Surface Functionalization of Polymer Latex Particles. III. A Convenient Method of Producing Ultrafine Poly(methylstyrene) Latexes with Aldehyde Groups on the Surface

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ABSTRACT: A convenient method of preparing ultrafine poly(methylstyrene) (PMS) latex particles with aldehyde groups on the surface is developed. PMS latexes in the size range 33–81 nm were prepared via microemulsion polymerization, using cetyltrimethylammonium bromide (CTAB) as surfactant. The surface of the PMS latexes was oxidized in the presence of *tert*-butyl hydroperoxide catalyzed by copper(II) chloride. As the degree of oxidation increased up to 6 h, the amounts of aldehyde group increased. Bigger particles were found to have a slightly higher rate of oxidation than small ones under the same oxidation conditions. The particle size underwent little change during oxidation; thus, the amounts of functional groups and the particle size could be controlled concurrently. Dialysis study of the oxidized PMS microlatexes indicated that the instability of highly oxidized PMS microlatexes was caused by the reduction of total surface charge density due to the presence of carboxylic acid groups. © 1998 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 36: 2103–2109, 1998

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INTRODUCTION

There has been an increased interest in ultrafine functional polymer particles in recent years because of their extremely large specific surface area which is of scientific and technical importance.[1-3] Polymer latexes prepared by emulsion polymerizations are bases of adhesives, paints, coatings, and solid supports.[4,5] Ultrafine particles (less than 100 nm in diameter) with surface functional groups may find many other applications, for example, as colloidal drug carriers, microencapulation, and detoxification agents.[6-10] The polymer particles containing aldehyde groups on the surface are particularly desirable in some of these applications because they can covalently bind with the amino group-containing biomolecules, e.g. proteins, drugs, and enzymes by the formation of a Schiff base at room temperature.[11-13] This kind of particle is generally prepared by the emulsion polymerization of acrolein under alkaline conditions or by the copolymerization of acrolein with styrene.[11,14,15] Okuba et al. reported a technique to produce submicron-size polymer particles bearing aldehyde groups via seeded aldol condensa-

tion polymerization of glutaraldehyde (GLA) in the presence of polystyrene particles of which size and monodispersity were preliminarily controlled.[16,17] Pichot et al. investigated emulsifier-free emulsion polymerization of *p*-formylstyrene in order to incorporate aldehyde groups on the surface of polystyrene latexes.[18] Furthermore, chemical modification of benzyl halide groups on the surface of poly(styrene-*co*-chloromethylstyrene) latexes to benzaldehyde groups by oxidation with 2-nitropropane in aqueous sodium methoxide was studied.[19]

Poly(methylstyrene) has recently received considerable commercial interest because of new monomer synthesis from toluene and ethylene that could result in low prices. Furthermore, methylstyrene exhibits reactivity analogous to that of styrene.[20] Stöver and his co-workers have reported a solvent-based selective oxidation of poly(4-methylstyrene) with cobalt acetate/sodium bromide to afford a polymer bearing both aldehyde and carboxylic acid groups.[21–23] We have also demonstrated a facile synthesis of functionalized poly(methylstyrene) latex particles (>100 nm in diameter) containing aldehyde and carboxylic acid groups on the surface via a metal-catalyzed oxidation in aqueous emulsion.[24,25]

Polymerization in microemulsion is a relatively new and versatile technique which allows for the synthesis of microlatexes less than 100 nm in diameter. In addition, well-defined size and narrowly distributed latexes can be easily obtained by controlling the surfactant to monomer ratio. Recently, Antonietti and his co-workers reported the copolymerization of styrene with various methacryl esters in microemulsion, giving microlatex sizes ranging from 25 to 50 nm in diameter.[9,26] Microemulsion copolymerization of styrene and acrylic acid in the presence of dodecyltrimethylammonium bromide has also been attempted.[27] However, control of both the size of microlatexes and the amounts of functionality on the surface is usually difficult to achieve concurrently. As part of our continuing studies on the catalytic surface functionalization of polymer particles, we now wish to report a convenient method of producing ultrafine poly(methylstyrene) microlatexes containing aldehyde and carboxylic acid functionalities on the surface. We first concentrated on the synthesis of well-defined microlatexes of poly(methylstyrene) via microemulsion polymerization and

then studied the catalytic oxidation conditions and the colloidal properties of the functionalized PMS microlatexes.

