Batch and Semicontinuous Emulsion Copolymerization of Vinylidene Chloride and Butyl Methacrylate. I. Kinetics in VDC-BMA Emulsion Polymerization and Surface and Colloidal Properties of VDC-BMA Latexes

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SYNOPSIS

Vinylidene chloride (VDC)-butyl methacrylate (BMA) comonomer mixtures with various composition (83 : 17, 60 : 40, 33 : 67 in mol %) were polymerized at 25°C using redox catalyst by batch and seeded semicontinuous emulsion copolymerization. The reactivity ratios determined in VDC (M_1)-BMA (M_2) emulsion copolymerization system were r_1 = 0.22 and r_2 = 2.41. Seven 35% solids (83 : 17 mol %) VDC-BMA copolymer latexes were prepared: one batch (G), one seeded batch (F), and 5 seeded semicontinuous polymerizations of 5 different monomer feed rates ranging from 0.27 (A) to 1.10 wt %/min (E). The kinetic studies of seeded semicontinuous polymerizations A-E showed that the rates of polymerizations (R_p) were controlled by the monomer addition rates (R_a). The conversion versus time curves for the polymerizations of 0 : 100-100 : 0 VDC-BMA mixtures by batch polymerization showed that the rate of polymerization (R_p) was a function of the number of particles, and that the rate of polymerization in a latex particle (R_{pp}) increased with increasing proportions of butyl methacrylate in the monomer mixture. All of the latexes had narrow particle size distributions. The greater particle number density in VDC polymerization and the greater water solubility of VDC suggest that the homogeneous nucleation mechanism is operative in VDC-BMA copolymerizations. The latex copolymers prepared by semicontinuous polymerization had lower number- and weight-average molecular weights than those of the corresponding batch copolymers, resulting from the monomer starvation occurring during the semicontinuous polymerization. The surface characterization study of the cleaned latexes showed that for the latexes by batch process, the surface charge density derived from strong-acid groups decreased with increasing proportion of VDC in the monomer mixture. On the other hand, for the latexes prepared by semicontinuous polymerization, the surface charge density derived from strong-acid groups did not depend on the monomer composition of the copolymers.

INTRODUCTION

It is well known that the nature of the polymerization process can affect the kinetic behavior, microstructure, molecular weight, and homogeneity of the resulting polymers.[1-6] The semicontinuous process is particularly effective in emulsion copolymerization for the monomer pairs, which do not form alternating copolymers in batch process. In semicontinuous process where the rate of polymerization (R_p) is controlled by the rate of monomer addition (R_a), When R_p is less than the maximum rate of batch polymerization ($R_{p,max}$), more uniform composition copolymers can be obtained.[7-9]

Table I shows some of the physical properties of monomers and homopolymers of vinylidene chloride

Table I Physical Properties of VDC and BMA[10,11]

Property	VDC	BMA
Monomer		
Molecular wt.	97.0	143.0
Density, g/cm^3	1.214	0.889
Solubility, g/100 mL H$_2$O	0.25	<0.01
Polymer		
T_g, °C	−17	20
Density, g/cm^3	1.7–1.9	1.05

(VDC) and butyl methacrylate (BMA).[10,11] The emulsion polymerization of VDC–BMA mixtures is expected to be influenced by the difference in reactivity ratios and water solubilities of the two monomers. The reactivity ratios in VDC (M_1)–BMA (M_2) emulsion polymerization were determined in the present work with $r_1 = 0.22$ and $r_2 = 2.41$. Therefore, in batch copolymerizations of VDC–BMA, the instantaneous copolymer compositions will change with conversion as shown in the simulation given in Figure 1, and the homopolymer of VDC will start to appear at 83, 93, and 98% conversion for the copolymerizations of 83 : 17, 60 : 40, and 33 : 67 (mol %) VDC–BMA, respectively.

The purpose of the present work is to study the kinetics of batch and semicontinuous emulsion copolymerization of VDC–BMA and the effects of comonomer composition and method of monomer ad-

dition on surface and colloidal properties of VDC–BMA copolymer latexes.

EXPERIMENTAL

Materials

VDC (Dow Chemical Co.), fractional distilled under nitrogen at 31.2°C after washing with 20 wt % aqueous NaOH solution, was immediately used for the experiments. n-BMA (Rohm and Haas Co.), distilled at 66°C under vacuum at 57 mmHg and nitrogen, was stored in a refrigerator prior to use. Ammonium persulfate, sodium metabisulfite, and ferrous sulfate (Fisher Scientific, reagent grades) were used as the oxidant, reductant, and activator, respectively. Aerosol MA-80 (American Cyanamid) was used as an emulsifier without further purification. The monomethyl ether of hydroquinone (Fisher Scientific, reagent grade) was used as a shortstopper for the gravimetric determination of conversion during the polymerization. Distilled-deionized water (DDI water) and nitrogen gas of zero grade were used.

