

Surface Functionalization of Polymer Latex Particles: 4. Tailor-Making of Aldehyde-Functional Poly(methylstyrene) Latexes in an Emulsifier-Free System

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Controlled synthesis of aldehyde-functional poly(methylstyrene) (PMS) latexes in an emulsifier-free system was achieved via an emulsifier-free emulsion polymerization of methylstyrene using V-50 as an initiator, followed by an in-situ surface oxidation catalyzed by copper(II) chloride and *tert*-butyl hydroperoxide. Our investigation of the effect of oxidant concentration, reaction time, and temperature demonstrated that controlling the surface concentration of aldehyde and carboxylic acid groups was readily accomplished by altering these three reaction parameters. The concentration of the catalyst, however, was found to have little affect on the rate of oxidation. Furthermore, the amounts of surface aldehyde and carboxylic acid groups were determined by conductometric and potentiometric titrations. Electrolyte stability of functionalized latexes was also examined with regard to their critical coagulation concentrations in various salt solutions. Finally, SEM studies were conducted and clearly showed that surface morphology of functional latexes hardly altered with a low degree of oxidation but became aggregates when highly oxidized latexes were formed.

Introduction

Emulsifier-free latex particles with well-defined particle size and functional groups on the surface are highly desirable materials because of their important applications in a broad range of fields, e.g. as binders in paints, adhesives, paper coating, and textile and as a solid support in the biochemical and biomedical field, as well as in catalysis and calibration standards.^{1–3} These functional groups include hydroxyl,⁴ aldehyde,^{5–11} carboxylic acid,^{12–14} amino,^{15–17} epoxy,¹⁸ vinyl,¹⁹ sulfhydryl,²⁰ and chloromethyl

groups.^{21,22} Among them, the aldehyde group is especially useful because it can be bound with amino group-containing biomolecules in a single step, via the Schiff base linkage, without prior activation. Polymer particles with aldehyde functional groups have generally been prepared by five different approaches. (1) Emulsion homopolymerization of monomer containing aldehyde group: For example, Margel and Wiesel reported that monodisperse polyacrolein microspheres were obtained via a single-step process by either aqueous polymerization of acrolein under alkaline conditions or by aqueous radical polymerization.⁵ (2) Emulsion copolymerization of styrene with monomer containing aldehyde group: Yan et al. studied emulsifier-free emulsion copolymerization of styrene and acrolein.⁸ Pichot also described a radical-initiated copolymerization of styrene and *p*-formylstyrene by solution polymerization⁹ and by emulsifier-free emulsion polymerization.¹⁰ (3) Seeded copolymerization to produce composite latexes: Slomkowski et al. prepared core-shell latexes containing polyacrolein on the surface layer, via a seeded polymerization of acrolein in the presence of polypyrrole latexes initiated with K₂S₂O₈,²³ and has recently published a review article about polyacrolein-containing microspheres.²⁴ Okubo et al. also reported that submicrometer-size monodisperse polystyrene/polyglutaraldehyde composite particles which had aldehyde groups on the surfaces could be synthesized by seeded aldol condensation polymerization of glutaraldehyde in the presence of polystyrene particles prepared by emulsifier-free emulsion polymerization.¹¹ (4) Grafting of polyacrolein onto polymer particles: Polyacrolein has been grafted onto poly(methyl methacrylate) or polystyrene

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- (1) Pichot, C. *Polym. Adv. Technol.* **1995**, *6*, 427–434.
- (2) Pichot, C.; Charleux, B.; Charreyre, M.; Revilla, J. *Macromol. Symp.* **1994**, *88*, 71–87.
- (3) Wang, Q.; Fu, S.; Yu, T. *Prog. in Polym. Sci.* **1994**, *19*, 703–753.
- (4) Charleux, B.; Pichot, C.; Llauro, M. F. *Polymer* **1993**, *34*, 4352–4359.
- (5) Margel, S.; Wiesel, E. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 145–158.
- (6) Margel, S. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3521–3533.
- (7) Rembaum, A.; Chang, M.; Richards, G.; Li, M. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 609–621.
- (8) Yan, C.; Zhang, X.; Sun, Z.; Kitano, H.; Ise, N. *J. Appl. Polym. Sci.* **1990**, *40*, 89–98.
- (9) Charleux, B.; Pichot, C. *Makromol. Chem.* **1992**, *193*, 187–203.
- (10) Charleux, B.; Fanget, P.; Pichot, C. *Makromol. Chem.* **1992**, *193*, 205–220.
- (11) Okubo, M.; Kondo, Y.; Takahashi, M. *Colloid Polym. Sci.* **1993**, *271*, 109–113.
- (12) Ceska, G. W. *J. Appl. Polym. Sci.* **1974**, *18*, 2493–2499.
- (13) Sakota, K.; Okaya, T. *J. Appl. Polym. Sci.* **1977**, *21*, 1025–1034.
- (14) Sakota, K.; Okaya, T. *J. Appl. Polym. Sci.* **1977**, *21*, 1035–1043.
- (15) Charreyre, M.; Razafindrakoto, V.; Veron, L.; Delair, T.; Pichot, C. *Macromol. Chem. Phys.* **1994**, *195*, 2153–2167.
- (16) Delair, T.; Marguet, V.; Pichot, C.; Mandrand, B. *Colloid Polym. Sci.* **1994**, *272*, 962–970.
- (17) Ganachaud, F.; Mouterde, G.; Delair, T.; Elaissari, A.; Pichot, C. *Polym. Adv. Technol.* **1995**, *6*, 480–488.
- (18) Kling, J. A.; Ploehn, H. J. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1107–1118.
- (19) Okubo, M.; Nakagawa, T. *Colloid Polym. Sci.* **1992**, *270*, 853–858.

