SYNTHESES OF SUPER-FINE MONO-DISPERSED PARTICLES OF POLY(STYRENE-*CO*-METHYL METHACRYLATE) BY DISPERSION COPOLYMERIZATION

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ABSTRACT

Poly(styrene-co-methyl methacrylate) particles with a spherical shape, smooth surface, and a size range of 0.3-1.5 μm with a narrow size distribution were obtained by dispersion copolymerization in ethanol/water media with azo-bisisobutyronitrile initiator and a polymeric dispersant of poly(N-vinylpyrrolidone). Without the dispersant, the copolymers were formed in sheets and lumps. Using the solvent mixture of ethanol and water, the particle size distribution was narrower in a mixture containing 10-30 parts of water. The average particle sizes decreased with increasing the dispersant concentration, polarity of the dispersion medium, or agitation rate. Increases in polymerization temperature or reaction time resulted in an increase in the average particle size. This article elucidates the synthesis techniques for super-fine, monodispersed copolymer formation by the theories of the solubility parameter, and dispersant anchoring.

INTRODUCTION

Monosized polymeric particles are used in a wide variety of applications including instrument calibration standards, such as determinations of pore size and the efficiency of filters, column packing materials for chromatographic separation, inks, coatings, ion-exchangers, pharmaceutical reagents, support materials for biochemicals, dry and liquid toners for laser-based printers and photocopying machines (xerography), medical diagnostic tests, microelectronics, etc.[1] The level of success for these applications ultimately depends upon the particle size and size distribution, the morphology of the particles and surface properties. For super-fine toner particles, control of the glass transition temperature and surface charging of the final copolymer beads may be particularly important.[2]

The interest in monosized polymeric particles for use as dry and liquid toners has led to detailed investigations of the dispersion copolymerization of styrene and methyl methacrylate in polar solvents as a method for the formation of polymeric particles. Dry xerographic toners consist of a colorant in a binder resin.[3] Beyond these essential ingredients, a particular toner design may contain charge control additives to control the charge level, surface additives to control flow and cleaning properties, magnetic additives to aid in toner control, and waxes to promote toner release from the fuser roll. Several different families of resins have found frequent applications in xerography depending on the fixing technique selected. The role of the resin in a toner is to bind the pigment to the paper or a transparency material to form a permanent image. This is typically done by selecting a polymer that will melt at a reasonable temperature when heat is applied in any of a number of ways or one that can be fused into the paper fibers

at high pressure without additional heat. Toner particle sizes are generally in the range of about 7 to 12 μm in diameter for dry toner; and 1 to 3 μm for liquid toner. Particle sizes significantly larger than this usually produce ragged lines and dots and thus degrade copy quality. Even if the average size is reasonable, a broad particle size distribution will introduce significant amounts of the small and large toner particles that cause dirt and copy quality problems. As a result, toner processing strives for the narrowest particle size distribution. This is typically done with well-designed micronization equipment followed by air classification and possibly sieving; however a narrow particle size distribution of resin is also of importance.

The objective of this research work is therefore to produce poly(styrene-*co*-methyl methacrylate) super-fine particles ranging from submicron- to micron size with narrow size distributions by dispersion copolymerization in polar solvents.

EXPERIMENTAL

Materials

Styrene and methyl methacrylate were purified by the conventional alkaline method. Azo-bisisobutyronitrile (AIBN) was recrystallised from methanol. Ethanol and methanol were purified by fractional distillation prior to use. Poly(N-vinylpyrrolidone), PVP K-30, $\bar{M}_v$ 40,000 was used, as a dispersant, without further purification.

Preparation of Poly(Styrene-*co*-Methyl Methacrylate)

All ingredients were weighed and mixed in a 1L four-necked round bottom flask, and were purged with nitrogen, capped, and sealed. For most of the experiments, the ratio of styrene to methyl methacrylate was fixed at 75:25; otherwise, its ratio will be mentioned. The temperature of the reaction mixture was constantly maintained at 60°C while stirring at a constant speed with a slow purging of nitrogen gas for 10 h. The polymerization was subsequently stopped by adding a hydroquinone/methanol solution to the reaction mixture sample and the reaction flask was cooled in an ice bath to room temperature. The polymeric beads were cleaned with methanol by a repeated sedimentation-redispersion process. The copolymers were isolated from the colloidal system by washing with methanol and allowed to sediment for 2-3 days at room temperature. After the PVP dispersant in the serum was decanted, the copolymer particles were then allowed to sediment again. This repeated process was aimed to remove the physical adsorption of PVP on the surface of the copolymer during the course of the reaction. The product was placed in an oven at 70°C for 24 h to remove the residual methanol.

Copolymer characterization

All the copolymers were subjected to IR analyses including pure polystyrene for investigation of anchoring absorption of samples prepared by dispersion copolymerization. The particle size and size distribution were examined by scanning electron microscopy (SEM). Four hundred particles are measured for each reaction product, from which the number average diameter, coefficient of variation of number-average size, standard deviation and size distribution were calculated. The average molecular weights were measured by using a gel permeation chromatography (GPC) with a refractive-index detector (RID-6A) and an ultraviolet-visible detector (SPD-10 AV) under the following conditions: a pair of Showa Denko columns (K-806 M; 300 mm x 8 mm I.D.; packing with styrene-divinylbenzene gels having a number of theoretical plates of 17,000).

RESULTS AND DISCUSSION

In this research, the reaction involving the dispersion copolymerization in ethanol/water is a single stage or a "one-shot" process. In the "one-shot" process, a solution of monomer, initiator and graft copolymer dispersant (PVP-g-Pdisp or monomer adsorption on PVP, where Pdisp is the polymer from dispersant on PVP) in a diluent (EtOH/water) is heated together with stirring under reflux. After a short time, solution polymerization takes place to produce very small "molecular" particles. These primary particles can aggregate with each other to form layer species by association with the graft copolymer dispersant. Afterwards, styrene and MMA are adsorbed into the polymer particles and polymerization proceeds at an increasing rate within the particle, as in a bulk copolymerization. To date, it may be concluded that dispersion polymerization proceeds through the solution polymerization and bulk polymerization mechanisms. Dispersion copolymerization of styrene and methyl methacrylate in the solvent mixture of ethanol and water in the presence of PVP K-30 as a polymeric dispersant was homogeneous and clear at the beginning. After an induction period of about 15 min. a faint opalescence was observed. It becomes more opalescent after just 25 min. and it turns into a milky white stable dispersion afterwards. Finally, the polymer product was in a fine powdery form.

According to Shen *et al.*,[4] The adsorption of the polymeric dispersant onto poly(styrene-*co*-methyl methacrylate) particles can be divided into two cases. The first case is the physical adsorption of PVP, which is relatively weak and reversible by washing with methanol. The other case is anchoring adsorption of graft copolymer (PVP-*g*-Pdisp), which is an irreversible adsorption, and it could not be desorbed by washing with methanol because the dispersant radicals continue to react through the respective polymerization as part of the polymer particle. In this regard, propagation is far more probable and would create polymers that are chemically bound or "anchored" to the particles and thus incapable of being desorbed.

Effect of Polymeric dispersant Concentration

The concentration of the polymeric dispersant is one of the most important factors controlling nucleation, i.e., the number of particles increases and their size decreases as the dispersant content is raised. Dispersion copolymerization was performed with six different PVP K-30 concentrations (0, 2, 6, 8, 10 and 12 wt%).

The characteristics and the surfaces of the copolymer particles prepared with different PVP K-30 concentrations are shown in Figure 1. Table 1 shows the effect of polymeric dispersant concentration on dispersion copolymerization of styrene and methyl methacrylate. It can be seen that these copolymer particles, controlled by the dispersant, have a micro-spherical shape with a smooth surface. Different dispersant concentrations also gave various copolymer particle sizes. The copolymer particle sizes obtained were in the range of 0.3 - 1.5 μm. The copolymer particles have a spherical shape and are stabilized in a dispersion medium because of repulsive forces generated by barriers of the soluble dispersant.[5] When two surfaces, each covered by a layer of adsorbed soluble polymer chains, approach each other within a distance less than the combined thickness of the adsorbed layers, an interaction between the polymer layers will occur. This is the source of steric stabilization generating a repulsive force between the opposing surfaces. When the system was polymerized without the dispersant, PVP K-30, agglomerated particles or even sheets were formed. It is explained that the polymerizing system without a dispersant brings about the attractive force which operates between two adjacent particles, usually called the Van der Waals force, originating in the interactions between the atoms and molecules of which the particles are composed.[6] The particles distributions of all

Table 1 Effects of Polymeric Dispersant Concentration on Dispersion Copolymerization of Styrene and Methy Methacrylate.[a]

No.	PVP (wt%)	$D_n^{b,c}$ (μm)	$CV^{d,c}$ (%)	$SD^{c,c}$ (μm)	PDI^f	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
P1[g]	0	-	-	-	-	-	-	-
P2	2	1.5	4.75	0.07	1.01	29,884	79,214	2.65
P3	6	0.6	8.72	0.05	1.02	119,717	216,576	1.81
P4	8	0.6	7.53	0.04	1.02	11,619	37,123	3.20
P5	10	0.5	8.59	0.05	1.02	39,629	157,979	3.99
P6	12	0.3	9.07	0.03	1.02	15,087	34,016	2.25

a Data were obtained under the following conditions: reaction time = 10 h, reaction temperature = 60°C, ethanol/water = 70/30 with 290 rpm stirring
b Calculated diameter, c Determined by scanning electron microscopy from which 400 particles are measured to obtain D_n
d Coefficient of variation of number-averaged size, e Standard Deviation, f Polydispersity Index, g Agglomerated particles

Table 2 Effects of the Ethanol/Water Ratio on Dispersion Copolymerization of Styrene and Methyl Methacrylate.

