Cationic diblock copolymer spheres as model templates for the production of hollow silica nanoparticles

Elizabeth R Jones[1*], O. O. Mykhaylyk[1], P. Wyman[2], R. Habets[2], S. P. Armes[1]

[1]*Department of Chemistry, University of Sheffield, Sheffield, United Kingdom*
[2] *DSM Ahead, P.O. Box 18, 6160 MD Geleen, The Netherlands*
**lizzy.jones@sheffield.ac.uk*

A poly(2-(dimethylamino)ethyl methacrylate) (PDMA) chain transfer agent (CTA) was used for the reversible addition-fragmentation chain transfer (RAFT) alcoholic dispersion polymerisation of benzyl methacrylate (BzMA) in ethanol at 70˚C [1]. THF GPC analysis indicated a well-controlled polymerisation with molecular weight increasing linearly with conversion. GPC traces also showed high blocking efficiencies with no homopolymer contamination apparent, and M_w/M_n values were less than 1.35 in all cases. ^{1}H NMR studies confirmed greater than 98% BzMA conversion when targeting PBzMA degrees of polymerization (DP) of up to 800. The PBzMA block becomes insoluble as it grows, leading to *in situ* formation of sterically-stabilised diblock copolymer nanoparticles *via* polymerisation-induced self-assembly (PISA). Fixing the mean DP of the PDMA stabilizer block at 99 units and systematically varying the DP of the PBzMA block enables a series of spherical nanoparticles of tunable diameter to be obtained.

Two methods were employed for the silicification of these spherical nanoparticles. The first protocol was based on that reported previously by Armes and co-workers using TMOS as a precursor [2], and the second protocol was based on a formulation involving TEOS and L-lysine reported by Nandiyanto et al. [3]. Various silica coating thicknesses were targeted and these silicified particles were then used to produce hollow silica spheres (via pyrolysis of the organic polymer template) [2]. Small angle X-ray scattering (SAXS) was used to investigate the structure of the silica layer produced by each method. In principle, this approach can be used to produce hollow silica spheres which could have various potential applications, such as catalysis, drug delivery, anti-reflective coatings or thermal insulation.

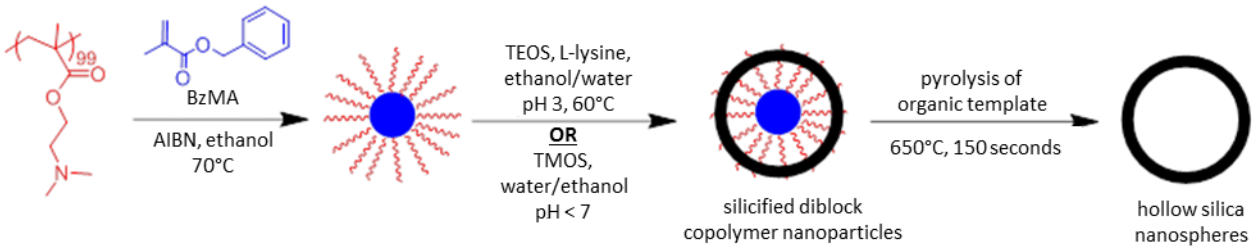

Figure 1: Chain extension of a poly(2-dimethylamino)ethyl methacrylate (PDMA) macro-CTA via ethanolic RAFT dispersion polymerisation of benzyl methacrylate (BzMA) to produce sterically-stabilised PDMA-PBzMA diblock copolymer nanoparticles. Subsequent silica deposition by one of two different methods affords silicified nanoparticles, which form well-defined hollow silica nanoparticles on calcination.

Acknowledgements DSM Research (Geleen, Netherlands) is thanked for funding a CASE award for ERJ's EPSRC PhD studentship and also for permission to present this research. SPA acknowledges a five-year ERC *Advanced Investigator* grant (PISA 320372) and also partial project funding from Stichting Innovatie Alliantie (Foundation Innovation Alliance).

[1] E. R. Jones, M. Semsarilar, A. Blanazs and S. P. Armes, *Macromolecules*, 2012, **45**, 5091.
[2] J.-J. Yuan, O. O. Mykhaylyk, A. J. Ryan and S. P. Armes, *J. Am. Chem. Soc.*, 2007, **129**, 1717.
[3] A. B. D. Nandiyanto, T. Iwaki, T. Ogi and K. Okuyama, *J. Colloid Interface Sci.*, 2013, **389**, 134.