

## Emulsifier-free cationic latexes based on vinylbenzyl chloride and 2-(dimethylamino)ethyl methacrylate with adjusted hydrophilic–hydrophobic properties

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**ABSTRACT:** Functional emulsifier-free cationic latexes based on styrenic monomer vinylbenzyl chloride (VBC) and acrylic monomer 2-(dimethylamino)ethyl methacrylate (DMA) were successfully prepared with dual quaternary ammonium ions (36–63 mol %) on both monomer moieties in two-stages. First, [2-(methacryloyloxy)ethyl]dimethylhexadecylammonium bromide monomer (DMA(C<sub>16</sub>)), prepared via quaternization of DMA with 1-bromohexadecane, was utilized as a comonomer (5–20%) as well as a surfactant in the emulsion polymerization of VBC. Next, the quaternization of chloromethyl groups in the VBC moiety in latex particles with trimethylamine and *N,N*-dimethylhexadecylamine created a second type of quaternized sites on the latex particles. The percentages of the quaternary ammonium ions of the first-stage latexes (P[VBC-DMA(C<sub>16</sub>-x)]) and the second-stage latexes (P[VBC(R)-DMA(C<sub>16</sub>-x)]) were determined using bromide and chloride ion-selective electrodes. The particles were characterized with a scanning electron microscope, Zetasizer, measuring water contact angles of their pellets. The polymer structure and the alkyl group length in their quaternary ammonium ions played an important role on the sizes, zeta potentials and hydrophilic–hydrophobic balances of the latexes. The water contact angles of the pellets of the latex particles varied from 50.3 to 109.6° depending on both the polymer structure and the alkyl group length. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42775.

**KEYWORDS:** colloids; emulsion polymerization; functionalization of polymers; latexes; surfaces and interfaces

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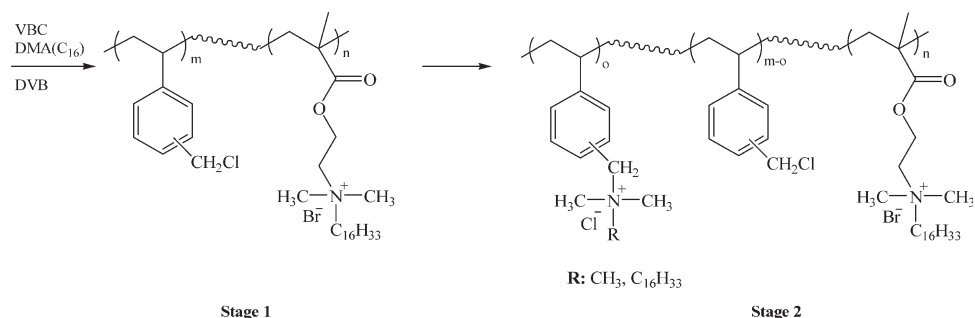
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### INTRODUCTION

Functional polymer latexes have become attractive materials due to their widespread use in both industrial and academic applications, such as catalysis, biotechnology, coating and thickeners, as well as in cosmetic and pharmaceutical areas.<sup>1,2</sup> The functional groups on the surfaces of latex particles play an extremely important role in the applicability of latexes. In preparations of functional polymer latexes, various approaches have been used to create certain functionalities on the particles and to adjust their surface properties. Of these, emulsifier-free emulsion polymerization with functional comonomers has many advantages, providing a facile way to obtain latex particles with specific surface functionalities, as well as clean and applicable surfaces.<sup>3–21</sup> In such preparations, various types of the comonomers in small quantities were added to the polymerization medium, while styrene was used mostly as a main monomer.

