

Preparation of Emulsifier-Free Polystyrene by Conventional Emulsion Polymerization with a Hydrolysable Emulsifier

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ABSTRACT: An alkali-hydrolyzable surfactant, (1-tetradecyloxycarbonyl)trimethylammonium chloride, was used as an emulsifier for emulsion polymerization of styrene in water. The polymerization yielded a high molecular-weight polymer almost quantitatively. Addition of a small amount of NaOH to the resulting latex solution precipitated the polymer immediately. Analysis of the centrifuged solid indicated almost perfection of both recovery of the

polymer and removal of surface-active species from it. Minimization of ionic species in the polymer solid was confirmed by a high contact angle of the polymer film with water. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 358–361, 2008

Key words: emulsion polymerization; latices; polystyrene; surfactants

INTRODUCTION

Emulsion polymerization in water is one of the most important and “environmentally friendly” techniques for the commercial production of polymers.¹ These polymers are typically prepared with ionic emulsifiers such as alkylsulfate and alkylbenzenesulfonate, and frequently used as solid materials, isolated from the aqueous latex solutions by addition of salts. In such cases, some of the emulsifiers and other additives remain in the polymer solids and are difficult to remove, which may influence product performance such as durability, water resistance, insulation, quick-drying, etc. Castro et al. recently demonstrated that polystyrenes (PSt) prepared by emulsion and bulk polymerizations have different film characteristics and that the former polymers have less stabilities to water and salt solutions due to the presence of residual surfactant molecules.²

In this context, cleavable surfactants or emulsifiers, which convert to non-surface-active or uncharged products, will be favorable.³ Several types of cleavable surfactants including photodegradable^{4–6} and hydrolysable^{7–9} ones have been applied to coagulate latices and decrease the surfactant content in the resulting polymers. We have recently demonstrated that

an UV-degradable surfactant, (*p*-dodecylbenzyl)trimethylammonium bromide, can be used not only as an emulsifier for microemulsion polymerization of methyl methacrylate but also as a useful “floculant” of latices that gives surfactant-free polymers.¹⁰ This system, however, has two drawbacks: (1) complete photolysis (i.e., conversion to a nonsurfactant) appears to be slow: it takes more than 60 min under a given condition, (2) opaque latex solutions will be inapplicable. The practical use in a wide range of applications thus requires surfactants to be easily cleavable after their use.

In the present article, we report that an alkali-hydrolyzable cationic surfactant with a betaine ester group, (1-tetradecyloxycarbonylmethyl)trimethylammonium chloride (C₁₄B), can be used as a cleavable emulsifier for emulsion polymerization of styrene (St). This type of surfactants is known to be hydrolyzed rapidly in alkali solutions.^{11–13}

EXPERIMENTAL

Materials

C₁₄B was prepared according to the literature¹² and recrystallized from a mixture of ethanol and acetone. Cetyltrimethylammonium chloride (CTAC) and 2,2'-azobis(2-amidinopropane) dihydrochloride (AIBA), purchased from Wako Chemical (Osaka, Japan), were used as received. Myristyltrimethylammonium chloride (MTAC) (Tokyo Kasei, Tokyo, Japan) was used as received. St (Wako Chemical) was distilled

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under reduced pressure before use. PSt prepared by bulk polymerization (PSt-b) (Wako Chemical) was used as received (molecular weight, 1.7×10^5).

Hydrolysis of C₁₄B

A known amount of C₁₄B in 2 mL of H₂O was mixed with 18 mL of 20 mM buffer solution (pH 6–11) and stirred for 10 min at 25°C, and the hydrolysis was terminated by adding a drop of conc. HCl: KH₂PO₄-NaOH (pH 6–8) and H₃BO₃-NaOH (pH 9–10) were used as buffers. The reaction mixture was extracted with 20 mL of hexane. To the solution, 1-hexadecanol (2 mM) was added as an internal standard and then directly injected into a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector and a packed column (OV-17, 5%). The hydrolysis yield was determined on the amount of a hydrolyzed product, 1-tetradecanol (C₁₄OH).

