Polymerization Conditions and the Development of a Core–Shell Morphology in PMMA/PS Latex Particles. 1. Influence of Initiator Properties and Mode of Monomer Addition

Jan-Erik Jönsson, Helen Hassander, and Bertil Törnell*

Department of Chemical Engineering II, Chemical Center, Lund Institute of Technology, P.O. Box 124, S-221 00 Lund, Sweden

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ABSTRACT: Latex particles containing equal amounts of poly(methyl methacrylate) (PMMA) and polystyrene (PS) were prepared by polymerizing styrene in the presence of PMMA seed particles using two different initiators, potassium persulfate (KPS) and *tert*-butyl hydroperoxide (*t*-BHP). Styrene was added either before polymerization (batch) or continuously during the polymerization. Particles prepared using batch addition of styrene showed no signs of a core–shell morphology, and the surface concentration of PS was lower than 50%. Particles with well-defined core–shell structures were obtained when styrene was added at a low feed rate. With *t*-BHP as initiator, the shell layer was compact and distinct and the surface concentration of PS high, whereas with KPS as initiator the shell layer was thicker and contained domains of PMMA. Composite particles prepared using a low styrene feed rate, but seed particles containing a chain-transfer agent, had PS domains distributed throughout the entire particle volume. Hence, the formation of particles with a core–shell structure was due to the suppression of radical transport to the interior of the seed particles, mainly because of the high internal viscosity of the latter. The structure and composition of the shell layer, however, depends on the chemical nature of the initiator.

Introduction

Morphology control during the preparation of multiphase latex particles by emulsion polymerization presents a problem of considerable technical significance. There is thus considerable interest in finding conditions which permit the reproducible production of two-phase latex particles with a core–shell morphology.

Previous work in the field suggests that particle morphology is controlled by many factors, including the hydrophilicity of the monomers and polymers,[1–3] the particle viscosity,[4] the molecular weight of the polymers,[5] the degree of grafting between the polymers,[6–8] the rate of transport of monomers, radicals, and oligomers,[9–12] and the interfacial free energy of the system.[12–15] Some of these factors are system specific and determined by the chemical structure of the monomer/polymer systems involved. The other factors are general and may, to a considerable extent, be controlled by the manner in which the polymerization process is conducted.

In order to be able to utilize the potential of controlling particle morphology by controlling the detailed process conditions, we have set out to study how particle morphology is affected by changes in polymerization conditions such as temperature, the manner of adding the second monomer, the type of initiator used, and the rate of initiation.

In a previous paper the morphology of polystyrene/poly(methyl methacrylate) (PS/PMMA) latex particles, prepared by adding methyl methacrylate to PS seed particles containing an oil-soluble initiator, was reported. Under these conditions a core–shell morphology was not observed, even when the MMA was added continuously and at a low feed rate. Although the seed particles were rather large and the polymerization temperature low compared with the glass transition temperature of the seed particles, the resulting particles contained PMMA domains distributed throughout the entire volume of the particles. Hence, under all conditions of practical interest, the rate of intraparticle monomer diffusion would generally be too high to make it possible to establish a monomer concentration gradient of sufficient sharpness to generate a core–shell structure in latex particles.[13]

The present paper reports results from a similar study, differing from the one referred to above mainly in the fact that water-borne instead of particle-borne primary radicals were used. Moreover, in the present study PMMA seed particles were used and styrene was the second monomer. This was done because PS is rather stable in the electron beam of an electron microscope, whereas PMMA is not. The use of styrene as the second monomer thus would facilitate the observation of the shell layer by electron microscopy. We also report on differences in morphology and surface composition of the particles induced by substituting potassium persulfate for *tert*-butyl hydroperoxide as initiator and by inducing chain-transfer reactions in the particles. The morphology of the composite particles was studied by electron microscopy on thin sections cut through the particles, and their surface composition by ESCA.

Methods

Chemicals. Methyl methacrylate (Merck) and styrene (Merck) were freed from inhibitors by passing the monomers through a column filled with active basic aluminum oxide (Merck). The purified monomers were kept at 8 °C before use. Potassium persulfate (Merck) and *tert*-butyl hydroperoxide (80% water solution, Merck) were of analytical grade and were used without further treatment. All other chemicals were of analytical grade and were used as supplied.

