Colloid Polym Sci (2006) 285:185–192
DOI 10.1007/s00396-006-1549-9

ORIGINAL CONTRIBUTION

Influence of additives on model emulsion polymerization of vinyl acetate (VAc) using poly(vinyl alcohol) (PVA) as a protective colloid

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Received: 6 December 2005 / Accepted: 23 May 2006 / Published online: 7 September 2006

Abstract To clarify the influence of additives on the grafting phenomenon as well as the particle behavior more precisely, we carried out a model emulsion polymerization of vinyl acetate (VAc) in a 1% aqueous solution with ammonium persulfate (APS) using poly (vinyl alcohol) (PVA) as a protective colloid in the presence of additives. The addition of alcohol to the system remarkably affected the particle formation, especially grafting. This is thought to be attributed to competition between hydrogen abstraction from PVA and alcohol with a sulfate radical. Especially, the addition of acetone to the system decreased grafting to a great extent, resulting in an increase in the particle size together with an increase in the number of polymer molecules in a polymer particle. This result is thought to arise from a combination of electron abstraction from acetone with a sulfate radical and the chain-transfer reaction of the propagation radical with acetone.

Keywords Emulsion polymerization · Grafting · Vinyl acetate · Poly(vinyl alcohol) · Additive effect

Introduction

Poly(vinyl alcohol) (PVA) as a protective colloid, in contrast to the common surfactants, is advantageous in importing a strengthening effect to emulsion films [1, 2]. PVA has been widely used industrially in the emulsion polymerizations of vinyl acetate (VAc) and VAc/ethylene using PVA. However, PVA has not been used in the emulsion polymerization of conjugated monomers such as the acrylic monomers and styrene/butadiene, owing to the lack of stability during polymerization. The key factor to determine the stability of an emulsion particle is thought to be the weak ability to graft these conjugated monomers onto PVA, as the growing chain radicals from the monomers are believed to be reactive in comparison with those from polyvinyl acetate (PVAc). In other words, the growing chain radical from PVAc is reactive due to non-conjugation in the polymer radical.

The authors have had doubts about the grafting mechanism: one is hydrogen abstraction from PVA with the growing chain radicals, and the other is with the primary radicals. To clarify the ability of grafting onto PVA in the case of acrylics with a sulfate radical, the authors have studied a model experiment utilizing methyl methacrylate (MMA) as a representative of acrylics, and a very dilute monomer concentration of (MMA/PVA/water=1/1/100) that can be regarded as the initial stage of emulsion polymerization, as emulsion polymerization starts in the water phase with the monomer contained in water. As the authors have reported in previous papers [3–8], new particle formation continued and the number of particles did not become constant during polymerization. Grafting took place during the model polymerization: about 95% of polymerized MMA and approximately 65% of PVA were grafted. PVA in the grafted polymers were supposed to act as the stabilizers of newly formed particles. In this case, the reaction times of the initiation of the sulfate radical with MMA (τ_1), of the propagation of the PVA radical (τ_2), of hydrogen abstraction from PVA with a sulfate radical (τ_3), and the time of entry of the sulfate radicals into a particle (θ) were calculated from kinetic treatment [6].

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In comparison with these times of reactions, the most important reaction was concluded to be hydrogen abstraction from PVA with a sulfate radical. To realize the grafting phenomenon more precisely in the model experiment, we studied the influence of additions on the model emulsion polymerization of MMA using PVA [3]. It was found that the addition of alcohol to the system strongly affected particle formation followed by grafting. This might arise from competition between the hydrogen abstraction reaction from PVA and alcohol with a sulfate radical, due to the high-rate constant. We studied the influence of additives on the grafting phenomenon in regard to the mechanism of particle formation on the model experiment of emulsion polymerization of vinyl acetate (VAc) using PVA.

The aim of this study is to clarify the influence of additives on the grafting of VAc onto PVA, the mechanism of particle formation, and the degree of polymerization of resulting polymers more precisely. The kinetic consideration of the experimental results will also be described.

Experimental

Materials

Polymerization grade vinyl acetate (VAc) was used, supplied by Kuraray, Japan. PVA (degree of hydrolysis 88%, degree of polymerization (DP) 580, supplied by Kuraray, Japan) was used after Soxhlet extraction with methanol to exclude sodium acetate. APS (Wako Pure Chemical Industries) and low-molecular-weight alcohols such as isopropyl alcohol (*i*-PrOH), *n*-propyl alcohol (*n*-PrOH), isobutyl alcohol (*i*-BuOH) and *t*-butyl alcohol (*t*-BuOH) (Nacalai tesque Co), were of reagent grade, and were used as received.

