

Preparation and Properties of Alkoxysilane/Butyl Acrylate/Methyl Methacrylate Copolymer Latices

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ABSTRACT: The incorporation of alkoxysilanes into latex systems is of major interest in the field of colloidal science. Two kinds of vinyl-containing alkoxysilanes, methacryloxypropyltrimethoxyl silane and vinyltriethoxysilane, were copolymerized with butyl acrylate and methyl methacrylate by seeded emulsion polymerization, and copolymer latices were obtained. The morphologies of the latex particles were characterized with transmission electron microscopy. Dynamic light scattering showed that the particle size increased

and the particle size distributions of all the copolymer latex particles were alike with increasing amounts of organosilane. The effects of the organosilane content on the morphology of the particles, the rheology, and the swelling properties were also investigated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 185–188, 2009

Key words: emulsion polymerization; lattices

INTRODUCTION

In recent years, researchers in the field of colloidal science have taken interest in the incorporation of alkoxysilanes into latex systems. Previously, organofunctional silanes were used as silane coupling agents to reinforce composite materials.¹ The reinforcement mechanism shows that the silane coupling agents located in the interlayer between the inorganic surface and organic surface form a chemical bond between the two layers. Osterholtz and Pohl² extensively studied the kinetics of both hydrolysis and condensation reactions in a series of silane compounds in aqueous solutions. Vinyl-containing silane is a sort of silane coupling agent. Usually, it is copolymerized with other monomers, mostly in organic solvents, to improve the performances of polymer materials, including the weather resistance, mar resistance, and stain resistance,^{3–5} or it is used in polysiloxane–polyacrylate copolymerization to enhance the miscibility of the two phases.⁶

As is well known, polyacrylates, industrially produced for many years, are widely used in adhesives, latex paints, paper coatings, floor tiles, and textile treatments. Their durability, transparency, flexibility, stability, and relatively low cost are attributes that contribute to industrial acceptance. However, because of their linear structure, most thermoplastic acrylic polymers, although they are tough and stable at room

temperature, become sticky at only slightly elevated temperatures. In addition, their water resistance is not good. To overcome their poor properties, acrylates are often copolymerized with other monomers. The copolymerization of vinyl-containing silanes and acrylic monomers is expected to result in copolymers with excellent properties.

In this study, copolymer latices of vinyl-containing silane, butyl acrylate (BA), and methyl methacrylate (MMA) were prepared. The effects of the organosilane monomer on the morphology of the particles, the particle size and its distribution, and the rheology, were examined in detail. Also, the water absorption property of the copolymer latex films was studied. These latices are proved useful for self-crosslinking coatings and adhesives. They could also find industrial applications as crosslinker agents and in the room-temperature vulcanization of silicone rubbers. In addition, these silanol-functionalized colloids could be used as elementary bricks for the elaboration of sophisticated organic–inorganic nanostructures.

EXPERIMENTAL

Materials

Methacryloxypropyltrimethoxyl silane (MATS) and vinyltriethoxysilane (VTES) were purchased from Wuhan University Chemical Plant (Wuhan, China) and were used without any further purification. BA and MMA were distilled in a stream of an inert gas and stored in a refrigerator. Ammonium persulfate (APS) was recrystallized. The nonionic emulsifier polyoxyethylene fatty alcohol ether (AEO15) and the anionic

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TABLE I
Recipe for the Preparation of Seed Emulsions

Ingredient	Amount (g)
BA	30
SDS	0.8
AEO15	0.8
NaHCO ₃	0.3
APS	0.15
Water	105

emulsifier sodium dodecyl sulfate (SDS) were analytical-grade and were used without purification.

Preparation of the seed emulsions

The seed emulsions were prepared according to the recipe given in Table I. The ionic and nonionic surfactants were first dissolved in deionized water. The other ingredients were then added, and the mixture was poured into a reactor equipped with a paddle agitator. After half an hour of mixing, the mixture was heated to 80°C. The polymerization was typically completed after 2 h.

Preparation of the copolymer latices

A typical recipe is given in Table II. The surfactant was first dissolved in deionized water in a 0.25-L dropping funnel equipped with a stirrer. Then, a mixture of all the monomers was added. After half an hour of mixing, the monomer emulsion was obtained. Seed emulsions were poured into another 0.5-L reactor equipped with a stirrer, reflux condenser, sampling device, and inert system for nitrogen. The seed emulsion was heated at 80°C. After 15 min, the monomer emulsions, kept stirring in the dropping funnel during the whole process, were poured into the seed emulsion by dropwise addition in 2.5 h. The dispersion was maintained for 1 h after the addition was completed.

Morphology of the latex particles

The morphology of the latex particles was observed with a JEM-100 SX transmission electron microscope (Akishima, Japan). The internal particle morphologies were examined with dried samples of the latices. The sections were stained with a phosphotungstic acid aqueous solution.

