The Mild Synthesis of
Zinc Oxide Nanoparticles and Nanocomposites via
hydrolysis of
Well-Characterised Zinc Organometallics

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for the degree of
Doctor of Philosophy

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Declaration

The work described in this thesis was conducted in the Department of Chemistry, Imperial College London, between October 2007 and September 2010, and is the work of the author unless otherwise stated.
Abstract

This thesis centres on the development of a clean, one step method for generating surface-functionalised zinc oxide (ZnO) nanoparticles for application in the synthesis of well-dispersed inorganic-organic nanocomposites. The nanoparticle synthesis method utilises the controlled hydrolysis of organometallic zinc compounds, employing diethylzinc as a bulk precursor and an alkylzinc carboxylate as a substoichiometric, secondary precursor to deliver the capping ligands.

A series of ethylzinc carboxylate species were synthesised and studied by NMR spectroscopy (EtZn(OOCR); R = H, CH₃, and (CH₂)ₙCH₃, where n = 4, 10, 16). The ligand stoichiometry of the complexes was found to depend on the nature of the solvent (coordinating vs. non-coordinating), and single crystal X-ray experiments indicated that the strength of the donor interaction of a coordinating solvent affects the nuclearity of the complex’s repeat unit in the solid state. In addition, the isolated complexes of the acetate derivative were active catalysts for the copolymerisation of CO₂ and cyclohexene oxide.

The ZnO nanoparticle synthesis route was first explored in the absence of a polymer matrix and was proven to yield hydrophobic nanoparticles with a narrow size distribution without the need for size selection steps (average particle size 3.6 ± 0.2 nm, σ = 15% using stearate; HR-TEM). The effect of varying different synthesis parameters on the resulting ZnO particle size and morphology was investigated. Additional inorganic zinc phases were observed on slowing the reaction rate, allowing insight into the mechanism of delivery of carboxylate groups to the growing nanoparticle surfaces.

Finally, in situ ZnO/epoxy resin nanocomposites were prepared. The degree of nanoparticle dispersion improved with surface-functionalisation in the order stearate < uncapped < benzoate (TEM), which correlated with the nature of the particle-matrix interaction (DSC). In situ prepared nanoparticles (uncapped) were also introduced into conventional microcomposites and found to improve the composite density and thermal conductivity relative to the highest loading of microparticles alone.
Acknowledgements

First and foremost I would like to thank Dr Charlotte Williams and Prof. Milo Shaffer for giving me the opportunity to carry out my PhD under their supervision. I am very grateful for all of the advice, expertise, ideas, and encouragement that they have given me throughout my time at Imperial, without which this project would not have been possible, nor as successful and enjoyable.

There are a number of people in the Department of Chemistry who have contributed to this thesis. Special thanks go to Dr. Andrew White, for his skill, patience, and hard work in determining the crystal structures of my compounds. Peter Haycock and Dick Sheppard carried out the PGSE and VT NMR experiments, and I greatly appreciate the time that they put into assisting with interpretation of the results. Additionally, I would like to thank Dave Anthony, Johann Cho, Richard Winchester and Tomi Herceg for providing various SEM images (not all of which made it into the final draft).

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Publications

The work in this thesis has resulted in, or will result in, the following publications:

‘Pentanuclear Complexes for A Series of Alkylzinc Carboxylates’
Katherine L. Orchard, Andrew J. P. White, Milo S. P. Shaffer, Charlotte K. Williams
*Organometallics* (2009), 28, 5828-5832.

‘Solvent Dependence of the Structure of Ethylzinc Acetate and its Application in CO$_2$/Epoxide copolymerization’
Katherine L. Orchard, Jonathan Harris, Andrew J. P. White, Milo S. P. Shaffer, Charlotte K. Williams

‘Surfactant-free, one-step synthesis of surface-modified ZnO nanoparticles and nanocomposites’
Katherine L. Orchard, Milo S. P. Shaffer, Charlotte K. Williams
*In preparation.*
List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>δ</td>
<td>chemical shift</td>
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<tr>
<td>υ</td>
<td>frequency</td>
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<tr>
<td>σ</td>
<td>standard deviation</td>
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<tr>
<td>atm.</td>
<td>atmospheres (pressure)</td>
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<td>br</td>
<td>broad</td>
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<tr>
<td>Bu</td>
<td>butyl</td>
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<tr>
<td>CHO</td>
<td>cyclohexene oxide</td>
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<tr>
<td>$C_p$</td>
<td>heat capacity</td>
</tr>
<tr>
<td>DGEBA</td>
<td>diglycidylether of bisphenol-A</td>
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<tr>
<td>DSC</td>
<td>dynamic scanning calorimetry</td>
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<tr>
<td>DSSSC</td>
<td>dye sensitized solar cell</td>
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<td>Et</td>
<td>ethyl</td>
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<td>GPC</td>
<td>gel permeation chromatography</td>
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<td>h</td>
<td>hours</td>
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<tr>
<td>HR-TEM</td>
<td>high resolution transmission electron microscopy</td>
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<tr>
<td>HPA</td>
<td>hexylphosphonic acid</td>
</tr>
<tr>
<td>IR</td>
<td>infra-red</td>
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<tr>
<td>LDH</td>
<td>layered double hydroxide</td>
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<tr>
<td>LED</td>
<td>light emitting diode</td>
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<tr>
<td>LFM</td>
<td>laser flash method</td>
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<tr>
<td>LHZA</td>
<td>layered hydroxide zinc acetate</td>
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<tr>
<td>m</td>
<td>multiplet</td>
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<tr>
<td>Me</td>
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<tr>
<td>MALDI-ToF</td>
<td>matrix-assisted laser desorption ionisation time-of-flight</td>
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<tr>
<td>$M_n$</td>
<td>number averaged molecular weight</td>
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<td>mol%</td>
<td>molar percentage</td>
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<td>Definition</td>
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<tr>
<td>$M_w$</td>
<td>weight averaged molecular weight</td>
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<td>carboxylate</td>
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<tr>
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<td>polydispersity index</td>
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<tr>
<td>PGSE</td>
<td>pulsed gradient spin echo</td>
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<tr>
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<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
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<tr>
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<td>propylene oxide</td>
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<tr>
<td>PPC</td>
<td>poly(propylene carbonate)</td>
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<td>parts per million</td>
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<tr>
<td>py</td>
<td>pyridine</td>
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<td>quartet</td>
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<td>RH</td>
<td>relative humidity</td>
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<td>rpm</td>
<td>revolutions per minute</td>
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<td>s</td>
<td>seconds, singlet</td>
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<tr>
<td>SA</td>
<td>stearate</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<td>sharp</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
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<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
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<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TOF</td>
<td>turn-over frequency</td>
</tr>
<tr>
<td>TON</td>
<td>turn-over number</td>
</tr>
<tr>
<td>TOPO</td>
<td>tri-octylphosphine oxide</td>
</tr>
<tr>
<td>UV</td>
<td>ultra violet</td>
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<tr>
<td>UV-vis</td>
<td>ultra violet-visible</td>
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<tr>
<td>vol%</td>
<td>percent by volume</td>
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<tr>
<td>w</td>
<td>weak</td>
</tr>
<tr>
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<td>percent by weight</td>
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<td>XRD</td>
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Chapter 1

Introduction

1.1 Project Motivation

1.1.1 Introduction to nanotechnology

The term “nanotechnology”, first used by Taniguchi in 1974,\textsuperscript{[1, 2]} refers to the development and study of materials with at least one dimension on the order of 1 - 100 nm. Nanotechnology is a rapidly growing and diverse field that impacts many areas of science and engineering, and has the potential to revolutionise a vast array of technologies, from power generation and electronics to disease detection and treatment.

The human use of nanoscale materials is not new: for example, colloidal gold has been deliberately studied for over a century,\textsuperscript{[3]} and has been applied in medical treatments since the late 1940s,\textsuperscript{[4]} but examples of its use as a pigment for glass and ceramics date back as far as the Roman era, such as in the Lycurgus Cup.\textsuperscript{[5]} Many of the ideas and possibilities for miniaturization to the atomic and nanoscale were famously outlined by Richard Feynman in his 1959 lecture “There’s Plenty of Room at the Bottom”;\textsuperscript{[6]} however, the most significant surge in nanomaterials research has occurred only in the last twenty-five years, driven by vast improvements in scientists’ ability to image and manipulate matter on the atomic scale, and by the realisation of the unique, size-dependent properties of materials on length scales of a few nanometers.\textsuperscript{[2, 3, 7]} As a result, the great promise of nanotechnology lies in the possibility of tuning macroscopic materials properties through the deliberate design of nanoscopic structures.

Two main factors control the size-dependent properties of nanoparticles.\textsuperscript{[8]} Firstly, the surface-area-to-volume ratio of a material is greatly increased with a decrease in particle
Figure 1.1 (a) Illustration of the change in surface area (A) to volume (V) ratio on decreasing particle size (based on Reference [9]) and (b) the decrease in proportion of surface atoms on increasing particle size (redrawn from Rogers et al.).

(size (Figure 1.1 (a)) and, correspondingly, the proportion of atoms residing at the surface increases as the total number of atoms decreases (Figure 1.1 (b)). The increase in the number of coordinatively unsaturated surface atoms is responsible for the enhanced catalytic activity of many nanoparticles compared with the equivalent volume of bulk solid. In addition, with an increase in surface area there is a corresponding increase in surface energy, which has been known to result in a change in lattice constants and crystal structures, as well as the depression of physical properties such as melting temperature.\[^2, 8, 10\] Secondly, when a particle is reduced to dimensions on the order of a few wavelengths of a free electron, quantum confinement is achieved: the density of electronic states within the particle becomes discrete at the edges of the band structure (Figure 1.2) and the separation between energy levels increases, which manifests as an increase in the bandgap, $E_g$, of semiconducting materials with decreasing size.\[^11\] The blue-shift in the absorption and emission wavelengths associated with the increase in $E_g$ has been applied in producing tuneable, coloured phosphors for light emitting diode (LED) technology.\[^12, 13\]
1.1.2 Nanocomposites and the importance of dispersion

One application of inorganic nanomaterials that has attracted increasing interest over the last 20 years is their use as filler materials in polymer nanocomposites.\cite{14} Conventional composites have a long history and fulfil an important role in engineering applications, either improving the properties of low cost polymers to match those of more expensive materials, or generating materials with otherwise unobtainable properties.\cite{15, 16} Many examples of micro- and nanocomposites are found in nature, such as bone, spider’s silk, and nacre, and much research activity has been inspired by studying - and attempting to emulate - these structures.

Compared to conventional micro- and macrocomposites (such as polymer-fibre composites), the use of nanoscale fillers has several advantages. Firstly, the unique properties of nanoscale materials give access to a wider range of potential composite properties and applications; in particular, the discovery of carbon nanotubes - with very high modulus, strength, and electrical properties at extremely low density - has led to great hopes for the production of a new generation of high performance materials.\cite{17} Secondly, the reinforcement properties of a filler improves with reduced dimensions, as the number of critical defects decreases with decreasing particle size.\cite{18} Importantly, the high surface-area-to-volume ratio of nanofillers results in an increase in interfacial area, which can cause changes in composite properties at much lower filler content than required for the equivalent microcomposite.\cite{19-21}

The interaction between the matrix and a particle surface results in a volume of interfacial polymer (interphase) with altered chain dynamics compared to that of the bulk; the
nature of the change in the behaviour of the interphase relative to the bulk depends on whether the interaction is favourable or unfavourable.\textsuperscript{[22]} The distance that the interphase extends away from the particle surface is approximately independent of particle size and is on the order of the radius of gyration of the polymer (3-30 nm); therefore, as the particle size decreases, the relative proportion of the polymer that resides in the interphase increases, and the interfacial volume surrounding an individual particle can be larger than the particle itself. Winey \textit{et al.} estimate that the percentage of interfacial polymer in a composite can increase 50-fold on decreasing the size of the filler by only one order of magnitude, with a negligible quantity of interphase formed for an equivalent volume of microfiller.\textsuperscript{[16]} When the filler loading is sufficiently high to allow the interfacial volumes on neighbouring particles to overlap, the matrix can essentially entirely consist of interfacial polymer, resulting in a composite with very different macroscopic properties to those of the pure polymer. Typically, nanocomposite properties can change at loadings as low as 5 volume percent (vol%), compared with 20-40 vol% for a comparable change in the equivalent microcomposite.\textsuperscript{[23]} The resulting benefits of such low filler loadings - aside from low cost - include greater retention of polymer transparency, processibility, and toughness compared with microcomposites.\textsuperscript{[24]}

The implication of the formation of the interphase is that, for the majority of materials, in order to optimise the bulk property enhancements the dispersion of the nanofillers must be maximised. Notable exceptions include applications where ordered arrays of particles are required, for example for iridescent or dichroic composites.\textsuperscript{[15, 25]} Unfortunately nanocomposites have widely been found to underperform due to the tendency of the filler particles to minimise surface energy by forming agglomerates.\textsuperscript{[26, 27]} Consequently, significant research effort is being invested in developing production methods to overcome or avoid filler aggregation.

\subsection*{1.1.3 Methods for nanocomposite fabrication}

Conventional nanocomposite fabrication techniques, including melt-blending and solution blending, are classified as \textit{ex situ} routes, as they involve simply mixing pre-prepared particles into the polymer (Figure 1.3 (a)). These routes are still by far the most widely used as they are the most facile and can easily be adapted to any nanoparticle/polymer combination. In addition, they offer the greatest control over particle quality as any nanoparticle fabrication method can be used and refinement steps can be carried out, such as
Figure 1.3 Illustration of nanocomposite synthetic methods.

size-selective precipitation and high temperature annealing. However, \textit{ex situ} routes are the most prone to issues of filler agglomeration, as aggregates tend to form on isolation and drying of the nanoparticle powders (prior to composite synthesis), and require large (often unachievable) amounts of energy to separate; the situation is enhanced for 1-D (tubes) and 2-D (platelet) structures where lines or areas of contact are formed, respectively. Poor polymer-particle compatibility and, subsequently, poor wetting can further hinder particle dispersion.

The most common approach to improve particle dispersion is to modify the particle surfaces with organic molecules, the benefits of which are two-fold: primarily, the surfactants act as a thermodynamic barrier to aggregation, as the free energy of the surface groups sharply increases as particles approach each other; secondly, the surface groups can be tailored to improve the compatibility of the surfaces with the polymer, minimising phase segregation.\cite{28} A common example is the functionalisation of silica and metal oxide particles with silane groups to create hydrophobic particle surfaces.\cite{22,29-31} Compatibility can be further improved by functionalising the nanoparticle surfaces with organic groups that are capable of bonding covalently to the matrix, a strategy often used in conventional fibre composites to maximise load transfer.\cite{21} Particles can also be functionalised with groups capable of initiating or taking part in polymerisation (e.g. halides or olefins) in order to
generate “hairy” particles by a “grafting-from” approach; in this way, particles can be functionalised with the same polymer as the bulk matrix.[32] The disadvantages of this approach are that complete particle separation prior to functionalisation is required and, particularly for polymer-functionalised particles, incomplete wetting can still occur once dispersed in the matrix.[32]

Other efforts have focused on improving the composite fabrication method, including the use of high-shear mixing, and the use of non-surfactant additives. Recently, exfoliated zirconium phosphate nanosheets were used to disperse uncapped zinc oxide nanoparticles in epoxy,[33] it was proposed that the presence of the platelets improved the solubility of the particles by changing the polarisation of the epoxy resin. The loadings of the particles within the polymer were, however, very low (0.2 - 0.4 vol%; 1 - 2 wt%), therefore it is uncertain how effective the method would be for higher nanoparticle loadings.

An alternative approach is to synthesise the particles in situ, directly within the polymer or pre-polymer (Figure 1.3 (b)). In situ methods intrinsically generate better particle dispersions as the small molecule precursors are easily and homogeneously dispersed prior to nanoparticle synthesis. The use of surface ligands is still beneficial for in situ routes as, in the absence of surface groups, the generated dispersions are only kinetically stable.[15] Organic-inorganic hybrids based on mixtures of extended silica networks embedded in cross-linking polymers have been synthesised via in situ sol-gel routes since the 1980’s, commonly using the hydrolysis of precursors such as tetraethoxysilane to generate the silica network.[34] Subsequent in situ routes to composites containing individual nanoparticles have also been primarily based on sol-gel synthesis. To date, surface-modification methods have largely relied on pendant functionality attached to the polymer backbone. For example, epoxy resin/TiO₂ nanocomposites have been prepared by cross-linking an epoxy pre-polymer with a trimethoxysilane-functionalised amine curing agent, and growing TiO₂ from the silane groups via the hydrolysis of Ti(O"Bu)₄;[35] ZnO/poly(methylmethacrylate) (PMMA) composites have been synthesised in which the PMMA binds to the ZnO through carboxylate groups, introduced either by incorporating zinc acrylate as a secondary monomer during polymerisation,[36] or by hydrolysing a small proportion of the methacrylate groups during the nanoparticle synthesis.[37]

Despite the great advantage of improved particle dispersion, the main drawback of in situ preparation is that the choice of nanoparticle synthesis method is limited to those that are compatible with the matrix: although physical synthesis routes to nanoparticles, such as
chemical vapour deposition and pulsed-laser deposition\cite{38} yield particles of high crystallinity and purity, they require high temperatures that are incompatible with organic components (often 800 °C and above)\cite{39}. In situ routes are therefore restricted to low temperature solution routes, many of which suffer the additional problem that they generate undesirable by-products\cite{15}. The bulk properties of the composite also strongly rely on the particle quality that can be achieved via the single, in situ synthetic step, as extra refinements are not possible. Therefore, in order to become widely viable, the challenge remains to develop in situ methods that provide the same level of particle control, matrix compatibility, and nanoparticle purity as ex situ routes.

1.1.4 Metal oxide nanomaterials

Among the materials investigated on the nanoscale, metal oxides have attracted a great deal of attention as they represent one of the most versatile and diverse classes of materials with regards to the range of obtainable crystal structures, metal oxidation states, and magnetic and electronic properties\cite{40,41}. Many metal oxides have more than one accessible polymorph, the relative stabilities of which may change on the nanoscale in response to the increase in surface energy\cite{10}. In the bulk, metal oxides are ubiquitous in industrial catalytic processes and electronics applications; on the nanoscale, further potential applications include gas sensing and magnetic storage, among others.

Zinc oxide in particular has been widely investigated as it is a semiconductor in the bulk, with a wide direct band gap of 3.30 eV at 300 K\cite{42}, and an exciton binding energy of 60 meV, leading to applications in ultra-violet (UV) LEDs, UV lasers\cite{43,44}, electro- and photoluminescence devices, and varistors\cite{45}. The sensitivity of the electrical conductivity of ZnO towards UV light and surface-adsorbed molecules makes it an excellent sensor\cite{46}. It is biocompatible and, accordingly, has found applications in the medical and cosmetic industries due to its UV-absorbing properties.

Although two cubic forms of ZnO are known (rock salt and zinc blende structures; Figure 1.4 (a) and (b)), the hexagonal wurtzite structure is the thermodynamically most stable form (Figure 1.4 (c)). Wurtzite is inherently anisotropic, which has allowed the facile fabrication of a variety of anisotropic nanostructures such as rods\cite{47}, rings\cite{48}, spirals\cite{49}, and pyramidal shapes\cite{50}. The crystal anisotropy also gives rise to piezoelectric behaviour, which has been exploited in composite fibres for low-frequency power generation fabrics\cite{51}.
Figure 1.4 Unit cells for the known crystal structures of ZnO: (a) the face-centred cubic (rock-salt) structure; (b) zinc blende; (c) wurtzite structure (right) and how it extends in hexagonal close-packing (left). The rock-salt structure is stable at elevated temperatures, whilst the zinc blende structure is only stable if ZnO is grown on other cubic templates. Lattice parameters taken from Özgur et al.\cite{42} (rock salt and zinc blende lattice parameters rounded to an average of the range reported).

Nanoscale ZnO has also been investigated for its luminescence properties. ZnO commonly exhibits a visible green fluorescence, which is believed to be due to the presence of surface defects such as oxygen vacancies and interstitial zinc(II) ions.\cite{52} There have been reports of changes in emission colour via surface modification;\cite{53} recently, ZnO nanoparticles with tuneable emission were synthesised via the encapsulation of particles of varying sizes in silica (core-shell particles).\cite{54}

A key application of ZnO is in photovoltaic devices. Metal oxide electrodes are commonly used in solid state solar cells, as well as in dye-sensitized solar cells (DSSCs).\cite{55} Due to its high conductivity and transparency in the visible region of the solar radiation spectrum, bulk ZnO has been investigated for thin-film applications and nanoparticulate ZnO has been used in both DSSCs (as an alternative to TiO$_2$) and ZnO/conjugated polymer hybrids to make bulk heterojunction photovoltaics.\cite{56,57}
1.1.5 Project aims

The focus of this project was to develop a clean, mild method for synthesising ZnO nanoparticles that could be adapted for in situ nanocomposite fabrication. Prior work by A. González-Campo et al. (Imperial College London) demonstrated that the facile fabrication of ZnO/epoxy nanocomposites could be achieved via the hydrolysis of diethylzinc (Figure 1.5 (a)). Relatively high loadings of ZnO in epoxy resin were achieved (up to 40 wt%, 12 vol%) with only a minimal reduction in the resin’s processibility (minimal increase in the resin viscosity prior to curing; Figure 1.5 (b)). The composites were homogeneous dispersions of secondary particles - small aggregates up to 100 nm in diameter (Figure 1.5 (c)). The low incidence of individual nanoparticles and the only modest improvements in bulk properties (thermal conductivity) were attributed to the poor particle-polymer interactions, both in terms of solubility and load transfer (phonon conduction).

The work contained in this thesis builds upon the work by González-Campo et al., with the specific aim of introducing organic groups to the ZnO particle surfaces, whilst still maintaining the “one-pot” nature of the synthesis. While many routes exist to introduce capping agents to nanoparticles, a key objective in making the method compatible with in situ synthesis was for capping to occur in one step, and for the organic ligands to be introduced in substoichiometric quantities to avoid the need for nanoparticle purification. It was envisaged that controlled capping of the particles could be achieved by introducing a second, heteroleptic organometallic zinc precursor, possessing one hydrolysable alkyl group and one non-hydrolysable ligand to act as the capping agent (Figure 1.6).

In the following sections, the hydrolysis of organometallic complexes will be reviewed in the context of the available metal oxide synthesis routes, and the choice of suitable zinc heteroleptic precursor compounds will be discussed. Finally, an overview of the scope of the thesis will be given.
Figure 1.5  (a) Reaction scheme for *in situ* synthesis of ZnO nanoparticles in epoxy resin; (b) change in viscosity on increasing nano-ZnO loading; (c) TEM image of nanoparticle dispersion of *in situ* prepared in epoxy resin; Courtesy of A. González-Campo.\(^{[58]}\)

Figure 1.6 Concept for one-step capping of ZnO nanoparticles using a combination of homoleptic and heteroleptic zinc precursors.
1.2 Solution Routes to Metal Oxide Nanoparticles

1.2.1 Overview of current approaches

Collectively, chemical (solution) routes to metal oxide nanoparticles are often referred to as “sol-gel”, as they are derived from the process of making expanded metal hydroxide and oxide gels from aqueous colloidal solutions of metal salts (“sols”). In the sol-gel process, a series of reactions take place which can be generalised as:

- **Hydrolysis:**

  \[
  H_2O + M-OR \xrightarrow{H} H:\xrightarrow{M-OR} HO-M\xrightarrow{O} HO-M + ROH
  \]

- **Alcoxolation:**

  \[
  M-OH + M-OR \xrightarrow{M} M:\xrightarrow{O} MO-M\xrightarrow{R} M-O-M + ROH
  \]

- **Oxolation:**

  \[
  M-OH + M-OH \xrightarrow{M} M:\xrightarrow{O} MO-M\xrightarrow{H} M-O-M + H_2O
  \]

Metal oxide nanoparticles can be prepared by calcination of the gel or precipitated metal hydroxide, however drying of the gel is a delicate procedure and control over the particle size and quality is difficult.

The vast majority of current methods are more accurately described as homogeneous precipitation routes, as the nanoparticles are formed directly from the reaction solution. These routes can be broadly categorised as: (1) basic hydrolysis, (2) non-aqueous thermolysis, and (3) organometallic hydrolysis. Additional variants have been investigated, including oxidation of metal nanoparticles, and preparations in microemulsions but these are not reviewed here.

The majority of the basic hydrolysis routes to ZnO nanoparticle synthesis are based on the method of Spanhel and Anderson, utilising the hydrolysis of zinc salts by alkaline hydroxides in an alcoholic medium. In the original method, zinc acetate dihydrate was first heated to 80 °C in ethanol, and then hydrolysed by addition of lithium hydroxide. Extensive study of the system found that several “magic sized” zinc o xoacetate complexes formed in the precursor solution prior to hydrolysis and acted as templates for the growing ZnO nuclei (Figure 1.7). To avoid the use of alkaline metals, which have been shown to
Figure 1.7 (a) Formation of “magic sized” zinc oxoacetate complexes during ZnO nanoparticle synthesis via hydrolysis of zinc acetate dihydrate in ethanol; (b) Schematic of the various zinc oxoacetate clusters. Image taken from Reference [61] © Copyright Springer Science + Business Media, LLC 2006.

adversely affect ZnO nanoparticle growth and optical properties, variations of the method have used alternative sources of hydroxide, such as tetrabutylammonium hydroxide, or in situ hydroxide generation via the deprotonation of water by methylhydrazine.

Basic hydrolysis routes have been successfully employed to prepare nanocomposites of ZnO and thermoplastic polymers, such as poly(acrylate). However, the route has the disadvantage that it generates salt by-products which need to be washed from the final composite. In addition, the use of reactive bases renders the method incompatible with sensitive matrices such as epoxy resin: the epoxide rings are prematurely opened by the base itself or by in situ generated alkoxide groups, preventing curing.

Non-aqueous thermolysis routes to metal oxides are analogous to those developed for metal chalcogenides, such as CdS and CdSe. The category encompasses both thermal decomposition of single-source, organometallic precursors through continuous heating, and hot injection syntheses, whereby the precursor is decomposed by being rapidly injected into
hot surfactant or coordinating solvent. As the syntheses are conducted in a dry, inert atmosphere, either the solvent or the organic ligands of the precursor must act as the oxygen source. For example, when [EtZn(O^iPr)] is heated to 200 °C in neat tri-octylphosphine oxide (TOPO), it decomposes to give TOPO-capped ZnO, ethane, and butane (determined by gas chromatography). Garnweitner and Niederberger developed a general route for metal oxide nanoparticle synthesis, via the thermolysis of metal salts in neat benzyl alcohol at 200 °C, when metal chlorides are used, the sole source of oxygen is the benzyl alcohol solvent. In a further example, 3 nm ZnO nanoparticles with narrow size distribution were generated by the rapid injection of a mixture of diethylzinc and oxygenated hexadecylamine into neat TOPO at 200 °C. The reaction of dialkylzincs with oxygen alone results in an amorphous product at room temperature, therefore elevated temperatures are required to form the crystalline oxide. The size of the particles was increased by multiple injections of the oxygenated-ZnEt_2 precursor at 200 °C, but the size distribution of the particles also increased.

The benefits of the moderate temperature routes include the fact that growth is temperature-dependent and can be quenched by cooling the reaction. In addition, highly crystalline particles with few defects are produced, as annealing occurs at the reaction temperature. However, the reactions are designed to cause the decomposition of carbon-oxygen bonds, therefore the temperatures used are not expected to be compatible with the in situ synthesis of particles within sensitive polymeric matrices - especially those containing carbon-oxygen bonds.

The hydrolysis of organometallic zinc complexes lies between the extremes of the basic hydrolysis and non-aqueous routes by introducing controlled (stoichiometric) amounts of water to an otherwise dry system. The method exploits the high reactivity of the metal precursor complexes to water and, as the hydrolysis reaction is highly exothermic, crystalline ZnO can be achieved at ambient conditions. By using alkylmetal or metal alkoxide precursors, the reaction can be very clean, generating only volatile by-products.

### 1.2.2 Organometallic hydrolysis

The hydrolysis of organometallic precursors has no doubt been accidentally carried out for many years, but deliberate hydrolysis and investigation of the products has only begun recently. A large body of work has been carried out by the group of Chaudret, applying the concept to the synthesis of Fe(II)O from [Fe{N(SiMe_3)_2}]_2, and ZnO from dicyclohexylzinc, [ZnCy_2], the latter was achieved by exposing solutions of
[ZnCy₂] and alkylamine surfactants to atmospheric moisture over a period of 4 days. A similar route has also been explored using the hydrolysis of a solution of [Zn(NiBu₂)₂]₂ and hexylamine in diethyl ether under moist air flow, yielding organic-capped ZnO nanoparticles in 2 - 4 days. Other researchers have used alkylzinc alkoxides, [RZn(OR')]₂, as precursors, often decomposed via the rapid hydrolysis of the precursor solutions with dilute mixtures of water, for example in tetrahydrofuran or methylimidazole. The analogous synthesis of ZnS by reaction of ZnEt₂ with a saturated solution of H₂S in toluene has also been reported.

