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ORIGINAL CONTRIBUTION

Effect of additives on the initial stage of emulsion polymerization of styrene (St) using poly(vinyl alcohol) as a protective colloid

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Abstract To realize the mechanism of particle formation followed by the grafting of styrene (St) onto poly(vinyl alcohol) (PVA) more precisely, we investigated the influence of additives on model experiments of emulsion polymerizations in 1 ml styrene (St) per 100 ml water at 70 °C using PVA as a protective colloid. In the case of a standard system without additive, experimental results indicate new particle formation, and that 30% of St feed and 30% of the PVA used were grafted. The sulfate radical seldom enters into particles but reacts with PVA, forming the PVA radical that yields the grafting of St onto PVA. The experimental results are thought to arise from a hydrogen abstraction from PVA with a sulfate radical. The addition of low-molecular-weight alcohol, such as isopropyl alcohol (i-PrOH) and n-propyl alcohol (n-PrOH), strongly affected the mechanism of particle formation in terms of a decrease in grafting, due to competition between hydrogen abstraction from PVA and the alcohols with a sulfate radical. Surprisingly, the addition of a low-reactive alcohol, such as t-butyl alcohol (t-BuOH), also resulted in the particle formation with a decrease in grafting, influenced the polymerization locus to be a monomer droplets dispersed by t-BuOH, and confirmed homogeneous nucleation with the increase in the solubility of St in the aqueous phase.

Keywords Emulsion polymerization · Grafting · Styrene · Poly(vinyl alcohol) · Protective colloid · Additive effect

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Introduction

Poly(vinyl alcohol) (PVA) has been used industrially as a dispersant in the synthesis of the (co) polymer emulsions of vinyl acetate (VAc). In polymer emulsion, the advantage of using PVA as a protective colloid, in contrast to the common surfactants, is the strengthening effect of PVA on the emulsion films [1, 2]. PVA as a polymer protective colloid instead of a surfactant such as sodium lauryl sulphate has been widely used in emulsion films. It is worthwhile in producing styrene/butadiene (SB) lattices using PVA for polymer industrial material fields such as adhesives, binders, paints, and coatings. However, it has not been employed in the emulsion polymerizations of conjugated monomers such as acrylic derivatives and styrene/butadiene due to the lack of stability during polymerization. The lack of stability has been believed to be caused by the weak reactivity of grafting conjugated monomers onto PVA. The authors had doubts about this because there should be two grafting mechanisms: one is hydrogen abstraction from PVA with the growing chain radicals, and the other is with the primary radicals. To investigate the possibility of grafting acrylics onto PVA with a sulfate radical, the authors employed a model experiment utilizing MMA as a representative of acrylics, and a very low monomer concentration (MMA/PVA/water = 1/1/100) that can be regarded as the initial stage of emulsion polymerization [2–6]. One part of our present investigation has already been reported: about 95% of polymerized MMA and approximately 65% of PVA were grafted [3–7]. On the basis of a kinetic consideration of the experimental results, the main reaction was concluded to be hydrogen abstraction from PVA with a sulfate radical. The authors also discussed the difference between the results in the MMA and VAc system [8]. Unexpectedly, no difference in the grafting behavior was observed in comparison with the VAc system. During the initial stage, large amounts of PVA were consumed by grafting to result in particle formation. The mechanism of the common emulsion polymerization of acrylic monomers using PVA as a protective colloid was discussed in terms of the instability of the soap-free particles formed after the consumption of free PVA in water by grafting the acrylic monomer onto PVA [9]. The reason for instability in soap-free particles of PMMA was concluded to be the low reactivity of the sulfate radical with MMA compared to that with VAc. On the other hand, in the case of an aromatic monomer, such as styrene (St), it has not been realized whether the grafting reaction would take place. There have not been any papers with regard to the stability of emulsion, particle formation, and grafting behavior in the emulsion polymerization of St using PVA as a protective colloid, owing to a low reactivity of the propagation radical with PVA. To clarify the reasons for the unsuitableness of utilizing PVA in the emulsion polymerization of St, the authors have studied the initial stage of the emulsion polymerization using a very low concentration of St in the presence of PVA. The aim of this study is to investigate the influence of low-molecular-weight alcohols, such as isopropyl alcohol (i-PrOH), n-propyl alcohol (n-PrOH), and t-butyl alcohol (t-BuOH) on model experiments of emulsion polymerization in a 1 vol.% St solution using PVA initiated by APS. Especially, in additional cases, such as t-BuOH, the experimental results will be discussed with respect to the grafting behavior, particle formation and polymerization locus dependent on the solubility of St by the addition of t-BuOH.

Experiments

Materials

PVA (degree of hydrolysis: 88%, degree of polymerization 580, supplied by Kuraray, Japan) was used after Soxhlet extraction with methanol to remove sodium acetate. Styrene (St) was distilled under reduced pressure before polymerization. APS (Wako Pure Chemical, Japan) of GR grade and low-molecular-weight alcohols, such as isopropyl alcohol (i-PrOH), n-propyl alcohol (n-PrOH), and t-butyl alcohol (t-BuOH) (Nacalai Tesque, Japan) were used as received.

Model emulsion polymerization

Prescribed amounts of PVA were added to a 200-ml flask equipped with an argon inlet tube, a vacuum-pumping cock, and a sampling cock, and an evacuation-argon introduction procedure was carried out three times. Model emulsion polymerization was mainly carried out under an argon atmosphere with the following recipe: St/PVA/APS/water=0.93/1/0.05/100 (weight ratio) in the presence of alcohol being a 10 vol.% at 70 °C for 2 h. With respect to the low viscosity of the dilution in the model experiments, the stirring speed was kept at 200 rpm with a magnetic stirrer.

