Synthesis of a Polydispersed Polybutadiene Latex. Direct Method for High-Solid Polybutadiene Emulsion Preparation

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ABSTRACT: A high solid, polydispersed polybutadiene latex of large particle size was synthesized. The reaction was carried out at a high monomer/water ratio and a small quantity of emulsifier (soap). Additions of a colloiddally active material with a high molecular weight and an electrolyte were effective in limiting the surface film of growing polymer particles governed by water structure or ionic environment and, also, in promoting the agglomeration of particles. A mixture of sodium alginate and magnesium sulfate was particularly effective, and provided a method with excellent reproducibility.

KEY WORDS Acrylonitrile–Butadiene–Styrene Resin / Polybutadiene
Latex / High-Solid Latex / Polydispersed Latex /

Acrylonitrile–butadiene–styrene (ABS) resin is a 3-component type thermoplastic resin formed from acrylonitrile (AN), butadiene (BD), and styrene (ST). Due to its high impact resistance, toughness and excellent molding characteristics, it finds wide application as a universal engineering plastic for the automobile, household electric appliance, building material industries and etc. Many manufacturing processes are developed according to these applications.¹ In general, AN and ST are grafted by emulsion polymerization onto polybutadiene latex. From the viewpoint of its intended use, it is demanded that the base material, polybutadiene latex, have large particle size and be polydispersed.^{2–4}

Various methods have been proposed in order to obtain a large particle polydispersed latex.⁵ The most common one is an emulsion polymerization wherein the monomer/water ratio is large and the quantity of the emulsifier should be small, and polymer particles are made to coalesce during the course of polymerization to form larger ones.^{6,7} This is achieved

by putting the polymer particles just before the critical condition in which an unstable system containing considerable prefloc and coalescing of particles occurs.

In such a direct, high concentration polymerization with a high monomer/water ratio, the reaction enters a thickening stage⁸ early on, that is, 20–30% conversion, and the stirring becomes difficult. At this moment, particles are clustered and become most compact. If the polymerization is continued, it goes out of control. On account of the small quantity of the emulsifier, the soap coverage⁹ of the particles decreases. This decreases the mechanical stability of the particles and promotes their coalescence. Careful stirring is necessary to remove the heat of polymerization evolved at this high viscous stage and to promote agglomeration, causing the reduction of viscosity and increase of soap coverage to stabilize the system.

A method like this suffers from the disadvantage that a precise reaction-controlling technique is required to prevent excessive

coagulation. Howland *et al.*,¹⁰ obtained a low viscosity and high solid latex by concentration of a low solid latex by adding 0.03–0.04 parts PVME (polyvinyl methyl ether). They pointed out that the addition of PVME and some electrolytes moderates the hydration of the particle surface and eliminates the surface film, so that particle coalescence proceeds well during the concentrating procedure.

In the present study, the effects of colloidally active materials such as gelatin, CMC (carboxymethyl cellulose) and sodium alginate in addition to PVME in combination with some electrolytes on the high solid polymerization were investigated. An advanced method to obtain a high solid, polydispersed polybutadiene latex having 0.1–1 μm size and lower viscosity using two or three additives to promote the particle agglomeration during the course of growth is reported.

EXPERIMENTAL

Monomer and Reagents

The following materials were used: butadiene (Nippon Petrochemicals Co., Ltd., 98.5% up), sodium rosinate (Toho Chemical Industry Co., Ltd. (DIPRODIN Na-15)), fatty acid soap (Kao Corporation (OS SOAP)), potassium persulfate (analytical grade, 98.0% up), *n*-dodecyl mercaptan (Kao Corporation (THIOKALCOL, 95% up)) and sodium alginate (Kamogawa Chemicals Co., Ltd. (DUCKALGIN, #NPSL, the viscosity of 1% aq. solution is 100 CP)).

Analysis

Extent of Polymerization. Approx. 1 g of aliquot was transferred to an aluminum dish and weighed. The total solid content in the aliquot was determined by evaporating the water and monomer under reduced pressure in a vacuum oven at 120°C and conversion was calculated.

Particle Size Distribution. Particle size distribution was determined by electron micro-

scope¹¹ and the alginate creaming method.¹² The reference sample for the electron microscope was a Dow monodispersed polystyrene latex (LS-1047-E, $d = 0.234 \pm 0.0026$).

Gel Content and Swelling Index. The polymer sample was immersed in benzene and left in a dark place for 24 h. The gel content and swelling index were then determined by the usual methods.

Viscosity. A Brookfield rotating viscometer was used.

