

**Nitroxides in Mechanistic Studies: Ageing of Gold
Nanoparticles and Nitroxide Transformation in Acids**

Yun Ma

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Abstract

The work described in this thesis includes the applications of nitroxide in the mechanistic studies of two very different research topics.

Chapter 2 describes the investigation of ageing of gold nanoparticles (AuNPs) and its mechanistic implications. By utilizing a customized bisnitroxide disulfide, ligand place-exchange reactions of AuNPs were studied by Electron Paramagnetic Resonance (EPR) Spectroscopy and a nitroxide spin label was introduced onto the gold surface in the process. Ageing of thiolate protected AuNPs results in reduced reactivity in the disulfide exchange. By studying the ligand and temperature dependence of this process and the effect of ageing on the maximum extent of exchange, the presence of different binding sites on the surface of AuNPs was proposed.

Chapter 3 describes the mechanistic studies of nitroxide-based polymerization inhibitors in various organic monomers. The presence of nitroxide radicals was utilized to report dissolved oxygen concentration which is essential in the inhibition of polymerization. Oxygen-related broadening was deconvoluted from the EPR spectra of nitroxide radicals using an oximetry fitting method. By adopting this method, the inhibition mechanism and associated chemistry of nitroxides in self-initiated polymerization of acrylic acid was investigated. The synergism of nitroxides with other types of inhibitors was proposed. An unusual decay of nitroxide radicals in acid at high temperature was observed.

Following Chapter 3, Chapter 4 describes the detailed mechanistic investigation of nitroxide decay in acid at high temperature. *N*-oxoammonium salt, a product of acid-catalyzed disproportionation of nitroxides, was found to decompose at high temperature. Mechanistic investigation of this reaction leads to identification of the important role of hydroxylamine in the mechanism of nitroxide inhibited polymerization of acidic monomers.

Declaration

This thesis is a summary of the research work carried out in the Department of Chemistry, University of York, between October 2006 and September 2010. It has not, either in part or as a whole, been submitted for a degree or diploma or other qualification at any other University.

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List of Abbreviations

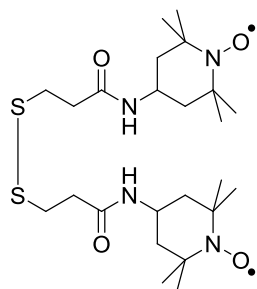
Abs – absorbance

aq – aqueous solution

a.u. – arbitrary units

AuNPs – gold nanoparticles

DIS3 –



EI – electron impact ionization

EPR – Electron Paramagnetic Resonance

ESI – electrospray ionization

EXP – experimental

FID – flame ionization detector

g – gram(s)

GC – Gas Chromatography

gem – germinal

GPC – Gel Permeation Chromatography

HR – high resolution

hrs – hour(s)

4HT – 4-hydroxy-TEMPO

IR – infrared

M – molar

MEHQ – monomethyl ether of hydroquinone (*4*-Methoxyphenol)

Me – methyl, CH₃

mg – milligram(s)

Mhz – megahertz

min – minute(s)

mL – millilitre(s)

μl – microlitre
MS – Mass Spectrometry
m/z – charge to mass ratio
n – normal
Na-ASC – sodium *L*-ascorbate
nm – nanometre(s)
NMR – Nuclear Magnetic Resonance
ns – nanosecond(s)
4OT – 4-oxo-TEMPO
p – para-
PhNHNH₂ – phenylhydrazine
PPh₃ – triphenylphosphine
ppm – part(s) per million
ppt – part(s) per trillion
PTZ – phenothiazine
R.T. – room temperature
s – second(s)
SOMO – singly occupied molecular orbital
TEM – Transmission Electron Microscopy
TEMPO(T) – 2,2,6,6-tetramethyl-1-piperidinyloxy
TEMPOH(TOH) – TEMPO hydroxylamine
TGA – Thermogravimetric
TH⁺ – protonated TEMPO
TLC – Thin Layer Chromatography
T=O⁺ – oxoammonium salt from TEMPO
TOAB – tetraoctylammonium bromide
TOH₂⁺ – protonated TEMPOH
UV-*vis* – Ultraviolet-visible
v/v – volume to volume ratio
w/w – weight to weight ratio

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