Fractionation of the polymers in emulsion

The polymers in the emulsion were fractionated into methyl ethyl ketone (MEK)-soluble (homo-PS) at the first stage, water-soluble (homo-PVA) at the second stage, and the insoluble part (grafted PVA) at the final stage. The last part was regarded as the graft polymers. The number-average molecular weights of the MEK-soluble part (homo-PS) and insoluble part (grafted PVA) were determined by GPC (Tosoh, TSK$_{\text{gel}}$ GMH$_{\text{HR}}$-M, polystyrene standard) at 40 °C in tetrahydrofuran after acetylating the polymers.

Measurement

Conversions during the polymerization were determined gravimetrically. The rates of polymerization were determined by initial slope of time-conversion curves. Particle diameters were measured by the dynamic light scattering (DLS, PAR-III, Otsuka Electronics, Japan). The monomer concentration in the aqueous phase was measured by gas chromatography analysis (G180, Gas chromatograph, Yanaco, Japan).

Results and discussion

Model emulsion polymerizations of St using PVA

Model emulsion polymerizations of St using PVA as a protective colloid were carried out. The monomer concentration was 1 ml St per 100 ml water. Emulsion polymerization started immediately after introducing APS (0.05 g). Figure 1 shows the time-conversion curves. In the standard system using 1 g of PVA, the conversions were only 50% at 2 h. The rate of polymerization (R_p) decreased to be 1.8×10^{-5} mol l^{-1} s^{-1}. The rate of polymerization slightly increased with increasing the amount of PVA. Figure 2 shows the particle diameters (a) and the number of particles (b) during polymerization. In this case of using 1 g of PVA, 85 nm polymer particles which nucleated at a very early stage gradually became large, whereas the number of particles increased to 2.0×10^{13}/ml, which indicates particle nucleation due to added PVA. On the other hand, in the absence of PVA, the process of particle growth was observed as shown in Fig. 2a,b. The resulting polymer in

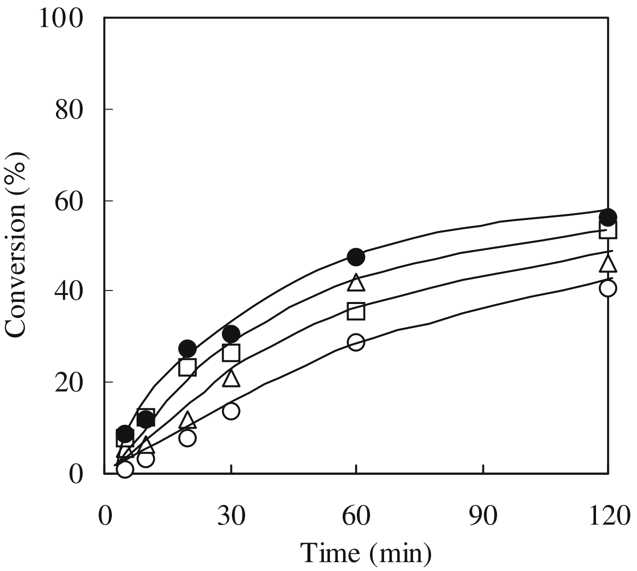

Fig. 1 Time-conversion curves of the model emulsion polymerization of styrene (St) using poly(vinyl alcohol) (PVA) as a protective colloid. Recipe: St 0.96 g, PVA; *Open circle* none; *open triangle* 0.5 g; *open square* 1.0 g; *closed circle* 2.0 g, APS 0.05 g, water 99 g, 70 °C, and 2 h

the emulsions was fractionated into three parts. The fractionation results are listed in Table 1. In the standard system using 1 g of PVA, about 33% of the St feed and 28% of the PVA used were grafted. The degree of grafting onto PVA with St increased with increasing the amount of PVA. Although the degree of grafting on PVA (grafted PVA) apparently increased to be 35% per 0.5 g of PVA used, the weight of grafting onto PVA (0.17 g) was found to be smaller than that (0.28 g) in the presence of 1 g of PVA. The weight of grafting onto PVA increased with increasing the amount of added PVA. This indicates evidence of the grafting of St onto PVA with a sulfate radical, notwithstanding the reactivity of the propagation radical with PS, owing to the higher reactivity of hydrogen abstraction from PVA than that of the propagation reaction.

Effect of additives on the emulsion polymerization of St using PVA

The influence of low-molecular-weight alcohols on the model emulsion polymerization of St using PVA was investigated. Figure 3 shows the time-conversion curves. In additional cases of alcohols, such as i-PrOH, n-PrOH, and t-BuOH at 10 vol.%, polymerization was achieved to be 100% during conversion for 2 h, where the rate of polymerization in these additional cases was higher than that in the absence of alcohol. Figure 4 shows the particle diameters (a) and the number of particles (b) during the polymerization. In the additional case of alcohol, such as i-PrOH, the particle size drastically increased to be about 90 nm in the range of 10–20% conversion and it gradually increased to be about 120 nm in the final stage. The number of particles kept constant at approximately 1×10^{13}/ml water. The addition of alcohols, such as i-PrOH and n-PrOH, to the system strongly affected the mechanism of particle nucleation, followed by a decrease in grafting. The experimental results are thought to arise from competition between hydrogen abstraction from PVA and alcohols with a sulfate radical, due to the high-rate constant. In the case of a low reactive alcohol, such as t-BuOH, although hydrogen abstraction from t-BuOH with a sulfate radical seems to be negligible [11], the particle size slightly increased to be about 95 nm, while the number of particles slightly increased to be 4×10^{13}/ml water, which indicates the mechanism of particle growth.