PMMA Seed Latex Preparation. The poly(methyl methacrylate), PMMA, seed latexes were prepared by soap-free emulsion polymerization at 70 °C, using potassium persulfate, KPS, as initiator. The monomer was fed continuously to the reactor, thus keeping the monomer concentration in the reactor low and avoiding new particle formation. Unreacted initiator was removed from the seed latex with a Dowex 2X8 OH^- ion-exchange column. The total solid content was determined after ion-exchange. The particle diameters of the final PMMA latexes were determined by quasi-elastic light scattering with a Coulter N4 MD. Data for the seed latexes are given in Table 1.

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* To whom correspondence should be addressed.

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Table 1. Data for the PMMA Seed Latexes

PMMA seed latex	S1	S2
solids content, wt %	15.75	4.68
particle diameter, nm	510	560
number of particles per gram of latex, 10^{12}	1.92	0.43

Table 2. Experimental Conditions Used in the Seeded Polymerization Step

polymerization mode and mixture	experiment						
	A	B	C	D	E	F	G
addition of styrene	batch	batch	cont	cont	cont	cont	cont
initiator	KPS	*t*-BHP	KPS	KPS	*t*-BHP	*t*-BHP	*t*-BHP
PMMA latex S1, g	80	80	80		80		80
PMMA latex S2, g				100		100	
SDS, g	0.15	0.15	0.15	0.11	0.15	0.11	0.15
$CBrCl_3$,[a] g							0.18
styrene, mL	12.0	12.0	12.0	5.1	12.0	5.1	12.0
styrene feed rate, mL/h			3.00	3.00	3.00	3.00	3.00

[a] Introduced in the seed particles (see text for details).

Table 3. Redox Initiator Systems Used in the Seeded Polymerization Experiments[a]

ascorbic acid, g	0.30
$VOSO_4 \cdot 5H_2O$, mg	5.0
initiator solution (KPS or *t*-BHP), mol/L	3.0×10^{-4}
initiator feed rate, mol/min	1.0×10^{-7}

[a] Ascorbic acid and vanadium(IV) oxide sulfate were added to the reactor mixture prior to polymerization.

Polymerization of Styrene in the Presence of PMMA Seed Particles. The seeded polymerization experiments were carried out at 60 °C in a 200-mL calorimetric reactor submerged in a carefully controlled water bath.[17] The experimental conditions are given in Table 2. The PMMA seed latex, sodium dodecyl sulfate, ascorbic acid, and vanadium(IV) oxide sulfate were charged into the reactor. Ascorbic acid and vanadium(IV) oxide sulfate were components of the redox initiator system used in these experiments (cf. ref 18). In experiments A and C (Table 2), all of the styrene monomer was charged to the reactor and allowed to diffuse into the seed particles overnight at room temperature. In experiments C–G, the styrene monomer was continuously pumped into the reactor by a motor-driven syringe at a constant feed rate (3.0 mL/h). The chain-transfer agent used in experiment G was introduced in the seed particles by first dissolving it in acetone. The acetone solution was poured into the PMMA latex. The latex was stirred overnight at room temperature. Prior to polymerization, the acetone was removed by vacuum distillation. The initiator solutions were prepared by either adding KPS or *tert*-butyl hydroperoxide (*t*-BHP) to water. The initiator solutions were fed continuously into the reactor by a motor-driven syringe pump at a controlled molar feed rate of 1.0×10^{-7} mol/min (cf. Table 3). Before the polymerization was started by adding initiator or initiator and monomer, the charged reactor, the vessels for the reactor feeds, and the pumping systems were repeatedly degassed by evacuation and refilling with nitrogen in order to supress oxygen inhibition. The monomer and initiator were fed into the reactor via steel tubes immersed in the water bath and syringe needles connected to membrane sealed valves in the bottom of the reactor. In this way the monomer and initiator solutions were preheated to the polymerization temperature before entering the reactor. The rate of polymerization was measured by monitoring the temperature difference between the water bath and the interior of the reactor (cf. ref 17 for details).

