

Emulsifier-Free Synthesis of Monodisperse Core–Shell Polymer Colloids Containing Chloromethyl Groups

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SYNOPSIS

Both the synthesis of *m,p*-trimethyl(vinylbenzyl)ammonium chloride (TMVBAC) and the synthesis of polymer colloids consisting of a shell of poly(vinylbenzyl chloride) grafted onto a well-defined, monodisperse poly(styrene–divinylbenzene) core are described. The preparation of the polymer latices consists of a sequence of different emulsifier-free emulsion polymerizations. First, monodisperse poly(styrene–divinylbenzene) seed latices, with 2,2'-azobis(2-amidinopropane) hydrochloride (AIBA · 2HCl) as cationic initiator, are prepared under batch conditions. These latices are used for the seeded polymerization of divinylbenzene (DVB), in order to synthesize monodisperse particles, with a well-defined spherical shape, which contain a sufficient amount of pendant vinyl groups for grafting of the vinylbenzyl chloride (VBC) monomer. After the graft polymerization, the chloromethyl groups can easily be modified with a postpolymerization reaction. As an example, the amination with trimethylamine (TMA) is described. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The use of insoluble polymer colloids as support for reagents and catalysts has been studied extensively.^{1,2} To overcome the difficulties of external mass transfer and intraparticle diffusion limitations, observed in conventional polymer-supported catalysts with particle sizes of 20–500 μm , colloidal polymer particles with particle sizes of less than 1 μm and with a nonporous surface morphology can serve as an alternative. The advantages of using polymer latices as support for reagents or catalysts are the narrow particle size distribution, a sufficient surface area, a high degree of control in their synthesis, and, as already mentioned above, avoidance of heat and mass transfer limitations. Examples include the inversion of sucrose,³ phase-transfer catalysis,⁴ and the cobalt(II)phthalocyanine-catalyzed thiol oxidation.⁵

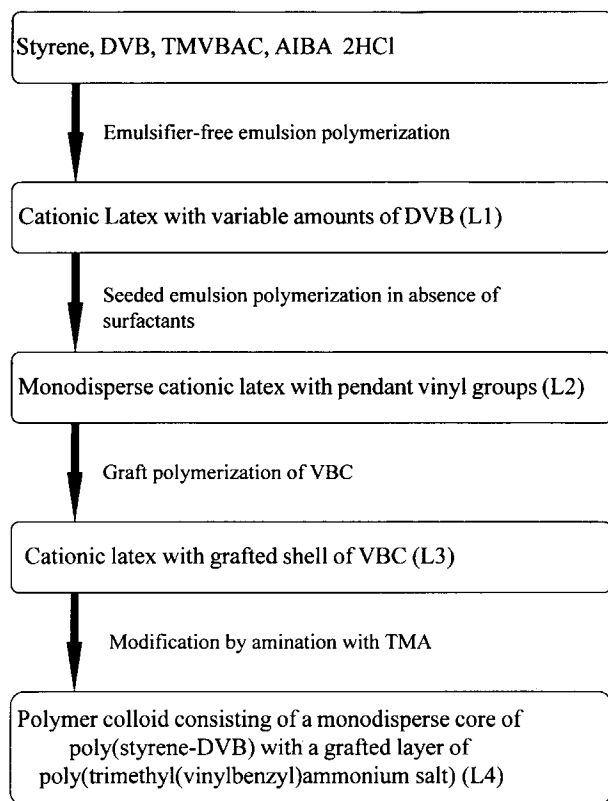
It is easy to understand that each polymer support applied in a process has to obey a set of specific demands. Therefore, the design and synthesis of a

universal polymer colloid, which can easily be modified with one postpolymerization reaction, would be an outcome.

An attempt was made to synthesize such a polymer colloid keeping in mind that the method of synthesis of the particles should avoid the use of non-polymerizable surfactants and minimize the production of water-soluble polymer. The particles should contain a functional group (e.g., chloromethyl) that can easily be modified to the functionality required for the application of the polymer colloid. An excellent review on the modification of chloromethyl groups is given by Camps et al.⁶

Moreover, the particles should be as monodisperse as possible, have a well-defined morphology and the colloids should have the ability to be (re)dispersed in both aqueous and organic media without losing their structure. In this article, the synthesis of the basic polymer colloid, consisting of a shell of poly(vinylbenzyl chloride) grafted onto a well-defined, monodisperse poly(styrene–divinylbenzene) core, as well as its modification to a polymer colloid having a poly[trimethyl(vinylbenzyl)ammonium salt] shell, by amination of the functional chloromethyl groups with trimethylamine (TMA), is described. The pathway

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Scheme 1 Flow chart showing a pathway for the various steps of the latex synthesis.

for the various steps of the latex synthesis is presented in Scheme 1.

EXPERIMENTAL

Materials

Styrene (Merck) was distilled under vacuum and divinylbenzene (DVB; Merck, 65 wt % divinylbenzene *m,p*-isomers, 33 wt % ethylvinylbenzene *m,p*-isomers) was washed with NaOH prior to use to remove the inhibitor. *m,p*-Vinylbenzyl chloride (VBC; kindly provided by DOW Benelux), trimethylamine (TMA; Janssen Chimica, 45 wt % aqueous solution), mixed-bed ion-exchange resin (Bio-Rad, AG501-X8 20-50 mesh, p.a.), and cobalt (II) phthalocyaninetetra (sodium sulfonate) [CoPc(NaSO₃)₄] (kindly provided by T.P.M. Beelen) were used as received. In all experiments we used deionized distilled water (Millipore super Q) that was stored under argon, and that had a conductivity of approximately 0.8–1.0 $\mu\text{C cm}^{-2}$. All other materials were of analytical grade, commercially available, and used as purchased.