Particle size and distribution

Particle size measurements were carried out by photon correlation spectroscopy with a Malvern Loc-FC-963 autosizer from Malvern Instruments (Malvern, UK). This apparatus gave the z-average diameter (d_z)

and polydispersity index (PDI). PDI ranged from 0 to 1. The lower the PDI value was, the more uniform the particles were.

Rheology properties

The viscosity of the latex was tested with an NDJ-1-type viscometer (Shanghai, China) with the cylinder torsion method at room temperature. The spin rate was set at 60 rpm.

Swelling properties of the latex film

The film, formed at room temperature by the casting of latices onto a polytetrafluoroethylene plate, was immersed in a swelling agent for 48 h at 25°C. The specimen was weighed immediately after the solvents attached to the surface were wiped off. The swelling degree was calculated according to the following equation:

$$\text{Swelling}(\%) = (W_s - W_g) / W_g \times 100\%$$

where W_s and W_g are the weights of the film and swollen film, respectively.

RESULTS AND DISCUSSION

Morphology of the copolymer latex particles

The morphology and size are closely related to the properties of latices. Figure 1(A,B) shows particles prepared by seeding emulsion polymerization with various amounts of MATS. Comparing all the micrographs, we can conclude that the morphology of the copolymer particles is spherical, and the size is relatively uniform. It is almost homogeneous in the particles. MATS is often used for copolymerization with acrylic monomers.^{7,8} It is commonly held that MATS can easily copolymerize with those monomers because there exists a $\text{CH}_2=\text{CH}(\text{CH}_3)\text{COO}-$ group with a similar structure.⁹ However, most copolymerizations are carried out in an organic solvent. In our study, the free-radical copolymerization of MATS

TABLE II
Typical Recipe for the Preparation of the Copolymer Latices

Ingredient	Amount (g)
Seed emulsion	137
Organosilane	10
BA	12
MMA	18
AEO15	1.6
APS	0.1
Water	52

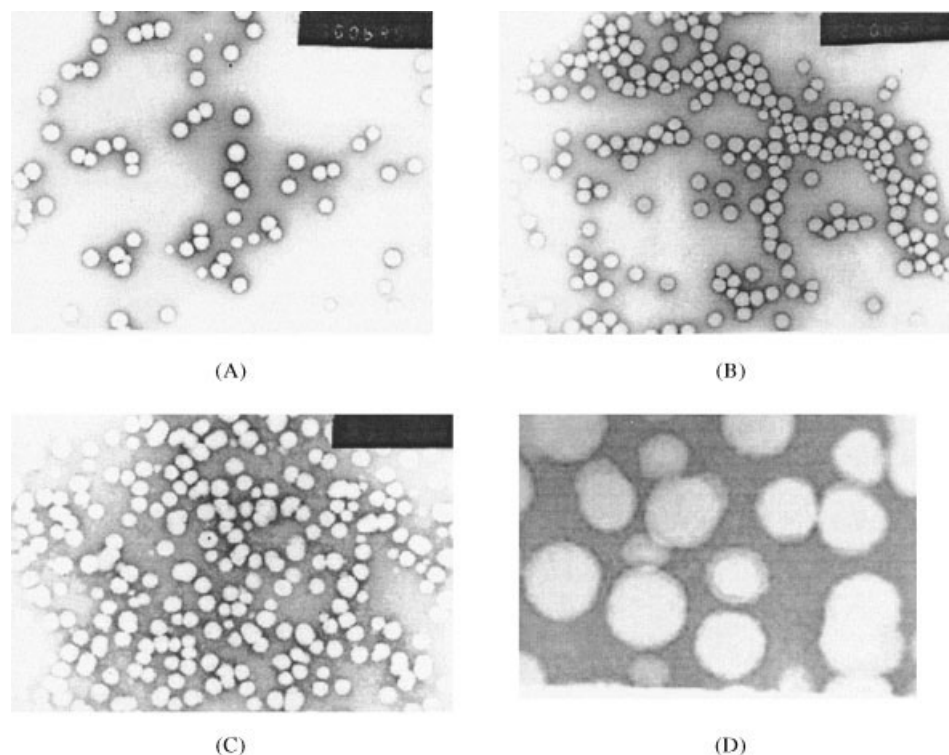


Figure 1 Transmission electron micrographs of the copolymer latex particles: (A) 18 g of MATS (30,000 \times magnification), (B) 26 g of MATS (30,000 \times magnification), (C) 14 g of VTES (30,000 \times magnification), and (D) 14 g of VTES (50,000 \times magnification).

with other monomers was conducted in an aqueous system. MATS, containing trimethoxy groups, can hydrolyze and then condense to form Si—O—Si bonds in an aqueous system. The rates of hydrolysis and condensation are pH-dependent; fast reactions occur at lower pHs and at higher pHs. The minimum rate of hydrolysis occurs at pH 7, and the minimum rate of condensation is at pH 4 for trifunctional silanes.² For these reasons, NaHCO₃ is used as a pH buffer reagent. Moreover, dropwise addition is applied to keep MATS at a low concentration and avoid the condensations of silanol groups resulting from hydrolysis. That is, most MATS can copolymerize into the polymer rapidly before condensation. The experimental results in Table III show that a batch process produces more coagulum than a dropwise process. This is mainly because the MATS concentration in the latter system is relatively low.