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 to remove oxygen in the system. Emulsion polymerization was mainly carried out by the following basic recipe: VAc/PVA (DP580, DH 88%)/water=0.93/1/103 (wt. ratio) with several additives at 70 °C for 2 h. Conversion was determined gravimetrically. The stirring speed of polymerization was kept at 200 rpm by mechanical stirring.

Fractionation of the polymers in emulsion

The polymers in the emulsion were fractionated into acetone-soluble (homo-PVAc), water-soluble (homo-PVA), and then insoluble (grafted PVA) parts as residuals by extraction in that order.

Measurement

Particle diameters were measured by dynamic light scattering (DLS, PAR-III, Otsuka Electronics). The degree of polymerization (DP) of the acetone-soluble (homo-PVAc) part was measured by GPC (Tosoh, TSK_{gel} GMH_{HR}-M, polystyrene standard) at 40 °C in tetrahydrofuran. A portion of the grafted polymer was acetylated with a mixture of acetic anhydride and acetic acid (1/1) in the presence of hydrogen chloride at 70 °C for 3 h, and then the degrees of polymerization of the resulting polymer were measured by GPC (Tosoh, TSK_{gel}, GMH_{HR}-M, polystyrene standard) at 40 °C in tetrahydrofuran.

Results and discussion

The model emulsion polymerization of vinyl acetate (1 ml VAc per 100 ml water) using 1 g PVA in the presence of isopropyl alcohol (*i*-PrOH) was carried out with changing the amounts of *i*-PrOH. APS (0.05 g) was used as initiator. The reaction system was at first homogeneous and became an emulsion just after introducing APS. Figure 1 shows the effect of the amounts of *i*-PrOH on the time–conversion curves. In the standard case in the absence of alcohol, the polymerization was achieved to be about 100% during conversion for 20 min, where the initial rate of polymerization (R_p) was obtained to be 4.87×10^{-5} (mol l^{-1} s^{-1}) with the initial slope of the polymerization curves. On the other hand, in the presence of *i*-PrOH (0.75 mol l^{-1}), the polymerization was achieved to be about 70% during conversion for 20 min,

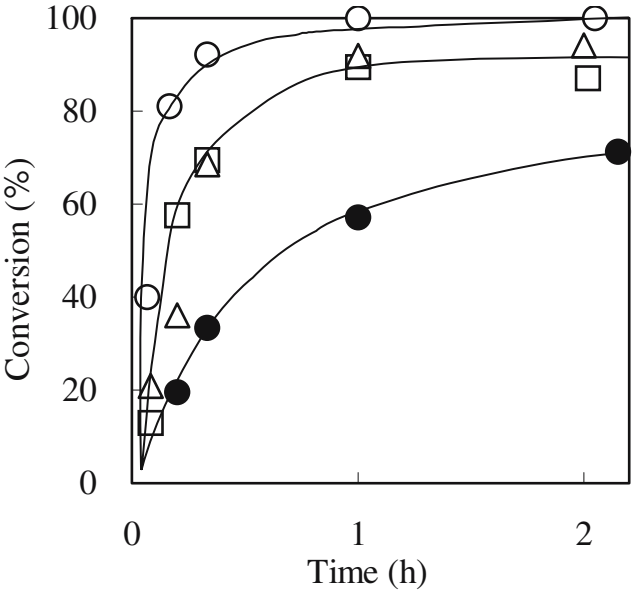


Fig. 1 Time–conversion curves of the model emulsion polymerization of vinyl acetate (VAc) using poly(vinyl alcohol) (PVA) in the presence of isopropyl alcohol (*i*-PrOH). Recipe: PVA 1 g, VAc 0.93 g, APS 0.05 g, water 103 g, *i*-PrOH (mol l^{-1}): 0 (*open circles*), 0.27 (*open squares*), 0.75 (*open triangles*), 1.50 (*solid circles*), 70 °C and 2 h

where the rate of polymerization, R_p, decreased to one-third compared with that in the standard case.

Figure 2 shows the effect of the amount of *i*-PrOH on the particle diameters (a) and the number of particles (b). In the standard case without *i*-PrOH, the particle size kept constant at about 70–80 nm, while the number of particles increased to approximately 3×10^{13}/ml, which indicates new particle formation during polymerization. When a considerable amount of *i*-PrOH (1.50 mol l^{-1}) was added to the system, the particle size increased to about 200 nm, while the number of particles slightly increased to 1.0×10^{12}/ml. The experimental result indicates the particle growth behavior during polymerization.