Electron Microscopy. Dried latex samples were embedded in epoxy resin and sectioned with an LKB Ultratome V microtome equipped with a diamond knife. The section thickness was about 600 Å. The sections were examined in a JEOL 100U transmission electron microscope. As PMMA decomposes in the electron beam, contrast between the polymer phases was obtained without staining.[19] In the micrographs, the PS appeared as dark domains and PMMA as bright domains. It can be seen from the micrographs that the sectioned particles are deformed. This was undoubtedly caused by compression during sectioning as the deformation is perpendicular to the cutting direction.

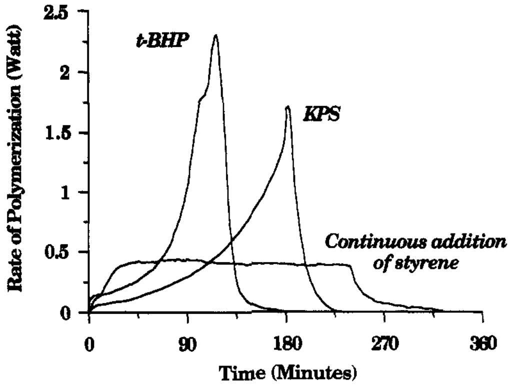

Figure 1. Rate of polymerization vs time for experiments A–C, E, and G.

Surface Analysis. Electron spectroscopy for chemical analysis, ESCA, was used to characterize the surface of the composite particles. In order to suppress the influence of nonpolymeric species in the ESCA analysis, the latex samples were cleaned with distilled water in a serum replacement cell using membranes with a 1-μm cut-off. About 5 mL of the latex was diluted with approximately 30 mL of distilled water. At least 100 mL of distilled water was passed through the cell. The cleaned latexes were dried on aluminum plates in a vacuum desiccator. The carbon and oxygen parts of the ESCA spectrum were analyzed using a Kratos 800 ESCA instrument. The surface composition was calculated from the carbon (C1s) and oxygen (O1s) signals.

Results and Discussion

Polymerization. The experiments carried out involve the polymerization of styrene in the presence of PMMA seed particles. In all cases, the amount of styrene used corresponded to the amount of PMMA in the seed particles. The composite particles would thus contain equal amounts of PS and PMMA. Fairly large seed particles were used in order to permit the morphology of the resulting particles to be studied by electron microscopy on thin sections.

Polymerization was initiated with radicals produced from either KPS or *t*-BHP by a rapid vanadium-catalyzed redox initiation system.[18] Vanadium(IV) oxide sulfate (catalyst) and ascorbic acid (for reduce the oxidized vanadium) were present in the reactor, and a solution of the initiator substance was pumped into the reactor at a constant feed rate. In all experiments the molar feed rate of initiator was the same, which means that, in the absence of side reactions, the rate of primary radical production in the reactor should also have been the same.

In the experiments, styrene was added either batchwise or continuously. In the batch experiments (A and B of Table 2), all of the styrene was added from the beginning and allowed to be absorbed in the PMMA seed particles. In these experiments the styrene concentration in the particles was initially about 50% and decreased during polymerization. The corresponding rate curves given in Figure 1 show the normal behavior of emulsion seed polymerizations under conditions where the rate of termination is subject to viscosity control from the beginning; an initial rapid increase of reaction rate as the radical population in the particles builds up, a phase during which the rate of polymerization grows as the rate constant for termination progressively decreases, a maximum (the gel peak), and a phase of decreasing rate of reaction, which sets in as the polymerization rate constant starts to decrease. A comparison between the two curves shows

