

Swelling of Poly(styrene-*co*-methacrylic acid) Latex by Isoprene

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ABSTRACT: Carboxylated polystyrene latex was used as seed and isoprene as the second-stage monomer in an inhibited, seeded emulsion polymerization recipe for studies of monomer swelling kinetics at 80°C during interval III of an emulsion polymerization. The isoprene was added to the reactor in small portions using a syringe, and changes in the reactor pressure were continuously measured. Isoprene was added until a free liquid monomer phase was formed; that was, interval II was reached, as indicated by no further pressure increase upon the addition of more monomer. When the observed pressure increment, Op_i , per unit isoprene added was plotted as a function of the volume fraction of polymer in the latex particles, v_p , the graph could be divided into 3 domains. The break points in the Op_i curve could, in an analogous emulsion polymerization, be identified as the glass transition temperature for the polymer, the so-called gel point in interval III and the onset of interval III. In the second domain, where the v_p was between the glass transition temperature, T_g , for the seed polymer and the gel point, the value of Op_i decreased significantly with increasing monomer concentration in the latex particles. This was due to the entropy of mixing and the monomer acting as a plasticizer in the seed polymer. The rate of sorption of monomer to the latex particles was low at high values of v_p . It then increased rapidly with increasing monomer concentrations in the latex particles, $[M]_p$, and a maximum was observed in domain 2. At lower values of v_p the sorption rate decreased in domain 3 and finally became zero as the free liquid monomer phase started to form. Results from batch polymerization suggested that the rate of diffusion of adsorbed monomer and oligo radicals into the particles was retarded. A simplified form of the Vanzo equation was used to estimate the monomer partitioning. It predicted too high a value of $[M]_p$, especially in domain 2 of the swelling process. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 2041–2051, 1998

Key words: two-stage; seeded emulsion polymerization; monomer swelling; monomer partitioning; particle viscosity; monomer vapor pressure.

INTRODUCTION

In order to fully understand the mechanism of emulsion polymerization, the distribution of the monomer between the aqueous phase and the

polymer particles in the dispersion must be known, as well as the rates of transfer of monomer between the different phases present in the reacting system. The rate of polymerization, and the molecular weight and composition of the polymer, are directly related to the partitioning of the monomers between the phases in the polymerizing system. The swelling of latex particles due to the absorption of a monomer has been studied using several techniques. Cen-

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trifugation¹⁻⁴ and ultracentrifugation,^{5,6} together with static pressure measurements,^{2,7-10} are commonly used methods for studying non-reacting latexes. The static pressure method can only be used below saturation, that is, in interval III of the polymerization process. The disappearance of monomer droplets² and a maximum in the reaction rate^{2,11} during polymerization indicate the onset of interval III and supply information on the saturation swelling of the particles. Many other methods have been used for the determination of monomer partitioning, for example Coulter counter measurements,¹² angular light scattering,¹³ small-angle neutron scattering (SANS),^{14,15} ultrasonic velocity,¹⁶ isothermal analysis,¹⁶ gas chromatography (GC),^{6,10,17} dialysis,⁶ and densimeter measurements.¹⁸

In a previous article,¹⁹ we discussed factors influencing the particle morphologies obtained in seeded emulsion polymerization, using a carboxylated polystyrene seed and isoprene and methacrylic acid as the second-stage monomers. Changes in the morphology due to variations in the internal particle viscosity during the second-stage polymerization process were studied by changing the phase ratio and by using different monomer addition techniques, that is, batch and semicontinuous, under starved, as well as flooded, conditions. The thermodynamically favored morphology was promoted by a low internal particle viscosity, which is, in turn, influenced by the polymerization temperature, the seed molecular weight, and the volume fraction of monomer.²⁰⁻²³

When discussing the influence of the viscosity on the particle morphology, it is necessary to know whether or not a separate phase of liquid monomer was present in a certain experiment, and, if so, the relative volume of this phase. In this connection, data on the swelling of a carboxylated polystyrene latex by isoprene under the experimental conditions used were required. The swelling data, combined with conversion data obtained from polymerization experiments, can be used to estimate the internal particle viscosity. In the present work, 1 of the carboxylated polystyrene seed latexes used for the morphological studies reported on previously¹⁹ was swelled with isoprene at 80°C. The isoprene vapor pressure was continuously recorded, and the partitioning of the isoprene was calculated.

THEORY

Saturation swelling of latex particles by a monomer having limited solubility in the aqueous phase has been studied by Morton, Kaizerman, and Altier.¹ When the swollen latex particle is in equilibrium with the free monomer phase, the partial molar free energy of the monomer can be expressed as

$$\Delta F_1 = \Delta F_{m1} + \Delta F_t \quad (1)$$

where ΔF_1 is the partial molar free energy of the monomer, ΔF_{m1} is the osmotic contribution, and ΔF_t is the contribution from the particle-water interfacial energy. At swelling equilibrium, ΔF_1 is zero, and the resulting expression is the so-called Morton-Kaizerman-Altier equation,¹ as follows:

$$\frac{2V_M\gamma}{RTr} = - \left[\ln(1 - v_P) + v_P \cdot \left(1 - \frac{1}{\bar{M}_n} \right) + \chi v_P^2 \right] \quad (2)$$

