Emulsion Polymerization of Transparent Core−Shell Latices with a Polydivinylbenzene Styrene and Vinyl Acetate

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ABSTRACT: There is today a big need for polymeric material with well-defined nanostructures. Especially the field of transparent biomaterials is an intensively investigated area. The question if seeded emulsion polymerization of vinyl acetate (VAc) onto polydivinylbenzene (PDVB) seed latices is an appropriate way to obtain transparent latices with a core−shell structure is especially interesting because this material is very promising due to its unique properties as biocompatible optical material. It is shown that vinyl groups on the surface of the PDVB inhibited the conversion of seeded VAc polymerization due to unfavorable reactivity ratios of VAc and styrene (Sty) groups. The results show that covering the vinyl groups of the PDVB seed latex with a layer of polystyrene (PSty) is an option to overcome the inhibition and still obtain transparent latices. The polymerization of VAc onto double-layer PDVB/PSty seed latices could be run up to 100% conversion. Transmission electron microscopy (TEM) measurements in combination with RuO_4 and uranyl acetate staining are a reliable tool for investigating the core−shell morphology of the extremely small PDVB/PSty/PVAc multilayer latices obtained.

Introduction

The optimal combination of properties of two different polymers can often be better achieved with structured particles than by blending the polymers. The fields to which structured particles are especially applied are waterborne paints and coatings, adhesives, and impact modifiers, but high-value-added products are also included, for example in the area of biotechnology.[1,2] Seeded emulsion polymerization is a commonly used technique to synthesize structured morphologies. Various heterogeneous structures can be expected, but generally the particles formed are referred to as core−shell particles, implying that the seed polymer is in the center of the newly formed particle, which is covered by a shell of the polymer formed from the monomer that was added later. The design and morphology of structured particles are complex, and both kinetic and thermodynamic factors affect the formation of latex particles with a core−shell structure.[2,3] Secondary particle formation is generally not wanted in the synthesis of structured particles but often observed during the synthesis of core−shell particles.

Ferguson studied secondary particle formation in the polymerizations of VAc onto PSty seeds.[4] While extensive research had already been done on ways to avoid secondary particle formation in seeded emulsion polymerization,[6−10] Ferguson et al. developed an easy, accessible model of experimental conditions under which no secondary nucleation occurs in core−shell polymerizations, rather than a comprehensive model covering all eventualities of the system. Final comparisons of Ferguson's model with more extended models showed good agreement and sufficient accuracy for serving the purpose.

The predictions for the polymerization of VAc onto PSty seeds, which where also proven right experimentally, resulted in two major conclusions: (1) At constant solid content a decrease in the seed latex size increases particle number and particle surface, thereby drastically lowering the degree of new particle formation. With a larger seed particle number, the probability of the growing oligomer chain entering a seed latex increases. (2) Higher solid content results in a decrease in secondary particle formation. This effect is again associated with the increase in the number of seed particles, which the growing oligomer chains can enter.

Ferguson also applied his simulations and experiments on systems under starved-feed conditions. Starved-feed conditions result in a lower monomer concentration in the seeded emulsion polymerization system. It was predicted in that scenario that a low monomer concentration decreases the degree of undesired secondary nucleation in a seeded emulsion polymerization system. This effect can be attributed to the reduction of aqueous phase propagation when monomer addition is slower than the maximum rate of monomer consumption in a monomer-saturated system. The oligomers have more time to diffuse and enter a seed particle before they reach critical chain length and form a new particle. Thus, starved conditions result in less secondary particle nucleation.

To limit secondary nucleation and encourage core−shell formation in seeded emulsion polymerization, the following requirements must be met: (i) small seed latex particles (smaller particles supply a larger surface at the same solid content); (ii) high amounts of solid content (increased seed particle surface area); (iii) low surfactant concentration (to preserve formation of micelles); (iv) semicontinuous addition of monomers (starved-feed conditions to keep the monomer concentration low).

The model compares well with the system investigated within this research of VAc emulsion polymerization in the presence of PDVB seeds, since the structure of DVB is chemically similar to that of Sty.[5] With PDVB seed latex particles having a radius of 15 nm and solid content of around 10%, the results imply that secondary nucleation of PVAc is expected to occur only

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to an insignificant degree. The formation of core−shell polymer morphologies should be the predominant reaction. The formation of nanoscale core−shell latex particles with a densely cross-linked PDVB core supplying the material with stability and a hydrophilic biocompatible PVAc shell is especially in the field of biomaterials interesting because it allows a possible use inside the human body.

