Alkoxysilane-Functionalized Acrylic Copolymer Latexes. I. Particle Size, Morphology, and Film-Forming Properties

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ABSTRACT: Via the conventional emulsion copolymerization of acrylic monomers and vinyl-containing alkoxysilane monomers with three siloxane groups, siloxane groups were added to acrylic copolymers to make alkoxysilane-functionalized acrylic copolymer latexes. In producing stable polymer latexes, seeded polymerization was superior to the other two processes, batch and continuous addition polymerization. The experimental results showed that vinyltriethoxysilane–acrylic copolymer latexes were capable of film forming. In contrast, the incorporation of methacryloxypropyl trimethoxysilane gave rise to the formation of highly crosslinked acrylic copolymer latexes, which had poor film-forming properties. Relatively small monodispersed particles with particle sizes of less than 100 nm were formed. These particles had a core–shell structure, although some of them were asymmetric. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 954–960, 2004

Key words: films; latices; morphology

INTRODUCTION

Acrylic polymer latexes, including thermoplastic and thermosetting latexes, are widely used in industry as, for example, adhesives and coatings[1] because of their specific properties, such as good UV resistance, gloss, and transparency, as well as good film-forming ability at room temperature. For thermosetting acrylic polymer latexes, comonomers with pendant reactive groups are required to provide the sites for subsequent crosslinking, normally at higher temperatures.[2] Among other functional groups, alkoxysilanes are promising[3] because they contain at least two kinds of functional groups, one reacting with organic materials and the other with inorganic materials, and they are therefore generally well known as coupling agents. In addition, they offer the possibility of curing at room temperature, which is very important for the production of room-temperature crosslinkable paints and so forth. The incorporation of alkoxysilane functional groups into acrylic (co)polymers can be achieved through the copolymerization of acrylic monomers and alkoxysilane monomers bearing vinyl groups. However, this is normally carried out in organic solutions, instead of aqueous media, because alkoxysilanes are easy to hydrolyze and then crosslinking can happen with ease, giving rise to unstable latexes with bad shelf stability. One exception is when alkoxysilanes are used as the coupling agents between acrylic (co)-polymers and polysiloxane polymers in aqueous media.[4,5] Therefore, making stable acrylic latexes with alkoxysilane functional groups is both interesting and challenging.

There are a number of ways to make relatively stable latexes. One is to use semicontinuous procedures; that is, the alkoxysilanes are usually added late in the reaction to avoid their prolonged contact with water.[3] Stable latexes can also be prepared through the copolymerization of vinyl-group-containing alkoxysilane monomers with protected siloxane functional groups.[6] In addition, applying sterically hindered alkoxysilanes[7] can minimize unexpected hydrolysis and, therefore, the crosslinking of siloxane groups. Furthermore, novel alkoxysilanes with a lower hydrolysis rate can be designed via the induction of one siloxyl group that has an electronegative character.[8]

Very recently, Marcu et al.[3] applied a promising approach, miniemulsion polymerization, to carry out the vinyl copolymerization of vinyltriethoxysilane (VTES) and *n*-butyl acrylate. This approach has real potential for incorporating high amounts of VTES into *n*-butyl acrylate latex systems by a one-step batch procedure because it yields significantly lower amounts of coagulum at high silane feed compositions in comparison with the conventional method. The reason behind this success is that the silane moiety is protected from the aqueous phase by the waterproof oil droplet formed in the miniemulsions before the

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polymerization, and so its hydrolysis and condensation are minimized.

Of course, the reaction conditions, such as the pH, temperature, and surfactants, have a very important influence on the hydrolysis of siloxane groups. It is well known that the hydrolysis of alkoxysilane is sensitive to both acids and bases. Therefore, a neutral pH is required for most systems to obtain the minimum hydrolysis rate.

In this article, we report a preliminary study on alkoxysilane-functionalized acrylic copolymer latexes acquired through the conventional emulsion copolymerization of acrylic monomers and two vinyl-containing alkoxysilane monomers bearing three siloxane groups, methacryloxypropyl trimethoxysilane (MATS) and VTES, with different polymerization processes. Seeded polymerization can produce stable polymer latexes with high concentrations of alkoxysilanes. However, the incorporation of MATS and VTES leads to the formation of copolymers that have significantly different film-forming properties. The particle size, particle size distribution, and morphologies of the latex particles have also been investigated.

