\tau = L^2 / 2D_p \tag{10}$$

$$\theta = 1/2\pi d_n D_w N_p \tag{11}$$

$$t = 1 \Big/ \left(k_p[M]_p\right) \tag{12}$$

where L is the diameter of the particle, D_p and D_w are the diffusion constant in the particle and in the aqueous phase, respectively. Table 2 lists the calculated values of τ, θ and t. The times of desorption of the chain-transferred monomer radical from the particle (τ) and entry of the oligomer radicals (θ) were much shorter than that of the propagation radical to the monomer to locate in the particle (t). The addition of a considerable amount of SLS caused the mechanism of particle nucleation during polymerization. Consequently, if the escape of a chain-transferred monomer radical from a polymer particle occurs faster than the time for the propagation radical to be added to a monomer unit, then this is an important factor that influences the kinetics, which controls the particle nucleation.

Effect of chain transfer agents

We have studied the influence of the chain transfer agents (CTA) *n*-dibutyl disulfide, *t*-dibutyl disulfide and L-cysteine on the emulsion polymerization. Figure 6 shows the influence of *n*-dibutyl disulfide on the time–conversion curves in the emulsion polymerization initiated by the water-soluble azo-initiator, V-50. The initial rate of polymerization (R_p) decreased with increasing amounts of CTA. The influence of the amounts of CTA on R_p can be explained by two factors. One is the desorption of the radical from the particle followed by a chain transfer reaction of the propagating radical to the chain transfer agents in the polymer particle. The second is a decrease of

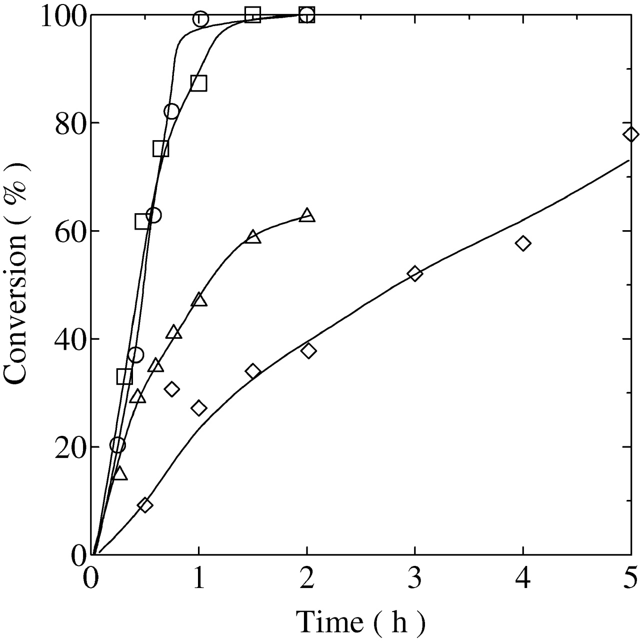

Fig. 6 Effect of *n*-dibutyl disulfide on time–conversion curves in the emulsion polymerization initiated by V-50 using SLS. Recipe: VPi 4.3 g, water 45 g, SLS 6.17 g, Na_2SO_4 0.07 g, V-50: 4.49×10^{-4} g, [*n*-dibutyl disulfide]/[VPi]: *open circles*, none; *open squares*, 1.2×10^{-5}; *open triangles*, 5.9×10^{-4}; *open diamonds*, 5.9×10^{-3}; Ar atmosphere, 50 °C

the effective concentration of radicals per particle with the recombination of the chain-transferred radicals in the polymer particle. The addition of sulfate oxygen at a pH less than 3.5 caused polymerization into the particle. Figure 7 and Table 3 show the influence of *n*-dibutyl disulfide on the particle sizes (a) and the number of polymer particles (b) during emulsion polymerization. The addition of increasing amounts of *n*-dibutyl disulfide caused a slight increase in the particle size from 27 to 45 nm using the V-50 initiator, except at the highest concentration of *n*-dibutyl disulfide wherein the number of polymer particles irregularly decreased over the range of 10.7×10^{15}–1.5×10^{15}/ml water. There was a regular decrease except at the highest mole concentration of *n*-dibutyl disulfide, which might to be due to a drastically increased rate of escape of chain-transferred radical from the polymer particle. The log–log plots of the rate of polymerization and the number of polymer particles vs the amount of *n*-dibutyl disulfide as shown in Fig. 8a reveal that, for the V-50 initiator, the rate of polymerization linearly decreased with increasing amounts of CTA, while the number of polymer particles first slightly decreased and then increased.

