

# Determination of the Interfacial Mass Transfer Coefficient of Vinyl Acetate Monomer Diffusion into Poly(vinyl acetate) and Polystyrene Latex Particles Stabilized with Different Stabilization Mechanisms Using a Vapor Phase Addition Method

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## SYNOPSIS

A vapor phase monomer addition method was used to measure the monomer transfer rate into latex particles. The classical mathematical model for the diffusion process was used to calculate the overall mass transfer coefficients of monomer between the vapor and the water phases, and between the water and the polymer particle phases. At the initial stage of the monomer transfer into the glassy polystyrene latex particles at 60°C, the rate-determining step was the monomer transfer inside the polymer. As more monomer transferred into the latex particles and the glass transition temperature of the swollen latex particles decreased below the experimental temperature, the rate-determining step became the monomer transfer across the interfacial surfactant layer. This transition was not observed with poly(vinyl acetate) latex, which was rubbery at the experimental temperature. The diffusion coefficients calculated were in the order of  $10^{-13}$  to  $10^{-14}$  cm<sup>2</sup>/s. These low values correspond to molecular diffusion of small molecules through a solid or glassy membrane. This was attributed to the resistance of the adsorbed surfactant layer. The mass transfer rates into latex particles stabilized with ionic, nonionic surfactants, and a water-soluble polymer were compared. In the case of the ionic surfactant, sodium dodecyl sulfate, when a large amount of electrolyte was added, the mass transfer rate decreased compared to the electrolyte addition free case. This was attributed to the formation of a "condensed" layer of adsorbed surfactant. Adsorbed nonionic surfactant or water-soluble polymer showed larger resistance to monomer transport compared to the ionic surfactant layer. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Surfactants play several major roles in the emulsion polymerization reaction. Some of these roles include: (1) solubilizing of highly water-insoluble monomers; (2) reducing the interfacial tension between phases; (3) controlling the number of particles nucleated and, thus, the rate of polymerization; and (4) main-

taining colloidal stability during the particle growth stage of polymerization. In the latex system, most of the surfactant molecules are adsorbed at the particle/water interface, and only a small fraction is adsorbed at the air/water interface or remains in the bulk aqueous phase as solute surfactant.

Harkins, in his postulated mechanism of micellar nucleation in emulsion polymerization, considered that the major source of particle nucleation was the monomer-swollen surfactant micelles.<sup>1,2</sup> According to Harkins, radicals generated in the aqueous phase enter the monomer-swollen micelles and initiate polymerization to form monomer-swollen polymer

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particle nuclei. The nuclei grow by polymerization of monomer supplied to the monomer-swollen particles by diffusion from the monomer droplets through the aqueous phase. The surfactant molecules required to stabilize the growing particles are supplied from the micelles, which have not been entered by radicals. The particle nucleation stage ends with the disappearance of the micelles. According to this hypothesis, the major locus of polymerization is the monomer-swollen polymer particles.

Diffusional and interfacial phenomena in conventional emulsion polymerization reactions have been studied by Brooks.<sup>3,4</sup> Four possible resistances to monomer transport were considered: (1) transfer from monomer droplets to the aqueous phase, (2) transfer through the aqueous phase, (3) transfer through the interfacial surfactant layer surrounding the particles, and (4) transfer within the monomer-swollen polymer particles. Brooks concluded that the diffusional process in the aqueous phase would not affect the polymerization, and the main resistance was the resistance to the monomer diffusion at the interface between the monomer-swollen polymer particles and the aqueous phase.

Implicit evidence has been given by Netschey et al.<sup>5-7</sup> for the existence of mass transfer resistance at the latex particle interface with an adsorbed "condensed" monolayer of surfactants or an adsorbed water-soluble polymer. In their study, they showed that a poly(vinyl acetate) seed latex, when stabilized with a water-soluble polymer, poly(ethylene oxide-*b*-vinyl acetate), and an ionic surfactant, sodium palmityl sulfate, exhibited a reduced rate of polymerization, which was attributed to the interfacial resistance to radical entry because of the higher local viscosity in the surfactant layer.

Delgado et al.<sup>8</sup> analyzed the monomer transport during the course of a miniemulsion copolymerization. They applied a mathematical model of diffusional monomer transfer to the miniemulsion copolymerization of a vinyl acetate-butyl acrylate monomer mixture. They studied the interfacial mass transfer resistance due to the adsorbed surfactant layer, and noted that the polymerization rate became monomer transport-controlled when the value of the mass transfer coefficient at the interface between the miniemulsion droplets and the aqueous phase became lower than  $10^{-4}$  cm/s. The result was a decrease in the polymerization rate of the miniemulsion latex particles.

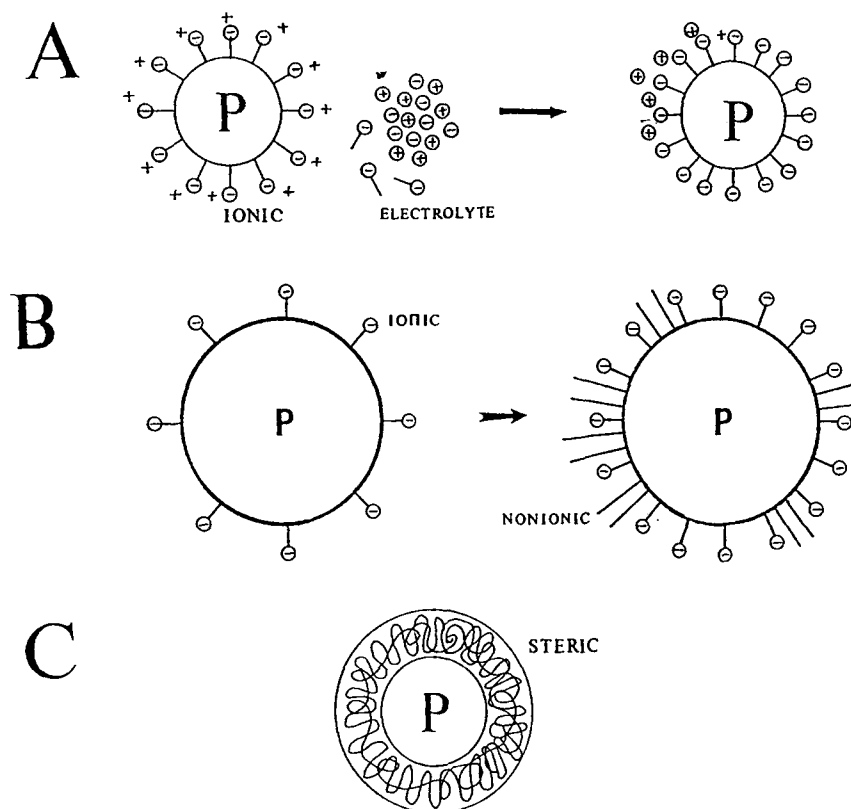
Rodriguez et al.<sup>9,10</sup> studied the interparticle monomer transport in the miniemulsion copolymerization of styrene-methyl methacrylate monomer mixture. They found that the mass transfer

coefficients of monomers across the surfactant layer of sodium dodecyl sulfate and hexadecane were in the range between  $1.0 \times 10^{-6}$  and  $3.0 \times 10^{-8}$  cm/s. They concluded that the mass transfer coefficients were not low enough for the rate of polymerization to be controlled by mass transfer.

