Synthesis of Ultrahigh Surface Area Monodisperse Porous Polymer Nanospheres

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ABSTRACT: Synthesis of vinyl benzyl chloride (VBC)/divinylbenzene (DVB) copolymers via surfactant-free emulsion polymerization yields near monodisperse chloromethylated polystyrene precursor nanospheres ∼400 nm in diameter. These are analogous to gel-type suspension polymerized particles typically of ∼100−500 μm in diameter and are essentially nonporous in the dry state having only a very nominal surface area (∼10 $m^2\ g^{-1}$). Cross-linking of appropriate dichloroethane swollen precursors with a high content of VBC residues in the presence of $FeCl_3$ (i.e., using a Davankov-type strategy) yields near monodisperse porous hyper-cross-linked nanoparticles with extremely high surface areas up to ∼1200 $m^2\ g^{-1}$. The latter display all the characteristics of Davakov-type resins in terms of their ability to sorb both thermodynamically "poor" and "good" solvents and in particular despite their superficial hydrophobic makeup are able to sorb significant quantities of water (up to ∼2.5 g/g). By adjusting the content of VBC in the precursor particles, the surface area of the near monodisperse nanoparticles can be adjusted in the range ∼15−1300 $m^2\ g^{-1}$.

Introduction

In our current research program aimed at synthesizing porous vinyl polymer particulates in a more rational and designed manner than is currently the case,[1] we have recently reported on the self-assembly of polymer microspheres from monodisperse vinyl polymer nanospheres[2] with the generation of porosity in terms of the interstitial voids in the hexagonally close-packed nanospheres. To progress this strategy, we wish to self-assemble similar monodisperse nanospheres where the latter already have intrinsic porosity involving smaller pores. However, the synthesis of such porous polymer nanoparticles does not seem to be recorded in the literature, despite the fact that such materials may be of more generic value in nanoscience and technology.

Initially, we attempted to adapt the attractive procedure of Ruckenstein et al.[3] to our particular materials needs, but we were able to produce particulates with surface area of only ∼20 $m^2\ g^{-1}$. The related procedure reported by Qin et al.[4] seemed even more attractive to us because of the cross-linked nature of the particles, but again in our hands this yielded particulates with a surface area of only <30 $m^2\ g^{-1}$. With our own experience in synthezising porous vinyl polymer resins of diameter ∼10−500 μm via suspension polymerization,[1d] we naively thought that application of similar polymerization mixtures involving solvent porogens in aqueous emulsion polymerization[5] might well deliver the porous nanospheres we required. However, there was no evidence in the literature that such an approach was readily transferable from a suspension to an emulsion vinyl polymerization methodology, and indeed it quickly became apparent that such a simple adaptive procedure was impossible. Despite the investigation of a broad range of comonomer/porogen compositions, the maximum surface area achieved with the particulates that were synthesized[6] was ∼60 $m^2\ g^{-1}$. An early paper by Hyde and Robb[7] described the polymerization of a vinyl monomer that was completely solubilized in surfactant micelles via use of appropriately high levels of surfactant. Their objective was to produce a nanosized "polymerized micelle". We felt that the inclusion of a cross-linking comonomer and a solvent porogen in such a procedure might yield the particles we sought, but in practice this approach resulted only in the formation of rather large particulates, ∼1 mm in diameter, presumably arising from aggregation of the smaller particles originally present.

Bearing in mind the relatively facile procedure for producing surfactant-free emulsion polymerization particles[8] that we ourselves have also exploited previously,[9] we wondered whether these could be chemically modified to produce porous analogues with high surface area. In parallel to the present work we have recently reported[10,11] on the synthesis of ultrahigh surface area suspension polymerized particles using the procedure originally introduced by Davankov and co-workers[12] and developed further by Jerabek et al.[13] and scientists at the Rohm and Haas Co.[14] We were also aware of the work by Ford and co-workers,[15] who demonstrated that cross-linked chloromethylated polystyrene emulsion particles can be readily aminated by direct reaction with simple tertiary amines. It therefore seemed plausible that monodisperse surfactant-free polystyrene-based emulsion polymerized nanospheres, heavily functionalized with chloromethyl groups, might yield ultrahigh surface area polymer nanospheres via Lewis acid-catalyzed Davankov-type hyper-cross-linking (Figure 1). As will be described, this indeed has proved to be the case. Furthermore, rather sensitive control of the ultimate surface area has proved to be possible. Interestingly, Davakov's own group have previously demonstrated the ability to intramolecularly hyper-cross-link individual linear polymer molecules[16] to produce soluble cross-linked polymer coils.