(20) Delair, T.; Pichot, C.; Mandrand, B. *Colloid Polym. Sci.* **1994**, *272*, 72–81.

(21) Sarobe, J.; Forcada, J. *Colloid Polym. Sci.* **1996**, *274*, 8–13.

(22) Okubo, M.; Iwasaki, Y.; Yamamoto, Y. *Colloid Polym. Sci.* **1992**, *270*, 733–737.

(23) Basinska, T.; Kowalczyk, D.; Miksa, B.; Slomkowski, S. *Polym. Adv. Technol.* **1995**, *6*, 526–533.

particles through a γ -irradiation technique.^{25,26} Similar approaches were also examined for the preparation of polyglutaraldehyde-based particles.^{27,28} (5) Surface modification of preformed latexes: For example, benzyl halide groups on the surface of poly(styrene-*co*-chloromethylstyrene) latexes were converted to benzaldehyde groups by oxidation with 2-nitropropane in aqueous sodium methoxide.²⁹ Although the above approaches have been successfully adopted in preparing aldehyde-functional polymer particles, some major drawbacks of these methods have been identified. First, there are significant differences in solubility and reactivity between functional and matrix monomers in heterogeneous systems, resulting in the formation of water-soluble polymers and low incorporation of the functional monomer on or into the particles. In addition, synthesis of emulsifier-free polymer particles with controlled particle size and aldehyde content on the surface is very difficult to achieve.

Recently, a simple and versatile method of producing aldehyde-functionalized poly(methylstyrene) (PMS) latexes via a surface oxidation of either anionic or cationic PMS latexes catalyzed by copper chloride in the presence of *tert*-butyl hydroperoxide has been developed by our research group.^{30–34} This method is capable of controlling the particle size and amounts of functional groups on the surface by first synthesizing the desirable size of PMS particles, followed by surface functionalization. In addition, it offers a way of bypassing the problems associated with the use of functional monomers. In this paper, as part of our continuing efforts on the catalytic surface functionalization of poly(methylstyrene) latexes, we wish to report on the synthesis and characterization of functional PMS latexes in an emulsifier-free emulsion system with controlled amounts of aldehyde units on the particle surface.

Experimental Section

Materials. Phenolic inhibitor in 3(4)-methylstyrene (60:40 *m-p*-methylstyrene) (Aldrich) was removed by washing three times with 10% sodium hydroxide solution and then deionized water until the pH of the monomer dropped to 7. It was further purified by vacuum distillation. Freshly deionized and distilled water was used as a dispersion medium. The initiator, 2,2'-azobis(2-amidinopropane) dihydrochloride (V-50), was from Wako Chemicals, and the analytical grade copper(II) chloride dihydrate was from BDH. *Tert*-butyl hydroperoxide (70%) and hydroxylamine hydrochloride ($\text{H}_2\text{NOH}\cdot\text{HCl}$) were purchased from Acros Organic Co. Other chemicals were all reagent grade and used without further purification.

Synthesis and Purification of Emulsifier-Free Poly(methylstyrene) Latexes. A detailed procedure for the synthesis of emulsifier-free poly(methylstyrene) latexes was described previously.³³ The mean particle size and polydispersity of the latexes obtained were 753 nm in diameter and 1.15, respectively. The PMS latexes prepared were dialyzed against

deionized water using a molecular porous membrane dialysis tube (Spectra/Pro) for 1 week in order to remove impurities such as residual initiators, low molecular weight oligomers, and electrolytes. The deionized water was replaced every 12 h and monitored with a conductivity meter. The serum replacement technique was also used to speed up the purification process. The diluted latex dispersion was placed in a filtration assembly with a filtration membrane (0.22 μm pore size). A mechanical stirrer was mounted above the filtration assembly, and the serum was replaced by filtration and addition of deionized water under continuous stirring.

Catalytic Oxidation of Poly(methylstyrene) Latexes. The cleaned poly(methylstyrene) (PMS) latex dispersion (20 mL, 1 g of PMS) was mixed with a prescribed amount of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (1:50 mole ratio to *t*-BuOOH) dissolved in 5 mL of deionized water. The mixture was heated to either 60 or 70 °C, and then *tert*-butyl hydroperoxide (0.025–0.7 M) was added dropwise to the mixture. The oxidation reaction was carried out under air with continuous stirring. The oxidized PMS latexes were isolated quantitatively by precipitation of the dispersion into hot methanol and characterized by FT-IR spectrophotometer (Nicolet 750) using KBr disks. Furthermore, the degree of oxidation was estimated by elemental analyses performed at MEDAC Ltd., Department of Chemistry, Brunel University, Middlesex, U.K.

Determination of Particle Size and Distribution. Particle size and distribution were determined using a Coulter LS-230 particle size analyzer. The average diameter was calculated on the volume base. The particle size and surface morphology of the latexes were also examined by scanning electron microscopy (SEM Stereoscan 440, Leica). A drop of diluted latex dispersion was spread onto a glass surface and dried in a dust-free environment at room temperature. The dried specimen was then coated under vacuum with a thin layer of gold to a depth of ca. 5 Å.

