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SHORT COMMUNICATION

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Effect of initiators on grafting in the initial stage of the emulsion polymerization of methyl methacrylate using poly(vinyl alcohol) as a protective colloid

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Abstract To make clear the reason of unsuitability of poly(vinyl alcohol) (PVA) protective colloid for the emulsion polymerization of conjugated monomers, a model experiment of emulsion polymerization of methyl methacrylate (MMA) was carried out with ammonium persulfate (APS) or azobis(isobutyronitrile) (AIBN) initiators, where a small amount of MMA (1/100th of the concentration compared with ordinary emulsion polymerization) was employed. This corresponds to the initial stage of the emulsion polymerization. Grafting of MMA onto PVA took place remarkably irrespective of the kind of the initiators. Formation of homo-poly(MMA) was observed to a small extent. The formation of new emulsion particles smaller than 100 nm continued to increase to almost the end of the polymerization. PVA molecules in the grafted polymer are supposed to act as stabilizers of newly formed particles. From kinetic treatment using the experimental data, the important issues were derived as follows. Firstly, the sulfate anion radical from APS is much more reactive than the isobutyronitrile radical from AIBN in terms of hydrogen abstraction from PVA. Secondly, high grafting ability of the latter initiator system, notwithstanding the much lower reactivity in the hydrogen abstraction compared with the APS system, is attributed to the relative reactivity of the primary radicals, i.e., hydrogen abstraction reaction from PVA to initiation reaction with MMA. The much slower rate of addition of the isobutyronitrile radical to the monomer compared with that of hydrogen abstraction from PVA facilitates the grafting, although the rate constant of hydrogen abstraction is far smaller than that with the sulfate anion radical by 10^{-4} times.

Keywords Emulsion polymerization · Initial stage · Grafting · Methyl methacrylate · Poly(vinyl alcohol)

Introduction

In the emulsion polymerization of vinyl monomers, water-soluble polymers can be utilized as a dispersant instead of low-molecular-weight emulsifiers. Among the protective colloids, poly(vinyl alcohol) (PVA) has been used industrially in the copolymer emulsions of vinyl acetate (VAc), VAc/ethylene, and so on. There are several reasons to adopt PVA in these commercial products. In the field of adhesives, which is an important application of commercial emulsions, primary tackiness, i.e., the tackiness of adhesives in the wet state, is especially necessary as well as the final strength of the adhesives. This is afforded by swollen PVA which exists at the surfaces of emulsion particles. The other key feature arising from PVA is the strengthening effect on the film properties [1]. The tensile strength and the creep resistance of the adhesive layer can be enhanced by PVA to a great extent; this is also a principal demand for adhesive polymers.

To afford the characteristic properties of PVA protective colloid to polymer emulsions, there have been several efforts to utilize PVA in commercial copolymer emulsions consisting of conjugated monomers such as styrene/butadiene and methyl methacrylate (MMA)/alkyl acrylates. To our knowledge, no polymer emulsions from these monomers using conventional PVA have been commercialized yet. This is attributed to the low grafting ability of monomers to PVA. In the case of reactive propagating radicals consisting of unconjugated monomers such as VAc and vinyl chloride, the grafting onto PVA can occur easily, whereas in the case of stable propagating radicals consisting of the conjugated monomers, the grafting does not take place easily. In fact, by using PVA having a reactive thiol group at one end (PVA–SH) instead of ordinary PVA, styrene, acrylates, and MMA/butyl acrylate were successfully polymerized, yielding stable emulsions, where block copolymer formation played an important role [2, 3]. To make clear the importance of grafting, we carried out a model experiment that relates to the initial stage of the emulsion polymerization of MMA using PVA as a protective colloid, where the MMA concentration in the system was only 1%. The polymerization system was at first homogeneous in this case. It was observed that grafting of MMA onto PVA occurred markedly in the early stage of the polymerization when using ammonium persulfate (APS) as an initiator. The high degree of grafting of MMA in the model emulsion polymerization indicates the important role of the primary radical on grafting instead of the propagating radical. A high degree of grafting of the monomer to PVA was also observed when using azobis(isobutyronitrile) (AIBN) as an initiator instead of APS [4]. This is noteworthy since the reactivity of the isobutyronitrile radical resulting from AIBN is believed to be much lower than the sulfate anion radical because of the conjugated structure of the former. In this work, we deal with the reason for the high degree of grafting in the model experiments using both of the initiators.