EXPERIMENTAL

Materials

3(4)-Methylstyrene and divinylbenzene from Aldrich Chemical Co. were freed from phenolic inhibitor by washing three times with 10% sodium hydroxide solution. The monomer was then washed with deionized water until the pH of the water dropped to seven. Azobis(isobutyronitrile) (AIBN) from China National Chemical Co. was purified by recrystallization in ethanol. The analytical grade of copper(II) chloride dihydrate (BDH) was used as received. *tert*-Butyl hydroperoxide (80%) was purchased from Riedel de Haën. Other chemicals were reagent grade and used without further purification.

Instruments

The particle size and size distribution of poly(methylstyrene) latexes were characterized at 25°C by a commercial dynamic laser light scattering spectrometer (ALV-5000, Langen in Hessen, Germany). An argon ion laser (Coherent INNOVA, operated at 448 nm and 400 mW) was used as the light source. The primary beam was vertically polarized. All measurements were completed at a 45° scattering angle. The latex dispersion was optimized for the light-scattering experiments by diluting the crude concentrated latexes with an excess of deionized water until the count rate of the resulting mixture was within the optimal range of the spectrometer. These dilute solutions were made dust-free by filtering them through Millipore HA 0.5 μm filters. The IR spectra were recorded using a Nicolet FT-IR spectrometer. All samples were prepared as KBr disks. Elemental analysis was performed at MEDAC Ltd., Brunel University, Middlesex, U.K.

Synthesis of Poly(methylstyrene) Microlatexes

Purified 3(4)-methylstyrene (2 g) and a mixture of divinylbenzene (55%) and ethylstyrene (45%) (0.08 g, for a cross-linking density $P_c = 1/50$ or one cross-link per 50 monomer units) as well as AIBN (50 mg) were stirred at room temperature

to form an oil phase. Cetyltrimethylammonium bromide (CTAB) ranging from 0.667 to 6.0 g was dissolved in deionized water to form a water phase. The oil and water phases with a total weight of 100 g were dispersed with a high-speed stirrer for 6 h at room temperature under N_2 atmosphere in order to supply sufficient dispersion energy to produce microemulsions with smaller size. The mixture was then heated to 70°C, and the reaction was completed after 72 h. The conversion generally exceeded 95% as determined by the mass of the isolated polymer. The latexes were used directly in dynamic laser light scattering measurement, dialysis study, and subsequent oxidation. The poly(methylstyrene) latexes were precipitated by addition of excess amounts of hot methanol. The surfactants were carefully removed from the PMS microgels in THF by multifold reprecipitation in hot methanol. The final white powder was dried *in vacuo* at 40°C for 72 h.

Catalytic Oxidation of Poly(methylstyrene) Microlatexes

The microemulsion (50 mL, equivalent to 1 g of PMS) was mixed with 5 mL of $CuCl_2$ (0.07 g) solution and stirred at 60°C under air. *tert*-Butyl hydroperoxide (1 mL, 80%) diluted in 5 mL of deionized water was added dropwise to the microemulsion, and the reaction was continued for 8 h. A study of oxidation kinetics was carried out by withdrawing 10 mL of emulsion at 2 h intervals for FT-IR spectrometry and elemental analyses.

Dialysis of Poly(methylstyrene) Microlatexes

Poly(methylstyrene) microlatexes (20 mL) were placed into a dialysis tube (model Spectra/pore 4, MWCO 12,000–14,000) and then immersed in 1 L of deionized water at 25°C. The dialysis procedure was monitored by the conductivity meter (Horiba, ES-14).