The aim of the work described was the synthesis of core−shell particles with a PDVB core and a PVAc shell. The control of the degree of VAc conversion by introducing an additional PSty layer between the PDVB and the PSty was a major part of the research. Also, the transparency of the obtained material and the analysis of the obtained latex structure were of great importance in the studies due to a possible use of the latex as biomaterial for optical devices.

Experimental Section

Characterization. A CHDF 2000 apparatus from Matec Applied Science was used to determine particle sizes. The CHDF eluent, ELUENT 1X, was used with a flow rate of 1.4 mL/min. Sodium benzoate was used as an internal marker. The average particle size by area was taken as the average particle size. To prevent blockage of the capillary, the latices were generally filtered through a 1 μm filter. The transmission measurements providing information on latex transparency were made on a Hewlett-Packard UV−vis diode array spectrophotometer (HP 8451 A) using a quartz cuvette of 1 cm optical path length. Measurements were performed at room temperature. Conversion was measured gravimetrically. Transmission electron microscopy (TEM) measurements were carried out at the Australian Key Centre for Microscopy and Microanalysis at the University of Sydney using a Phillips EM 499 instrument. Uranyl acetate negative staining was done by placing a drop of the sample in a 0.1% uranyl acetate solution. After 10 min a drop of the solution was placed on a TEM copper grid and allowed to dry. Some samples were stained with RuO_4 damps when placed in a special staining chamber over a RuO_4 solution at 40 °C for few minutes. Further details can be found in the literature.[5] For the cryo-TEM measurements, which were done at the Universiteit Maastricht, a TEM copper grid was dipped into the sample. Excess sample was blotted with filter paper. The film was vitrified in liquid ethylene and analyzed in a Phillips TEM (CM 12) at −170 °C.

Materials. DVB (industrial grade, 80%, Aldrich), Sty (99%, Merck), and VAc (99%, Aldrich) were used after being purified of inhibitor by passing them over a column filled with an inhibitor remover package (Aldrich). Sodium dodecyl sulfate (SDS, 96.0%, Fluka) and sodium peroxodisulfate (SPS, 99+%, Merck) were used as received. Deionized water was used in all experiments.

Sty Polymerization in the Presence of PDVB Seed Latices. A typical polymerization procedure was performed in a 300 mL double-walled glass reaction vessel with attached Teflon stirrer, reflux cooler, a gas inlet, and a peristaltic pump for the starved-feed monomer addition. First the vessel was fed with 4 g of SDS sealed and purged with argon for about 10 min. After that, 147 mL of water, which had been made oxygen-free by purging for about 20 min with argon, was added. The mixture was stirred at 400 rpm for 30 min at the reaction temperature of 60 °C to dissolve the surfactant under an argon atmosphere. Following this, 6 g of DVB monomer was added. The mixture was stirred for a further 45 min to allow the monomer to emulsify. After forming an emulsion, it was initiated with dissolved radical initiator, typically 0.3 g of SPS in 3 mL of water, and allowed to polymerize for 45 min. Then 6 g of Sty was added under starved-feed conditions at a rate of 0.05 mL/min. After the addition of Sty was completed the mixture was allowed to react for 2 h.

VAc Polymerization in the Presence of PDVB Seeds or PDVB−PSty Core−Shell Seeds. A typical polymerization procedure was performed in a 300 mL double-walled glass reaction vessel with attached Teflon stirrer, reflux cooler, gas inlet, and a peristaltic pump for the starved-feed monomer addition. First the vessel was fed with seed latex, typically 120 g. It was then sealed and purged with argon for 30 min at 60 °C and 300 rpm. The initiator SPS, typically 0.2 g dissolved in 4 mL of water, was added, and then the semicontinuous addition of the shell monomer VAc, typically 5 mL, was started, usually at a feeding rate of 0.03 mL/min. After the total amount of monomer was added, the mixture was allowed to react for up to 5 h.

