

Preparation and Surface Modification of Poly(vinylbenzyl Chloride) Latices

Y. CHONDE,* L.-J. LIU, and I. M. KRIEGER, *Departments of Chemistry and Macromolecular Science, Case Institute of Technology, Case Western Reserve University, Cleveland, Ohio 44106*

Synopsis

Monodisperse stable latices with reactive methyl chloride surface functionalities were prepared in the presence of mixed surfactants using vinylbenzyl chloride in various ways: as a homopolymer, crosslinked with divinylbenzene, copolymerized with styrene, and overpolymerized onto uniform polystyrene latices. In homopolymerization of vinylbenzyl chloride, the effect of monomer content and concentration and type of surfactant are reported. Nucleophilic displacement of the surface chloride by sulfite ions was accomplished by reaction with aqueous sodium sulfite, without change in latex particle size. Also discussed are ways to control the amount of water-soluble polyelectrolyte produced as a result of the sulfonation reaction.

INTRODUCTION

Emulsion polymerization techniques have been used to prepare latices containing highly uniform spherical polymer particles.¹⁻⁵ Such monodisperse latices are used in medical research and as model systems for the study of physical properties such as rheology, stability, and light scattering. The physical properties are determined by colloidal properties, such as particle size, polymer content, and surface charge density. Various researchers have reported on the effect of polymerization conditions on colloidal properties of latices. In the case of latices prepared by emulsifier-free recipes, Goodwin et al.² and Juang⁵ have reported empirical equations relating the particle diameter to initiator concentration, monomer concentration, ionic strength and reaction temperature. These methods permit only approximate control of particle size, however, and fail to give adequate control of the important variable of surface charge density.

In general, one can control the latex surface charge either by varying the latex preparative recipe,⁵⁻⁷ or by modifying the final latex surface.⁸⁻¹⁰ The modification of the final latex surface is attractive for producing a series of latices with the same particle size but different surface charge. However, depending on the type of monomer used to prepare the latex particles, the surface modification experiment can be very cumbersome. For example, Chan and Goring⁸ suspended polystyrene latex particles in dichloroethane for sulfonation with SO₃/triethylphosphate complex, and then redispersed them in water. In an attempt to bypass the tedious resuspension steps, Liu¹⁰ sulfonated styrene-butadiene latex with aqueous sodium bisulfite. This process produced extensive amounts of weak acid.

Modification of the latex surface charge would be greatly facilitated by the presence of reactive functional groups at the surface of the particles. This can

* Present address: Diamond Shamrock Corp., P.O. Box 348, Painesville, OH 44077.

be accomplished by using reactive vinyl monomers such as vinylbenzyl chloride (VBC). Nucleophilic displacement of chloride can be accomplished prior to polymerization, to make ionic comonomer,¹¹ or in posttreatment of the latex particles, to modify their surface charges.¹²⁻¹⁴ There are four different ways of using VBC monomer to control the particle surface charges. They are as follows: (1) the use of salts derived from VBC as ionic comonomers, (2) copolymerization of VBC with styrene, etc., followed by nucleophilic displacement of the surface chlorides, (3) overpolymerization of a shell of PVBC on polystyrene latex, followed by nucleophilic displacement of the surface chlorides, and (4) posttreatment of a PVBC homopolymer latex with nucleophiles.

As with most monomers there are certain disadvantages associated with the use of VBC. The monomer is expensive and toxic. The hydrolyzability of the chloride group above 40°C limits the choice of initiators for its polymerization. In addition, low-molecular-weight oligomers are formed during the nucleophilic displacement of the chloride on the latex surface. Despite these shortcomings, VBC is potentially very useful in preparing polymer latices for use as model systems.

The present report includes a study of the polymerization of vinylbenzyl chloride latices in water at 30°C using persulfate-bisulfite/Fe(II) redox initiator in the presence of added emulsifiers, to yield monodisperse latices at ~40–45% polymer. The effect of various parameters on the final latex particle size and particle surface charge in the homopolymerization of VBC and in copolymerization of VBC and styrene are discussed. We are also reporting a preliminary study of a seeding technique using polystyrene latex particles as the core, onto which a thin shell of VBC is polymerized.