Lohr<sup>11</sup> used a vapor pressure technique to measure the monomer transfer rate from the aqueous phase into the latex particles. He used an apparatus that was similar to that developed by Vanzo et al.<sup>12</sup> and Morton et al.<sup>13</sup> In this study, the pressure profile of a system of latex particles swollen with monomer was measured after the addition of a known amount of monomer. They concluded that there was no interfacial mass transfer resistance of monomer into the latex particles.

The hypothetical condensed surfactant layer can be explained conceptually by Figure 1. An ionic surfactant is composed of a hydrophobic "tail" and a hydrophilic "head." If the ionic strength of the aqueous phase increases, electrostatic repulsion between the ionic heads decreases, and more surfactant molecules are adsorbed on the particle surface.<sup>14</sup> Tonge found that the rate of polymerization of vinyl acetate (VAc) changes with the ionic strength of the aqueous phase.<sup>15</sup> Klein et al. investigated the threshold concentration of potassium sulfate added as electrolyte to a poly(vinyl acetate) (PVAc) latex and showed it to be  $2 \times 10^{-4} M$ .<sup>16</sup> Below the threshold concentration, the repulsive force between the ionic head groups dominates, and the surfactant layer is assumed to be in the gaseous state, but, above the threshold concentration, surfactant molecules condense on the surface because of the dominant van der Waals forces. In the mixed system of ionic and nonionic surfactants, the electrostatic repulsion between the neighboring ionic surfactant molecules is reduced because of the shielding effect of the nonionic surfactant, and the adsorption of the surfactant molecules increases accordingly. In the water-soluble polymeric surfactant system, the microscopic local viscosity in the thick steric barrier is higher than in the aqueous phase, which can cause the retardation of molecular transport. During the constant-rate period of conventional emulsion polymerization, or in seeded emulsion polymerization, monomer transfer from the aqueous phase through the condensed surfactant layer may become an important factor.

In the present study, the mass transfer rates will be measured for latex particles stabilized by ionic, nonionic, or water-soluble polymeric surface layers, and the mass transfer coefficients will be compared.



**Figure 1** Conceptual drawings of the condensed surfactant layer. (A) Ionic surfactant system with electrolyte; (B) mixed system of ionic and nonionic surfactant; (C) water-soluble polymeric surfactant system.

## EXPERIMENTAL

### Equipment and the Materials Used

The experimental apparatus, shown in Figure 2, consists of a glass chamber in which latex is swollen and a separate microburette from which monomer molecules transfer through the vapor phase.

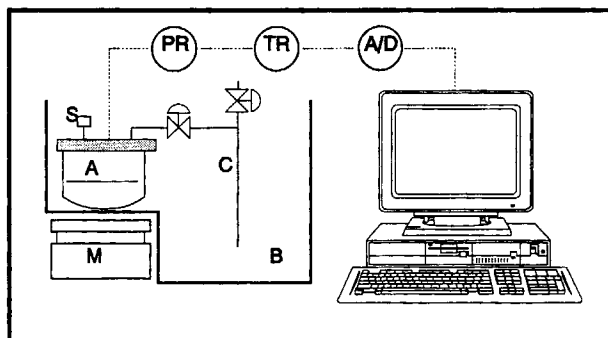
Pressure transducers (Omega Engineering Co., Type PX-425-015av, range = 0–15 psi) were used for reliable and accurate measurement of the pressures of the glass chamber and of the microburette. A thermistor (Omega Engineering, range = 0–100°C) was used to measure and control the temperature inside the glass chamber. Analog signals from the pressure transducers and thermistor were converted to digital signals by an analog-digital converter and computer. The volumetric transfer rate of monomer from the microburette was measured using a cathetometer (max. error range = 0.002 mL) at the same time the pressure was measured. The equipment was immersed in a thermostated bath maintained at a temperature of  $60 \pm 0.1^\circ\text{C}$ .

The monodisperse polystyrene latex (PS-160;  $D_w = 158$  nm, Morton Thiokol International Co.), stabilized with an ionic surfactant, sodium dodecyl sulfate (SLS), was cleaned using the serum replacement technique.<sup>21</sup>

The vapor phase addition method and the model polystyrene latex used in this study are more fully described in the previous article.<sup>17</sup> Monodisperse PVAc latex was prepared by emulsifier-free polymerization in the aqueous phase.<sup>18</sup> The weight-average diameter,  $D_w$ , was 600 nm, with a standard deviation of 29 nm. Sodium dodecyl sulfate, ionic surfactant, Igepal CO-660 (GAF), with 10 ethylene oxide units, was used as the nonionic surfactant, and PVP K-30 (polyvinyl pyrrolidone,  $M_w = 40,000$ , GAF) was used as the water-soluble polymeric stabilizer. The surfactants and the polymer were used without further purification.

### Mathematical Model for the Monomer Transport into the Latex System

A mathematical model was used to calculate the overall mass transfer coefficients of monomer be-



- A Glass Chamber  
 B Waterbath  
 C Microburet  
 S Monomer Injection  
 M Magnetic Stirrer  
 PR Pressure Transducer  
 TR Thermistor  
 A/D Analog-Digital Converter

**Figure 2** Experimental apparatus of the vapor addition method.

tween the vapor and the water phase, and between the water and the polymer particle phase. It was postulated, based on classical theory in an agitated system, that in the absence of a chemical reaction, the number of mol of a species transported per unit time from a given phase to an adjacent phase is proportional to the transfer area,  $A$ , and to the difference between the concentration of the material in the phase under consideration that which would be in equilibrium with the actual concentration in the adjacent phase,  $C_e$ , and its actual concentration,  $C$ , in the given phase. The transport equations for the monomer transport from the vapor phase to the aqueous phase and polymer phase can be expressed as follows:

#### Monomer Transport from the Vapor Phase to the Aqueous Phase.

$$(dN_{vw}/dt)^* = (dN_w/dt)^* \\ = K_{vw}^* A_w (C_{w,e} - C_w) \quad (1)$$

Where superscript \* represents the monomer transport experiment into the water-surfactant solution, which has the same amount of water and surfactant as those of the latex. The transport equations for monomer into the latex system can be also expressed as follows:

