

# Prediction and Experiment of Core–Shell Particle Morphology of Vinyl Acetate and Butyl Acrylate

PEIQIN SUN, KE ZHAO, DAZHUANG LIU, DONGXIA HUO

Department of Chemical Engineering, Zhengzhou University of Technology, Zhengzhou 450002, China

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**ABSTRACT:** In this article, the particle morphology in emulsion polymerization of the poly(vinyl acetate) (PVAc)/poly(butyl acrylate) (PBA) system is investigated. With the use of the basic data in literature, the relevant interface tensions and viscosity are estimated with the equation proposed in literature. The time achieved to equilibrium morphology is predicted with cluster dynamics proposed by Gonzalez. The experiment result is consistent with that of prediction. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2930–2937, 2002; DOI 10.1002/app.10297

**Key words:** latex particles; morphology; seeded emulsion polymerization; poly(butyl acrylate); poly(vinyl acetate)

## INTRODUCTION

It has been found that when hydrophobic monomers are polymerized in the presence of highly hydrophilic polymer seed particles, the second-stage hydrophobic polymers form cores surrounded by the first-stage hydrophilic polymers, resulting in an inverted core–shell latex. In the process of forming the inverted core–shell, the hydrophilic polymer chains migrate from seed to outer layer.<sup>1</sup> It is known that the viscosity resistance will strongly affect the rate of chain migration. Because the amount of monomer inside the particle in the process of a semicontinuous polymerization is lower than that in batch process, the interior viscosity of the particle in the semicontinuous process is larger than that in the batch process. The result will be that the time to achieve the final morphology in the semicontinuous process will be longer than the time to achieve the batch process. The starvation feeding is an extreme mode in the semicontinuous process. In

that case, the amount of monomer is little or negligible in the particle. Therefore, the study of the formation of inverted core–shell by starvation feeding mode should provide valuable information.

Vinyl acetate-butyl acrylate (VAc-BA) emulsion copolymers that are widely used in many technical applications also provide researchers with model latices for investigating structure–property relationships. For such a system, the glass transition temperature of both poly(vinyl acetate) (PVAc, 32°C) and butyl acrylate (PBA, –54°C) is lower than that of polymerization reaction, so chain migration can be carried out at the reaction temperature, even without the monomer. This allows us to study with no trouble the semicontinuous starved feeding mode. Kong<sup>2</sup> performed a study of two-stage batch polymerization of the system VAc-BA. It was found that at the end of the experiment, PVAc is formed at an outer layer in the core–shell structure and either PVAc or PBA is used as seed. On the basis of the above-mentioned study, the following article deals with the two-stage polymerization by the semicontinuous starved feeding mode. PVAc is selected as

Correspondence to: P. Sun (sunpq@public2.zz.ha.cn).

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**Table I** The Surface Tension of Polymers and Water with SLS<sup>9</sup>

Substance	Temperature (°C)	$\gamma \times 10^3$ (N/M)	$\gamma^d \times 10^3$ (N/m)	$\gamma^p \times 10^3$ (N/m)	$-d\gamma/dT \times 10^3$ (N/m)/°C	$X^p$
PVAc	20	36.5	24.5	12	0.066	0.329
	70	33.2	22.28	10.92	—	—
PBA	20	33.7	30.4	3.3	0.070	0.098
	70	30.2	27.24	2.96	—	—
Water (SLS)	20	39.5	12.01	27.49	0.2275	0.696
	70	28.12	8.55	19.57	—	—

seed, whereas BA is selected as the second-stage monomer.

In recent years, great advances have been made in the theoretical study of core-shell latex particle morphology. Sundberg et al.<sup>3,4</sup> proposed a thermodynamic rationale for the formation of two-stage particle structures: the thermodynamically preferred morphology is the one that has minimum interfacial energy change. Gonzalez-Ortiz and Asua<sup>5-7</sup> proposed cluster dynamics to simulate and estimate the whole process in the evolution of particle morphology. The main idea of cluster dynamics is as follows: (a) The polymer chains are formed at a given position in a polymer particle. (b) If the newly formed polymer chain is incompatible with the seed polymer chain, phase separation occurs. Phase separation leads to the formation of clusters. (c) To minimize the Gibbs free energy, the clusters migrate toward the equilibrium morphology. The motion of the clusters is due to the balance between the van der Waals forces and the viscosity forces. Interfacial tension and viscosity are the basic parameters in the calculation. This has made it possible to study the effect of various factors on the chain migration by mathematics simulation method.