where γ is the value of the interfacial energy at swelling equilibrium, r is the particle radius at swelling equilibrium, V_m is the partial molar volume of the monomer, v_P is the volume fraction of polymer in the latex particles, \bar{M}_n is the number-average degree of polymerization, R is the gas constant, T is the temperature, and χ is the Flory-Huggins interaction parameter.²⁴ Morton and coworkers found that the amount of monomer in the swollen latex particles at equilibrium was a direct function of the particle diameter and an inverse function of the interfacial energy at the surface of the particles. Above 100,000, the molecular weight of the polymer had no effect on the equilibrium swelling. The swelling experiments were carried out in the presence of excess surfactant. When the authors lowered the concentration of the surfactant, the amount monomer taken up by the latex particles decreased, and this was explained by an increase in the particle-water interfacial energy in the absence of surfactant. The amount of surfactant used in the investigation was above the critical micelle concentration (CMC), and it seems likely that there were micelles present, which then would absorb monomer. Nilsson et al.⁸ obtained results, which indicated that monomer partitioning was affected by

the amount of emulsifier present with surfactant concentrations below the CMC. On the other hand, Maxwell et al.²⁵ noted no effects of surfactant at different concentrations below the CMC on the monomer partitioning in swelling experiments on methyl acrylate.

In the swelling of latex particles in emulsion polymerization, the monomer is assumed to have a limited solubility in water, and the aqueous phase should become saturated with monomer. Even if the monomer is a good solvent for the polymer and is miscible with the polymer at any ratio in bulk, only a limited amount of monomer will be absorbed by the latex particles as the surface free energy increases upon swelling partially compensates for the free energy of mixing; that is, the osmotic driving force is limited by the interfacial tension at the polymer–water interface. Since common monomers have a considerable interfacial tension relative to water, the total restraining force increases as the particle becomes swollen and as polymerization causes an increase in the particle radius. At some point, the forces balance each other, and equilibrium swelling will be attained. In an emulsion system, the presence of emulsifier greatly decreases the interfacial tension and allows a substantial amount of swelling. Antonietti, Kaspar, and Tauer¹⁸ showed that for polystyrene latex particles in the size range of $15 \text{ nm} < r < 100 \text{ nm}$, having different types of covalently bound stabilizing groups, the toluene swelling ratio in the absence of emulsifier was considerably lower than predicted by equation (2). Furthermore, they observed a pronounced dependence of the swelling ratio on particle size and also that charge stabilization resulted in higher swelling ratios and significantly lower values for the interfacial energy than with steric stabilization. The authors also reported that even at small particle sizes, neither moderate crosslinking, nor different molecular weights had any effect on the swelling ratio. Similar results were obtained by Maxwell et al.⁶ Other authors have reported effects of crosslinking on particle swelling^{2,26,27} and have included an elastic energy term in the expression for the Gibbs free energy to account for elastic deformation during swelling and the crosslinking density.

In the absence of monomer droplets, the latex particles are not saturated by monomer, and Vanzo et al.⁷ showed that the partial molar energy is given by

$$\Delta F = RT \ln a \quad (3)$$

where a is the activity of the monomer. The monomer activity can be approximated by the ratio p/p_0 ,⁷ where p is the vapor pressure of the monomer at a given volume fraction of polymer, and p_0 is the vapor pressure at saturation swelling. For partial swelling of latex particles by monomers and solvents, p can be related to the volume fraction of polymer in the latex particles, v_P , via the following so-called Vanzo equation:⁷

$$\ln(1 - v_P) + v_P \cdot \left(1 - \frac{1}{M_n}\right) + \chi v_P^2 + \frac{2V_M \gamma}{RT r} = \ln\left(\frac{p}{p_0}\right) \quad (4)$$

Maxwell and coworkers⁶ used the approximation that p/p_0 can be replaced by the ratio of aqueous phase solubilities of the monomer below and at saturation, as follows:

$$\frac{p}{p_0} = \frac{[M]_{\text{aq}}}{[M]_{\text{aq,sat}}} \quad (5)$$

where $[M]_{\text{aq}}$ is the concentration of monomer in the aqueous phase, and $[M]_{\text{aq,sat}}$ the saturation concentration of monomer in the aqueous phase. They found that for partial swelling of methyl acrylate and poly(methyl acrylate-co-styrene) systems in the presence of emulsifier, the monomer partitioning was insensitive to temperature, polymer composition, and even latex particle radius. Their results also indicated that at higher values of v_P the conformational entropy of mixing for the monomer and the polymer will determine the degree of latex particle swelling by the monomer. They introduced an empirical approach to estimate the value of the sum of the residual free energy and the particle–water interfacial free energy terms in the Vanzo equation from the saturation swelling volume fraction of the polymer. On the basis of the Morton–Kaizermann–Altier equation, they calculated a correction term, as follows:

$$\text{corr} = - [\ln(1 - v_{P,\text{sat}}) + v_{P,\text{sat}}] \quad (6)$$

where $v_{P,\text{sat}}$ is the volume fraction of polymer in the latex particles at saturation swelling due to the monomer. This correction term was then used in the Vanzo equation (4), as follows:

$$\ln(1 - v_p) + v_p + \text{corr} = \ln\left(\frac{[M]_{\text{aq}}}{[M]_{\text{aq,sat}}}\right) \quad (7)$$

In using this equation, some assumptions were made. Firstly, the effect of polymer molecular weight upon the partial molar free energy of mixing of the monomer and the polymer was ignored. Secondly, the interfacial free energy and the residual free energy terms were, as pointed out by the authors, incorrectly assumed to be independent of the volume fraction of polymer. However, these terms were considered to be small compared with the conformational entropy term. Using equation (7), Maxwell and coworkers obtained satisfactory results for the MA–poly(methyl acrylate-*co*-styrene) system.