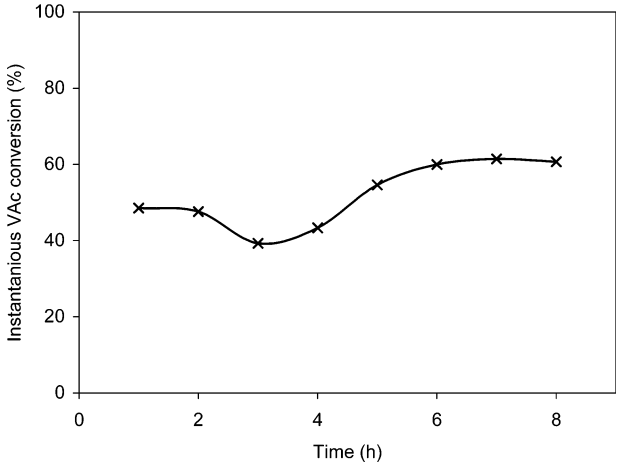

Figure 1. Conversion as a function of time of a seeded emulsion polymerization of VAc on DVB latex under starved-feed conditions at an addition rate of 0.03 mL/min.

Results and Discussion

Emulsion Polymerization of VAc on PDVB Seeds. The starting point of the experiments was the seeded emulsion polymerization of VAc in the presence of PDVB. Since the chemical structures of DVB and Sty are similar, VAc emulsion polymerization on PSty seeds or PDVB seeds was expected to behave in a comparable manner. PDVB latex was chosen with the smallest particle size in relation to a high solid content and a low surfactant concentration as a seed.[11] The PDVB latex used was stabilized with 1.7% methacrylic acid (MAA) and had an average particle size of around 26 nm and a solid content of 8%. Preliminary surfactant titration surface tension measurements and conductivity measurements determined whether the surfactant concentration of the latex was under the cmc or whether the latex had to be dialyzed before core−shell polymerization.

Polymerizing one part VAc under starved-feed conditions relative to 2.5 parts PDVB seed latex resulted in around 60% conversion. Repetition of the experiments gave the same results.

Figure 1 shows the conversion as a function of time for the seeded VAc emulsion polymerization in the presence of PDVB. The addition of monomer ended after 3 h. It can be seen that the reaction stopped at 60% conversion after ~6 h. Under starved-feed conditions the instantaneous conversion was still around 50%, which means that no complete instantaneous conversion of monomer was occurring; thus inhibition was taking place.

To exclude any systematic error, the same reaction process was performed in the presence of PSty and 100% conversion of the VAc was obtained. Additional seeded polymerizations of VAc in the presence of PDVB varying reaction temperature, seed stabilization, seed solid

content, surfactant concentration in the seed, initiator, stirring speed, monomer feeding rate, and amount of monomer and buffering of the system did not lead to higher conversions.

To understand the inhibition of the VAc emulsion polymerization on PDVB seeds, the inhibiting effect of Sty in VAc polymerization was considered, since DVB is chemically similar to Sty.

The copolymer reactivity ratios r_1 and r_2 show the inclination of the two monomers to copolymerize. For the Sty (M_1) and VAc (M_2) system it was found that $r_1 = 56$ and $r_2 = 0.01$ at 60 °C, which indicates that the copolymerization of Sty and VAc is very unfavorable.[12] The propagating chain with a VAc end group is very active when adding Sty. However, the affinity of a propagating Sty radical to VAc is very low, which indicates that the reaction will be practically inhibited.[13] The PDVB seed in our polymerization system can be considered as latex particles with reactive Sty bound at its surface, which explains the inhibition in the seeded emulsion polymerization of VAc in the presence of PDVB seeds.

The reason why VAc can nonetheless be polymerized up to a conversion of 60% is probably because VAc is moderately water-soluble. The initiation of the VAc polymerization starts in the water phase before the VAc oligomers enter the seed particle. Because the initiator continuously forms radicals in the aqueous phase, where VAc is present, the conversion increases. After a certain amount of PVAc has been adsorbed by the seed particles, a PVAc shell is formed that swells with monomer and drastically reduces the monomer concentration in the aqueous phase. Since no propagation occurs in the polymeric phase and monomer concentration in the aqueous phase is decreased, the reaction stops at ~60% conversion.

Emulsion Polymerization of Sty in the Presence of PDVB. A possible way to solve the problem of inhibition in the seeded emulsion polymerization of VAc onto PDVB seed latex is the formation of a multilayer structure. As previously described, seeded emulsion polymerization of VAc in the presence of PSty can result in up to 100% conversion. Because of the fact that no transparent latex can be obtained in the emulsion polymerization of Sty, the idea was to polymerize a PSty layer onto the small, transparent PDVB latex particles in order to cover all inhibiting vinyl bonds of PDVB with PSty. Because of its structural similarity with DVB, it should be possible to polymerize a PSty shell onto PDVB seeds.