Emulsion Polymerization

The recipes used in making VDC–BMA latexes by both processes are given in Table II. The polymerization reactor was a standard 500-mL four-necked
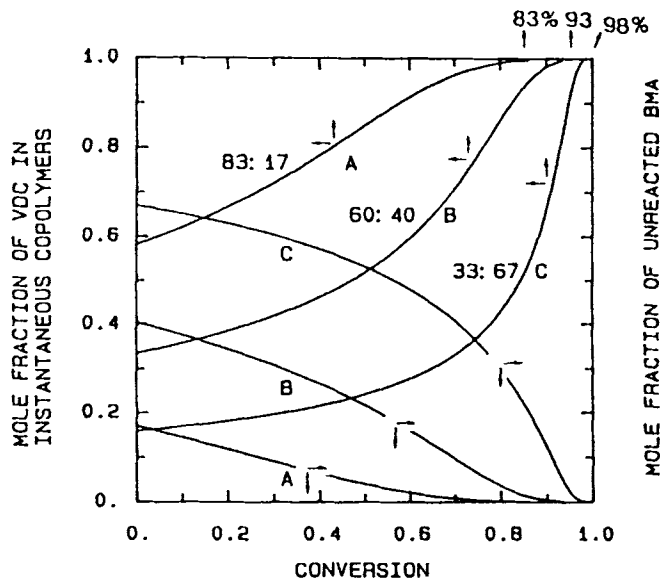

Figure 1 VDC–BMA copolymerizations of 83 : 17, 60 : 40, 33 : 67 (in mol %) by batch process.

Table II Polymerization Recipes of VDC–BMA by Batch and Semicontinuous Processes[a]

	Mol %			Ingredients
	VDC	BMA		
1	100	9	B	Batch
2	83	17	B (G)	Monomer mixture: 80.0 g
			SB (F)	Emulsifier: Aerosol-MA (80%), 1.5 g (1.6%)[b]
			S[a] (A–E)	Catalyst:
3	60	40	B	$FeSO_4 \cdot 7H_2O$, 2.20×10^{-3} g (0.0027%)[b]
				$(NH_4)_2S_4O_8$, 0.28 g (0.35%)[b]
				$Na_2S_2O_5$, 0.28 g (0.35%)[b]
			S	H_2O: 152.0 g
4	33	67	B	Seeded
			S	Monomer mixture: 80.0 g
				Monomer for seeding: 8.0 g
				(VDC = 4.0 g, BMA = 4.0 g) (10%)[b]
				Monomer for addition: 72.0 g (90%)[b]
5	0	100	B	Emulsifier, catalyst, H_2O: the same as above.

[a] B = Batch polymerization, S = seeded semicontinuous polymerization: 0.27 wt %/min in monomer feed rate, SB = seeded batch polymerization; S[a] = for 83 : 17 VDC–BMA semicontinuous polymerization, monomer feed rates were varied in the range of 0.27–1.10 wt %/min: (A) 0.27, (B) 0.39, (C) 0.55, (D) 0.79, (E) 1.10 in wt %/min.

[b] Based on total monomer wt % (80 g). Theoretical solids content: 35.0 wt %; reaction temperature: 25°C.

flask immersed in a constant-temperature bath at 25°C and equipped with a lune-type Teflon blade, glass stirrer fitted with a Teflon trubore adapter, a precise thermometer of 0.1°C scale, spiral reflux condenser in which −15°C coolant circulating to prevent the VDC vapor during the polymerization, and the sampling device to withdraw the sample during the polymerization. For the batch polymerization, the total monomer mixture with DDI water and emulsifier was added at the beginning of the polymerization, and polymerized by an addition of activator, oxidant, and reductant solution (dissolved in DDI water) at 25°C. For the semicontinuous polymerization, the seed formation was first completed, and the remaining monomer mixture was fed into the reactor at the constant feed rate using the compact syringe pump (Harvard Apparatus Company) throughout the polymerization. For the seed formation, 10 wt % of the total monomer mixture (VDC = 4.0 g; BMA = 4.0 g), with DDI water and emulsifier, was charged and maintained under nitrogen atmosphere for half an hour and polymerized by an addition of activator, oxidant, and reductant solution (dissolved in DDI water) at 25°C. The formation of seed latex was entirely completed within 30 min. After the additional 20 min at 25°C, the remaining monomer mixture was fed into the reactor at a constant feed rate using the compact syringe pump throughout the polymerization, as shown in

Table II. After the monomer addition was completed, the polymerization was allowed to proceed for an additional 4 h to complete the reaction. The final conversion was measured gravimetrically.

Conversion Measurement

After the polymerization was started, 1–2 mL of the reaction mixture was sampled at appropriate intervals throughout the polymerization for the conversion measurement. The latex was placed in a tared aluminum weighing dish along with three drops of shortstop solution (0.06 g monomethyl ether of hydroquinone in 20 mL isopropanol) and dried in an oven at 70°C overnight. The percent solids and percent conversion of each sample were determined gravimetrically from the dried sample weights based on the total amount of monomer mixture in the recipe.