In the present study, the Maxwell approach described above has been applied to the isoprene-poly(styrene-*co*-methacrylic acid) system. Instead of measuring the monomer concentration in the aqueous phase, as was done by Maxwell et al., we measured the partial isoprene pressure, as originally suggested by Vanzo⁷; therefore, the term $\ln\left(\frac{[M]_{\text{aq}}}{[M]_{\text{aq,sat}}}\right)$ in equation (7) was replaced by the term $\ln\left(\frac{p}{p_0}\right)$, as in equation (8) below.

$$\ln(1 - v_p) + v_p + \text{corr} = \ln\left(\frac{p}{p_0}\right) \quad (8)$$

Apart from this, the same assumptions as above were made.

EXPERIMENTAL

Seed Latex Polymerization

Styrene (S) (Merck, Germany, pro analysi) and methacrylic acid (MAA) (Merck, Germany, pro analysi) were purified by passing them through a column filled with aluminium oxide (Merck, active base). The purified monomers were stored at 8°C until use. All other chemicals were of analytical grade and used as supplied. Distilled, deionized water was used. The seed latex was prepared through batch copolymerization of S and 2 wt % MAA using potassium persulphate (KPS) as the initiator and sodium dodecyl sulphate (SDS) as the emulsifier. The SDS concentration was 2 g L⁻¹. Further details on the seed preparation are given elsewhere.¹⁹ The surface mean diameter,

D_s , of the seed latex particles was determined to 74 nm from transmission electron microscopy (TEM) micrographs.²⁸ The solid content of the latex was 20.0 wt %.

Swelling Experiments

The swelling experiments were carried out in a 200-mL Chemisens (Lund, Sweden) RM2 calorimetric reactor designed for pressures up to 25 bar. The reactor temperature and pressure were continuously monitored. The reactor temperature did not deviate by more than $\pm 0.05^\circ\text{C}$ from 80.0°C during the experiments. A WIKA Tronic 891.13.530 piezoelectric pressure transducer, with an accuracy of 0.005 bar absolute pressure, was used. The reactor lid was equipped with a heater, which kept the lid at a temperature slightly above the reactor temperature in order to avoid condensation of isoprene on any surfaces in contact with the vapor phase.

In the experiments, 100.0 g of the PS seed were weighed and added to the reactor. To prevent polymerization during the swelling experiments, 0.1 g 4-methoxyphenol (Aldrich-Chemie, Germany) was added to 20 g of the isoprene (Janssen Chimica, Belgium), which already contained 100 ppm 4-*tert*-butylcatechol as an inhibitor. In order to remove dissolved gases, the isoprene and the reactor contents were repeatedly purged with nitrogen and degassed at room temperature. The reactor temperature was then raised to 80°C. The measurements started at a slightly reduced pressure in the reactor, which was set as the zero level. Isoprene was added through an inlet valve in the reactor lid in small portions (0.1–0.3 g) by means of a syringe.

Second-Stage Polymerization

Isoprene was polymerized in a seeded batch process using the same reactor equipment as in the swelling experiments. The isoprene (Merck, pro analysi) was purified by passing it through a column filled with aluminium oxide (Merck, active base) and was stored at 8°C until use. In order to remove dissolved gases, the isoprene, the initiator solution, and the seed latex were repeatedly degassed at room temperature under vacuum and purged with nitrogen. 100.0 g of the PS seed were added to the reactor. The reactor was evacuated, and 20.0 g of isoprene was added from a pressurized vessel. After 1 h at room temperature, with stirring, the reactor temperature was raised to

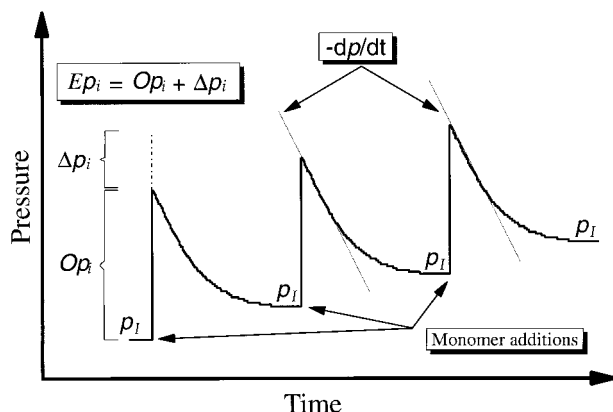


Figure 1 The pressure response after monomer additions.

80°C, and the calorimeter was calibrated. The reaction was started by injecting a KPS solution through a membrane at the inlet valve by means of a syringe. The KPS concentration was $2.5 \times 10^{-3} \text{ mol L}^{-1}$ based on the aqueous phase, and no emulsifier was added. The isoprene vapor pressure and the instantaneous heat of polymerization were continuously measured and used for calculation of the conversion and the polymerization rate.