Sheu et al. prepared core−shell latices by seeded emulsion polymerization of Sty onto PSty latices that had previously been cross-linked with amounts of DVB varying from 0.1 to 6%.[14,15] Their experiments were performed with rather large monodisperse PSty latices with a particle size of 5.2 μm that were cross-linked with DVB. The cross-linked latices were then swollen with shell polymer (Sty) and polymerized in a batch process. The resulting latex particle structures were investigated with scanning electron microscopy (SEM). Sheu et al. were able to show that with an increasing degree of cross-linking in the seed latex the shell structure changed. Sty formed a homogeneous shell onto un-cross-linked PSty seed. The morphology of the shell changed to a snowman structure when PSty seed was cross-linked with around 0.2% DVB. At 6% added DVB the shape of the shell changed into a kind of raspberry

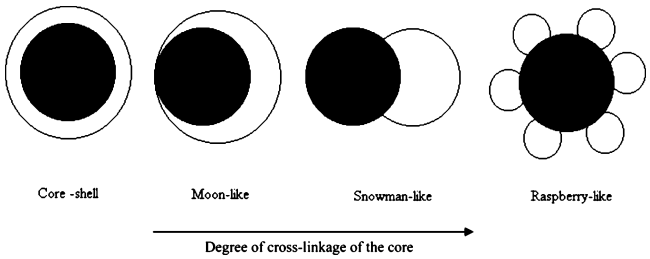

Figure 2. Schematic drawings of core−shell structures of PDVB/PSty latices with increasing cross-linking of the core latex following Sheu et al.[14,15]

structure. Figure 2 shows this trend in core−shell morphologies, as observed by Sheu et al.

Tests showed that best results for the synthesis of the PDVB/PSty core−shell structure formation were obtained in a one-pot reaction where Sty was added before 100% conversion of the DVB, and the polymerization was carried out at low PDVB seed concentrations (4%) under starved-feed Sty addition. The starved-feed addition might prevent secondary nucleation of PSty, but it also lowers the risk of structured raspberry-type shell formations. All reactions could be run up to 100% conversion. Table 1 gives the results for the polymerization of various amounts of Sty onto PDVB seeds.

Figure 3 shows the conversion/time and diameter/time history of a seeded emulsion polymerization of 2 parts Sty onto 1 part PDVB seed latex with a solid content of 4%. The conversion is related to both monomers DVB and Sty because Sty was added before the conversion of DVB was complete. The Sty addition finished after 7 h.

TEM and cryo-TEM measurements show spherical core−shell particle morphologies. Because of resolution limits of TEM and cryo-TEM with respect to the small sized latex particles, and because of the shape of the PDVB seeds, an absolute statement about structure is not possible. The expectation that the formation of secondary nucleated PSty particles will be very low is supported by results shown in Table 1. The seeded emulsion polymerization of Sty in the presence of PDVB seed led to the formation of transparent latices with a small particle size. CHDF measurements indicated that polymerization of 1 part Sty onto 1 part PDVB latex led to a measured growth of seed particles of only 2 nm to an average particle size of 28.5 nm, whereas a size of 33 nm would be expected. The latex obtained was transparent. To check whether secondary PSty polymerization occurred, the same amount of Sty was starved-fed and polymerized in an additional experiment without seed latex, at higher free surfactant concentrations than present in the seeded polymerization (0.1 mol/L). The latex obtained was opaque and had an average particle size of 37.3 nm. Previous experiments indicated that even small amounts of larger sized particles led to a drastic increase in the opaqueness of the latex.[11] This was not seen in the seeded emulsion polymerization of Sty onto PDVB latices.

