

Simple Method of Related Sensitivity Range To Predict the Thermodynamic Equilibrium Morphology of a Core–Shell Latex Particle

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ABSTRACT: The equilibrium morphologies of different core–shell latices are predicted, and a related sensitivity analysis is given for the predictions. This article proposes a related sensitivity range for estimating the accuracy of predictions, made with the simple method, of the thermodynamically preferred morphology of a core–shell latex particle in two-stage seeded emulsion polymerization. The related sensitivity range of the predictions is defined and calculated, and the results show that different core–shell

lattices have different sensitivity ranges. The wider the sensitivity range is, the more reliable the prediction is of the morphology of the core–shell latex. The simple method of related sensitivity range has been verified in the literature and with experiments. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3144–3152, 2004

Key words: core-shell polymers; morphology; emulsion polymerization; thermodynamics

INTRODUCTION

The morphology of composite latex particles is a very complicated topic in two-stage seeded emulsion polymerization. A composite latex can have a thermodynamic equilibrium morphology or a nonequilibrium morphology, which can develop into an equilibrium morphology with time. Torza and Mason¹ proposed the sprawling coefficient method 30 years ago to predict the thermodynamically preferred morphology of composite latices, and Sundberg et al.² proposed a theory in which the thermodynamically preferred morphology is the one with a minimum interfacial free energy change in four possible equilibrium morphologies (core–shell, inverted core–shell, individual particle, and hemisphere). Sundberg et al.² and Chen et al.^{3–6} designed many strict experiments to validate the theory. To make the theory easier, Gonzalez-Ortiz and Asua⁷ recently suggested that synthetic parameters be used to predict the thermodynamic equilibrium morphology of composite latices.

The theory proposed by Sundberg et al.² is very useful in research on the equilibrium morphology of core–shell latices. One of the further developments of the theory is the prediction of the equilibrium morphology of the core–shell latices before the related experiments. On the basis of the product function and

the knowledge of the core–shell morphology, we can predict and design the core–shell equilibrium morphology and the monomer composition with the theory. The difference between the method used to predict and design the equilibrium morphology of the core–shell latex before the related experiments and the method used to judge and validate the theory for the related equilibrium morphology is as follows. The method and the related experiments used to judge and validate the theory are very strict and complicated. However, the method used to predict and design the equilibrium morphology of the core–shell latex before the related experiments should be convenient.

In fact, more information is needed for the prediction of the equilibrium morphology of a core–shell latex in addition to the theory. There are two kinds of methods used to predict the equilibrium morphology. One is based on the theory, but some related experiments should be added to obtain some related parameters. This method of predicting the related morphology is very complicated and difficult; it is called the strict method of prediction. The other is also based on the theory, and some related calculations are necessary to obtain some related parameters. Because no other supplementary experiments are necessary, this method is easier, and it is called the simple method of prediction.

If the strict method of prediction, in which some related experiments to obtain some related parameters are added, is more complicated and difficult than the related experiment for the equilibrium morphology of the core–shell latex, as far as actual practice is concerned, the strict method of prediction is less valuable,

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and it is better to perform the related experiment for the equilibrium morphology of the core-shell latex without the prediction.

Before the related experiments, the prediction of the equilibrium morphology of the core-shell latex is useful. However, the prediction may be right or wrong and more or less accurate, regardless of which method of prediction is used. Therefore, the sensitivity range of the prediction should be given at the same time with the prediction. Then, the prediction results for the equilibrium morphology should be judged by the following experiments for the equilibrium morphology of the core-shell latex.

On the basis of Sundberg et al.'s² theory, this article reports the prediction method and related sensitivity range of the prediction of the equilibrium morphology of the core-shell latex by a calculation method used to obtain the related parameters. The equilibrium morphology of different core-shell latices is predicted with the simple method proposed by Huo and coworkers,^{8,9} and a proposed related sensitivity range of prediction is given at the same time.

Recently, Huo and coworkers^{8,9} proposed the simple calculation method to obtain the related parameters to predict the equilibrium morphology of a poly(butyl acrylate) (PBA)/poly(styrene-*co*-methyl methacrylate) core-shell latex with Sundberg et al.'s² theory. Sun and coworkers^{10,11} used and developed a method of predicting the morphology of a composite latex of poly(vinyl acetate) (PVAc) and PBA, in which the basic data comes from the related literature. The results are good, and the prediction method is easier than the others, especially when the thermodynamically preferred morphology can be predicted before the experiments. This article develops the method of predicting many systems of core-shell latices and examines the possibility of this method being used in a more popular way. However, the methods proposed by Huo and coworkers^{8,9} and Sun and coworkers^{10,11} simplify the calculations of the related parameters in actual practice, but the accuracy of the prediction is partly sacrificed. Therefore, this article analyzes the accuracy of the prediction, and the related sensitivity range of the prediction is supplemented.