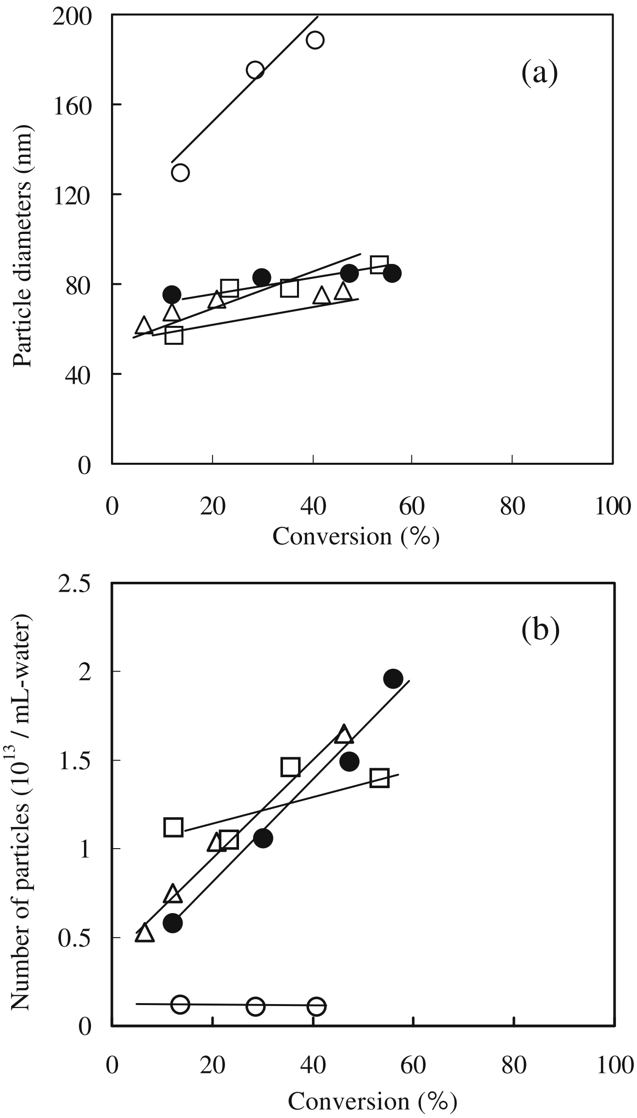

Fig. 2 Particle diameters (**a**) and the number of particles (**b**) during polymerization. Recipe and marks: the same as in Fig. 1

Table 1 Effect of the amounts of PVA on the particle diameters, number of particles, and grafts

PVA (g)	Particle diameter (D_n) (nm)	Number of particles (10^{12}/ml)	Grafted PS (%)	Grafted PVA (%)
			Polymerized St	Feed PVA
None	195	1.1	–	–
0.5	80	16.5	13	35
1.0	90	14.0	33	28
2.0	83	19.6	76	58

Recipe is the same as in Fig. 1.

The influence of additives on the grafting of St onto PVA was investigated. Table 2 lists the effect of alcohols on the grafting behavior. In comparison with that in the standard case without alcohol, 33% of the polymerized St and 28% of the feed PVA were grafted, due to the low solubility of St (0.03 vol.%). On the other hand, the additional case of i-PrOH at 10 vol.% remarkably decreased the grafting of St onto PVA (grafted PVA) to about 9%, that is, an increase of the homo-polymer of PS with an increase of the solubility of St to 0.35 vol.%, while the grafting of St (grafted PS) slightly decreased to 20%. In the case of another addition, such as n-PrOH, the functional results with respect to the grafting of St onto PVA were found to be similar to that in the case of i-PrOH: 12% of the feed PVA and 23% of the polymerized St were grafted. This result is thought to arise from the competition between the hydrogen abstraction from PVA and alcohols with a sulfate radical, due to the high-rate constant [3, 4, 11]. Surprisingly, the addition of t-BuOH to the system strongly affected the grafting of St onto PVA, where 9% of the polymerized St and 52% of the feed PVA were grafted, and the solubility of St increased to 0.24 vol.% by the addition of t-BuOH.

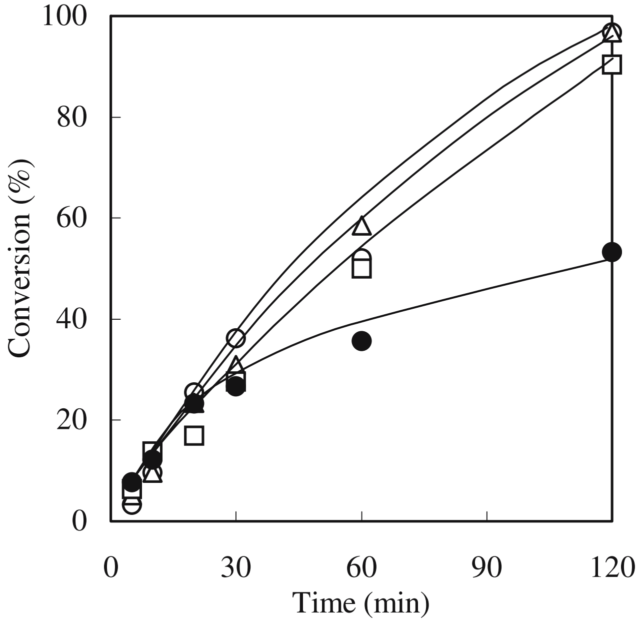

Fig. 3 Time-conversion curves in several cases. Recipe: St 1 ml, continuous phase 100 ml, alcohol (10 vol.%): *closed circle* none, *open circle* t-BuOH, *open triangle* n-PrOH, *open square* i-PrOH