EXPERIMENTAL

Materials

Butyl acrylate (BA) and methyl methacrylate (MMA) (CP) were purchased from Tianjin Dihua Chemical Limited Company (Tianjin, China), and distilled under reduced pressure before use. MATS and VTES (CP) were acquired from the Chemical Plant of Wuhan University (Wuhan, China). Ammonium persulfate (APS, CP) was from the Tianjing Organic Chemical Plant (Tianjin, China). Sodium dodecylsulfate (SDS, CP) was purchased from Nacalai Tesque (Kyoto, Japan). A nonionic surfactant and a pH buffer were made in our laboratory.

Preparation of the copolymer latexes

Batch process

All the monomers, emulsifiers, and initiators were mixed at 35°C for 0.5 h, and then the temperature was increased to 80°C and kept there for 2 h.

Seeded polymerization

Some BA, emulsifiers, and initiators were mixed at 35°C for 0.5 h and then polymerized at 80°C for 1 h to obtain the poly(butyl acrylate) (PBA) latex. This PBA latex was used as the seed latex for the second-stage polymerization of the pre-emulsified monomers left. The addition of the monomer emulsion to the seeded latex was finished in 2.5 h, and the emulsion was

TABLE I
Typical Recipe for Seeded Emulsion Polymerization

| Material | Content (wt %) | |
	Seed emulsion	Copolymerization emulsion
Seed emulsion		60.5
Silane		2.6
MMA		7.9
BA	21.9	5.3
SDS	0.6	
NaHCO$_3$	0.2	
Nonionic surfactant	0.6	0.7
APS	0.1	0.1
H$_2$O	76.6	22.9

polymerized for another 1 h. Table I shows a typical recipe for this process.

Continuous addition process

All the monomers and two-thirds of the emulsifiers and initiators were mixed with water at 35°C for 0.5 h. The obtained emulsion was added to a water solution containing the remaining emulsifiers and initiators at 80°C, and this temperature was kept for 1 h after the addition of the monomer emulsions.

Stability (σ) of the polymerization process

After the completion of the emulsion polymerization, the latexes were filtered, and the precipitates were washed with water and dried in a vacuum oven to a constant weight. σ of the emulsion polymerization process was calculated as follows:

$$\sigma = W_1/W_2 \times 100\% \tag{1}$$

where W_1 and W_2 are the weights of the precipitate and monomers, respectively.

Morphology and size of the latex particles

Morphologies of latex particles were determined by transmission electron microscopy (TEM, JEM-100SX.JEOL, Akishima, Japan). Particle sizes and distributions were determined with Malvern Autosizer Loc-FC-963 (Malvern, Worcestershire, U.K.).

RESULTS AND DISCUSSION

σ of the polymerization processes

Table II shows the experimental results of σ (%) for different polymerization processes. Seeded polymerization yields the lowest value of σ (%) and therefore the best σ value for polymerization. This is straight-

TABLE II
σ Under Different Polymerization Processes

Process	σ (%)
Batch	0.89
Seeded	0.06
Continuous	4.66

MATS: 2.6 wt % in the copolymerization emulsion, corresponding to 7.9 wt % in copolymer.

forward because in seeded emulsion polymerization, MATS monomers are added during the second stage of the polymerization, and this reduces the time of contact with water. This is the advantage of applying a semicontinuous process.[3,4]

For the seeded polymerization process, the effect of the alkoxysilane concentration on σ of emulsion polymerization is shown in Table III. σ does not change much with the alkoxysilane concentration increasing up to around 30%. Obviously, even larger amounts of alkoxysilane can be incorporated, with the polymerization procedure kept stable. Seeded polymerization is pretty successful in making stable polymer latexes under the experimental conditions.

### Particle size and distribution

Figure 1 shows that the particle size increases with the time of polymerization. This is a common phenomenon in emulsion polymerization. However, the particle sizes are relatively small, in the range of 60–75 nm. The particle size distributions are pretty narrow (Fig. 2 and Table IV), largely in the range of 50–100 nm. This is not expected because conventional emulsion polymerization normally leads to the formation of particles with wide distributions on account of the coexistence of micelle, homogeneous, and droplet nucleation mechanisms.[9,10] One possibility is that there are no new particles produced during the second stage of

TABLE III
Effect of the Alkoxysilane Concentration on σ of the Seeded Emulsion Polymerization

