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SHORT COMMUNICATION

Synthesis of bifunctional core–shell particles with a porous zeolite core and a responsive polymeric shell

S. Ziesmer · N. Stock

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Abstract The aim of our work is the synthesis and characterization of colloidal core–shell particles with a zeolite core and an environmentally responsive shell. We have synthesized colloidal ZSM-5 zeolite and modified the surface with 3-(trimethoxysilyl)propyl methacrylate in order to introduce double bonds at the surface. The cross-linked polymeric shell was prepared by precipitation polymerization using the functionalized zeolite particles as seeds. We employed thermoresponsive poly(*N*-isopropylacrylamide) and pH-responsive poly(vinylpyridine) as the polymeric shell, respectively. The temperature- and pH-depending swelling and deswelling of the core–shell particles were characterized with dynamic light scattering techniques. Transmission electron microscopy pictures show the morphology of the synthesized particles. It is proposed that these types of bifunctional core–shell particles could be of use for controlled uptake and release applications and separation of molecules.

Keywords Zeolite · Hydrogel · Temperature-responsive · pH-responsive · Core–shell particles

Introduction

The synthesis of functional materials that are able to react to external stimuli is a fascinating and very important field in material science. Environmentally responsive polymeric core–shell particles in the nano- to micrometer range have attracted great attention in recent years due to their practical and potential applications in controlled release systems, encapsulation and heterogeneous catalysis, etc. [1–6]. The diffusion through the polymer shell can be controlled by external stimuli (temperature [7, 8], pH value [9–11], solvent quality [12, 13], and magnetic [14, 15] and electric field [16]) which directly influence the transport properties of guest molecules in and out of the inner core.

Silica is often used as a core material [17] as it can be readily removed by etching with hydrofluoric acid, producing a hollow sphere [18, 19], although polymer latex particles may also be used for the same purpose [20]. But there is a lack of information about the use of materials with well-defined porosity (e.g., zeolites) as core particles. Zeolites are crystalline microporous solids with pores in the range of approximately 0.3–1 nm in diameter of various shapes, sizes, and topologies that control the reactivity and shape-selective properties of these materials [21, 22]. These characteristics are the basis for their immense importance in catalysis, separations, and ion exchange. Zeolites can also be used as host materials for guest molecules in slow release applications [23, 24]. The well-defined porosity of zeolites restricts the diffusion of molecules in and out of the pores based on their size. For fast exchange processes, nanocrystalline zeolites have been shown to be advantageous due to the short diffusion pathway [25].

The most widely studied class of responsive polymers used as shells in core–shell particles are temperature-responsive poly(acrylamides), specifically poly(*N*-isopropylacrylamide) (PNIPAm). This has been well documented, e.g., in review articles [1, 2]. Purely organic core–shell particles have been mainly described, for example, double temperature sensitive [26] and poly(styrene) (PS)–PNIPAm particles [27, 28]. PNIPAm exhibits a coil–globule transition in aqueous solution at a lower critical solution temperature (LCST) of about 32 °C [29]. By raising the temperature above the

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S. Ziesmer · N. Stock (✉)
Institute of Inorganic Chemistry, University of Kiel,
24098 Kiel, Germany
e-mail: stock@ac.uni-kiel.de

transition temperature, water bound to the polymer chain is released and the soluble polymer coils start to form solid globular particles. Thus, below the LCST the polymer shell is in a swollen state and permeable, which allows free molecular exchange between the inner core and the bulk medium while above the LCST diffusion is hindered.

Poly(vinylpyridine) (PVP) is a well-known pH-responsive polymer [30]. At low pH values, PVP becomes positively charged due to the protonation of the pyridine nitrogen. Water becomes increasingly incorporated into the polymer network producing an increase in the polymer volume and particle swelling occurs. In this state, the polymer is permeable for guest molecules. When the PVP is uncharged (pH >4.8), hydrophobic interactions dominate, the polymer shrinks, and the permeability for molecules is restricted [31]. PVP polymer gels have been shown to reversibly swell and deswell upon decreasing and increasing pH, respectively, over many cycles [30].