The effect of *n*-dibutyl disulfide on R_p and N_p might be caused by termination reactions among chain transfer agents in the polymer particle and subsequent re-entry of the chain-transferred radicals into the particle. The reason for the decrease of the rate of polymerization with the addition of a small amount of CTA is thought to arise from a decrease of the average number of radicals per particle being less than 0.5 and yields a considerable desorption of *n*-butyl disulfide radical from the polymer particle. The chain transfer reaction of agents such as *n*-dibutyl disulfide and *t*-dibutyl disulfide might cause a chain transfer reaction on the particle surface to escape from the particle. The considerable increase of radical desorption from the particles caused by suitable chain transfer agents can be seen as a kind of “promoting effect” and affords a decrease of the degree of polymerization of the resulting polymer

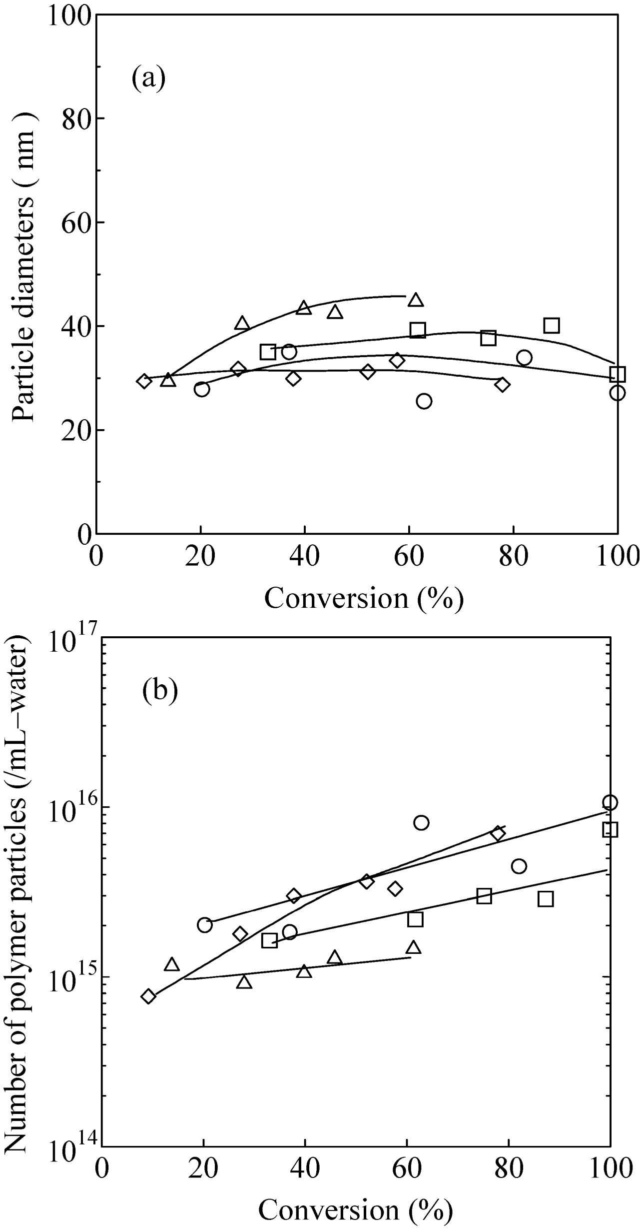

Fig. 7 Effect of *n*-dibutyl disulfide on the particle diameters (**a**) and the number of particles (**b**) obtained in the emulsion polymerization. Recipe and symbols: the same as in Fig. 6

Table 3 Effect of the amounts of chain transfer agents (CTA) on the particle sizes (d_p), the number of polymer particles (N_p), the number average degree of polymerization ($\overline{P_n}$) of the resulting polymer and the number of polymers in a particle in the emulsion polymerization initiated by KPS and V-50

