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

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ABSTRACT: An alkali-hydrolysable surfactant, (1-tetradecyloxycarbonylmethyl)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.

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 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 films’ 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[4,5] and hydrolysable[6,7] 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 an useful ‘flocculant’ of latices that gives surfactant-free polymers.[8] This system, however, has two drawbacks: (1) complete photolysis (i.e., conversion to a non-surfactant) 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 paper, we report that an alkali-hydrolysable cationic surfactant with a betaine ester group, (1-tetradecyloxycarbonylmethyl)trimethylammonium chloride ($C_{14}B$), 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.[9-11]

EXPERIMENTAL

Materials

$C_{14}B$ was prepared according to the literature[10] and recrystallized from a mixture of ethanol and acetone. Cetyltrimethylammonium chloride (CTAC) and 2,2'-azobis(2-amidinopropane) dihydrochloride (AIBA), purchased from Wako Chemical, were used as received. Myristyltrimethylammonium chloride (MTAC) (Tokyo Kasei) was used as received. St (Wako Chemical) was distilled 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 $C_{14}B$

A known amount of $C_{14}B$ in 2 ml of H_2O was mixed with an 18 ml of 20 mM buffer solution (pH 6-11) and stirred for 10 min at 25 ^{o}C and the hydrolysis was terminated by adding a drop of conc. HCl: KH_2PO_4-NaOH (pH 6-8) and H_3BO_3-NaOH (pH 9-10) were used as buffers. The reaction mixture was extracted with a 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 ($C_{14}OH$).

Surface activities

Critical micelle concentration (CMC) and foaming, solubilizing, and dispersing powers of surfactants were determined as reported previously.[12] After complete hydrolysis of $C_{14}B$ in a 10 mM of aqueous NaOH solution for 20 min at 30 ^{o}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.[13] 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 $C_{14}B$ or CTAC, and 50 g of water a 0.049 g (0.18 mmol) of AIBA in 5 g of water was added and stirred (250 rpm) at 60 ^{o}C for 6 h under nitrogen atmosphere. The resulting latices were named PSt/$C_{14}B$ and PSt/CTAC, respectively. A portion of the latex solution was lyophilized. The resulting polymers were named PSt/$C_{14}B$-l and PSt/CTAC-l, respectively. The conversion was determined gravimetrically.

Hydrolysis and salting out of latices

A typical hydrolysis procedure for the PSt/$C_{14}B$ 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 $C_{14}B$ 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 and finally the collected solid was dried in vacuo. Salting out of PSt/$C_{14}B$ and PSt/CTAC latices with NaCl (0.1-2.4 mmol) was carried out in the similar manner. The resulting polymers were named PSt/$C_{14}B$-h, PSt/$C_{14}B$-s, and PSt/CTAC-s, respectively. The conversions (recovery yields of polymers) were determined gravimetrically.

Polymer characterization

Molecular weight (Mw) 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 ^{o}C. The calculations for these parameters were defined in the ISO standard document 13321:1996 E.

^{1}H NMR spectra were recorded on a Bruker AVANCE400 spectrometer at room temperature. Weighted polymer solids were dissolved in $CDCl_3$ 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); $C_{14}B$, δ 4.95 ppm (s, 2H, $-CO-CH_2-N-$); 1-tetradecanol ($C_{14}OH$), δ 3.62 ppm (t, 2H, J=6.6 Hz, $-C-CH_2-OH$); St (monomer), δ 5.23 and 5.74 ppm (dd, 2H, $-C=CH_2$).

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.

RESULTS AND DISCUSSION

Hydrolytic and surface-active properties of $C_{14}B$

It is well known that surface-active betaine esters, in particular $C_{14}B$, are extremely susceptible to alkali-hydrolysis because of the inductive effect and the 'micellar catalyst' of the quaternary ammonium groups.[9,10] In order to confirm this, pH dependence of the hydrolysis of $C_{14}B$ (2 mM) itself was examined in 18 mM of buffer solutions at 25 ^oC (Figure 1). The hydrolysis yield increased above pH 8 and reached to almost 100 % at pH 10 within 10 min. The increase of the $C_{14}B$ concentration and the solution ionic strength slightly decreased the yield, the latter of which is obviously due to the decreased 'micellar catalyst' effect.[9,10] In such cases, lengthening the reaction time or increasing the solution pH could complete the hydrolysis.

In Table I, several surface-active properties of $C_{14}B$ before and after hydrolysis are compared with classical surfactants, CTAC and MTAC. While $C_{14}B$ 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 CH_2 groups.[10,14] On addition of a little excess of NaOH to the aqueous $C_{14}B$ solution at 30 ^{o}C, leading to the complete hydrolysis, its surface activities disappeared immediately, indicating the conversion to a non-surfactant. In contrast, only a little apparent changes were observed for CTAC.