Some emulsifier-free emulsion polymerization studies aimed to prepare latexes for investigation of their hydrophobic–hydrophilic nature and surface properties and to consider them in applications where the hydrophobic–hydrophilic balance of the

surface is important. Non-ionic hydrophilic monomer 2-hydroxyethyl methacrylate was used in various amounts in the preparation of emulsifier-free polystyrene (PS) latexes of different hydrophilic–hydrophobic character.<sup>5</sup> Fluorinated surface active monomers and block-copolymer stabilizers were also effectively used to obtain more hydrophobic surfaces on PS latex films.<sup>12,22</sup> Poly(vinylbenzyl chloride) (PVBC) based quaternary ammonium ion containing latexes has been synthesized and used successfully as a catalyst support in the hydrolysis of certain organic phosphates.<sup>18–20</sup> The catalytic efficiency in the hydrolysis increased as the hydrophobicity of the PVBC latexes increased. The hydrophobicity of the latex particles was adjusted through the quaternization of chloromethyl groups in VBC moieties with alkyl dimethylamines in varying quantities. The alkyl groups in the tertiary amines were methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-hexadecyl. Aliphatic latex particles, based on alkyl methacrylates in the presence of a small amount of VBC, were also prepared and treated with trimethylamine and *n*-tributylamine.<sup>21</sup> These hydrophilic latexes were used in the hydrolysis of certain phenyl alkanoate compounds.



**Scheme 1.** Preparation of cationic latexes with dual quaternary ammonium ions.

Although studies have been carried out to control the hydrophilicity and hydrophobicity of the functional latexes and used them in various applications, the functionalities on these latexes were provided solely by one type functional group. It appears that there is a dearth of research on the ability of functional latexes to create multi-functionalities on particles, as well as to adjust their hydrophobic–hydrophilic balance. In this study, we aim to prepare functional emulsifier-free latexes based on styrenic monomer vinylbenzyl chloride (VBC) and acrylic monomer 2-(dimethylamino)ethyl methacrylate (DMA) with dual quaternary ammonium ions on both monomer moieties. [2-(Methacryloyloxy)ethyl]dimethylhexadecylammonium bromide monomer (DMA(C<sub>16</sub>)) prepared from DMA and 1-bromohexadecane was utilized as a comonomer (5–20%) as well as a surfactant in the emulsion polymerization of VBC. The hydrophilic–hydrophobic balances of the latex particles were further altered via quaternization of chloromethyl groups in the VBC moiety in the polymers with trimethylamine and *N,N*-dimethylhexadecylamine.

## EXPERIMENTAL

### Materials

DMA (from Merck), VBC (mixture of 3- and 4-isomers) (from Aldrich), divinylbenzene [DVB, 80% active, remaining is ethylvinylbenzene (EVB)] (from Fluka), 1-bromohexadecane (from Aldrich), trimethylamine (from Aldrich), *N,N*-dimethylhexadecylamine (from Fluka), and potassium persulfate (KPS) (from Merck) were purchased from different sources. Deionized water was used in all of the experiments.

[2-(Methacryloyloxy)ethyl]dimethylhexadecylammonium bromide (DMA(C<sub>16</sub>)) was synthesized from DMA and 1-bromohexadecane in accordance with the literature.<sup>23</sup>

### Preparation of Emulsifier-Free Latexes

Latexes with different DMA(C<sub>16</sub>) contents were prepared using conventional emulsifier-free emulsion polymerization of VBC and DMA(C<sub>16</sub>) according to the literature.<sup>6,7</sup> The monomer–water ratios were about 1 : 10 by mass in the polymerizations. A typical emulsifier-free emulsion polymerization procedure was as follows: Distilled water (50 mL) was poured into a 100 mL three-necked flask, stirred magnetically, and purged with nitrogen for 30 minutes. A mixture of the cationic monomer DMA(C<sub>16</sub>) (0.75 g; 1.62 mmol), VBC (4.25 g, 27.86 mmol), and cross linker DVB (0.26 g, contains 80 mol % of DVB) was added to the flask. While stirring at 600 rpm, the flask contents were heated to 60°C and then polymerization was initiated with

the addition of KPS (1% of total monomer, by mass). The polymerization continued for 24 hours under a nitrogen atmosphere. A latex product containing ca. 5 mol % DMA(C<sub>16</sub>) and 5 mol % DVB in the polymerization feed was coded as P[VBC-DMA(C<sub>16</sub>-5)]. Similarly, a 5.0% DVB cross-linked 10, 15, and 20 mol % DMA(C<sub>16</sub>) containing P[VBC-DMA(C<sub>16</sub>-10, -15, -20)] latexes was prepared.

