

Functionalization of poly(methylstyrene) latex particles in an emulsifier-free system

Pei Li^{a,*}, Jianjun Xu^a, Chi Wu^b

^aDepartment of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, People's Republic of China

^bDepartment of Chemistry, The Chinese University of Hong Kong, N.T., Hong Kong, People's Republic of China

Abstract

Poly(methylstyrene) (PMS) latex particles in an emulsifier-free emulsion were first synthesized by using 2,2'-azobis-(2-amidinopropane) dihydrochloride (V-50) as an initiator. Purification of the latexes by dialysis was followed in order to remove residual monomer, initiator and electrolytes. The cationic poly(methylstyrene) latexes were then oxidized in the presence of *t*-butyl hydroperoxide catalyzed by copper chloride at 60°C under air. The degree of oxidation increased with reaction time, but the emulsions of highly oxidized poly(methylstyrene) latexes were found to be unstable. An increase of oxidant concentration enhanced the rate of oxidation, while the catalyst concentration had little influence on it. The effect of reaction temperature and pH value on the catalytic oxidation of poly(methylstyrene) latexes was also investigated. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Poly(methylstyrene); Catalytic oxidation; Functional latex particles; Emulsifier-free emulsion

1. Introduction

Functional latex particles with well-defined particle size and surface properties in the emulsifier-free emulsion system are highly desirable because of their wide range of applications in both biomedical and biochemical fields [1]. Among the possible functionalities on a particle surface, aldehyde and carboxylic acid groups are especially useful for covalent bonding of amino

groups containing biomolecules under mild conditions [2,3]. Polymer particles bearing surface aldehyde or carboxylic acid groups in the emulsifier-free emulsion system are commonly prepared by the co-polymerization of styrene and functional monomers [4–6]. Recently, we have reported a novel approach to introduce aldehyde and carboxylic acid functional groups onto a particle via a surface oxidation of either anionic or cationic poly(methylstyrene) latexes catalyzed by copper chloride in the presence of *t*-butyl hydroperoxide [7,8]. Hence, as part of our continuing studies on the surface functionalization of polymer latexes,

* Corresponding author.

we report here our studies on the metal-catalyzed surface oxidation of poly(methylstyrene) latexes in the emulsifier-free emulsion system.

2. Experimental

2.1. Materials and instruments

3(4)-Methylstyrene from Aldrich Co. was freshly distilled. 2,2'-Azobis-(2-amidinopropane) dihydrochloride (V-50) from Wako, copper (II) chloride dihydrate (BHD) and *t*-butyl hydroperoxide (70% solution in water) from Acros Organic Co. were all used as received. Infrared spectra were recorded on a Nicolet 750 FT-IR spectrophotometer using KBr disks. Particle size was determined by using a Coulter LS-230 Particle Size Analyzer. Elemental analyses were performed at MEDAC Ltd., Department of Chemistry, Brunel University, U.K.

2.2. Preparation of poly(methylstyrene) latexes

A 500-ml three-necked round-bottle flask containing 280 g of deionized water was placed in a water bath. After stirring for 20 min under nitrogen at 70°C, freshly distilled 3(4)-methylstyrene (15 g) was added to the vessel, and stirring continued for 15 min prior to the addition of 2,2'-azobis-(2-amidinopropane) dihydrochloride (0.7 g) dissolved in 5 ml of deionized water. The mixture was then stirred at 350 rev./min for 24 h to reach above 90% conversion, and the mean diameter of the particles was 562 nm.

2.3. Purification of latexes

The resulting poly(methylstyrene) latexes were dialyzed against deionized water by using a molecular porous membrane dialysis tube (Spectra/Pro) for 1 week in order to remove impurities such as residual initiator, low molecular weight oligomers and electrolytes. The deionized water was replaced every 12 h and monitored by using a conductivity meter.

