

NOTE

Synthesis of High Solid Latices by Thermally Initiated Emulsion Polymerization

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INTRODUCTION

Recent interest in synthetic emulsion products has shifted from mass-produced solid materials to specialty products such as paints, adhesives, and binders. High solid content latices are typically prepared in industrial practice, and used for coatings and adhesives. These latices offer definite advantages for most of the commercial applications, for example, low shipping costs and less energy to remove water. One of the major difficulties encountered in the preparation of these latices is the increase in viscosity once a certain value of the particle volume fraction is achieved. It is well known that this increase in the viscosity is due to the effect of particle–particle interactions and the formation of complex flow elements, which become crucially important when the volume fraction of the dispersed phase approaches the maximum packing density.

The preparation of polymer emulsions with broad particle size distribution is an area of considerable industrial interest. High solid content,^{1,2} good film-formation characteristics, and improved mechanical

and rheological properties can be obtained from polymer emulsions with broad particle size distribution. The polymer emulsions with broad size distribution have higher maximum packing concentration of polymer particles than that with monodisperse rigid spheres. Usually, semibatch and multiple-shot processes are the most common techniques for preparation of this type of latex to ease the extensive heat of polymerization by controlling the reaction rate. Inevitably, carefully controlled addition of monomers is required as well as use of sophisticated controlling devices. Molecular weight is lower than that of the batch process.

High solid content emulsion copolymerization of styrene, butyl acrylate, and methacrylic acid has been carried out, and polymer latices with a multimodal particle size distribution (PSD) prepared by introducing additional surfactants during the semicontinuous emulsion polymerization.³ Bimodal and trimodal PSD polymer latices can be obtained by this method, and the secondary generation of particles is greatly affected by the nature and the amount of additional surfactants, as well as the moment at which they are introduced. High solid content (>65%), low viscosity, and coagulum-free latices have been obtained through the secondary nucleation of polymer particles, and a minimum in viscosity was observed when the weight fraction of the large particles was around 80%.

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The miniemulsion polymerization process is also a possibility for the production of the multimodal latex,^{4,5} because a much longer nucleation period results in polydispersity of particles. El-Aasser et al.⁶ reported on the preparation of high solid content poly(*n*-butyl acrylate) latices through miniemulsion polymerization. Fluid and coagulum-free poly(*n*-butyl acrylate) latices, with up to 61 wt % solid content with broad size distribution, were prepared by using two-stage polymerization. It was shown that, when the breadth of the particle size between the largest and smallest particle of the latices was smaller than 550 nm, the viscosity increased significantly, and the latices became nonfluid pastes once the limit of 55 wt % solid was reached. On the other hand, when the breadth of the PSD was broader than 550 nm, coagulum-free, fluid latices with solid contents up to 61 wt % were successfully prepared without addition of any extra stabilizing agent.

In thermally initiated emulsion polymerization without the addition of initiator, the generation rate of radical is very slow, and leads to prolonged nucleation in the aqueous phase due to the slow entry of radicals and low radical capture efficiency of polymer particles. Consequently, polymer latex with broad size distribution was formed.^{7,8}

In this article, the longer and slower nucleation period of the thermal process is taken as an advantage to obtain broad size distribution of the polymer particles, and the preparation of high solid content polymer latices is reported.

EXPERIMENT

Material

All the reagents, unless stated otherwise, were purchased from Kishida Chemical Co. Ltd. Styrene (ST), vinyl acetate, butyl acrylate, and methyl methacrylate were commercial grade, and distilled under reduced pressure, except for vinyl acetate, which was distilled at atmospheric pressure. Acrylic acid was used as received. Sodium dodecyl sulfate (SDS, biochemistry grade, from Merck Co.), polyvinyl alcohol (PVA, degree of polymerization: 2000, extent of hydrolysis: 98.5–99.4% Kuraray), Sodium sulfate (Na₂SO₄, reagent grade, Wako Pure Chemical Industries Ltd., Japan), and sodium hydrogen carbonate (NaHCO₃, reagent grade, Wako Pure Chemical Industries Ltd., Japan) were used as received. Tetrahydrofuran (THF, commercial grade) was used as a carrier solvent for GPC. Deionized and distilled (DDI) water was used throughout for polymerization reactions and analysis.

Polymerization

The thermally initiated emulsion polymerization was carried out in a four-necked, 300 or 500-mL flask im-

mersed in a thermostat. The flask was equipped with a stirrer, condenser (nitrogen outlet), nitrogen inlet tube, and the inlet for the ingredients. A slow stream of nitrogen was introduced into the reaction mixture for 2 h after the weighed portion of monomer and DDI water with dissolved SDS and Na₂SO₄ were added into the flask. The stirrer was rotated from 200 to 350 rpm, then the mixture was heated to the reaction temperature in 30 min with a programmed heating device (Yamato Thermo-Mate BF 600, Yamato). A blanket of nitrogen atmosphere was maintained throughout the reaction period.

