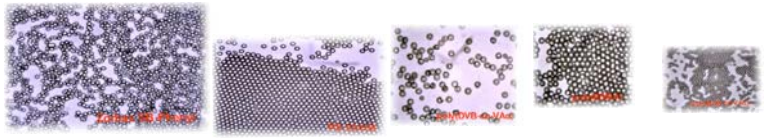
Preparation of Monodisperse Porous Polymer Particles as Stationary Phases for High Temperature Chromatography



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High temperature liquid chromatography has become an area of increasing interest over recent years. In particular, the use of superheated water as a mobile phase at temperatures above 100 °C has attracted attention due to its green credentials (particularly in the light of the current acetonitrile shortage) and potential performance advantages brought about by reduced viscosity and polarity etc.

Wider uptake of this approach is currently hampered by the lack of available stationary phases that are stable under such conditions, and available with an appropriate range of surface functionality to be applicable over a wide spectrum of analyte polarity. With this in mind, we have chosen to investigate the performance of cross-linked polymeric materials, since by custom-synthesis the polarity and surface chemistry of these materials can be tuned to give the required retention properties.

Experimental Techniques, Results and Discussion

Micron-size polystyrene seed particles were prepared based on a dispersion polymerisation method [1,2]. Different initiator concentrations and 1,1-Diphenylethylene (DPE) were utilised to control the size and the molecular weight of the seed.

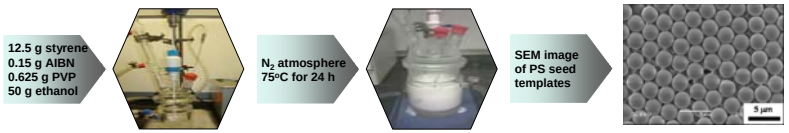


Figure 1 Schematic diagram of PS seed preparation by dispersion polymerisation

All ingredients used to prepare different polystyrene seed particles are summarised in Table 1.

Table 1 Recipe for preparing polystyrene seed particles

Sample	Styrene (mL)	AIBN (g)	Ethanol (mL)	PVP K-90 (g)	DPE (g)	Size (µm)	Mw (kDa)
PS 1 (1x I•)	12.5	0.15	50	0.625	-	2.8	128
PS 2 (4x I•)	12.5	0.6	50	0.625	-	6.2	12
PS 3 (DPE)	11	0.15	50	0.55	0.25	5	-

References

1. Wang, D.N., et al., *Seeded dispersion polymerization.* Journal of Applied Polymer Science, 2002. **84**(14): p. 2710-2720.
2. Tuncel, A., M. Tuncel, and B. Salih, *Electron microscopic observation of uniform macroporous particles. I. Effect of seed latex type and diluent.* Journal of Applied Polymer Science, 1999. **71**(14): p. 2271-2290.
3. Caglayan, B., et al., *Monodisperse porous poly(vinyl acetate-co-divinylbenzene) particles by single-stage seeded polymerization: A packing material for reversed phase HPLC.* Journal of Separation Science, 2006. **29**(7): p. 936-944.

Porous polymer particles were produced using a single-step swelling and polymerisation method according to the diagram given in Figure 2 [3].

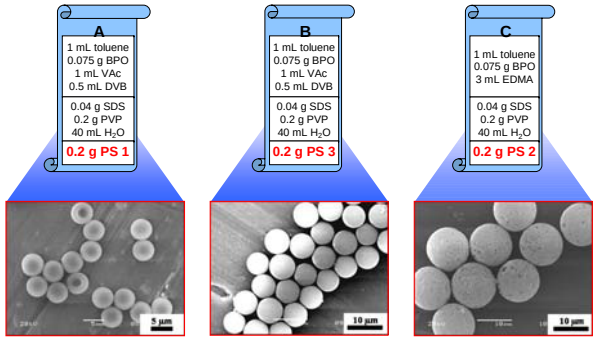
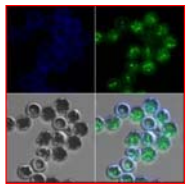


Figure 2 Recipes and microscopic images of particles of (A and B) poly(divinylbenzene-co-vinyl acetate) and (C) poly(ethylene dimethacrylate).

The results showed that the particles obtained were usually monodisperse and spherical, but the outcome was highly dependent on the molecular weight of the polystyrene seed.



SEM and confocal microscope images confirmed that the particles produced by using high molecular weight PS 1 were collapsed due to phase separation of the seed PS into the particle interior, where it precipitated causing the particles to collapse.

Figure 3 Confocal microscope image of fluorescently-labelled PS phase (green) separating in collapsed particles (blue).

Acknowledgement

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More polar poly(ethylene dimethacrylate) particles were produced using a similar method, packed into a 4.6x150 mm stainless column and used as packing material for high temperature HPLC using 100% H_2O as a mobile phase. A standard mixture of uracil, pyridine and phenol was injected while the temperature of the column was set between 30°C and 150 °C.

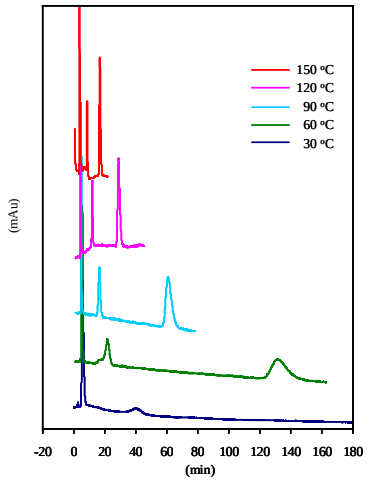

Figure 4 HPLC chromatograms of uracil, pyridine and phenol (from left to right) showing isothermal separations at temperatures between 30°C and 150°C.

Conclusion

Porous monodispersed polymer particles were successfully produced for use as stationary phases for high temperature HPLC. By controlling molecular weight of the PS seed particles, well-defined porous polymer particles can be obtained. Our initial results show that these polymer particles are stable under superheated water conditions. 35 sequential injections of the test mixture at 150°C showed no evidence of particle degradation. The chromatographic peaks show good symmetry but the column efficiency is rather low (approx 6200-12000 plates/m) for poly(ethylene dimethacrylate) packing material. This may be due to its low porosity ($30 m^2/g$).