

# One-Stage Method of Preparing Core-Shell Particles

W. HE,<sup>1,\*</sup> J. TONG,<sup>1</sup> M. WANG,<sup>1</sup> C. PAN,<sup>1</sup> and Q. ZHU<sup>2</sup>

<sup>1</sup>Department of Material Science and Engineering and <sup>2</sup>Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui, People's Republic of China

## SYNOPSIS

A one-stage method of preparing core-shell particles was developed for the system containing silicone oils and glycidyl methacrylate (GMA). Although the formation of core-shell particles for the systems containing silicone oils and methyl methacrylate (MMA) or styrene (ST) is possible in view of thermodynamics, the core-shell particles were not obtained. Factors such as better compatibility of silicone oils with vinyl monomers, higher swelling degree of silicone rubber in the vinyl monomers, and larger addition rate of the vinyl monomers with Si—H during the crosslinking of silicone oil containing vinyl group and Si—H (SVB and SHB) do not favor the formation of core-shell particles. X-ray photoelectron spectrometer (ESCA) was used in determining the formation of core-shell particles. The mechanism of the formation of core-shell particles is discussed. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Recently, the studies of preparation, characterization, and applications of core-shell particles have been attracting more and more attention due to their interesting morphology and applications in various aspects, such as plastics toughening and rubber reinforcement.<sup>1</sup> Generally, core-shell particles were prepared by adding monomers into a seeded emulsion using batch or continuous method.<sup>2-4</sup> The core-shell architecture was characterized by transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and differential scanning calorimetry (DSC).<sup>1</sup> The quantitative determination of the monomer composition of the surface of acrylate copolymer latex was made by Pijpers and Donners<sup>5</sup> on electron spectroscopy for chemical analysis (ESCA).

Efforts have been made to study the mechanism of the formation of core-shell architecture. For two-stage latex, Berg and co-workers proposed that core-shell architecture was formed only when  $\Delta G < 0$  in Eq. (1).<sup>6,7</sup>

$$\Delta G = (\gamma A)_i \quad (1)$$

where  $A$  and  $\gamma$  are the interface area and the interfacial free energy of component  $i$ , respectively, and  $G$  is Gibbs' free energy. It can be predicted that hydrophobic polymers mainly located in the core region of the particles are based on Eq. (1). In addition kinetics factors also affect the formation of core-shell particles in two-stage latex polymerization. The hydrophilic/hydrophobic two-stage polymer systems have a tendency to invert, but the diffusion of polymers limits complete inversion.<sup>8</sup>

In studying the preparation of core-shell particles, we designed a one-stage method of preparing core-shell particles as follows: In a mixture of silicone oils containing Si—H and vinyl group, respectively, vinyl monomers were emulsified in water. During the crosslinking reaction between Si—H and Si—CH=CH<sub>2</sub>, the hydrophilic monomers were excluded to the surface layer of the particles. Then the monomers were polymerized by an appropriate method. In the work, this method of preparing core-shell particles is described and the results are discussed.

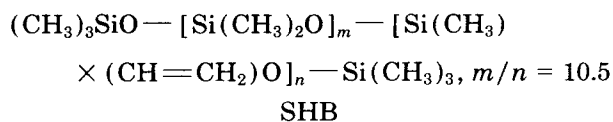
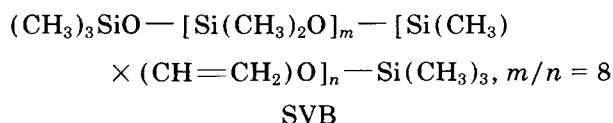
## EXPERIMENT

### Materials

Silicone oil containing vinyl group (SVB) was purchased from BongBu Organic Silicone Factory and

\* To whom correspondence should be addressed.

its equivalence was 826. Silicone oil containing Si-H (SHB) was prepared according to the method described in the literature,<sup>9</sup> and its equivalence measured by nuclear magnetic resonance (NMR) equals 987. Methyl methacrylate (MMA) and styrene (ST) were analytical reagents (AR) and purified before use. Glycidyl methacrylate (GMA) was synthesized by using the method described in the literature.<sup>10</sup> Platinum catalyst was prepared by the reaction of  $\text{H}_2\text{PtCl}_6$  with tetramethyl divinyl silicone ester according to the method described in the literature.<sup>8</sup> The vinyl polymers were obtained by bulk polymerization of related monomers with BPO as initiator at 80°C.