Figure 3 shows the effect of grafting by increasing the amount of *i*-PrOH. In the standard case in the absence of alcohol, about 90% of polymerized VAc and about 45% in added PVA were grafted, owing to hydrogen abstraction from PVA with a sulfate radical. On the other hand, in the presence of *i*-PrOH (0.75 mol l^{-1}), grafted-PVAc slightly decreased to about 85%, and grafted PVA remarkably decreased to about 1%. The addition of a considerable amount of *i*-PrOH (1.5 mol l^{-1}) to the system strongly decreased the grafting: 65% in grafted PVAc and 0% in grafted PVA. Increasing the amount of the additive influenced the grafting behavior. This is thought to be attributed to competition between hydrogen abstraction from PVA and alcohol with a sulfate radical, due to the high-rate constant. The effect of other alcohols was also investigated and the results are listed in Table 1. The addition of alcohols as listed in Table 1 affected the grafting of VAc on PVA as well as the particle behavior, except for *t*-butyl alcohol (*t*-BuOH), which showed almost no effect.

Let us consider the influence of additives on the mechanism of grafting VAc onto PVA. In the absence of alcohol, elementary reactions involving the sulfate radical from PVA and grafting can be written as follows:

1. Initiation and propagation

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

2. Abstraction of hydrogen and grafting

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

$$\bullet PVA + VAc \xrightarrow{k_{i,2}} PVA\text{ - }VAc\bullet \xrightarrow{k_p} PVA-(VAc)_n\bullet$$

where $k_{i,1}$, and $k_{1,2}$ are the initiation-rate constants of the sulfate and PVA radicals, respectively. The propagation-rate

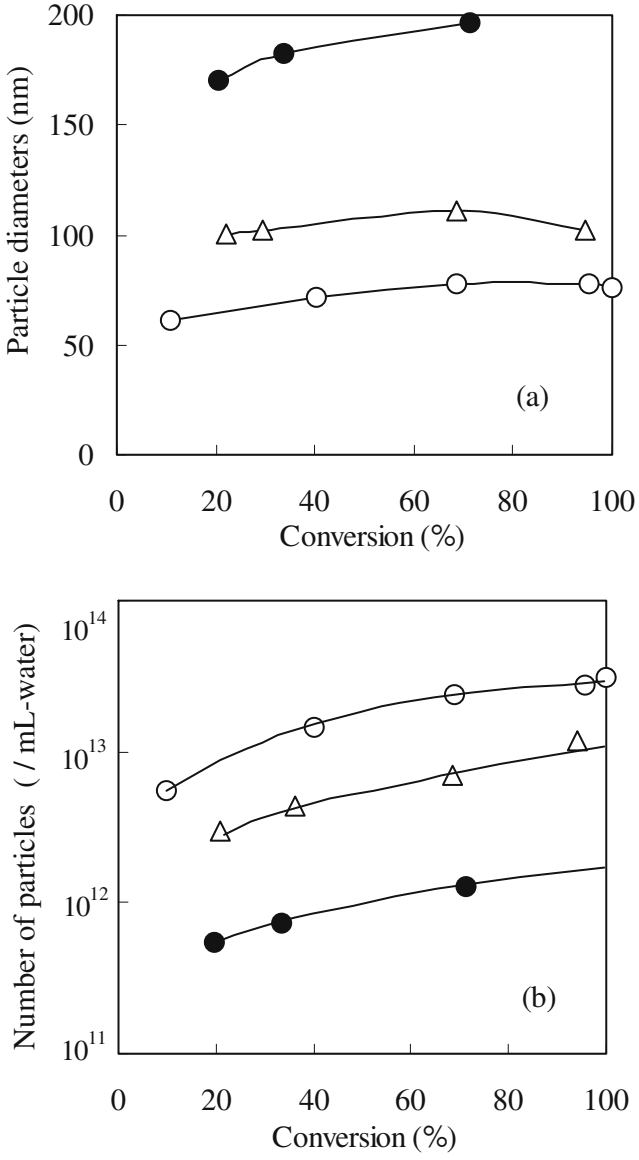


Fig. 2 Influence of the amount of *i*-PrOH on particle diameters (**a**) and the number of particles (**b**) during polymerization. Recipe and symbols: the same as shown in Fig. 1

