Dispersion Copolymerization

Dispersion copolymerization was carried out in a reactor equipped with a reflux condenser and a magnetic stirrer that was placed in an oil bath equipped with a temperature control. A typical procedure for dispersion copolymerization of styrene with VBA-PAspNa is presented below: 0.107 g of AIBN and 1.34 g of styrene were dissolved in 27 mL of ethanol and was added into 18 mL of aqueous solution containing of 0.10 g VBA-PAspNa. The mixture was polymerized in the reactor at 343 K for 6 h under nitrogen atmosphere. The resultant particles were refined by three centrifugating washes with water.

Measurements and Characterization

^{1}H NMR spectra were measured using a NMR spectrometer (JEOL, AL300 SC-NMR). Molecular weights of PSI were determined by a gel permeation chromatography (GPC, TOSOH HLC-8120 GPC system) using polystyrene standards with DMF as an eluant. The flow rate and the column temperature were 0.6 mL/min and 313 K, respectively. The particle diameter and the diameter distribution were determined by scanning electron microscopy (SEM, Hitachi *S*-4700). The number-average particle diameter was obtained by counting 200 particles in SEM photographs. Coefficient of variation (CV) of the particle diameter was calculated from the following equation:

$$\mathrm{CV}(\%) = \frac{\text{Standard derivation } (\mu\text{m})}{\text{Number-average particle diameter } (\mu\text{m})} \times 100 \quad (1)$$

Styrene monomer conversion was calculated from the unreacted styrene monomer concentration, which is measured by high-performance liquid chromatography. Small amount of samples withdrawn at different polymerization intervals were added to methanol with 4-*t*-butylpyrocatechol to terminate polymerization. These solutions were centrifuged at 30,000 rpm for 15 min to remove the particles. Unreacted styrene concentration in the supernatant was measured by high-performance liquid chromatography (TOSOH SC-8010 system) with a UV–vis detector (UV-8010, $\lambda = 254$ nm) with the mixture of methanol/water = 7/3 (vol/vol) as an eluant. The column was a TSK-Gel ODS-80Ts QA (150 × 4.6 mm^2, TOSOH). The flow rate and the column temperature were 0.8 mL/min and 313 K, respectively. Particle number was calculated on the basis of the particle diameter and styrene monomer conversion. ζ-Potential of the particles was measured by using an electrophoretic light scattering spectrophotometer (Otuka Electronics ELS-6000).

RESULTS AND DISCUSSION

Synthesis and Characterization of PAspNa Macromonomers

In this study, the feed molecular fractions of VBA to succinimide unit of PSI were 5, 10, 15, and 20 mol %. Weight-average molecular weight (M_w) of PSI used for the synthesis of VBA-PAspNa were between ~6000 and ~30,000.

The typical ^{1}H NMR spectra of VBA-PSI and VBA-PAspNa are shown in Figure 1. Hydrolysis of PSI units was confirmed by decrease of the peak at 5.3 ppm for a methine proton of a succinimide unit and the appearance of the peaks at 4.5 and 4.7 ppm for methine protons of aspartic acid units. Though the hydrolysis of succinimide units was completed, the peak at 4.5 ppm remained. This peak is based on the *trans*-vinyl proton in the side chain.

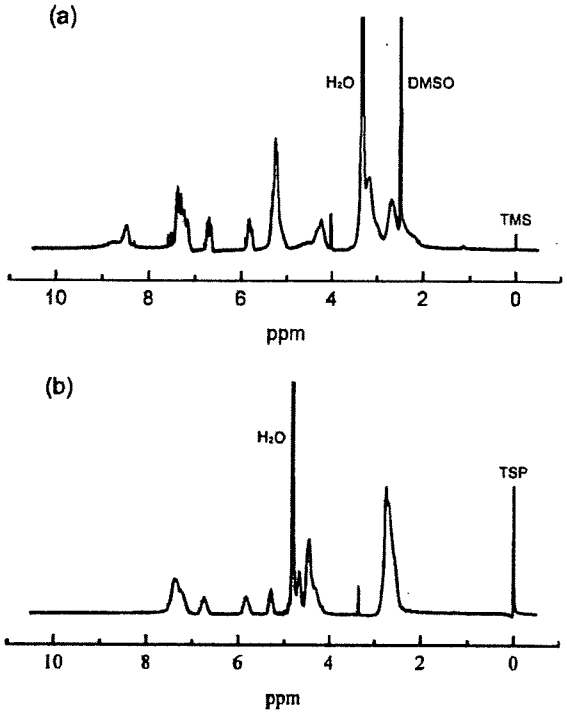


Figure 1. ^{1}H NMR spectra of (a) VBA-PSI in DMSO-d_6 and (b) VBA-PAspNa in D_2O.

Table 1. Conditions of Synthesis and Vinyl Group Fraction of VBA-PaspNa

Sample	PSI		VBA/SI[b] (mol %)	Vinyl Group Fraction[c] (mol %)
	M_w[a]	M_w/M_n[a]		
VBA-5-PAspNa-30k	3.0×10^4	2.9	5	5
VBA-9-PAspNa-6k	6.0×10^3	3.5	10	9
VBA-9-PAspNa-31k	3.1×10^4	2.3	10	9
VBA-10-PAspNa-30k	3.0×10^4	2.9	11	10
VBA-13-PAspNa-31k	3.1×10^4	2.3	15	13
VBA-18-PAspNa-31k	3.1×10^4	2.3	20	18

[a] Measured by GPC.
[b] Molecular fraction of VBA to succinimide unit of PSI.
[c] Determined by ^{1}H NMR spectrum.

Vinyl group fraction was calculated by integration values of a vinyl proton peak at 5.8 ppm and a methine proton peak of a succinimide unit at 5.3 ppm in the ^{1}H NMR spectrum of VBA-PSI. Table 1 shows the vinyl group fraction of VBA-PAspNa. The feed mole ratios of VBA and succinimide units to PSI mostly corresponded to the vinyl group fraction calculated by a ^{1}H NMR spectrum. The feed mole ratios of VBA and succinimide units to PSI can control the vinyl group fraction in VBA-PAspNa.

Preparation of Polymeric Particles

Figure 2 shows the time courses of styrene monomer conversion, particle diameter, CV, and particle number in dispersion copolymerization of styrene with VBA-PAspNa in a mixture of ethanol and water. The conversion approached approximately constant (>90%) within 3 h. Particle diameter also gradually increased with progress of polymerization time. These show quite similar tendency. Particle number was stabilized at a constant value, during the polymerization, after its fast increase. The CV of particle diameter increased up to 45 min, then became almost constant. From these results, we consider that this polymerization mechanism is as follows: Particle nucleation and aggregation has occurred in the initial stage to form stable particles. As the nucleation and aggregation proceed simultaneously, the CV value increases during this period. After this stage, the propagation of particles is developed by capturing monomers and/or oligomers from the continuous phase.

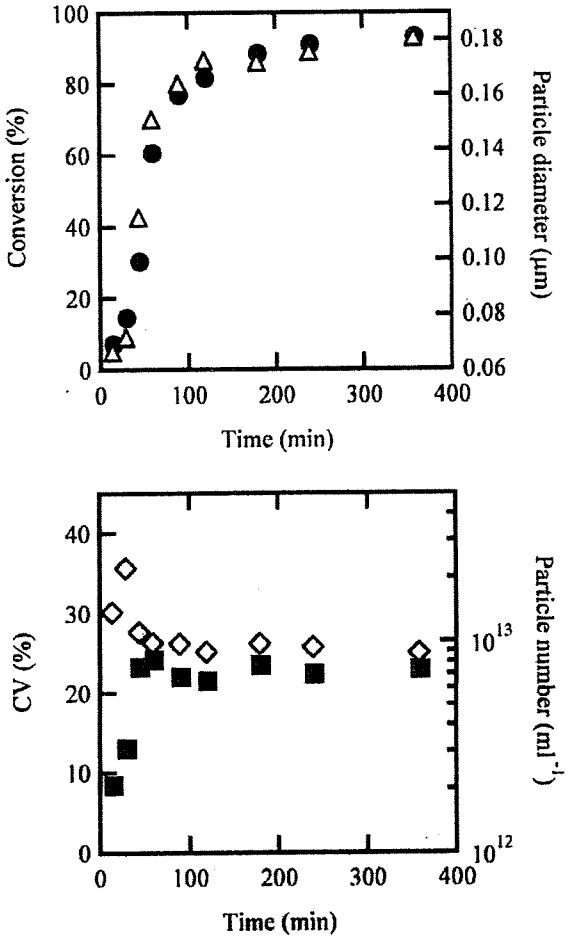


Figure 2. Time courses of styrene monomer conversion (●), particle diameter (△), CV (■), and particle number (◇) in dispersion copolymerization of styrene with VBA-10-PAspNa-30k, [VBA-PAspNa] = 1.11 g/L.

Table 2. Particle Diameter and CV of Particle Prepared by Dispersion Copolymerization with VBA-PaspNa

Macromonomer	Concentration (g/L)	dp^a (μm)	CV^b (%)
VBA-9-PAspNa-31k	0.22	0.277	16.7
	2.22	0.177	24.4
	4.44	0.157	21.9
VBA-9-PAspNa-6k	2.22	0.173	25.4
VBA-5-PAspNa-30k	2.22	0.208	22.0
VBA-13-PAspNa-31k	2.22	0.168	16.0
VBA-18-PAspNa-31k	2.22	0.150	20.2

[a] Number-average particle diameter determined by SEM.
[b] Coefficient of variation.

Particle diameter and CV of the particles prepared with various concentrations, vinyl group fractions, and molecular weight of VBA-PAspNa are shown in Table 2. In spite of low macromonomer concentration (<1 g/L), stable particles with submicron size were obtained. The particles prepared in this study were smaller than those prepared with PEO macromonomer under similar conditions.[15] The particle diameter distribution was broad irrespective of the concentration, the vinyl group fraction, and molecular weight of the VBA-PAspNa.

