

Effect of Poly(vinyl acetate/vinyl alcohol) Copolymer with a Thiol End Group as a Steric Stabilizer on Dispersion Polymerization of Styrene

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SYNOPSIS

In dispersion polymerization of styrene in ethanol, effects of a reactive steric stabilizer, poly(vinyl acetate/vinyl alcohol) copolymer with a thiol end group (P(VAc/VA)-SH), were investigated. In the absence of the thiol end group, the dispersion coagulated at the middle stage of the polymerization, while in the presence of the thiol end group, the polymerization proceeded successfully to result in close to monodisperse particles. The reactive thiol group acts as a site of formation of the block copolymer, that is, polystyrene-*b*-P(VAc/VA), which is utilized as an effective dispersant. From the measurement on molecular weights during the course of polymerization, two polymerization loci were realized. Addition of butyl methacrylate to styrene affected markedly not only rate of polymerization but also particle size.

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INTRODUCTION

Since the research works performed by Barrett,¹⁻² many articles have been reported on dispersion polymerization of styrene (St) and methyl methacrylate.³⁻²¹ In dispersion polymerization, the reaction medium is at first homogeneous and becomes heterogeneous because of the insolubility of resulting polymer in the medium, where the polymer is stabilized with so-called steric stabilizer, yielding mainly micron-size particles. It is never the rare case to obtain monodisperse particles, which is realized to be of importance from both academic and industrial points of view. Many kinds of solvents have been reported to be useful, and solvency plays an important role to determine the particle size and its distribution.^{4,5,10,14,16-18} Several kinds of polymers such as hydroxypropylcellulose,^{5,7,8,10,12-15} poly(acrylic acid),^{4,15} poly(vinyl pyrrolidone) (PVP),^{4,6,11,15,17,18,20,21} polyisobutylene,⁹ and so on have been utilized as the steric stabiliz-

ers. In some cases, ionic low molecular weight compounds are used as a costabilizer.^{4,6,11,15,20} The steric stabilizer is thought to adsorb onto the surface of particles (or aggregates) and/or to form graft polymer that can stabilize the particles by anchoring the grafted portion into the resulting polymer, while the original portion of the steric stabilizer is soluble in the medium.^{12,13-15,20,21} Block copolymers were also reported as a steric stabilizer.^{3,19} Molecular weight of the resulting polymers are reported to be rather low,^{4,5,7,10,11,13} although they are high in the case of the presence of remarkable gel effect.^{1,17,18} Partitioning behavior of monomer between the particle and the continuous phase was studied during the polymerization.^{1,7,11} Differing from the case of emulsion polymerization, monomer is present mainly in the continuous phase. This coincides with the above mentioned low molecular weight of the resulting polymers. In other words, low molecular weight polymers are formed in the continuous phase and precipitate out, followed by their capture by the existing particles.²¹ The second polymerization locus was also reported to exist in the particles.¹¹

The authors have reported the synthesis of polymers with a reactive thiol end group using a chain transfer reaction of propagating radicals to thioacetic acid followed by weak alkaline treat-

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ment.^{19,22-26} In the presence of the polymer with a thiol end group, a second monomer can be polymerized, yielding mainly A-B-type block copolymer. In a previous paper,¹⁹ we reported the versatility of the block copolymer composed of poly(vinyl acetate/vinyl alcohol) copolymer and polystyrene in the dispersion polymerization of St in ethanol.

In this paper the results of dispersion polymerization of St in ethanol using P(VAc/VA) with a reactive thiol end group (P(VAc/VA)-SH), which is the precursor of the block copolymer mentioned above, as a steric stabilizer will be reported with respect to the role of block copolymerizability of the steric stabilizer. Interesting behavior of a comonomer, butyl methacrylate (BMA), and the degrees of polymerization of both cases will be also dealt with.

EXPERIMENTAL

Reagents

St and BMA were distilled under reduced pressure before use. Ethanol of GR grade and azobisisobutyronitrile (AIBN) of analytical grade were used as received. P(VAc/VA)-SH was synthesized by polymerizing vinyl acetate (VAc) in methanol in the presence of purified thioacetic acid, which was supplied continuously during the course of polymerization to keep the ratio of thioacetic acid to VAc constant. The detailed method of the synthesis was reported elsewhere.^{22,23,25} Polyvinyl acetate with an acetylthio end group was partially hydrolyzed in methanol in the presence of a small amount of sodium hydroxide. Degree of hydrolysis (DH) of the resulting partially hydrolysed polymer was measured by the usual method, hydrolyzing the residual acetyl groups with excess sodium hydroxide followed by back-titration.

