

Influence of Reaction Between Second Monomer and Vinyl Group of Seed Polysiloxane on Seeded Emulsion Polymerization

WEI-DONG HE,^{1,2} CAI-YUAN PAN¹

¹ Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

² Open Laboratory of Bond Select Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

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ABSTRACT: Seeded emulsion polymerization of methyl methacrylate (MMA) or styrene (ST) was carried in the presence of different vinyl-containing polysiloxane latices (SV-*) and the core-shell particles with poly(methyl methacrylate) (PMMA) or polystyrene (PST), as the shells were obtained under different polymerization conditions. Besides the compatibility of the vinyl monomer and its polymer with polysiloxane and the reaction between vinyl monomer with vinyl group of polysiloxane, the content of vinyl group of seed polysiloxane has influence on the morphology and component of the resulted composite particles. The mechanism for the formation of core-shell structure is discussed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2752–2758, 2001

Key words: core-shell particles; seeded emulsion polymerization; polysiloxane

INTRODUCTION

Core-shell particles have a vast of application in coating modification, plastics toughening, and rubber strengthening. Many efforts have been devoted to the preparation of core-shell particles by staged emulsion polymerization and the investigation of the formation mechanism of core-shell structure. With the view of thermodynamics, the more hydrophilic component will be localized in the outer layer of the particles.¹ The hydrophilicity of the particle surface tends to increase with the seeded emulsion polymerization after the introduction of ionic end-group to polymer chains.² The kinetics factors, including polymerization rate,³ mode and rate of

monomer addition,⁴ grafting reaction,^{5,6} and diffusion of species,^{7,8} play important role in the formation of core-shell structure.

In previous work, we demonstrated that the morphology of particles prepared in the presence of linear vinyl-containing and crosslinked polysiloxane is quite different, indicating the chemical reaction between monomer and the vinyl group of polysiloxane also affect the morphology of the resulted particles.^{9,10} In the present study, seeded emulsion polymerization of ST or MMA was carried out in the presence of different linear vinyl-containing polysiloxane to study this influence in more detail.

EXPERIMENTAL

Materials

Ocatmethyl cyclotetrasiloxane (Me-D4) and tetramethyl tetravinylcyclotetra-siloxane (Vi-D4) were

Correspondence to: W.-D. He (E-mail: wdhe@ustc.edu.cn).

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Table I Synthesis of Seed Polysiloxane Latex

Latex	Mole Fraction of Monomer		Composition of Copolysiloxane (Mole Fraction)		Polymer Content (wt %)	Conversion of Monomer (%)
	Me-D4	Vi-D4	Me-D4 Residue	Vi-D4 Residue		
SV-1	0.88	0.12	0.89	0.11	11.6	44.1
SV-2	0.76	0.24	0.75	0.25	9.7	36.1
SV-3	0.54	0.46	0.60	0.40	8.0	29.2

purchased from Bengbu Organic Silicone Factory. Styrene (ST) and methyl methacrylate (MMA) were analytical reagents; the inhibitor was removed by vacuum distillation before polymerization. Sodium dodecyl benzene sulfonate (Na-DBSA) was used as received.

Preparation of Seed Latex

Distilled water (500 mL), Na-DBSA (2 g), and 98 % sulfuric acid (1 mL) were added into a three-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. When the temperature of the mixture rose to 80°C, a mixture of Me-D4 and Vi-D4 (150 g) at a specific ratio was added while strongly stirring. After the reaction mixture stood for 6 h, it was neutralized with saturated sodium carbonate aqueous solution. An oily layer of siloxane oligomer and unreacted monomer floated on the reaction mixture and was removed with a separate funnel. Thus, linear vinyl-containing polysiloxane latex was obtained. Crosslinked polysiloxane latex was prepared by heating the linear vinyl-containing polysiloxane latex in the presence of potassium persulfate ($K_2S_2O_8$) at 80°C for 12 h. The polysiloxane content in seed latex was determined gravimetrically after evaporating water of weighted seed latex under vacuum at 60°C.