Before quaternization of the chloromethyl groups of the P[VBC-DMA(C<sub>16</sub>-x)] (x = 5, 10, 15, and 20) latex particles with *N,N*-dimethylhexadecylamine, about 500 mg particles of each latex was recovered from their emulsions after ultrafiltration through 0.10 μm cellulose acetate/nitrate membranes. The particles were redispersed in THF and treated with stoichiometric amounts of *N,N*-dimethylhexadecylamine under reflux for 25 hours. The quaternized particles were then precipitated with 10 mL of acetone, filtered, washed with 10 mL of acetone and redispersed in distilled water. In the case of quaternization of latexes with trimethylamine, a similar procedure to the one described above was applied, except the reactions were carried out in water at 40°C for 18 hours. These VBC-quaternized latexes were coded as P[VBC(Me)-DMA(C<sub>16</sub>-5)], P[VBC(C<sub>16</sub>)-DMA(C<sub>16</sub>-5)], P[VBC(Me)-DMA(C<sub>16</sub>-10)], P[VBC(C<sub>16</sub>)-DMA(C<sub>16</sub>-10)], P[VBC(Me)-DMA(C<sub>16</sub>-15)], P[VBC(C<sub>16</sub>)-DMA(C<sub>16</sub>-15)], and P[VBC(C<sub>16</sub>)-DMA(C<sub>16</sub>-20)].

### Characterization of Latex Particles

The morphologies of the latex particles were examined by scanning electron microscope (SEM; Carl Zeiss ULTRA Plus). The hydrodynamic diameters of the particles were measured by dynamic light scattering using a Malvern Zetasizer Nano ZS. The same instrument with an MPT-2 autotitrator was used to measure the zeta potentials of the particles at different pH values. The water contact angles of the pellets from the latex particles were determined using a Krüss DSA 100 Drop Shape Analyzer. Polymer pellets were prepared from 100 mg of the latex particles dried under vacuum at 60°C for 3 days. The water contact angles were measured by adding a drop of distilled water (75 μL) to the surfaces of the pellets at room temperature. Measurements were repeated six times for each polymer pellet and an average angle value was reported.

### Characterization of Polymer Structures

Bromide (Mettler Toledo, DX280-Br Bromide half-cell) and chloride (Mettler Toledo, perfectION comb Cl, 51344706) ion-selective electrodes were used to determine the quaternary ammonium ion contents of the latex particles. The latexes were

directly titrated with  $\text{AgNO}_3(aq)$  without any separation process of the particles.<sup>24</sup> For titration, 1.0 mL of ionic strength adjuster and a certain amount of the P[VBC-DMA( $C_{16-x}$ )] latex containing 15 mg of polymer particles were put in a 100 mL beaker. The total latex volume was then topped up to 50 mL with deionized water. Next, the latex sample was titrated with 0.050 M  $\text{AgNO}_3(aq)$  after the pH was adjusted to 2.0 with  $\text{HNO}_3$  to allow the passage of bromide counterions in the polymers into an aqueous phase. The millimoles of bromide ion per gram of the latex particles were calculated from the volume of consumed  $\text{AgNO}_3(aq)$  required to precipitate the bromide ions as  $\text{AgBr}(s)$ . In this way, the mole percentages of the DMA( $C_{16}$ ) moieties, which are equal to those of the  $\text{Br}^-$  ions, were determined for the first-stage P[VBC-DMA( $C_{16-x}$ )] latexes.

Similarly, the amount of chloride counterions of (vinylbenzyl)alkyldimethyl ammonium ions in the P[VBC(Me)-DMA( $C_{16-x}$ )] and P[VBC( $C_{16}$ )-DMA( $C_{16-x}$ )] latexes was determined by titration with  $\text{AgNO}_3(aq)$ . The amount of silver ion reacting with the bromide ion was taken into consideration during the calculations of the millimoles of the chloride ion per gram of the latex particles. In this way, the mole percentages of (vinylbenzyl)alkyldimethyl ammonium ions, which are equal to those of  $\text{Cl}^-$  ions, were determined for the second-stage latex particles.