From the results of Table 2, particle diameter decreased with increasing vinyl group fraction of the VBA-PAspNa. In the system of dispersion copolymerization with macromonomer, homopolymers and graft copolymers (polymerized chains of monomers and macromonomers) were supposed to be formed. The aggregation of homopolymers and graft copolymers results in the particle nuclei. When the concentration or the vinyl group fraction of VBA-PAspNa is high, the copolymerization of VBA-PAspNa and styrene is enhanced, and the influence of graft copolymers is also increased. Thus, the aggregation of particle nuclei is prevented by graft copolymers, resulting in the increase of the particle number formed at the beginning of polymerization. Eventually, the smaller particles are obtained.

The molecular weight of VBA-PAspNa did not significantly affect the particle diameter. A particle diameter is determined by the surface area occupied by the macromonomer chains.[5] Because VBA-PAspNa is a random copolymer bearing vinylbenzyl groups, VBA-PAspNa is expected to attach at multiple sites on the particle surface. That is why the amount of grafted VBA-PAspNa onto the particle surface is independent of the molecular weight of VBA-PAspNa. Therefore, surface area per unit weight of macromonomer was not changed even though the macromonomer chain length was increased.

Effect of VBA-PAspNa Concentration

Dispersion stabilizer concentration is a representative parameter affecting particle diameter in dispersion polymerization. The effect of VBA-PAspNa on the particle diameter is shown in Figure 3. The particle diameter decreased with increasing VBA-PAspNa concentration and is expressed as the following equation:

$$d_p = [\text{VBA} - \text{PAspNA}]^{-0.19}$$

It was found that the vinyl group fraction of VBA-PAspNa did not affect the dependence of macromonomer concentration. The value of exponent is much smaller than that of a theoretical value for dispersion copolymerization with macromonomer, −0.50, predicted by Kawaguchi et al.[5] However, several values of exponent between −0.30 and −0.93 were obtained from experimental results on the dispersion copolymerization of styrene with PEO macromonomer.[8,9,11,15] It may depend on the polymerization condition. The dispersion copolymerization of methyl methacrylate

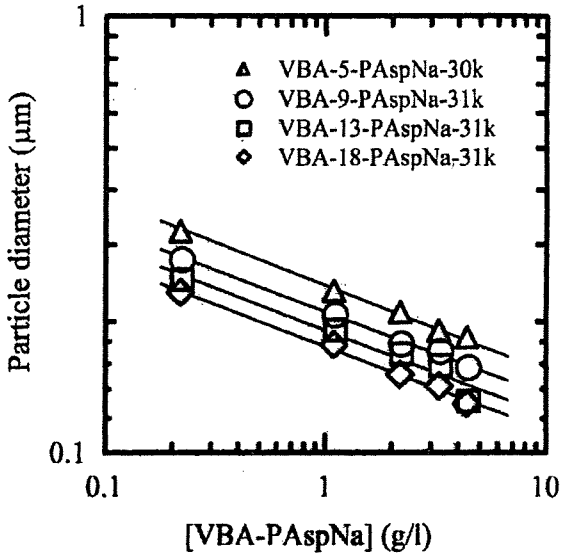
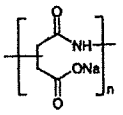
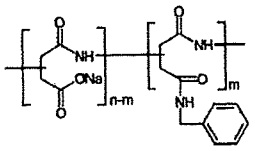
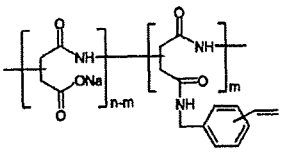


Figure 3. Effect of VBA-PAspNa concentration on particle diameter of the particles prepared by dispersion copolymerization of styrene with VBA-PAspNa.

Table 3. Chemical Structures and Composition of Dispersion Stabilizers Based on PAspNa

Dispersion Stabilizer	Structure	M_w of PSI[a]	Pendant Group Fraction[b] (mol %)
PAspNa (Homopolymer)		4.3×10^4	–
BA-PAspNa (Amphiphilic copolymer)		3.1×10^4	10
VBA-PAspNa (Macromonomer)		3.1×10^4	9

[a] Measured by GPC.
[b] Determined by ^{1}H-NMR spectrum.

with poly(methacrylic acid) macromonomer showed the different dependencies of macromonomer concentration on particle diameter with varying polarity of the medium.[19] When the polymerization was carried out in the mixture of ethanol and water (5:5), the particle diameter was constant regardless of macromonomer concentration. On the other hand, in the case of the polymerization in the mixture of ethanol and water (7:3), the particle diameter increased with increasing macromonomer concentration. These results are interpreted by the solubility decrease of macromonomer in a solvent. This implied that the dependence of macromonomer concentration on the particle diameter was influenced by the solubility of macromonomer in a solvent. Since ethanol is a poor solvent for PAspNa, the solubility of VBA-PAspNa in a mixture of ethanol and water was not sufficient. This may result in a low value of exponent in dispersion copolymerization with VBA-PAspNa.

Effect of Chemical Structure of Dispersion Stabilizers

In general, dispersion stabilizers used in dispersion polymerization are classified as follows: (a) homopolymers, (b) amphiphilic copolymers, and (c) macromonomers. To confirm the effect of vinyl groups of a dispersion stabilizer, the diameter of particles prepared using PAspNa macromonomer (VBA-PAspNa) was compared with that using PAspNa homopolymer (PAspNa) and a PAspNa derivative containing benzyl pendant groups (BA-PAspNa). Chemical structures and composition of dispersion stabilizers used in this section are summarized in Table 3.

The comparison of dispersion stabilizers to the particle diameter is shown in Figure 4. Micron-sized particles were prepared in dispersion polymerization using PAspNa-43k[27] or BA-10-PAspNa-31k as a dispersion stabilizer. The diameter of particles prepared using BA-10-PAspNa-31k was much smaller than that using PAspNa-43k. When low concentrations of BA-10-PAspNa-31k ([BA-PAspNa] = 0.22–1.1 g/L) was used, the particles with bimodal particle diameter distribution were obtained. On the other hand, the diameter of particles using VBA-9-PAspNa-31k was decreased to submicron size, and we did not observe bimodal particle diameter distribution.

The small particles obtained using BA-10-PAspNa-31k were due to the hydrophobicity of benzyl groups in the side chain involving in the

adsorption of BA-10-PAspNa-31k onto the particle nuclei. However, VBA-9-PAspNa-31k gave much smaller particles than that obtained by BA-10-PAspNa-31k. This comparison result indicated that an important factor for particle stabilization is not hydrophobicity but reactivity of vinylbenzyl pendant group.

Characterization of Particle Surface

Macromonomers copolymerize with monomers and bind to the particles. The presence of macromonomer chains on the surface significantly affect the properties, such as a dispersion stability, of resultant particles. To confirm the presence of macromonomer on the surface of particles prepared with VBA-5-PAspNa-30k, ζ-potential of the particles was measured. The surface has negative charge from the carboxylate group of PAspNa chains, if the particles surface is covered with macromonomers. The results of ζ-potential measurement of the particles prepared with different VBA-5-PAspNa-30k concentrations is shown in Figure 5. As shown in this figure, the particles after refinement had a high negative charge on the surface. This indicated that PAspNa chains having a negative charge were fixed onto the surface of particles. Consequently, VBA-PAspNa is bound to the particle surface and gives dispersion stability to the particles through dispersion copolymerization method. Moreover, since PAspNa can be modified with various functional pendant groups,

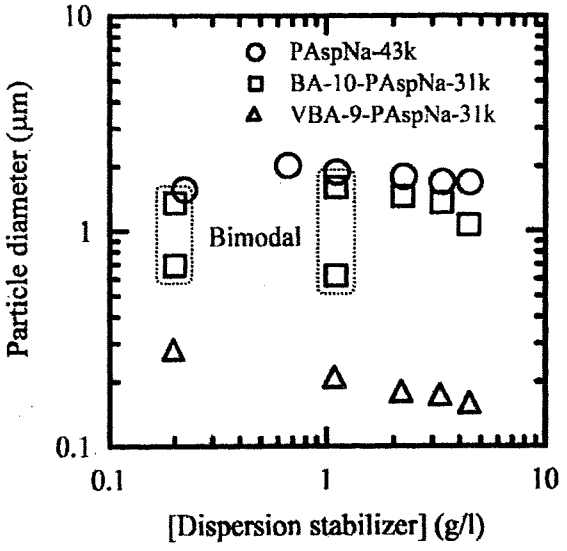


Figure 4. Comparison results of particle diameter with different type of dispersion stabilizers.

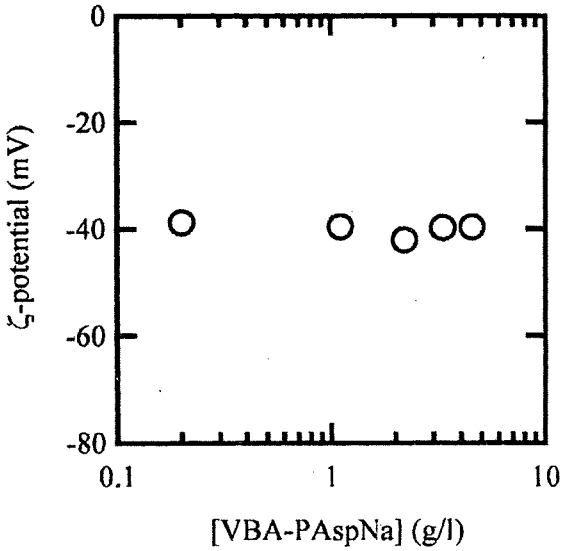


Figure 5. ζ-Potential of the particles prepared by dispersion copolymerization with different VBA-5-PAspNa-30k concentrations.

it will be a promising way to prepare functional polymeric particles.