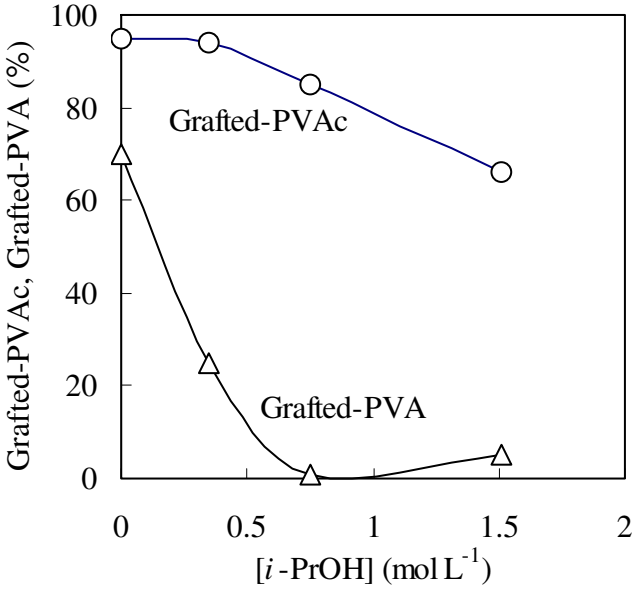


Fig. 3 Influence of the amount of *i*-PrOH on the grafting of VAc onto PVA in the system. Remarks: grafted PVAc (*open circles*), grafted PVA (*open triangles*). Recipe: the same as shown in Fig. 1

constants for the shortest chain lengths, k_p (1), were one order of magnitude or more larger than those for macromolecular chain lengths, k_p (n). We adopted k_p=4,600 (mol^{-1} l s^{-1}) [10] instead of 3,800 (mol^{-1} l s^{-1}) as k_p (n). $k_{a,APS}$ denotes the rate constant of hydrogen abstraction from PVA with the sulfate radical.

The reaction time of the sulfate radical with VAc (τ_1), that of the addition of VAc 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 with the following equations [3–5, 10, 11]:

$$\tau_1 = 1\Big/\left(k_{i,1}[VAc]_0\right) \quad (1)$$

$$\tau_2 = 1/\left(k_p[VAc]_0\right) \quad (2)$$

$$\tau_3 = 1\Big/\left(k_{a,APS}[PVA]_0\right) \quad (3)$$

where $[VAc]_0$ and $[PVA]_0$ denote the initial concentrations of VAc and PVA (expressed by the vinyl alcohol unit), respectively. Referring to Eqs. (1–3) using the rate constant of the initiation, $k_i=10^8$ (mol^{-1} l s^{-1}) [9], that of the propagation, k_p=4,600 (mol^{-1} l s^{-1}) [10], and that of hydrogen abstraction from PVA with a sulfate radical, $k_{a,APS}=5\times10^8$ (mol^{-1} l s^{-1}) [4], and substituting [VAc]=0.1 mol l^{-1} and [PVA]=0.2 mol l^{-1}, we obtained $\tau_1=10^{-7}$ (s), $\tau_2=2.2\times10^{-3}$ (s), and $\tau_3=1.7\times10^{-8}$ (s). The rate of hydrogen abstraction from PVA with a sulfate radical was the fastest, resulting in the ability to graft VAc onto PVA. The rate of the propagation reaction of the PVAc radical in the aqueous phase was much slower in comparison with the other two reactions. In general, the accepted opinion for the mechanism of particle nucleation in the common emulsion polymerization of VAc using SLS suggests that the primary radical are initiated with monomer to produce oligomers in aqueous phase, and the oligomer entry into micelle to nuclear the polymer particles in initial stage of polymerization. In the case of model experiments of emulsion polymerization using PVA, the oligomers were similarly assumed to enter into polymer particles to nuclear the polymer particle on the basis of a diffusional entry model [11]. The time of entry of oligomer radicals into a particle (θ) can be expressed as follows:

