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

Yun Ma

PhD

2010

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.

Yun Ma

Acknowledgements

Firstly, I would like to thank my family for their support and patience during my PhD study. It was the most amazing experience that the entire family were supporting me even at the most difficult times.

I would also like to thank my supervisor, Dr Victor Chechik for the continuous help and guidance in this research work as well as proof reading this thesis. Thank my IPM, Prof. Ian J. S. Fairlamb for his help and advice. Dr Philip Helliwell and Dr Paul Elliott helped me with some analysis work. The experimental officers and technicians in the department are thanked for their support. Dr James Hopkins and Miss Shalini Punjabi are thanked for their help on the headspace analysis. Thank Gareth Moody for his help on the GC analysis.

The Nufarm R&D team in Wyke are thanked for the useful discussions and the nice lunches. Especially I'm thankful for Angela Glossop and James Hunt for the IC analysis and synthesis of oxoammonium salt.

A special thank you to Dr Marco Conte for his help, advice and encouragement during my PhD study. Present (Muhammad Warsi, James Wallace, Thomas Newby, Kazim Raza and Jamie Gould) and past (Marco Conte, Eleanor Hurst, Riccardo Garzelli, Gabriella and Petre Ionita, Brendan Garret, Xuetong Zhang and Leonie Jones) group members are thanked for the wonderful and not so wonderful days we have spent together. I'm also grateful for the many good friends I met in York, who have made the life colourful here.

Nufarm Ltd. and University of York (Wild Fund) are thanked for the financial support.

I would also like to thank Sir Timothy Berners-Lee for inventing the World Wide Web 20 years ago. I would never finish this thesis without his invention.

List of Abbreviations

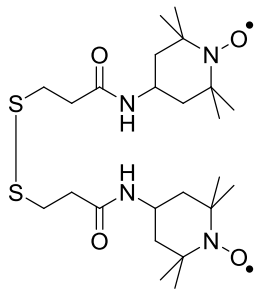
Abs – absorbance

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, CH_3

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-

$PhNHNH_2$ – phenylhydrazine

PPh_3 – 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-piperidinyloxyl

TEMPOH(TOH) – TEMPO hydroxylamine

TGA – Thermogravimetric

TH^+ – protonated TEMPO

TLC – Thin Layer Chromatography

$T{=}O^+$ – oxoammonium salt from TEMPO

TOAB – tetraoctylammonium bromide

TOH_2^+ – protonated TEMPOH

UV-*vis* – Ultraviolet-visible

v/v – volume to volume ratio

w/w – weight to weight ratio

Table of Contents