Determination of Reactivity Ratios in VDC–BMA Emulsion Polymerization

The reactivity ratios of VDC and BMA in emulsion copolymerization were determined by elemental analysis method, using the Lewis and Mayo equation.[12] Six pairs of monomer mixtures over the entire range of composition were prepared as described in Table III and polymerized using the same recipe and

Table III   Emulsion Copolymerization of VDC (M_1) and BMA (M_2)

Sample No.	Monomer (mol %)		C, H, Cl wt % in Polymer[a]				Polymer (mol %)	
	M_1	M_2		C	H	Cl	$d[M_1]$	$d[M_2]$
1	96.53	3.47	E	37.96	4.22	50.87	77.05	22.95
			T	37.75	4.43	50.87		
2	80.39	19.61	E			33.04	54.64	45.36
			T			33.04		
3	64.15	35.85	E	55.14	7.89	21.02	37.09	62.91
			T	55.29	7.62	21.02		
4	54.50	40.50	E	57.61	8.38	16.92	30.17	69.83
			T	57.84	8.08	16.92		
5	38.55	61.45	E			10.11	19.00	81.00
			T			10.11		
6	20.51	79.47	E			4.73	9.18	90.82
			T			4.73		

[a] Determined by elemental analysis. E = experimental value; T = calculated value.

the same polymerization conditions as described in Table II. The polymerizations were shortstopped at about 5% conversion by adding a shortstop solution. The dried copolymers were analyzed for the C, H, and Cl content using combustion method to determine the monomer compositions in copolymers.

Average Molecular Weight and Molecular Weight Distribution

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a Waters Associates 201A instrument coupled to a differential refractometer detector. Four microstyragel columns were used with pore sizes 10^3, 10^4, 10^5, and 10^6. Monodisperse Polystyrene (PS) samples with the molecular weights of 4000, 17,500, 35,000, 128,000, 390,000, 770,000, and 3,000,000 were used as references. All polymer samples were dissolved in tetra hydrofuran (THF) at concentrations of 0.1–0.2 wt %.

Particle Size Measurements

Particle sizes of the latexes were determined by a Philips 300 transmission electron microscope. A drop of latex with a concentration of 1–3% was placed on a carbon-coated Formvar electron microscope grid, and most of the drop was removed by contacting it with filter paper. The sample was then stained with 2% phosphotunstic acid (PTA) to improve the contrast. The transmission electron micrographs of the latexes were taken at room temperature. In order to calibrate the magnification of the electron microscope, a micrograph of a carbon

replica of a diffraction grating was taken at the same setting as that used for the latex particles. The diameter of the latex particles was measured by a Carl Zeiss Mop-3 instrument. A computer program was used to determine the weight- and number-average particle diameters, as well as particle size distribution.

Latex Cleaning and Surface Characterization

The latexes were cleaned with DDI water using serum replacement and characterized by conductometric titration.[13,14] The latex samples were diluted
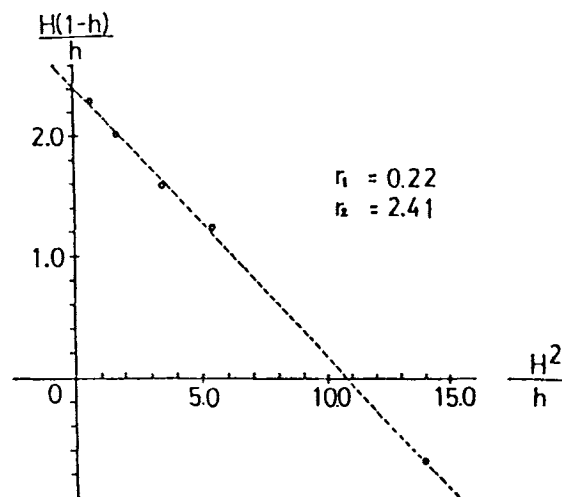

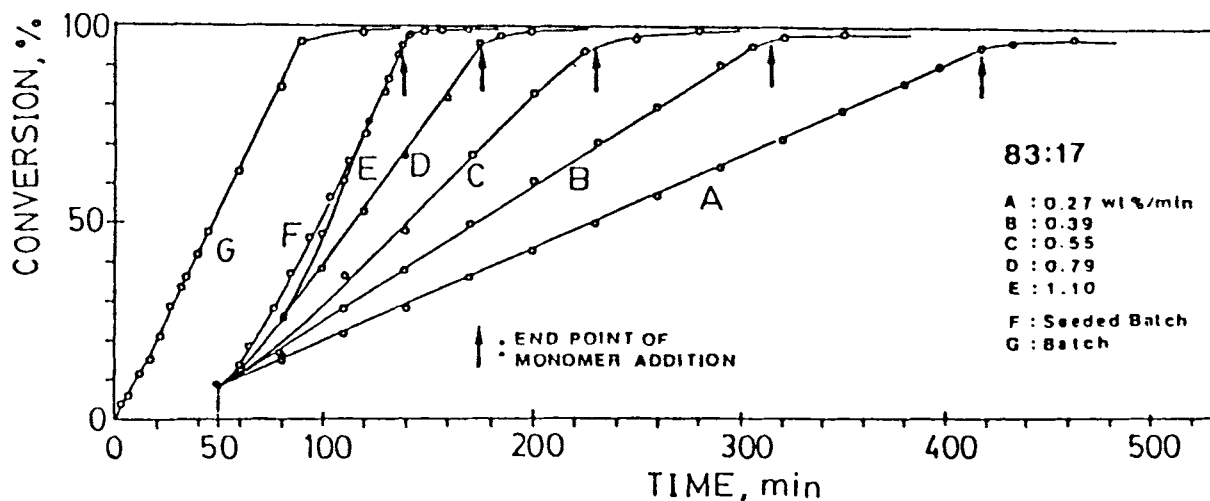**Figure 2**   Reactivity ratios determined by Lewis and Mayo equation.