Experimental

Materials

MMA was purified by vacuum distillation. Water was distilled after being ion-exchanged. APS and AIBN were used as received. PVA (degree of hydrolysis 88%, degree of polymerization 580, supplied by Kuraray) was used after Soxhlet extraction with methanol to exclude sodium acetate.

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. Water (100 ml) and MMA (1 ml) deaerated with argon were added to the reactor. After reaching 70 °C, the initiator solution deaerated with argon was added.

Fractionation of the polymers

The polymers in the emulsion were fractionated into acetone-soluble, water-soluble, and insoluble parts. The last part was regarded as the graft polymers.

Measurement

The particle diameters were measured by dynamic light scattering (Otsuka Electronics).

Results and discussion

In the presence of PVA, MMA was polymerized in aqueous solution at 70 °C by adding initiator. The concentration of the monomer was 1 vol/wt %, which was about 1/100th of ordinary emulsion polymerization. APS (0.0523 g, 2.21×10^{-3} mol/l) and AIBN (0.0132 g, 7.77×10^{-4} mol/l) were used, where the rate of formation of the primary radicals was kept constant in both cases [5, 6]. The amounts of PVA used were 0.5 or 1 g. Time–conversion curves are shown in Fig. 1. Polymerization was completed within 1 h. The polymerization rate using APS was higher than that using AIBN, although the rate of formation of the primary radicals was the same in both systems. The particle diameters during the polymerization are shown in Fig. 2. As is clear from Fig. 2, the particle diameters were almost constant at 80–90 nm during the course of the polymerization, except in the case of 0.5 g PVA using AIBN, where the particle diameter gradually became larger.

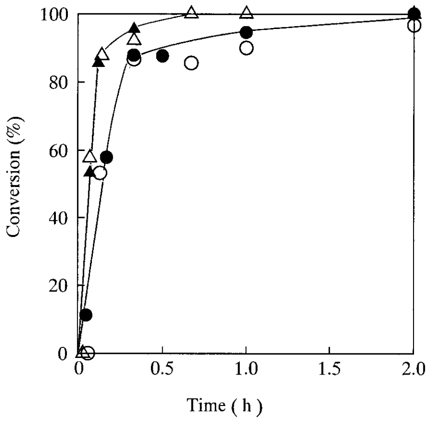

Fig. 1 Time–conversion curves: methyl methacrylate 0.93 g, water 103 ml, 70 °C. Ammonium persulfate system (*triangles*), azobis(isobutyronitrile) system (*circles*). 0.5 g poly(vinyl alcohol) (*PVA*) (*open symbols*), 1 g PVA (*filled symbols*)

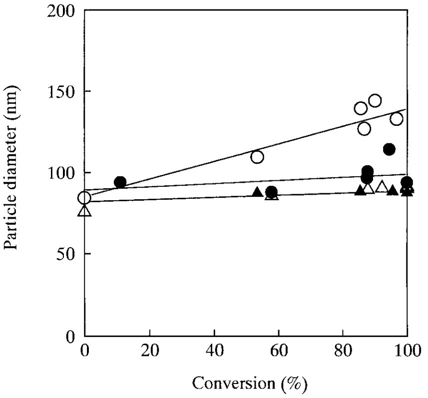

Fig. 2 Change in particle diameters during the polymerization Recipe and symbols the same as in Fig. 1

This means a lack of stability of the system. The change in the number of particles during the polymerization is shown in Fig. 3. The number of particles increased from 2×10^{12}/ml H_2O at about 10% conversion to 2×10^{13}/ml H_2O at final in the case of APS initiator. In other words, new particle formation continued and the number of particles did not become constant in this model emulsion polymerization using APS, which corresponds to the initial stage of ordinary emulsion polymerization.