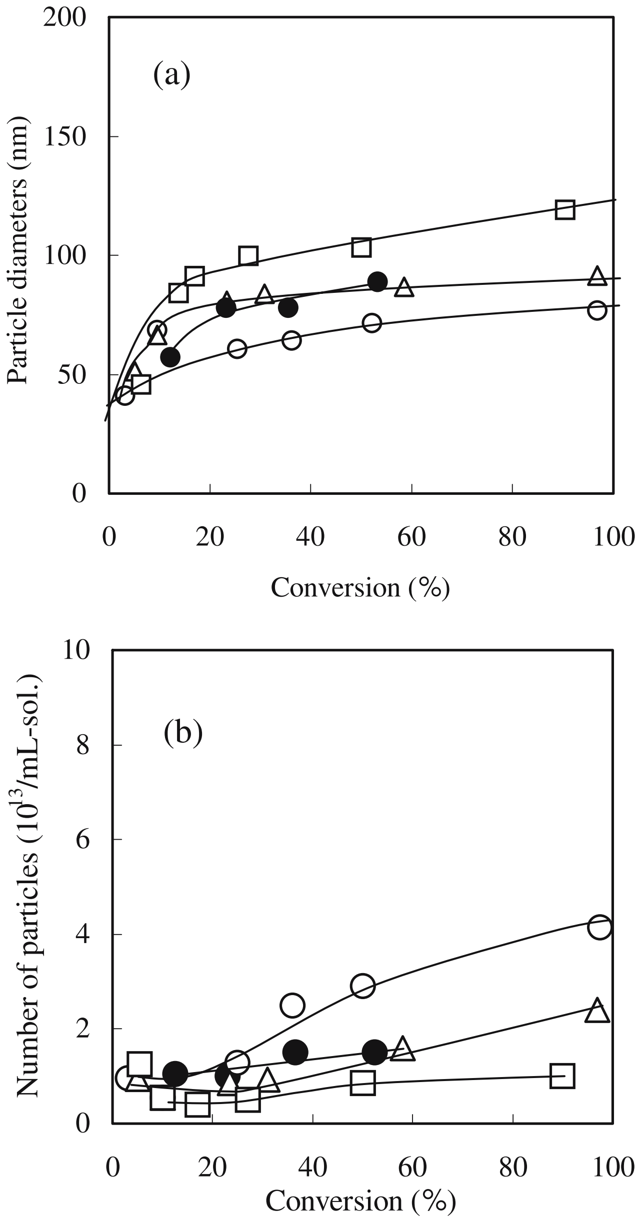

Fig. 4 Effect of additives on the particle diameters (**a**) and the number of particles (**b**). Recipe and marks: the same as shown in Fig. 1

We studied the effect of the amount of t-BuOH on the emulsion polymerization, although the reactivity of t-BuOH with a sulfate radical seems to be negligible, due to the low-rate constant, which is 8.4×10^5 l mol^{-1} s^{-1} [11]. Figure 5 shows the time-conversion curves in the t-BuOH system. In the small amount of t-BuOH (0–30 vol.%), the initial rate of polymerization increased with increasing the amount of t-BuOH. In a large amount of t-BuOH (40 vol.%), the rate of polymerization slightly decreased. Figure 6 shows the effect of the amount of t-BuOH on the particle sizes (a) and

Table 2 Effect of additives on particle diameters, the number of particles, grafts, and solubility of St in aqueous phase

Alcohol	Con. (%)	Particle diameter (D_n) (nm)	Number pf particles (10^{13}/ml)	Grafted PS (%) / Polymerized St	Grafted PVA (%) / Feed PVA	Solubility of St in aqueous phase (vol.%)
None	53	89	1.4	33	28	0.03
i-PrOH	90	119	1.0	20	9	0.35
n-PrOH	97	92	2.4	23	12	0.50
t-BuOH	97	77	4.2	9	52	0.24

Recipe: St 1 ml, APS 0.05 g, water 99 g, alcohol 10 vol.%, 70 °C, 2 h

the number of particles (b) in the case of polymerization. In a small amount of t-BuOH (10 vol.%), the particle size slightly increased to about 70 nm and the number of particles remarkably increased to about 4.0×10^{13}/ml water, which indicates new particle formation during polymerization. The polymerization system became a monomer droplet nucleation with a small amount of t-BuOH. However, in a rather large amount of t-BuOH (40 vol.%), the particle size drastically increased to about 110 nm during 10–30% conversion, while the number of particles kept constant at about 1×10^{13}/ml water. The addition of the large amount of t-BuOH affected the mechanism of particle growth, owing to the homogeneous nucleation of the polymerization locus with an increase in the solubility of St by the addition of t-BuOH. Table 3 lists the influence of the amount of t-BuOH on the grafting behavior in the model emulsion polymerization. In a small range of t-BuOH at 10–20 vol.%, the degree of grafting onto PVA with St (grafted PVA) slightly decreased to be in the range of 40–50%, while almost all of the St homo-polymerized