EXPERIMENTAL

Apparatus

Polymerization Reactors

Two different types of reaction vessels were used during this study. For exploratory purposes, 12 oz citrate of magnesia bottles were charged with ingredients, purged with N₂, capped, and then placed in a 30°C thermostatted water bath, commonly known as a bottle polymerizer. The polymerizer was equipped with a rotor to which were attached cages for the bottles. The polymerization proceeds in a closed system, with agitation resulting from end-over-end rotation of the bottles. The large-scale reactions were conducted in a three-neck two-liter round-bottom flask equipped with a stirrer (half-moon Teflon blade), a condenser, and a nitrogen gas inlet. The flask is immersed in a 30°C water bath for temperature control.

Electron Microscopy

The electron microscope used was a JEM-100B (Japan Electron Optics Laboratory, Ltd.). The technique used in this study is described in a previous article.⁴

Conductivity Apparatus

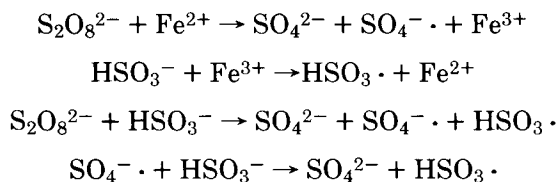
Conductivity was measured by means of a dip-type glass conductivity cell (Matheson Scientific Co.) and a 60-cycle Wheatstone bridge (Leeds & Northrup Co.) in a 30°C water bath under a nitrogen atmosphere.

Reagents

Styrene (reagent, Eastman Kodak Co.) and divinylbenzene (technical, Dow Chemical Co.) were passed through an activated alumina column before use to remove inhibitor. Vinylbenzyl chloride (technical, Dow Chemical Co.) was washed with 0.5% NaOH to remove inhibitors, then nitromethane was added to prevent Friedel-Crafts acylation. Anionic surfactant Siponate DS-10 (sodium dodecylbenzene sulfonate from Alcolac Chemical Co.) and nonionic surfactant Triton X-100 (polyoxyethylene isooctylphenyl ether from Rohm and Haas Co.) were used as received. Analytical grade potassium persulfate (Mallinkrodt Chemical Works) was used as received. All the other chemicals are commonly used reagent grade chemicals. Mixed-bed ion-exchange resin (Rohm and Haas MB-3) was rinsed before use with double-distilled water until the specific conductance of the eluate under a nitrogen atmosphere measured $(0.3-0.5) \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$. Distilled water was used in all reactions.

POLYMERIZATION

Benzyl chloride hydrolyzes readily at elevated temperatures,¹² so that thermally activated substances such as persulfates cannot be used to initiate polymerization. Therefore, these latices were prepared at 30°C using a persulfate-bisulfite/Fe(II) redox initiator and mixed anionic and nonionic emulsifiers. Berry and Petersen¹⁵ suggest the following reaction as the mechanism for the free radical generation of the redox initiator activated by iron(II) salts.



The same experimental procedures are followed for homopolymerization of VBC and copolymerization of VBC with styrene. Two typical recipes are shown in Table I. Nitromethane is used in these recipes to inhibit possible Friedel-Crafts acylation, which would lead to undesired crosslinks. The reagents are charged in the order given in the table. The surfactants and $\text{K}_2\text{S}_2\text{O}_8$ were in aqueous stock solutions. The stirring in the three-neck round-bottom flask was kept at 400 rpm for 45 min before the initiator system was added; then the stirring was cut down to 150 rpm. The reaction vessel was purged continuously with O_2 -free nitrogen. In the bottle polymerization all the ingredients were charged except the initiator systems; then the mixture was degassed for 15 min, after which the initiator system was added. Once more the mixture was degassed for 2 min before the bottle was capped, shaken, and placed in the polymerizer.

Seed polymerization was conducted in a three-neck round bottom flask.