RESULTS AND DISCUSSION

Synthesis of Poly(methylstyrene) Microlatexes

Ultrafine microlatex particles $(20 < d < 100$ nm) can be prepared by using the microemulsion polymerization technique.[28-30] A well-established relationship between the amount of surfactant and
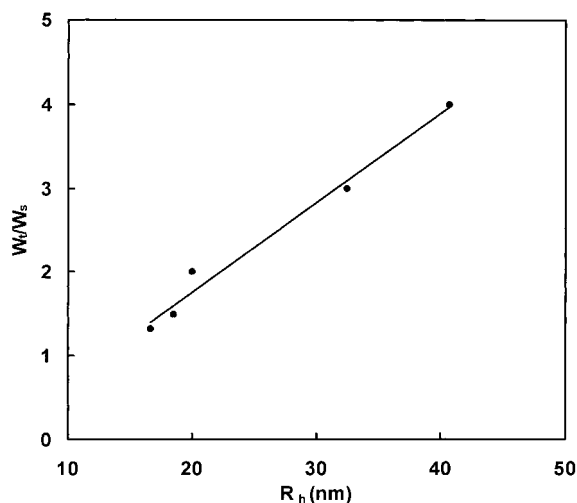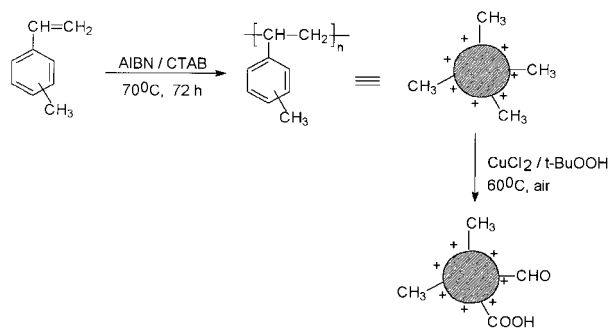

Figure 1. Plot of the macroscopic weight ratio of total (W_t) to CTAB (W_s) versus the hydrodynamic radius (R_h), where W_t = weight of monomer (W_m) + weight of surfactant (W_s).

particle size has been reported by Wu and Antonietti.[31-34] Their results show that the size of latex particles in the system of styrene/cross-linker/CTAB/water, initiated with AIBN, can be directly controlled by the relative amount of CTAB, based on a simple geometric micelle model. Since methylstyrene exhibits reactivity analogous to that of styrene, it is conceivable that different sizes of poly(methylstyrene) microlatexes can be prepared by varying the surfactant to monomer ratio. Microemulsion polymerization of 3(4)-methylstyrene and divinylbenzene initiated by AIBN was carried out in the presence of various amounts of cetyltrimethylammonium bromide (CTAB). Figure 1 shows a plot of W_t/W_s versus R_h, where W_t is the total weight of monomer (W_m) plus surfactant (W_s) and R_h is the hydrodynamic radius of the microlatexes measured by the dynamic laser light scattering spectrometer. A linear relationship between W_t/W_s and the hydrodynamic radius (R_h) was obtained, which was in agreement with Wu's findings for the polystyrene system. These PMS microlatexes with different particle sizes were used directly for the subsequent oxidation reactions.
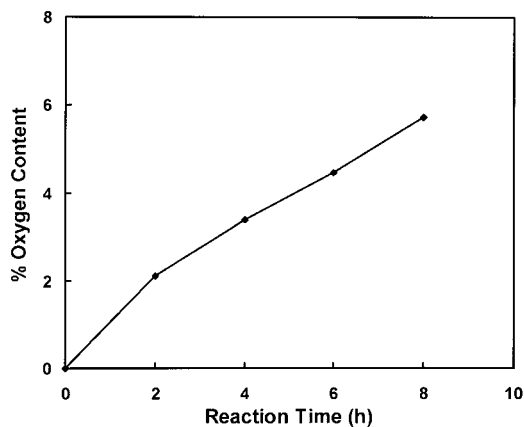
Oxidation of Poly(methylstyrene) Microlatexes

We previously developed the $CuCl_2/t$-BuOOH catalytic system, which could selectively oxidize the methyl groups on the PMS particle to the corre-
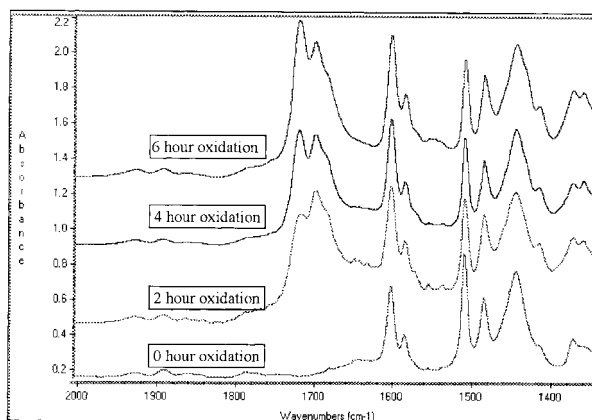
Scheme 1. Copper-catalyzed oxidation of poly(methylstyrene) microlatex.