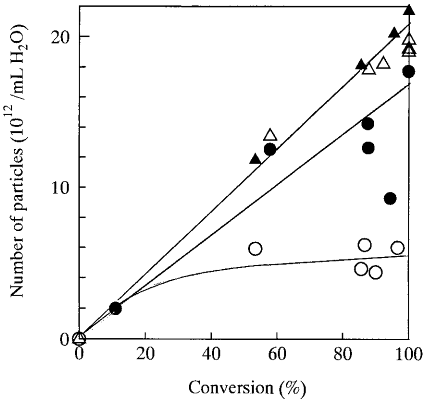

Fig. 3 Change in number of particles during the polymerization Recipe and symbols the same as in Fig. 1

Polymers in the emulsions were fractionated into three parts, i.e., acetone soluble [homo-poly(MMA)] (homo-PMMA), water-soluble (homo-PVA), and insoluble (graft polymers) parts. The fractionation results are listed in Table 1. As is clear from Table 1, almost all the polymerized MMA was grafted irrespective of the kind of initiator. The amount of grafted PMMA decreased with a decrease in the amount of PVA, especially in the case of AIBN. The amount of grafted PVA was larger in the APS system compared with the corresponding AIBN system.

In the case of the highly reactive sulfate radical, the high degree of grafting may be reasonable; however, in the case of the isobutyronitrile radical from AIBN, the high grafting ability should be noticeable, since the reactivity of the isobutyronitrile radical can be regarded to be much lower because of delocalization of the electron owing to the conjugated structure. In fact, AIBN is industrially utilized in solution polymerization of VAc and other monomers as a mild initiator having no induced decomposition. Let us consider the reason for the high grafting ability of the initiators.

Elementary reactions involving the sulfate radical from APS can be written as follows:

1. Initiation and propagation

$$\cdot^{-}SO_4 + MMA \overset{k_{i1}}{\rightarrow} {}^{-}O_4S\text{-}MMA\cdot \overset{k_p}{\rightarrow\rightarrow\rightarrow} {}^{-}O_4S\text{-}(MMA)_n\cdot$$

2. Abstraction of hydrogen and grafting

$$\cdot^{-}SO_4 + PVA \overset{k_{a,APS}}{\rightarrow} PVA\cdot,$$

$$PVA\cdot + MMA \overset{k_{i2}}{\rightarrow} PVA\text{-}MMA\cdot \overset{k_p}{\rightarrow\rightarrow\rightarrow} PVA\text{-}(MMA)_n\cdot,$$

where k_{i1} and k_{i2} are the initiation rate constants of the sulfate and PVA radicals, respectively, $k_{a,APS}$ denotes the rate constant of hydrogen abstraction from PVA with the sulfate radical, and A and B express propagating radicals of PMMA with a sulfate end group and PMMA with PVA, respectively.

Homo-PMMA is formed by termination between A radicals, and disproportionation termination of A with a B radical. The graft polymer is formed by termination between B radicals, coupling termination of A with B radicals, and disproportionation termination of A with

Table 1 Fractionation results of the polymers in emulsions obtained in the model experiments using poly(vinyl alcohol) (*PVA*) in the presence of ammonium persulfate (*APS*) or azobis(isobutyronitrile) (*AIBN*)

Initiator	PVA (g)	PMMA Grafted (%)	Homopolymer (%)	PVA Grafted (%)	Homopolymer (%)
APS	0.5	93.3	6.7	70	30
	1.0	97.8	2.2	54	46
AIBN	0.5	97.8	2.2	47	53
	1.0	98.8	1.2	20	80

B radicals. Disproportionation termination of A with B is regarded to yield equal amounts of homo-PMMA and grafted PMMA. Consequently the rates of formation of homo-PMMA and grafted PMMA can be expressed by the following equations:

$$\frac{\mathrm{d}[\text{homo - PMMA}]}{\mathrm{d}t} = k_\mathrm{t}[\mathrm{A}]^2 + 0.5\lambda k_\mathrm{t}[\mathrm{A}][\mathrm{B}] \ , \tag{1}$$

$$\frac{\mathrm{d}[\text{grafted PMMA}]}{\mathrm{d}t} = k_\mathrm{t}[\mathrm{B}]^2 + (1 - 0.5\lambda)k_\mathrm{t}[\mathrm{A}][\mathrm{B}] \ , \tag{2}$$

where λ denotes the ratio of disproportionation termination to the total termination and k_t is termination rate constant. The value of λ has been estimated to be about 0.7 in the polymerization of MMA [7]. Assuming a stationary state to PVA·, [A], and [B], the following equations can be derived:

$$\frac{\mathrm{d}[\mathrm{PVA}\cdot]}{\mathrm{d}t} = k_\mathrm{a,APS}[\cdot^{-}\mathrm{SO_4}][\mathrm{PVA}] - k_\mathrm{i2}[\mathrm{PVA}\cdot][\mathrm{MMA}] = 0,$$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_\mathrm{i1}[\cdot^{-}\mathrm{SO_4}][\mathrm{MMA}] - k_\mathrm{t}[\mathrm{A}]^2 - k_\mathrm{t}[\mathrm{A}][\mathrm{B}] = 0,$$