#### Monomer Transport from the Vapor Phase to the Aqueous Phase

$$(dN_w/dt) = (dN_{vw}/dt) - (dN_{wp}/dt) \\ = K_{vw} A_w (C_{w,e} - C_w) - K_{wp} A_p (C_{p,e} - C_p) \quad (2)$$

#### Monomer Transport from the Aqueous Phase into the Latex Particles

$$(dN_{wp}/dt) = (dN_p/dt) = K_{wp} A_p (C_{p,e} - C_p) \quad (3)$$

where  $dN_{vw}/dt$  and  $dN_{wp}/dt$  (mol/min) are the molar transfer rates of monomer from the vapor phase to the aqueous phase and from the aqueous phase to the polymer phase, respectively, and  $dN_w/dt$  and  $dN_p/dt$  are the accumulation rates of monomer in the aqueous and polymer phases. The subscript  $v$  refers to the vapor phase,  $w$  refers to the aqueous phase, and  $p$  refers to the polymer phase.  $K_{vw}$  and  $K_{wp}$  (cm/min) are the mass transfer coefficients of monomer per unit area between the vapor and the aqueous phases, and between the aqueous and the polymer phases, respectively.  $A_w$  and  $A_p$  are the total transfer areas between the vapor and the aqueous phases, and between the aqueous and polymer phases, respectively.  $A_p$  can be obtained from the particle size measurements, but  $A_w$  is difficult to measure because of the surface ripples due to agitation. From monomer transport experiments using the vapor phase addition method, we can obtain  $K_{vw} A_w$  and  $K_{wp} A_p$ , from which the overall mass transfer coefficient of monomer into the latex particle,  $K_{wp}$ , can be computed.

## RESULTS AND DISCUSSION

### Effect of Electrolyte Concentration in an Ionic Surfactant System

In the case of the ionic surfactant, the adsorption isotherm was shown to change with the electrolyte concentration in the aqueous phase.<sup>19</sup> A series of experiments with different amounts of potassium sulfate ( $K_2SO_4$ ) in the aqueous phase were performed to determine the ionic strength effect on the monomer transfer rate into the latex particles. Table I shows the experimental conditions and the computed values of  $K_{wp}$  from this study.

As is shown in Table I, the adsorption area of SLS changed from 101 to 87  $\text{\AA}^2$ /molecule when  $1 \times 10^{-4} M$  of  $K_2SO_4$  was added to the latex, which was stabilized with SLS. With the addition of a

**Table I Experimental Conditions for the Study of the Effect of the Ionic Strength of the Aqueous Phase on the VAc Transfer Rate into 160 nm PS Latex Particle**

Run No. <sup>a</sup>	K <sub>2</sub> SO <sub>4</sub> (M)	Adsorption (A <sup>2</sup> /Molecule Surfactant)	K <sub>wp</sub>
RS-120	None	101	6.6 × 10 <sup>-7</sup>
RS-121	1 × 10 <sup>-4</sup>	87	7.2 × 10 <sup>-7</sup>
RS-122	1 × 10 <sup>-3</sup>	24	5.6 × 10 <sup>-7</sup>

<sup>a</sup> PS160 5.26 wt %, D<sub>w</sub> = 158 nm, Water = 45 g, Polymer = 2.5 g.

larger amount of K<sub>2</sub>SO<sub>4</sub> (1 × 10<sup>-3</sup> M), the adsorption area changed dramatically to 24 A<sup>2</sup>/molecule. The molecular surface area determined by Ahmed at the maximum adsorption of SLS on 190 nm PS latex particles without any electrolyte was 43 A<sup>2</sup>/molecule.<sup>20</sup> The surfactant layer became "condensed" due to compact packing of the SLS molecules on the surface of the particles when large amounts of K<sub>2</sub>SO<sub>4</sub> was added to the aqueous phase. A comparison of particle size distributions before and after the additions of K<sub>2</sub>SO<sub>4</sub> showed no electrolyte-induced coagulation. Figure 3 shows that K<sub>wp</sub> does not change much when the SLS surface area changes from 101 to 87 A<sup>2</sup>/molecule, due to electrolyte addition, RS-120 and RS-121. But when the surface becomes densely populated with SLS, (24 A<sup>2</sup>/molecule, RS-122), K<sub>wp</sub> decreased by 16%.

#### Effect of Nonionic and Water-Soluble Polymeric Stabilizers

To study the effect of the stabilization mechanism on the monomer transfer rate, polystyrene latexes that were stabilized by the electrostatic mechanism (ionic surfactant) or by the steric mechanism (nonionic surfactant or water soluble polymer) were prepared. After cleaning of the latexes with distilled deionized water using serum replacement technique,<sup>21</sup> a certain amount of surfactant was added and the mixture was allowed to stand for a day until equilibrium was reached. Vacuum filtration was used to separate the serum from the latex, and the surfactant concentration in the aqueous phase was determined. The concentration of Igepal CO-660 in the aqueous phase was measured by UV spectroscopy at the wavelength of 275 nm, and that of PVP K-30 [Poly(vinyl pyrrolidone), M<sub>w</sub> = 40,000] was measured with a refractometer.<sup>22</sup> All the experiments were performed at an agitator speed, 400–500 rpm, which assured the measurement of the interfacial mass transfer resistance.<sup>17</sup> Table II shows the ex-

perimental conditions used to see the effect of the stabilization mechanism on the monomer transfer rate into the latex particles. Figure 4 shows the total amount of VAc transferred into the latex system, while Figure 5 shows the VAc transfer rates into latexes with different types of surface layers. The amount of VAc transferred is higher in RS-81 (using an ionic surfactant, SLS) than for RS-88 (using a nonionic surfactant, Igepal CO-660) or RS-89 (using a water-soluble polymeric surfactant, PVP K-30). To compare the interfacial mass transfer resistance of the latex particles, K<sub>wp</sub> was calculated as was explained previously. Figure 6 shows that the overall mass transfer coefficient (K<sub>wp</sub>) of VAc into the PS latex particles with different surfactant layers. The K<sub>wp</sub> for run No. RS-81, which used an electrostatic stabilizer, SLS, is 1.26 to 1.30 times larger than the other systems that use the steric stabilizer, CO-660, or PVP K-30. In this study, we can see the difference in the mass transfer resistance of the interfacial surfactant layer surrounding the latex particle. Higher viscosity in the steric stabilizer seems to be a reason for the resistance to monomer transport.