## RESULTS AND DISCUSSION

### The Synthesis of the Polymer Latexes

The polymer latexes with adjusted hydrophilic–hydrophobic properties were prepared in two-stages. In the first stage, the latexes were prepared with the monomers VBC, [2-(methacryloyloxy)ethyl]dimethylhexadecylammonium bromide (DMA( $C_{16}$ )) (5, 10, 15, and 20 mol %) and DVB (5 mol %) by emulsifier-free emulsion copolymerization. DVB forms cross-links and prevents the dissolution of the latex particles. In the second stage, the treatment of the first stage latex particles with trimethylamine and *N,N*-dimethylhexadecylamine partly converted the chloromethyl groups in the particles to corresponding (styrylmethyl)trimethylammonium chloride and (styrylmethyl)hexadecyldimethylammonium chloride ions. This two-stage procedure enabled us to obtain functional cationic latex particles containing two types of quaternary ammonium ions attached to styrenic and acrylic moieties of the polymers, containing different alkyl group combinations of methyl and *n*-hexadecyl, and *n*-hexadecyl and *n*-hexadecyl on them (Scheme 1). In addition, the quaternary ammonium ions on both moieties were of different quantities solely and relatively in the latex particles. Thus, interplaying with the relative moles of VBC and DMA( $C_{16}$ ), changing the quaternization agent trialkylamine for the quaternization of the VBC moiety and achieving different quaternization percentages of this moiety, affected the hydrophilic–hydrophobic features of the latexes. We also attempted to incorporate more than 20 mol % DMA( $C_{16}$ ) monomer in the latex particles. However, a gel type polymer instead of a latex formed when the polymerization recipe included 25 mol % DMA( $C_{16}$ ). We believe that the gel type polymer is a coagulum of the latex particles.

The entries 1–4 in Table I provide certain properties of the first-stage latexes. The incorporation percentages (6–18%) of

**Table I.** Certain Quantitative Properties of Latexes

Entries	Latex	$\text{Br}^-$ (mmol/g polymer)	$\text{Cl}^-$ (mmol/g polymer)	$\text{N}^+\text{R}_4\text{Br}^-$ (mol %)	$\text{N}^+\text{R}_4\text{Cl}^-$ (mol %)	$\text{N}^+\text{R}_4\text{X}^{\text{a}}$ (mol %)	Hydrodynamic diameter (nm)	Zeta potential <sup>b</sup> (mV)	Contact angle <sup>c</sup> (°)
1	P[VBC-DMA( $C_{16}$ -5)]	0.37		6		6	116	48.5	90.00 ± 0.53
2	P[VBC-DMA( $C_{16}$ -10)]	0.56		10		10	164	42.8	90.50 ± 0.34
3	P[VBC-DMA( $C_{16}$ -15)]	0.73		14		14	425	39.0	91.10 ± 1.14
4	P[VBC-DMA( $C_{16}$ -20)]	0.87		18		18	585	37.1	93.40 ± 0.90
5	P[VBC(Me)-DMA( $C_{16}$ -5)]	0.32 <sup>d</sup>	1.98		38	44	144	42.8	50.30 ± 0.86
6	P[VBC(Me)-DMA( $C_{16}$ -10)]	0.49 <sup>d</sup>	1.78		26	36	259	41.2	59.00 ± 0.60
7	P[VBC(Me)-DMA( $C_{16}$ -15)]	0.63 <sup>d</sup>	1.30		27	41	467	38.3	65.00 ± 0.83
8	P[VBC( $C_{16}$ )-DMA( $C_{16}$ -5)]	0.18 <sup>d</sup>	1.75		57	63	493	39.6	96.40 ± 0.77
9	P[VBC( $C_{16}$ )-DMA( $C_{16}$ -10)]	0.29 <sup>d</sup>	1.48		45	55	241	37.0	99.30 ± 0.98
10	P[VBC( $C_{16}$ )-DMA( $C_{16}$ -15)]	0.38 <sup>d</sup>	1.42		44	58	373	38.0	103.50 ± 1.75
11	P[VBC( $C_{16}$ )-DMA( $C_{16}$ -20)]	0.48 <sup>d</sup>	1.19		37	55	363	34.2	109.60 ± 0.43

<sup>a</sup>Total mole percentages of  $\text{N}^+\text{R}_4\text{Cl}^-$  ve  $\text{N}^+\text{R}_4\text{Br}^-$  in the latexes.