TABLE I
Typical Recipes for Preparing Monodisperse Poly(vinylbenzyl Chloride) Latices

Latex Code No.	N-1	S-1
Water (ml)	150	150
10% (w/w) Triton X-100 (ml)	40	40
1.0% (w/w) Saponate DS-10 (ml)	40	40
0.1N KOH (ml)	60	60
0.01% (w/w) FeSO ₄ ·7H ₂ O (ml)	10	10
Vinylbenzyl chloride (ml)	240	149
Divinylbenzene (ml)	10	
Styrene (ml)	—	91
1.0% (w/w) NaHSO ₃ (ml)	40	40
3.0% (w/w) K ₂ S ₂ O ₈ (ml)	20	20
CH ₂ NO ₂ (g)	0.27	0.17
Diameter (μm)	0.19	0.20

Distilled water, monodisperse PS latex, and anionic emulsifier (DS-10) are charged together in the flask and degassed for 30 min before vinylbenzyl chloride is added. In these recipes only 70% of the total amount of emulsifier required to cover the particle surface was used. After vinylbenzyl chloride was added, the mixture was stirred at ~300 rpm for 3 hr, then the persulfate-bisulfite/Fe(II) redox initiator system was charged into the flask. The stirring was adjusted to 150 rpm. The reaction was run for 24 hr under a continuous nitrogen atmosphere.

LATEX SULFONATION

Poly(vinylbenzyl chloride) latices were sulfonated in the aqueous phase using different sulfonating reagents. The solid content and particle size of the latex were measured before sulfonation to determine how much sulfonating reagent would theoretically be needed to attain a desired final charge density. The latex was then diluted to a proper solids content. To prevent the latex particles from coagulating during sulfonation, anionic emulsifier was added to the latex. The amount of emulsifier added was determined from a graph of surface tension versus the volume of concentrated emulsifier solution.

The following is a typical recipe for sulfonation. In a one-liter three-neck round-bottom flask equipped with a stirrer and a condenser, 150 ml of poly(vinylbenzyl chloride) latex (solid content 41%), 350 ml of 100 ppm *t*-butylcatechol solution, and 100 ml 1% DS-10 solution were mixed. The *t*-butylcatechol solution was added to prevent further polymerization during the sulfonation process. Three grams of sodium sulfite in 300 ml of water was then added to the flask over a period of 30 min. The flask was then immersed in a 65°C water bath and the stirring speed was adjusted to 40 rpm. The reaction was run for 48 hr. Electron microscopy and light scattering showed no detectable change in the particle size as a result of sulfonation.

Water-soluble polyelectrolyte not removed by ion exchange will augment the apparent surface charge, as determined by titration with base. Qualitative and quantitative determinations of water-soluble polyelectrolyte formed during sulfonation were carried out by centrifuging followed by ultraviolet spectrometry of the supernatant at 254 nm.

RESULTS

A systematic series of polymerizations of vinylbenzyl chloride was carried out in the bottle polymerizer. The effects of monomer concentration and of surfactant concentration on the final latex particle diameter and on uniformity were investigated. The effect of monomer content with constant initiator concentration, surfactant concentration, and ionic strength is shown in Figure 1. Particle size increases linearly with increasing monomer content.

In an emulsion polymerization system with emulsifier, the number of particles is determined by the initial concentration of micelles; therefore, parameters like initiator concentration, ionic strength, and pH value should have some effect on the final latex particle size. However, as shown in Figure 2 and Table II, the latex particle size is greatly affected by the ratio of anionic to nonionic surfactant. The particle size is more sensitive to variation in anionic surfactant content than to nonionic surfactant. Polydisperse latices resulted when a comparable amount of either surfactant type was used separately. The effect of surfactant on particle size and uniformity agreed well with the previously reported effect in styrene systems.⁴

The copolymerization of vinylbenzyl chloride with styrene was conducted under conditions similar to those employed in the homopolymerization of vinylbenzyl chloride. Apparent surface charges were determined after sulfonation and ion exchange. With other parameters held constant, the final latex particle size increased with an increase in the mole ratio of styrene to vinylbenzyl chloride. However, as shown in Figure 3, the apparent surface charge per unit area decreased drastically with increase in the mole ratio of styrene to vinylbenzyl chloride.

A preliminary study of seed polymerization of a small amount of vinylbenzyl chloride (~2% w/w of VBC/styrene) on polystyrene latex has produced encouraging results. As shown in Table III, a shell of PVBC only a few hundred angstroms thick is formed around each polystyrene particle. The thickness of this shell is easily controlled by varying the amount of vinylbenzyl chloride used. Thus, this technique does enable one to vary the surface properties of a latex particle without much change of original particle size.