Analyses

The polymer yield and the conversion of monomer were determined gravimetrically. Methanol was used to precipitate the polymer. The precipitated polymer was collected by a centrifuge, thoroughly washed with methanol two times, dried at 333 K in a drier, and weighed.

The average diameter of the particles was determined by direct measurement of 200 particles in a scanning electron microscope photograph (SEM, JSM-5310, JEOL).

The number- and weight-average molecular weights of polymer, \bar{M}_n and \bar{M}_w , were measured by gel permeation chromatography (GPC, HLC-8020, Tosoh, Japan) with the column system calibrated with standard PS. Commercial grade tetrahydrofuran was used as a carrier solvent.

The zeta potential of polymer latices was determined by direct measurement of the electrophoretic rate of particles in a 45-V direct current field, and automatically calculated by a zeta potential analyzer (ZC-050, Microtech Nichion Co., Japan).

RESULTS AND DISCUSSION

Synthesis of High Solid Latices of Polystyrene

The high solid latex was prepared by thermally initiated emulsion polymerization of styrene. The recipes are shown in Table I, the analyzed properties of latices and the SEM photographs are shown in Table II and Figure 1, respectively. From Table II, the monomer conversions almost reached 100 wt % at 373 K for 24 h. Stable latices with about 70 wt % solid content were prepared.

In run 5930, the samples were withdrawn by a syringe at finite time intervals. The polymer yield vs. reaction time curve, and the average particle diameter and number of polymer particles vs. polymer yield curves are shown in Figures 2 and 3, respectively. From Figure 2 and Table II, it can be seen that the monomer conversion reached up to about 88 wt %

Table I Recipes for Synthesis of High Solid Latices of Styrene

Run No.	ST (g)	SDS (g)	Na ₂ SO ₄ (g)	Water (g)	Agitation Rate (rpm)	T (K)
5901	250	10.5	5.2	234.3	350	373
5902	350	14	5.2	130.8	350	373
5903	350	10.5	5.2	134.3	350	373
5913 ^a	210	6.3	4.2	79.5	200	373
5918 ^a	180	6.3	4.3	109.4	200	373
5930 ^a	180	6.3	4.3	109.4	300	373

Reaction times are 24 h.

^a Runs 5913, 5918, and 5930 were scaled down; a 300-mL separator flask was used.

at 373 K for 24 h. The lower monomer conversion, compared with run 5918, is probably due to the repeated sampling. From Figure 3, it is clear that the particle diameter and the number of polymer particles increased with the polymerization progress. In our kinetic investigation of thermally initiated emulsion polymerization,⁸ the initiation mechanism was considered to be as follows: the decomposition of hydroperoxides in monomers controls the initial stage of polymerization because it was consumed in 1.5 h; the Mayo mechanism⁹ worked when the content of charged styrene was higher; and the initiation from the complex formed between monomers and hydrophilic additives proposed by Imoto-Ouchi¹⁰ mainly applied to the soap micelles and polymer particles where a majority of soap molecules are present. Due to the lower polymerization rate, the entry of radicals to polymer particles is slow, and the radical capture

efficiency of polymer particles is low. Consequently, new particles are generated throughout the polymerization process, and the polymer particles have broad size distribution. The SEM photographs at different monomer conversion of run 5930 are shown in Figure 4.

All runs shown in Table II, the stable latices were obtained by introducing electrolyte Na₂SO₄, and no coagulum was formed. As shown in Figures 1 and 4, the polymer particles dispersed well. The addition of electrolyte in emulsion polymerization contribute to the increase in the amount of surfactant adsorbed on the surface of polymer particle and to the extent of counterion binding.^{11,12} It is clear that the negative ζ potential value, as shown in Table II, is much higher than those observed in the previous experiments without the addition of electrolyte (−20 to −30 mV),⁸ and are slightly lower than that of the conventional persulfate-initiated latices (−80 to −100 mV). This implies that the addition of electrolyte increased the amount of surfactant adsorbed on the surface of polymer particle, and stabilized the polymer latices. On the other hand, because no coagulum was formed in all runs, it means that the concentrations of electrolyte used in the present system are below the critical coagulation concentration of latices.