Aside from the reactivity with protic sources, alkylzinc precursors are relatively inert towards a wide range of polymer matrices, including epoxy resins, allowing for general compatibility of the method. A few examples have been reported for the in situ synthesis of ZnO from ZnEt₂ in thin films of ethylene-vinyl acetate copolymers (EVA), polyphenylene vinylene (PPV) and poly(3-hexylthiophene) (P3HT).

The detailed mechanism and the identities of the intermediates involved in the hydrolysis reaction are currently unclear, however a proposed route for the hydrolysis of ZnEt₂ is shown in Figure 1.8. Ethylzinc hydroxide (EtZnOH) has been shown to be the product of the reaction between ZnEt₂ and water, and it is believed that colloids of EtZnOH act as the nucleating species for ZnO; EtZnOH colloids form a yellow solution which is observed immediately prior to nanoparticle formation.

![Figure 1.8 Proposed mechanism of diethylzinc hydrolysis, based on Kuran and Czernecka](image-url)
Lizandara-Pueyo \textit{et al.} recently studied the hydrolysis of methylzinc tert-butoxide, [MeZn(ÔBu)]₄, using \(^1\)H NMR spectroscopy.\cite{86} Based on \(pK_a\) arguments, and due to the history of alkylzinc reagents as alkylating agents, it was expected that the alkyl group would be hydrolysed prior to the alkoxide group; however, the reverse was found. An unidentified, transient methyl group resonance was observed, and assigned to a methyl-zinc intermediate (Figure 1.9); it is possible that the methyl-zinc intermediate was methylzinc hydroxide (MeZnOH). The ethyl group of ethylzinc alkoxides has previously been reported to be much less reactive than the ethyl groups of diethylzinc,\cite{93} as evidenced by the very slow alcoholysis of [EtZn(OR)] species. This lowered reactivity may go some way to explain the order of ligand hydrolysis observed by Lizandara-Pueyo \textit{et al.}. The proposed mechanism is also consistent with the observed decrease in reactivity of the derivatives prepared with tertiary alkoxides compared with primary alkoxides.\cite{86} Both of the mechanisms (Figures 1.8 and 1.9) propose an alkylzinc hydroxide tetramer (with a cubic structure) as the nucleating species, suggesting that the nucleation mechanism is essentially the same independent of the organometallic zinc precursor.

For this project, the proposed introduction of a non-hydrolysable ligand onto the zinc precursor was expected to act to block certain growth sites. The cubes in Figures 1.8 and 1.9 can condense in three dimensions (along all edges and faces). By introducing small amounts of non-hydrolysable ligand, some edges would be blocked, terminating growth along that edge or face. In an ideal mechanism, multiple growth termination events would define the edges and therefore, ultimately, the surfaces of the nanoparticle. If the particle synthesis could be manipulated such that the particles always grew to the appropriate size to achieve full surface coverage, then it is envisaged that the size of the particles could be dictated by the quantity of ligand: a lower quantity of ligand would give rise to a lower total surface area per mole of particles, corresponding to bigger particles.
1.3 Nanoparticle Surface-Modification

1.3.1 The role of ligands in nanoparticle growth

A variety of organic ligands have been previously used to functionalise metal oxide nanoparticle surfaces. Examples of dynamic ligands include phosphine oxides (such as TOPO), amines, alcohols, and carboxylic acids. Alternative surface modifiers include physisorbed surfactants such as polymers, and covalently bound ligands such as silanes and phosphonates.\[28]\n
Dynamic ligands or adsorbed polymers are almost always used during nanoparticle synthesis to prevent aggregation, but, by dynamically binding to the growing nanoparticle surfaces, they also act to moderate growth and can be used to generate anisotropic particles. For example, the wurtzite crystal structure has polar, hexagonal ±(0001) faces and non-polar sides of the form \{0110\}; these faces differ in the magnitude of their surface energy and, therefore, grow at different rates. The three fastest growth directions are shown in Figure 1.10; the polar ±(0001) faces are the highest energy and therefore are the fastest growth planes.

Under slow growth conditions, nanoparticles tend towards structures that minimise the total surface energy, often forming spherical or nearly spherical shapes;\[94]\ however, at high precursor concentrations or in the presence of surfactants the differences in the relative growth rates become important. At high concentrations, growth is very rapid and favoured at the highest energy face. Surfactants may preferentially bind to certain faces over others, enhancing or altering the difference in the relative growth rates.

Manna et al. showed that, for CdSe (also wurtzite structure), the use of mixtures of TOPO and hexylphosphoric acid could enhance the growth rate of (000\(\bar{1}\)) relative to the other faces such that rods were preferentially formed.\[94]\ By adding further precursor to the solution after the initial injection of precursors, the rods could be elongated, indicating that growth was unidirectional and sustainable. By allowing additional, slow growth of the particles, the high energy (fastest growing) surfaces were gradually replaced by the lower energy (slow growing) faces, giving shapes such as arrows and pine trees (Figure 1.11).

Chaudret et al. found that, in the slow hydrolysis of [ZnCy\(_2\)], the presence of alkylamines also yielded nanorods.\[76]\ The aspect ratio of the rods increased with increasing alkyl-chain length (Figure 1.12), which is likely to be related to the efficiency of transport of
Figure 1.10 The three fastest growth directions of ZnO: (a) [0001] (from the (0001) plane); (b) [0110] (from the [0110] plane); (c) [2110] direction.

ions through the layer of surfactant: the longer the chain, the greater the reduction in growth rate along each of the fastest growth directions and, consequently, the greater the enhancement of the relative rate of growth along the [0001] direction.

In contrast, nanodisks and nanorings have been achieved by using poly(acrylamide) to selectively bind to the (0001) surfaces, allowing for enhanced growth outwards from the centre. The rings represent a later stage in the growth where the zinc ions in the centre of the disks - the region with the highest defect density - dissolve and transfer to the growing edges.

Different combinations of ligand can also affect the micro- and macroscopic behaviour of the nanoparticles. For example, amphiphilic polymers have been used to induce nanoparticle solubility in both polar and non-polar solvents, and the use of combinations of amines and carboxylic acids has been reported to lead to electrostatically-driven 3-D self-assembly of ZnO nanoparticles, through the formation of a charged ligand bilayer at the particle surfaces.
Figure 1.11 Transmission electron microscopy images of CdSe nanoparticles synthesised by injection of organometallic precursors into hot TOPO/HPA mixtures: (a) to (c) effect of increasing the ratio of HPA:TOPO (8, 20, and 60 %, respectively); (d) to (e) elongation of the nanoparticles by multiple injections of precursor; (g) to (i) demonstrating the formation of pine trees by aging to replace high energy surfaces. Scale bar refers only to images (a) to (e). Images taken from Manna et al.[94] © Copyright American Chemical Society 2000.
Figure 1.12 Transmission electron microscopy images of ZnO nanoparticles synthesised by hydrolysis of ZnCy\textsubscript{2} in neat amine: (a) hexadecylamine; (b) dodecylamine; (c) octylamine. Images taken from Kahn et al.\textsuperscript{[76]} © Copyright WILEY-VCH Verlag GmbH &Co. KGA, Weinheim 2005.

1.3.2 Choice of surface modifier

The main aim of the project was to develop a method of introducing ligands to the nanoparticle surfaces in one step. While many preparation methods introduce surfactants during the synthesis, in the vast majority of examples they are present in great excess. In the case of dynamic ligands the excess is required precisely because the ligands are dynamic - the ligands continuously exchange between the bound and free states such that, in dilute solutions, the surfaces may be sufficiently unprotected to allow aggregation to occur. The presence of excesses of ligands or reactive small molecules is undesirable for in situ nanocomposite preparation; for epoxy resin systems in particular - which are commonly cured by amines - an excess of amine in the resin would affect the cross-linking density and therefore the mechanical properties of the final composite.\textsuperscript{[96]} More strongly bound ligands do not require such an excess - for example, thiols have been used to fully quench ZnO growth in alcoholic solution in microlitre quantities (sufficient for one monolayer of thiol per particle).\textsuperscript{[97]}
It was reasoned that, by using an additional heteroleptic zinc precursor with a non-hydrolysable ligand, the capping agent could be introduced in substoichiometric quantities; the Zn-ligand bonds would be conserved and therefore result in full surface-coverage without the need for excess surfactant. Bound carboxylate groups (rather than free carboxylic acids) were considered a good choice of ligand as, in a non-aqueous environment, the free carboxylate (charged species) is not expected to be favourable, and dissociation will not occur. From estimates of $pK_a$, exchange of a proton between zinc-bound water and the zinc-bound carboxylate to give the free carboxylic acid should also be unfavourable: the $pK_a$ of a typical carboxylic acid is around 5 whereas that of zinc-bound water is around $7^{[98, 99]}$, for comparison, the $pK_a$ of an alcohol is approximately 15,$^{[100]}$ which is consistent with the observation that Zn-OR groups are readily hydrolysed. As such, although some dynamic behaviour is expected due to the bridging nature of carboxylate ligands, the carboxylate group is expected to remain strongly bound to the zinc during synthesis, and the heteroleptic precursor was, therefore, chosen to be an alkylzinc carboxylate.

1.4 Summary

The facile preparation of well-dispersed nanoparticles within a polymer matrix still remains a challenge, but is considered to be key to achieving the theoretically optimum reinforcement properties of nanocomposites. Both in situ nanoparticle synthesis and surface-modification have been shown to improve the homogeneity of nanocomposites; this thesis aims to develop a method which utilises both of these principles. Organometallic hydrolysis is a clean, low temperature method for generating metal oxide nanoparticles which is ideally suited for in situ synthesis within a range of polymer resins, including sensitive thermosetting polymers.

The proposed method of ZnO nanoparticle synthesis is illustrated in Figure 1.13. By using a substoichiometric amount of surface capping ligand, introduced via an ethylzinc carboxylate precursor, nanoparticle surface-modification can be achieved without the need for excess reagents.
1.5 Scope of the Thesis

This thesis encompasses the development of in situ ZnO nanocomposite synthesis from the molecular to the macroscopic level.

In Chapter 2, the nature of the ZnO nanoparticle precursor solution is explored with respect to the structure and behaviour of the aliphatic ethylzinc carboxylate species. Although ethylzinc carboxylates as reagents have been reported in the literature, they have not previously been extensively studied in their own right. Crystal structures and solution studies for these species are presented, exploring the sensitivity of the structures and nuclearity of the complexes to the reaction solvent. In addition, zinc carboxylate motifs are common in catalysts for polymer synthesis; therefore, preliminary studies were also carried out into the activity of ethylzinc carboxylates for the copolymerisation of CO₂ and epoxides, with a view to low cost polymer production. High or moderate catalytic activity of these complexes for the copolymerisation could potentially lead to future production of ZnO/poly(alkylene carbonate) composites via polymerisation and ZnO nanoparticle synthesis from a common precursor mixture.

In Chapter 3, the nanoparticle synthesis itself is presented. The effect of varying certain reaction parameters on the size and shape of the particles is investigated and the implications of the observed formation of unexpected impurities are discussed.

Finally, in Chapter 4, the application of the method to in situ ZnO/epoxy resin nanocomposite synthesis is demonstrated and the nature of the interfacial interaction is investigated for uncapped particles and for two types of surface carboxylate groups.
Composites were also prepared using mixtures of uncapped *in situ* ZnO nanoparticles and *ex situ* ZnO microparticles, to investigate the extension of the method to the preparation of hierarchical structures.
Chapter 2

The Synthesis and Characterisation of a Series of Ethylzinc Carboxylates

2.1 Introduction to Alkylzinc carboxylates

2.1.1 Synthesis and characterisation to date

Organozinc compounds were one of the earliest classes of organometallic compounds, dating back to the discovery of diethylzinc by Frankland in 1848.\textsuperscript{[101, 102]} Subsequently, homoleptic and heteroleptic alkylzinc species (RZnX, where X = halide, alkoxide, amine, amide, aryloxide etc) have become established as useful reagents in organic synthesis, notably in Negishi cross-coupling reactions and addition reactions with carbonyl compounds.\textsuperscript{[103-108]}

Dialkylzincs (ZnMe\textsubscript{2}, ZnEt\textsubscript{2}, EtZnMe, etc.) exist as monomers in solution, whereas diphenylzinc can form dimers via bridging phenyl groups.\textsuperscript{[109, 110]} In contrast, heteroleptic organozinc compounds can access a variety of structures. For example, alkylzinc alkoxides can form dimers ([RZn(\mu-OR')]\textsubscript{2}), tetramers ([RZn(\mu\textsubscript{3}-OR')]\textsubscript{4} “cubes”), and heptamer complexes ([Zn\textsubscript{7}(\mu\textsubscript{3}-OR')\textsubscript{8}(R)\textsubscript{6}]), depending on the nature of the ligand (steric bulk), the alcohol to ZnR\textsubscript{2} ratio, and the solution concentration (Figure 2.1).\textsuperscript{[82, 111, 112]} In relation to their use in ZnO nanoparticle synthesis, the nuclearity of the precursor complex has been proposed to affect the morphology of the nanoparticles, by imposing differences in the probability of alignment of the growing faces of the hydrolysed ethylzinc alkoxide precursors.\textsuperscript{[82]} This theory should, however, be considered with caution as it is based on the assumption that the nuclearity of the crystal is maintained in solution, and in the presence of coordinating ligands.
Figure 2.1 Structures observed for alkylzinc alkoxide complexes: (a) dimeric (DBP = 2,6-di-
(tert-butyl phenyl); (b) tetrameric (for the cyclic alcohols, n = 3, 4), and (c) heptameric.
(which is unlikely, *vida infra*). Additionally, in light of the mechanism proposed for the
hydrolysis of alkylzinc alkoxides in Chapter 1, the preference for a particular complex
nuclearity and structure may not be maintained after the loss of the alkoxide ligand.

The synthesis of heteroleptic alkylzinc carboxylate species, from the reaction between
equimolar amounts of dialkylzinc and carboxylic acid, has been known since the 1960s.\[113\] These species have found application as modified Smith-Simmons reagents for
cyclopropanation reactions,\[114\] and as precursors for zinc oxocarboxylates [Zn₄O(OOCR)₆]
and zinc sulfidocarboxylates, which can be used as building blocks for high porosity metal-
organic frameworks, investigated for chemical storage.\[115\] However, despite having been
synthesised and used for over 40 years, the chemistry of alkylzinc carboxylates has been
relatively little explored and, in comparison to other organozinc compounds, very little
structural information is known.

In 1965, Coates and Ridley reported the synthesis of methylzinc acetate, a compound
which was insoluble in benzene and proposed to have a polymeric structure.\[113\] Since then,
Figure 2.2 Structures of alkylzinc carboxylate species (a) dimeric ethylzinc 2,6-bis-(2,4,6-trimethylphenyl)benzoic acid;\textsuperscript{116} hexameric ring structure of ethylzinc benzoate;\textsuperscript{115} Zn atoms have been highlighted in gold, and carboxylate (O-C-O) groups highlighted in red, for clarity; original image taken from Lewinski et al.\textsuperscript{115} © Copyright WILEY-VCH Verlag GmbH &Co. KGA, Weinheim 2008; (c) cyclic tetrameric ethylzinc \( \alpha,\alpha \)-diphenylglycine;\textsuperscript{117} (d) Polymeric ethylzinc 3-mercaptopropionic acid.\textsuperscript{118}

crystal structures have been determined for a small number of aryl carboxylate derivatives: the reaction between diethylzinc and 2,6-bis-(2,4,6-trimethylphenyl)benzoic acid in dichloromethane (DCM) yielded a dimeric product of the form \([\text{EtZn}(\mu_2\text{-OOCR})_2]\) (Figure 2.2 (a));\textsuperscript{116} the equivalent reaction with benzoic acid in tetrahydrofuran yielded ethylzinc benzoate, which crystallised from DCM/hexane (76% yield) as a cyclic hexamer of the form \([\text{EtZn}(\mu_3\text{-OOC}(\text{C}_6\text{H}_5))_6]\) (Figure 2.2 (b)).\textsuperscript{115} Of the aliphatic carboxylate derivatives, several complexes have been prepared for which the carboxylate group contains a second coordinating functionality, \([\text{RZn(OOCR'X)}]\) (X = OH, NH\textsubscript{2}, SH);\textsuperscript{117-120} a variety of structures have been observed, including tetrameric rings of \([\text{RZn}(\mu_2\text{-OOCR'}(\mu_2\text{-X}))]\) units (R = Et; R’X = CPh\textsubscript{2}(NH\textsubscript{2}); Figure 2.2 (c)), more complex structures such as
and extended polymers such as \([RZn(\mu_2-OOCR'(\mu_2-X))(py)]_n\) (R = Et; R’X = (CH₂)₂SH; Figure 2.2 (d)).\(^{[118]}\) Prior to the work in this thesis, however, no crystal structures of simple aliphatic derivatives had been reported and the solution behaviour of these species had not been studied.

### 2.1.2 Solvent dependence of organometallic complexes

The effect of the reaction solvent on the structure and reactivity of organometallic reagents in general can be striking: for example, Grignard reagents become less reactive for alkyl substitution reactions as the polarity and electrophilicity of the solvent increases, due to stabilisation of the metal centre and the carbanion, respectively.\(^{[121]}\) A few examples also demonstrate that the nuclearity of complexes can be affected, yielding different cluster sizes in polar and non-polar solvents.\(^{[122, 123]}\) For the ethylzinc alkoxides, the primary effect of a coordinating solvent such as pyridine is to reduce the nuclearity of complexes from the \([EtZnOR]_4\) cubane to a \([EtZnOR(py)]_2\) dimer (solvent adduct).\(^{[82]}\) As described previously, for ethylzinc carboxylates, the presence of a second coordinating functionality pendant to the carboxylate group has resulted in extended coordination to cyclic or polymeric structures.\(^{[117, 118]}\) In the work by Coates and Ridley, methylzinc acetate became soluble in benzene on the addition of pyridine and a discrete, dimeric \([MeZn(\mu_2-OCCCH_3)(py)]_2\) species was proposed, although the molecular weight determined by cryoscopy decreased with increasing dilution.

During the course of this project, it was found that, for straight-chain alkyl carboxylates, the nature of the solvent (coordinating vs. non-coordinating) strongly affects the ligand stoichiometry of the complexes, and the strength of the donor interaction of a coordinating solvent (THF vs. pyridine) was found to affect the nuclearity of the complex’s repeat unit in the solid state.

### 2.1.3 Potential as polymerisation catalysts

Aside from nanoparticle synthesis, another area of research in which organozinc compounds have shown significant promise is as catalysts for polymer synthesis; of particular interest is their use as catalysts for the alternating copolymerisation of epoxides and CO₂ to
Scheme 1.1 The copolymerization of CO$_2$ and an epoxide (X = initiating group provided by the catalyst, such as halide or carboxylate; EG = polymer end group). Ideally y = 0 (polymer entirely alternating copolymer).

form poly(alkylene carbonates) such as poly(propylene carbonate), PPC (Scheme 1.1). PPC itself has poor mechanical strength but is a low cost polymer, making it a good candidate for reinforcement by nanofillers. Carbon dioxide is an attractive reagent for use as a monomer in polycarbonate synthesis as it is inexpensive, abundant, and sustainable, being the waste product of many chemical processes. In addition, it is non-flammable and non-toxic, making it a particularly attractive alternative to current (toxic) polycarbonate synthetic routes using carbon monoxide or phosgenes.$^{[124]}$

The copolymerisation of propylene oxide (PO) and CO$_2$ was first reported by Inoue et al. in 1969, using ZnEt$_2$/water as the catalyst mixture;$^{[125]}$ since this early discovery, many advances in activity, selectivity and polymer quality have been made, and several detailed and comprehensive reviews have been published.$^{[126-130]}$ Zinc carboxylate motifs are common amongst catalysts for this copolymerisation; many early zinc catalysts were based on mixtures of ZnEt$_2$ and di- and trihydric ligands, including dicarboxylic and hydroxycarboxylic acids,$^{[128]}$ and the most widely applied heterogeneous catalyst for the copolymerisation of PO and CO$_2$ is zinc glutarate [Zn(O$_2$C(CH$_2$)$_3$CO$_2$)$_n$.$^{[131]}$ Recently, Eberhardt et al. prepared zinc glutarate derivatives from diethylzinc, glutaric acid, and SO$_2$, which showed excellent activities.$^{[132]}$

In contrast to di-carboxylic acids (such as glutaric acid), mono-carboxylate zinc catalysts have been much less explored. An early study by Inoue et al.$^{[128]}$ showed only low activity of ZnEt$_2$/mono carboxylic acid mixtures (acetic acid, benzoic acid) towards the copolymerisation of PO and CO$_2$, in dioxane at 35 °C and 40 atmospheres of CO$_2$; however, to the author’s knowledge, detailed studies using more forcing conditions or with other epoxides have not been carried out for these catalyst systems.
2.1.4 Scope

The ultimate aim of the project was to use long-chain alkyl carboxylate derivatives as the secondary precursor for ZnO nanoparticle synthesis, as longer chains are expected to prevent aggregation and enhance the solubility of the particles more effectively than a small moiety such as acetate. However, the acetate derivative was studied as a model compound, based on the simplicity of its spectral characterisation (NMR, IR) and relative ease of crystallisation compared to long-chain derivatives.

Alkylzinc carboxylates can be prepared via several routes, most commonly by alkane elimination in the reaction of a dialkylzinc with one equivalent of the respective acid. In this work, however, a different route was favoured, utilising ligand exchange between the dialkylzinc and the zinc bis(carboxylate) (Scheme 2.2); this route minimises the introduction of small traces of water that are unavoidable with the use of free carboxylic acids. It was found that the primary product formed was the same using either route (1H NMR spectroscopy).

In this chapter, the structure and solution behaviour of the model compound “ethylzinc acetate” will be presented and discussed. The results for the formate derivative and the long-chain aliphatic carboxylate derivatives will be briefly compared, with regards to generalisation of the findings and to assess the suitability of the complexes for ZnO nanoparticle synthesis. The key results are summarised in Scheme 2.2.

Finally, the activity of the “ethylzinc acetate” complexes toward the copolymerisation of CO\(_2\) with epoxides will be presented.

![Scheme 2.2](image-url)
2.2 Characterisation Techniques

2.2.1 Common analytical techniques

The organic ligand ratio (carboxylate:ethyl) and the nuclearity of the complexes was assessed using nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, and single-crystal X-ray crystallographic analysis. X-ray crystallography was carried out by Dr A. J. P. White, Imperial College London. Elemental analysis was carried out by Mr S. Boyer, London Metropolitan University.

2.2.2 Infra-red spectroscopy

Infra-red spectroscopy (IR) is commonly used to characterise organometallic complexes, allowing identification of ligands based on the presence of characteristic vibrational frequencies of functional groups, as well as giving structural (symmetry) information based on the number of normal modes of vibration.

In the context of metal-carboxylate complexes, IR can also be used to assign the carboxylate coordination mode. The coordination modes considered are (Figure 2.3): chelating (bidentate; structure I), bridging ($\mu_2$-coordination, structure II), and multi-centre bridging ($\mu_3$-coordination, structure III). It is possible to distinguish between structures I and II by the magnitude of the difference, $\Delta$, between the asymmetric and symmetric stretches of the carboxylate group ($\nu_s$(COO) and $\nu_A$(COO) respectively): $\Delta$ values for II are greater than those for I, which are typically on the order of between 100-200 cm$^{-1}$ (II) and <100 cm$^{-1}$ (I).$^{[133]}$ There is currently insufficient data reported for complexes with $\mu_3$-coordination to determine whether it is possible to distinguish between $\mu_2$- and $\mu_3$-coordination in a similar way.

![Figure 2.3](image-url) Bridging modes of carboxylate ligands. Adapted from Reference [133].
2.2.3 Pulsed Gradient Spin Echo NMR spectroscopy

Pulsed gradient spin echo (PGSE) NMR spectroscopy is a technique that measures the translational motion of molecular species in solution, and can be used as a comparative method for assessing molecular size. During an experiment, the solution is subjected to pulsed gradients of magnetic field and the spin-echo signal detected. The spin-echo intensity of a spin-active nucleus, $I$, is related to the diffusion coefficient of the molecule by:

\[
\ln \left( \frac{I}{I_0} \right) = -\gamma^2 \delta^2 G^2 \left( \Delta - \frac{\delta}{3} \right) D
\]

where $\gamma$ is the gyromagnetic ratio, $\delta$ is the length of a gradient pulse, $G$ is the gradient strength, and $\Delta$ is the delay between gradient midpoints. The hydrodynamic radius $r$ is related to the diffusion coefficient by the Stokes-Einstein equation:

\[
D = \frac{k_B T}{6 \pi \eta r}
\]

where $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\eta$ is the solvent viscosity at the measured temperature. The molecules are assumed to be spherical due to rapid rotation in solution.

The calculated hydrodynamic radius can be compared to the radius of a molecular repeat unit determined by X-ray crystallographic analysis. In this work, PLATON software was used to determine the packing efficiency of the unit cell, which was then used to estimate the volume per molecular repeat unit. The expected radius of the repeat unit in solution was estimated from the calculated volume, assuming a spherical shape.

The values of hydrodynamic radii determined by PGSE should not be taken as an absolute measure of the size of a complex, however the technique can usefully be used to compare species with large size differences, for example, in the investigation of monomer-dimer equilibria, and to assign the nuclearity of organometallic complexes in solution.\[134,135\]

PGSE experiments for the ethylzinc carboxylate complexes, and the subsequent data processing to give two-dimensional diffusion ordered spectroscopy (DOSY) plots, were carried out by Mr. P. Haycock, Imperial College London.
2.3 Ethylzinc Acetate

2.3.1 Behaviour in Aromatic Solvents

The reaction between anhydrous zinc bis(acetate) and diethylzinc in toluene yields compound 1 as a white powder (81% yield). Crystals were obtained either directly from the reaction mixture (concentrated by slow evaporation of a saturated toluene solution) or from a saturated hexane solution at -37 °C. In both cases, X-ray crystallographic analysis showed the formation of an unusual pentanuclear structure with the molecular formula [Zn₅(OAc)₆(Et)₄]. The complex crystallised with two independent molecules (A and B) in the asymmetric unit (Figure 2.4).

The complexes contain one central, six-coordinate Zn connected to four, tetra-coordinate Zn centres via bridging acetate ligands. Each acetate group ligand adopts a \( \mu_3 \)-coordination mode, analogous to the coordination of benzoate ligands in the structure of ethylzinc benzoate reported by Lewinski et al.\(^{115} \) The complex is constructed of fused networks of four-, six- and eight-membered heterocycles (two, six, and two of each type of heterocycle, respectively).

Although pentameric zinc complexes have been observed previously, largely as motifs in extended metal-organic frameworks,\(^{116-138} \) only one other discrete complex has been reported with a similar structure to that of 1. Ullrich et al. found that [Zn₅(ONMe₂)₆(iPr)₄] has a similar central, six-coordinated Zn, and four outer Zn(iPr) units which bind to the six O-N units by either an N,O,O- or an N,N,O coordination mode.\(^{139} \) As such, the binding of the hydroxylamine ligands is equivalent to that of the acetate groups in 1.

The structure of [Zn₅(ONMe₂)₆(iPr)₄] differs from that of 1 in that it is of higher symmetry: in [Zn₅(ONMe₂)₆(iPr)₄], the two four-membered rings are related by a \( C_2 \) axis, whereas 1 is chiral-at-metal. The Zn-O bond lengths of 1 are comparable to those observed in [Zn₅(ONMe₂)₆(iPr)₄], falling within the range 1.997(2) - 2.1695(17) Å (Table A1, Appendix), but are longer than those in anhydrous zinc acetate (Zn-O bond lengths 1.949(2) - 1.965(2) Å, in the monoclinic form);\(^{140} \) the greater length of the Zn-O bonds may be related to the \( \mu_3 \)-bridging nature of the acetate groups in 1 compared with the \( \mu_2 \)-bridging coordination in zinc acetate. The O-Zn-O bond angles observed in the four-membered rings are similar to those in [Zn₅(ONMe₂)₆(iPr)₄], ranging between 75.67(7) and 79.63(7)° (average 78.1°). Although the structure shown in Figure 2.4 is chiral-at-metal, the crystal space group is centrosymmetric, and there are equal numbers of both enantiomers present in the crystal.
Figure 2.4 The molecular structures of the two crystallographically independent molecules present in the crystals of 1, showing the five zinc atoms, the six bridging acetates (dark bonds) and the four ethyl units (open bonds). The only significant difference between the two structures is in the position of the terminal methyl of the Zn(4)-bound ethyl moiety (see also Figure A1, Appendix).

