

Determination of Interfacial Tensions for Latex Particles

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SYNOPSIS

The possibility of measuring *in situ* the interfacial tension at the monomer-swollen polymer-water interface of synthetic latices is considered in detail. Experimental measurements of certain liquid or vapor phase properties of the latex can, in principle, yield values of the desired interfacial tension. This technique requires the evaluation and comparison of the Flory-Huggins term and the Morton term of the thermodynamic expression for the chemical potential of the monomer in the latex particle. While each term can be evaluated, it turns out that the relative magnitudes of the two terms are such that unrealistically high precision is required in the experimental measurements for this technique to be useful for obtaining reasonably accurate interfacial tensions. At saturated swelling conditions with highly surface-active emulsifiers (e.g., sodium dodecyl sulfate), the interfacial tension values obtained have a precision of only about $\pm 50\%$. The reliability of these approximate values degrades rapidly as one moves away from saturation conditions, so as to render *in situ* experimental techniques inappropriate for gaining accurate knowledge about the surface energy at the latex particle-water interface at any monomer-polymer ratio. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Recently, there has been a significant amount of research on the parameters that lead to latex particle morphology control. From this body of work it has become clear that the interfacial tensions within and at the surface of latex particles are critically important in controlling the morphology of such composite particles. A number of papers¹⁻¹⁰ have presented predictive models based on an equilibrium thermodynamic analysis of the particle morphology and have been able to quantify the dependency of morphology on the interfacial tensions. Although most of the published models deal only with the conditions that apply at the end of a seed latex polymerization, two groups^{6,7} have offered versions that employ conversion-dependent interfacial tensions. This added detail, albeit still at conditions of equilibrium, offers the possibility of predicting the evolution of particle structure throughout the polymerization reaction. Chen et al.⁴⁻⁶ considered the effect of the conversion-dependent polymer-polymer interfacial

tension upon the evolution of morphology while restricting the polymer-water interfacial tensions to constant values. Winzor^{7,8} further advanced this type of analysis to include the variation of all interfacial tensions with conversion. It has become apparent from the progress made in understanding the control of the latex particle morphology that there have been few reliable measurements of the associated interfacial tensions reported in the literature. This is not surprising given the state of development of this research area and the fact that such interfacial tensions are dependent on a significant number of variables, notably including surfactants, polymeric end groups, monomer-polymer type, and temperature. All of the interfacial tensions that we are aware of that have been reported for use in latex morphology predictions have been measured in the bulk state using contact angles or drop-weight volume techniques. Given that it would be more desirable to measure these by using *in situ* techniques for monomer swollen latices, we have investigated this possibility in some detail. The purpose of this work was to determine the polymer-water interfacial tension by measuring the liquid or vapor properties of the latex. As it turns out this is not a completely straightforward task.

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BACKGROUND

A monomer- or solvent-swollen polymer latex can be considered a general system composed of three phases: the aqueous, the polymer particle, and the vapor phases. All of them contain some monomer or solvent (Fig. 1). In the analysis described in this study the polymer and the water are considered completely demixed. The vapor phase is also assumed to be composed only of water and monomer or solvent (no ambient gases).

If the system is at monomer saturation (all three phases are saturated by monomer), we can consider a fourth phase constituted of pure monomer in equilibrium with the others. The monomer chemical potentials in each phase are as follows: aqueous phase, μ_{MA} ; vapor phase, μ_{MG} ; polymer-particle phase, μ_{MPP} . The chemical potential of the pure monomer in its phase μ_{M^0} is taken as the chemical potential reference and arbitrarily set equal to zero. The chemical potential of the monomer in the aqueous phase can be written¹¹:

$$\mu_{MA} = \mu_{M^0} + RT \ln \frac{a_M}{a_{M^0}} \quad (1)$$

where a_M is the activity of the monomer in the water and a_{M^0} the activity at saturation. A general expression of the activity is $a_M = \gamma_M X_M$, with γ_M the activity coefficient and X_M the mole fraction of mono-