$$\theta = [R\bullet]/\rho = 1/2\pi D_n D_w N \quad (4)$$

where [R•] is the stationary state concentration of the oligomer radicals in the aqueous phase, ρ refers to the rate of radical entry into particles, and D_n, N, and D_w denote the particle diameter, the number of particles, and the diffusion constant of radicals in water, respectively [12]. From the calculation of Eq. (4) using D_n, N, and the diffusion constant in the aqueous phase, ($D_w=1.0\times10^{-5}$ cm^2 s^{-1}), we obtained $\theta=10^{-4}$ (s), which is much slower than that in the hydrogen abstraction reaction ($\tau_3=1.0\times10^{-8}$ s). This indicates that the oligomer radicals seldom enter into particles, but sulfate radicals react with PVA, forming the PVA radicals that yield the grafting of the monomer. The propagation rate of the grafting chains may not be fast, as the reaction rate, τ_2, is longer (2.2×10^{-3} s). Consequently, shortly after that hydrogen abstraction from PVA with a sulfate radical occurred in the aqueous phase, the grafted chain forms particles by coagulation together with the other grafted chains as a homogeneous nucleation in aqueous phase. The number of PVAc molecules in a particle can be estimated, assuming the chain length of the grafted PVAc to be identical with degree of polymerization of the homo-PVAc. There were 6.5×10^5 monomer units in PVAc particles of 80 nm, where the PVAc core was covered with a PVA shell of 15 nm, when the degree of polymerization being 580 of PVA was used [7]. Accordingly, 2.1×10^6 grated molecules are presumed to get together to form a PVAc particle.

The addition of isopropyl alcohol (*i*-PrOH) strongly influenced particle formation, followed by the grafting behavior. This is thought to arise from the two mechanisms of kinetic consideration: one is hydrogen abstraction from *i*-PrOH with a sulfate radical [12], and the other is the chain-transfer reaction of the propagation polymer radical with alcohol. The elementary reactions involving competition between hydrogen abstraction from PVA and alcohol with a sulfate radical and the chain transfer of the propagation polymer radical to alcohol can be written as follows:

1. Abstraction of hydrogen from alcohol with a sulfate radical:

$$\bullet SO_4^- + RCH_2OH \xrightarrow{k_{i,3}} SO_4^{2-} + \dot{R}CHOH \quad (5)$$

2. Chain-transfer of propagation polymer radical (VAc •) to alcohol:

$$(VAc)_n\bullet + RCH_2OH \xrightarrow{k_{tr,s}} PVAc + \dot{R}CHOH \quad (6)$$

where $k_{i,3}$ and $k_{tr,s}$ are rate the constants of the hydrogen abstraction reaction from alcohol with sulfate radical, and

Table 1 Influence of low-molecular-weight alcohols on particle size, the number of polymer particles, and grafting

Additives	D_n (nm)	N (10^{13}/ml)	Grafted PVAc (%)	Grafted PVA (%)
			Polymerized Vac	Used PVA
None	79	2.8	95	70
n-propyl alcohol	114	0.8	92	19
Isopropyl alcohol	103	1.2	85	1
Isobutyl alcohol	78	2.8	94	26
t-butyl alcohol	105	1.2	96	50

Recipe: PVA 1 g, additives 0.75 mol l^{-1}, VAc 0.93 g, APS 0.06 g, water 99 g, 70 °C, 2 h

the chain-transfer reaction of the propagation radical to alcohol. Many rate constants of hydrogen abstraction from low-molecular-weight alcohols with a sulfate anion radical have been reported [3].

The time of hydrogen abstraction from alcohol with a sulfate radical, and the time of the chain-transfer of the propagation polymer radical to alcohol can be expressed with the following equations:

$$\tau_4 = 1 \Big/ \left(k_{i,2}[alcohol]\right) \tag{7}$$

$$\tau_5 = 1 \Big/ \left(k_{\ tr,s}[alcohol]\right) = 1 \Big/ \left(C_s k_p[alcohol]\right) \tag{8}$$

where C_s ($=k_{tr,s}/k_p$) refers to the chain-transfer constant and [alcohol] is the concentration of alcohol in the aqueous phase. In the additional case of *i*-PrOH at 0.75 mol l^{-1}, τ_4 was obtained to be 1.6×10^{-8} (s) by referring the Eq. (7) with data: $k_{i,2}=0.86\times10^8$ (l mol^{-1} s^{-1}) [3]. The time of hydrogen abstraction from alcohol with sulfate was faster in comparison with that from PVA with a sulfate radical (10^{-8} s). Referring to $k_{tr,s}=C_s k_p=3.5$ using the reaction rate constant, k_p=4,900 (l mol^{-1} s^{-1}) [10], and $C_s=7.11\times10^{-4}$ for propanol at 70 °C [10], and [*i*-PrOH]=0.75 (mol l^{-1}), we obtained $\tau_5=3.8\times10^{-1}$ (s). The chain-transfer reaction was negligible due to the low rate constant, $k_{tr,s}$=3.5 (l mol^{-1} s^{-1}).