The fact that the particle sizes obtained for the core−shell latices are smaller than expected may have two causes. The first one is the limitations of the measurement techniques. Because of the fact that we measure CHDF close to the lower cutoff value and the possible presence of not spherical morphologies, CHDF measurements may give particle sizes that are too low for the core−shell particles. The other cause may be that secondary nucleation occurred, and rather small sec-

Table 1. Sty Amounts Relative to PDVB Seed, Particle Size, and Transmissions of the Unfiltered and Filtered PDVB/PSty Core−Shell Latices

Sty relative to PDVB (wt %)	particle size (nm)	transmission unfiltered latex (%)			transmission filtered latex (%)		
		450 nm	550 nm	650 nm	450 nm	550 nm	650 nm
0	26.7	63.7	82.9	90.8	69.8	87.2	93.7
33	27.2	63.1	83.0	91.1	65.1	84.7	92.5
67	27.8	57.5	79.0	88.7	57.7	81.1	90.8
100	28.5	36.4	66.0	81.0	57.1	79.8	89.5
133	28.5	36.5	66.6	82.0	37.4	67.5	82.8
167	28.8	21.0	52.7	72.3	21.0	53.2	73.4

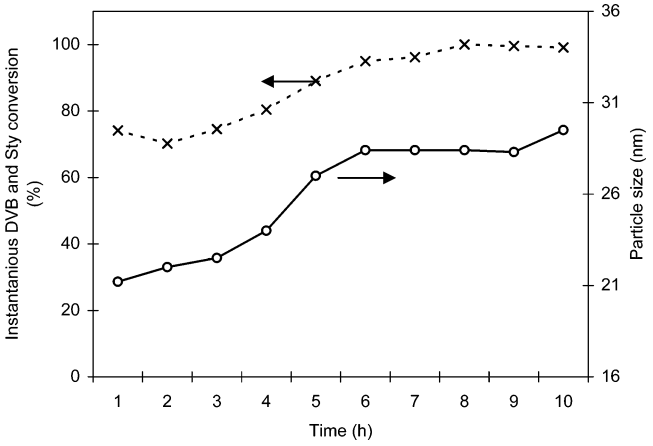

Figure 3. Conversion and particle size as a function of time of a seeded emulsion polymerization of Sty onto PDVB seed latices with a solid content of 4%.

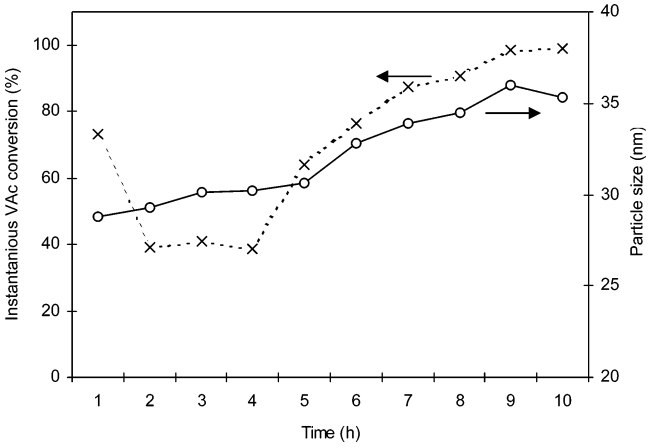

Figure 4. Conversion and particle size as a function of time of seeded emulsion polymerization of VAc onto PDVB/PSty core−shell seed latices with a solid content of 12%.

ondary PSty latices were created. Homopolymerization of Sty resulted in rather large particle sized, opaque latices. Since the seeded emulsions resulted in transparent latices, a low amount of secondary PSty particles was expected.

In summary, it can be concluded that seeded emulsion polymerization of Sty in the presence of PDVB latex was successful. The latices obtained remained transparent even when high amounts of Sty were polymerized onto PDVB seeds.

Emulsion Polymerization of VAc in the Presence of PDVB/PSty Core−Shell Seeds. Experiments were carried out on seeded emulsion polymerization of VAc onto PDVB/PSty core−shell seed latices, to see whether polymerization of Sty onto the PDVB seed latices would cover the vinyl bonds of PDVB, which is believed to be the reason for inhibition in the VAc shell polymerization onto PDVB seeds.

Figure 4 shows the conversion/time and diameter/time history of the seeded emulsion polymerization of 2 parts VAc onto 3 parts PDVB/PSty core−shell seed latex with a solid content of 12%. The VAc addition ended after 5 h. It can be seen in Figure 4 that, in contrast to shell polymerization of VAc on PDVB, conversion of VAc could be run up to 100% when the PDVB was sufficiently covered with PSty. The latex particle size increased simultaneously with the conversion.

