

Preparation and Properties of Core [Poly(styrene-*n*-butyl acrylate)]–Shell [Poly(styrene–methyl methacrylate–vinyl triethoxide silane)] Structured Latex Particles with Self-Crosslinking Characteristics

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ABSTRACT: Structured latex particles with a slightly crosslinked poly(styrene-*n*-butyl acrylate) (PSB) core and a poly(styrene–methyl methacrylate–vinyl triethoxide silane) (PSMV) shell were prepared by seed emulsion polymerization, and the latex particle structures were investigated with Fourier transform infrared, thermogravimetric analysis, differential scanning calorimetry, transmission electron microscopy, and dynamic light scattering. The films that were formed from the structured core (PSB)–shell (PSMV) particles under ambient conditions had good water repellency and good

tensile strength in comparison with films from structured core (PSB)–shell [poly(styrene–methyl methacrylate)] latex particles; this was attributed to the self-crosslinking of $\text{CH}_2=\text{CH}-\text{Si}(\text{OCH}_2\text{CH}_3)_3$ in the outer shell structure. The relationship between the particle structure and the film properties was also investigated in this work. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1824–1830, 2006

Key words: core-shell polymers; crosslinking; emulsion polymerization

INTRODUCTION

Polyacrylic and poly(acrylic–styrene) latices and corresponding latex products have been widely used in coatings, paints, adhesives, and so forth because of specific properties, such as good film-forming, gloss and transparency, and mechanical properties. On the other hand, polyacrylic and poly(acrylic–styrene) latices have many weaknesses, such as poor water resistance and weather resistance, because of their chemical structure. These weaknesses give polyacrylic and poly(acrylic–styrene) latices many disadvantages in applications. In contrast, because of the existence of Si–O–Si, polysiloxane has many excellent properties, such as a low glass-transition temperature and surface tension, good water repellency, weather resistance, and thermal stability. Therefore, it is possible to modify polyacrylics and poly(acrylic–styrene) with polysiloxanes or siloxanes to improve their physical and chemical properties.

In the past decades, much research on siloxane (or polysiloxane)-modified polyacrylics and poly(acrylic–styrene) has been conducted by many researchers, and

great progress has been made.¹ This work includes the formation of mixtures through the addition of siloxane (or polysiloxane) to polyacrylic [or poly(acrylic–styrene)] latices,^{2–5} copolymerization with acrylics (or acrylic–styrene) and siloxane (or polysiloxane),^{6,7} the formation of complex polymers such as interpenetrating polymer networks,^{8,9} and core–shell-structure polymer particles^{10–12} In particular, because the core or shell structure can be easily changed for achieving certain functions, the core–shell-structure polymer particles of siloxane-modified acrylics and acrylic–styrene have been investigated extensively and deeply.^{1,6,10–15}

Despite the many excellent properties of siloxanes, the poor compatibility between polysiloxane and acrylics (or acrylic–styrene) brings disadvantages to their polymerization and products, so vinyl trialkoxysilane has often been used as a crosslinking agent to form a middle transition layer between the core and shell to improve the compatibility between polysiloxane and polyacrylics [or poly(acrylic–styrene)].⁶ Much research on the crosslinking of polysiloxane products and the effect of the crosslinking on improving product properties has been reported;^{16–18} however, reports about the self-crosslinking properties of organosilicone acrylic emulsions with vinyl trialkoxysilane have seldom been seen. In this work, vinyl triethoxysilane (VITS) was introduced into the outer shell of core [poly(styrene-*n*-butyl acrylate) (PSB)]–shell [poly(styrene–methyl methacrylate–vinyl triethoxide silane)]

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(PSMV)] latex particles to give them self-crosslinking properties in the film-forming process. The properties of these latex particles were investigated.

EXPERIMENTAL

Materials

Aerosol 501 (A-501; 35% aqueous solution of disodium isodecyl sulfosuccinate) was bought from Special Chemical Reagent Co. (Shanghai, China). Styrene (St), diethylene glycol diacrylate (DEGDA), methyl methacrylate (MMA), and *n*-butyl acrylate (BA) were purchased from Tianjin Chemical Reagent Factory (Tianjin, China) (analytical reagents); the inhibitor was removed by vacuum distillation before use. VITS was purchased from Tianjin Chemical Reagent Factory (Tianjin, China) and was used as received. Potassium persulfate ($K_2S_2O_8$; 99.99%) was recrystallized in deionized water before use. Deionized water was purchased from the chemical plant of Nankai University.