Experimental Section

Materials. Divinylbenzene (DVB) (80% grade), styrene (S), and vinylbenzyl chloride (VBC) (mixed isomers) were from the Aldrich Chemical Co. and were freed from inhibitors by passing through a silica column. 2,2′-Azobis(2-amidinopropane) dihydrochloride

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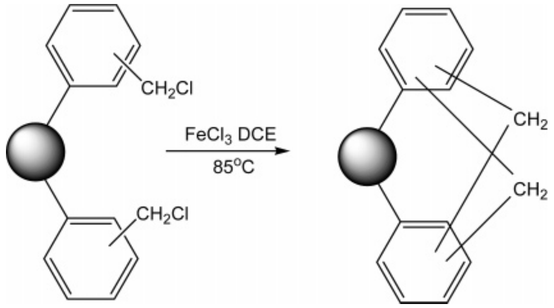

Figure 1. Hyper-cross-linking of precursor gel-type VBC−DVB nanoparticles.

(V-50), $FeCl_3$, and anhydrous 1,2-dichloroethane (DCE) were also from the Adrich Chemical Co.

Synthesis of Precursor Gel-Type VBC−DVB Nanoparticles (E1−4). Surfactant-free emulsion polymerizations were carried out in a 1 L water-jacketed glass reactor charged with distilled water (250 mL) and brought to 75 °C, the reaction temperature. While stirring at 500 rpm the comonomer mixture (VBC, DVB, and S when appropriate) (13 cm^3, 5 vol % of total aqueous phase) was added. Following attainment of a uniform dispension (∼15 min) V-50 (0.21 g, $\sim 2.95 \times 10^{-3}$ mol L^{-1}) dissolved in distilled water (10 cm^3) was added. The polymerization was carried out under N_2 for 6 h. The cooled emulsion was dried by rotary evaporation followed by freeze-drying to give a free-flowing fine white powder.

Hyper-Cross-Linking of Precursor Nanoparticles. These reactions were carried out by adding the dry precursor polymer (**E1−3,** 1.0 g) to a 500 cm^3 three-necked round-bottomed flask containing DCE (80 cm^3). Following sonication to produce a good dispersion the mixture was stirred at 400 rpm for 1 h, before a solution of $FeCl_3$ (0.8 g) in DCE (80 cm^3) was added. Heat was then applied via a preheated oil bath at 85 °C, and the reaction was allowed to proceed for 6 h (**HXLE1,** samples A−C being replicas), 3 h (**HXLE2**), and 1 h (**HXLE3** and **-4**). (*Note*: in parallel work on suspension polymerized resins[11] it was shown that the development of surface area under these conditions was complete after 1 h with essentially no further increase with longer reaction time, and this is the case also here. A 1 h reaction period was eventually therefore adopted as standard.) The reaction mixture was cooled, and the DCE was removed on a rotary evaporator. The dark brown particles (**HXLE1−4**) were washed by sonication in aqueous HNO_3 (pH 1), the latter being removed by decantation. They were then sonicated sequentially in methanol, water, and acetone with the residues of the latter being removed by rotary evaporation to yield a free-flowing pale tan powder.

Characterization of Hyper-Cross-Linked Nanoparticles. Elemental analyses were performed on a Perkin-Elmer 2400 analyzer and Fe analyses carried out using a Milestone MLS 1200 mega digestion system and a Perkin-Elmer Optima 3000 ICP spectrometer. N_2 sorption porosimetry was performed on a Micromeritics ASAP 2000, and the data were manipulated using the custom software supplied to yield the relevant porosity parameters. For electron microscopic analysis spreads of wet particles were prepared on carbon-backed Formvar-coated 200 mesh support grids. Each sample was then imaged on a Zeiss 912 energy filtering transmission electron microscope operating in zero-loss mode at 120 kV. Images were acquired via a 2K Proscan camera using AnalySIS EsiVision software. Solvent uptake data were determined gravimetrically (g/g) using a small glass sinter stick and centrifugation (3000 rpm, 3 min) to remove interstitial solvent.[17] Nanoparticles were contacted with solvent for 3 h prior to centrifugation. In the case of *n*-hexane and toluene the particles appeared to be more dense than each solvent and were readily and efficiently centrifuged free of excess solvent. In the case of water, however, the particles floated and tended to adhere to the sides of the sinter stick. This made removal of the excess water problematical, and so the accuracy of these data is lower.

