Notes

Shell-Layer Stability in Core−Shell Particles Prepared with Different Initiators

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Introduction

We have previously reported that potassium persulfate (KPS) and *tert*-butyl hydroperoxide (*t*-BHP), when used as initiators in semicontinuous seed emulsion polymerization of styrene in the presence of poly(methyl methacrylate) seed particles (PMMA) containing polymer anchored sulfate end groups, produced core−shell particles having shells with different structure.[1] We now report that the difference in shell structure caused a large difference in the tendency of the particles to undergo phase inversion when swollen with a solvent. Polymerization with *t*-BHP gave a shell which served as a good barrier to phase inversion of solvent swollen particles, whereas the shell formed in polymerization with KPS seemed to present no resistance to phase rearrangement. Hence, the choice of initiator may play a significant role in preparation of core−shell latexes. Recent industrial experience has confirmed this. Thus, film-forming core−shell latexes, having the same monomer composition but prepared using either KPS or *t*-BHP as second stage initiator, have been found to behave quite differently as film formers in certain paint applications.[2]

Characteristic Properties of the Core−Shell Particles Studied

The preparation and morphology of the two types of core−shell particles used in the present study have been described in a previous publication.[1] The two sets of particles had the same polymer composition (PMMA/PS, 50/50) and derived from the same PMMA seed latex, prepared by soap-free emulsion polymerization using KPS as initiator and continuous addition of monomer. Before being used, the seed latex was freed from excess initiator. Except for the use of different initiator substances, the second polymerization steps leading to the core−shell particles were carried out using identical process conditions (see Experimental Section). Size exclusion chromatography indicated no significant molecular weight difference between the two sets of particles ($\bar{M}_n$, as calculated from a PS calibration curve, 290 000 and 310 000 for particles prepared using KPS and *t*-BHP, respectively). As reported,[1] transmission electron microscopy studies of unstained thin sections of the particles embedded in epoxy resin revealed that, in particles prepared with KPS as initiator, the interface between the polystyrene (PS) shell and the PMMA core was diffuse and irregular in shape. The shell seemed to be made up of small spherical PS domains (Figure 1a). The domain structure of the shell layer was rather clearly seen as graininess in sections cut through the upper or lower shell caps of the particles. In particles prepared with *t*-BHP as initiator, however, the interface between the PS shell and the PMMA core was smooth and rather sharp (Figure 1b). As was also reported, ESCA analysis indicated that the surface concentration of PS was higher in particles from the experiment with *t*-BHP (85%) than in those prepared using KPS (50%).[1]

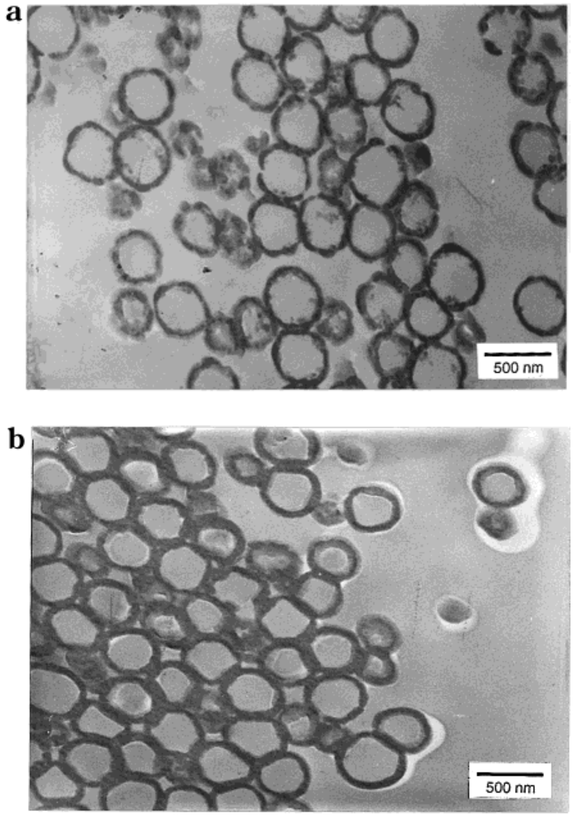

Figure 1. TEM images of unstained sections from epoxy embedded core−shell PMMA/PS particles prepared from PMMA seed particles using continuous addition of styrene and (a) KPS or (b) *t*-BHP as second stage initiator.

