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Preparation of Hybrid Nanocapsules

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Summary: Hybrid nanoparticles with a polystyrene core and a hybrid copolymer shell were used to produce hybrid nanocapsules by dissolving the polystyrene core from the previously elaborated core-shell particles. Following previous works, the core-shell particles were prepared by emulsion polymerization of styrene and subsequent addition of γ-methacryloxy propyl trimethoxy silane (MPS) to produce the shell by copolymerization reaction of MPS with the residual styrene. Core extraction was performed by diluting the core-shell particles in an excess of tetrahydrofuran (THF). Two procedures were investigated to separate the dissolved polymer chains from the nanocapsules. In the first procedure, the polymer was isolated by successive centrifugation and redispersion in THF, whereas in the second procedure, the free polymer chains were removed by dialysis. The polymer molecular weight was optimized in order to promote dissolution of the polymer chains and allow them to diffuse through the shell.

Keywords: core-shell polymers; diffusion; hybrid nanocapsules; emulsion polymerization; sol-gel

Introduction

Hollow particles have found increasing interest in recent years because of their potential applications in multiple areas of material science such as decorative paper coatings, paints and drug delivery.[1,2] Hollow spheres can be elaborated in a variety of ways. Structured latexes with a carboxylated core and one or several polymeric shells were developed by the Rohm and Haas Company.[3] The polyelectrolyte interior of the particles was ionized to expand the core and generate micro void domains. By light scattering, hollow latexes contribute to increase hiding and are very efficient as synthetic pigments in coating applications. Voided particles can also be generated by phase separation techniques either in emulsion[4] or miniemulsion polymerization.[5] Other synthetic methods include interfacial polycondensation,[6] layer-by-layer adsorption of polyelectrolyte films on colloidal templates[7] and sol-gel nanocoating.[8–11] In these last two approaches, the hollow spheres are produced by removing the template by dissolution, thermal decomposition or chemical etching.

On the other hand, organic-inorganic polymer hybrids offer very attractive properties in various domains of material science and have attracted increased interest in recent literature.[12–15] Pioneering works in this field were done by Schmidt,[16] Mark,[17] and Wilkes,[18] who developed the co-reaction of alkoxysilane-functionalized polymers with tetraalkoxysilanes in solvents or performed sol-gel reactions within elastomeric networks. The intimate combination of organic and inorganic components into hybrid materials allows the elaboration of new products with enhanced compatibility between both components.

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For instance, by controlling phase separation between the organic and inorganic parts, it is possible to create materials which are harder and fully transparent due to the elimination of light scattering.

The objective of this work is to produce organic/inorganic hybrid nanocapsules using polystyrene latexes as sacrificial templates. Core-shell particles with a polystyrene core and a hybrid shell were prepared in two steps as detailed in previous studies[19]. First, a polystyrene latex core was synthesized in batch up to 70% conversion. Then, the hybrid shell was produced in a subsequent step by reacting MPS with the residual amount of styrene through seeded emulsion polymerization. For the reader's convenience, the method of synthesis of the core-shell particles is reminded in the experimental section while in the discussion section, we have provided the most relevant information related to the core-shell particles structure and properties as this will be useful to understand and interpret the present data.

In this work, hollow nanocapsules have been produced by dissolution of the polystyrene core of the previously elaborated core-shell particles in tetrahydofuran (THF) and subsequent extraction by two procedures. The first one consisted of extracting the free polymer chains by successive centrifugation and redispersion in THF, a good solvent for polystyrene, while in the second procedure, the dissolved polymer chains were separated from the nanocapsules by dialysis. The polymer molecular weight of the core was optimized in order to facilitate polymer dissolution and diffusion through the hybrid shell. The influence of the silence concentration in the shell on the diffusion rate of the core through the shell is studied.

Experimental Part

Materials

Styrene (Aldrich) was distilled under vacuum before use. Potassium persulfate (Acros Organics) was used as initiator while dodecyl thiol (Aldrich) was used as chain transfer agent. The surfactant, dimethyl propylammonium sulfonate (Ralufon, Aldrich) and 3-trimethoxysilyl propyl methacrylate (MPS, Aldrich) were used without any purification. Water was deionized on mixed bed resins.