Results and Discussion

Typically in the present work monodisperse lightly cross-linked gel-type chloromethylated polystyrene nanospheres were produced by surfactant-free emulsion polymerization of vinylbenzyl chloride (VBC) and divinylbenzene (DVB) (**E1−4**, Table 1), yielding milky white emulsions. Following cleaning and drying, white powders were obtained in respectable nonoptimized yields of 70−80 mass %. The measured Cl content (20.4%) of E1 prepared using a VBC/DVB volume ratio of 98/2 was below the theoretically expected value, but this was not unexpected from the long time (6 h) in contact with water and the known tendency for VBC to undergo hydrolysis.[10,18] In the case of analogous precursor suspension polymerized resins we and our analytical chemistry collaborators have quantified the typical level of hydrolysis that occurs, but it seems that about half of the benzyl alcohol groups so formed subsequently participate in the methylene bridging hyper-cross-linking reaction.[10] Be this as it may, the chloromethyl group content was totally adequate for the second stage of the synthesis. Examination by transmission electron microscopy (TEM) showed the precursor particles to be spherical with a near monodisperse particle size with a diameter ∼420 nm (Figure 2, left).

The dried precursor particles were sonicated in 1,2-dichloroethane (DCE) to obtain a good dispersion, and following addition of $FeCl_3$ in DCE the stirred mixture was heated at 85 °C (oil bath) for 6 h. The resulting particles, **HXLE1A−C**, were recovered essentially quantitatively and were washed sequentially with aqueous HNO_3 to remove the $FeCl_3$, methanol, water, and acetone. Finally, they were dried in a vacuum oven (40 °C) (see Experimental Section for details). Reexamination by TEM showed that the particles had retained their integrity but were somewhat enlarged, ∼550 nm in diameter (Figure 2, right). This is consistent with the gel-type precursor particles being hyper-cross-linked in a solvent-swollen state, followed by drying to reveal a rigid porous structure. Indeed, a comparison of the TEM images in Figure 2 tentatively suggests some increased transparency to the electron beam in the case of the hyper-cross-linked particles, indicative of a lower mass density. The results in Table 1 summarize the characterization data for the various precursor and hyper-cross-linked particles prepared. For **E1** the three replica hyper-cross-linked products, **HXLE1A−C**, show a substantial fall in the Cl content from ∼20 to ∼4 wt % (average) consistent with the reaction of pendent chloromethyl groups to form methylene cross-linking groups, corresponding to a conversion of ∼80%. The residual Cl probably arises in part from unreacted sterically inaccessible $-CH_2Cl$ groups and partly from trapped chloride salts. In addition, all three samples retained Fe residues of 500−1000 ppm compared with 15 ppm in the precursor, **E1**, analyzed as a control. No attempt has yet been made to minimize the Fe residues or to exploit other Lewis acids in place of $FeCl_3$ although other Lewis acids have been used in related work involving suspension polymerized resins.[14]

The surface area, pore volume, and average pore diameter of **E1** and **HXLE1A−C** calculated using standard procedures from N_2 sorption data are shown in Table 1. These demonstrate very dramatically the generation of extensive porosity in the particles during hyper-cross-linking, and the data themselves are remarkably similar to those obtained following the hyper-cross-linking of much larger suspension polymerized VBC−DVB resin particles.[10−14] The precursor gel-type **E1** (also **E2−E4**, see later) is essentially nonporous in the dry state with a nominal surface area (N_2 BET) of ∼10 m^2 g^{-1}. This rises sharply to a remarkably high value ∼1100−1300 m^2 g^{-1} in **HXLE1A−C** with the generation of pores with an average diameter of ∼4