An object proposed in this article is that the inverted core-shell morphology will be set at the end of the experiment. The research method is that suitable condition is found by computer simulation method, and then experimental verification is carried out. The simplified conditions are as follows: (1) In the semicontinuous polymerization process, because the reaction rate is roughly equal to the adding rate of monomer, the effect of monomer on the interfacial tension and viscosity can be roughly neglected. (2) The same initiator is used in the two-stage polymerization; so, the polymer polarity change caused by different initiators can be reduced. (3) The parameters are obtained by calculation from the equation proposed in the literature.

## THE CALCULATION OF THE BASIC PARAMETER

### Estimation of the Interfacial Tension

Both harmonic mean and geometrical mean are applied to estimate the interfacial tension from the surface tension. Sundberg et al.<sup>3</sup> used the harmonic mean to estimate the interfacial tension of mineral oil and poly(methyl methacrylate) (PMMA). Huo et al.<sup>8</sup> has, respectively, used harmonic mean and geometrical mean to estimate various interfacial tension in systems of polystyrene (PSt)/PMMA, PBA/PSt, PBA/PMMA, and PBA/poly(styrene-co-methyl methacrylate). All the equilibrium morphologies predicted were consistent with the experiment results. In this article, sodium lauryl sulfate (SLS) is used as emulsifier; the surface tension of PBA, PVAc, and water with SLS are listed in Table I.

The equation of harmonic mean is

$$\sigma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad (1)$$

The equation of geometrical mean is

$$\sigma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} - 2(\gamma_1^p \gamma_2^p)^{1/2} \quad (2)$$

In Table I and the above equation,  $\gamma$  is the surface tension,  $\gamma^d$  and  $\gamma^p$  are the dispersive components and the respective polar components of the surface tension, respectively,  $X^p$  is the fractional polarity, and  $\sigma$  is the interfacial tension. The calculated results of the interfacial tension are listed in Table II.

### Estimation of the Viscosity

Viscosity  $\mu$  of polymer melt changes with temperature and molecular weight. The simplified equation is as follows<sup>6</sup>:

**Table II The Interfacial Tension between Polymer and Water and Polymer and Polymer at 70°C**

70°C	Harmonic Mean	Geometrical Mean
$\sigma_{\text{PVAc/w}} \times 10^3$ (N/m)	8.57	4.48
$\sigma_{\text{PBA/w}} \times 10^3$ (N/m)	22.01	12.58
$\sigma_{\text{PVAc/PBA}} \times 10^3$ (N/m)	5.06	2.75

$$\mu = \frac{\mu_0^* \exp\left\{\frac{E_\mu}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right\} M^{3.4}}{M_R^{3.4}} \quad (3)$$

where  $\mu_0^*$  is the viscosity at the reference values of temperature;  $T_R$  is the polymer molecular weight,  $M_R$ ; and  $T$  and  $M$  are the actual temperature and polymer molecular weight, respectively.

If PVAc is seed and the reaction temperature is at 70°C, the values of viscosity of PVAc in different molecular weights can be calculated by eq. (3).

In general, the molecular weight of PVA is between  $10 \times 10^4$  and  $150 \times 10^4$ . According to literature,<sup>10</sup>  $M_R = 1 \times 10^5$ ;  $T_R = 200$  °C;  $\mu_0^* = 2 \times 10^2$  Pa s;  $E_\mu = 67$  (KJ/mol). The results are listed in Table III.

### The Prediction of the Time of Achieving Equilibrium Morphology

#### The Prediction of the Equilibrium Morphology

Let us consider a seed semicontinuous emulsion polymerization of monomer 1 (BA) on a seed of polymer 2 (PVAc). The aqueous phase will be denoted as phase 3. The final equilibrium morphology of the particle can be predicted by Gonzalez's method by using the interfacial tension obtained by harmonic or geometrical mean:

$$\begin{aligned} \text{Harmonic mean: } \sigma_{23} &= 8.57 \times 10^{-3} \text{ (N/m)} \quad \sigma_{13} \\ &= 22.01 \times 10^{-3} \text{ (N/m)} \quad \sigma_{12} = 5.06 \times 10^{-3} \text{ (N/m)} \end{aligned}$$