#### Determination of Hydrophobicity of Polymers

Vinyl polymers were dissolved in benzene and the obtained solutions were cast onto the smooth surface of glass. After the solvent was evaporated completely at room temperature, the obtained films were dried in vacuum. The contact angles of PGMA, PMMA, and PST with water were measured on the T-Y-82 Contact Angle Apparatus. Silicone oils of SVB and SHB with equivalence ratio of 1 : 2 containing Pt catalyst were cast onto the glass surface and then crosslinked at 60°C. A piece of the silicone rubber was used to determine its contact angle with water on the same instrument.

#### Swelling Degree of Silicone Rubber in Vinyl Monomers

The silicone rubber resulted from the bulk cross-linking reaction of SVB (1 eq.) and SHB (2 eq.) was immersed in one of the monomers containing an inhibitor at 60°C for 24 h. The swelling degree of the silicone rubber in the various monomers was calculated.

#### Determination of the Addition Reaction Rates of SHB with SVB or Monomers

A solution of SHB (2 eq.) with SVB or different monomers (1 eq.) in D-benzene was put into the

NMR tubes. The conversions of the vinyl group at 60°C were traced on the FX-Q90 FT-NMR spectroscopy.

#### Preparation of Core-Shell Particles

A mixture (100 weight parts) of SVB and SHB at mole ratios of 1 : 2 was mixed with different weight parts of monomers; then several drops of platinum catalyst were added into the mixture. A suspension obtained by stirring organic compounds in water (600 weight parts) containing 1.5% (wt) octamethylenebenzyl polyethylene glydiol ether with  $D_p = 10$  (OP-10) was cycled two times at 40 MPa in a homogenizer, and a stable latex was obtained. The latex was kept at 60°C for 6 h while stirring, then irradiated under  $\gamma$ -ray of  $^{60}\text{Co}$  resource at 1.10 rad/s for 5.5 h. The solid products were obtained by adding anhydrous  $\text{Na}_2\text{SO}_4$  into the latex while stirring; it was then filtered, washed with water, and dried under vacuum.

#### Characterization and Determination of Vinyl Polymer Concentration in the Surface Layer of Final Latex Particles

The final latex were diluted with distilled water, several drops of the diluted latex were put onto copper network, and then the architecture of the latex particles was observed on the Hitachi H-800 TEM instrument.

The films of vinyl polymers and a small piece of pure silicone rubber were used to determine the mole ratios of Si/C of pure polymers on the VG ESCALAB MK-2 ESCA instrument. The latex particles were fixed on stainless steel with adhesive and their mole ratios of Si/C were obtained on the same instrument; then the vinyl polymer concentrations in the surface layer of the latex particles were calculated. The detecting depth was about 100 Å.

