Poster 5

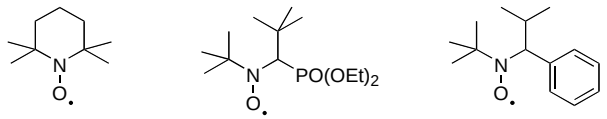
Nitroxide-Mediated Polymerisation in Miniemulsion using TIPNO-based Alkoxyamines

Robert J. Blanchard[1], Neil R. Cameron[2], Olivier Lagrille[2] and Peter A. Lovell[1]

[1]Materials Science Centre, School of Materials, The University of Manchester
Grosvenor Street, Manchester, M1 7HS, United Kingdom
[2]IRC in Polymer Science and Technology, University of Durham
Department of Chemistry, South Road, DH1 3LE, United Kingdom

Nitroxide-mediated polymerisation (NMP) has become a well-established means for achieving controlled radical polymerisation of a range of olefinic monomers following the pioneering work of Rizzardo and Solomon [1,2] and Georges et al. [3] with 2,2,6,6-tetra-methyl-piperidine-*N*-oxyl (TEMPO) as the nitroxide. The control results from fast reversible exchange between dormant alkoxyamine species and active propagating radical species, which gives rise to a very low radical concentration and thus drastically reduces the probably of radical-radical termination reactions. Several new acyclic ∝-H-bearing nitroxides and the corresponding alkoxyamines have been developed by many authors. Compared to TEMPO, these nitroxides can control the polymerisation of styrene and acrylates over a shorter timescale, giving predictable molar masses and narrow molar mass distributions.

Recently, NMP has been carried out successfully in aqueous dispersed systems, especially in miniemulsion using *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (SG1) and 2,2,5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) or their derivatives as nitroxides [e.g., 4-8].



TEMPO SG1 TIPNO

Nitroxide Structures

The present work concerns design and synthesis of hydrophobic acyclic nitroxides for effecting miniemulsion polymerisation below 100 °C. The TIPNO skeleton was chosen because it is more amenable to the introduction of bulky, hydrophobic species. The aim was to prepare a family of nitroxides and alkoxyamines with controlled structural variations and to investigate effects of nitroxide and alkoxyamine structure on bulk and miniemulsion polymerisation of styrene and n-butyl acrylate. This paper will describe some of the new hydrophobic nitroxides [9] and will report results from initial studies of the use of TIPNO-derived alkoxyamines in bulk and miniemulsion polymerisation of styrene at 125 °C and 90 °C.

1. D.H. Solomon, E. Rizzardo, P. Cacioli, U.S. Patent 4,581,429, 1985
2. D.H. Solomon, *J. Polym. Sci., Polym. Chem.*, 2005, *43*, 5748-5764.
3. M.K. Georges, R.P.N. Veregin, P.M. Kazmaier, G.K. Hamer, *Macromolecules*, 1993, *26*, 2987-2988
4. C. Farcet, M. Lansalot, B. Charleux, R. Pirri, J.P. Vairon, *Macromolecules*, 2000, *33*, 8559-8570
5. B. Keoshkerian, A.R. Szkurhan, M.K. Georges, *Macromolecules*, 2001, *34*, 6531-6532
6. M. Lansalot, C. Farcet, B. Charleux, J.P. Vairon, R. Pirri, P. Tordo, in *Controlled / Living Radical Polymerization*, K. Matyjaszewski (Ed.), *ACS, Symp. Ser.*, 2000, *768*, Chapter 10
7. C. Farcet, B. Charleux, R. Pirri, *Macromolecules*, 2001, *34*, 3823-3826
8. J. Nicolas, B. Charleux, O. Guerret and S. Magnet, *Macromolec*ules, 2004, 37, 4453-4463
9. O. Lagrille, N.R. Cameron, P.A. Lovell, R. Blanchard, A.E. Goeta and R. Koch, *J. Polym. Sci., Polym. Chem.*, 2006, *44*, 1926-1940