Surface charge modification of homopolymer of VBC and copolymer of VBC with styrene was carried out by nucleophilic displacement of the surface chloride by sulfide ions. As shown in Tables IV and V the degree of sulfonation increased with the concentration of sulfite ions and the reaction temperature. As the

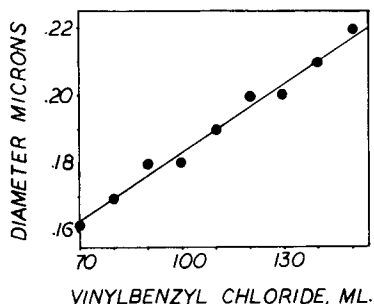


Fig. 1. Effect of initial charge (in ml) on the final latex particle diameter. Recipe content: 147 g of water, 0.25 g of $K_2S_2O_8$, 0.16 g of $NaHSO_3$, 0.0004 g of $FeSO_4 \cdot 7H_2O$, 0.16 g DS-10, 1.6 g of Triton X-100.

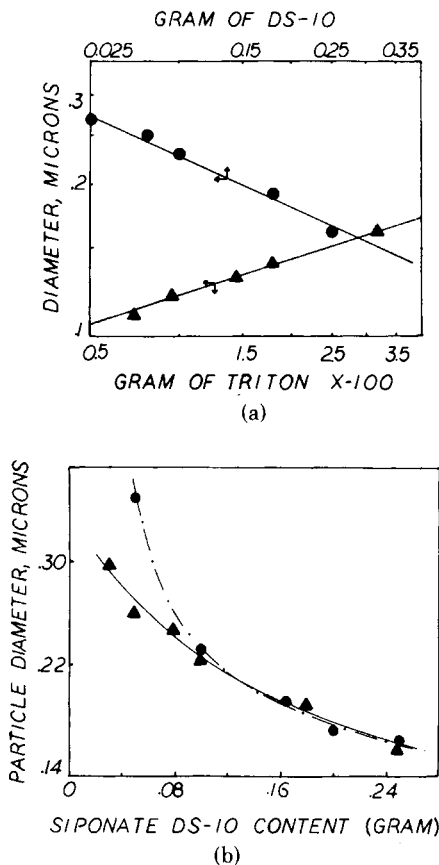


Fig. 2. (a) Effect of varying surfactant content on the final latex particle diameter. Recipe content: 92.6 g VBC, 0.25 g of $K_2S_2O_8$, 0.16 g $NaHSO_3$, 0.0004 g of $FeSO_4 \cdot 7H_2O$, total volume of mixture 264 ml. (●) 4.5 g of Triton X-100; (▲) 0.25 g of DS-10. (b) Effect of anionic surfactant on the final latex particle diameter. Same recipe as in (a). (●) 1.64 g of Triton X-100; (▲) 4.5 g of Triton X-100.

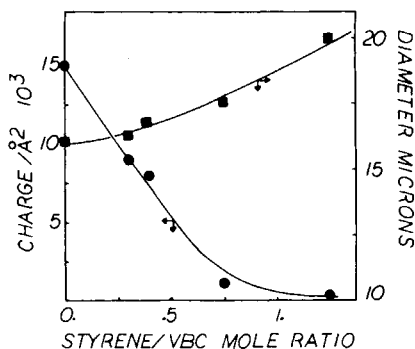


Fig. 3. Effect of varying the mole ratio of styrene to vinylbenzyl chloride on the final particle diameter and apparent charge density of deionized latex.

sulfonation reaction progressed, the electrostatic repulsion between sulfonated neighbors resulted in chain uncoiling and desorption of water-soluble oligomer fragments. The concentration of oligomers diminished as the percent of

TABLE II
Effect of Varying (a) Anionic and (b) Nonionic Surfactant Content on the Latex Particle Size