Alkoxysilane[a]	Alkoxysilane[b]	σ (%)
0	0	0.05
MATS 2.6	7.9	0.06
MATS 4.2	12.7	0.06
MATS 5.8	17.5	0.07
MATS 7.6	23	0.08
MATS 9.1	27.5	0.08
MATS 10.4	31.4	0.1
VTES 2.6	7.9	0.05
VTES 5.8	17.5	0.07
VTES 9.0	27.2	0.15

[a] Weight percentage in the copolymerization emulsion.
[b] Corresponding weight percentage in the copolymer.
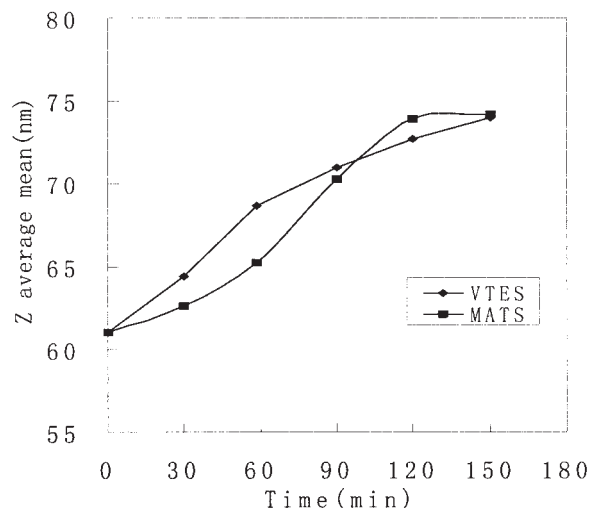
Figure 1 Particle size evolution versus the polymerization time (7.9 wt % silane in the copolymer).

polymerization because of the good control over the addition of monomer emulsions; this assumes that micelle nucleation is the predominant mechanism, and homogeneous and droplet nucleation has been eliminated. The prerequisite for this probability is that the seed latex particles are monodispersed. However, the particle size distribution of the seed latex of PBA is multidispersed [shown later in Fig. 4(A)], and this leaves unclear the origin of the aforementioned monodispersed particles.

Similar monodispersed particles have been obtained in the emulsion copolymerization of silicons (octomethyltetracyclosiloxane and MATS) and acrylic monomers,[4] and a semicontinuous process has also been used. However, no details about the monodispersity of the particles have been given. Obviously, there must be something in common between these two different systems that gives rise to the monodispersed particle sizes, and more effort is needed to determine their origins (discussed later).

Figure 3 shows the particle size obtained with different concentrations of alkoxysilane monomers. The particle sizes are still 50–100 nm, but they become larger with an increasing concentration of alkoxysilane. The latter is straightforward. The particle size of the VTES–acrylic copolymer latex, for example, increases from about 72 to 93 nm, that is, approximately 30%, corresponding roughly to the increased amount of VTES (~29%) in the system. However, the MATS–acrylic copolymer latex particle size increases from about 72 to 88 nm, that is, approximately 22%, whereas the amount of MATS increases approximately 31% in the system. In other words, the increase in the particle size is less than the amount of MATS incorporated, and this suggests a volume reduction. This might be due to a higher crosslinking density when MATS is used (discussed later).
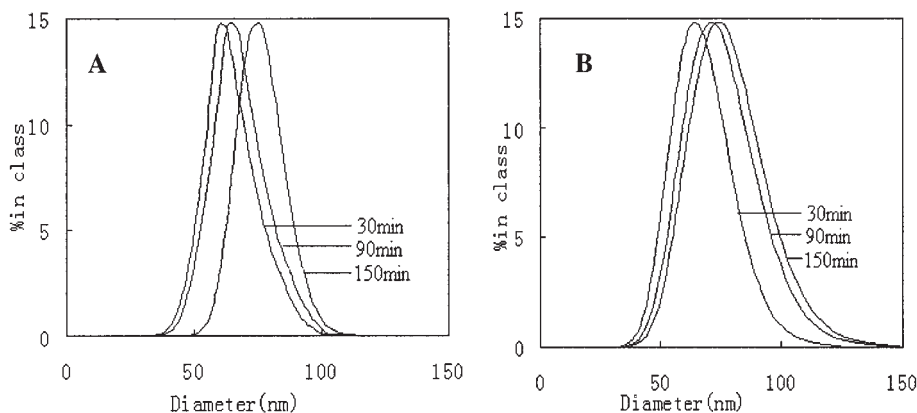
Figure 2 Variation of the particle size distribution with the time (7.9 wt % silane in the copolymer): (A) MATS and (B) VTES.