Surface activities

Critical micelle concentration (CMC) and foaming, solubilizing, and dispersing powers of surfactants were determined as reported previously.¹⁴ After complete hydrolysis of C₁₄B in a 10 mM of aqueous NaOH solution for 20 min at 30°C, its foaming, solubilizing, and dispersing powers were determined. Under the same conditions, the properties of CTAC were also examined.

Emulsion polymerization

Emulsion polymerization of St was carried out by a conventional method using AIBA as an initiator.¹⁵ A typical polymerization procedure was as follows: To a mixture of 6.24 g (60 mmol) of St, 0.21 g (0.6 mmol) of C₁₄B or CTAC, and 50 g of water and 0.049 g (0.18 mmol) of AIBA in 5 g of water were added and stirred (250 rpm) at 60°C for 6 h under nitrogen atmosphere. The resulting latices were named PSt/C₁₄B and PSt/CTAC, respectively. A portion of the latex solution was lyophilized. The resulting polymers were named PSt/C₁₄B-l and PSt/CTAC-l, respectively. The conversion was determined gravimetrically.

Hydrolysis and salting out of latices

A typical hydrolysis procedure for the PSt/C₁₄B latices was as follows: The latex solution was diluted to one fifth with deionized water. To a 10 mL of the diluted solution including 0.02 mmol of C₁₄B, a 0.4 mL of aqueous NaOH solution (0.02–0.08 mmol) was added and stirred for 10 min at room temperature. The solid precipitated was collected on a glass filter, washed with deionized water, and then dispersed in deionized water. This cycle was repeated three times

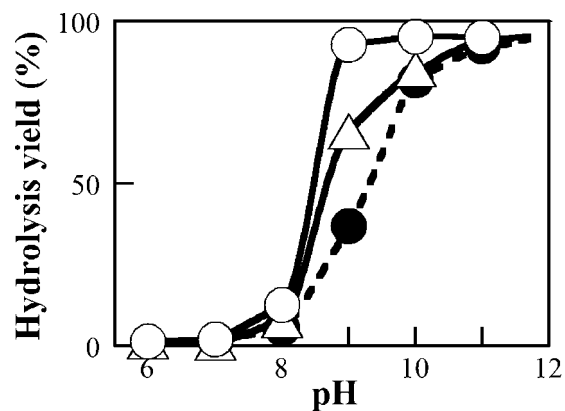


Figure 1 pH dependence of hydrolysis of C₁₄B in 18 mM buffer solutions at 25°C. ○: [C₁₄B] = 2 mM, △: [C₁₄B] = 10 mM, ●: [C₁₄B] = 2 mM; [NaCl] = 80 mM, hydrolysis time: 10 min.

and finally the collected solid was dried *in vacuo*. Salting out of PSt/C₁₄B and PSt/CTAC latices with NaCl (0.1–2.4 mmol) was carried out in the similar manner. The resulting polymers were named PSt/C₁₄B-h, PSt/C₁₄B-s, and PSt/CTAC-s, respectively. The conversions (recovery yields of polymers) were determined gravimetrically.

Polymer characterization

Molecular weight (M_w) was estimated by using a Jasco liquid chromatography system with a UV detector (Jasco UV-975) and a Shodex KF-805 column. Monodisperse polystyrene samples were used as standards.

Particle size (Z-average size) and distribution (polydispersity index: PDI) of latices were measured by a Zetasizer Nano Series (3 mW He-Ne laser, 633 nm) (Malvern Instruments, UK) at 25°C. The calculations for these parameters were defined in the ISO standard document 13321:1996 E.

¹H NMR spectra were recorded on a Bruker AVANCE400 spectrometer at room temperature. Weighted polymer solids were dissolved in CDCl₃ containing a known amount of terephthalonitrile (δ 7.80 ppm) as an internal standard. Compositions were quantified by measuring the area of the following peaks: PSt, δ 6.2–7.4 ppm (m, 4H, aromatic); C₁₄B, δ 4.95 ppm (s, 2H, –CO–CH₂–N–); 1-tetradecanol (C₁₄OH), δ 3.62 ppm (t, 2H, J = 6.6 Hz, –C–CH₂–OH); St (monomer), δ 5.23 and 5.74 ppm (dd, 2H, –C=CH₂).