$$\begin{aligned} A_{121} &= 0.992 \times 10^{-20} \text{ (J)} \quad A_{123} = -0.821 \\ &\times 10^{-20} \text{ (J)} \quad A_{131} = 4.315 \times 10^{-20} \text{ (J)} \end{aligned}$$

$$\begin{aligned} T &= |\sigma_{13} - \sigma_{12}| / \sigma_{23} = 1.9778 \quad U = \sigma_{12} / \sigma_{13} \\ &= 0.2299 \end{aligned}$$

where  $\sigma_{12}$ ,  $\sigma_{23}$ ,  $\sigma_{13}$  are interfacial tensions of polymer1 and polymer2, polymer2 and water, and polymer1 and water, respectively.  $A_{ijk}$  is the Hamaker constant of material  $i$ ,  $k$  in a continuous phase  $j$ . The values of the Hamaker constants can be estimated from the interfacial tensions.

Because  $\alpha_{123} < 0$ ,  $T > 1$ ,  $U < 1$ , the equilibrium morphology will be the inverted core-shell structure in this condition:

$$\text{Geometrical mean: } \sigma_{23} = 4.48 \times 10^{-3} \text{ (N/m)}$$

$$\sigma_{13} = 12.58 \times 10^{-3} \text{ (N/m)} \quad \sigma_{12} = 2.75 \times 10^{-3} \text{ (N/m)}$$

$$A_{121} = 0.539 \times 10^{-20} \text{ (J)}$$

$$A_{123} = -0.524 \times 10^{-20} \text{ (J)}$$

$$A_{131} = 2.466 \times 10^{-20} \text{ (J)}$$

$$T = |\sigma_{13} - \sigma_{12}| / \sigma_{23} = 2.1942$$

$$U = \sigma_{12} / \sigma_{13} = 0.2186$$

Because  $\alpha_{123} < 0$ ,  $T > 1$ ,  $U < 1$ , the equilibrium morphology will also be the inverted core-shell structure in this condition.

Although there is some difference between the interfacial tension calculated by harmonic mean and geometrical mean, the predicting equilibrium morphology is consistent.

The prediction of the time achieving equilibrium morphology is as follows.

#### Mathematics Model and Calculation Step

When we predict the time of the core-shell particle to achieve the final equilibrium morphologies after getting the parameters of interfacial tension and viscosity, the first problem is how to determine the initial state, the volume ( $V_0$ ), and the number ( $N$ ) of the initial clusters. In general, because the values of  $V_0$  and  $N$  are related to the

**Table III The PVAc Viscosity in Different Molecular Weight at 70 and 30°C**

$M$ ( $\times 10^{-4}$ )	$T = 70^\circ\text{C}$ $\mu$ (Pa s)	$T = 30^\circ\text{C}$ $\mu$ (Pa s)
10	$1.27 \times 10^5$	$2.83 \times 10^6$
20	$1.35 \times 10^6$	$2.99 \times 10^7$
50	$3.03 \times 10^7$	$6.73 \times 10^8$
100	$3.20 \times 10^8$	$7.11 \times 10^9$
150	$1.27 \times 10^9$	$2.82 \times 10^{10}$

three-element phase diagram, cluster nucleation, and dynamics in polymerizing system, accurate values of  $V_0$  and  $N$  are unknown. Fortunately, sensitivity analysis<sup>7</sup> showed that the final particle morphology was not significantly affected by either the volume or the cluster nucleation rate constant. Therefore, we apply the simplified condition as follows: (1) When the volume of the second-stage monomer and polymer is equal to 1% of the volume of the original seed, the cluster formation begins. (2) The simulation result was not significantly affected by the number of the initial clusters (such as 30, 50, 100) after comparing calculation results; thus, the number of the initial clusters was chosen  $N = 50$ .