2.4. Catalytic oxidation of poly(methylstyrene) latexes

The clean PMS latex emulsion (20 ml, equivalent to 1 g of PMS) was mixed with 0.0289 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in 5 ml of deionized water, followed by the addition of *t*-butyl hydroperoxide (1.14 ml, 70% in water). The reaction mixture was stirred at 60°C under air. The oxidized PMS was isolated quantitatively by precipitation of the emulsion into hot methanol.

3. Results and discussion

The purified PMS latexes were oxidized catalytically with copper (II) chloride in the presence of *t*-butyl hydroperoxide at 60°C up to 10 h. The degree of oxidation was monitored by withdrawing a small amount of sample at 2-h intervals for FT-IR spectrometry and elemental analyses. As shown in Fig. 1, the percent oxygen content increased significantly in the first 8 h. However, the oxidized PMS latexes became less stable after 6 h. The decrease of latex stability might result from a decrease of total surface charge density, which probably happened when the surface cationic charges were neutralized by the newly formed carboxylic acid group on the particle surfaces.

Fig. 2 shows the FT-IR spectra of PMS latexes oxidized at different oxidant concentrations. The peaks at 1720 cm^{-1} and 1690 cm^{-1} represent the aldehyde and carboxylic acid groups, respectively. These two functional groups were formed concu-

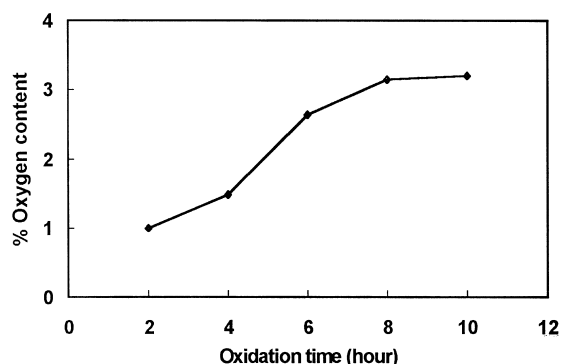


Fig. 1. Rate of oxidation of PMS latexes in the emulsifier-free emulsion system catalyzed by $\text{CuCl}_2/t\text{-BuOOH}$ at 60°C. Percent oxygen content was determined by the elemental analysis.

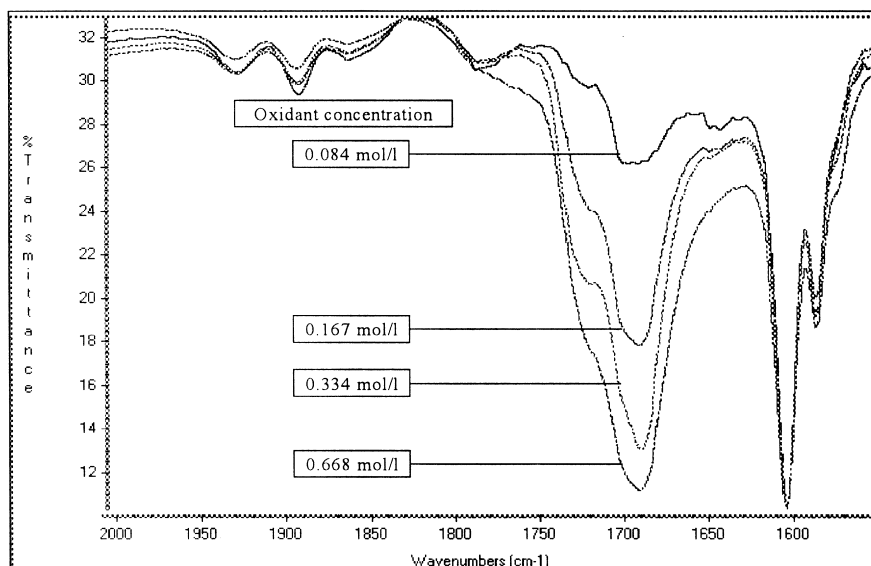


Fig. 2. FT-IR spectra of the PMS latexes oxidized with various oxidant concentration. The mole ratio of oxidant to catalyst remained at 50:1, and all reactions were carried out at 70°C for 4 h under air.

rently during the oxidation, with the carboxylic acid group being the major one. The intensity of the carbonyl peaks in the IR spectra at different oxidant concentrations indicated that the degree of oxidation increased with the increase of *t*-BuOOH concentration. However, when the concentration of oxidant exceeded 0.5 M, the latexes became unstable.

