Hypercrosslinked polystyrene microspheres by suspension and dispersion polymerization

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Abstract: To determine the influence of particle size on the specific surface area of hypercrosslinked poly(styrene-*co*-divinylbenzene) (PS) microspheres, two methods were chosen for preparation of particles, suspension and dispersion polymerization. While the former method produced hundred micrometer-sized PS-S microspheres, the latter yielded PS-D particles of ca. 1-μm size. Dispersion copolymerization of styrene (St) and divinylbenzene (DVB) in ethanol was stabilized by (hydroxypropyl)cellulose (HPC) and initiated with dibenzoyl peroxide (BPO). Monodisperse 1.4-μm PS-D microspheres were prepared only in the presence of 3.6 wt% HPC. All microspheres were chloromethylated with chloromethyl methyl ether (CMME), chloromethyl ethyl ether (CMEE) or chloromethyl octyl ether (CMOE) to investigate the effect of the chloromethylation agent on the specific surface area of microspheres. Chloromethylated microspheres were hypercrosslinked in 1,2-dichloroethane (DCE) in the presence of a Lewis acid (SnCl$_4$). The effects of the crosslinker (DVB) and DCE/microsphere ratio on properties of the product were studied. The specific surface area, pore volume and pore size distribution of the microspheres were analyzed by dynamic desorption of nitrogen, cyclohexane regain and mercury porosimetry.

Introduction

Hypercrosslinked polystyrene (PS) particles with a very high specific surface area (> 1000 m^2 g^{-1}) and high micropore (< 2 nm) content (~ 0.6 ml g^{-1}) were introduced by Davankov [1-6] as early as in the1970's. Even though the topic was initially somewhat ignored, a recent renewed interest in hypercrosslinked particles possessing high sorption capacity stems from their applications as packings in high-performance liquid chromatography [7], ion exchangers [8, 9], specific sorbents [10-13], for hydrogen storage [14-18] and in water treatment for removal of hydrocarbon traces [19]. Hypercrosslinked sorbents are promising also for elimination of distillation [20] and removal of inorganic ions from acid solutions [21] or toxic proteins from blood in kidney failure [22]. Palladium catalysts for the Suzuki reaction were incorporated in hypercrosslinked sorbents to facilitate their separation from the reaction mixture [23].

Formation of hypercrosslinked networks is completely different from that of conventional macroporous systems; in the former case microphase separation occurs. Hypercrosslinked polymers are mostly prepared by swelling (or dissolution) of uncrosslinked or lightly crosslinked precursors in a thermodynamically good solvent to introduce voids between polymer chains, followed by crosslinking of precursor chains by three bonds at least [2, 24]. The type of the crosslinks between polymer chains depends on the bifunctional reagents used; the crosslinking agents

may be aliphatic (e.g., chloromethyl alkyl ethers or dimethoxymethane) or aromatic (e.g., 4,4'-bis(chloromethyl)biphenyl) [25]. Then rapid crosslinking locks the polymer chain in an extended conformation. Although 70% of chloromethyl groups rapidly transform to methylene bridges in the beginning, only those formed at later stages from rather less accessible chloromethyl groups are responsible for a very high specific surface area [24]. Besides micropores (< 2 nm) responsible for high specific surface area, also mesopores (2-50 nm), macropores (50 nm – 1 μm) and superpores (> 1 μm) occur in the polymers [26]. Various methods are generally used for characterization of porous structures. For example, mercury porosimetry determines the pore diameters ranging 3.8 nm - 116 μm; smaller pores are typically characterized by dynamic desorption of nitrogen using BET isotherm [27].

Conventional microspheres with a large particle size (50-500 μm) and a broad particle size distribution are prepared by suspension polymerization [28]. Heterogeneity of the particle size distribution results in an inefficient packing of columns. This requires a classification of particles to narrow fractions suitable for sorption. Compared with those of a large size, small particles generally give a better resolution and improve the efficiency of separation. Monodisperse particles or those with a narrow distribution prepared by dispersion polymerization show high separation efficiency in chromatography due to uniform physical and chemical properties. In order to improve manipulation in separation processes, it is convenient to introduce impart magnetic response to the particles. The magnetic cores are typically incorporated into a polymer shell in polymerization (emulsion, inversion emulsion, dispersion, etc.) [29].