Determination of Aldehyde Content. The amount of aldehyde on the particle surface was determined according to a pH 2.5 method reported in the literature.¹¹ The cleaned latex dispersion (30 mL, approximately 3% solid content) was placed in a 100 mL beaker. The pH value of the dispersion was adjusted to 2.5 with 0.1 N HCl solution. Hydroxylamine hydrochloride ($\text{N}_2\text{HOH}\cdot\text{HCl}$) aqueous solution (1 N, 30 mL), which had been preadjusted to pH = 2.5 with 0.1 N HCl solution, was then added to the latex dispersion. The mixture was stirred for 1 h at room temperature, followed by titration with 0.005 N NaOH solution until the pH value of the mixture reached 2.5. The number of moles of aldehyde group was calculated on the basis of the volume of NaOH consumed. For example, with assumption that volume V_1 (mL) of latex dispersion with a solid content of $X\%$ was titrated with 0.005 M sodium hydroxide aqueous solution, a volume of NaOH (V_2) was consumed. The aldehyde content was then calculated according to the following equations:

$$\text{aldehyde (mol/g of particles)} = 0.005 \times V_2/1000 \times V_1 \times X$$

$$\begin{aligned} \text{aldehyde (mol/m}^2) &= \frac{\text{aldehyde (mol/g of particles)}}{\text{surface area (m}^2/\text{g of particles)}} \\ &= \frac{5 V_2 \rho D}{6 \times 10^7 V_1 X} \end{aligned}$$

Here ρ is the density of a latex particle (PMS = 1.05 g/cm³) and D is the mean particle size in diameter.

$$\text{no. of aldehyde/m}^2 = N_A \times \text{aldehyde (mol/m}^2)$$

where N_A is the Avogadro's constant.

$$\begin{aligned} \text{average surface area (\AA}^2/\text{aldehyde)} &= \\ &= 1/(\text{no. of aldehyde/m}^2) \times 10^{20} \end{aligned}$$

Determination of Carboxylic Acid Content. The amount of carboxylic acid groups on the surface of the oxidized latexes was determined by both potentiometric and conductometric titration methods. Latex dispersion (40 mL) was titrated under nitrogen atmosphere with 0.005 M NaOH solution, both poten-

(24) Slomkowski, S. *Prog. Polym. Sci.* **1998**, *23*, 815–874.

(25) Margel, S.; Beitler, V.; Ofarin, M. *J. Cell. Sci.* **1982**, *56*, 157.

(26) Yen, R.; Rembaum, A. *Enzyme Microb. Technol.* **1984**, *6*, 317.

(27) Rembaum, A.; Margel, S.; Levy, J. *J. Immunol. Methods* **1978**, *24*, 239.

(28) Margel, S.; Zisblatt, S.; Rembaum, A. *J. Immunol. Methods* **1979**, *28*, 341.

(29) Oenick, M. D. B.; Warshawsky, A. *Colloid Polym. Sci.* **1991**, *269*, 139.

(30) Li, P.; Liu, J. H.; Yiu, H. P.; Chan, K. K. *J. Polym. Sci. A: Polym. Chem.* **1997**, *35*, 1863–1872.

(31) Li, P.; Liu, J. H.; Wong, T. K.; Yiu, H. P.; Gau, J. *J. Polym. Sci. A: Polym. Chem.* **1997**, *35*, 3585–3593.

(32) Li, P.; Xu, J.; Wu, C. *J. Polym. Sci. A: Polym. Chem.* **1998**, *36*, 2103–2109.

(33) Xu, J.; Li, P.; Wu, C. *J. Polym. Sci. A: Polym. Chem.* **1999**, *37*, 2069–2074.

(34) Li, P.; Xu, J.; Wu, C. *Colloids Surf., A* **1999**, *153*, 363–366.

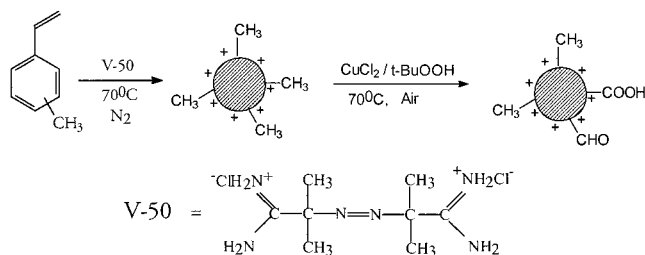


Figure 1. Synthesis and surface oxidation of poly(methylstyrene) latex particles.

tiometrically and conductometrically, in the same vessel at room temperature. In these titration experiments, solid content between 3 and 4% w/w was most suitable. The potentiometric titration was performed with an Orion pH meter (model 250A) equipped with a glass electrode, and a Horiba conductivity meter (model ES-14 E) was used for the conductometric titration.

Determination of Critical Coagulation Concentration of PMS Latexes. Stability measurements of the functionalized latexes were performed by a turbidity method. The functionalized latex dispersion was diluted to a latex volume fraction of 2×10^{-4} . In coagulation experiments, 0.1 mL of the latex dispersion was added to 1.9 mL of salt solution with the desired concentration. The critical coagulation concentration of the latexes at different salt concentrations was determined by turbidity at wavelength of 400–600 nm using an Orbeco-Hellige turbidimeter. Relative turbidities τ_0/τ were plotted against $\log c$, where c was the salt concentration and τ_0 and τ were the turbidities of the latexes before and after addition of salt. The turbidity was measured at a distinct time period after salt addition, usually 1 min.

Results and Discussion

Synthesis of Emulsifier-Free Poly(methylstyrene) Latexes. Highly monodispersed emulsifier-free cationic poly(methylstyrene) latexes were prepared via an emulsifier-free emulsion polymerization of 3(4)-methylstyrene using 2,2'-azobis(2-amidinopropane) dihydrochloride (V-50) as an initiator (Figure 1). The optimal reaction conditions have been studied systematically and reported elsewhere.^{33,34} The mean particle size and its polydispersity were found to be 753 nm in diameter and 1.15, respectively. Prior to the oxidation reaction, the PMS latex dispersion was purified by either dialysis or serum replacement methods in order to remove impurities such as residual initiators, water-soluble oligomers, and electrolytes.