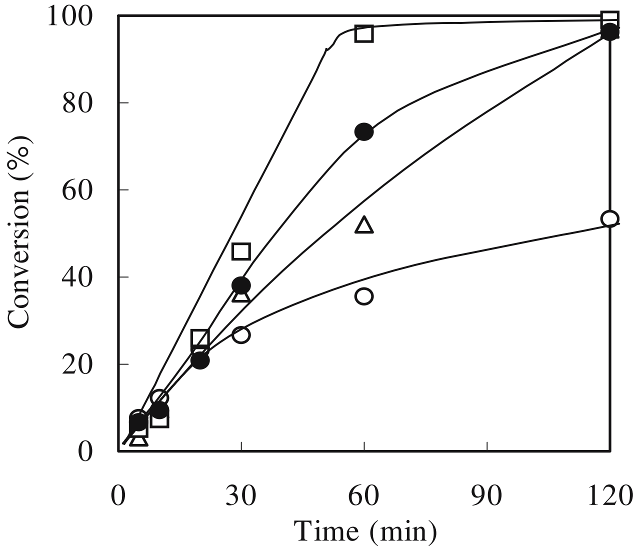

Fig. 5 Effect of the amounts of t-BuOH on the time-conversion curves in the model emulsion polymerization. Recipe: St 1 ml, continuous phase 100 ml, t-BuOH; *open circle* 0 vol.%, *open triangle* 10 vol.%, *open square* 20 vol.%, *closed circle* 40 vol.%

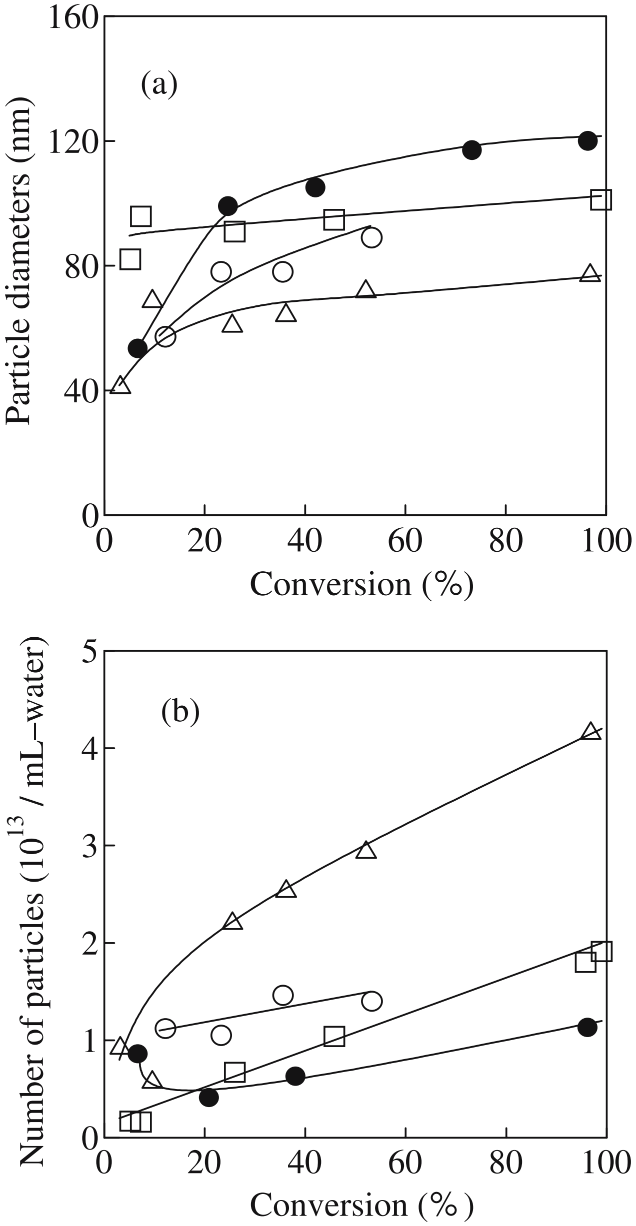

Fig. 6 Effect of the amounts of t-BuOH on the particle diameters (**a**) and the number of particles (**b**). Recipe and marks: the same as shown in Fig. 5

Table 3 Effect of the amounts of t-BuOH on particle diameters, the number of particles, grafts, and degree of polymerization of the resulting polymer

t-BuOH (vol.%)	Particle diameter (D_n) (nm)	Number of particle (10^{13}/ml-H_2O)	Grafted PS (%) / Polymerized St	Grafted PVA (%) / Feed PVA	Homo-PS (P_n)
0	88	1.5	33	28	150
10	76	4.2	9	52	330
20	100	1.9	8	42	330
40	118	1.1	60	29	280

Recipe: St 1 ml, APS 0.05 g, continuous phase 99 ml, t-BuOH (various values), 70 °C, and 2 h

increased to about 92%. This is thought to be attributed to the polymerization locus being limited to the monomer droplet dispersed by t-BuOH. In a considerable amount of t-BuOH (40 vol.%), the degree of grafting St onto PVA (grafted PVA) increased to 60%, while the degree of grafting St (grafted PS) decreased to about 30%. The polymerization system became a homogeneous nucleation in the aqueous phase with an increase in the solubility of St. Consequently, the addition of t-BuOH to the system irregularly changed the mechanism of particle formation as well as the polymerization locus with dependence on the solubility of St in the aqueous phase.

To realize the effect of the amount of t-BuOH on the polymerization locus in more detail, we carried out soap-free emulsion polymerization of St using t-BuOH. Figure 7 shows the time-conversion curves. In the no additional case, soap-free polymerization was successfully achieved to be about 40% during conversion for 2 h. In the presence of t-BuOH, the soap-free polymerization was achieved at about 80% during conversion for 2 h. The addition of t-BuOH to the system slightly increased the rate of polymerization. Figure 8 shows the particle sizes (a) and the number of particles (b) during polymerization. The addition of t-BuOH to the system also affected mechanism of particle nucleation. The size of the polymer particles nucleated at the initial stage slightly increased to 130 nm, while the number of particles kept constant at about 10^{13}/ml water during polymerization. The experimental result of the particle behavior indicates that the polymerization locus was limited to monomer droplets dispersed by t-BuOH.