The stoichiometry of the complex is strongly supported by $^{1}$H NMR spectroscopy as the $^{1}$H NMR spectrum of 1 consistently showed ratios of the methyl group resonances, on the acetate and ethyl ligands, of 3:2 (Figure 2.5 (a), peaks labelled a and b respectively). The reaction between equimolar quantities of ZnEt$_2$ and Zn(OAc)$_2$, in situ in d$_6$-benzene, was monitored by NMR spectroscopy (Figure 2.5 (b)). The spectrum shows the resonances for [Zn$_5$(OAc)$_6$Et$_4$], with an integration ratio for OOC$_3$H$_3$:CH$_3$ of 3:2 as before; however, resonances corresponding to the excess ZnEt$_2$ also appear (Figure 2.5b, labelled d and e). The sum of the integrations for the methyl groups of ZnEt$_2$ and [Zn$_5$(OAc)$_6$Et$_4$] gives a ratio of OOC$_3$H$_3$:[total ethyl CH$_3$] of 1:1, consistent with the original equimolar stoichiometry.

When a solution of equimolar ratios of Zn(OAc)$_2$ and ZnEt$_2$ reacted in situ in toluene-d$_8$ was heated, the ethyl peaks were found to coalesce at 80 °C (Figure 2.6), suggesting that the ethyl groups are in dynamic exchange. Although the formation of the heteroleptic species may be considered to be an equilibrium process, the apparent 3:2 ligand ratio is not the result of the position of an equilibrium between the heteroleptic species and
the solvated homoleptic species: addition of excess ZnEt$_2$ to the system simply increased the area of the ZnEt$_2$ resonances and the ligand ratio of the product resonances remained the same (Figure 2.7). Similarly, application of a dynamic vacuum removed the excess diethylzinc and yielded a product with a $^1$H NMR spectrum equivalent to that shown in Figure 2.5 (a). In other words, changing the diethylzinc content of the system does not affect the measured ligand ratio of 3:2, indicating that the ligand ratio is the true intramolecular ratio of the product.

Heating a sample which contains no excess diethylzinc did not reveal any peak broadening or change in chemical shift of the ethyl resonances, further suggesting that the dynamic behaviour is not a true equilibrium but simply an exchange mechanism; for this sample, heating did not alter the $^1$H NMR spectrum, indicating the thermal stability of the complex.

The reagent stoichiometry (3:2) can also be derived from the apparent conversion of ZnEt$_2$. For the 1:1 ZnEt$_2$:Zn(OAc)$_2$ experiment, the [Zn$_5$(OAc)$_6$(Et)$_4$] ethyl resonances constitute 64% of the total ethyl resonances. Assuming that 100% of the Zn(OAc)$_2$ is converted, the ratio of OAc:Et is 100:64 or 3.0:1.9. Note that Zn(OAc)$_2$ has negligible solubility in C$_6$D$_6$; therefore all of the acetate signal must arise from [Zn$_5$(OAc)$_6$(Et)$_4$] acetate groups.

In addition, the preparation of 1 in bulk proceeds cleanly from a 3:2 ratio of Zn(OAc)$_2$:ZnEt$_2$. Elemental analysis supports the stoichiometry of the pentanuclear complex (calculated carbon content 30.12, found 30.08 wt%). A gas evolution study indicated 13.7 wt% hydrolysable ethyl content which matches the calculated value for the pentanuclear complex (14.6 wt%) to within the accuracy of the testing method.

The diffusion coefficient for 1 was measured by PGSE NMR spectroscopy to be $8.2 \times 10^{-10}$ m$^2$s$^{-1}$ which gave an estimate of the hydrodynamic radius of 4.4 Å. The radius estimated from the X-ray crystal structure is 5.1 Å, given that there are four molecules per unit cell and the molecules occupy 69% of the unit cell volume. The radius estimates are comparable, suggesting that the pentanuclear complex persists in solution (benzene).
Figure 2.5 $^1$H NMR spectra (in C$_6$D$_6$) for (a) “ethylzinc acetate” prepared from a 3:2 mixture of Zn(OAc)$_2$ and ZnEt$_2$, and (b) “ethylzinc acetate” prepared *in situ* from a 1:1 mixture of ZnEt$_2$ and Zn(OAc)$_2$. In (b), the remaining ZnEt$_2$ peaks are indicated by d (methyl) and e (methylene). The peak at 0.3 ppm (marked with ‘**”) is due to silicone grease contamination.
Figure 2.6 $^1$H NMR (C$_7$D$_8$) spectra for solutions of 1:1 ZnEt$_2$ + Zn(OAc)$_2$ (a) at 293 K, (b) 353 K. The spectrum shown in (b) has been scaled to allow clearer viewing of the broad, coalesced peaks. The peak at 0.3 ppm (marked with ‘*’) is due to silicone grease contamination.
Figure 2.7 $^1$H NMR ($C_6D_6$) for varying ratios of Zn(OAc)$_2$:ZnEt$_2$. The peak marked with ‘*’ is due to silicone grease contamination.

2.3.2 Behaviour in the Presence of Coordinating Solvents

2.3.2.1 Pyridine

The addition of 1 equivalent of pyridine (py) per Zn to a toluene solution containing equimolar quantities of ZnEt$_2$ and Zn(OAc)$_2$ enabled isolation of compound 2 [EtZn(OAc)(py)] in 72% yield. The $^1$H NMR spectrum of 2 showed ligand ratios of OAc:Et:py of 1:1:1 (Figure 2.8). As shown in Table 2.1, the $^1$H NMR chemical shifts of the ethyl and acetate resonances of 2 were shifted much further downfield compared to 1. Both the $^1$H and $^{13}$C{$^1$H} NMR spectra showed that the pyridine resonances were shifted relative to free py in $d_6$-benzene, demonstrating that the pyridine is strongly bound to the complex in solution.

Crystals of 2 were obtained directly from the saturated reaction mixture (toluene) and X-ray crystallographic analysis confirmed the 1:1 ligand ratio, showing 2 to consist of EtZn(OAc)(py) monomeric units (Figure 2.9) that link together to form an extended polymer
chain (Figure A2, Appendix). In contrast to 1, the acetate groups of 2 are bound in a \( \mu_2 \)-bridging coordination, with pyridine occupying the fourth coordination site of each tetrahedrally coordinated zinc. The Zn-O bond lengths (Table A2, Appendix) of 2 (2.014(3) and 2.046(2) Å) are comparable to the Zn-O bond lengths of 1, and the Zn-N bond length (2.111(3) Å) is comparable to Zn-N bond lengths in related carbamato species (2.0786(17) Å),\(^{[117]} \) and to previously reported Zn-bound py species (2.0339(8) Å).\(^{[141]} \)

The PGSE NMR spectrum of 2 in C\(_6\)D\(_6\) gave an estimate of the diffusion coefficient of 1.0 \( \times \) 10\(^{-9} \) m\(^2\) s\(^{-1} \) which corresponds to a hydrodynamic radius of 3.5 Å; this value exactly matches that estimated from the crystal data for the monomeric [EtZn(OAc)-py] unit, based on four monomers per unit cell and a unit cell occupancy of 68\%. Based on the agreement between the two values, it is likely that 2 exists as a monomer in solution. The coordination of the pyridine groups in the solid state is also supported by IR data; the absorption bands associated with the vibrations of the pyridine ring are shifted to higher frequency (free pyridine vibrations at 1581, 1030, and 604 cm\(^{-1} \); adduct vibrations at 1605, 1041, 614 cm\(^{-1} \) respectively).\(^{[142]} \) The difference, \( \Delta \), between the asymmetric and symmetric carboxylate stretches is 113 cm\(^{-1} \), within the range for bridging acetate groups, but slightly lower than that for 1 (165 cm\(^{-1} \)), which may be an indication of the difference in the acetate bridging mode (\( \mu_2 \) for 2 compared to \( \mu_3 \) for 1).

**Figure 2.8** \(^1\)H NMR (C\(_6\)D\(_6\)) of 2, the pyridine adduct of ethylzinc acetate.
Table 2.1 Comparison of the chemical shifts (in $C_6D_6$) of [EtZn(OAc)(py)]$_x$, 2, with [Zn$_5$(OAc)$_6$(Et)$_4$], 1, and free pyridine (py).$^{[143]}$

<table>
<thead>
<tr>
<th>Group</th>
<th>$^1$H NMR chemical shift (ppm)</th>
<th>$^{13}$C($^1$H) NMR chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>-OOCCH$_3$</td>
<td>1.89</td>
<td>2.07</td>
</tr>
<tr>
<td>-CH$_2$CH$_3$</td>
<td>1.56</td>
<td>1.71</td>
</tr>
<tr>
<td>py ortho</td>
<td>-</td>
<td>8.60</td>
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<tr>
<td>py para</td>
<td>-</td>
<td>6.81</td>
</tr>
<tr>
<td>py meta</td>
<td>-</td>
<td>6.55</td>
</tr>
</tbody>
</table>

Figure 2.9 The molecular structure of the monomeric repeat unit of the chain polymer of 2, the pyridine adduct of ethylzinc acetate. The extended polymer structure is shown in the Appendix.
2.3.2.2 Tetrahydrofuran

The addition of one equivalent of tetrahydrofuran (THF) to a toluene solution of ZnEt₂ and Zn(OAc)₂ yielded an opaque suspension that could not be fully characterised. However, the reaction between equimolar quantities of Zn(OAc)₂ and ZnEt₂ directly in THF yielded a product, 3, with the molecular formula EtZnOAc, in 81% yield (¹H NMR spectroscopy, Figure 2.10). The use of an excess of Zn(OAc)₂ (3:2 OAc:Et, as found for 1) yielded the same product, 3, contaminated with the excess Zn(OAc)₂ (¹H NMR; Figure 2.11). Crystals of the product were obtained by slow evaporation from a THF solution, and X-ray diffraction showed that the structure consisted of dimeric [EtZn(OAc)]₂ units (Figure 2.12 (a)). The asymmetric units are connected to one another via bridging of neighbouring μ₃-acetate groups to form two-dimensional sheets of 16-membered [Zn(OAc)]₄ rings joined by Zn₂O₂ nodes (herringbone structure; Figure 2.12 (b); see also Figure A3, Appendix). All of the Zn centres are tetrahedrally coordinated, with no covalent interaction between the sheets. Interestingly, no molecules of THF remained bound in the solid state, despite the great excess present during crystallisation. The Zn-O bond lengths (Table A3, Appendix) in the structure are comparable to those for 1, lying within the range 1.977(7) - 2.137(7) Å. The O-Zn-O bond angles of the dimeric repeat unit are 75.1(3) and 77.0(3)° which are comparable to the O-Zn-O angles of the four-membered rings of 1; the remaining O-Zn-O angles range between 92.5(3) and 107.9(3)°.

The 1:1 ligand ratio and absence of bound THF is supported by elemental analysis (calculated C 31.30 H 5.25, found C 31.27 H 5.14 wt%) and ¹H NMR spectroscopy (Figure 2.10); the only THF signals observed in the spectrum are due to the solvent residual signals.

The PGSE NMR spectrum of 3 in THF-d₈ gave a calculated diffusion coefficient of 1.7 × 10⁻⁹ m² s⁻¹ which corresponds to a hydrodynamic radius of 2.7 Å. The radius of the dimeric unit estimated from the crystal data is 3.7 Å, based on four dimers per unit cell and a unit cell occupancy of 75%. The values are comparable, indicating that the sheet structure is likely to be disrupted and that 3 exists as a discrete dimer when solvated by excess THF. It seems likely that the acetate groups would favour a μ₂-bridging coordination in the discrete dimer, as solvent molecules could occupy the fourth coordination site of the zinc atoms; however, this is a hypothesis and no evidence for such a change in coordination has been obtained.
Figure 2.10 $^1$H NMR spectrum (THF-$d_8$) of 3. Peak marked with “•” is residual solvent; peak marked with “Δ” is due to small amounts of (dissolved) ethane.$^{[143]}$

Figure 2.11 Comparison of the $^1$H NMR spectrum ($d_8$-THF) of 3 (1:1 OAc:Et) with that of anhydrous Zn(OAc)$_2$ and the product of the reaction between ZnEt$_2$ and an excess of Zn(OAc)$_2$ (2:3; middle spectrum); in the middle spectrum, the acetate resonance is shifted relative to 3, toward that of free Zn(OAc)$_2$. The peak marked “•” is residual protonated solvent.
Figure 2.12 (a) The molecular structure of the dimeric repeat unit of 3, demonstrating the tetrahedrally coordinated zinc atoms and the acetate bridging arrangement that leads to (b) the extended polymeric sheet structure.

2.3.3 Changing Solvents

To investigate the solvent dependence and lability of the structures of the complexes, isolated 1 and 3 were dissolved in $d_8$-THF and $d_6$-benzene, respectively, and their structures studied by $^1$H NMR spectroscopy. Isolated 3 was largely insoluble in $d_6$-benzene at room temperature but, when heated, yielded a clear solution which persisted on cooling to 25 °C. The $^1$H NMR spectrum of the cooled solution showed resonances of the 3:2 pentanuclear complex (1) and those of free ZnEt$_2$; the sum of the integration of the ethyl peaks gave a ratio of [OAc]:[total Et] of 1:1, as expected. Similarly, attempted dissolution of isolated 1 in $d_8$-THF at room temperature yielded a suspension with a large amount of undissolved solid but, on heating the mixture to reflux (70 °C), the solid dissolved to give a clear solution which persisted on cooling to 25 °C. The $^1$H NMR spectrum of the cooled solution showed total ligand ratios of 3:2 [OAc]:[Et], but the acetate resonance was shifted downfield with respect to that of 3, towards that of free Zn(OAc)$_2$ (comparable to Figure 2.11). PGSE of the clear solution at room temperature gave an estimate of the hydrodynamic radius of the species in solution of 2.5 Å, comparable to 3. From the $^1$H NMR data, it is believed that the solution contained the dimeric 1:1 species (3) and excess Zn(OAc)$_2$ in dynamic exchange, rather than the pentanuclear complex. Addition of one equivalent of ZnEt$_2$ per mol of [Zn$_5$(OAc)$_6$(Et)$_4$] to the solution gave a $^1$H NMR spectrum equivalent to that of 3.
It can be concluded that the pentanuclear complex, 1, is strongly favoured in aromatic solvents and ethylzinc carboxylates dissolved in aromatic solvents will revert to the pentanuclear complex regardless of their ligand stoichiometry prior to dissolution. The process of interchanging between the 1:1 dimer and the 3:2 pentanuclear structure is accelerated by heating, presumably acting disrupt the extended sheet and discrete complex structures, respectively.

2.4 Further Derivatives

In order to investigate whether the observed ligand stoichiometry was common for all alkylzinc alkyl-carboxylates, the formate, hexanoate, dodecanoate, and stearate derivatives were also studied (carbon chain lengths of 1, 6, 12, and 18, respectively).

2.4.1 Long-chain alkyl carboxylates

The complex formed by reaction between zinc bis(stearate) and ZnEt$_2$ in toluene, [Zn$_5$(OOCR)$_6$(Et)$_4$], 4, can be isolated in the bulk as a white powder (37% yield). Although the flexibility of the stearate chain prevented successful crystallisation, elemental analysis of 4 supported the stoichiometry of the pentanuclear complex (calculated C 64.98 H 10.81, found C 64.90 H 10.87 wt%). The difference, \( \Delta \), between the asymmetric and symmetric carboxylate stretches in the IR spectrum of 4 was 140 cm$^{-1}$ and the spectrum shares many comparable features with that of 1.

Despite considerable effort, it was not possible to isolate the hexanoate and dodecanoate derivatives, therefore full characterisation could not be performed. These complexes were highly solvophilic (toluene, hexane, pentane) and the solvent could not be fully removed even after extended times under high vacuum. However, the hexanoate and dodecanoate derivatives were prepared and studied \emph{in situ} in $d_6$-benzene. For all three derivatives (including 4), the $^1$H NMR spectra show integration ratios for OOCR:Et of 3:2, based on the methylene peaks (Figure 2.13). For each, the apparent conversion from a solution prepared from a 1:1 ratio of Zn(OOCR)$_2$:ZnEt$_2$ gives a 3:2 ratio as found for 1. Additionally, variable temperature $^1$H NMR spectra of each derivative demonstrated coalescence with diethylzinc peaks, where excess diethylzinc was present.
Preparation of the dodecanoate derivative directly in THF yielded a compound, 5, which, when dissolved in C₆D₆ (with heating) showed resonances for the 3:2 complex as well as those for free ZnEt₂, with a [OOCR]:[total Et] ratio of 1:1 (Figure 2.14).

By analogy to the behaviour of the fully characterised acetate derivatives 1 and 3, it is believed that formation of a pentanuclear complex occurs in aromatic solvents but formation of a 1:1 complex in coordinating solvents is common to this series of ethylzinc carboxylate compounds: acetate, hexanoate, dodecanoate, stearate.

Figure 2.13 ¹H NMR spectra (C₆D₆) of the long chain alkyl carboxylates of [Zn₅(OOCR)₆(Et)₄] (a) hexanoate, (b) dodecanoate, (c) stearate.
Figure 2.14 $^1$H NMR ($C_6D_6$) of ethylzinc dodecanoate, 5, prepared directly in THF.
Resonances for the pentanuclear complex are present, along with those for free diethylzinc.
The peak at 0.29 ppm is due to grease.

2.4.2 Formate

The reaction between equimolar amounts of zinc bis(formate) and ZnEt$_2$ was studied in situ in deuterated solvent ($C_6D_6$). In contrast to the ethylzinc acetate system, the $^1$H NMR spectrum showed a product with an intramolecular ligand ratio of OOCH:Et of 4:3, but which formed at a much lower conversion: a large amount of undissolved solid remained in the reaction mixture and the $^1$H NMR spectrum showed an excess of free diethylzinc greater than would be expected if the reaction had gone to completion to form a product with a ligand stoichiometry of 4:3 (Figure 2.15 (a) and Table 2.2). Two series of experiments were carried out with varying ratios of [ZnEt$_2$]:[Zn(OOCH)$_2$]: (1) maintaining the concentration of ZnEt$_2$ as 0.3 M but varying the loading of Zn(OOCH)$_2$, and (2) maintaining the loading of Zn(OOCH)$_2$ but varying the concentration of ZnEt$_2$; the value quoted in Table 2.2 as [Zn(OOCH)$_2$] is the maximum concentration of this species assuming all of the solid had dissolved. For series 2, the quantity of undissolved solid appeared not to vary (visually) with varying the excess of diethylzinc; for series 1, the quantity of undissolved solid decreased with increasing ratio of [ZnEt$_2$]:[Zn(OOCH)$_2$], resulting in a clear solution with very few
Figure 2.15 $^1$H NMR spectra ($C_6D_6$) of various ratios of ZnEt$_2$:Zn(OOCH)$_2$, reacted *in situ*. As the true stoichiometry of “ethylzinc formate” is not known, the Zn and ligand ratios are represented as $x$, $y$, and $z$. The peak marked with ‘$\Delta$’ is due to traces of ethane; the peak marked with ‘$*$’ is due to silicone grease contamination.
Table 2.2 Expected and observed conversion of ethyl groups (expected conversion based on full conversion to ethylzinc formate complex with 4:3 [OOCH]:[Et])

<table>
<thead>
<tr>
<th>Series</th>
<th>Ratio [ZnEt₂]:[Zn(OOCH)₂]</th>
<th>[ZnEt₂] /M</th>
<th>[Zn(OOCH)₂] /M</th>
<th>Conversion %</th>
<th>[Product] /M</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1:1</td>
<td>0.30</td>
<td>0.30</td>
<td>75</td>
<td>0.042</td>
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<tr>
<td></td>
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<td>0.30</td>
<td>0.15</td>
<td>38</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>5:1</td>
<td>0.30</td>
<td>0.06</td>
<td>15</td>
<td>0.014</td>
</tr>
<tr>
<td>2</td>
<td>3:4</td>
<td>0.08</td>
<td>0.10</td>
<td>100</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>0.10</td>
<td>0.10</td>
<td>75</td>
<td>0.015</td>
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<tr>
<td></td>
<td>2:1</td>
<td>0.20</td>
<td>0.10</td>
<td>38</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>4:1</td>
<td>0.30</td>
<td>0.10</td>
<td>19</td>
<td>0.006</td>
</tr>
</tbody>
</table>

particulates for a ratio of [ZnEt₂]:[Zn(OOCH)₂] of 5:1. The 4:3 ligand ratio in the product was maintained in all samples (Figure 2.15 (b) and (c)).

Comparing the results of the two series, simple dilution does not significantly improve the apparent conversion and subsequently leads to lower calculated product concentrations. Therefore, it can be concluded that the discrepancy is not simply a result of low solubility of the product (as the calculated product concentration would be expected to vary only with variation of Zn(OOCH)₂ loading). For series 2, the conversion remains poor up to a reagent ratio of 4:1, whereas for series 1 the conversion improves with increasing ratio, to approximately full conversion at a ratio of 5:1. The 5:1 sample is both the most dilute in Zn(OOCH)₂ and the most concentrated with respect to ZnEt₂, which suggests that the formation of the heteroleptic complex is dependent on both the solubility of Zn(OOCH)₂ and the concentration of ZnEt₂ – varying these factors independently does not significantly improve the conversion.

In order to form the heteroleptic species, the zinc bis(carboxylate) must interact with ZnEt₂ to go from the solid (reagent) phase to the dissolved (product) phase (neither Zn(OAc)₂ nor Zn(OOCH)₂ are significantly soluble in aromatic solvents alone). For the acetate derivative, the formation of the heteroleptic species is favoured and therefore no excess of ZnEt₂ is required – the rate of formation is slow (approximately 2 days if unstirred or 1 hour if stirred) but the reaction proceeds to completion. In contrast, for the formate derivative, it appears that the formation of the heteroleptic species is unfavourable and requires great
excess of ZnEt₂ in sufficient concentration to act as a “solubilising” agent in order to proceed to full conversion.

Attempts to obtain X-ray quality crystals of the formate derivative have not been successful; as such it is not possible to confidently assign the structure. However, as Zn(OOCH)₂ is not soluble in C₆D₆ it is believed that the 4:3 ratio is genuine, and a possible structure analogous to the heptameric alkylzinc alkoxide double-cube is proposed (Figure 2.16).

Addition of 1 equivalent of pyridine (py) per Zn to a 1:1 solution of Zn(OOCH)₂ and ZnEt₂ yielded a product, 6, as a clear, viscous oil. ¹H NMR spectroscopy (Figure 2.17) and elemental analysis supported a ligand ratio of [OOCH]:[Et]:[py] of 1:1:1, analogous to 3. The formation of 6 demonstrates that, in the presence of an additional, strongly coordinating ligand, the behaviour of the formate derivative is dramatically changed and the heteroleptic species is favoured; the reason for this difference is proposed to be due to the enhanced solubility of Zn(OOCH)₂ and the stability of the heteroleptic species that are imparted by the presence of py.

**Figure 2.16** Proposed structure for “ethylzinc formate” with a 4:3 (8:6) ratio of (OOCH):Et, analogous to the heptameric structure observed for ethylzinc alkoxides. The Zn-Et groups are highlighted in blue for clarity. The proposed structure consists of 8- and 6-membered rings.
Figure 2.17 $^1$H NMR spectrum (C$_6$D$_6$) of “ethylzinc formate”, 6, prepared in toluene in the presence of 1 equivalent of pyridine per Zn.

2.5 Discussion

The donor ability (donor number), polarity (expressed as the dielectric constant) and acceptor number of the solvents investigated are given in Table 2.3.$^{[121]}$ Both of the polar, donating solvents impose a preference for a 1:1 ligand ratio in the ethylzinc carboxylate complexes but, whereas pyridine acts as an additional, permanent ligand, THF acts as a labile ligand which does not remain bound in the solid state. The pyridine adduct, 2, forms as monomers of [EtZn(OAc)(py)] whereas the product formed in THF, 3, forms [EtZn(OAc)]$_2$ dimers. Both 2 and 3 form extended polymers in the solid state. The difference between the behaviour of pyridine and THF can be explained by the higher donor number of py compared to THF and by the higher polarity (greater driving force to bind to the metal centre). The enhanced electrophilic nature of py compared to THF may allow a small degree of back-donation (metal-to-ligand transfer) to occur through the Zn-py bond, as evidenced by a yellow colour observed in [ZnEt$_2$(py)] solutions; however, the significance of the effect in 2 is not clear.

The formation of a discrete complex with unequal numbers of ligands (3:2 OAc:Et for the acetate derivative) in toluene and benzene solutions is explained by the need to minimise
Table 2.3 Comparison of the donor number, dielectric constant and acceptor number of the solvents investigated for this project.\[121\]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Donor Number /kcalmol$^1$ (kJmol$^1$)</th>
<th>Dielectric Constant</th>
<th>Acceptor Number</th>
</tr>
</thead>
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<tr>
<td>Benzene</td>
<td>0.1 (0.4)</td>
<td>2.3</td>
<td>8.2</td>
</tr>
<tr>
<td>THF</td>
<td>20.0 (83.7)</td>
<td>7.6</td>
<td>8.0</td>
</tr>
<tr>
<td>Pyridine</td>
<td>33.1 (138.5)</td>
<td>12.3</td>
<td>14.2</td>
</tr>
</tbody>
</table>

The polarity of the complex with respect to its outer coordination shell: in I, the ethyl and acetate methyl groups are directed outwards towards the solvent, keeping the polar Zn-O bonds more protected towards the centre of the structure. It is not clear, however, whether the observed structure “appears” less polar than would a hypothetical 1:1 cubane structure similar to that seen for the ethylzinc alkoxides. It may be that the pentanuclear arrangement is structurally more compact than other, higher structures or any attainable structures with 1:1 ligand ratios.

The formation of the heteroleptic formate derivative is much more unfavourable than for the acetate derivative which may reflect the lower solubility and lower stability in toluene of a complex with just a proton on the carboxylate group. Complex formation is only favoured when an additional ligand – py – is introduced to improve both the solubility of the starting zinc bis(carboxylate) and the stability of the final (1:1) complex.

The tendency for the complexes to revert to the ligand ratio and structure dictated by the preference of the solvent (regardless of the structure that the solid possesses prior to dissolution) indicates the lability of the complexes and, importantly, how great an influence the solvent parameters have on the organometallic complexes. In the absence of coordinating solvent, the dynamic exchange of ethyl groups between the complex and any excess diethylzinc present is also an indication of the lability of the complexes; this behaviour is thought to be a promising indicator of the ability of the ethylzinc carboxylate species to interact with nucleating ethylzinc hydroxide species during nanoparticle growth and to act to deliver carboxylate groups to the nanoparticle surfaces, as intended.
2.6 Catalytic Activity of Ethylzinc Acetate Species

2.6.1 Mechanism and previous findings

The copolymerisation of CO$_2$ and epoxides proceeds by a coordination-insertion mechanism, using a Lewis acidic metal catalyst of the form L$_n$M-X, where L$_n$ represents permanent ligands, and X can be a halide, carboxylate or alkoxide initiating group (Scheme 2.3). The reaction proceeds via alternating insertion of the epoxide into a metal carbonate bond, followed by insertion of CO$_2$ into a metal alkoxide bond; where X is a carboxylate or halide, the insertion of the epoxide is the initiating step (as shown in Scheme 2.3); where X is an alkoxide, insertion of CO$_2$ is the initiating step. Side reactions can occur by back-biting (to form the cyclic carbonate species) and by chain transfer through reaction with ROH, to give a hydroxyl-terminated copolymer (ROH = water or alcohol). In addition, some catalysts can also homopolymerise epoxides, leading to a certain proportion of ether linkages in the final polymer.

The key criteria for assessing catalysts for this copolymerisation are:

- Polymer quality (proportions of carbonate and ether linkages; ideal polymer is 100% carbonate);
- Selectivity (percentage cyclic product)
- Activity, as measured by turn-over frequency (TOF, moles of epoxide consumed per mole of metal per hour)
- Productivity (g polymer per g metal)
- Molecular weight control (the ideal is a linear relationship between molecular weight and conversion, with a narrow weight distribution)

In addition, the general properties of an ideal catalyst system include low toxicity, lack of colour or odour, and low cost.