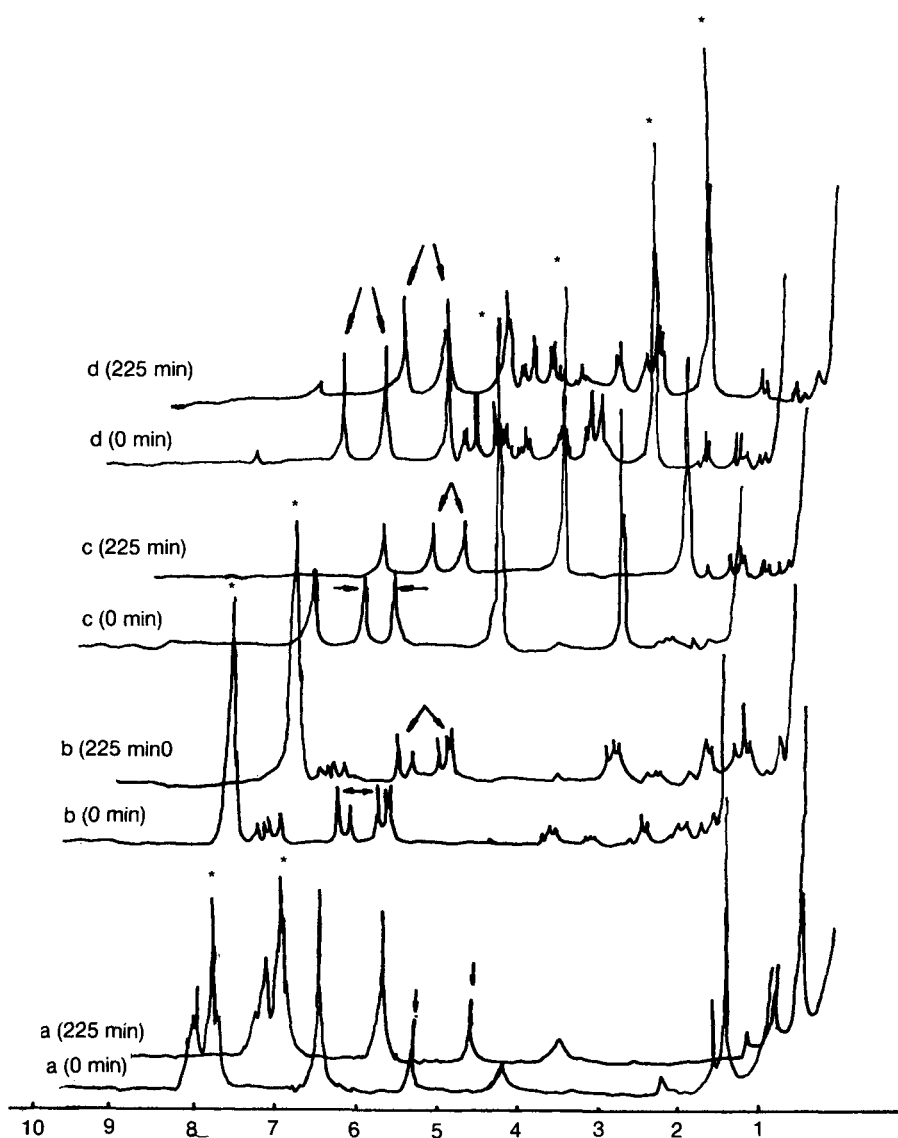
## RESULTS AND DISCUSSION

Many investigations on the preparation of core-shell particles concentrated on the seeded emulsion polymerization with two stages.<sup>2-4</sup> It is interesting to study the formation of core-shell particles by polymerizing a mixture of SVB, SHB, and vinyl monomers with only one stage. It demands that the addition reaction occurred only between Si-H of SHB and vinyl group of SVB during the crosslinking reaction, and the unpolymerized monomers would

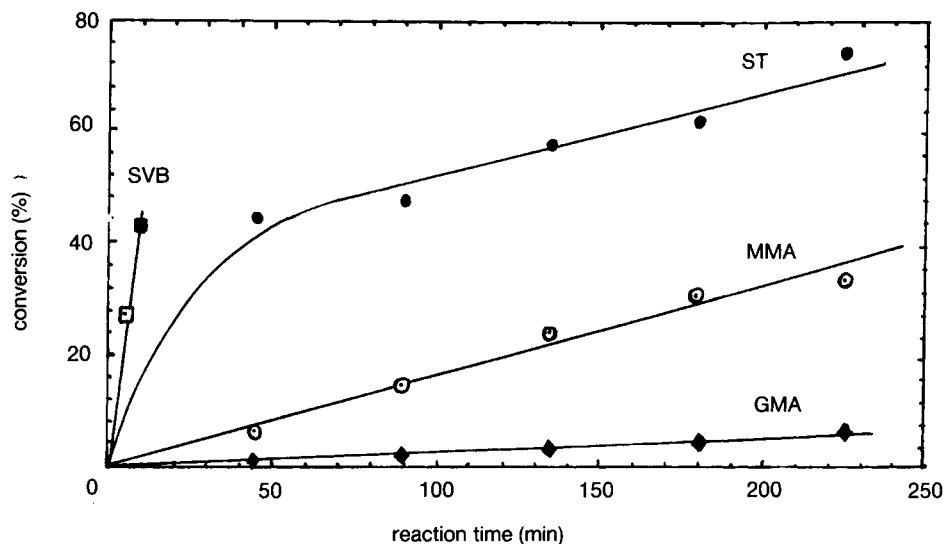
be excluded to the surface of the particles, then polymerized or grafted. Therefore, the addition reaction rates of SHB with SVB, MMA, GMA, or ST were measured using NMR instrument. The NMR spectra of the reaction systems of SHB with different monomers or SVB are shown in Figure 1.