No.	Ethanol/Water	$D_n^{b,c}$ (μm)	$CV^{d,e}$ (%)	$SD^{e,c}$ (μm)	PDI^f	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
S1[a]	100/0	*	*	*	*	6,413	11,265	1.76
S2[a]	90/10	1.3	4.12	0.05	1.03	5,839	15,008	2.57
S3[a]	80/20	0.7	8.57	0.06	1.07	6,001	13,283	2.21
S4[a]	70/30	0.5	10.21	0.09	1.08	3,222	4,691	1.46
S5[a]	60/40	**	**	**	**	18,807	67,170	3.57
S6[a]	0/100	***	***	***	***	22,518	56,538	2.51

a Reaction temperature = 70°C, reaction time = 8 h with PVP = 8 wt% and 290 rpm stirring; *, **, ***, **** = very broad particle size distribution.
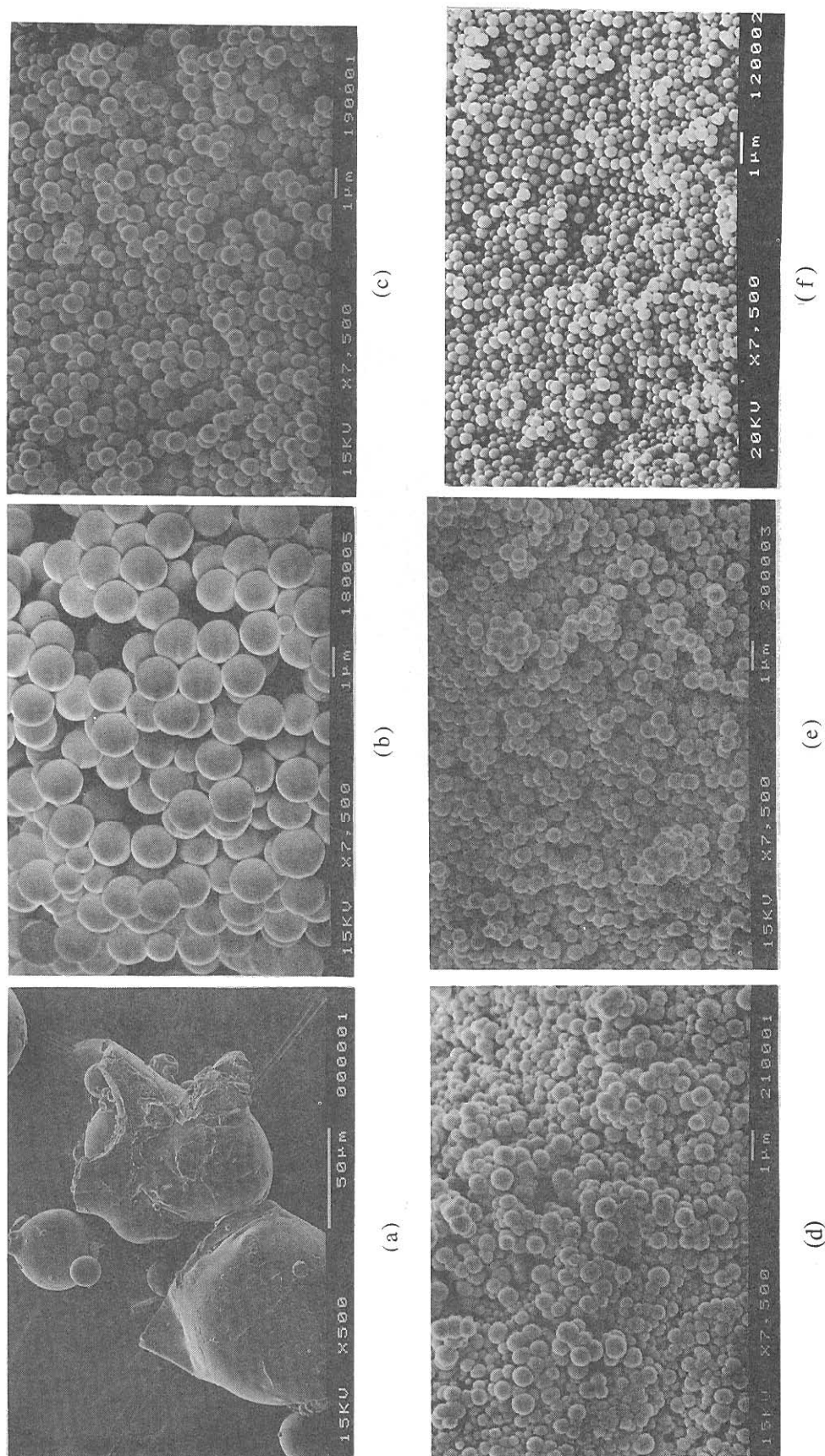
Fig.1 SEM micrographs of poly(Styrene-*co*-methyl methacrylate) particles synthesized presence of (a) 0, (b) 2, (C) 6, (d) 8, (e) 10 and (f) 12% of PVP.

batches synthesized with PVP are relatively monodispersed with a cv of less than 10%. The molecular weights are varied from a couple tens of thousands to hundreds of thousands with an $\overline{M}_w/\overline{M}_n$ of not larger than 4.

Since we have recognized the role of polymeric dispersant in dispersion polymerization, its function in particle growth should be emphasized. The nature and amount of this material used in a dispersion copolymerization has a profound effect on the occurrence of nucleation and the particles formed grow in size and number until the dispersant is insufficient to cover the surface effectively and prevent flocculation. We further characterize the adsorption of the polymeric dispersant. The cleaned copolymer particles were dried as described above. The PVP segments of the copolymer, either presumed to be graft copolymers or otherwise, could be analyzed by infrared spectrophotometry. This is confirmed by comparing the spectrum to the reference peaks of the standard PVP and polystyrene.

The IR spectra of the PVP K-30 standard and polystyrene prepared by the dispersion copolymerization are shown in Figure 2. In this figure, the vibration at 1666 cm^{-1} indicates the C=O group of PVP, whereas the bands at 1940, 1890, 1800 and 1740 cm^{-1} indicate mono-substituted aromatic rings. The band at 1660 cm^{-1} indicates the aromatic ring vibration. Besides these two bands, there are no additional bands. The IR spectrum of polystyrene prepared by dispersion polymerization in the presence of PVP shows an additional peak of C=O at 1684 cm^{-1}. Its peak indicates the residual PVP in polystyrene. The result proves the importance of anchoring adsorption of PVP. The adsorption of PVP on poly(styrene-*co*-methyl methacrylate) particles can be explained as both a physical adsorption and anchoring adsorption from which the latter case is an irreversible adsorption leading to PVP that cannot be desorbed just by a simple washing with methanol, a good solvent for PVP.

Increasing the PVP K-30 concentration implied an increase in both the physical adsorption rate of PVP and the viscosity of the continuous phase, which in turn reduced the mobility of oligomer chains, decreased the diffusion velocity of the precipitated oligomer radicals to result in a decrease of the aggregation of precipitated oligomer radicals, and decreased the number of precipitated oligomer chains and the chain length in each nucleus. The dependence of dispersant content is very marked up to a certain level, beyond which further additions have a much less significant effect. For very high levels of the dispersant, or high dispersion chain solvency, the efficiency of stabilization is seriously impaired and it may be possible that secondary aggregation of primary particles occurs, so that the final particle size is not very sensitive to the dispersant content. From Table 1, after the addition of dispersant higher than 6 wt%, there is no marked effect on the particle sizes observed. At low levels of PVP (2 wt%), the particles have a higher average size.