Polymerization

The appropriate amounts of water, emulsifier, mercaptan and agglomeration promoters consisting of sodium alginate and MgSO_4 were introduced into a glass-lined autoclave provided with a sightwindow and mechanical stirrer with Brumagin-type turbine blades.^{13,14} After replacing the air in the vessel with nitrogen, the pressure was reduced, and butadiene was charged. The vessel was then heated with stirring and, when the temperature reached the specified value, an aqueous solution of potassium persulfate was pressure-injected to start the polymerization. During polymerization, the reaction temperature was further raised, then booster solution¹⁵ (consisting of emulsifier, mercaptan and aqueous solution of potassium persulfate) and another emulsifier solution were added. After 60–70 h, the conversion reached over 95%.

The following is the most typical procedure for synthesis. Monomer/water ratio is 100/52, 1 part of emulsifier (sodium rosinate) being added, and polymerization is started at 46 or 52°C. Sampling is carried out at 1 h intervals, the total solids in the samples are measured and the conversion is calculated. When the conversion attains 10%, the temperature is raised to 52°C in case of 46°C start, and when it reaches 40%, the temperature is raised to 66°C. An additional emulsifier is induced as a stabilizer at a conversion range from 50 to 70%, to prevent excessive coagulation; the above booster solution is added at 60% con-

version to generate new particles and compensate for the decreased rate of polymerization due to the decrease of particles.

After the polymerization, the reaction mixture is cooled and unreacted butadiene is removed. Total amounts of solids, viscosity and particle size distribution in the latex obtained are measured. A polydispersed latex with a large particle size on the average remains at a practical viscosity until the total solid content approaches a high solid, 60–70%. The viscosity of the latex can be a quick guide to particle size and polydispersibility.¹⁶ In addition, part of the latex is evaporated to dryness, and the gel content and swelling index of the polymer were determined.

RESULTS AND DISCUSSION

The Effect of the Addition of Electrolytes

Figure 1 shows typical time-conversion curves for some systems. The addition of some electrolytes in the emulsion polymerization induces the reduction of viscosity at the thickening stage and may contribute to coalescence of the polymer particles. Table I shows the results of the polymerization with the addition of 0.1–0.5 parts KCl and Na₂SO₄ to 100 parts monomer to control the process of the high-solid polymerization and shows also that highly viscous latices were obtained without electrolyte, while the addition of KCl or Na₂SO₄ promoted agglomeration and decreased the viscosity, but showed less reproducibility. This tendency is increased with the amounts of additives.

Effects of the Addition of High Molecular Weight, Colloidally Active Materials

The effects of the addition of colloidally active materials such as gelatin, CMC (carboxymethyl cellulose), PVME and sodium alginate on the high-solid polymerization were investigated. The addition of the colloidally active materials lead to the preferential formation of coagulum or destruction of the

Figure 1. Time-conversion curves in the case of KCl addition. Butadiene, 100 g; water, 52 g; Na-rosinate, 1 g; KPS, 0.3 g; *n*-DDM, 0.25 g; temp = 46°C, 52°C, 66°C; additive, KCl; (1) ○, none; (2) ●, 0.2 phr; (3) ⊙, 0.5 phr; (4) ●, 0.5 phr.

emulsion system as shown in Table II. This result is different from Howlands' work.¹⁰

Concurrent Use of High Molecular Weight Materials and Electrolytes for High Solid Polymerization

High solid polymerizations with combined additives, *i.e.*, CMC-KCl, CMC-MgSO₄, PVME-MgSO₄, sodium alginate-KCl, sodium alginate-ZnSO₄ and sodium alginate-Al₂(SO₄)₃ were carried out. In all cases, a large quantity of coagulated or paste polymer formed. Table II shows a comparison of the effects on the particle agglomeration for the PVME system and PVME-MgSO₄ one, as an example. The high molecular weight, colloidally active material apparently has an effect on the coalescence of the particles and this tendency increased with the amount of electrolyte, even if only slight. As for reproducibility, polymerization systems other than sodium alginate-MgSO₄ were not appropriate, and also impossible to avoid coagulation due to partial destruction of the emulsion.

Table I. Effects of the addition of KCl and Na₂SO₄ on the high solid polymerization^a

Electrolyte		Temp °C	Time h	Conversion %	Total solid %	Viscosity CP
KCl phr	Na ₂ SO ₄ phr					
—	—	44—66	70	78.6	57.4	859
—	—	44—66	72	Coagulate	—	—
—	—	44—66	71	83.0	59.1	394
0.1	—	52—66	70	84.2	54.7	320
0.1	—	46—66	70	85.6	59.4	600 ^b
0.2	—	52—66	110	78.0	55.6	95
0.2	—	52—66	70	Coagulate	—	—
—	0.2	44—66	70	Coagulate	—	—
—	0.2	44—66	72	91.1	47.0	250
—	0.5	44—66	72	86.2	48.7	100
—	0.5	52—66	69	Coagulate	—	—