Synthesis of the Capsules

The polystyrene core was synthesized through emulsion polymerization using KPS as initiator, dodecyl thiol as chain transfer agent and Ralufon as surfactant.[9–11,19] The polymerizations were carried in batch at 70 °C under a nitrogen atmosphere up to 70% conversion. After 70% conversion of styrene, a given amount of MPS was added to the reaction medium and the copolymerization of styrene and MPS was continued until the steady-state conversion was reached. The pH value of the suspension was fixed at 7 by adding equivalent quantities of ammonium dihydrogenphosphate and disodium hydrogenphosphate. A typical recipe is as follows: styrene, 90 g; KPS, 0.7 g; chain transfer agent, 5.4 g; surfactant, 0.8 g; buffer, 0.2 g; water, 210 g; and various quantities of MPS. In the following, the core-shell particles will be referred to as polystyrene@(polystyrene-co-MPS).

Unless stated otherwise, the nanocapsules were prepared as follows: 10 g of the latex suspension was poured in 70 g of THF and the mixture was stirred for 120 minutes at ambient temperature.

In a first procedure, the hybrid nanocapsules were purified by successive centrifugation/ dissolution in THF. The dissolved polymer, contained in the supernatant was discarded and the operation was repeated until there was no more polymer detected in the serum as determined by UV spectroscopy from previously established calibration curves. The UV/VIS spectra were recorded on a UV/VIS UVIKON 922 spectrophotometer using quartz cells.

In a second procedure, the dissolved polymer chains were separated from the nanocapsules by dialysis. Typically, 100 g of the suspension was dialyzed against 2000 g pure THF using 22 nm-diameter Spectra-Por cellulose ester membranes tubing with a molecular weight cutoff of 50000. At least five replacements of THF were required to ensure complete removal of the polymer chains from the core.

Characterizations

The overall conversion during the formation of the nanoparticles was determined gravimetrically. The particle diameter of the latex particles was measured using a dynamic light scattering (DLS) Malvern Autosizer Lo-C instrument. Infrared spectra were recorded using a Nicolet FTIR 460 spectrometer on powder-pressed KBr pellets. Polymer samples were prepared by putting the latex into an oven at 100 °C for half an hour and then drying under vacuum at 50 °C for 5 h in order to remove most of the water and the residual amount of monomer.

The glass transition temperature (Tg) of the synthesized hybrid materials was measured using differential scanning calorimetry (DSC). Appropriate amounts of samples were sealed in aluminum sample pans and prepared by compression molding. DSC thermo-scans of the hybrid materials were then conducted under a dry nitrogen atmosphere at a heating rate of 20 °C/min from −80 °C to 180 °C, in two scans using a Setaram DSC 131 apparatus.

Transmission electron microscopy analysis (TEM) was performed with a Phillips CM10 electron microscope operating at 80 kV. In a typical experiment, one drop of the colloidal dispersion was put on a carbon film supported by a copper grid and allowed to dry before observation.

The condensation reactions were followed by ^{29}Si solid state nuclear magnetic resonance (NMR) measurements. The samples were immediately cooled, centrifuged and dried under vacuum. ^{29}Si solid state NMR measurements were performed on a Bruker DSX-300 spectrometer operating at 59.6 MHz using cross polarization of protons. The contact time was 5 ms, the recycle delay 1 s (sufficient for a full relaxation of protons) and the spinning rate 5 kHz. The ^{29}Si NMR spectra were simulated using the DM-FIT program for quantitative analysis.

The rate of MPS hydrolysis was monitored by gas chromatography (GC) by measuring the concentration of released methanol. Samples of latex were dissolved in appropriate amounts of THF which was used as an internal standard for GC calibration.

Results and Discussion

Synthesis of Core-Shell Colloids

The different reactions involved in the synthesis of the hybrid copolymer shell are illustrated in Figure 1.

Three types of reactions can take place simultaneously during shell growth: i) copolymerization of styrene with MPS, ii) hydrolysis of the methoxy silyl groups into silanols and shell cross-linking through condensation of the silanol groups.

As shown in our previous works, the extent of hydrolysis/condensation strongly depends on the suspension pH and on the MPS concentration. Table 1 shows the hydrolysis rate obtained with different MPS concentrations at pH 7.