The main reason why KPS produced shells with a different structure than *t*-BHP is most probably due to the fact that KPS gives negatively charged, but *t*-BHP uncharged, primary radicals and oligomers. Thus, with KPS, the mechanism of shell formation and growth is associated with electrostatic interactions, which are unimportant in the case of *t*-BHP. With KPS, shell formation involves capture of negatively charged pri-

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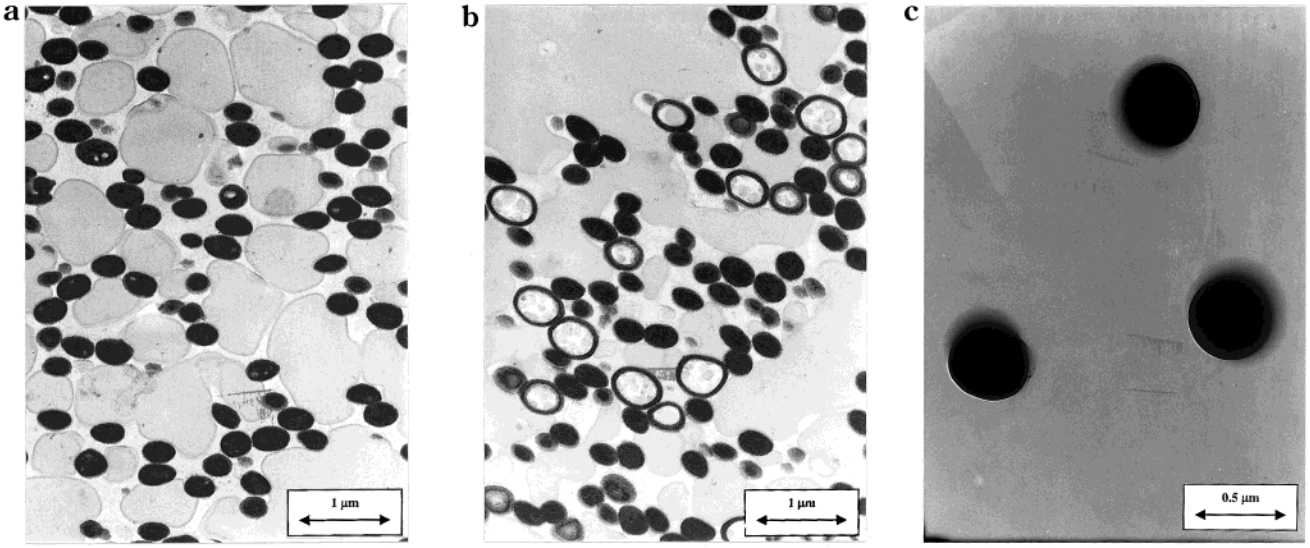

Figure 2. TEM images of stained sections (ruthenium tetroxide) from epoxy embedded samples of solvent-treated core–shell particles prepared using (a) KPS or (b) *t*-BHP as second stage initiator and (c) whole unstained, solvent-treated core–shell particles prepared using KPS as initiator.

mary radicals or oligomers by particles having a rather high surface concentration of sulfate end groups. This would tend to push in-coming growing radicals into the low dielectric constant region below the highly charged seed particle surface.

Results and Discussion

We here report results from experiments that provide additional information about the properties of the shell layers generated by the two initiators. In these experiments, the two types of particles discussed were first subjected to intermittent swelling with methylene chloride. The morphology of the solvent-treated particles was then studied by transmission electron microscopy. In these experiments, 5 g of the latex under study was diluted by 65 mL of water and charged to a small stirred reactor. Methylene chloride was added in an amount corresponding to 10 times the volume of the latex particles. After stirring the mixture for 5 h at 60 °C, the reactor valve was opened, and methylene chloride was removed by evacuation. This technique was previously used to investigate the equilibrium morphology of two-phase latex particles of similar size and polymer composition but prepared in a different type of process.[3]

The deswelled particles were embedded in epoxy resin and sectioned in an ultra-microtome (LKB Ultratome V) equipped with a diamond knife. The sections were stained with ruthenium tetroxide[4,5] and studied with transmission electron microscopy. Representative micrographs from stained, thin sections of the solvent-treated particles are shown in Figure 2a,b. The dark areas represent the stained PS phase. The micrograph in Figure 2a shows that methylene chloride swelling of particles prepared using KPS as initiator caused the PS shell layers of the original particles to form almost homogeneous, compact PS domains containing only a few occasional inclusions of PMMA, seen as bright spots in the dark PS areas. Micrographs from the same sections but with higher resolution (not shown) indicated that the large PS domains in Figure 2a were partly surrounded by the former PMMA core polymer. The micrograph of the unsectioned and unstained whole particles in Figure 2c confirms this structure and suggests that the equilibrium morphology in this case corresponds to a PS particle partly engulfed in PMMA.