Kinetic consideration of the experimental results

Let us consider the mechanism of particle formation as well as the grafting reaction. Elementary reactions such as initiation and propagation plus hydrogen abstraction and grafting can be written as follows:

1. Initiation and propagation

$$\bullet{}^{-}SO_4 + St \xrightarrow{k_{i,1}} {}^{-}O_4S - St \xrightarrow{k_p} {}^{-}O_4S - (St)_n\bullet \tag{1}$$

2. Hydrogen abstraction and grafting

$$\bullet{}^{-}SO_4 + PVA \xrightarrow{k_{a,APS}} PVA\bullet$$

$$\bullet PVA + St \xrightarrow{k_{i,2}} PVA - St\bullet \rightarrow \xrightarrow{k_P} \rightarrow PVA - (St)_n \tag{2}$$

where $k_{i,1}$, $k_{a,APS}$, and $k_{i,2}$ are the rate constants of the initiation and propagation, hydrogen abstraction from PVA with a sulfate radical, and the initiation of grafting, respectively.

The reaction time of the sulfate radical with St (τ_1), that of the addition of St to the propagation radicals in the aqueous phase (τ_2), and that of hydrogen abstraction from PVA with a sulfate radical (τ_3) can be expressed as follows:

$$Initiation\ \ t_1 = \left(1/k_{i,1}[St]\right) \tag{3}$$

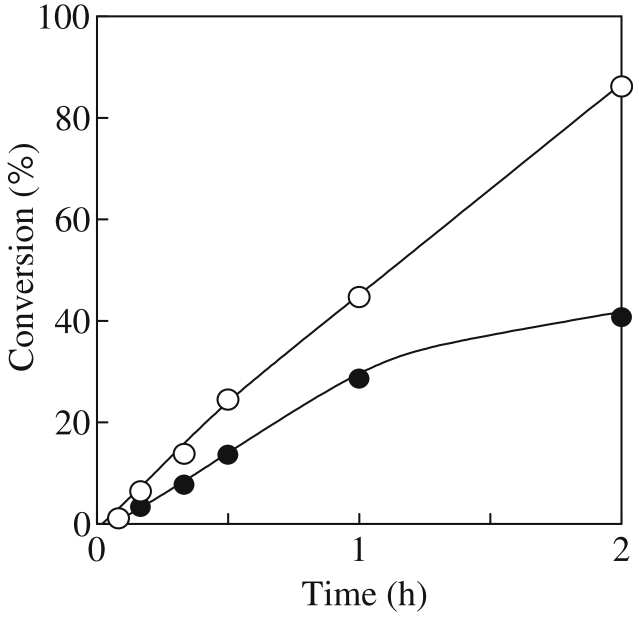

Fig. 7 Time-conversion curves in the soap-free emulsion polymerization of St using t-BuOH.Recipe: St 1 ml, APS 0.05 g, continuous phase 100 ml, t-BuOH; *open circle* 10 vol.%, *closed circle* 0 vol.%

$$\text{Propagation } t_2 = 1/(k_p[St]) \quad (4)$$

$$\text{Hydrogen abstraction } t_3 = 1/(k_{a,APS}[PVA]) \quad (5)$$

where [St] and [PVA] denote the concentrations of the St monomer and PVA (expressed by a vinyl alcohol unit) in the aqueous phase, respectively. Using the data, $k_{\mathrm{i}}=2\times10^9$ l mol^{-1} s^{-1} [10], $k_{\mathrm{p}}=240$ l mol^{-1} s^{-1} [11], and $k_{\mathrm{a,APS}}=4.1\times10^8$ l mol^{-1} s^{-1}, as reported in our other papers [6–9]. The times of τ_1, τ_2, and τ_3 were obtained to be 1.7×10^{-7} s, 1.4 s, and 1.3×10^{-8} s, respectively. The time of τ_3 was very fast, and yielded a high degree of grafting St onto PVA with a sulfate radical. The time of τ_1 was very slow. The reasons for grafting can be explained as follows: one is a low concentration of styrene in the aqueous phase, and the other is the low reactivity of the primary sulfate radical with the α-position on the double bond in styrene, due to electron delocalization. By Eq. 4, using the experimental parameters, time τ_2 in 2.2 s was slow, owing to the low reactivity of the propagation radicals with the monomer.

On the other hand, the time of entry of the radical into the polymer particle (θ) can be calculated as follows:

$$\theta = \frac{1}{2\,\pi\,D_n N\,D_w} \quad (6)$$

where D_{n}, N, and D_{w} denote the particle size, the number of particles, and the diffusion constant in the aqueous phase (1.01×10^{-5} cm s^{-1}), respectively. The time of the entry of radicals into a particle (θ) was estimated to be about 2.8×10^{-4} s, assuming the particle size to be 54 nm, and 1.0×10^{13}/ml to be the number of particles in the initial stage [2–4]. The time of θ was much slower than the hydrogen abstraction reaction time, τ_3 (10^{-8} s). From a comparison with other reaction times, a sulfate radical seldom enters into particles but reacts with the PVA radical, that is, yields the grafting of St on PVA, due to the high reaction rate. The propagation rate of the grafting chains in the aqueous phase may not be fast. The main reaction was concluded to be the particle nucleation mechanism by grafting St onto PVA. In additional cases, such as i-PrOH and n-PrOH, the rate constant of the hydrogen abstraction from alcohol with PVA may be more than five times larger than that from alcohol. The experimental results can be explained by the competition between hydrogen abstraction from PVA and alcohol with a sulfate radical, due to the high-rate constant [12]. In the case of a low reactive alcohol, such as t-BuOH, the rate constant of hydrogen abstraction with a sulfate radical is much smaller (one tenth, compared with i-PrOH). An additive such as a low reactive compound like t-BuOH did not affect the grafting substantially. The grafted chains were aggregated with each other to form a polymer particle. The degree of aggregation of homo-polymers in a PS particle was estimated with a theoretical consideration using the experimental data [5, 6]. In the absence of alcohol, the graft-polymers conjugated with a PS polymer of 2.9×10^5 units of St in a polymer particle of 90 nm, where the PS core was covered with a PVA shell of 27 nm in the PVA of DP 580 [1]. Consequently, the number of PS molecules in a PS particle was estimated to be 150, assuming the chain length of the grafted PS polymer to be