CONCLUSIONS

PAspNa macromonomers having vinylbenzyl pendant groups (VBA-PAspNa) were synthesized. VBA-PAspNa with different vinyl group fraction were synthesized by changing feed VBA. Submicron sized polymeric particles were prepared by dispersion copolymerization of styrene with VBA-PAspNa in a mixture of ethanol and water. In the present polymerization system, styrene monomer conversion and particle diameter increased with the progress of polymerization, they showed similar tendency, and particle number was constant in 1 h. The particle diameter decreased with increasing concentration and vinyl group fraction of VBA-PAspNa. Comparing the results of dispersion polymerization using PAspNa or benzylamine-modified PAspNa derivative, it was found that VBA-PAspNa is an effective stabilizer in dispersion polymerization in a mixture of ethanol and water. The presence of PAspNa chains anchored onto the particle surface was confirmed by ζ-potential measurement. In PAspNa, functional groups can be easily introduced into the side chain; thus the present method is a process for preparation of polymeric particles with various functional polymer chains on the surface.

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ORIGINAL CONTRIBUTION

Design of polylactide-grafted copolymeric stabilizer for dispersion polymerization of D,L-lactide

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Abstract Poly(D,L-lactide) (PDLLA) microspheres with narrow diameter distribution were prepared by dispersion polymerization of D,L-lactide in xylene/heptane (1:2, *v/v*) using poly(dodecyl methacrylate)-*g*-poly(D,L-lactide) (PDMA-*g*-PDLLA) as a dispersion stabilizer. The particle diameters of PDLLA microspheres were controlled from 200 nm to 5 μm by altering the concentration and the graft chain number of PDMA-*g*-PDLLA. The effect of the copolymer composition on the particle diameter was investigated to clarify an important factor of the copolymer structure for the control of the particle diameter. As a result, it was necessary for anchor block in diblock copolymer as a dispersion stabilizer to have low solubility in the solution rather than the compatibility with particles. Moreover, we confirmed by dynamic light scattering measurement that PDMA-*g*-PDLLA formed micelles in the solution. In conclusion, it was clarified that PDLLA microspheres with a wide range of particle diameter were prepared due to the different kinetic stability of micelles.

Keywords Poly(D, L-lactide) · Microsphere · Dispersion polymerization · Graft copolymeric stabilizer · Copolymeric micelles

Introduction

Heterogeneous polymerization has been of increasing interest for the last three decades, due to the simple preparation of polymeric microspheres with narrow diameter distribution and a wide range of particle diameter [1]. This technique is classified into two methods. The first is emulsion polymerization, which is able to prepare the polymeric microspheres with submicrometer size using reaction medium not dissolving almost monomer. The polymerization takes place in the micelles composed of monomer and emulsifier. The second is dispersion polymerization, which is able to prepare the polymeric microspheres with micrometer size using reaction medium dissolving monomer but not dissolving polymer. The polymerization takes place in reaction medium until the polymer reaches critical molecular weight to precipitate, then the precipitated particles are stabilized by a dispersion stabilizer.

In dispersion polymerization, the dispersion stabilizer which affects the stability of the precipitated particles plays an important role for microsphere preparation. Many workers have prepared monodisperse polymeric microspheres using homopolymeric stabilizers such as poly(vinyl pyrrolidone) and hydroxypropyl cellulose [2–4]. They found that smaller microspheres were obtained at a higher dispersion stabilizer concentration and molecular weight. On the other hand, Dawkins and coworkers have made near-monodisperse polymeric microspheres using diblock copolymeric stabilizer such as poly(styrene-*b*-ethylene-*co*-propylene) and poly(styrene-*b*-dimethylsiloxane) [5–8]. They have investigated the effect of the molecular structure in diblock copolymer such as molecular weight and the alkyl group number of anchoring block on the resultant particle diameter. Winnik et al. confirmed the existence of regular micelles comprising several hundred diblock copolymers and micellar clusters corresponding to the aggregate of tens of micelles in aqueous solution by dynamic light scattering measurement [9–10]. They also

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described that block copolymer with low molecular weight should be used as a stabilizer for dispersion polymerization of styrene in methanol to prepare large and monodisperse microspheres [11].

On the other hand, there have been few papers describing the use of graft copolymer as a stabilizer in dispersion polymerization. Slomkowski et al. reported that Poly(D,L-lactide) (PDLLA) and poly(L,L-lactide) (PLLA) microspheres with narrow diameter distribution were prepared by dispersion polymerization of D,L-lactide and L,L-lactide using poly(dodecyl acrylate)-*g*-poly(ε-caprolactone) as a dispersion stabilizer, respectively [12–13]. They investigated the critical micelle concentration (cmc) of the dispersion stabilizer in 1,4-dioxane/heptane (1:4, *v/v*) as a reaction medium. The polymerization occurred at lower concentrations than its cmc, it was found that the particle diameter and the diameter distribution depend on the molecular structures of the dispersion stabilizer [14]. We have also reported that PDLLA microspheres with narrow diameter distribution were prepared by PLLA-grafted copolymer, poly(dodecyl methacrylate)-*g*-poly(L,L-lactide) (PDMA-*g*-PLLA), as a dispersion stabilizer [15]. In this work, we investigated the effect of the molecular structures in PDMA-*g*-PDLLA on the particle diameter of PDLLA microspheres prepared by dispersion polymerization of D,L-lactide in xylene/heptane (1:2, *v/v*) to clarify an important factor of molecular structures in the graft copolymeric stabilizer for the control of the particle diameter.

Experimental

Materials

D,L-lactide purchased from Purac Biochem BV (Gorinchem, The Netherlands) was purified by the recrystallization from toluene. 2-Hydroxyethyl methacrylate (HEMA) and dodecyl methacrylate (DMA) purchased from Wako Pure Chemical Industries was purified by the distillation under reduced pressure. Toluene, xylene, and heptane (dehydrated-grade) were purchased from Wako Pure Chemical Industries were treated with 4 Å molecular sieves to remove dissolved water. PME-4000, poly(ethylene glycol) macromonomer (MA-PEG), was kindly provided by NOF. FM-0721, polydimethylsiloxane macromonomer (MA-PDMS), was purchased from Chisso were used as received. Other reagents were purchased from Wako Pure Chemical Industries and used as received.

Measurements

Gel permeation chromatography (HLC 8120, Tosoh, GPC) was performed on the basis of the polystyrene standards with tetrahydrofuran as an eluent to determine the number-averaged molecular weight (*Mw*) and the polydispersity index (*Mw/Mn*) of synthesized polymer. ^{1}H NMR (AL300 SC-NMR, JEOL) measurement was conducted using $CDCl_3$ as a solvent and tetramethylsilane (TMS) (1%, *v/v*) as an internal standard to determine the molecular structure of synthesized polymer. Scanning electron microscopic observation (S-4700, Hitachi, SEM) was performed to determine the particle diameter (*dp*) and the diameter distribution (coefficient of variation, CV) of prepared PDLLA microspheres. Differential scanning calorimetric measurement (SSC5200H, Seiko Instruments, DSC) was conducted to determine the glass transition temperature (T_g) of PDMA-*g*-PDLLA and PDLLA microspheres. The heating rate was kept at 5 K/min, and the atmospheric temperature was scanned from 253 K to 373 K. Dynamic light scattering measurement (FPAR-1000, Otsuka Electronics, DLS) was carried out at 293 K to determine the hydrodynamic diameter (R_h) of micelles that consist of PDMA-*g*-PDLLA in xylene/heptane (1:2, *v/v*).

Synthesis

PDMA-g-PDLLA

The preparation of PDMA-*g*-PDLLA serves as a typical example for PDLLA-grafted copolymer. MA-PDLLA was synthesized by ring-opening polymerization of D,L-lactide using HEMA as an initiator in the presence of stannous 2-ethylhexanoate as a catalyst [16]. MA-PDLLA (*Mw*= 3,700, 0.42 mmol), DMA (9.65 mmol), and dehydrated toluene 18 ml as a solvent were placed into a round-bottom reactor. After nitrogen was admitted to remove oxygen, the reactor was immersed in an oil bath at 358 K. Dehydrated toluene dissolving benzoyl peroxide (BPO) (0.63 mmol) was added to initiate the polymerization. The polymerization was conducted for 3 h. After the polymerization, the reaction mixture was poured into excess methanol to remove DMA. The precipitate was recovered and added to 1,4-dioxane/heptane (1:4, *v/v*) to remove the remaining MA-PDLLA. After the purification, the polymer was dried under reduced pressure at 313 K.

The number of PDLLA chains in PDMA-*g*-PDLLA, *CN*, was calculated from the ^{1}H NMR spectrum using the integration ratio of DMA and PDLLA unit. It was defined by the following equation:

$$S_{\mathrm{MA-PDLLA}} = \frac{A_{\mathrm{MA-PDLLA}}}{\mathrm{PD}}$$

$$S_{DMA} = \frac{A_{DMA}}{2}$$

where $A_{\mathrm{MA\text{-}PDLLA}}$ and A_{DMA} denote the peak areas of CH for PDLLA unit of MA-PDLLA and $COOCH_2$ for DMA