Oxidation Kinetic of Poly(methylstyrene) Latexes. The surface of PMS latexes was oxidized in the presence of *tert*-butyl hydroperoxide catalyzed by copper(II) chloride at 70 °C under air for up to 24 h to obtain functional PMS latexes containing aldehyde and carboxylic acid groups (Figure 1). The oxidation mechanism was described in our previous paper.³⁰ During the reaction, samples were drawn out at various time intervals in order to study the oxidation kinetic. Figure 2 demonstrated that the reaction proceeded rapidly, reaching 3.21% oxygen content during the initial 8 h, and then the rate of reaction decreased significantly. This decrease could be explained by two possible reasons: (i) decrease in oxidant concentration; (ii) instability of the latexes resulting in decreasing the total particle surface area. After 6 h of oxidation, flocculation of the latexes started to appear. This instability might be caused by a significant reduction of the total cationic surface charge density, which could occur when the surface cationic charges were partly neutralized by the newly formed carboxylic acid group on the particle surface.

Effect of Oxidant Concentration. The oxidant concentration played a key role in the catalytic oxidation

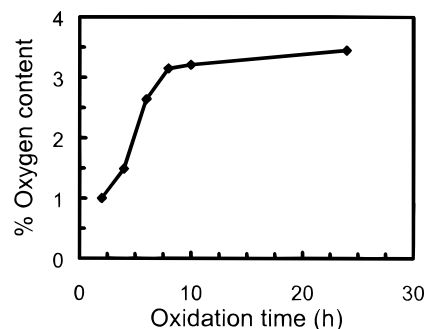


Figure 2. Oxidation kinetic of PMS latexes catalyzed by $\text{CuCl}_2/t\text{-BuOOH}$ at 60 °C. The percentage of oxygen content was determined by elemental analyses.

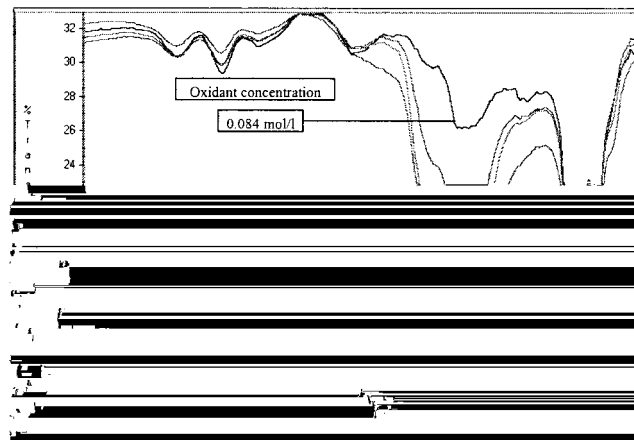


Figure 3. FTIR spectra of PMS latexes oxidized with different oxidant concentrations. The mole ratio of oxidant to catalyst was kept at 50:1, and all reactions were carried out at 70 °C for 4 h under air.

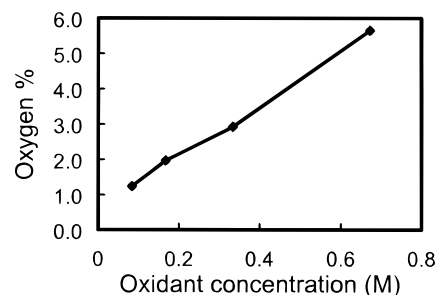


Figure 4. Oxygen content of the oxidized PMS as a function of oxidant concentration.

reaction. No oxidation was observed when only oxygen was bubbled through the latex dispersion containing copper(II) chloride at 60 °C. The effect of *tert*-butyl hydroperoxide (*t*-BuOOH) concentration on the rate of oxidation was investigated by varying its concentration from 0.084 to 0.668 M as shown in Figure 3. A strong and broad peak between 1690 and 1720 cm^{-1} indicated the formation of both aldehyde and carboxylic acid functionalities concurrently, with the carboxylic acid groups being the major ones on the latexes. The intensity of the peak increased notably with the rise of *t*-BuOOH concentration. Similar results were also obtained on the basis of the elemental analyses of the oxidized products as shown in Figure 4. However, when the concentration of oxidant exceeded 0.5 M, the latexes became unstable.

Effect of Catalyst Concentration. The effect of catalyst concentration on the degree of oxidation was examined by varying the concentration of copper(II) chloride from 0.0034 to 0.034 M. Results in Table 1 indicate

Table 1. Effect of Copper(II) Chloride Concentration on Oxidation of PMS Latexes^a

concn of CuCl ₂ (mol/L)	mole ratio of BuOOH:Cu ²⁺	oxygen content ^b (%)
0.034	1:0.1	2.85
0.017	1:0.05	2.88
0.0034	1:0.01	2.84

^a Reactions were carried out in the presence of 0.34 M of *t*-BuOOH and 0.017 M CuCl₂·2H₂O for 4 h under air. ^b The percentage oxygen content was determined by elemental analysis.