#### Transition of Monomer Transfer Rate into the Latex Particles

There are several steps for monomer to be transferred from the separate microburette via the vapor phase, to the aqueous phase, and finally into the latex particles. The resistance of the monomer transfer from the microburette to the aqueous phase was shown to be smaller than that of the interfacial surfactant layer at the high agitator speeds that were used in the series of the monomer transport experiments.<sup>17</sup> The rate of pressure increase of the PS-160 system in which the model latex particles are swollen with VAc monomer transferred from the microburette shows the transition as is shown in Figure 7 (run No. RS-81). In the early stage of the monomer transport experiment, using the vapor

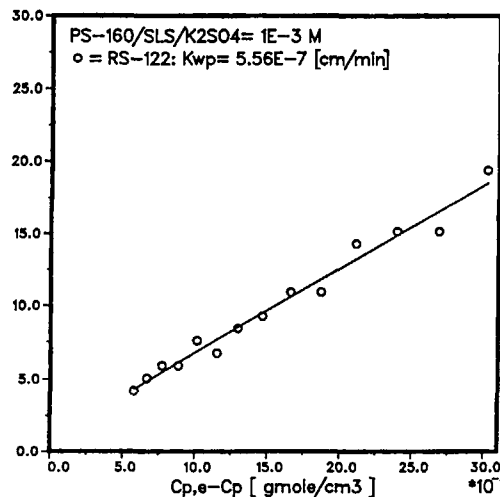
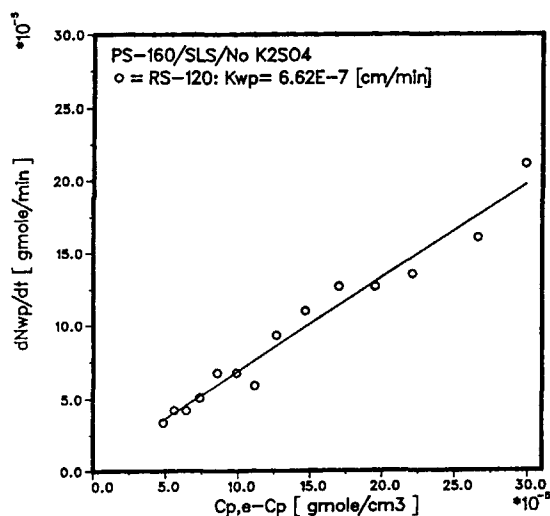
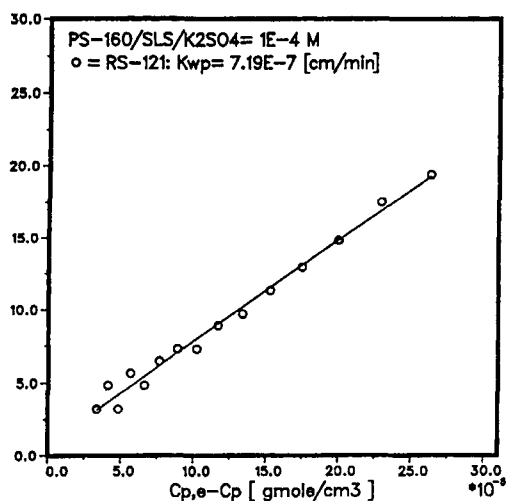


Figure 3 (continued)



**Figure 3** Overall mass transfer coefficient  $K_{wp}$  of VAc into the PS latex particles, which are stabilized with ionic surfactant, SLS, with different concentration of  $K_2SO_4$  in the aqueous phase: (1) RS-120: No  $K_2SO_4$ , extent of adsorption =  $101 \text{ \AA}^2/\text{molecule}$ ; (2) RS-121:  $K_2SO_4 = 1 \times 10^{-4} \text{ M}$ , Extent of adsorption =  $87 \text{ \AA}^2/\text{molecule}$ ; and (3) RS-122:  $K_2SO_4 = 1 \times 10^{-3} \text{ M}$ , Extent of adsorption =  $24 \text{ \AA}^2/\text{molecule}$  (see Table 1 for details).

phase addition method, monomer transfer occurs mainly into the water phase, and the amount of monomer inside the latex particles is less than 8%. With a small amount of VAc inside the particles, PS remains in the glassy state at  $60^\circ\text{C}$ . As the amount of monomer inside the particles increases, PS latex particles change from the glassy state to the rubbery state. Friis et al.<sup>23</sup> measured the glass transition of PS latex vs. the conversion of styrene monomer. According to their measurement, the PS

latex particles, which contain about 5–8 wt % of monomer, have a glass transition temperature of  $60^\circ\text{C}$ . Figure 8 shows the volume fraction of monomer in the latex particles and the corresponding glass transition temperature of the swollen PS latex particles according to time. The volume fraction of VAc vs. time data is from the experiments, and the  $T_g$  data is adapted from Friis et al. As is shown in this figure, swollen latex particles have a  $T_g$  of  $60^\circ\text{C}$  after around 10 min of the monomer transfer. PS latex particles remain in the glassy state up to that time and then change to the rubbery state because of the increased concentration of monomer inside the latex particles.

Figure 9 shows simulated values and experimental data for  $dN_{vw}/dt$ , the molar flow rates from the vapor to the aqueous phase,  $dN_w/dt$ , the accumulation rate of monomer in the aqueous phase, and  $dN_{wp}/dt$ , the molar flow rates from the aqueous to the polymer phase according to  $(C_{w,e} - C_w)$ , the driving force of the monomer transport from the vapor to the aqueous phase. Equations (1) and (2) are solved simultaneously using Euler's method. Initial values of  $C_w$  and  $C_p$  were obtained from the experiment at the time of 10 min. It was chosen in order to simulate the experimental data after the transition of the PS latex particles. Parameters obtained from the experiment RS-81 (PS-160 10 wt %, SLS, VAc monomer) were used in this case;  $K_{vw}A_w$  and  $K_{wp}A_p$  are 14.26 and  $1.36 \text{ cm}^3/\text{min}$ , respectively. In this figure, lines show the simulated values and the symbols (○) represent the actual experimental data. As was shown earlier, the experimental data obtained are in the region of the rubbery PS latex particles. The simulation was extended to the region of the glassy

**Table II** Experimental Conditions for the Study of the Effect of the Surfactant Stabilization Mechanism of the VAc Transfer Rate into 160 nm PS Latex Particles

Run No. <sup>a</sup>	Surfactant	Adsorption (Å <sup>2</sup> /Molecule Surfactant)	$K_{wp}$ (cm/min)
RS-81	SLS	109	$7.1 \times 10^{-7}$
RS-88	CO-660	72	$4.4 \times 10^{-7}$
RS-89	PVP K-30	660	$4.1 \times 10^{-7}$