SIMPLE METHOD OF PREDICTING THE THERMODYNAMICALLY PREFERRED MORPHOLOGY

Based on Sundberg et al.'s² theory, the important factor in predicting the equilibrium morphology of composite latex particle is that the three kinds of interfacial tension (a polymer of the seed and water, a new polymer and water, and a polymer of the seed and new polymer) must be known before the prediction. However, the related three interfacial tensions are very difficult to obtain under the reaction conditions. Chen et al.,³⁻⁶ Omi et al.,¹² Catherine et al.,¹³ and Kan et al.¹⁴ researched the morphology of composite latices in extensive experimental programs or theoretical pathways, and the equilibrium morphology was predicted with the method proposed by Sundberg et al.² In the studies, the three interfacial tensions were obtained by experiments or with the method proposed by Broseta et al.¹⁵ This method for obtaining the three interfacial tensions is very complicated and difficult and is named the strict method of prediction. To obtain the three interfacial tensions in a simple way, Huo and coworkers^{8,9} used the simple calculation method to get the three interfacial tensions to predict the equilibrium morphology of a composite latex; this is named the simple method of prediction. The limited conditions in the simple calculation method are as follows:

1. The surface tension (γ) of water (with an emulsifier, if present) is taken into account and can be determined by experimentation or from the literature.
2. The same initiator in two stages is adopted, and so the effects of the residual segment of the initiator on the polymers are neglected.
3. If only a little monomer exists, the effects of the monomer are not taken into account.

Under these conditions, the three interfacial tensions can be calculated by the harmonic mean method, and then the equilibrium morphology of the composite latex can be predicted with the method proposed by Sundberg et al.,² which is introduced later.

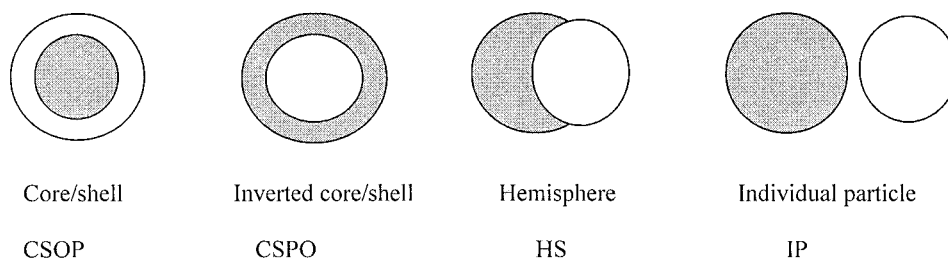


Figure 1 Four kinds of possible equilibrium morphologies of core-shell latices.



Figure 2 Related processing method of hemispheres.

The four kinds of possible equilibrium morphologies of core-shell lattices and their related calculation methods are as follows. In Figure 1, the dark area is the seed polymer, and the white area is the second-stage polymer.

The total interfacial free energy change (ΔG) for all the different types of possible equilibrium morphologies can be expressed as follows:

$$\Delta G = \sum_i (\sigma_{ij}A_{ij}) - \sigma_{1w}A_0 \quad (1)$$

where σ_{ij} is the interfacial tension of the i th and j th interfaces and A_{ij} is the corresponding interfacial area of the i th and j th interfaces. σ_{1w} is the interfacial tension of seed polymer phase 1 suspended in the water phase (with an emulsifier, if present), and A_0 is its interfacial area. Therefore, the reduced interfacial free energy change per unit of surface area of the original polymer 1 particle ($\Delta\gamma$) is obtained by the division of the expression for ΔG by A_0 :

$$\Delta\gamma = \Delta G/A_0 = \sum_i (\sigma_{ij}A_{ij})/A_0 - \sigma_{1w} \quad (2)$$

It is also advantageous to work in terms of the volume fraction (ϕ_p) of polymer 2 in the final particle:

$$\phi_p = V_p/(V_p + V_0) \quad (3)$$

where V_p and V_0 are the volumes of polymer 2 and polymer 1, respectively.