Preparation of the poly(styrene-*n*-butyl acrylate) [P(St-BA)] seed latex

Deionized water (40 mL), $K_2S_2O_8$ (0.35 g), A-501 (1.5 g), DEGDA (0.27 g), and a selected amount of St and BA (the total of the two was 22 g) were added to a 250-mL, four-necked, round-bottom flask equipped with a mechanical stirrer, a thermometer, a dropping funnel, and N_2 -controlled equipment. The flask was then purged of oxygen with bubbling nitrogen for 30 min at room temperature, with stirring at about 210 rpm. After that, the flask was placed in a water bath of a controlled temperature of 75°C. Ten minutes later, the remainder of the monomer mixture of St and BA was continuously dropped into the flask through a dropping funnel for 2 h with strong stirring. The reaction process continued for 30 min after the dropping was finished.

Seeded emulsion polymerization of St-MMA-VITS onto the P(St-BA) latex particles

In the seeded polymerization, no additional surfactant was added to the system. Although the amount of VITS was varied in the experiments, the total weight was kept constant (20 g), and the weight ratio of St to MMA was invariable (11.5/8.5). $K_2S_2O_8$ (0.05 g) and 0.35 g of $NaHCO_3$, which was dissolved in 10 mL of water, were first charged to the reactor after the monomers were dropwise added in the first step. Thirty minutes later, the monomer mixture was added dropwise at a low rate of about 10 mL/h. The reaction mixture stood for an additional 3 h when the addition was completed.

Characterization of the composite particles

Solid film samples that were formed in a polypropylene mold were extracted successively with *n*-hexane for 24 h. The chemical composition of the polymer was determined with a Bio-Rad FTS 135 Fourier transform infrared (FTIR) spectrometer.

The measurement of the transmission electron microscopy (TEM) was performed on a JEOL (Japan) TEM-100. Before the TEM measurement, the emulsion samples were diluted with distilled water and placed in a copper grill covered with a carbon membrane.

The measurement of the dynamic light scattering (DLS) was performed on a BI-200SM. The measurements were performed at 25°C with an Ar laser light wavelength of 514.5 nm, and the measurement angle was 90°.

The saturated water adsorption of the solid film, which had been dried for 48 h in a vacuum drying oven at 60°C and then kept for 24 h at room temperature, was characterized by the immersion of about 1 g of the solid film in deionized water at room temperature and the comparison of the weights of the solid sample before immersion (W_1) and after immersion (W_2); the saturated water adsorption was defined as $(W_2 - W_1)/W_1 \times 100\%$.

The differential scanning calorimetry (DSC) thermograms were recorded with a Netzsch (Germany) DSC 204 at a heating rate of 20°C/min under an N_2 atmosphere from -100 to 200°C, and thermogravimetric analysis (TGA) was performed in Netzsch TG 209 at a heating rate of 20°C/min under an N_2 atmosphere from 0 to 500°C.

Stress-strain characteristics were determined on a Testometric (England) M500-25kN at a tensile rate of 20 mm/min at 25°C

RESULTS AND DISCUSSION

Copolymerization stability of VITS with BA, St, and MMA

VITS is an important copolymerization monomer containing one C=C group and three $SiOCH_2CH_3$ groups. It can not only undergo radical polymerization with acrylic and St monomers but also condense with Si-OH groups originating from the hydrolysis of $SiOCH_2CH_3$ groups to self-crosslink in film formation. However, the Si-O-C bond in VITS molecules is much easier to hydrolyze and condense both in acidic media and in alkali media, and this brings instabilities to the polymerization process and storage process that must be prevented. Therefore, it is the key factor for controlling the hydrolyzation and condensation reactions, which are determined mainly by the emulsion pH, $SiOCH_2CH_3$ group content, and method of adding VITS. To avoid coagulation in the emulsion polymerization process and storage process, $NaHCO_3$

TABLE I
Influence of the VITS Content and Adding Mode on the Emulsion Stability

VITS (wt %)	0	2	4	6	8	10
Mode	I	I	I	I	I	II
Stability (6 months later)	Stable	Stable	Stable	Stable	Stable	— ^a

^a Coagulation appeared 2 days later after emulsion polymerization.