The aim of this work is to design and prepare monodisperse micrometer-sized particles by dispersion copolymerization of styrene (St) with divinylbenzene (DVB) and to hypercrosslink them to get a high specific surface area. Pore properties, such as porosity, specific surface area and pore size are investigated to facilitate prospective applications. The particles are compared with those obtained by suspension polymerization and subsequent hypercrosslinking.

Results and discussion

Poly(styrene-divinylbenzene) (PS-S) microspheres by suspension polymerization

The particles produced by suspension polymerization, which is a common method for the preparation of PS, were investigated first. Such particles containing 0.3 wt% DVB, denoted as PS-S, were rather polydisperse (PDI 1.29), with the average size 57 μm (Fig. 1 a).

With the aim to investigate the effect of microsphere size on the properties of particles after hypercrosslinking, dispersion polymerization was selected as a method of choice for the preparation of microspheres smaller by an order of magnitude than those obtained by suspension polymerization.

Poly(styrene-divinylbenzene) (PS-D) particles by dispersion polymerization

Dispersion copolymerization of styrene and divinylbenzene with dibenzoyl peroxide as initiator was carried out in ethanol. Incorporation of DVB, even in low amounts (0.3 and 1 wt%), is important because crosslinking prevents dissolution of polystyrene particles in some organic solvents. Moreover, crosslinking preserves spherical shape even after hypercrosslinking [25].
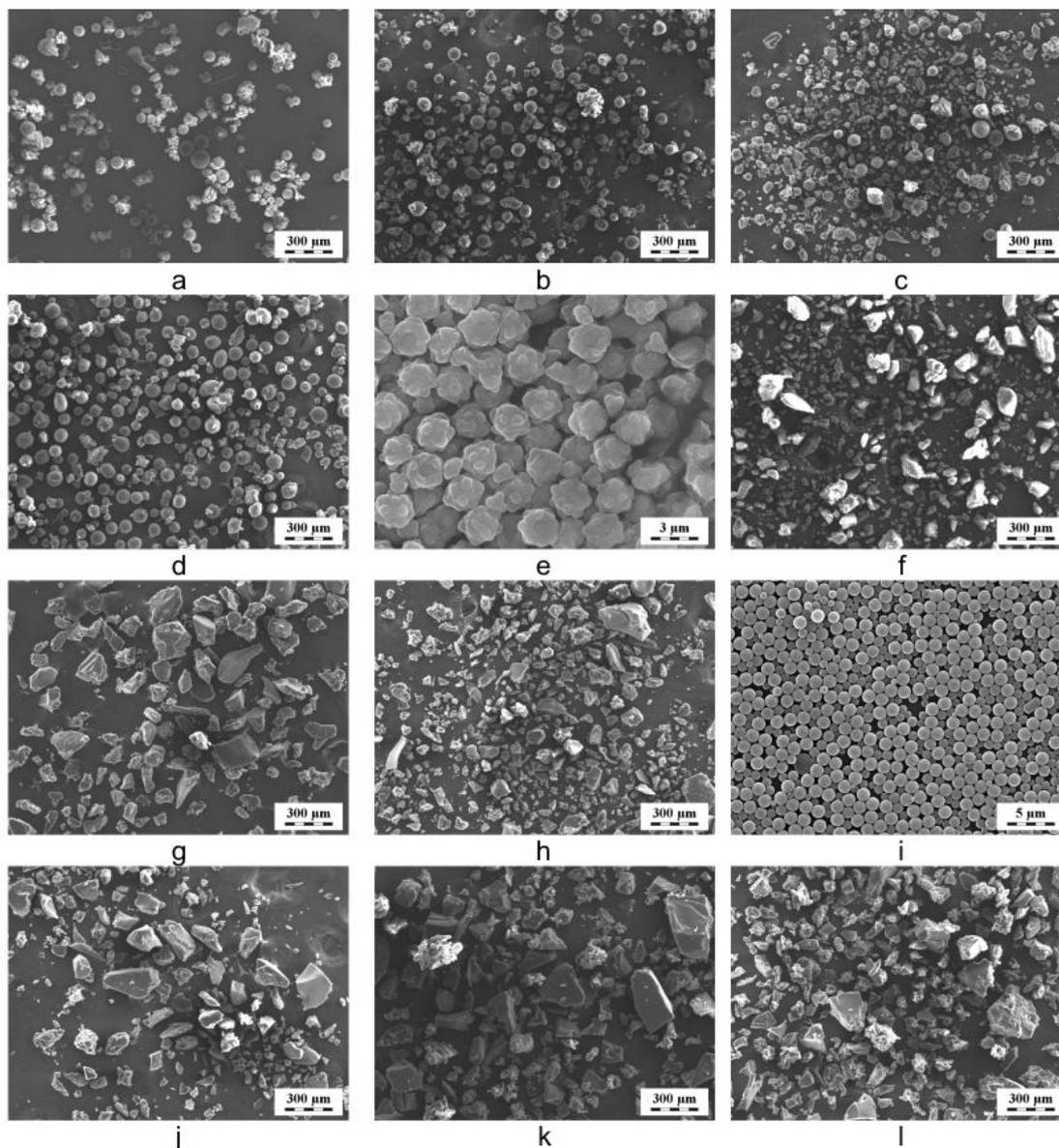
Fig. 1. SEM micrographs of 57 µm PS-S (a-d), 2.4 µm PS-D-1 (e-h) and 1.4 µm PS-D-2 microspheres (i-l) before (a, e, i) and after hypercrosslinking. Chloromethylation was done with CMME (b, f, j), CMEE (c, g, k) and CMOE (d, h, l). Microspheres were crosslinked with 0.3 wt% DVB.