Figure 3. FT-IR spectra of the oxidized poly(methylstyrene) at various reaction times. Refer to the general procedure for the reaction conditions.

sponding aldehyde and carboxylic acid functionalities. Similar oxidation conditions were adapted for this system, and the oxidation conditions are shown in Scheme 1. Since there was a large amount of CTAB present in the microemulsion, oxidation of an aqueous solution of pure CTAB was examined under the standard reaction conditions, and little oxidation of CTAB was detected, based on the FT-IR spectrometry analysis.

Oxidation kinetics of PMS microlatexes synthesized from 1 : 1 ratio of W_m/W_s, with a particle size of 40.0 nm in diameter, was studied in the presence of $CuCl_2$ and t-BuOOH at 60°C under air. Figure 2 shows that percentage oxygen content of the oxidized poly(methylstyrene) increases with reaction time, indicating an increase in the degree of oxidation. The FT-IR spectra show two strong peaks at 1720 and 1704 cm^{-1}, representing the carbonyl groups of aldehyde and carboxylic acid

stretching bands (Fig. 3). It is noted that as the degree of oxidation increases, the amounts of aldehyde groups increase, which is contrary to the oxidation of anionic PMS latexes. In general, copper-catalyzed oxidation in the presence of t-Bu-OOH undergoes a free radical autoxidation, and the aldehyde group is oxidized rapidly to the corresponding carboxylic acid group. However, our results indicate that aldehyde is the major functional group up to 6 h reaction. Such high selectivity for aldehyde functionality may be due to the effect of the electrostatic double layer structure around the cationic particle surface, which may slow down the rate of aldehyde oxidation to the corresponding acid.

Effect of Particle Size on the Oxidation of Poly(methylstyrene) Microlatexes

Oxidation of various sizes of poly(methylstyrene) microlatexes was investigated, as shown in Table I. In all of these experiments, the concentration of oxidant used was the same. In general, the rate of oxidation is governed by both the concentration of oxidant and the total surface area of particles. Bigger particles that have smaller surface areas are expected to react more slowly than the smaller ones. However, our experimental results showed that the degree of oxidation increased slightly with the increase of the particle size. It was anticipated that this effect might be caused by the excess amounts of surfactant used in the microemulsion. In order to verify this assumption, oxidation of PMS mi-

Figure 2. Degree of oxidation of PMS microlatexes catalyzed by $CuCl_2$ in the presence of t-BuOOH at 60°C in air. The percentage oxygen was determined by elemental analysis.

Table I. Effect of Particle Size on the Oxidation of Poly(methylstyrene) Microlatexes[a]

Ratio of W_m/W_s	Particle Size in Diameter (nm)	Elemental Anal.		
		C (%)	H (%)	O (%)
1 : 3	33.2	83.60	8.22	5.03
1 : 2	37.0	83.78	8.14	5.29
1 : 1	40.0	83.70	8.19	5.73
2 : 1	65.0	82.49	8.35	6.14
3 : 1	81.4	82.40	7.87	6.81

[a] Reaction conditions: 50 mL of emulsion containing PMS (1 g), copper chloride (0.07 g), and t-BuOOH (1 mL) was reacted at 60°C for 8 h under air.

crolatexes of the same size in different amounts of CTAB was examined. Microlatexes with $W_m/W_s = 3 : 1$ were first polymerized according to the procedure described in the experimental section. After polymerization, an extra CTAB was added to this microemulsion to make up microemulsions with $W_m/W_s = 1 : 1$ and 1 : 3, allowing the influence of the free surfactant in the microemulsion to be studied. Table II shows that, under the same oxidation conditions, the percentage oxygen contents for $W_m/W_s = 1 : 1$ and $W_m/W_s = 1 : 3$ systems are 3.42% and 2.12% after 8 h reaction, while 6.81% was obtained for the $W_m/W_s = 3 : 1$ system. These results indicate that excess amounts of surfactant inhibit the oxidation reaction. The formation of smaller particles requires a higher concentration of surfactant, and a higher number of free micelles are therefore expected in the microemulsion. Some of the oxidant molecules may be trapped inside of these empty micelles, resulting in a loss of efficiency.