Polymerization Procedure

A 1-L Pyrex glass reactor equipped with an anchor-type stirrer, a reflux condenser, a thermometer, a burette sealed with nitrogen gas, and a nitrogen inlet tube with a sampling way was used. Polymerization was started in nitrogen atmosphere by adding a prescribed amount of AIBN dissolved in ethanol through a sampling way. Conversion was measured gravimetrically.

Measurement

Molecular weights of polystyrene and poly(St/BMA) copolymer were measured by gel permeation chro-

matography using columns made by Showa Denko Co. (Shodex A-803/S \times 2 and A-80M/S \times 2) at 40°C in tetrahydrofuran and were calibrated based on the standard polystyrene.

Particle size was determined by measuring about 100 particles of scanning electron microscope photographs that were taken on samples vacuum-dried at -10°C. Two types of average particle size were mainly used: number average (d_n) and volume-surface average (d_s), ($d_n = \sum n_i \cdot d_i / N$, $d_s = \sum n_i \cdot d_i^3 / \sum n_i \cdot d_i^2$). Particle size distribution was shown mainly by d_s/d_n .

RESULTS

Dispersion polymerization of St in ethanol was carried out using P(VAc/VA) copolymer as a steric stabilizer. Figure 1 shows the effect of a thiol end group of the copolymer on the rate of polymerization. In the absence of the thiol group at an end of the copolymer, i.e., a usual copolymer (DP 890), the dispersion coagulated at 40% conversion. A usual copolymer with lower DP (DP 280, DH 23%) afforded a similar result (coagulated after 5 h polymerization). On the other hand, in the presence of the thiol group at an end of the copolymer, the polymerization proceeded smoothly, resulting in microspheres with about 0.8 μm particle diameter. This indicates that a chain transfer reaction took place from polystyrene radicals to the thiol groups to yield the block copolymer that is composed of polystyrene and P(VAc/VA), as the authors have already reported elsewhere.^{19,25,26} Since the P(VAc/VA) por-

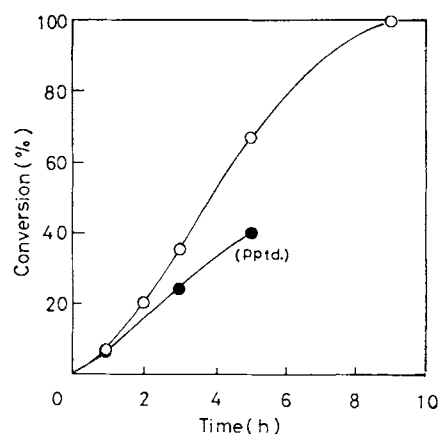


Figure 1 Time-conversion curves of polymerization of styrene using P(VAc/VA) as a steric stabilizer. St: 60 g, Ethanol: 400 mL, AIBN: 0.6 g, Steric stabilizer: 6 g. Polymerization temperature: 70°C. (●) P(VAc/VA), DP 849, DH 23%; (O) P(VAc/VA)-SH, DP 281, DH 24%.

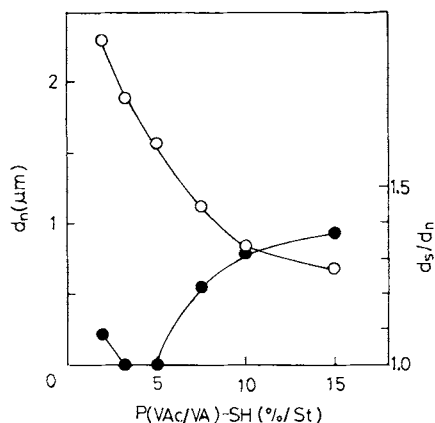


Figure 2 Effect of amount of P(VAc/VA)-SH on particle size and particle size distribution. St: 60 g; ethanol: 400 mL; AIBN: 0.6 g; P(VAc/VA)-SH: DP 274, DH 24%. Polymerization temperature: 70°C. (O) Particle size; (●) d_s/d_n .

tion of the block copolymer is soluble in ethanol, the block copolymer seems to play an important role at the surface of the particles. Weak gel effect can be seen in the case of P(VAc/VA) with a thiol end group.

