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Synthesis of Different Mesoporous SiO_2 Structures by Using PNIPAM-*co*-PS Particles as Templates

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Summary: Different mesoporous SiO_2 structures were synthesized by a novel process in which poly(N-isopropyl acrylamide)-*co*-polystyrene (PNIPAM-*co*-PS) copolymer particles with 10 and 35 wt% styrene, respectively, acted as templates. The copolymer particles were prepared by direct miniemulsion polymerization and subsequently assembled by sedimentation-aggregation with the silica precursor tetraethyl orthosilicate (TEOS). After a sol-gel process the polymeric cores were removed by calcination at 650 °C. The influence of temperature of the sol-gel process on the morphology of the mesoporous silica was investigated. Choosing the temperature below or above the lower critical solution temperature (LCST) of the copolymer allows fine-tuning of the pore size and pore distribution.

Keywords: mesoporous silica; microgel nanoparticles; miniemulsion polymerization; soft-sphere templating

Introduction

A mesoporous system is generally described as a material with a regularly arranged pore system with pores in the range of 2 to 50 nm. Due to these pores, the materials possess a high degree of order and a very large and homogeneous surface in the range from 800 to 1500 $m^2 \cdot g^{-1}$. Because of these specific properties they are of interest for nanostructured materials that possess novel electronic, optical, photochemical and catalytic properties as needed for separation technologies and production of chemicals. At the beginning, the only available well ordered porous materials were natural and synthetic zeolites which are microporous crystalline molecular sieves. The diameter of their pores is in the range of 0.4 to 1.5 nm.[1] With the discovery of high surface area silica and aluminosilicate materials in 1988 (the fold sheet material, FSM) and in 1992 (the M41S family), a new field of well-ordered molecular sieves with diameters in the range of 2 to 10 nm was available.[2] The synthesis based on self-assembled charged or neutral surfactant molecules like poly(ethylene oxide) polymers and triblock copolymers poly(ethylene oxide-*b*-propylene oxide-*b*-ethylene oxide) as templates during the sol-gel process of the precursor leads to mesoporous materials with pore sizes up to 30 nm.[3] Materials with even bigger macropores with an average diameter of 200 to 800 nm can be obtained by using monodisperse polystyrene (PS) beads as templates in the sedimentation-aggregation technique.[4]

Here we report the use of a new type of thermoresponsive poly(N-isopropyl acrylamide)-*co*-polystyrene (PNIPAM-*co*-PS) hydrogel particles with a size of 120 to 320 nm as templates during the sedimentation-aggregation synthesis of a mesoporous material. The particles were synthesized by miniemulsion polymerization[5,6] which allows to form particles with a high homogeneity of the copolymer composition.[7] To the best of our knowledge, up to now only hard-sphere particles like PS or

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poly(methyl methacrylate) (PMMA) beads were used as templates in the sedimentation-aggregation process. Because of their hydrogel properties PNIPAM-*co*-PS particles can be considered as soft-sphere particles. The size of the particles and the thermoresponsive shrinking rate depend on the monomer ratio in the hydrogel particles. The synthesis of mesoporous SiO_2 matrices is accomplished by using soft-sphere particles as templates and the pore size of the silica matrix can be influenced directly by changing the temperature during the sedimentation-aggregation process.

Experimental Part

Preparation of PNIPAM-*co*-PS Nanoparticles as Templates

Methylene bis(acrylamide) (MBA) cross-linked PNIPAM-*co*-PS particles were synthesized using the miniemulsion technique. Two different particles were synthesized with 10 wt% and 35 wt% of styrene. In a typical synthesis, the monomer N-isopropylacrylamide (NIPAM) was dissolved in the comonomer styrene. Hexadecane was added as ultrahydrophobe. This solution was added to the continuous phase consisting of water, the surfactant SDS, and the cross-linker MBA. The disperse phase was homogenized by ultrasonication. The obtained miniemulsion was heated up to 72 °C and the polymerization was initiated by adding KPS. The obtained particles were analyzed upon the thermoresponsive change of the particle size by dynamic light scattering measurements at different temperatures between 20 °C and 55 °C.