^b Coagulation appeared a month later after emulsion polymerization.

is used as a buffer to maintain a pH value of about 7 before VITS is brought to the reactor.¹ The influences of the other two factors on the polymerization and storage processes are shown in Table I.

To determine the effect of the method of adding the VITS monomer on the polymerization process, mode I and mode II were compared (based on a theoretical solid concentration of 45 wt % and a VITS concentration of 8 wt %). In mode I, the VITS monomer was mixed with St and MMA in advance and then dropped into a reactor that contained the prepared PSB seed emulsion. In mode II, VITS was dropped when the St and MMA dropping had finished. The emulsion prepared in mode I was very stable, whereas the emulsion coming from mode II coagulated after 2 days. The results indicated that the VITS monomer in mode I was dispersed effectively by monomers St and MMA in the polymerization process and then was separated well by St and MMA in the shell, so the condensation and crosslinking of the Si—OH groups were limited and the emulsion was stable. However, in mode II, the VITS monomer was added after St and MMA were dropped, and this increased the density of the Si—OH groups in the outer layer of the shell and facilitated the condensation, so the emulsion showed coagulation.

To investigate the effects of different VITS concentrations on the polymerization and storage stabilities, emulsion polymerizations were carried out with VITS concentrations of 0, 2, 4, 6, 8, and 10 wt % (based on a constant theoretical solid concentration of 45%) in

mode I. The results are shown in Table I. The emulsion polymerization process was very stable when the VITS concentration was less than 8%; however, coagulation appeared in the copolymerization process and the emulsion coagulated completely a month later when the VITS concentration was 10 wt %. It is thought that increasing Si—OH groups with increasing VITS concentration resulted in the instabilities of the polymerization and storage processes.

The following samples in this work were prepared according to mode I with not more than 8 wt % VITS.

TEM and DLS analysis of the latex particles

From the transmission electron micrographs in Figure 1, it can be seen that core-shell structures were successfully formed in the composite particles. Because of the high electron cloud density of the silicone atoms, compared with that of carbon atoms, VITS showed a deeper color than BA and St in the micrographs.¹ The core-shell structure was not well defined but was still distinguishable by the deep color in the edge layer and the light color inside. We think the responsible aspect was the good compatibility between the core and the shell because the composition of the core (BA—St) and the composition of the shell (MMA—St—VITS) were similar. In contrast to 70 nm in Figure 1(c), the latex particle diameters in Figure 1(b,c) are about 100 nm. Because the particles accumulated together in the test-

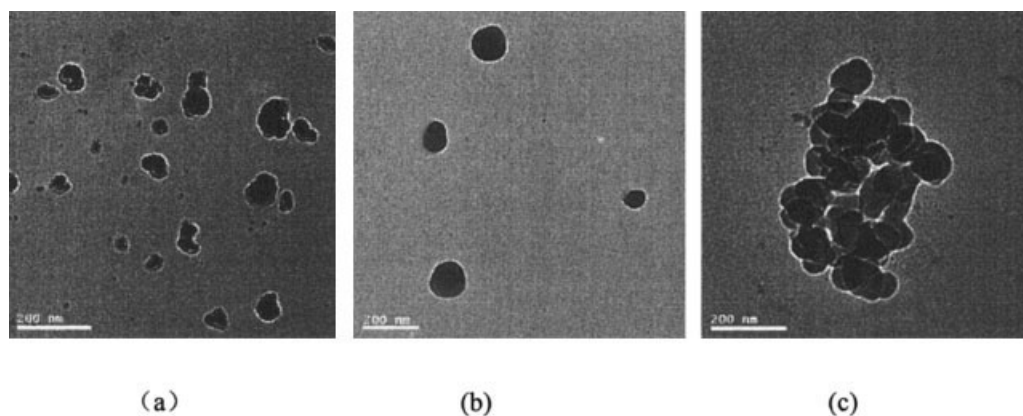


Figure 1 TEM micrographs of latex particles from different VITS samples: (a) 0, (b) 4, and (c) 6 wt %.