Seeded Emulsion Polymerization

Monomer (3.0 mL) and an appropriate amount of $K_2S_2O_8$ (53 mg) were added into seed polysiloxane latex (50 mL) while being magnetically stirred. The obtained mixture was then added dropwise into an aqueous solution (50 mL) of Na-DBSA (80 mg) and sodium hydrogen sulfite ($NaHSO_3$) (80 mg), which was purged with nitrogen at 80°C. The addition was completed in 4 h, and the reaction mixture stood for additional 4 h. The precip-

itate was obtained by adding anhydrous sodium sulfate (Na_2SO_4) while stirring at elevated temperature and by filtering and washing with warm distilled water. After drying under vacuum at 60°C, a white powder or adhesive solid was obtained.

Characterization of Composite Particles

Latex was thinned with distilled water and treated with an ultrasonic cleaner. Two or three drops of the thinned latex were put onto copper network and the morphology of latex particles was observed under Hitachi H-800 transparent electron microscopy (TEM).

Solid products were extracted successively with petroleum ether and benzene for 48 hrs, respectively. The chemical composition of polymer was determined on Nicole 150SX FTIR with crosslinked polysiloxane and vinyl polymer as the standard.

RESULTS AND DISCUSSION

Synthesis of Polysiloxane Seed Latex

Linear polysiloxane latex was prepared by ring-opening emulsion polymerization of cyclosiloxane. 1H -NMR was used to determine the mole fraction of Me-D4 and Vi-D4 residues of polysiloxane in the seed latex particles.⁹ The recipe of polymerization and the composition of polysiloxane were listed in Table I. The content of polysiloxane in the seed latex was determined gravimetrically. Therefore, the overall conversion of monomers to latex particles was calculated and the results were also listed in Table I.

Because most of monomers were converted into oligomer floating on the reaction mixture, overall conversion of monomers into latex particles was

Table II Seeded Emulsion Polymerization of MMA or ST

Latex	Seed Latex	Polysiloxane (g)	Monomer (mL)	Conversion of Monomer ^b (%)
X3-M	SV-3, crosslinked	4.00	MMA (3.0)	97
Y3-M	SV-3, linear	4.00	MMA (3.0)	98
Y2-M	SV-2, linear	4.85	MMA (3.0)	96
Y1-M	SV-1, linear	5.80	MMA (3.0)	96
X3-S	SV-3, crosslinked	4.00	ST (3.0)	92
Y3-S	SV-3, linear	4.00	ST (3.0)	95
Y2-S	SV-2, linear	4.85	ST (3.0)	93
Y1-S	SV-1, linear	5.80	ST (3.0)	94

MMA, methyl methacrylate; ST, styrene.

fairly low. Linear vinyl-containing latex was crosslinked in the presence of $K_2S_2O_8$. The disappearance of the absorption at 1690 cm^{-1} of the crosslinked polysiloxane latex indicates the complete reaction of vinyl group of linear polysiloxane.⁹

Morphology of Composite Latex Particles

In order to investigate the influence of copolymerization between vinyl monomer and vinyl group of linear polysiloxane, seeded emulsion polymerization of MMA or ST in the presence of different seed latex was carried out as shown in Table II. The latex prepared by seeded polymerization of MMA in the presence of linear and crosslinked SV-3 was marked as Y3-M and X3-M, respectively. For ST, the latex was Y3-S and X3-S, respectively.

TEM photos of those latex particles were shown in Figures 1 and 2. Core-shell structure was found for X3-S and Y3-M latex particles. On the contrary, no core-shell structure was found for X3-M latex particles while the serious aggregation occurred.