The equations for $\Delta\gamma$ for each case are as follows. For the core-shell (CSOP),

$$(\Delta\gamma)_{CSOP} = \sigma_{12} + \sigma_{2w}(1 - \phi_p)^{-2/3} - \sigma_{1w} \quad (4)$$

For the inverted core-shell (CSPO),

$$(\Delta\gamma)_{CSPO} = \sigma_{1w}[(1 - \phi_p)^{-2/3} - 1] + \sigma_{12}[(\phi_p/(1 - \phi_p))^{2/3}] \quad (5)$$

For individual particles (IP),

$$(\Delta\gamma)_{IP} = \sigma_{2w}[\phi_p/(1 - \phi_p)]^{2/3} \quad (6)$$

The case for hemispherical morphology is more complicated in a geometrical sense, and an approximate analysis is useful at this point. Figure 2 presents this approximation and defines the new parameters h and R , which are related to the volume fraction of polymer 2. The related processing method of hemispheres (HS) is as follows:

$$(\Delta\gamma)_{HS} = (1 - \phi_p)^{-2/3}\{\sigma_{2w}(h/2R) + \sigma_{1w}[1 - (h/2R) - (1 - \phi_p)^{2/3}] + \sigma_{12}(h/2R)[1 - h/2R]\} \quad (7)$$

The supplemented equation is

$$\phi_p = 3(h/2R)^2 - 2(h/2R)^3 \quad (8)$$

Equations (7) and (8) are calculated together to obtain the value of $(\Delta\gamma)_{HS}$. Except for the explanations of the aforementioned symbols, in eqs. (1)–(8), σ_{2w} is the interfacial tension between the new polymer and water (with an emulsifier, if present), and σ_{12} is the interfacial tension between the new polymer and seed polymer. The equilibrium morphology of a core-shell latex is the one that corresponds to the minimum value of $\Delta\gamma$.

Equation (7) is a simplified formula used to calculate $(\Delta\gamma)_{HS}$. Chen et al.⁵ presented more rigid expressions to calculate $(\Delta\gamma)_{HS}$. They introduced two angle parameters: the angles between the line that connects the two centers of the hemispheres and the line that connects the centers and the three-phase point. Naturally, the calculation is very tedious in comparison with eq. (7). For the hemisphere particle, θ is greater than 0° and less than 180° . When θ is 0° , there is no three-phase point, and the particle is individual; when θ is 180° , the particle is inverted core-shell. When θ is 90° , the hemisphere particle can be approximately determined (Fig. 2); eq. (7) can be used to calculate $(\Delta\gamma)_{HS}$. This simplified model is a lot easier.

TABLE I
Thermodynamic Data for H₂O, PVAc, PBA, PMMA, and PSt

	H ₂ O	PVAc	PBA	PMMA	PSt
γ (mN/m, 20°C)	36.2	36.5	33.7	41.1	40.7
χ^p	0.696	0.329	0.098	0.281	0.168
$-d\gamma/dt$ (mN m ⁻¹ /°C)	0.228	0.066	0.07	0.067	0.07

TABLE II
Prediction of the Thermodynamic Equilibrium Morphology
of PVAc/PBA and PVAc/PSt

	PVAc/PBA = 1 : 1	PVAc/PSt = 1 : 1
σ_{1w} (mN/m)	8.6	8.57
σ_{2w} (mN/m)	22.0	19.5
σ_{12} (mN/m)	5.1	2.67
$\Delta\gamma$ (mN/m; core-shell)	31.4	25.1
$\Delta\gamma$ (mN/m; inverted core-shell)	10.1	7.7
$\Delta\gamma$ (mN/m; individual particles)	22.0	19.5
$\Delta\gamma$ (mN/m; hemisphere)	17.7	14.8
Prediction by Sundberg	Inverted coreshell	Inverted core-shell
Experiment	Inverted core-shell ^{10,11,19-22}	Inverted core-shell ^{7,23,24}

With eqs. (1)–(8), the interfacial tensions σ_{ij} (σ_{1w} , σ_{2w} , and σ_{12}) can be calculated between the i th and j th interfaces by the harmonic mean equation:

$$\sigma_{ij} = \gamma_i + \gamma_j - \frac{4\gamma_i^d\gamma_j^d}{\gamma_i^d + \gamma_j^d} - \frac{4\gamma_i^p\gamma_j^p}{\gamma_i^p + \gamma_j^p} \quad (9)$$

where γ^d and γ^p are the dispersive and polar components of the surface tension, respectively. The related three kinds of interfacial tensions σ_{ij} (σ_{1w} , σ_{2w} , and σ_{12}) can be calculated from γ and γ^p of the i th and j th interfaces with eq. (9).