The simulation steps are as follows:

- (1) In the initial state, the particle contains  $N$  (50) tiny clusters of the same size randomly distributed in the seed particle. The total volume of these initial clusters is equal to 1% of the volume original seed. The seed's sphere center coordinate is 0, 0, 0; the cluster's center coordinate is  $X_i, Y_i, Z_i$ , radius as  $r_i, i = 1 \sim N_0$ . The values of the Hamaker constants need to be calculated. As polymerization proceeds, polymer 1 is produced in both clusters and polymer 2 matrix. It was considered that polymer 1 can be formed in the matrix diffused instantaneously to the clusters; the distribution of polymer 1 between clusters is proportional to the interfacial clusters–matrix area of each cluster. The size of the clusters varies because of coagulate; simultaneously with polymerization, they move and coagulate because of the van der Waals forces.
- (2) Selecting a small time increment  $\Delta t$  to calculate the change of cluster's position and radius because of the migration and coagulation of cluster by the follow equations after the time passed  $\Delta t$ .

The motion of the clusters is caused by the balance between the forces of van der Waals and the forces of viscosity. For small movements, that is,  $|X_{j0} - X_j| < 1$  nm, the equation of motion is

$$X_j = X_{j0} + \frac{F_j t}{b_j \mu} \quad (4)$$

where  $X_j$  is the vector giving the position of cluster  $j$ ,  $F_j$  is the net van der Waals force acting on cluster  $j$ ,  $t$  is the time,  $\mu$  is the viscosity of phase 2 [ $\mu$  can be calculated by eq. (3)], and  $b_j$  is the friction factor of cluster  $j$ . The friction factor of a sphere is as follows:

$$b_j = 6\pi r_j \quad (5)$$

where  $r_j$  is the radius of the cluster. The net van der Waals force is given by

$$F_j = F_{j3} + \sum_{h=i, h \neq j}^H F_{jh} \quad (6)$$

where  $F_{j3}$  is the force on cluster  $j$  resulting from the interaction of cluster  $j$  and phase 3.  $F_{jh}$  is the force resulting from the interaction of clusters  $j$  and  $h$ , and  $H$  is the total number of clusters. These forces can be obtained from the energies of interaction,  $E_j$ , by using the equation:

$$F_j = -\nabla E_j \quad (7)$$

The interaction energies  $E_j$  relate to Hamaker constants, cluster's position, and radius.

Because the time scale for coagulation is generally much shorter than the time scale for the motion of the clusters, it was assumed that instantaneous coagulation of cluster is formed when they contact. Selecting cluster  $i$  and calculating the acting forces  $F_j$  of other clusters and water on it. By the force of  $F_j$ , calculating the migration distance of cluster  $i$ , cluster's center coordinate will change. If the migration distance of cluster is bigger than 1 nm, the time increment  $\Delta t$  should be decreased and recalculated by sequence. Sequencing calculates every cluster's migration distance and the change of the cluster center coordinate. When two clusters touch each other, they will coagulate immediately, the number of clusters diminishes, and the cluster's radius accumulates.

- (3) Combining the material balances equation with the reaction kinetics equation,

**Table IV** The Time Achieving the Final Equilibrium Morphology at Different Viscosity

$\mu$ (Pa s)	$T = 70^\circ\text{C}$	$M (\times 10^{-4})$	Harmonic Mean		Geometrical Mean	
			$R_0 = 50$ nm $t$ (min)	$R_0 = 200$ nm $t$ (min)	$R_0 = 50$ nm $t$ (min)	$R_0 = 200$ nm $t$ (min)
$1 \times 10^6$		18.3	39	87	48	99
$1 \times 10^7$		36.1	76	204	86	249
$1 \times 10^8$		71.1	118	689	161	839
$1 \times 10^9$		139.9	274	1954	333	2417
$1 \times 10^{10}$		275.5	759	6481	933	8098

calculating every cluster's growth because of the polymerization in the time  $\Delta t$ .

- (4) The time passes by  $\Delta t$ , the time changes to  $t + \Delta t$ , the number of cluster changes to  $N'$ , the cluster center coordinate changes to  $X_i'$ ,  $Y_i'$ ,  $Z_i'$ , and cluster radius changes to  $r_i'$ . Then we should return to (2) and redo the calculation.
- (5) Repeating the calculation from (2)-(4) until clusters move to spherical center entirely and the inverse core-shell morphology is formed.

To observe the morphology of the particle more directly, the figures of the three-dimensional sphere should be changed to the figures of the two-dimension plane. The figures are the projections of the clusters on a vertical plane that rotates  $180^\circ$  about the vertical axis of the polymer particles.