It was thought that the reaction between vinyl monomer and vinyl group of polysiloxane might affect the morphology of obtained particles in the course of seeded emulsion polymerization in the presence of linear polysiloxane latex. Therefore, the reactivity ratios of the copolymerization of vinyl monomer with vinyl group of polysiloxane were determined using ^1H -nuclear magnetic resonance (NMR), as reported in our previous article.¹⁰ The results are $r_{\text{SV}} = 2.01$, $r_{\text{MMA}} = 0.78$, and $r_{\text{SV}} = 1.08$, $r_{\text{ST}} = 1.44$. At the same time, the propagating chain produced in the reaction media would be absorbed by the preexisting particles to form the shell or aggregate each other to give out

vinyl polymer particles. Those two tendencies are controlled by the compatibility of seed particles with vinyl polymers. Moreover, it is known that lower interfacial tension between PST and polysiloxane than that between PMMA and polysiloxane favors the precipitation of PST propagating chain onto the preexisting seed particles. At the same time, better solubility of ST monomer in the seed particles favors the polymerization in preexisting particles other than in the reaction media. For example, about 90 % monomers of ST and 54 % monomers of MMA stay in the particles of linear SV3 latex, respectively.¹⁰

In the presence of crosslinked SV-3 seed latex, the crosslinkage hindered the penetration of PST propagating chain into the particles, but the better compatibility of PST with polysiloxane favored the spread of PST over the surface of pre-existing particles. Therefore, core-shell structure was found for X3-S latex as shown in Figure 1(a). The incompatibility between PMMA and polysiloxane expelled the PMMA chains away from the preexisting particles and the aggregation of X3-M latex particles happened, as shown in Figure 2(a). By contrast, ST copolymerized well with vinyl groups of polysiloxane during its seeded emulsion polymerization in the presence of linear SV-3 latex and the resulted copolymer further improved the compatibility of PST with the particles. Therefore, it was easier for ST and PST chain to penetrate into the particles and homogeneous particles of Y3-S were obtained as shown in Figure 1(b). At the same time, the copolymerization of MMA with vinyl groups of linear polysiloxane in the corona of pre-existing particles did happen and increased the compatibility of PMMA with the particles. So core-shell structure of Y3-M was formed as shown in Figure 2(b).