Chain transfer agents (CTA)	Initiators	[CTA]/[VPi] (mol/mol)	Conv. (%)	d_p (nm)	N_p (10^{15}/ml)	$\overline{P_n}$	Number of polymers in a particle
n-dibutyl disulfide	V-50	0	100	27	10.7	4,650	13
		1.2×10^{-5}	100	31	7.3	2,810	30
		5.9×10^{-4}	61	45	1.5	6,290	43
		5.9×10^{-3}	78	29	7.0	680	102
	KPS	0	100	38	10.6	9,360	18
		1.2×10^{-5}	100	31	5.0	1,250	71
		1.2×10^{-4}	100	32	5.5	1,280	76
		5.9×10^{-3}	100	24	1.3	1,420	30
		5.0×10^{-2}	98	11	54.5	160	24
		1.0×10^{-1}	55	9.7	1.3×10^{2}	91	30
t-dibutyl disulfide	KPS	0	100	38	10.6	9,360	18
		1.0×10^{-3}	100	28.6	9.1	2,900	54
		1.0×10^{-2}	100	24.8	13.9	840	24

Recipe: VPi 4.3 g (1.69 mol L^{-1}), water 45 g, Na_2SO_4 0.07 g, SLS 6.17 g, chain transfer agents: several mole-ratio of CTA to monomer, V-50 0.0004 g, KPS 0.01 g, Ar atmosphere 50 °C

due to the chain transfer reaction into the polymer particle with the extremely low solubility of CTA in the aqueous phase.

We also investigated the relationship between the rate of polymerization and the number of particles produced as a function of the mole-ratio of *n*-dibutyl disulfide to VPi for the case of the water-soluble initiator KPS. As shown in Fig. 8b, for small amounts of *n*-dibutyl disulfide the rate of polymerization stayed constant, but beyond a value of [*n*-dibutyl disulfide]/[VPi] of about 10^{-2}, R_p decreased rapidly. As Table 3 shows, large amounts of *n*-dibutyl disulfide caused a gradual decrease of the particle size to less than 10 nm, while the number of particles increased substantially to about 1.3×10^{17}/ml. The addition of *n*-dibutyl disulfide caused a decrease of the number average degree of polymerization of the resulting polymer. These results can be explained by the following arguments. The first is that an acceleration of the desorption of the chain-transferred radical will decrease the number average radical per particle to less than 0.5, if the polymerization loci are limited in the polymer particle. The chain transfer reaction to CTA caused a decrease of the number average degree of polymerization of the resulting polymer. A second reason is that the chain transfer agent may play the role of a co-surfactant to stabilize the emulsion particle to less than 10 nm under conditions of constant ionic strength by the addition of sodium sulfate. In this case, the addition of chain transfer agents caused the stabilization of the monomer droplets leading to a low efficiency of the mass transfer in the aqueous phase, that is, the control of an Ostwald ripening by the CTA.

Lastly, we investigated the influence of L-cysteine on the emulsion polymerization initiated by V-50. The initial rate of polymerization did not depend on the amounts of L-cysteine (not shown in the figures). As detailed in Table 4, the addition of L-cysteine in the largest amount caused an increase of the particle size, but in a bimodal distribution at about 69 and 130 nm. The resulting number of polymer particle ranged from 1×10^{14}/ml for the large particles to 8×10^{14}/ml for the small particles. The addition of L-cysteine caused a decrease in the degree of polymerization. These experimental results can be qualitatively described as due to a reduced desorption of chain transfer radical from the polymer particle when V-50 and L-cysteine were used due to a low chain transfer reaction rate constant of L-cysteine because of its low solubility in the polymer particle.

The discussion of the CTA experiments above was qualitative. Now, we turn to a quantitative description. On the basis of the theoretical consideration previously proposed by the present authors [30], the total rate coefficient for radical desorption (k_f) from the particles is given by

$$kf = K_0\,m\left(\frac{k_{\mathrm{mf}}[T]p}{K_{0\,\mathrm{m}}\overline{n} + kp[M]p}\right) + K_{0\,T}\left(\frac{k_{T\mathrm{f}}[T]p}{K_{0\,T}\overline{n} + k_{i\,T}[M]p}\right) \tag{13}$$

$$K_{0\,T} = \frac{12D_{\mathrm{w}}\,\delta}{m_{\mathrm{d}}D_{\mathrm{p}}^2} \qquad C_{\mathrm{m}T} = \frac{\cdot\,k_{\mathrm{m}T}}{k_{\mathrm{p}}} \tag{14}$$