Contact angles of cast films with water were obtained using the sessile drop method with a contact angle meter (Kyowa Interface Science, CA-VP) at room temperature. PSt films were solvent cast from 2 wt % of chloroform solutions. The contact angle reported was an average of more than five readings at different places on the same sample.

TABLE I
Surface-Active Properties of Surfactants Before and After Hydrolysis at 30°C^a

Hydrolysis	Surfactant	CMC ^b (mM)	Foaming ^c (mL)	Dispersing ^d (%)	Solubilizing ^e (mg/L)
Before	C ₁₄ B	1.7 (1.9) ^f	23	74	26
	CTAC	1.5 (1.5) ^g	28	72	47
	MTAC	5.6 (4.5) ^g	2	75	14
After ^a	C ₁₄ B	–	<1	4	1
	CTAC	–	15	55	–

^a Measured after hydrolysis in 10 mM of aqueous NaOH for 20 min at 30°C.

^b Determined by conductivity method.

^c Foam volume of shaken solution, [surfactant] = 0.023 wt %.

^d % Absorption of carbon-black-dispersed solution (after dilution to 1/125), [surfactant] = 0.25 wt %.

^e Solubility of Oil Orange SS in aqueous solution, [surfactant] = 0.25 wt %.

^f Ref. 16.

^g Ref. 17.

RESULTS AND DISCUSSION

Hydrolytic and surface-active properties of C₁₄B

It is well known that surface-active betaine esters, in particular C₁₄B, are extremely susceptible to alkali hydrolysis because of the inductive effect and the “micellar catalyst” of the quaternary ammonium groups.^{11,12} To confirm this, pH dependence of the hydrolysis of C₁₄B (2 mM) itself was examined in 18 mM of buffer solutions at 25°C (Fig. 1). The hydrolysis yield increased above pH 8 and reached to almost 100% at pH 10 within 10 min. The increases of the C₁₄B concentration and the solution ionic strength slightly decreased the yield, the latter of which is obviously due to the decreased micellar catalyst effect.^{11,12} In such cases, lengthening the reaction time or increasing the solution pH could complete the hydrolysis.

In Table I, several surface-active properties of C₁₄B before and after hydrolysis are compared with classical surfactants, CTAC and MTAC. While C₁₄B had only a slightly larger CMC value and somewhat smaller foaming and solubilizing powers than CTAC, these surface activities were superior to those of MTAC. These results are consistent with the fact that the CMC values of betaine chloride alkyl esters are close to those of *n*-alkyltrimethylammonium

chlorides with an alkyl chain longer by two CH₂ groups.^{12,16} On addition of a little excess of NaOH to the aqueous C₁₄B solution at 30°C, leading to the complete hydrolysis, its surface activities disappeared immediately, indicating the conversion to a non-surfactant. In contrast, only little apparent changes were observed for CTAC.

Emulsion polymerization

Two latices, PSt/C₁₄B and PSt/CTAC, were prepared by conventional emulsion polymerization of St in water.¹⁵ The characteristics of the polymer latices are summarized in Table II. For both surfactants, the conversions reached 90%, and stable latices of monodispersity with a narrow size distribution were obtained: the mean diameters were ca. 70 nm and the polydispersity index (PDI) values were lower than 0.1. In addition, the obtained polymers had high molecular weights (ca. 4 × 10⁵). Thus, C₁₄B, as well as CTAC, is safely said to be a “good” emulsifier for emulsion polymerization of St.

TABLE II
Emulsion Polymerization of St^a

Latex	Conversion (%)	M _w	Particle diameter (nm)	PDI ^b
PSt/C ₁₄ B	90	4.7 × 10 ⁵	72	0.016
PSt/CTAC	92	3.6 × 10 ⁵	70	0.055

^a [St] = 60 mmol, [surfactant] = 0.6 mmol, [AIBA] = 0.18 mmol, polymerization temperature: 60°C, polymerization time: 6 h.

^b Polydispersity index of particle diameter.