Figure 2 shows the effect of the amounts of P(VAc/VA) with a thiol end group (P(VAc/VA)-SH) on particle size and particle size distribution. With an increase in the amounts of P(VAc/VA)-SH, the particle size decreased and the particle size distribution became broader, except in the case of the lowest amount of P(VAc/VA)-SH of 2%/monomer where a slight coagulation took place. It should be noticed that monodisperse particles of 1.9–1.6 μm were obtained at the narrow range of P(VAc/VA)-SH concentration (3.3–5%/monomer). Standard deviations of the former and of the latter were 0.035 μm (1.8%) and 0.029 μm (1.9%), respectively.

Table I Change in Particles During the Course of Dispersion Polymerization of Styrene

Time (h)	Conversion (%)	Particle Size (μm)		
		d_n	d_s	d_s/d_n
0.5	0.4	0.88	0.90	1.02
1	3.6	1.32	1.33	1.01
2	10.2	1.64	1.70	1.03
3	18.0	1.84	1.92	1.04
5	35.8	2.29	2.36	1.03
7	52.8	2.54	2.60	1.03
11	70.8	2.75	2.84	1.03

Styrene: 60 g; ethanol: 400 mL; AIBN: 0.6 g; P(VAc/VA)-SH (DP 274, DH 24%): 2.1 g. Polymerization temperature: 70°C.

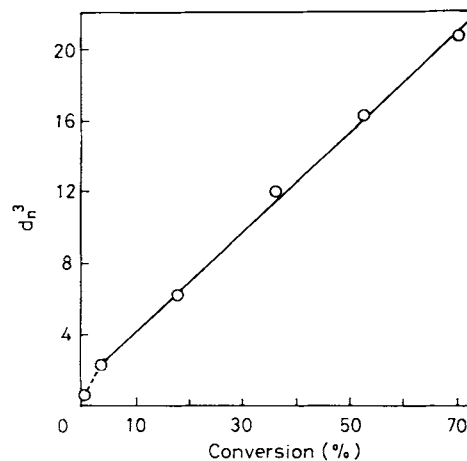


Figure 3 Relationship between conversion and numbers of particles expressed by d_n^3 . Conditions the same as in Table I.

In Table I are listed the changes in particles during the course of the dispersion polymerization. In this case, the polymerization rate was slower than that shown in Figure 1. Increase in particle diameter in accordance with increase in conversion did not bring about change in the particle size distribution, which indicated almost constant to be 1.03 of d_s/d_n during the polymerization. Figure 3 shows the relation between conversion and numbers of particles expressed by d_n^3 . Linear relationship can be seen in Figure 3, except at the very low conversion of 0.4%.

Addition of BMA to St were carried out. Figure 4 shows the time-conversion curves of the dispersion copolymerization of St with BMA. With an increase

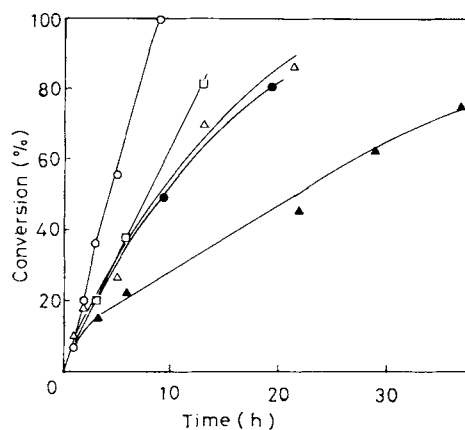


Figure 4 Time-conversion curves of copolymerization of St and BMA. St+BMA: 60 g; ethanol: 400 mL; AIBN: 0.6 g; P(VAc/VA)-SH: 6 g; DP 274, DH 24%. Polymerization temperature: 70°C. Weight ratio of St/BMA: (O) 100/0; (□) 90/10; (△) 80/20; (▲) 70/30; (●) 70/30 (P(VAc/VA)-SH 9 g).