Figure 1(C,D) shows the VTES/BA/MMA copolymer particles. These particles are not as spherical as the MATS/BA/MMA copolymer particles. Core-shell-structure particles can be observed. Some particles adhere to one another. Because a seeded emulsion polymerization is used, it is understandable that the copolymer reaction of VTES and the other acrylic monomer occurs almost at the end of the polymerization. VTES has been incorporated into the surface of the latex particles. The copolymer chain is not com-

patible with the poly(butyl acrylate) chain. Consequently, a heterogeneous structure is formed.

Particle size and distribution

Table III indicates the effect of the amount of organosilane on the particle size and its distribution. With an increase in the amount of organosilane, d_z increases and PDI remains almost constant in both cases. The organosilanes copolymerize with acrylic monomers by free-radical polymerization or condensation. With

TABLE III
Particle Sizes and Their Distributions

Organosilane	Amount (g)	Mean d_z (nm)	PDI	Coagulum (g)
None	0	72.2	0.05	0.03
MATS	6 (batch)	57.3	0.04	0.89
MATS	6	74.3	0.05	0.04
MATS	10	79.1	0.05	0.04
MATS	14	83.2	0.05	0.06
MATS	18	84.3	0.03	0.07
MATS	22	85.1	0.04	0.07
MATS	26	86.8	0.04	0.09
VTES	6	73.6	0.03	0.03
VTES	14	79.1	0.04	0.05
VTES	22	92.2	0.03	0.12

an increasing amount of organosilane, particles become bigger. However, the size distributions of all the copolymer latex particles are alike. The reason may be that the same kind of seed emulsion has been used, and new particles have hardly been generated.

Figure 2 presents a diagram of the dependence of the viscosity on the amount of organosilane. The key factors by which organosilane affects the rheology of the copolymer latices are the solvation effect and crosslinking reaction. The silanol groups, located on the surface of the latex particles, are able to form H-bonds with water molecules. As the amount of organosilane increases, the solvation effect between particles and water becomes stronger, and the crosslinking degree resulting from condensation increases; this causes the viscosity to increase.

Swelling properties of the latex film

The MATS/BA/MMA copolymer latices cannot form a film at room temperature even when the MATS concentration is equal to 6 wt % of the total monomer mass. As for VTES, the water absorption of the latex film decreases with an increase in the amount of organosilane, as shown in Table IV. There is no doubt that organosilane acts as a crosslinker in the system. The MATS/BA/MMA copolymer macromolecule,

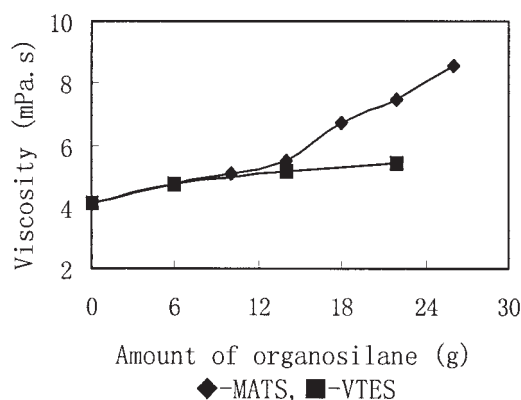


Figure 2 Effect of the amount of organosilane on the viscosity of the latices.

TABLE IV
Effect of VTES Amount on the Water Absorption Properties of the Films

VTES (g)	Water absorption (%)
0	38.0
6	34.1
14	25.0
22	8.8

bearing a long side chain with the functional group $-\text{OCOCH}_2\text{CH}_2\text{CH}_2\text{SiOH}$, may crosslink more easily than that of VTES, for which shorter $-\text{SiOH}$ is constrained.

CONCLUSIONS

Two novel alkoxy silane/BA/MMA copolymer latices have been obtained through seeding emulsion polymerization. The morphologies of the particles are quite different. As the amount of organosilane increases, the particle size and viscosity of both latices increase, but the size distributions of all the copolymer latex particles are alike. The MATS/BA/MMA copolymer latices cannot form films at room temperature. However, films of the VETS/BA/MMA copolymer latices show excellent water resistance.

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