The total desorption rate coefficient equation is constructed from two parts: one is the desorption rate

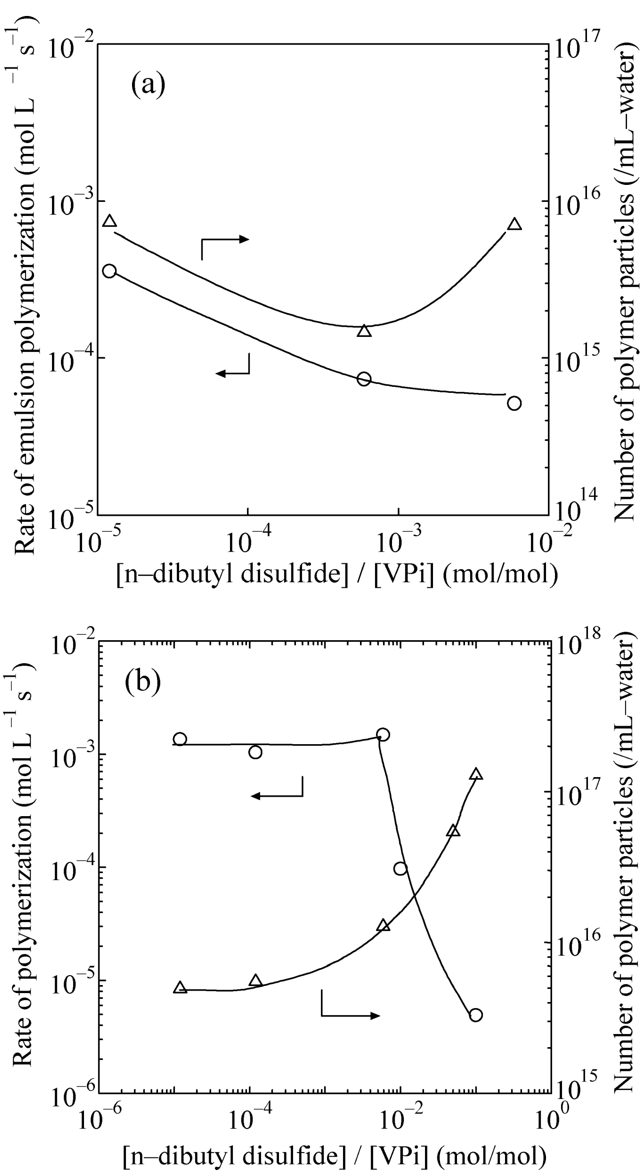

Fig. 8 Effect of the amounts of *n*-dibutyl disulfide on the initial rate of polymerization and the number of polymer particles in the emulsion polymerizations initiated by V-50 (**a**) and KPS (**b**). Recipe: VPi 4.3 g, water 45 g, SLS 6.17 g, Na_2SO_4 0.07 g, V-50 0.0004 g, KPS 0.01 g, several mole-ratio of *n*-dibutyl disulfide to VPi, Ar atmosphere, 50 °C

coefficient of chain-transferred monomer radicals, the other is the desorption rate coefficient of chain-transferred chain transfer agents. Here, $K_{0\mathrm{m}}$, K_{0T} are the desorption ratio coefficients of the chain-transferred monomer radicals and those of the chain transfer agent radicals, respectively. k_{mf} and $k_{T\mathrm{f}}$ are the chain transfer rate constants to the monomer and to the chain transfer agent, respectively. $k_{\mathrm{i}T}$ is the re-initiating rate constant of the chain transfer agent radical. $[T]_{\mathrm{p}}$ and $[M]_{\mathrm{p}}$ are the concentrations of the chain transfer agent and the monomer in the polymer particles, respectively. In (Eq. 14), δ is the ratio of the water–side mass transfer resistance to the overall mass transfer resistance around the particle for chain transfer agent radicals and satisfies the inequality $0<\delta<1$, and $C_{\mathrm{m}T}$ is chain transfer rate constant to chain transfer agent. In this case, the average number of radicals per particle $\overline{n}$ can be expressed by the following equation:

$$\overline{n} = \frac{1}{2}\left[-C + \left(C^2 + 2C\right)^{1/2}\right] \quad C = \frac{r_{\mathrm{i}}}{k_{\mathrm{f}} N_{\mathrm{p}}} \tag{15}$$