Table II Particle Size and Particle Size Distribution with Change in Monomer Composition

Composition of Monomers (Wt. Ratio)	Particle Size (μm)		
	d_n	d_s	d_s/d_n
Styrene/Butyl Methacrylate			
100/0	0.83	1.15	1.30
90/10	2.18	2.23	1.02
80/20	5.61	6.53	1.16
70/30		pptd.	
70/30 ^a	7.48	9.34	1.25

Monomers: 60 g; ethanol: 400 mL; AIBN: 0.6 g; P(VAc/VA)-SH (DP 274, DH 24%): 6 g. Polymerization temperature: 70°C. ^a 9 g of P(VAc/VA)-SH was used.

in the ratio of BMA, the rate of polymerization decreased remarkably, and the copolymerization did not proceed to conversion 100%. Table II indicates the particle size and particle size distribution obtained in the experiments shown in Figure 4. Particle size increased markedly from 0.83 to 7.48 μm with an increasing fraction of BMA. Particle size distribution was the narrowest in the case of 90/10 composition of St/BMA. In the case of 70/30 composition of St/BMA, the dispersion was unstable to become coagulated, but in the presence of P(VAc/VA)-SH of 15%/monomers instead of 10%/monomers, polymerization proceeded smoothly.

Trials to substitute the stabilizer without a thiol end group for a part of that with a thiol end group were investigated at comonomer composition of 70/30 (St/BMA). Table III reveals the effect of the ratios of both of the stabilizers on particles. In the

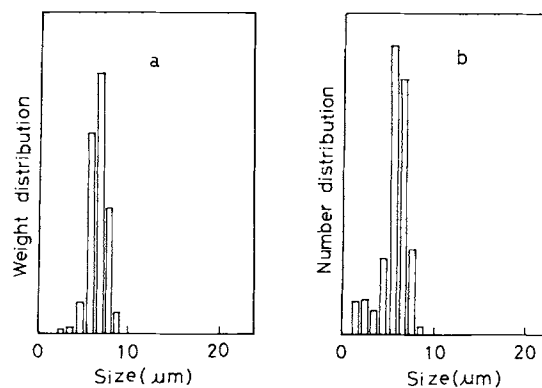


Figure 5 Particle size distribution at conversion 5.8% using a mixture of equal amount of P(VAc/VA)-SH and P(VAc/VA) as steric stabilizer. (a) Weight distribution; (b) number distribution. St+BMA: 90 g; ethanol: 400 mL; AIBN: 0.9 g; steric stabilizer: P(VAc/VA)-SH(DP 201, DH 22%) 4.5 g; P(VAc/VA)(DP 199, DH 25%); 4.5 g, Polymerization temperature: 65°C.

case of equal amounts of both of the stabilizers, particle size and its distribution during the copolymerization were investigated, as also shown in Table III. The experimental conditions listed in Table III did not afford a satisfactory dispersion at the last stage of the copolymerization, even when the stabilizer was composed of only P(VAc/VA)-SH. The particles obtained in the case were golf-ball-like sized. With an increase in the amounts of the stabilizer without a thiol end group, the stability of the particles became worse, and large amounts of flocculant occurred at equal amounts of both stabilizers. Figures 5 and 6 show the change in particle size distribution in terms of weight distribution and of number distribution during the course of the copo-

Table III Effect of Addition of P(VAc/VA) with Unmodified End Group to P(VAc/VA)-SH on Particle Size and Particle Size Distribution

Steric Stabilizer P(VAc/VA)-SH ^a /P(VAc/VA) ^b (Wt. Ratio)	Polymerization		Particle			Remarks
	Time (h)	Conversion (%)	d_n (μm)	d_s (μm)	d_s/d_n	
100/0	23.0	87.0	6.35	7.53	1.19	Not sphere ^c
70/30	22.0	80.4	6.95	11.79	1.67	Weak floc. ^d
50/50	1.0	5.8	5.58	6.15	1.10	
	16.0	63.4	3.73	11.48	3.08	
	23.5	80.7	—	—	—	Almost floc.

Monomers: 88 g (St/BMA = 7/3, wt. ratio); ethanol: 400 mL; AIBN: 0.88 g; steric stabilizer: 8.8 g. Polymerization temperature: 65°C.

^a DP 201, DH 22%.

^b DP 199, DH 25%.

^c Golf-ball like.

^d Weak flocculation.