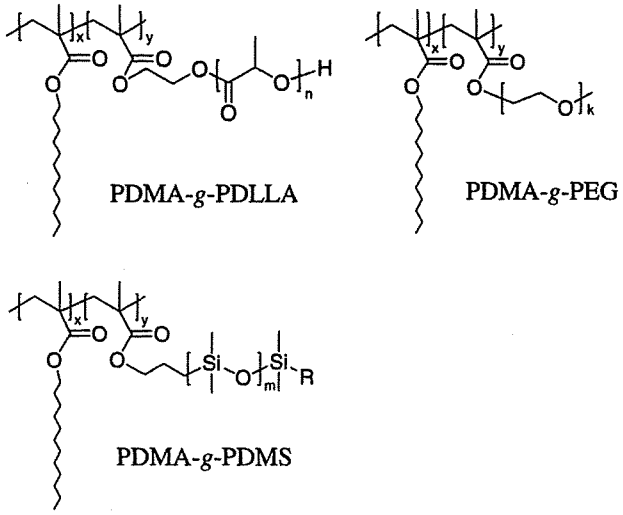


Fig. 1 Chemical structures of the graft copolymeric stabilizers

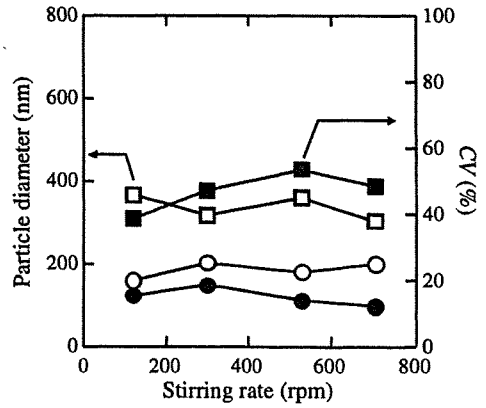


Fig. 2 Effect of stirring rate on the particle diameter and the diameter distribution of PDLLA microspheres prepared using (*open square, close square*) G_2 and (*open circle, close circle*) G_4 copolymers with different molecular structures; [PDMA-*g*-PDLLA]=10 g/l

unit in ^{1}H NMR spectrum of PDMA-*g*-PDLLA, respectively. And PD denotes the polymerization degree of MA-PDLLA. The number of DMA unit per MA-PDLLA unit, *N*, was defined by

$$N = \frac{S_{DMA}}{S_{MA-PDLLA}}$$

$$CN = \frac{Mw_{copolymer}}{(Mw_{DMA} \cdot N + Mw_{MA-PDLLA})}$$

where $Mw_{copolymer}$, Mw_{DMA}, and $Mw_{MA\text{-}PDLLA}$ denote the weight-averaged molecular weight of PDMA-*g*-PDLLA, DMA, and MA-PDLLA, respectively.

PDMA-g-PEG

MA-PEG (*Mw*=4,200, 0.55 mmol), DMA (14.49 mmol), and dehydrated toluene 18 ml as a solvent were placed into a round-bottom reactor. After nitrogen was admitted to remove oxygen, the reactor was immersed in an oil bath at 358 K. Dehydrated toluene dissolving BPO (0.47 mmol) was added to initiate the polymerization. The polymerization was conducted for 3 h. After the polymerization, the reaction mixture was poured into excess methanol to remove the remaining MA-PEG and DMA, and then the precipitate was recovered. After the purification, the polymer was dried under reduced pressure at 313 K.

PDMA-g-PDMS

MA-PDMS (*Mw*=8,400, 7.96 mmol), DMA (7.96 mmol), and dehydrated toluene 18 ml as a solvent were placed into a round-bottom reactor. After nitrogen was admitted to remove oxygen, the reactor was immersed in an oil bath at 358 K. Dehydrated toluene dissolving BPO (0.94 mmol) was added to initiate the polymerization. The polymerization was conducted for 3 h. After the polymerization, the reaction mixture was poured into excess methanol. The precipitate was recovered and added to methanol/2-propanol (1:2, *v/v*) to remove the remaining MA-PDMS. After the purification, the polymer was dried under reduced pressure at 313 K.

Table 1 Molecular structures of PDMA-*g*-PDLLA

Code	Graft copolymer	*Mw*[a]	*Mw/Mn*[b]	Macromonomer		*N*[e]	*CN*[f] (PDLLA)
				Mw[c]	*Mw/Mn*[d]		
G_1	PDMA-*g*-PDLLA	41,300	2.31	3,700	1.30	116	1.3
G_2	PDMA-*g*-PDLLA	34,500	2.23	3,700	1.30	54	2.0
G_3	PDMA-*g*-PDLLA	36,500	2.04	3,700	1.30	27	3.4
G_4	PDMA-*g*-PDLLA	30,700	2.53	6,600	1.40	24	2.4

[a,b,c,d] Determined by GPC
[e] Number of DMA units per MA-PDLLA unit
[f] A grafted PDLLA chain number in a copolymer

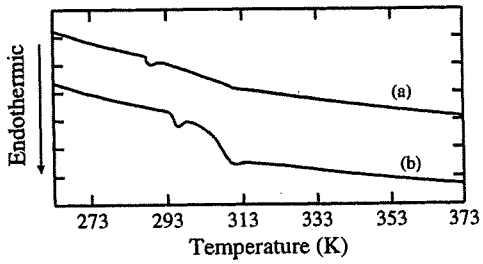


Fig. 3 DSC curves for (*a*) G_4 copolymer and (*b*) PDLLA microspheres prepared with G_4 copolymer; [PDMA-*g*-PDLLA]=10 g/l

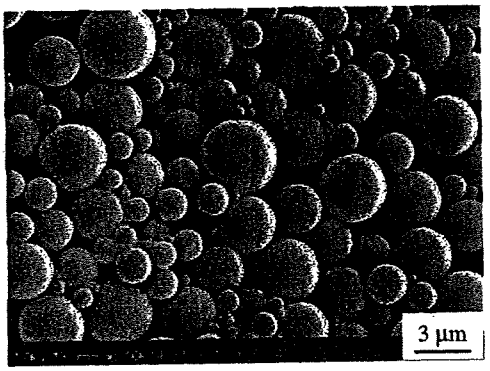


Fig. 4 SEM image of PDLLA microspheres prepared with PDMA-*g*-PEG as a dispersion stabilizer; (*dp*=1,420 nm, CV=48.2%), [PDMA-*g*-PEG]=10 g/l

Preparation of PLA microspheres

The preparation of PDLLA microspheres is shown as a typical example. D,L-lactide (0.5 g, 3.47 mmol) was added into 17 ml of dehydrated xylene/heptane (1:2, *v/v*) dissolved PDMA-*g*-PDLLA. In this study, the concentration of dispersion stabilizer ranged from 0.01 to 0.2 g. The solution was stirred at 120 rpm with a magnetic stirrer. Three milliliters of dehydrated xylene/heptane (1:2, *v/v*) dissolving stannous 2-ethylhexanoate (0.0475 g, 0.12 mmol) as a catalyst and lauryl alcohol (0.011 g, 0.06 mmol) as an initiator was prepared. The solution was added with a syringe and the polymerization was conducted at 368 K for 9 h. After the polymerization, the reaction solution was poured into excess cold heptane. The solution was centrifuged for 5 min at 9,000 rpm and the microspheres were redispersed into excess heptane. The solution was filtered to obtain the prepared microspheres.

Results and discussion

Synthesis of PDMA-*g*-PDLLA

Figure 1 shows the chemical structures of synthesized graft copolymers with different grafted polymer chains. MA-PDLLA was synthesized by ring-opening polymerization of D,L-lactide using HEMA as an initiator. Subsequently, MA-PDLLA was copolymerized with DMA by free radical polymerization using BPO as an initiator to obtain PDMA-*g*-PDLLA. The ^{1}H NMR spectrum of PDMA-*g*-PDLLA had peaks in the range of 1.5–1.7 ppm (CH_3 for PDLLA unit), 5.1–5.3 ppm (CH for PDLLA unit) and around 3.9 ppm ($COOCH_2$ for DMA unit). Furthermore, peaks at 5.6 and 6.2 ppm (CH_2=CH for MA-PDLLA) were not detected in the spectrum. Therefore, PDMA-*g*-PDLLA was finally identified. The molecular structures of synthesized PDMA-*g*-PDLLA were summarized in Table 1.

Synthesis of PDMA-*g*-PEG

PDMA-*g*-PEG was synthesized by free radical polymerization of DMA and MA-PEG as a macromonomer using BPO as an initiator. The ^{1}H NMR spectrum of PDMA-*g*-PEG had peaks in the range of 3.6 ppm ($COOCH_2CH_2$ for PEG unit) and around 3.9 ppm ($COOCH_2$ for DMA unit). Furthermore, peaks at 5.5 and 6.1 ppm (CH_2=CH for MA-PEG) were not detected in the spectrum. Therefore, PDMA-*g*-PEG was finally identified. The MA-PEG number in PDMA-*g*-PEG, *CN*, was calculated by the similar method to PDMA-*g*-PDLLA.

Synthesis of PDMA-*g*-PDMS

PDMA-*g*-PDMS was synthesized likewise using MA-PDMS. The ^{1}H NMR spectrum of PDMA-*g*-PDMS had

Table 2 Molecular structures of graft copolymeric stabilizers

Graft copolymer	*Mw*[a]	*Mw/Mn*[b]	Macromonomer		*N*[e]	*CN*[f] (Macromonomer)
			Mw[c]	*Mw/Mn*[d]		
PDMA-*g*-PEG	27,500	2.38	4,200	1.09	22	2.8
PDMA-*g*-PDMS	39,000	2.05	8,400	1.11	23	2.8

PEG poly(ethylene glycol), *PDMS* poly(dimethyl siloxane)
[a,b,c,d] Determined by GPC
[e] Number of DMA units per macromonomer unit
[f] A grafted macromonomer chain number in a copolymer

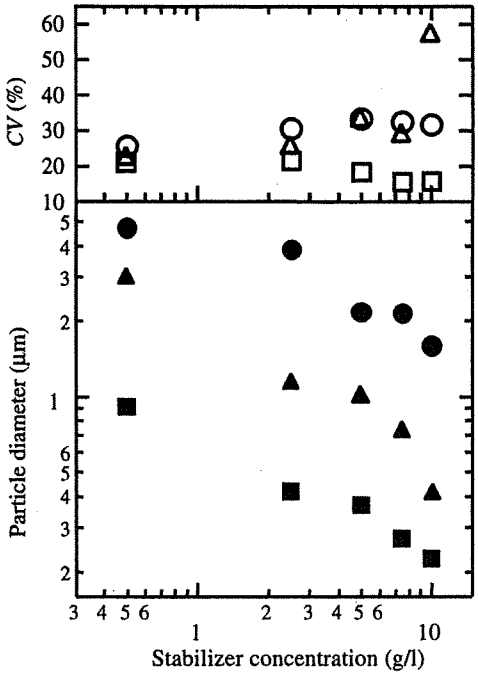


Fig. 5 Effect of concentration of (*open circle*, *close circle*) G_1, (*open triangle*, *close triangle*) G_2, and (*open square*, *close square*) G_3 copolymers with different number of graft chains on the particle diameter and the diameter distribution of PDLLA microspheres