<sup>b</sup>Measured at pH 6.50.

<sup>c</sup>The uncertainties are the standard errors of the means.

<sup>d</sup>Calculated from the  $\text{Br}^-$  equivalent amounts in P[VBC-DMA( $C_{16-x}$ )] latexes.

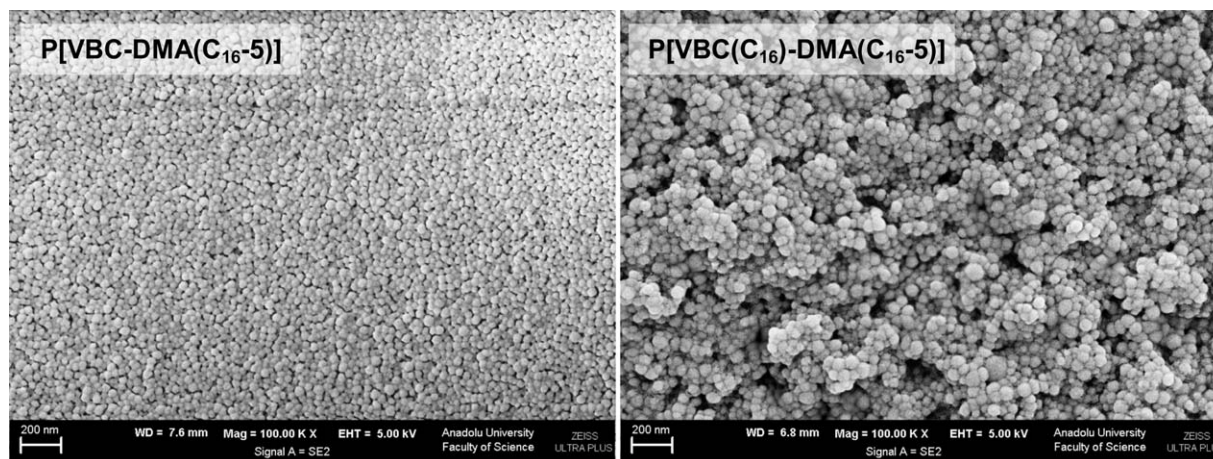


Figure 1. Examples of the SEM images of the functional latexes.

the DMA( $C_{16}$ ) monomer into the latex particles are very close to the polymerization feed percentages of this monomer. Aiming for two types of quaternary ammonium ion functionalities on the same latex particles, it appears that we succeeded in incorporating one of them in significant quantities. This also places our latexes in a position different to conventional emulsifier-free functional latexes reported in the literature. Conventional latexes usually contain a few percent and only one type of quaternary ammonium functionality. Generally, quaternary ammonium ions on the latexes reported in the literature come from polymerizable surfactants (cationic or anionic monomers) which are utilized to form micelles and to stabilize latex particles. In this respect, our first-stage latexes are different to these and contain as much as 18% quaternary ammonium ions (Table I). High quaternary ammonium percentages of the latexes enable them to have high functional group density, a high anion exchange capacity, a high binding capacity, and so on; all which may be important in certain applications.

The SEM micrographs of our first-stage latexes show that the particles are of spherical shape (Figure 1) (left). An increase in the percentages of the DMA( $C_{16}$ ) moiety in the particles results in an increase in their hydrodynamic diameters (entries 1–4, Table I), a decrease in their zeta potentials (Figure 2) and an increase in their contact angles. Because the DMA( $C_{16}$ ) is a highly hydrophobic monomer and its concentration in the polymerization feeds is extremely high (much higher than its CMC ( $1.0 \times 10^{-3}$  M)<sup>23</sup>), we believe that a micellar nucleation mechanism, rather than homogenous nucleation and monomer droplet nucleation mechanisms, may have been substantially involved in our preparations.<sup>25</sup> It is well established that the diameter of latex particles decreases when the concentration of cationic monomer increases in the conventional emulsifier-free emulsion polymerization, and the polymerization proceeds inside monomer-swollen particles via droplet nucleation mechanism.<sup>13</sup> As the concentration of cationic monomer gets higher, more stabilized particles form and this leads to smaller diameters in the final polymer particles.<sup>6</sup> However, when the concentration of cationic monomer is too high, micellar nucleation becomes the dominant mechanism<sup>13</sup> and the diameter of the latex particles increases with an increase in the concentra-