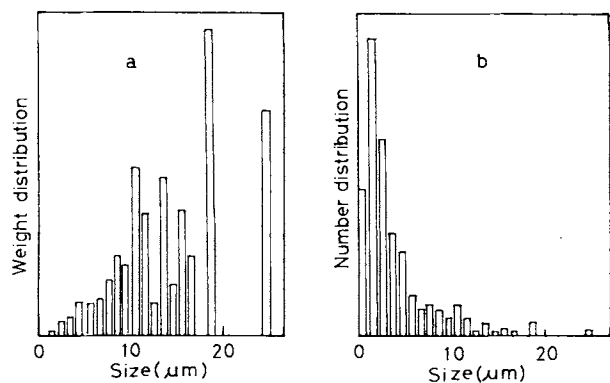


Figure 6 Particle size distribution at conversion 63.4% using a mixture of equal amount of P(VAc/VA)-SH and P(VAc/VA) as steric stabilizer. (a) Weight distribution; (b) number distribution. Conditions the same as in Figure 5.

lymerization in the case of equal amounts of both stabilizers. Clear broadening of the particle size distribution can be seen in this case. At the low conversion of 5.8%, the distribution was not so broad, but at the high conversion of 63.4%, it became remarkably broader.

Degrees of polymerization of resulting polymers during the course of polymerizations were measured. Table IV lists the results of two sets of experiments: one is St polymerization, and the other is St/BMA copolymerization. Degrees of polymerization were determined on the whole polymers. The authors made several trials to separate the block copolymer, homopolystyrene and nonblocked P(VAc/VA), but their efforts ended in failure. Influence of the P(VAc/VA) portion in the whole polymers are mostly not large in the GPC measurement except at the lowest conversion (5.5%) in Table IV. In the last case, although the presence of the larger

amounts of P(VAc/VA) portion should not be negligible, it is still understandable to estimate the polymerization phenomenon using the GPC result.

In the case of St, with increase in conversion, weight average degree of polymerization (\overline{P}_w) increased, and number average degree of polymerization (\overline{P}_n) increased to reach maximum followed by marked decrease. Accordingly, polydispersity index, $\overline{P}_w/\overline{P}_n$, increased remarkably from 2.02 at conversion 5.5% to 6.74 at the last stage of polymerization. On the other hand, in the case of St/BMA copolymerization, \overline{P}_n and \overline{P}_w were almost kept constant except the last stage of copolymerization, where both of the degrees of polymerization became smaller, and $\overline{P}_w/\overline{P}_n$ varied slightly.

Figures 7 and 8 show changes in the molecular weight distributions (MWDs) of the both cases in Table IV in terms of weight frequency and of number frequency. The change in MWD in terms of number frequency in the case of St indicates an interesting phenomenon [Fig. 7(b)]. That is, at the early stage of the polymerization (conversion 5.5%), MWD revealed a single peak, whereas at the middle stage (conversion 52.5%) there were two peaks, and finally a strong peak of very low molecular weight of 1000–2000 (degree of polymerization of 10–20) and a broad peak of much larger molecular weight. MWDs in terms of weight frequency indicate clearly the increase in \overline{P}_w and the broadening of $\overline{P}_w/\overline{P}_n$ described above. The changes in MWD in terms of number frequency as well as weight frequency in the case of St/BMA are coincident with the result in Table IV described above.

Here the influence of the block copolymer and remaining P(VAc/VA)-SH to the MWDs should not be neglected, especially in lower conversion. But the MWDs in the lower conversions (5.5% in Fig.

Table IV Degrees of Polymerization during the Polymerization

No.	St/BMA (Wt. Ratio)	AIBN (g)	Time (h)	Conversion (%)	Particle Size (μm)			Degree of Polymerization		
					d_n	d_s	d_s/d_n	\overline{P}_n	\overline{P}_w	$\overline{P}_w/\overline{P}_n$
1 ^a	100/0	0.6	1	5.5	—	—	—	132	267	2.02
			5	52.5	—	—	—	265	962	3.62
			24	100	2.29	2.48	1.09	153	1031	6.74
2 ^b	70/30	0.88	1	8.5	7.73	10.23	1.32	165	273	1.66
			7	42.3	—	—	—	164	278	1.71
			30	89.4	9.50	15.66	1.65	125	239	1.91

Ethanol: 400 mL. Polymerization temperature: 70°C.