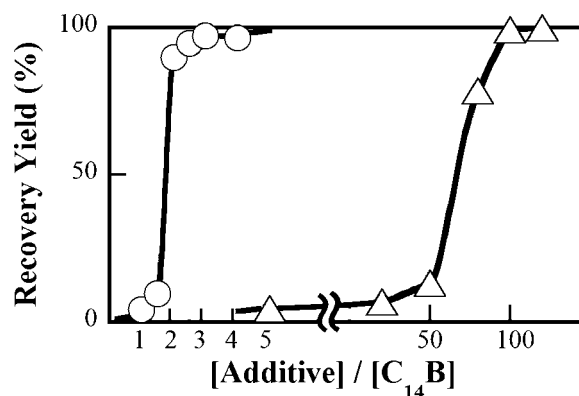


Figure 2 Effect of NaOH or NaCl on recovery of polymers from PSt/C₁₄B latices. ○: hydrolysis ([NaOH] = 0.02–0.08 mmol), △: salting out ([NaCl] = 0.1–2.4 mmol), [C₁₄B] = 0.02 mmol, reaction time: 10 min.

TABLE III
Compositions of Polymer Solids Recovered by Lyophilization, Hydrolysis, and Salting Out^a

Polymer	Component (mol%)			
	PSt	Surfactant	C ₁₄ OH	St
PSt/C ₁₄ B-1 ^b	97.6	0.9	–	0.6
PSt/C ₁₄ B-s ^c	97.8	0.9	–	0.3
PSt/C ₁₄ B-h ^d	98.5	0	1.0	0.2
PSt/CTAC-1 ^b	98.2	1.0	–	0.4
PSt/CTAC-s ^d	98.0	1.0	–	0.6

^a Determined by ¹H NMR.

^b Recovered by lyophilization of latex solution.

^c Recovered by salting out with aqueous NaCl (2.4 mmol).

^d Recovered by hydrolysis in aqueous NaOH (0.08 mmol).

Hydrolysis and salting out of polymer latices

To achieve a complete hydrolysis of C₁₄B in PSt/C₁₄B, the sample solution was diluted one fifth with deionized water and then a small amount of aqueous NaOH was added. As shown in Figure 2, addition of only two times of excess NaOH to C₁₄B in the latices precipitated the polymer immediately and almost quantitatively. This clearly indicates that conversion of C₁₄B to a nonsurfactant labilizes the latices, promoting the coagulation. In contrast, addition of more than 100 times of excess NaCl (>0.2M) to C₁₄B in the latices was necessary to salt out the polymer quantitatively.

The precipitates obtained by hydrolysis and salting out were washed with deionized water three times and then analyzed by ¹H NMR spectroscopy. As references, the polymers recovered by simple lyophilization of the latex solutions were also examined. Table III summarizes the compositions in the recovered polymers. The polymers recovered by lyophilization and salting out had almost the same compositions for both C₁₄B and CTAC, indicating that the salting out can not remove the surfactants from the latices under the present conditions. As expected, the polymer obtained by hydrolysis (PSt/C₁₄B-h) contained a nearly quantitative amount of a hydrolyzed product, C₁₄OH, as an alternative to C₁₄B. Thus the latter polymer solid had little ionic species.

Surface wettability of polymer films

To investigate the surfactant effect on the surface wettability for the present polymers, the cast films of PSt-b and PSt/C₁₄B were characterized by contact angle goniometry with water. The obtained contact angle of PSt-b film (90°), in accordance with the literature value,^{2,18} indicates the hydrophobic surface. In contrast, the surfaces of PSt/C₁₄B-1 (10°) and PSt/

C₁₄B-s (12°) were found to be remarkably hydrophilic. This might be a result of chemical heterogeneity on the surfaces: the residual surfactant molecules in hydrophobic films tend to migrate to the film/air interface.² It should be noted that the PSt/C₁₄B-h film has a contact angle (88°) as high as the PSt-b film, i.e., a small amount of C₁₄OH that remained in the former polymer has little effect on the hydrophobicity of the film.

CONCLUSIONS

This work has shown that a high molecular weight of PSt containing a negligibly small amount of surface-active species can be prepared by conventional emulsion polymerization using a hydrolyzable cationic emulsifier (C₁₄B). Such easy cleavage of the emulsifier under mild conditions and easy recovery of polymers without a large quantity of additives could be useful for preparation of polymers with high quality and performance on a large scale.

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