Effect of the Ethanol-to-Water Ratio

The process of particle formation is strongly influenced by increasing the solvency of the medium for the polymer which is being produced: The onset of particle formation is often retarded; the duration of particle formation is prolonged; fewer particles are produced. They are correspondingly larger and usually of a wide particle size distribution. The solvency of the reaction medium controls the critical chain length of precipitated oligomers, which affects the critical molecular weight and the size of the copolymer particles. SEM photographs of microspheres prepared with different ethanol/water ratios in the presence of 8 wt% PVP K-30 are shown in Figure 3. The copolymer particles prepared in 90/10 have a narrower size distribution than those in ratios of 80/20 and 70/30 ethanol/water. The copolymer particles
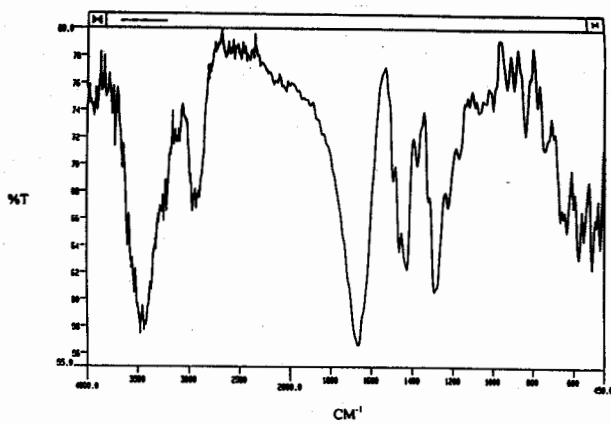
(a)
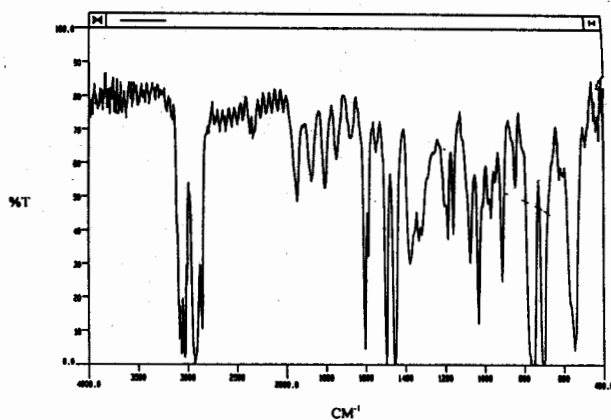
(b)
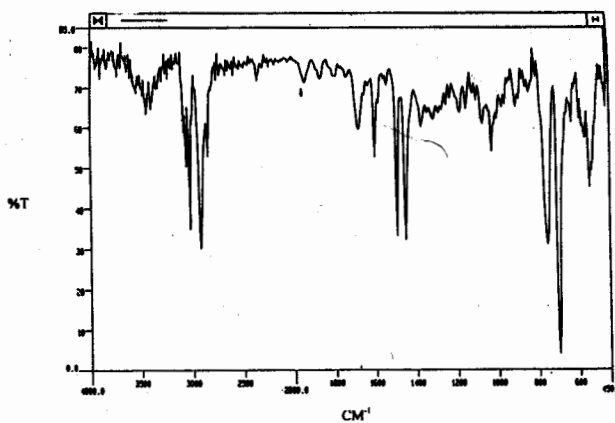
(c)

Fig.2 IR spectra of (a) PVP K-30, (b) standard polystyrene, and (c) polystyrene synthesized by dispersion polymerization.
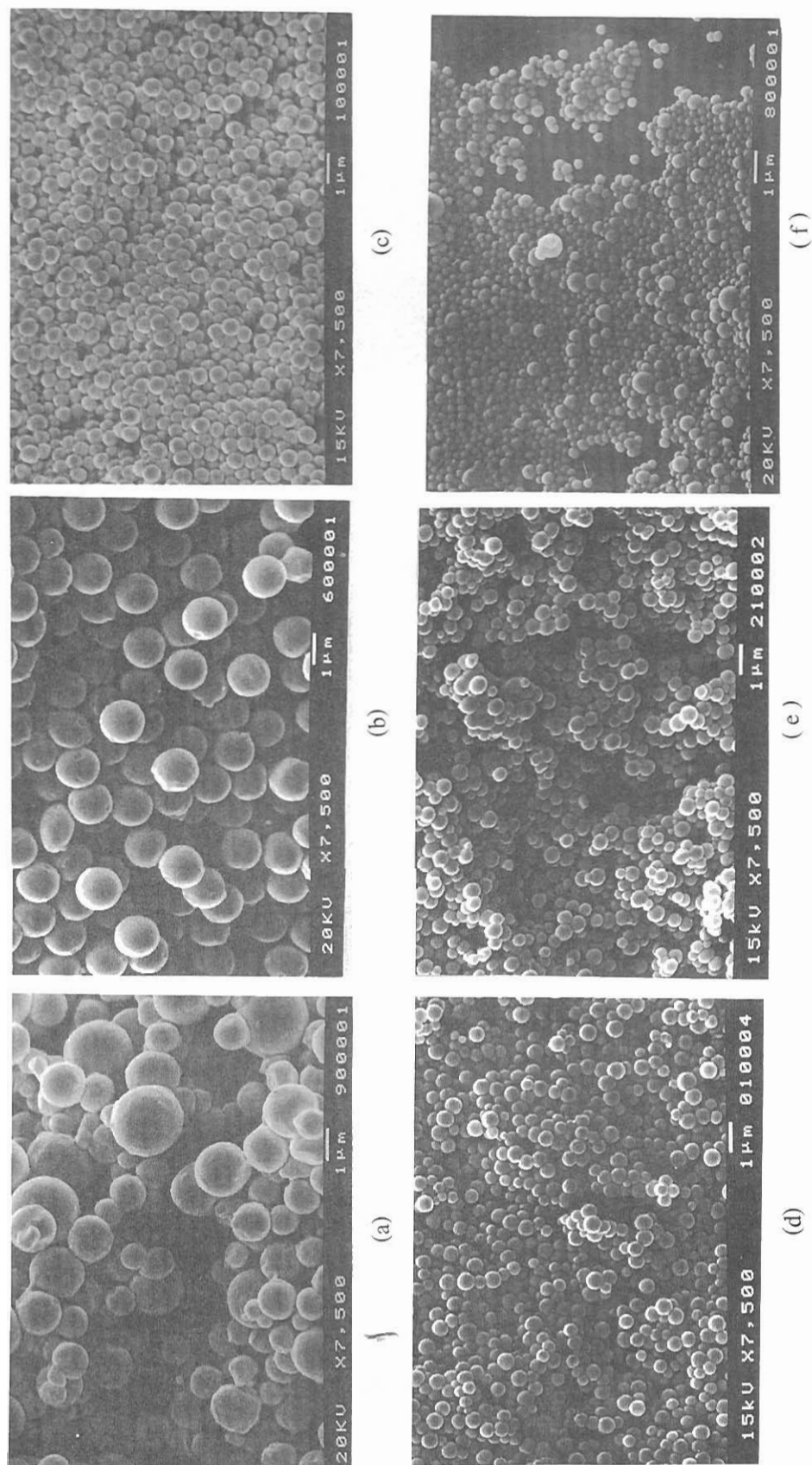
Fig.3 SEM micrographs of poly(styrene-*co*-methyl methacrylate) particles synthesized in ethanol/water ratios of (a) 100/0, (b) 90/10, (C) 80/20, (d) 70/30, (e) 60/40 and (f) 0/100

prepared in 60/40 ethanol/water have the broadest size distribution because the poor solvent (water) for the polymeric dispersant was increased, and the PVP chains entangle and precipitate in the poor solvent to change the morphology of the PVP dispersant to a coil form, which leads to greater excluded free volume within the dispersant chains in the polymer solution. The particle size distribution is thus additionally controlled by the excluded free volume of the dispersant solution. Therefore, the broad particle size distribution was found.[7] When using a good solvent for the dispersant in the reaction medium the resulting particle size distribution is narrow because the morphology of the dispersant is an expanded chain. The dispersant can dissolve easily and its chains disentangle and then stretch freely in that medium. The expanded dispersant chains have almost equal free volumes (or free space) in the dispersant solution, which morphologically controls the particle size of the copolymer.

The higher the polarity of the reaction medium, the smaller the average size at a dispersant concentration because water is a poorer solvent for poly(styrene-*co*-methyl methacrylate) than ethanol, the critical chain length of precipitated oligomers decreased, and the rate of adsorption of the dispersant onto the nuclei and the rate of nuclei formation increase with increasing water content. Figure 3f shows the SEM micrographs and particle size distribution of poly(styrene-*co*-methyl methacrylate) in water. Accordingly, the above behavior might affect the decrease of free volume in the polymeric solution that controls particle sizes of the copolymers when increasing water content.

For pure ethanol, the copolymers have the largest size and a broad size distribution because the pure ethanol is a very good solvent for the oligomer radicals, and the formation of the critical chain length of the oligomer radicals is very long resulting the formation of particle nuclei from these growing oligomer chains as a self-nucleation mechanism. (See Figure 3(a)), the SEM micrographs showing the particle size and size distribution of poly(styrene-*co*-methyl methacrylate) in ethanol). However, some oligomer radical chains are shorter, resulting from the aggregating mechanism, so a smaller particle size was also produced. These various particle sizes led to a broad particle size distribution. At 100% water (polar component solubility parameter, $\delta_p = 16$ (MPa)$^{1/2}$), the copolymer contains more styrene monomers ($\delta_p = 1.0$ (MPa)$^{1/2}$ than methyl methacrylate ($\delta_p = 18$ (MPa)$^{1/2}$), because $\Delta\delta_{p(STY\text{-}H_2O)}$ is large than $\Delta\delta_{p(MMA\text{-}H_2O)}$; therefore, most MMA stays in the aqueous phase of water. The critical chain length of oligomer radical chains in water is shorter than in ethanol. Therefore, in 100% water, the copolymer particle size becomes smaller. In addition, the copolymers have a broad size distribution because pure water (total solubility parameter, $\delta_T = 47.9$ (MPa)$^{1/2}$) acts as a poor solvent for the PVP dispersant ($\delta_T = 25.6$ (MPa)$^{1/2}$) when compared with ethanol ($\delta_{EtOH} = 26.0$ (MPa)$^{1/2}$). The PVP dispersant chains entangle or aggregate to a coiled form in the poor solvent. The particle size distribution is thereby controlled by the excluded free volume in solution of the dispersant, the broad particle size distribution of the copolymer was consequently obtained.