At the end of the reaction in the second-stage seeded emulsion polymerization, the amount of the residual monomer is small, and the simple calculation method for obtaining the three interfacial tensions is reasonable when only the equilibrium morphology of the core-shell is taken into account. The literature¹⁴ also reports the use of the harmonic mean equation to estimate the interfacial tension between the seed polymer and second polymer in the two-stage seeded emulsion polymerization. However, a different emulsifier and a different initiator can have great effects on the interfacial tension, so it is a rough method to presume that the effects from the same initiator in the two-stage polymerization counteract. In the same way, it is also a rough method to assume that the γ

value of water (with an emulsifier, if present) is not changed in the reaction. Although it is a rough method to estimate the three interfacial tensions in two-stage seeded emulsion polymerization under the three limited conditions, the prediction of the equilibrium morphology of a core-shell latex is easier than the others. The method of prediction can be easily tested to judge its value through a comparison of the results of the prediction with the results from the experiments of the equilibrium morphology of the core-shell latex, as shown later. The reliability of the prediction is different under the three limited conditions, and the sensitivity range of the prediction should be discussed and supplemented. The related comparisons are as follows.

First we examine the equilibrium morphology of the composite latices of PVAc and PBA, PVAc and polystyrene (PSt), PSt and poly(methyl methacrylate) (PMMA), and PBA and PSt, which have been investigated in the literature. In the PVAc/PBA composite latex, PVAc is the seed and PBA is the second-stage polymer. Similarly, in the other systems (PVAc/PSt, PSt/PMMA, and PBA/PSt), the first polymers are the seeds and the second polymers are the second-stage polymers.

To avoid the deviation caused by the basic thermodynamic data in different publications, we have taken

TABLE III
Prediction of the Thermodynamic Equilibrium Morphology of PSt/PMMA and PBA/PSt

	PSt/PMMA = 1 : 1	PBA/PSt = 1 : 1
σ_{1w} (mN/m)	19.5	22.01
σ_{2w} (mN/m)	12.2	19.53
σ_{12} (mN/m)	1.4	1.39
$\Delta\gamma$ (mN/m; core-shell)	1.2	10.39
$\Delta\gamma$ (mN/m; inverted core-shell)	12.8	14.32
$\Delta\gamma$ (mN/m; individual particles)	12.2	19.53
$\Delta\gamma$ (mN/m; hemisphere)	6.2	11.51
Prediction by Sundberg	Core-shell	Core-shell
Experiment	Core-shell, inverted core-shell hemisphere ^{3-6,25,26}	Core-shell, inverted core-shell hemisphere ^{8,9,27,28}

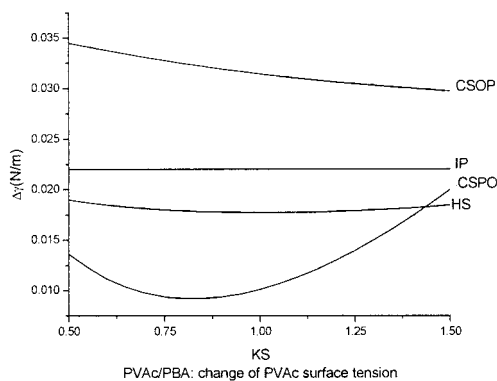


Figure 3 Changes ($\pm 50\%$) in γ of PVAc.

the basic thermodynamic data from only one source,¹⁶ from which Huo and coworkers,^{8,9} Sun and coworkers,^{10,11} Omi et al.,¹² Catherine et al.,¹³ Kan et al.,¹⁴ and Gonzalez-Ortiz and Asua^{7,17,18} took the basic thermodynamic data, and in which the basic thermodynamic data came from the melted or liquid polymer. The data are listed in Table I; χ^p is the polarity, and $-d\gamma/dt$ is the surface tension coefficient changing with the temperature. $\gamma = 36.20$ was determined by the experiments; the sodium dodecyl sulfate, an emulsifier, was applied at a concentration of 1% (w/w). The other values were obtained from the literature.¹⁶ The results of the predictions and the experiments reported in the literature are listed in Tables II and III. The weight ratios of the seed polymer and new polymer were 1 : 1.

Tables II and III show that the predictions of the equilibrium morphology of PVAc/PBA and PVAc/PSt agree with the experiments, but the predictions about PSt/PMMA and PBA/PSt are different from the experiments. We further examine why the predictions for different composite latex particles have different accuracies with the simple method,^{8,9} and we propose a related sensitivity range to judge the accuracy of the predictions.