In this work, we chose the nanocrystalline zeolite ZSM-5 as the core material and the thermoresponsive PNIPAm as well as the pH-responsive PVP for the shell material.

Experimental

Materials

Tetraethyl orthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH, 20 wt.% aqueous solution), aluminum isopropoxide, 3-(trimethoxysilyl)propylmethacrylate (MPS), ammonia solution (25 wt.% in water), ethanol (96%), *N*-isopropylacrylamide monomer (NIPAm), *N*,*N'*-methylenebis(acrylamide) (BIS), 2-vinylpyridine (VP), divinylbenzene (DVB), sodium dodecylsulfate (SDS), α,α'-azodiisobutyramidine dihydrochloride (V 50), and potassium persulfate (KPS) were all purchased from Sigma-Aldrich and used as received. The water used in all synthesis and washing steps was ion exchanged.

Preparation of the ZSM-5 zeolite

The ZSM-5 zeolite was prepared from a clear gel solution according to the procedure described by Mintova and Bein [32]. The synthesis gel composition for the ZSM-5 synthesis is $9TPAOH:0.25Al_2O_3:25SiO_2:599H_2O$. The starting materials TEOS (5.7 mL), TPAOH solution (9 mL), and aluminum isopropoxide (0.1 g) were mixed in water and stirred at room temperature for 24 h to ensure complete hydrolysis of TEOS and aluminum isopropoxide. To remove the ethanol and the isopropyl alcohol, the solution was heated to 50 °C for 5 h. After aging for 48 h, the solution was transferred into a polypropylene vessel and treated hydrothermally for 24 h at a temperature of 90 °C. The zeolite particles resulting from the hydrothermal treatment were purified by separation from the mother liquid by three steps of centrifugation. After each centrifugation cycle, the particles were redispersed in ion-exchanged water, while after the third centrifugation step the particles were dispersed in ethanol. The concentration of the zeolite particles in the final dispersion was 6.5 wt.%.

MPS modification of the ZSM-5 particles

The zeolite dispersion was diluted with ethanol to a concentration of 1 wt.%. Zeolite dispersion of 125 mL was mixed with 500 µL MPS and 100 µL ammonia solution and stirred for 48 h at room temperature. To remove the unreacted MPS and MPS oligomers from the dispersion, four cycles of centrifugation and redispersion in ethanol were performed. After the last centrifugation step, the MPS-modified zeolite was dispersed in 10 mL ethanol.

Synthesis of the zeolite–PNIPAm core–shell particles

The zeolite–PNIPAm core–shell nanoparticles were prepared by aqueous free radical precipitation polymerization under a nitrogen atmosphere. In this polymerization process, the amounts of NIPAm and BIS were varied (Table 1). As an example, 1 mL of the ethanolic MPS-modified zeolite dispersion was added to 25 mL deionized water. The mixture was heated to 70 °C and 3 mL water solution of 0.25 g NIPAM and 0.037 g BIS was injected. After treating the solution with N_2 gas for 15 min, a solution of 6 mg KPS in 1 mL water was added. The reaction mixture was stirred at 70 °C for 2.5 h and cooled down to ambient temperature. The dispersion was dialyzed for 10 days against deionized water to remove unreacted starting materials and oligomers.

Synthesis of the zeolite–PVP core–shell particles

The zeolite–PVP core–shell nanoparticles were prepared by aqueous emulsion polymerization. The amounts of the starting materials used for the synthesis are listed in Table 2. In a typical synthesis, 1 mL of the ethanolic MPS-modified zeolite dispersion was added to 25 mL deionized water and

Table 1 Quantity of educts used for the synthesis of zeolite–PNIPAm core–shell particles

Sample	NIPAm [mg]	BIS [mg]	KPS [mg]
CS 1	250	37.5	6
CS 2	250	18.75	6
CS 3	250	50	6
CS A	125	37.5	6
CS B	375	37.5	6

Table 2 Quantity of educts used for the synthesis of zeolite–PVP core–shell particles

Sample	VP [μl]	DVB [μl]	Initiator [mg]	SDS [mg]
P 1	125	15	8 (KPS)	10
P 2	125	15	8 (KPS)	–
P 3	125	15	8 (V 50)	10

heated to 70 °C; 125 μL VP, 12.5 μL DVB, and a solution of 10 mg SDS in 1 mL water were injected. The mixture was treated with N_2 gas in order to remove oxygen. After 15 min, a solution of 8 mg KPS in 1 mL water was added. The reaction mixture was stirred at 70 °C for 2.5 h and cooled down to ambient temperature. The dispersion was dialyzed for 10 days against deionized water to remove unreacted starting materials and oligomers.