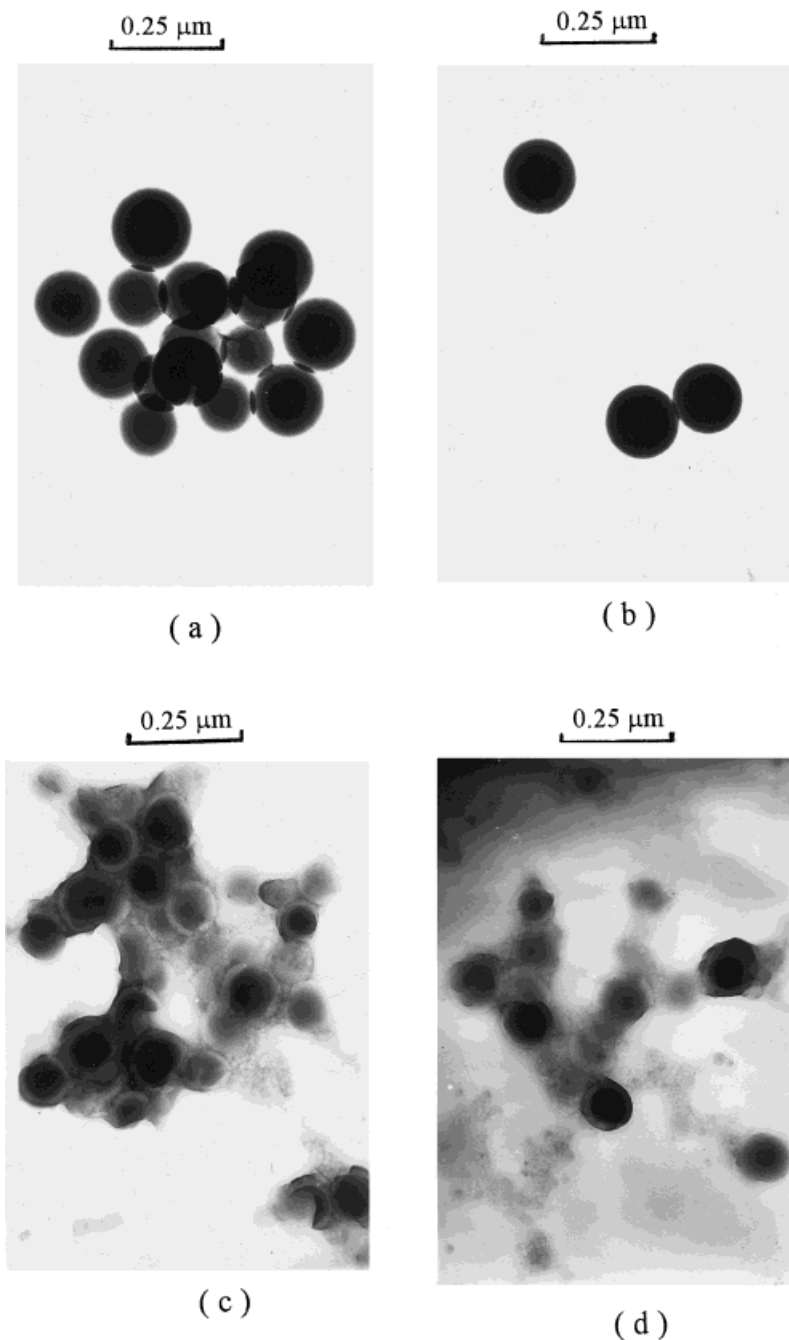


Figure 1 Transmission electron micrographs of latex particles prepared by polymerization of ST. (a) X3-S; (b) Y3-S; (c) Y2-S; (d) Y1-S

With decreasing the vinyl content of polysiloxane in seed particles, the opportunity of copolymerization between vinyl-containing polysiloxane and styrene decreased and little improvement of the miscibility of the particles with ST was obtained. Therefore, the increase of crosslinking degree of the obtained particles would happen due

to greater probability for vinyl group of seed particles to polymerize with each other. The higher crosslinking degree might prevent PST from mixing homogeneously with polysiloxane in the latex particles. Therefore, core-shell structure of both Y2-S and Y1-S latex was formed as shown in Figure 1(c) and (d). At the same time, the copoly-