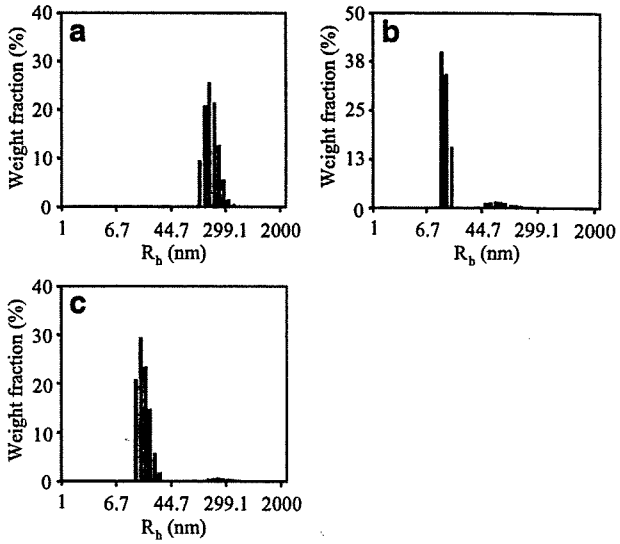
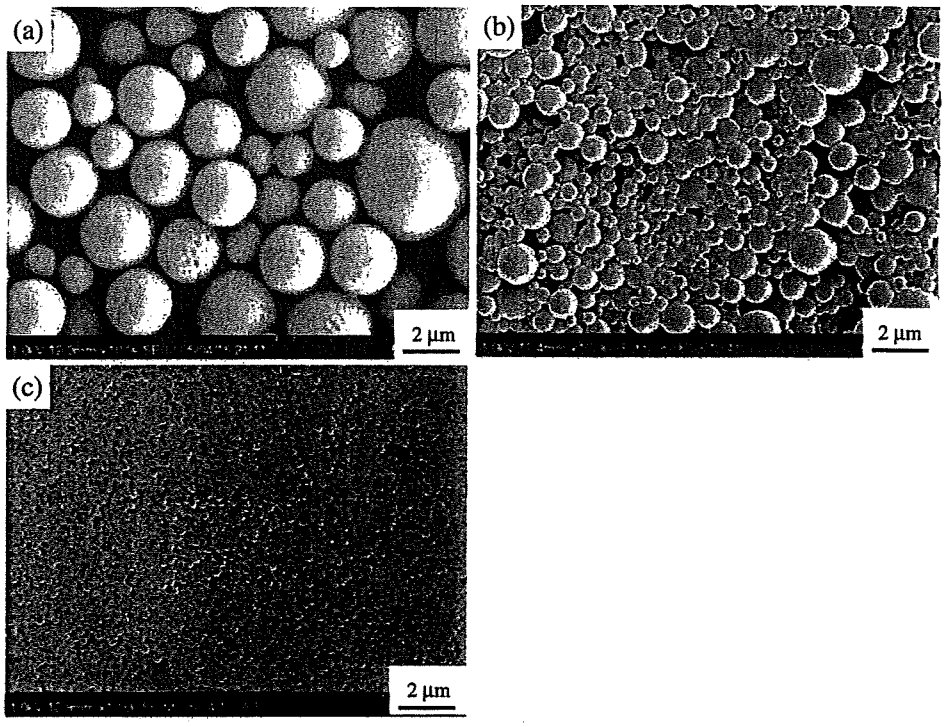


Fig. 7 Size distributions for micellar aggregates of **a** G_1 (R_h=194 nm), **b** G_2 (R_h=13 nm, 93 nm) and **c** G_3 (R_h=18 nm, 276 nm) copolymers in xylene/heptane (1:2, *v/v*) at 293 K; [PDMA-*g*-PDLLA]=10 g/l

peaks in the range of 0.0 ppm ($Si(CH_3)_2$ for PDMS unit) and around 3.9 ppm (OCH_2 for DMA unit). Furthermore, peaks at 5.4 and 6.0 ppm (CH_2=CH for MA-PDMS) were not detected in the spectrum. Therefore, PDMA-*g*-PDMS was also finally identified. The MA-PDMS number in PDMA-*g*-PDMS, *CN*, was calculated likewise.

Fig. 6 SEM images of PDLLA microspheres using **a** G_1 (*dp*= 1,600 nm, CV=31.6%), **b** G_2 (*dp*=414 nm, CV=57.2%), and **c** G_3 (*dp*=225 nm, CV=15.8%) copolymers. They have different number of graft chains; [PDMA-*g*-PDLLA]=10 g/l



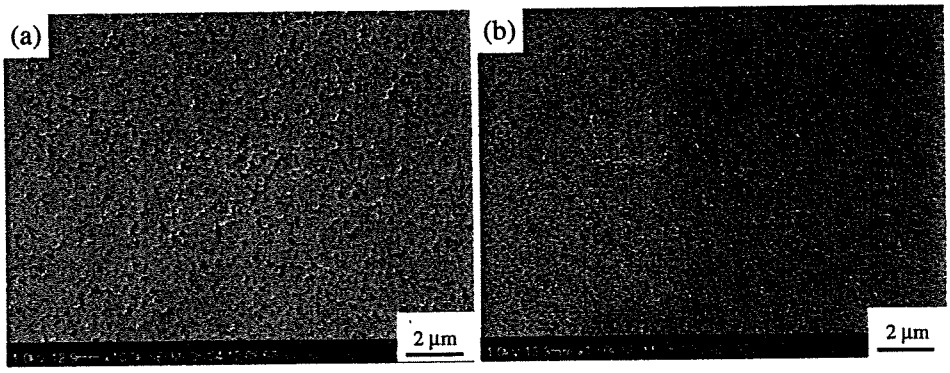


Fig. 8 SEM images of PDLLA microspheres using **a** G_3 (dp=225 nm, CV=15.8%) and **b** G_4 (dp=160 nm, CV=15.4%) copolymers. They have different graft chain length; [PDMA-*g*-PDLLA]=10 g/l

Effect of stirring rate

Figure 2 shows the effect of the stirring rate in the solution on the particle diameter of PDLLA microspheres prepared using G_2 and G_4 copolymers with different molecular structures. As shown in this figure, the stirring rate did not affect the particle diameter.

In addition, in the case with G_2 copolymer, the particle diameter exhibited larger than that in the case with G_4 copolymer. This result implied that the adsorption rate of G_4 copolymer was larger than that of G_2 copolymer because G_4 copolymer shows lower solubility in the solution than G_2 copolymer. As a result, G_4 copolymer prevented primary particles from further aggregation, leading to the formation of small particles with narrow diameter distribution. Thus, it was suggested that the particle diameter depended on the adsorption rate of PDMA-*g*-PDLLA on the surface of primary particles. Namely, it was expected that the particle diameter of PDLLA microspheres was controlled by the molecular structures in PDMA-*g*-PDLLA.

The surface characterization of polymeric microspheres prepared by dispersion polymerization using a dispersion stabilizer with nitrogen element has been performed with X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) [17–18]. They exhibited the existence of diblock copolymeric stabilizer immobilized on the surface of the polymeric microspheres. For PDMA-*g*-PDLLA, however, XPS and FT-IR are not available. Therefore, we confirmed the existence of PDMA-*g*-PDLLA with ^{1}H NMR. Moreover, we also confirmed the T_g based on PDMA-*g*-PDLLA with DSC. Figure 3 shows the DSC curves of G_4 copolymer and PDLLA microspheres prepared by dispersion polymerization with G_4 copolymer. From this figure, T_g based on PDMA in G_4 copolymer was 287 K. In addition, T_g of G_4 copolymer was confirmed from the DSC curve of the resultant PDLLA microspheres and the T_g shifted higher to 294 K. Therefore, it was suggested that PDLLA anchor blocks in G_4 copolymer were strongly adsorbed on surface of the primary particles.

Effect of graft chain structure

We investigated the effect of the molecular structures in PDMA-*g*-PDLLA on the particle diameter to clarify an important factor of the molecular structure for the adsorption on the surface of primary particles. As the first point, Ober et al. reported that the anchor block in copolymeric stabilizer should be compatible with the particles [19]. In contrast, Baines et al. suggested that the compatibility was not an essential requirement [20]. We synthesized copolymers with different grafted polymer chains to experimentally prove the point mentioned above. PDLLA and PDMS bring hydrophobicity to the copolymer but PEG brings hydrophilicity. In addition, PDLLA and PEG show low solubility in xylene/heptane (1:2, *v/v*) during dispersion polymerization. In contrast, PDMS shows high solubility in the solution. The characteristics of the synthesized graft copolymers were summarized in Table 2. Figure 4 shows the SEM image of PDLLA microspheres prepared by dispersion polymerization with PDMA-*g*-PEG as a stabilizer. As a result, in cases with PDMA-*g*-PDLLA and PDMA-*g*-PEG, PDLLA microspheres were prepared. Thus, PDMA-*g*-PEG played a role of a dispersion stabilizer even PEG chain brought no good compatibility with PDLLA particles. In contrast, PDMA-*g*-PDMS gave rise to an undefined-shaped product in the solution even PDMS chain had better compatibility with PDLLA particles than PEG chain. In conclusion, it is necessary for an anchor block in diblock copolymer as a dispersion stabilizer to have low solubility in the solution rather than the compatibility with particles.