In this report, HPC, a commonly used stabilizer for dispersion polymerization in ethanolic media [32], was selected. Before polymerization, the system was homogeneous, i.e., the monomers, stabilizer and initiator were dissolved in ethanol, but the polymer particles precipitated during the polymerization. As it is known that crosslinking agents interfered with the particle nucleation stage and immobilized the stabilizer, thus inducing flocculation [33], the addition of DVB was postponed to the end of the nucleation stage, an hour after the beginning of the reaction. Both the concentrations of styrene and BPO in ethanol were maintained constant during the experiments, only the HPC concentration was varied and its effect on properties of the resulting microspheres was investigated.
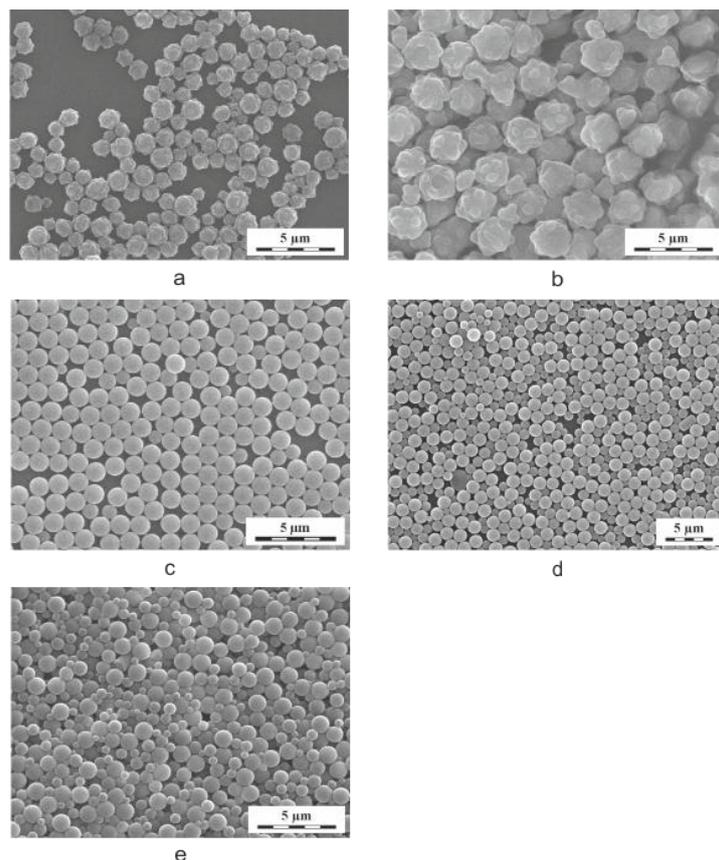
Fig. 2. SEM micrographs of PS-D (0.3 wt% DVB) microspheres prepared by dispersion polymerization in ethanol (a-e) and stabilization with 1 (a), 2.3 (b), 3.6 (c), 5 (d) and 6.5 wt% HPC (e).
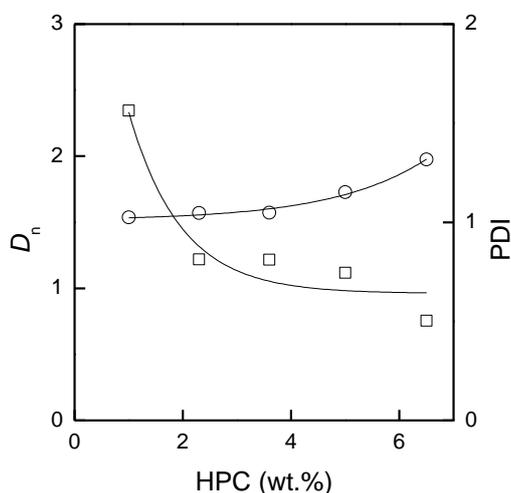