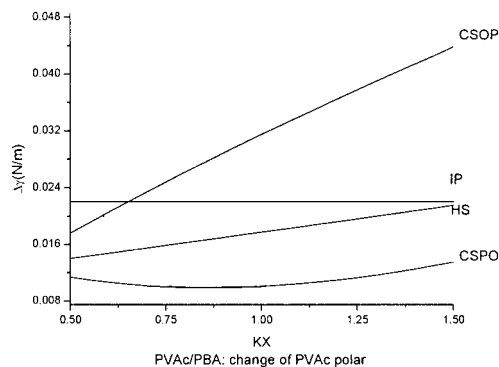


Figure 4 Changes ($\pm 50\%$) in χ^p of PVAc.

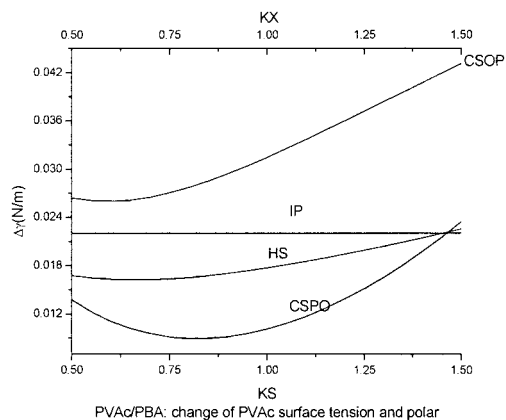


Figure 5 Changes ($\pm 50\%$) in γ and χ^p of PVAc. The directions of the changes are the same.

RELATED SENSITIVITY RANGE OF THE PREDICTION

Under real reaction conditions, the three interfacial tensions can be the same as or different from the ones calculated with eq. (9) with the data in Table I; if they are different, the difference between the calculation and experiment can exert an effect on the prediction. However, the reliability of the prediction is different for different composite lattices, and so the accuracy of the prediction should be investigated. In other words, some systems of the possible equilibrium morphology of a core-shell latex are sensitive to the three interfacial tensions, and others are not. We can use the method to predict the possible equilibrium morphology of a core-shell latex before the related experiment, when the possible equilibrium morphology is not sensitive to the three interfacial tensions. However, the method could be a failure in predicting the possible equilibrium morphology of a core-shell latex before the related experiment, when the possible equilibrium morphology is sensitive to the three interfacial ten-

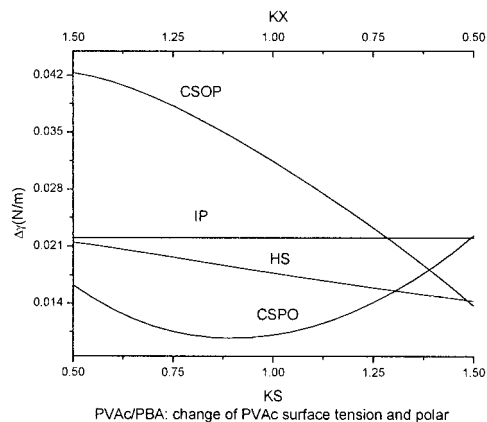


Figure 6 Changes ($\pm 50\%$) in γ and χ^p of PVAc. The directions of the changes are the opposite.

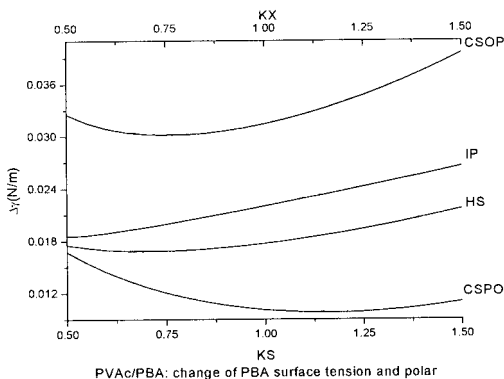


Figure 7 Changes ($\pm 50\%$) in γ and χ^p of PBA. The directions of the changes are the same

sions. The most important thing is to judge the sensitivity, which involves the relationship between the possible equilibrium morphology of a core-shell latex and the three interfacial tensions.

Based on eq. (9), γ and γ^p can have important effects on the three interfacial tensions. The nature of the polymers, emulsifier, and initiator can influence γ and γ^p , so possible changes in γ and γ^p can reveal the nature of the polymers, emulsifier, and initiator and have important effects on the three interfacial tensions and, therefore, on the possible equilibrium morphology. We discuss the problem of how changing the range of γ and γ^p influences the possible equilibrium morphology. Based on the basic thermodynamic data in Table I, γ and χ^p (γ^p/γ) are related to the nature of water and the polymer, but the effects of the emulsifier and initiator are not taken into account. We use KS and KX to represent the possible changing ranges of γ and χ^p of the water and polymer with the effects of the emulsifier and initiator; KS is the percentage of change of γ , and KX is the percentage of change of χ^p . KS = 1 and KX = 1 mean γ and χ^p are not changed.