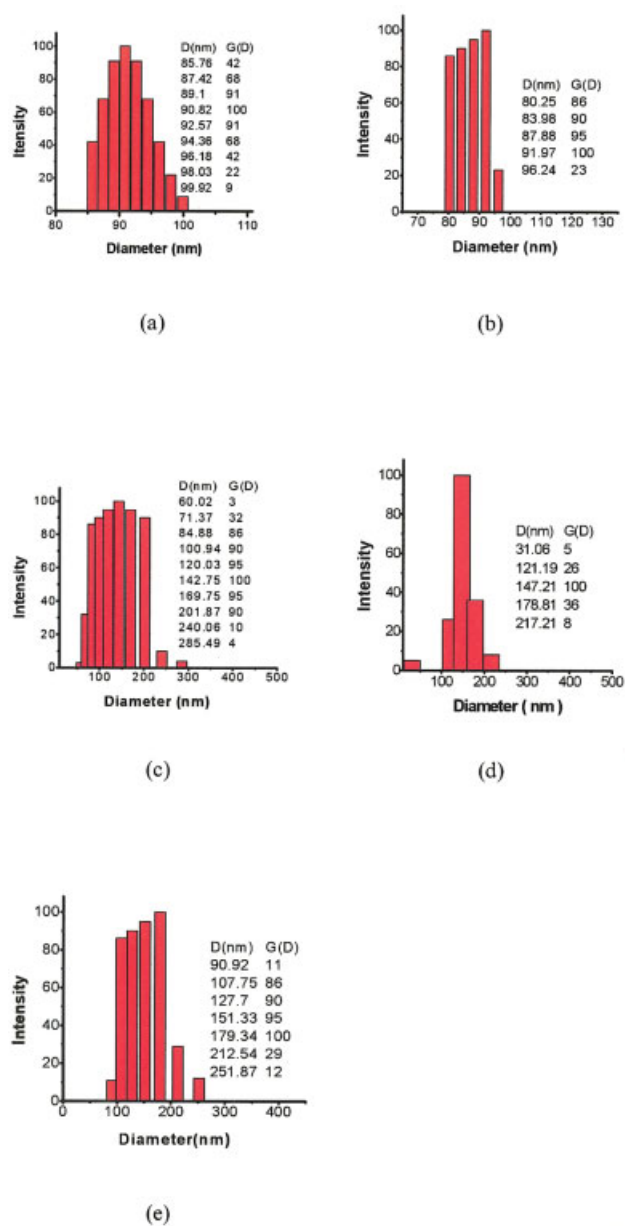


Figure 2 Latex particle size distributions of different VITS concentrations: (a) 0 wt % (mean diameter = 86.9 nm, polydispersity = 0.030), (b) 2 wt % (mean diameter = 91.3 nm, polydispersity = 0.103), (c) 4 wt % (mean diameter = 136.1 nm, polydispersity = 0.079), (d) 6 wt % (mean diameter = 149.9 nm, polydispersity = 0.15), and (e) 8 wt % (mean diameter = 149.1 nm, polydispersity = 0.121). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ing samples, it was difficult to determine accurately the size and size distribution of the particles by TEM, so the task was completed with DLS.

The size and size distribution of the particles measured by DLS are shown in Figure 2. Figure 2 shows that with an increase in the weight concentration of VITS in the copolymers, the particle size increased and the particle size distribution became wider. When the