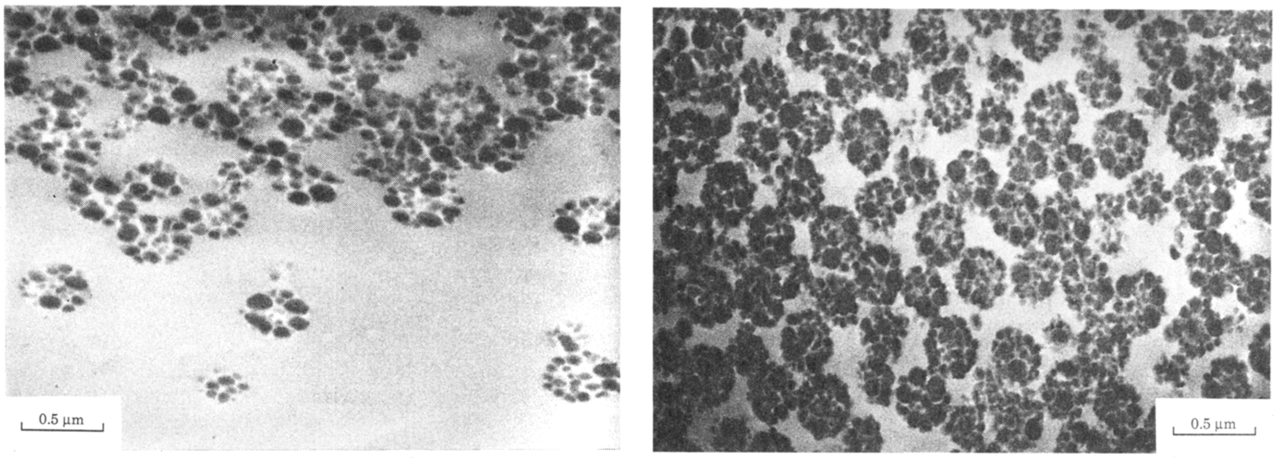

Figure 2. TEM micrographs of sectioned particles prepared by batchwise addition of styrene. Experiment A with KPS as initiator (left) and experiment B with *t*-BHP as initiator (right).

that the two initiators gave different reaction times. With KPS the time elapsed before the appearance of the gel peak was about 3 h, whereas with *t*-BHP the gel peak appeared after about 2 h. Similar differences in reaction time have been observed in other experiments with these initiators, *viz.* in seeded emulsion polymerization of styrene using PS seed particles,[20] which indicates the presence of a genuine difference in the reaction behavior of these initiators with respect to reduction by vanadium(IV), or between the resulting radicals. There is presently no explanation of this difference. In a previous study of batch seed emulsion polymerization of styrene, it was suggested that growing polymeric radicals containing sulfate end groups, because of electrostatic repulsion within the particles, would have a tendency to accumulate in the outer part of the particles and that the resulting increase in the local radical concentration would lead to an increase in the rate of termination and, hence, a lower rate of polymerization.[20] The magnitude of this effect is not known. The results discussed below, showing that *t*-BHP by polymerization under starvation conditions gave core–shell particles with a thinner shell layer than persulfate, does not support the idea that this electrostatic effect is an important one. The sulfate radical is known to be a powerful oxidant, and it can by no means be excluded that a certain fraction of the sulfate radicals are simply consumed in side reactions.

In the experiments with continuous addition of styrene (C–G of Table 3), the polymerization rates corresponded to the monomer feed rate, except during the periods before a stationary monomer concentration in the particles was reached or after the monomer feed was stopped. Thus, in comparable experiments, almost identical rate curves were obtained (Figure 1) irrespective of the initiator substance used. In these experiments, the reaction rate started to decay immediately after stopping the monomer feed. This proves that the polymerizations were performed under so-called starved conditions and that only a negligible amount of liquid monomer was present in the reactor. By integrating the tail part of the rate curves (from the moment at which the monomer feed was stopped), the concentration of monomer in the particles at the end of the constant rate period was estimated to be approximately 0.45 mol/L in experiments C, E, and G and 1.1 mol/L in experiments D and F, in excess of the monomer concentration in the particles at zero rate of polymerization. Considering the fact that the total particle volume increased by a factor of 2 during the experiments, it can be estimated that the stationary-state monomer concentration in the particles in experiments C, E, and G varied between about 0.90 and 0.45 mol/L, and in experiments D and F from about 2.2 to 1.1 mol/L. The higher monomer concentration in experiments D and F was due to the fact that in these experiments the volume of the seed particles was lower (cf. Table 1) but the monomer feed rate the same as in experiments C, E, and G.

The experiments differed mainly with respect to the monomer concentration in the particles and the nature of the primary free radicals used. The monomer concentration in the particles determines the intraparticle viscosity and thus the mobility of the various species present in the particles. Thus, the mobility of oligomeric radicals in the particles should have been much higher in the batch experiments than in those carried out under starvation conditions.