RESULTS AND DISCUSSION

Swelling of a carboxylated polystyrene latex by isoprene was studied under conditions similar to those used in the seeded emulsion polymerization reported on previously.¹⁹ The swelling experiments were carried out in order to relate the observed latex particle morphologies to changes in the internal particle viscosity during polymerization and phase separation. The experiments were performed in a calorimetric reactor equipped with a pressure transducer, and 100 g of PS latex corresponding to 20 g of polymer were charged into the reactor. The void volume in the reactor was initially approximately 150 mL.

Figure 1 shows typical pressure responses after an injection of isoprene into the reactor. The expected pressure increment, $E p_i$, corresponds to the pressure that would be obtained if no isoprene had been absorbed in the liquid phase. The difference, Δp_i , between $E p_i$ upon monomer addition and the observed pressure increment, $O p_i$, is a measure of the fraction of the added isoprene, which rapidly entered the aqueous phase in the

reactor, either entering the particles, causing them to swell, or forming monomer droplets. The rate of absorption of monomer into the seed particles was calculated from the initial rate of pressure reduction, $-\frac{dp}{dt}$, observed in the reactor after each monomer addition (see Fig. 1). The increase in the particle surface area due to swelling and the decreasing gas phase volume due to the increasing liquid volume in the reactor were taken into account in the calculations. The equilibrium vapor pressure of isoprene, p_I , at a given volume fraction of monomer (or polymer) in the particles, was determined as the limiting pressure obtained when no further pressure reduction occurred, approximately 2 h after a monomer injection. The presented values of p_I are corrected for the initial pressure in the reactor.

The results obtained from the swelling of carboxylated PS latex with isoprene at 80°C are shown in Figure 2. The isoprene equilibrium pressure, p_I , is plotted in the figure both as a function of the total amount of isoprene charged (filled circles) and as a function of the amount of isoprene absorbed into the latex particles (diamonds). The first injections of isoprene saturated the gas phase and aqueous phase with monomer. This can be seen as the initially steep increase in p_I at charge levels lower than 0.6 g isoprene. After the first few monomer additions, the 2 curves in the figure differed in their slopes up to approximately 3.3 g total isoprene charged. The difference between the 2 curves represents the amount of monomer that has accumulated in the gas phase, approximately 1.1 g at a charge level of

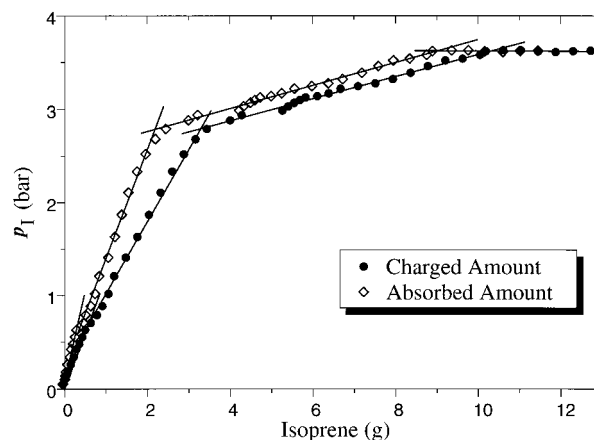


Figure 2 The isoprene vapor pressure, p_I , as a function of the charged amount isoprene (\diamond) and as a function of the absorbed amount isoprene (\bullet).

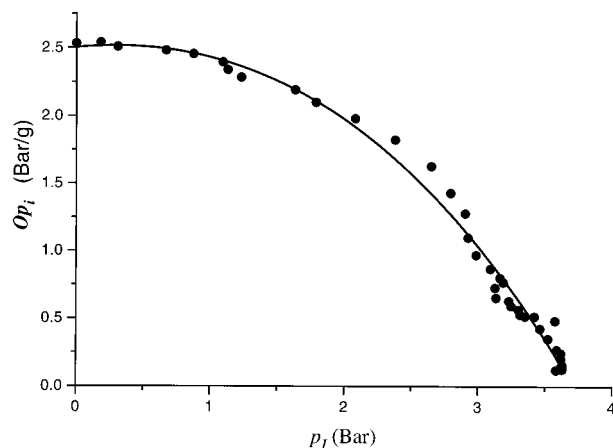


Figure 3 The observed pressure increment after a monomer addition, Op_i , as a function of the isoprene vapor pressure, p_I .

3.3 g. In the next interval, from 3.3 up to 10.3 g of charged monomer, an additional 0.25 g of isoprene accumulated in the gas phase, corresponding to an increase of 25 wt %. In the same interval p_I increased by 30%. The 2 curves were thus almost parallel in this interval, and, consequently, the main part of the absorption of monomer into the seed particles occurred here. At a charge level of approximately 10.3 g, no further increase in p_I was observed upon the addition of isoprene, and p_I settled at 3.68 bar, corresponding to a saturated gas phase at 80°C. The observed value is somewhat lower than the vapor pressure of 3.77 bar reported in the literature for pure isoprene at 80°C.²⁹

This experiment shows that a large fraction of the monomer can accumulate in the gas phase if the vapor pressure of the monomer is high at the polymerization temperature, especially under starved conditions in semicontinuous emulsion polymerization. Consequently, when calculating the monomer partitioning, the monomer fraction remaining in the gas phase must be considered. Provided pressure and conversion data are available, the concentration of monomer in the latex particles can be accurately calculated and, thereby, the internal particle viscosity. This will give further means of controlling the latex particle morphology.