Fig. 3. Dependence of PS-D microsphere diameter D_n (□), and polydispersity index PDI (o) on the concentration of HPC stabilizer in ethanol.

The PS-D microspheres (0.3 wt% DVB) produced by dispersion polymerization in ethanol were observed by SEM to analyze their morphology (shape, polydispersity, size) in the dry state (Fig. 2 a-e). When the HPC concentration in ethanol was low (1 or 2.3 wt%), the polymerization mixture was not stable and the primary microspheres

(e.g., PS-D-1) aggregated into cauliflower-like particles of a rather irregular shape (Fig. 2 a, b). This can be also associated with higher reactivity of DVB compared with St interfering thus with the nucleation mechanisms; as a result, irregular particles or agglomerates are formed. The surface roughness was observed in many dispersion polymerizations carried out in the presence of crosslinkers [34]. At higher HPC concentrations in ethanol (3.6-5 wt%), regular PS-D microspheres with smooth surface (e.g., PS-D-2) were obtained (Fig. 2 c-e). At the same time, monodispersity was achieved indicating that the nucleation was fast [35] and HPC effectively stabilized the system. At very high concentrations of HPC (> 6 wt%), however, two kinds of microspheres were again formed, thus broadening the particle size distribution (Fig. 2 e). Obviously, this was a result of the prolonged nucleation stage; particles were formed later after the polymerization started and enough HPC was present to stabilize them. The microsphere size decreased from 2.4 to 0.8 µm with increasing the HPC concentration (Fig. 3), because the larger surface area was protected at higher HPC concentrations. In other words, more particles of smaller size were stabilized with a higher amount of the stabilizer. An increase in the crosslinking density of PS-D-3 microspheres (1 wt% DVB) resulted in the formation of two kinds of microspheres and in broadening the particle size distribution (PDI 1.43; Fig. 4 a).
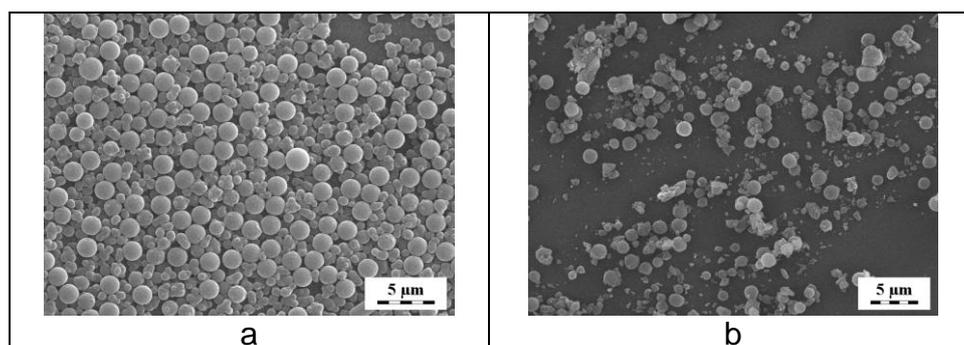

| a | b |

Fig. 4. SEM micrographs of 1-µm PS-D-3 (1 wt% DVB) microspheres before (a) and after chloromethylation with CMME and hypercrosslinking (b). Starting microspheres were prepared by dispersion polymerization in ethanol and stabilization with 2.3 wt% HPC.

Hypercrosslinked microspheres

Hypercrosslinked microspheres were prepared by the Friedel-Crafts reaction of PS-S and PS-D particles swollen in anhydrous 1,2-dichloroethane (DCE) with a SnCl₄ catalyst using three chloromethylation agents: chloromethyl methyl ether (CMME), chloromethyl ethyl ether (CMEE) and chloromethyl octyl ether (CMOE) (Scheme 1). For obtaining microspheres with a very high specific surface area, the hypercrosslinking reaction has to be faster than particle deswelling in order to fix the microstructure formed by solvent swelling of weakly crosslinked polymers.