The ZnEt$_2$/water catalytic system, reported by Inoue et al. in 1969, yielded high molecular weight copolymers of propylene oxide (PO) and CO$_2$ (approximately 150,000 g mol$^{-1}$) with high carboxylate content (88%), at atmospheric pressure (in benzene); however the conversion was low (3%). The conversion increased (7%) when the copolymerisation reaction was carried out at 50 atm. but at the expense of molecular weight (lowered to 44,000 g mol$^{-1}$). Subsequently, the same research group reported catalytic mixtures of ZnEt$_2$ and di- and trihydric ligands with improved performance: for example,
Scheme 2.3 Overview of the coordination-insertion mechanism of the metal catalysed copolymerisation of CO₂ and an epoxide.\[126]\n
ZnEt₂:m-hydroxybenzoic acid (1:1) in dioxane, at 40 atm. CO₂, produced PPC with molecular weight of 110,000 g mol⁻¹ at a turn-over frequency of 0.45 h⁻¹, and 72% conversion.\[128]\n
Since these early systems, the greatest advances in terms of polymer quality and activity have been achieved with small molecule, homogeneous catalysts. Of note are the zinc phenoxide and zinc β-diminate systems, which were the first highly active, well-defined catalysts;\[144-146]\nfor example, TOFs of ~250 - 730 h⁻¹ were achieved at 7 atm. CO₂, with narrow weight distribution (polydispersity indices of <1.2; see section 2.6.2.3) and selectivity of up to 99 % using zinc β-diminate complexes. Since then, many metal catalysts with ligand systems including porphyrins, salens, and macrocyclic groups have been developed, showing high activity, selectivity, and molecular weight control at pressures as low as 1 atm.;\[130, 147]\nhowever, for these systems, the molecular weight is often low (1,000 - 10,000 g mol⁻¹) and the complexity of the catalysts currently makes them cost-prohibitive for large-scale co-polymer synthesis. Heterogeneous catalysts, such as zinc glutarate, are still the system of choice for multi-kilogram scale synthesis of high molecular weight polycarbonate, despite their lower activity (70 g copolymer per g Zn; 40 h reaction time) and broader molecular weight.
distributions (PDI 2 - 3 for highly crystalline zinc glutarate).\cite{131,148-150} As such, there is still interest both in developing heterogeneous catalysts and in re-visiting cheap, simple homogeneous catalysts, such as Al(O\textsubscript{i}Pr)\textsubscript{3}.\cite{151}

Recently, Eberhardt \textit{et al.} demonstrated that ethylzinc sulfinate groups could be active for the initiation of the copolymerisation of CO\textsubscript{2} and PO.\cite{152} By converting 25\% of the ethyl groups of a 1:1 mixture of ZnEt\textsubscript{2} and glutaric acid to ethylsulfinate groups, the TOF was increased 16-fold compared to ZnEt\textsubscript{2}/glutaric acid alone (ZnGA(0));\cite{132} the weight-average molecular weight (\textit{vida infra}) was high (110,000 g mol\textsuperscript{-1}), with a high proportion of carbonate linkages (93\%) and a relatively low polydispersity (2.5 compared with 7.9 for ZnGA(0)).

Due to the precedence for ZnEt\textsubscript{2}/carboxylic acid catalytic systems, and the lack of prior, detailed study of ethylzinc carboxylate systems, the well-defined complexes 1 and 3 were tested for their catalytic activity towards epoxides. Preliminary experiments demonstrated no activity towards PO copolymerisation for either catalyst, however both were active towards cyclohexene oxide (CHO). Testing was carried out using conditions commonly used for similar systems (e.g. the zinc phenoxide compounds); however, whereas CO\textsubscript{2} pressures of up to 50 atm. are commonly used, the pressure was restricted to 15 atm. in this work.

\section*{2.6.2 Key polymer characterisation methods}

\subsection*{2.6.2.1 Degree of carbonate linkages}

The extent of incorporation of CO\textsubscript{2} into carbonate linkages was determined by \textsuperscript{1}H NMR, and was based on the integration of the protons alpha to the carbonate and ether linkages, centred at 4.6 and 3.4 ppm, respectively. A peak at 4.0 ppm was assigned to the \textit{trans} cyclic carbonate product. The \textit{cis} cyclic product is expected to resonate at 4.6 ppm; as this resonance was masked by that of the protons alpha to the carbonate linkages, the quantity of \textit{cis} cyclic product was estimated to be equal to that of the \textit{trans} cyclic product (both were observed in the IR spectrum of the copolymer).

\subsection*{2.6.2.2 Activity}

The activity of the catalysts was expressed as follows:

\begin{equation}
\text{Conversion (\%)} = \frac{100 \times [W_p - W_c]}{M_m \times [142.1 F_c + 98.1 F_c]} \quad (2.1)
\end{equation}
\[ \text{Turn over frequency (TOF)} = \frac{M_m \times \left( \frac{C}{100} \right)}{M_{Zn} h} \] (2.2)

where \( W_p \) and \( W_c \) are the masses of the isolated polymer and the mass of the catalyst, respectively; \( M_m \) and \( M_{Zn} \) are the number of moles of monomer and zinc, respectively; \( F_C \) and \( F_e \) are the fractions of carbonate and ether linkages, respectively (based on \(^1\)H NMR analysis); \( h \) is the reaction time in hours.

### 2.6.2.3 Molecular Weight

The molecular weight of the polymers was determined by Gel Permeation Chromatography (GPC). The polymers were dissolved in THF, injected into the chromatograph and the concentration of polymer in the eluted solution was measured (by light scattering) as a function of time. In GPC analysis, the detector response is calibrated to be linear with concentration, such that the intensity of the signal is a reflection of the absolute number of chains at a given retention time. In this work, the molecular weight was calibrated using poly(styrene) standards, therefore the measured molecular weight is a relative value. A typical chromatograph is shown in Figure 2.18.

![Figure 2.18 Example gel permeation chromatograph for poly(cyclohexene oxide).](image)
Two values for molecular weight are typically obtained from GPC analysis: the number average molecular weight, $M_n$, is the mean of the weight distribution:

$$M_n = \frac{\text{total weight of sample}}{\text{total number of chains}} = \frac{\sum_i M_i N_i}{\sum_i N_i}$$  \hspace{1cm} (2.3)$$

where $N_i$ is the number of chains with mass $M_i$. The weight average molecular weight, $M_w$, is the second moment average, which gives a measure of the “width” of the distribution:

$$M_w = \frac{\sum_i M_i^2 N_i}{\sum_i M_i N_i}$$  \hspace{1cm} (2.4)$$

The ratio $M_w/M_n$ gives the polydispersity index (PDI), which is an indication of how broad the distribution is: the lower the PDI, the more uniform the molecular weight of the sample. For a polymerisation to be considered controlled (or “living”), the PDI should be between 1.0 and 1.2.

2.6.3 Results

The results of CO$_2$/CHO copolymerisation studies using 1 and 3 are summarized in Table 2.4.

The donating abilities of epoxides towards zinc complexes have been reported to be lower than that of THF;\textsuperscript{144} however, it is plausible that the same preference for the 1:1 ligand ratio occurs for CHO as for THF. It may be expected, therefore, that 1 would segregate into the 1:1 complex (3) and excess Zn(OAc)$_2$; as such, 1, 3, and Zn(OAc)$_2$ alone were tested in the copolymerisation reactions to compare activity.

In the absence of CO$_2$ (1 atm. N$_2$), both 1 and 3 were active catalysts for the homopolymerisation of neat CHO, yielding a highly viscous liquid (polycyclohexene oxide) after 10 hours (Table 2.4, rows 1 and 2). The yields of the isolated poly(cyclohexene oxide) were similar for both catalysts and, although the conversion was low (7 and 5\% for 1 and 3, respectively) the $M_n$ values were high. The low conversion and high molecular weight are comparable to the results found for epoxide homopolymerisation catalysed by alkylzinc alkoxides,\textsuperscript{129} indicating that only a small proportion of the metal sites were active for catalysis. The molecular weights ($M_n$) and conversions obtained in this work correspond to approximately 2\% of the zinc sites being active during polymerisation. The low PDIs of the polymers ($M_w/M_n = 1.6$ and 1.5 for 1 and 2, respectively) demonstrate that, although only a tiny fraction of the zinc sites are active, the rate of growth is higher than the rate of initiation.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T/°C$</th>
<th>$p$(CO$_2$)/atm.</th>
<th>time/h</th>
<th>% conversion</th>
<th>% carbonate</th>
<th>% cyclic carbonate</th>
<th>$M_n×10^3$/gmol$^{-1}$</th>
<th>PDI</th>
<th>TOF</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>0</td>
<td>10</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>464.1</td>
<td>1.6</td>
<td>2</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>0</td>
<td>10</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>234.1</td>
<td>1.5</td>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td>[(cC$_5$H$_9$)$_7$Si$<em>7$O$</em>{11}$ (OSiMePh$_2$)$_2$]Zn$_4$Me$_4$, Ref.[153]</td>
<td>120</td>
<td>0</td>
<td>24</td>
<td>13</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>80</td>
<td>15</td>
<td>3</td>
<td>24</td>
<td>39</td>
<td>4</td>
<td>44.8</td>
<td>2.5</td>
<td>24</td>
<td>128</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>15</td>
<td>3</td>
<td>32</td>
<td>66</td>
<td>2</td>
<td>10.8</td>
<td>10.2</td>
<td>31</td>
<td>184</td>
</tr>
<tr>
<td>1</td>
<td>80</td>
<td>15</td>
<td>7.5</td>
<td>39</td>
<td>66</td>
<td>4</td>
<td>12.9</td>
<td>9.9</td>
<td>16</td>
<td>240</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>15</td>
<td>7.5</td>
<td>41</td>
<td>66</td>
<td>2</td>
<td>12.9</td>
<td>9.9</td>
<td>16</td>
<td>240</td>
</tr>
<tr>
<td>Zn(OAc)$_2$</td>
<td>80</td>
<td>15</td>
<td>7.5</td>
<td>31</td>
<td>67</td>
<td>2</td>
<td>5.33</td>
<td>14.2</td>
<td>13</td>
<td>185</td>
</tr>
<tr>
<td>[(cC$_5$H$_9$)$_7$Si$<em>7$O$</em>{11}$ (OSiMePh$_2$)$_2$]Zn$_4$Me$_4$, Ref.[153]</td>
<td>80</td>
<td>80</td>
<td>24</td>
<td>34</td>
<td>92</td>
<td>2</td>
<td>10.6</td>
<td>10.8</td>
<td>3</td>
<td>95</td>
</tr>
<tr>
<td>SiO$_2$-tethered ZnEt$_3$, Ref.[153]</td>
<td>120</td>
<td>80</td>
<td>24</td>
<td>6</td>
<td>93</td>
<td>-</td>
<td>9.00</td>
<td>5.3</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Al(O’Pr)$_3$, Ref.[151]</td>
<td>90</td>
<td>20</td>
<td>18</td>
<td>51</td>
<td>9.1</td>
<td>-</td>
<td>15.0</td>
<td>2.0</td>
<td>9</td>
<td>579</td>
</tr>
</tbody>
</table>

Table 2.4 Copolymerisation results with cyclohexene oxide (CHO) and CO$_2$ (CHO:catalyst ratio 300:1)

At 15 atm. CO$_2$ and in neat CHO, both 1 and 3 were moderately active catalysts for the copolymerisation. The TOFs decreased with increasing reaction time (3 h to 7.5 h), which corresponded to a decrease in reaction rate due to an increase in the viscosity of the reaction mixture. The conversion was marginally higher for 3 than 1 at the 3 h timepoint (Table 2.4; rows 4 and 6), and 1 had a much higher proportion of ether linkages after 3 h than 3. By 7.5 h, the discrepancy had disappeared and both catalysts had approximately the same conversion and the same proportion of ether linkages. The molecular weight of the copolymer catalysed by 1 was considerably higher after 3 h than both the equivalent copolymer catalysed by 3 and the polymer catalysed by 1 after 7.5 h ($M_n$ 44,800, 12,900, and 12,900 gmol$^{-1}$, respectively). The reduction in $M_n$ with time for 1 is thought to be caused by initial homopolymerisation to generate high molecular weight poly(cyclohexene oxide) chains (which represent a higher proportion of the total chains) followed by copolymerisation and chain transfer reactions to give shorter chains. Additionally, it is likely that chain transfer reactions result in shorter chains and a broadening of the molecular weight distribution. The copolymers catalysed by 1 and 3 were analysed by matrix-assisted laser deposition time-of-flight (MALDI-ToF) mass spectrometry, which showed that, for both catalysts, the only observable polymer end-groups were hydroxyl groups (Figure 2.19), indicative of a chain transfer mechanism; it should be noted that MALDI-ToF mass spectrometry generally has an
upper limit for mass to charge ratio on the order of $10^3 - 10^4$ (approximately 10 - 100 repeat units for poly(cyclohexene carbonate)), therefore the analysis is only representative of the lower end of the polymer size distribution. In-line with the $^1$H NMR spectroscopy results, the MALDI-ToF spectrum of the polymer catalysed by 1 showed much higher quantities of ether linkages after 3 h compared to the equivalent copolymer catalysed by 3.

Despite the reported\textsuperscript{128} lack of activity towards PO, Zn(OAc)$_2$ alone was surprisingly active under the current reaction conditions and yielded a copolymer with an equivalent proportion of ether and carbonate linkages after 7.5 h to that produced by 1 and 3. In general, however, both 1 and 3 showed a higher activity and higher performance in terms of productivity (per gram Zn); in comparison to the Zn(OAc)$_2$, the $M_n$ of the copolymers formed by 1 and 3 were higher and the PDIs narrower, demonstrating the better performance of these catalysts. In light of the expected segregation of 1 to 3 plus Zn(OAc)$_2$, the slightly lower activity of 1 compared to pure 3 after 3 h is explained by the lower activity of Zn(OAc)$_2$; the difference in reactivities means that the copolymer catalyzed by 3 reaches a high viscosity earlier than that catalysed by 1, allowing the rates to become comparable after 7.5 h (16 Zn$^{-1}$h$^{-1}$).

The results for 1 and 3 are comparable to recently reported anchored alkylzinc species (Table 2.4, rows 10 and 11) and the related metal alkoxide Al(OPr)$_3$ (Table 2.4, row 12); however, although the weight-average molecular weights ($M_w$) of the polymers catalyzed by 1 and 3 are high and the catalyst activities are moderate, the overall quality of the polymers is low. The catalytic performance of 1 and 3 may be improved by rigorous optimisation; for example, it is expected that CO$_2$ pressures of 40 atm. and above would improve the carboxylate content of the co-polymers.\textsuperscript{144}
Figure 2.19 Parts of the MALDI-ToF spectra of the copolymer of CO₂ and cyclohexene oxide (3 h reaction time) catalysed by (a) 1 and (b) 3.
2.7 Summary

The structure and solution behaviour of a series of ethylzinc carboxylate species has been investigated. The stoichiometry and nuclearity of the complexes has been found to be strongly dependent on the nature of the solvent in which they are dissolved and the presence of additional, strongly coordinating ligands (Scheme 2.4). For the acetate derivative, a pentanuclear complex with a ligand ratio of 3:2 is favoured in non-coordinating solvents (toluene, benzene) whereas a 1:1 ligand ratio is favoured in coordinating solvents; in THF, the asymmetric repeat unit of the solid state crystal structure is dimeric whereas, in the presence of pyridine, the complex is monomeric. The behaviour of the long-chain alkyl carboxylate derivatives is comparable to that of the acetate derivative. In contrast, for the formate derivative, formation of the heteroleptic species is only favourable in the presence of a strongly coordinating ligand (py). The ethyl groups of the complexes exchange with those of any excess ZnEt₂ on the NMR timescale, indicating the lability of these groups.

The two acetate derivatives 1 and 3 are active catalysts for both the homopolymerisation of CHO and the copolymerisation of CHO with CO₂. The broad PDIs of the copolymers indicate multiple initiating groups and an uncontrolled polymerisation mechanism, but the quality of the polymers may improve with optimisation of the polymerisation conditions.

Scheme 2.4 Summary of the solvent dependence of the structure of ethylzinc acetate.
Chapter 3

ZnO Nanoparticle Synthesis

3.1 Introduction

The primary aim for the work in this chapter was to demonstrate that surface-functionalised ZnO nanoparticles can be produced in one step using substoichiometric quantities of capping agent. As the properties of nanoparticles and nanocomposites are so dependent on size and shape, control over these parameters remains an important goal for nanomaterials synthesis. Therefore, the ZnO synthesis method was explored with respect to the effect of varying the synthetic parameters, with the ultimate goal of developing the method to be adaptable for systematic, homogeneous variation of particle size and morphology.

3.1.1 Nanoparticle nucleation and growth

All particle synthesis involves a nucleation step followed by growth. Ideally, these stages must be separated temporally, such that no further nucleation occurs once growth begins and all particles have a common growth history. Separation of nucleation and growth can be achieved by using heterogeneous nucleation, whereby small, pre-synthesised nuclei are introduced to the system to act as a template for nanoparticle growth, or by homogeneous “burst nucleation” as described by LaMer and Dinegar in the 1940s. The ideal conditions for homogeneous nucleation are shown schematically in Figure 3.1, represented by the change in concentration of nucleating species (monomers) in solution over time. Initially, the concentration of monomers increases steadily until a critical supersaturation concentration \( C_{\text{crit}} \) is achieved. Prior to \( C_{\text{crit}} \), although supersaturation is
Figure 3.1 LaMer diagram, demonstrating the growth conditions required to produce a homogeneous dispersion of particles. Figure reproduced from Sugimoto et al.© Copyright 2000 Elsevier Science B. V.

achieved ($C \geq C_s$), the energy barrier to nucleation is so high that the rate of nucleation is lower than the rate of re-dissolution, such that any nuclei that do form in this stage are transient and unstable.\textsuperscript{154} Above $C_{\text{crit}}$, the energy barrier to nucleation can be overcome and the formation of stable nuclei occurs (Stage II). Nucleation causes the monomer concentration to drop until, below $C_{\text{crit}}$, the rate of nucleation becomes negligible. Diffusion controlled growth occurs whilst there is a balance between generation of monomers by the chemical reaction and elimination of the species by diffusion to the nuclei and the concentration is maintained above $C_s$ (Stage III). In this regime, focusing of the size distribution can occur: the number of particles remains approximately constant but the growth rate is inversely proportional to the particle radius, therefore the smallest particles grow the fastest. Once the concentration decreases below supersaturation, defocusing can occur, whereby larger particles grow at the expense of smaller particles due to the strong dependence of nanoparticle solubility on size (Ostwald ripening).

Classic nucleation theory describes the barrier to nucleation thermodynamically; the Gibbs free energy of homogeneous nucleation (formation of spherical particles of radius $r$) is given by:\textsuperscript{154,157}

$$
\Delta G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_v = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \left(\frac{-RT \ln(S)}{V_m}\right)
$$

(3.1)

where $\gamma$ is the surface energy per unit area, and $\Delta G_v$ represents the free energy change between the nucleating (reactant) species in solution and the unit volume of the bulk crystal;
\( V_m \) is the molar volume of the bulk material, \( R \) is the gas constant, \( T \) is the temperature and \( S \) is the supersaturation condition.

The supersaturation condition is given by:

\[
S = \frac{[A][B]}{K_{sp}} \tag{3.2}
\]

where [\( A \)] and [\( B \)] represent the concentration of reacting species (assuming a binary reaction system – for example, \( \text{Zn}^{2+} \) and \( \text{O}^{2-} \) for \( \text{ZnO} \)) and \( K_{sp} \) is the solubility product of the final metal oxide, representing the equilibrium concentration of dissolved ions in solution.

Differentiating equation 3.1 with respect to \( r \) and rearranging gives the critical radius \((d\Delta G/dr = 0)\) above which a particle will grow and below which a particle will dissolve as:

\[
r^* = \frac{2\gamma V_m}{RT \ln(S)} \tag{3.3}
\]

Following nucleation, the final particle size then depends on the number of nuclei, total number of monomers available for growth, and the diffusion conditions during growth.\(^{[155]}\) Qualitatively, it is predicted that, for a constant quantity of reagents, the higher the number of nuclei initially formed, the smaller the resulting particle size will be, as the remaining monomers are distributed equally between all growing nuclei.

Based on equation 3.3, the number of nuclei initially formed will increase with a decrease in the critical radius, which can be achieved by an increase in \( S \) or \( T \), and a decrease in \( \gamma \). These predictions are supported by theoretical calculations carried out by Park et al. (Figure 3.2).\(^{[154]}\) The conditions that induce the most rapid nucleation (high \( S \), high \( T \) or low \( \gamma \)) also result in the fastest drop in monomer concentration, leading to aging mechanisms occurring earlier in the reaction; this trend is reflected in the slow decrease in particle concentration with time for the top curve in Figure 3.2 (b)-(d).

Based on equation 3.3, it is predicted that the final size of the particles can be increased by decreasing the reaction temperature, decreasing the monomer concentration (causing a decrease in \( S \)) and by increasing \( \gamma \), for example by using a solvent with low polarity.

The influence of synthetic parameters on particle size has been demonstrated experimentally. For example, in the case of iron oxide nanoparticles, prepared by a hot injection method,\(^{[158]}\) a higher reagent concentration led to faster nucleation and smaller particles, and a low reaction temperature led to larger particles; however, the sample polydispersity also increased when the temperature was lowered. In another example, the size
Figure 3.2 Numerical simulation of nanoparticle formation and growth. (a) Change in particle concentration and supersaturation as a function of time. (b)-(d) Change in particle concentration with time for varying synthetic parameters: (b) supersaturation, (c) temperature, (c) surface free energy ($\gamma$). Figures reproduced from Park et al.$^{[154]}$ © Copyright 2007 Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim.

of CdSe particles, synthesised by hot injection, was systematically decreased from 5.5 to 3.6 nm by increasing the concentration of bis-(2,2,4-trimethyl-pentyl)phosphonic acid; the acid acts as a surfactant, decreasing $\gamma$ and stabilising the growing nuclei.$^{[159]}$ However, the precise effect of additives such as surfactants can be complicated, as they may play several roles.$^{[160]}$ In addition to stabilising nuclei, they can enhance the solubility of the particles by stabilising the metal ions in non-polar solvents, and alter the reactivity of the precursor complexes, affecting the nucleation rate.

The effect of varying certain synthetic parameters on the size of ZnO particles synthesised by the hydrolysis of methylzinc alkoxides was recently studied by Lizandara-Pueyo et al.$^{[86]}$ In line with the theoretical predictions, it was found that the average particle size decreased with increasing solvent polarity (as expressed by dielectric constant); however, contrary to expectations (equations 3.2 and 3.3), the measured particle size increased with increasing concentration. The proposed explanation for the increase in size with increasing concentration was that the particle size was growth-dominated rather than dependant on the
number of nuclei formed: following the nucleation event, the quantity of precursor available to feed the growing nuclei increases with increasing concentration, leading to bigger particles. An alternative explanation could be that the number of nuclei increases, as predicted by thermodynamic arguments, but as the concentration increases the rate of ripening processes (the growth of larger particles at the expense of smaller particles) also increases due to the effective proximity of the nuclei. The effect of temperature was found to be complex, with an apparent increase in particle size with increasing temperature up to a peak at 25 °C, after which the size decreased with increasing temperature; however, the total change in particle diameter (measured using X-ray diffraction) was on the order of 1 nm and it is unclear whether this size change is significant.

3.1.2 Scope

In this chapter, the novel precursor system for generating organic-capped ZnO nanoparticles in one step is presented and discussed. The effects of varying the synthetic parameters on particle size and morphology are investigated. In particular, variation of the carboxylate loading and decreasing the nucleation rate were trialled as means to systematically increase the particle size; two independent methods are presented for delaying the nucleation rate, namely lowering the reaction temperature and decreasing the rate of water addition. Finally, the identity of a secondary phase, found to appear when the reaction rate was decreased, was determined and the implications for the mechanisms of nanoparticle growth and functionalisation are discussed.

3.2 Key Analytical Techniques

3.2.1 X-ray powder diffraction

X-ray powder diffraction (XRD) exploits the diffraction of X-rays by periodic crystal lattices which have a repeat distance on the order of ångströms – equivalent to the wavelength of the X-rays. The conditions under which the scattered rays constructively interfere with one another, to form peaks in intensity, are described by Bragg’s Law:[161]

\[ n\lambda = 2d \sin \theta \]  

(3.4)

where \( n \) is an integer, \( \lambda \) is the wavelength of the incident radiation, \( d \) is the interplanar spacing and \( \theta \) is the scattering angle. By convention, X-ray diffraction patterns are routinely
recorded for values of $2\theta$ and the observed Bragg peaks act as a fingerprint, allowing for crystal phase identification.

Bragg’s Law is, however, only strictly valid for ideal crystals (perfect crystals of infinite size): it is found that the conditions for destructive interference also rely on the periodicity of the crystal with the result that, in non-infinite crystals, X-rays scattered at angles which are small deviations from the exact Bragg angle are not fully annulled. Finite crystal size leads to a broadening of the line-width of the peaks, which can be quantified using the Scherrer formula: \[^{161}\]

$$t = \frac{0.9\lambda}{B \cos \theta}$$  \hspace{1cm} (3.5)

where $t$ is the thickness of the crystal in a direction normal to the planes which produce scattering at angle $\theta$, $B$ is a measure of the broadening, conventionally taken as the full-width at half-maximum, in radians, of the peak of interest. $B$ represents an angular width in terms of $2\theta$, not a linear width. Thus, XRD can be used to estimate the average particle size. Differences in the size measurement from different planes can indicate the likely aspect ratio (for example, spheres vs. rods), however, the proportion of particles of a particular size and shape cannot be deduced.

XRD has the advantage that the sample size can be very large and hence the apparent average particle size is likely to be representative. However, when the particles are very small, the peaks can be very broad and the signal intensity to noise ratio can be low, which can lead to inaccuracy in calculation. Relative peak intensities are related to the multiplicity of the reflection (the number of symmetry-related planes), the atom type, the relative positions of the atoms, and the interplanar spacing. In addition, the peak broadening can also be affected by lattice strain, which is not accounted for by the Scherrer formula and is particularly apparent at surfaces (of which nanoparticles have a high proportion) and at defect sites (such as oxygen vacancies). \[^{162}\]

The ZnO reference line pattern is shown in Figure 3.3, and the corresponding lattice planes for the first few lines are given in Table 3.1. In this work, the Bragg peaks were fitted using fitting software (Fityk, version 0.9.0). Where possible, the average crystal size was measured using the full-width half-maximum of each peak, however, it was often not possible to reliably fit the (100), (002) and (101) peaks due to the high degree of broadening and overlap; the clearest peaks were those due to scattering from the (102) and (110) planes and, as a minimum, these were the two peaks used to calculate average particle size; where
Figure 3.3 Reference line pattern for ZnO (PDF no. 36-1451, ICDD PDF4+ database)

Table 3.1 Lattice plane data for first five Bragg peaks of ZnO
(data taken from PDF no. 36-1451, ICDD PDF4+ database)

<table>
<thead>
<tr>
<th>hkl</th>
<th>(100)</th>
<th>(002)</th>
<th>(101)</th>
<th>(102)</th>
<th>(110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl</td>
<td>(10(\bar{1})0)</td>
<td>(0002)</td>
<td>(10(\bar{1})1)</td>
<td>(10(\bar{1})2)</td>
<td>(11(\bar{2})0)</td>
</tr>
<tr>
<td>(2\theta) (°)</td>
<td>31.770</td>
<td>34.422</td>
<td>36.253</td>
<td>47.539</td>
<td>56.603</td>
</tr>
<tr>
<td>(d) (Å)</td>
<td>2.8143</td>
<td>2.6033</td>
<td>2.4759</td>
<td>1.9111</td>
<td>1.6247</td>
</tr>
</tbody>
</table>
the measured particle sizes from the two reflections were similar (± 1 nm), an average was taken. The (102) plane has a component along the unique $c$-axis whereas the (110) plane does not; therefore a comparison of the particles sizes measured from the corresponding Bragg peaks was taken as a qualitative representation of the aspect ratio of the particles.

The broadening due to the instrument was measured to be 0.06 – 0.08° $2\theta$, which was corrected for in the size measurements. The strain component of the broadening was not separated from the size component; however, as the calculated sizes based on the Scherrer equation were in good agreement with the sizes measured by other techniques (UV-vis spectroscopy and High Resolution Transmission Electron Microscopy), the effect of strain was assumed to be negligible.

3.2.2 High Resolution Electron Transmission Microscopy

High resolution Electron Transmission Microscopy (HR-TEM) is an imaging technique used for obtaining information about particle morphology and crystallinity. Elemental analysis can be carried out using energy-dispersive X-ray spectroscopy (EDX) or electron energy loss spectroscopy (EELS). HR-TEM can be a powerful technique for analysing number-average particle size and the particle size distribution; however, its significance is limited by the small sample size: very small quantities of particles are deposited on each grid and only a few areas can be measured at one time, which increases the chances that the region measured is not characteristic of the whole sample.