Table 2 shows the condensation rate obtained with 20 wt% of MPS relative to styrene at pH 7 and pH 8.5. The different silicon-based species are called according to the conventional T^j nomenclature where T is the trifunctional alkoxysilane and j designates the number of siloxane groups bounded to the silicon atom. Under basic conditions, most of the hydrolyzed species have condensed to form mainly T^3 (−68 ppm) and T^2 (−60 ppm) sites whereas under neutral conditions, only T^0 (−44 ppm) species could be identified in the NMR spectrum of the original latexes.

From the thermodynamic point of view, the final morphology of the particles should minimize the Gibb's free energy of the system. From this thermodynamic criterion, it can be concluded that the smaller the surface tension of the shell material, the easier the formation of the core-shell

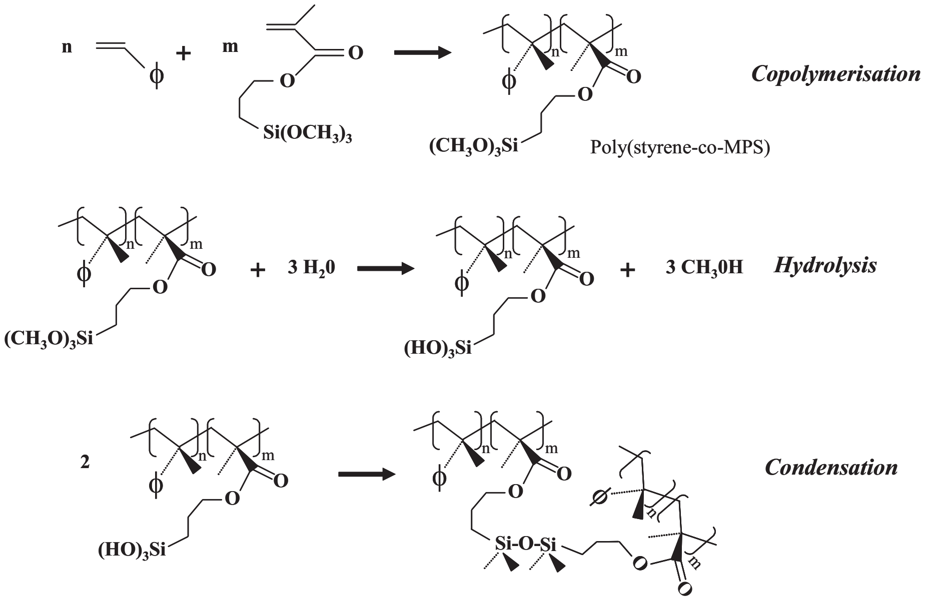

Figure 1.
Alkoxysilane-based copolymerization mechanism.

Table 1.
Extent of hydrolysis obtained by gas chromatography at various MPS concentrations and pH 7.

MPS concentration (wt% relative to styrene)	5%	10%	20%
Amount of methanol (g/100 g emulsion)	0.026	0.083	0.288
Percentage of hydrolyzed Si-OMe groups	4.5%	7.3%	12.6%

structure. In the system under consideration, the particles surface contains hydrophilic SiOH groups formed by hydrolysis of the alkoxysilyl moieties of the copolymer.[11] The presence of these SiOH groups is expected to significantly decrease the surface tension of the shell which promotes the formation of the above-mentioned core-shell structure. In the meantime, crosslinking of the shell through siloxane bounds formation prevents the movement of chain segments and stabilizes therefore the core-shell morphology.

A TEM image of the latex particles is shown on Figure 2. The core-shell structure cannot be identified by TEM as the core and shell materials display nearly the same contrast. However, the fact that the particles exhibit a narrow size distribution (there is no formation of a secondary population of particles) and that their diameter, determined either by TEM or by DLS (Figure 3), increases after copolymerization supports the assumption of formation of core-shell particles. The mean particles size increased from 126 nm before adding MPS

Table 2.
Results of the deconvolution of the ^{29}Si NMR spectra of a series of hybrid core-shell latexes. [MPS] = 20 wt% relative to styrene.

pH value	T^0	$T^1 + T^2$	T^3	$100\ (T^1 + T^2 + T^3)/T^0$
7	100	0	0	0
8.5	18	22	60	82