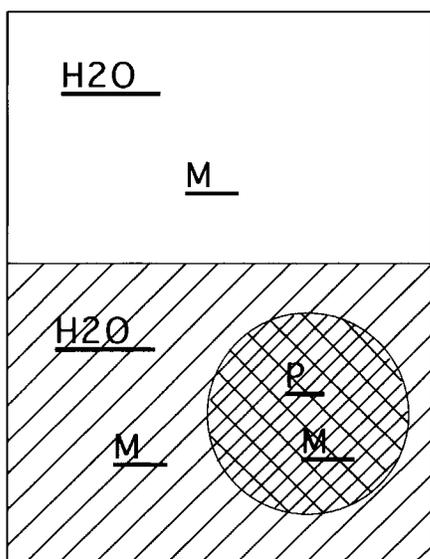


Figure 1 Simplified representation of a polymer latex. All three phases contain some monomer M. The aqueous (H₂O/M), the polymer particle (P/M), and the vapor phase (H₂O/M).

mer. Since the solubility of most monomers in water is very low, it is reasonable to consider the activity coefficient γ_M equal to unity. Thus Eq. (1) can be rewritten as

$$\mu_{MA} = RT \ln \frac{X_M}{X_{M^0}} \quad (2)$$

where X_{M^0} is the monomer solubility in the aqueous phase expressed as mole fraction.

The case of the vapor phase is very similar to the aqueous phase. Here the chemical potential of the monomer can be written¹¹

$$\mu_{MG} = \mu_{M^0} + RT \ln \frac{f_M}{f_{M^0}} \quad (3)$$

where f_M is the fugacity of the monomer in the vapor phase and f_{M^0} the fugacity of the pure monomer. At low to moderate pressure, the vapor phase can be considered to be an ideal gas mixture. Equation (3) then becomes

$$\mu_{MG} = RT \ln \frac{P_M}{P_{M^0}} \quad (4)$$

where P_M is the partial pressure of the monomer and P_{M^0} the pure component vapor pressure of the monomer.

The polymer particle phase is more complex. The case of a polymer latex involves an interface between the polymer and the aqueous phase. The contribution to the chemical potential of the polymer-monomer interaction is described by the Flory-Huggins term¹²

$$RT[\ln \Phi_M + (1 - \Phi_M)(1 - m) + \chi_{M/P}(1 - \Phi_M)^2] \quad (5)$$

and the interfacial contribution is described by the Morton term¹³:

$$2 \frac{V_M \gamma_{A/P}}{r^0} (1 - \Phi_M)^{1/3} \quad (6)$$

where Φ_M is the volume fraction of monomer in the particle, $\chi_{M/P}$ the Flory-Huggins monomer-polymer interaction parameter, $m = V_M/V_p$ (V_M , V_p the molar volumes of the monomer and the polymer, respectively), $\gamma_{A/P}$ the interfacial tension between the particle and the aqueous solution, and r^0 the radius of the unswollen particle. Thus the chemical

potential of the monomer in the polymer particle can be expressed as follows:

$$\begin{aligned} \mu_{M^{PP}} = \mu_{M^0} + RT[\ln \Phi_M + (1 - \phi_M)(1 - m) \\ + \chi_{M/P}(1 - \phi_M)^2] + 2 \frac{V_M \gamma_{A/P}}{r^0} (1 - \phi_M)^{1/3} \quad (7) \end{aligned}$$

Under equilibrium conditions the chemical potential of the monomer is the same in all phases. This can be written as

$$\mu_{M^A} = \mu_{M^{PP}} = \mu_{M^G} \quad (8)$$

A particularly interesting case is that of monomer saturation (sat). A fourth phase composed of pure monomer is created in thermodynamic equilibrium with the other three, and one can write

$$[\mu_{M^G}]_{\text{sat}} = [\mu_{M^{PP}}]_{\text{sat}} = [\mu_{M^A}]_{\text{sat}} = \mu_{M^0} = 0 \quad (9)$$

Thus Eq. (7) can be solved for $\gamma_{A/P}$ at saturation as

$$\gamma_{A/P}^{\text{sat}} = - \frac{r^0 RT [\ln \Phi_{M^{\text{sat}}} + (1 - \Phi_{M^{\text{sat}}})(1 - m) + \chi_{M/P}(1 - \Phi_{M^{\text{sat}}})^2]}{2V_M(1 - \Phi_{M^{\text{sat}}})^{1/3}} \quad (10)$$

This interfacial tension can be calculated if one knows the radius of the particle before and after swelling to saturation, the interaction parameter at that swelling ratio, and the molecular weight of the polymer.

