

Hydrolyzable-Emulsifier-Containing Polymer Latices as Dispersants and Binders for Waterborne Carbon Black Paint

Yoshihiro Itoh, Kaori Ozaki, Ryosuke Maezawa

Functional Polymer Science Course, Division of Chemistry and Materials, Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

Correspondence to: Y. Itoh (E-mail: yositoh@shinshu-u.ac.jp)

ABSTRACT: Poly(styrene-*co*-butyl methacrylate) and poly(styrene-*co*-butyl acrylate) latices were prepared by emulsion polymerization with alkali-hydrolyzable and nonhydrolyzable cationic emulsifiers and were used as a dispersant and binder for waterborne carbon black (CB) paint. CB was dispersed in the latex solutions and then coated on filter paper pretreated with dilute aqueous Na₂CO₃ under mild conditions. The styrene (St)-rich rigid copolymer latices easily dispersed the CB but fixed a little amount of the pigment on the paper surface. In contrast, the methacrylate- and acrylate-rich soft latices tended to increase the adhesibility on it. We also demonstrated that the hydrolyzable-emulsifier-containing latices always had a higher adhesibility than the nonhydrolyzable-emulsifier-containing ones. Thus, the hydrolyzable-emulsifier-containing latices with an appropriate St content had the highest paintability, rapid adhesion, quick drying, reduced fading, superior fastness, and so on. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3869–3873, 2013

KEYWORDS: coatings; dyes/pigments; emulsion polymerization; latices; surfactants

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INTRODUCTION

Waterborne paints, usually made of synthetic resins, pigments, and low amounts of coalescing solvents, have been evaluated as environmentally friendly alternatives to solvent-based paints because of the significantly lower content of the volatile organic compounds in the former. Water-soluble components in waterborne paints, such as surfactants and water-soluble polymers, play a critical role in stabilizing dispersions, which becomes important further in paints containing hydrophobic organic pigments and carbon black (CB).^{1–3} However, the slow evaporation of water and the persistent surface activity of amphiphiles may inhibit the adhesion to substrates and the formation of continuous films; this leads to a decrease in the performance of the final products in elements such as quick-drying ability, water resistance, toughness, durability, and other paint qualities.⁴ Significant efforts have been made to diminish the amounts of the components or to mask their surface activity; these include surfactant-free emulsion polymerization,^{5,6} polymeric surfactants,⁷ polymerizable surfactants,^{8,9} and fluorine- or silicone-containing polymer latices and surfactants.^{10–15} In most cases, however, posttreatments such as crosslinking and high-temperature annealing should be required, and moderate amounts of surface-active components still remain in the final products. In this context, cleavable surfactants, which lose the

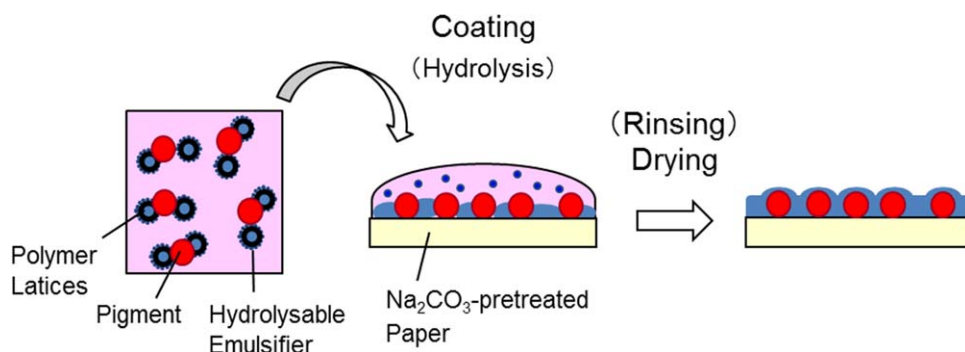
surface activity under mild conditions after their use,¹⁶ merit attention. Mohlin et al.¹⁷ indicated a potential use of hydrolyzable surfactants for alkyl ketene dimer, a water-insoluble sizing agent, in paper making, where a surfactant is needed at one stage of the process but unwanted at a later stage.

We succeeded in the preparation of perfectly surfactant-free styrene (St) and (meth)acrylate polymers by conventional emulsion polymerization using an alkali-hydrolyzable cationic emulsifier, (1-tetradecyloxycarbonylmethyl)trimethyl ammonium chloride (C₁₄B), followed by hydrolysis under mild conditions.^{18,19} We also demonstrated that the surface of filter paper pretreated with dilute aqueous Na₂CO₃ can be polymer-coated rapidly with the previous polymer latices at room temperature and that the surface immediately becomes water-repellent.^{20,21} The facile hydrolysis of C₁₄B in the latices has been presumed to induce the coalescence of latex particles and their adhesion to the paper surface.