Latex code	A	B	C	D	E	F
(a)						
Water (ml)	45	52	60	62	65	67
18% Triton X-100 (ml)	25	25	25	25	25	25
1% DS-10 (ml)	25	18	10	8	5	3
0.1N KOH (ml)	24	24	24	24	24	24
0.10% FeSO ₄ ·7H ₂ O (ml)	4.1	4.1	4.1	4.1	4.1	4.1
VBC (ml)	100	100	100	100	100	100
1% NaHSO ₃ (ml)	16.4	16.4	16.4	16.4	16.4	16.4
1% K ₂ S ₂ O ₈ (ml)	24.6	24.6	24.6	24.6	24.6	24.6
CH ₃ NO ₂ ^a						
Diameter (μm)	0.16	0.19	0.23	0.25	0.26	0.30
(b)						
Water (ml)	52	60	62	65	67	
18% (w/w) Triton X-100 (ml)	18	10	8	5	3	
1% (w/w) DS-10 (ml)	25	25	25	25	25	
0.1N KOH (ml)	24	24	24	24	24	
0.01% FeSO ₄ ·7H ₂ O (ml)	4.1	4.1	4.1	4.1	4.1	
VBC (ml)	100	100	100	100	100	
1% NaHSO ₃ (ml)	16.4	16.4	16.4	16.4	16.4	
1% K ₂ S ₂ O ₈ (ml)	24.6	24.6	24.6	24.6	24.6	
CH ₃ NO ₂ ^a						
Diameter (μm)	0.16	0.14	0.13	0.12	0.11	

^a 0.8316 g CH₃NO₂ in 770 ml VBC.

crosslinking of PVBC latex increased (see Table VI). The same effect was observed in VBC copolymerized with styrene, as the mole ratio of styrene to VBC increased. The kinetics of sulfonation is shown in Figure 4.

DISCUSSION

It is evident from the work described above that uniform and stable reactive latices can be prepared by several routes: by direct polymerization of vinylbenzyl chloride, by seed polymerization of vinylbenzyl chloride onto monodisperse polystyrene latex, or by copolymerization of vinylbenzene chloride with styrene.

TABLE III
Typical Recipe for Seed Polymerization of Vinylbenzyl Chloride onto Polystyrene Latex

Latex code No.	P-2
Water (ml)	150
Latex P ($D = 0.147 \mu\text{M}$, 10% solids) (ml)	100
10% (w/w) DS-10 (ml)	5.7
0.01% (w/w) FeSO ₄ ·7H ₂ O (ml)	0.6
Vinylbenzyl chloride (ml)	28
1% (w/w) NaHSO ₃ (ml)	3
3% K ₂ S ₂ O ₈ (ml)	3
Diameter (μm)	0.172

TABLE IV
Effect of Concentration of Na_2SO_3 on the Sulfonation of Poly(vinylbenzyl Chloride) Latex^a
at 55°C

Mole ratio of surface chloride/sulfite ion	$\frac{\text{g of polyelectrode}^b}{\text{g of polymer latex}} (\times 10^3)$	Residual surface charge ^c / $\text{\AA}^2 (\times 10^4)$
1:1	9.0	2.4
1:2	9.6	3.1
1:3	13.6	6.8
1:4	14.0	
1:5	14.5	7.6

^a Latices in Tables IV and V are ion-exchanged using mixed-bed MB-3 resin.

^b Water-soluble oligomer.

^c Residual surface charge refers to bound surface charge on the latex particle after repeated centrifugation and redispersion of ion-exchanged latex sample.

In the homopolymerization of vinylbenzyl chloride, the effect of mixed surfactant concentration on the latex particle size and uniformity is in accord with the mixed micelle theory of emulsion polymerization proposed by Woods et al.⁴ for polystyrene latex: (1) uniform particle latices are obtained when both ionic and nonionic surfactant are used, but polydisperse latices result when a comparable

TABLE V
Effect of Temperature on Sulfonation of Poly(Vinylbenzyl Chloride) Latex^a at $[\text{Na}_2\text{SO}_3] = 3.6 \times 10^{-2}$ for 30 hr

Temperature (°C)	Apparent surface charge ^b / \AA^2 ($\times 10^4$)
30	1.4
40	3.8
65	25

^a See Table IV.

^b Apparent surface charge refers to the total titratable acid groups in the latex. This includes the contribution from water-soluble oligomers in the bulk phase and from the latex particles.

TABLE VI
Effect of Crosslinking on the Formation of Polyelectrolyte During Sulfonation of Vinylbenzyl Chloride Latices^a

Type of latex	Sulfonation		$\frac{\text{g of polyelectrolyte}}{\text{g of polymer}}$
	Temperature (°C)	Time (hr)	
VBC (homopolymer)	45	20	2.82
VBC overpolymerized on PS	65	24	1.8×10^{-2}
VBC 2% crosslinked with DVB	65	24	2.8×10^{-2}
VBC 8.6% crosslinked with DVB	45	20	1.35×10^{-2}
Copolymer of VBC + Styrene (styrene/VBC mole ratio of 0.3)	65	24	8.5×10^{-3}

^a Ratio of Na_2SO_3 to initial surface Cl, 4:1; latices ion exchanged after sulfonation.