where r_{i} is the rate of radical production in the aqueous phase and N_{p} is the number of polymer particles. Equations (13)–(15) indicate that the rate of polymerization, $R_{\mathrm{p}} = k_{\mathrm{p}}\overline{n}[M]_{\mathrm{p}}N_{\mathrm{p}}$ and $\overline{n}$ decreased with increasing values of k_{f}, assuming that the number of polymer particles and the rate of radical production of KPS and V-50 in the aqueous phase remain constant. According to (Eq. 13), the value of k_{f} should increase with increasing solubility of chain transfer agents $[T]_{\mathrm{p}}$ in the particles and with the chain transfer constant, $k_{T\mathrm{f}}$, for individual chain transfer agents.

Experimentally, we found that the addition of the chain transfer agents: *n*-dibutyl disulfide and *t*-dibutyl disulfide caused an increase of the value of k_{f} by increasing the concentration in the monomer droplets when the pH was controlled at 3.5 by addition of sodium sulfuric. We ascribe this behavior to the high reaction rate constant of the chain transfer agents as evidenced by the values of the following experimental parameters: the chain transfer constant (C_x) of vinyl acetate (VAc) at 60 °C to *n*-dibutyl disulfide is about 1.0 and to *t*-dibutyl disulfide is <1.0 [26]. We suppose that these values reflect the influence of the amount of initiator on the value of k_{f}.

Table 4 Effect of the amounts of L-cysteine on polymer particles

[L-cysteine]/[VPi]	d_{p} (nm)	N_{p} (10^{14}/ml)	$\overline{M_n}$ (10^5)	$\overline{M_w}$ (10^5)	$\overline{P_n}$	$\overline{M_w}/\overline{M_n}$
0	69, 81	6.4, 4.0	13.4	43.5	10,500	3.2
1.0×10^{-6}	96	2.3	6.8	23.8	5,300	3.5
1.0×10^{-5}	83	4.0	3.7	19.6	2,900	5.3
1.0×10^{-4}	64, 130	8.0, 1.0	2.7	14.0	2,000	5.3

The particle diameter (d_{p}), number of polymer particles (N_{p}), the number ($\overline{M_n}$) and weight average ($\overline{M_w}$) molecular weights and the number average degree ($\overline{P_n}$) of polymerization of the resulting polymer obtained in the emulsion polymerization

Recipe: VPi 5.0 ml (3.4×10^{-2} mol), H_2O 45 g, Na_2SO_4 0.07 g, SLS 0.467 g, V-50 0.004 g, Ar atmosphere 50 °C

The addition of L-cysteine to the polymerization caused a decrease of the value of k_f with a decrease of $[T]_p$ in the particles. This is thought to be attributed to a small chain transfer rate constant of acrylamide to L-cysteine of 0.17 at 30 °C [31]. The rate of polymerization, R_p decreased with increasing k_f, as expected from an increase of the chain transfer constant of the CTA and the high solubility of chain transfer agents in the particle. Consequently, we concluded that the influence of the amounts of chain transfer agents on the kinetic mechanism could be quantitatively understood in terms of the dependence on the chain transfer reaction rate, the solubility of CTA and the efficiency of mass transfer in the aqueous phase on the desorption of the chain transfer agents from the particle.

When the termination reactions of radicals occur via coupling reactions in the polymer particle, that is, assuming that the termination reaction is negligible in the aqueous phase, the instantaneous degree of polymerization of resulting polymers $\overline{P_n}$ is given by

$$\overline{P_n} = \frac{k_{\mathrm{p}}[M]_{\mathrm{p}}\overline{n}\,N_{\mathrm{p}}}{(\rho_{\mathrm{w}}/2)\lambda + \rho_{\mathrm{w}}(1-\lambda) + k_{T\mathrm{f}}[M]_{\mathrm{p}}\,\overline{n}\,N_{\mathrm{p}}} \tag{16}$$

where ρ_w is the rate of radical production in the aqueous phase and λ is the probability of radical termination, assuming that the termination reaction is a combination reaction (λ=0 for VPi) and k_{Tf} is the chain transfer constant to the chain transfer agents. The instantaneous number average degree of polymerization would decrease from the effect of a decrease in $\overline{n}$ resulting from an increase of k_{Tf}, owing to the desorption of the chain transfer radical from the polymer particle. The cumulative degree of polymerization, $\overline{P_N}$ with X as conversion of the monomer is given by