The peaks at  $\delta = 7.70$ , 4.69, and 2.43 ppm, which correspond to phenyl protons of ST, esteric methyl protons of MMA, and methyl protons on carbon-carbon double bond of GMA, respectively, were used as internal standards because they did not change during the addition reaction of Si-H with carbon-carbon double bond. For the system containing SVB,

a certain amount of chlorobenzene was added as an internal standard. The peak height of the protons of carbon-carbon double bond for SVB at  $\delta = 6.52$  ppm, ST at  $\delta = 6.24$ , 5.76 ppm, and MMA at  $\delta = 6.60$ , 5.47 ppm decreased with the increase of the reaction time as shown in Figure 1. However, almost no change of the peak height of the protons of carbon-carbon double bond for GMA  $\delta = 6.08$ , 5.58 ppm was observed as shown in Figure 1. The conversions of the vinyl group could be calculated from the height of the peaks of the various vinyl groups and standard peaks. The results are shown in Figure 2. It was found that the addition reactivities of Si-H with



**Figure 1** NMR spectra of addition reaction products of SHB and vinyl compounds: (a) SHB with SVB, (b) SHB with ST, (c) SHB with MMA, (d) SHB with GMA, (\*) standard peak, and (↓) peak of the proton of vinyl group.



**Figure 2** The dependence of conversion of vinyl groups with the reaction time: (●) ST, (○) MMA, (◆) GMA, (□) SVB, and (■) gelation point for SVB.

various vinyl compounds had the following order:



From the discussion above, it is expected that the core-shell particles would be formed only in the case of silicone oils with GMA since the addition reaction rate of carbon-carbon double bond with Si-H was almost zero. As a comparison, three kinds of particles were prepared from silicone oils with ST, MMA, or GMA, respectively. The architectures of final particles were measured on a TEM instrument. The appearance of two layers in the particles of silicone