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 that the concentration of CuCl_2 catalyst has little effect on the degree of oxidation of the PMS latex particles.

Table 1
Effect of copper (II) chloride concentration on the oxidation of PMS latexes^a

Concentration of CuCl_2 (M)	Mole ratio of BuOOH: Cu^{2+}	Percent oxygen content ^b (%)
0.034	1:0.1	2.85
0.017	1:0.05	2.88
0.0034	1:0.01	2.84

^aReactions were carried out in the presence of 0.34 M of *t*-BuOOH at 70°C for 4 h under air.

^bThe percent oxygen content was determined by the elemental analysis.

Table 2
Effect of reaction temperature on the oxidation of PMS latexes^a

Reaction temperature (°C)	Reaction time (h)	Percent oxygen content ^b (%)
60	4	1.49
70	4	2.88
80	4	3.98

^aReactions were carried out in the presence of 0.34 M of *t*-BuOOH and 0.017 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ for 4 h under air.

^bThe percent oxygen content was determined by the elemental analysis.

Table 2 shows that the degree of oxidation of the PMS latexes increases with the increase of reaction temperature. Since our research interest is mainly focused 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.

The influence of pH value on the degree of oxidation was examined at three different pH values. The purified latex emulsions were first treated with HCl (1 M) and NaOH (0.5 M) solu-

tions at room temperature to pH 2.2 and pH 10.0, respectively. The latexes were then oxidized for 4 h at 70°C according to the procedure described in Section 2. Only slight oxidation was found at both pH 2.2 and 10.0, indicating that the catalytic oxidations of PMS latexes were inhibited in both acidic and basic conditions, yet it reacted well under the neutral conditions.

During the reaction, oxidation first occurred at the particle surface, then in the inner layer. Control of the surface oxidation could be achieved by manipulating the reaction conditions. For example, oxidation of PMS latexes using 0.025 M *t*-BuOOH catalyzed by CuCl₂ for 1 h gave the functionalized PMS particles containing aldehyde groups of 1.07×10^{-5} (mol/g particle), which was determined using 2.5 pH method proposed by Smith et al. [9]. Little change in the mean diameter of the particles was detected. Detailed study on the control of both particle size and aldehyde content will be reported in our subsequent paper.

Acknowledgements

We are grateful to the Hong Kong Polytechnic University for the financial support of this research.

References

- [1] C. Pichot, *Polym. Adv. Technol.* 6 (1995) 427.
- [2] S. Margel, *J. Polym. Sci., Polym. Chem. Ed.*, 22 (1984) 3521.
- [3] M. Kumakura, M. Suzuki, I. Kaetsu, *J. Colloid Interface Sci.* 97 (1984) 157.
- [4] Q. Wang, S.K. Fu, T.Y. Yu, *Prog. Polym. Sci.* 19 (1994) 703.
- [5] C. Yan, X. Zhang, Z. Sum, H. Kitano, N. Ise, *J. Appl. Polym. Sci.* 40 (1990) 89.
- [6] B. Charleux, P. Fanget, C. Pichot, *Makromol. Chem.* 193 (1992) 205.
- [7] P. Li, J.H. Liu, H.P. Yiu, K.K. Chan, *J. Polym. Sci., Part A: Polym. Chem.* 35 (1997) 1863.
- [8] P. Li, J.H. Liu, T.K. Wong, H.P. Yiu, J. Gau, *J. Polym. Sci., Part A: Polym. Chem.* 35 (1997) 3585.
- [9] D.M. Smith, J. Mitchell, Jr., *Anal. Chem.* 22 (1950) 750.