Photodegradative Surfactants: *p*-Dodecylbenzyltrimethylammonium Bromide as a Photodegradative Emulsifier for Microemulsion Polymerization

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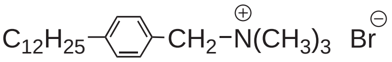
A photodegradative surfactant, *p*-dodecylbenzyltrimethylammonium bromide, was used as an emulsifier for micro-emulsion polymerization of methyl methacrylate in water. The resulting polymer latex was coagulated during UV irradiation. The analysis of the centrifuged solid after irradiation indicated almost perfection of both recovery of the polymer and removal of surface-active species from it.

In emulsion polymerization, surfactants are essential for emulsification of monomer droplets and stabilization of latex particles, but they have drawbacks in latex applications such as reduced water-resistance and electrical insulation of coatings. A simple way to overcome these problems is emulsifier-free polymerization. In most cases, however, small or moderate amounts of additives (e.g., polymerizable emulsifiers) have been added,[1] and then "truly" surfactant-free polymers have been scarcely obtained. An alternative and promising approach involves the use of cleavable surfactants.[2] Yamamura et al.[3] demonstrated that acid-hydrolyzable surfactants containing ketal and sulfonate groups lower the content of ionic species in the resulting polymer. Nuyken et al.[4] reported that *p*-dodecylphenyldiazosulfonate can control the latex coagulation process simply by exposing the dispersion to UV irradiation.[5]

In this paper, we report that a photodegradative surfactant, *p*-dodecylbenzyltrimethylammonium bromide ($C_{12}BA$) (Scheme 1),[6] can be used not only as an emulsifier for microemulsion polymerization of methyl methacrylate (MMA) but also as a useful "flocculant" of latices that gives surfactant-free polymers.

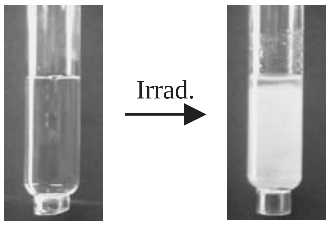


$C_{12}BA$

Scheme 1.

Poly(MMA) (PMMA) latices were prepared according to the method of Ming et al.[7] with some modification.[8] The polymerization proceeded smoothly and the conversion went up to over 95%. The resulting transparent latex solution was stable over several weeks.

The latex solution became turbid after UV irradiation for 20 min, its turbidity reached to the maximum after 45 min, and then the polymer was partially precipitated (Figure 1).[9] This clearly indicates that in the time range the conversion of $C_{12}BA$ to a non-surfactant labilizes the latices, promoting their coagulation. By contrast, no apparent change was observed for the latices prepared with a non-degradative surfactant, hexadecyltrimethylammonium chloride, or a photodegradative one, hexade-



(a) before (b) after

Figure 1. Photographs of PMMA/$C_{12}BA$ latex solution (a) before and (b) after UV irradiation for 90 min.

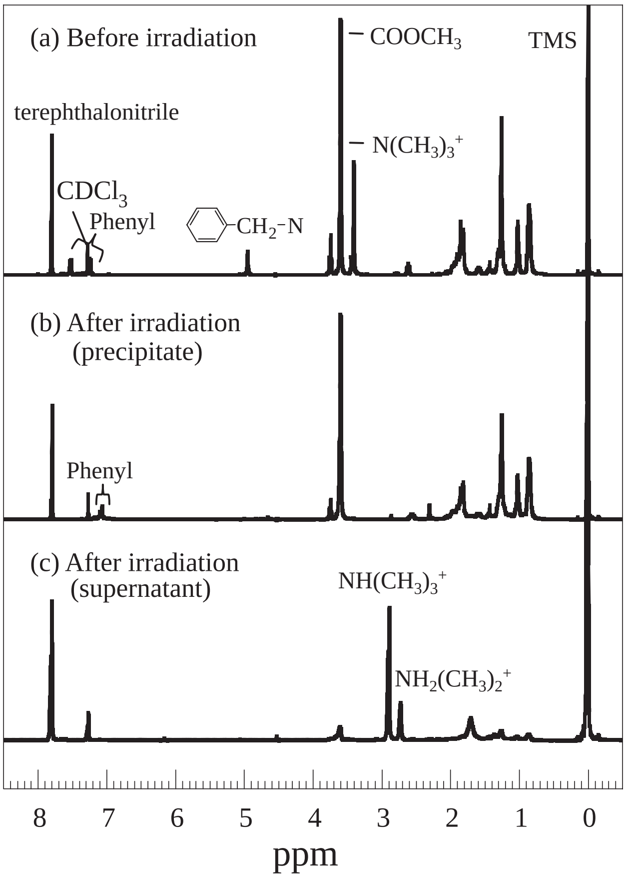


Figure 2. ^1H NMR spectra of PMMA/$C_{12}BA$ lattices dissolved in $CDCl_3$ (a) before irradiation, (b) precipitate after irradiation, and (c) supernatant after irradiation: terephthalonitrile (δ 7.80 ppm) and tetramethylsilane (TMS: δ 0.00 ppm) were added as internal standards.

