Synthesis of Spherical Ultra-High Surface Area Monodisperse Amphipathic Polymer Sponges in the Low Micrometer Size Range[**]

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Davankov's group was the first to report on the synthesis of hypercrosslinked polystyrenes.[1] These are remarkable species that possess ultra-high specific surface areas (> 1000 m^2 g^{-1}) and an ability to sorb significant amounts of water, in spite of their apparently hydrophobic nature. The original methodology developed by Davankov and co-workers involved the exhaustive crosslinking of linear polystyrene chains using a Lewis acid generated 'external' bis-electrophile. Scientists at Rohm and Haas Co.[2] developed similar products, and more recently Jerábek and his co-workers[3] used similar, commercially-sourced chloromethylated suspension polymerized polystyrene resin particles as the starting material, with the generation of 'internal' electrophiles as the crosslinking mechanism. We ourselves have employed in-house prepared vinylbenzyl chloride (VBC)-divinylbenzene (DVB) copolymer resin particles, typically ~ 50-500 μm in diameter, with $FeCl_3$ as a particularly efficient Lewis acid catalyst[4] (Scheme 1). This methodology allows much better control over the porous morphology of the hypercrosslinked products. Recently, we have also succeeded in adapting our procedure to hypercrosslink VBC-DVB emulsion polymerized particles, typically ~ 400 nm in diameter.[5] This success convinced us that the Davankov methodology is a generic one and that it should be possible to synthesize monodisperse polymer particles with similar morphology and with diameters in what is probably the more immediately interesting technologically relevant size scale lying between emulsion and suspension polymerized particulates, *i.e.*, in the low micrometer size range. We have now investigated this strategy using precursor particles prepared *via* a non-aqueous dispersion (NAD) polymerization procedure[6] and particles prepared using a precipitation polymerization (PP) procedure.[7]

The overall strategy we have adopted is to synthesize precursor polymer particles from VBC using a restricted level of crosslinking, and then to further crosslink these particles extensively in a thermodynamically 'good' solvent, exploiting the pendent chloromethyl groups as an 'internal' electrophile source. Unfortunately, the methodology of NAD polymerization for synthesizing monodisperse particles with diameters in the low micrometer size range is most effective for *non*-crosslinked particles, although low levels of crosslinking

can sometimes be tolerated.[6] On the other hand, the technique of PP produces good yields of highly monodisperse particles in the desired size range (micrometer) when relatively higher levels of crosslinker are employed.[7] To some extent, therefore, neither of the precursor synthetic methodologies is considered to be ideal.

In the case of NAD polymerizations, discrete crosslinked particles, as opposed to aggregates, were obtained using levels of comonomer DVB in the range of 0.4–2% (w/w, relative to total monomer in the feed) but, unfortunately, in all cases these particles were not monodisperse. Nevertheless, a series of NAD precursors (**NAD1-4**) were synthesized using 1.5% (w/w) DVB with a range of VBC/styrene (St) ratios in order to investigate the effect of varying the content of chloromethyl groups. The data in Table 1 summarizes the findings. All the samples, **NAD1-4**, were polydisperse, although the particles were spherical and do fall in the low micrometer size range (Figure 1). The recoveries were moderate to good and the % Cl content correlates well with the proportion of VBC in the monomer feed. In all cases, the N_2 sorption BET derived specific surface area was very low, ~ 2 $m^2\ g^{-1}$, and the particles are essentially non-porous in the dry state. Exploitation of the pendent chloromethyl groups present in each sample in Lewis acid ($FeCl_3$) catalyzed hypercrosslinking readily yields the modified particles **HXLNAD1-4** with very good recoveries. The overall integrity of particles is retained (Figure 1), although surface roughness or contamination is obvious. Furthermore, the significant fall in the % Cl content (Table 1) confirms the high level of crosslinking that is achieved, which, at least in the case of **HXLNAD1** and **HXLNAD2**, must involve multiple bridging between aromatic groups. Of more practical importance, however, is that fact that each sample shows a remarkable rise in specific surface area (up to ~ 1,600 $m^2\ g^{-1}$) clearly indicative of the generation of a highly microporous morphology (Table 1). Only when the feed ratio of VBC to styrene in the precursor particles falls below 50% (**HXLNAD4**) does the specific surface area generated in its hypercrosslinked derivative fall to below 1,000 $m^2\ g^{-1}$.