^a Monomer/water ratio, 100/52; Na-rosinate, 1 g; KPS, 0.3 g; *n*-DDM, 0.25 g.^b Particle size distribution of marked latex/%

0.1 μm under	0.1—0.2 μm	0.2—0.3 μm	0.3—0.4 μm	0.4—0.8 μm	0.8 μm over
22	29	10	16	20	3

Table II. Effects of the addition of PVME and PVME-MgSO₄ on the high solid polymerization^a

PVME phr	MgSO ₄ phr	Temp °C	Time h	Viscosity ^b CP	Particle size distribution/%				
					0.2 μm under	0.2—0.3 μm	0.3—0.4 μm	0.4—0.8 μm	0.8 μm over
—	—	44—66	70	ca. 2000					
—	—	52—66	72	—					(Viscous latex)
0.04	—	52	41	280	17	17	13	47	6 (Coagulation)
0.01	—	52	50	310					Gelation occur
									(Partially paste polymer formed)
0.01	0.01	52	42	180	10	30	25	29	6 Gelation occur
0.01	0.02	52	47	210	8	30	20	37	5 Gelation occur

^a Monomer/water ratio, 100 g/52 g; Na-rosinate, 1 g; KPS, 0.3 g; *n*-DDM, 0.25 g.^b Measurement of latices concentrated to 55% solids.

Concurrent Use of Sodium Alginate and MgSO₄

Table III shows the results of the polymerization with the addition of sodium alginate and MgSO₄. Gelation and formation of paste polymer as observed on adding of PVME did not occur and reproducibility was very good. The optimum condition was ascertained as

that of 0.001 parts sodium alginate and 0.02 parts MgSO₄ to 100 parts monomer. Table IV shows that the reproducibility was not affected by the scaling up of the reaction vessel, of 10 l, 20 l, 60 l, and 1700 l. Figure 2a shows typical time-conversion curves. These similar profiles imply that the desired high solid, large particle, polydispersed latices were obtained with good

Table III. Effects of the addition of sodium alginate-MgSO₄ on the high solid polymerization^a

Sodium alginate	KCl	MgSO ₄	Temp	Time	Total solid	Viscosity	Particle size distribution/%					
							0.1 μm under	0.1—0.2 μm	0.2—0.3 μm	0.3—0.4 μm	0.4—0.8 μm	0.8 μm over
phr	phr	phr	°C	h	%	CP						
0.0005	—	—	46—66	68	58.8	560						(Paste polymer formed)
0.001	—	—	46—66	68	56.5	330						(Paste polymer formed)
0.005	—	—	46—66	71	55.3	270						(Paste polymer formed)
0.001	0.1	—	46—66	72	56.9	140						(Partially coagulation occur)
0.001	0.2	—	46—66	73	—	—						(Coagulation occur)
0.005	0.1	—	46—66	70	60.7	1090						(Partially paste polymer formed)
0.001	—	0.01	46—66	70	57.3	150						
0.001	—	0.01	46—66	69	59.8	500	10	43	20	16	8	1
0.001	—	0.01	46—52—66	69	58.9	300	10	39	26	8	14	3
0.001	—	0.02	46—52—66	69	58.0	130						
0.001	—	0.02	46—52—66	71	57.9	100	7	15	38	10	23	7
0.001	—	0.02	46—52—66	71	58.7	70	3	24	33	7	23	10
0.002	—	0.02	46—52—66	70	56.0	190						(Partially paste polymer formed)
0.001	—	0.05	46—52—66	72	55.9	140						(Partially coagulate)

^a Monomer/water ratio, 100 g/52 g; Na-rosinate, 1 g; KPS, 0.3 g; *n*-DDM, 0.25.

Polydispersed Polybutadiene Latex

Table IV. Properties of high solid latex manufactured by large scale vessel^a

Reactor vol l	Time h	Total solid %	Viscosity	Gel content %	Swelling index	Particle size distribution/%					
			CP			0.1 μ m under	0.1—0.2 μ m	0.2—0.3 μ m	0.3—0.4 μ m	0.4—0.8 μ m	0.8 μ m over
10	72	61.9	160	78	12	9	20	40	5	22	4
20	73	62.9	140	83	16	3	24	33	7	23	10
60	—	60.0	260	83	13	12	23	27	8	19	12
1700	60	60.0	190	84	15	2	19	38	8	23	10

^a Monomer/water ratio, 100 g/52 g; N-rosinate, 1 g; KPS, 0.3 g; *n*-DDM, 0.25 g; Na-alginate, 0.001 g; MgSO₄, 0.02 g. Temp condition = 101, 201, and 601, 46→52→66°C; 1700 1, 52→66°C.

reproducibility.