AQUEOUS PHASE ANALYSIS

Theoretical Possibilities

The measurement of the interfacial tension $\gamma_{A/P}$ at different concentrations of monomer in the polymer particle is made possible by measuring the concentration of monomer in the aqueous phase. Combination of Eqs. (2), (7), and (8) gives

$$\begin{aligned} \ln \frac{X_M}{X_{M^0}} = [\ln \Phi_M + (1 - \phi_M)(1 - m) \\ + \chi_{M/P}(1 - \phi_M)^2] + 2 \frac{V_M \gamma_{A/P}}{r^0 RT} (1 - \phi_M)^{1/3} \quad (11) \end{aligned}$$

and this equation can be solved for $\gamma_{A/P}$ as

$$\begin{aligned} \gamma_{A/P} = \frac{r^0 RT}{2V_M(1 - \phi_M)^{1/3}} \left\{ \ln \frac{X_M}{X_{M^0}} - [\ln \Phi_M \right. \\ \left. + (1 - \phi_M)(1 - m) + \chi_{M/P}(1 - \phi_M)^2] \right\} \quad (12) \end{aligned}$$

In this equation the molecular weight of the polymer, the molar volumes of the monomer and polymer, the temperature of the thermodynamic equilibrium, the monomer solubility in the aqueous phase X_{M^0} , and the radius of the swollen particle are required constants whose values may readily be known. The parameters $\chi_{M/P}$ and X_M are functions of Φ_M and may not be readily known. However, when all these parameters are determined, Eq. (12) can be used to calculate the function $\gamma_{A/P} = f(\phi_M)$. The main experimental problem would appear to be determining the concentration of the monomer in the aqueous phase at any swelling ratio so as to obtain X_M . However, $\chi_{M/P}$ and its variation with swelling ratio is a different matter and will be discussed separately.

Experimentation

The system we studied was composed of a polystyrene (PS) latex that was swollen by *n*-butyl methacrylate (BuMA) monomer. The PS seed latex had been synthesized in a batch process. Styrene from Aldrich Company had been previously vacuum distilled and stored at -18°C , and sodium dodecyl sulfate (SDS) from Fluka was used without further purification. The polymerization was carried out in a stirred jacketed reactor. The recipe used is shown in Table I along with the final characteristics of the latex.

Particle size determination was made with a disc centrifuge photosedimentometer (Brookhaven DCP 1000), and the latex solids content was determined

Table I Recipe and Characterization of the Base PS Latex

Experiment Number	EP1
Temperature ($^\circ\text{C}$)	70
DI water (g)	1364.2
SDS (g)	1.4435
NaHCO ₃ (g)	1.1029
K ₂ S ₂ O ₈ (g)	1.106
Styrene (g)	130
Time (h)	5.5
Size (nm) DCP	259
Weight-average molecular weight (g/mol)	398,000
Polydispersity of particles	1.03
Solid content (wt %) of latex	8.59

Table II Volume Fractions of BuMA in Swollen EP1/PS Latices

Experiment Number	BuMA (g)	BuMA/PS g/g	Calculated Particle Density (g/cm ³)	ϕ_M (vol. frac.)
EP2-1	1.06	0.124	1.032	0.126
EP2-2	1.99	0.232	1.020	0.214
EP2-3	3.02	0.352	1.009	0.292
EP2-4	4.02	0.468	1.000	0.355
EP2-5 ^a	5.01	0.583	0.992	0.406
EP2-6 ^a	6.03	0.702	0.985	0.452
EP2-7	7.06	0.822	0.979	0.491
EP2-8	8.07	0.939	0.974	0.524
EP2-9	9.22	1.007	0.969	0.557
EP2-10	10.08	1.173	0.965	0.579
EP2-sat	23	2.677	0.936	0.757

^a Experiments highlight samples for which density of aqueous phase and particle were too close for separation.

gravimetrically (average of three samples dried over night at 110°C). The determination of the polymer molecular weight was made by using the Zimm method with a Brookhaven B1-90 quasielastic light scattering instrument. The weight average molecular weight was 398,000 g/mol ($\pm 3.3\%$).