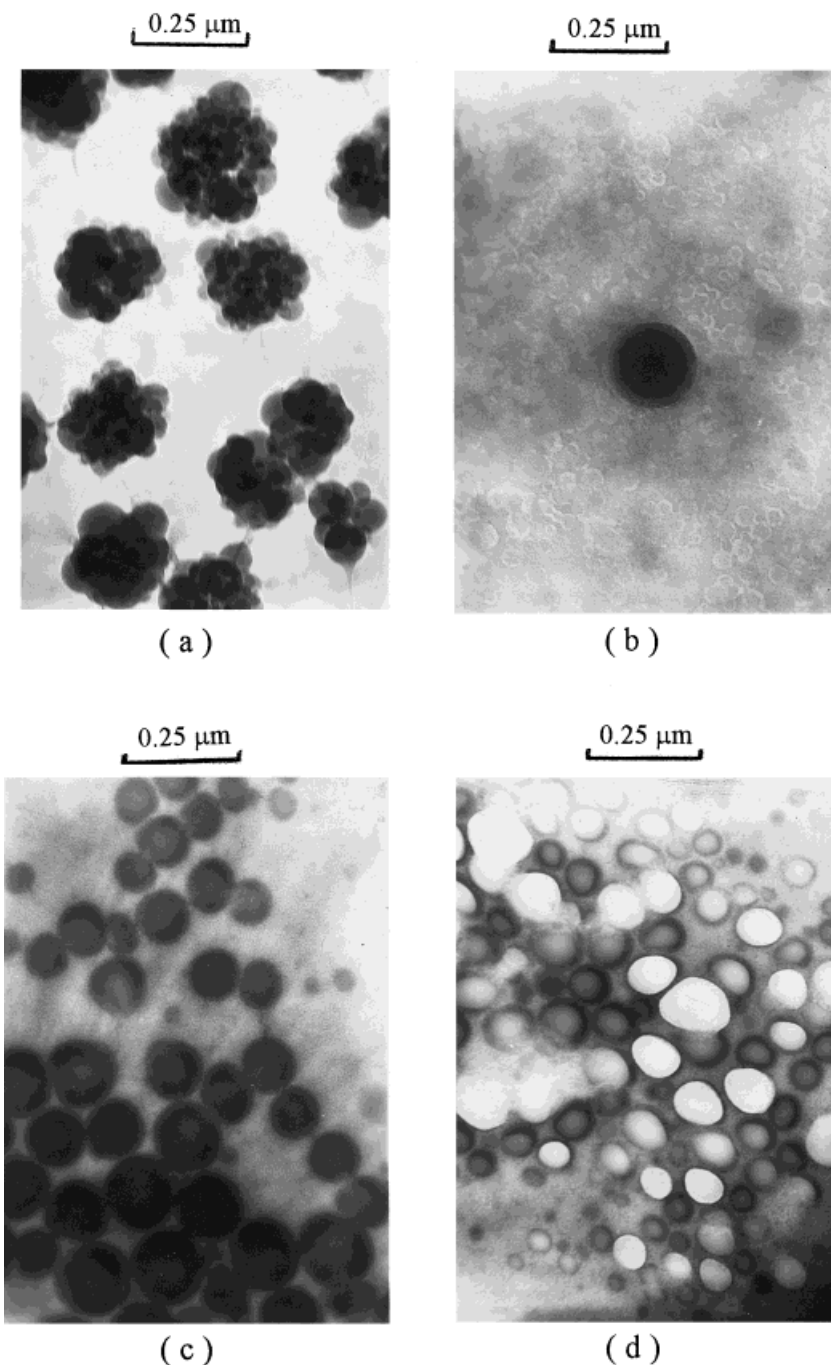


Figure 2 Transmission electron micrographs of latex particles prepared by polymerization of MMA. (a) X3-M; (b) Y3-M; (c) Y2-M; (d) Y1-M.

merization between MMA and vinyl group of polysiloxane led to the graft of PMMA onto the pre-existing particles and improved the compatibility of PMMA with the particles. Therefore, the core-shell structure was seen from TEM photos of Y2-M and Y1-M latex particles as shown in Figure 2(c) and (d).

Component of Composite Particles

The latex particles were extracted with petroleum ether first, followed by benzene. The weight percent (wt %) of remaining polymer after extraction (Wp) was determined gravimetrically and the composition of the obtained particles was determined using

Table III Composition Analysis of Latex Particles After Extraction

Latex	Before Extracting R_{w0}	Extracting With Petroleum Ether				Further Extracting With Benzene			
		W_{p1}	R_{w1}	R_{SV1}	R_{VP1}	W_{p2}	R_{w2}	R_{SV2}	R_{VP2}
X3-M	0.68	0.90	0.80	0.84	0.98	0.75	0.63	0.81	0.71
Y3-M	0.71	0.85	0.78	0.80	0.92	0.89	0.75	0.77	0.84
Y2-M	0.53	0.88	0.61	0.84	0.91	0.88	0.63	0.81	0.90
Y1-M	0.47	0.87	0.52	0.84	0.97	0.81	0.53	0.77	0.90
X3-S	0.64	0.91	0.71	0.88	0.96	0.85	0.60	0.87	0.81
Y3-S	0.66	0.47	0.80	0.42	0.54	0.31	0.64	0.31	0.31
Y2-S	0.56	0.62	0.72	0.55	0.75	0.52	0.56	0.51	0.54
Y1-S	0.44	0.78	0.58	0.70	0.95	0.69	0.46	0.67	0.72

FTIR. The calibration curve for FTIR measurement was established by mixing crosslinked polysiloxane and vinyl polymer at different weight ratio. The characteristic vibration absorption of Si-C at 800 cm^{-1} for polysiloxane, phenyl ring at 699 cm^{-1} for PST and carbonyl group at 1730 cm^{-1} for PMMA was chosen for composition analysis, respectively. The weight ratio of vinyl polymer to polysiloxane (R_w) and W_p were listed in Table III.