The aim of this study was to explore the availability of this type of polymer latices in waterborne paints that require the dispersion of hydrophobic pigments. Our methodology is shown in Scheme 1: pigments were dispersed in an aqueous solution with the aid of the hydrolyzable-emulsifier-containing latices as dispersants, and then, the Na₂CO₃-pretreated paper surface was

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Scheme 1. CB dispersion and coating processes with hydrolyzable-emulsifier-containing polymer latices. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coated by the simple loading of the dispersed solution followed by hydrolysis of the emulsifier. In this method, the pigment adhesion was expected to be achieved without the addition of binder, evaporation of water, or other thermal and chemical treatments. Here CB was used because it is one of the most common and important black pigments used in widespread industrial applications.²²

EXPERIMENTAL

Chemicals

C₁₄B was prepared and purified as reported previously.¹⁸ Graphitized CB was purchased from Sigma-Aldrich Japan (Tokyo, Japan) and was used as received. The average diameter of the particles dispersed in an aqueous surfactant solution determined by dynamic light scattering was about 200 nm. All of the other chemicals were those reported previously^{18–21} or commercially available. St, butyl methacrylate, and butyl acrylate (BA), purchased from Tokyo Kasei (Tokyo, Japan), were distilled under reduced pressure before use.

Emulsion Polymerizations

The emulsion copolymerization of St with butyl methacrylate or BA with C₁₄B or cetyltrimethyl ammonium chloride (CTAC) as emulsifiers was carried out according to the previous method.^{18,19} Characterizations of the resulting polymers and polymer latices were also carried out as described previously.^{18,19} The polymerization conditions and results are summarized in Table 1 in the Supporting Information. Polystyrene (PSt) latices containing different concentrations of C₁₄B (1, 2, 4, and 10 mol % on the basis of the St monomer) were also prepared similarly. The resulting latices will hereafter be referred to as polymer(*x*)/emulsifier where *x* indicates the St content (mol %) in the copolymer.

Dispersion of CB

To 50 mg of CB in a test tube, 1 mL of 10 wt % latex solution was added; this was stirred for 1 min in a vortex mixer and then sonicated for 5 min with an SND sonicator US-10KS (240 W). The supernatant solution was used in the following experiment. The carbon black dispersability (*D*_{rel}; %) was determined spectroscopically; the supernatant fraction of the solution was diluted by 1000 times, and the absorption efficiency (%) at 500 nm in a 1-cm cuvette was recorded on a Hitachi U-3210 spectrophotometer.

Adhesion of CB to Filter Paper

Quantitative filter paper (ADVANTEC, No. 5C; thickness = 0.22 mm; cut into 25-mm squares) was pretreated by the loading of 0.5 mL of aqueous Na₂CO₃ solution (0.2 mol/L) and then air-drying overnight. The paper was placed on a hotplate (IKA, C-MAG HP7) at temperatures of 30–70°C. An amount of 0.1 mL of the CB-dispersed latex solution was spot-loaded gently at the center of the paper and allowed to stand for 1–3 min. The paper was then sonicated in water for 10 min and air-dried overnight. The CB adhesion to the paper surface was estimated roughly by measurement of the relative attenuation of reflected light from the paper surface: the paper was placed in a film holder attachment within a Hitachi F850 fluorescence spectrophotometer; the reflected light intensities at 500 nm for the paper substrate (*I*_P) and the CB-loaded portion (*I*_{CB}) were recorded, and the carbon black adhesibility (*A*_{rel}) was then calculated from eq. (1):

$$A_{\text{rel}}(\%) = 100 \times (I_P - I_{CB}) / I_P \quad (1)$$

Several pieces of paper were also coated all over with 1 mL of the CB-dispersed latex solution and then posttreated as described previously.