Synthesis of *m,p*-Trimethyl(vinylbenzyl)ammonium Chloride (TMVBAC)

m,p-Trimethyl(vinylbenzyl) ammonium chloride (TMVBAC) was synthesized, to serve as a cationic comonomer, in order to enhance colloidal stability of the cationic latex particles prepared by emulsifier-free emulsion polymerizations. The quaternary ammonium salt TMVBAC is formed by the Menschutkin reaction, using VBC and TMA as reagents. Acetone was kept over molsieves (4 Å) under an argon atmosphere at -20°C and was used as a solvent. Despite its only moderate polarity, acetone affords the advantage of being a nonsolvent for the product (the reaction is favored by polar solvents). VBC (5.0 g) was added to 50 mL of acetone in a dry crimp top flask (100 mL). The temperature was kept below -20°C by occasional cooling with liquid nitrogen.

TMA (aq) (50 g) was poured into a round-bottomed flask (250 mL) equipped with a magnetic stirring bar and an Allihn condenser. The aqueous solution of TMA was heated up to 40°C using a thermostated silicone oil bath. The temperature was raised to 50°C during the experiment. The TMA gas liberated was purged through a gas-washing bottle, filled with CaCl₂ as a drying agent. The dried TMA gas was condensed and dissolved in the cooled VBC/acetone mixture for a period of about 2 h.

After this, the vial was capped with a Teflon-coated rubber gasket, and the reaction mixture was kept under argon atmosphere and stored at -20°C for 48 h. The product obtained at the end of this time period (needlelike white crystals) was filtered using a glass funnel and was thoroughly washed four times with 25 mL acetone. The crystalline mass was dried. All of these actions were performed under an argon blanket.

The product obtained was very hygroscopic and liable to spontaneous polymerization, when allowed to stand in open air at room temperature. Therefore, the product must be stored under an argon atmosphere at low temperature (-20°C). Needle-like white crystals (acetone), yield 80%; ¹H-NMR (D₂O) δ 2.90 [s, 9H, (CH₃)₃—N⁺ (*p*)], δ 2.92 [s, 9H, (CH₃)₃—N⁺ (*m*)], δ 4.28 [s, 2H, CH₂—Ar (*p*)], δ 4.30 [s, 2H, CH₂—Ar (*m*)], δ 5.19–5.24 (d, 1H, $J_{\text{cis}} = 10.5$, HC=C—Ar), δ 5.71–5.78 (d, 1H, $J_{\text{trans}} = 17.7$, HC=C—Ar), δ 6.61–6.68 (dd, 1H, =CH—Ar), δ 7.25–7.51 (m, 4H, Ar). The product was characterized by ¹H-NMR as a 2 : 1 mixture of *m*- and *p*-TMVBAC.

Emulsifier-Free Emulsion Polymerizations

The experiments performed for synthesizing the "basic" polymer colloid will now be presented. First, the synthesis of cationic, potentially crosslinked, latices with or without the use of TMVBAC as cationic comonomer is described. After this the seeded experiments with divinylbenzene (DVB) and the graft polymerization performed on these latices with vinylbenzyl chloride (VBC) are described.

All experiments were carried out under argon in a jacketed all-glass reactor (1 L), thermostated at $70 \pm 0.5^\circ\text{C}$ (for the grafting of VBC at $25 \pm 0.5^\circ\text{C}$) and equipped with a mechanical six-bladed turbine stirrer. The stirring speed was kept at 200 rpm. Before polymerization, the reaction mixture was degassed and purged with argon three times. The polymerizations were stopped after 24 h and the products were filtered through a filter paper. The solids content (SC) during and after the reaction was determined gravimetrically.

Emulsifier-Free Emulsion Polymerization without Ionic Comonomer

Styrene (50 g) was polymerized in 450 mL of a water/methanol mixture (2 : 1) in absence of a surfactant. AIBA · 2HCl was used as initiator, at $8.194 \text{ mmol L}^{-1}$. Note that the latex prepared in this experiment (L0) was used as a reference polymer colloid. The reaction was carried out under semibatch conditions. The amount of styrene monomer was added dropwise to the reactor over a period of 4 h. (Note: Chonde and Krieger⁷ studied the effect of methanol addition on the emulsifier-free emulsion polymerization of styrene with an ionic comonomer. They suggested that the presence of methanol increases the solubility of styrene and growing oligomeric radicals decreases the dielectric constant of the medium and changes the decomposition rate of the initiator.)

Emulsifier-Free Emulsion Polymerization with Ionic Comonomer (TMVBAC)

The basic recipe for the surfactant-free emulsion polymerizations carried out with a varying amount of DVB under batch conditions, is given in Table I (i.e., DVB/styrene ratios by weight: L1-A 0; L1-B 0.01; L1-C 0.43).

Seeded Polymerization with a Commercial Divinylbenzene Mixture

The recipes for seeded emulsion polymerization of DVB were based on the parameters listed in Table II.

Table I Recipe for the Emulsifier-Free Emulsion Polymerization of Styrene with TMVBAC as Ionic Comonomer and Variable Amounts of DVB (i.e., L1-A, L1-B and L1-C)^a

Component	Amount
Styrene	49.65 - x g
DVB	x g
TMVBAC	0.35 g
AIBA · 2HCl	2.049 mmol L ^{-1b}
Water	0.450 L

^a L1-A, $x = 0$ g; L1-B, $x = 0.50$ g; L1-C, $x = 14.96$ g.

^b Concentration is based on the volume of the amount of water used at room temperature.

The seed latex, DVB, and TMVBAC were added to the major part of the water in a laboratory bottle (1 L) and this was purged with argon. After the bottle had been sealed tightly with a Teflon screw cap and Teflon sealing tape, the seed latex was allowed to swell for 24 h, while shaking the mixture. In order to suppress spontaneous polymerization of the DVB monomer while swelling, a small amount of the inhibitor was maintained and the swelling procedure was carried out at room temperature. After this the reaction mixture was poured into the reactor. The experiment was continued following the general procedures of a seeded, batch emulsion polymerization experiment.