Eleven samples of 100 g each from latex EP1 were placed in 250-mL bottles. Some BuMA from Aldrich without further purification was added to the latices to swell them (Table II). The swelling was conducted under stirring for 48 h at room temperature (25°C). No excess monomer was evident after the stirring was stopped. A final sample was prepared with an excess of monomer using the same procedure. In this sample the excess monomer was removed from the latex using a separatory funnel. Table II lists the characteristics of the 11 swollen latices.

In order to calculate $\gamma_{A/P}$ via Eq. (12), one needs to determine the value of X_M for each swelling ratio. Several attempts to separate the serum (aqueous solution) from the polymer particles were made. The best results were obtained by using a two-step separation. First, the samples were centrifuged under 47,000g for an hour at 10°C. Then the serum was collected with a pipet. A final cleaning of the serum was made with 200-nm filters (from Satorius). The samples were stored at 5°C while awaiting analysis. The polymer particles from EP2-5 and EP2-6 had a density too close to that of the water to be separated by the centrifuge. Results from these two samples have not been included in the following discussion.

At first it was thought that simple UV absorption spectra would provide measurements of BuMA concentration in the serum, but at 214 nm (maximum absorbance for BuMA) other materials in the

aqueous phase also absorb UV light. Thus we turned to high-pressure liquid chromatography (HPLC) analysis, which showed that at least four products were present in the aqueous phase. A variable wavelength UV detector tuned at 214 nm with a Delsi Enica 10 integrator and a 30-cm Microbondapack C18 column was used for this procedure. The mobile phase was an acetonitrile–water solution, 60/40 in volume. The pump speed was 1 mL/min, the injection loop had a volume of 10 μ L, and the column was at room temperature. The column provided good separation of the components within the aqueous phase. A calibration of nine samples with aqueous concentration in BuMA from 0.03 to 2 g/L was constructed. The calibration gave a good logarithm regression between the peak areas and the BuMA concentration as shown in Figure 2.

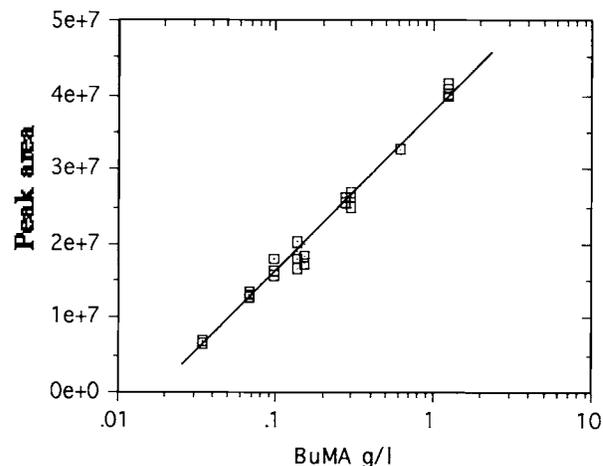


Figure 2 Calibration curve of the HPLC. Correlation of the data gives the relation: Peak area = $[3.772 + 2.151 \times \log_{10}(\text{[BuMA g/L]})] \times 10^{+7}$.

Discussion

In order to use the thermodynamic relationships discussed earlier to evaluate the latex particle–aqueous phase interfacial tension, one needs to have values of Φ_M and $\chi_{M/P}$ at each condition of interest. Values for $\chi_{M/P}$ for this, or most other systems, are not available in the literature, and thus we have measured them over the monomer–polymer range of interest for us. This was not straightforward and involved the preparation and use of variably cross-linked PS samples swollen with BuMA monomer. These measurements are reported in a separate communication¹⁴ and resulted in the relationship $\chi_{M/P} = 0.902 - 0.42\Phi_M$ for polystyrene of $\bar{M}_w = 398,000$.