Swelling Behavior

The observed pressure increment at 80°C, Op_i , is plotted as a function of p_I in Figure 3 (filled cir-

cles). During the first monomer injection, Op_i assumed high values due to monomer accumulation in the gas phase, but at increasing charge levels, Op_i decreased and approached zero when the monomer partial pressure, p_I , approached p_0 , that is, the saturation vapor pressure at 80°C. The Op_i data were fitted to equation (9) by polynomial regression, as follows:

$$Op_i = 2.504 + 0.0894p_I - 0.1423p_I^2 - 0.0170p_I^3 \quad (9)$$

This is represented by the line in Figure 3. Solving equation (9) for p_I at $Op_i = 0$ gives a value of p_0 corresponding to 3.72 bar, which is in fair agreement with the experimental value of 3.68 bar and the literature value²⁹ of 3.77 bar.

The swelling of the PS seed particles can be visualized as in Figure 4, where the value of Op_i is plotted as a function of the volume fraction of polymer, v_p , in the swollen latex particles. The volume fraction was calculated from pressure and sorption data. The curve clearly shows 3 different slopes, and the swelling process can consequently be divided into 3 domains, 1, 2, and 3. Monomer addition starts in domain 1 at $v_p = 1.00$. The aqueous phase is saturated after the first monomer injections, and the particles will start to absorb the monomer. The pressure increment after each monomer injection is large due to slow absorption, and most of the added monomer accumulates in the gas phase.

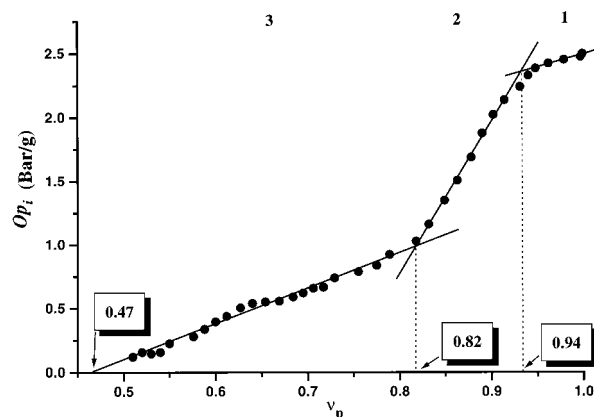


Figure 4 The observed pressure increment after a monomer addition, Op_i , as a function of the volume fraction of polymer in the latex particles, v_p (experimental data, ●; —, linear approximations). Domains 1, 2, and 3 are indicated by dotted lines.

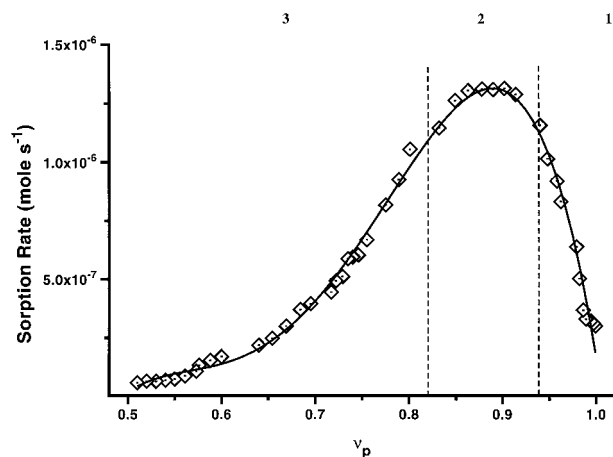


Figure 5 The sorption rate of isoprene into the seed polymer as a function of the volume fraction of polymer in the latex particles, v_p . Domains 1, 2, and 3 are indicated by dotted lines.

In domain 2, beginning at $v_p = 0.94$, the glass transition temperature of the polystyrene particles has decreased to 80°C due to the plasticizing effect of the absorbed monomer. The monomer can now diffuse freely in the particles, and there is a large entropy contribution from the polymer to the free energy of mixing. The steep decrease in the slope of the Opi curve in Figure 4 corresponds to the rapidly increasing segmental mobility of the polymer and decreasing internal particle viscosity. However, no gross movements of polymer molecules are possible.

At $v_p = 0.82$, domain 3 is reached, and a low internal viscosity now allows polymer molecules to diffuse in the particles. A polymer solution will form in the particles on further addition of monomer. The concentrated solution phase will continue to absorb, but the slope of the Opi curve becomes less steep as the monomer activity in the particles is slowly approaching that of the pure monomer, as the solution is diluted. The internal particle viscosity will further decrease until the equilibrium concentration of monomer in the latex particles at 80°C is reached, at $v_p = 0.47$. If more monomer is added after this point, monomer droplets will start to form in the aqueous phase and no more swelling of the particles will occur.

Sorption Rate

The swelling process may also be described by the rate of sorption of monomer. Figure 5 shows the rate of sorption of isoprene into the seed particles

as a function of the volume fraction of polymer, v_p . The 3 domains described above are indicated in the figure. The sorption rate was calculated from the rate of pressure reduction, $\frac{dp}{dt}$, after each monomer injection (see Fig. 1).