^a Monomer 60 g, AIBN 0.6 g, P(VAc/VA)-SH (DP 274, DH 24%) 1.2 g.

^b Monomers 88 g, AIBN 0.88 g, P(VAc/VA)-SH (DP 274, DH 24%) 8.8 g.

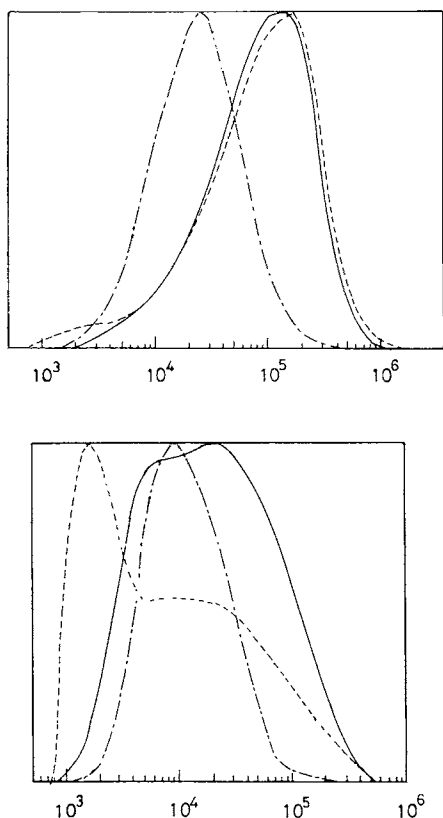


Figure 7 MWD of polystyrene during the course of dispersion polymerization. (a) Weight frequency; (b) number frequency. St: 60 g; ethanol: 400 mL; AIBN: 0.6 g; P(VAc/VA)-SH: 1.2 g; DP 274, DH 24%. Polymerization temperature: 70°C. (---) 5.5%, 1 h; (—) 52.5%, 5 h; (· · · · ·) 100%, 10 h.

7, 8.5% in Fig. 8) are relatively sharp single peaks, and the MWD changes are very large at higher conversions in the case of styrene. The polymerization phenomenon therefore may be understood approximately from the change of MWD in the course of the polymerization.

DISCUSSION

It is evident that the block copolymer formation *in situ* plays an important role in this study. This is revealed by the experimental result that in the absence of the thiol group, the dispersion flocculated at the middle stage of the polymerization, as shown in Figure 1, and that by mixing the steric stabilizer without a thiol end group to the one with a thiol end group, the dispersion became unstable, where broadening of the particle size distribution took place, as shown in Table III and Figures 5 and 6.

In solution polymerization of St in the homogeneous state, the degree of polymerization (DP, expressed in the following equation as P) can be written as the following equation:

$$\frac{1}{P} = C_m + \frac{C_s[S]}{[M]} + \frac{C_x[X]}{[M]} + \frac{k_t R_p}{2k_p^2[M]^2}$$

where C_m , C_s , and C_x are chain transfer constants to monomer, solvent, and chain transfer agent, respectively; $[S]$, $[X]$, and $[M]$ are concentrations of solvent, chain transfer agent, and monomer, respectively; k_t and k_p are rate constants of termination and propagation, respectively; and R_p denotes rate of polymerization. By adopting following values^{27,28} $C_s = 0.6 \cdot 10^{-4}$, $C_s = 2 \cdot 10^{-4}$, $C_x = 18$, $k_t = 11.7 \cdot 10^7$ L · mol⁻¹ · s⁻¹, and $k_p = 389$ L · mol⁻¹ · s⁻¹, and using appropriate R_p , DP can be calculated as listed in Table V. The DP values are in the range of 50 to 60 in the case of 10% steric stabilizer to St and 80 to 90 in the case of 2% steric stabilizer to St, depending