In the case of the charged monomer content of 50 wt % (run 5901), the final latex was a stable, flowing emulsion. When the charged monomer content rose to 60 wt % (runs 5918 and 5930), the final latex yielded a stable flowing emulsion immediately after the polymerization, then became a fluid and creamy latex after it was placed at room temperature for 12 h. Moreover, when the charged monomer content rose to 70 wt % (runs 5902, 5903, and 5913), the final latices were fluid

Table II Main Properties of High Solid Latices of Styrene

Run No.	Conv. (wt %)	Solid Content (wt %)	\bar{d}_p (μ m)	N_p ($10^{17}/\text{dm}^3$)	CV ^a (%)	\bar{M}_w (10^5g/mol)	\bar{M}_n (10^5g/mol)	\bar{M}_w/\bar{M}_n (−)	ζ potential (mV)
5901	91.1	45.6	0.14	3.17	28.7	11.5	6.12	1.87	−49.7
5902	95.6	66.9	0.15	3.79	31.5	12.6	6.25	2.01	−100
5903	99.2	69.5	0.19	1.93	35.8	7.45	3.08	2.42	−50.1
5913	99.0	69.1	0.20	1.65	33.7	13.5	7.30	1.85	−45.5
5918	90.7	54.4	0.17	2.11	25.6	5.00	1.87	2.68	−63.1
5930	87.7	52.6	0.16	2.45	32.5	13.1	5.90	2.22	−52.3

In all runs, the latex was stable, and no coagulum was formed.

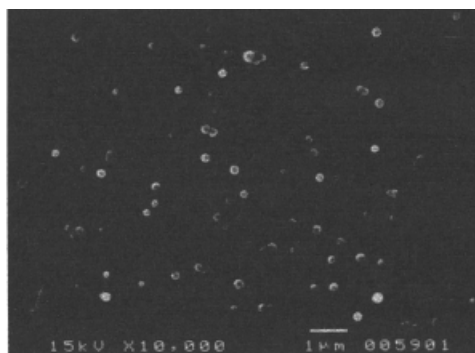
^a Coefficient of variation = (standard deviation)/(average diameter) \times 100

Run 5901: flowing latex.

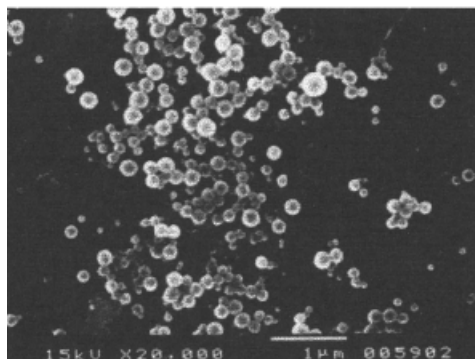
Runs 5918 and 5930: flowing latex immediately after the polymerization, then it became fluid and creamy latex after it was placed at room temperature for 12 h.

Runs 5903 and 5913: fluid and creamy latices.

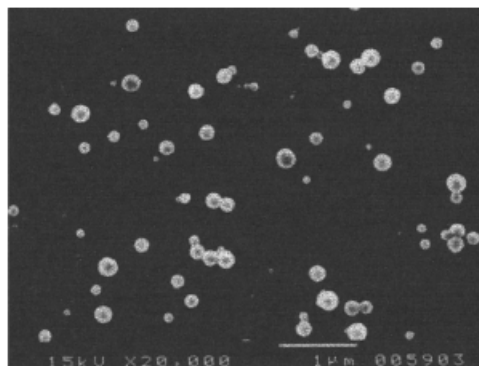
Run 5902: nonfluid and soufflet-like latex.



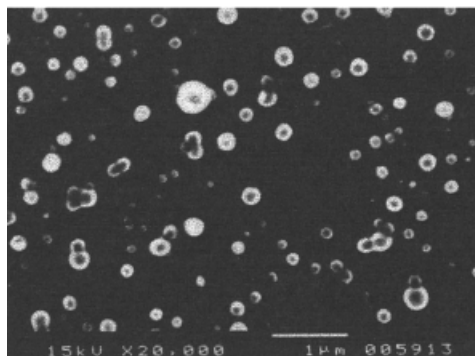
a) run 5901, solid content 45.6 wt.%



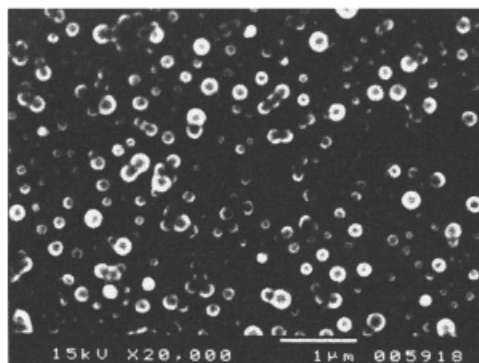
b) run 5902, solid content 66.9 wt.%



c) run 5903, solid content 69.5 wt.%



d) run 5913, solid content 69.1 wt.%



e) run 5918 solid content 54.4 wt.%

Figure 1 SEM photographs of polymer particles of high solid latices of polystyrene.

and creamy for runs 5903 and 5913, and nonfluid and paste-like for run 5902, probably reflecting the differences in the ζ potential and the particle size.