Methods

X-ray powder diffraction patterns of the ZSM-5 were recorded with a Stoe Stadi/P diffractometer using monochromated CuKα_1 radiation. Scanning electron microscope (SEM) images of the ZSM-5 nanocrystals were collected using a JEOL JSM 6500F scanning electron microscope. Infrared (IR) spectra of the MPS-modified ZSM-5 were recorded on a Bruker IFS 66v/S Fourier transform (FT)IR spectrometer in the spectral range 4,000–400 cm^{-1} using the potassium bromide disk method. Transmission electron microscopy (TEM) images of the core–shell particles were obtained using a JEOL JEM 2011 transmission electron microscope operating at 200 kV. Hydrodynamic diameters of the core–shell particles were measured using the ZetaPlus apparatus (Brookhaven Instruments, USA) by the dynamic light scattering (DLS) technique.

Results and discussion

In order to be able to form core–shell particles, the surface of the zeolite was modified with the organosilicon coupling agent 3-(trimethoxysilyl)propyl methacrylate (MPS) to introduce double bonds on the zeolite surface (Scheme 1). The cross-linked polymer shell was prepared by precipitation polymerization using the functionalized zeolite particles as seeds. The double bonds on the zeolite surface react with the growing radicals during the polymerization. The surface modification by MPS is essential to avoid the preparation of pure polymer particles containing no zeolite core [33]. An alternative mechanism for very small nonporous SiO_2 particles was recently described where the hydrophobic MPS-functionalized SiO_2 particles are included in the emulsion droplets of the NIPAm monomer prior to polymerization [17].

Synthesis and characterization of nanocrystalline ZSM-5

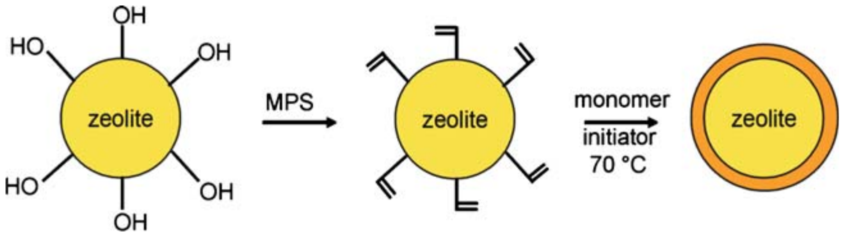
Powder X-ray diffraction (XRD) patterns confirm the successful synthesis of the zeolite ZSM-5 (Fig. 1a). The measured diffraction pattern agrees well with the diffraction pattern expected for ZSM-5. A SEM image of the ZSM-5 sample is shown in Fig. 1b. The particles are evenly shaped and have an average diameter of approximately 100 nm. The monodispersity was corroborated by dynamic light scattering measurements. The hydrodynamic diameter of the particles measured by DLS was 114 nm.

MPS modification of the ZSM-5 particles

In order to obtain a functionalized surface, MPS which contains a C=C double bond was added and reacted with the Si–OH groups on the zeolite surface by hydrolysis. The functionalization of the inner pore wall is not likely since template ions (tetrapropylammonium ions) are in the channels and cages of the zeolites. Figure 1 also displays the IR spectra of the zeolite before (Fig. 1c) and after (Fig. 1d) grafting MPS on the surface. The IR spectra after the MPS modification displays additional bands at 1,719 cm^{-1} (ν C=O), 2,842 cm^{-1} (ν CH_2), and 2,925–2,950 cm^{-1} (ν CH_3) which gave evidence for a successful grafting of MPS on the zeolite surface [33].