$$\overline{P_N} = \frac{X}{\int_0^X \left(1/\overline{P_n}\right)dX} \tag{17}$$

The relationship of the number average degree of polymerization ($\overline{P_n}$) with the amount of the disulfide chain transfer agents are summarized in Table 3. In the cases of the water-soluble initiators, V-50 and KPS, the values of $\overline{P_n}$ of the resulting polymer decreased with increasing amounts of chain transfer agent. In particular, the use of *n*-dibutyl disulfide combined with V-50 produced a marked decrease in $\overline{P_n}$ and increased the number of polymer molecules in a particle up to 102, thanks to fast chain transfer reactions to chain transfer agents on the boundary surface. In the case where we used a ratio of 1/10 KPS to *n*-dibutyl disulfide in the emulsion polymerization, $\overline{P_n}$ decreased to about 90 and the number of polymer molecules per particles dropped to 30. We attribute these effects to a high solubility of *n*-dibutyl disulfide in the polymer particle and a large concentration of primary sulfate radical in the aqueous phase. These conditions would have the effect of decreasing $\overline{n}$ by increasing k_{Tf} and ρ_w, that is, increasing the rate of desorption of the chain transfer radical from the polymer particle. In the reactions with *t*-dibutyl disulfide, the addition of the most concentrated solution (0.01× 1.64 mol L^{-1}) caused a decrease of $\overline{P_n}$ to 840 and yielded only 24 polymer molecules per polymer particle.

There was only a slight difference in the behavior of different CTAs on the degree of polymerization of the resulting polymers. These subtle variations are thought to arise from two sources. One is a slight difference in the chain transfer reaction rate constant between *t*-dibutyl disulfide (C_s<1.0) and *n*-dibutyl disulfide (C_s=1.0) [26], that is, a lower rate of desorption of the chain transfer radical from the polymer particle in the case of *n*-dibutyl disulfide. Another reason is the variations in solubility of the chain transfer agents in the polymer particle. In the case where L-cysteine was used in the emulsion polymerization initiated by V-50, the number average degree of polymerization of the resulting polymer decreased somewhat with increasing CTA concentration. These results can be described by a low rate of desorption of the chain transfer radical from the polymer particle due to a low rate constant of L-cysteine resulting from a low solubility in the polymer particle. Overall, the influence of chain transfer agents on the mechanism of particle nucleation and the number average degree of polymerization of the resulting polymer can be described theoretically in terms of the dependence of the desorption of chain transfer radicals from the polymer particles on the chain transfer rate of CTA, its solubility in the polymer particle and the efficiency of the mass transfer of CTA from the aqueous phase to the monomer droplets.

Conclusion

We have studied the kinetics and mechanism of particle nucleation in the emulsion polymerization of VPi as a function of the amount of SLS using water-soluble initiators such as KPS and V-50. In the standard case, there was a relationship between the initial rates of polymerization, R_p, and the number of polymer particles, N_p, with respect to increasing the amount of SLS and KPS ($R_p \propto [\mathrm{SLS}]^{0.16}$, $N_p \propto [\mathrm{SLS}]^{0.77}$, $R_p \propto [\mathrm{KPS}]^{0.32}$ and $N_p \propto [\mathrm{KPS}]^{0.46}$). On the basis of a kinetic analysis using the Ugelstad plots, we were able to make a qualitative comparison between the theoretical and experimental behaviors of the average number of radical per particle $\overline{n}$ as function of the model parameter $\alpha_\omega = \rho_\omega V_p / k_{tp} N_p$. The behavior of $\overline{n}$ vs α_ω in this system was similar to that in the emulsion polymerization of styrene varied with various amounts of SLS. This result can be understood using a kinetic model consideration featuring low levels of adsorption of the chain-transferred monomer radical from the particle. The addition of the chain transfer agents: *n*-dibutyl disulfide and *t*-dibutyl disulfide caused a decrease in the number average molecular weight of the resulting polymer together with a decrease in the size of the polymer particle in the aqueous phase. The experimental results indicate a considerable desorption of the chain transfer radicals from the polymer particle having the effect of decreasing $\overline{n}$ resulting from an increase of solubility of CTA into the polymer particle, as predicted theoretically. On the other hand, in the case of L-cysteine used in the emulsion polymerization initiated by V-50, the addition of L-cysteine caused a slight decrease of the number average degree of polymerization. This result can be ascribed to a small amount of desorption of chain transfer radicals from the polymer particle due to a low reaction rate of L-cysteine resulting from a low solubility in the particle. The general role of chain transfer agents in these emulsion polymerizations is to modify the escaping of chain-transferred radicals from the polymer particles. A kinetic analysis reveals that the molecular weight, size and degree of polymerization of the product depend on the solubility of the CTA in the monomer droplets and the efficiency of its mass transfer from the monomer droplet to the aqueous phase.