VITS concentration was 0 wt %, the particle size distribution [Fig. 2(a)] showed a very narrow band in the range of 80–96 nm. The mean particle diameter was 87 nm, and the polydispersity was only 0.030. With 2 wt % VITS [Fig. 2(b)], the particle size distribution showed a similar band in the range of 86–100 nm; the mean diameter was 87 nm. In parallel, the polydispersity was increased (0.103). However, when the VITS concentration was more than 4 wt %, the particle diameters had obvious variations, and the particle size distributions also showed a broad band [in Fig. 2(c), the mean particle size is 136 nm, and it is distributed in the range of 60–285 nm; in Fig. 2(d), the particle size is 121–217 nm, and the mean diameter is 150 nm; and in Fig. 2(e), the particle size is 100–251 nm, and the mean diameter is 149 nm]. For Figure 2(b), there are not obvious variations in the mean diameter and the particle size distribution in comparison with Figure 2(a), and this implies that the low concentration of VITS did not make agglomerates of the particles in the processes of preparation and storage (6 months). However, from Figure 2(c) to Figure 2(e), the particle sizes are obviously larger than those of Figure 2(a,b), and it may be considered that VITS was not inhibited from hydrolyzing fully in the preparation and storage processes, and with increasing VITS concentration, the latex particle conglomeration became easy. This agrees with the earlier analysis.

FTIR confirmation of the copolymerization of VITS with BA, St, and MMA and the self-crosslinking of VITS

The FTIR spectra of polystyrene (PSt), poly(styrene-*n*-butyl acrylate/styrene-methyl methacrylate), poly(vinyl triethoxysilane) (PVITS), and the copolymer poly(styrene-*n*-butyl acrylate/styrene-methyl methacrylate-vinyl triethoxide silane) [P(SB/SMV)] are shown in Figure 3. Figure 3(D) reveals the composition of P(SB/SMV). The characteristic peaks of C—H of the benzene ring at 3100–3000 cm^{-1} and at 1068 and 1025 cm^{-1} , C=C ring stretching at 1650–1450 cm^{-1} [Fig. 3(A)], and a C=O stretching peak at 1736 cm^{-1} [Fig. 3(B)] still exist, and new characteristic peaks appear: the characteristic peaks at 1106 and 1080 cm^{-1} , which can also be observed in Figure 3(C), were contributed by Si—O—Si. The new peaks indicate the copolymerization of VITS with St, BA, and MMA and the crosslinked structure of the latex particles. The peaks are not strong at 1106 and 1080 cm^{-1} because of the low concentration of Si—O—Si. The IR analyses are well supported by TGA results for the copolymer samples. The end weight loss decreased with an increase in the VITS concentration, and this definitely pointed toward a VITS concentration increase in the copolymers.

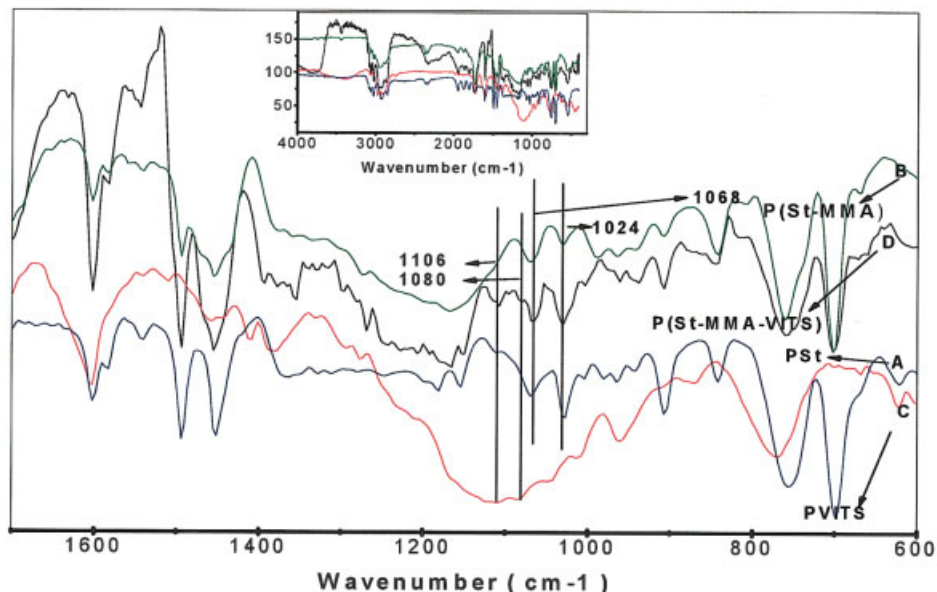


Figure 3 FTIR spectra of (A) PSt, (B) poly(styrene-*n*-butylacrylate/styrene-methyl methacrylate) [P(St-MMA)], (C) PVITS, and (D) poly(styrene-*n*-butylacrylate/styrene-methyl methacrylate-vinyl triethoxide silane). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TGA results for the copolymers

