Photoactivation with copper(II) and disproportionation of copper(I) of acrylamides and acrylates for compatibilisers

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Abstract

End functional and block copolymers where the end group/a-block is designed to interact with one substrate and the B-polymer designed to interact with a continuous phase are a main stay of compatibilisation. In order to achieve this as efficiently as possible, effective living polymerisation methods are required. The use of radical based chemistry allows for many functional groups to be used without laborious purification and protecting group chemistry. This is essential for making these new materials in an economically viable way. Two new methods of using copper complexes at ambient and sub ambient temperature will be presented 1) using visible light with copper(II) complexes and 2) utilising rapid disproportionation of copper(I) in water and aqueous media. Photo-activated living radical polymerization of acrylates, in the absence of conventional photo-initiators or dye sensitizers upon irradiation with UV radiation ($\lambda_{\text{max}} \sim 360$ nm) will be described. In the presence of low concentrations of copper(II) bromide and an aliphatic tertiary amine ligand (Me$_6$-Tren), near-quantitative monomer conversion (> 95%) is obtained within 80 minutes yielding poly(acrylates) with dispersities as low as 1.05 and excellent end group fidelity (>99%). The control retained during polymerization is confirmed by MALDI-ToF-MS and exemplified by in situ chain extension upon sequential monomer addition furnishing higher molecular weight polymers with an observed reduction in dispersity ($D = 1.03$). Similarly, efficient one-pot block copolymerization by sequential addition of PEGA$_{480}$ to a poly(methyl) acrylate (PMA) macroinitiator without prior work-up or purification is also reported. Minimal polymerisation in the absence of light confers temporal control and alludes to potential application at one of the frontiers of materials chemistry whereby precise spatiotemporal “on/off” control and resolution achieved.

A new approach to perform single-electron transfer living radical polymerization (SET-LRP) in water will be also described. The key step in this process is to allow full disproportionation of CuBr/Me$_6$TREN to Cu(0) powder and CuBr$_2$ in water prior to addition of both monomer and initiator. This provides an extremely powerful tool for the synthesis of functional water-soluble polymers with controlled chain length and narrow molecular weight distributions (PDI approx. 1.10), including poly- NIPAM, DMA, acrylamide, zwitterionic monomers, PEG acrylate, HEA and an acrylamido glyco monomer. (1, 2)
Acknowledgements: We appreciate financial support from the University of Warwick and China Scholarship Council (QZ). Equipment used in this research were supported by the Innovative Uses for Advanced Materials in the Modern World (AM2), with support from Advantage West Midlands (AWM) and partially funded by the European Regional Development Fund (ERDF). D.M.H is a Royal Society/Wolfson Fellow.

References
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Short Biography
David Haddleton has been working in the area of controlled polymer synthesis for over 25 years since being employed at ICI. His PhD “Photochemistry of some organometallic ethene compounds” was under the supervision of Robin Perutz at the University of York in 1986. He spent one year at the University of Toronto as a PDRA working with Geoff Ozin on metal vapour synthesis and intra zeolite encapsulation of organometalics. He joined ICI in 1988 and spent one year at the University of Southern Mississippi working with polymer liquid crystals. Moving back to the UK in 1988 he spent 5 years working on GTP and anionic polymerisation prior to moving to Warwick in 1993 and was promoted to full Professor in 1998. He has published over 300 papers and has a google h-index = 61 with over 12000 citations. Current work in the group is in different aspects of developing new polymerisation methodology and using this for novel polymers for industrial applications, polymers for personal care applications, (hair and skin care) and for biomedical and nano medicinal applications (new and targeted peptide and protein conjugation). Recent work includes new conjugation strategy, glycopolymers, monomer sequence control and polymerisation in biological media. He was, and remains, the founding Editor in Chief of the RSC journal Polymer Chemistry and is an adjunct Professor and a Chair Professor at Soochow University.