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Table 1. Yields (%) of species in irradiated $C_{12}BA$/PMMA latex solution

Irrad.[a]	Fraction	PMMA[b]	$C_{12}BA$[c]	Hydrophobe[d]	Ion[e]
Before	Total	100	100	—	—
After	Total	100	4	86	93
	Precipitate	96	3	79	3
	Supernatant	4	0	0	68[f]

[a] $[C_{12}BA] = 3$ mM; [PMMA] = 29 mM; irradiation time, 90 min; products yields are based on the initial $C_{12}BA$ concentration. [b] Determined by peak area at 3.60 ppm. [c] Determined by peak area at 3.42 ppm. [d] Total yield of *p*-dodecylbenzyl alcohol, *p*-dodecyltoluene, and other minor products determined by peak area at 2.55 ppm. [e] Total yield of dimethyl- and trimethylammonium bromides, determined by peak areas at 2.73 and 2.89 ppm, respectively. [f] Partially insoluble in $CDCl_3$.

cylbenzyldimethylammonium chloride.[6] This is because the latices still hold a surface-activity after irradiation.

After irradiation for 90 min (almost 100% conversion), the suspended PMMA/$C_{12}BA$ solutions were centrifuged and the precipitate and supernatant were analyzed by ^{1}H NMR spectroscopy.[10] Figure 2 shows the spectra where some of assigned structures are indicated. Table 1 summarizes the quantitative data. As described below, the photoproducts of $C_{12}BA$ obtained in the latex were the same as those in water. The signals of PMMA (δ 0.8–2.1 ppm and 3.60 ppm) were observed in the precipitate (Figure 2b), whereas those in the supernatant were little (Figure 2c). In fact, the recovery of the polymer, calculated from the area for the methyl proton at 3.60 ppm, was 96% of the total. Most of the signal of the *N*-methyl proton in $C_{12}BA$ at 3.42 ppm disappeared both in the precipitate and supernatant, and those of the corresponding water-soluble products, dimethyl- and trimethylammonium bromides (2.73 ppm and 2.89 ppm, respectively) in the supernatant. In the same manner, the benzene protons in $C_{12}BA$ (7.2–7.6 ppm) disappeared, and those of the corresponding hydrophobic products, *p*-dodecylbenzyl alcohol, *p*-dodecyltoluene, and others (7.0–7.2 ppm), appeared in the precipitate. From those data, the conversion of $C_{12}BA$ was determined to be 96% and the removal of ionic species from the precipitate to be at least 94% (Table 1). Therefore, the photolysis of $C_{12}BA$ not only can recover the polymer but also can remove ionic species from it almost perfectly. It should be noted that salting-out of the unirradiated PMMA/$C_{12}BA$ latex with aqueous saturated NaCl solution recovered 87% of the total polymer and removed only 15% of $C_{12}BA$ from it. Such a large difference in ionic content would affect the performances of the resulting polymers. Preliminary experiments showed that ionic dyes were little adsorbed on the film and solid of the "photo"-precipitated polymer, though, containing some photo-products. This might be indicative of improved water-resistance or electrical insulation of the polymer coating.[11]

The photoreactivities of $C_{12}BA$ in the latex and H_2O are compared in Table 2.[12] Although the conversion of $C_{12}BA$ slightly decreased in the latex, the same products were obtained and their yields were not much different. It is thus concluded that $C_{12}BA$ in the polymer latex is photodegradated similarly to that in water (quantum yield = 0.45).[6]

In conclusion, the irradiation of the PMMA/$C_{12}BA$ latex can precipitate the polymer and can remove ionic species from it almost quantitatively, which may find various applications in polymer industry. For improvement of the reactivity and the sensitivity to a longer-wavelength light (>300 nm), the synthesis of different surfactants is in progress.

Table 2. Product yields (%) for photolysis of $C_{12}BA$ in PMMA latex and H_2O[a]

Sample	Conversion[b]	Alcohol	Alkyl	sec-A	tert-A
latex	85	7	26	32	4
$C_{12}BA$	95	9	23	37[c]	57[c]

[a] $[C_{12}BA] = 10$ mM; [PMMA] = 26 mM; irradiation time, 60 min; products yields are based on the initial $C_{12}BA$ concentration; Alcohol, *p*-dodecylbenzyl alcohol; Alkyl, *p*-dodecyltoluene; *sec*-A, dimethylammonium bromide; *tert*-A, trimethylammonium bromide. [b] Conversion yield of $C_{12}BA$ in %. [c] Irradiation time, 90 min.

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8 A typical polymerization procedure was as follows: To a mixture of 0.5 g of MMA, 0.6 g of $C_{12}BA$, and 45 g of water a 0.04 g of 2,2′-azobis(2-isobutylamidine) dihydrochloride in 5 g of water was added and heated to 60 °C under nitrogen atmosphere. Then 1 g of MMA was slowly added into the solution, which was kept at 60 °C for another 3.5 h. A portion of the resulting latex solution was lyophilized and weighed. The polymerization yield was 97%. The weight-average molecular weight of the obtained polymer was determined to be 80,000 by GPC.
9 The diluted polymer latex solution ($[C_{12}BA] = 3$ mM) in a quartz tube (13 mmϕ) was irradiated without deaeration at 25 °C with all light emitted from a 500-W high-pressure mercury lamp in a merry-go-round apparatus.
10 Irradiated samples were prepared as follows: the suspended solutions were centrifuged and the precipitate was dissolved in $CDCl_3$ containing a known amount of terephthalonitrile as an internal standard (δ 7.80 ppm). The supernatant solution was lyophilized and then re-dissolved in the above $CDCl_3$ solution. Non-irradiated samples were obtained by direct lyophilization or salting-out with NaCl followed by dissolution in $CDCl_3$.
11 Detailed characterization of the polymers is in progress.
12 The latex composition was slightly different from the above case.

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