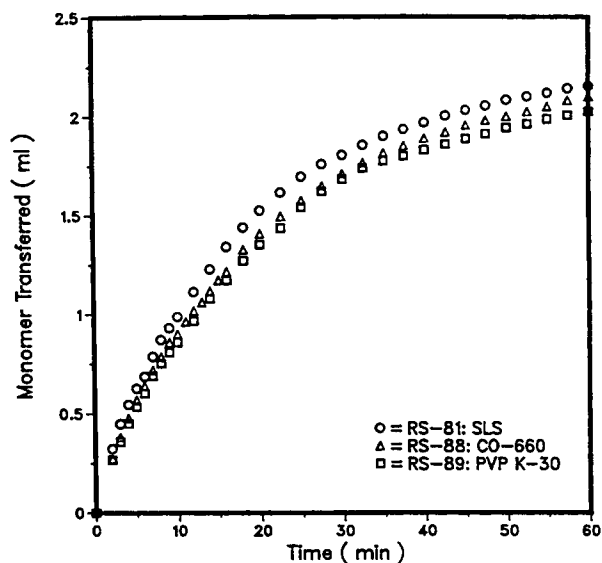
<sup>a</sup> PS160 10.0 wt %,  $D_w = 158$  nm, Water = 45 g, Polymer = 5.0 g.

PS latex particles, and no transition was found in the plot of  $dN_w/dt$  and  $dN_{wp}/dt$ .

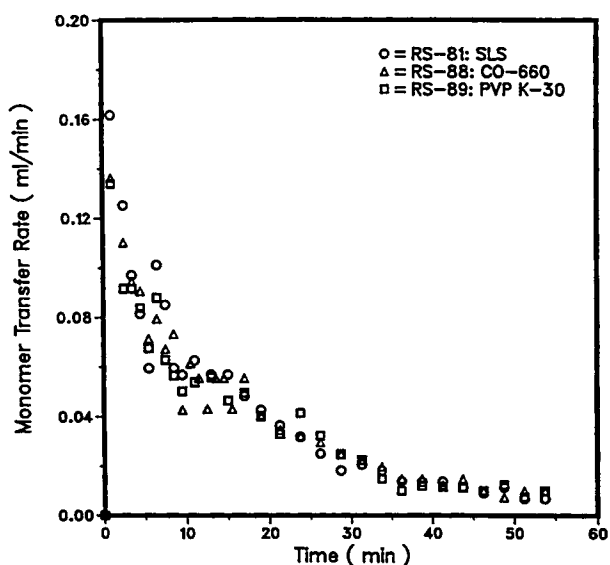
Figure 10 is similar to Figure 9, but in this plot, two different values of  $K_{wp}A_p$  were used. When PS latex particles are in the glassy state (initial time period of the experiments), the overall mass transfer coefficient inside the particles seems to be lower than that across the interfacial surfactant layer. In this region, an arbitrary value of the overall mass transfer coefficient,  $1.10 \text{ cm}^3/\text{min}$ , which is 80% of the overall mass transfer coefficient across the surfactant layer, was used for the simulation. As is clearly shown in this figure,  $dN_w/dt$ , the accumulation rate of monomer in the aqueous phase, and  $dN_{wp}/dt$ , the molar flow rates from the aqueous to the polymer phase

according to  $(C_{w,e} - C_w)$ , show definite transition between the two regions in which the two different values of the mass transfer coefficients were used. It must be pointed out that the simulated values represent the actual experimental data well, which means that the hypothesis of the transition in the mass transfer coefficients due to the transition of PS latex particles from the glassy to the rubbery phase is most likely valid.

The diffusion coefficients of small molecules in glassy materials are in the range of  $10^{-12}$  to  $10^{-14} \text{ cm}^2/\text{s}$ ,<sup>8,24,25</sup> and the diffusion coefficients of monomer or monomeric radicals in rubbery materials are in the range of  $10^{-6}$  to  $10^{-9} \text{ cm}^2/\text{s}$ .<sup>26-30</sup> The controlling step was already shown to be an interfacial resistance due to the adsorbed surfactant layer. If the



**Figure 4** Total amount of VAc transferred into the latex systems with different stabilization mechanisms. RS-81: electrostatic stabilization mechanism (ionic surfactant, SLS); RS-88: steric stabilization mechanism (nonionic surfactant, CO-660); and RS-89: steric stabilization mechanism (water-soluble polymeric surfactant, PVP K-30) (see Table 2 for details).



**Figure 5** VAc transfer rate into latexes with different stabilization mechanisms. RS-81: electrostatic stabilization mechanism (ionic surfactant, SLS); RS-88: steric stabilization mechanism (nonionic surfactant, CO-660); and RS-89: steric stabilization mechanism (water-soluble polymeric surfactant, PVP K-30) (see Table 2 for details).

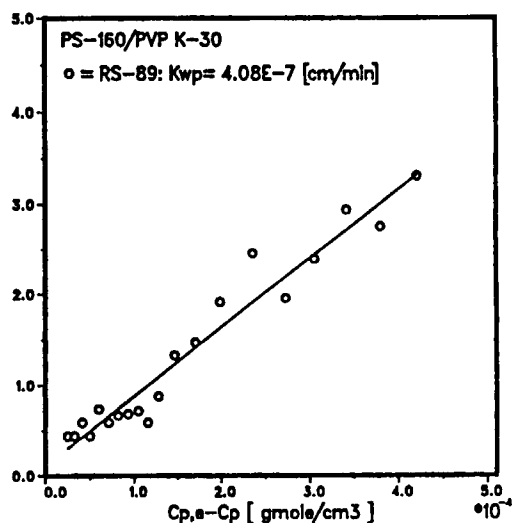
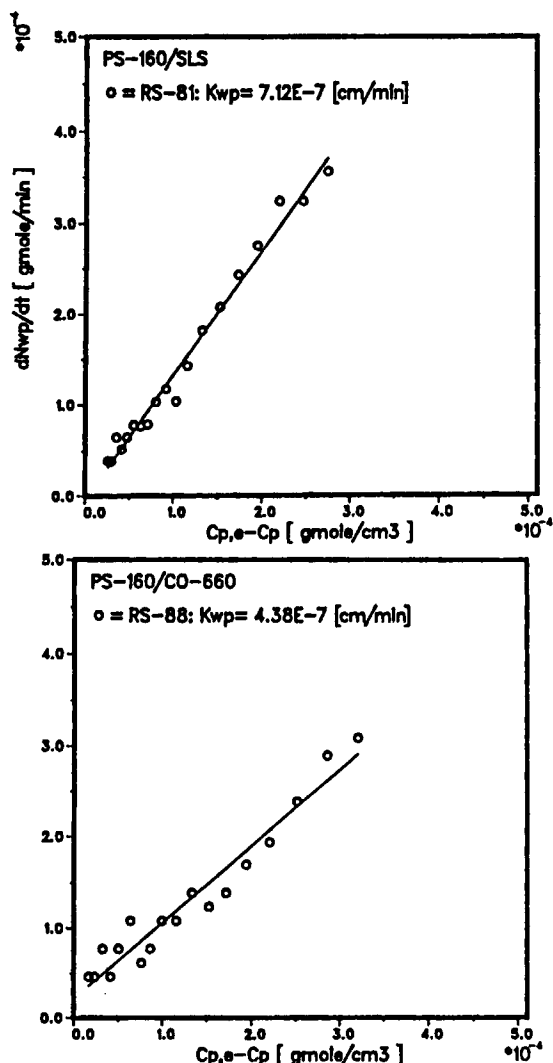