Measurements

Water contact angles for the all-over CB-coated samples were measured at regular intervals by the static sessile drop method at room temperature.¹⁸

RESULTS AND DISCUSSION

Dispersion of CB

The CB particles used in this study seemed to have a slightly negatively charged surface from a simple experimental result in which CB was dispersed better in aqueous cationic surfactant solution than in an anionic surfactant one. The C₁₄B-containing cationic latices were thus expected to be candidates for CB dispersants. Then, to select appropriate latices as dispersants, preliminary dispersion experiments with several kinds of homopolymer latices containing different amounts (1–10 mol % feed monomer) of C₁₄B, prepared in our laboratory, were carried out. We found that the latices consisting of 4 mol % or less of C₁₄B and those of homopolymers with a glass-transition temperature (*T*_g) lower than room temperature could not disperse 5 wt % CB stably in an aqueous solution. That is, the *D*_{rel}

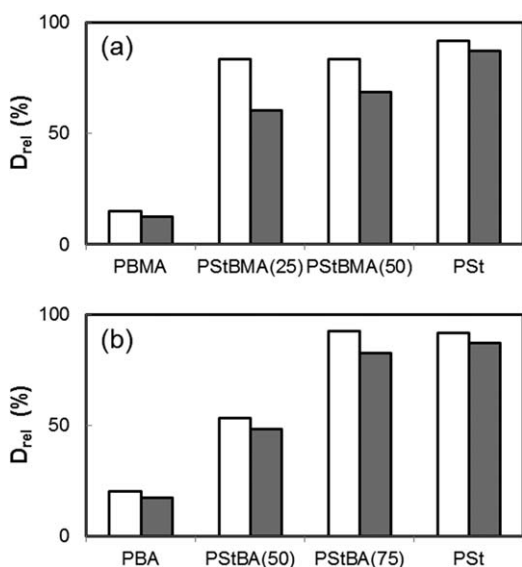


Figure 1. D_{rel} values in 10 wt % (a) PStBMA(x) and (b) PStBA(x) latex solutions, where the open bars represent the CTAC-containing latices and the closed bars represent the $C_{14}B$ -containing latices (5 wt % CB was initially loaded).

values were 47, 61, 71, and 87% for 1, 2, 4, and 10 mol % $C_{14}B$ -containing PSt latices (PSt/ $C_{14}B$), respectively, and those for 10 mol % $C_{14}B$ -containing poly(butyl methacrylate) (PBMA) and poly(butyl acrylate) (PBA) latices (PBMA/ $C_{14}B$ and PBA/ $C_{14}B$) were 12 and 17%, respectively. We thus prepared poly(styrene-*co*-butyl methacrylate) (PStBMA) and poly(styrene-*co*-butyl acrylate) (PStBA) latices containing 10 mol % CTAC or $C_{14}B$ (Table 1 in the Supporting Information).

Figure 1 shows the D_{rel} values in aqueous solutions of the copolymer latices with different x values. We found that the D_{rel} values of both latices tended to increase with increasing x , that is, the polymer's T_g and the polymer latices with a T_g higher than room temperature could disperse CB efficiently. For reference, the literature values²³ and the expected values calculated with the Fox equation²⁴ are shown in Supporting Table 1. These results are plausible because the dispersion process added mechanical stress constantly to the polymer latices, and this resulted in the structural collapse of the soft latices. In fact, lumps of CB and polymers precipitated in the PBMA and PBA latex solutions, and then CB was scarcely dispersed. The D_{rel} values of the $C_{14}B$ -containing latices were slightly but always smaller than those of the CTAC-containing ones. We had no clear reason for this. However, with our previous result that the solubilizabilities of several substrates in aqueous $C_{14}B$ solution were somewhat lower than those in the CTAC one,²⁵ $C_{14}B$ might form less stable latices and decrease D_{rel} .

Adhesion of CB to Filter Paper

By modification of the previous coating method,²¹ the CB-dispersed latex solution was spot loaded on the filter paper pretreated with Na_2CO_3 . On the basis of the result that the paper surface coated with $C_{14}B$ -containing latices dried immediately after the coating process and became water repellent,²¹ the CB-

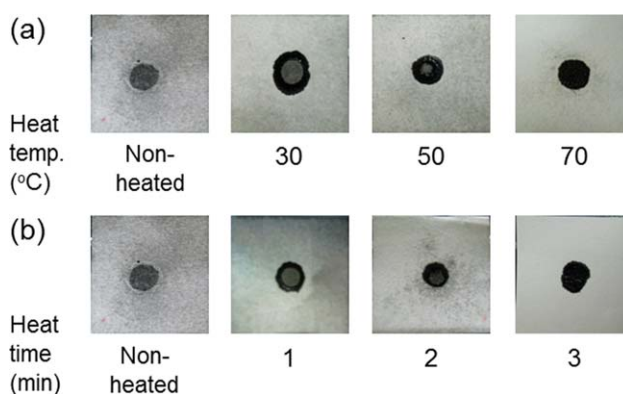


Figure 2. Photographs of pieces of heat-treated paper coated with CB-dispersed PStBMA(25)/ $C_{14}B$ latices: (a) heat temperature dependence (heat time = 3 min) and (b) heat time dependence (heat temperature = 70°C). A CB-dispersed latex solution was loaded onto the paper followed by heating, rinsing, and then air-drying.