Table 1. Characterization Data for Hyper-Cross-Linked Nanoparticles and Their Precursors

							solvent uptake (g/g)		
sample	VBC/S/DVB ratio (vol %)	BET SA[a] ($m^2 g^{-1}$)	BJH[a] V_p ($cm^3 g^{-1}$)	BJH[a] D_p (nm)	% Cl content	Fe (ppm)	*n*-hexane	toluene	H_2O
E1	98/0/2	~10	*b*	*b*	20.4	15	0.5	1.3	0.8
HXLE1A	98/0/2	1280	0.25	3.9	3.3	1065	0.9	2.0	2.0
HXLE1A	98/0/2	1350	0.28	3.9	5.4	1060	1.7	2.5	2.5
HXLE1B	98/0/2	1060	0.22	3.8	4	440	1.8	2.3	2.6
HXLE1C	65/33/2	~15	*b*	*b*	14.8		0.6	1.7	0.8
E2	65/33/2	870	0.27	4.4	2.8		2.1	2.2	1.1
HXLE2	49/49/2	~15	*b*	*b*	11.3		0.6	1.8	0.9
HXLE3	49/49/2	570	0.21	4.8	2.2		1.6	2.2	0.6
E4	25/73/2	~15	*b*	*b*	6.3		0.7	2.2	0.8
HXLE4	25/73/2	~25	*b*	*b*	1.2		0.7	2.4	0.7

[a] SA = surface area; V_p = average pore volume; D_p = average pore diameter; each determined from N_2 adsorption isotherm. [b] Adsorption data too low to allow meaningful calculation (see data for **E1**, Figure 3).

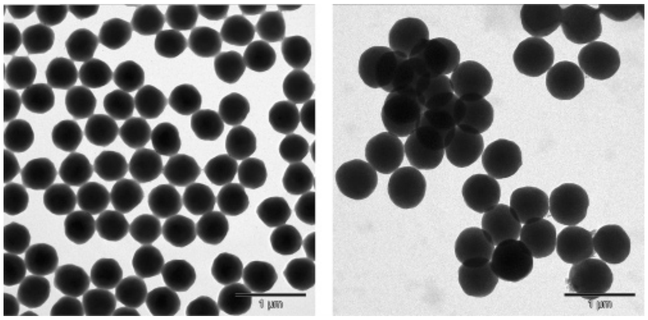

Figure 2. Transmission electron micrographs of gel-type precursor **E1** (left) and its porous hyper-cross-linked derivative **HXLE1B** (right).

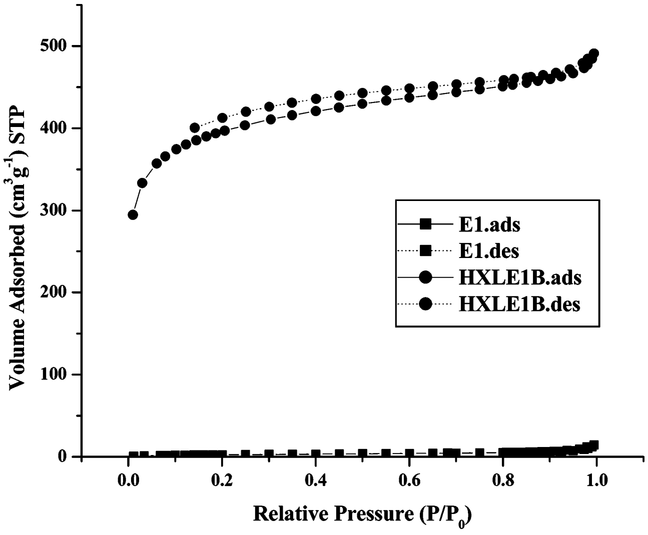

Figure 3. N_2 adsorption/desorption isotherms of gel-type precursor **E1** (■) and its porous hyper-cross-linked derivative **HXLE1B** (●).

nm and a pore volume of ~0.25 cm^3 g^{-1}. The N_2 sorption isotherms (Figure 3) and the pore size distribution curve (Figure 4) are typical of porous materials with a very narrow unimodal pore size distribution in the micropore range, e.g., zeolites. The response of the particles to the solvents *n*-hexane, toluene, and water is demonstrated by the solvent uptake data in Table 1. Again these show the changes characteristic of hyper-cross-linked networks. Not only do the uptake data for the thermodynamically compatible solvent, toluene, increase relative to the precursor in the case of **HXLE1A−C**, but also the two thermodynamically "poor" solvents, *n*-hexane and water, also show a measurable rise. The significant and unusual sorption of water by these hydrophobic polystyrene-based particles is diagnostic of Davankov-type morphology.[12]