Effect of Surfactant Content

Runs 5902 and 5903 were carried out under the same styrene monomer and electrolyte Na_2SO_4 content, but the amount of surfactant SDS was varied. From

Table II, even though the solid content of the final latex of run 5903 was higher than that of run 5902, the final latex of run 5903 was fluid, but the latter was not fluid. The number of polymer particles of run 5902 was higher than run 5903, but the ζ potential of the particle implies that the particles were well stabilized by extensive adsorbed surfactant on the surface of the polymer particles. These factors led to the higher latex viscosity. On the other hand, although the CV was not so different with run 5902, the ζ

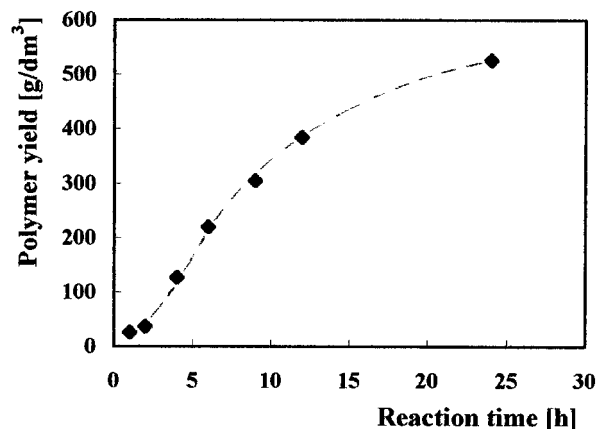


Figure 2 Polymer yield vs. reaction time curve of run 5930.

potential of latex 5903 was not sufficient enough to stabilize each particle, which implies that the particles were loosely flocculated together, and the apparent number density was not as high as was calculated.

Effect of Agitation Rate

The high solid latex of PS was also prepared at different agitation rates. In runs 5918 and 5930, the agitation rate was 200 and 300 rpm, respectively; the other reaction conditions are the same. From Table II it can be seen that the number-average diameter decreased when the agitation rate was increased from 200 rpm to 300 rpm, although the monomer conversions of the two runs are slightly different. In our previous work,⁸ it was clear that the particle size decreased with increased SDS concentration.

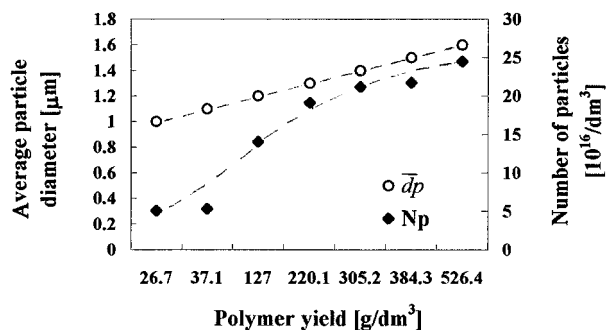
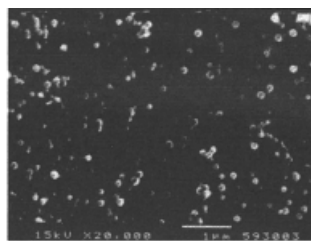
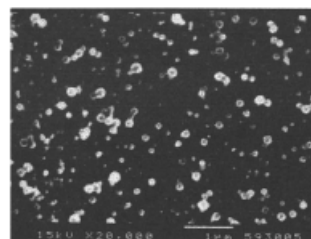


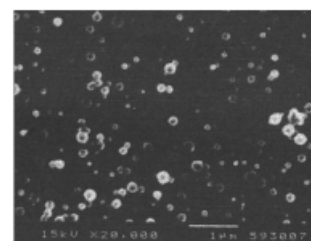
Figure 3 Variation of average particle diameter and number of polymer particles during polymerization for run 5930.



a) monomer conversion 21.2 wt.%, $\bar{d}_p = 0.12 \mu\text{m}$



b) monomer conversion 50.9 wt.%, $\bar{d}_p = 0.14 \mu\text{m}$



c) monomer conversion 87.7 wt.%, $\bar{d}_p = 0.16 \mu\text{m}$

Figure 4 SEM photographs at different monomer conversion of run 5930.