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_\mathrm{i2}[\mathrm{PVA}\cdot][\mathrm{MMA}] - k_\mathrm{t}[\mathrm{B}]^2 - k_\mathrm{t}[\mathrm{A}][\mathrm{B}] = 0 \ .$$

From these equations, we obtain Eq. (3):

$$\frac{k_\mathrm{a,APS}[\mathrm{PVA}]}{k_\mathrm{i1}[\mathrm{MMA}]} = \frac{[\mathrm{B}]}{[\mathrm{A}]} \ . \tag{3}$$

In the case of AIBN instead of APS, the same type of equation can be derived:

$$\frac{k_\mathrm{a,AIBN}[\mathrm{PVA}]}{k_\mathrm{i3}[\mathrm{MMA}]} = \frac{[\mathrm{B}]}{[\mathrm{A}]} \ , \tag{4}$$

where $k_\mathrm{a,AIBN}$ is the rate constant of hydrogen abstraction from PVA with the isobutyronitrile radical and k_i3 denotes the initiation rate constant of the isobutyronitrile radical.

In our model experiments described earlier, the fraction of grafted PMMA was much larger than that of homo-PMMA, especially in the case of 1 g PVA. This enables us to consider that concentration of the B radical (PVA–PMMA·) is much larger than that of the A radical (PMMA·). Consequently Eqs. (1) and (2) can be simplified as follows:

$$\frac{\mathrm{d}[\text{homo - PMMA}]}{\mathrm{d}t} = 0.35k_\mathrm{t}[\mathrm{A}][\mathrm{B}] \ , \tag{5}$$

$$\frac{\mathrm{d}[\text{grafted PMMA}]}{\mathrm{d}t} = k_\mathrm{t}[\mathrm{B}]^2 \ . \tag{6}$$

From Eqs. (5) and (6), Eq. (7) can be derived:

$$\frac{\mathrm{d}[\text{grafted PMMA}]}{\mathrm{d}[\text{homo - PMMA}]} = \frac{k_\mathrm{a,APS}[\mathrm{PVA}]}{0.35k_\mathrm{i1}[\mathrm{MMA}]} \ . \tag{7}$$

Although the concentrations of PVA and MMA change with time, let us regard the decrease in the both concentration as almost the same rate. Then, Eq. (8) can be derived from Eqs. (3) and (7):

$$\frac{k_\mathrm{a,APS}}{k_\mathrm{i1}} = \frac{[\text{grafted PMMA}]}{[\text{homo - PMMA}]} \times 0.35 \times \frac{[\mathrm{MMA}]_0}{[\mathrm{PVA}]_0} \ . \tag{8}$$

In the case of AIBN initiator, Eq. (9) can be obtained:

$$\frac{k_\mathrm{a,AIBN}}{k_\mathrm{i3}} = \frac{[\text{grafted PMMA}]}{[\text{homo - PMMA}]} \times 0.35 \times \frac{[\mathrm{MMA}]_0}{[\mathrm{PVA}]_0} \ . \tag{9}$$

Using the data in Table 1, we can calculate the values $k_\mathrm{a,APS}$ and $k_\mathrm{a,AIBN}$ from Eqs. (8) and (9) since k_i1 is reported and k_i3 may be estimated by the following procedure. The rate constant of the polymethacrylonitrile radical to MMA can be obtained from the propagation rate constant of polymethacrylonitrile [9] and the monomer reactivity ratios that are calculated from *Q*–*e* values of the two monomers. The value thus obtained was 64 l/mol/s. In the free-radical polymerization of methyl acrylate, styrene, and methacrylonitrile, Moad and coworkers [10–12] have reported the marked chain length dependence of the propagation rate constants. The values for the shortest chain lengths, $k_\mathrm{p}(1)$, were 1 order of magnitude or more larger than those for macromolecular chain lengths, $k_\mathrm{p}(n)$. Taking this into account, we adopted 10^3 instead of 64 as k_i3. The calculated values of $k_\mathrm{a,APS}$ and $k_\mathrm{a,AIBN}$ are listed in Table 2.