Figure 3 Overall conversion versus time curves of 83 : 17 VDC–BMA emulsion copolymerizations.

to 2.5–3.0% solids with DDI water and placed in the serum replacement cell equipped with 0.1 or 0.2 μm-diameter Nucleporemembrane. The capacity of the cell was 400 mL; filtration membrane was 76 mm in diameter. The cleaned latex was treated with about 1 gal of $10^{-5}N$ hydrochloric acid to replace the Na^+ and NH_4^+ ions by H^+ ions, and was again washed with DDI water until the conductance of the filtrate was about the same as that of the feed water. The cleaned latexes were titrated using $0.02N$ standard sodium hydroxide solution conductometrically

to determine the amount of surface strong-acid and weak-acid groups on the surface of the particles.

RESULTS AND DISCUSSIONS

Reactivity Ratios of VDC–BMA in Emulsion Copolymerization

The experimental results for the determination of reactivity ratios of VDC–BMA in emulsion copoly-
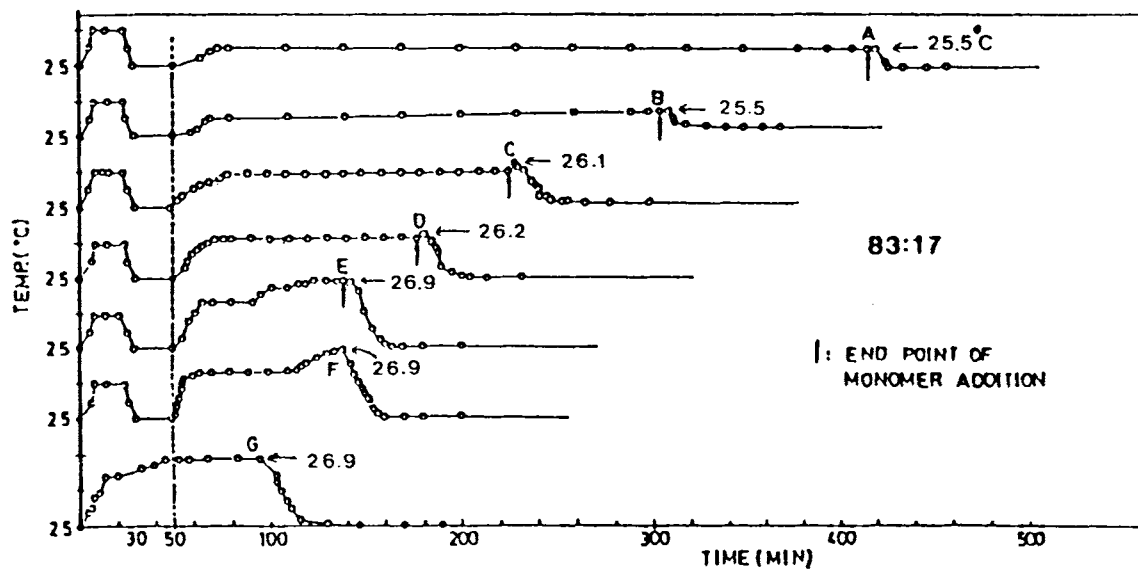

Figure 4 Reaction temperature versus time curves of 83 : 17 VDC–BMA emulsion copolymerizations.
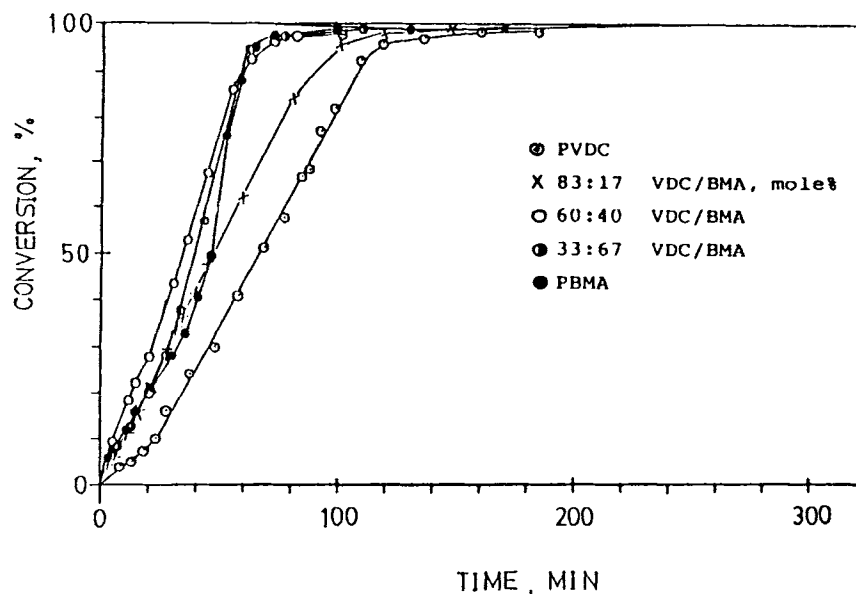
Figure 5 Conversion versus time curves for VDC–BMA batch polymerizations.

merization are shown in Table III. The calculated values of the proportions of C and H in the copolymers, based on the %Cl determined by elemental analysis, agreed well with the experimentally determined values. The reactivity ratios determined in the present study were $r_1 = 0.22$ and $r_2 = 2.41$, as shown in Figure 2. Therefore, in the batch polymerization, the copolymer composition will drift with conversion, resulting in BMA-rich copolymers at the beginning and VDC-rich copolymers at the end of the copolymerization.