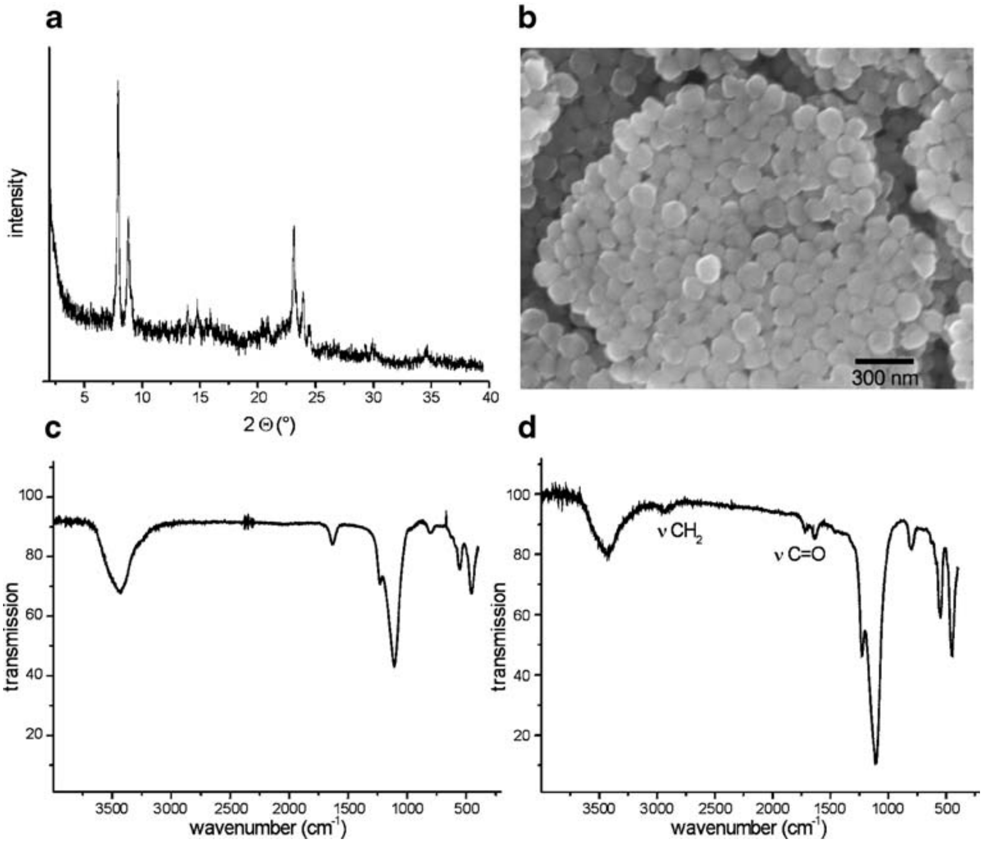
Synthesis of the zeolite–PNIPAm core–shell particles

Zeolite–PNIPAm core–shell particles were synthesized through emulsion polymerization of NIPAm and BIS with MPS-grafted zeolite particles which were used as seeds in the polymerization process. Because of the water insolubility



Scheme 1 Schematic representation of the synthesis route of the core–shell particles

Fig. 1 Characterization of the zeolite ZSM-5. XRD (**a**) and SEM image (**b**) of the zeolite ZSM-5; FTIR spectra of the zeolite ZSM-5 before (**c**) and after (**d**) MPS modification