In the case of the nanoparticles produced in this project, the TEM images typically had poor contrast between the particle edges and the carbon film background, due to the small size of the particles (and therefore high transparency relative to the support) and the presence of organic molecules on the surface (Figure 3.4). The poor resolution is likely to have introduced systematic errors in size measurement. In addition, as larger particles are easier to see, it is likely that there was a slight systematic measurement bias towards larger particle sizes.
3.2.3 Optical Absorption Spectroscopy (UV-vis)

The ultraviolet absorption spectra of bulk semiconducting materials are largely associated with transitions between the valence band and the conduction band and, as such, give a measure of the band-gap of the material. It should be noted that transitions can also occur which relate to structural defects. In the nano-regime, quantum size effects cause the semiconductor electronic bands to become more like molecular orbitals, leading to a widening of the band-gap with decreasing size. Below a certain size, the blue-shift in the absorption spectrum associated with the increase in band-gap becomes observable, and it is possible to use this shift to estimate particle size (for ZnO the critical size is approximately 7 – 10 nm). In the regime of strong confinement - where the average crystalline radius, \( r \), is much lower than the exciton Bohr radius - the effective mass model developed by Brus may be applied: \(^{163}\)

\[
eE_g = eE_g^{\text{bulk}} + \frac{\hbar^2 \pi^2}{2r^2} \left( \frac{1}{m_e m_0} + \frac{1}{m_h m_0} \right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 r} + \text{smaller terms} \tag{3.6}
\]

where \( E_g^{\text{bulk}} \) is the bulk energy gap (3.37 eV), \( r \) is the particle radius, \( m_e \) is the effective mass of the electrons, \( m_h \) is the effective mass of the holes, \( m_0 \) is the free electron mass, \( \hbar \) is Planck’s constant divided by \( 2\pi \), \( \varepsilon \) and \( \varepsilon_0 \) are the relative permittivity of the material and free space respectively, and \( e \) is the charge on the electron (\( m_e = 0.24 \), \( m_h = 0.45 \), \( \varepsilon = 3.7 \)).
The Brus model is a good approximation for some semiconductors but ZnO has a limited deviance from an $r^{-2}$ dependence of energy.\[^{162}\] Some have shown that the Brus model is a reasonable approximation,\[^{67, 97}\] however it is only applicable when $\lambda_{\text{max}}$, the wavelength for which the absorption is at a maximum, is used.\[^{61}\] For ZnO nanoparticles $\lambda_{\text{max}}$ can be difficult to determine as the absorption curve is not symmetrical and does not have a defined maximum (Figure 3.5). Several groups have used the absorption onset as an approximation of $E_g$. In the current study, however, the choice of onset was unclear: an onset based on extrapolation from the baseline and the absorption edge (the red end of the peak) is highly subjective and will be affected by any broadening in this region; an onset based on extrapolation from the blue end of the peak is difficult to measure as there is no flat region below 350 nm (i.e. “in front” of the peak maximum). Instead, it was decided that the approximation empirically derived by Meulenkamp would be used.\[^{164}\] The wavelength at which the absorption was at half the maximum value, $\lambda_{1/2}$, was related to the particle diameter, $d$, by:

$$\frac{1240}{\lambda_{1/2}} = 3.556 + \frac{799.9}{d^2} - \frac{22.64}{d}$$

Equation 3.7 is valid for particle diameters between 2.5 and 6.5 nm. The value of $\lambda_{1/2}$ was estimated as the maximum in the derivative of the absorption spectrum for each sample, which is expected to deviate from the true $\lambda_{1/2}$ by less than 1 nm. For the current study, the results calculated by this method were in excellent agreement with the results obtained from HR-TEM and XRD measurements.

Optical absorption spectra analysed in this way give an estimate of the volume-weighted average particle size: the measured absorption is related to the cross-sectional area of absorption (larger particles have a larger absorption area therefore the intensity of the signal from these particles will be disproportionately larger than the signal for smaller particles). Because of this bias toward larger particles, the apparent average particle size calculated from UV-vis spectra is expected to be larger than the number-averaged particle size.
3.2.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measures the weight loss of a sample as a function of temperature. In the current context, TGA gives a measure of the amount of organic component present and can be used to estimate the percentage of the particle surface area covered by carboxylate ligands (percentage coverage). The theoretical total surface area \( S_T \) of the samples is given as:

\[
S_T = S_p \times N_p
\]  

(3.8)

where \( S_p \) is the surface area per particle and \( N_p \) is the total number of particles, given by:

\[
N_p = \frac{nV_m}{V_p}
\]  

(3.9)

where \( n \) is the number of moles of ZnO, \( V_m \) is the molar volume of ZnO (1.4353 x 10^{-25} \text{ Å}^3 \text{mol}^{-1}) and \( V_p \) is the volume per particle. Assuming that the particles are perfect spheres, rearranging equations 3.8 and 3.9 gives:

\[
\frac{S_T}{S_p} = \frac{nV_m}{V_p} \rightarrow \frac{S_T}{4\pi r^2} = \frac{nV_m}{(\frac{4}{3}\pi r^3)} \rightarrow S_T = \frac{3nV_m}{r}
\]  

(3.10)

where \( r \) is the radius of the particles (average of measurements by HR-TEM, UV-vis, and XRD analysis).
The number of moles of carboxylate per mole of ZnO, \( n_c \), for each sample was calculated from the organic content measured by TGA:

\[
n_c = \left( \frac{W_0/M_c}{W_i/81.39} \right) \tag{3.11}
\]

where \( W_0, W_i \) are the weight percent (wt\%) of organic and inorganic components, respectively, and \( M_c \) is the molecular weight of the carboxylate.

The surface area per carboxylate molecule was estimated as 20 Å\(^2\), based on reported areas for self-assembled carboxylate monolayers.\[^{165, 166}\] The theoretical surface area that could be occupied by carboxylate groups, \( S_s \), was then calculated as:

\[
S_s = Z \times n_c \times 20 \, \text{Å}^2 \tag{3.12}
\]

where \( Z \) is Avogadro’s number, and \( n_c \) is the number of moles of carboxylate (calculated from the total organic content). The ratio of \( S_s \) to \( S_T \) (with \( n \) in equation 3.10 set as 1) gives the percentage coverage.
3.3 Synthesis of ZnO Nanoparticles by Rapid Hydrolysis

The general form of the nanoparticle synthesis is shown in Scheme 3.1. The synthetic conditions were based on those of previous reports for the hydrolysis of ethylzinc alkoxide precursors, and that detailed by González-Campo et al.. Briefly, the organometallic zinc precursors were mixed in dry toluene and, under inert atmosphere, a dilute solution of distilled water in acetone (one equivalent per ethyl group; two equivalents per diethylzinc) was added dropwise over 4 minutes. Growth was continued for 2 h before isolation of the particles by centrifugation.

Acetone was chosen as the solvent for delivery of water as it is miscible with both water and organic solvents, it is non-protic (i.e. it won’t react directly with diethylzinc to eliminate ethane, as an alcohol would) and is a slightly weaker donor than tetrahydrofuran (donor numbers 17.0 and 20.0, respectively), therefore interference in the nanoparticle growth was expected to be minimised. Toluene was chosen as the standard reaction solvent as all of the ethylzinc carboxylates are fully soluble in toluene and, as it is aromatic, was considered an appropriate mimic for polymer systems such as epoxy resins based on the diglycidyl ether of bisphenol A (DGEBA) – the system of interest for later work (see Chapter 4).

The size and quality of the nanoparticles was found to be equivalent (HR-TEM, UV-vis, XRD) regardless of whether the ethylzinc carboxylate precursor was pre-prepared (isolated and dried prior to use) or generated in situ from diethylzinc and the zinc bis(carboxylate) (Zn(OOCR)$_2$); for the majority of experiments, the ethylzinc carboxylate was generated in situ for ease of handling and in order to maintain the “one-pot” nature of the method.

![Scheme 3.1 General form of the ZnO nanoparticle synthesis](image-url)
3.3.1 Standard Synthesis

The standard synthesis conditions utilised a precursor ratio of diethylzinc to zinc bis(stearate) (ZnSA₂) of 9:1, resulting in a carboxylate loading, [OOCR]/[Zn], of 0.2 (R = (CH₂)₁₆CH₃; n = 0.11 in Scheme 3.1). No colour change was observed during the reaction until, after approximately 60% of the water had been added, a very viscous “gel” phase occurred which became fluid again after approximately 5 seconds, yielding a hazy solution which did not precipitate on standing. The particle suspension could be reversibly dissolved and precipitated on addition of excess toluene and acetone, respectively. After drying in air, the isolated product paste formed a hard, clear pellet; the pellet was assumed to be an amorphous glassy arrangement of the particles, encouraged by interaction of the surface organic groups. On grinding with a pestle and mortar, the particles formed a white, flowing powder. Once isolated and dried, the particles could be easily re-dissolved in toluene or chloroform by heating; toluene solutions (1 mgmL⁻¹) precipitated a white film after standing for two days, but the film could be easily re-dissolved again by heating.

XRD analysis was positive for crystalline, wurtzite ZnO (Figure 3.6 (a)) with extra, broad peaks at low angle due to the organic component (see discussion, section 3.4.2). HR-TEM (Figure 3.6 (c)); showed the particles to be roughly spherical, non-agglomerated, and nearly monodisperse, with a narrow size-distribution (standard deviation, σ = 15%). The average size of the particles was reproducibly between 3 and 4 nm with excellent agreement between the size measurement techniques (mean result of 10 trials: 3.6 ± 0.4 nm by HR-TEM, 3.6 ± 0.2 nm by UV-vis spectroscopy, 3.1 ± 0.4 nm by XRD). The photoluminescence spectrum of the particles (excitation wavelength, λ = 360 nm) is shown in Figure 3.6 (d); the broad peak centred at 520 nm is consistent with the green luminescence previously observed for ZnO nanoparticles, attributed to the presence of oxygen vacancies.⁵³

TGA of the particles indicated a high organic content (38 wt% measured content; 41 wt% expected content) and infra-red (IR) spectroscopy confirmed the presence of carboxylate groups; the carboxylate antisymmetric and symmetric vibrational modes were broadened and shifted compared to ZnSA₂, at 1550 and 1418 cm⁻¹, respectively (1537 and 1398 cm⁻¹, respectively for ZnSA₂). The difference, Δ, between the two modes is 132 cm⁻¹, indicating that the stearate groups still adopt a bridging arrangement (see Chapter 2).¹³³ The presence of a high carboxylate content in the TGA and IR analyses, combined with the lyophilic behaviour of the nanoparticles, was taken as good evidence for the efficient surface-functionalisation of the particles. From the measured organic content, based on an average
Figure 3.6 Example of analyses of nanoparticles synthesized by the rapid hydrolysis method ([OOCR]/[Zn] = 0.2; OOCR = stearate): (a) XRD pattern, with reference pattern (blue lines; PDF no. 36-1451, ICDD PDF4+ database), and a broad peak due to the organic content \((2\theta \approx 20^\circ)\) is marked with “*”; (b) UV-vis spectrum; (c) HR-TEM image with (inset) individual particle showing (101) lattice planes, and size distribution histogram; (d) Photoluminescence spectrum of the particles.

Particle size of 3.6 nm, the calculated surface coverage was 87%. A broad, weak absorption centred at approximately 3400 cm\(^{-1}\) was also present in the IR spectrum, which may be due either to small amounts of residual moisture or to additional surface functionalisation with OH groups.

No meaningful information could be gathered from the \(^1\)H NMR spectrum of the particles, which showed only very broad peaks in the alkyl region.
3.3.2 Particle growth over time

The average particle size as a function of time was determined by taking aliquots from
the reaction mixture at times from 1 - 2880 min (48 h) after the final water addition (note that
a timepoint of 1 min after the final water addition corresponds to 5 min after water addition
began). The trends based on UV-vis spectroscopy and HR-TEM are shown in Figure 3.7.

The results suggest that there is rapid nucleation (t < 1 min) to yield particles of
3 - 4 nm, which are stable until between 2 and 4 h; from 4 h, there is a slow aging process to
yield larger particles. HR-TEM showed samples taken at 2 h and below to be predominantly
spherical particles, whereas there was a greater incidence of ellipsoid particles in the aged
samples (Figure 3.8), suggesting that aging occurs in a manner which increases the
anisotropy of the particles. Qualitatively, the dispersibility of the dried particles also
decreased over time, with the aged (30 - 48 h) samples difficult to re-disperse in toluene than
earlier samples.

Figure 3.7 Plots of the average particle size (measured by UV-vis spectroscopy and TEM)
over time for ZnO particles prepared with a stearate loading of [SA]/[Zn] = 0.2. The error
bars shown are representative of the standard deviation measured for 10 trials of the 2 h
timepoint.
Figure 3.8 Example HR-TEM demonstrating increase in dispersity of particle morphology with reaction time for the standard rapid hydrolysis experiment ([OOCR]/[Zn] = 0.2; OOCR = stearate), from (a) roughly spherical at 30 min after final water addition, to (b) higher incidence of ellipsoid particles at 8 h.

3.4 Variation of Synthetic Parameters

3.4.1 Alkyl chain length

Variation of the alkyl chain length of a surfactant can be beneficial in a variety of ways. For nanocomposite applications it is desirable to have as low a surfactant content as possible in order to minimise the plasticising effect of the surface groups on the polymer matrix; one way of lowering the effective organic content (by weight) of surfactant is to reduce the alkyl chain length. In addition, as discussed in Chapter 1, decreasing the alkyl chain length of surfactants (e.g. amines)\textsuperscript{76} has been found to decrease the aspect ratio of ZnO nanoparticles.

For the rapid hydrolysis method, decreasing the carboxylate alkyl chain length resulted in a slight increase in average particle size but the increase was less than 1 nm overall (stearate, dodecanoate, hexanoate; average size = 3.6 \pm 0.2, 3.9 \pm 0.4, and 4.1 \pm 0.4 nm, by HR-TEM respectively), and no change in particle morphology was observed. The effective organic content was reduced to 20 wt% by using hexanoate (TGA; 22 wt% expected), but a very high calculated surface coverage was maintained (99%).
3.4.2 Carboxylate loading

As the standard synthesis conditions (section 3.3.1) yielded nearly monodisperse nanoparticles with high calculated surface coverage, it was hypothesised that, by reducing the carboxylate content of the reaction, the final particle size could be increased: if the stearate molecules preferentially arranged on the surface in a close-packed monolayer arrangement, then a lower quantity of stearate per mole of Zn would impose a lower total surface area requirement, and hence larger particles.

Solutions were prepared such that the ratio of carboxylate molecules to zinc ions varied but the total concentration of zinc species remained the same. The carboxylate loadings are detailed in Table 3.2; in effect, the total hydrolysable ethyl content and absolute concentration of free diethylzinc increased with decreasing carboxylate loading.

As shown in Figure 3.9, the carboxylate loading had little effect on the particle size; there is a slight increase in the average size (as measured by HR-TEM and XRD), but the overall change is less than 1 nm and is within the standard deviation for each sample.

Representative TEM images and particle size distribution histograms for samples a, c, d, and e (Table 3.2) are shown in Figure 3.10; for samples d and e the polydispersity is broader than for a and c. Qualitatively, samples d and e were more difficult to re-dissolve once dried (e and f were the only samples which precipitated during the synthesis without addition of excess acetone) and agglomerates were observed for both samples by HR-TEM; it was difficult to determine whether the agglomerates were permanent or whether they had occurred during TEM grid preparation.

For the control reaction (sample f, Table 3.2), the primary crystallite size was measured to be $4.0 \pm 0.7$ nm by XRD but HR-TEM showed the particles to be largely agglomerated, forming aggregates on the order of 50 nm – 2 µm (Figure 3.11 (a)); regions between the particles had an appearance similar to that of sintered particles, indicating that the particles had aggregated and become permanently fused during synthesis. Heating the sample to 100 °C for 6 hours resulted in an increase in the measured average size (XRD) to $10.0 \pm 0.2$ nm, indicative of crystallisation within the aggregates; the estimated particle size was confirmed by HR-TEM (Figure 3.11 (b)). In contrast, particles prepared by the standard synthesis (sample b, Table 3.2) showed no size change on heating to 100 °C, demonstrating the stability imparted to the particles by the stearate capping groups.
Table 3.2 Variation in the effective concentration of free diethylzinc with the variation of carboxylate loading (calculated based on full conversion of ZnSA$_2$ to [Zn$_5$(SA)$_6$(Et)$_4$];

SA = stearate = OOC(CH$_2$)$_{16}$CH$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>[SA]/[Zn]</th>
<th>ZnEt$_2$ /mmol</th>
<th>ZnSA$_2$ /mmol</th>
<th>Free ZnEt$_2$ /mmol</th>
<th>Free ZnEt$_2$ /M</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.33</td>
<td>0.833</td>
<td>0.167</td>
<td>0.722</td>
<td>0.108</td>
</tr>
<tr>
<td>b</td>
<td>0.20</td>
<td>0.900</td>
<td>0.100</td>
<td>0.833</td>
<td>0.124</td>
</tr>
<tr>
<td>c</td>
<td>0.10</td>
<td>0.950</td>
<td>0.050</td>
<td>0.917</td>
<td>0.137</td>
</tr>
<tr>
<td>d</td>
<td>0.05</td>
<td>0.975</td>
<td>0.025</td>
<td>0.958</td>
<td>0.143</td>
</tr>
<tr>
<td>e</td>
<td>0.01</td>
<td>0.995</td>
<td>0.005</td>
<td>0.992</td>
<td>0.148</td>
</tr>
<tr>
<td>f</td>
<td>0.00</td>
<td>1.000</td>
<td>0.000</td>
<td>1.000</td>
<td>0.150</td>
</tr>
</tbody>
</table>

Figure 3.9 Measured average particle size for ZnO nanoparticles prepared with varying carboxylate loadings. The error bars shown represent the standard deviation for multiple repeat reactions (10 trials for loading of 0.20, 4 trials for loading of 0.00, 2 trials for all other loadings).
Figure 3.10 Representative HR-TEM images and size distribution histograms for ZnO nanoparticles prepared with varying carboxylate loadings: [OOCR]/[Zn] = (a) 0.33, (b) 0.10, (c) 0.05, and (d) 0.01.

Figure 3.11 Representative HR-TEM images for ZnO nanoparticles prepared from ZnEt₂ alone (a) dried at room temperature (in air) and (b) after heating in air at 100 °C for 6 h.
XRD showed crystalline, wurtzite ZnO for all carboxylate loadings, but the appearance of the peaks at low angle differed (Figure 3.12). For sample a ([SA]/[Zn] = 0.33) the peaks between 5 - 25° 2θ were sharp and well-defined, and matched those of ZnSA₂. However, the intensities of the peaks between 18 – 28° 2θ were greater relative to those between 5 – 10° than in the reference pattern. Peaks between 18 – 28° are associated with lateral chain packing, whereas peaks at low angle are associated with inter-layer spacing.\textsuperscript{[167]} Therefore, the difference in relative intensities of ZnSA₂ reflections in sample a compared with those of the highly crystalline reference pattern is thought to be due to reduced long-range order (order between ZnSA₂ layers) in a relative to the degree of short-range order (order between SA chains of the same layer).

The IR spectra of the particles are shown in Figure 3.13, along with that of ZnSA₂. The spectrum for sample a matched that of ZnSA₂, supporting the assignment of the observed additional XRD peaks. The carboxylate absorbances broadened and shifted to higher frequency with decreasing carboxylate loading, suggesting that the predominant form of the stearate groups in these samples was a bound, bridging state on the nanoparticle surfaces, rather than as Zn(SA)₂.

The total carboxylate content (TGA) matched the intended loading for each sample which, based on the measured average particle size, corresponds to a decrease in surface
Figure 3.13 Infra-red spectra for ZnO nanoparticles with varying stearate loadings, compared to zinc bis(stearate). Assignments taken from Taylor et al.;[167, 168] “ν” refers to a stretching mode, “δ” refers to a bending mode, and “ρ” refers to a rocking mode.

coverage with decreasing loading (Figure 3.14). The calculated coverage for sample a was greater than 100% (154%), which is consistent with the presence of excess Zn(SA)$_2$.

For the control reaction, TGA showed a mass loss of 9.4 wt%, consisting of a broad loss centred at around 140 °C followed by a second, sharper loss (4 wt%), centred at 370 °C (onset approximately 300 °C). IR spectroscopy (Figure 3.13) indicated that carboxylate groups were present. A possible source of the organic content in the form of acetate groups is by the insertion of oxygen into Zn-ethyl bonds during the hydrolysis reaction. Insertion of oxygen in this way has been shown to generate carboxylate groups for some alkylzinc species;[169] however, the temperature of the second thermal decomposition stage is higher than that for zinc-bound acetate groups (150-282 °C for zinc acetate dihydrate);[170] and the IR carboxylate stretches are shifted relative to zinc acetate: 1588 and 1423 cm$^{-1}$ compared with 1565 and 1450 cm$^{-1}$ for the $\nu_{\text{asymmetric}}$ and $\nu_{\text{symmetric}}$ of the nanoparticles and zinc acetate, respectively. An alternative source is via reaction with carbon dioxide in the air to form species such as zinc carbonate at the surface of the nanoparticles, as has been observed during
The degradation of zinc oxide nanowires.\textsuperscript{[171]} The TGA profile did not entirely match that of zinc carbonate or zinc-bound acetate, therefore it is not possible to draw definite conclusions.

It can be concluded that, for rapid hydrolysis, the particle size is primarily determined by the nucleation step (number of nuclei formed) and that, instead of growth occurring until the size is limited by the formation of a close-packed monolayer of carboxylate on the surface, the particles grow to 3–4 nm and the carboxylate groups are either distributed over the surfaces to give a lower coverage ([OOCR]/[Zn] ≤ 0.2) or are segregated into Zn(OOCR)\textsubscript{2} ([OOCR]/[Zn] > 0.2). From the TGA data, it is estimated that approximately 10 mol\% of Zn is segregated into Zn(OOCR)\textsubscript{2} for the 0.33 loading (60 mol\% of carboxylate groups); it is difficult to estimate the Zn(OOCR)\textsubscript{2} content for the lower loadings as the calculated coverage is less than 100 \% and the IR and XRD peaks corresponding to the organic content are broad.
3.4.3 Precursor Concentration

Precursor solutions ([stearate]/[Zn] = 0.2) were prepared such that, after addition of the acetone/water solution (2.3 mL), the total concentration of zinc species varied from 0.3 M to 0.025 M.\textsuperscript{a} Contrary to the findings of Lizandara-Pueyo \textit{et al.},\textsuperscript{[86]} the particle size was found not to change with concentration (Figure 3.15); this result suggests that the final size is not dictated by number of nuclei formed at the beginning of the reaction but by growth and aging events. The different factors involved are likely to be complex and were not fully explored. However, it may be that the balance between solubility of the monomers (which decreases with increasing concentration) and number of nuclei always favours the same final particle size. That the particle size does not change with increasing concentration is a promising result from the point of view of scale-up of the method: if the quantity of solvent used can be reduced, the method becomes far more viable for large scale production.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.15.png}
\caption{Effect on average particle size of ZnO nanoparticles prepared with varying total zinc concentration (measured by UV-vis spectroscopy; [stearate]/[Zn] = 0.2). Error bars represent the standard deviation measured for 10 trials of the 0.15 M concentration.}
\end{figure}

\textsuperscript{a} Prior to the addition of water, the concentration varied from 1 to 0.027 M.
3.4.4 Solvent

Particles prepared by the standard synthesis in hexane were found to have an average particle size of $4.8 \pm 0.2 \text{ nm}$ and $4.6 \pm 0.2 \text{ nm}$ by UV-vis spectroscopy and HR-TEM, respectively (average of 3 trials). The increase in particle size on going from toluene to hexane as the reaction solvent is consistent with expectations based on the difference in surface energy of the growing particles imposed by each solvent (hexane less polar than toluene). XRD analysis showed wurtzite ZnO but the peaks due to the organic content were sharper than seen for the equivalent reaction in toluene, and were identified as the zinc bis(carboxylate); the XRD pattern was similar in appearance to that of sample a (section 3.4.2) The percentage coverage was estimated as 121%, consistent with the presence of excess Zn(OOCR)$_2$.

3.4.5 Delayed nucleation

3.4.5.1 Low temperature reaction

The standard synthesis ([OOCR]/[Zn] = 0.2; OOCR = stearate; solvent = toluene) was carried out at 0 °C and -78 °C, and the effect of temperature on the average particle size is shown in Figure 3.16; in each case, the solution was kept at the respective temperature during water addition and then for a further 2 h. The solutions were allowed to warm to room temperature for 30 min before isolation.

Overall, decreasing the temperature resulted in an increase in measured average particle size, with good agreement between the measurements by each technique (Figure 3.16). However, the XRD analysis indicated an increase in particle anisotropy with decreasing temperature: the particle size measurement using the (110) reflection was always larger than that of the (102) reflections, as expected from the wurtzite structure anisotropy, but whereas the difference was less than 1 nm for the standard synthesis (20 °C), the difference between the two measurements increased with decreasing temperature (Figure 3.17). In contrast to the effect seen for amine groups (increase in anisotropy along c-axis), the change in anisotropy is along the non-polar directions, from which it can be inferred that the carboxylate groups bind preferentially to the (0001) surfaces. Where larger, apparently round particles were seen by TEM, it is possible that these features were discs rather than spheres.
Figure 3.16 Effect of reaction temperature on the average ZnO nanoparticle size. The error bars represent the standard deviation measured of 10 trials for the 20 °C data point.

Figure 3.17 Plot to show the discrepancy between the average particle size calculated based on the (102) and (110) Bragg reflections (XRD). The error bars for the 20 °C and -78 °C data points are the standard deviations of multiple repeat reactions (10 and 4 repeats, respectively); the error bars for the 0 °C data point are an average of the standard deviations of the 20 and -78 °C data points.
An additional series was carried out at -78 °C with varying carboxylate loading (analogous to section 3.4.2). The average particle sizes, measured by XRD, are shown in Figure 3.18. The discrepancy between (102) and (110) was common for all carboxylate loadings; where available, the measurements using the (002) and (100) reflections are also shown in Figure 3.18. For all samples containing carboxylate, the (100) and (110) measurements were comparable to each other, as were the (002) and (102). For the control sample (diethylzinc only), the (002) measurement was comparable to the (100) and (110) measurements, suggesting that crystallites formed in the absence of carboxylate groups were still roughly spherical; the particle morphology is confirmed by HR-TEM (Figure 3.19).

As seen for the room temperature experiment, the particle size and measured aspect ratio does not vary with carboxylate loading, demonstrating that the nucleation rate is the primary factor in determining the ZnO particle size. In the low temperature reactions, the nucleation rate is slow yielding large particle sizes but increased polydispersity relative to the room temperature reaction (as seen in Figure 3.19).

![Figure 3.18](image)

**Figure 3.18** Plot to show the discrepancy between the average particle size calculated by XRD for ZnO nanoparticles prepared at -78 °C with varying carboxylate loadings. The error bars for the 0.20, 0.10, 0.05, and 0.00 data points are the standard deviations of multiple repeat reactions (minimum 3 repeats); the error bars for the 0.14 and 0.06 data points are an average of the standard deviations for the 0.20-0.00 loadings.
3.4.5.2 Slow Hydrolysis Method

Adding the acetone/water solution at a slower rate (total addition time 58 min, 0.03 equivalents water per Zn per min) was found not to significantly affect the average particle size (HR-TEM: 3.9 nm; UV-vis spectroscopy 4.1 nm), therefore slow hydrolysis by exposure to atmospheric moisture was trialled.

The precursors were prepared in dry toluene with a concentration of total zinc species of 1.0 M. The solution was then made up to volume in vials with either toluene or hexane to a final concentration of 0.15 M, in-line with the final concentration after addition of water in the rapid hydrolysis experiments.

In order to maintain a constant, reproducible humidity atmosphere and to minimise solvent loss during the experiment, the samples were placed into a glass tank that had been equilibrated for at least 18 h with a saturated salt solution and the lid was sealed with vacuum grease. Two relative humidities were chosen: 32% (CaCl_2·6H_2O) and 11% (LiCl). It was not possible to monitor the humidity during the experiment; however the humidity was verified with a digital hygrometer during equilibration and was found not to change during removal and replacement of the lid. Relative humidity (RH) is defined as the ratio of the
absolute measured humidity and the maximum absolute humidity of air at the measured temperature. The reactions were carried out at 20 ± 2 °C which corresponds to a change in absolute humidity of ± 0.5 gm⁻³ (± 0.02 mmoldm⁻³) for the 32% RH solution and ± 0.2 gm⁻³ (± 0.01 mmoldm⁻³) for the 11% RH solution, which was considered negligible.[172]

Once placed inside the tank, the atmosphere was allowed to equilibrate for a further 5 min before stirring began. In preliminary experiments it was observed that, for samples reacted for 2-4 h, the liquid decanted from the samples after centrifugation became hazy on standing, indicating that the reaction was incomplete at this time. Therefore, a longer reaction time of 24 h was used.

The size results were found to be the same (to within the standard deviation) for reactions carried out in hexane and toluene. The size was also found to be independent of carboxylate alkyl chain length.

The average particle sizes measured by XRD for all samples for each relative humidity (RH) over a range of carboxylate loading are shown in Figure 3.20. For both series, a linear region exists, where the average particle size depends on carboxylate loading, but the control experiments (diethylzinc only) yielded much larger crystallites (outside that predicted by linear extrapolation). For each loading, the measured particle size was larger for the 11% RH series than for the 32% RH series.