The simulation is as follows. PVAc is a seed at first stage; BA is added to reactor by semicontinuous starvation mode at second stage, and the polymerization rate is roughly equal to the adding rate. The weight ratio of BA and VAc is 1 : 1. In general, the polymerization temperature is  $70^\circ\text{C}$ , and the feeding time is about 2 h. Then heat preservation reacts for some time (2 h in general). Now, suppose the PVAc seed's radius is 50 or 200 nm; by using the interfacial tensions by harmonic or geometrical mean, we can predict the time in which particles achieving the final equilibrium morphology at different viscosities. The time at which particles achieving the final equilibrium morphology at different viscosity are given in Table IV.

Table IV shows that viscosity and seed radius significantly influence the time achieving the equilibrium morphology; the lower the viscosity and the smaller the seed radius, then the shorter

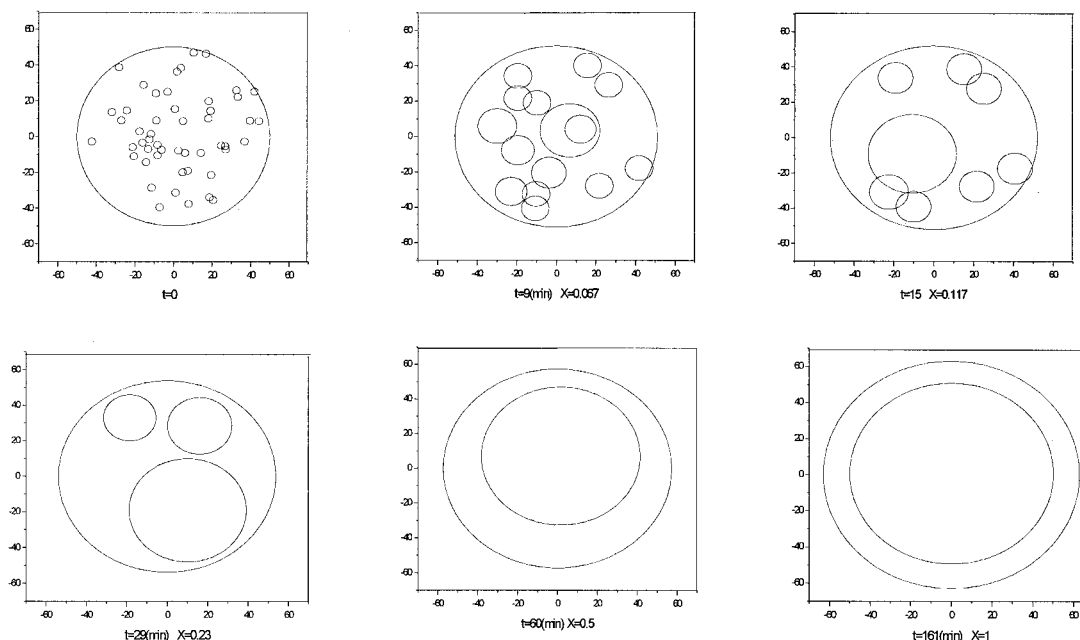
the time achieving the equilibrium. Though the difference of the interfacial tensions obtained by harmonic mean and geometrical mean has influence on the time achieving the equilibrium morphology, there is no order of magnitude difference. As an estimated method, the influence can be neglected. As an example,  $R_0 = 50$  nm,  $\mu = 1 \times 10^8$ . Evolution of the particle morphology for calculation by the interfacial tension from geometrical mean are presented in Figure 1. Evolution of the particle morphology at other conditions is similar to Figure 1, just as the time achieving the inverted core-shell morphology is different.

If the object of experimental design is that the inverted core-shell morphology sets at the end of experiment, that is, the total time achieving the inverted core-shell morphology is  $< 4$  h (240 min), Table IV shows that the time achieving the inverted core-shell morphology is very long when the viscosity is high and the seed radius is large. The inverted core-shell morphology cannot set at the end of experiment. According to the simulation results, some procedures should be followed in the experiment: (1) to get the small seed radius, ion-emulsifier should be added in the experiment only; (2) to decrease the viscosity, chain transfer should be added in the experiment.