Reports on the thermal stabilities of polysiloxanes have been published by many researchers.^{19–23} For linear molecules, the generally accepted view is that the degradation mechanism is siloxane bond cleavage with the formation of a cyclic four-centered intermediate as the rate-determining step.^{16,19} In contrast to this point, the thermal degradation of our experimental samples was C—C bond scission rather than siloxane bond cleavage because the BA-St-MMA-VITS copolymers could not form linear polysiloxane and further a cyclic four-centered intermediate. On the other hand, the thermal stability of any polymer material is largely determined by the strength of the covalent bond between the atoms forming the polymer molecules. The C—C bond energy is less than that of C—Si, C=C and Si—O bonds.²⁴ Therefore, with an increase in the VITS concentration, the rudimental networks formed by VITS increased, and the weight loss of the sample decreased. In Figure 4, the weight loss is consistent with the analysis. The influence of the VITS concentration on the decomposition temperature was not obvious, and the changes were random.

DSC analysis of the copolymers

The glass-transition temperatures of the samples were determined by DSC (see Fig. 5). Figure 5 illustrates the DSC curves of the polymers with 0, 2, 4, 6, and 8 wt % VITS. All the samples had two different glass-transition temperatures; the lower values (T_{g1}) were attributed to the core PSB, and the higher ones (T_{g2}) were

attributed to the shell PSMV. This was consistent with the results earlier observed by TEM.

All the samples had almost the same T_{g1} , which corresponded to the same core composition (BA and St were kept invariable). However, there was a small variation of T_{g2} for the different samples, which was affected by the VITS concentration. Because of the self-crosslinking that was formed by the condensation between VITS molecules, the movement of the polymer segments in the shell was subjected to severe limitations. Much more energy was needed to make

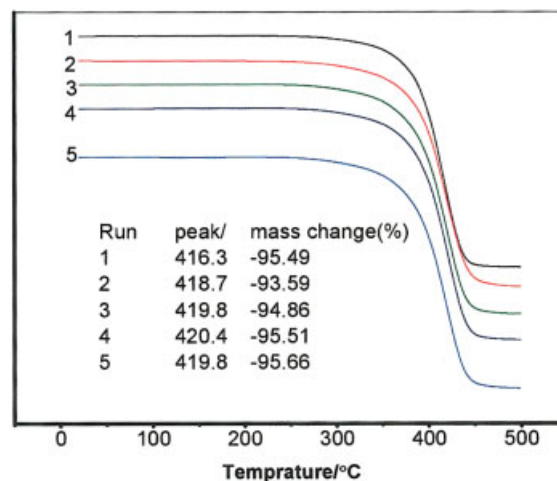


Figure 4 TGA curves of copolymers of different VITS concentrations: (1) 8, (2) 6, (3) 4, (4) 2, and (5) 0 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

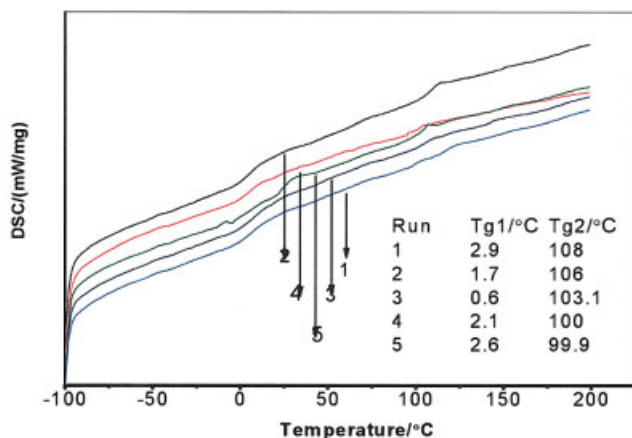


Figure 5 DSC curves of different VITS concentrations: (1) 8, (2) 6, (3) 4, (4) 2, and (5) 0 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

these limited segments move. Therefore, with the VITS concentration increasing, T_{g2} became higher.