Graft Polymerization with Vinylbenzyl Chloride

The graft polymerizations were carried out at 25°C , by using a redox-initiator system with sodium formaldehyde sulfoxylate (SFS) as reducing agent, Feⁿ⁺(EDTA) complex as mediator with EDTA as a sequestering agent, and cumene hydroperoxide (CHP) as oxidizing agent. The SFS/Feⁿ⁺(EDTA) complex/CHP redox-initiator system used is based on the parameters listed in Table III. The graft re-

Table II Recipe Parameters for the Seeded Emulsion Polymerization of DVB in Absence of Surfactants (i.e., L2)

Parameter	Value
Monomer/polymer ratio	0.80 g g ⁻¹
TMVBAC/DVB ratio	0.02 g g ⁻¹
Final solids content	3.60 wt %
AIBA · 2HCl	1.881 mmol L ^{-1a}
Water (total amount)	0.490 L

^a Concentration is based on the total volume of the reaction medium at room temperature.

Table III Recipe Parameters for the SFS/Feⁿ⁺ (EDTA) Complex/CHP Redox-Initiator System

Parameter	Value
SFS/VBC ratio	2.51 mmol mol ⁻¹
Fe ⁿ⁺ /VBC ratio	54.9 μmol mol ⁻¹
EDTA/VBC ratio	54.9 μmol mol ⁻¹
CHP/VBC ratio	2.51 mmol mol ⁻¹

actions were carried out with a variable monomer/polymer ratio [i.e., M/P = 0.2; 0.85 (L3); 1.6] and a total solids content (SC) after reaction of ca. 2–3 wt %. The amount of the cationic comonomer TMVBAC was 1 wt % of the amount of VBC. The seed latices with pendant vinyl groups were purified by ultrafiltration prior to use, in order to reduce the ionic strength of the aqueous phase, so that any possible coagulation of the latices upon addition of the graft components (compression of the double layer due to enhancement of ionic strength) was excluded.

The amounts of seed latex, CHP, TMVBAC, and VBC were added to the major part of the water in a laboratory bottle (1 L). The swelling procedure described above for the seeded experiments with DVB was followed, with the exception that the mixture was now tumbled end-over-end instead of shaken (because of the density of VBC). After this the reaction mixture was poured into the reactor. The experiment was continued following the general procedures of a seeded, batch emulsion polymerization experiment. Note that aqueous solutions of SFS and the Feⁿ⁺(EDTA) complex (acidic) were injected into the reactor in order to activate the redox-initiator system.

Amination of Latices

The chloromethyl groups, present in the latices (i.e., L3), were treated with a 10-fold molar excess of trimethylamine (TMA), calculated from the added amount of VBC monomer in the graft polymerization.

The required amount of an aqueous solution of TMA was added to the latex in a round-bottomed flask. The flask was tightly sealed with a stopper and parafilm. The reaction mixture was shaken for several minutes after which the system was allowed to stand for 48 h at room temperature. Afterward, the excess of TMA was removed by purging the polymer latex with argon. The solids contents of the aminated latices were determined gravimetrically.

Sample Purification Method for Solid-State Characterization Techniques

A sufficient amount of the latex sample was ultracentrifugated using a Centrikon T-2060 ultracentrifuge in order to separate the latex particles from the aqueous phase. The supernatant was removed and the precipitated polymer was redispersed in a good solvent for the residual monomer component (solids content of 1–3 wt %). For the poly(styrene-divinylbenzene) latices ethanol was used. After graft polymerization with VBC acetone was applied, which meets the additional requirement of being a solvent for poly(vinylbenzyl chloride). After reacting the chloromethyl groups with trimethylamine, water was used to redisperse the polymer colloids. The dispersion was allowed to stand for 24 h, after which it was ultracentrifugated again. Next the polymer was redispersed in water and the latex was again allowed to stand for 24 h. Finally, the latex was freeze-dried using a Hetosicc freeze dryer.

The supernatant of the latex samples was tested for polymer occurrence by UV analysis [the presence of water-soluble polycationic polymer was determined upon addition of CoPc(NaSO₃)₄ (cobalt titration) as reported by van Welzen et al.⁸]. The UV/VIS spectrophotometric measurements were performed on a Hewlett Packard 8451 A diode array spectrophotometer using 1.000 cm quartz cuvettes. The cells were kept in a thermostat at 25.0 ± 0.5 °C.

The amount of residual monomer of a latex sample was determined by HPLC analysis (Waters equipment). Purification procedures were continued until all tests showed a negative result. Aqueous solutions were additionally checked on conductivity.

Fourier Transformed Infrared Spectroscopy (FTIR)

The FTIR spectra were recorded on a Mattson Polarix FTIR spectrometer with KBr pellets at a resolution of 1.0 cm⁻¹. In order to determine, quantitatively, the composition of the poly(styrene-DVB) latex samples, the IR spectra were interpreted as reported by Bartholin et al.⁹

Carbon-13 Solid-State Nuclear Magnetic Resonance Spectroscopy

¹³C CP-MAS spectra were recorded on a Bruker MSL 400 NMR spectrometer. ¹³C CP-MAS (effective 90° proton pulse length 7 μs, contact time 500 μs, acquisition time 8 ms, rotation speed 5 kHz, repetition time 5 s) δ 40–41 (polymer backbone), δ 46–47 (benzylic Ar—CH₂Cl), δ 53–54 [methyl

—N⁺(CH₃)₃], δ 69 (benzylic Ar—CH₂—N⁺), δ 127–128 (monosubstituted phenyl ring), δ 138 (disubstituted phenyl ring), δ 146–148 (pendant vinyl groups).