The reaction conditions, such as the alkylation agent/PS ratio 1/2 (w/w) and the SnCl₄/PS ratio 1.25/1 (w/w), were selected analogously to a previous work [3] they were kept constant in all experiments. The PS-S microspheres did not change their shape after chloromethylation with CMME, CMEE or CMOE and SnCl₄-catalyzed hypercrosslinking (Fig. 1 b-d). Even though a majority of PS-S particles preserved spherical shape after hypercrosslinking, some particles were damaged, probably due

to abrupt changes in swelling and collapse after drying (Fig. 1 b-d). The size of hypercrosslinked PS-S particles (63 µm) was higher than that of initial PS-S ones (57 µm). This could be explained by formation of rigid crosslinks between polymer chains, which prevented shrinkage of the network after deswelling. In contrast, 1.4-µm PS-D-1 and 2.4-µm PS-D-2 microspheres agglomerated during hypercrosslinking after addition of the SnCl$_4$ catalyst to the reaction mixture. They had to be mechanically disintegrated by sieving on 250-µm mesh, resulting in irregular particles up to the 300 µm size (Fig. 1 f-h and j-l). The aggregation was partly avoided by a higher dilution of the microspheres with DCE and by a higher degree of crosslinking (PS-D-3 microspheres with 1 wt% DVB; Fig. 4 b). The microspheres changed their size from 1 µm to 1.1 µm after hypercrosslinking.
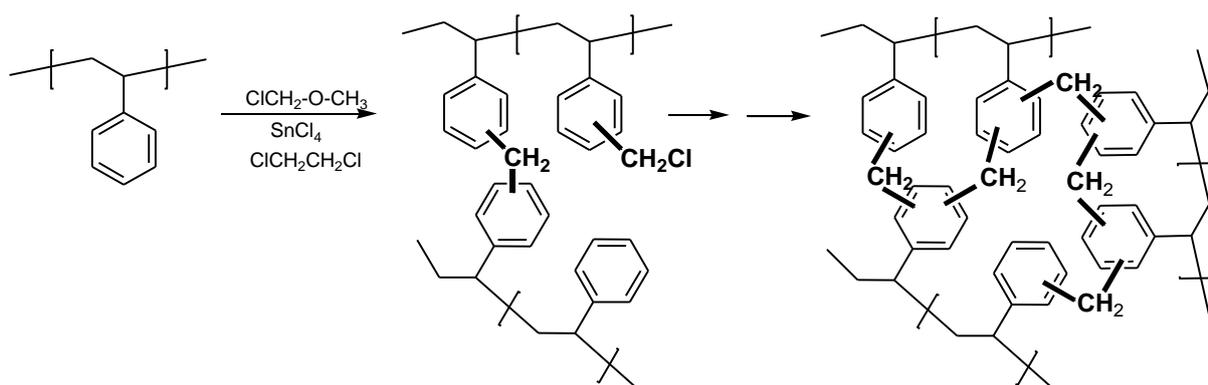
Scheme 1. Chloromethylation of polystyrene microspheres with chloromethyl methyl ether and their hypercrosslinking.

Pore properties of hypercrosslinked microspheres were determined by dynamic desorption of nitrogen, cyclohexane regain and mercury porosimetry.

Specific surface area

The results of dynamic desorption of nitrogen from microspheres are summarized in Table 1. They showed that hypercrosslinking mostly increased the specific surface area of the microspheres depending on the selection of the chloromethylation agent. The ultimate specific surface areas 1577 m^2/g, 396 m^2/g and 124 m^2/g were obtained by post-crosslinking 57-µm PS-S microspheres with CMME, CMEE and CMOE, respectively (Table 1). Hypercrosslinking of PS-D-2 (0.3 wt% DVB) microspheres resulted in lower specific surface areas of 707 m^2/g, 87 m^2/g and 81 m^2/g using CMME, CMEE and CMOE as chloromethylation agents, respectively. Even lower specific surface areas were obtained by post-crosslinking of PS-D-1 and PS-D-2 microspheres. However, hypercrosslinked PS-D-3 microspheres chloromethylated with CMME possessed the specific surface area 1457 m^2/g because they were prepared at a high DCE dilution, which suppressed particle aggregation. Thus CMME can definitely be considered as the chloromethylation agent of first choice, which is superior to CMEE and CMOE in producing particles with a very high specific surface area. CMME, which penetrates more easily and deeply into the bulk of the microspheres due to its small molecules, obviously provides more methylene crosslinks in para positions of benzene rings compared with CMEE or CMOE. CMME is capable to form chloromethylene groups even in locations otherwise accessible only with difficulties rendering thus the microspheres with very high values of specific

surface area after hypercrosslinking [24]. Molecule-size thus plays a critical role in hypercrosslinking, affecting the number of pores. It should also be noted that the specific surface area decreased with decreasing microsphere size (Table 1). This can be explained by the fact that small particles tend to aggregate (Fig. 1 f-h and j-l).