Table 2. Effect of Reaction Temperature on Oxidation of PMS Latexes^a

reacn temp (°C)	reacn time (h)	oxygen content ^b (%)
60	4	1.49
70	4	2.88
80	4	3.98

^a Reactions were carried out in the presence of 0.34 M of *t*-BuOOH and 0.017 M CuCl₂·2H₂O for 4 h under air. ^b The percentage oxygen content was determined by elemental analysis.

that the concentration of CuCl₂ catalyst had little effect on the degree of oxidation of the PMS latexes. Metal-catalyzed decomposition of alkyl hydroperoxide (ROOH) into the corresponding RO₂[·] and RO[·] radicals has been extensively employed for many oxidation reaction.³⁵ It is well-known that the reaction undergoes an autoxidation mechanism under air. Thus the catalyst concentration had little influence on the rate of oxidation.

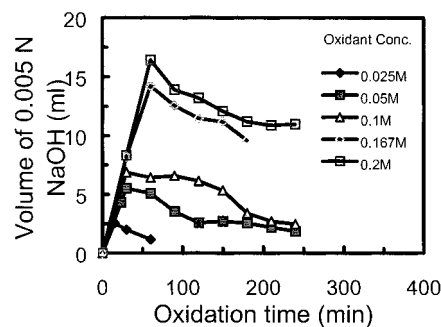
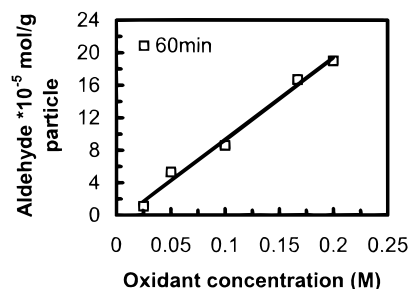
Effect of Reaction Temperature. Table 2 shows that the degree of oxidation of the PMS latexes increases with the increase of reaction temperature. This may be a result of enhancing the decomposition rate of alkyl peroxide. Since our research interest focuses mainly on producing the aldehyde functionality on the PMS particle surface, higher reaction temperatures may not be suitable because they lead to more rapid conversion of aldehyde to the corresponding carboxylic acid groups, thus reducing the quantity of aldehyde groups. Therefore, the reaction temperature was generally set at 70 °C.

Concentration of Surface Aldehyde Groups. Controlling the surface functionalization is one of the most important and challenging aspects of the synthesis of functional latexes. An ideal functional particle should contain functional groups located on the surface of latex particles. For example, for PMS particles with mean diameter of 753 nm and density $\rho = 1.05 \text{ g/cm}^3$, if a cross-sectional area of 24 Å is taken for the aldehyde group (the value for alcohol³⁶), theoretically speaking, the number of moles of aldehyde needed to cover the surface of 1 g of latex particles is $5.26 \times 10^{-5} \text{ mol/g}$, which corresponds to an oxygen content of 0.084%. If all the functional groups located on the latex surface are assumed to be carboxylic acid groups, the oxygen content required should be 0.168%. In other words, if only the surface oxidation occurs, the maximal oxygen content should be lower than 0.168%. When these theoretical values were compared with our elemental analysis results for the oxidized PMS, it was found that the oxidation reaction occurred not only on the particle surface but also into the inner layer of the particles, especially when higher oxidant concentration was utilized.

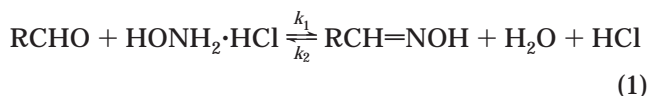
(35) Sosnovsky, G.; Rawlinson, D. J. In *Organic Peroxides*, Swern, D., Ed.; Wiley-Interscience: New York, 1971, Vol. II, p 269; 1972; Vol. III, p 141.

(36) LeDissez, C.; Wong, P. C.; Mitchell, K. A. R.; Brooks, D. E. *Macromolecules* **1996**, *29*, 953–959.

(37) Yan, C.; Zhang, X.; Sun, Z.; Kitano, H.; Ise, N. *J. Appl. Polym. Sci.* **1990**, *40*, 89–98.

**Figure 5.** Effect of *t*-BuOOH concentrations on surface concentration of aldehyde.**Figure 6.** Relationship between surface concentration of aldehyde and the *t*-BuOOH concentration based on 60 min of oxidation.

Determination of Aldehyde Content on the Particle Surface. Two common methods have been reported in the literature for the determination of surface concentration of aldehyde. They are the colorimetric assay method based on reaction with dinitrophenylhydrazine (DNPH)^{23,36} and conductometric titration based on the release of HCl.^{5,11,37} In this study, the conductometric titration has been employed because of its simple experimental procedure. The basic reaction is shown in eq 1.



Aldehyde groups could easily react with hydroxylamine hydrochloride at room temperature to form oxime and hydrochloric acid (HCl). The concentration of HCl released from this reaction could be simply determined by titration with NaOH solution, thus the amount of aldehyde groups on the latex could be estimated. A detailed procedure using a pH 2.5 method has been described in the Experimental Section. Figure 5 showed that the volume of NaOH solution used for the titration of oxidized PMS latexes obtained in the initial reaction reached a maximum, and then decreased gradually. These results suggested that amounts of surface aldehyde increased very rapidly in the initial stage of the oxidation for all oxidant concentrations and then slowly reduced due to their further oxidation to the corresponding carboxylic acid groups. Figure 6 demonstrated a typical plot of the surface concentration of aldehyde versus oxidant concentration after 60 min of reaction. An almost linear relationship between the oxidant concentration and the surface concentration of aldehyde was discovered. In other words, the desired amount of aldehyde on the particle surface could be easily obtained by controlling the oxidant concentration.