In complete contrast to the NAD precursors, the precursors prepared using PP (**PP2–5**) were near monodisperse, perfectly spherical particles each with a diameter of ~ 5 μm (Figure 2). Only when the DVB content was reduced to 5% (w/w, relative to total monomer in the feed) were no particles produced (Table 2). The recoveries of product were rather low (~ 25–35%) but such recoveries are typical for dilute solution polymerizations such as these at the crosslinker levels employed.[7] Once again, the % Cl content in **PP2-4** correlates well with the VBC/DVB feed ratio, and the specific surface area of each sample is very low, ~ 5 m^2 g^{-1}. Subsequent $FeCl_3$ catalyzed crosslinking yielded the modified particles **HXLPP2-4**, again with respectable recoveries (54–70%) (Table 2). Very importantly, the high quality spherical monodisperse nature of all the particles is retained (Figure 2), possibly with a small increase in the diameter in the dry state, and once again with a remarkable rise in the specific surface area (up to ~ 1,300 m^2 g^{-1}).

Overall, the hypercrosslinking results show that to produce porous polymer particles with specific surface areas > 1,000 m^2 g^{-1} the VBC content of the precursor needs to be ~ 50% (w/w) or higher such that, statistically, 100% of the polystyrene pendent aromatic groups become methylene bridged at least once, and preferably more than once. This is consistent with our earlier quantitative solid state magic angle spinning ^{13}C nuclear magnetic resonance (SS MAS ^{13}C NMR) spectroscopic analysis of commercially sourced polystyrene-based hypercrosslinked resins, which indicated that the ratio of protonated to non-protonated aromatic C atoms is such that multiple methylene bridges must be present.[8]

The responses of all the samples when contacted with hexane, toluene and water are summarized in the solvent up-take data presented in Figures 3 and 4. The overall pattern displayed by the NAD precursors, **NAD1-4,** and the PP precursors, **PP2-PP4**, is similar. Likewise, the changes that arise when each precursor is hypercrosslinked are also similar. However, the larger up-take figures for the NAD samples, which arise from the very low level of crosslinking (1.5% w/w) in the precursors, show these trends more clearly. For the

precursors **NAD1-4** (Figure 3) the up-take of toluene is significantly larger than the figures for hexane and water, reflecting the fact that toluene is a thermodynamically compatible solvent with polystyrene, whereas the other two solvents are not. In this series the major change is the increase in the up-take of toluene from **NAD1** to **NAD4**; presumably, this trend reflects the increase of the styrene content in this series. In the case of the precursors **PP2-PP4**, yet again toluene is the best sorbed solvent but, overall, the data remains relatively unchanged across the series. *By far the most important effect* is seen on hypercrosslinking the precursors, where there is a sharp rise in the up-take of water, with a parallel increase in the toluene up-take figures. The effect with **HXLNAD1** (Figure 3) is particularly remarkable. Interestingly, the relative rise in water up-take *decreases* in the series **HXLNAD1** to **HXLNAD4** and this correlates with a *fall* in the feed content of VBC in the precursor, *i.e*., in the degree of methylene bridging that is achievable. *This confirms, therefore, that the water up-take data are intimately associated with the level of crosslinking achieved*. In the case of the **HXLPP** series a very similar dependence is seen in terms of both the water and the toluene data. The explanation for why apparently hydrophobic polystyrene-based materials sorb significant levels of water once they are hypercrosslinked has been reviewed a number of times by Davankov *et al*.[1] Our naive understanding is that the intense hypercrosslinking is carried out with the polymer chains in a swollen state. When the solvent is removed, collapse of the polymer network is frustrated, generating considerable stress in the matrix. On contact with even a poorly compatible small molecule, such as water, the matrix experiences plasticization, relaxation of the stress and subsequent expansion. This is manifest macroscopically as a significant volume up-take of water and, in some cases, other poorly compatible solvents such as hexane.