Many steps are involved in the sorption process. Gaseous isoprene will first dissolve into the aqueous phase and condense into droplets. The monomer will diffuse through the aqueous phase into the polymer particles. Finally, the isoprene will adsorb onto and diffuse into the seed particles. The absorption process is probably affected by a surface layer on the particles consisting of methacrylic acid (MAA) copolymers and adsorbed surfactants.²⁸ The rates of the separate events are not known for the present system and are not explicitly included in the discussion. However, a qualitative evaluation of the sorption process may be possible if the swelling of the seed polymer is assumed to be rate-determining, and all other rates are considered to be constant during the swelling process.

At 20°C , the solubility of isoprene is 0.055 g per 100 g water.³⁰ After the first monomer injection, the aqueous phase is saturated, as noted above. On further injections, only a small fraction of the monomer will dissolve in the aqueous phase due to the pressure increase. The major proportion will remain in the gas phase or dissolve into the particles.

Initially, the absorption of isoprene into the polymer particles will be restricted, as can be seen in Figure 5, by the low molecular mobility of the polymer, which is in the glassy state.³¹⁻³³ In domain 1, the sorption rate increases significantly and passes through a maximum in domain 2, corresponding to the sharp drop observed in the pressure increase, as discussed previously (Fig. 4). The sorption rate maximum can be explained by the decrease in T_g of the seed polymer due to the plasticizing effect of the monomer, leading to a significant increase in the diffusion rate of the isoprene in the particles.³¹⁻³³ Furthermore, the latex particles still have a relatively low isoprene concentration, and this, in turn, will result in a large entropic driving force for the absorption of more monomer.

The higher isoprene concentration in the seed particles in domain 3 leads to a slowly decreasing entropic driving force for the sorption of monomer into the particles, and the rate will consequently slowly decrease. Close to equilibrium swelling, the sorption rate decreases towards zero, and a

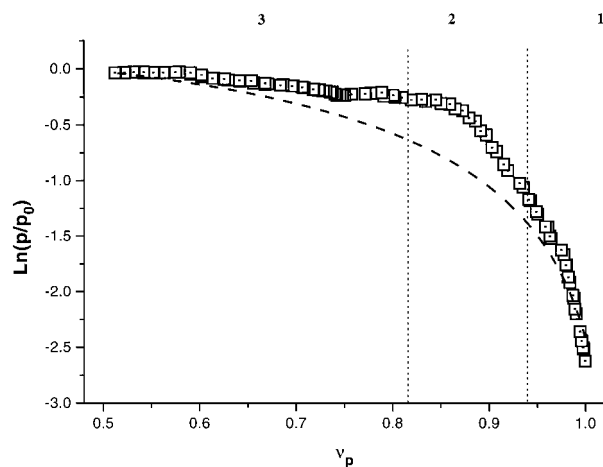


Figure 6 Comparison of theoretical predictions using equation (8) (dashed line) and experimental data (\square). Domains 1, 2, and 3 are indicated by dotted lines.

separate liquid monomer phase will eventually form.

The Estimated Vanzo Equation

The use of the Vanzo equation [eq. (4)] to calculate the monomer partitioning between the different phases in the system requires that both the interaction parameter, χ , and the particle–water interfacial tension, γ , be known. Both these parameters are probably volume-dependent and would be difficult to determine by independent experiments.⁶ An empirical approach to estimating the monomer partitioning by equation (7) has been presented by Maxwell et al.^{6,25} To describe the swelling of the poly(styrene-*co*-methacrylic acid) latex by isoprene in the present study, the Vanzo equation was used in the form it is presented in equation (8). In Figure 6, $\ln(p_I/p_0)$ is plotted versus v_p ; and, as can be seen from the figure, there is fair agreement between the values calculated from equation (8) and the actual values at high and low values of v_p . In the region of the diagram that corresponds to domain 2, above, there is a considerable mismatch between the estimated and the experimental data. In this domain, the monomer activity, expressed as p_I/p_0 , was notably higher than that predicted by equation (8). The reason for the deviation is unclear, but it may be a consequence of the rapidly increasing molecular mobility in this region, as a result of the glass transition. Other studies have for some combinations of polymers and swelling monomers obtained results in agreement with

equation (8), but for monomers having large interactions with the polymer, the observed monomer activity was higher than predicted by equation (8).^{10,34}

Second-Stage Polymerization

In seeded emulsion polymerization, one can assume that the break points in the Op_i curve in Figure 4, $v_p = 0.47, 0.82$, and 0.94 , correspond to the onset of stage III, at which no free monomer droplets are present in the aqueous phase, the gel point, and the final conversion, respectively, according to the Smith–Ewart³⁵ terminology.

In order to verify this assumption, seeded emulsion polymerization was carried out under conditions analogous to those in the swelling experiments described above. The polymerization was carried out in a calorimetric reactor and repeated 3 times with identical results. The instantaneous heat of polymerization, R_p , was used as a measure of the rate of polymerization. In Figure 7, R_p is given as a function of time, together with the reactor pressure, p_I , and the conversion. Furthermore, it was assumed that a free monomer phase was present as long as the pressure was constant in the reactor and that the system was initially in equilibrium.