tion of the cationic monomer. This type of behavior is reported when 1-ethyl-2-methyl-5-vinylpyridinium bromide,<sup>14</sup> [2-(methacryloyloxy)ethyl]trimethylammonium chloride,<sup>11</sup> a cationic monomer of *N,N*-dimethylaminoethyl methacrylate quaternized with epichlorohydrin,<sup>17</sup> and 3-[2-(acryloyloxy)ethoxy]-3-oxopropyl(phenyl)phosphinic sodium<sup>26</sup> are used as monomers in high concentrations. Our findings for an increase in the diameters of the latex particles agree with findings in the literature for the preparation of latexes with high concentrations of cationic monomers. We conclude that our emulsion-free polymerization of VBC initiated with KPS in the presence of DMA( $C_{16}$ ) proceeds via a micellar nucleation mechanism.

Figure 2 gives zeta potential versus pH curves of the first-stage latexes. These measurements indicate that the zeta potential values decrease with an increase in the amount of DMA( $C_{16}$ ) in the particles. The isoelectric points (IEPs) for these latexes were not observed due to the absence of labile hydrogen(s) on the quaternary ammonium group.

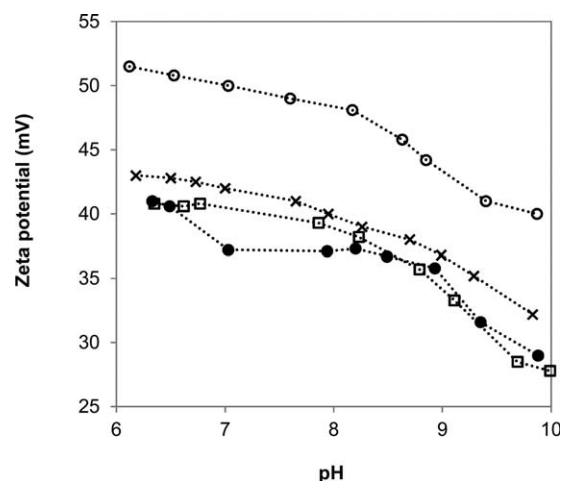
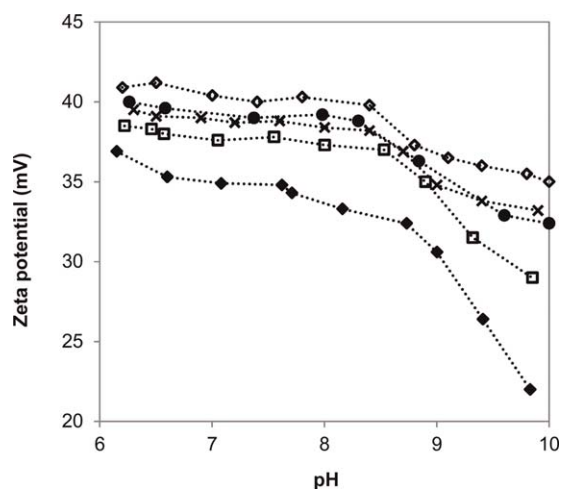


Figure 2. Zeta potential versus pH curves for the first-stage latexes (○) P[VBC-DMA( $C_{16}$ -5)], (×) P[VBC-DMA( $C_{16}$ -10)], (□) P[VBC-DMA( $C_{16}$ -15)], and (●) P[VBC-DMA( $C_{16}$ -20)].