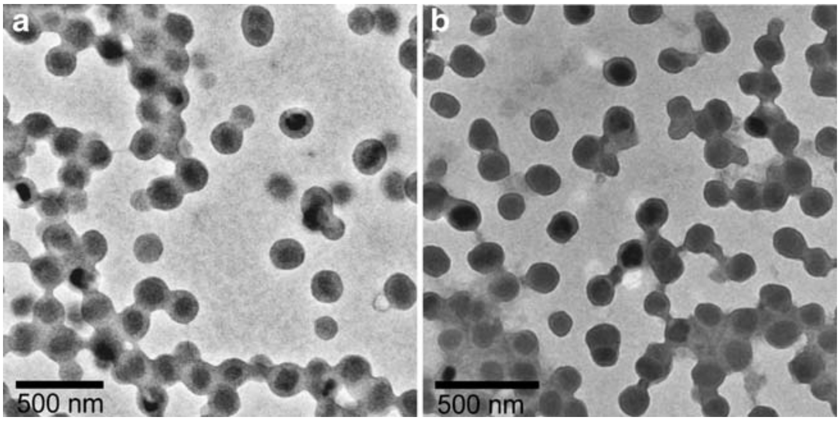


of PNIPAm at the polymerization temperature of 70 °C, the growing polymer radicals prefer precipitating onto the zeolite surface when they reach the critical length in water. The radicals continue to grow on the surface and form a cross-linked microgel. For a detailed characterization, dynamic light scattering experiments were performed to determine the particle size of the core–shell particles during the coil to globule transition and TEM micrographs were recorded to show the morphology of the synthesized particles.

Figure 2 displays TEM images of the resulting core–shell particles. Nearly all of the spherical particles reveal core–shell structures. Only a few particles have not only one single core and some particles consist of pure microgel without core. The particles of the sample CS 1 exhibit a thicker shell as the particles of sample CS A which is due to the higher monomer content used in the polymerization process. When the amount of added NIPAM monomer is increased to a NIPAm–ZSM–5 weight ratio of 5>3, the formation of pure hydrogel and the flocculation of the particles is possible [19].

The thickness of the shell of the core–shell particles depends on a number of parameters: the size and the concentration of the core particles as well as the amount of NIPAm and BIS during the polymerization. DLS measurements have shown that the thickness of the core–shell particles decreased when the temperature is increased above

Fig. 2 TEM images of the zeolite–PNIPAm core–shell particles. **a** Sample CS 1, **b** sample CS A



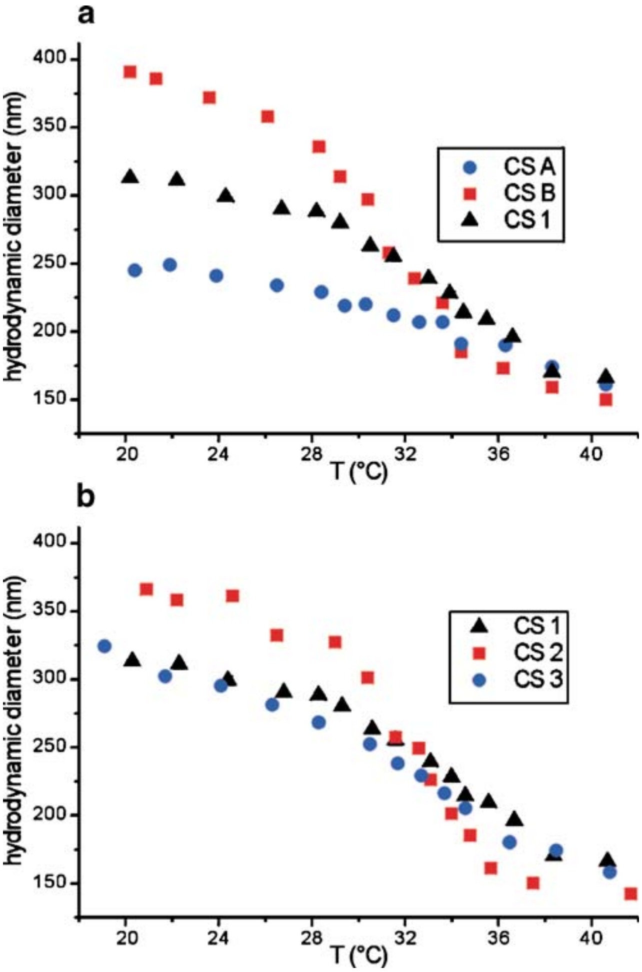


Fig. 3 Hydrodynamic diameter of the zeolite–PNIPAm core–shell particles at different temperatures. **a** Variation of the monomer content and **b** variation of the cross-linker content during the polymerization process