Particle Morphology. As can be seen from the micrographs in Figures 2–5, the morphology of the composite particles was strongly dependent on the prevailing polymerization conditions. The particles prepared by the batchwise addition of styrene (Figure 2) exhibited several PS domains distributed throughout the whole particle volume. Moreover, the electron micrographs do not indicate a higher PS concentration at the outer part of the particles. This indicates that polymerization during most of the conversion period occurred over the whole particle volume. It seems as if the radicals and the monomer have had access to the whole particle volume during a considerable part of the polymerization processes. The fairly large size of the PS domains suggests that transport of even large molecules might be possible under the conditions that prevailed in the particles during these experiments.

The morphology of the particles obtained in experiments C, E, and F, where styrene was added continuously, exhibited a PMMA core surrounded by PS shell. In these experiments the effective polymerization volume in the particles was limited to their outermost surface layer. This must, at least partly, be a result of the high viscosity within the particles, preventing oligomeric radicals from being transported to the interior of the particles.

The particles obtained in experiment D had a different morphology from that of those prepared in experiments C, E, and F (cf. Figures 3 and 4). Although the particles from experiment D were surrounded by a PS shell, PS domains were also present in the interior of the seed particles. This indicates that, under the same experimental conditions (experiments D and F), radicals derived from KPS, when captured by the particles, had a higher mobility in the slightly styrene swollen PMMA phase than

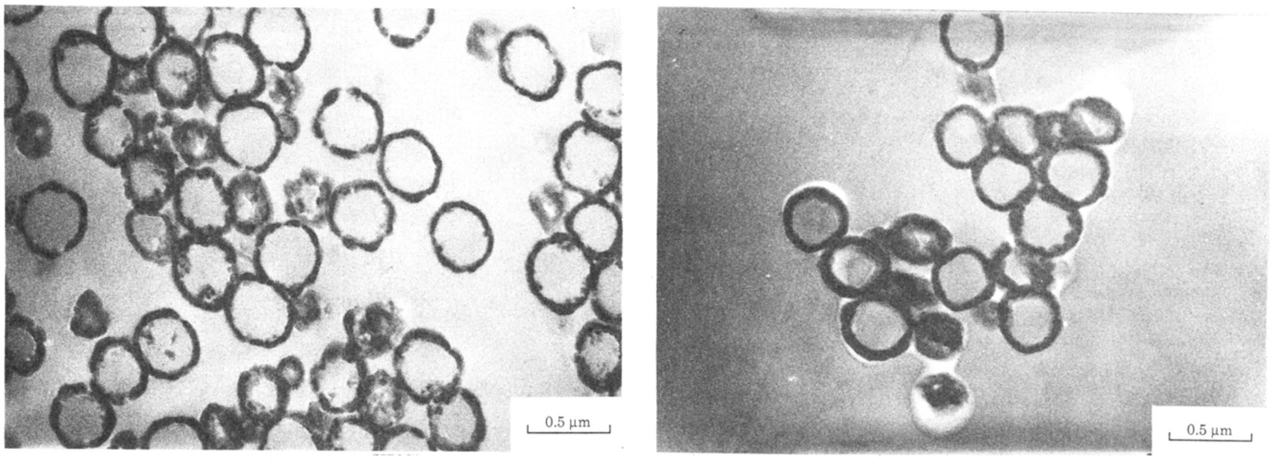

Figure 3. TEM micrographs of sectioned particles prepared by continuous addition of styrene using seed latex S1. Experiment C with KPS as initiator (left) and experiment E with *t*-BHP as initiator (right).