Synthesis of Mesoporous SiO_2 Structures

A mixture of 8 mL ethanol and different amounts of H_2O was stirred for 5 min. Then different amounts of the aqueous polymer latex were added and the reaction batch stirred for another 45 min. The solution was adjusted to pH 2 by dropwise addition of HCl and was then given to different amounts of the silica-precursor tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$). Different batches were prepared at 25 °C and 40 °C to analyze the influence of the thermoresponsive change of the template particle size on the pore size of the obtained SiO_2 matrix. The gelation time was varied depending on the temperature. At 25 °C the gelation time was 24 h and at 40 °C samples were taken after 4 h and 24 h. All samples were centrifuged at 20000 rpm for 6 h at 25 °C or 40 °C. After centrifugation, the obtained pellets were calcinated at 650 °C for 5 h to remove the templates. For comparison pure polystyrene particles as hard templates were also employed. The different steps of the process are shown in Figure 1. The composition of the different samples, the reaction temperature, and the gelation time are summarized in Table 2.

Characterization

The morphology and the pore size of the mesoporous SiO_2 samples were examined using a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). The silica powders were dispersed in acetone before. For SEM one droplet was placed on an aluminium plate. The samples were dried at room temperature. Before examination with SEM the aluminium plates were sputtered with Pd/Au.

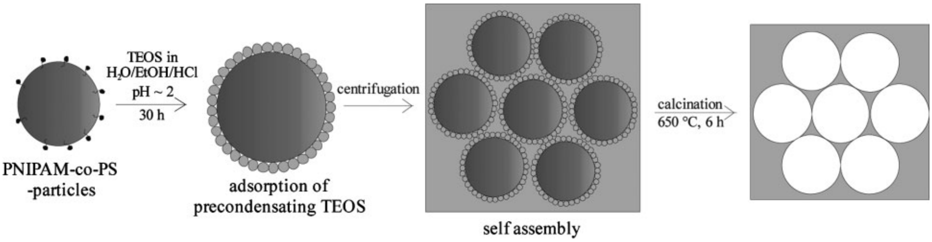

Figure 1.
Sedimentation-aggregation-technique for the synthesis of mesoporous SiO_2 matrices.

Table 1.
T_g of the polymers in the PNIPAM (P1) and the comonomer PNIPAM-co-PS template particles P2 and P3 as obtained in the miniemulsion polymerization process.

Particles	wt.% styrene	T_g (2^{nd} heat)
P1	0	123 °C
P2	10	96 °C
P3	35	82 °C

The hydrodynamic diameters of the nanoparticles in water were determined by dynamic light scattering (DLS) with a Nicomp particle sizer (model 380, PSS, Santa Barbara, CA) at a fixed scattering angle of 90°.

Results and Discussion

PNIPAM-co-PS nanoparticles with two different copolymer composition were synthesized by miniemulsion polymerization. In order to investigate the homogeneity of the monomer distribution in the copolymers the glass transition temperatures (T_g) were determined and compared with that of pure PNIPAM particles. There is a clear descend of T_g with increasing content of styrene (Table 1).

For all samples, only one glass transition is observed which indicates that both monomers are statistically distributed in the polymer network and no blocky structure was formed.

PNIPAM is one of the best known polymers exhibiting a lower critical solution temperature. Figure 2 shows that the thermoresponsiveness is still preserved and that the particle size of both particles decreases with increasing temperature. The size change is fully reversible (not shown).

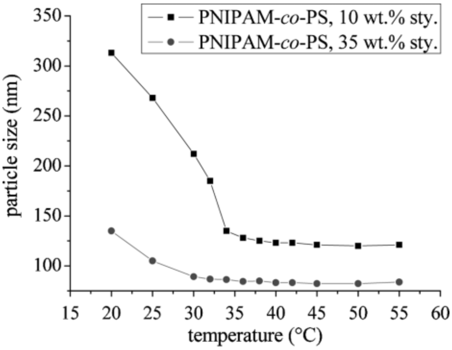

Figure 2.
Thermoresponsive decrease of the particle size with increasing temperature.

As known from the literature,[8] a comonomer content of 10 wt% styrene has only a little influence on the thermoresponsiveness of the particle size compared to pure PNIPAM (upper curve in Figure 2). The lower critical solution temperature (LCST) of the PNIPAM-*co*-PS particles is shifted from 37 °C to ~ 34 °C. This is induced by the incorporation of the hydrophobic comonomer in the hydrophilic hydrogel network. If the content of the comonomer is increased to 35 wt%, the decrease of particle size with increasing temperature is much less expressed (lower curve in Figure 2). No more clear LCST is observed and only a small decrease in particle size from $d_{25\,°C} = 140\,\text{nm}$ to $d_{50\,°C} = 80\,\text{nm}$ is observed.