Effect of the Reaction Temperature

The effect of the reaction temperature on the dispersion copolymerization of styrene and methyl methacrylate was investigated. Figure 4 shows SEM photographs of microspheres of the copolymer. The copolymer particle size increased with increasing reaction temperature in the range from 50°C to 70°C and then decreased with increasing temperature up to 80°C. However, the particle size distribution was narrower when increasing the polymerization temperature. Such increases are due to increases in both the decomposition rate of the initiator and polymerization rate of monomers at higher temperatures which may lead to the larger agglomerates.

Table 3 Effects of the Reaction Temperature on Dispersion Copolymerization of Styrene and Methy Methacrylate.[a]

No.	Temp (°C)	$D_n^{b,c}$ (μm)	$CV^{d,c}$ (%)	$S^{e,c}$ (μm)	PDI[f]	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
T1	50	0.5	25.94	0.13	1.19	10,461	21,714	2.08
T2	60	0.6	7.53	0.04	1.02	11,619	37,123	3.20
T3	70	0.8	8.77	0.07	1.02	82,445	125,050	1.52
T4	80	0.6	5.96	0.07	1.01	3,676	9,217	2.51

[a]Reaction time = 10 h, PVP = 8 wt%, EtOH/water = 70:30, 290 rpm stirring; [b]Calculated diameter, [c]Determined by Scanning Electron Microscopy, [d]Coefficient of variation of number-averaged size, [e]Standard Deviation, [f]Polydispersity Index

Table 4 Effects of the Agitation Rate on Dispersion Copolymerization of Styrene and Methyl Methacrylate.[a]

No.	Agitation Rate (rpm)	$D_n^{b,c}$ (μm)	$CV^{d,e}$ (%)	$SD^{e,c}$ (μm)	PDI[f]	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
A1	80	0.8	8.72	0.07	1.02	35,125	156,218	4.45
A2	150	0.8	8.32	0.06	1.02	31,336	143,985	4.59
A3	200	0.7	9.86	0.07	1.03	34,413	150,799	4.38
A4	290	0.6	7.53	0.04	1.02	11,619	37,123	3.20

[a]Reaction temperature = 60°C, reaction time 10 h, PVP = 8 wt%, EtOH/water = 70:30, [b]Calculated diameter, [c]Determined by Scanning Electron Microscopy, [d]Coefficient of variation of number-averaged size, [e]Standard Deviation, [f]Polydispersity Index
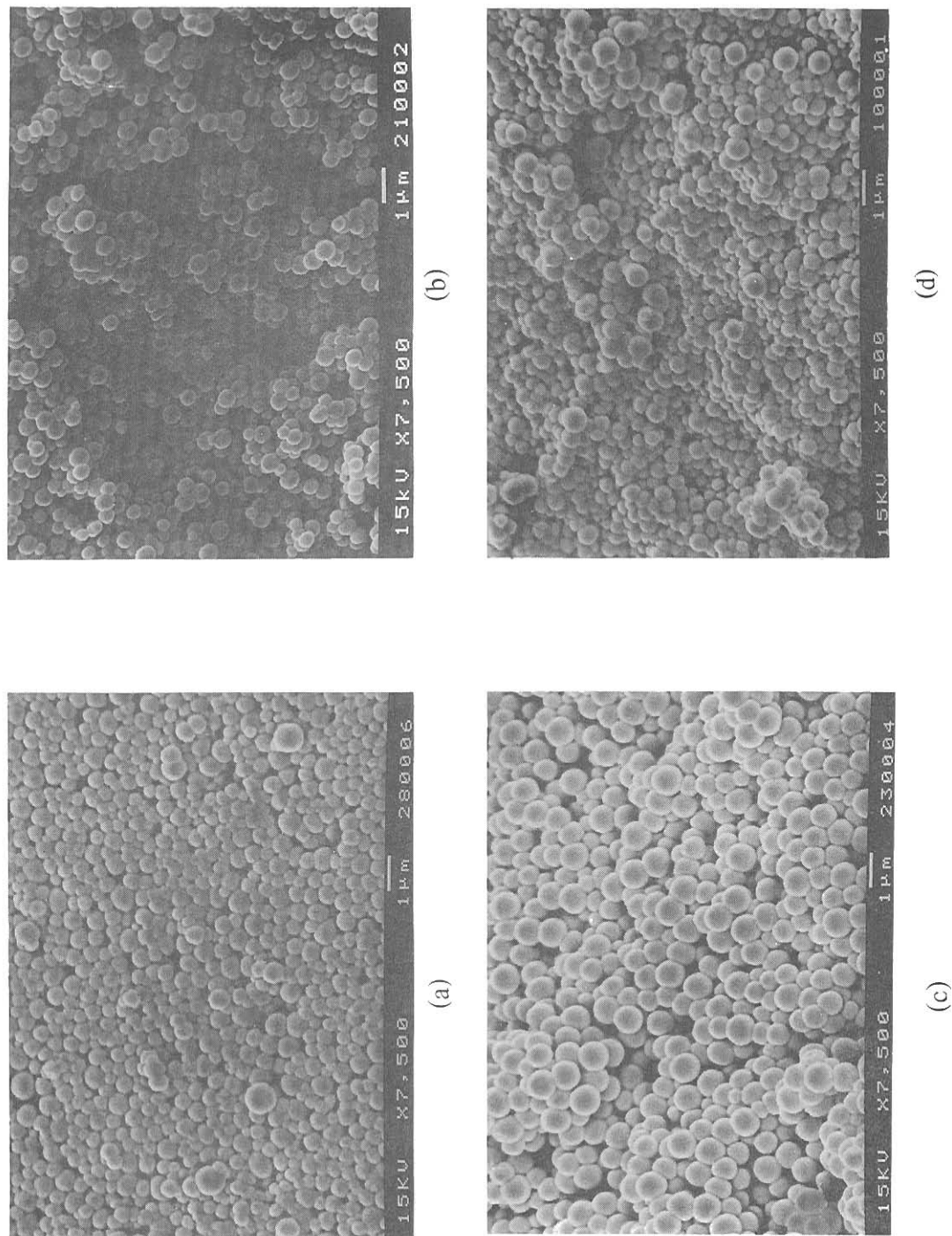
Fig.4 SEM micrographs of poly(styrene-co-methyl methacrylate) particles synthesized at (a) 50, (b) 60, (C) 70, and (d) 80°C.

Increasing the reaction temperature initially resulted in an increase in the particle size of the polymer because the critical chain length of precipitated oligomer chains was increased due to an increase in the solubility of the oligomer chain in the continuous phase at the higher reaction temperatures.

When increasing the reaction temperature from 50°C to 60°C, the average molecular weight increased gradually and then increased rapidly at the reaction temperature of 70°C. The average molecular weight then decreased rapidly when increasing the reaction temperature up to the reaction temperature of 80°C as shown in Table 3. Another attribute could be the decrease in viscosity of the continuous phase and the adsorption rate of the polymeric dispersant due to its increasing solubility. Table 3 shows the particle size range from 0.5 to 0.8 μm with a cv range of 6 to 26% and the PSD of 1.01 to 1.2. Molecular weight averages and polydispersity of the particles prepared at 70°C seem to be quite narrow with relatively high weight averages.

Effect of the Agitation Rate

In dispersion copolymerization, the mixture was polymerized with stirring in the reactor for 10 h. The rates of stirring were varied from 80 to 290 rpm. The sizes of copolymer particles are in the range of 0.6-0.8 μm as shown in Table 4. It was found that upon increasing the rate of mixing, the particle size of the copolymers decreases as shown in Figure 5. The smallest particle size obtained from the highest agitation rate gave the narrowest size distribution. This could be due to the free volume in the polymeric solution becoming smaller at increasing rates of mixing due to the system being more disturbed. The higher the agitation, the faster the chain diffusion and termination and the lower the molecular weight. That is, when increasing the rate of mixing as high as 290 rpm, the shearing force exerted on the solution viscosity to permit faster segmental diffusion in the polymer solution increases, and the average molecular weight of the copolymer is therefore decreased.

Effect of the Reaction Time

Table 5 shows the effect of the reaction time on dispersion copolymerization. The sizes of copolymer particles are in the range of 0.3-0.6 μm as increasing the reaction time.