References

1. Yamamoto T, Yoda S, Sangen O, Fukae R, Kamachi M (1989) Polym J 21:1053
2. Marten FL (1985) In: Mark HF, Bikales NM, Menges CG, Kroschewitz JI (eds) Encyclopedia of polymer science and engineering, Wiley, New York, 17:167–180
3. Masuda M (1991) In: Finch CA (ed) Polyvinyl alcohol—evelopments, Wiley, New York, pp403–422, p 711
4. Yamaura K, Hoei Y, Matsuzawa S, Go Y (1971) Kolloid-Z Z Polym 7:243
5. Ghim HD, Kim JP, Lyoo WS (2003) Polymer 44:895
6. Galeska I, Kim T-K, Patil SD, Bhardwaj U, Chatttopadhyay D, Papadimitrakopoulos F, Burgess DJ (2005) AAPS J 7:E231
7. Kobayashi H, Kato M, Matsuda A, Taguchi T, Kataoka K, Tanaka J (2004) Trans Mater Res Soc Jpn 29:2897
8. Chu KC, Jordan KJ, Battista JJ, Van Dyk J, Rutt BK (2000) Phys Med Biol 45:955
9. Kinoshita A, Yamada K, Ito M, Yamazaki M, Taneda M, Hayakawa T (1994) Neuroradiology 36:65
10. Brown KT, Brody LA, Decorato DR, Getrajdman GI (2001) J Vasc Inter Radiol 12:882
11. Kwark YJ, Lyoo WS, Ha WS (1996) Polym J 28:851
12. Yeum JH, Ji BC, Noh SK, Jeon HY, Kwak JW, Lyoo WS (2004) Polymer 45:4037
13. Lyoo WS, Kim JH, Ghim HD (2001) Polymer 42:6317
14. Lyoo WS, Kwak JW, Yeum JH, Ji BC, Lee CJ, Noh SK (2005) J Polym Sci, A, Polym Chem 43:789
15. Smith WJ, Ewart RH (1948) J Chem Phys 16:592
16. Smith WJ (1948) J Am Chem Soc 70:3695
17. Smith WJ (1949) J Am Chem Soc 71:4077
18. O’Toole JT (1965) J Appl Polym Sci 9:1291
19. Ugelstad J, Mφrk PC, Aasen JQ (1967) J Polym Sci, A-1, Polym Chem 5:2281
20. Ugelstad J, Mφrk PC, Dahl P, Rangnes P (1969) J Polym Sci, C 27:49
21. Nomura M (1987) Kobunshi 36:684
22. Nomura M, Minamino Y, Fujita K, Harada M (1982) J Polym Sci Polym Chem Ed 20:1261
23. Harada M, Nomura M, Eguchi W, Nagata S (1971) J Chem Eng Jpn 4:54
24. Nomura M (1976) Polymer Colloid Group Newsletter 6 (1) (May)
25. Nomura M, Harada M, Eguchi W, Nagata S (1976) In: Piirma I, Gardon JL (eds) Emulsion polymerization. Am Chem Soc Symp Ser 24:102
26. Clarke JT, Howard RO, Stockmayer WH (1960) Eingegangen Am 21:427
27. Stockmayer WH (1957) J Polym Sci 24:314
28. Nomura M, Fujita K (1985) Makromol Chem Suppl 10/11:25
29. Nomura M, Kubo M, Fujita K (1983) J Appl Polym Sci 28:2767
30. Nomura M (1982) In:Piirma I (ed) Emulsion polymerization. Academic, p 191
31. Kikuchi K, Ueno Y, Okaya T (2003) Kobunshi Ronbunshu 60:448