Morphologies of the latex particles

As mentioned previously, the PBA seed latex has a wide particle size distribution, as shown in Figure 4(A). This is common in traditional emulsion polymerization because of the coexistence of three nucleation mechanisms. The low glass-transition temperature (T_g) of PBA ($\sim -56°C$) might also contribute to the nonuniform particle morphologies, as well as the combination among particles.

After the second stage of the polymerization of BA monomers left and all the MMA monomers, the latex particles of composite PBA (core)/poly(butyl acrylate-methyl methacrylate) [P(BA–MMA); shell] latexes have a relatively uniform spherical shape [Fig. 4(B)]. Obviously, the spherical shape of the PBA/P(BA–MMA) composite latex particles comes from the copolymerization of the MMA monomers in the shell layer, the homopolymer of which has a high T_g around 100°C, which contributes to the rigidity of the particles. This shape is kept after the incorporation of alkoxysilane monomers [Fig. 4(C,D) shows the results for MATS only]. This is understandable because the siloxane groups in alkoxysilanes are easy to hydrolyze into hydroxyl groups. The Si—OH groups that form can produce a condensation reaction in latex particles, leading to crosslinked structures, which will further increase the rigidity of the particles. This conclusion has been verified by the poor film-forming properties

of MATS-functionalized acrylic copolymer latexes (discussed later).

The same question discussed previously arises: why do the PBA/P(BA–MMA) composite latex particles become relatively monodispersed, whereas the P(BA–MMA) copolymers grow on multidispersed PB seed latex particles? At first glance, there is a striking similarity if this is compared to the evolution of the particle size distribution in the miniemulsion copolymerization of styrene and BA,[10] for which the particle size distribution is broader at the beginning of the polymerization and becomes narrower as the polymerization proceeds. At the end of the polymerization, monodispersed particles are formed. However, these two situations are significantly different in nature, in that the broad particle size distribution obtained at the beginning of the miniemulsion copolymerization of styrene and BA actually refers to monomer droplets only. In the study reported here, however, the broad particle size distribution at the beginning of the seeded polymerization refers to PBA polymer latex particles only. In other words, there is no issue of molecular diffusion from larger monomer droplets to growing polymer particles, which become smaller and approach the mean population, as in the miniemulsion copolymerization of styrene and BA.[10] Again, more effort is needed to determine the origins of this unusual behavior.

TABLE IV
Variation of the Polydispersity Index[a] with Time

	Time (min)				
	30	60	90	120	150
Polydispersity index (MATS[b])	0.0200	0.0234	0.0239	0.0230	0.0206
Polydispersity index (VTES[b])	0.0338	0.0412	0.0381	0.0400	0.0497

[a] The polydispersity Index is a variable indicating the particle size distribution. The value varies between 0 and 1. The closer to 0 it is, the narrower the particle size distributionis.
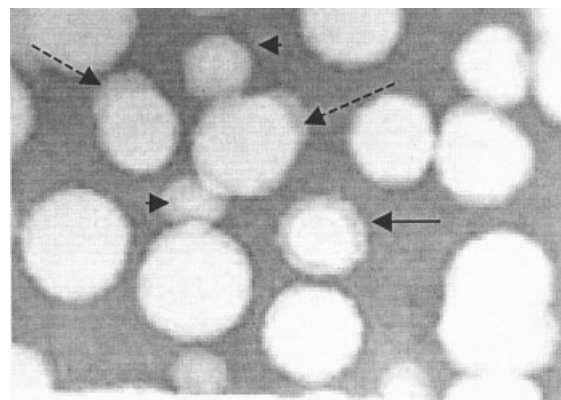[b] Silane-7.9 wt % in the copolymer.
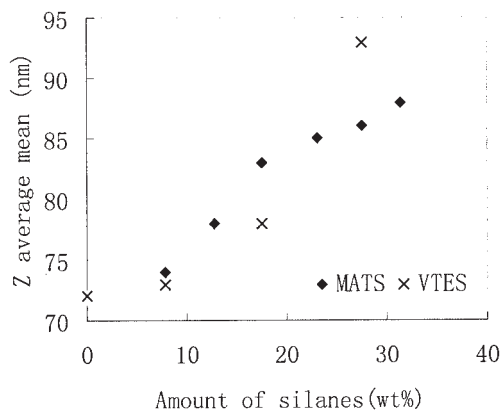
Figure 3 Effect of the silane concentration on the particle size.