Transmission Electron Microscopy (TEM)

The TEM pictures were recorded on a Joel 2000-FX transmission electron microscope. The average particle sizes and the polydispersity (PD) of the latex as well as the particle morphology were determined using TEM pictures (L1-A: $D_n = 114$ nm, PD = 1.016); (L1-B: $D_n = 102$ nm, PD = 1.017); (L2: $D_n = 107$ nm, PD = 1.021); (L0: $D_n = 269$ nm, PD = 1.017); (L1-C: PD \gg 1.05).

Conductometric Titrations

The surface charge (N_c) and the surface charge density (σ_c) of diluted and purified latex samples (SC 1 wt %), were determined by conductometric titration under argon with a standard 0.01N HCl solution using a Metrohm dosimat and conductometer ($c = 0.80$ cm⁻¹, freq. = 2 kHz), equipped with a magnetic stirring bar. During the titration, the conductivity of the sample was monitored and the critical point was obtained by calculating the intersection point of two straight lines, obtained by linear regression. The titration of each sample was performed twice.

The latex samples were extensively purified by ultrafiltration and mixed bed ion-exchange techniques before analysis. The latex samples as well as the supernatant of the ultrafiltration process were tested for purity, as described above.

RESULTS AND DISCUSSION

The first step in the preparation of the desired polymer colloid is the synthesis of a crosslinked, monodisperse seed latex with pendant vinyl groups in order to obtain the core of the ultimate polymer colloid having a well-defined, permanent shape and to provide the seed latex with a sufficient number of reactive sites for graft polymerization (the pendant vinyl groups).

Emulsifier-Free Emulsion Polymerization with Ionic Comonomer (TMVBAC)

The easiest method for preparing the seed latex without the use of surfactants would be polymerizing styrene and a commercial divinylbenzene (DVB)

mixture in a single step under batch conditions with 2,2'-azobis(2-amidinopropane) hydrochloride (AIBA · 2HCl) as initiator. The synthesized TMVBAC was used as a cationic comonomer in order to enhance colloidal stability.

Therefore, several polymerizations were performed with a constant TMVBAC/(DVB–styrene) ratio and a varying DVB/styrene ratio in the polymer recipe (i.e., DVB/styrene ratios by weight: L1-A 0; L1-B 0.01; L1-C 0.43; see Table I for a standard recipe). The conversion–time plots of the emulsifier-free emulsion polymerizations are depicted in Figure 1. The overall rates of polymerization of latex samples L1-A and L1-B are similar. After 3 h most of the monomer was polymerized (conversion over 96%), no coagulum was observed, and the synthesized latex particles were spherically shaped with a nearly smooth particle surface (see Fig. 2) and a monodisperse particle size distribution. The introduction of a small amount of DVB in the polymer recipe (L1-B) leads to a reduction of the average particle size (i.e., L1-A: $D_n = 114$ nm; L1-B: $D_n = 102$ nm). This was caused by an increase in the particle number, as a result of the enhanced possibility for

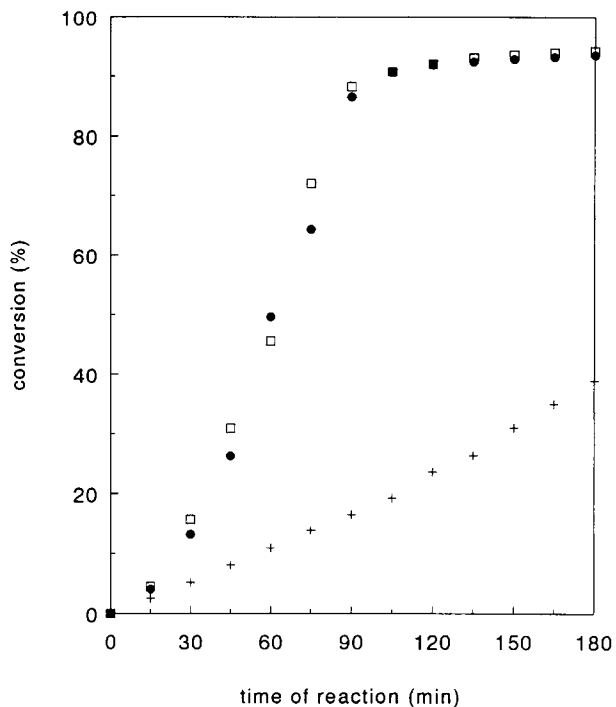


Figure 1 Monomer conversion versus time of reaction for (□) L1-A, (●) L1-B, and (+) L1-C. Emulsifier-free emulsion polymerizations with a constant TMVBAC/(DVB–styrene) ratio and a varying DVB/styrene ratio in the polymer recipe (see Table I: DVB/styrene ratios by weight: L1-A 0; L1-B 0.01; L1-C 0.43).

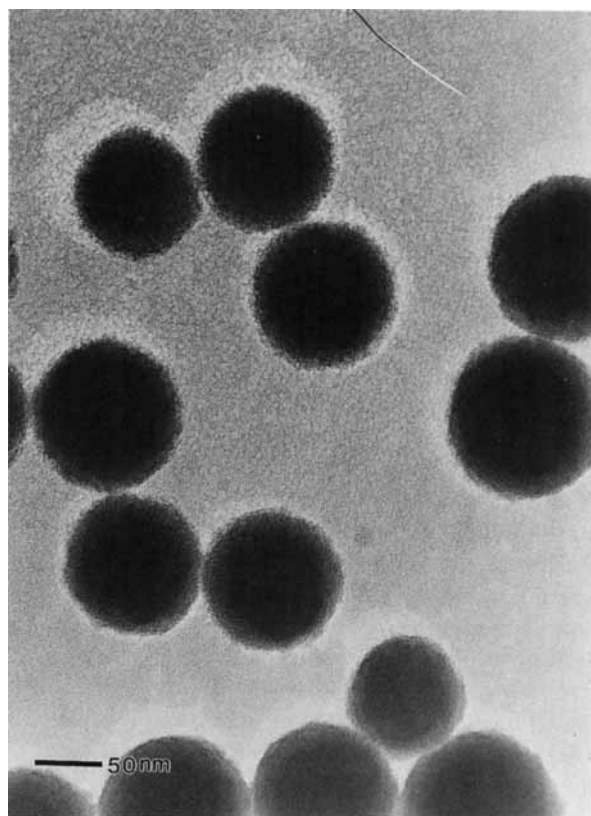


Figure 2 TEM picture of a polystyrene seed crosslinked with a small amount of divinylbenzene (L1-B). The latex is monodisperse ($D_n = 102$ nm; PD = 1.017). The particles are spherically shaped with a nearly smooth particle surface.