Kinetic Study

All of the VDC–BMA emulsion polymerization, carried out by both batch and semicontinuous polymerization at the present study, gave stable latexes of almost 100% conversion with negligible coagulum.

Figure 3 shows the overall conversion versus time curves of seven 83 : 17 mol % VDC–BMA emulsion copolymerizations A to G as determined by the gravimetric method. In the seeded semicontinuous polymerizations A–E, the rate of polymerization (R_p) increased with increasing monomer feed rate (R_a), i.e., the rate of polymerization was controlled by the monomer feed rate. Specifically, the monomer feed rates in the polymerizations A–D ($1.40 - 4.12 \times 10^{-4}$ mol L^{-1} s^{-1}) were less than the observed maximum rate of batch polymerization ($R_{p,max}$, 5.79 $\times 10^{-4}$ mol L^{-1} s^{-1}), indicating that the monomer

concentrations in the latex particles in polymerizations A to D are much lower than those of the batch and seeded batch polymerizations G and F, respectively. In other words the polymerizations A–D occurred under monomer-starved conditions. However, for the polymerization E, which used the highest monomer feed rate (5.77×10^{-4} mol L^{-1} s^{-1}), the corresponding conversion versus time curve was nearly the same as those obtained in the batch polymerization G and the seeded batch polymerization F, indicating that the polymerization E occurred under near-flooded condition.

Figure 4 shows the temperature inside the reactor as a function of time during these seven copolymerizations. In the seeded polymerizations A–F, the temperatures rose from the designated polymerization temperature, 25°C, during the formation of the seed, and returned to the designated temperatures at the end of the polymerization. With the addition of the monomer mixture, the temperature rose again to a maximum, and leveled off. During the seed formation of polymerizations A to F, the maximum reaction temperature was 26°C. The maximum reaction temperature found during the monomer feed increased with increasing monomer feed rate (R_a), i.e., the maximum reaction temperature was controlled by the feed rate. For polymerization E, which used the highest monomer feed rate, the corresponding maximum reaction temperature was the same as those obtained for seeded batch (F) and

Table IV   Rates of Polymerization in VDC–BMA Batch Polymerizations

VDC–BMA	$R_p \times 10^{4\ a}$	$N_p/L \times 10^{-17\ b}$	$R_{pp} \times 10^{21\ c}$
Rates of polymerization at the beginning of second stage of batch polymerization			
100/0	5.87	8.56	0.69
83/17	5.79	2.89	2.00
60/40	8.14	2.35	3.46
33/67	4.55	1.20	3.79
0/100	6.06	1.27	4.77
Rates of polymerization at the end of second stage of batch polymerization			
100/0	5.87		0.69
83/17	6.08		2.10
60/40	9.33		3.97
33/67	9.34		7.78
0/100	16.05		12.64

[a] R_p = overall rate of polymerization; mol L^{-1} s^{-1}.
[b] N_p = number of particles/unit volume.
[c] R_{pp} = rate of polymerization per particle; mol particle^{-1} s^{-1}.

batch polymerizations (G). The results are found to be consistent with those obtained in Figure 3.

Figure 5 shows the conversion versus time curves, determined by gravimetry, for the VDC–BMA batch polymerizations. For the VDC and 83 : 17 VDC–BMA polymerizations, an oily flow appeared on the wall of the reaction flask during the polymerization, which might result from the coalescence of monomer droplets owing to the shortage of emulsifier.[15,16] However, the slowdown in polymerization rate at the beginning of the second stage in these conversion versus time curves was not observed in the present study. The transition from stage II to stage III occurred at progressively lower conversions, and the length of stage II was also progressively shorter, as the amount of BMA in monomer mixture was increased, indicating that the extent of swelling of the polymer particles by monomer plays an important role in stage II of VDC–BMA copolymerizations.

Table IV shows the rate of polymerization (R_p) and rate of polymerization per particle (R_{pp}) at the beginning and end of stage II of the polymerizations. The rate of polymerization was determined from the slope of the conversion versus time curves, and the rate of polymerization per particle was obtained from the ratio of the overall rate of polymerization to the number of latex particles. The rate of polymerization per particle increased with increasing BMA concentration in the monomer mixture, and the particle number density was the dominant factor for the overall rate of polymerization. The extent of au-

toacceleration increased with increasing concentration of BMA.

Particle Size and Size Distribution

Table V shows the average particle diameters of 83 : 17 VDC–BMA copolymer latexes determined by transmission electron microscopy (TEM). The copolymer latexes A–F prepared by seeded polymerization showed almost the same number-average particle diameters of about 120–125 nm, all with narrow size distributions. Figure 6 shows a TEM picture of these latexes. These results indicate that no secondary particle nucleation took place after the