Figure 5 TEM photograph (50,000×) of the VTES–acrylic copolymer latex particles ([VTES] = 17.5 wt %).

Because of the seeded polymerization process used, it is expected that a core–shell structure for the particles should be formed on account of the composition difference between the core and shell layers. Figure 5 shows a TEM photograph of VTES–acrylic copolymer latex particles under larger magnification (50,000×). Particles with a core–shell structure have been formed (see the particle labeled with a long-tail solid arrow), although there is obviously room to improve the contrast between the core and shell layers.

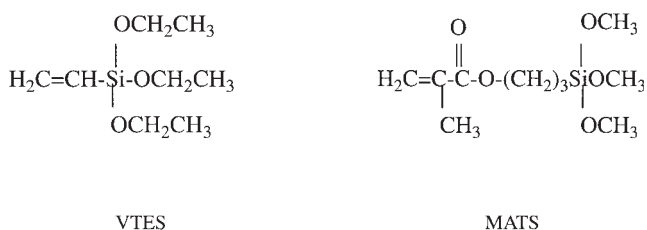Some particles have an asymmetric spherical shape (the particles labeled with dashed arrows), with the shell layer growing largely in one direction; this resembles the uniform nonspherical particle morphology of polystyrene latex interpenetrating polymer networks[11] prepared by the seeded emulsion polymerization of styrene–divinylbenzene mixtures. However, their origins are different. In the latter case, the uniform nonspherical particles are formed by the separation of the second-stage monomer from the crosslinked seed network during swelling and polymerization. The kinetics of phase separation reveal that the phase separation is induced by the relaxation of polymer chains before polymerization begins and is
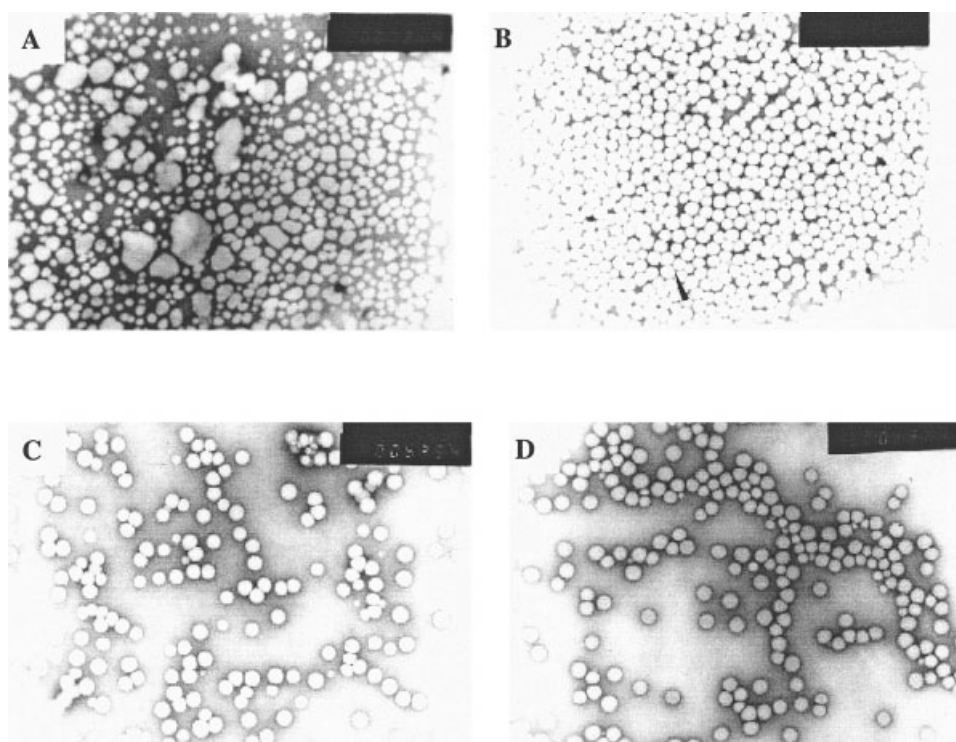
Figure 4 TEM photographs of (A) PBA seed particles (20,000×) and (B–D) MATS–acrylic copolymer latex particles (30,000×). The MATS concentration in the copolymer was (B) 0, (C) 17.5, or (D) 31.4 wt %.