The development of R_p with pressure and polymerization time is difficult to explain. The monomer pressure, p_I , remained stationary until approximately 30% of the monomer had been consumed and then decreased steadily. This behavior indicates the presence of an initial free monomer phase. However, according to the results of the swelling experiments, the free monomer phase

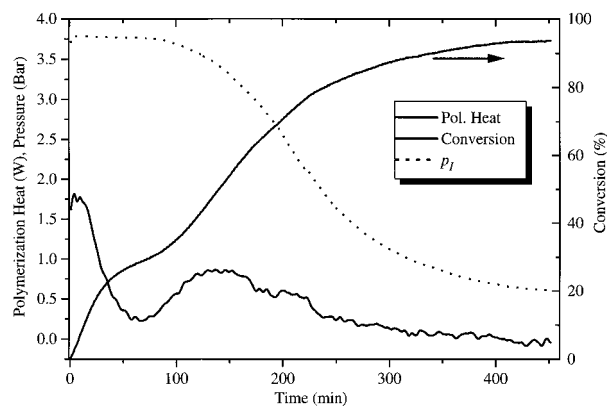


Figure 7 Results of emulsion polymerization in a calorimetric reactor. The left Y-axis corresponds to R_p and p_I . The right Y-axis corresponds to the conversion.

should only be present up to approximately 10% conversion. R_p showed an initial peak and then decreased steeply, reaching a minimum that coincided with the onset of the pressure drop. R_p then passed through a maximum, presumably due to the Tromsdorff effect, and slowly decreased towards zero. According to theory, R_p should have been more or less constant during the consumption of the free monomer phase. As can be seen in Figure 7, during the observed decrease in R_p the reactor pressure was constant, which led us to the conclusion that the monomer and the oligo radical diffusion into the particles may have been retarded due to, for example, the presence of a surface layer of adsorbed emulsifier and chemically anchored methacrylic acid copolymers²⁸ obstructing monomer absorption.^{13,36} A fraction of the monomer may also be solubilized in the layer of adsorbed emulsifier on the latex particles.⁸ The vapor pressure of this fraction should be close to the saturation pressure of isoprene.

Figure 8 shows a TEM micrograph of the latex particles after second-stage polymerization. The morphology is that of an occluded simplified hemisphere^{19,37} with the polystyrene seed phase forming a shell around the second-stage polyisoprene. The large polyisoprene domain present in the particles was presumably formed during the first part of the second stage of polymerization, when the viscosity was low enough to allow diffusion of polyisoprene molecules. During this period, the monomer concentration in the particles drops rapidly. From Figure 7, it can be deduced that the polymerization process then entered a region with diffusion-controlled termination, resulting in an increase in polymerization rate. The small occlusions seen in the particles were probably formed during this phase of polymerization as a result of a high internal viscosity due to a low monomer concentration in the particles. No diffusion of polymer would take place under these conditions, and crosslinking of the polyisoprene domains would further decrease the molecular mobility. The final conversion in the polymerization was 94%, which corresponds to $v_p = 0.96$ and $[M]_p = 0.36 \text{ mol} \cdot \text{L}^{-1}$. From the swelling experiments, $v_p = 0.94$ and $[M]_p = 0.55 \text{ mol} \cdot \text{L}^{-1}$ were predicted, but since the polyisoprene phase formed has a glass transition temperature well below 80°C, the final monomer concentration will be lower than that in the swelling experiments with the polystyrene latex.³⁸

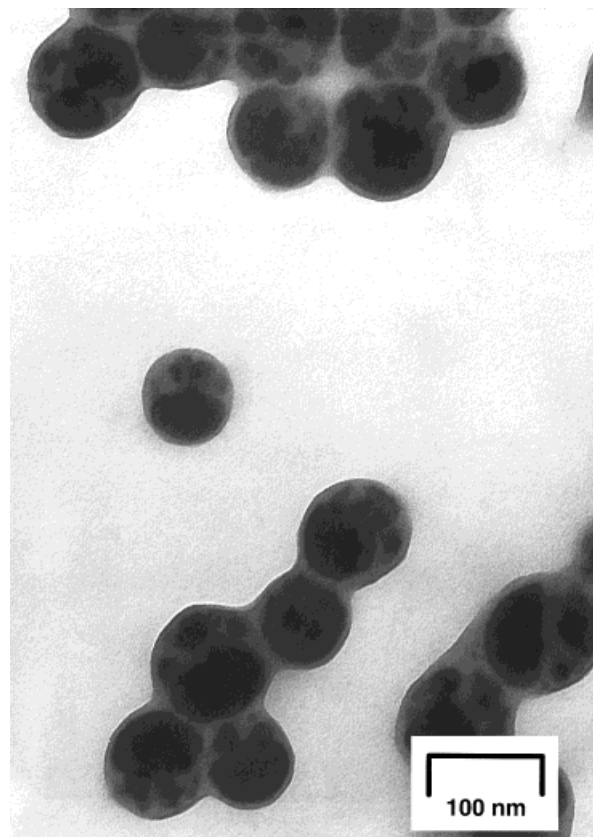


Figure 8 TEM micrograph showing the latex prepared in the emulsion polymerization process depicted in Figure 7. The dark phase domains are osmium-stained polyisoprene and the light phase domains are polystyrene.