Figure 6 (continued)

Figure 6 Overall mass transfer coefficient  $K_{wp}$  of VAc into the PS latex particles with different stabilization mechanisms. (1) RS-81: electrostatic stabilization mechanism (ionic surfactant, SLS); (2) RS-88: steric stabilization mechanism (nonionic surfactant, CO-660); and (3) RS-89: steric stabilization mechanism (water-soluble polymeric surfactant, PVP K-30) (see Table 2 for details).

controlling step in the overall monomer transport process is not a resistance due to the interfacial surfactant layer, but a resistance of the latex particle itself, the ratio of the values of the mass transfer coefficients before and after the transition should be higher than  $10^3$ . This is apparent from the fact that the mass transfer coefficients can be directly related to the diffusion coefficients. In Figure 10, the actual experimental data is shown with a ratio of 0.8 for the mass transfer coefficients before and after the transition. This indicates that the molecular diffusion of the monomer through a tightly packed surfactant layer resembles the diffusion through a

solid or a glassy state membrane. Delgado et al.<sup>8</sup> and Rodriguez et al.<sup>10</sup> obtained similar results in case of miniemulsions, in which SLS and a cosurfactant (hexadecane or cetyl alcohol) were used. They postulated that the high interfacial resistance might be due to the high level of surfactant adsorbed onto the miniemulsion.

#### Monomer Transport into the PVAc Latex Particles

In the previous section, it was shown that the controlling step in the overall monomer transport pro-

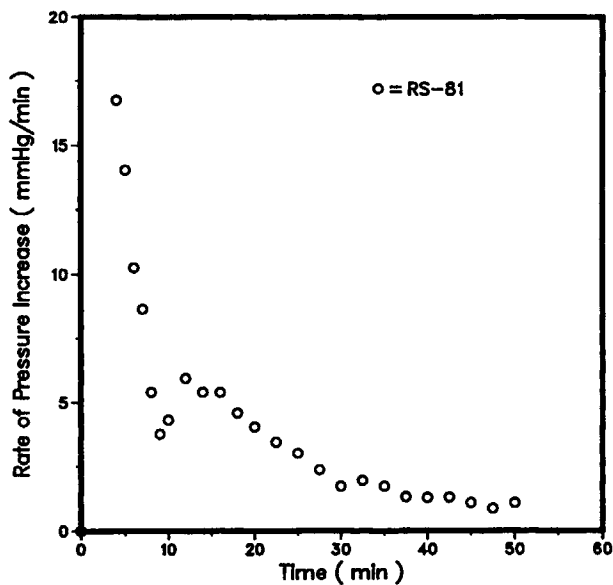
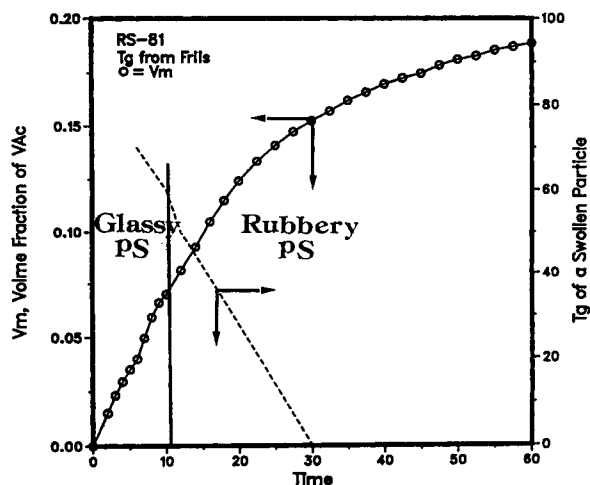


Figure 7 The rate of pressure increase of the system with the PS-160 latex particles swollen with the monomer transferred from the microburet as a function of time. Run No. = RS-81.



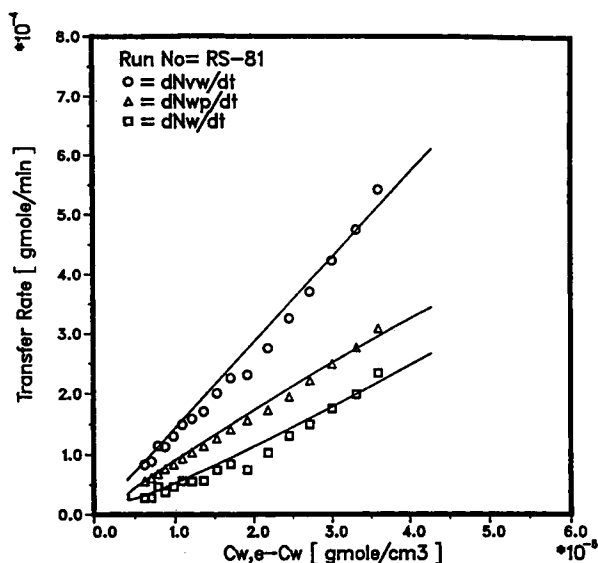


**Figure 8** Volume fraction of monomer inside the latex particle, which is swollen with VAc as a function of experimental time and corresponding glass transition temperature of the swollen latex particles. Run No. RS-81.  $T_g$  data is adapted from the work of Friis et al.