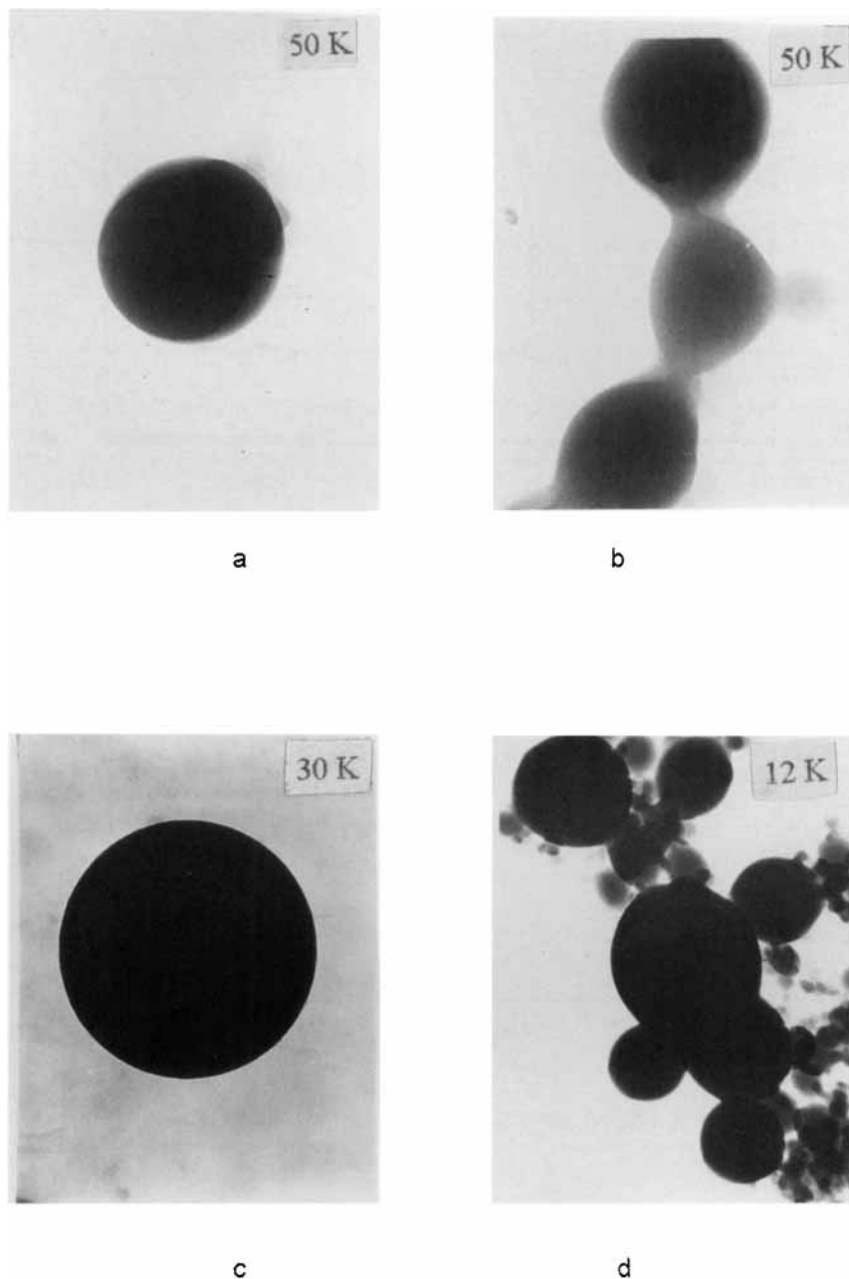
rubber-GMA (13) and silicone rubber-GMA (7) on their TEM pictures demonstrates the formation of core-shell particles as shown in Figure 3(a) and 3(b). The systems containing silicone rubber-ST and silicone rubber-MMA did not show the existence of core-shell architecture as shown in Figure 3(c) and 3(d).

To estimate the concentrations of vinyl polymers in the surface layer of the particles ( $C_s$ ) is very useful for determining whether the core-shell particles were formed. The Si/C atom ratios of silicone rubber-vinyl polymer particles were calculated from the counts of C and Si in the ESCA spectra as shown in Figure 4. A system error for the Si/C atom ratios

**Table I** Vinyl Polymer Concentration in the Surface Layer of Latex Particles

Sample	Monomer and wt. Ratio of Monomer/Silicone Oils	Si/C of Initial Mixture (Mole Ratio)	Si/C of Final Particle (Mole Ratio) <sup>a</sup>	Vinyl Polymer/Silicone Rubber (wt. Ratio)
ST(100)	ST 1.00	0.1309	0.4390	0.2140
ST(26)	ST 0.26	0.2902	0.4962	0.1345
ST(13)	ST 0.13	0.3690	0.4412	0.2104
PST	ST —	0	0.0719	—
MMA(100)	MMA 1.00	0.1768	0.4856	0.2467
MMA(13)	MMA 0.13	0.4708	0.4360	0.3703
PMMA	MMA —	0	0.1050	—
GMA(13)	GMA 0.13	0.4089	0.3127	0.7817
GMA(7)	GMA 0.07	0.4489	0.2905	0.9141
PGMA	GMA —	0	0.0613	—
Silicone rubber	0 —	0.5067	0.5784	—

<sup>a</sup> Data from ESCA.