Figure 6 shows the SEM micrographs of poly(styrene-*co*-methyl methacrylate) particles. After the ingredients are mixed, no new polymer nuclei are formed after the initial precipitation of polymer particles because they are inaccessible and the size distribution is very narrow. Following the nucleation stage, subsequent polymerization is confined to further growth of the polymer particles formed initially. Therefore, the special feature of polymerizing systems, involving growth of individual molecules, permits rapid attainment of steady-state conditions of nucleation. The chain-length or the size of particles of the polymer therefore increases with increasing reaction time. As the average molecular weight gradually increases, the completion of polymerization or high conversion gives larger particle sizes with higher average molecular weights.

Effect of the Feed Ratio of Styrene/Methyl Methacrylate

The copolymer particles were prepared with different styrene/methyl methacrylate ratios of 100/0, 75/25, 50/50, 25/75, and 0/100 in a 70:30 ethanol:water medium. Table 6 shows the effects of styrene feed on dispersion copolymerization of styrene and methyl methacrylate. Varying the feed ratio of styrene/methyl methacrylate, the smallest particle size (0.30 μm) was obtained from the homopolymer of polystyrene and a very large particle size (11.82 μm) with a broad size distribution was obtained from the homopolymer of poly(methyl methacrylate).
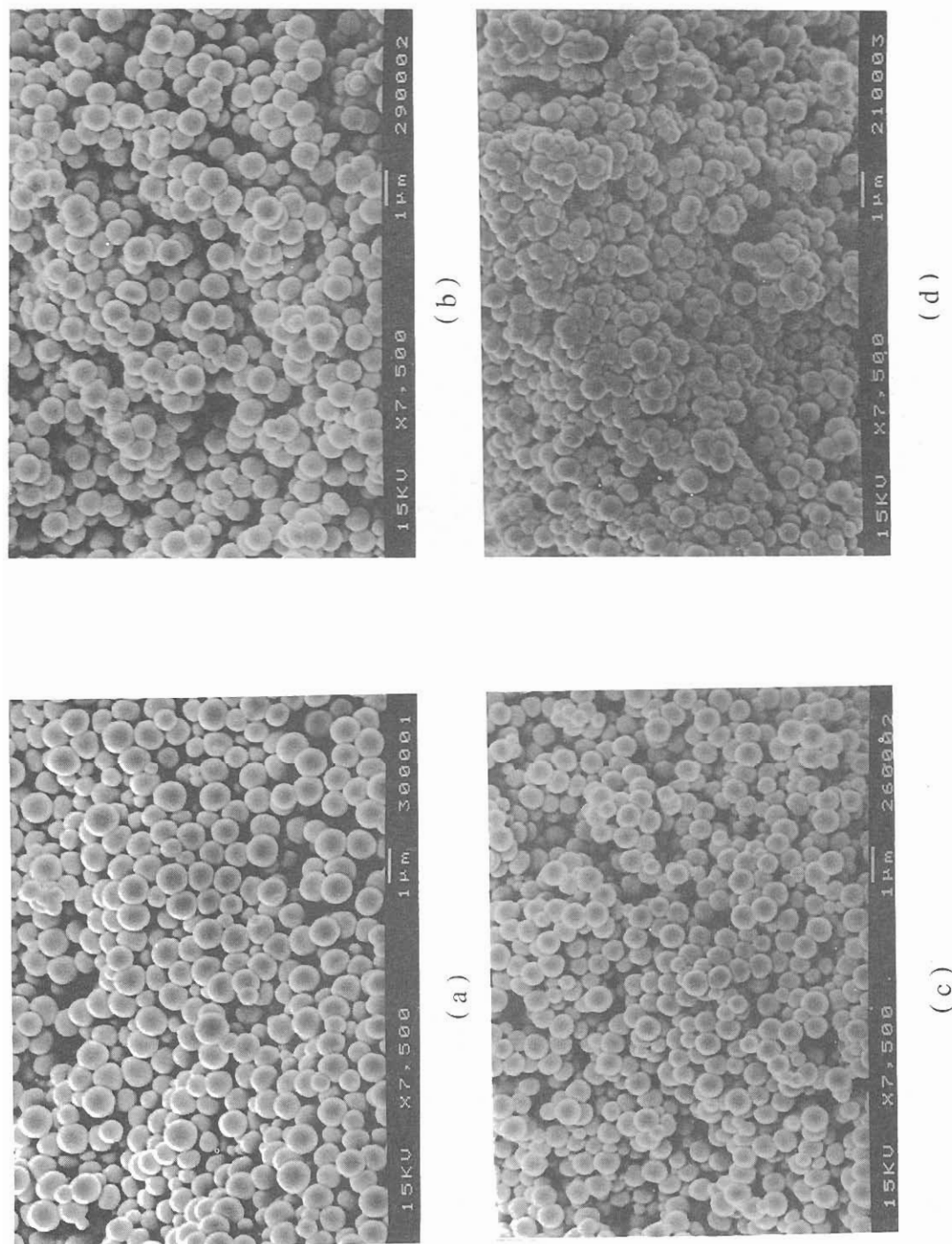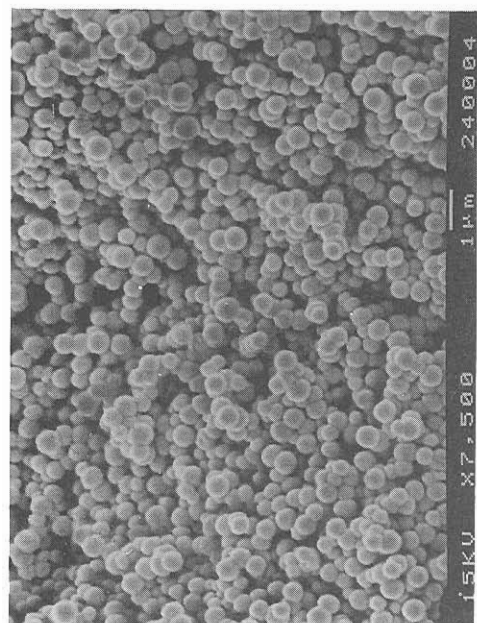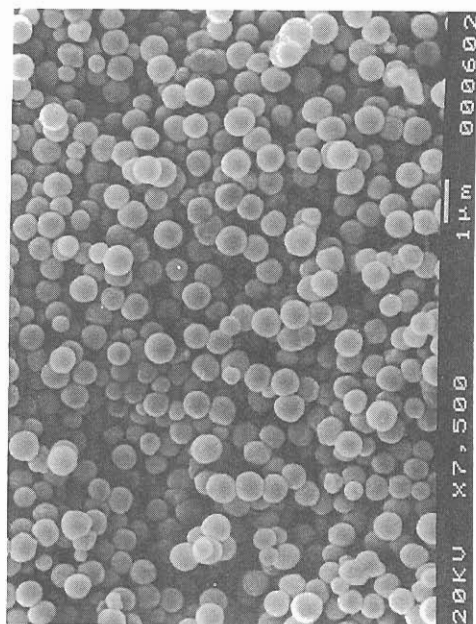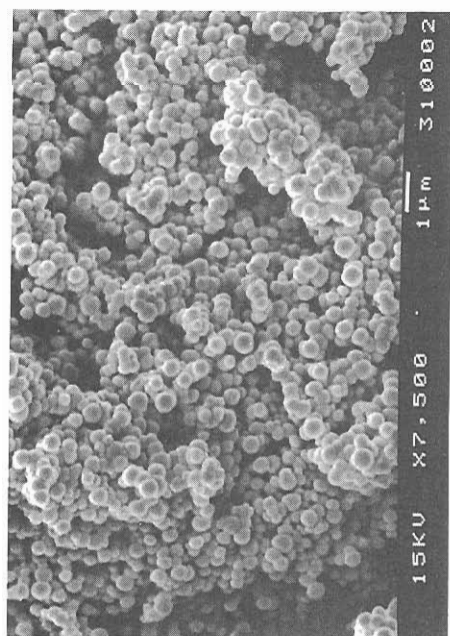
Fig.5 SEM micrographs of poly(styrene-*co*-methyl methacrylate) particles synthesized at (a) 80, (b) 150, (C) 200, and (d) 290 rpm stirring.
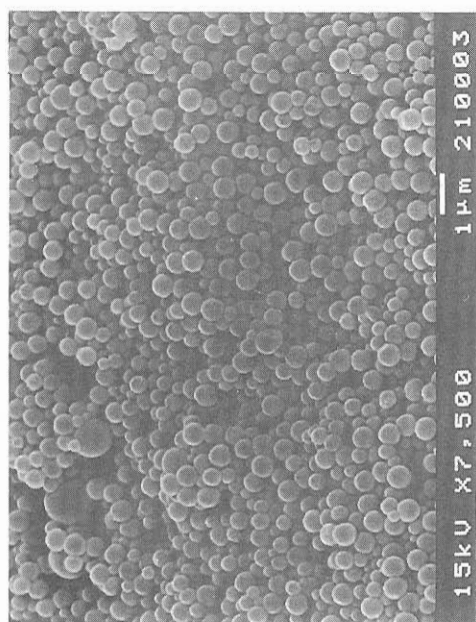
Fig.6 SEM micrographs of poly(styrene-co-methyl methacrylate) particles synthesized for (a) 6, (b) 8, (C) 10, and (d) 15 h.