The most important reaction was not the chain transfer of the propagation radical to alcohol but hydrogen abstraction from PVA with a sulfate radical. Low-molecular-weight alcohol radicals formed from hydrogen abstraction with sulfate radical may also add VAc, yielding homo-PVAc. Especially, the addition of *i*-PrOH strongly retarded the grafting (in Table 1). The experimental results might not have arisen from the chain-transfer of the propagation polymer radical to alcohol, but from the considerable competition between hydrogen abstraction from PVA and *i*-PrOH with a sulfate radical, owing to the high-rate constant, 0.86×10^8 (l mol^{-1} s^{-1}) [3]. The addition of another alcohol such as *n*-propyl alcohol (*n*-PrOH) and *i*-butyl alcohol (*i*-BuOH) to the system also decreased grafting, due to the high-rate constant (in Table 2). However, the addition of a low reactive alcohol such as *t*-butyl alcohol (*t*-BuOH) with a sulfate radical did not affect the grafting, as hydrogen abstraction from *t*-BuOH was negligible, due to the low-rate constant (0.084×10^8 l mol^{-1} s^{-1}) [13].

Table 2 Rate constants of hydrogen abstraction from alcohols with sulfate radical [3]

Alcohol	Rate constants of hydrogen abstraction with SO_4^- (10^8, 1 mol^{-1} s^{-1})
n-propyl alcohol	0.59
Isopropyl alcohol	0.86
Isobutyl alcohol	1.3
t-butyl alcohol	0.0084

We investigated the influence of additives such as acetone, acetonitrile, and acetic acid on the grafting as well as particle formation more precisely. Figure 4 shows the time–conversion curves in these systems. In the presence of additives such as acetonitrile and acetic acid (0.75 mol l^{-1}), polymerizations were achieved to be 93% during conversion for 2 h. The addition of acetonitrile and acetic acid only slightly affected the rate of polymerization. On the other hand, the addition of acetone to the system strongly affected polymerization. Polymerization was achieved to be about 73% during conversion for 2 h, with a decrease in the rate of polymerization. Table 3 lists the effect of additives on the particle behavior and the grafting of VAc onto PVA. Additives to the system strongly decreased the grafting (cf. 47% grafted PVAc and 45% grafted PVA for acetone, 59 and 56% for acetonitrile), yielding an increase in particle size. This is thought to be attributed to competition between hydrogen abstraction from PVA and alcohol with sulfate radical.

On the other hand, the addition of a low reactive additive such as acetonitrile only slightly affected the grafting and the degree of polymerization of the resulting polymer, due to the low chain transfer rate constant of propagation radical to acetonitrile (C_s) of 10×10^{-4} [14].

However, the addition of acetone influenced particle formation, followed by grafting. Table 4 lists the particle

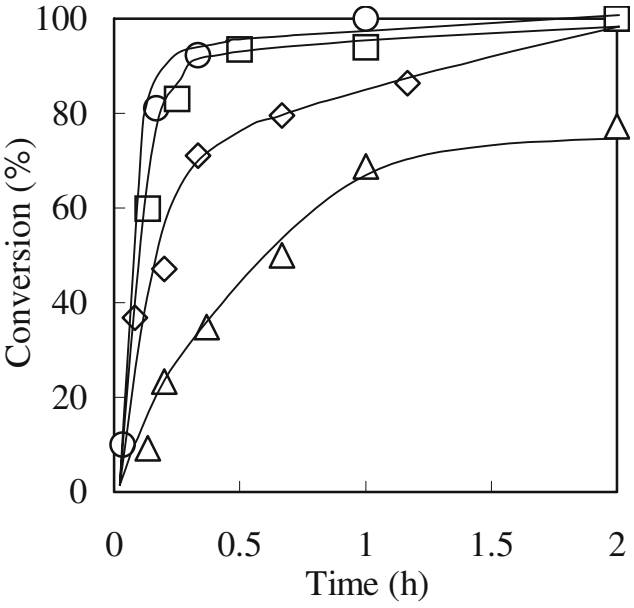


Fig. 4 Influence of additives on time–conversion curves of the model emulsion polymerization. Recipe: PVA 1 g, VAc 0.93 g, continuous phase 99 g, additives: 0.75 mol l^{-1}. None (*open circles*), acetone (*open triangle*), acetate acid (*open squares*), acetonitrile (*open diamonds)*, APS 0.05 g, 70 °C and 2 h