As described, different amounts of Sty were polymerized onto the PDVB in order to see which amount afforded sufficient coverage of the PDVB vinyl groups with PSty. Figure 5 shows how the conversion of the seeded emulsion polymerization of VAc onto PDVB/PSty changes as coverage of PDVB with PSty increases. When in the seed latex the ratio between PSty and PDVB is 1:1, the conversion of VAc becomes nearly 100%. From this it can be concluded that at this degree of coverage sufficient or full coverage of the vinyl groups

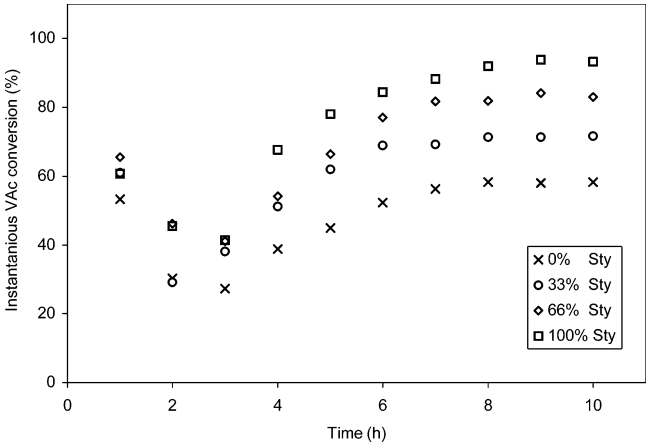

Figure 5. Conversion as a function of time of a seeded emulsion polymerization of VAc onto PDVB/PSty core−shell seed latices with PSty ratios relative to PDVB of 0%, 33%, 66%, and 100%.

on the surface of the PDVB latex particles has been obtained. Emulsions with seed latices containing less PSty showed variations in the VAc conversions, indicating that slightly different morphologies may have been formed when coverage of the PDVB vinyl groups was insufficient.

The addition of VAc to the polymerizations in Figure 5 was ended after 3 h. The particle sizes of the latices shown in Table 2 are qualitative rather than quantitative. Because of the "soft" character of PVAc, CHDF is not an ideal analytical tool for this type of latice, but one can see an increase in the particle size of the particles compared to the seed latex (Table 2). The latex particle sizes in Table 2 are probably not large enough for CHDF measurements to supply a sufficiently accurate estimation. The polymerizations in Figure 4, on the other hand, resulted in larger particle sizes, so a

Table 2. VAc Conversions, Particle Sizes, and Optical Transparencies of Latices Obtained after Seeded Emulsion Polymerization of VAc onto PDVB/PSty Seeds of Varying PSty Content

sty relative to PDVB (wt %)	particle size (nm)	conversion of VAc (%)	transmission unfiltered latex (%)			transmission filtered latex (%)		
			450 nm	550 nm	650 nm	450 nm	550 nm	650 nm
0	29.2	58	53.6	77.7	87.2	58.7	82.3	90.9
33	29.8	71	44.6	70.0	82.0	59.5	78.8	87.0
67	28.8	83	31.0	56.3	70.4	47.1	73.8	85.8
100	29.3	93	33.0	60.3	74.1	38.6	68.1	82.4
133	30.0	98	30.5	61.3	77.4	29.8	61.4	78.2
167	30.6	97	12.0	40.3	61.9	14.1	42.1	61.6

more accurate measurement could be made. Transmission of the latices obtained was still sufficient but decreased as conversion of the VAc and particle size increased. It is important to keep in mind that we did not stabilize the latices in addition to the surfactant initially present during polymerizations. Stabilization can increase the transparency of the latices.

In conclusion, the shielding of the vinyl groups on the surface of PDVB latex particles with PSty is an efficient tool of increasing the conversion of seeded emulsion polymerization of VAc onto PDVB/PSty core−shell seed latices. Particle size and transparency of the latices obtained remain sufficient for use as optically transparent material.

Analysis of the Core−Shell Latices with TEM and Cryo-TEM. TEM and cryo-TEM are powerful tools in the examination of latex morphologies. TEM investigations on the morphology of the obtained latices were performed at the University of Sydney, Australia, together with the team led by Professor R. Gilbert. The core−shell latices obtained were analyzed by using a special technique developed by Ferguson, which had proven to efficiently confirm core−shell morphologies of latices obtained by seeded emulsion polymerizations of VAc onto PSty seeds.[4,5]

For the TEM measurements PDVB/PSty/PVAc latex samples were stained for several minutes with RuO_4 fumes. RuO_4 is known to react with several functional groups, e.g., unsaturated hydrocarbons, ethers, and aromatics. Literature mentions that RuO_4 reacts with PSty (PDVB) but not with PVAc.[4,5] Therefore, treatment with RuO_4 provides a larger contrast for TEM measurements between PDVB/PSty areas (which reacts and darkens), on one hand, and PVAc, on the other. To enhance the contrast, uranyl acetate negative staining