As seen for the low temperature reactions, there was a discrepancy between the size measurements based on the (102) and the (110) peaks which was greater for the 11% RH series than the 32% RH series (Figure 3.21). For a carboxylate loading of 0.05, it was possible to fit the (002) peak and the size measurement from this peak supported the apparent increase in aspect ratio (measured particle size from (002) 3.6 ± 0.2 nm). HR-TEM also showed particles with sizes and aspect ratios that agreed well with the results from XRD analysis (Figure 3.22)

The majority of samples with carboxylate loadings lower than 0.2 were difficult to redisperse once isolated and dried, hindering characterisation by HR-TEM and UV-vis spectroscopy. The low solubility was attributed to low surface coverage. On decreasing the carboxylate loading from 0.20 to 0.05, the surface coverage was estimated to vary from 100 - 71% for the 11% RH series and from 93 – 48% for the 32% RH series; however, a proportion of the measured carboxylate content is thought to be sequestered to phases other than ZnO (see section 3.5).
Figure 3.20 Effect of carboxylate loading and relative humidity on the average particle size (measured by XRD) of ZnO nanoparticles prepared by the slow hydrolysis method. The error bars represent the standard error in the estimation of the mean for multiple repeat reactions of each data point (6 repeats for 11% RH; 4 repeats for 32% RH). The results are inclusive of all reactions performed in hexane and toluene, and all alkyl chain lengths trialled (hexanoate, dodecanoate, stearate).
Figure 3.21 Plots to show the discrepancy between the average particle size calculated based on the (102) and (110) Bragg reflections (XRD) for ZnO nanoparticles prepared with varying carboxylate loadings, by slow hydrolysis at (a) 32% RH, and (b) 11% RH. The error bars represent the standard error in the estimation of the mean for multiple repeat reactions of each data point (6 repeats for 11% RH; 4 repeats for 32% RH). The results are inclusive of all reactions performed in hexane and toluene, and all alkyl chain lengths trialled.
Figure 3.22 HR-TEM images showing the change in aspect ratio from (a) roughly spherical ([OOCR]/[Zn] = 0.2) to (b) predominantly high aspect ratio ([OOCR]/[Zn] = 0.05) ZnO nanoparticles prepared by slow hydrolysis (11% RH).

UV-vis spectroscopy data taken using the wet product paste (after centrifugation and one washing step) showed the same size trend as the XRD measurements based on the (102) peak, whereas TEM measurements of grids taken from the same samples showed average particle sizes in agreement with the average of the measurements from the (102) and (110) peaks. Some small, spherical particles were observed in all samples (not shown), indicating that the polydispersity of these samples was high; however, TEM observations were in line with XRD measurements that the anisotropy increased with decreasing carboxylate loading (Figure 3.22). The polydispersity in the samples may be a result of particle aging due to the extended reaction time, or may indicate that nucleation and growth are not separated (small particles continue to nucleate whilst larger particles grow).
3.5 Impurity Phases

In both the slow hydrolysis and low temperature experiments, an impurity phase was observed in the XRD patterns of all samples, with intense but broad peaks at $2\theta < 15^\circ$ and two additional peaks at $2\theta = 33$ and $59^\circ$ (e.g. Figure 3.23); the intensity of the additional peaks increased in proportion to the carboxylate loading. The positions and relative intensities of the peaks below $15^\circ$ varied with the carboxylate chain length but the peaks at 33 and $59^\circ$ were common to all experiments.

For the 32% RH slow hydrolysis experiment, it was found that the impurity was largely separated from the bulk ZnO during centrifugation: XRD analysis of solid material from the supernatant showed it to be predominantly the impurity phase whereas the precipitated (bulk) material contained ZnO and sharp peaks at low angle corresponding to the respective Zn(OOCR)$_2$ (Figure 3.24). The fraction of the total product sequestered to the impurity phase increased with increasing carboxylate loading (Table 3.3). There was no significant difference between the carboxylate regions of the IR spectra of the impurity and the isolated ZnO, but there was an increase in absorption due to hydroxyl species for the impurity phase (approximately 3400 cm$^{-1}$).

![Figure 3.23 Example XRD pattern of ZnO nanoparticles containing the impurity phase (peaks marked with “*” are impurity peaks common to all impure samples); blue lines are characteristic ZnO reflections (PDF no. 36-1451).](image)
Figure 3.24 Comparison of XRD patterns of (a) bulk isolated powder and (b) material isolated from the supernatant (“wash material”) for 32% RH series, [OOCR]/[Zn] = 0.2; OOCR = dodecanoate. Black reference lines are ZnO (PDF no. 036-1451); blue reference lines are for zinc bis(dodecanoate) (internal reference).

Table 3.3 Comparison of the percentage of the total isolated solid represented by the bulk (ZnO) powder and the material isolated from the wash liquid for each carboxylate loading (slow hydrolysis method, 32% RH).

<table>
<thead>
<tr>
<th>[OOCR]/[Zn]</th>
<th>Bulk ZnO (%)</th>
<th>Wash Material (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>53.5</td>
<td>46.5</td>
</tr>
<tr>
<td>0.14</td>
<td>51.6</td>
<td>48.4</td>
</tr>
<tr>
<td>0.10</td>
<td>92.6</td>
<td>7.4</td>
</tr>
<tr>
<td>0.06</td>
<td>99.5</td>
<td>0.5</td>
</tr>
<tr>
<td>0.05</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>
In contrast, the impurity could not be separated from samples from the 11% RH slow hydrolysis experiments or the low temperature experiments. The quantity of material isolated from the supernatant was generally on the order of 2 mg or less (insufficient to fully analyse) and the impurity peaks were present in the XRD patterns of the bulk material.

In addition, the same impurity peaks were observed in the standard rapid hydrolysis experiment ([OOCR]/[Zn] = 0.2) when aged for 8 h or more.

Peaks at $2\theta = 33$ and 59° have been observed as an impurity in ZnO previously but have been attributed to a variety of products. For ZnO nanoparticles prepared from zinc bis(acetate) and lithium hydroxide, the impurity was proposed to be a “basic zinc-lithium-acetate complex”, related to basic zinc acetate (zinc oxoacetate, Zn₅O(OAc)₆). The assignment was based on ion chromatography and acid titration methods but no further structural characterisation was carried out.

Recently, Lizandara-Pueyo et al. reported the presence of the impurity peaks in ZnO prepared by the hydrolysis of an alkylzinc alkoxide in the presence of poly(vinylpyrrolidone) (PVP). It was proposed that the impurity was a metastable form of ZnO with α-boron nitride structure. The assignment was based primarily on fitting the experimental XRD pattern with a calculated pattern for the impurity and on HR-TEM observations of a sheet-like structure. The quantity of the impurity was increased by decreasing the reaction temperature and by increasing the reagent concentration; additionally, the phase was found to transform into wurtzite ZnO between 220–280 °C.

Hosono et al. prepared ZnO from alcoholic solutions of zinc bis(acetate) in the absence of base and attributed the impurity peaks to layered hydroxide zinc acetate (LHZA), $\text{Zn}_5(\text{OH})_8(\text{Ac})_2\cdot 2\text{H}_2\text{O}$, by comparison with the powder pattern of LHZA previously reported by Poul et al.. LHZA was proposed to have a brucite structure, with sheets of Zn(OH)$_2$ arranged in edge-sharing octahedra and with one-quarter of the Zn$^{2+}$ sites vacant; Zn$^{2+}$ ions lie above and below the vacancy, occupying tetrahedral sites (Figure 3.25).

The intense, low angle peaks in XRD patterns of the impure samples prepared in this study (Figure 3.23 for example) resemble XRD patterns of related, reported layered hydroxides prepared with long chain alkyl functionalisation. As the quantity of the impurity is strongly correlated with the presence of carboxylate groups (see later), and both IR and TGA analysis show that the impurity contains carboxylate groups, the most likely source of the impurity peaks is a layered double hydroxide compound (LDH), of the form $\text{Zn}_5(\text{OOCR})_x(\text{OH})_{10-x}$. 
Comparison of the TGA profiles for the impurity and for the bulk ZnO isolated from the same experiment are shown in Figure 3.26. The curves appear to be identical with the exception that the curve for the impurity peak is off-set by a mass loss between 100 - 200 °C. It was reported that heating LHZA to 120 °C led to dehydration of the compound, including destructive dehydroxylation to form zinc oxoacetate and ZnO.\textsuperscript{[174]} It is therefore likely that the loss at this temperature in the impurity is also due to a dehydroxylation process. Additionally, all ZnO samples which contain the impurity exhibit a sharp mass loss at 100 - 140 °C in their TGA profile. Samples without the impurity either show a very broad, steady mass loss due to moisture (1–2%) or no loss at this temperature. From the TGA data in Figure 3.26, assuming that the sharp mass loss between 100-140 °C was entirely due to dehydroxylation of OH groups, it was estimated that the composition of the impurity was approximately Zn\textsubscript{5}(OH)\textsubscript{9.5}(OOCR)\textsubscript{0.5}; the intended carboxylate loading of the sample was 0.1 (i.e. [Zn]/[OOCR] = 10) which is consistent with the calculated formula.

The proposal of a layered structure is also supported by the observation of layered species in HR-TEM images of nanoparticle samples; individual strands have been observed in some rapid hydrolysis samples (Figure 3.27 (a) and (b)), whereas large areas of layering have been observed in slow hydrolysis samples with high carboxylate loading (Figure 3.27 (c)). The selected area electron diffraction pattern of a region of the layered compound is shown in Figure 3.27 (d); the most intense rings are measured to lie at spacings which correspond to the powder diffraction reflections at 33 and 59°. In the image
Figure 3.26 TGA profiles of bulk ZnO powder and material isolated from the wash liquid for ZnO nanoparticles prepared by the slow hydrolysis method ([OOCR]/[Zn] = 0.10; OOCR = dodecanoate).

shown, the average layer spacing for the coherent regions was measured to be 30.2 ± 0.3 Å, which matches the distance calculated for a bilayer arrangement of dodecanoate molecules (30.2 Å) and correlates well with the spacing calculated from the powder diffraction pattern (29.4 Å).

To aid the identification of the source of the impurity, the pure ethylzinc carboxylate species were prepared in situ in dry solvent and hydrolysed with excess water (as a dilute solution in acetone, analogous to the rapid hydrolysis experiments). The resulting white powders were isolated after 2 h by removal of the volatile components in order that all phases would remain in the final product (the products would not be separated by washing steps).

The XRD patterns of each derivative are shown in Figure 3.28. The patterns of the long chain alkyl derivatives all possess sharp peaks at low angle which can be identified as the respective zinc bis(carboxylate) as well as additional broad peaks at low angle and the common impurity peaks at 33 and 59°. The broad peaks at low angle match those seen in impure ZnO samples, supporting the assignment that these broad peaks are associated with the impurity. From the broadened peaks it was possible to calculate gallery spacings for each derivative, shown in Figure 3.29. The measured gallery spacings are in good agreement with the estimated lengths of a bilayer of the carboxylates (Figure 3.30 (a)). Both the measured values and the increase in spacing with alkyl chain length (2.2 Å per CH₂ unit) agree with literature values for carboxylate/layered hydroxide hybrids reported in the literature.[31]
Figure 3.27 HR-TEM images of layered compounds: (a) and (b) individual strands, and (c) large area of layered compound, with corresponding selected area diffraction pattern, (d).
Figure 3.28 XRD patterns for hydrolysed pentanuclear complexes, \([\text{Zn}_5(\text{OOCR})_6(\text{Et})_4]\), \text{OOCR} = (a) acetate, (b) hexanoate, (c) dodecanoate, (d) stearate. Reference lines are the respective zinc \textit{bis}(carboxylate); (b) and (c) in-house reference; (a) reference code 00-033-1464; (d) reference code 00-055-1618. Peaks attributed to the LDH species are marked with “*”.
Figure 3.29 Change in gallery spacing (measured by XRD) with alkyl chain length for the LDH species (dark circles) compared to the zinc bis(carboxylate) species (white squares). The value for the stearate derivative (C18) is estimated based on the spacing measured for the (004) Bragg reflection; the values for the other derivatives were estimated directly from the lowest angle peak.

The XRD pattern of the acetate derivative also has sharp peaks - which match well with those of zinc bis(acetate) dihydrate - and a broad peak corresponding to a gallery spacing of 14.8 Å. The measured gallery spacing agrees with the literature value for LHZA (14.7 Å), corresponding to a structure as shown in Figure 3.30 (b).

The IR spectra for the long-chain alkyl derivatives match the spectra for the respective zinc bis(carboxylates) but with an increased absorption in the OH region (centre ~3400 cm\(^{-1}\)), analogous to the impurity material separated from the supernatant of the 32% RH ZnO syntheses. In the case of the acetate derivative, the carboxylate region is broadened slightly relative to zinc bis(acetate).

The TGA profiles for each derivative are shown in Figure 3.31. Each derivative has a sharp mass loss between 100-200 °C, followed by a loss due to carboxylate. For the acetate and stearate derivatives, the sharp loss after 100 °C appears to be separated into two stages, with the onset of the latter stage at 120 °C, in line with LHZA; for the hexanoate and dodecanoate derivatives, the loss appears to only consist of one stage.
Figure 3.30 Schematics for the proposed structures of the LDH species and indicating the gallery spacing: (a) bilayer arrangement for long-chain carboxylates (re-drawn based on Iyi et al.)\textsuperscript{[31]}; (b) arrangement of acetate groups and intercalated water for LHZA (re-drawn based on Poul et al.).\textsuperscript{[174]}

For the stearate and dodecanoate derivatives, the mass of the residual solid after TGA (assumed to be ZnO) matched that which would be expected for the motif $[\text{Zn}_5(\text{OOCR})_6(\text{OH})_4]$ – the product expected for simply hydrolysing all of the ethyl groups of the pentanuclear complex. However, for the hexanoate and acetate derivatives the residual mass was lower than expected (Table 3.4). Basic zinc acetate $[\text{Zn}_4\text{O}($\text{OAc}$)_6]$ has been reported to have a greater mass loss on thermolysis than expected (20-28 wt\% compared to the calculated value of 52 wt\%)\textsuperscript{[170]} and, during the course of this project, pure ethylzinc acetate has also been observed to sublime. Although not previously reported for the pure LHZA, it is possible that some components of the hydrolysed ethylzinc sublime at high temperature. Elemental analysis for each derivative correlates with the expected carboxylate content based on the motif $[\text{Zn}_5(\text{OOCR})_6(\text{OH})_4]$ (Table 3.4).

Heating the acetate and stearate derivatives to 140 °C for 6 hours yielded samples containing ZnO (XRD). IR spectroscopy showed that carboxylate groups were still present after heating; for the stearate derivative, the carboxylate content was identified as ZnSA$_2$ and was seen by XRD to be the predominant phase. The two-phase hypothesis is supported by the observation that, at temperatures above the melting point of ZnSA$_2$ (mp 133-135 °C), the sample vial contained a white solid phase mixed with a clear, molten phase. Heating the hydrolysed complexes in solution did not yield ZnO. It is proposed that the hydrolysis of the pentanuclear ethylzinc carboxylate complexes proceeds by hydrolysis of the ethyl groups (as expected) followed by segregation of a theoretical intermediate to give a mixture of zinc bis(carboxylate) and carboxylate-functionalised LDH (Scheme 3.2); the proposed mixture would give an elemental analysis result equivalent to that expected for $[\text{Zn}_5(\text{OOCR})_6(\text{OH})_4]$, consistent with the observed results.
**Figure 3.31** TGA profiles of the hydrolysed ethylzinc carboxylate complexes; inset is the expanded profile of the stearate derivative to show two-step decomposition in the region 100 – 200 °C

**Table 3.4** Elemental analysis and TGA results for the hydrolysed ethylzinc carboxylate complexes (C_n refers to carbon chain length of the respective derivative: acetate, hexanoate, dodecanoate and stearate). Calculated (calc.) values based on [Zn₅(OOCR)₆(OH)₄]

<table>
<thead>
<tr>
<th>C_n</th>
<th>C</th>
<th>H</th>
<th>OOCR</th>
<th>C</th>
<th>H</th>
<th>OOCR</th>
<th>Calc.</th>
<th>Found</th>
<th>Residual ZnO</th>
<th>OOCR</th>
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<tr>
<td>2</td>
<td>19.24</td>
<td>2.96</td>
<td>47.28</td>
<td>19.16</td>
<td>3.11</td>
<td>47.1</td>
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<td>6</td>
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<tr>
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<td>8.77</td>
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<td>25.8</td>
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<td></td>
</tr>
<tr>
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<td>61.89</td>
<td>10.29</td>
<td>81.16</td>
<td>61.75</td>
<td>10.37</td>
<td>81.0</td>
<td>19.4</td>
<td>18.9</td>
<td>79.1</td>
<td></td>
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</table>
Scheme 3.2 Proposed intermediates for the hydrolysis of the pentanuclear ethylzinc carboxylate species and their interaction with excess ethylzinc hydroxide species to form organic-capped ZnO nanoparticles.

3.6 Discussion

Based on the results of the nanoparticle syntheses, three distinct phases have been identified to occur: (1) ZnO, (2) Zn(OOCR)$_2$, and (3) LDH. The relative quantities of each of the phases have been semi-quantitatively estimated and this information is represented qualitatively in Figure 3.32.

The suggested explanation for the phase distributions, and hence the mechanism for the particle formation, is that the formation of both the ZnO and the LDH are kinetically controlled processes. It is expected that diethylzinc will hydrolyse faster than the ethylzinc carboxylate and both are expected to proceed via a hydroxide intermediate (a product with a Zn-OH group). For the rapid hydrolysis reactions, excess water is added over a relatively short period of time, which minimises the effective difference in reactivities of the various products. In all samples a momentary gel stage is formed which might be a zinc hydroxide/carboxylate gel which then breaks down to give ZnO of uniform sizes.

When the reaction is slowed, by decreasing the water addition rate or by lowering the temperature, the reactivities of both the ethylzinc carboxylate and diethylzinc are slowed, leading to each species spending more time as the respective hydroxide before nucleation and growth occurs. In particular, the stability of ethylzinc hydroxide has been shown to increase.
Figure 3.3.2 “Map” to show the estimated percentage of zinc ions in each of three distinct phases (red = Zn(OOCR)$_2$, blue = LDH, yellow = ZnO), for each set of synthesis conditions.

For the rapid hydrolysis (-78 °C) and slow hydrolysis 11% RH samples, the values were estimated based on the assumption that all mass loss between 100 – 140 °C was due to LDH dehydroxylation; for the slow hydrolysis, 32% RH samples, the values were based on the assumption that all of the material isolated from the wash liquid was pure LDH.

with decreasing temperature: alone or in the presence of excess diethylzinc, ethylzinc hydroxide has a half-life of 6 minutes at 30 °C, 35 minutes at 15 °C and 220 minutes at 0 °C (no information is available regarding the half-life in the presence of excess water). As no hydroxide species were observed in the control samples and the quantity of layered hydroxide increased with increasing carboxylate loading, it follows that the presence of carboxylate groups stabilises the hydroxide intermediates. With increasing loading of carboxylate, a greater quantity of diethylzinc species can be segregated to and stabilised as the hydroxide phase. A corollary of the stabilisation is that a large proportion of the carboxylate groups remain in the hydroxide phase and therefore are not as available to functionalise the surfaces of the growing nanoparticles, leading to the low dispersibility of the nanoparticle samples. However, the increased aspect ratio of the particles resulting from these syntheses implies that some carboxylate is still present on the nanoparticle surfaces to impose anisotropic growth. Alternatively, the anisotropy of the particles may be a direct result of the conversion of the layered structure (innately anisotropic) to ZnO.

A further factor to consider is that, at low temperature, the dynamic exchange between the ethyl groups of the diethylzinc and ethylzinc carboxylate species is slowed; it may be that the incorporation of the carboxylate groups onto the surface of the particles at
room temperature is facilitated by the dynamic exchange mechanism, therefore when this mechanism is slowed, the ethylzinc carboxylate species is encouraged to form and remain in the hydroxide phase.

The presence of the layered hydroxide in aged samples implies that it can also be a by-product of aging; it may be that, if the particles remain in solution, some particles can transform to the hydroxide – taking excess carboxylate away from the surfaces – while larger particles grow. The hydrolysis of pure ethylzinc dodecanoate was followed over time and the intensity of the LDH peaks (XRD) did not change, ruling out the possibility that the appearance of LDH with time is due to crystallisation of LDH which had already formed at the beginning of the reaction.

For this system, it is clear that isotropic increases in particle size cannot be achieved by simply slowing particle formation. Anisotropic growth might be avoided by adding a small amount of a second, dynamic surfactant (e.g. an amine) to slow the growth along the \{100\} directions, however care would need to be taken over the quantity used. Amines introduce particle anisotropy themselves and any size effect imposed by the carboxylate groups may be negated if too large a quantity of amine is used.

An alternative approach could be to fully separate nucleation and growth by seeding – adding extra diethylzinc to a solution containing pre-prepared nuclei. Several trials were carried out during this project in an attempt to grow larger particles by adding diethylzinc to pre-prepared, stearate-capped particles. However, as the measured size of the particles did not increase, it is thought that the carboxylate capping is not sufficiently dynamic to allow growth before the excess diethylzinc nucleates as extra particles of the same size. A possibility could be to use particles stabilised with another surfactant such as an amine or TOPO; however, as mentioned above, the influence of these surfactants on the morphology of the particle and, if applied in a nanocomposite, on the properties of the final product must be considered.

A final possibility could be to add a very small quantity of water (<< 1 equivalent) to a solution of diethylzinc and then add the carboxylate at varying stages after the water addition. It would be necessary to add less than one equivalent of water in order to prevent the nanoparticles forming and aggregating prior to adding the carboxylate. Again, a great deal of method development may be required in order to achieve the correct balance between nucleation and growth and to target the correct timepoint at which to add the carboxylate.
3.7 Summary and Conclusions

It has been demonstrated that, using the standard method ([OOCR]/[Zn] = 0.2), it is possible to prepare organic-capped ZnO nanoparticles that are non-agglomerated and nearly monodisperse, with an average size of 3-4 nm. When isolated after 2 h, washing steps are not required as levels of impurity species are low. The carboxylate content can be as low as 20 wt% if hexanoate is chosen as the capping species. The method is therefore highly applicable to “one-pot”, in situ nanocomposite synthesis.

The size of the particles appears to increase with reaction time due to aging: the size change is less than 1 nm over 24 h for the standard experiment in toluene, but is greater when the reaction is carried out in hexane and for samples with lower loading of carboxylate.

Varying the carboxylate loading at room temperature does not give a significant change in size for the rapid hydrolysis reaction, suggesting that the particle size is controlled by nucleation: size selection occurs based on the number of nuclei initially formed, and the carboxylate groups simply spread out over the particle surfaces or are segregated into the respective zinc bis(carboxylate). A corollary of the constant particle size at room temperature is that the nanoparticle surface coverage can be controlled, which may be advantageous to other nanoparticle applications that require a certain amount of free oxide surface (such as catalysis).

The average particle size can be increased by lowering the temperature or by slowing the rate of reaction (slow hydrolysis by exposure to air). For the slow hydrolysis reactions, the largest particle size was achieved for the lowest tested humidity and therefore slowest reaction rate. However, the increased particle size also corresponded to an increase in polydispersity and increased anisotropy for the lowest carboxylate loadings. The presence of small particles in all samples may be indicative of extended nucleation (nucleation occurring simultaneous to growth) or Ostwald ripening.

A layered hydroxide species occurs when the reaction rate is slowed and during aging; the quantity of layered hydroxide decreases with decreasing carboxylate loading. It is proposed that the layered hydroxide compound is a by-product of the hydrolysis of the ethylzinc carboxylate species and represents an intermediate that is formed during the nucleation and growth processes of ZnO formation.
Chapter 4

ZnO/epoxy Nanocomposites

4.1 In situ ZnO/Epoxy nanocomposites

4.1.1 Introduction

The primary goal of this thesis was to develop a clean, “one-step” synthetic method for generating nanocomposites with homogeneous dispersions of nanoparticles, with a target model system of ZnO nanoparticles in an epoxy resin.

Epoxy resins are thermosetting polymers, the majority of which are based on the diglycidyl ether of bisphenol-A (DGEBA; Figure 4.1), cured by reaction with cross-linking agents such as amines or anhydrides, or by homopolymerisation over a catalyst. Epoxies are widely used engineering materials, applied as adhesives, moulding compounds, encapsulants, coatings, and electrical insulators.[179] Owing to the versatility of epoxy resins, they have been widely investigated as matrices for nanocomposite applications with inorganic fillers. For example, the toughening of epoxy with silica nanoparticles has been investigated,[180-182] and both aluminium nitride and boron nitride have been added to epoxy to yield thermally conductive resins.[183-185] In addition, a large body of carbon nanotube composite research has been carried out using epoxy matrices.[186]

ZnO nanoparticles have been investigated as nanofillers for a variety of electronics applications, including photovoltaics, dielectric materials,[187] and diodes,[188] however, the primary uses of nano–ZnO have been as a UV absorber, both to protect sensitive...
polymers,\cite{68, 88, 189, 190} and to act as a luminescent material.\cite{30} One application of an \textit{ex situ} ZnO/epoxy nanocomposite, for example, was as a phosphor for solid state lighting.\cite{191, 192}

As discussed in Chapter 1, homogeneous nanoparticle dispersions can be achieved and maintained by preparing nanoparticles that are sterically stabilised (to prevent aggregation) and that have surface-functionalisation which is compatible with the polymer matrix (to maximise particle wetting). The primary interest for this section of this chapter was therefore to assess the degree of dispersion that could be achieved using the \textit{in situ} ZnO nanoparticle synthesis method developed in Chapter 3, and relate it to the nature of the particle/epoxy interfacial interaction.

\subsection*{4.1.1.1 Characterisation of interfacial interaction and nanoparticle dispersion}

The degree of nanoparticle dispersion is commonly characterised using microscopy techniques to image the particles and the separation between them directly; in general, smaller mean particle-particle distances are interpreted as improved dispersion.\cite{22} Often the degree of dispersion is directly used as an indication of the nature of the interfacial interaction, with better dispersion associated with favourable interaction and improved wetting.\cite{32}

Another common property used as a means of assessing the nature of the interfacial interaction and degree of nanoparticle dispersion is the composite glass transition temperature, $T_g$. The glass transition temperature represents the temperature below which the polymer is largely amorphous (glassy) and brittle, and above which the polymer chains can freely change their conformation and deform elastically in response to an applied load (rubbery behaviour); as such it is an important engineering property, which describes the behaviour and useful working temperature range of the polymer.

Several methods exist for obtaining a value of $T_g$, based on measurable changes in a property as a function of temperature (such as heat capacity, viscosity, modulus). There is no absolute value of $T_g$; as the glass transition is a dynamic property, relating to a change in the mobility of the polymer chains relative to one another, the precise value obtained is sensitive
to the measurement conditions; however, there are several common factors which determine
the relative $T_g$’s of similar polymers measured in the same way. In general, $T_g$ is increased by
inclusions that restrict polymer motion, such as covalent cross-links or side-groups that
introduce extra regions of chain-chain interaction. Conversely, $T_g$ is decreased by factors that
introduce a higher degree of free volume per chain, such as introducing non-interacting side
groups or by decreasing the molecular weight (increasing the number of chain ends).

The use of $T_g$ to characterise nanocomposite interfaces is derived from, and correlated
with, observed changes in $T_g$ in ultrathin (nanometer scale) films.\cite{20,193,194} It has been shown
that the $T_g$ of a thin film shifts relative to that of the equivalent bulk polymer due to the
formation of regions of polymer with altered mobility at the film surfaces. In free-standing
films and films sandwiched between de-wetting substrates, $T_g$ decreases due to the formation
of a liquid-like layer of surface polymer.\cite{193} Conversely, if the polymer-substrate interfacial
interaction is attractive (wetting), $T_g$ of the film is increased.\cite{194,195} In both cases, the
magnitude of the shift in $T_g$ increases with decreasing film thickness, associated with an
increase in surface area to volume ratio (more of the polymer behaves like the surface).