In summary, therefore, we have succeeded in preparing, for the first time, spherical ultra-high specific surface area monodisperse polymer particles with diameters in the low micrometer size range. Furthermore, these polymer particles are capable of sorbing significant levels of both hydrocarbon solvents and water, acting in effect as *amphipathic*

micro-sponges. We believe that these novel particles provide exciting possibilities for exploitation, particularly as the basis of new stationary phases in HPLC and related methodologies, and we are currently investigating with some urgency a number of applications in this area. Furthermore, being polystyrene-based, these particles will be amenable to versatile chemical derivatization and will display good thermal and chemical stability. Therefore, scientists with interests in diagnostics, sensors, delivery vehicles and catalysis may also find that these species provide new, exciting opportunities.

Experimental Methods

NAD polymerizations were performed at 70 °C under N_2 in a jacketed, baffled 1 L glass reactor with a four-bladed Teflon stirrer and a water condenser. The reactor was maintained at 70 ºC during the reaction. 95% of the dispersion medium [comprising the dispersant poly(vinyl pyrrolidone), 13% w/w relative to total mass of monomer in the feed, and the solvent (ethanol/toluene 77/23, v/v)], 70% of the monomer mixture (15% w/w based on total mass of dispersion medium) and DVB (80% grade; 0-2% w/w relative to total monomer in the feed) were introduced to the reactor at 70 ºC, and stirred at 120 rpm. After 1h, AIBN (5.2% w/w relative to total monomer in the feed) was dissolved in the remaining dispersion medium (5%) and the remaining monomer mixture (30%) and added dropwise to the reaction mixture, which was then allowed to polymerize for 24h under constant agitation. The particles formed were washed four times in total by centrifugation (2 x ethanol, then 2 x methanol) and then left on a roller in ethanol for 12 hours, before being recovered by vacuum filtration on a nylon membrane filter (0.2 µm) and dried *in vacuo* at 40 ºC overnight.

For the PP particles the comonomers (VBC and DVB) (2% w/v total monomer in feed relative to solvent) and AIBN (2 mol% relative to polymerizable double bonds) were added to acetonitrile (200 mL) in a polypropylene bottle (PPB) (250 mL).The VBC content (relative to DVB) was varied from 0-95% (w/w) with the balance being DVB. The monomer solution was de-oxygenated with N_2 at 0 °C and then the PPB placed on a low-profile roller (Stovall) in a

temperature-controllable incubator (Stuart Scientific, Surrey, UK). The temperature was ramped from ambient to 60 °C over a period of ~ 2 hours and the polymerization allowed to proceed at 60 °C for a further 46 hours. The resulting particles were separated from the reaction medium by filtration on a 0.2 μm nylon membrane filter, washed successively with methanol, toluene and acetone, before drying *in vacuo* at 40 °C overnight.

For the hypercrosslinking reactions the NAD or PP precursor particles (1.5 g) were added to 1,2-dichloroethane (DCE) (40 mL) in a round-bottomed flask (100 mL) and were left to swell fully under N_2 at room temperature for 1 hour. $FeCl_3$ (1:1 mole ratio with respect to the CH_2Cl content of particles) in DCE (40 mL) was added and the mixture heated at 80 °C for 18 hours. The resultant particles were recovered as described above and washed with MeOH and several times with aqueous HNO_3 (pH 1). The particles were then extracted overnight with acetone in a Soxhlet extractor and were washed again with MeOH and diethyl ether before drying *in vacuo* overnight at 40 °C.

Specific surface areas were calculated using a BET treatment of N_2 adsorption isotherm data generated on a Micromeritics ASAP 2000 porosimeter.

Scanning electron microscopy (SEM) micrographs were acquired using a JEOL 6400 instrument. Samples were coated in gold prior to analysis.

Solvent up-take data were measured gravimetrically using an adaptation of a literature procedure[9] involving a small SPE cartridge fitted a 0.45 μm nylon filter, excess solvent being removed by application of a vacuum to the SPE reservoir.