Tab. 1. Pore properties of poly(styrene-*co*-divinylbenzene) microspheres hypercrosslinked with chloromethylation agents.

Code	% DVB (wt%)	Starting microsphere size (μm)	Chloromethyl methyl ether				Chloromethyl ethyl ether				Chloromethyl octyl ether			
			S_{BET} (m²/g)	V_{CX} (ml/g)	V_{Hg} meso (ml/g)	D_{Hg} meso (nm)	S_{BET} (m²/g)	V_{CX} (ml/g)	V_{Hg} meso (ml/g)	D_{Hg} meso (nm)	S_{BET} (m²/g)	V_{CX} (ml/g)	V_{Hg} meso (ml/g)	D_{Hg} meso (nm)
PS-D-1	0.3	1.4	347	4.24	0.27	9.2	345	6.75	0.27	9.8	19	3.20	0.14	9.6
PS-D-2	0.3	2.4	707	2.39	0.20	9.4	87	4.64	0.13	9.2	81	4.37	0.28	9.8
PS-D-3	1	1	1457	4.30	0.30	18.0	945	3.66	0.25	9.4	558	2.87	0.27	6.0
PS-S	0.3	57	1577	3.14	0.23	9.4	396	2.81	0.26	32.2	124	2.29	0.26	9.8

% DVB – weight percentage of divinylbenzene in starting poly(styrene-*co*-divinylbenzene) microspheres, S_{BET} - specific surface area, V_{CX} - pore volume by cyclohexane regain, $V_{Hg\ meso}$ - mesopore volume, by mercury porosimetry, $D_{Hg\ meso}$ - most frequent mesopore diameter, by mercury porosimetry

Pore volume and size

Cyclohexane is a θ-solvent for polystyrene at 34.5 °C [36] and a poor solvent at 23 °C. However, it can swell polystyrene microspheres that are in the collapsed state after drying. Cyclohexane regain of the microspheres is thus a result of both filling their pores and particle swelling. The hypercrosslinked PS-S and PS-D microspheres showed the cyclohexane regain in the range 2.29-6.75 ml/g (Table 1), reflecting the differences in the pore volume. However, it should be mentioned that it was difficult to measure the cyclohexane regain of PS-D-1 and PS-D-2 microspheres due to their aggregation. A very high cyclohexane regain of PS-D-1 microspheres amounting up to 6.75 ml/g could be explained by the presence of large pores within the aggregates of micrometer-size particles. In contrast, non-agglomerated PS-D-3 microspheres showed an expected decrease in cyclohexane regain when replacing the chloromethylation agent CMME with CMEE and CMOE in hypercrosslinking due to a decrease in the micropore content as documented by specific surface area measurements.

As the pore size is an important factor governing the relationship between the pore volume and surface area, mercury porosimetry was used for the determination of both the pore size distribution and pore volume of hypercrosslinked PS (Fig. 5). However, the method is limited by the maximum available pressure of mercury (400 MPa) corresponding to the pore size 4 nm. As mercury, in contrast to cyclohexane, does not penetrate into pores smaller than 4 nm, the specific pore volumes from mercury porosimetry, ranging typically from 0.1 to 0.6 ml/g, were lower than those obtained with cyclohexane. On the other hand, another limitation of mercury porosimetry consists in the lowest possible pressure (0.1 kPa), which limits