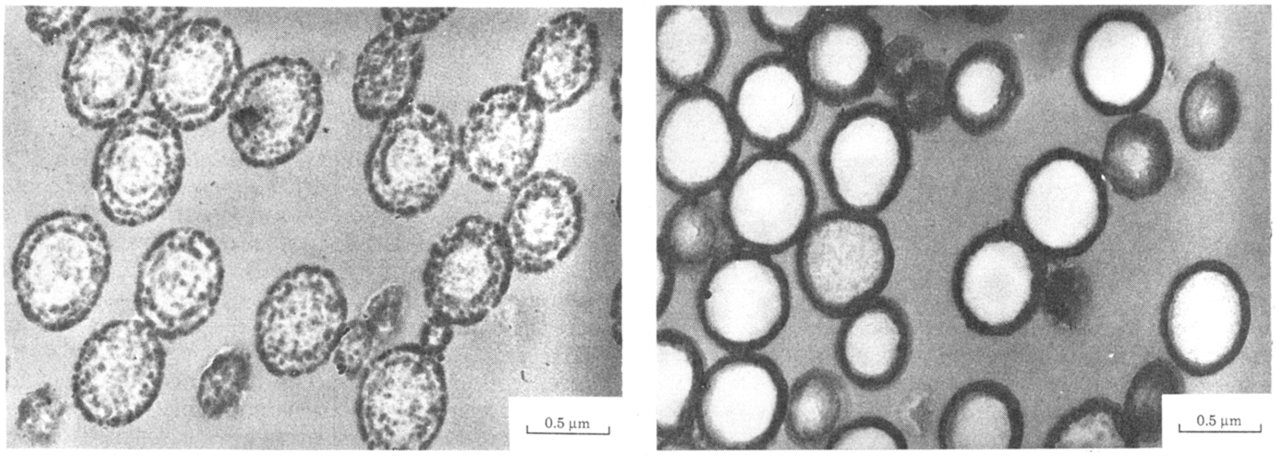

Figure 4. TEM micrographs of sectioned particles prepared by continuous addition of styrene using seed latex S2. Experiment D with KPS as initiator (left) and experiment F with *t*-BHP as initiator (right).

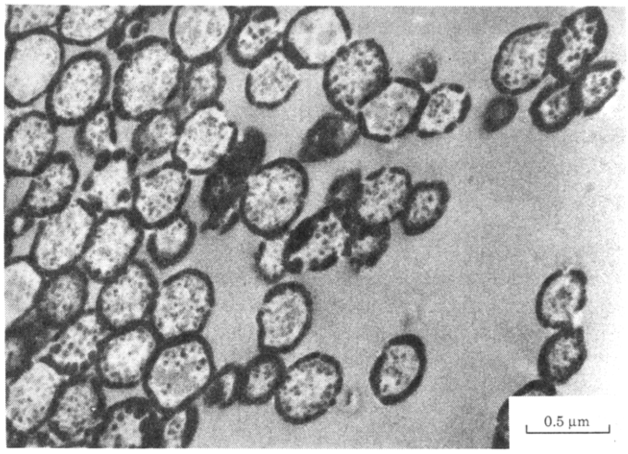

Figure 5. TEM micrograph of sectioned particles prepared as in experiment E (Figure 3) but with particles containing $CBrCl_3$ as a chain-transfer agent.

those from *t*-BHP. Such a difference in mobility is in agreement with results from other experiments to be presented in a subsequent paper.[21] It may also offer an explanation of the difference in the PS shell layer structure observed in this study and discussed below.

It is obvious that the type of initiator used had a strong effect on the morphology of the particles prepared under starvation conditions. Particles prepared with *t*-BHP as initiator exhibited a dense shell layer with a rather well defined interface between PS and PMMA. In the particles from experiment C, which used KPS as initiator, the shell layer appeared cloudy and seemed to be "diluted" with PMMA domains. In this case the shell layer was thicker and more irregular in shape than that in experiments E and F. Similar differences in shell-layer morphology produced by substituting KPS for *t*-BHP have been observed in a number of experiments and seem to reflect a genuine difference in properties which must be related to the structure of the primary radicals. For particles from experiments E and F, in which *t*-BHP was used as initiator, the ratio between the particle and core diameters was close to $2^{1/3}$, which corresponds to a shell layer of the same volume as that of the core, i.e., an ideal core–shell structure in particles containing equal amounts of the two polymers.

Experiment G was performed under conditions similar to those of experiment E, except for the fact that the seed particles contained a chain transfer agent, bromotrichloromethane. The particles obtained from experiment G (Figure 5) consisted of a PS shell layer surrounding a PMMA core containing small PS domains. This proves that, during polymerization at very low feed rates, monomer is present within the whole particle volume and might undergo polymerization if radicals can be transported in the highly viscous particles. Chain transfer in this case led to the formation of free radicals, having the size of about a monomer unit. Obviously, such radicals are able to diffuse from the particle surface into the center of even unusually large latex particles before effectively losing their mobility due to growth.