The micrograph in Figure 2b shows sectioned particles prepared using *t*-BHP as initiator after intermittent swelling with methylene chloride. As can be seen, a considerable fraction of these particles retained their core–shell structure during the solvent treatment. It can also be seen that treatment with methylene chloride caused the PS shells of a majority of the particles to form single, compact spherical PS domains. In this case, electron microscopy of whole, unsectioned, solvent-treated particles did not reveal the presence of an unsymmetrically placed, outer PMMA phase of the type shown in Figure 2c. The likely explanation is that these particles had been converted to inverted core–shell particles. Considering the fact that the PS phase in this case contained no hydrophilic end groups, while the PMMA polymer phase did, the inverted core–shell structure would represent the expected equilibrium morphology of these particles.

The dark, compact PS disks seen in Figure 2b represent sections cut through inverted core–shell particles or the upper or lower cap of core–shell particles. A sectioned core–shell particle will show up as a dark ring in TEM only if the entire section is taken somewhere from below the upper to above its lower shell caps. Other sections through the particle will show up as dark disks. Considering the core size (about 510 nm), the thickness of the shell layer (about 66 nm), and the section thickness (about 60 nm), the probability that a microtome section randomly taken from the particle will appear as a dark ring or a dark disk was calculated to be 0.64 and 0.36, respectively. Similarly, the probability that a random microtome cut through an inverted core–shell particle (assumed to have a 510 nm diameter PS core and a 66 nm thick PMMA shell) would contain a slice of the PS core and show up as a dark disk in TEM was calculated to be 0.81. Considering these probabilities, data from TEM images containing stained sections through 1089 particles, 23% of which appeared as dark rings, suggested that 31% of the original particles retained their core–shell structure on solvent treatment under stirring conditions. In contrast, not a single dark ring could be seen in micrographs representing several thousand solvent-treated particles derived from the experiment with KPS as initiator. The two sets of particles thus differed considerably in their stability against phase inversion in the swollen state.

The fact that a considerable fraction of the particles prepared using *t*-BHP retained their core–shell structure strongly indicates the presence of a kinetic barrier to phase rearrangement. A continuous layer of solvent swollen PS separating the PMMA phase from the aqueous phase would provide such a barrier. Hence, a likely explanation to the fact that a large fraction of the particles retained their original morphology is that the shell surrounding the swollen particles was devoid of holes or channels through which the solvent swollen PMMA phase could reach contact with the outside aqueous phase. This explanation suggests that the phase-inverted particles seen in Figure 2b were formed because their continuous shells were broken up by mechanical forces induced by stirring, thus enabling contact between the PMMA core phase and water. The fact that none of the particles prepared using KPS as second stage initiator retained their core–shell morphology suggests that this initiator gave shells with a PS/PMMA two-phase structure. The results strongly indicate that the choice of the second stage initiator may affect the shell properties of core–shell latexes.

Experimental Section

The starting material was a monodisperse PMMA seed latex prepared at 70 °C, using a soap-free emulsion polymerization process with continuous monomer addition and KPS as initiator. Excess initiator was removed by anion exchange. The final seed latex contained 15.8 wt % PMMA and particles with an average diameter of 510 nm.

Core–shell particles containing about equal amounts of PMMA and PS were prepared at 60 °C in a 200 mL, stirred calorimetric reactor, submerged in a carefully controlled water bath (cf. ref 6). The reactor was charged with 80 g of the seed latex, 0.15 g of sodium dodecyl sulfate, 0.30 g of ascorbic acid, and 5.0 mg of $VOSO_4 \cdot 5H_2O$. Ascorbic acid and vanadium(IV) oxidisulfate were components of the redox initiator system (cf. ref 7). Oxygen was removed from the reactor, the pump system, and the feed vessels by repeated evacuation and nitrogen refilling steps. Polymerization was started by activating two metering feed pumps: one feeding styrene at a constant rate of 3 mL/h and the other an aqueous solution of initiator (either KPS or *t*-BHP). With either initiator, the initiator feed pump was adjusted to give a continuous feed of 6×10^{-6} mol/h of initiator substance. After 4 h, the monomer feed pump was stopped, while the initiator feed pump was allowed to run until the power signal from the calorimetric reactor reached the baseline.

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References and Notes

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