The value of Φ_M for use at equilibrium swelling in Eq. (10) is readily obtained by measuring the swollen particle volume through material balance without regard to the monomer concentration in the aqueous phase. However, at unsaturated conditions there is the need to measure the mole fraction of monomer in the aqueous phase (X_M) at both the condition of interest and at saturation. This allows the use of the Eq. (12) for calculating $\gamma_{A/P}$. As described earlier, the HPLC was used to obtain values for X_M . Figure 3 shows the values of X_M plotted against the corresponding Φ_M .

Utilization of Eq. (12) with the experimental data at a variety of particle swelling ratios (i.e., Φ_M) gave completely unrealistic answers for $\gamma_{A/P}$. In order to understand such results, comparisons of the Flory and Morton terms were made at each swelling ratio, and it was found that at low Φ_M 's, the Morton term was very small compared to the Flory term {i.e., $2(V_M\gamma_{A/P}/r^0)(1 - \phi_M)^{1/3}$ and $RT[\ln \Phi_M + (1$

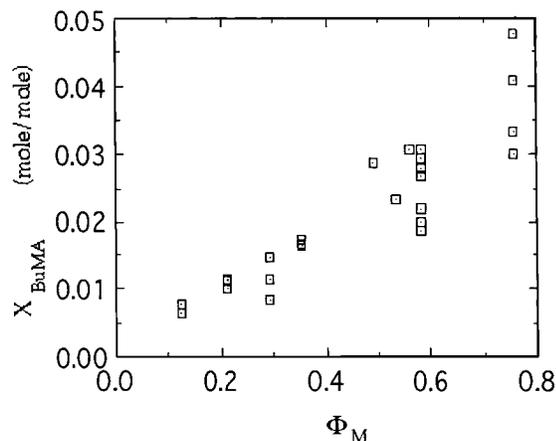


Figure 3 Experimental concentration of monomer in the aqueous phase. Dependence on the monomer fraction Φ_M in the polymer particle (of latex EP2-1 to EP2-4 and EP2-7 to EP2-10 and EP2-sat).

Table III Comparative Contribution of the Morton Term and the Flory Term to the Monomer Chemical Potential in the Swollen Latex EP2

Φ_M	$\gamma_{A/P}$	Morton Term [Eq. (6)]	Flory Term [Eq. (5)]	Chemical Potential [Eq. (7)]
0.001	3.3	4.30	-11003	-10999
0.1	3.3	4.16	-1552	-1548
0.2	3.3	4.00	-630	-626
0.3	3.3	3.82	-274.2	-270.4
0.4	3.3	3.63	-116.6	-113.0
0.5	3.3	3.42	-46.24	-42.84
0.6	3.3	3.17	-16.54	-13.37
0.7	3.3	2.88	-5.352	-2.469
0.76	3.3	2.68	-2.672	0.004
0.9	3.3	1.20	-0.472	1.527
0.9999	3.3	0.20	-9.8E-05	0.20

$-\phi_M)(1 - m) + \chi_{M/P}(1 - \phi_M)^2$], respectively} as shown in Table III. Close to saturation both terms have values of similar magnitude. The unrealistic answers at the unsaturated conditions apparently arise from the need to compute the difference between the Morton and the Flory terms in Eq. (12).

Considering this problem, theoretical curves (at constant interfacial tension) of the monomer concentration versus the swelling ratio were plotted. Equation (12) was solved for X_M as:

$$X_M = X_{M^0} \exp \left\{ [\ln \Phi_M + (1 - \phi_M)(1 - m) + \chi_{M/P}(1 - \phi_M)^2] + 2 \frac{V_M \gamma_{A/P}}{r^0 RT} (1 - \phi_M)^{1/3} \right\} \quad (13)$$

Equation (13) is plotted in Figure 4 for values of $\gamma_{A/P} = 30$ mN/m and $\gamma_{A/P} = 0.5$ mN/m with all other parameters set at the values characteristic of the experimental situation. The swelling term is so small over this range of Φ_M that the difference between the two curves can barely be seen, and the experimental points are far apart from the curves. From this comparison it is concluded that the accuracies of the experimental measurements are far too low for this technique to yield useful results.