Therefore, we use the changing ranges of KS and KX to represent the equilibrium morphology of a core-

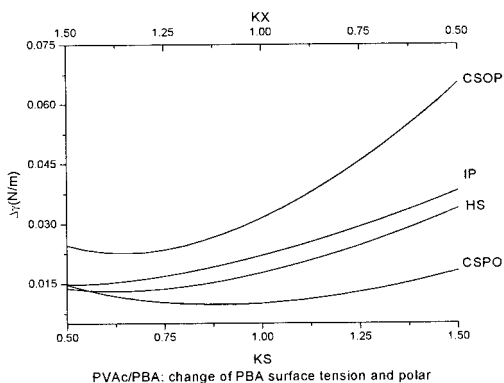


Figure 8 Changes ($\pm 50\%$) in γ and χ^p of PBA. The directions of the changes are the opposite.

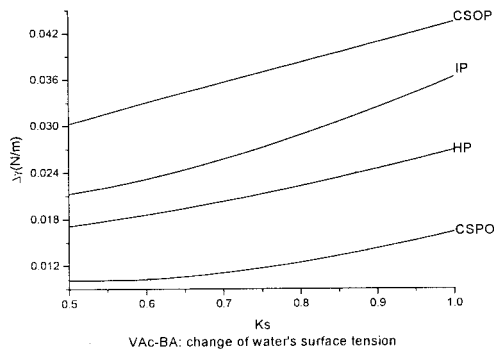


Figure 9 Changes (-50%) in γ of water.

shell latex and how it is related to the effects of the emulsifier and initiator. When the core-shell equilibrium morphology is unchanged in the more greatly changing ranges of KS and KX, we can decide that the equilibrium morphology is not sensitive to the effects of the emulsifier and initiator. When the equilibrium morphology is unchanged in the less changing ranges of KS and KX, we can decide that the equilibrium morphology is sensitive to the effects of the emulsifier and initiator. The changing ranges of KS and KX, in which the equilibrium morphology of a core-shell latex is kept unchangeable, represent the sensitivity range for the effects of the emulsifier and initiator. The sensitivity range is seriously related to the changing ranges of KS and KX. Therefore, we can use the calculation method to obtain the sensitivity range, which is introduced as follows:

1. An emulsifier causes the reduction of γ and χ^p of water, and the extent is -50% from pure water, which has $\gamma = 72 \text{ mN m}^{-1}$ (20°C) and $\chi^p = 0.696$.
2. An initiator can change γ and χ^p of polymers, and the extent is $\pm 50\%$ from the data in Table I. The direction of the changes in γ and χ^p of polymers is taken into account.
3. The three interfacial tensions are calculated with the aforementioned harmonic mean equation,

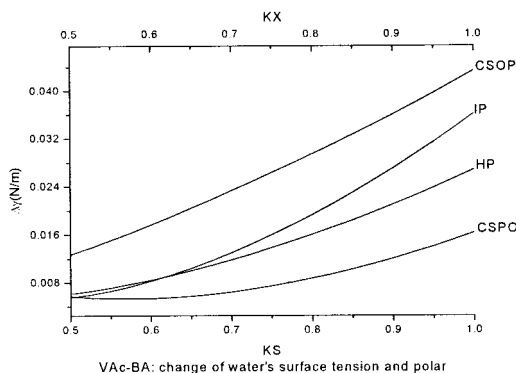


Figure 10 Changes (-50%) in γ and χ^p of water.

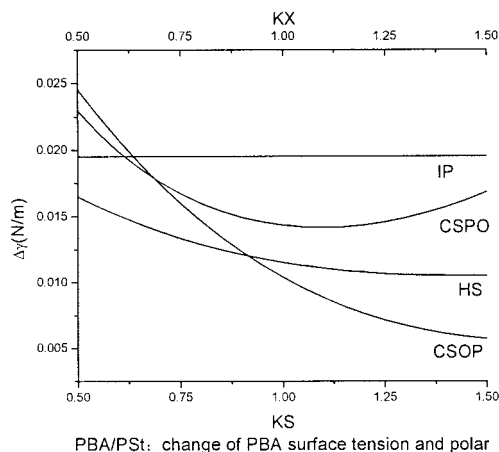


Figure 11 Changes ($\pm 50\%$) in γ and χ^p of PBA. The directions of the changes are the same.

and the interfacial free energy change curves ($\Delta\gamma$), related to the four possible equilibrium morphologies, are calculated with eqs. (1)–(8). The minimum interfacial free energy change curve crosslink range can be obtained from the charts.