It can be concluded that the self-crosslinking reaction appeared in two kinds of places: in the shell of the same latex particle and among different shells of latex particles. The self-crosslinking reaction greatly depended on the VITS concentration induced, whether it appeared in the same latex particle shell or among different latex particle shells. When the VITS concentration was low, the self-crosslinking reaction occurred mainly among different latex particle shells in the film-forming process, whereas in the same shell, the self-crosslinking reaction was relatively less because the VITS units were separated by St and MMA in the shell. With increasing VITS induced to the shell, the total self-crosslinking reactions of the two positions were strengthened. Therefore, in comparison with sample 5, there was rarely a change for T_{g2} of sample 4, but those of samples 1–3 were obvious.

Mechanical properties and water-absorbing behavior

The stress–strain characteristics and water-absorbing behaviors of all the copolymer films are shown in Figure 6. Figure 6 shows the stress–strain curves for several copolymers with different VITS concentrations. Evidently, all the copolymers exhibited larger stress as VITS was incorporated, and this indicated that the mechanical response of the copolymers was affected by the VITS self-crosslinking. It was also possible to verify that their stress–strain curves were similar to those commonly obtained for plastic materials. Comparing curves 1–4, we found that as the VITS concentration increased, the samples did not obey the same order with respect to the tensile stress. At a higher VITS concentration (8 wt %), the stress value

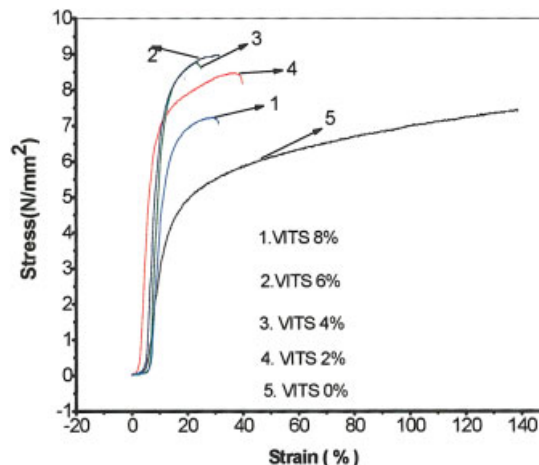


Figure 6 Stress–strain curves of self-crosslinking polymer films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was smaller, and it was possible to think that the VITS self-crosslinking reaction occurring greatly in the same shell contributed relatively less to the film tensile stress and that the self-crosslinking reaction among different shells, which could strengthen the tensile stress, was in contrast reduced.

The influence of the crosslinking density of the outer shell PSMV on the water-adsorption behavior is shown in Figure 7. An obvious change can be observed: the water adsorption decreased as the VITS concentration increased. When the VITS concentration was 0%, the water adsorption was about 8% at 250 h, but the water adsorption was much lower when the VITS concentration was 2, 4, or 6 wt %. In particular, the water adsorption was less than 4% when the VITS concentration was 6 wt %. An important requirement for the design of core (PSB)–shell (PSMV) latex parti-

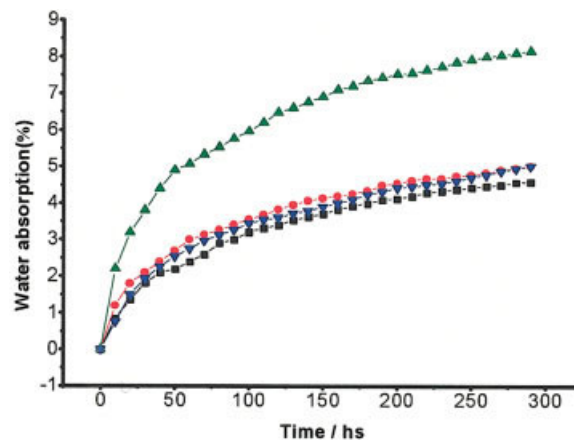


Figure 7 Water adsorption of copolymer latex films: (\blacktriangle) 0, (\blacklozenge) 2, (\blacktriangleright) 4, and (\blacksquare) 6 wt % VITS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cles with self-crosslinking characteristics is that the —Si—O—Si— network formed by the VITS components of the shell PSMV appears on the surfaces of the latex particles so that the structured particles have good water resistance. It is also thought that self-crosslinking maintains the stability of the core-shell particles in the film-forming process, which contributes to the good latex film properties. The results in Figures 6 and 7 confirm the desirable properties.