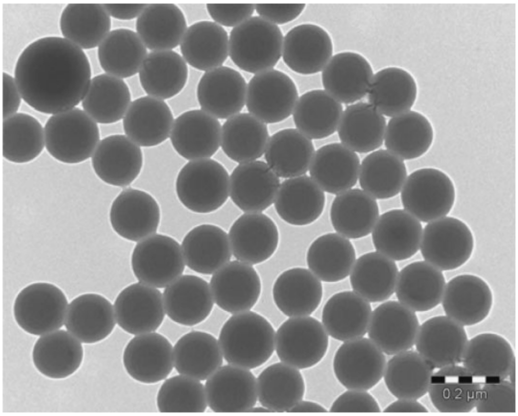

Figure 2.
TEM image of the polystyrene@(polystyrene-co-MPS) core-shell particles.

to 155.7 nm after copolymerization as measured by DLS at pH 7 with 10 wt% of MPS relative to styrene. A similar result was obtained from the TEM micrographs analysis.

Nanocapsules Formation

The synthesized hybrid particles can be used to form hollow nanocapsules. In order to do so, the core must be extracted from the core-shell particles by dissolution in a solvent. Only the polystyrene core is dissolved since the shell is reticulated. In order to promote polystyrene dissolution, we introduced a chain transfer agent at the beginning of the reaction to decrease the polymer molecular weight. Optimization of the core molecular weight allows a better dissolution and later on a better diffusion through the shell. As the chain transfer agent is mainly consumed during styrene polymerization, it is not expected to influence the molecular weight of the polymer chains formed during the copolymerization reaction. After dissolution, the core is allowed to diffuse through a dialysis

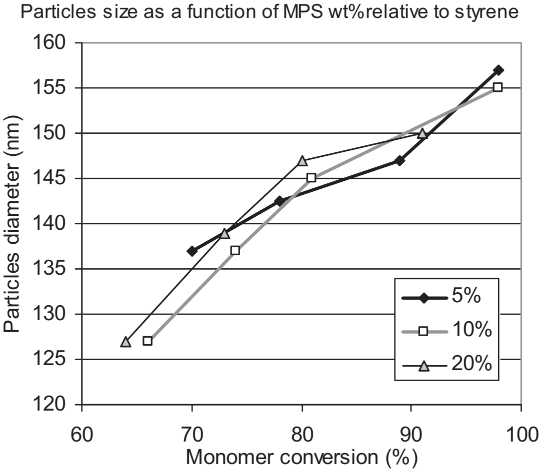

Figure 3.
Evolution of the particles size as a function of the overall monomer conversion while varying the MPS concentration in the shell.

membrane in order to separate it from the nanocapsules or is extracted by an exhaustive centrifugation/redispersion procedure.

Solubility of Polystyrene in a Mixture of THF and Water

When the latex is diluted into THF, the solvent molecules penetrate the nanoparticles. The polystyrene core thus swells and progressively dissolves in the continuous phase which is composed of THF and water. The dissolved polystyrene chains go out of the capsules until equilibrium of the concentration of polystyrene in the solvent is obtained between the interior and the exterior of the nanoparticles. The flux of the polymer through the capsules depends on the gradient of polymer concentration between the interior and the exterior of the nanocapsules and on the permeability of the shell that in turn depends on the degree of cross linking.

The concentration of the dissolved core which is determined by the polystyrene solubility in the surrounding medium is therefore of great importance. Figure 4 shows the evolution of the polystyrene solubility as a function of the THF:water weight ratio for different polymer molecular weights. It is worthwhile to mention that the solids content of the latex was 30% before dilution in THF. The data shows that using a chain transfer agent significantly increases the solubility of polystyrene in the THF/water mixture as expected. The average number molecular weight of the core was fixed at 10219 g/mol using 6% of chain transfer agent whereas without chain transfer agent it was about 96,000 g/mol. In addition, the higher the amount of THF, the higher is the amount of dissolved polystyrene. Therefore, in the following experiments the THF:water will be fixed at 7 and the core-shell particles will be synthesized in the presence of 6 wt% of chain transfer agent.