loaded paper was rinsed with water and air-dried in the same manner, although these processes are unnecessary for the practical uses of paints. At room temperature, unfortunately, CB could not be fixed on the paper surface in several minutes, and most of the CB was desorbed easily by rinsing, and this gave a dirty and smeared surface. Figure 2 shows the photographs of the pieces of heat-treated paper coated with CB-dispersed PStBMA(25)/ $C_{14}B$ latex solution (where the number indicates the St content in molar percentage). Figure 2(a,b) indicates the effects of the heat-treatment temperature and time, respectively. As shown clearly in the figure, heat treatment at 70°C for 3 min was sufficient for CB adhesion to the paper surface; this

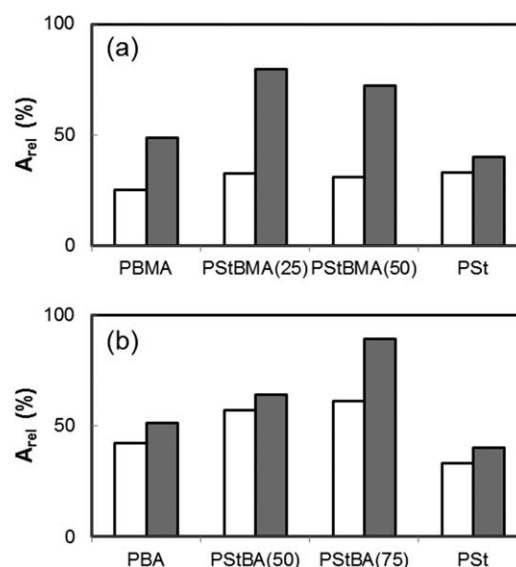


Figure 3. A_{rel} values on the paper surface coated with (a) PStBMA(x) and (b) PStBA(x) latices, where the open bars represent the CTAC-containing latices and the closed bars represent the $C_{14}B$ -containing latices. CB-dispersed solutions (Figure 1) were spot-loaded onto the paper followed by heating at 70°C for 3 min, rinsing, and then air-drying.

yielded a clear spot. The samples were then prepared under these conditions.

Figure 3(a) shows the A_{rel} values of the PStBMA latices. When all of the CB particles loaded on the paper were fixed, the A_{rel} value increased monotonously with the D_{rel} value, that is, x (Figure 1). However, the values of PStBMA(x)/CTAC latices were almost independent on x , whereas those of the PStBMA(x)/C₁₄B latices showed a convex dependence. It should also be noted that the latter values were always higher than the former ones. For CB adhesion, the latices needed to coalesce with each other and with CB particles and then to adhere to the paper surface (Scheme 1). The presence of nonhydrolyzable CTAC in the PStBMA(x)/CTAC latices may have interfered with the latex coalescence under these conditions, rinsing out a significant amount of CB and thus decreasing the overall A_{rel} values for all of the latices. In contrast, the C₁₄B molecules in the PStBMA(x)/C₁₄B latices hydrolyzed easily when in contact with Na₂CO₃ on the paper surface; this facilitated the latex coalescence and thus increased the A_{rel} value. This desirable effect should have been more pronounced for the soft latices consisting of PStBMA(x) with a lower x or T_g ; this had a lower D_{rel} value. Thus, the trade-off relationship between the dispersability and adhesibility led to the convex dependence of A_{rel} for the PStBMA(x)/C₁₄B latices.

Figure 3(b) shows the CB adhesibilities of the PStBA latices. Both the CTAC- and C₁₄B-containing latices showed a convex dependence similar to that in the PStBMA(x)/C₁₄B latices, where the values of the PStBA(x)/C₁₄B latices were slightly higher than the PStBA(x)/CTAC ones. The intrinsically high adhesibility and low T_g of BA moieties in the copolymer²⁶ may have facilitated the latex coalescence with or without the surfactant hydrolysis. It is worth noting that the PStBMA(25)/C₁₄B and PStBA(75)/C₁₄B latices, which showed the highest adhesibility, had similar T_g values of around 35°C (Table 1 in the Supporting Information). This clearly indicated that the rigidity of