Table V   Particle Sizes of of 83 : 17 VDC–BMA Copolymer Latexes

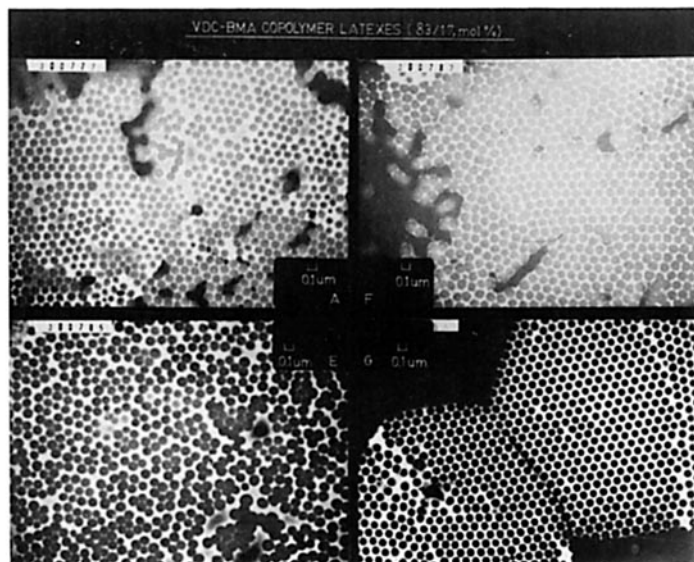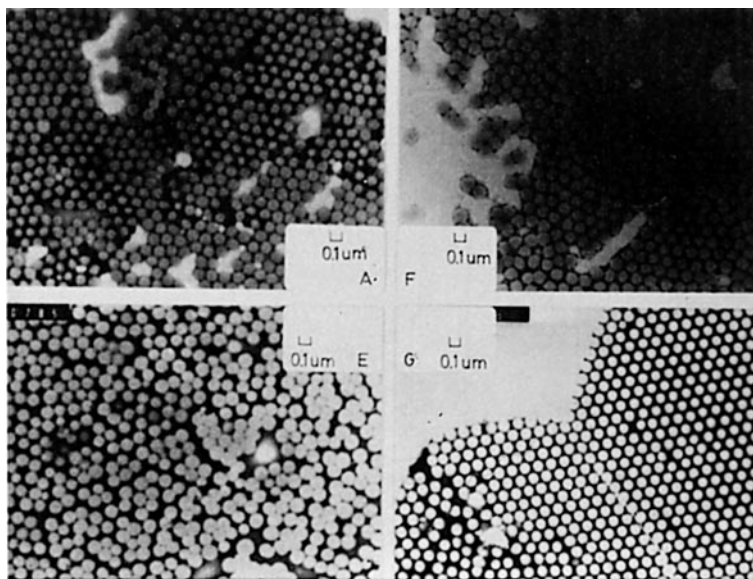|	Particle Sizes		
Latexes	$\bar{D}_n$ (nm)	$\bar{D}_w$ (nm)	$\bar{D}_w/\bar{D}_n$
Seed	56	57	1.022
A	121	124	1.024
B	120	125	1.035
C	125	130	1.033
D	124	126	1.022
E	120	123	1.023
F	124	126	1.018
G	113	116	1.020

Figure 6 Transmission electron micrographs of 83 : 17 VDC–BMA copolymer latexes.

seeding process. The seeding with 10 wt % of the monomer ensured that most of the emulsifier was adsorbed on the particle surface, so that the secondary generation of new particles would be avoided.

The polymerization G, carried out by conventional batch polymerization, resulted in a latex with a number-average particle diameter of 113 nm and a narrow size distribution. This average particle size was slightly smaller than those of the latexes prepared by seeded polymerization. VDC is much more water soluble than BMA (VDC = 0.25; BMA = less than 0.01, g/100 mL H_2O).[10,11] If the copolymerization favors initiation in the aqueous phase (homogeneous nucleation),[17,18] the radicals generated

Table VI   Particle Sizes of VDC–BMA Latexes

Latex Composition VDC–BMA, mol %	Batch (nm)			Semicont. (nm)		
	$\bar{D}_n$	$\bar{D}_w$	$\bar{D}_w/\bar{D}_n$	$\bar{D}_n$	$\bar{D}_w$	$\bar{D}_w/\bar{D}_n$
(1) 100/0	77	82	1.057			
(2) 83/17	113	116	1.020	121	124	1.024
(3) 60/40	125	128	1.025	127	130	1.018
(4) 33/67	162	164	1.010	136	139	1.022
(5) 0/100	168	171	1.017			

in the aqueous phase add VDC monomer and polymerize until the oligomeric radicals exceed their solubility and precipitate. The precipitated oligomeric radicals adsorb emulsifier and absorb monomer to become primary particles. These primary particles formed in the early stage of polymerization may persist as nuclei for the capture of other primary particles. Therefore, in the copolymerization of VDC–BMA mixture, the number of nuclei generated would be proportional to the content of VDC monomer in the monomer mixture. In the same way, the latex G prepared by batch polymerization has a larger number of nuclei than those of latexes by seeded polymerization.

Table VI also shows the average particle diameters of the VDC–BMA latexes prepared by both batch and seeded semicontinuous polymerization, determined by TEM. The number-average particle diameter of the latexes prepared by seeded semicontinuous polymerization increased with increasing amount of BMA in the monomer composition, from 121 to 136 nm; all latexes had narrow particle size distributions, indicating that apparently no secondary nucleation took place after the seed formation. The number-average particle diameters of the latexes prepared by the batch polymerization increased with increasing amount of BMA in the monomer composition, from 77 nm for PVDC to 168 nm for PBMA, all with narrow particle size distributions. TEM pictures of the VDC–BMA copolymer latexes prepared by batch polymerization are given in Figure 7. The number of particles increased with increasing amounts of VDC in the VDC–BMA copolymerization. This might be explained by the higher water solubility of VDC and the mechanism of homogeneous nucleation in the aqueous phase. Therefore, in VDC–BMA copolymerization, the number of nuclei generated is proportional to the content of VDC in the monomer mixture.