Extraction of the Core from the Core-Shell Particles

Two different techniques were used to extract the core from the core-shell particles and to form the nanocapsules. In the first technique, the dispersion was centrifuged and redispersed in THF. The procedure was repeated until complete extraction of the core. In the second technique, the 30% solid content latex was dissolved in THF (the THF:water ratio used for dissolution was 7:1) and introduced into a dialysis membrane that was put in THF in order to promote the dissolved polystyrene to diffuse through the membrane pores.

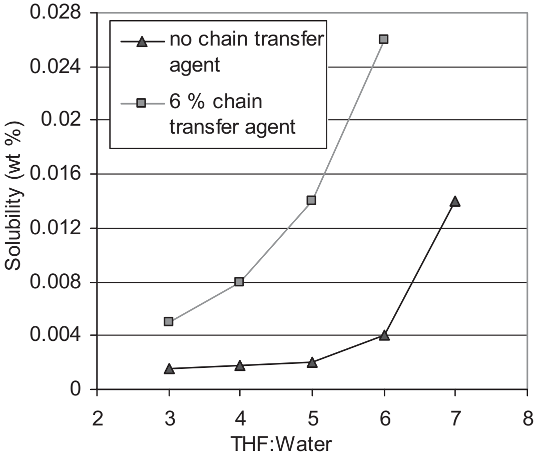

Figure 4.

Polystyrene solubility in a THF:water mixture as a function of polystyrene molecular weight. Mn = 10219 g/mol with 6% of chain transfer agent and Mn = 96000 g/mol without chain transfer agent.

Figure 5 shows the TEM images of particles obtained by both techniques. It seems that the first technique (centrifugation/redispersion) influences the morphology of the capsules (Figure 5b–c). Indeed, the strong mechanical force applied during centrifugation destroys the original spherical shape of the capsules and the nanoparticles tend to collapse on the TEM grid.

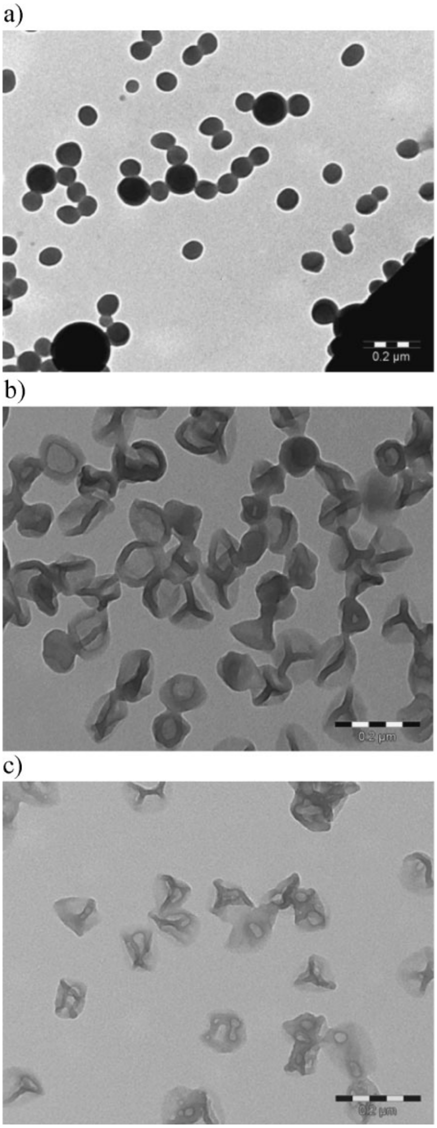

Figure 5.
TEM images of (a) hybrid nanocapsules obtained by dialysis (b) hybrid nanocapsules obtained by centrifugation/redispersion in THF of core-shell particles with a styrene to MPS ratio of 3:1 (c) hybrid nanocapsules obtained by centrifugation/redispersion in THF of core-shell particles with a styrene to MPS ratio of 3:2.

On the other hand, intact spherical capsules could successfully be obtained by the dialysis technique, as illustrated in Figure 5a. Water in the mixed solvent goes out of the membrane first which greatly increases the solubility of the polymer core and makes it easier to extract. By this way, the polymer extracted out of the core can go out of the membrane gradually and a suspension of nanocapsules is obtained. However, the driving force in the process of dialysis is the difference of polymer concentration between inside and outside the membrane which is quite weak. Therefore, it is likely that some polystyrene chains remain entrapped inside of the capsules. The procedure must be thus repeated a sufficient number of times to ensure complete removal of the core.