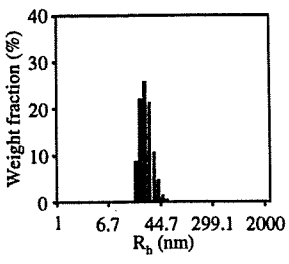


Fig. 9 Size distribution for micellar aggregates of G_4 copolymer in xylene/heptane (1:2, *v/v*) at 293 K; R_h=24 nm, [PDMA-*g*-PDLLA]=10 g/l

Effect of graft chain number

Figure 5 shows the effect of the graft chain number and the concentration of PDMA-*g*-PDLLA on the particle diameter and the diameter distribution of PDLLA microspheres. As shown this figure, the particle diameter decreased with increasing the graft chain number and the concentration of G_1, G_2, and G_3 copolymers. Moreover, it was able to control the particle diameter from 200 nm to 5 μm by altering the graft chain number and the concentration of PDMA-*g*-PDLLA. However, as regarding the particle diameter distribution, they were not correlated. Figure 6 shows the SEM images of PDLLA microspheres using G_1, G_2, and G_3 copolymers. In the case with G_1 copolymer, large PDLLA microspheres were prepared. In contrast, in the case with G_3 copolymer, small PDLLA microspheres with narrow diameter distribution were prepared. In addition, in the case with G_2 copolymer, PDLLA particle with a bimodal size distribution were prepared. From these results, it was suggested that the adsorption rate of PDMA-*g*-PDLLA on the surface of primary particles was determined by the kinetic stability of PDMA-*g*-PDLLA micelles in the reaction medium. Winnik et al. and Stejskal et al. reported similar opinions in dispersion polymerization of styrene and methyl methacrylate using poly(ethylene oxide-*b*-styrene) and poly(styrene-*b*-ethylene-*co*-propylene) as a dispersion stabilizer, respectively [11, 21]. The copolymers with low molecular weight in the micelles can undergo relatively rapid exchange with unimers because the copolymer acts as a steric stabilizer. In contrast, high molecular weight copolymers slowly exchange with unimers, causing the polymerization to take place within the micelles. We measured the hydrodynamic diameter (R_h) of PDMA-*g*-PDLLA micelles in xylene/heptane (1:2, *v/v*) by DLS measurement. Figure 7 shows the size distributions for the micelles of G_1, G_2, and G_3 copolymers in xylene/heptane (1:2, *v/v*) at 293 K. It was confirmed that the G_1 copolymer exhibited a single size distribution and formed larger micelles than that of G_2 and G_3 copolymers because the longer PDMA segment shows higher solubility in the solution. In contrast, G_2 and G_3 copolymers exhibited a bimodal size distribution. It was suggested that both peaks corresponded to the micelles with different R_h because the graft copolymer with various graft chain number exists in the synthesis by free radical polymerization. The micelles of G_3 copolymer are thermodynamically less stable than that of G_1 and G_2 copolymers because G_3 copolymer shows the lowest solubility in the solution. Therefore, the adsorption capability of PDMA-*g*-PDLLA on the surface of primary particles was increased with increasing the graft chain number.

Effect of graft chain length

Figure 8 shows the SEM images of PDLLA microspheres prepared using PDMA-*g*-PDLLA with different graft chain length. From this figure, the particle diameter was decreased with increasing the graft chain length in PDMA-*g*-PDLLA. Figure 9 shows the size distribution of G_4 copolymeric micelles in xylene/heptane (1:2, *v/v*) at 293 K. It was confirmed that the micelles of G_4 copolymer showed a similar size to those of G_2 and G_3 copolymers. This result indicated similar tendency to the effect of the graft chain number. Thus, it was concluded that the particle diameter strongly depended on the kinetic stability of copolymeric micelles in the solution.

Particle formation mechanism

Based on the results in above sections and the proposed mechanism of anionic dispersion polymerization of styrene [22, 23], a particle formation mechanism in the dispersion polymerization of D,L-lactide in xylene/heptane (1:2, *v/v*) is proposed as shown in Fig. 10. The graft copolymeric stabilizer, PDMA-*g*-PDLLA, forms micelles in the solution. D,L-lactide does not swell the micelles and D,L-lactide is completely soluble in the solution. Therefore, the polymerization of D,L-lactide takes place in the homogeneous medium until the polymer chains achieve a critical chain length to precipitate from the medium. After particle nuclei are formed by the aggregation of precipitated polymer chains, the graft copolymeric stabilizer adsorbs on the

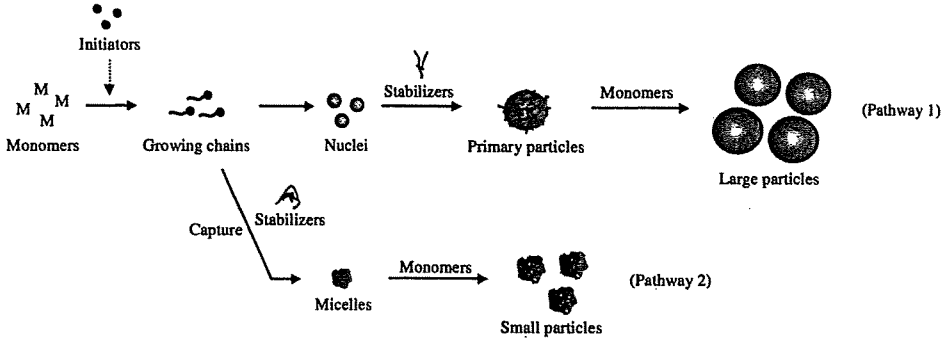


Fig. 10 Schematic representation of particle formation and growth in dispersion polymerization of D,L-lactide with PDMA-*g*-PDLLA

surface of aggregates of particle nuclei to prevent further aggregation. The process of stabilizer adsorption continues until all the surface is occupied, and which forms primary particles. Then the polymerization in the particle goes on through the monomer diffusion from the medium to the particle inside (pathway 1). Moreover, we suggested that the graft copolymeric stabilizer with low solubility in the medium such as G_3 copolymer rapidly exchanged to unimer state and it captured the precipitated polymer chains in the micelles before aggregation. Subsequently, further polymerization of D,L-lactide takes place within the micelles, leading to the formation of small particles with narrow size distribution (pathway 2).

Conclusions

We investigated the effect of molecular structures in the graft copolymer, PDMA-*g*-PDLLA, on the particle diameter of PDLLA microspheres prepared by dispersion polymerization of D,L-lactide in xylene/heptane (1:2, *v/v*). The particle diameters of prepared PDLLA microspheres were controlled from 200 nm to 5 μm by altering the concentration and the graft chain number of PDMA-*g*-PDLLA. The anchor block having low solubility in the solution was important for the graft copolymer as a stabilizer. Such copolymers readily formed micelles in the solution. Thus, PDLLA microspheres with a wide range of particle diameter were prepared due to the different kinetic stability of micelles. In addition, the graft chain number and length of PDMA-*g*-PDLLA affect the kinetic stability of micelles. In conclusion, the particle diameter of PDLLA microspheres in dispersion polymerization is controllable by the molecular design of graft copolymeric stabilizer.

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Heterogeneous Polymerization with Polyaspartate Macromonomer Having Vinyl Pendant Groups. II. Control of Particle Diameter and Diameter Distribution in Dispersion Copolymerization

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ABSTRACT: To control particle diameter and particle diameter distribution in dispersion copolymerization of styrene and sodium polyaspartate macromonomer containing vinylbenzyl pendant groups, effects of some polymerization parameters, water contents, initiator concentration, styrene monomer concentration, reaction temperature, and type of initiator on the particle diameter and the diameter distribution were investigated. Variation of the water contents from 20 to 80 vol % controls the resultant particle diameter from 0.066 to 0.47 μm. The diameter increased with increasing initiator concentration. This tendency is similar to dispersion polymerization system using a nonpolymerizable stabilizer. Particle diameter distribution broadened with increasing styrene monomer concentration. This trend was attributed to the increase of a period of particle formation. This result indicated that the period of particle formation affected the resultant particle diameter distribution. Particle diameter distribution was successfully improved (CV = 9.1 from 23.6%) by shortening of decomposition time of initiator. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 47: 2281–2288, 2009

Keywords: colloids; dispersion polymerization; macromonomers; particle nucleation; particle size distribution

INTRODUCTION

Nano- and microparticles immobilized with polymer chains on the surface have been remarked in recent years. These functional particles have been used for biomedical tools,[1] particulate emulsifier,[2] catalyst,[3–6] and colloidal crystal.[7,8] Functionalization of the polymer chains on the surface can expand the application of these particles.

It is known that heterogeneous polymerization with macromonomer, such as emulsion copolymerization[2,9–13] or dispersion copolymerization,[1,2,13–21] is a one-pot method for preparing particles immobilized with polymer chains on the surface. In this polymerization system, macromonomer plays a role of not only a dispersion stabilizer but a comonomer. Therefore, prepared particles secure high stability and functionality derived from macromonomer chains immobilized onto the surface. Poly (ethylene oxide) (PEO) macromonomer has been used in almost all studies on the heterogeneous polymerization.[11–13,15–21] However, the functionalization of PEO chains is difficult owing to the chemical stability of ethylene oxide units.

We synthesized sodium polyaspartate (PAspNa) macromonomer with vinylbenzyl

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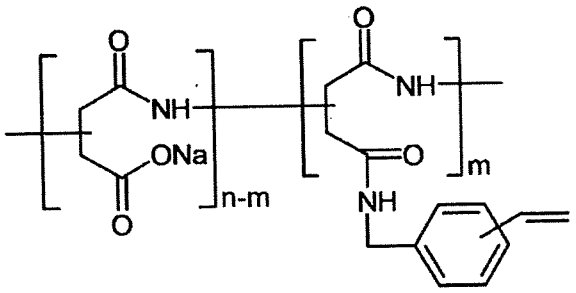

Figure 1. Chemical structure of VBA-PAspNa.

pendant groups (VBA-PAspNa; Fig. 1) as a polymerizable stabilizer in dispersion polymerization.[22] Since poly(succinimide) (PSI), precursor of PAspNa, reacts with various amine compounds without any coupling agent, PAspNa derivatives with various functional pendant groups are easily designed.[23–26] Therefore, dispersion copolymerization with VBA-PAspNa is promising to prepare polymeric particles with polymer chains functionalized as desired on the surface. Submicron sized polymeric particles with broad diameter distribution were obtained by dispersion copolymerization of styrene with VBA-PAspNa in a mixture of ethanol and water.[22]

Adequate ranges of particle diameter in each application fields are different. In addition, monodisperse particles are required for many applications. Therefore, to apply the functional particles produced by dispersion copolymerization with VBA-PAspNa for various application fields, the extension of the control range of particle diameter and improvement of the diameter distribution are important. Many studies about the effects of polymerization parameters on the particle diameter and the distribution in dispersion polymerization have been reported by researchers.[14,15,19–21,27–37] However, there are relatively few studies which discuss the formation mechanism of polydisperse particles in dispersion polymerization in detail. Paine proposed the model of particle formation in dispersion polymerization.[38] In this model, polydisperse diameter distribution results from newborn particle formation and/or coalescence of the particles after stable particle formation. These phenomena result in changes of particle number and diameter distribution of the particles during polymerization. Thus, the investigation of time courses of the particle number and the diameter distribution in dispersion copolymerization is important for elucidation of the formation mechanism of polydisperse particles. In our best knowledge, however, there is no study which discusses about polydispersity of the particle diameter in the term of the time courses of the particle number and the diameter distribution.