the maximum size of measured pores to 116 µm. Such pores are not pertinent to the present study and, therefore, only pores with a diameter smaller than 50 nm were considered (Table 1). Moreover, in contrast to cyclohexane, mercury does not swell microspheres. All these factors contribute to the fact that the pore volumes obtained from mercury porosimetry were lower than those from the cyclohexane regain.
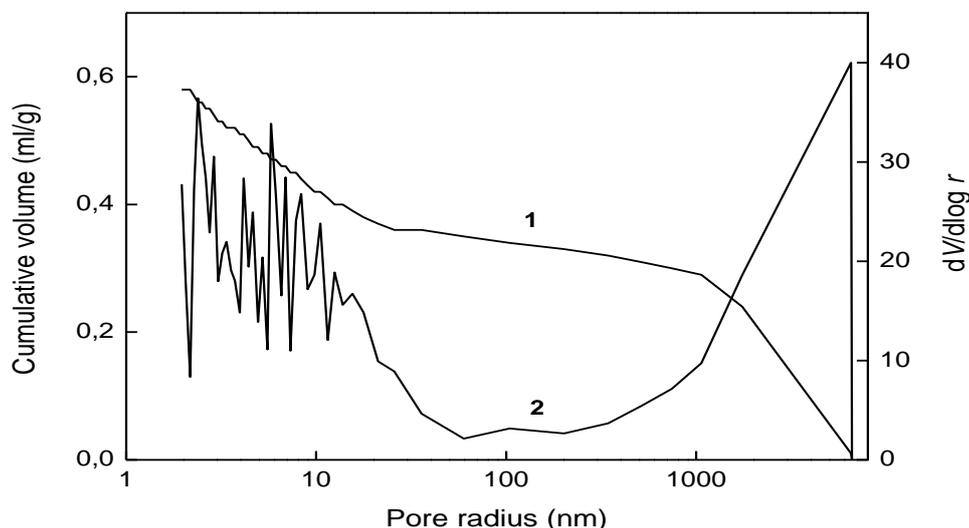

Fig. 5. Cumulative pore volume *V* (1) and pore size distribution d*V*/dlog *r* curves (2) of CMME-hypercrosslinked PS-D-3 (1 wt% DVB) microspheres determined by mercury porosimetry.

It could be thus noted that the cumulative volume (~ 0.24 ml/g) and the most frequent mesopore diameters (4-22 nm) were typically similar for all hypercrosslinked PS-S and PS-D microspheres chloromethylated with CMME, CMEE or CMOE (Table I). While PS-S microspheres chloromethylated with CMME and CMOE had the most frequent mesopore diameter around 10 nm, those chloromethylated with CMEE showed the mesopore size *ca.* 30 nm with broad distribution.

Conclusions

Dispersion polymerization of styrene (containing 0.3 wt% divinylbenzene) in ethanol produced monodisperse crosslinked microspheres. Their size could be controlled and kept in the range 0.8-2.4 µm by changing reaction conditions. At a low concentration of the stabilizer ((hydroxypropyl)cellulose), deformed non-spherical particles were obtained. The concentration window of the stabilizer in ethanol for formation of regular microspheres with smooth surface and narrow size distribution was 3.6-5 wt%. The microspheres were compared with those produced by suspension polymerization in terms of hypercrosslinking. The latter particles were polydisperse and larger than the former by an order of magnitude. Hypercrosslinked particles were obtained by crosslinking the above microparticles with alkyl chloromethyl ethers catalyzed by a Lewis acid, preferably with chloromethyl methyl ether. Hypercrosslinking with chloromethyl ethyl and chloromethyl octyl ethers produced lower specific surface areas and cyclohexane regains compared with the chloromethyl methyl ether. While microspheres obtained by suspension

polymerization did not agglomerate during hypercrosslinking, the particles obtained by dispersion polymerization did because their dilution with DCE was low (1/10 w/w). This problem was overcome by increased crosslinking (1 wt% DVB) and a higher dilution of particles with dichloroethane (1/20 w/w). As a result, 1-µm PS-D-3 microspheres with the specific surface area 1457 m^2/g, pore volume 4.3 ml/g and mesopore size 9 nm were prepared by chloromethylation with the chloromethyl methyl ether followed by hypercrosslinking. Such pore size is sufficiently large for prospective precipitation of iron oxide inside the microspheres forming thus a new kind of magnetic particles. Specifically functionalized magnetic hypercrosslinked microspheres seem suitable for carriers in immunosensors for electrochemical detection of proteins.