The most important feature for the formation of a mesoporous matrix with

Table 2.
Reaction parameters for the different SiO_2 matrices (Template particles: P1: PS, P2: PNIPAM-co-PS with 10% PS, P3: PNIPAM-co-PS with 35% PS).

Sample	Ratio/g mL^{-1}	Template	V_{H2O}/mL	$V_{Ethanol}$/mL	$V_{template\ latex}$/mL	$V_{precursor}$/mL	$t_{reaction}$/h	$T_{reaction}$/°C
Si-PS	0.0516	PS	24	2.7	0.85	1.3	24	25
Si-R1	0.413	P3	72	8	20	4	24	25
Si-R2(4h)	8.26	P3	62	8	20	0.2	4	40
Si-R2(24h)	8.26	P3	62	8	20	0.2	24	40
Si-R3	0.414	P2	72	8	32	4	24	25
Si-R4(4h)	3.01	P2	62	8	20	0.4	4	40
Si-R4(24h)	3.01	P2	62	8	20	0.4	24	40

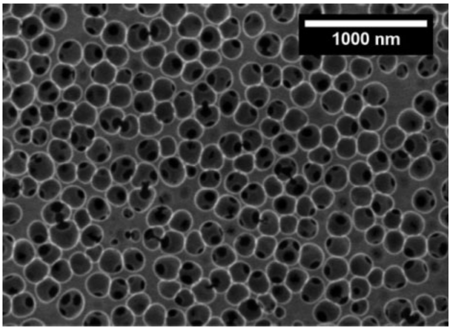

Figure 3.
SEM picture of the SiO_2 matrix (sample Si-PS) with PS particles as template.

well-ordered pores generated by particulate templates is the ratio R of the mass of template (in g) and volume of precursor (in mL). For every batch this ratio R was calculated concerning the size of the template particle at the given temperature.

PS Particles as Template

The first synthesis (Si-PS) was performed using PS particles ($d = 185$ nm) as typical hard-sphere template for comparison with $R_{styrene} = 0.0516\,g\,mL^{-1}$. The SiO_2 matrix was synthesized as described above by the sedimentation-aggregation technique with a gelation time of 24 h. The SEM picture of the obtained mesoporous matrix after the calcination step at 650 °C is shown in Figure 3.

The picture displays a uniform porous structure over large areas. The average pore size is 190 nm in good accordance with the size of the PS particles (185 nm). This confirms that the PS particles function very well as templates for the pore formation.

PNIPAM-*co*-PS Particles with 35 wt% Styrene as Template

In the next set of syntheses, PNIPAM-*co*-PS template particles (P3) with 35 wt.% of styrene were used for the formation of a silica matrix in the sedimentation-aggregation process at a reaction temperature of 25 °C. Despite of the relatively large amount of styrene in the copolymer, these particles still show a noticeable change in diameter when increasing the temperature (see Figure 2). So, at 25 °C these particles should be considered as soft-sphere particles in contrast to the pure PS particles (see above). The SiO_2 matrix was synthesized as described above with a ratio $R_1 = 0.413\,g\,mL^{-1}$ and a gelation time of 24 h. The SEM pictures of the obtained mesoporous SiO_2 matrix are displayed in Figure 4 showing a uniform porous structure over large areas. Figure 4b reveals that the entire matrix is completely permeated with uniform pores. The average pore size is 90 nm. The small discrepancy between the diameter of the template particles (105 nm, see Figure 2) and the resulting pores can be traced to several factors. One reason might be the deformation and compression of the soft-sphere particles during the centrifugation step. Another reason for shrinking was described by Li et al.[9] They showed that the contraction of the lattice during calcination is caused by the removal of the template and a subsequent condensation of the remaining silanol groups.

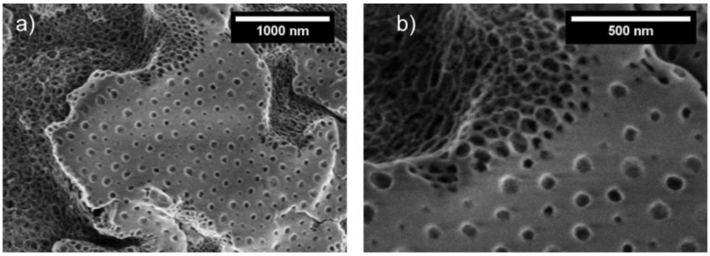

Figure 4.
SEM-images in different magnifications of the SiO_2 matrix (sample Si-R1) using the copolymer particles P3 as template ($R_1 = 0.413\,g\,mL^{-1}$, $T_{reaction} = 25\,°C$, $t_{gelation} = 24\,h$).