Since the amount of the surface aldehyde groups could be manipulated by oxidant concentration and reaction

Table 3. Surface Concentrations of Aldehyde Using Different *t*-BuOOH Concentrations^a

time (min)	$10^5 \times$ aldehyde ^b for [<i>t</i> -BuOOH] of				
	0.025 M	0.05 M	0.10 M	0.167 M	0.20 M
15	2.66	4.48			
30	2.08	5.76	9.05		
45	1.22				
60	1.07	5.31	8.58	16.7	19.0
90		3.69	8.74	15.0	15.4
120		2.71	8.27	14.1	15.4
150		2.83	7.44	13.5	13.0
180		2.66	4.49	11.1	13.5
210		2.29	4.70	3.79	13.2
240		1.93	4.45		13.3

^a Reaction conditions: PMS:CuCl₂ = 50:1, at 70 °C under air. Mean particle size = 753 nm. ^b The number of moles of aldehyde per gram of latexes.

time, a series of functional latexes was prepared using an oxidant-to-catalyst ratio of 50:1 at 70 °C under air. Four *t*-BuOOH concentrations, 0.025, 0.05, 0.167, and 0.2 M, were examined at various reaction periods, and results are summarized in Table 3. The percentage surface coverage by aldehyde groups could be estimated by the following calculation. For example, when the PMS particles were oxidized for 15 min at 70 °C in the presence of 0.05 M *t*-BuOOH, the concentration of aldehyde groups was 4.48×10^{-5} mol/g, which translated to an area per group of about 28.82 Å. Assuming a cross-sectional area of 24 Å for the aldehyde group (the value for an alcohol³⁶), the implication was that approximately $24/28.82 = 83\%$ of the particle surface was occupied by aldehydes, if they were uniformly distributed. On the basis of this calculation, it can be seen from Table 3 that the percentage of surface coverage by aldehyde groups exceeded 100% when *t*-BuOOH concentration was higher than 0.10 M. These results were similar to the elemental analysis suggesting that the oxidation occurred also in the inner layer of particles. Therefore, to obtain a desirable quantity of aldehyde groups on the surface, it was important to control both the oxidant concentration and reaction time. Low oxidant concentration (such as 0.05 M *t*-BuOOH) and short reaction time (e.g. 30 min) were the most appropriate conditions to achieve high surface aldehyde functionality.

Determination of Carboxylic Acid Groups on the Particle Surface. The amount of carboxylic acid groups was determined by titrating the latex dispersion with NaOH under a nitrogen atmosphere. Figure 7a shows the titration curves of the purified virgin PMS latexes. The equivalent points determined by both potentiometric and conductometric titrations were in good agreement. The titration curves showed that only strong acid was present, which were H⁺ ions originating from the initiator (V-50). As demonstrated in Figure 7b, both potentiometric and conductometric titrations of the functionalized PMS latexes which were oxidized with 0.025 M *t*-BuOOH after 1 h gave two equivalent points, corresponding to a strong acid group (HCl) and a weak acid group (-COOH), respectively. On the basis of the volume of the NaOH consumed, the surface concentration of carboxylic acid was calculated to be 1.05×10^{-4} mol/g of particle. Comparing this value with the amount of aldehyde groups (1.07×10^{-5} mol/g of particle) reported in Table 3, we could conclude that carboxylic acid groups were the major functionality, which was consistent with FT-IR studies.

Surface Morphology of Latexes. Surface morphologies of latexes during the oxidation were investigated by scanning electron microscopy. The particle sizes were also determined using a Coulter's particle size analyzer at the same time. Figure 8b-d displays the SEM micrographs

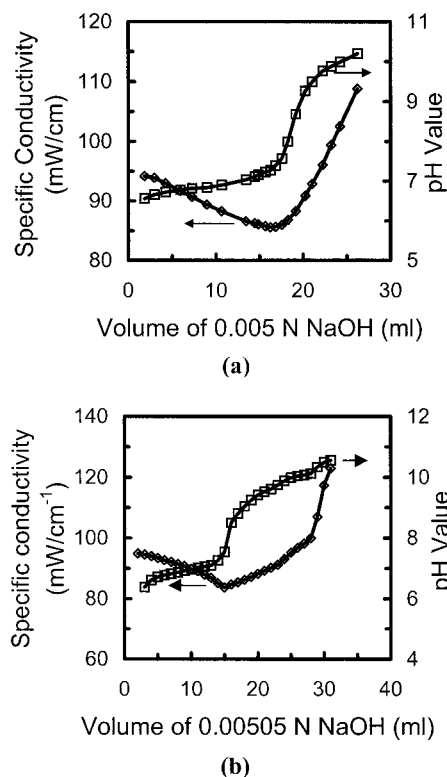


Figure 7. Conductometric and potentiometric titration curves: (a) pure PMS latexes; (b) functionalized PMS latexes after 60 min oxidation.

of poly(methylstyrene) particles oxidized for 15, 30, and 60 min, using *t*-BuOOH (0.025 M) and CuCl₂ (5.0×10^{-4} M) at 70 °C under air. The PMS particles prior to the oxidation were highly monodispersed as shown in Figure 8a. As the oxidation proceeded, a majority of particles remained the same size except for a few small particles. This study demonstrated that the particle size and surface morphology of the functionalized particles changed little when low oxidant concentration and short reaction time were employed. In other words, this method allows us to prepare functional-aldehyde poly(methylstyrene) particles with controlled particle size as well as controlled functionality. Figure 8e,f shows SEM micrographs of the PMS particles oxidized using higher concentration of *t*-BuOOH (0.167 M) for a longer time. After 8 h of oxidation, an aggregation of particles was obviously noted, suggesting that the system became unstable. As the reaction proceeded further, e.g. for 24 h, more and more large aggregates and precipitates were observed even though the dispersion was under vigorous stirring. The aggregation of highly oxidized latex particles was also confirmed by the particle size analysis at different reaction times as shown in Figure 9. The original particles were highly monodispersed. After oxidation with relatively high concentration of *t*-BuOOH (0.167 M) for 2 h, aggregates were detected, which had an average size about 2 μm. The peak of larger aggregates in the distribution curve rose with an increase in reaction time. After 12 h of oxidation, a bimodal size distribution appeared. The instability of the highly oxidized poly(methylstyrene) latexes might be attributed to the interaction between the negatively charged carboxylic acid groups and the positively charged imidino ions on the particle surface. As a result, the total surface charge density was substantially decreased, leading to the coagulation of the particles.