## EXPERIMENTAL

### Experimental Method

According to the above design, the experiment is prepared as follows. The experiment is carried out in a five-neck glass reactor with jacket; the composite latex particles are prepared by seed semicontinuous feeding mode. The experiment recipe is given in Table V, where KPS (potassium per-



**Figure 1** Evolution of the particles morphology:  $R_0 = 50$  nm,  $\mu = 1 \times 10^8$ ; interface tension is calculated by geometrical mean.

sulfate) is applied as initiator, and DDM (dodecyl mercaptan) is applied as chain transfer.

The experimental procedure is as follows: SLS, 2.5 g;  $\text{NaHCO}_3$ , 0.5 g; and  $\text{H}_2\text{O}$ , 300 mL are put into the reactor. The temperature rises to  $70^\circ\text{C}$ ; then drops 10 g VAc, DDM 0.15 g, and 0.25 g KPS to the reactor. After reacting for half an hour, the rest of the 50 g VAc is added at a rate of  $0.01 \text{ mL s}^{-1}$ . When the addition is over, the reaction continues for 1 h more at  $70^\circ\text{C}$ , and then the temperature rises to  $90^\circ\text{C}$  and stays constant for 1 h more, so as to make VAc conversion entire and to exhaust the initiator. After that, the temperature is dropped to  $70^\circ\text{C}$ , and 0.25 g KSP, DDM 0.15 g is added to the reactor; 60 g BA is added at a rate of  $0.01 \text{ mL s}^{-1}$ . The reaction continues for another 2 h at a constant  $70^\circ\text{C}$ . Then the experiment is ended.

### Experiment Results

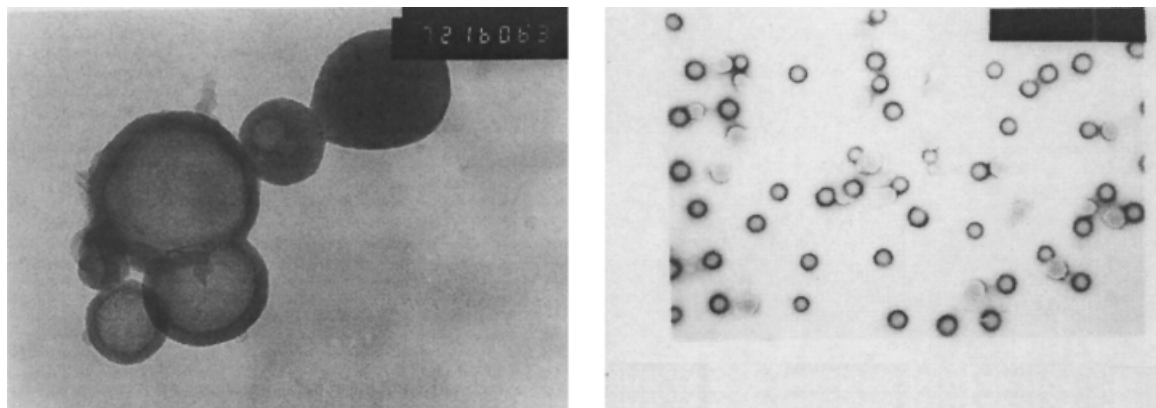
- (1) Determination of the conversion: During the reaction, the conversion was determined

by gravimetry. It is found that the reaction rate is roughly equal to the adding rate.

- (2) Determination of the particle diameter: The particle diameter is determined by the granularity instrument of Malven Co., the Autosizer IIC type, made in Britain. The seed mean diameter is  $D_1 = 73.5$  nm (seed mean radius,  $R_0 = 36.8$ ). After the second stage of the polymerization, the mean diameter of particles is  $D_2 = 92.6$  nm.
- (3) Determination of the molecular weight: The molecular weight is determined by a Waters 208 LC/GPC, made in America. The weighted mean molecular weight of the seed polymer is  $21.94 \times 10^4$ .
- (4) Determination of the particle morphology: The particle morphology at the end of the experiment is observed by TEM of JEM-100CX made in Japan, work voltage, 100 kV; amplification factor, 48–72,000. Phosphotungstic acid was used as a staining agent,  $\text{pH} = 2.0$ . The particle TEM pho-

**Table V** Experiment Recipe

Ingredient	VAc	BA	KPS	DDM	SLS	$\text{NaHCO}_3$	$\text{H}_2\text{O}$
Weight	60g	60g	0.5g	0.3g	2.5g	0.5g	300ml



**Figure 2** TEM photograph of particles, at the end of the experiment.

tography in Figure 2 shows that the PBA color is white, the PVAc color is black, and the particle morphology is inverted core-shell.