Emulsion polymerization

Two latices, PSt/$C_{14}B$ and PSt/CTAC, were prepared by conventional emulsion polymerization of St in water.[13] The characteristics of the polymer latices are summarized in Table II. For both surfactants, the conversions reached to 90 % and stable latices of monodisperse with a narrow size distribution were obtained: the mean diameters were ca. 70 nm and the polydisperse index (PDI) values were lower than 0.1. In addition, the obtained polymers had high molecular weights (ca. 4×10^{5}). Thus $C_{14}B$, as well as CTAC, is safely said to be a ‘good’ emulsifier for emulsion polymerization of St.

Hydrolysis and salting out of polymer latices

To achieve a complete hydrolysis of $C_{14}B$ in PSt/$C_{14}B$, 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 excess NaOH to $C_{14}B$ in the latices precipitated the polymer immediately and almost quantitatively. This clearly indicates that conversion of $C_{14}B$ to a non-surfactant labilizes the latices, promoting the coagulation. In contrast, more than 100 times excess NaCl (>0.2 M) to $C_{14}B$ in the latices were 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 ^{1}H 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 $C_{14}B$ 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/$C_{14}B$-h) contained a nearly quantitative amount of a hydrolyzed product, $C_{14}OH$, as an alternative to $C_{14}B$. Thus the latter polymer solid had little ionic species.

Surface wettability of polymer films

In order to investigate the surfactant effect on the surface wettability for the present polymers, the cast films of PSt-b and PSt/C_{14}B were characterized by contact angle goniometry with water. The obtained contact angle of PSt-b film (90 °), in accordance with the literature value,[2,16] indicates the hydrophobic surface. In contrast, the surfaces of PSt/C_{14}B-l (10 °) and PSt/C_{14}B-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/C_{14}B-h film has a contact angle (88 °) as high as the PSt-b film: i.e., a small amout of C_{14}OH 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 hydrolysable cationic emulsifier (C_{14}B). 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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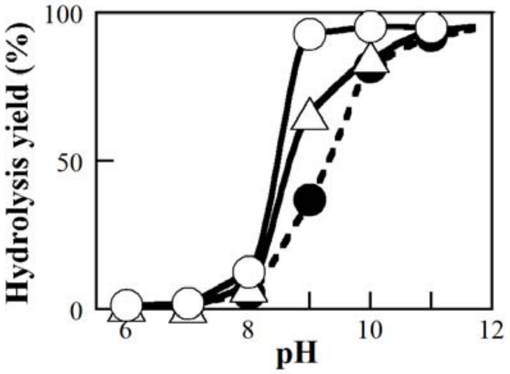

Figure 1: pH dependence of hydrolysis of $C_{14}B$ in 18 mM buffer solutions at 25 ^{o}C. ○: $[C_{14}B]$=2 mM, △ : $[C_{14}B]$=10 mM, ● : $[C_{14}B]$=2 mM; [NaCl]=80 mM, hydrolysis time: 10 min.

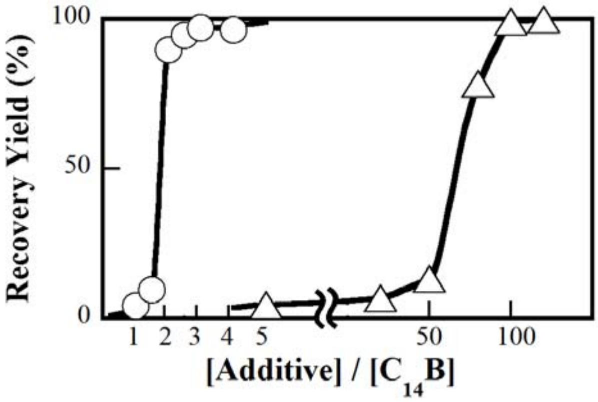

Figure 2: Effect of NaOH or NaCl on recovery of polymers from PSt/$C_{14}B$ latices. ○: hydrolysis ([NaOH]=0.02-0.08 mmol), △ : salting out ([NaCl]=0.1-2.4 mmol), $[C_{14}B]$=0.02 mmol, reaction time: 10 min.

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 shaked 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. 14.

[g] Ref. 15.

Table II: Emulsion polymerization of St[a]

Latex	Conversion (%)	Mw	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, polym. temp.: 60 °C, polym. time: 6 h.

[b] Polydispersity index of particle diameter.

Table III: Compositions of polymer solids recovered by lyophilization, hydrolysis, and salting out[a]

	Component (mol%)			
Polymer	PSt	Surfactant	$C_{14}OH$	St
PSt/C_{14}B-l[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-l[b]	98.2	1.0	—	0.4
PSt/CTAC-s[d]	98.0	1.0	—	0.6

[a] Determined by ^{1}H 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).