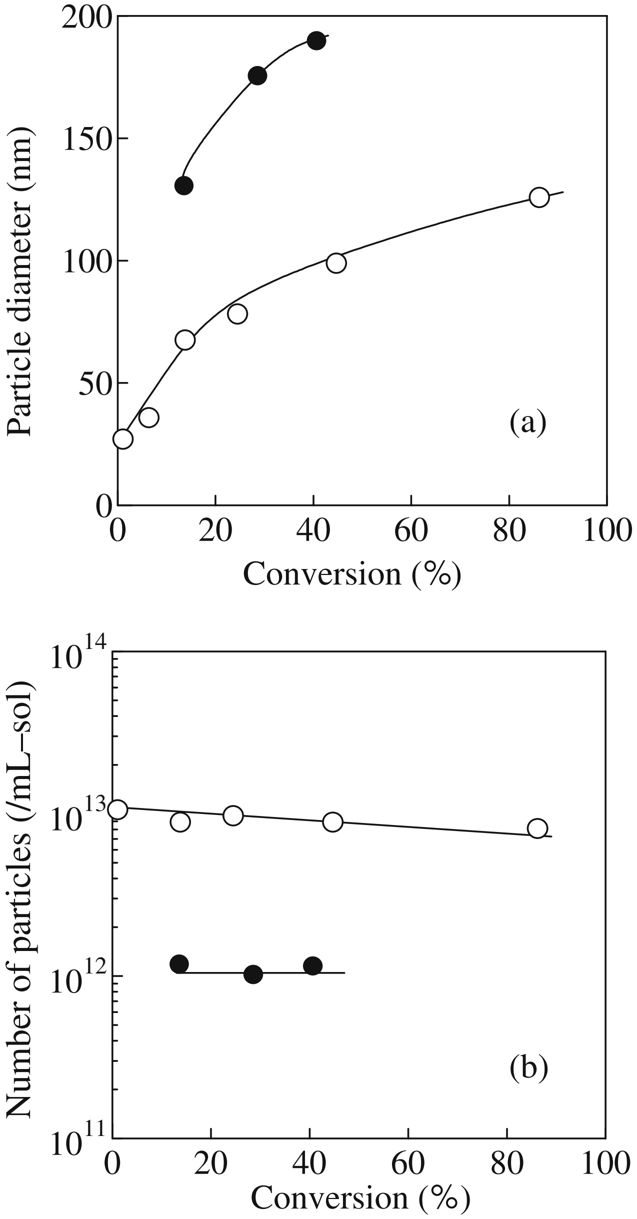

Fig. 8 Effect of t-BuOH on particle diameters (**a**) and the number of particles (**b**) during the soap-free emulsion polymerization. Recipe and marks: the same as shown in Fig. 5

identical with the degree of polymerization of the homopolymer in PS measured by GPC. On the other hand, the addition of an alcohol such as i-PrOH to the system slightly decreased to 270 degrees of polymerization of the resulting polymer (cf. 300 for n-PrOH, 330 for t-BuOH). The effect of alcohols such as i-PrOH and n-PrOH on the degree of polymerization of the resulting polymer can be explained by the chain-transfer reaction from the propagation radical with the alcohol, which is dependent on the rate constant [13–15]. However, the addition of a low reactive compound like t-BuOH did not affect the degree of polymerization, because the rate of the chain-transfer reaction of the propagation radical with t-BuOH is much smaller [15]. The addition of t-BuOH to the system slightly decreased the number of polymers in a particle by decreasing the particle size.

Judging from the results shown in Figs. 5 and 6a,b, the particle formation mechanism in the presence of t-BuOH was different from that in the additional cases of alcohols such as i-PrOH and n-PrOH. The observation of particle formation in the former case, as shown in Figs. 7 and 8a,b, indicates that the addition of t-BuOH decreased the monomer droplet size in the aqueous phase. The time of the entry of the radicals into the monomer droplet dispersed with t-BuOH (θ) was estimated in accordance with the formulation in Eq. 6. In a small amount of t-BuOH at 10–20 vol.%, the time of θ was estimated to be a very short term of 10^{-6}–10^{-8} s, depending on the monomer droplet size. The polymerization system indicates the mechanism of the monomer droplet nucleation dispersed by the addition of t-BuOH. The grafting of St (grafted PS) decreased to about 9% and grafting onto PVA (grafted PVA) increased to more than 50%. The experimental results are thought to be attributed to a competition of the entry of the radical into the monomer droplet dispersed with t-BuOH and the hydrogen abstraction from PVA with a sulfate radical. On the other hand, in a considerable amount of t-BuOH (40 vol.%), the time of entry of the radical into the monomer droplet dispersed by t-BuOH was fast, assuming the dispersed monomer droplet to be 17 nm in the aqueous phase. The addition of t-BuOH remarkably increased the grafting of St (grafted PS) with increasing the solubility of St in the aqueous phase. This is thought to be attributed to the polymerization system becoming a homogeneous nucleation mechanism.

