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NEW NITROXIDES DESIGNED FOR CONTROLLED RADICAL MINIEMULSION POLYMERIZATION

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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). Since then several new acyclic nitroxides and the corresponding alkoxyamines have been developed. Compared to TEMPO, they control polymerisation of styrene and acrylates over a shorter timescale, giving predictable molar masses and narrow molar mass distributions. More recently, NMP has been used successfully in aqueous media with *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].

This paper will describe the design and synthesis of new hydrophobic acyclic nitroxides for effecting miniemulsion polymerisation at temperatures 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 the effect of nitroxide and alkoxyamine structure on bulk and miniemulsion polymerisation of styrene and n-butyl acrylate.

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