In this article, the effects of polymerization parameters such as water contents in media, initiator concentration, styrene monomer concentration, reaction temperature, and type of initiator on the particle diameter and the diameter distribution were examined. Moreover, time courses of the particle number and the diameter distribution during polymerization were investigated with changing the polymerization parameter, which was found to affect the diameter distribution.

EXPERIMENTAL

Material

Styrene, 2,2′-azobisisobutyronitrile (AIBN), 2,2′-azobis(2,4-dimethylvaleronitrile) (ADVN), 4-*t*-butylpyrocatechol and ethanol were obtained from Wako Pure Chemical Industries. Styrene was purified by distillation under reduced pressure. AIBN and ADVN were purified by recrystallization from ethanol. 4-*t*-Butylpyrocatechol was used without purification. Water was purified by a Millipore Milli-Q purification system.

Synthesis of PAspNa Macromonomers

VBA-PAspNa was synthesized by the reaction between PSI and vinylbenzylamine (VBA) and the hydrolysis reaction with sodium hydroxide. The detailed synthesis procedure was described in our previous article.[22] A vinyl group fraction of VBA-PAspNa used in this study was fixed at 10 mol %. Weight-average molecular weight (M_w) and the distribution (M_w/M_n) of the PSI was 29,700 and 2.9, which were measured by gel permeation chromatography (GPC) with polystyrene standard.

Dispersion Copolymerization

Dispersion copolymerization was carried out in a reactor equipped with a reflux condenser and a magnetic stirrer, and which was placed in an oil bath equipped with a temperature control. A typical procedure for dispersion copolymerization of styrene with VBA-PAspNa is presented below: 0.107 g of AIBN and 1.34 g of styrene were dissolved in ethanol 27 mL, and it added into the aqueous solution containing of 0.05 g VBA-

PAspNa 18 mL. The mixture was polymerized in the reactor at 343 K for 6 h under nitrogen atmosphere.

Measurements and Characterization

The diameter and the diameter distribution of particles were measured by scanning electron microscopy (SEM, Hitachi *S*-4700). The number-average particle diameter was obtained by counting 200 particles in SEM photographs. Coefficient of variation (CV) of the particle diameter was calculated from the following equation:

$$CV(\%) = \frac{\text{Standard derivation } (\mu m)}{\text{Number} - \text{average particle diameter } (\mu m)} \times 100 \quad (1)$$

Styrene monomer conversion was calculated from the unreacted styrene monomer concentration measured as follows: Small amount of samples withdrawn at different polymerization intervals was added to methanol with 4-*t*-butylpyrocatechol to terminate polymerization. This solution was centrifuged at 30,000 rpm for 15 min to precipitate and collect polymers, and unreacted styrene concentration in the supernatant was measured by high-performance liquid chromatography (TOSOH SC-8010 system) with a UV–VIS detector (UV-8010, λ = 254 nm) with the mixture of methanol/water = 7/3 (vol/vol) as an eluant. The column was a TSK-Gel ODS-80Ts QA (150 × 4.6 mm, TOSOH). The flow rate and the column temperature were 0.8 mL/min and 313 K, respectively. Particle number was calculated from the particle diameter and the styrene monomer conversion.

RESULTS AND DISCUSSION

Effect of Water Contents in Medium

The polarity of medium significantly affects the diameter of the particles prepared by dispersion polymerization.[27,29–33,37] When oligomers have larger molecular weight than the critical value for precipitation, these are precipitated and coagulated to form particle nuclei. The particle nuclei subsequently coagulate among each other and the number of particle nuclei decreases until enough stabilizers adsorb to stabilize them. Yielding a large number of particle nuclei results in the decrease in the diameter of final particles. The

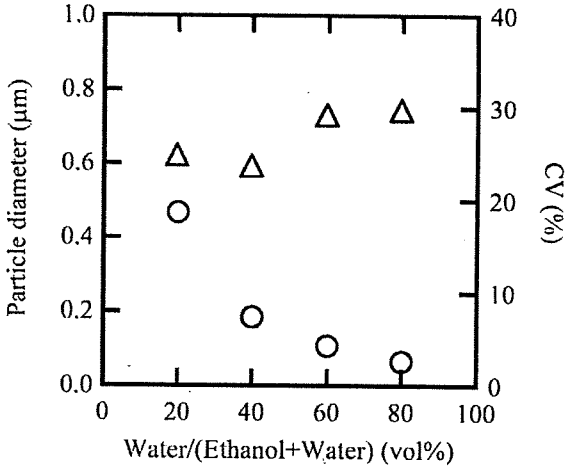

Figure 2. Effect of water contents in the media on particle diameter (○) and CV (△). [Styrene] = 29.8 g/L, [Initiator] = 8 wt %-monomer.

critical value for precipitation strongly depends on the solubility of oligomers in the medium. In addition, since polarity of medium also affects the solubility of dispersion stabilizers, it determines their adsorption behavior and stability. Therefore, the polarity of medium is a principal parameter affecting resultant particle diameter in dispersion polymerization.

The solvents used in this study were a mixture of ethanol and water because the ratio of the solvent controls the polarity of the medium. Water contents of the standard condition was 40 vol %. Dispersion copolymerization was carried out in the media with different water contents was carried out to examine the effect of the water contents on the particle diameter and CV. Styrene monomer was not completely solved in the media with more than 60 vol % of water, and the polymerization occurred in the heterogeneous system. Effect of the water contents in media on the particle diameter and CV is shown in Figure 2. Particle diameter was significantly decreased with increasing water contents. Variation of the water contents from 20 to 80 vol % facilitates the control of particle diameter from 0.066 to 0.47 μm. The decrease in diameter with increasing water contents is explained as follows: (1) Increasing water contents induces further formation of particle nuclei because the solubility of polystyrene in water is lower than that in ethanol. (2) Since PAspNa is insoluble in ethanol and soluble in water, the solubility of VBA-PAspNa is enhanced with increasing water contents. Thus, the PAspNa chains on the surface of particle nuclei provide

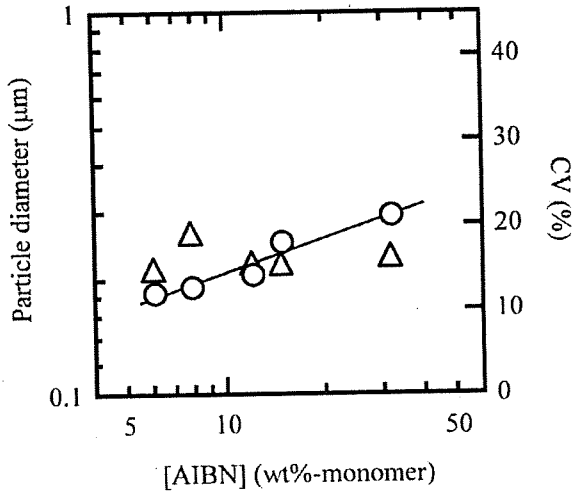

Figure 3. Effect of initiator concentration on particle diameter (○) and CV (△). [Styrene] = 7.5 g/L, ethanol/water = 3/2.

high dispersion stability to the particle nuclei and prevent from coagulating, resulting in the formation of a large number of particle nuclei.

Diameter distribution of the particles prepared in water-rich media was slightly broader than that prepared in ethanol-rich media. When dispersion copolymerization in water-rich solvents is considered, the particle diameter distribution is supposed to be monodisperse because of the high dispersion stability. However, this result indicated opposite tendency to our prediction. Therefore the polymerization was probably occurred in heterogeneous phase.

Effect of Initiator Concentration

Effect of initiator concentration on the diameter and the CV of particles obtained is shown in Figure 3. As seen in this figure, the particle diameter increased with increasing initiator concentration as the follow equation:

$$dp = [\text{Initiator}]^{0.30}$$

Many researchers have reported that a particle diameter increased with increasing initiator concentration in dispersion polymerization with homopolymer as a nonpolymerizable dispersion stabilizer.[28,29,32,36,37] This behavior is explained as follows. The molecular weight of polystyrene formed is decreased by termination reactions with increasing initiator concentration. In dispersion polymerization using homopolymer as a dispersion stabilizer, free radicals generated in the solution abstract the hydrogen atoms from the homopolymer chain during polymerization. Graft polymerization of monomer from these radical sites occurred and led to produce the graft copolymers which adsorb onto the particles. The graft copolymers with shorter polystyrene segment are formed at higher initiator concentration, which make it more soluble in the medium and thus less effective as a stabilizer. This leads to low number of particle nuclei and large particles. Since VBA-PAspNa is a macromonomer containing multiple vinyl groups in the side chains, we can imagine that the stabilization mechanism of VBA-PAspNa is similar to that of homopolymer. Thus, the effect of initiator concentration on the polymerization behavior using VBA-PAspNa was corresponding to that using homopolymer.