**Figure 3.** Zeta potential versus pH curves obtained for some of the second-stage latexes (●) P[VBC(C<sub>16</sub>)-DMA(C<sub>16</sub>-5)], (□) P[VBC(C<sub>16</sub>)-DMA(C<sub>16</sub>-15)], (◆) P[VBC(C<sub>16</sub>)-DMA(C<sub>16</sub>-20)], (◇) P[VBC(Me)-DMA(C<sub>16</sub>-10)] (×) P[VBC(Me)-DMA(C<sub>16</sub>-15)].

The quaternization of VBC moieties in the P[VBC-DMA(C<sub>16</sub>-x)] latexes with trimethylamine and *N,N*-dimethylhexadecylamine results in cationic latexes containing 36–63 mol % quaternary ammonium ions attached to the VBC and DMA(C<sub>16</sub>) moieties (entries 5–11, Table I). An SEM image of one of the second-stage latexes is given in Figure 1 (right). The type of quaternization agent greatly affected particle size and the hydrophilic–hydrophobic nature of the latexes. It was observed that the particle size increased after treatment of some of the first-stage latexes with trimethylamine (entries 5–7, Table I). The same increase trend for the particles of the latexes P[VBC-DMA(C<sub>16</sub>-5)] and P[VBC-DMA(C<sub>16</sub>-10)] was observed after the quaternization of the VBC moiety with *N,N*-dimethylhexa-

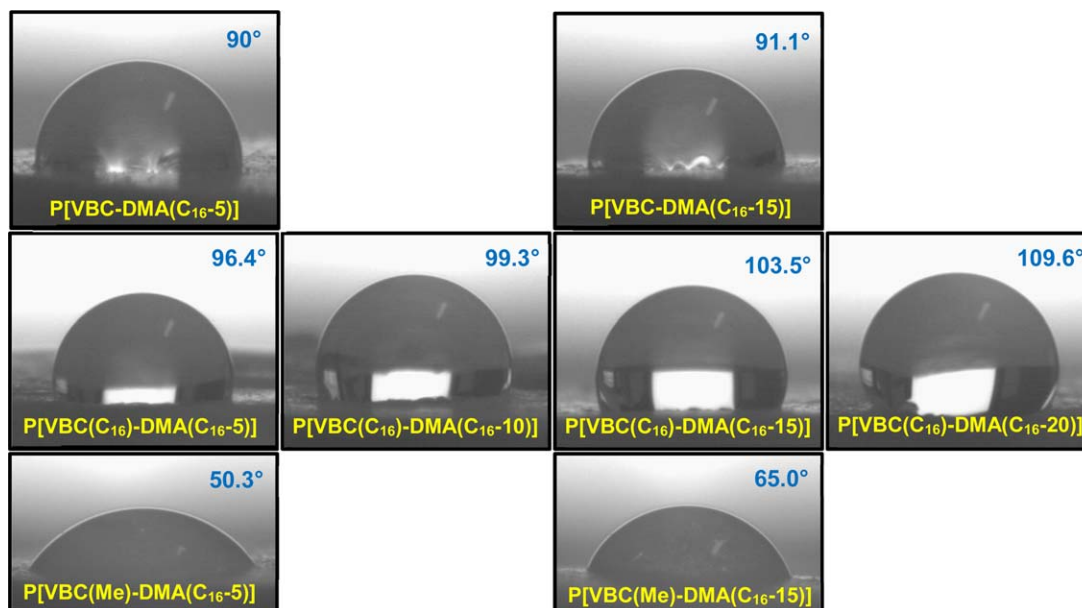
decylamine, whereas the treatment of the P[VBC-DMA(C<sub>16</sub>-15)] and P[VBC-DMA(C<sub>16</sub>-20)] latexes with the same tertiary amine caused a decrease of particle size (entries 10 and 11, Table I). It appears that incorporating the *n*-hexadecyl group into particles with a high percentage, combined with the high percentages of the same alkyl group on the DMA moieties, led to highly hydrophobic particles; the particles eventually dehydrated and shrank. The water contact angle measurements, to be discussed later, support an increase in the hydrophobicities of these latexes. We previously reported a similar decrease in the hydrodynamic diameters of latexes as the percentage of the *n*-hexadecyl group increases.<sup>27</sup> Zeta potential values also decreased as the hydrophobicity of the latexes increased (Figure 3), and the IEPs for the second-stage latexes were not observed as expected because of an absence of the labile H atom(s) on the quaternized sites.