The chain-transfer agent used in this experiment was very efficient. According to the literature the chain-

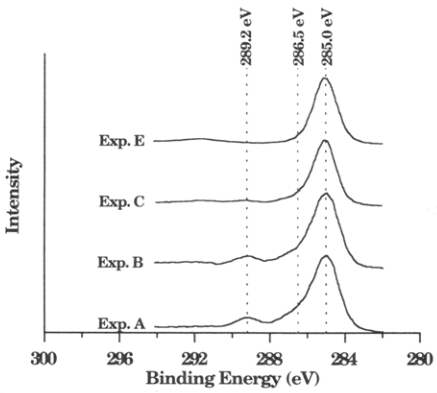

Figure 6. Carbon (C1s) spectra from the ESCA analysis of particles from experiments A–C and E. The dotted lines correspond to the binding energy of aliphatic and aromatic carbons (285.0 eV), ether carbons (286.5 eV), and ester carbons (289.2 eV).

Table 4. Results from the ESCA Analysis

experiment	O1s/C1s integrated intensity ratio	O/C[a] molar ratio	CO/AC[a] integrated intensity ratio
A	0.73	0.28	0.32
B	0.63	0.24	0.23
C	0.57	0.22	0.16
E	0.10	0.04	0.03

[a] See text for details.

transfer constant has been determined to be 65.[22] It is therefore most likely to belive that the chain-transfer agent was consumed long before the polymerization was completed. This explains the unusual morphology of the resulting particles. The PS shell which can be seen in the micrographs (cf. Figure 5) to a large extent was most likely formed after the transfer agent was consumed. Hence, the PS domains that appear inside the particles were formed at the very beginning of the polymerization process.

Surface Analysis. ESCA analysis was used to determine the PS surface content of the particles, using two different approaches. The first employed the ratio of the peak areas obtained for oxygen and carbon, here denoted as the O1s/C1s ratio. This ratio may be converted to a molar ratio, denoted as the O/C ratio, by using sensitivity factors, which take into account the fact that different elements interact differently with the X-ray photons.[23] The sensitivity factors for our instrument have been determined to be 0.25 for C1s and 0.66 for O1s. In the second approach the carbon peak was resolved into components corresponding to aliphatic and aromatic carbons at 285 eV (AC carbons) and to ether carbons (286.5 eV) and ester carbons (289.2 eV). In resolving the carbon peak, advantage was taken of the fact that in PMMA the two latter peaks should be equal in size. From the CO/AC ratio, where CO refers to the sum of ether and ester carbons, it is possible to estimate the amount of PS at the particle surface. The carbon peaks from the ESCA analysis are shown in Figure 6. The more skewed to higher binding energies, the more ether and ester carbons are present in the sample surface. The data obtained from the ESCA analysis are presented in Table 4, and the amount of PS at the particle surface calculated from these data is given in Figure 7.

Although the values of the PS surface content for a given sample differed by between 2 (experiment E) and 22 mol % (experiment C), depending on the method of evaluation, the two methods ranked the samples in the same order. The difference in PS surface content between the two methods mainly depends on the fit of the sum of the resolved carbon peaks to the original curve. The best fit was obtained with experiment E (showing a negligible difference) and the worst fit with experiment C.

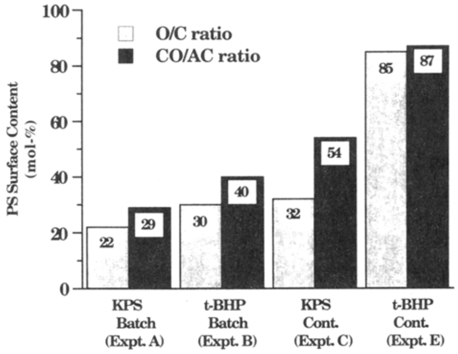

Figure 7. The ESCA surface content of PS for particles from experiments A–C and E.

Generally, it can be seen that polymerizations with *t*-BHP as initiator gave higher PS contents at the particle surface than with KPS. This is true for particles from experiments with batch addition as well as continuous addition of the monomer. Continuous addition of the monomer gave particles with a higher PS surface content than batchwise addition. A rather surprising result was the large difference in PS surface concentration observed between particles from experiments E and C, which differed only with respect to the initiator used.