Table 5 Effects of the Reaction Time on Dispersion Copolymerization of Styrene and Methyl Methacrylate.[a]

No.	Time (h)	$D_n^{b,c}$ (µm)	$CV^{d,e}$ (%)	$SD^{e,c}$ (µm)	PDI^f	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$F^{g,h}$ (mole%STY)
t1	6	0.3	16.97	0.05	1.08	14,099	28,198	2.00	73.56
t2	8	0.4	14.09	0.06	1.07	19,183	48,559	2.53	81.99
t3	10	0.6	7.53	0.04	1.02	11,619	37,123	3.20	81.66
t4	15	0.6	8.33	0.05	1.05	112,036	214,032	1.91	79.18 (78.04)i

[a]Reaction temperature = 70°C, PVP = 6 wt% in 70:30 EtOH:water at 290 rpm stirring, [c]Determined by Scanning Electron Microscopy, [d]Coefficient of variation of number-averaged size, [e]Standard Deviation, [f]Polydispersity Index, [g]Copolymer composition, determined by Nuclear Magnetic Resonance, [h]Known mole% styrene =75 mole%, [i]Determined by elemental analysis

Table 6 Effects of Styrene Feed on Dispersion Copolymerization of Styrene and Methyl Methacrylate.[a]

No.	Styrene (mole%)	$D_n^{b,c}$ (µm)	$CV^{d,e}$ (%)	$SD^{e,c}$ (µm)	PDI^f	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	F^g (mole%STY)
F1	0	*	*	*	*	-	-	-	0h
F2	25	0.7	2.86	0.02	0.09	16,278	41,078	2.52	42.15
F3	50	0.7	15	0.06	1.17	4,097	7,916	1.93	55.85
F4	75	0.6	8.72	0.05	1.02	119,717	216,576	1.81	80.18
F5	100	0.3	20	0.06	1.15	6,757	18,779	2.78	94.02

[a]Reaction temperature 60°C, reaction time 10 h, PVP = 6 wt%, EtOH:water = 70:30, [b]Calculated diameter, [c]Determined by Scanning Electron Microscopy, [d]Coefficient of variation of number-averaged size, [e]Standard Deviation, [f]Polydispersity Index, [g]Copolymer composition, determined by elemental analysis, [h]100.51 mole% methyl methacrylate, *Very broad particle size distribution.

Methyl methacrylate is more hydrophilic than styrene, a hydrophobic monomer. The solubility of the former monomer in the medium is better than the latter. A different monomer concentration could be the main explanation of the particle size difference.

In the range of 25% styrene to 100% styrene, the particle sizes obtained are in the size range of 0.7-0.3 μm, as shown in Figure 7. A different monomer interaction with the polymeric dispersant, PVP, during the particle nucleation, could be the main reason. In-situ grafting of the initiator on the polymeric dispersant involves abstraction of hydrogens from the PVP molecules to create free radical sites (PVP$^\bullet$) which can accept monomers. Styrene monomer is adsorbed much more strongly on the PVP$^\bullet$ than is the methyl methacrylate monomer, because styrene monomer is a stronger electron donor for PVP (an electron acceptor). The particle sizes of the copolymers containing more styrene content are thus smaller.

The reactivities of styrene and methyl methacrylate in radical copolymerization are 0.52 and 0.46, respectively.[8] The reactivity of the styrene monomer toward the poly(methyl methacrylate) radical ($1/r_{mma} = 2.2$) is higher than the reactivity of the methyl methacrylate monomer toward the polystyrene radical ($1/r_{sty} = 1.9$), leading to a large particle size of higher MMA feed ratio.

The weight average molecular weight of the copolymers of the particles are around 18,000 - 40,000. With an increasing styrene feed, a copolymer with a lower average molecular weight is produced and the adsorption of the styrene monomer on the PVP dispersant is enhanced, as is the adsorption rate of PVP. This produces short chain lengths of the polymer to give a lower average molecular weight. When the methyl methacrylate content was as high as 75 mole%, the gel effect might possibly occur and the chain length increased to give a higher overall molecular weight. The gel effect has been shown to result from a decrease in the termination rate as the viscosity of the polymerization medium increases. Although diffusion of monomers is still possible within the increasingly viscous medium, the diffusion of the much larger growing polymer radicals is considerably retarded and makes them much less likely to terminate with each other. Though the polymer growth continues largely unhindered, the termination rate is considerably reduced. The larger increases in $k_p/k_t^{1/2}$ accompanying the gel effect lead to greater increases in the sizes of the polymers produced when the polymerization proceeds.[7] For all the reasons, there has been a corresponding increase in the chain length or size of PMMA with increased conversion. The diminution of the termination rate in the polymerization of MMA has been similarly ascribed to hindered radical-radical termination due to the formation of tightly-coiled macroradicals. Besides, the monomer used is a frequent solvent for their own polymers. The overall solvency of the continuous phase for polymers changes as the monomers are consumed. Consequently, the precipitation of polymers formed in solution changes throughout the copolymerization.

Considering the structure of the styrene monomer and monomer reactivities, the latter corresponds to the order of increased resonance stabilization by the particular substituent of the radicals formed by the monomer. It also shows that the phenyl substituent increases the reactivity of monomers attacking the PVP radical. Substituents composed of unsaturated linkages are most effective in stabilizing the radicals because of the loosely held π-electrons,[7] which are available for resonance stabilization as in the case of the styrene monomer. Due to this resonance effect the overall activation energy of the monomer and its polymer radicals is low. Hence the stage of aggregation of oligomer radical chains is in a short time range after the faster particle stabilization. Therefore, the number of aggregated oligomer chains in each particle is smaller resulting in a smaller particle size.
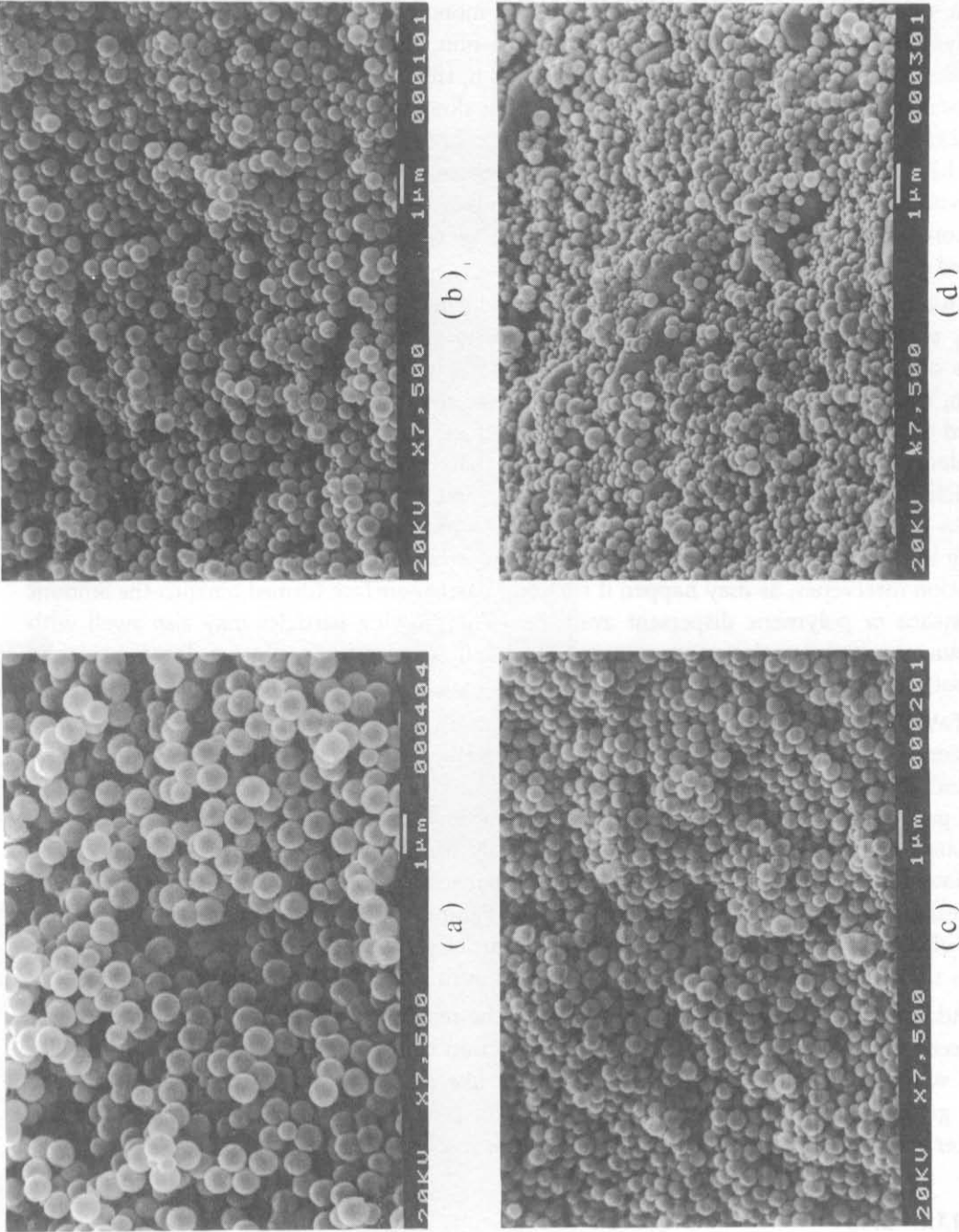
Fig.7　SEM micrographs of poly(styrene-*co*-methyl methacrylate) particles synthesized by styrene content of (a) 0, (b) 25, (c) 50, (e) 75, and (f) 100 mole%.