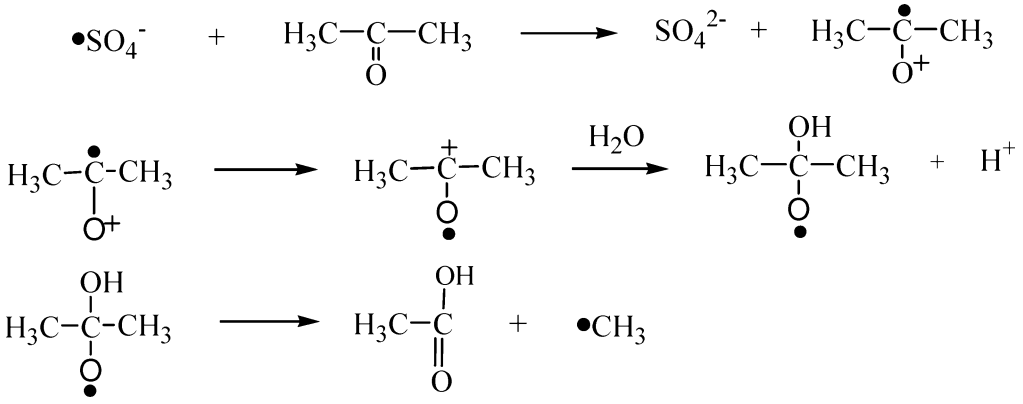
Table 3 Influence of additives on particle sizes, the number of polymer particles, grafting, and the number-average degrees of polymerization of resulting polymers

Additive	D_n (nm)	N (10^{13}/ml)	Grafted PVAc (%)	Grafted PVA (%)	Homo-PVAc (DP)[a]
			Polymerized Vac	Used PVA	
None	79	2.8	95	70	110
Acetone	86	1.9	47	45	60
Acetic acid	103	1.3	85	62	110
Acetonitrile	95	1.5	59	56	170

Recipe: PVA 1 g; additives 0.75 mol l^{-1}; VAc 0.93 g, APS 0.06 g, water 99 g, 70 °C and 2 h
[a] Measured by GPC

behavior, grafting behavior, and grafting as a function of the amount of acetone. In the case of a considerable amount of acetone (1.5 mol l^{-1}) added to the system, the particle size increased to approximately 120 nm, and the number of particles decreased to 0.7×10^{13}/ml. The addition of acetone to the system increased the particle size, and decreased the grafting to a great extent: the degree of grafting of VAc onto PVA (grafted PVA) with each other to form a polymer particle, the polymerization became a heterogeneous system. The influence of acetone on the mechanism of particle growth and grafting of VAc onto PVA are thought to arise from several side reactions.

Let us describe the kinetic considerations in regard to the a retardation of grafting as follows:



(9)

drastically decreased to about 24%, while the degree of the grafting of VAc (grafted PVAc) became low (73%). The degree of polymerization of the resulting polymer (homo-PVAc) decreased to about 30. A comparison between the experimental and theoretical results indicates the influence of additives on the degree of polymerization of the resulting polymer. The theoretical results were slightly different from the theoretical consideration, assuming the polymerization locus to be a homogeneous nucleation in the aqueous phase in the initial stage. The number of PVAc molecules in a particle was estimated to be 2.8×10^5, assuming the chain length of the grafted PVAc to be identical with the degree of polymerization of the homo-PVAc, 2.8×10^5 polymers with about 30 short lengths coagulated with each other to form the particle in the initial stage. After the coagulation where a primary radical with high reactive electrophilic nature may attack the electro-rich portion of a carboxyl group in acetone. The methyl radical with low reactivity for grafting might be added to the double bond in the main chain of VAc to homo-polymerize PVAc, which indicates the mechanism of particle growth followed by propagation reaction. This is thought to arise from the consumption of a sulfate primary radical by the electron abstraction from acetone with a sulfate radical, although the rate constant of hydrogen abstraction from acetone with sulfate has not been reported.

Investigation of the influence of additives on the experimental degrees of polymerization (DP) of the obtained polymers (homo-PVAc) was done, and is described in Fig. 3. Especially, the addition of acetone decreased the experimental degree of polymerization (DP) of the resulting polymers, and increased the number of grafted

Table 4 Influence of the amount of acetone on particle sizes, the number of polymer particles, grafting, and the number-average degrees of polymerization (DP) of resulting polymers

[Acetone] (mol l^{-1})	D_n (nm)	N (10^{13}/ml sol.)	Grafted PVAc (%)	Grafted PVA (%)	Homo-PVAc (DP)[a]
			Polymerized Vac	Feed PVA	
0	79	2.8	95	70	110
0.75	86	1.9	–	45	60
1.50	117	0.7	73	24	30

