Di-*tert*-alkyl Nitroxyl Radicals. Synthesis, Physical Properties and Applications as Inhibitors of Vinyl Polmerization at Elevated Temperatures

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Hydrogenation of Alkenes and Alkynes, Di-*tert*-alkyl Amines, Di-*tert*-alkyl Nitroxyl (Aminoxyl) Radicals, Polymerization Inhibitors

Stable di-*tert*-alkylnitroxyl radicals, *tert*-butyl-*tert*-pentylnitroxyl (**4a**), di-*tert*-pentylnitroxyl (**4b**) and *tert*-octyl-tert-pentylnitroxyl (**4c**), the homologs of di-*tert*-butylnitroxyl (**1**), were synthesized from *tert*-alkyl amines **7a-c** via the 3-*tert*-alkylamino-3-methyl-1-butynes **8a-c**. Oxidation of **8a,b** with hydrogen peroxide lead to relatively unstable N-*tert*-alkyl-N-(1,1-dimethyl-prop-2-ynyl)nitroxyl radicals **15a,b**. The thermal stability, vapor pressure data, ultraviolet, visible and electron paramagnetic resonance spectra of **4a-c** were recorded. The radicals were explored as potential inhibitors of unwanted alkene polymerization reactions at elevated temperatures, in comparison with the aliphatic di-*tert*-butyl nitroxyl (**1**), the alicyclic nitroxyl radicals 2,2,6,6-tetramethylpiperidin-1-oxyl (**2**) and 4-hydroxy-2,2,6,6-tetramethyl-piperidin-1-oxyl (**3**), some commercial polymerization inhibitors, such as diethyl-hydroxylamine (Pennstop, **16**), ammonium salt of N-hydroxy-N-nitrosobenzenamine (Cupferron, **17**), bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin 770, **18**), and the well-known spin traps 2-methyl-2-nitrosopropane (**19**) and *tert*-butylhydroxylamine (**20**).