The silane content in the shell also influences the morphology of the capsules. Figure 5b shows that increasing the concentration of MPS in the capsules increases their softness. This was also confirmed by DSC which showed that the Tg of the hybrid copolymer decreased from 91.0 to 86.3 °C when the MPS concentration was increased from 5 to 20 wt% relative to styrene.

The hybrid nanocapsules were characterized by FTIR (Figure 6). The spectrum shows characteristic vibrations of polystyrene at 1601, 1492, 1452, 1028, 906, 757 and 697 cm^{-1} as well as absorption bands

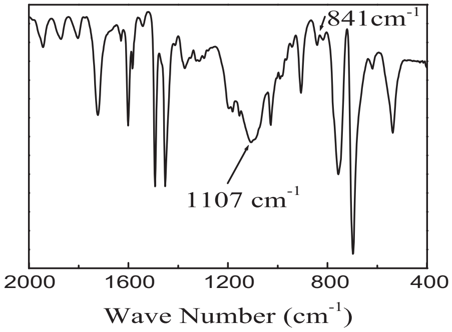

Figure 6.
FTIR spectrum of the polystyrene-*co*-MPS hybrid nanocapsules.

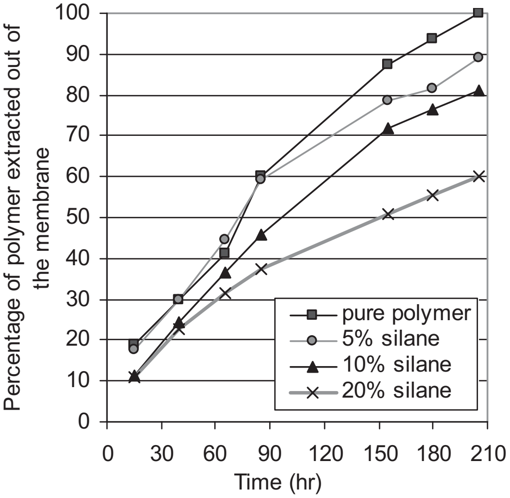

Figure 7.
Effect of the MPS concentration (in wt% relative to styrene) on the amount of extracted polystyrene (in wt% of the total amount of polymer) as determined by UV analysis of the solution outside of the dialysis membrane as a function of time.

corresponding to MPS (1724 and 1107 cm^{-1}) and supports the formation of the hybrid structure.

UV analysis was used to quantity the amount of polymer separated from the polymer particles. The part of polymer that goes out of the membrane is assumed to be equal to the total amount of polymer extracted from the polymer particles. Figure 7 shows that the amount of polymer extracted depends on the silane content in the copolymer. With low silane concentrations, the polymer diffuses easily through the membrane while the diffusion is slowed down when increasing the silane content. This is probably due to the difficulty of diffusion of polystyrene through a shell composed of networks. The polymer chains diffusion gets slower as the cross link density gets higher.

Conclusions

In this work, hybrid nanocapsules were produced from polystyrene@(polystyrene-co-MPS) core-shell nanoparticles by dissolution of the polystyrene core in THF. The dissolved polymer chains were removed from the suspension either by dialysis or by a series of centrifugation-redispersion cycles in THF. In order to facilitate dissolution and accelerate diffusion through the shell, the molecular weight of the core was decreased by adding a chain transfer agent. A significant effect on the solubility of the polystyrene chains was observed using 6% of chain transfer agent and when using a large excess of THF.

It was found that the centrifugation-redispersion technique altered the shape of the capsules while intact spherical nanocapsules were obtained by dialysis. However, this last procedure did not enable to extract all the polystyrene from the core-shell particles.

The higher was the amount of MPS in the shell, the slower was the diffusion of the polystyrene chains through the hybrid shell. Even though the Tg of the copolymer was lower than that of polystyrene, the incorporation of MPS in the copolymer induced cross linking and gave rise to a low shell permeability. These hybrid functional capsules could be used for encapsulation and diffusion-controlled release of active substances with potential applications in biology or cosmetics.

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