Figure 2b shows the rate of the polymerization calculated from the curve (2) in Figure 2a. This figure also shows the change of the number of polymer particles, observed by electron microscope of aliquot hourly taken out (small particles produced by the addition of the booster solution were excluded). The electron micrographs (Figures 3a—d) of the particles in aliquots taken at 10, 20, 30, and 40% conversion also show the change in particle diameter.

For mutual polymerizations, the rate of reaction, R_p , is defined by the following eq 1,

$$R_p = K_p \cdot r \cdot M \cdot N \quad (1)$$

where K_p denotes the propagation rate constant, r the average number of free-radicals in each particles, M the monomer concentration in a particle and N the number of particles. Generally, R_p increases in the initial stage (1st stage) where the number of particles is increasing, and reaches the stationary state (R_p = constant) where the number of particles is constant. This stage is called a 0 order reaction zone (2nd stage) proposed by Omi *et al.*¹⁷ However the present high-solid polymerization did not have the 2nd stage, the region where R_p = constant. R_p begins to decline almost instantly due to the decrease of the number of the particles by particle agglomeration after the 1st stage. A direct observation through the sight window of the reaction vessel

Figure 2a. Time-conversion curves in the case of agglomeration promoter (Na alginate & MgSO₄) addition. Butadiene, 100 g; water, 52 g; Na-rosinate, 1 g; KPS, 0.3 g; *n*-DDM, 0.25 g; Na-alginate, 0.001 g; MgSO₄, 0.02 g; temp = 46°C, 52°C, 66°C. Impeller speed (1700 l vessel): (1) ●, 100 rpm; (2) ○, 120 rpm; (3) ●, 140 rpm.

indicated that the viscosity of the polymerization system begins to decrease at this stage. This fact also supports the above-mentioned consideration of particle agglomeration.

Even if the polymerization temperature was raised at this stage, the rate was not necessarily increased. This fall-off in the rate was considered a decrease in the concentration of living radicals. To keep the polymerization rate high, a booster solution was added. R_p was increased again, showing the onset of a new emulsion polymerization. Finally, the

Figure 2b. Dependence on conversion of R_p and number of particles in the high solid polymerization. Curve (a) was obtained by the calculation from curve (2) in Figure 2a and curve (b) was obtained from the photographs of the particles in aliquots taken at each conversion.

Figure 3. Electron micrographs of particles in aliquots taken at: (a) 10% conversion; (b) 20% conversion; (c) 30% conversion; (d) 40% conversion.

concentration of monomer in the polymer particles decreased, and the polymerization rate gradually fell off. In this manner, the conversion reached about 90% or above and, thus polydispersed high solid latices were obtained.

In general, a water soluble polymer is adsorbed on the latex particles,^{18,19} and controls hydration²⁰ and interaction of the particles.²¹ In the present study, it is thought that the coalescence of polymer particles was controlled by water soluble magnesium alginate and the agglomeration proceeded very smoothly. Figure 4 shows its speculated model. Though the specificity of magnesium alginate is not clearly explained, a half molar amount of MgSO_4 to the sodium alginate is the most effective. This means that magnesium alginate acts on the electric double layer film²² of the present polymer particles covered with emulsifier and coalescence them effectively.

It appears to that the water-soluble magnesium alginate reacts with the emulsifier which covers the polymer particle and spills out the emulsifier with aid of magnesium ions in the alginate and then the alginate is adsorbed on the particles and aggregates with them.

Effects of the Booster Solution

The addition of booster solution in the final stage of the reaction, which generates small particles, reduces the fall-off in the rate of polymerization due to the drop in the number of the particles, and also makes the particle concentration high. The presence of small particles is essentially disadvantageous to the following graft polymerization for ABS resin synthesis.²³ Thus, the best time for examining is when the booster solution is charged into the reaction mixture.

Figure 5 shows the relation between the generation of small particles and the charging time of the booster solution.

It is reported that there is no free monomer remaining when the conversion reaches 50% in

Figure 4. Action of magnesium alginate on the coalescence of polymer particles covered with emulsifier.

Figure 5. Relation between conversion on adding the booster solution and the content of small particles in the high solid latex obtained.

the emulsion polymerization of butadiene.²⁴ The newly produced particles generated by the addition of the booster solution are formed by the polymerization of monomer eluted out from the large polymer particles existing already in the system. Figure 5 shows that the quantity of small particles produced by the addition of the booster solution decreases with the time of addition. This means that the number of newly produced particles is related to the amount of the monomer eluted out from the particles.

In conclusion, by the addition of the new agglomeration promoters, the combination of sodium alginate and MgSO_4 , under precise reaction control, the direct manufacturing process of a high solid, polydispersed polybutadiene latex of large particle size with excellent reproducibility is possible.

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