To investigate the effect of reaction between vinyl monomer and vinyl group of polysiloxane on the seeded emulsion polymerization further, the ratio of the remaining polysiloxane after extracted with petroleum ether to seed polysiloxane (R_{SV1}) and that of the remaining vinyl polymer to vinyl polymer produced (R_{VP1}) were calculated according to

$$R_{SV1} = \frac{(W_{SV0} + W_{VP0}) \times W_{p1}}{(1 + R_{w1}) \times W_{SV0}} \quad (1)$$

$$R_{VP1} = \frac{(W_{SV0} + W_{VP0}) \times W_{p1}}{(1 + 1/R_{w1}) \times W_{VP0}} \quad (2)$$

where W_{SV0} , and W_{VP0} is the weight of polysiloxane in the seed particles and vinyl polymer produced by seeded emulsion polymerization, respectively. The subscript of 1 means being extracted with petroleum ether.

After being extracted further with benzene, these ratios of latex particles could be obtained according to similar equations to eq. (1) and (2) by replacing W_{p1} and R_{w1} with W_{p2} and R_{w2} , respectively. The subscript of 2 means being extracted further with benzene. All the results were listed in Table III.

Probably as a result of the poor compatibility of PMMA with polysiloxane, R_{VP2} of X3-M latex was

lower than that of X3-S latex indicating that fewer monomers of MMA were grafted to the pre-existing particles while R_{SV1} and R_{VP1} of both X3-M and X3-S latex particles were nearly equal. However, rather different results were obtained for Y3-* latex prepared in the presence of linear polysiloxane latex with high content of vinyl group. The fact that both R_{SV1} and R_{VP1} of Y3-S were very low demonstrated that much of polysiloxane and PST were removed by extraction with petroleum ether. It might be caused by the lower crosslinking degree of the obtained particles and the formation of linear polysiloxane grafted with short chains of PST, which could be expected with view to the reactivity ratio. The latter also led to the further fall of R_{VP} and R_{SV} after the latex particles were extracted with benzene as shown in Table III. By contrast, R_{VP1} and R_{SV1} of Y3-M hardly changed compared with X3-M, but its R_{VP2} was obviously higher than that of X3-M, which resulted from the copolymerization of MMA with vinyl groups of seed polysiloxane.

With the decreased vinyl content in seed polysiloxane, the considerable increase of R_{VP} and R_{SV} was expected because of less copolymerization of vinyl groups of polysiloxane with vinyl monomers and higher crosslinking degree of the resulted latex. At the same time, R_{VP2} of Y*-M latex was higher than that of X3-M because more vinyl polymers were grafted to the crosslinked particles.

CONCLUSIONS

Seeded emulsion polymerization of MMA and ST was carried in the presence of different linear vinyl-containing polysiloxane latices. Core-

shell structure was formed for all cases of PMMA despite the vinyl content of seed polysiloxane. Compared with the latex particles prepared by the polymerization of ST, the higher weight of the remaining PMMA in the latex particles after extracted indicated more PMMA chains were grafted to polysiloxane with higher crosslinking degree, which favored the formation of core-shell structure. Core-shell morphology was observed when polysiloxane latex with lower vinyl content was used as the seed latex for seeded emulsion polymerization of ST. The larger weight loss of PST and polysiloxane for Y*-S latices after the extraction indicated the crosslinking degree of particles was lower and the formation of grafted polysiloxane with short chains of PST. Therefore, good copolymerization of ST with vinyl group of polysiloxane led to the formation of homogenous particles when polysiloxane latex with high vinyl content was used as the seed latex.

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