**Figure 3** TEM photos of silicone rubber-vinyl monomers particles: (a) silicone rubber-GMA(13), (b) silicone rubber-GMA(7), (c) silicone rubber-ST(100), and (d) silicone rubber-MMA(100).

of pure polymers was found; thus it should be considered in calculating the concentrations of the vinyl polymers in the surface layer (100 Å) of the particles, according to Eq. (2).

$$\frac{100 \times 38/2800 + C_s Q_1 A/M + 100 \times 38/2800 \times (Q_2 - Q'_2)/Q'_2}{100 \times 77/2800 + C_s A/M} = \text{Si/C}^* \quad (2)$$

where  $C_s$  is the weight ratios of the vinyl polymer to silicone rubber in the surface layer (100 Å) of the particles,  $Q_1$  is the value of Si/C mole ratio of the pure vinyl polymer obtained from ESCA,  $A$  is the amount of C atom per monomer, and  $M$  is the molecular weight of the vinyl monomer.  $Q_2$  is the value of Si/C mole ratio of silicone rubber obtained from ESCA and  $Q'_2$  is calculated based on the composition of silicone rubber. Si/C\* is the value of Si/C mole

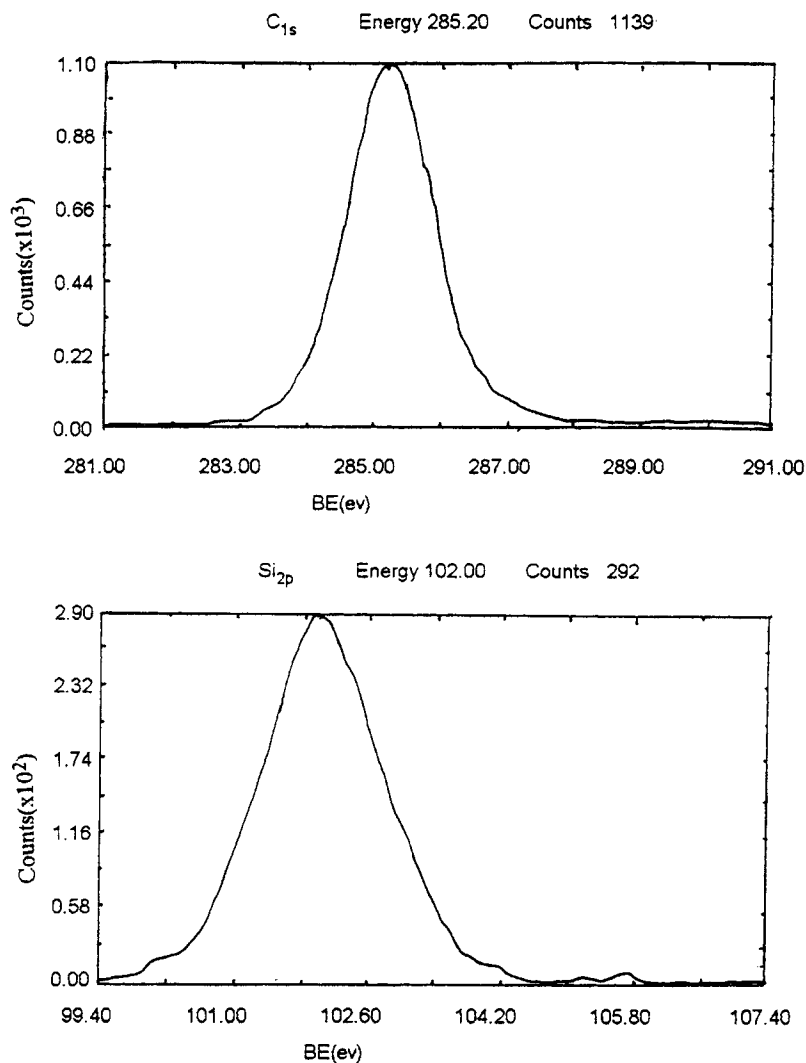


Figure 4 ESCA spectra of silicone rubber-GMA (13).

ratio of the particles obtained from ESCA. The results were listed in Table I.