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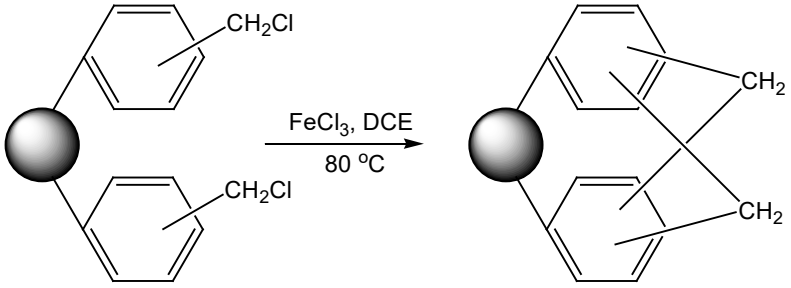

Scheme 1. Schematic representation of Lewis acid catalysed ‘internal’ hypercrosslinking of VBC-DVB precursor particles.

Table 1. Compositional and analytical data for NAD precursor particles and their hypercrosslinked derivatives.

Particles	VBC/St[a] (w/w)	D[b] (μm)	Coef. Var. (%)	Yield (%)	Microanalysis			S.A.[c] (m^2 g^{-1})
					%C	%H	%Cl	
NAD1	100/0	3.8 ± 0.3	8.2	50	72	5.8	21.0	~2
NAD2	75/25	4.6 ± 1.7	36.2	77	76	6.2	17.0	~2
NAD3	50/50	4.2 ± 1.4	33.2	60	80	6.7	12.6	~2
NAD4	25/75	10.9 ± 3.1	28.6	56	86	7.1	6.6	~2
HXLNAD1	100/0	4.0 ± 1.0	9.3	82[c]	85	6.2	5.1	1620
HXLNAD2	75/25	4.3 ± 1.7	38.5	82[c]	87	6.0	3.0	1480
HXLNAD3	50/50	3.8 ± 1.3	35.3	86[c]	88	6.3	2.7	1150
HXLNAD4	25/75	10.2 ± 5.2	50.5	45[c]	90	6.9	0.8	70

[a] Mass of VBC + St = 98.5% (w/w) of total monomer in the feed, with the balance (1.5%) being DVB-80; [b] D = average particle diameter ± standard deviation (S.D.) achieved with ImageJ software by counting 100 individual particles from SEM micrographs; [c] S.A. = specific surface area computed from N_2 sorption isotherms and BET analysis. [c] Relative to the mass of the corresponding (non-hypercrosslinked) precursor particles.

Table 2. Compositional and analytical data for PP precursor particles and their hypercrosslinked derivatives.

Particles	VBC/DVB (w/w)	D[a] (µm)	Yield (%)	Microanalysis			S.A.[b] (m^2 g^{-1})
				%C	%H	%Cl	
PP1	95/5	no particles	-	-	-	-	-
PP2	75/25	~ 4-5	27	78	6.5	14.5	~4
PP3	50/50	~ 5	25	83	7.0	8.5	~4
PP4	25/75	~ 4-5	30	88	7.5	4.0	~5
PP5	0/100	~ 3	33	91	7.6	-	210
HXLPP2	75/25	~ 4-5	70[c]	84	6.0	4.5	1320
HXLPP3	50/50	~ 5	61[c]	85	6.5	3.0	1080
HXLPP4	25/75	~ 4-5	54[c]	81	6.4	3.0	880

[a] D = particle diameter deduced visually from SEMs; [b] S.A. = specific surface area computed from N_2 sorption isotherms and BET analysis. [c] Relative to the mass of the corresponding (non-hypercrosslinked) precursor particles.