#### Determination of Polymer Structural Compositions

Data from the ion-selective electrode measurements were used to determine the amounts and percentages of the quaternary ammonium ions of the P[VBC-DMA(C<sub>16</sub>-x)], P[VBC(Me)-DMA(C<sub>16</sub>-x)], and P[VBC(C<sub>16</sub>)-DMA(C<sub>16</sub>-x)] latexes. The amounts of the bromide and chloride counterions correspond to the amounts of the quaternary ammonium ions in the DMA and VBC moieties, respectively. The bromide and chloride ions were titrated with AgNO<sub>3</sub>(aq). It was found that the P[VBC-DMA(C<sub>16</sub>-x)] latexes contained 0.37–0.87 mmol DMA(C<sub>16</sub>) moiety per gram of polymer, corresponding to 6–18 mol % DMA(C<sub>16</sub>) in the structures (Table I). The quaternary ammonium ion contents on the VBC moieties of the polymers latexes range from 26 to 57 mol % (Table I).

#### Contact Angle Measurements

The hydrophilic–hydrophobic nature of the latex particles was assessed by measuring the water contact angles of their pellets.



**Figure 4.** Digital images of water contact angles of some of the polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The water contact angle values are given in Table I. The results demonstrate that the contact angles vary with polymer structure; mainly the alkyl group length in their quaternary ammonium ions: (1) The contact angle increases gradually, but not significantly, with an increase in the amount of DMA(C<sub>16</sub>) in the P[VBC-DMA(C<sub>16</sub>-x)] latexes (entries 1–4, Table I); (2) The contact angles further and significantly increase in the resulting polymers after the quaternization of the chloromethyl groups of VBC of the first-stage latexes with *N,N*-dimethylhexadecylamine (entries 8–11, Table I); (3) The quaternization of the chloromethyl groups of the VBC moiety of the first-stage latexes with trimethylamine lead to a substantial decrease in the contact angles of the resulting polymers (entries 5–7, Table I). These results show that the hydrophilic–hydrophobic nature of the latexes can be simply tuned to interplay with the structural compositions of their particles and the amounts of the quaternary ammonium ions in the polymers.

Figure 4 shows images of the contact angles of some of the polymer pellets with water. Typically, the water contact angle of a hydrophobic surface is above 90°. It can be clearly observed that the alkyl group length on the quaternary ammonium ions of the VBC moiety plays an important role in the hydrophobicities of the functional P[VBC(C<sub>16</sub>)-DMA(C<sub>16</sub>-x)] latexes.

## CONCLUSIONS

Varying the surface properties and functionalities of the latex particles creates a potential for latexes to be used in different applications. Here, we report easy preparation of functional cationic latexes with dual type quaternary ammonium ions in high contents, leading to different hydrophilic–hydrophobic properties on the latex particles. Emulsifier-free emulsion polymerization of VBC, and various amounts of a monomer bearing quaternary ammonium ions DMA(C<sub>16</sub>) (5–20%), results in P[VBC-DMA(C<sub>16</sub>-x)] latexes. DMA(C<sub>16</sub>) acts as a comonomer, as well as a polymerizable surfactant. The resulting latex particles had high colloidal stability due to their amphiphilic structure. The quaternization of the chloromethyl functionality of the VBC moiety in the polymers enables adjustment of the hydrophilic–hydrophobic balances of particles of the P[VBC(R)-DMA(C<sub>16</sub>-x)] latexes. Bromide and chloride ion-selective electrodes were used successfully in the characterization of the structural compositions of the P[VBC-DMA(C<sub>16</sub>-x)] and P[VBC(R)-DMA(C<sub>16</sub>-x)] latex particles. Water contact angle measurements show that the hydrophilic–hydrophobic balances of the latex particles can be adjusted with polymer structural composition, mostly the alkyl group length, in their quaternary ammonium ions.

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