Particle growth and conversion

Table 7 shows the particle growth and conversion. It can be seen that the sizes of copolymer particles increase gradually with conversion as the polymerization progresses. Figure 8 shows the changes in particle size during conversion. Within 19 min of the beginning of the reaction, oxygen suppresses the polymerization of monomers. At the reaction time of 20 min, the polymerization occurred only to 0.1%. At 28 min, the polymerization was increased to only 3%. During the reaction time of 0.6 h to 0.73 h, the particle growth was constant. There might be some retardant in the reaction system that slows down the particle growth. However, in this case, the polymerization still occurs but at a slower rate (from 3.44% at 0.6 h to 5.12% at 0.73 h). The retarder was less effective and it took up only a portion of the radicals. Within the polymerization time of 10 h, the conversion increased from 9% at 1 h to 78% at 10 h. After dispersion polymerization for 1 h, the average size of the particles was 0.7 μm and was increased to 1.3 μm at the reaction time of 8 h.

In a typical dispersion polymerization, producing polymers which are insoluble in the diluent, the stage of particle formation is normally completed very quickly within a few seconds or tens of seconds after the start of the reaction. During the growth stage of the reaction, the stabilized particles efficiently scavenge smaller particles so that new nuclei are captured almost immediately, before they have a chance to become stabilized themselves. All the evidence from electron micrographs indicates that very few particles form after the stage of particle formation unless the solvency of the medium is drastically altered or substantial amounts of additional dispersant are added. The number of particles, therefore, remains virtually unchanged throughout the remaining course of polymerization, unless some form of aggregation intervenes, as may happen if the total particle surface formed outruns the amount of dispersant or polymeric dispersant available. The growing particles may also swell with their own monomers and capture growing oligomer particles from solution, leading to solid phase polymerization of much higher molecular weights that terminated in solution.

Table 7 shows a relatively constant diameter after six hours of polymerization, while conversion increases steadily. The particles subsequently grew without the formation of new nuclei and without agglomeration of particles. When enough particles are formed, the formation of new particles is inhibited. The present observation agrees with that of Takahashi *et al.*,[9] who stated that nearly all the oligomeric radicals formed within the free volume in the continuous phase were captured by the existing particles before they could form new nuclei but continued to propagate within the particle. Figure 9 shows the conversion and particle growth of poly(styrene-*co*-methyl methacrylate) particles in terms of percentage conversion vs. reaction time, and particle volume vs. conversion during the growth of the particles.

Additionally, we can state that increasing the reaction time allows the polymerization to proceed. The particles formed after a short reaction time were soft and relatively irregular spheres with an indented half-circle at the edge like a cherry. During polymerization, the particle growth increased gradually and the rate of polymerization increased slowly within 1 h; after this time, it increased rapidly until the reaction time reached 8 h.

CONCLUSIONS

Dispersion copolymerization of styrene and methyl methacrylate in the presence of the PVP polymeric dispersant in an ethanol-water system has been studied with a goal of obtaining a narrow size distribution of the copolymer particles. The present research has succeeded in preparing styrene/methyl methacrylate copolymer particles that have a narrow size distribution

Table 7 Investigation of the Particle Growth of Poly(styrene-comethyl methacrylate) and Conversion.

Time (h)	D_n(μm)	CV(%)	SD	PDI	% Conversion (p)
0.33	*	-	-	-	0.1
0.47	*	-	-	-	3.0
0.6	0.6	8.33	0.05	1.08	3.4
0.73	0.6	10.6	0.06	1.02	5.1
1	0.7	8.03	0.06	1.07	9.4
2	0.9	5.21	0.05	1.02	27.5
4	1.2	4.13	0.05	0.99	45.5
6	1.3	3.08	0.04	1.02	62.2
8	1.3	4.12	0.05	1.03	74.9
10	1.3	3.32	0.04	1.02	77.7