Experimental part

Reagents

Styrene (St) and divinylbenzene (DVB; 54 % meta and 20 % para isomers, 24 % ethylvinylbenzene) from Kaučuk Co. (Kralupy nad Vltavou, Czech Republic) were vacuum- distilled. 1,2-Dichloroethane (DCE), ethanol for UV spectroscopy, diethyl ether and cyclohexane were from Lach-Ner (Neratovice, Czech Republic). Chloromethyl methyl ether (CMME), chloromethyl ethyl ether (CMEE), chloromethyl octyl ether (CMOE) and (hydroxypropyl)cellulose (HPC; M_w 100,000) were from Aldrich (Steinheim, Germany). Dibenzoyl peroxide (BPO; crystallized from ethanol, moistened with 20 % of water) was from Fluka. PS-S is St-DVB copolymer (0.3 wt% DVB) produced by suspension polymerization in Spolchemie Co. (Ústí nad Labem, Czech Republic). All other solvents and chemicals, chemically pure or reagent grade, were supplied by Aldrich and were used without further purification.

Preparation of microspheres

Dispersion polymerization of styrene

Polymerization was performed in a glass vessel equipped with an anchor stirrer (100 rpm). In a typical procedure, the reactor was charged with 0.9 g HPC dissolved in 34.1 g of ethanol, 5 g St and 0.1 g BPO under nitrogen. The reactor was heated under stirring at 70 °C for 18 h. One hour after starting polymerization, 0.015 g DVB was added. At the end of the reaction, the resulting polymer (PS-D) microspheres were removed by centrifugation (2,600 rpm) and washed with ethanol (10 × 100 ml) to ensure complete removal of impurities (HPC, unreacted monomers, initiator residues) and finally dried in vacuum at 23 °C. Polymerization conversion: 98 wt.%.

Preparation of hypercrosslinked microspheres

Microspheres were hypercrosslinked using the modified Davankov procedure [3]. In a typical experiment, 2 g of PS-D microspheres (0.3 wt% DVB) were placed for 20 h in a 100-ml flask with 20 g anhydrous DCE to swell the particles. The reaction mixture was cooled to -15 °C in an ice/NaCl bath under magnetic stirring, 0.77 g CMME was added and the mixture kept at this temperature for 1 h. 2.49 g $SnCl_4$ was added and the mixture refluxed for 20 h at 80 °C. Hypercrosslinked particles were then kept in anhydrous DCE for 12 h, then filtered off, washed successively with DCE, ethanol and diethyl ether and finally dried in vacuum at 40 °C.

Characterization

Microspheres were observed in an Opton light microscope III (Oberkochen, Germany) and photographed with a Canon EOS 400D camera (Tokyo, Japan). The particle size and its distribution in the dry state were analyzed by scanning electron microscopy (SEM; JEOL JSM 6400). The number-average diameter (D_n), weight-average diameter (D_w) and dispersity (polydispersity index PDI = D_w/D_n) were calculated using Atlas software (Tescan Digital Microscopy Imaging, Brno, Czech Republic) by counting at least 500 individual particles in SEM micrographs. The D_n and D_w can be expressed as follows:

$$D_n = \frac{\sum n_i \cdot D_i}{\sum n_i} \tag{1}$$

$$D_w = \frac{\sum n_i \cdot D_i^4}{\sum n_i \cdot D_i^3} \tag{2}$$

where n_i and D_i are the number and diameter of the *i*-th particle, respectively.

The cyclohexane regain (CXR) of equilibrium-swollen (24 h) microspheres was determined by centrifugation [30] in glass columns with fritted disc at 1400 *g* for 10 min and immediately weighed (w_{CX} – weight of swollen microspheres), then vacuum-dried for 20 h at 40 °C and again weighed (w_d – dry weight). Cyclohexane regain (CXR, g/g) was calculated from Eq. 3

$$CXR = \frac{w_{CX} - w_d}{w_d} \tag{3}$$

CXR and pore volume V_{CX} (ml/g) are summarized in Table 1.The results are averages from two measurements.

Specific surface areas (S_{BET}) of microspheres were determined by dynamic desorption of nitrogen in a Quantasorb apparatus (Quantachrome, Greenvale, USA).

The specific pore volumes and pore size distributions of dry microspheres were determined with a Pascal 140 and 440 mercury porosimeter (Thermo Finigan, Rodano, Italy) in two pressure ranges, 0-400 kPa and 1-400 MPa, allowing for determination of meso-, macro- and superpores. In this study, only the volume and size of mesopores were evaluated. The pore volumes and the most frequent mesopore diameters were calculated from cumulative pore volume curves under the assumption of a cylindrical pore model using the Pascal program and the Washburn equation describing capillary flow in porous materials [31].

The modified microspheres were analyzed using a Perkin Elmer 2400 Series CHNS/O elemental analyzer (Shelton, Connecticut, USA).

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