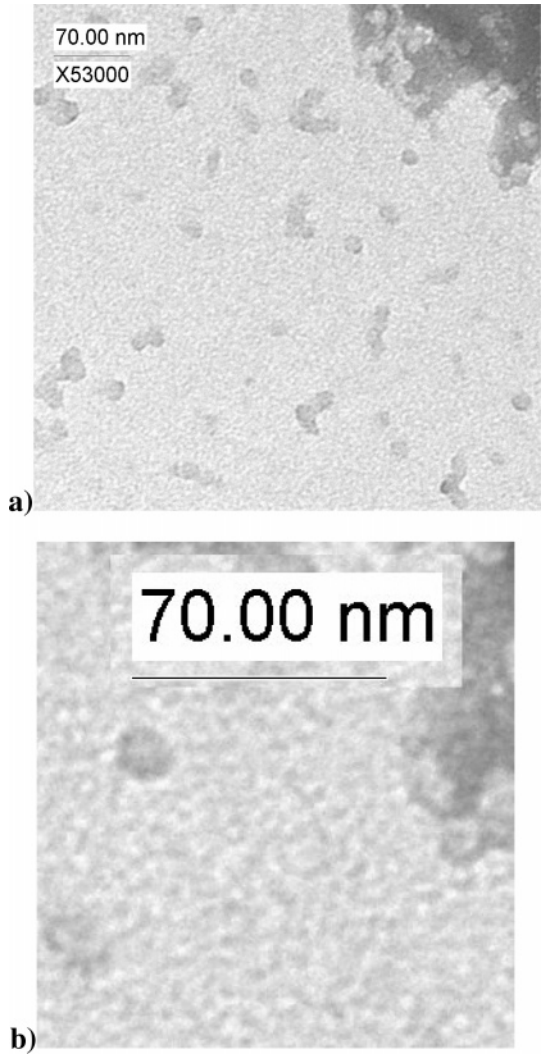

Figure 6. (a) TEM picture of RuO_4-stained PDVB/PSty seed latex particles. (b) A magnification.

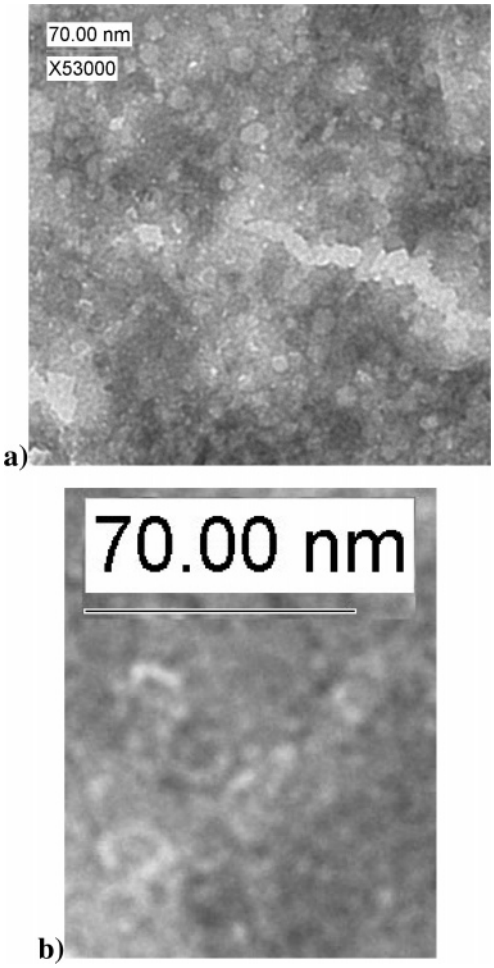

Figure 7. (a) TEM picture of RuO_4-stained PDVB/PSty/PVAc core−shell particles. (b) A magnification.