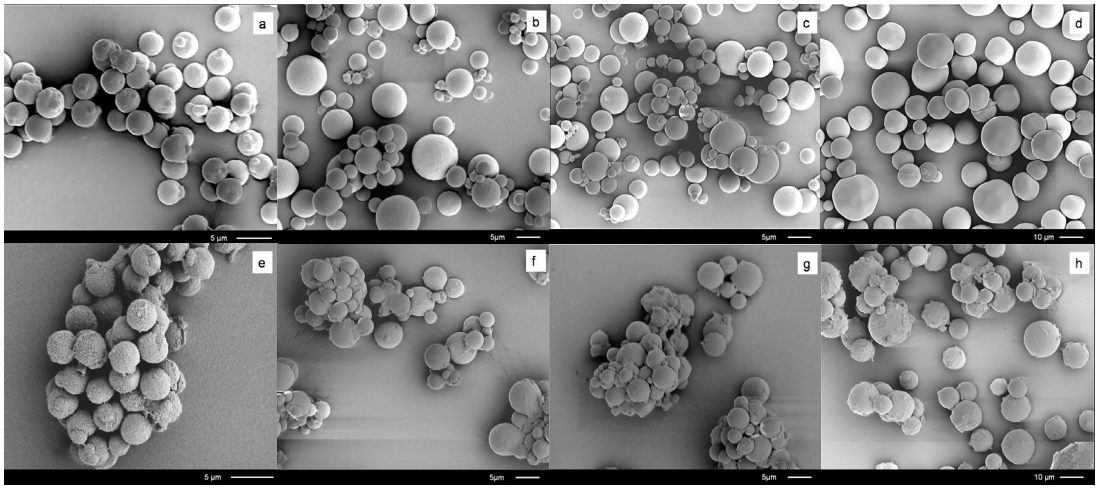

Figure 1. SEM images of VBC-St-DVB precursor particles prepared by NAD polymerization with different VBC/St w/w ratios and a fixed DVB content: (a) **NAD1**, 100%VBC/0%St; (b) **NAD2**, 75%/VBC/25%St; (c) **NAD3,** 50%VBC/50%St; (d) **NAD4,** 25%VBC/75%St, and their hypercrosslinked derivatives: (e) **HXLNAD1**; (f) **HXLNAD2**; (g) **HXLNAD3**; (h) **HXLNAD4**. The applied acceleration voltage of the incident electron beam was 3 kV.

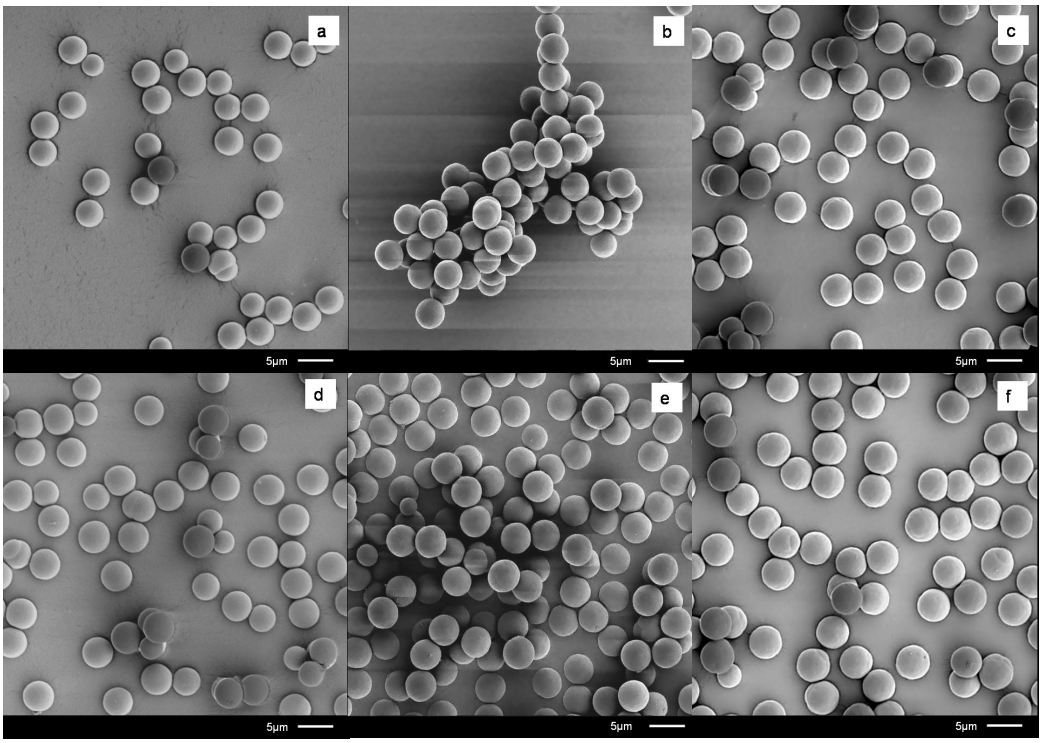

Figure 2. SEM images of precursor particles prepared by PP with different VBC/DVB w/w ratios: (a**)** **PP2**, 75%VBC/25%DVB; (b) **PP3**, 50%VBC/50%DVB; (c) **PP4,** 25%VBC/75%DVB, and their hypercrosslinked derivatives: (d) **HXLPP2**; (e) **HXLPP3;** (f) **HXLPP4**. The applied acceleration voltage of the incident electron beam was 3 kV.