Effect of Styrene Monomer Concentration

Effect of styrene monomer concentration on particle diameter and CV is shown in Figure 4. Particle diameter was almost constant regardless of styrene monomer concentration in dispersion copolymerization with VBA-PAspNa. CV of the resultant particles increased with increasing styrene monomer concentration. In the conventional dispersion polymerization of styrene, the particle diameter increases with increasing feed monomer concentration.[28–30] Styrene monomer in a medium acts as a good solvent for the polymer, polystyrene, formed in dispersion polymerization. Thus, at

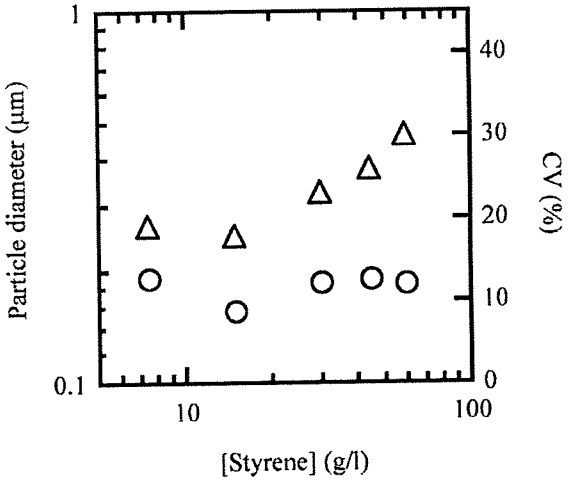

Figure 4. Effect of styrene monomer concentration on particle diameter (○) and CV (△). [Initiator] = 8 wt %-monomer, ethanol/water = 3/2.

high styrene monomer concentration, large particles are produced as described in the above section. However, dispersion copolymerization of styrene with VBA-PAspNa showed a different tendency.

Paine proposed that polydisperse diameter distribution resulted from newborn particle formation and/or coalescence of the particles after initial particle formation. In this model, broadening of the diameter distribution involving increase in the particle number is due to the newborn particle formation, and that involving decrease in the particle number is due to the coalescence of the particles. To clarify the reason why the diameter distribution was broadened with increasing styrene monomer concentration, the time course of particle number and CV in dispersion copolymerization with different monomer concentrations were investigated. The results are shown in Figure 5(a,b). In all of the polymerization conditions, CV increased with polymerization time and then reached on almost constant value. Particle number also increased from the beginning of polymerization and then decreased to a constant value. The period of increase in CV and particle number indicated that particle nucleation continues to occur in this period. Since the newborn particles are smaller than the old particles, the CV was enhanced by the newborn particle formation. Decrease of particle number after the maximum value is probably caused by coagulation of the particles. The particles formed at initial polymerization stage grew to increase the surface area of particles. The increase of surface area advanced the coagulation of particles, and this led to decrease the particle number.

It was found that the both periods in which CV and particle number increased were extended and therefore these final values increased with increasing styrene monomer concentration. This means that the particle nucleation period was prolonged with increasing styrene monomer concentration. The time courses of the amount of unreacted styrene and the CV of particle diameter at a different styrene monomer concentration are shown in Figure 5(b,c). From these results, the CV was gradually increased when styrene remained in the system. This indicated that newborn particles were produced as long as styrene monomer was available for polymerization. In general, since particle nuclei after the initial particle nucleation are instantly captured by the growing particles, no formation of newborn particles occurs during polymerization.[27,37] However,

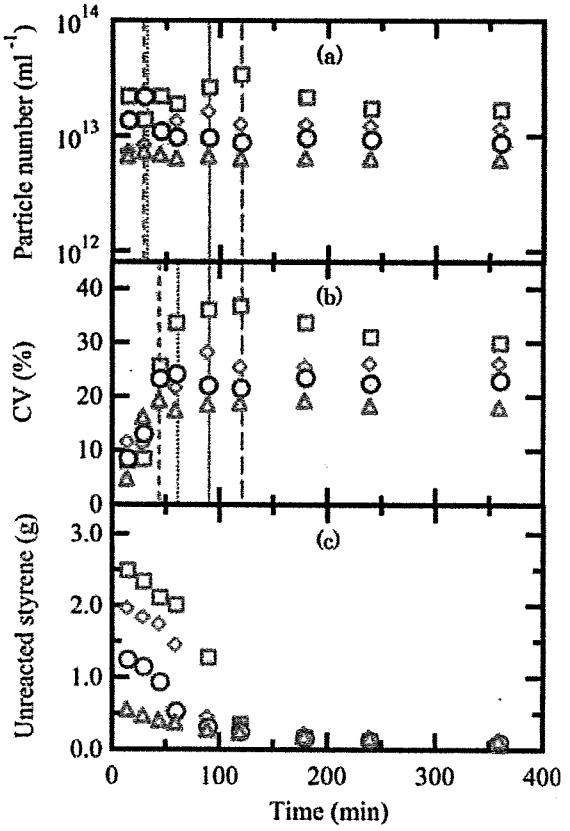

Figure 5. Time courses of (a) particle number, (b) CV, and (c) unreacted styrene amounts in dispersion copolymerization with various concentration of styrene monomer: [Styrene]= 14.9 g/L (△, - - -), 29.8 g/L (○, ·····), 44.7 g/L (◇, —), 59.6 g/L (□, – – –). The lines indicate the times for maximum values of the particle number and CV during polymerization.

Figure 5 implies that capturing particle nuclei by the growing particles is difficult. The surface of particles prepared with VBA-PAspNa would be significantly covered with PAspNa chains at the initial polymerization stage. During dispersion polymerization, styrene oligomers are generated in solution. The oligomers are precipitated and coagulate among each other to form particle nuclei. Graft copolymers are also generated in the solution and adsorb to the particle nuclei to stabilize them. Therefore, stabilizer chain density on the particle surface increases with progress with polymerization.[38] The low solubility of VBA-PAspNa in the ethanol-rich solvent leads to fast adsorption of VBA-PAspNa onto the particle surface. It seems that sufficient surface coverage of PAspNa chains prevents from capturing particle nuclei. The no dependency of styrene

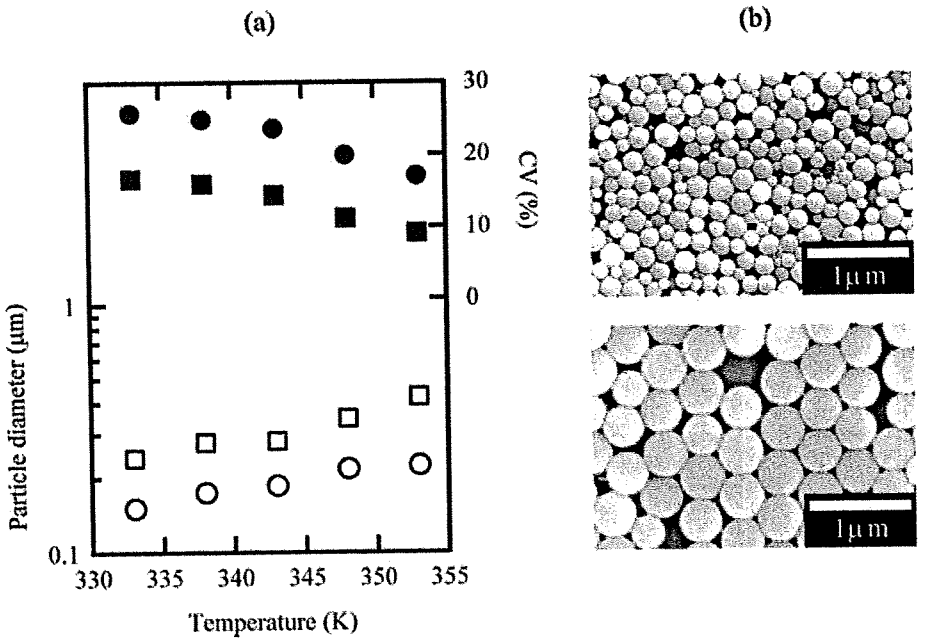

Figure 6. (a) Effects of reaction temperature on particle diameter (open key) and CV (close key) with AIBN (○, ●), ADVN (□, ■) as an initiator. [Styrene] = 29.8 g/L, [Initiator] = 8 wt %-monomer, ethanol/water = 3/2. (b) SEM images of particles prepared with AIBN at 343 K (top) and with ADVN at 353 K (bottom).

concentration on particle diameter is also explained by the decrease in the number-average particle diameter along with the small newborn particle formation.

Effect of Reaction Temperature and Type of Initiator

As mentioned above, the long period of particle nucleation gives rise to broader particle diameter distribution in dispersion copolymerization with VBA-PAspNa. To reduce the CV of the prepared particles, the nucleation time needs to be shortened. Radical generation relates to the particle nucleation. Thus, the period of particle formation expects to decrease by fast decomposition rate of initiator. The decomposition rate of initiator depends on the reaction temperature and the molecular structure. To demonstrate the effect of initiator decomposition rate on the particle diameter distribution, dispersion copolymerization with different reaction temperatures and initiators were carried out. Reaction temperature was varied from 333 K to 353 K. AIBN or ADVN was used as an initiator. The decomposition rate is faster at higher temperature. In addition, the half-life time of ADVN, ~36 min at 343 K, is shorter than that of AIBN, ~340 min at 343 K. The effects of reaction temperature on the particle diameter and the CV of particles with AIBN and ADVN are shown in Figure 6(a). Figure 6(b) shows SEM images of the particles prepared with AIBN at 343 K and with ADVN at 353 K. These results indicated that the elevation of reaction temperature increased the particle diameter and decreased the CV. In addition, large particles with narrow diameter distribution were obtained by using ADVN. The increase of the particle diameter by fast decomposition rate of initiator might be similar to the phenomenon at high initiator concentration.

As expected, dispersion copolymerization with ADVN at high temperature produced particles with low CV. The time courses of particle number and CV of particles prepared by dispersion copolymerization at different reaction temperatures are shown in Figure 7. These results showed that the period of increase in particle number and CV, the period of particle nucleation, was shorter at higher reaction temperature. Likewise, the time courses of particle number and CV of particles prepared by dispersion copolymerization with using AIBN or ADVN are shown in Figure 8. When using AIBN, the CV increased until 60 min. Conversely, when using ADVN, the CV was