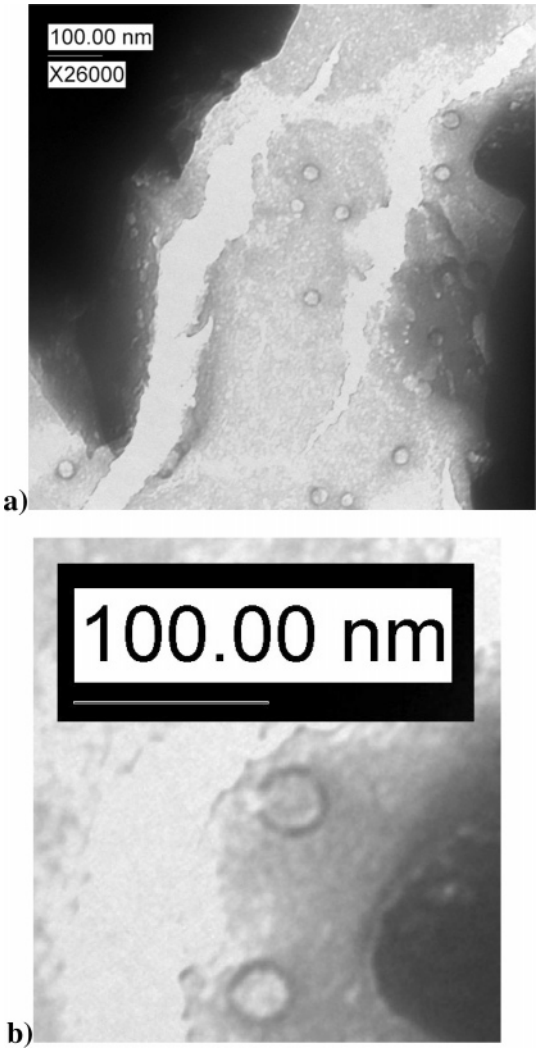

Figure 8. (a) TEM picture of RuO_4- and uranyl acetate-stained PDVB/PSty/PVAc core−shell particles. (b) A magnification.

was also performed on some samples. The electron dense uranium atoms have greater electron scattering than the polymer particles, and hence the area around the latex particle appears darker.

The main obstacle in the analysis was the resolution of the TEM optical system. The sizes of the PDVB/PSty/PVAc latex particles were at the lower resolution cutoff of value the TEM instrument used. Therefore, the results could not be used for quantitative measurements of the system. Nevertheless, the pictures could be analyzed qualitatively, and they showed much evidence that our particles have a core−shell structure. The TEM measurements showed no evidence of secondary nucleation in the seeded VAc polymerizations in the presence of PDVB/PSty seeds.

The TEM measurements in combination with RuO_4 and uranyl acetate staining gave a good idea of the latex morphology and according to the experienced staff in Sydney (C. Ferguson) evidence of core−shell morphology.

Figure 6 shows a TEM measurement of PDVB/PSty seed latex particles that were previously exposed to RuO_4 fumes. Single particles with a size of around 20 nm can be seen very well.

Figure 7 shows a TEM measurement of PDVB/PSty/PVAc multi layer core−shell latex particles that were exposed to RuO_4 fumes prior to measurement. The particle concentration is rather high, but core−shell structures with a dark RuO_4-stained PDVB/PSty core and a light PVAc shell can be recognized very well.

Figure 8 shows a TEM picture of PDVB/PSty/PVAc multilayer core−shell latex particles that were exposed to RuO_4 fumes and negatively stained afterward with uranyl acetate. Because of the negative staining, a dark ring appears around the core−shell particles.

Conclusions

The seeded emulsion polymerization of vinyl acetate (VAc) in the presence of polydivinylbenzene (PDVB) seed latices was investigated. The experiments show that because of the incompatibility of vinyl groups on the surface of the PDVB seed latex with VAc, the polymerization could only be run up to conversions of around 60%. A core with a layer of polystyrene (PSty) polymerized onto the PDVB seed latex to shield the inhibiting vinyl groups was suggested as a solution to the problem.

Seeded emulsion polymerization of various amounts of styrene (Sty) in the presence of PDVB seed latices was successfully performed. 100% conversions were reached, and particle sizes and transparency of the latices obtained gave much evidence of a core−shell morphology.

VAc was polymerized with conversions up to 100% onto PDVB/PSty seed latices. It was observed that the conversion of VAc rose with increasing amounts of PSty on the PDVB seed latices. 100% conversion of VAc was obtained with double-layer seed latex that had a PDVB:PSty weight ratio of 1:1, corresponding to a PSty interlayer of 3.5 nm. The latices obtained were still transparent.

TEM measurements in combination with RuO_4 and uranyl acetate staining gave evidence that the PDVB/PSty/PVAc multilayer latices had core−shell morphology. Indications of secondary nucleation were not found.

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