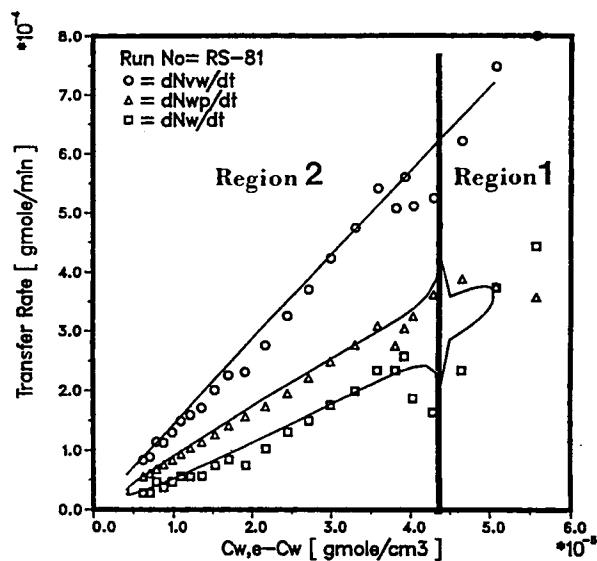
cess into the PS latex particles changes from the glassy PS itself to the interfacial surfactant layer when the glassy polymer becomes rubbery with a high volume fraction of monomer inside the particles. In order to check this hypothesis, some experiments were performed with a monodisperse PVAc latex, which is in the rubbery state at 60°C. It is well known that SLS tends to form a complex with the PVAc or penetrate into the polymer.<sup>31-35</sup> Therefore, the exact amount of SLS on the particle was not determined precisely. For the run RV-08,  $9.75 \times 10^{-3} M$  of SLS was introduced into the cleaned PVAc latex and was allowed to stand for 1 day to reach equilibrium. To check for the presence of a transition in the controlling step of monomer transport, the rate of pressure increase plot as a function of time, which is similar to Figure 7, was prepared with the PVAc latex. Figure 11 shows no transition for the PVAc system, which is rubbery throughout the monomer transport experiment. The experimental results for the PVAc system, when compared with those for the PS, imply that the transition observed in Figure 7 is due to the glassy/rubbery transition of the PS latex.

**Simulation of Monomer Transport into the PS Latex Particles**

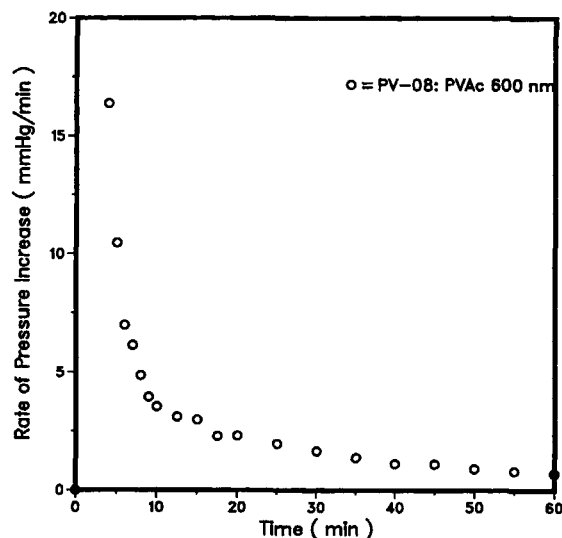
The mathematical equations for the monomer diffusion were used to simulate the monomer transport from the microburette into the latex particles. Cleaned PS-160, which has a particle diameter of



**Figure 9** Molar flow rates of VAc into the latex system as a function of the driving force ( $C_{w,e} - C_w$ ).  $dN_{vw}/dt$  = molar flow rate of VAc from the vapor to the aqueous phase,  $dN_w/dt$  = accumulation rate of VAc in the aqueous phase, and  $dN_{wp}/dt$  = molar flow rate of VAc from the aqueous to the polymer phase. line; simulation and (O); experimental.  $K_{vw}A_w = 14.26$  and  $K_{wp}A_p = 1.36$  cm<sup>3</sup>/min. Run No. RS-81.



**Figure 10** Molar flow rates of VAc into the latex system as a function of the driving force ( $C_{w,e} - C_w$ ).  $dN_{vw}/dt$  = molar flow rate of VAc from the vapor to the aqueous phase,  $dN_w/dt$  = accumulation rate of VAc in the aqueous phase, and  $dN_{wp}/dt$  = molar flow rate of VAc from the aqueous to the polymer phase. line; simulation and (O); experimental.  $K_{vw}A_w = 14.26$  and  $K_{wp}A_p = 1.10$  (in region 1) and 1.36 cm<sup>3</sup>/min (in region 2). Run No. RS-81.



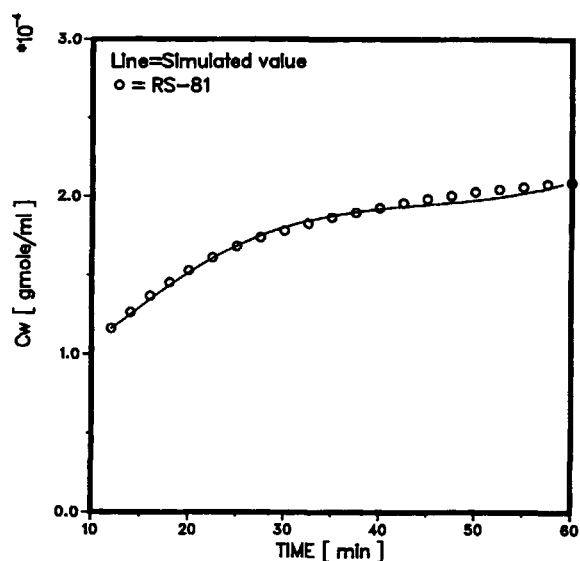
**Figure 11** The rate of pressure increase of the system with the PV-600 latex particles swollen with the monomer transferred from the microburette as a function of time. Run No. RV-08.

158 nm, was used for this latex. The latex particles are assumed to be monodisperse throughout the experiments, with a diameter of 163 nm. This value was calculated when the volume fraction of monomer inside of a swollen latex particle was 8% (half of total monomer transferred inside the particle). The values of  $K_{vw}A_w$  and  $K_{wp}A_p$  are 14.26 and 1.36  $\text{cm}^3/\text{min}$ , respectively (run No. RS-81).

Figures 12 and 13 show the model prediction for the monomer concentration profiles in the aqueous and the polymer phases, respectively. Monomer concentrations in each phase after the transition of PS latex particles from the glassy state to the rubbery state were compared with the experimental data. It is noted that the mathematical simulation of the vapor phase monomer addition method predicts the experimental data quite well. Also, simulated values of the total mol of VAc in the aqueous and the polymer phase were compared with the experimental data in Figure 14. It is shown that the mathematical simulation predicts the diffusional monomer transport into the latex system very well.