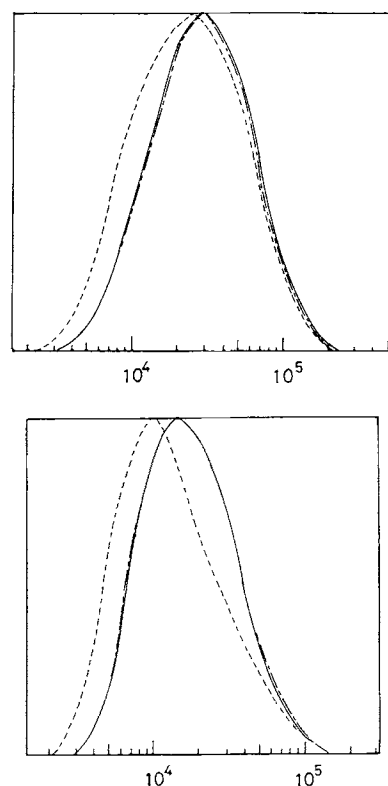


Figure 8 MWD of poly(St/BMA) copolymer during the course of dispersion copolymerization. (a) Weight frequency; (b) number frequency. St: 63 g; BMA: 27 g; ethanol: 400 mL; AIBN: 0.9 g; P(VAc/VA)-SH: 9 g; DP 274, DH 24%. Polymerization temperature: 70°C. (---) 8.5%, 1 h; (—) 42.3%, 7 h; (· · · · ·) 89.4%, 30 h.

Table V Calculation of Degrees of Polymerization of Polystyrene and Ratio of Blocked Polystyrene to Total Polystyrene at Low Conversion Regarding the Medium as Homogeneous

P (VAc/VA)-SH (g)	$[X]^*/[M]$ (10^{-4})	Rate of Polymerization (%/h)	Degree of Polymerization	Ratio of Blocked Polystyrene to Total Polystyrene ^b
6	5.0	7.5	56	0.50
		10	50	0.45
1.2	1.0	7.5	93	0.17
		10	77	0.14

St: 60 g; ethanol: 400 mL. Polymerization temperature: 70°C.

^a Concentration of thiol group.

^b Calculated by dividing $C_x [X]/[M]$ by DP.

on the rate of polymerization. In the former case, the ratio of blocked polystyrene to total polystyrene is ca. 50%, whereas in the latter case, it is ca. 15%. Because the actual medium is not homogeneous, the calculation described above must differ from the real kinetics. However, from the fact that the DP of 132 at 5.5% in No. 1 in Table IV is rather close to the calculated values of 80 to 90, the difference between the calculation and the real one may not be so large.

In the chain transfer reaction using a reactive reagent having C_x larger than unity, caution against the consumption of the chain transfer agent is needed.²⁴ According to our calculation on solution polymerization, the ratios of remaining thiol compound having C_x of 18 to initial concentration are 40, 15, and 1.8% at conversion 5, 10, and 20%, respectively. In other words, the thiol end groups are consumed with rapid chain transfer reaction at the early stage of polymerization to yield the block copolymer. The actual medium was not homogeneous. However, the real polymerization locus seems to be close to homogeneous at the early stage of polymerization, since the main polymerization locus was not in the particles but in the continuous phase, as will be described later.

Consequently, the mechanism of polymerization in this study appears to proceed as following scheme. St polymerizes yielding not only homopolymer but also a large amounts of block copolymer, where the ratio of blocked polystyrene to total polystyrene depends on the amount of P(VAc/VA)-SH. The thiol end groups in the steric stabilizer are almost consumed at the early stage of polymerization less than 10% conversion. The block copolymer thus formed plays a role of a dispersant of aggregated particles that precipitate from solution by exceeding the critical chain length, as Shen et al.²¹ described recently on the dispersion polymerization of methyl methacrylate. The result shown in Figure 3 clearly in-

dicates that the particle formation period is at very low conversion and that after the period of particle formation, propagating polymers and dead polymers in continuous phase do not form new particles but are absorbed to the existing particles.

Graft copolymerization of St onto P(VAc/VA) is less important compared with the block copolymerization, because chain transfer reaction of polystyrene radicals to P(VAc/VA) is much less probable compared with that to thiol groups. Ratio of grafting to blocking can be estimated roughly to be 1 to 200, regarding average C_s of vinyl acetate and vinyl alcohol portions in the stabilizer as $5 \cdot 10^{-4}$ (using values of ethyl acetate and isopropyl alcohol²⁷). Although the amounts of the graft copolymer are much less, it must affect the polymerization to some extent because the polymerization proceeded up to 40% in the presence of P(VAc/VA) without a thiol end group, and particle size distributions became broader using a mixture of P(VAc/VA) and P(VAc/VA)-SH. In the P(VAc/VA)-SH, there are inevitably a small amounts of P(VAc/VA) without a thiol end group, the ratio of which is about 5% in the polymer used in this study.²³ This might be a reason for the difficulty to obtain complete monodisperse particles.