The relevance of thin film behaviour to that of nanocomposites lies in the analogy of
film thickness to interparticle distance, where particle-particle separation in nanocomposites
is decreased by increased dispersion and increased particle loading. The equivalence of the
two systems has been demonstrated using a range of nanoparticle/thermoplastic polymer
combinations.\cite{20,193-195} for example, the relationship between $T_g$ and surface-surface spacing
for SiO$_2$/polystyrene nanocomposites and films was investigated by Bansal et al.
(Figure 4.2 (a)).\cite{193} Schadler et al. showed that the magnitude and shift of $T_g$ for a variety of
composite systems could be correlated with the strength of the interfacial interaction,
expressed as the difference in solubility parameters [$\delta_s - \delta_p$] of the surface polymer with the
particle surface and the bulk polymer, respectively (Figure 4.2 (b)).\cite{20} For uncapped
particles, and those capped with small molecules, the degree of wetting is primarily
determined by changes in the enthalpy of the system on the inclusion of nanoparticles. For
particles grafted with polymer chains, an entropic contribution becomes important, with
wetting occurring only when the molecular weight of the grafted polymer is close to equal to
or greater than the molecular weight of the bulk polymer.\cite{20,32}

Epoxy nanocomposites have been shown to follow the same trends as thermoplastics
in some cases;\cite{22} however, a recent study showed that the direction and magnitude of the
shift in $T_g$ can be affected by the inherent cross-link density of the bulk matrix. In a recent
Figure 4.2 (a) Comparison between the change in glass transition temperature ($T_g$) with interparticle spacing for SiO$_2$/polystyrene nanocomposites and thin films (image taken from Reference [16], original data from Reference [193]); (b) Change in $T_g$ as a function of the difference in the polymer solubility parameters multiplied by surface area (image taken from Reference [16]). © Copyright Materials Research Society 2007.
study by Putz et al.,[96] the inclusion of carbon nanotubes with favourable interfacial interaction increased the $T_g$ of epoxy resins with low cross-link density, as expected, but decreased the $T_g$ of resins with high cross-link density. It was proposed that an increase in matrix cross-link density corresponded to a reduction in the relative distance that the region of interfacial polymer (interphase) extends away from the particle surfaces; as a result, the observed trend in $T_g$ arises from a trade-off between the formation of a favourable interphase (increase in $T_g$) and the disruption of the otherwise highly dense polymer network by the nanoparticles (decrease in $T_g$). Therefore, for epoxy resins with relatively low cross-link density, $T_g$ is expected to be increased by increasing loadings of nanoparticles with attractive surface-functionality and decreased by increasing loadings of nanoparticles with repulsive surface-functionality, as the formation of the interphase is the dominant factor. For epoxy resins with high cross-link density, $T_g$ will be unchanged or decreased by inclusions of nanoparticles until a particle loading is reached for which neighbouring regions of interphase overlap (percolation).

4.1.2 Scope

In this section, the one-step synthesis of organic-capped ZnO nanoparticles developed in Chapter 3 is applied to the in situ preparation of ZnO/epoxy nanocomposites. Comparison is made between composites prepared without surface-functionalisation (uncapped particles) and those prepared with aliphatic (steaerate, in-line with Chapter 3) and aromatic (benzoate) surface-functionalisation. Both the degree of dispersion, as measured by microscopy, and the relative values of $T_g$ will be used to discuss the nature of the interfacial interaction for each type of composite.
4.1.3 Sample Preparation

A commercially available, two-component epoxy resin system was used, comprising of a low molecular weight derivative of DGEBA ("pre-polymer") and an amine curing agent (Figure 4.3). Both components were viscous liquids at room temperature. The epoxy pre-polymer was dried and degassed under vacuum for 6 h at 65 °C prior to the addition of the organometallic zinc complex(es); the water content of samples of pre-polymer dried in this manner was measured to be between 130 and 170 ppm (Karl Fischer). The measured water content is equivalent to approximately 0.01 mmol H$_2$O per g of resin, which is substoichiometric with respect to the precursor.

The nanocomposite preparation method was the same as that developed by A. Gonzalez-Campo et al. with the exception that hexane was replaced by toluene as the reaction solvent as both the ethylzinc carboxylate precursors and the epoxy pre-polymer were significantly more soluble in toluene than in hexane. Briefly, precursor solutions of 1.0 M [Zn] were mixed with the epoxy pre-polymer and hydrolysed by adding 2 equivalents of water as a solution in acetone. The solvent was then removed, the amine hardener added, and the mixture transferred to moulds for curing. The pre-polymer/curing agent mixture (100:23 pre-polymer:curing agent, by weight) was degassed in the moulds by heating to 100 °C under vacuum, then cured by heating under air at 120 °C for 2 h and 140 °C for 2 h.

For the surface-modified particle composites, the loading of carboxylate [OOCR]/[Zn] was 0.2, in-line with the method used in Chapter 3. The ZnEt$_2$/“EtZn(OOCR)” precursor mixtures were equilibrated for 18 h prior to use, and both the stearate and benzoate derivatives gave clear solutions after gentle heating.

![Figure 4.3 Composition of the amine hardener.](image)

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4.1.4 Analytical Techniques

4.1.4.1 ZnO content

The inorganic content of all of the composite samples was measured by thermogravimetric analysis (TGA). For composites containing uncapped particles, the ZnO content by weight (wt%) was taken directly as the wt% of inorganic residue from the TGA measurement, which was converted to ZnO content by volume (vol%) using:

\[
Vol\% = 100 \times \frac{W/\rho_{ZnO}}{\left(\frac{W}{\rho_{ZnO}} + \frac{(1-W)}{\rho_{epoxy}}\right)}
\]  

where \(W\) is the weight fraction (wt%/100) of ZnO. For surface-modified nanocomposites, the calculation was modified as:

\[
Vol\% = 100 \times \frac{W/\rho_{ZnO}}{\rho_{composite}}
\]  

It should be noted that, although the wt% and vol% of ZnO with respect to the total composite weight and volume is accurate, the relative vol% of epoxy resin is slightly lower in the surface-modified particle composites, due to the presence of the organic groups.

4.1.4.2 X-ray diffraction

The presence of ZnO in the samples was confirmed by X-ray diffraction (XRD): discs of the cured nanocomposites were mounted onto aluminium sample holders for analysis. Detailed discussion of XRD is given in Chapter 3.

4.1.4.3 Transmission Electron Microscopy

The extent of particle dispersion was assessed by transmission electron microscopy (TEM). Slices approximately 90 nm thick were cut from thin bar specimens (2 mm by 2 mm) using a diamond knife microtome and mounted onto a copper grid; slices were taken “through-thickness”. Samples were imaged using an accelerating voltage of 100 kV, to minimise sample damage. Further discussion of TEM is given in Chapter 3.
4.1.4.4 Dynamic Scanning Calorimetry

The glass transition temperatures of the composites were measured using Dynamic Scanning Calorimetry (DSC). DSC is a technique used for measuring changes in the heat capacity of materials as a function of temperature. During a measurement, a sample and a reference are simultaneously heated at a constant rate and the difference in the energy required to heat the sample compared to the reference is recorded (normalised by the mass of the reference and sample pans). The glass transition appears as a step in the resulting heat-flow-temperature curve. The value of \( T_g \) will differ depending on which part of the step transition is analysed (Figure 4.4): the onset of the transition (A) and the point of inflection of the curve (B) are often used, although the choice of \( T_g \) is not often specified; in this thesis both the onset and midpoint are reported, for completeness.

Samples were tested in hermetically sealed aluminium pans and, under \( \text{N}_2 \) flow, subjected to two cycles of heating to 220 °C at 10 °C/min and cooling at 10 °C/min. \( T_g \) was measured from the second heating cycle.
4.1.5 Results and discussion

With the exception of nanocomposites prepared with greater than 10 wt% stearate-capped ZnO nanoparticles, all uncured nano-ZnO/epoxy pre-polymer/curing agent mixtures were easily processible, and behaved in an equivalent manner to the pure epoxy pre-polymer/curing agent mixture on moulding. Above 10 wt% (2 vol%) of stearate-capped nanoparticles, the uncured composite mixtures were highly viscous and unmouldable. Qualitatively, once cured, uncapped and benzoate-capped nanocomposites were stiff and difficult to manually break whereas the stearate-capped composites were brittle; for the 10 wt% stearate loading, some specimens fractured on removal from the moulds.

The XRD patterns of comparable loadings (1 vol%) of uncapped, stearate-capped and benzoate-capped nanocomposites are shown in Figure 4.5; all three patterns show characteristic reflections for ZnO but the reflections are broad and the patterns could not be satisfactorily fitted to give a reliable size measurement. The peak broadening is likely to be due to a combination of the small particle size, and the experimental set-up. As the inorganic content of the resins is low, the penetration depth of the X-rays into the material is on the order of hundreds of microns. Reflections are therefore collected from particles at varying heights relative to the incident beam and the detector, giving rise to shifts in the measured positions of the Bragg reflections.\[199]\n
Transmission electron microscopy (TEM) showed that the nature of the surface modification greatly affects the particle distribution (Figure 4.6). In the absence of capping groups (Figure 4.6 (a) and (d)), the overall distribution of particles throughout the resin was homogeneous, but the dispersion is considered poor as the particles largely formed aggregates (50-100 nm); these findings are equivalent to those previously reported.\[58]\ When stearate was introduced, large agglomerated regions of nanoparticles formed (Figure 4.6 (b) and (e)): despite both the stearate-capped nanoparticles and the epoxy pre-polymer being soluble in toluene, on removal of the solvent the two components phase-segregated. As shown in Figure 4.6 (e), although the particles are aggregated, the particles are separated from one another (they are not permanently fused), indicating segregation due to surface groups. When the capping agent was benzoate – an aromatic moiety compatible with the epoxy resin – well-dispersed and well-distributed ZnO nanoparticles were formed (Figure 4.6 (c) and (f)). The nanoparticle sizes in both Figure 4.6 (e) and (f) are measured to be 3 - 4 nm, in good agreement with the results presented in Chapter 3.
Figure 4.5 XRD patterns of ZnO/epoxy nanocomposites (1 vol% ZnO loading), prepared with different particle surface-functionalisation (vertical lines are the ZnO reference pattern; PDF no. 36-1451, ICDD PDF4+ database).

Figure 4.6 Representative TEM images of ZnO/epoxy nanocomposites with uncapped particles (ZnEt₂ used as single precursor; (a) and (d)), stearate-capped particles ((b) and (e)), and benzoate-capped particles ((c) and (f)).
Figure 4.7 Comparison of $T_g$ for each type of ZnO/epoxy nanocomposite (a) measured from the point of inflection of the glass transition; (b) measured from the onset of the glass transition. Error bars represent the standard deviation of measured values for pure epoxy (4 repeats).

The $T_g$ values for each type of nanocomposite are shown in Figure 4.7. Figure 4.7 (a) illustrates that $T_g$ increased relative to the pure epoxy resin for the uncapped nanocomposites, with a peak at 10 wt% (2 vol%). The increase in $T_g$ - indicating a favourable interfacial interaction between the filler and the matrix - was unexpected based on results seen for related (ex situ) metal oxide/epoxy nanocomposites (such as TiO$_2$). It is suspected that the in situ nature of the synthesis is responsible for the formation of the favourable interaction: the epoxide moieties of the epoxy pre-polymer can coordinate to the diethylzinc precursor prior to - and during - hydrolysis in an analogous manner to that observed for the binding of tetrahydrofuran (and epoxide monomers) to ethylzinc carboxylate species in Chapter 2. Coordination prior to hydrolysis could result in residual adsorption or chemisorption of the polymer to the nanoparticle surface after curing.

The changes in $T_g$ for the surface-functionalised derivatives correlate well with the TEM observations and the expected interfacial interaction: the benzoate-capped nanocomposite $T_g$ increased relative to pure epoxy, in-line with a favourable interfacial interaction; the 5 wt% (1 vol%) stearate-capped nanocomposite had a $T_g$ profile that was very similar to that of the pure epoxy resin but the 10 wt% (2 vol%) sample $T_g$ was markedly lower, in-line with an unfavourable interface. It could be argued that the presence of high
quantities of long-chain alkyl groups could act as plasticisers in the matrix, lowering $T_g$; however, the TEM evidence strongly suggests that phase segregation is the most likely and primary contributing factor to the decrease in $T_g$.

Comparison of Figures 4.7 (a) and 4.7 (b) indicates that, for the uncapped series, the breadth of the transition for a loading of 10 wt% (2 vol%) was comparable to that of the pure epoxy resin ($[T_g, \text{midpoint} - T_g, \text{onset}] = \Delta = 9 \, ^\circ\text{C}$), but that the transition was broad below 2 vol% ($\Delta = 31 \, ^\circ\text{C}$ at 1 vol%), and increased with increasing loading above 2 vol% ($\Delta = 40 \, ^\circ\text{C}$ at 12 vol%). The benzoate-capped nanocomposite also showed a sharp transition ($\Delta = 9 \, ^\circ\text{C}$, 1 vol% loading), whereas the transition was broadened for the stearate-capped nanocomposites ($\Delta = 20 \, ^\circ\text{C}$ at 1 vol%). Broadening of the glass transition has previously been proposed as indirect evidence that percolation (interaction of neighbouring interfacial volumes) is not achieved, whereas a complete shift in $T_g$ gives evidence of percolation.[22] Although percolation could not be proven in this study, the $T_g$ data could be interpreted as an indication that percolation is reached at or near 2 vol% of uncapped particles whereas percolation is reached at or near 1 vol% for benzoate-capped particles. However, further testing of both types of composite is required in order to reliably determine whether the properties of benzoate-capped ZnO nanocomposites are significantly improved compared to uncapped composites of equivalent loading.

A possible reason for broadening of the glass transition for the uncapped nanocomposites at high loadings could be an increase in particle aggregation and segregation. In increasing the loading of ZnO, the precursor concentration and volume of solvent increases (Table 4.1); as such, the method increasingly becomes a solution-blending method (potentially comparable to an ex situ method). At high precursor concentration and, correspondingly, high epoxy dilution, the growing particles may have greater opportunity to aggregate, giving rise to larger secondary particles with lower incidence of epoxy-ZnO surface binding relative to a composite with lower ZnO loading. For composites with larger aggregates of nanoparticles, the resulting surface-area to volume ratio would be reduced, leading to larger regions of bulk polymer unaffected by the interphase.
Table 4.1 Example reagent quantities to demonstrate increase in ZnEt$_2$ concentration with increasing intended nanocomposite loading.

<table>
<thead>
<tr>
<th>ZnO /wt% (vol%)</th>
<th>Epoxy /cm$^3$</th>
<th>1.0 M ZnEt$_2$ /cm$^3$</th>
<th>[Zn] /moldm$^{-3}$</th>
<th>Solvent/epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 (1)</td>
<td>3.75</td>
<td>3.6</td>
<td>0.49</td>
<td>0.96</td>
</tr>
<tr>
<td>10 (2)</td>
<td>3.48</td>
<td>7.0</td>
<td>0.67</td>
<td>2.01</td>
</tr>
<tr>
<td>20 (4)</td>
<td>4.03</td>
<td>18.3</td>
<td>0.82</td>
<td>4.54</td>
</tr>
<tr>
<td>30 (8)</td>
<td>2.91</td>
<td>22.6</td>
<td>0.89</td>
<td>7.77</td>
</tr>
<tr>
<td>40 (12)</td>
<td>2.46</td>
<td>29.7</td>
<td>0.92</td>
<td>12.09</td>
</tr>
</tbody>
</table>

4.2 Hierarchical Composites

4.2.1 Motivation

A final application of the *in situ* method of interest for this project was in the preparation of hierarchical composites of fillers on different length scales, as a means of improving the properties of conventional microcomposites. Hierarchical structures are common in nature, often forming very strong, tough structures from relatively weak, brittle constituents.\sup{[200]} Similarly, in man-made composites, combinations of nano- and microscale fillers have been explored in order to overcome inherent weaknesses in the respective nano-only and micro-only composites. For example, epoxy resins with enhanced toughness have been prepared using mixtures of rubber microparticles and silica nanoparticles, with each filler providing a different and complementary reinforcement mechanism,\sup{[180]} and the growth of nanotubes or nanofibres on conventional macroscale fibres (such as carbon fibre or natural fibres) has been shown to alter the mechanical properties of both the fibre itself and those of the subsequent polymer composites.\sup{[201]}

One application of composites comprising fillers on different length scales that is attracting growing attention is in the synthesis of thermally conductive resins, where metal oxides, such as SiO$_2$ and Al$_2$O$_3$, and binary compounds such as silicon carbide, aluminium nitride, and boron nitride are common filler materials.\sup{[184, 202-204]} When the filler particles are of low aspect ratio (such as spheres), to improve the conductive properties of an insulating
polymer matrix, high loadings of micron-sized particles are desirable in order to maximise the volume of conductive material - forming a percolating network whilst minimising the polymer-particle interfacial resistance.

There are several potential benefits of the addition of nanoparticles to thermally conductive microcomposites. Firstly, theoretical and experimental studies of polymer composite systems have shown that an increase in particle size polydispersity can enhance thermal conductivity through increasing the particle packing efficiency and maximising the particle-particle contact area.\textsuperscript{[183, 205]} The effect can be synergistic:\textsuperscript{[204, 206]} for example, a recent study showed that the improvement in the thermal conductivity of polyimide films was greater for composites containing mixtures of 70 nm and 1 µm particles of boron nitride (70:30 micro:nano) than for comparable loadings of either micro or nanoparticles alone.\textsuperscript{[206]} Secondly, as previously discussed, the addition of nanofillers is expected to introduce secondary reinforcement mechanisms, yielding composites with improved mechanical properties. Finally, high loadings of microparticles can result in (pre)polymer melts with high viscosity, hindering processing (moulding, extruding). In contrast, \textit{in situ} prepared nanoparticle composite (pre)polymers show a relatively low increase in viscosity with loading;\textsuperscript{[58]} therefore, it is expected that better quality composites of high loading, with improved density and processibility, can be achieved using micro/nano mixtures than with microparticles alone. To the author’s knowledge, maximising filler loading in this way has not previously been investigated.

\textbf{4.2.2 Scope and aims}

The primary aim of this section was to prepare ZnO/epoxy resins with the maximum achievable, processible loading of microparticles and to use the \textit{in situ} ZnO nanoparticle synthesis method to increase the total particle loading. The effect of the inclusion of nanoparticles on the composite density and thermal conductivity, in particular with regards to whether the thermal conductivity was improved beyond that of the microcomposite with the highest microparticle loading alone, was used to assess the success of the method. As thermal conductivity is a through-thickness (volume-averaged) property, the loading of microparticles was kept at a constant volume fraction while nanoparticle loading was increased.
4.2.3 Sample Preparation

Submicron sized fillers were sourced from Strem Chemicals, with an average particle size of 0.3 ±0.2 µm (SEM, courtesy of D. Anthony; Figure 4.8). A reference series of composites (referred to as microcomposites from herein) were prepared by melt blending of the submicron particles into the epoxy pre-polymer at 65 °C.

A series of hierarchical composites was prepared by diluting portions of a stock solution of in situ nano-ZnO/epoxy pre-polymer/curing agent, containing 20 wt% (4.9 vol%) uncapped nano-ZnO, prepared by the method described in 4.1.3 (see also 6.3.2.1) and adding submicron-ZnO by melt-blending at 65 °C.

4.2.4 Analytical Techniques

4.4.2.1 Thermal Conductivity

The thermal conductivity, λ, of a material is given by:

\[ \lambda = \alpha \times C_p \times \rho \]  

(4.8)

where \( \alpha \) is the thermal diffusivity, \( C_p \) is the heat capacity, and \( \rho \) is the density of the material.

4.2.4.2 Density

The density of the composite samples was measured using Archimedes’ principle: the mass of the sample was recorded in air and suspended in distilled water and the density calculated using the relations:
\[ \rho_s = \frac{M_s}{V_s} = \frac{M_s \cdot \rho_w}{M_s - M_s'} \]  

(4.3)

where \( \rho_s, \rho_w \) are the densities of the sample and water, respectively, \( M_s \) is the sample mass in air, \( M_s' \) is the apparent mass of the sample when suspended in water, and \( V_s \) is the volume of the sample. The ambient temperature of the room was recorded at the time of measurement and the density of water was adjusted accordingly.

The expected density of the composites was estimated using the Rule of Mixtures:

\[ \rho_c = f_f \rho_f + f_m \rho_m \]  

(4.4)

where \( \rho_c, \rho_f, \rho_m \) are the densities of the composite, filler, and matrix, respectively, and \( f_f, f_m \) are the volume fractions of filler and matrix, respectively. The density of ZnO was taken to be 5.61 g cm\(^{-3}\)\[^{[172]} \] and the density of the pure epoxy resin was measured to be 1.145 g cm\(^{-3}\) (assumed to be void-free). More sophisticated methods for estimating the properties of nanoscale composites are commonly in use, particularly for anisotropic particles;\[^{[181]} \] however, for spherical nanoparticles and for the purposes of this project, rule of mixtures is a reasonable first approximation.

4.4.2.2 Thermal diffusivity

Thermal diffusivity is a measure of how quickly a material can change its temperature, and is an indication of a material’s heat transfer properties. In this project, the thermal diffusivity was measured using the Laser Flash method (LFM).

LFM uses a laser pulse to supply an immediate heat change to one side of the sample and the rise in temperature on the opposite side is recorded (for example, using an IR detector; Figure 4.9 (a)). A temperature response curve is obtained (Figure 4.9 (b)) which is fitted to a theoretical model to calculate the diffusivity (in this project the Cowan model was used). In the simplest case where there is no heat loss, diffusivity is calculated as:\[^{[207]} \]

\[ \alpha = 0.1388 \cdot \frac{l^2}{t_{50}} \]  

(4.5)

where \( l \) is the sample thickness (in cm) and \( t_{50} \) is the time taken (in seconds) for the opposing face temperature to reach half of its maximum value.
Figure 4.9 (a) Schematic of the experimental set-up for thermal diffusivity measurement by the Laser Flash Method; (b) Example thermal response curve.

4.4.2.3 Heat capacity

Heat capacity can be calculated from the heat flow data recorded by DSC, by the relation:

\[ C_p = \frac{Q}{m\Delta T} \]  (4.6)

where \( Q \) is the energy (heat flow), \( m \) is the specimen mass and \( \Delta T \) is the change in temperature.

The heat capacities measured by DSC were found to have errors which were larger than any observable trend (Figure A5, Appendix). The precise reason for the large error is unknown but it is thought that small errors in mass measurement, and non-uniformity of the specimen sizes - and therefore specimen volumes - may be contributing factors. Other factors could include differences in moisture content of each sample; however this is considered a small factor, as samples taken from the same batch of composite also varied in the measured heat capacity value.
Heat capacity can also be measured indirectly using the LFM by comparison of the thermal response of a sample with that of a reference sample with known heat capacity. In order for the measurement to be valid, the experimental set-up, material thickness, and the distance between the top surface and the IR detector must be the same for the sample and the reference. Assuming that the energy absorbed by the sample is the same as the reference, the heat capacity of the sample can be calculated using:

\[
(mC_p\Delta T)_{\text{sample}} = (mC_p\Delta T)_{\text{reference}}
\]  

(4.7)

The specific equation used by the software used in this project (LFA Analysis) is included in the Appendix.

As the interest in thermal conductivity in this project was as a comparative measure rather than in determining the absolute values, the values of the heat capacities of the composites were measured using the LFM. An average heat capacity-temperature profile for pure epoxy resin was created using the DSC measurements for 7 samples, and this was used to create a reference sample. The resulting trend in $C_p$ was a slight decrease with increasing filler loading, as predicted by rule of mixtures (Figure 4.10).

\[C_p \; [\text{Jg} \cdot \text{K}^{-1}] \]

**Figure 4.10** Change in heat capacity ($C_p$) with ZnO filler loading, as measured using the Laser Flash Method. Error bars represent the error in the measurement of heat capacity (DSC) for the pure epoxy sample (7 samples).
4.2.5 Results and Discussion

The maximum processible loading of microparticles was found to be 50 wt% (17 vol%); up to and including this loading, the ZnO/pre-polymer/curing agent mixtures were mouldable and, once cured, were free from visible voids. A sample of 60 wt% was prepared but the composite mixture was highly viscous; although the sample could be moulded, full degassing prior to curing was hindered, resulting in a cured resin containing large, visible voids. As expected, the prepared microcomposites had much lower transparency compared with nanocomposites of equivalent loading (Figure 4.11).

A series of hierarchical composites was prepared, maintaining a constant loading of microparticles of 17 vol% but increasing the total ZnO loading using a stock solution of in situ nanoparticles/epoxy prepolymer/curing agent (Table 4.2). Hierarchical composites A and B were easily processible and gave cured resins that were free from visible voids in the bulk. Hierarchical composite C was mouldable prior to curing but, after curing, gave a composite that was very brittle, with little structural integrity; therefore, C was not tested.

Figure 4.11 Photograph of nanocomposites (top) compared to microcomposites (bottom) with equivalent loadings of (left to right) 0, 1, 5, 10, 20, and 40 wt%; samples are discs of 1.6 cm diameter, 2 mm thickness.
Table 4.2 Proportions of stock nano-ZnO/epoxy pre-polymer/curing agent and microparticles used to prepare the hierarchical composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stock$^a$/g (cm$^3$)</th>
<th>Resin Mixture /g (cm$^3$)</th>
<th>μ-ZnO /g (cm$^3$)</th>
<th>Total Vol% ZnO$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.565 (0.41)</td>
<td>0.478 (0.42)</td>
<td>0.951 (0.170)</td>
<td>19</td>
</tr>
<tr>
<td>B</td>
<td>0.848 (0.62)</td>
<td>0.242 (0.21)</td>
<td>0.951 (0.170)</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>1.130 (0.83)</td>
<td>-</td>
<td>0.951 (0.170)</td>
<td>21</td>
</tr>
</tbody>
</table>

$^a$ Stock solution contained the equivalent of 20 wt% (4 vol%) ZnO nanoparticles.

$^b$ Total vol% is the expected value.

Scanning electron microscopy (SEM; Figure 4.12, courtesy of T. Herceg) showed that the distribution of the particles within the microcomposites was generally good, with aggregate sizes up to 1 - 2 μm; in a few instances, aggregates of particles on the order of 10 - 30 μm were observed (Figure 4.12 (g) and (h)).

Figure 4.13 shows the change in density with ZnO loading for the microcomposites and hierarchical composites A and B, compared with the series of uncapped in situ nanocomposites (see section 4.1.3). The densities of the nanocomposites matched those predicted by rule of mixtures for all loadings, and fitting of the data (Figure A6, Appendix) gave an extrapolated density of the nano-ZnO of 5.64 ±0.02 gcm$^{-3}$ which is in agreement with the literature value for bulk ZnO.$^{[172]}$

In contrast the microcomposites only achieved full density up to 20 wt% (5 vol%); the density fell to 97% of that expected for a loading of 50 wt% (17 vol%) and the density of the 60 wt% microcomposite was 85% of the expected value. Fitting of the microcomposite data between 0-50 wt% (Figure A7, Appendix)) gave an extrapolated value of the submicron-ZnO density of 5.20 ± 0.2 gcm$^{-3}$, which implies the introduction of either surface-bound moisture or voids (air bubbles) around the particles. Other than air, the most likely source of vapour bubbles generated in the curing resins is the volatile component of the hardener which can then become trapped in the viscous resin mixture. It is possible that water adsorbed on the particle surfaces could generate bubbles, however, it seems unlikely that water is a major source of vapour bubbles as water is deliberately added to the precursor solutions in the nanocomposite synthesis and these composites are fully densified.
Figure 4.12 Example SEM images of tensile fracture surfaces of ZnO/epoxy microcomposites, at increasing magnification (left to right), showing the dispersion of particle agglomerates (dense white regions) within the resin: (a), (b), (c) 5 wt% (1 vol%); (d), (e), (f) 30 wt% (8 vol%); (g) and (h) isolated regions of poor dispersion observed in 20 wt% (4 vol%) sample.
Importantly, the hierarchical composites were fully dense, implying that the nanoparticles enhanced the mixing of the polymer and filler particles. These results are contradictory to those of Yung et al. who found that hierarchical composites had a lower density than micro or nano alone;\textsuperscript{[185]} however, in their study, both types of particle were introduced \textit{ex situ} which is likely to have influenced void formation.

One explanation for the increased density is that the nanoparticles migrate to the interface between the submicron particles and the polymer, filling voids that might otherwise be less dense. In light of the findings of section 4.1.5, the favourable interface between the nanoparticles and the matrix could enhance the microparticle-epoxy interface by creating regions of epoxy-nanoparticle favourable interface around the microparticle surfaces. Alternatively, the nanoparticles may simply alter the overall polarity of the matrix to improve wetting of the microparticles. A further possibility is that the nanoparticles act as nucleation sites for vapour bubble formation, leading to better removal of volatiles during curing and hence a more dense composite.

The microcomposites showed a greater overall improvement in thermal conductivity ($\lambda$) with ZnO loading than the nanocomposites (Figure 4.14); neither set of results followed a
linear increase, with only a small change in $\lambda$ at low loadings. Similar findings have previously been attributed to the need to have a high enough loading to begin to form particle networks (percolation) before conductivity properties begin to improve.\textsuperscript{[185]}

Importantly, while the thermal conductivity of hierarchical composite A was comparable to the 50 wt\% (17 vol\%) microcomposite alone, hierarchical composite B showed a relative improvement in $\lambda$, which is attributed to the formation of conductive networks of nanoparticles between the microparticles. To an extent, there may also be a stiffening of the matrix as a whole, leading to greater conduction of phonons in the matrix itself. However, with only two successful hierarchical composite loadings, it is not possible to determine the trend in the data, especially with respect to whether the observed result is comparable to or improved in comparison to that expected for a linear combination of the respective volume fractions of submicron and nano-ZnO.

The fact that hierarchical composite C did not cure to give a good quality resin is suspected to be due to the loading of microparticles being close to the limit of particle wetting and the limit of composite processibility. Therefore, in order to obtain valuable information regarding the effect of nanoparticle inclusion on the mechanical and thermal properties of
conventional composites, future work should be carried out at lower loadings of microparticles, such as 5-10 vol%, where processibility and composite density is good.