the LCST of PNIPAm (Fig. 3). The volume phase transitions of the different core–shell particle samples are close to 32 °C but their volumetric contractions are different. In agreement with the results observed for PS–PNIPAm core–shell particles [5], the sample CS A with the highest monomer content exhibits the largest change of the hydrodynamic diameter between 20 and 40 °C (Fig. 3a). For a given monomer concentration, the increase of cross-linker concentration will lead to broadening of the transition region. In our experiment, the monomer–cross-linker molar ratio was not constant. Instead, with increasing monomer content the monomer–cross-linker molar ratio decreased. Therefore, at low monomer concentrations, a high cross-linker concentration is present and thus a broad volume phase transition region is observed. With increasing cross-linking density, the maximum deswelling decreases (Fig. 3b). McPhee et al. [34] observed the same effect on PNIPAm microgel particles. The particle sizes from the DLS measurement are larger than those from TEM measurement due to the loss of water under vacuum.

Synthesis of the zeolite–PVP core–shell particles

The preparation of the zeolite–PVP core–shell particles was similar to the synthesis of the PNIPAm-coated particles. Sample P 3 flocculated during the polymerization. This could be due to the initiator used (V 50) that leads to positively charged microgel which could form heteroaggregates with the negatively charged zeolite particles. It is known that surfactants like SDS could stabilize the growing particles during polymerization but, in this case, the addition of SDS has no positive influence on the stability of the particles.

The use of KPS led to stable colloidal dispersions. Figure 4a shows a TEM image of the sample P 1. The PVP shell around the zeolite core is not so uniformly distributed as the PNIPAm shell. The pH-responsive behavior of the samples P 1 and P 2, measured by DLS, is presented in Fig. 4b. As reported in the literature, a sharp volume phase transition undergoes between a pH value of 4 and 5.

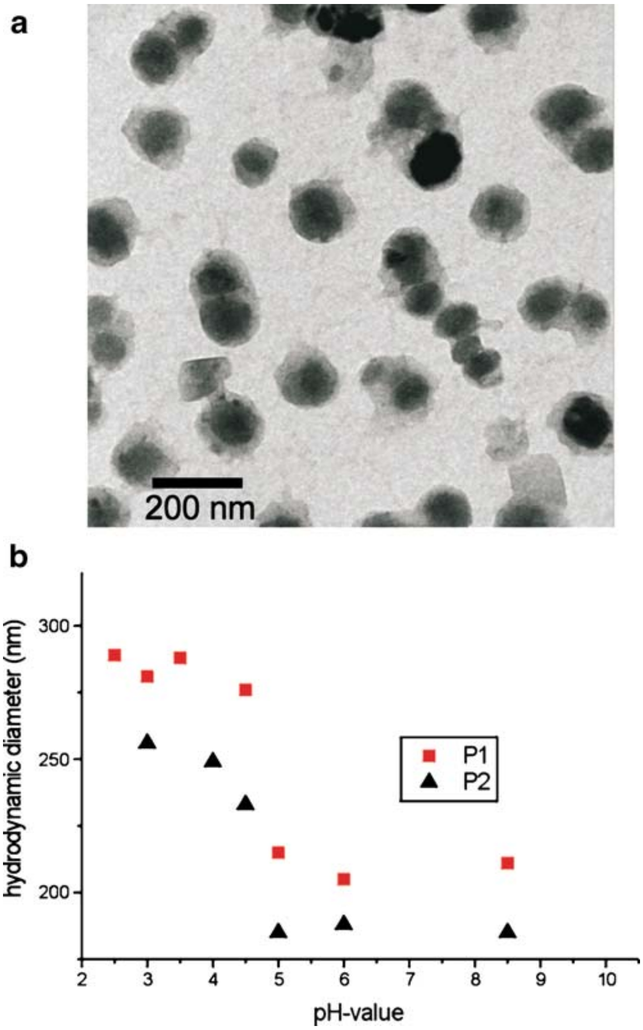


Fig. 4 TEM image (**a**) of the sample P 1 and hydrodynamic diameter (**b**) of the samples P 1 and P 2 at different pH values