- (5) Determination of the glass transition temperature ( $T_g$ ) is determined by the differential scanning calorimeter of Perkin-Elmer DSC-7. There are two  $T_g$ 's in latex polymer; the high value is  $T_g = 23.83^\circ\text{C}$ , near to the  $T_g$  of PVAc.

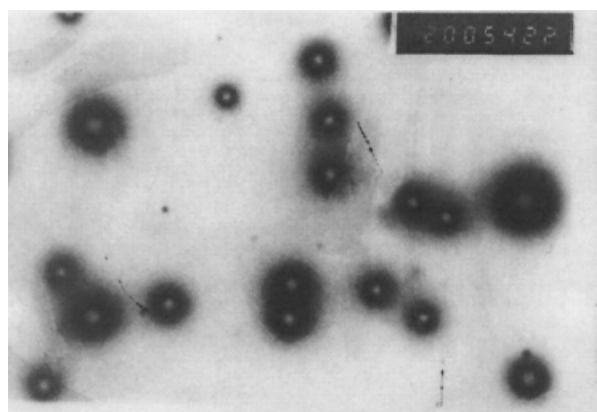
#### The Particle Morphology in the Polymerization

In the above experiment, the seed mean radius  $R_0 = 36.8$ , and the molecular weight of the seed polymer is  $21.94 \times 10^4$ . Compared to the results of the Table IV, a similar condition is the result obtained when the seed radius is  $R_0 = 50$ , molecular weight is  $18.3 \times 10^4$ , and the time to achieve the inverted core-shell morphology is 48 min. If the result is convincing, the inverted core-shell morphology will be formed far before 240 min. Then the monomer

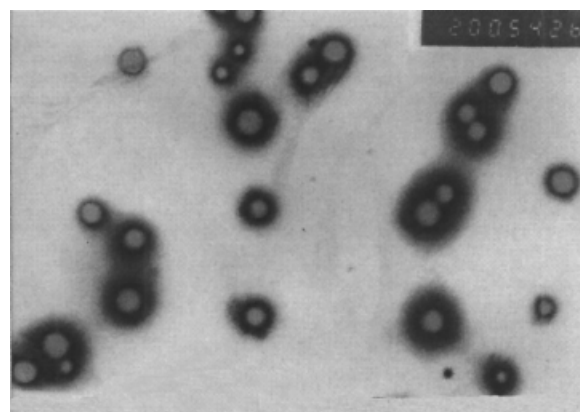
continuously added transforms into the polymer and enters into the cores, which expand continuously. The experiment was carried out again to prove the simulated result. Samples are taken out in the process of reaction to observe the morphology of the particles. The particle TEM photographs at different times are as shown in Figures 3 and 4. Figures 3 and 4 show that, as expected, the inverted core-shell formed at  $t = 35$  min, because the amount of PBA is small at initial stages. The white core is smaller than the black shell, and as the time prolongs, the proportion of white core rather than black shell increased. The final result was displayed in Figure 2. This experiment shows that the simulated results can be used to guide the experimental design.

#### CONCLUSION

The cluster dynamics theory is applied to simulate formation of the VAc/BA inverted core-shell



**Figure 3** TEM photograph of particles,  $t = 35$  min.



**Figure 4** TEM photograph of particles,  $t = 80$  min.

with the semicontinuous starved feeding mode. The effect of various factors on the time achieving the final equilibrium core-shell morphology is discussed. These factors include particle radius and viscosity of the seed, interface tensions of the polymer-polymer and polymer-water with emulsifier. The object of the experiment design is that inverted core-shell morphology forms at the end of the experiment. According to the conditions obtained from simulation, the experiment is carried out. It is found that the result of the experiment is consistent with that of the design prediction.

In the calculation processes, the harmonic and geometric mean methods are used to calculate interface tension of the PVAc-PBA, PVAc-water (with SLS), PBA-water (with SLS) from the surface tension of PBA, and PVAc and water (with SLS), which comes from the literature. It is found that these methods are simple and convenient, which is easy to operate to test the aim set in the prediction.

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