precursor particles to grow through propagation, rather than to coagulate with other precursors. This increase in the number of particles would result in a higher rate of polymerization for L1-B compared to L1-A. However, the smaller amount of monomer imbibed in the slightly crosslinked latex particles compensated this effect and, therefore, similar overall rates of polymerization were observed.

In order to provide a sufficient number of reactive pendant vinyl groups, a high fraction of the divinylbenzene mixture is preferred. This decreases the swellability of the precursor particles, due to an increase of the crosslinking degree of these precursors. An increase in the rate of polymerization would be observed, due to an earlier onset of the Trommsdorff effect and the higher number of precursor particles. However, the smaller amount of monomer imbibed creates monomer-starved conditions in the particles, resulting in a decreasing rate of polymerization. This latter effect dominates, as can be observed in Figure 1 for latex L1-C with a DVB/styrene ratio of 0.43.¹⁰

The high DVB/styrene ratio led to incomplete conversion and formation of small amounts of coagulum. A broad particle size distribution, consisting of very small particles (< 100 nm) and larger agglomerated particles, was obtained. This can be ascribed to irreversible agglomeration and polymerization of monomer droplets, as reported by Funke et al.^{10,11} Note that enlarging the amount of ionic comonomer in the polymerization recipe may suppress the intermolecular reaction, but broad particle size distributions will be obtained due to a dual particle nucleation mechanism.¹²

When using a small fraction of commercial divinylbenzene (DVB) in the polymerization recipe, the remainder of pendant vinyl groups is very low and, therefore, these particles are not suitable for the grafting process. No residual double bonds were observed in the poly(styrene-DVB) latex L1-B by IR analysis. Characterization of latex L1-C by IR analysis showed that approximately 25% of the *m,p*-divinylbenzene content in the polymer colloid had a remaining vinyl group after polymerization ($x_{c=c}$). However, this latex was not suitable for further synthesis, because of its moderate colloidal stability (coagulation upon storage and after addition of small amounts of electrolytes, e.g., NaCl, was observed) and its broad particle size distribution.

Seeded Polymerization with Divinylbenzene

The obvious alternative to evade most difficulties is to polymerize under seeded conditions. Monodisperse polystyrene particles prepared by surfactant-free emulsion polymerization (i.e., L1-B), conceivably slightly crosslinked by using a small fraction of divinylbenzene, served as a seed latex and were swollen with a certain amount of the commercial divinylbenzene mixture. The presence of monomer droplets is avoided, by keeping the monomer/polymer swelling ratio below its maximum value, and therefore polymerization will start in interval III of the emulsifier-free emulsion polymerization. In the seeded experiments performed (i.e. L2; recipe parameters are given in Table II) limited conversions were observed. An explanation for this is that instantaneously, a polymer network was formed. An early onset of the Trommsdorff, or gel, effect was the result, causing a rapid polymerization of the DVB monomer imbibed in the seed particle. However, the network formation rapidly reduced the relative diffusion rate of the monomer to the sites of radical reaction, and outweighed the suppression of biradical termination by the gel effect. This resulted

in a reduction in rate of the emulsion polymerization, already at moderate conversions.

The latices obtained from the seeded experiments were monodisperse and the particles were in all cases spherically shaped. However, the particle surface was not smooth, but slightly cockled, as shown in Figure 3. This can be explained by assuming the formation of very small, but distinctly separated domains, due to the high crosslink density.¹³ The results of the IR analysis of latex L2 are presented in Table IV. From these results it is easy to calculate that the fraction of divinylbenzene (65 wt % of the commercial mixture) from which only one group has reacted ($x_{c=c}$) has a value of 0.402. Note that composition drift during the polymerization has not been taken into account. The overall conversion of the monomer mixture calculated from these results has a value of 49.3%. However, from the gravimetric analysis a conversion of 81.2% was obtained. The accuracy of this result can be doubted because the samples (provided with a small amount of hydro-

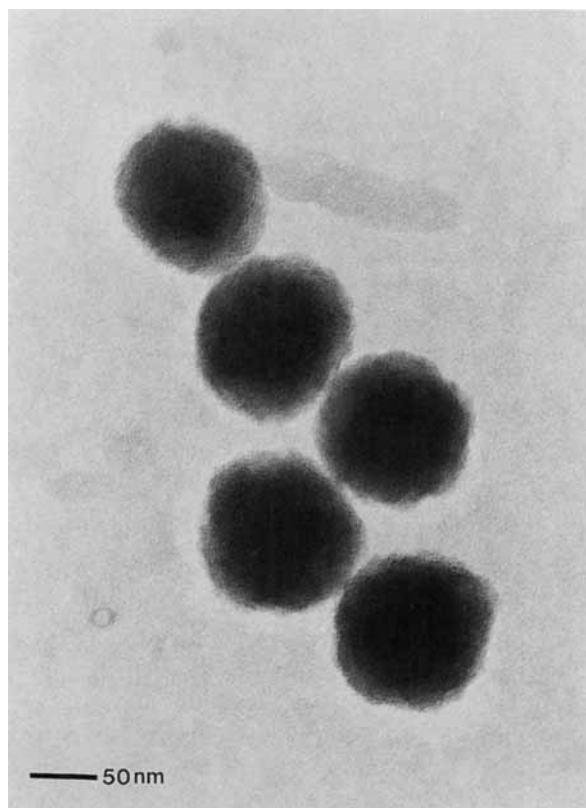


Figure 3 TEM picture of the polymer colloid after seeded polymerization with the commercial divinylbenzene mixture (L2). The latex is monodisperse ($D_n = 107$ nm; PD = 1.021). The particles are spherically shaped with a slightly cockled particle surface.