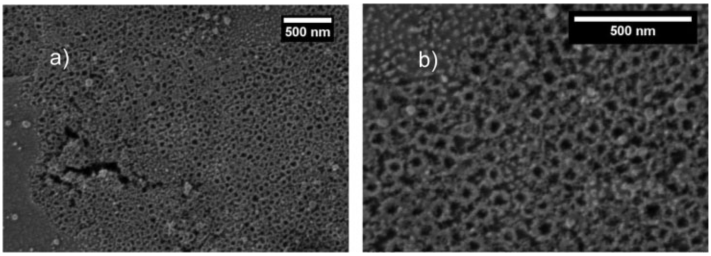

Figure 5.
SEM images in different magnifications of the SiO_2 matrix using P3 as template particles ($R_2 = 8.26\,g\,mL^{-1}$, $T_{reaction} = 40\,°C$, $t_{gelation} = 4\,h$).

When the reaction temperature was increased to 40 °C the amount of precursor had to be adjusted because of the thermoresponsive shrinking of the template particles which causes a decrease of the total volume of template. The reaction at 40 °C and with the template particles P3 was performed with a ratio of $R_2 = 8.26\,g\,mL^{-1}$. Samples were taken after a gelation time of 4 h (sample Si-R2(4h)) and 24 h (Si-R2 (24h)). The centrifugation step took also place in a centrifuge at 40 °C. The SEM pictures of the obtained SiO_2 matrices after calcination are displayed in Figure 5.

Figure 5 shows a uniform porous structure with a fairly uniform arrangement of the pores and an average pore size of about 50 nm. This indicates that the discrepancy between the diameter of the template particles at 40 °C (82 nm) and the resulting pores is relatively more expressed compared to the matrix obtained by the syntheses at 25 °C. The second sample taken after a gelation time of 24 h is shown in Figure 6. The SEM image in Figure 6 shows a breaking edge of the obtained SiO_2-matrix revealing the inside of the matrix. It shows a uniform porous structure with an average pore size of 28 nm.

The even larger discrepancy between the particle size of the template (82 nm, see Figure 2) and the resulting pore size compared to the syntheses at 25 °C might be attributed to the diffusion and subsequent sol-gel process of TEOS into the more hydrophobic particles above the LCST. The more pronounced effect at longer gelation time confirms the kinetic influence of the diffusion on this process.

PNIPAM-*co*-PS Particles with 10 wt% Styrene as Template

In the next step, PNIPAM-*co*-PS particles (sample P2) with 10 wt% of styrene were used as template in the sedimentation-aggregation process. Because of the small amount of the hydrophobic comonomer styrene, these particles show a strong hydrogel-like behavior with increasing temperature as shown in Figure 2. So at 25 °C these particles can be truly considered as soft-sphere particles. The SiO_2 matrix was synthesized as described above with a ratio $R_3 = 0.414\ g \cdot mL^{-1}$ and a gelation time of 24 h. The SEM pictures of the obtained mesoporous SiO_2 matrix are displayed in Figure 7. Both images show small areas with a uniform porous structure (circles in Figure 7). The average pore size in these areas is 15–30 nm.

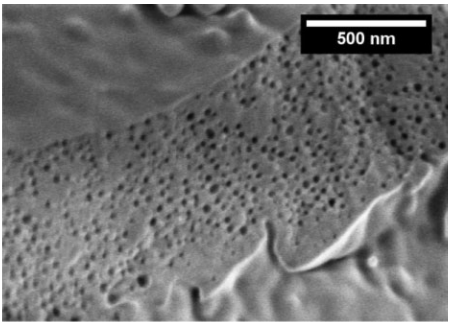

Figure 6.
SEM image SiO_2 matrix using P3 as template ($R_2 = 8.26\,g\,mL^{-1}$, $T_{reaction} = 40\,°C$, $t_{gelation} = 24\,h$).