At the same polymerization conditions, it seems that *t*-BHP gave composite particles with a higher PS surface concentration than KPS. The difference was particularly obvious for particles prepared under starvation conditions. In this case, the two initiators gave core–shell particles with shell layers of different structure: *t*-BHP a thin and well-defined shell; KPS a thicker, less homogeneous shell with a stronger tendency to partly invade the core particle. It might have been anticipated that PS with charged sulfate end groups from KPS would be located preferentially at the particle surface and that PS with uncharged end groups from *t*-BHP might be more prone to penetrate into the particles. However, both electron microscopy and ESCA indicate the reverse situation.

As discussed above, and also demonstrated by the comparison in Figure 4, the results have shown that PS prepared using *t*-BHP has a stronger tendency to remain at the surface of the seed particles than PS prepared using persulfate. This difference in behavior has been observed in numerous experiments, and we are fully convinced that the difference is genuine and must be referred to chemical factors. Presently, it is not possible to pinpoint the mechanism underlying the observed initiator effect. This is due to the complex nature of the polymerizing system and the lack of basic knowledge of radical and initiator reactivities in systems of this type. Accordingly, a discussion of the initiator effect has to be speculative. Presupposing that the two initiators react with the vanadium catalyst to form *tert*-butyloxy and sulfate radicals, respectively, the initiator effect should be related to the different reactivity and charge of these radicals. The initiator effect might be caused by a difference in size of the radical species as these enter the particles. Such differences might arise from water-phase polymerization, if the primary radicals differ in reactivity toward styrene dissolved in the aqueous phase. According to this suggestion, the rather deep PS penetration observed in experiments with KPS should be due to a low reactivity of sulfate radicals toward styrene compared to that of *tert*-

butyloxy radicals. This idea, however, is in disagreement with the fact that results from radiolytic studies of styrene addition to sulfate radicals in water have shown this reaction to be rapid and to occur at a rate closely approaching the limit of diffusion control.[24] Moreover, this idea would imply that the extent of PS penetration should be sensitive to variations in the number concentration of seed particles, or rather to the total particle surface per unit volume of water used in the second polymerization. As will be shown in a future communication, this does not seem to be the case. The primary radicals under discussion also differ in charge and interact with negatively charged seed particles. Thus, electrostatic repulsion between negatively charged species (sulfate radicals, oligomeric styrene radicals and polymer molecules with a sulfate end group), which have entered the particles, would force charged species to move away from each other. In a medium of rather low dielectric constant like PMMA, electrostatic repulsive forces would be fairly long ranged and might cause a broadening of the surface shell layer. It is also possible that the initiator effect is due to as yet unknown reactions between the primary radicals and components of the system other than the monomer, creating a situation favoring a particular structure of the shell layer. Chain transfer to polymer by a very reactive primary radical might create such a situation.

Conclusions

The generation of a core-shell structure in two-phase latex particles presupposes that radicals are prevented from being transported from the particle surface region into the interior of the seed particles. This requires that the intraparticle viscosity of the seed particles be kept high during polymerization of the second monomer by polymerizing at a low temperature and adding the second monomer at a low rate. Thus, in the present case, when all of the styrene was added to the PMMA seed particles before starting the polymerization, a core-shell differentiation could not be observed. However, when the styrene was added slowly during polymerization, particles with a distinct core-shell morphology were obtained.

With seed particles containing a low molecular weight chain-transfer agent, PS domains were formed also in the interior of the particles, although the second monomer was added a low rate. This indicates that the transport of small radicals in the particles is rapid compared with the growth processes leading to slowly diffusing oligomeric radicals.

The surface composition and the morphology of the shell layer were found to depend on the type of initiator used. Thus, the use of *t*-BHP as initiator resulted in particles with a shell of PS, having a thickness that corresponded quite well to the amount of styrene used. The surface concentration of PS was high. On the other hand, when KPS was used as initiator, the shell layer was thicker and less homogeneous. It had a cloudy appearance, a blurred interface with the PMMA core, and a fairly high surface concentration of PMMA.

Finally, the core-shell morphologies described in this work are kinetically controlled structures and far from thermodynamic equilibrium. In the present case, the persistance of the structures might be entirely due to the fact that both polymers have high glass transition temperatures. In systems of greater technical interest, where the second polymer is in the rubbery state, phase migration may cause shelf-life problems.

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