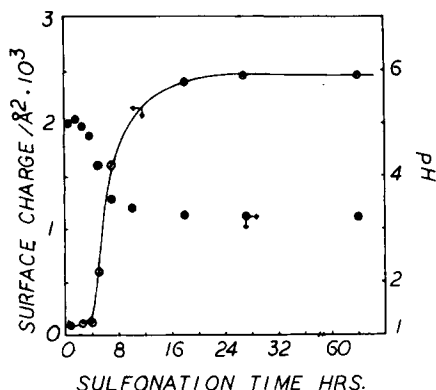


Fig. 4. Kinetics of sulfonation of poly(vinylbenzyl chloride) latex $[\text{Na}_2\text{SO}_3] = 3.65 \times 10^{-2}$, at 65°C .

amount of either surfactant is used; (2) an increase in the content of ionic surfactant results in decreasing the latex particle size; (3) an increase of nonionic surfactant content increases the particle size, but it has a much smaller effect than ionic surfactant.

In copolymerization of vinylbenzyl chloride with styrene, the particle size increases with the mole ratio of styrene to vinylbenzyl chloride, but the titratable charge decreases rapidly. The decrease in titratable charge is due both to lower particle surface charge and to a lesser tendency to form polyelectrolyte. Seed polymerization of the vinylbenzyl chloride shell around a core of polystyrene latex has produced a stable latex with reactive chloride endgroups.

The surface modification study has shown some interesting results. In sulfonation of homopolymer, the formation of polyelectrolyte is a problem. However, crosslinking or copolymerization with styrene greatly reduce the amount of polyelectrolyte formed by treatment with sulfite. Even in the case of sulfonated homopolymer, repeated centrifugation and redispersion of the latex was shown to remove almost all polyelectrolyte.¹⁶ By varying the extent of sulfonation, it should be possible to produce a series of latices of the same particle size but different surface charge densities.

This work was partially supported by a grant from the Paint Research Institute.

References

1. F. A. Bovey, I. M. Kolthoff, A. I. Medalia, and E. J. Meehan, *Emulsion Polymerization*, Interscience, New York, 1955.
2. J. W. Goodwin, J. Hearn, C. C. Ho, and R. H. Ottewill, *Colloid Polym. Sci.*, **252**, 464 (1974).
3. J. N. Shaw, *J. Polym. Sci., Part C*, **27**, 237 (1969).
4. M. E. Woods, I. S. Dodge, I. M. Krieger, and P. E. Pierce, *J. Paint Technol.*, **40**, 527 (1968); **40**, 541 (1968).
5. M. S. Juang and I. M. Krieger, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 2089 (1976).
6. J. Stone-Masui and A. Watillon, *J. Colloid Interface Sci.*, **52**, 479 (1975).
7. W. C. Wu, Ph.D. thesis, Lehigh University, 1977.
8. F. S. Chan and D. A. I. Goring, *Can. J. Chem.*, **44**, 725 (1966).
9. P. Swaraj and R. Bengt, *Macromolecules*, **9**, 337 (1976).
10. Li-Jen Liu, Ph.D. thesis, Case Western Reserve University, 1978.
11. G. D. Jones, U.S. Patent No. 2,909,508 (1959).
12. W. G. Lloyd and J. F. Vitkuske, *J. Appl. Polym. Sci.*, **6**, (24), S58 (1962).

13. W. G. Lloyd and T. E. Durocher, *J. Appl. Polym. Sci.*, **7**, 2025 (1963).
14. W. G. Lloyd and T. E. Durocher, *J. Appl. Polym. Sci.*, **8**, 953 (1964).
15. K. L. Berry and J. H. Peterson, *J. Am. Chem. Soc.*, **73**, 5195 (1951).
16. Y. Chonde and I. M. Krieger, *J. Colloid Interface Sci.*, to appear.

Received December 4, 1979

Accepted January 31, 1980