Molecular Weight of High Solid Latex

A significant decrease of molecular weight was observed in run 5903 [$\bar{M}_w = 7.45 (10^5)$] and run 5918 [$\bar{M}_w = 5.00 (10^5)$] compared with run 5902 [$\bar{M}_w = 12.6(10^5)$] and run 5930 [$\bar{M}_w = 13.1 (10^5)$], respectively. The only differences in these results are that runs 5902 and 5903 employed different SDS concentrations, and runs 5918 and 5930 used different agitation rates. The main factors deducible from these experiments are the slightly higher value of the number of polymer particles, and that runs 5902 and 5930 probably progressed with a higher nucleation rate of polymer particles than runs 5903 and 5918, respectively, hence, with a higher reaction rate. Figure 5 shows the variation of molecular weight of run 5930 during the polymerization. It is clear that both number-average and weight-average molecular weight almost stayed constant during the polymerization. The slightly higher molecular weights of the initial samples may be due to the lower temper-

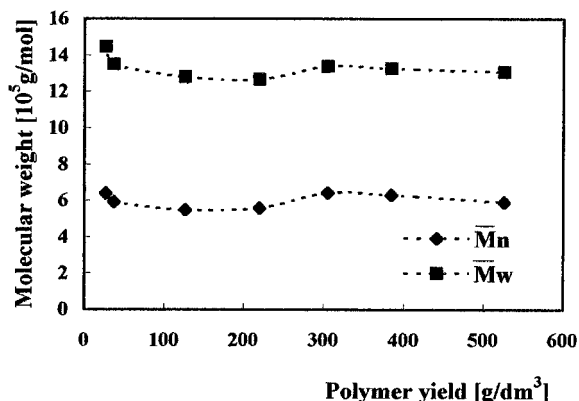


Figure 5 Variation of molecular weight during polymerization of run 5930.

ature polymerization when nitrogen purging and heating were in progress.

Synthesis of High Solid Latices of Vinyl Acetate and Acrylates

The high solid latices were also investigated by thermally initiated homopolymerization, copolymerization, and terpolymerization involving VAc as a main monomer, and employing 60 wt % monomer content. The SDS was used as a surfactant, and the polymerization was carried out at 373 K. In the copolymerization of VAc and BA (VAc/BA = 100/200), the latices remained stable up to 60 wt % monomer conversion after 24 h. However, further continuation of the polymerization yielded phase separation of the latex. When the charged amount of hydrophilic monomer increased, the phase separation occurred at lower conversion. It is well known that the copolymerization ability of VAc is very poor. To improve the copolymerization ability, the semibatch process was employed, but an amount of coagulum formed in the later stage of polymerization.

Even though the electrolyte was added, coagulum formed in the later stage of polymerization in the homopolymerization of 30 wt % MMA. The present conclusion is that high solid latices are difficult to produce when hydrophilic monomers are present in the formulation.

Stannett et al.¹² studied the effect of ionic strength and temperature on vinyl acetate emulsion polymerization. It was found that, although the amount of surfactant adsorbed on the surface of polymer particles was increased by the addition of electrolyte, at the higher ionic strength, the increase of reaction temperature resulted in an increase of interfacial tension at the particle/water interface due to monomer desorption from polymer particles. In the present system, a higher reaction temperature is required, and it may lead to a high interfacial tension at the particle/water interface.

Consequently, the coagulation of polymer particles or phase separation occurred.

The thermally initiated emulsion polymerization of vinyl acetate was also carried out at 353 K for 48 h. Stable latices could be obtained, but the monomer conversion stopped at about 60 wt %. Further, longer time polymerization resulted in the coagulation between polymer particles.

CONCLUSION

High solid latices of polystyrene up to 70 wt % solid were produced by employing thermally initiated emulsion polymerization. The reaction was carried out at 373 K for 24 h. Sodium dodecyl sulfate (SDS) and the addition of an adequate amount of sodium sulfate provided stable emulsions with nearly 100 wt % monomer conversion. The longer and slower nucleation period of polymer particles, and the resulting broader size distribution compared to the conventional initiation system are considered an advantage. The addition of electrolyte increased the amount of surfactant adsorbed on the surface of polymer particle and the extent of counterion binding, hence increasing the stability of polymer particles.

On the other hand, the attempts at homopolymerization, copolymerization, and terpolymerization involving VAc as a main monomer failed to produce stable latices with high solids content and monomer conversion. The high solid latices are difficult to produce because of the higher reaction temperature required for thermally initiated emulsion polymerization.

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