#### Monomer Diffusion Coefficients across the Interfacial Surfactant Layer

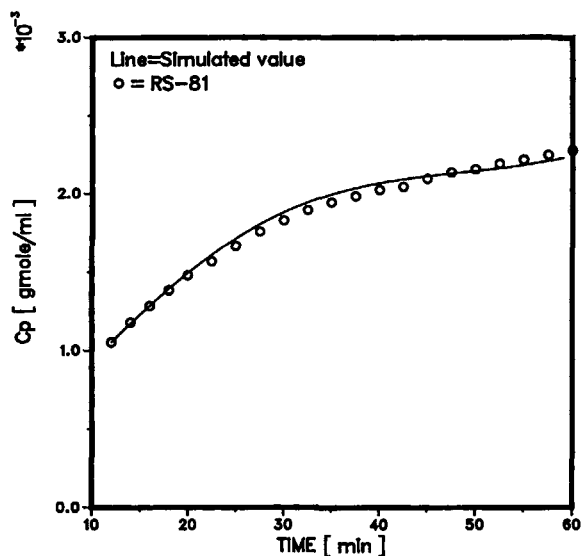
It was already shown that the mass transfer coefficient of VAc across the interface was independent of the agitator speed.<sup>17</sup> When there is no effect of mixing on the interfacial surfactant layer, diffusional mass transfer into the latex particle can be thought



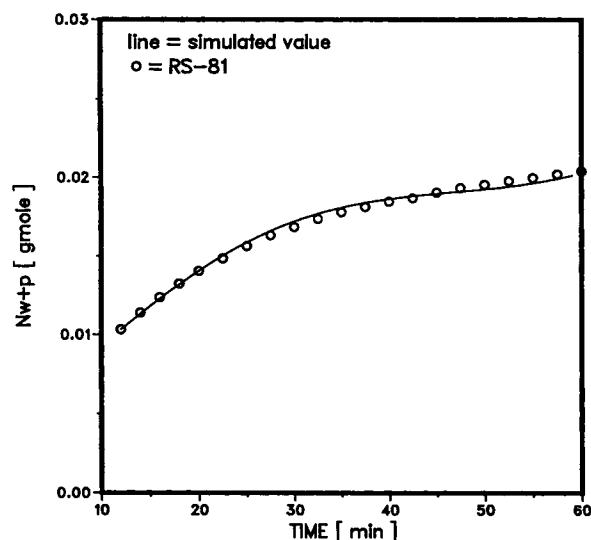
**Figure 12** Concentration of VAc in the aqueous phase as a function of time. line; simulation and (O); experimental. Run No. RS-81.

to be the same as the diffusional process from the stagnant liquid into the particles.<sup>36</sup> At the experimental agitator speeds, the latex particles tended to move with the water. In this case, the Sherwood number, defined in eq. (4), is 2.

$$Sh = K_{wp} \frac{d_p}{D} \quad (4)$$



**Figure 13** Concentration of VAc in the polymer phase as a function of time. line; simulation and (O); experimental. Run No. RS-81.



**Figure 14** Total mol of VAc in the PS-160 latex as a function of time. line; simulation and (O); experimental. Run No. RS-81.

where  $d_p$  is the particle diameter,  $K_{wp}$  is the overall mass transfer coefficient, and  $D$  is the diffusion coefficient of monomer across the interface. From this, the diffusion coefficient of  $9.7 \times 10^{-14} \text{ cm}^2/\text{s}$  was obtained. This low value of the diffusion coefficient is another indication of the "condensed" nature of the adsorbed surfactant around the latex particles.

## SUMMARY AND CONCLUSIONS

A vapor phase addition method was used to determine the interfacial mass transfer resistance of vinyl acetate monomer diffusing into polystyrene latex particles stabilized with ionic or nonionic surfactants, or water-soluble polymer. Using the mathematical model for the diffusional process, mass transfer coefficients of monomer into the particles were calculated and compared. In case of the ionic surfactant, sodium dodecyl sulfate, the mass transfer coefficient, did not change much when a small amount of electrolyte (potassium sulfate),  $1 \times 10^{-4} M$ , was added. But, with a larger amount of potassium sulfate added,  $1 \times 10^{-3} M$ , the extent of adsorption was increased and the mass transfer coefficient decreased by 16%. The latex particles stabilized with steric stabilizers such as Igepal CO-660 or PVP K-30 showed lower monomer transfer rates compared with that of the ionic stabilizer, sodium dodecyl sulfate. Higher local viscosity in the interfacial surfactant layer of the steric stabilizers seems to be the reason for the increased interfacial resis-

tance of monomer transport. The mathematical simulation of the diffusional mass transfer of monomer into the latex particles predicted the concentration of monomer in the aqueous and polymer phases well. The mass transfer coefficient across the surfactant layer showed the transition when the PS latex particles changed from the glassy state to the rubbery state due to the increased monomer concentration inside the particles. The rate-determining step in the overall monomer transport process in the vapor phase addition method was found to be the interfacial mass transfer resistance due to the adsorbed surfactant layer. Transition in the mass transfer rate into the latex particles was also observed by simulation with different values of  $K_{wp}$  before and after the transition. The diffusion coefficient of the monomer through the interface seems to be low. This value represents the molecular diffusion of a small molecule through a solid or glassy membrane. This might be due to the resistance of the adsorbed surfactant or the incompatibility of nonpolar species against the polar ends of the surfactant on the latex particles.

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## NOMENCLATURE

$A_w$	Total interfacial area of the vapor/water interface ( $\text{cm}^2$ )
$A_p$	Total interfacial area of the water/polymer interface ( $\text{cm}^2$ )
$C_v$	Concentration of monomer in the vapor phase ( $\text{mol}/\text{cm}^3$ )
$C_w$	Concentration of monomer in the aqueous phase ( $\text{mol}/\text{cm}^3$ )
$C_p$	Concentration of monomer in the polymer phase ( $\text{mol}/\text{cm}^3$ )
$C_{w,e}$	Equilibrium concentration of monomer in the aqueous phase with the concentration of monomer in the vapor phase ( $\text{mol}/\text{cm}^3$ )
$C_{p,e}$	Equilibrium concentration of monomer in the polymer phase with the concentration of monomer in the aqueous phase ( $\text{mol}/\text{cm}^3$ )
$N_v$	The number of mol of monomer in the vapor phase (mol)
$N_w$	The number of mol of monomer in the aqueous phase (mol)
$N_p$	The number of mol of monomer in the polymer phase (mol)

$N_{vw}$	The number of mol of monomer transferred from the vapor to the aqueous phase (mol)
$N_{wp}$	The number of mol of monomer transferred from the aqueous to the polymer phase (mol)
$K_{vw}$	The overall mass transfer coefficient at the interface between vapor and water (cm/min)
$K_{wp}$	The overall mass transfer coefficient at the interface between polymer and water (cm/min)
$V_w$	Volume of the aqueous phase (cm <sup>3</sup> )
$V_p$	Volume of the polymer phase (cm <sup>3</sup> )
$D_w$	Weight-average particle diameter determined by TEM (nm)
$p$	Pressure of the system (mmHg)
$t$	Time (min)

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