Although the authors have had no data with respect to the stabilization of polystyrene particles with physical adsorption of P(VAc/VA) in ethanol, it seems to be almost impossible to stabilize the particles with the physical adsorption, because ethanol is a good solvent for P(VAc/VA) and the affinity of the copolymer to polystyrene is assumed to be not strong.

Dawkins et al.²⁹ reported quite recently that dispersion polymerized polystyrene using P(VAc/VA) with unmodified end group was very close to monodisperse. Their result looks different from ours. However, the amount of the steric stabilizer (18%/

St) in their study was much larger than those in this study (<10%/St). As they mentioned, decreasing the amounts to 9% caused significant increases both in particle size and distribution, which is close to our results.

As shown in Figure 2, there exists the preferable region in the amounts of P(VAc/VA)-SH to afford monodisperse particles. This is well-known behavior in dispersion polymerization. In the presence of too large amounts of the stabilizer, resulting smaller particles may aggregate with each other because of contact of the steric stabilizer on surface of particles. In the case of too small amounts of the stabilizer, absorption of propagating and dead polymers by existing particles may be incomplete, resulting in unstable polymer aggregates. Recently Yabuuchi et al.³⁰ reported a similar result.

Lu et al.¹¹ reported the molecular weight and MWD of dispersion polymerized polystyrene in ethanol using stabilizers composed of PVP and di-2-ethylhexyl ester of sodium sulfosuccinic acid. They concluded that there exist two polymerization loci in the dispersion polymerization of St in ethanol: one is in continuous phase, and the other in polymer particles in which concentrations of monomer and ethanol are much less than those in continuous phase. Our results shown in Figure 7(a) are similar to their results (Fig. 9 of Ref. 11). The other curves shown in Figure 7(b), which is based on the number frequency instead of the weight frequency as in Figure 7(a), indicate the existence of two polymerization loci. At the early polymerization stage (conversion 5.5%), molecular weight is rather close to the calculated value as described previously, and MWD was rather sharp, which indicates the polymerization locus being in continuous phase. At the middle stage of polymerization, the MWD was clearly composed of two peaks: the lower part appears to be formed in continuous phase, whereas the higher one must be formed in particles where the weak gel effect occurs, as mentioned previously. The molecular weight of polymer formed in the continuous phase at the last stage of polymerization became extremely lower to be DP 10–20 because of decrease in monomer concentration, whereas the initiator concentration in the continuous phase was still high.

In the case of St/BMA copolymerization, \overline{P}_n , \overline{P}_w , and $\overline{P}_w/\overline{P}_n$ are kept constant at the early stage to the middle stage of polymerization, as shown in Table IV, and \overline{P}_n and \overline{P}_w decreased at the last stage (conversion 89.4%, time 30 h) to some extent. Figure 8(a) and (b) show that the single peak of MWD is kept even at the last stage. This appears to be thor-

oughly different from the case of St. The behavior can be realized as follows. In the case of St/BMA, there existed no gel effect in polymerization judged from the time-conversion curves. By adding more polar BMA to St, solvency that is an important characteristic of the medium,^{10,14} as well as polarity of the resulting copolymer, are changed to a great extent, resulting in longer critical chain lengths to precipitate and in larger particle sizes. Moreover, the resulting particles are supposed to contain relatively larger amounts of solvent than in the case of St. This may be one of the reasons for the absence of gel effect. Then the polymerization in the particles is thought to play less important role compared with the St case. Absence of gel effect is thought to cause less amounts of copolymer polymerized in the particles and to suppress the formation of the copolymer of higher molecular weight. The reason for the absence of extremely low molecular weight portion in Figure 8(b), which is one of the large difference between St system and St/BMA one, is thought to arise from the incompleteness of the copolymerization even after the longer polymerization time. This comes from the fact that the copolymerization rate of St/BMA (70/30) was much lower compared with the polymerization rate of St, as is shown in Figure 4. According to calculation, only $\frac{1}{64}$ amounts of the initiator remained after 30 hours at 70°C. This caused a marked decrease in rate of copolymerization, so that the extremely low molecular weight copolymers, which should have been formed at the final stage, were not formed.

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