When there was not enough PVA in the aqueous phase, the soap-free emulsion particles were stabilized with sulfate end groups. In the soap-free polymerization of St in the absence of alcohol, as shown in Fig. 8a, the particle behavior represents the process of particle growth, where the particle size increased to 200 nm, the number of particles kept constant at about 10^{12}/ml water. As shown in Fig. 8b, the addition of t-BuOH to the system decreased the rate of the process of particle growth in the case of polymerization. The addition of t-BuOH influenced the mechanism of particle formation followed by changing polymerization locus.

The effect of t-BuOH on the solution behavior of St was investigated to clarify the polymerization locus in the polymerization system. In a 1 vol.% St solution mixed with t-BuOH in the range of 10–20 vol.%, as listed in Table 4, the solution behavior of St in the aqueous phase appeared opaque, where the monomer droplets dispersed to be 145–860 nm in size, due to the inhibition of Ostwald Ripening with t-BuOH. The equilibrium solubility increased to 0.43 vol.%. The monomer droplet size decreased with increasing the amount of t-BuOH. The time of entry of the radical to the monomer droplet was estimated to be in the range of 1.8×10^{-4}–5.0×10^{-6} s, in accordance with Eq. 6, using the size of the monomer droplet dispersed by t-BuOH. On the other hand, in the case of large amounts of t-BuOH (40 vol.%) mixed with St in the aqueous phase, oil-droplets dispersed to be 17 nm in the dilute solution, while the solubility of St increased to 0.75 vol.%. The time of 6.9×10^{-8} s for the entry of the radical to the monomer droplet was much faster in comparison with that of hydrogen abstraction from PVA with a sulfate radical in the polymerization system as a homogenous nucleation. Consequently, the addition of t-BuOH to the system may be an important factor to control the polymerization loci, grafting behavior, and particle formation with the solubility of St by the addition of t-BuOH.

We made a trial to carry out an ordinary emulsion polymerization of St using PVA, where the soap-free emulsion particles coagulated with each other to yield unstable polymer particles in emulsion after the consumption of PVA for grafting. We recognized that the addition of t-BuOH by using a continuing addition of PVA confirmed

Table 4 Effect of the amounts of t-BuOH on solubility of St in aqueous phase, monomer droplet sizes dispersed by t-BuOH, and times (θ) of entry of radical into the monomer droplet particle

t-BuOH (vol.%)	Solubility of St in aqueous phase (%)	Size of emulsified St (nm)[a]	Remarks	θ(s)[c]
None	0.03	–	Separation	–
10	0.04	856	Opaque[b]	1.8×10^{-4}
20	0.43	144	Opaque[b]	5.0×10^{-6}
40	0.75	17	Clear	6.9×10^{-8}

Recipe: St 1 ml, t-BuOH (0, 10, 20, and 40 vol.%), continuous phase 100 g, 70 °C, and 2 h

[a] Emulsified by ultrasonic-homonizer

[b] Emulsification

[c] Calculated by Eq. 1: $\theta(s)=1/(2\pi D_n N D_w)$, D_n: monomer droplet size, N the number of particles, D_w diffusion constant in the aqueous phase (1.01×10^{-5} cm s^{-1})

the stability of particle growth, grafting of St onto PVA, and the polymerization locus, owing to an increase in the solubility of St by the addition of t-BuOH. This technique is thought to be an important factor for controlling the mechanism of particle formation and grafting in a common emulsion polymerization using PVA. This technique has been already applied for industrial products of acrylate-emulsion and SB rubber with a common emulsion polymerization using PVA [16, 17]. The emulsion polymerization with a continuing addition of a mixture of St in the PVA solution and ethanol successfully achieved stabile polymer particles in emulsion followed by a decrease in grafting St onto PVA. This may arise from competition between hydrogen abstraction from PVA and ethanol with a sulfate radical, and restrain the consumption of PVA for grafting by supplying PVA into the polymerization system. The emulsion particles obtained from the emulsion polymerization of St using PVA were found to have good advantage for industrial characterizations and physical properties such as film-strength and resistance against coagulation with salts. This technique can be expected to pioneer several new varieties for the purpose of industrial products.

Conclusion

We carried out model experiments of emulsion polymerization of St (1 ml-St/100 ml water) using PVA as a protective colloid. In the standard polymerization in a 1-g PVA recipe, observation of the particle size and the number of particles indicate new particle formation. About 30% of St feed and 30% of the PVA used in the emulsion were grafted. On the basis of a kinetic consideration of the experimental results, the main reaction was concluded to be hydrogen abstraction from PVA with a sulfate radical, due to the high-rate constant. One thousand four hundred grafted polymers were coagulated with each other to form a polymer particle in the initial stage. The addition of low-molecular-weight alcohol such as i-PrOH and n-PrOH strongly affected the particle formation, and decreased the grafting of St on PVA. The experimental results are thought to arise from competition between hydrogen abstraction from PVA and alcohol with a sulfate radical, owing to the high-rate constant. However, the addition of a low reactive alcohol such as t-BuOH did not affect grafting with respect to the amount of t-BuOH. In a small amount of t-BuOH, the polymerization system appeared to become the mechanism of monomer droplet nucleation as the polymerization locus into the monomer droplet was stabilized by t-BuOH. The addition of a large amount of t-BuOH confirmed homogeneous nucleation in the polymerization system, owing to an increase in the solubility of St by t-BuOH. Consequently, the addition of t-BuOH was concluded to be an important key factor for controlling the grafting of St onto PVA, the polymerization locus, and the mechanism of particle formation with the solubility of St by t-BuOH.

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