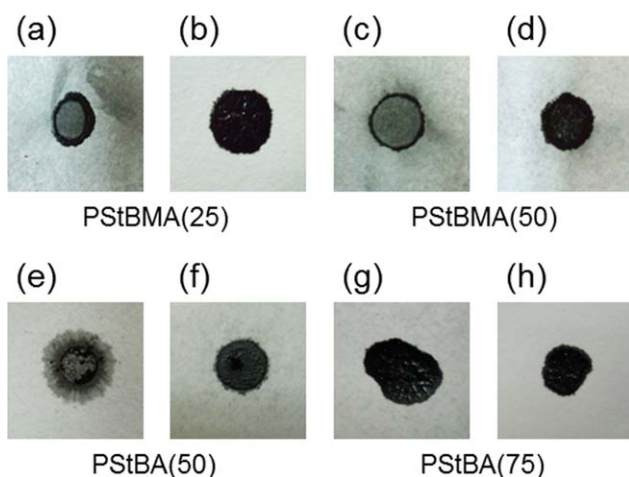


Figure 4. Photographs of pieces of paper coated with CB-dispersed PStBMA(25)/C₁₄B latices: (a) PStBMA(25)/CTAC, (b) PStBMA(25)/C₁₄B, (c) PStBMA(50)/CTAC, (d) PStBMA(50)/C₁₄B, (e) PStBA(50)/CTAC, (f) PStBA(50)/C₁₄B, (g) PStBA(75)/CTAC, and (h) PStBA(75)/C₁₄B. The samples are those shown in Figure 3.

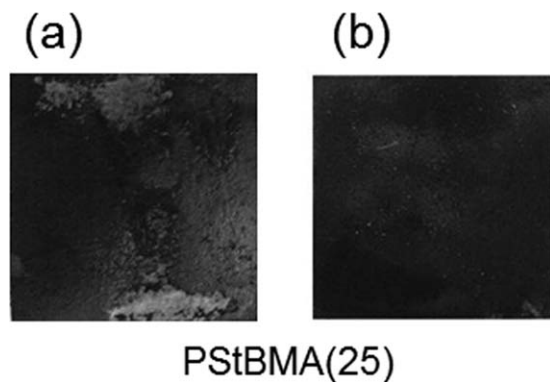


Figure 5. Photographs of two pieces of paper coated over all with the CB-dispersed copolymer latices: (a) PStBMA(25)/CTAC and (b) PStBMA(25)/C₁₄B.

the polymer latices was a dominant factor for the hybrid functions of dispersant and binder.

Surface Properties of the CB-Loaded Paper

Photographs of pieces of the CB-loaded paper are shown in Figure 4. It was evident that CB was desorbed easily through rinsing from the paper surface treated with CTAC-containing latices; this gave a dirty and faded spot, whereas CB was fixed on the surface treated with the C₁₄B-containing latices, and this yielded a sharp and clear spot. In addition, the latter surface was quickly dried and showed better fastness to rubbing.

The higher adhesibility of the C₁₄B-containing latices was also confirmed not only visually for the pieces of paper coated all over with the CB-dispersed PStBMA(25) latices (Figure 5) but also gravimetrically for them: the fixed yields of CB were 40 and 69% for the PStBMA(25)/CTAC and PStBMA(25)/C₁₄B latices, respectively. We further found that the latter surface became water repellent; although a water drop immediately penetrated into the former paper (the water contact angle rapidly decreased from about 90 to 0° within 3 min), the penetration was remarkably retarded, though imperfectly, for the latter one (the angle gradually decreased from about 110° over 5 min).

CONCLUSIONS

In this article, we demonstrated the usefulness of hydrolyzable-emulsifier-containing polymer latices in waterborne paints for paper. The results indicate that the latices of the poly(meth)acrylates with an appropriate T_g higher than room temperature functioned efficiently as dispersants and binders for waterborne CB paint; this led to easy and good painting on the paper surface and gave it quick drying and water-repellent properties. Film formation without the evaporation of water is one of the strengths of this novel method, which requires no additional treatments such as crosslinking or high-temperature annealing. We thus believe there will be many potential applications for this in the paint and coatings industry. The dispersion and adhesion efficiencies, however, were not sufficient; for example, the CB concentration in the dispersed solution was 5 wt % at most, heat treatment was still needed, and a perfectly blackened and water-repellent surface was not obtained. Further increases

in the performances should require the minimization of surface-active components and improvements in each process. Because polymeric surfactants are good dispersants for hydrophobic pigments,^{1-3,7} we now plan to prepare hydrolyzable ones.

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