Given the lack of sensitivity of Eq. (13) to $\gamma_{A/P}$, it is instructive to calculate what experimental accuracy is necessary to be able to use the equation. So far we have done a variety of conditions and found that in order to achieve an accuracy of ± 1 mN/m for $\gamma_{A/P}$, it is necessary to measure X_M to within $\pm 0.05\%$ for a 260-nm particle. The need for such great accuracy is lessened at smaller particle sizes, but is still at 0.5% for 50-nm particles. Table IV

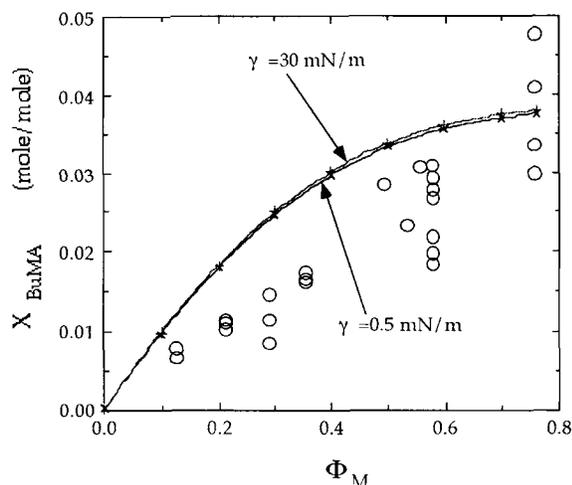


Figure 4 Comparison between theoretical and experimental concentrations of BuMA. The two continuous curves represent the theoretical monomer concentration for interfacial tension of 30 and 0.5 mN/m depending on the monomer fraction inside the polymer particles Φ_M . Open circles represent experimental measurements from this work.

shows the results of other calculations for achieving greater accuracy in the interfacial tension.

The required accuracies on X_M were computed with the assumption that all of the other parameters in Eq. (12) (e.g., r^0 , Φ_M , and $\chi_{M/P}$) were known with absolute precision. Obviously, this cannot be the case. Considering the experimental difficulties involved in this approach, it appears that there is no realistic chance of using this technique to obtain *in situ* measurements if $\gamma_{A/P} = f(\Phi_M)$ even if the HPLC analysis can be done with high accuracy.

At saturation conditions the situation is somewhat different and approximate values of $\gamma_{A/P^{sat}}$ can be measured with ordinary experimental precision. For the PS-BuMA system studied here, $\gamma_{A/P^{sat}} = 3$ mN/m, which is favorably compared with values found by Morton et al.¹³ for different solvents, and to recent measurements from a pendant drop apparatus.¹⁵ The value of 3 mN/m is only an approx-

Table IV Estimation of the Accuracy Required for the Aqueous Phase Method^a

	$\gamma \pm 0.1$ mN/m	$\gamma \pm 1$ mN/m
$D = 260$ nm	$\pm 0.005\%$	$\pm 0.05\%$
$D = 50$ nm	$\pm 0.05\%$	$\pm 0.5\%$

^a The numbers in % in the table represent the accuracy required on the determination of the monomer concentration in the aqueous phase for a given particle diameter D and a desired accuracy of γ .

imation since its precision is about $\pm 50\%$ as determined by assessing the accuracy of the various parameters (r^0 , Φ_M , and $\chi_{M/P}$) to $\pm 1\%$ in Eq. (10). For this reason we have reported this value to the nearest whole number.

As this article was being prepared, Maxwell et al.^{16,17} presented excellent discussions of the partial swelling of latex particles with one and two monomers, respectively. Although their emphasis was on developing a model for predicting monomer partitioning between the latex particle and the aqueous phase, they too found that at partial swelling their results were insensitive to the values of $\gamma_{A/P}$. However, at saturation conditions their results were much more sensitive to the interfacial tension value. This is as it must be since it is well known that the Morton term containing $\gamma_{A/P}$ is the reason for the limited swelling of a latex particle at saturation conditions. While our conclusions regarding the insensitivity of Eq. (13) to $\gamma_{A/P}$ are the same as those of Maxwell et al., we would suggest that the $\gamma_{A/P}$ value of 45 mN/m they used to fit their methyl acrylate (MA) monomer partitioning experiments (partial swelling of PMA latex stabilized with Aerosol MA80) is unrealistic. Wu¹⁸ reported the surface tension of PMA as 41 mN/m at 20°C, and it must be that its interfacial tension against water containing a surfactant will be substantially lower than its surface tension. With a polar monomer like MA partially swelling the latex particle, one should expect that the $\gamma_{A/P}$ value would be yet lower. Our results suggest that it is very unlikely that one will be able to determine a unique set of values of $\gamma_{A/P}$ and $\chi_{M/P}$ that will allow Eq. (13) to accurately fit monomer partitioning data under swelling conditions.