$$H_2C=CH-\underset{\underset{OCH_2CH_3}{|}}{\overset{\overset{OCH_2CH_3}{|}}{Si}}-OCH_2CH_3$$

VTES

$$H_2C=\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{\|}}{C}-O-(CH_2)_3\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{Si}}OCH_3$$

MATS

Scheme 1 Molecular structures of VTES and MATS.

enhanced by increased conversion. A nucleation-and-growth mechanism has been proposed to describe the phase separation. In the study reported here, however, the following two factors might be the possible reasons for the appearance of nonuniform spherical particles. One is the combination of regularly big particles and relatively smaller particles, labeled by arrows with no tails. The other is that the incorporation of VTES monomer units is not homogeneous in the shell layer, and this gives rise to the uneven distribution of siloxane groups in the shell layer. The latter being the case would have some effect on the surface properties of the latex films formed, and it has been verified by the significantly different film-forming properties of the VTES–acrylic copolymer latex and MATS–acrylic system, as discussed later.

Film-forming properties

The composite polymer latex of PB/P(BA–MMA) produced by the seeded polymerization process is capable of film forming at room temperature, and the film is soft and transparent. After the incorporation of MATS into the shell layer, however, the latexes produced cannot form films. This is obviously due to the crosslinking formed in the shell layer of the latex particles, which prevents the latex particles from deforming and melting together. In contrast, the latexes produced via the incorporation of VTES are capable of film forming.

Both MATS and VTES have three alkoxy groups. However, the copolymer latexes after the incorporation of these two monomers have quite different film-forming properties. One possible reason is that, compared with MATS, VTES is much harder to incorporate into the acrylic copolymer, and so fewer crosslinks and a low crosslinking density will be formed. This is because VTES has larger ethoxysilane groups closer to the vinyl functional group (Scheme 1), and this leads to a significant screening effect on the copolymerization of the latter. This can be interpreted by the large difference in the reactivity ratios between VTES and acrylic monomers, such as BA.[3] The reactivity ratio of BA is two orders of magnitude larger than that of VTES.[3] This indicates that BA and MMA in our system will polymerize with the exclu-

sion of VTES, and so only a small amount of VTES would be incorporated into the outer layers of acrylic copolymer latex particles. The majority of the VTES monomers would then polymerize via the free-radical process to form some low-molecular-weight homopolymers or via a hydrolysis/condensation process to form some branched or crosslinked polysiloxanes, both as free chains in latex particles or graft chains on the surface of acrylic copolymer latex particles. This outcome gives rise to the uneven distribution of alkoxysilane groups in a latex particle, which could be one of the reasons for the appearance of nonuniform spherical particles discussed in a previous section.

In addition to easier copolymerization with acrylic monomers, the smaller CH_3— group and longer side chain [—$COOCH_2CH_2CH_2Si(OCH_3)_3$] of MATS, compared with those of VTES, might also facilitate the hydrolysis of —$Si(OCH_3)_3$ groups and the condensation reaction of —SiOH groups formed thereafter, giving rise to the high crosslinking density in MATS–acrylic copolymer latex particles, which is consistent with the previous finding that MATS–acrylic copolymer latex particles have a significant volume reduction, whereas VTES–acrylic copolymer latex particles do not.

In summary, under this experimental condition, MATS is not applicable to the production of conventional polymer latexes when the film-forming property is important to their applications. However, it is practical to use VTES to make self-crosslinkable latex materials at room temperature.

CONCLUSIONS

A preliminary study on the synthesis of alkoxysilane-functionalized acrylic copolymer latexes has been carried out. Siloxane groups have been added to the acrylic copolymers through the copolymerization of acrylic monomers with alkoxysilane monomers bearing vinyl groups. Seeded polymerization has been found to produce more stable polymer latexes than the other two processes, batch and continuous addition polymerization. In addition, relatively small monodispersed particles with particle sizes of less than 100 nm have been formed. However, more work is needed to determine the origins of this monodispersity. These particles have core–shell structures, with some of them asymmetric, probably because of the combination of regularly big and relatively small particles or the uneven distribution of siloxane groups in the shell layer. The experimental results show that the incorporation of MATS leads to the formation of premature crosslinking in acrylic copolymer latexes, which are not be able to form films. However, acrylic copolymer latexes containing VTES are able to be film-forming

because of the low crosslinking density in the copolymer latex particles.

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