Since the poly(methylstyrene) microlatexes were crosslinked preliminarily, the particle size underwent little change during oxidation. For example, for the system $W_m/W_s = 1 : 2$, the diameter of the particle changed from 37.0 nm to only 39.4 nm after 8 h reaction, giving 5.29% oxygen content. This is definitely a very unique approach toward controlling the amounts of functional groups on the particle surface and the particle size concurrently. A desirable size of microlatexes containing carbonyl functionalities can be therefore prepared by the synthesis of specific size poly(methylstyrene) particles based on the well-established microemulsion polymerization procedure, followed by the cata-

lytic oxidation of the particle surface to give the desired amounts of functional groups which can be controlled easily by varying the oxidation conditions such as oxidant concentration and reaction time.

## Dialysis of the Functionalized Poly(methylstyrene) Microlatexes

After 24 h of oxidation, flocculation of the highly oxidized PMS particles was observed. In order to gain some insight into the instability of the highly functionalized microlatexes, a dialysis study of the particles before and after oxidation was conducted. During the dialysis of the latexes, CTAB molecules and other ions such as H^+ and Br^- diffused across the membrane to 1 L of deionized water until an equal ion concentration was achieved on both sides. A conductivity meter was used to measure the change of conductivity with time in the dialysate. The contribution of the copper chloride present in the oxidized PMS microemulsion to the specific conductance was taken into account by adding an equal concentration of copper ion into the pure PMS microemulsion. Figure 4 shows that the microlatexes obtained after 8 h of oxidation have a much larger slope at the beginning of dialysis than the latexes without oxidation. Such a large variance in the conductivity for PMS microlatexes before and after oxidation may be due to the fact that some methyl groups on the particle surface are oxidized to the corresponding carboxylic acid groups, which are negatively charged. Interaction between the cationic surfactants and the carboxylic acid groups releases H^+ and Br^- ions. These two ions are much smaller ions than CTAB, resulting in a

Table II. Effect of CTAB Concentration on the Oxidation of Poly(methylstyrene) Microlatexes[a]

Particle Size in Diameter (nm)	Ratio of W_m/W_s	Elemental Anal.		
		C (%)	H (%)	O (%)
81.4	3 : 1	82.40	7.87	6.81
81.4	1 : 1[b]	87.47	8.31	3.42
81.4	1 : 3[b]	87.90	8.50	2.12

[a] Refer to general procedure for reaction conditions.
[b] The microlatexes using $W_m/W_s = 3 : 1$ was first polymerized, followed by the addition of CTAB to make up the microemulsion with $W_m/W_s = 1 : 1$ and 1 : 3.
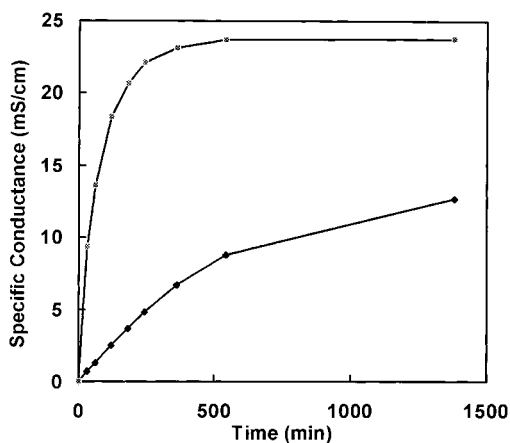
Figure 4. Plot of the specific conductance versus dialysis time for the microlatexes prepared by using $W_m/W_s = 3 : 1$: (■) after oxidation; (♦) before oxidation.

higher dialysis rate. Furthermore, they have better conductance. The remarkable increase in the conductivity after oxidation indicates that the total positive surface charges have been reduced due to the presence of carboxylic acid groups. Therefore, for highly oxidized PMS microlatexes, the surface charge density is substantially decreased which leads to coagulation of the polymer particles.

CONCLUSIONS

Ultrafine poly(methylstyrene) latex particles with both the aldehyde and carboxylic acid groups on the surface were prepared via microemulsion polymerization, followed by an *in-situ* oxidation catalyzed by copper(II) chloride and *tert*-butyl hydroperoxide. The diameters of particle studied were in the range 33–81 nm, and aldehyde groups were obtained as the major functional groups for up to 6 h of reaction. The degree of oxidation increased slightly as the particle size increased. The excess amounts of surfactant in the microemulsion could reduce the rate of oxidation. The dialysis study indicated that the instabilities of the highly oxidized PMS microlatexes were a result of reduction of total surface positive charges on the particle. We have demonstrated a convenient method of preparing ultrafine latex particles with a desired particle size and a controlled amount of functional groups on the surface.

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