Recipe: the same as shown in Table 1
[a] Measured by GPC

molecules in a PVAc core particle to form the polymer particle. The theoretical degree of polymerization of the resulting polymers of homo-PVAc can be estimated with the numerical formula in Eq. (10), assuming the polymerization locus to be homogeneous in the aqueous phase

$$\frac{1}{\overline{Pn}} = C_M + C_S\frac{[Solvent]}{[VAc]_0} + C_p\frac{[PVAc]}{[VAc]_0} + \frac{(1+\lambda)k_tR_p}{2k_p^2[VAc]_0^2} \quad (10)$$

where C_M, C_s, and C_p denote the chain-transfer constants to VAc, solvent, and polymer (C_M=4.7×10^{-3} l mol^{-1} s^{-1} [15], C_s=variable constants, C_p=4×10^{-4} l mol^{-1} s^{-1} [16]), respectively. R_p refers to the rate of polymerization and k_t and k_p denote the rate constants of the termination reaction, (k_t=1.61×10^8 l mol^{-1} s^{-1} [17], k_p=3,800 mol^{-1} l s^{-1}), and the rate constants of polymerization, respectively. λ is the probability of disproportionation in the total termination reaction (λ=0 for VAc). $\overline{P}_n$ is the number-average degree of polymerization of the polymer. The third term, C_p [PVAc]/$[VAc]_0$ on the right-hand side of Eq. (10) was simplified to C_p (1.48×10^{-4} l mol^{-1} s^{-1}) with the concentration of the polymer (expressed by the monomer unit) during conversion at 100%.

Referring to Eq. (10) with the experimental parameters: initial concentration of the monomer and solvent, $[VAc]_0$=0.1 (mol l^{-1}), [Solvent]=0.75 (mol l^{-1}), the rate of polymerization (R_p) with acetone, acetic acid, and acetonitrile being 2.9×10^{-3}, 1.39×10^{-2}, and 6.00×10^{-2} (mol l^{-1} s^{-1}), respectively (obtained by Fig. 4), and the chain-transfer rate constant of the propagation radical to the additive (C_s) being 25.6×10^{-4} for acetone [18], 2.0×10^{-5} for acetic acid [19], and 25.6×10^{-3} for acetonitrile [18], the theoretical number-average degrees of polymerization of homo-polymers ($\overline{P}_n$) influenced by additives such as acetone, acetic acid, and acetonitrile were calculated to be about 45, 200, and 45, respectively.

A qualitative comparison between the theoretical and experimental results indicates the strong influence of the additives on the degree of polymerization of the resulting polymer. However, the theoretical degree of polymerization only slightly differed from the experimental results: (cf. 110 for the standard system in the absence of an additive, 60, 110, and 170 for acetone, acetic acid, and acetonitrile, respectively, as listed in Table 3. The assumption that the polymerization locus was a homogeneous nucleation in the aqueous phase did not quantitatively explain the influence of additives on the experimental number-average degree of polymerization of the resulting homo-polymer as a function of the amount of additives.

In the additional cases, after several grafted polymers coagulated with each other to form the polymer particle, the polymerization locus changed to become a heterogeneous nucleation on the basis of the mechanism of particle growth followed by propagation reaction. The influence of additives on the mechanism of particle formation, the grafting of VAc onto PVA, the degree of polymerization of the resulting polymer, and several grafted molecules in a PVAc core particle to form the emulsion particle, are thought to arise from kinetic considerations with respect to side reactions such as the chain-transfer reaction of the propagation radical to additives, and hydrogen abstraction from additives with a sulfate radical.

Conclusion

We have studied the influence of low-molecular-weight alcohols such as *i*-PrOH, *n*-PrOH, *i*-BuOH, *t*-BuOH, and additives such as acetone, acetic acid, and acetonitrile on the mechanism of particle nucleation, grafting of VAc onto PVA in model experiments of emulsion polymerization of VAc in a 1% aqueous solution with 1 g of PVA using APS. The addition of the alcohols strongly affected particle formation, followed by the grafting of VAc onto PVA. The decrease in the grafting of VAc onto PVA with the addition of alcohol is thought to arise from competition between the hydrogen abstraction reaction from PVA and alcohols with a sulfate radical. On the other hand, the addition of acetone

to the system decreased the grafting to a great extent to result in an increase in the particle size and increased the number of polymer molecules in a particle. The influence of acetone on the experimental results can be explained by kinetic consideration on the basis of side reactions such as electron abstraction from acetone with a sulfate radical and the chain-transfer reaction of the propagation radical to acetone.

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