- Under real reaction conditions, many factors can affect the equilibrium morphology of a composite latex, and so the sensitivity analysis should take the worst conditions into account. The sensitivity range is defined as the minimum range in the entire minimum interfacial free energy change curve crosslink range.

In this article, the initiator can change γ and χ^p of polymers, and the range is $\pm 50\%$ from the data in Table I. According to the definition of the sensitivity range in this article, in the $\pm 50\%$ changing range of KS and KX, the equilibrium morphology of a core-shell latex can be changed, and the sensitivity range is less than -50 to 50% . In fact, the initiator can seriously change γ and χ^p of a polymer, but the more greatly changing range of KS and KX does not influence the sensitivity range in the definition in this article. The influence of the emulsifier is the same. The sensitivity range of the prediction is defined and calculated in the simple way, and it can be used in a comparison of the effects of the emulsifier and initiator on the equilibrium morphologies of different core-shell latices. Therefore, we can more easily judge that the equilibrium morphologies of core-shell latices of some systems are more sensitive or less sensitive to the three interfacial tensions.

As an example, a sensitivity analysis of the prediction of the equilibrium morphology for PVAc/PBA and PBA/PSt has been calculated, and Figures 3–14 present the effects on the minimum interfacial free energy change curve crosslink range, which come

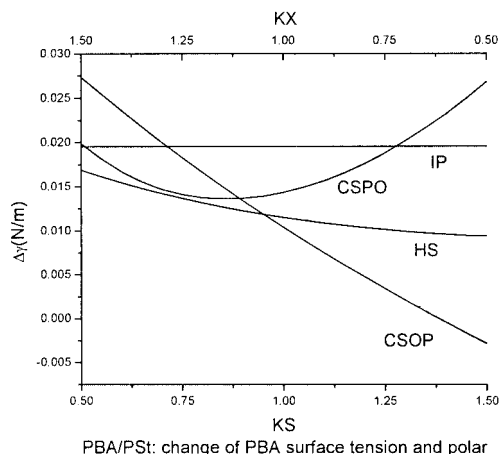


Figure 12 Changes ($\pm 50\%$) in γ and χ^p of PBA. The directions of the changes are the opposite.

from the changes in γ and χ^p in eqs. (1)–(4). In Figures 3–14, $\Delta\gamma$ is related to the four kinds of possible thermodynamic equilibrium morphologies, which were determined by Sundberg et al.² When KS and KX change in the range proposed in this article, the three interfacial tensions can be calculated with eq. (9), $\Delta\gamma$ -KS and $\Delta\gamma$ -KX curves can be obtained, and the minimum interfacial free energy change curve crosslink range can be found. Then, the sensitivity range is defined as the minimum range in the entire minimum interfacial free energy change curve crosslink range. The sensitivity analysis of the prediction of the equilibrium morphology for PVAc/PBA is as follows.

Effects of the initiator

The ranges of γ and χ^p of polymers of PVAc and PBA change $\pm 50\%$ from the basic data in Table I, and the

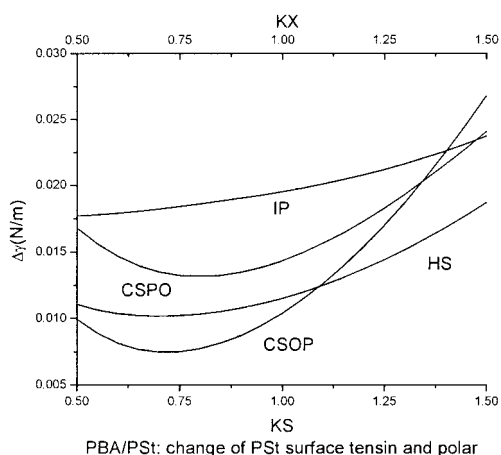


Figure 13 Changes ($\pm 50\%$) in γ and χ^p of PSt. The directions of the changes are the same.