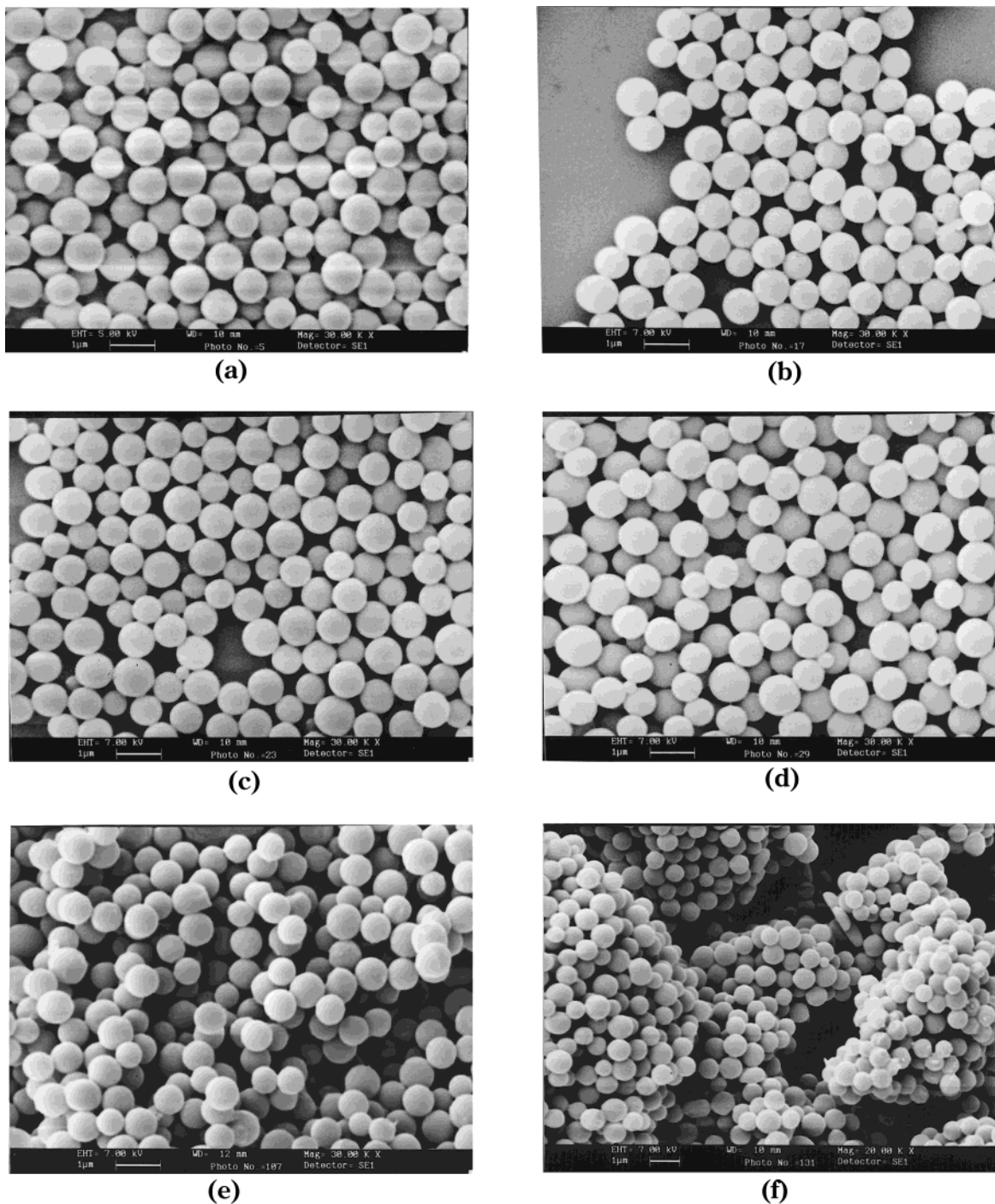


Figure 8. SEM micrographs of PMS latexes: (a) without oxidation; (b) oxidized for 15 min; (c) oxidized for 30 min; (d) oxidized for 60 min; (e) oxidized for 8 h; (f) oxidized for 24 h.

Stability of Latexes. In general, addition of inorganic salts caused the latex dispersion to coagulate. To determine the stability of functional PMS latexes with respect to the degree of oxidation, a series of latexes with various aldehyde content on the particle surface were examined using a turbidity method. Figure 10 shows four curves for the functionalized PMS with various degrees of oxidation in NaCl solution. These curves consist of two approximately linear sections. In the first section, the stability of the latex decreases rapidly with the increase in concentration of electrolyte, whereas, in the second section, it is independent of electrolyte concentration. The intersection of the two linear parts corresponds to the transition from the region of slow coagulation to that of rapid coagulation. Consequently, the critical coagulation can

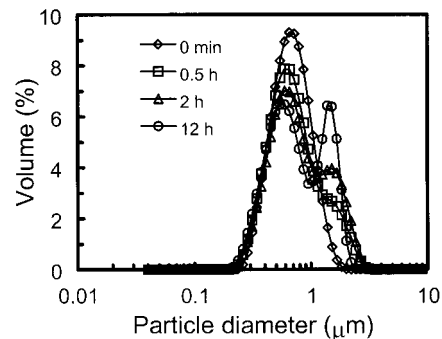


Figure 9. Variation of particle size distributions of PMS latexes during the oxidation.

