Preparation of Well-defined Biocompatible Macromonomers and their use as Steric Stabilisers in Latex Syntheses

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A range of well-defined methacrylic macromonomers based on the biomimetic monomer, 2-(methacryloyloxy)ethyl phosphorylcholine (MPC), has been synthesised by Atom Transfer Radical Polymerisation (ATRP) in alcoholic media using N-(dimethylamino)ethyl-2-bromoisobutyrylamide. This tertiary amine-functionalised initiator was used to produce homopolymer precursors of various chain lengths. These polymerisations were relatively well controlled with $M_w/M_n \leq 1.30$, providing that the target degree of polymerisation (DP) did not exceed 30. For higher target DPs, polymerisations were poorly controlled and characterised by broad molecular weight distributions ($M_w/M_n = 1.50 – 2.31$). The tertiary amine end-group of each near-monodisperse homopolymer precursor was then quaternised using 4-vinylbenzyl chloride (4-VBC) to afford the corresponding styrene-functionalised macromonomers.

$PMPC_{30}$ macromonomer proved to be an effective reactive steric stabiliser for the formation of polystyrene latex particles, provided that it is employed at 10 w/w % based on monomer. Submicrometer-sized and micrometer-sized latexes were synthesised by aqueous emulsion and alcoholic dispersion polymerisation respectively, as judged by scanning electron microscopy and dynamic light scattering studies. Attempted alcoholic dispersion polymerisation syntheses conducted either in the presence of the $PMPC_{30}$ homopolymer precursor or in the absence of any macromonomer resulted in macroscopic precipitation, with no evidence of particle formation. Such control experiments confirmed the importance of the terminal styrene groups on the macromonomer chains for latex formation. FT-IR spectroscopy indicated the presence of the $PMPC_{30}$ macromonomer within the polystyrene latex and XPS studies indicated that these stabiliser chains are located at (or very near) the latex surface, as expected. Using $PMPC_{20}$ and $PMPC_{10}$ macromonomers for the alcoholic dispersion polymerisation of styrene led to latexes with substantially broader size distributions. Finally, approximately micrometer-sized latex particles could also be prepared by aqueous dispersion polymerisation of 2-hydroxypropyl methacrylate in the presence of the $PMPC_{30}$ macromonomer.