VAPOR PHASE ANALYSIS

Theoretical Possibilities

In this case consideration is made of obtaining the interfacial tension $\gamma_{A/P}$ at different monomer fractions in the polymer by measuring the total pressure above the latex.¹⁹ Equations are very similar to the ones shown for the aqueous phase. Combination of (7) and (4) as allowed by (8) yields:

$$\ln \frac{P_M}{P_{M^0}} = [\ln \Phi_M + (1 - \Phi_M)(1 - m) + \chi_{M/P}(1 - \Phi_M)^2] + 2 \frac{V_M \gamma_{A/P}}{r^0 RT} (1 - \Phi_M)^{1/3} \quad (14)$$

This last equation can be solved for $\gamma_{A/P}$ as

$$\gamma_{A/P} = \frac{r^0 RT}{2V_M(1 - \Phi_M)^{1/3}} \left\{ \ln \frac{P_M}{P_{M^0}} - [\ln \Phi_M + (1 - \Phi_M)(1 - m) + \chi_{M/P}(1 - \Phi_M)^2] \right\} \quad (15)$$

The constants needed for application of this equation are the same as in the aqueous case except the monomer saturation vapor pressure P_{M^0} . Then there remains two unknown functions of ϕ_M , which are $\chi_{M/P}$ and P_M . When all these parameters are determined, Eq. (15) may be used to calculate the function $\gamma_{A/P} = f(\phi_m)$.

Experimental Realities

To get the partial pressure of the monomer over the latex, a setup composed of a three-neck flask and two "feeding flasks" have been designed. The main flask is agitated with a magnetic stirring bar. A pressure gauge provides the total pressure of the main flask. A vacuum pump and a water vapor tank are also connected to the flask (Fig. 5).

At the beginning of the experiment the main flask is to be empty and under vacuum (V_1 open). The vacuum valve is closed (V_1), and the vacuum is broken with water vapor (V_2 is open). The latex is then added to the main flask (V_3 then V_4 are open), and the total pressure over the latex is the saturation water vapor pressure $P_{H_2O^0}$. A known amount of monomer is added to the latex (V_5 and V_6 are opened then closed) and stirred to reach equilibrium. The total pressure is now $P_{H_2O^0} + P_M$. Monomer saturation is reached step by step (increasing amount

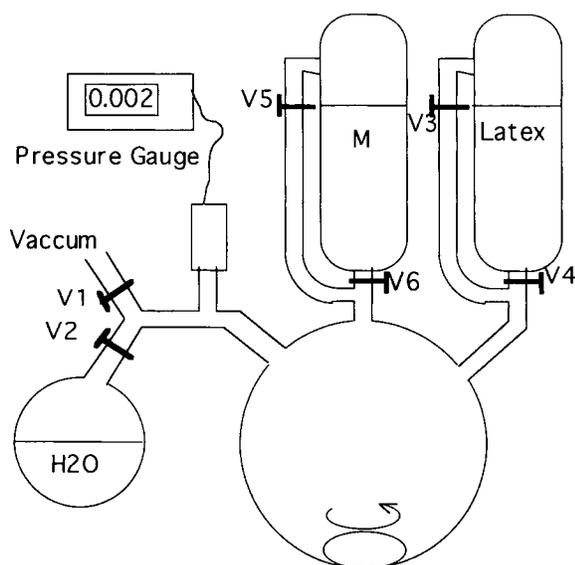


Figure 5 Experimental setup to measure vapor pressure.