From the data in Table I it is easily seen that the possibility of forming core-shell particles for the studied systems has the following order:

$$\text{GMA} > \text{MMA} > \text{St}$$

The swelling degrees ( $D_S$ ) of silicone rubber in the various vinyl monomers is calculated according to the following equation and listed in Table II:

$$D_S = (W - W_0)/W_0 \quad (3)$$

where  $W_0$  is the initial weight of silicone rubber and  $W$  is the weight of silicone rubber after swelling in vinyl monomers at 60°C for 24 h. From the data

listed in Table II, the swelling degree of silicone rubber in various monomers has the following order:

$$\text{ST} > \text{MMA} > \text{GMA}$$

Thus GMA migrate easier to the surface of particles than other vinyl monomers during the addition reaction.

Table II Swelling Degree of Silicone Rubber in Vinyl Monomer

Monomer	GMA	MMA	ST
Swelling degree (%)	25.59	53.64	177.59

**Table III** Interface Free Energy of Polymers to Water

Sample	Contact Angle $\theta$	$\gamma_{s-g}^a$ ( $10^{-3}$ J/m $^2$ )	$\gamma_{s-water}^b$ ( $10^{-3}$ J/m $^2$ )	$\Delta G'$ ( $10^{-3}$ J/m $^2$ )
Silicone rubber	$106.17 \pm 0.25$	9.38	29.41	0
PST	$92.52 \pm 0.18$	16.45	19.61	-9.80
PMMA	$76.53 \pm 0.51$	27.35	10.59	-18.82
PGMA	$65.05 \pm 0.07$	36.37	6.01	-21.70

<sup>a</sup>  $\gamma_{s-g}$  was calculated according to the following equation<sup>11</sup>:  $\gamma_{s-g} = \gamma_{l-g} (1 + \cos \theta)^2 / 4$ .

<sup>b</sup>  $\gamma_{s-g}$  and  $\gamma_{l-g}$  were the surface free energy of polymers and water, respectively.

According to Eq. (1), the change in interface free energy for forming core-shell and inverted particles can be expressed as following:

$$-\Delta G_{\text{core-shell}} = \gamma_{A-B} + \gamma_{B-water} - \gamma_{C-water} \quad (4)$$

$$-\Delta G_{\text{invert}} = \gamma_{A-B} - \gamma_{A-water} - \gamma_{C-water} \quad (5)$$

where  $\gamma_{A-B}$  is the interface free energy of the two polymers A and B;  $\gamma_{C-water}$  is the interface free energy of the initial latex particles against water.  $\gamma_{B-water}$  and  $\gamma_{A-water}$  are the interface free energy of polymer A against water and polymer B against water, respectively.

$$(4)-(5): \Delta G = (-\Delta G_{\text{core-shell}}) - (-\Delta G_{\text{invert}}) \quad (6)$$

$$= \gamma_{B-water} - \gamma_{A-water}$$

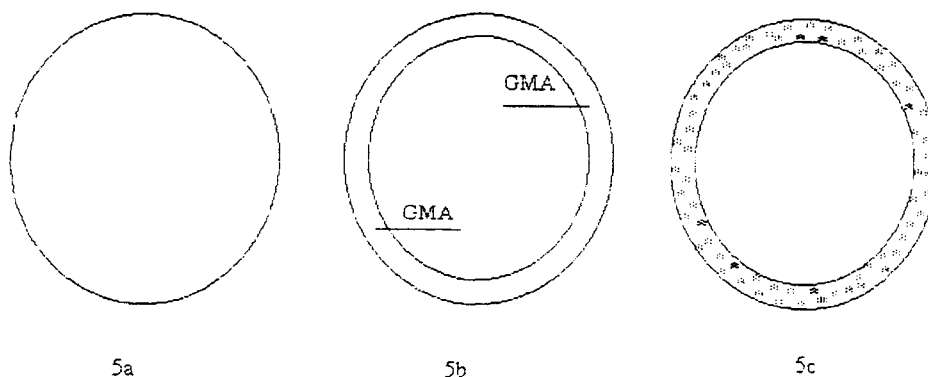
The contact angles of various polymers to water were measured and  $\Delta G$  was calculated. The results are listed in Table III.  $\Delta G$  for GMA is the smallest. Thus the system containing silicone oils and GMA is the easiest to form the core-shell particles. The formation process of core-shell particles can be pro-

