

Preparation of Diblock Copolymer Nanoparticles by RAFT Dispersion Polymerization in Non-Polar Media and their use as Nanoreactors for the In Situ Synthesis of Silica or Titania

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Well-defined diblock copolymer nanoparticles are prepared via reversible addition-fragmentation chain transfer (RAFT) dispersion polymerization of 2-hydroxyethyl methacrylate (HEMA) in a poly(α -olefin) at 90 °C using a poly(lauryl methacrylate) (PLMA) precursor. This formulation produces a colloidal dispersion of spherical PLMA-PHEMA nanoparticles at 10% w/w solids. The nanoparticle cores can be swollen with 30% w/w aqueous HCl based on the PHEMA mass and then used as nanoreactors for the *in situ* synthesis of silica or titania using either tetraethyl orthosilicate (TEOS) or titanium *t*-butoxide, respectively. The nanoparticles are characterized by TEM, DLS and SAXS. The former technique indicates that core-swelling leads to a subtle change in copolymer morphology from pseudo-spherical to perfectly spherical nanoparticles. DLS and SAXS indicate the formation of near-monodisperse nanoparticles of 92-117 nm diameter with colloidal stability being retained after the nanoreactor syntheses. For the silicified nanoparticles, turbidimetry and SAXS studies suggest a reaction timescale of around 50 min at 25 °C. In this case, the final nanoparticle dispersion is highly transparent, whereas the corresponding titania-loaded nanoparticles form a highly turbid dispersion. Thermogravimetric analyses indicate silica and titania mass loadings of 17% and 21%, respectively. In both cases, the inorganic phase is amorphous rather than crystalline.

Keywords:

RAFT, PISA, Synthesis, Nanoreactor, Silica

References:

- [1] Chohan, P.; György, C.; Mykhaylyk, O. O.; Prentice, G. M.; Filip, S. V.; Payne, M. J.; Manna, G.; Armes, S. P. RAFT Dispersion Polymerization of 2-Hydroxyethyl Methacrylate in Non-Polar Media. *Macromolecules* **2024**, *57*, 11738–11752.
- [2] Chohan, P.; Xie, A.; Mykhaylyk, O. O.; Prentice, G. M.; Atkinson D. J.; Armes, S. P. Diblock Copolymer Nanoparticles act as Nanoreactors for the Synthesis of Sterically-Stabilized Inorganic Oxide Particles in Non-polar Media. Unpublished work.