Table V Estimation of the Accuracy Required for the Vapor Phase Method^a

	$P_{M^0} = 0.1$ atm	$P_{M^0} = 0.5$ atm
$D = 260$ nm	± 0.000004 atm	± 0.00002 atm
$D = 50$ nm	± 0.00002 atm	± 0.0001 atm

^a The numbers in atm in the table represent the accuracy required on the pressure gauge to get $\gamma = 5 \pm 0.1$ mN/m. All other parameters reflect a system composed of PS ($M_w = 398,000$) swollen with BuMA.

of added monomer). The final total pressure at saturation is $P_{H_2O^0} + P_{M^0}$. Through such an experiment one can get (at a given temperature) P_M at different swelling ratios of the polymer particles.

Equation (14) can be solved for P_M to yield

$$P_M = P_{M^0} \exp \left\{ [\ln \Phi_M + (1 - \phi_M)(1 - m) + \chi_{M/P}(1 - \phi_M)^2] + 2 \frac{V_M \gamma_{A/P}}{r^0 RT} (1 - \phi_M)^{1/3} \right\} \quad (16)$$

This equation can be used to determine the required accuracy on the pressure gauge to obtain $\gamma_{A/P}$ values of any accuracy of interest. Given that values of $\gamma_{A/P}$ for swollen latices will be near 5 mN/m, a useful accuracy of $\gamma_{A/P}$ will be considered to be 0.1 mN/m. For the two cases of latex particle sizes of 50 and 260 nm, and the two choices of $P_{M^0} = 0.1$ and 0.5 atm (reflecting expected conditions for BuMA at normal polymerization temperatures), it is predicted (Table V) that the pressure must be measured within 0.00002 atm for a total pressure of nearly one atmosphere. This is clearly unrealistic even if the temperature was controlled precisely. Temperature fluctuations of even $\pm 0.01^\circ\text{C}$ will cause pressure changes of about 0.00002 atm in a perfect gas ($\Delta P = P \Delta T/T$, at $P = 0.5$ atm and $T = 323$ K).

CONCLUSION

Our attempts to measure *in situ* the latex particle-aqueous phase interfacial tension as a function of monomer swelling have failed for reasons that can be explained by thermodynamics. While it is possible to obtain approximate values of $\gamma_{A/P}$ at maximum particle swelling, the accuracy falls off precipitously as swelling is decreased. This is due to the relative sizes of the Flory term and the Morton term in the thermodynamic expression for the chemical potential of the monomer in the latex. In principle the measurement of $\gamma_{A/P}$ can be made by determining the aqueous phase concentration of the monomer

or the partial pressure of the monomer above the latex. However, it was shown that the precision required in such measurements is not possible in a practical sense. Therefore it appears that latex particle interfacial tensions and their dependency on monomer concentration will have to be obtained by indirect methods.

We are grateful for financial support provided by Rhône-Poulenc. We wish also to thank Flavien Melis for the molecular weight determination by the Zimm method and some particle size determinations.

Abbreviations and Symbols

a_M	monomer activity
a_{M^0}	monomer activity at saturation
f_M	monomer fugacity
f_{M^0}	monomer fugacity at saturated vapor pressure
m	molar volume ratio between monomer and polymer
M_M	monomer molecular weight
M_w	polymer molecular weight
P_M	monomer partial vapor pressure
P_{M^0}	monomer saturated vapor pressure
r^0	particle radius (before swelling)
R	perfect gas constant
T	temperature (K)
V_M	monomer molar volume
V_P	polymer molar volume
X_M	monomer concentration (mol/mol)
X_{M^0}	monomer concentration at saturation (mol/mol)
$\gamma_{A/P}$	(aqueous solution)/(swollen polymer particle) interfacial tension
Φ_M	monomer volume fraction in the polymer particle
$\Phi_{M^{\text{sat}}}$	monomer volume fraction in the polymer particle at saturation
μ_{M^A}	monomer chemical potential in the aqueous phase
μ_{M^G}	monomer chemical potential in the vapor phase
$\mu_{M^{PP}}$	monomer chemical potential in the polymer particle

μ_{M^0}	monomer chemical potential in its pure phase; taken as reference
$\chi_{M/P}$	monomer/polymer interaction parameter

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