Table IV Results from FTIR Analysis of Latex Sample L2

Component	Amount (meq g ⁻¹)
IR results	
Pendant vinyl group	0.59
Polymerized DVB/EVB	2.26
Polymerized styrene	6.72
Theory ^a	
Polymerized DVB/EVB	3.53
Polymerized styrene	5.17

^a Calculated from the actual polymerization recipe at 100% conversion.

quinone) were air dried at 50°C for 24 h. After this period there is still a substantial amount of the divinylbenzene monomer present in the samples. This residual amount may be removed by increasing the drying temperature (the temperature must, preferably, be higher than the glass-transition temperature of the polymer sample; in this case, taken into account the formation of the polymer network, $T > 130^\circ\text{C}$). However, at these elevated temperatures, side reactions, such as Diels-Alder cycloadditions followed by molecular assisted homolysis of the intermediate, cannot be excluded.

The large difference in the fraction divinylbenzene from which only one vinyl group has reacted ($x_{c=c}$), between the seeded experiments (i.e., L2; $x_{c=c} = 0.402$) and the single step polymerization L1-C ($x_{c=c} = 0.246$), can be explained by several facts. First, in the seeded experiments all the monomer is imbibed in the particle. Therefore the concentration of the second double bond from DVB units already polymerized once is small in the initial stage of the polymerization process, when compared to the concentration of "free" DVB monomeric vinyl groups. Moreover, this is enhanced by the validity of the difference in intrinsic reactivities of the vinyl groups at the beginning of the polymerization. The consumption of the second double bond, therefore, is smaller, when compared to its consumption in a single step polymerization under batch conditions, as has been reported by Guyot.¹⁴ Also, network formation with a higher crosslinking density in the seeded experiments resulted in an increase in viscosity and steric hindrance. Thus, the second double bond was not in reach for the growing polymer radical and has remained intact. Both of these effects result in a larger fraction of singly reacted DVB in the polymers obtained in the seeded experiments.

However, the formation of a network with a high crosslinking density in the seeded experiments gave

rise to an earlier onset of the Trommsdorff, or gel, effect resulting in both suppression of bimolecular termination and longer diffusion times for the monomer to the reaction loci, when compared with the single-step styrene-DVB polymerization. This favors the consumption of the second double bond and, therefore, a smaller fraction of singly reacted DVB under seeded conditions can be expected.

From the IR results it can be concluded that the two effects with a positive contribution outweigh the Trommsdorff effect and, therefore, a higher fraction of singly reacted DVB ($x_{c=c}$) was observed when polymerizing under seeded conditions (i.e., L2) than in the single step emulsifier-free emulsion polymerization of a styrene-DVB-TMVBAC mixture (i.e., L1-C).

The latices obtained from the seeded experiments with DVB had well-defined particle morphologies and were provided with a sufficient number of pendant vinyl groups. Therefore, these latices are suitable for graft polymerization of VBC, despite the fact that a considerable amount of the residual double bonds present in the latices cannot serve as reactive sites for grafting because of the shielding effect, caused by both steric hindrance and high viscosity in the inner regions of the polymer network.

Graft Polymerization with Vinylbenzyl Chloride

The emulsifier-free graft polymerizations of the functional monomer, *m,p*-vinylbenzyl chloride (VBC), onto the styrene-DVB seed latices (i.e., L2) were performed at ambient temperature, in order to restrict possible side reactions (i.e., hydrolysis, and hydrogen and/or chlorine abstraction). The redox-initiator system SFS/Feⁿ⁺(EDTA) complex/CHP was used as initiator.

Under the experimental conditions, the vinylbenzyl chloride (VBC) monomer and the cumene hydroperoxide (CHP) are both imbibed in the seed particle. The remaining two components of the redox-initiator system are mainly present in the aqueous phase. It is assumed that radical decomposition of the CHP takes place near the surface of the particle, almost immediately followed by radical entry. However, due to the highly crosslinked nature of the seed particle, the mobility of the radical was restricted, resulting in an enhanced average time, required for the growing radical to diffuse to the interior of the particle. The high viscosity and steric hindrance inside the particle, as well as the anchoring of the growing radical by polymerizing with a pendant vinyl group, "excluded" reaction loci in the

inner regions. Therefore, polymerization took place mainly in the shell region of the latex particle.

The particles obtained from the graft polymerization of VBC were nonspherical, consisting of a well-defined, monodisperse core with a spherical shape, whose size was about the same as the size of the original seed latex particles, and a sharp cockled shell of grafted VBC (see Fig. 4). This particle morphology can be explained by assuming the occurrence of shell polymerization and phase separation. The formation of separate domains of poly(vinylbenzyl chloride) can be ascribed to several parameters of the specific polymer system. It was confirmed from a series of experiments varying the monomer/polymer ratio that higher monomer/polymer swelling ratios favor the nucleation of new phase domains. The multiphase domains observed in TEM pictures of L3 can be ascribed to the high crosslinking degree of the seed particles.