Molecular Weight and Molecular Weight Distribution

Table VII shows the average molecular weights of the VDC–BMA copolymers prepared by batch and semicontinuous polymerization, determined by GPC. The determination of the molecular weights of the PVDC and the 83 : 17 VDC–BMA latex copolymer prepared by batch polymerization was impossible because of their insolubility at room temperature. In general, both the number-average and weight-average molecular weights of the copolymers
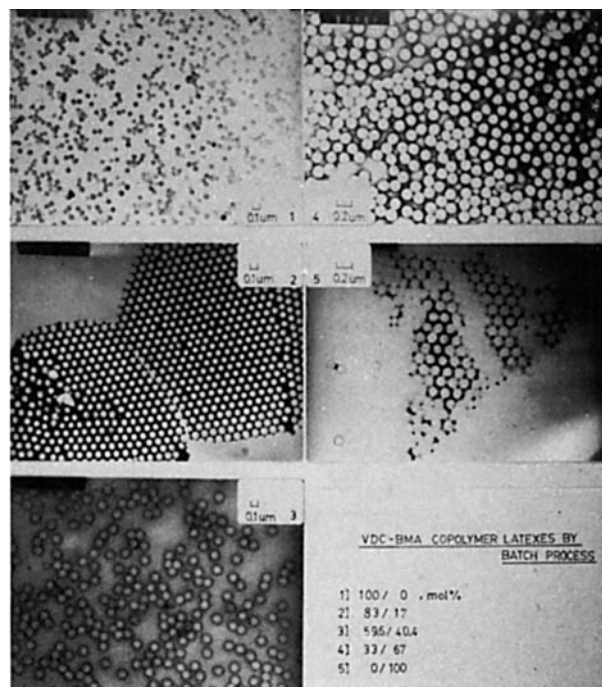

Figure 7   Transmission electron micrographs of VDC–BMA copolymer latexes.

Table VII Average Molecular Weight and Molecular Weight Distribution

VDC–BMA mol %	Batch × 10⁻⁵			Semicont. × 10⁻⁵		
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
100/0						
83/17				0.10	0.40	4.04
60/40	0.30	5.60	18.79	0.11	0.41	3.71
33/67	0.28	5.80	20.71	0.24	2.00	8.37
0/100	0.67	9.40	14.13			

83 : 17 mol % VDC–BMA Copolymers	(× 10⁻⁵)		
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A	0.10	0.40	4.04
B	1.80	7.50	4.18
C	2.90	5.80	1.97

prepared by seeded semicontinuous polymerizations were lower than those of their batch counterparts, which can be explained by the lower monomer concentration during the semicontinuous polymerizations. Especially, even for the 83 : 17 VDC–BMA emulsion copolymerizations A–C, prepared by seeded semicontinuous process, their number- and weight-average molecular weights increased with increasing monomer feed rate. The VDC–BMA latex copolymers prepared by batch polymerization were also found to have broader molecular weight distributions than their semicontinuous counterparts.

This phenomenon might be due to the occurrence of the compositional drift in the batch polymerization, resulting in BMA-rich copolymers of high molecular weight at the beginning and VDC-rich copolymers of lower molecular weight at the end of polymerization.

Surface Characterization

The surface groups of the VDC–BMA copolymer latexes are derived from two main sources: (1) the initiator fragments and their hydrolysis, and oxi-

Table VIII Surface Characterization of Cleaned VDC–BMA Latexes

Latex Composition VDC–BMA (mol %)	Concentration of End Groups (μeq/g polymer)			Surface Charge Density (μC/cm²)	
	Strong Acid	Weak Acid	Total	Strong Acid	Weak Acid
	Batch Process				
100/0	11.98	11.06	23.04	2.61	2.41
83/17	10.50	8.10	18.60	3.11	2.40
60/40	10.01	7.87	17.88	2.95	2.32
33/67	10.20	6.49	16.69	3.40	2.17
0/100	16.00	5.20	21.20	4.55	1.48
	Semicontinuous Process				
83/17	10.00	12.00	22.00	3.17	3.80
60/40	10.50	7.76	18.26	3.15	2.33
33/67	11.20	6.49	17.69	3.14	1.82

dation products (sulfonate, sulfate, hydroxyl, and carboxyl groups); and (2) the hydrolysis of methacrylate ester in the polymer chains (carboxyl groups).

