Production of polystyrene spheres for use as a templating material for polyaniline monolith structures

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Polystyrene (PS) spheres are potentially useful as a reproducible, sacrificial templating material for monolith columns once they can be utilised to create a uniform microstructured packing which enables a higher monolith batch to batch reproducibility. To achieve PS spheres which can meet these requirements, their synthesis was optimised. Parameters investigated included variation of reactant concentrations, along with optimisation of reaction conditions temperature, agitation speed and nitrogen flow during aeration. Temperature and agitation played vital roles in the size and homogeneity of the synthesised PS spheres. Temperature affected the equilibrium concentration of monomer in the aqueous phase. When reaction temperature was increased, sphere size reduced and as reaction temperature decreased sphere size increased. A similar trend was seen when agitation speed was varied. At higher agitation speed average PS sphere size decreased as the rate of polymerisation increased. At lower agitation speed the average PS sphere size increased as the rate of polymerisation decreased. Ensuring fluctuations in both temperature and agitation were kept to a minimum was key to maintaining reproducibility. Any fluctuation above ~10% in either temperature or agitation speed affected standard deviation irreversibly. The facile dissolution of the PS spheres was also investigated. If the spheres produced could not be dissolved, their use as a sacrificial templating material would not be possible. By decreasing the original concentration of cross-linker, dissolution increased dramatically.

Monolithic vs. Particulate stationary phases

Monolith
- •Lower back pressure
- •Increased flow rate
- •Reduced run times
- •decreased reproducibility

Fig.1.a schematic illustration of a monolith based stationary phase

Particle
- •High Reproducibility
- •High pressure required
- •Longer run time

Fig.1.b schematic illustration of a particle based stationary phase

Experimental

The method described by Shim, S. E et al to synthesis PS spheres was used with some modifications.

Table 1a and Table 1b list the effects on the final PS spheres of optimising agitation speed, temperature and styrene volume and the optimal conditions determined for each parameter.

Table 1a: Optimised parameters for initiating polymer growth

Stage.1 formation of polymer - Conditions	Lower	Optimum	Higher
Temperature	% deviation increased average sphere size increased	70°C	% deviation increased average sphere size decreased.
Agitation speed	Sphere size increased % deviation unchanged ~10%	150 rpm	Sphere size reduced % deviation unchanged ~10%
styrene volume	sphere size/viscosity decreased	10 mL	sphere size/viscosity increased

Table 1b: Optimised parameters for continuing polymer growth

Stage.2 continued polymer growth - conditions	Lower	Optimum	Higher
Temperature	% deviation increased average sphere size increased	70°C	% deviation increased average sphere size decreased.
Agitation speed	Sphere size increased % deviation unchanged ~10%	150 rpm	Sphere size reduced % deviation unchanged ~10%
styrene Volume	Viscosity reduced uniform sphere size (reaction more controlled)	10 mL	Viscosity increased dramatically, fluctuating sphere size resulted

Fig.2.

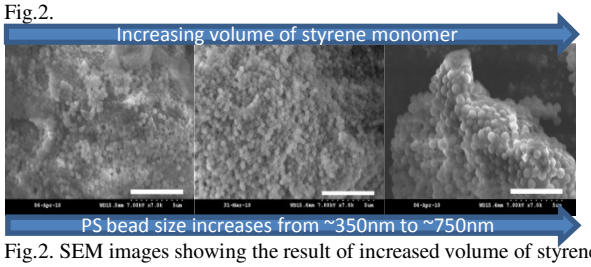

Fig.2. SEM images showing the result of increased volume of styrene monomer

Results & Discussion

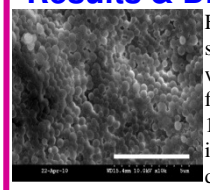

Fig.3.a PS spheres formed with temperature fluctuations of 5-10%, spheres irreversibly damaged.

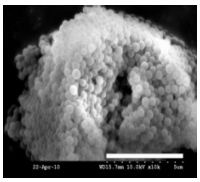

Fig.3.b PS spheres formed with temperature constant . Spheres are uniform with low % deviation.

The effect of temperature and agitation on the reaction is illustrated in the SEM images above. If reaction conditions are not strictly controlled, reproducibility of the PS spheres will be lost. It was shown that by varying temperature and agitation a wide and varying range of PS sphere sizes can be produced. It was also observed as temperature was increased rate of polymerisation increased, as temperature was decreased rate of polymerisation decreased. A similar trend was seen as agitation was varied. As agitation increased, sphere size reduced and as agitation decreased, sphere size increased due to polymerisation increasing with higher agitation speeds.

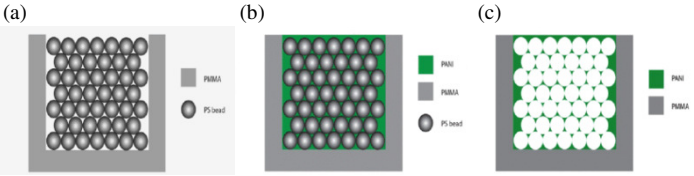

Fig.4. Schematic illustration of how microstructured PANI is obtained using a sacrificial PS sphere template

By packing PS spheres within a PMMA chip (a) the spheres can act as a sacrificial templating material. The growth of a PANI layer (green) around the PS spheres (b) followed by dissolution of the spheres, which was achieved by decreasing the concentration of the cross-linking agent DVB, resulted in the formation of an inverse opal structure (c). Once the PS spheres were successfully synthesised to the required specifications, they were packed into the separation channel in the micro fluidic chip using capillary forces. The resulting colloidal PS sphere structures are imaged in Fig. 5.

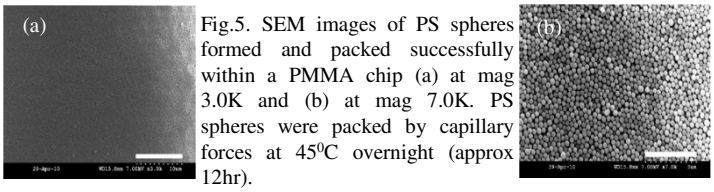

Fig.5. SEM images of PS spheres formed and packed successfully within a PMMA chip (a) at mag 3.0K and (b) at mag 7.0K. PS spheres were packed by capillary forces at 45°C overnight (approx 12hr).

Conclusions

The production of PS spheres suitable for use as a sacrificial template material for PANI monoliths was successfully achieved. PS sphere with uniform size and shape were produced with low standard deviation (~10% in the majority of cases) with as low as 4% achieved. It was shown that the main factors affecting uniform sphere formation were temperature and agitation speed. If large fluctuations were noted in either the temperature or agitation speed the resulting PS spheres were shown to have increased standard deviations and low uniformity. By reducing fluctuation PS spheres with low RSD along with uniform size and shape can be reproducibly produced which are suitable for use as a sacrificial templating material for PANI monoliths.

References

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