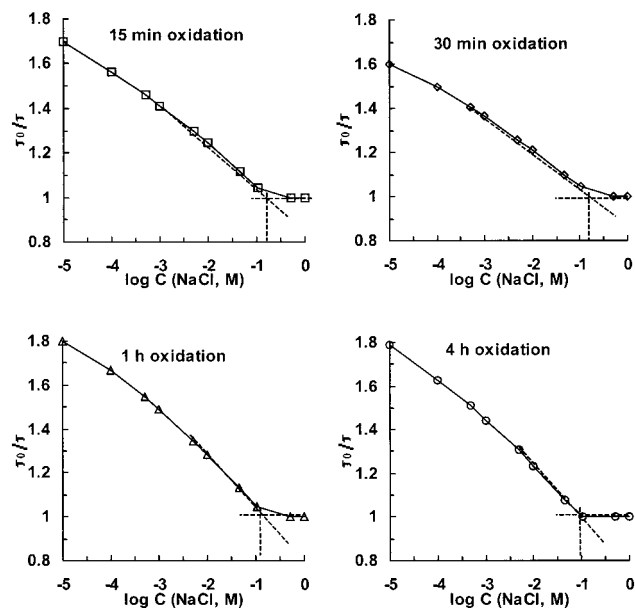


Figure 10. Turbidity studies of various oxidized PMS latexes in NaCl solution.

Table 4. Critical Coagulation Concentration of PMS Latexes with Different Types of Salt^a

salt	no oxidn	after 15 min of oxidn ^b	after 30 min of oxidn ^b	after 1 h of oxidn ^b	after 4 h of oxidn ^b
LiCl	200	195	182	166	111
NaCl	158	158	141	126	79
KCl	63				
NaF	250				
NaCl	158	158	141	126	79
NaI	35	33	25	16	11
MaCl ₂	20	18	17	14	7
CaCl ₂	11				

^a Critical coagulation concentration (C_{crit}) was determined by the turbidity method. The concentration unit was $\text{mmol}\cdot\text{L}^{-1}$. ^b The latexes were oxidized by using *t*-BuOOH (0.025 M) and CuCl_2 (5.0×10^{-4} M) at 70 °C.

be obtained from this intersection point. Detailed results of the critical coagulation concentrations (C_{crit}) of all latexes determined by the turbidity method are listed in Table 4.

A closer inspection of the coagulation process for univalent counterions indicated that the effect of both cations and anions on C_{crit} was very significant. The cations followed the order for C_{crit} of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, while the anions had the order for C_{crit} of $\text{F}^- > \text{Cl}^- > \text{I}^-$. In addition, the stability of the latexes against divalent cationic electrolytes was very poor, and the critical coagulation concentration for the same latexes was 10–50 times smaller than the univalent electrolytes. Finally, critical coagulation concentrations of the functionalized PMS latexes decreased with the increase in degree of oxidation in the same electrolyte solution.

The difference in critical coagulation concentration in our investigation can be readily interpreted in terms of an exchange process at the solid and liquid phase. The latexes prepared by the emulsifier-free emulsion polymerization were spherical particles with smooth surfaces and were stabilized by the surface charge originating from the initiator segments. When some electrolyte, e.g. NaI, was added to the dispersion, any ion in the vicinity of the amidino groups was displaced by the iodine ion which was weakly hydrated. Some of the ions might bind directly to the amidino groups to form an inactive ion pair, resulting in the decrease of latex stability. On the contrary, addition of the same amount of sodium chloride did not cause aggregation to larger flocs because of strong hydration forces arising from the binding of more hydrated chloride. Finally, the decrease of critical coagulation concentration with increasing degree of oxidation might be caused mainly by the decrease of surface charge density as a result of higher carboxylic acid content.

Conclusions

Functionalization of poly(methylstyrene) latex particles in the emulsifier-free system was successfully achieved in this study, using the $\text{CuCl}_2/t\text{-BuOOH/air}$ system. By manipulation of the reaction conditions, surface concentration of aldehyde groups could be tailored from 2.7×10^{-5} to 1.67×10^{-4} mol/g depending on the oxidant concentration, reaction time, and temperature. The degree of oxidation increased with reaction time, but the dispersion of the highly oxidized poly(methylstyrene) latexes was found to be unstable. An increase in oxidant concentration enhanced the rate of oxidation, while the catalyst concentration had little influence on it. Raising reaction temperature also increased both the rate and degree of oxidation. Surface characterization of the functional latexes by conductometric and potentiometric titrations suggested that mild oxidation conditions were more appropriate in order to obtain high surface occupancy of aldehyde groups with little change in particle size and surface morphology. However, highly oxidized particles became unstable, and aggregation later occurred. The critical coagulation concentration of latexes depended on the type of salt and the degree of oxidation of the latexes. A higher oxidation degree gave a lower particle stability in NaCl solution. Finally, our method has clearly demonstrated that functional-aldehyde poly(methylstyrene) particles with controllable particle size and amounts of functionality can be conveniently produced, which will lead to an improvement for potential applications of functional particles in the biochemical and biomedical fields.

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