As shown in Table 2, the rate constant of hydrogen abstraction from PVA with the sulfate anion radical is larger than that with the isobutyronitrile radical by about 5×10^4 times. The extremely large rate constant

Table 2 Calculation of the parameters in Eqs. (8) and (9)

Initiator	PVA (g)	$\frac{[\text{grafted PMMA}]}{[\text{homo - PMMA}]} \times 0.35 \frac{[\mathrm{MMA}]_0}{[\mathrm{PVA}]_0}$	k_i1 (l/mol/s)[a]	k_i3 (l/mol/s)[b]	$k_\mathrm{a,APS}$ (l/mol/s)	$k_\mathrm{a,AIBN}$ (l/mol/s)
APS	0.5	4.0	10^8		4.0×10^8	
	1.0	6.4	10^8		6.4×10^8	
AIBN	0.5	12.8		10^3		1.3×10^4
	1.0	11.9		10^3		1.2×10^4

[a] Ref. [8]

[b] Estimated from the rate constant of the polymethacrylonitrile radical to MMA, which was obtained from the calculated monomer reactivity ratio from *Q* and *e* values

($4–6 \times 10^8$ l/mol/s) of hydrogen abstraction with the sulfate anion radical may be reasonable. Many rate constants of hydrogen abstraction from low-molecular-weight alcohols such as ethanol and 2-propanol with the sulfate anion radical have been reported. Clifton and Huie [13] and other researchers reported many data to be about 10^7–10^8 l/mol/s. The k_{i1} value adopted here is not the real initiation rate constant of the sulfate anion radical, but the decay rate constant of the sulfate radical in the presence of MMA [8]. Consequently, the true k_{i1} value may be smaller than 10^8 l/mol/s and result in decrease in $k_{a,APS}$ to some extent. The rate constant of hydrogen abstraction from PVA with the isobutyronitrile radical is remarkably smaller than that with the sulfate anion radical by 10^{-4} times. The low reactivity of the former may be due to its conjugated (and superconjugated) structure [12]. Irrespective of the low reactivity of the isobutyronitrile radical compared with the sulfate anion radical, a high grafting ability of the former radical was observed, as described before. It should be noted that factors affecting the grafting are not determined only by the reactivity of the primary radical with hydrogen in PVA. The ratio of the reaction rate constant of hydrogen abstraction in PVA to that of monomer addition with the primary radical is an important factor to determine the grafting. In other words, there is no relation between the ability of grafting with primary radicals and the hydrogen abstraction ability by the radicals. It is necessary to compare the reactivity of hydrogen abstraction with that of the initiation rate, although it is difficult to obtain both of the rate constants from the literature.

The rate of polymerization of the APS system was larger than that of the AIBN system, as shown in Fig. 1, and may be associated with the much smaller rate constant of addition of the isobutyronitrile radical to the monomer compared with the sulfate anion radical.

Conclusion

A model experiment of emulsion polymerization of MMA using PVA as a protective colloid was carried out in the presence of APS or AIBN, where a small amount of MMA (1/100th of the quantity compared with ordinary emulsion polymerization) was employed. This corresponds to the initial stage of the emulsion polymerization. Grafting of MMA onto PVA took place remarkably irrespective of the kind of the initiators. The formation of homo-PMMA was observed to a small extent. The formation of new emulsion particles smaller than 100 nm continued to increase to almost the end of the polymerization. PVA molecules in the grafted polymer are supposed to act as stabilizers of newly formed particles. From kinetic treatment using the experimental data, the important issues were derived as follows. Firstly, the sulfate anion radical from APS is much more reactive than the isobutyronitrile radical from AIBN in terms of hydrogen abstraction from PVA. Secondly, the high grafting ability of the latter initiator system, notwithstanding the much lower reactivity in the hydrogen abstraction compared with the APS system, is attributed to the relative reactivity of the primary radicals, i.e., hydrogen abstraction reaction from PVA to initiation reaction with MMA. The much slower rate of initiation of the isobutyronitrile radical compared with the rate of hydrogen abstraction from PVA facilitates the grafting, although the rate constant of hydrogen abstraction is far smaller than that with sulfate anion radical by 10^{-4} times.

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