Internal Particle Viscosity

The results of the swelling experiments show that different ratios between the second-stage monomer and the seed will lead to considerable differences in the internal particle viscosity during polymerization. For example, in two-stage batch emulsion polymerization with a second-stage monomer-to-seed ratio of 50 : 50, there may be a free monomer phase present in the second polymerization step up to 10–30% conversion. At a second-stage monomer-to-seed ratio of 72 : 28, that is, similar to the experiments reported previously,¹⁹ the free monomer phase would be present up to a second-stage conversion of approximately 50%. The monomer supply is thus abundant, and, consequently, the internal particle viscosity should be low. If the polymer produced has a low glass transition temperature, as in the present case, the internal particle viscosity in the end of the polymerization process will be lower

due to the higher molecular mobility of the soft polymer phase.^{31–33,38} For most of the second-step polymerization process, the diffusion of the polymer molecules will not be restricted. In the experiment with the 50 : 50 ratio between the second-stage monomer and the seed, most of the second polymerization step will take place without any free monomer being present, resulting in restricted polymer (and monomer) diffusion. It seems reasonable to assume that some of the differences in the particle morphologies observed in the previous study¹⁹ are related to the internal particle viscosity.

CONCLUSIONS

The observed pressure increment, Op_i , corresponding to an addition of monomer, plotted against the volume fraction polymer in the latex particles, v_p , gave a curve with 3 domains. At a low concentration of monomer in the particles, $[M]_p$, the value of the observed pressure increment, Op_i , was high and almost constant as the polymer temperature was above its glass transition temperature, T_g . A shift in the Op_i curve indicated that the plasticizing effect of the monomer at this particular $[M]_p$ was large enough to decrease the glass transition of the polymer particles to below 80°C, that is, the temperature of the experiment. Between the glass transition and the so-called gel point, corresponding to a region of limited segmental mobility, Op_i decreased significantly with decreasing v_p . The monomer acted as a plasticizer for the polymer with a substantial decrease in the internal particle viscosity, which was seen as a strong response in the Op_i curve upon each addition of monomer. The entropic gain of the seed polymer was large and contributed to a large driving force for the sorption of monomer in this domain, which was seen as a maximum in the sorption rate. On further addition of monomer, domain 3 was reached, which is the region between the gel point and the appearance of a free monomer phase in the aqueous phase. In this domain, the segmental mobility is high. The response of the Op_i curve was not as marked as in domain 2 because the plasticizing effect had decreased and the change in viscosity was not as dramatic as in domain 2. The sorption rate slowly decreased and became zero when the formation of a free monomer phase occurred.

The modified Vanzo equation predicted too high monomer concentrations in the polymer par-

ticles, especially in domain 2 in the Op_i curve, and could not be used in for prediction of monomer partitioning in the isoprene–poly(styrene-*co*-methacrylic acid) system with the pressure method.

Analogous emulsion polymerization experiments were performed to check the swelling experiments. The results of the polymerization experiments indicated a retarded monomer and oligo radical diffusion into the particles, due to the presence of monomer “adsolubilized” in a “hairy” layer consisting of poly(styrene-*co*-methacrylic acid) and adsorbed surfactants surrounding the particles.

The swelling study was initiated by questions arising from the particle morphology dependence on viscosity, and the results show that in the investigated system, seeded batch polymerization with second-stage monomer-to-seed ratios of 50 : 50 and 72 : 28, a free monomer phase could be present at levels of approximately 10 and 50% conversion, respectively. There will be a large difference in the internal particle viscosity during polymerization, in these 2 experiments, which, in turn, will significantly affect the latex particle morphology.

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NOMENCLATURE

ΔF_1	partial molar free energy of monomer (J mol ⁻¹)
ΔF_{m1}	osmotic contribution to ΔF_1 (J mol ⁻¹)
ΔF_t	particle–water interfacial energy (J mol ⁻¹)
$[M]_p$	monomer concentration in latex particles (mol L ⁻¹)
$[M]_{p,sat}$	monomer concentration in latex particles at saturation (mol L ⁻¹)
$[M]_{aq}$	monomer concentration in the aqueous phase (mol L ⁻¹)
$[M]_{aq,sat}$	monomer concentration in the aqueous phase at saturation (mol L ⁻¹)
v_p	volume fraction of polymer in the latex particles
$v_{p,sat}$	volume fraction of polymer in the latex particles at saturation
\bar{M}_n	number-average degree of polymerization
R	gas constant (J K ⁻¹ mol ⁻¹)
T	temperature (K)

χ	Flory–Huggins interaction parameter
r	particle radius at swelling equilibrium (m)
γ	particle–water interfacial tension (N m^{-1})
V_m	partial molar volume of the monomer (L mol^{-1})
D_s	surface mean diameter (m)
a	activity of the monomer
p	vapor pressure of the monomer at a given volume fraction of polymer (bar)
p_I	isoprene vapor pressure (bar)
p_0	vapor pressure at saturation swelling of the monomer (bar)
Ep_i	expected pressure increment after a monomer addition (bar)
Op_i	observed pressure increment after a monomer addition (bar)
Δp_i	difference between Ep_i and Op_i (bar). Gives the amount of added isoprene remaining in the liquid state after a monomer addition
R_p	polymerization heat (watt)

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