References

1. Kan, C. Y.; Kong, X. Z.; Yuan, Q.; Liu, D. S. *J Appl Polym Sci* 2001, 80, 2251.
2. Yang, M. J.; Dan, Y. *J Appl Polym Sci* 2004, 92, 2522.
3. Lee, Y. J.; Akiba, I.; Akayama, S. *J Appl Polym Sci* 2003, 87, 375.
4. Inoue, H.; Matsumoto, A.; Matsukawa, K.; Ueda, A.; Nagai, S. *J Appl Polym Sci* 1990, 41, 1815.
5. Lee, Y. J.; Akiba, I.; Akayama, S. *J Appl Polym Sci* 2002, 86, 1736.
6. Kan, C. Y.; Liu, D. S.; Kong, X. Z.; Zhu, X. L. *J Appl Polym Sci* 2001, 82, 3194.
7. Bajaj, P.; Gupta, D. C. *Eur Polym J* 1979, 15, 271.
8. Turner, J. S.; Cheng, Y. L. *Macromolecules* 2000, 33, 3714.
9. Zhou, P. G.; Frisch, H. L.; Rogovina, L.; Makarova, L.; Zhdanov, A.; Sergeienko, N. *J Polym Sci Part A: Polym Chem* 1993, 31, 2481.
10. He, W. D.; Pan, C.-Y. *J Appl Polym Sci* 2001, 80, 2752.
11. Seggali, I.; Dimonie, V. L.; El-Aasser, M. S.; Soskey, P. R.; Mylonakis, S. G. *J Appl Polym Sci* 1995, 58, 401.
12. He, W. D.; Cao, C.-T.; Pan, C.-Y. *J Appl Polym Sci* 1996, 61, 383.
13. Kong, X. Z.; Kan, C. Y.; Yuan, Q. *Polym Adv Technol* 1996, 7, 888.
14. Kan, C. Y.; Kong, X. Z.; Yuan, Q.; Liu, D. S. *J Appl Polym Sci* 2001, 80, 2251.
15. Matsumoto, M.; Urabe, T.; Kato, M.; Tammori, K. *Jpn. Pat.* 09208642/A2 (1997).
16. Zhang, T.; Xi, K.; Chen, H.; Yu, X. H. *J Appl Polym Sci* 2004, 91, 190.
17. Patel, M.; Morroll, P. R.; Skinner, A. R. *J Appl Polym Sci* 2002, 180, 109.
18. VanAert, H. A. M.; Sijbesma, R. P.; Fischer, H.; Dewaal, B. F. M.; Gilberts, J.; Maas, J. H.; Broer, D.; Meijer, E. W. *Acta Polym* 1999, 37, 293.
19. Funt, J. M.; Parekh, R. D.; Magill, J. H.; Shah, Y. T. *J Polym Sci Polym Chem Ed* 1975, 13, 2181.
20. Smith, S. D.; Longt, T. E.; Mcgrath, J. E. *J Polym Sci Part A: Polym Chem* 1994, 32, 1747.
21. Mayes, N.; Green, J.; Cohen, M. S. *J Polym Sci Part A-1: Polym Chem* 1967, 5, 365.
22. Thomas, T. H.; Kendrick, T. C. *J Polym Sci Part A-2: Polym Phys* 1970, 8, 1823.
23. Grubbs, G. R.; Kleppick, M. E. *J Appl Polym Sci* 1982, 27, 601.
24. Orgasilicone Research Group of the Chenguang Research Institute of Chemical Industry. *Orgasilicone Monomers and Polymers* (in Chinese); Chemical Industry: Beijing, 1986.