*Could not be measured by SEM, because there was too little product to be measured. PVP = 6 wt%, EtOH:water = 70:30, reaction time = 70°C with 290 rpm stirring.
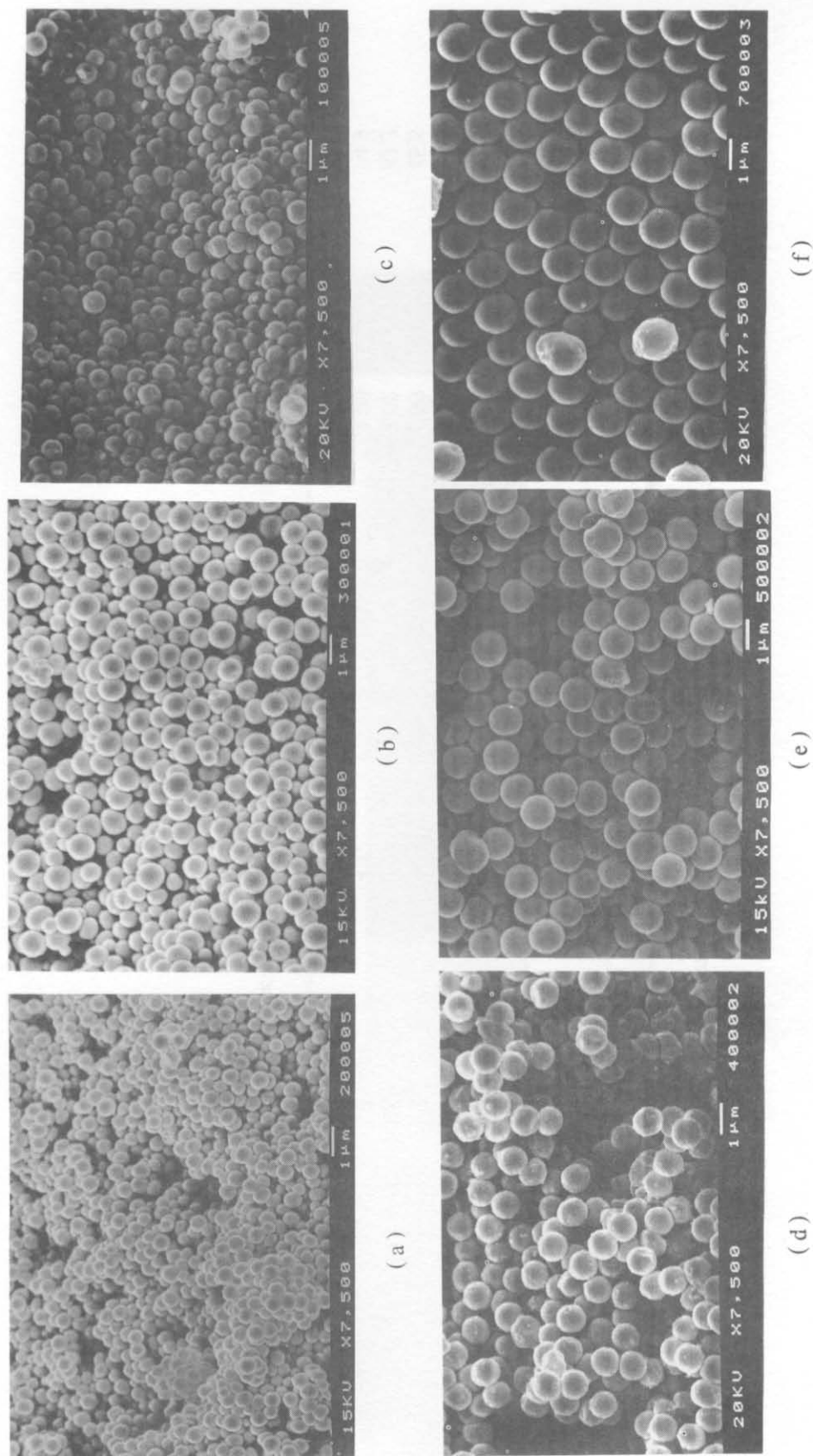
Fig.8 SEM micrographs of poly(styrene-*co*-methyl methacrylate) particles at various times of (a) 0.6, (b) 0.73, (c) 1, (d) 2, (e) 4, (f) 6, (g) 8, and (h)10 h.
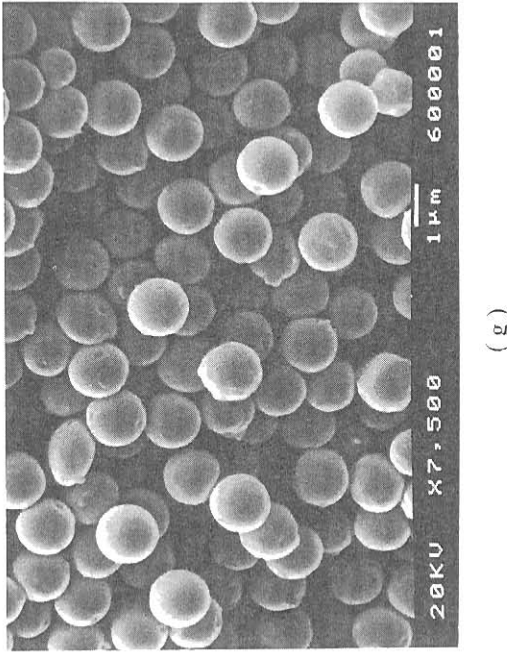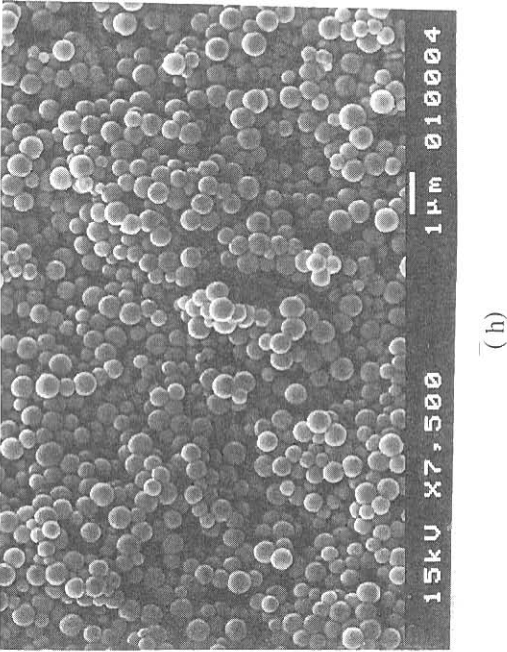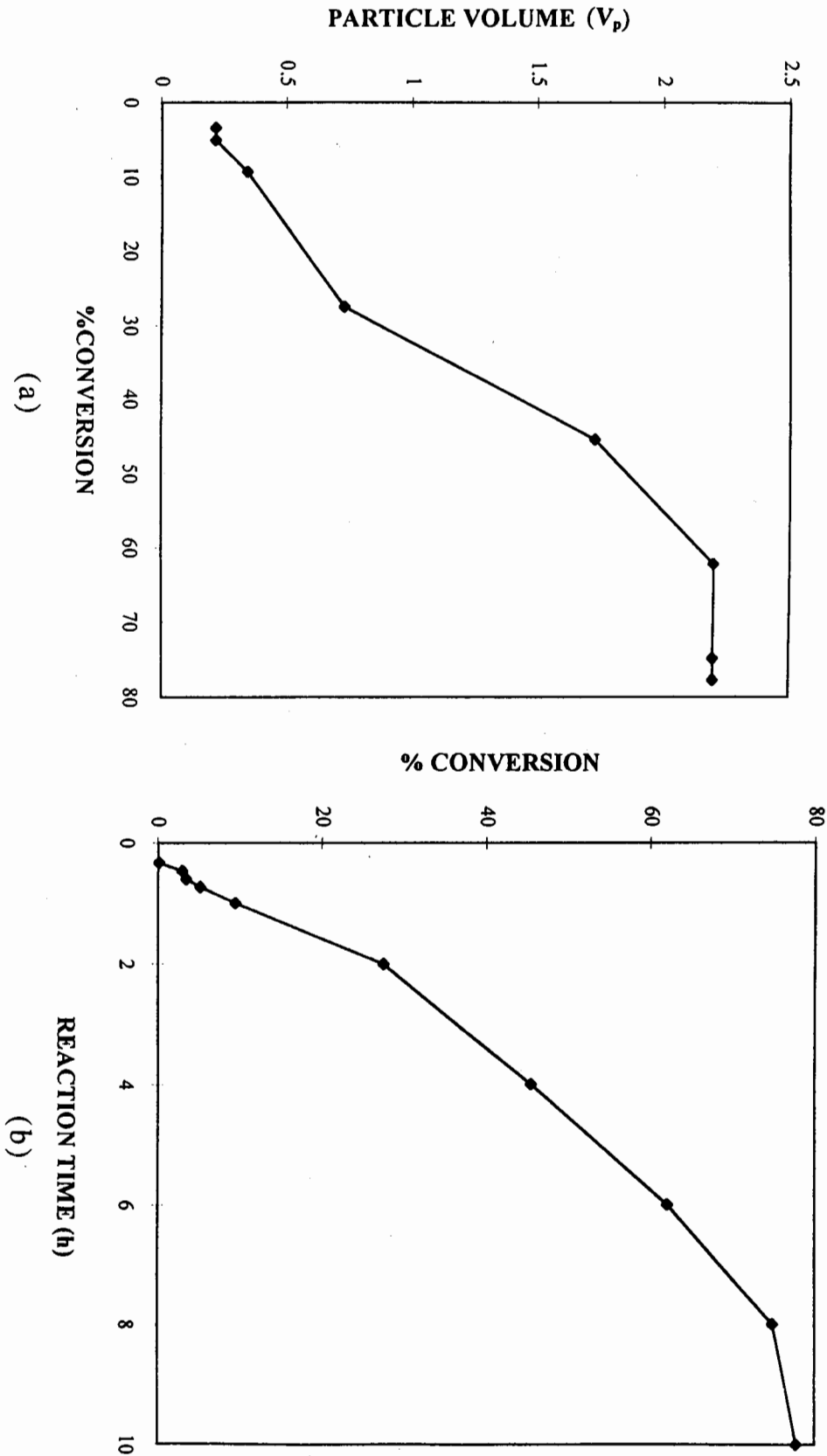
(h)

(g)

Fig.8 (Continued)

Fig.9 Conversion and particle growth of poly(styrene-*co*-methyl methacrylate): (a) percent conversion vs. reaction time (h), (b) particle volume vs. conversion during growth of the particles

(monodispersed) with a cv smaller than 10%, which is similar to the results of Takahashi *et al.*[9]

The individual particles could be stabilized by the role of the polymeric dispersant in anchoring adsorption as proven by IR spectrometry of polystyrene particles synthesized by dispersion polymerization. The largest poly(styrene-*co*-methyl methacrylate) particles with a narrow size distribution of 1.5 μm (cv = 4.75%) could be obtained by using 2 wt% PVP K-30 at the reaction temperature of 60°C whereas the same system containing 12 wt% PVP K-30 gave the smallest particle size with a narrow size distribution of 0.3 μm (cv = 9.07%). Additionally, the optimum reaction temperature for controlling the narrow molecular weight distribution of the copolymer is 70°C because the molecular weight distribution produced at this temperature is 1.51. The copolymer particle size and size distribution so obtained are suitable for use in both dry and liquid toner technology.

The size of the resulting poly(styrene-*co*-methyl methacrylate) particles decreased with increasing PVP K-30 concentration, increasing polarity of the reaction medium, increasing agitation rate and a high feed ratio of styrene (75%). The particle dispersity of most copolymer particles is still of a narrow size distribution. Under some polymerizing conditions, a particle size distribution as broad as 1.07 - 1.17 (cv > 10%) was obtained, with a reaction temperature of 50°C and a reaction medium having a water/ethanol ratio of 40/60. When 100% water or pure ethanol was used as the reaction medium instead of a water/ethanol mixture, the copolymer particles had a broad size distribution. Using a water/ethanol mixture, the particle size becomes smaller and decreases with increasing water content. That is, the ratio between a good and poor solvent (expressed in terms of solubility parameters) greatly affects the particle size and size distribution.

The particle size and size distribution of the resulting copolymers were mainly controlled by changing the morphology of the polymeric dispersant in solution by varying the mixed solvent polarity. In this research, the narrow particle size distribution of the copolymers was obtained when the solvent mixture of ethanol/water containing 10-30% of water were used. The mixture containing 10-30% of water acts as a better solvent for poly(N-vinylpyrrolidone) dispersant. The dispersant can dissolve easily and its chains disentangle and then stretch freely in that medium. The expanded dispersant chains give the free volume (or free space) in the dispersant solution, which morphologically controls the particle size of the copolymer. However, pure water and an ethanolic water mixture containing 40% of water act as rather poor solvents for the dispersant. The polymeric dispersant chains entangle or aggregate to become a coiled form in the poor solvent. The particle size distribution is controlled by the excluded free volume in solution of the dispersant, so a broad particle size distribution of the copolymer is obtained.

For particle growth, the phenomenon of the free volume within the dispersant chains is a main factor in controlling the particle formation. The larger the free volume in solution within the dispersant chains, the larger the size of the copolymer. The copolymer particles so obtained as a function of reaction time have a narrow size distribution, that is, these particles are controlled by the possibly equal free volumes of the dispersant chains in solution.

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