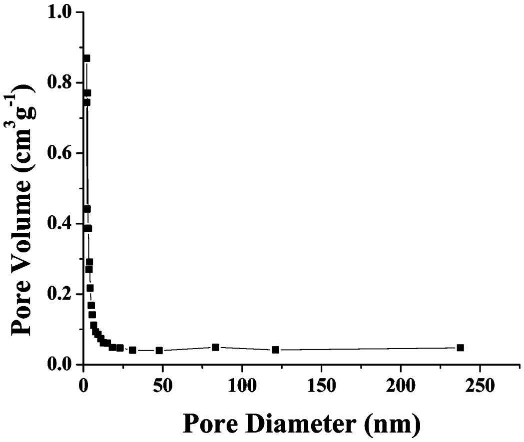

Figure 4. Pore size distribution curve for **HXLE1B** derived from N_2 adsorption isotherm.

The ability to synthesize monodisperse very high surface area porous polymer nanoparticles provides opportunities for exploitation in a number of areas, and we felt that the flexibility to tune the surface area would be additionally attractive. With this in mind gel-type VBC−DVB precursor nanoparticles **E2−E4** were synthesized with a DVB feed of 2 vol % similarly to **E1**, but with the content of VBC reduced progressively and balanced by appropriate addition to styrene (S) (Table 1). Hyper-cross-linking of each of these as before yielded **HXLE2−4**, respectively (Table 1). Our expectation was that the surface area might decline in this series but that some limit to the VBC content would be reached, below which the porosity characteristics of Davankov-type networks would be lost, simply because insufficient cross-links could be generated. In the event a systematic fall in the surface area is observed, the relationship between surface area and VBC feed content being essentially linear. This provides a convenient methodology for the synthesis of porous polymer nanoparticles with targeted surface areas.

However, although the pore volume and average pore diameter data for **HXLE2** and **3** are similar to those of **HXLE1**, the response to solvents, and notably to water, is different, suggesting that these networks do not possess all the structural features of hyper-cross-linked materials. Solvent uptake by cross-linked polymers can be regarded as having two components: one arising from pore filling and one from swelling of the network. Veverka and Jerabek[13] have made a similar point but in terms of adsorption and absorption effects. The uptake of toluene, a thermodynamically "good" solvent for these particular networks, remains fairly constant down the series **HX1E1−4**, and this solvent is able to both fill pores and swell the network. In contrast, the uptake of both *n*-hexane and water, both thermodynamically “poor” solvents for these networks, tends to decline down the series. Somewhat oversimplistically these two solvents can be regarded as nonswelling in the case of polystyrene-based networks. The decline observed in the uptake of these two solvents can therefore be attributed to a shift from the special characteristics of Davankov-type networks (**HXLE1A−C**) through a network with intermediate characteristics (**HXLE2**) to more conventional networks (**HXLE3** and **-4**). In the case of **HXLE4** with an original VBC content in its precursor of only 25 vol %, the porosity characteristics are significantly diminished and approach those of its precursor, **E4**. However, **HXLE4** cannot be regarded as a simple gel type, since its surface area is significant (∼25 m^2 g^{-1}) as is its solvent uptake, notably that of toluene. Nominally **HXLE4** has ∼50% of aromatic groups methylene bridged (from its 25 vol % of VBC), and a corresponding suspension polymerized styrene−DVB resin prepared with ∼50% DVB would be expected to have a very low capability to sorb even toluene. (*Note*: the toluene uptake for a 0.5% DVB resin is ∼13 g/g, falling to ∼2.5 g/g for a 5% DVB, and although it is difficult to extrapolate these data to provide a value for a 50% DVB resin the uptake by the latter will clearly be very low indeed.) The difference in behavior presumably arises because the network in **HXLE4** was methylene bridged while its precursor was swollen in DCE, whereas the network in the hypothetical 50% DVB resin would be formed in the absence of any additional solvent.

Conclusions

We have therefore developed a relatively simple but nevertheless potentially important synthetic procedure for the production of near monodisperse highly porous polymer nanospheres where the dry state surface area can be tailored in the range ∼20−1200 m^2 g^{-1}. In the case of the very high surface area species the porosity involves a very narrow unimodal pore size distribution in the micropore range, and these materials, though intrinsically hydrophobic, are able to sorb significant levels of water as well as solvents such as *n*-hexane and toluene.

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