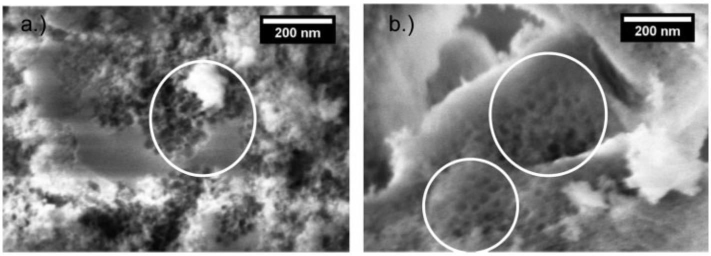

Figure 7.
SEM-images of SiO_2 matrices (Si-R3) using P2 as template ($R_3 = 0.414\,g\,mL^{-1}$, $T_{reaction} = 25\,°C$, $t_{gelation} = 24\,h$).

When the reaction temperature was increased to 40 °C the amount of the template was adjusted due to a decrease of the total volume of the template particles with $R_4 = 3.01\ g \cdot mL^{-1}$. Samples were taken after a gelation time of 4 h and 24 h and centrifuged at 40 °C. The SEM pictures of the obtained SiO_2 matrices are displayed in Figure 8.

Both images in Figure 8 show a uniform porous structure over large areas of the matrix with an average pore size of 37 nm. In Figure 8b the porosity of the whole "brush-like" matrix is nicely visible.

If the gelation time is increased to 24 h, an object with uniform porous structure is visible in some areas (see Figure 9). One of these areas is marked and shown in a higher magnification. The average pore size in this area is 34 nm.

Therefore, it could be shown that the syntheses of a mesoporous SiO_2 matrix with larger areas of uniform porous structure were successful for the reactions performed

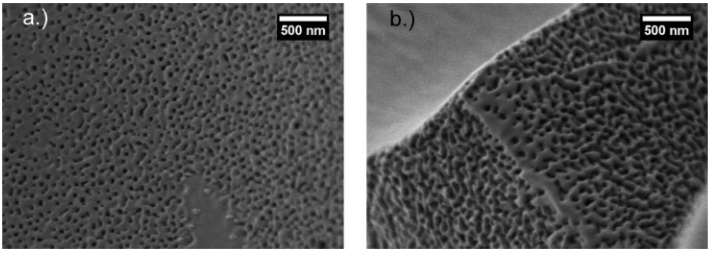

Figure 8.
SEM images of SiO_2 matrices using particles P2 as template ($R_4 = 3.01\ g \cdot mL^{-1}$, $T_{reaction} = 40\,°C$, $t_{gelation} = 4\,h$).

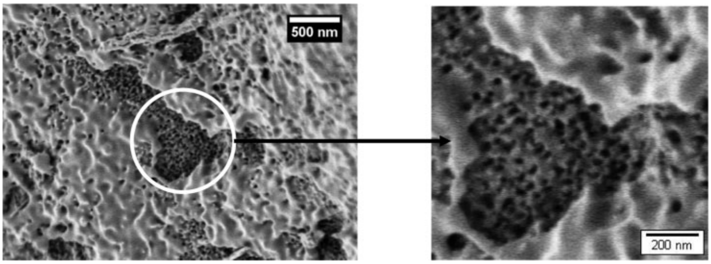

Figure 9.
SEM image of SiO_2 matrix Si-using P2 as template ($R_4 = 3.01\,g\,mL^{-1}$, $T_{reaction} = 40\,°C$, $t_{gelation} = 24\,h$) (left) and with detailed view of the marked area (right).

at 40 °C with PNIPAM-*co*-PS particles with 10wt% of styrene as templates. The synthesis at 25 °C results in objects with only small domains of uniform porous structures. Furthermore, the pore sizes (15 to ca. 40 nm, see above) seem to be quite independent of the template particle sizes (ca. 270 and 120 nm, respectively, see Figure 2). Hence we assume that the particles still act as template for the pore formation but TEOS diffuses probably even stronger into the particles than in the case of the 35 wt% styrene copolymer. We attribute this finding to the specific solubility of TEOS in the PNIPAM network. This might be also a reason for the lack of large areas of a uniform porous structure at 25 °C.

Conclusion

Mesoporous SiO_2 structures with uniform pores were successfully prepared. The syntheses were performed by a sol-gel process of a silica-precursor (TEOS) in combination with the sedimentation-aggregation-technique. Two different PNIPAM-co-PS copolymer particles with 10 and 35 wt % of styrene were used as templates. The pore size of the synthesized silica matrices could be influenced by the reaction temperature and was determined by SEM. If the temperature was increased above the LCST of the template particles, the pore size decreased noticeably. These reactions revealed that "soft" sphere particles like hydrogel particles are also suitable as templates for the syntheses of mesoporous silica matrices.

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