Conclusions

We have synthesized for the first time colloidal core–shell particles on the basis of the microporous zeolite ZSM-5 as the core material and thermoresponsive poly(*N*-isopropylacrylamide) and pH-responsive poly(vinylpyridine) as the polymeric shell, respectively. TEM pictures show the morphology of the particles. Quantitative encapsulation of the zeolite particles was observed. These particles reveal a reversible swelling transition upon changing the temperature (PNIPAm) or the pH value (PVP). The swelling behavior of the synthesized core–shell particles was characterized by DLS measurements. The swelling ratio was controlled by cross-linking density and the monomer concentration at the polymerization process. The use of other porous materials for the formation of core–shell particles is highly interesting since the pore diameter and form as well as the inner surface chemistry can be varied to a large extent. For this purpose, compounds like porous carbon, periodic mesoporous silica, or metal organic frameworks are highly desirable. Currently, we work on the use of these types of core–shell particles for controlled release applications and separation of molecules.

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References

1. Nayak S, Lyon LA (2005) Angew Chem 117:7862
2. Pelton R (2000) Adv Coll Interface Sci 85:1
3. Pelton RH (1988) J Polym Sci 26:9
4. Jones CD, Lyon LA (2000) Macromolecules 33:8301
5. Xiao XC, Chu LY, Chen WM, Wang S, Xie R (2004) Langmuir 20:5247
6. Li D, Qiang H, Cui Y, Li J (2007) Chem Mater 19:412
7. Hirokawa Y, Tanaka T (1984) J Chem Phys 81:6379
8. Hoffmann AS (1987) J Control Release 6:297
9. Park TG, Hoffmann AS (1992) J Appl Polym Sci 46:659
10. Chen G, Hoffmann AS (1995) Nature 373:49
11. Kiser PF, Wilson G, Needham D (1998) Nature 394:459
12. Ricka J, Tanaka T (1984) Macromolecules 17:2916
13. Hooper HH, Baker JP, Blanch HW, Prausnitz JM (1990) Macromolecules 23:1096
14. Seida Y, Nakano Y (1991) J Chem Eng Jpn 24:755
15. Homma M, Seida Y, Nakano Y (2001) J Appl Polym Sci 82:76
16. Tanaka T, Nishio I, Sun ST, Ueno-Nishio S (1982) Science 218:467
17. Karg M, Pastoriza-Santos I, Liz-Marzán LM, Hellweg T (2006) ChemPhysChem 7:2298
18. Zha L, Zhang Y, Yang W, Fu S (2002) Adv Mater 14:1090
19. Gao H, Yang W, Min K, Zha L, Wang C, Fu S (2005) Polymer 46:1087
20. Nayak S, Gan D, Serpe MJ, Lyon LA (2005) Small 1:416
21. Davis ME, Lobo RF (1992) Chem Mater 4:756
22. Cundy SC, Cox PA (2003) Chem Rev 103:663
23. Horcajada P, Marquez-Alvarez C, Ramila A, Perez-Pariente J, Vallet-Regi M (2006) Solid State Sci 8:1459
24. Zhang H, Kim Y, Dutta PK (2006) Microporous Mesoporous Mater 88:312
25. Tosheva L, Valtchev VP (2005) Chem Mater 17:2494
26. Berndt I, Richtering W (2003) Macromolecules 36:8780
27. Lu Y, Mei Y, Drechsler M, Ballauff M (2006) Angew Chem Int Ed 45:813
28. Hellweg T, Dewhurst CD, Eimer W, Kratz K (2004) Langmuir 20:4330
29. Heskins M, Guillet JE (1968) J Macromol Sci Chem 2:1441
30. Loxley A, Vincent B (1997) Coll Polym Sci 275:1108
31. Fernandez-Nieves A, Fernandez-Babero A, Vincent B, de las Nieves FJ (2000) Macromolecules 33:2114
32. Mintova S, Bein T (2001) Adv Mater 13:1880
33. Bourgeat-Lami E, Lang J (1998) J Colloid Interface Sci 197:293
34. McPhee W, Tam KC, Pelton R (1993) J Colloid Interface Sci 156:24