The characteristic IR bands for the chloromethyl group are at 1266 and 707 cm⁻¹. The IR spectra of

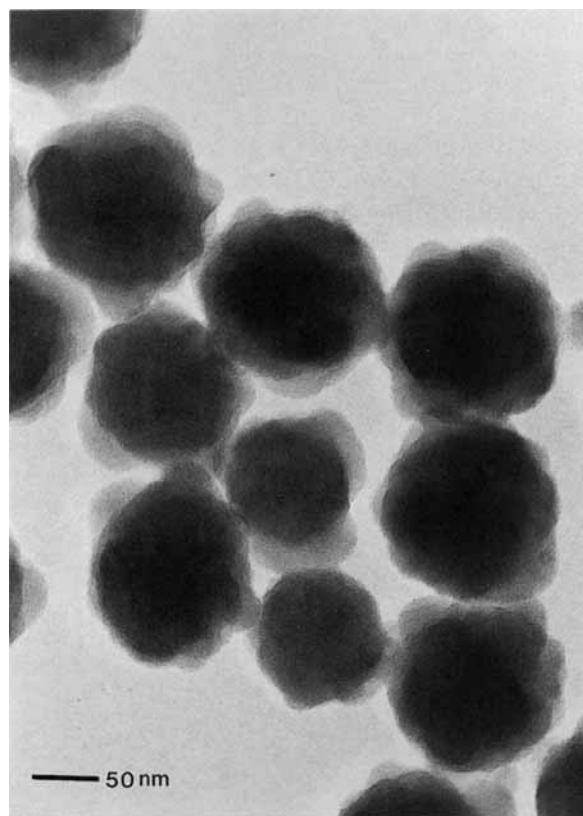


Figure 4 TEM picture of the polymer colloid after graft polymerization with vinylbenzyl chloride (L3). The particles are nonspherical, consisting of a well-defined, monodisperse core with a spherical shape, whose size is about the same size of the original seed latex particles (see Fig. 3; L2), and a sharply cockled shell of grafted VBC.

the VBC grafted latices showed a very clear band at 1266 cm^{-1} . The band at 707 cm^{-1} was difficult to track because of the occurrence of superposition. Absence of the 1010 cm^{-1} band indicated that hydrolysis of the chloromethyl groups could be neglected.

The amount of VBC grafted onto the seed could only be interpreted qualitatively by both IR analysis and ^{13}C CP-MAS measurements. The accuracy of the IR method using the ratio of the 1266 cm^{-1} C—Cl stretching band to the aromatic band at 1452 cm^{-1} , as reported by Revillon et al.,¹⁵ can be doubted in this case, because of broadening of the 1452 cm^{-1} band, due to the presence of both mono- and disubstituted phenyl rings in the IR sample, making it inadequate for precise quantitative determinations. Note that side reactions, such as crosslinking by radical transfer and hydrolysis, should also be taken into account in the determination of the content of chloromethyl groups.

The graft polymerization should have resulted in a decreased concentration of vinylic double bonds present in the polymer colloid (meq g^{-1}), as a result of dilution as well as reaction. However, comparison of the IR spectra of samples after graft polymerization (i.e., L3) with the spectra of samples from the seed latices (i.e., L2), showed that the relative intensities of the bands assigned to the pendant vinyl groups approximately remained the same.

This can be explained by the large amount of pendant vinyl groups in the seed latices. The ratio of vinyl groups in the polymer seed to the vinyl groups from the VBC monomer was large. A considerable fraction of the pendant vinyl groups could not have served as active sites for graft polymerization, due to the shielding effect. Moreover, the relative intrinsic reactivity of the pendant vinyl groups was smaller and, therefore, a large amount of residual double bonds in the polymer seed remained unreacted.^{16,17} Beside this, chain transfer reactions, induced by the presence of Fe^{n+} , could possibly have introduced new vinyl groups (from VBC monomer). Thus, a decrease in residual double bonds upon grafting would not be observed.

Several attempts to synthesize noncrosslinked poly(vinylbenzyl chloride) by emulsifier-free emulsion polymerization under batch conditions, in order to provide a reference latex, failed. Polymerizing at 70°C resulted in a nonsoluble crosslinked polymer with a considerable degree of hydrolysis of the chloromethyl group. Polymerizing at ambient temperatures, using the SFS/ Fe^{n+} (EDTA) complex/CHP redox-initiator system to suppress both side reactions still resulted in a nonsoluble polymer. It can

be postulated that the presence of Fe^{n+} accelerates side reactions (homolytical bond cleavage and one electron transfer), resulting in crosslinking (i.e., hydrogen and chlorine abstraction).

Amination

The final polymer colloid was obtained after amination of the chloromethyl groups of the polymer particle, grafted with vinylbenzyl chloride (VBC), using a tenfold excess of trimethylamine (TMA).¹⁸⁻²⁰

The aminated particles had a well-defined, monodisperse and spherical shaped core, which stemmed from styrene-divinylbenzene, surrounded by a grafted layer of poly[trimethyl(vinylbenzyl)ammonium salt] (see Fig. 5). The IR spectra of the aminated latices showed a total disappearance of the 1266 cm^{-1} band ($\mu_{\text{C-Cl}}$). This suggests a nearly complete conversion of the chloromethyl groups to quaternary ammonium salts. Due to superposition,