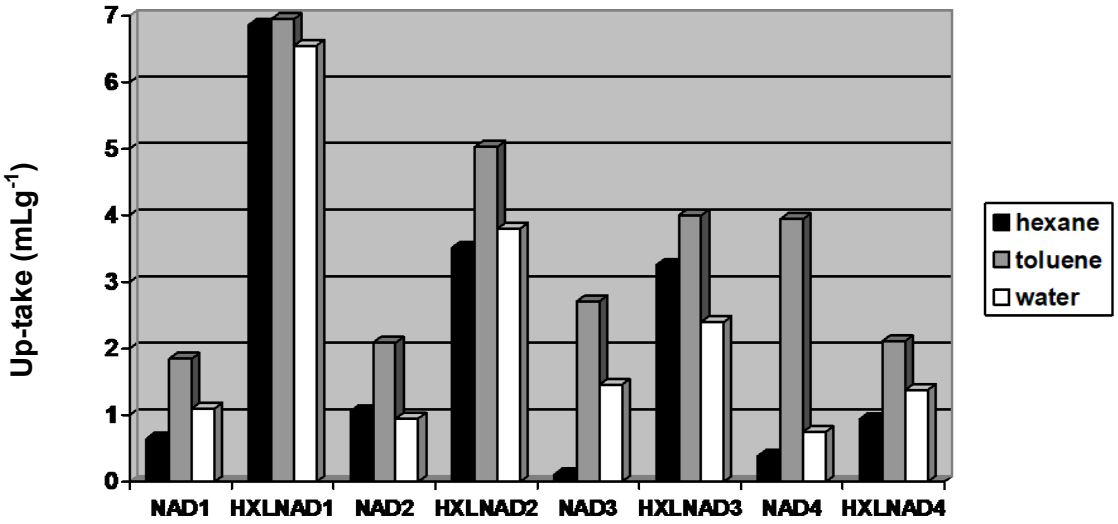

Figure 3. Solvent up-take data for NAD precursor particles and their hypercrosslinked derivatives.

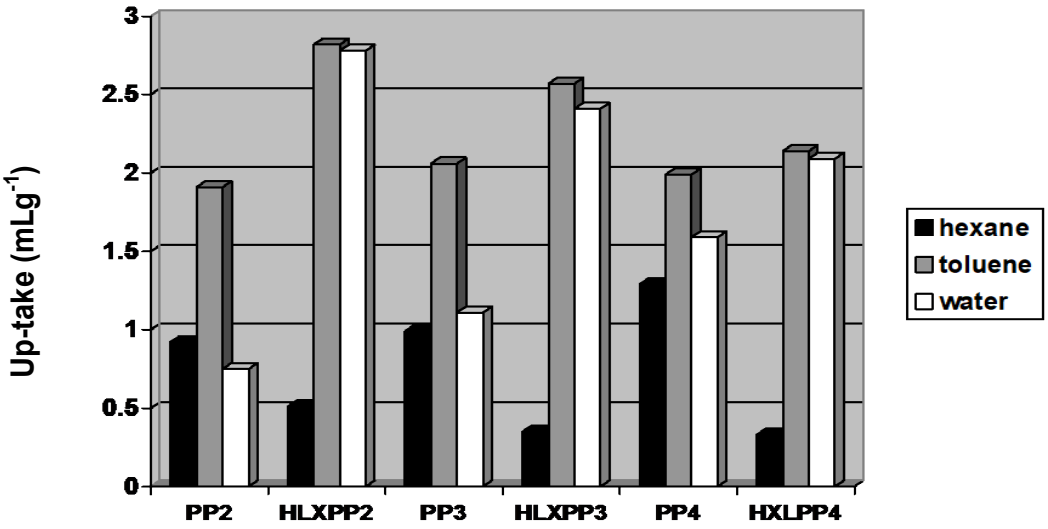

Figure 4. Solvent up-take data for PP particles and their hypercrosslinked derivatives.