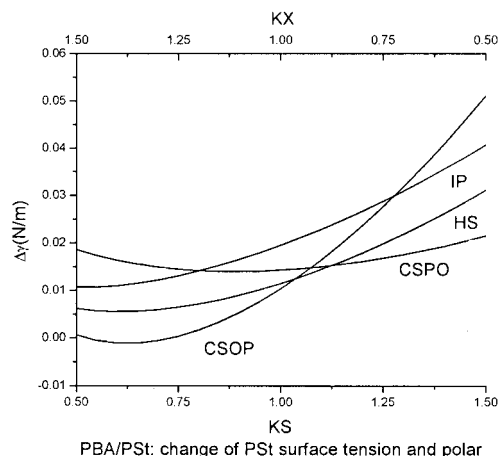


Figure 14 Changes ($\pm 50\%$) in γ and χ^p of PSt. The directions of the changes are the opposite.

others remain unchanged. The four kinds of possible equilibrium morphology interfacial free energy change curves are as follows.

In Figures 3–6, when γ and χ^p of a polymer of PVAc are changing together, the equilibrium morphology is more easily changed than when γ or χ^p of a polymer of PVAc is changing. Therefore, we only consider γ and χ^p of a polymer of PBA changing together.

Figures 3–8 show that the equilibrium morphology of a core-shell latex can be changed when KS and KX are changing beyond the crosslink range.

Effects of the emulsifier

The range of γ and χ^p of water is -50% from the basic data of pure water; the others are the same as those in Table I.

The results show that although an emulsifier can have an effect on $\Delta\gamma$, the equilibrium morphology is unchanged.

On the basis of the definition of the sensitivity range in this article, the sensitivity range of a PVAc/PBA composite latex is -45 to $+30\%$, which can be easily obtained from Figures 6 and 8. The results show that when γ and χ^p of a polymer are changing beyond -45 to $+30\%$ around $KS = 1$ and/or $KX = 1$, the equilibrium morphology of the composite latex can be

changed. Inside the range of -45 to $+30\%$, the equilibrium morphology is inverted core-shell.

For a PBA/PSt composite latex, the effect of the emulsifier on the equilibrium morphology is also small, and the effect of the initiator on the equilibrium morphology is calculated in Figures 11–14.

On the basis of the definition of the sensitivity range in this article, the sensitivity range of a PBA/PSt composite latex is -4 to 10% , which can be easily obtained from Figures 12 and 14.

In the same way, the sensitivity ranges of core-shell latices for different systems are listed in Table IV; the weight ratio of the seed polymer to the new polymer is 1 : 1.

According to Table IV, for the some systems, such as PVAc/PBA and PVAc/PSt, the sensitivity range is -45 to 30% . We can call them no-sensitivity systems: the equilibrium morphology is not easily changed, and the prediction agrees with the experiment. The same equilibrium morphologies are reported in the literature for PVAc/PBA^{10,11,19–22} and PVAc/PSt.^{7,23,24} For the other systems, such as PSt/PMMA, PBA/PMMA, and PBA/PSt, the sensitivity range is less than -20 to 15% . We can call these sensitivity systems: the equilibrium morphology of the core-shell latex is sensitive to the experimental conditions, and the prediction does not agree with the experiment. Different equilibrium morphologies have been reported in the literature for PSt/PMMA,^{3–6,25,26} PBA/PSt,^{8,9,27,28} and PBA/PMMA.^{29,30} Whether they are sensitivity or no-sensitivity systems, the equilibrium morphologies can be predicted with the method proposed in this article. Perhaps the sensitivity range proposed in this article can be used as a method of prediction and design for the equilibrium morphology of a core-shell latex before the related experiments.

CONCLUSIONS

This article provides a related sensitivity analysis of the simple prediction method. The related sensitivity range of the prediction is defined and calculated in this article, and the results show that different systems of composite latices have different sensitivity ranges of the prediction. The sensitivity ranges of the prediction of the equilibrium morphology for PVAc/PBA

TABLE IV
Equilibrium Morphology Prediction and Sensitivity Range of Composite Latices

	Composite latex				
	PVAc/PBA	PVAc/PSt	PSt/PMMA	PBA/PMMA	PBA/PSt
Equilibrium Morphology	Inverted Core-shell	Inverted Core-shell	Core-shell	Core-shell	Core-shell
Sensitivity range	-45 to 30%	-45 to 30%	-20 to 15%	-10 to 15%	-4 to 10%

and PVAc/PSt are -45 to 30% , and the predictions agree with the experiments. However, the sensitivity ranges of the prediction of the equilibrium morphology for PSt/PMMA, PBA/PMMA, and PBA/PSt are less than -20 to 15% , and the predictions do not agree with the experiments. A comparison of the predictions and the experiments shows that the wider the sensitivity range is, the more reliable the prediction is. Therefore, the related sensitivity range can be helpful in the prediction of the equilibrium morphology of a composite latex before the experiment.

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