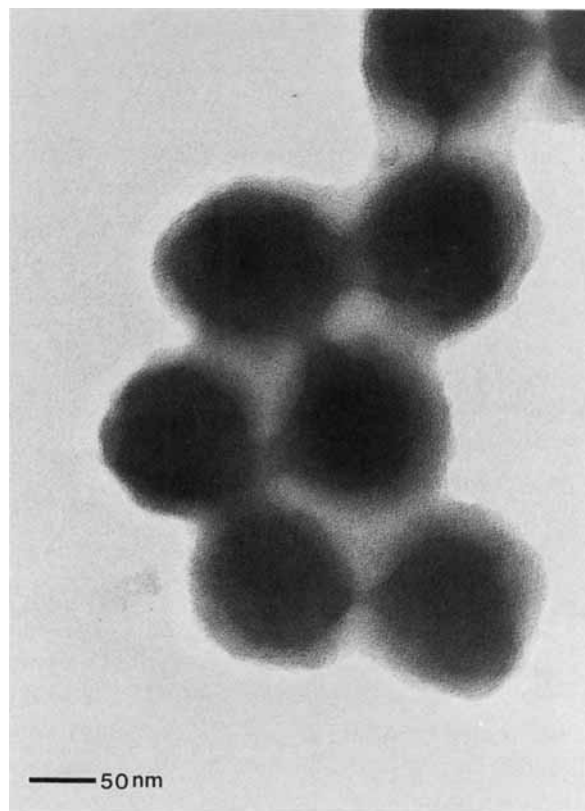


Figure 5 TEM picture of the polymer colloid after amination with trimethylamine (L4). The aminated latex particles have a well-defined, monodisperse and spherical shaped core, which stemmed from styrene-divinylbenzene, surrounded by a grafted layer of poly[trimethyl(vinylbenzyl)ammonium salt].

Table V The Surface Charge (N_c) and the Surface Charge Density (σ_c) Calculated from the Conductometric Titration Results

Latex Sample	N_c (meq g ⁻¹)	σ_c ($\mu\text{C cm}^{-2}$)
L4 ^a	1.14	219
L3 ^b	0.045	8.64
L0 ^c	1.89	8.66

^a For D_n the particle size of the core is taken, $D_n = 107$ nm; estimated $\rho_p = 1.12$ g cm⁻³.

^b $D_n = 107$ nm; estimated $\rho_p = 1.12$ g cm⁻³.

^c $D_n = 269$ nm; estimated $\rho_p = 1.06$ g cm⁻³.

probably caused by the hygroscopic character of the product, the appearance of the 3400 cm⁻¹ band corresponding to the quaternary ammonium salt could not be observed. ¹³C CP-MAS measurements showed similar results. A total disappearance of the peak assigned to the benzylic carbon atoms with a chlorine substituent at δ 46–47 ppm was observed. Both the peak at δ 69 ppm, from the benzylic atoms with an ammonium substituent, and the peak at δ 53–54 ppm, assigned to the carbon atoms from the methyl groups, were observed.

The results from the conductometric titrations performed on latices L0, L3, and L4 are presented in Table V. When both the surface charge (N_c) and the surface charge density (σ_c) are compared with the results of similar titrations performed on the latex before amination (L3) as well as on a monodisperse, cationic latex prepared by emulsifier-free emulsion polymerization of styrene with AIBA · 2HCl as initiator under semibatch conditions and the use of methanol as cosolvent (L0), they show that a considerable amount of N⁺ was present on the final polymer colloid (L4).

Now the amount of grafted VBC in the previous step of the synthesis can be calculated, assuming that

- The amount of N⁺ from the AIBA · 2HCl initiator fragments and TMVBAC comonomer, used in the total synthesis of the final polymer colloid, can be neglected.
- The side reactions of VBC (i.e., hydrolysis and crosslinking) can be neglected.
- Complete amination of the chloromethyl groups had occurred.
- No quaternary ammonium groups are present in the inner regions of the particle.

Under these assumptions, the composition of the polymer colloids consisting of a shell of poly-

(vinylbenzyl chloride) grafted onto a well-defined, monodisperse poly(styrene–divinylbenzene) core, can be calculated. The results are represented in Table VI. From these results it is easy to calculate that the actual amount of VBC that is grafted onto the styrene–DVB seed particle, is ca. 27% of the amount introduced in the polymer recipe (under the assumptions made above).

CONCLUSIONS

A method was developed to synthesize *m,p*-trimethyl(vinylbenzyl)ammonium chloride (TMVBAC) in high yields (80%). The product was very hygroscopic and liable to spontaneous polymerization, when allowed to stand in open air at room temperature.

Single step emulsifier-free emulsion (co)polymerization of a styrene–DVB monomer mixture, with the use of TMVBAC as cationic comonomer, under batch conditions, resulted in monodisperse latices with a neglectable amount of pendant vinyl groups, at low DVB/styrene ratios. A higher DVB/styrene ratio in the polymer recipe increased the amount of residual double bonds, however, latices with only moderate colloidal stability and broad particle size distributions were obtained.

From the emulsifier-free seeded experiments with DVB, using a monodisperse, cationic crosslinked seed latex, monodisperse “network-containing” latices with a considerable amount of residual vinyl groups were obtained (40% of the divinylbenzene molecules that polymerized reacted once).

In the graft experiments, shell polymerization of the VBC monomer occurred, as a result of the high viscosity and steric hindrance inside the crosslinked seed particles.

Table VI The Composition of the VBC Grafted Polymer Colloids (L3)

Component	Amount (meq g ⁻¹)
Conductometric titration results	
Polymerized VBC	1.22
Polymerized DVB/EVB	1.84
Polymerized styrene	5.47
Theory	
Polymerized VBC	2.99
Polymerized DVB/EVB	1.23
Polymerized styrene	3.65

^a Calculated from the actual polymerization recipe at 100% conversion.

Multiphase domains of poly(vinylbenzyl chloride) were formed, because of the presence of the polymer network.

Hydrolysis of the chloromethyl groups was not observed. However, the presence of the Fe^{n+} (EDTA) complex appears to result in cross-linking of the grafted shell and, possibly, in the introduction of "new" pendant vinyl groups (from the VBC monomer).

Complete conversion of the chloromethyl groups by amination with TMA was obtained.

The final, modified, latex particles had well-defined monodisperse, spherically shaped cores, which stemmed from the styrene-DVB, surrounded by a grafted "shell" layer of poly[trimethyl(vinylbenzyl) ammonium salt].

The aminated polymer colloids had a very high surface charge (N_c) of 1.14 meq g^{-1} .

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