Table VIII shows the results of the surface characterization of cleaned VDC–BMA copolymer latexes prepared by both batch and semicontinuous polymerization. These latexes were cleaned with DDI water using the serum replacement technique.[13,14] For latexes prepared by batch polymerization, the surface charge density (in $\mu C/cm^2$) derived from the strong-acid groups decreased, and the surface charge density derived from the weak-acid groups increased, with increasing VDC content in the copolymer. This phenomenon might be due to the catalytic effect of hydrochloric acid (generated by the degradation of the VDC units) and of sulfuric acid (generated from the hydrolysis of the sulfate end groups) on the hydrolysis of strong-acid groups and probably the oxidation reaction of the hydroxyl groups. The data of average molecular weights of VDC–BMA copolymers by GPC showed that the semicontinuous copolymers have lower number- and weight-average molecular weights than the batch copolymers, suggesting that the semicontinuous copolymers should, on the average, have a larger number of acid end groups per unit weight of the polymer. For latexes prepared by semicontinuous polymerization, the concentration of both strong- and weak-acid groups were found to be similar to those in the batch latexes. However, taking into consideration the possibility of a high degree of burial of acid end

groups inside the particles and the longer reaction times, it is likely that the semicontinuous copolymer latexes have higher concentration ($\mu eq/g$ polymer) of surface acid end groups than the batch copolymer latexes.

Table IX lists the results of the surface characterization of cleaned VDC–BMA latexes after heat treatment for 24 h at 85°C. The reason for choosing 85°C for the experiment is that, after 24 h at this temperature, the PVDC latex became discolored, changing from blue-white to yellow. This indicates that some degradation took place with the evolution of hydrochloric acid and the formation of conjugated double bonds on VDC sequences in the copolymers. For the latexes prepared by batch polymerization, the surface charge density derived from the strong-acid end groups decreased with increasing content of VDC in the copolymer, and the surface charge density derived from the weak-acid end groups did seem to increase with increasing content of VDC in the copolymer. These results indicate that heat treatment for 24 h at 85°C and H^+ generation resulted in the hydrolysis of both strong-acid end groups and methacrylate ester groups, and probably the oxidation of the hydroxyl end groups. The trends are consistent with the occurrence of a core–shell morphology in VDC–BMA copolymer latexes prepared by batch polymerization. On the other hand, for the latexes prepared by semicontinuous polymerization, the surface charge density derived from both strong- and weak-acid groups was virtually independent of the composition of the copolymers, in-

Table IX   Surface Characterization of Cleaned VDC–BMA Latexes, Heat Treated for 24 hr at 85°C

Latex Composition VDC/BMA (mol %)	Concentration of End Groups ($\mu eq/g$ polymer)			Surface Charge Density ($\mu C/cm^2$)	
	Strong Acid	Weak Acid	Total	Strong Acid	Weak Acid
Batch Process					
100/0	5.65	22.44	28.09	1.23	4.89
83/17	6.75	17.74	24.49	2.00	5.26
60/40	7.27	16.30	23.57	2.14	4.80
33/67	9.26	13.07	22.33	3.09	4.57
0/100	10.27	15.24	25.52	2.92	4.32
Semicontinuous Process					
83/17	8.25	14.77	23.02	2.61	4.68
60/40	8.58	13.75	22.33	2.58	4.12
33/67	8.12	14.73	22.85	2.28	4.14

Table X   Surface Characterization of Cleaned VDC–BMA Copolymer Latexes, Aged for 4 Months

Latex Composition VDC–BMA (mol %)	Concentration of End Groups (μeq/g polymer)			Surface Charge Density (μC/cm²)	
	Strong Acid	Weak Acid	Total	Strong Acid	Weak Acid
Batch Process					
100/0	6.92	11.95	18.87	1.51	2.60
83/17	8.13	10.60	18.73	2.41	3.14
60/40	7.52	9.74	17.26	2.22	2.87
33/67	9.01	11.54	20.55	3.00	3.85
0/100	8.45	9.60	18.05	2.40	2.72
Semicontinuous Process					
83/17	8.53	14.77	23.30	2.70	4.68
60/40	9.21	12.90	22.11	2.77	3.87
33/67	9.14	11.30	20.44	2.57	3.17

dicating that the semicontinuous copolymers have a more homogeneous composition on the surface of particles.

Table X shows the results of the surface characterization of cleaned VDC–BMA copolymer latexes aged for 4 months at room temperature. For the latexes prepared by batch polymerization, the surface charge density derived from the strong-acid groups decreased with increasing amount of VDC in the copolymer, and the surface charge density derived from the weak-acid groups was virtually independent of the composition of the copolymer. These results indicate that aging of the latexes at room temperature also resulted in the hydrolysis of both strong-acid end groups and methacrylate ester groups, and probably the oxidation of the hydroxyl end groups. On the other hand, for the latexes prepared by semicontinuous polymerization, the surface charge density derived from the strong-acid groups was virtually independent of the composition of the copolymer.

CONCLUSIONS

The mode of monomer addition and the comonomer composition were found to have a remarkable effect on the kinetics and mechanisms in VDC–BMA emulsion copolymerization, and particle number density and surface properties of VDC–BMA copolymer latexes as well as the molecular weight of the copolymer. VDC–BMA copolymerizations, car-

ried out under monomer-starved condition using slow monomer feed technique, had lower monomer concentrations in latex particles, resulting in lower molecular weights, and more homogeneous copolymer compositions on the surface of latex particles. In contrast, VDC–BMA copolymerizations, carried out by conventional batch process, had monomer-saturated conditions in latex particles, resulting in higher molecular weight, and more heterogeneous copolymer compositions on the surface of latex particles along with the occurrence of the composition drifts with conversion. The greater particle number density in VDC-rich copolymerizations and the greater water solubility of VDC suggest that the homogeneous nucleation mechanism is operative in VDC–BMA copolymerizations.

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