posed as shown in Figure 5. Homogeneous particles were obtained by pumping the mixture of silicone oils and GMA into a homogenizer, as shown in Figure 5(a). When the addition reaction of SVB and SHB took place in the presence of platinum complex, the phase separation gradually occurred because of poor compatibility of GMA with silicone rubber. Hydrophilicity of GMA causes the movement of monomers toward the surface of particles. The formation of stable core-shell particles is expected as shown in Figure 5(b). After the latex solution is irradiated under  $\gamma$ -ray of  $^{60}\text{Co}$ , the particles with PGMA-rich shell was obtained as shown in Figure 5(c).

The lack of formation of core-shell particles for silicone rubber-ST and silicone rubber-MMA was attributed to the rapid addition reaction of SHB with the monomers and the better compatibility of these monomers with silicone rubber.

## CONCLUSION

A one-stage method of preparing core-shell particles is developed successfully only for the system of sil-



**Figure 5** Formation of core-shell particles for silicone rubber with GMA system: (a) latex particle before addition reaction, (b) latex particle after addition reaction, and (c) latex particle after irradiation polymerization.

icone oils–GMA in the studied systems: silicone oils–MMA, ST, and GMA. The core–shell architecture was confirmed by TEM and ESCA. The results demonstrate that there are three factors favoring the formation of core–shell particles:

1. Lower interface free energy of PGMA with water than that of silicone rubber with water
2. Much lower addition reaction rates of GMA with SHB than that of SVB with SHB
3. Worse compatibility of GMA with silicone rubber

Under these conditions, the unreacted monomer of GMA can be excluded to the surface of latex particles during the crosslinking reaction between SHB and SVB; then polymerized or grafted to form the PGMA-rich shell.

## REFERENCES

1. (a) L. M. Wu, B. G. Li, Z. Z. Yu, and Z. R. Pan, *Gaofenzi Yuebao*, **2**, 71 (1990). (b) J. D. Tong, R. K. Bai, Y. F. Zou, and C. Y. Pan, *J. Appl. Polym. Sci.*, in press.
2. T. L. Min, A. Klein, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2845 (1983).
3. J. L. Jönsson, H. Hassander, L. H. Jansson, and Bertil Törnall, *Macromolecules*, **24**, 126 (1991).
4. J. D. Tong, R. K. Bai, Y. F. Zou, and C. Y. Pan, *Macromol. Rep.*, **A(30)**, 407 (1993).
5. A. P. Pijpers and W. A. B. Donners, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 453 (1985).
6. J. Berg, D. Sundberg, and B. Kronberg, *Polym. Mat. Sci. Eng.*, **54**, 367 (1986).
7. D. Sundberg, A. Cassasa, J. Pantazopoulos, and M. Muscat, *J. Appl. Polym. Sci.*, **41**, 1425 (1990).
8. S. Lee and A. Rudin, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 865 (1992).
9. Organic Silicone Laboratory of Chenguang Chemical Technology Institute, in *Monomers and Polymers of Organic Siloxanes*, China Chemical Industry Press, Beijing, 1986.
10. J. D. Tong, Master Thesis, University of Science and Technology of China, 1992.
11. R. J. Good, *Advances in Chemistry Series*, Vol. 43, Amer. Chem. Soc., Washington, 1964.

Received January 26, 1994

Accepted May 16, 1994