In addition, in this preliminary work, the microcomposite synthesis method was not optimised. A rigorous study would require more detailed work into developing the best blending and curing procedures to ensure that particle dispersion and resin curing is homogeneous. Although local variations in distribution or density do not significantly affect a volume-averaged measurement, such as thermal conductivity, other, more local, properties may be less reliable. For example, aggregates of particles can act as point defects, causing premature failure in tensile testing.

4.3 Summary

The in situ method of preparing organic-capped nanoparticles was shown to be successful, as individual particles were prepared when stearate or benzoate were used as capping agents. The degree of particle dispersion was found to be dependent on the nature of the matrix/capping agent interaction, with a homogenous distribution of well-dispersed particles achieved with benzoate-capped nanoparticles.

For the chosen epoxy pre-polymer/curing agent system, uncapped particles were found to form a favourable interface with the matrix, demonstrating the benefit, and potential improvement in properties, achieved by the in situ method compared with ex situ metal oxide/epoxy nanocomposite routes. In this case in particular, the in situ route can change the nature of the interfacial interaction.

Based on the results of this investigation, it is currently inconclusive as to whether a good dispersion of individual, capped nanoparticles shows an improvement over a reasonable dispersion of secondary (aggregated) uncapped particles at the same nanoparticle loading. However, in-line with expectations, a significant difference was observed between composites with a poor dispersion of individual (stearate-capped) particles and composites with a good dispersion of individual (benzoate-capped) particles. In addition, as the $T_g$ was increased for nanocomposites with favourable interfacial interactions, it can be concluded that the formation of the interphase was a stronger factor than disruption of the cross-linking network in this system.

The in situ method was also found to be effective in producing hierarchical composites with high density and improved thermal conductivity. It would be valuable to test
lower loadings of microparticles than used in this study in order to assess the effect of addition of nanoparticles on the mechanical properties of the composites.
5.1 Summary and Conclusions

Within the field of polymer nanocomposites, one of the main challenges remains to achieve good dispersions of particles with well-controlled surface interactions with the matrix. *In situ* nanoparticle preparation gives the greatest promise for generating well-dispersed and well-distributed particles but traditional sol-gel routes can often generate by-products and/or uncapped particles which are incompatible with the matrix and therefore still show a tendency to agglomerate. The work in this project has gone some way towards addressing the need for a clean *in situ* method for generating surface-modified nanoparticles which interact favourably with (and therefore are wet by) the matrix.

By using a non-stoichiometric mixture of diethylzinc and an ethylzinc carboxylate, carboxylate-capped ZnO nanoparticles were generated, which were of high crystallinity (wurtzite structure; XRD) and had a narrow size distribution ($\sigma = 15\%$; HR-TEM). By using a benzoate capping group, the nanoparticle surfaces were rendered compatible with the diglycidyl ether of bisphenol A and the method was successfully employed *in situ* to generate an epoxy resin with a homogeneous dispersion of individual nanoparticles (TEM).

The method is believed to be versatile with respect to the choice of carboxylate, therefore the system could, in future, be tailored to target further desired surface properties and be applied in a variety of polymeric matrices.

During the course of the project, ethylzinc carboxylate species have been characterised with respect to their solution and solid-state structures, and the solvent-dependence of their structures has been explored.
The effect of varying the reaction parameters on the size and morphology of the ZnO nanoparticles has been studied. The particle size was found to be independent of the carboxylate loading or the absolute concentration of zinc species; therefore the method is considered robust in terms of scale-up and method development (e.g. optimising nanoparticle-surface modifier-matrix loadings and ratios). The particle size increased on lowering the reaction temperature and, by lowering the carboxylate loading, the aspect ratio of the particles increased; however, polydispersity also increased. The same effect was seen for particles prepared by slow hydrolysis (exposure to atmospheric moisture). By slowing the reaction in these two ways, an impurity, believed to be a layered double hydroxide, was formed as a by-product.

Finally, the in situ method was also applied in the preparation of hierarchical micro-ZnO/nano-ZnO/epoxy composites, demonstrating that the inorganic loading of microcomposites could be increased by the addition of in situ prepared nanoparticles. The increase in $T_g$ of nanocomposites relative to that of the pure matrix, implies that the properties of conventional composites can be tuned and improved by the addition of small amounts of nano fillers; however, further investigation is required to verify this claim.

5.2 Future Directions

5.2.1 Alkylzinc Carboxylates

The most interesting avenue for future work in this area is in catalysis of the copolymerisation of CO$_2$ and epoxides, with a view to optimisation of the conditions. As was found by Darensbourg et al., higher pressures of CO$_2$ and, to a lesser degree, higher temperatures are likely to improve the carbonate content of the copolymers.$^{[144]}$ Altering the carboxylate group or sulfitation of the ethyl groups to improve the reactivity (in-line with Eberhardt et al.)$^{[152]}$ could also be investigated. However, work in this area should be undertaken with care so as not to lose the main advantage (low cost) of the acetate derivatives. Further work is already being carried out in the Williams/Shaffer groups to study related arylzinc compounds.
5.2.2 ZnO Nanoparticle Synthesis

One aspect of the synthesis that was not achieved was the systematic control of the nanoparticle size in one step and, as discussed in Chapter 3, alternative methods could be explored. However, it is likely that in order to effect size control some of the simplicity of the method will inevitably be lost due to either the introduction of additional ligands, or the use of additional steps such as seeding.

Alternative directions for building on the synthetic method developed here can be divided into two general categories: (i) development of functional ligands, and (ii) application to alternative nanoparticles.

Many applications utilise surface-modified nanoparticles, with the surface modifier playing a variety of roles. For some, such as inkjet printing or liquid based low refractive index lenses, the primary function of the ligands is to induce solubility and prevent aggregation. For biological applications the modifier can be functionalised to, for example, carry a drug or covalently bind with specific proteins.\[208\]

Within the context of nanocomposites, carboxylate ligands could be introduced to the nanoparticle surfaces which contain functionality for covalent binding with the matrix (e.g. amine groups for binding with epoxy resins or PMMA, or halide groups for grafting-from radical polymerisation reactions). The method would need to be fully optimised with regards to the effect of the ligands on the matrix and any effective cross-linking density or interruption of cure kinetics that might occur.

Much work has been done in the area of self-assembling and self-healing polymer networks, comprising telechelic oligomers functionalised with hydrogen bonding units.\[209-212\] It is envisaged that a new kind of self-assembling nanocomposite could be constructed by functionalising nanoparticles with one kind of hydrogen-bonding unit and simply mixing them with oligomers functionalised with a complementary unit; in theory, the loading of inorganic filler could be varied very easily and could be very high, but the composite would remain easily processible. The main limitation would be in the low melting temperature inherent to these materials, related to the breaking of multiple hydrogen bonds.

In applying the nanoparticle synthesis method to alternative nanoparticles, there are again several avenues of research. One would simply be to confirm the prediction that the method is applicable to other metal oxides and chalcogenides. The route is expected to be directly applicable to ZnS and ZnSe; ZnS has already been prepared from diethylzinc and H$_2$S,\[87\] and H$_2$Se is readily available. Polymeric methylaluminium oxide forms on the
reaction of one or two equivalents of water with AlMe$_3$, however no information has been reported for the product of the addition of excess water (to the author’s knowledge). Therefore it is not know whether the reaction is truly transferrable to Al$_2$O$_3$ preparation at present. Related work in forming magnesium oxide from alkylmagnesium alkoxides has recently been carried out, and might also be a material of interest.$^{[213]}$

Another area is in the synthesis of doped nanoparticles. Work has already been carried out by the groups of Driess and Polarz, among others, in doping ZnO with lithium, chromium and aluminium for various applications, such as catalysis and for the preparation of p-type ZnO.$^{[214, 215]}$ The preparation method involves hydrolysis of the alkylzinc alkoxide “cube”, in which one of the corner zinc atoms either possesses a pendant ligand which contains the target metal or has been directly replaced by the desired metal. Manganese-doped ZnS has also been prepared by the introduction of small amounts of in situ prepared diethylmanganese into the reaction mixture of diethylzinc and H$_2$S.$^{[87]}$ Similar routes could be explored using the alkylzinc carboxylates to generate soluble, doped ZnO nanoparticles.

5.2.3 Hierarchical Composites

Building on the preliminary results reported here, a valuable study would be to prepare a range of benzoate-capped ZnO/epoxy nanocomposites in order to fully characterise the mechanical and thermal properties and hence fully explore the effects of the improved nanoparticle dispersion and the favourable nanoparticle/epoxy interfacial interaction. This type of study could also be extended to involve any future work in changing the carboxylate ligand to one which can covalently bind with the matrix to examine whether the overall composite properties improve.

An investigation of the cure kinetics of the nanocomposite resins was not possible in this project but this should be included in any further work in this area following this project.

Additionally, the hierarchical project could be usefully extended to preparing much more rigorous series of composites to look in-depth at the effect of filler size on properties. Future investigations could include mixtures of fillers on three different length-scales (in situ 3-5 nm, 30-50 nm, and 0.3 µm).

Finally, other types of hierarchical structures can be explored. Diethylzinc has previously been applied in the in situ synthesis of ZnO within a photoactive polymer for photovoltaic devices.$^{[89]}$ The group of J. Nelson (Dept. Physics, Imperial College London) has developed photovoltaic cells using combinations of TiO$_2$ and ZnO nanorods;$^{[216]}$ during
this project a collaboration was established to investigate the addition of *in situ* synthesised ZnO nanoparticles to arrays of nanorods embedded in photoactive polymers. At the time of writing, results were yet to be finalised.
Chapter 6

Experimental Methods

6.1 General Methods and Materials

All reactions involving air-sensitive reagents were conducted under a nitrogen atmosphere using either standard Schlenk techniques or in a nitrogen-filled glovebox.

6.1.1 Solvents and reagents

Solvents were distilled from either sodium (toluene, hexane and tetrahydrofuran) or calcium hydride (dichloromethane and pyridine) and stored under nitrogen. Unless otherwise stated, solvents were freshly degassed prior to use by performing at least three freeze-pump-thaw cycles. Deuterated solvents and cyclohexene oxide were dried by placing over calcium hydride, performing three freeze-pump-thaw cycles, refluxing under vacuum for at least 48 h, distilling under vacuum and storing under nitrogen. Diethylzinc was purchased from Aldrich, vacuum distilled and stored in an ampoule, under nitrogen, at -38 °C. Zinc bis(hydroxide) was prepared by salt metathesis of ZnCl₂ and NaOH in aqueous solution. Research grade carbon dioxide from BOC was used for CO₂/epoxide copolymerisation studies. Unless otherwise stated, all other reagents were purchased from commercial suppliers and used as received.
6.1.2 Characterisation methods

6.1.2.1 Chemical characterisation

In general, NMR spectra were collected on a Bruker AV-400 machine. The $^1$H PGSE (DOSY) experiments were performed on a Bruker AV-500 spectrometer, equipped with a z-gradient bbo/5mm tuneable probe and a BSMS GAB 10 amp gradient amplifier providing a maximum gradient output of 5.35 G/cmA. All experiments were measured using the stebpgp1s pulse program (TopSpin 2.1.3 software) at a constant temperature of 300 K and a gas flow of 400 L per hour. The spectra were collected at a frequency of 500.13 MHz with a spectral width of 4000 Hz (centred on 4 ppm) and 32768 data points. A relaxation delay of 10 s was employed along with a diffusion time ($\Delta$) of 70ms. Bipolar gradient pulses ($\delta/2$) of 2.2 ms and homospoil gradient pulses of 1.1 ms were used. The gradient strength of the homospoil pulse was -17.13%. 32 experiments were collected with the bipolar gradient strength, initially at 2% (1st experiment), linearly increased to 95% (32nd experiment). All gradient pulses were sine shaped and after each application a recovery delay of 200 $\mu$s was used. The spectra were processed using an exponential function with a line broadening of 2Hz. Further processing was achieved using the Bruker dosy software or DOSYm software (©NMRtec); PGSE data collection and analysis carried out by Mr P. Haycock, Imperial College London.

Infra-red (IR) spectroscopy was carried out using a Perkin Elmer Spectrum 100 Fourier Transform IR spectrometer: powder samples were analysed using the Attenuated Total Reflection (ATR) accessory; air-sensitive samples were analysed in Nujol mull, using dried NaCl plates. Melting points were measured using a Reichert melting point apparatus, calibrated against benzoic acid. Elemental analysis was carried out using a Carlo Erba CE1108 Elemental Analyser and samples manipulated under inert atmosphere (helium glovebag); analysis performed by Mr S. Boyer at London Metropolitan University, North Campus, Holloway Road, London, N7.

Hydrolysable ethyl content was determined by a liquid displacement method described in the Appendix (section A2).

Gel-permeation Chromatography (GPC) was carried out using a Polymer Laboratories PL GPC-50 instrument, with THF as the eluent and a flow rate of 1 mLmin$^{-1}$; two Polymer Laboratories Mixed D columns were used in series. The instrument was calibrated against narrow $M_w$ poly(styrene) standards.
MALDI-ToF spectra were collected using a Micromass MALDI micro MX mass spectrometer, using a dithranol matrix (in THF). MALDI-ToF spectra were collected by Mr. J. Barton, Imperial College London.

6.1.2.2 Nanoparticle characterisation

Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris 1 TGA machine, under a flow of dry air, from 50 to 800 °C, at a heating rate of 10 °C/min.

Optical absorption spectra were collected on a Perkin Elmer Lambda 950 spectrophotometer using toluene as the solvent and a nanoparticle concentration of 10 μg/mL. Photoluminescence measurements were carried out using a CaryEclipse spectrometer, using chloroform as the solvent and a nanoparticle concentration of 1 μg/mL.

High-resolution Transmission Electron Microscopy (HRTEM) was carried out using a JEOL 2010 microscope at an operating voltage of 200 kV; samples were mounted on 300-mesh, holey carbon-coated copper films (Agar Scientific). Digital images were analysed for particle sizing using the software ImageJ, version 1.40g (W. Rasband, National Institute of Health). Particles were measured manually.

X-ray Diffractometry (XRD) was performed using an X’Pert Pro diffractometer (PANalytical B. V., The Netherlands) and X’Pert Data Collector software, version 2.2b. The instrument was used in the theta/theta reflection mode, fitted with a nickel filter, 0.04 radian Soller slit, 10 mm mask, ¼° fixed divergence slit, and ½° fixed antiscatter slit. Samples were analysed with a step size of 0.0041778°, at a scanning speed of 0.027852° s⁻¹. The diffraction patterns were analysed using Fityk (version 0.9.0; Marcin Wojdyr, 2010): the peaks were fitted to a Pseudo-Voigt function using the Levenberg-Marquardt algorithm and the particle size was calculated using the fitted full-width half-maximum.

6.1.2.3 Composite characterisation

Differential scanning calorimetry was carried out using a TA Instruments Q2000 Differential Scanning Calorimeter. Through-thickness fragments (approximately 2 x 2 x 2 mm) were made from rectangular beam specimens and placed in hermetically sealed pans. The samples were subjected to two temperature scans from 10 to 220 °C at a heating (and cooling) rate of 10 °C/min.

The thermal diffusivity of the samples was performed using a Netzsch LFA 447 NanoFlash Xenon flash apparatus. Test specimens were round discs with diameter
16.1 (± 0.08) mm and thickness 1.50 (± 0.05) mm, polished to give parallel, smooth surfaces. Test specimens were coated on both sides with graphite and loaded into a round sample holder with a 12.7 mm aperture, covered by a mask with a 9.8 mm aperture. The measurement was carried out five times per specimen, at 25 °C (after initial automatic optimisation by the Nanoflash 0.96c software), and the value of the thermal diffusivity was calculated by fitting the thermal response curve using the Cowan model in the LFA Analysis software.
6.2 Synthetic Procedures

6.2.1 Ethylzinc carboxylates

6.2.1.1 Zinc bis(carboxylates)

**Zinc bis(formate), Zn(OOCH)\(_2\)** (based on Wang *et al.*\(^{[217]}\)) Triethylamine (20 mL, 150 mmol) was added dropwise to a solution of formic acid (8.75 mL, 244 mmol) in methanol (30 mL) at -78 °C. The formic acid solution was then allowed to warm to 20 °C and then added to a solution of zinc chloride (12.9 g, 94.5 mmol) in a mixture of water (15 mL) and methanol (10 mL). The mixture was agitated gently and then allowed to stand with a holey film covering over the flask. Colourless, needle-like crystals formed after 1 h; the mixture was cooled to 0 °C and the crystals collected after 2 weeks (8.05 g, 60% based on Zn(OOCH)\(_2\)·2H\(_2\)O). A portion of the crude product (3.16 g) was dried under dynamic vacuum at 90 °C for 6 h, yielding white crystals (2.56 g, 19% mass loss).

**Elemental analysis (%)**: C 15.43, H 1.34 (calculated for C\(_2\)H\(_2\)O\(_4\)Zn: C 15.46, H 1.30)

**IR (ATR)**: \(v = 1651, 1591, 1563, 1357, 1350, 821, 784\) cm\(^{-1}\).

**Zinc bis(hexanoate), Zn(OOC(CH\(_2\)_\(_4\)CH\(_3\)\(_2\))** (as Berkesi *et al.*\(^{[218]}\)). Hexanoic acid (7.6 mL, 6.99 g, 60.2 mmol) was added to a suspension of zinc bis(hydroxide) (1.99 g, 20.0 mmol) in n-octane (200 mL), heated to reflux and stirred for 20 min. The solution was allowed to cool slowly to 20 °C and the resulting white solid was filtered and washed with n-octane (3 \times 20 mL). Crude yield: 5.85 g (99 %). A portion of the crude product (0.505 g) was dissolved in boiling chloroform and filtered. White, needle-like crystals were obtained after 2 days at 0 °C (0.467 g, 93%).

**Elemental analysis (%)**: C 48.83 H 7.44 (calculated for C\(_{12}\)H\(_{22}\)O\(_4\)Zn: C 48.75 H 7.50)

**Melting point**: 140 – 143 °C (lit. 141 - 143 °C\(^{[219]}\), 144 - 145 °C\(^{[218]}\))

**IR (ATR)**: \(v = 2957 ((\text{CH}_3)\text{asymm.}), 2926 ((\text{CH}_2)\text{asymm.}), 2870 ((\text{CH}_2)\text{symm.}), 1588 (w), 1547 (br), 1528 \text{ (br, (COO)asymm.)}, 1467 (\delta(\text{CH}_2)\text{symm.}), 1452 (\delta(\text{CH}_3)\text{asymm.}), 1409, 1398 ((\text{COO})\text{symm.}), 1347, 1296, 1231, 1119 (C-C), 1052, 1008, 954, 892, 847, 725 (\rho(\text{CH}_2)), 579 (\tau(\text{COO})), 547 (\rho(\text{COO}))\) cm\(^{-1}\). Assignments from Taylor *et al.*\(^{[167]}\).
Zinc bis(dodecanoate), Zn(OOC(CH$_2$)$_{10}$CH$_3$)$_2$ (as Berkesi et al.$^{[218]}$). Dodecanoic acid (12.0 g, 60.0 mmol) was added to a suspension of zinc bis(hydroxide) (1.99 g, 20.0 mmol) in n-octane (200 mL), heated to reflux and stirred for 20 min. The solution was allowed to cool slowly to 20 °C and the resulting white solid was filtered and washed with n-octane (3 × 20 mL). Crude yield: 9.32 g (> 100%). A portion of the crude product (0.950 g) was recrystallised from boiling chloroform (150 mL) yielding a crystalline white solid (0.485 g, 51%).

Elemental analysis (%): C 62.09 H 9.89 (calculated for C$_{24}$H$_{50}$O$_4$Zn: C 62.13 H 9.99)

Melting point: 135 – 136 °C (lit. 131 - 132 °C;$^{[218]}$ 133 - 135 °C$^{[168]}$)

IR (ATR): $\nu =$ 2953 ((CH$_3$)asymm), 2917 ((CH$_2$)asymm), 2847 ((CH$_2$)symm), 1536 (sh, (COO)asymm), 1459 (δ(CH$_3$)asymm), 1396 ((COO)symm), 1317, 1257, 1196, 1085, 951, 866, 777, 744, 722 (ρ(CH$_2$)), 576 (τ(COO)), 547 (p(COO)) cm$^{-1}$. Assignments based on Taylor et al.$^{[167,168]}$.

Zinc bis(stearate), Zn(OOC(CH$_2$)$_{16}$CH$_3$)$_2$ (as Taylor and Ellis$^{[168]}$). Stearic acid (28.4 g, 100 mmol) was dissolved in hot ethanol (200 mL) and potassium hydroxide (5.62 g, 100 mmol) was added to give a white suspension. A solution of zinc chloride (6.82 g, 50.0 mmol) in distilled water (10 mL) was added dropwise. Ethanol (20 mL) was added to aid stirring. The flask was then allowed to cool to 20 °C and stirred for 1 h. The resulting white solid was filtered and washed with distilled water (2 × 50 mL), ethanol (2 × 50 mL) and acetone (2 × 50 mL). The product was then washed in hot toluene and filtered to yield a fine, white powder (27.7 g, 87%).

Elemental analysis (%): C 68.31, H: 11.08 (calculated for C$_{36}$H$_{70}$O$_4$Zn: C 68.38 H 11.16)

Melting point: 134 – 136 °C (lit. 128 - 129 °C;$^{[218]}$ 135 - 136 °C$^{[168]}$)

IR (ATR): $\nu =$ 2950 ((CH$_3$)asymm), 2915 ((CH$_2$)asymm), 2848 ((CH$_2$)symm), 1535 (sh, (COO)asymm), 1461 (δ(CH$_3$)asymm), 1397 ((COO)symm), 1103, 946, 742, 723 (ρ(CH$_2$)), 578 (τ(COO)), 550 (p(COO)) cm$^{-1}$. Assignments based on Taylor et al.$^{[167,168]}$.
6.2.1.2 Ethylzinc carboxylates, bulk preparation

1, [Zn(OCOCCH₃)₆(Et)₄]. Diethylzinc (0.496 g, 4.02 mmol) was added to a suspension of anhydrous zinc bis(acetate) (1.11 g, 6.03 mmol) in toluene (5 mL) and stirred for 6 h to give a hazy solution which became clear on heating. Volatiles were removed in vacuo to yield a fine, white powder (1.30 g, 1.63 mmol, 81%).

¹H NMR (C₆D₆): δ = 1.89 (s, 18 H, OOCC₃H₃), 1.56 (t, 12 H, CH₂C₃H₃), 0.61 (q, 8 H, J = 8.0 Hz, CH₃CH₂) ppm;

¹³C{¹H} NMR (C₆D₆): δ = 181.19 (-C=O), 24.76 (H₃CCOO-), 12.90 (CH₃CH₂-), -0.14 (CH₃CH₂) ppm.

Elemental analysis (%): C 30.08 H 4.72 (calculated for C₂₀H₃₈O₁₂Zn: C 30.12 H 4.80)

IR (Nujol mull): ν = 1572 (br, (COO) asymm.), 1545 (br), 1407 ((COO) symm.), 1350, 1226 (w), 1176 (w, δ(Zn-Et)), 1027 (br), 990, 953, 921, 694, 623 (Zn-Et rock), 520 (w, Zn-Et) cm⁻¹.

Assignments based on Coates and Ridley.¹¹³

Hydrolysable ethyl: 13.7% (calculated 14.5%).

2, EtZn(OCOCCH₃)·(C₅H₅N). Diethylzinc (1.0 M in toluene, 1.90 mL, 1.90 mmol) was added to a suspension of anhydrous zinc bis(acetate) (0.346 g, 1.89 mmol) in toluene (3 mL). Pyridine (0.32 mL, 3.97 mmol) was added, forming a yellow solution. The mixture was stirred for 2 h, giving a clear, colourless solution with no particulates. Volatiles were removed in vacuo to yield a sticky white solid. The solid was washed with hexane (5 mL) to yield a dry, white powder (0.317 g, 72%).

¹H NMR (C₆D₆): δ = 8.60 (m, 2 H, pyridine ortho), 6.81 (m, 1 H, J₁ = 1.6 Hz, J₂ = 7.7 Hz, pyridine para), 6.55 (m, 2 H, pyridine meta), 2.07 (s, 3 H, -OOCCCH₃), 1.71 (t, 3 H, J = 8.0 Hz, -CH₂CH₃), 0.81 (q, 2 H, J = 8.0 Hz, -CH₂CH₃) ppm.

¹³C{¹H} NMR (C₆D₆): δ = 179.65 (-C=O), 149.46 (pyridine ortho), 138.47 (pyridine para), 124.88 (pyridine meta), 24.31 (-OOCCCH₃), 13.97 (-CH₂CH₃), -0.80 (-CH₂CH₃) ppm.

Elemental analysis (%): C 46.38, H 5.62, N 5.84 (calculated for C₉H₁₃O₂NZn: C 46.47, H 5.63, N 6.02).

IR (Nujol mull): ν = 1605 (sh, py (C=C) symm.), 1552 (br; (COO) asymm.), 1443, 1342, 1305 (w), 1259, 1217 (sh), 1156, 1071 (sh, py (C=C)), 1040 (sh, py (C=C)), 1013 (py (N-C)), 974, 941, 910, 796, 761, 703, 681, 635 (sh, py γ(CNC), γ(CCC)), 613, 590 cm⁻¹. Assignments based on Perelygin and Klimchuck.¹⁴² and Coates and Ridley.¹¹³
3, EtZn(OOCCH₃). Diethylzinc (0.400 g, 3.24 mmol) was added to a suspension of zinc bis(acetate) (0.593 g, 3.23 mmol) in tetrahydrofuran (5 mL). The mixture was stirred for 4 h to yield a clear, colourless solution. Volatiles were removed in vacuo to yield a fine white powder (0.840 g, 5.47 mmol, 85%).

¹H NMR (THF-d₈): δ = 1.97 (s, 3 H, -OOCCH₃), 1.13 (t, 3 H, J = 8.0 Hz, -CH₂CH₃), 0.09 (q, 2 H, J = 8.0 Hz, -CH₂CH₃) ppm;

¹³C¹H NMR (THF-d₈): 180.24 (-C=O), 23.67 (-OOCCH₃), 13.03 (-CH₂CH₃), 1.71 (-CH₂CH₃) ppm;

Elemental analysis (%): C 31.27 H 5.14 (calculated for C₄H₇O₂Zn C 31.30 H 5.25).

IR (Nujol mull): ν = 1582 (br, (COO) asymm.), 1421 ((COO) symm.), 1362, 1319, 1232, 1177 (δ(Zn-Et)), 1165, 1039 (br), 1022, 995, 957, 928, 900(w), 857(w), 723, 696, 623 (Zn-Et rock), 524 ((Zn-Et)) cm⁻¹. Assignments based on Coates and Ridley.[113]

4, [Zn₅(OOC(CH₂)₁₆CH₃)₄(Et)₄]. Diethylzinc (0.054 g, 0.437 mmol) was added to a suspension of zinc bis(stearate) (0.380 g, 0.601 mmol) in toluene (10 mL) and stirred for 19 h. The resulting suspension was heated gently to give a clear solution with a few undissolved particulates. The solution was filtered and the solvent reduced to yield a swollen, solvated white solid. The product was re-suspended in cold pentane and all volatiles removed in vacuo to yield a white solid (0.160 g, 0.07 mmol, 37%).

¹H NMR (C₆D₆): δ = 2.54 (t, 12 H, J = 8.0 Hz, OOCCH₂(CH₂)₁₂CH₃), 1.72 (m, 24 H, CH₂CH₂ + OOCCH₂CH₂(CH₂)₁₂CH₃), 1.35 (m, 168 H, OOCCH₂CH₂(CH₂)₁₄CH₃), 0.93 (t, 18 H, J = 6.8 Hz, OOC(CH₂)₁₆CH₃), 0.80 (q, 8 H, J = 8.0 Hz, CH₃CH₂) ppm.

¹³C¹H NMR (C₆D₆): δ = 183.51 (-C=O), 38.42, 32.38, 30.28 – 29.65 (12 C, carboxylate chain), 26.41, 23.16, 14.41, 12.85 (CH₃CH₂), -0.16 (CH₃CH₂) ppm.

Elemental analysis (%): C 64.90 H 10.87 (calculated for C₁₁₆H₂₃₀O₁₂Zn₅: C 64.98 H 10.81).

IR (Nujol mull): ν = 1566 ((COO) asymm.), 1540, 1426 ((COO) symm.), 1410 (w), 1399 (w), 1337 (w), 1268 (w), 1169 (w) (δ(Zn-Et)), 668, 614 (Zn-Et rock), 530 (w) ((Zn-Et)) cm⁻¹. Assignments based on Coates and Ridley.[113]
5, EtZn(OOC(CH$_2$)$_{10}$CH$_3$). Diethylzinc (0.970 g, 7.85 mmol) in tetrahydrofuran (5 mL) was added dropwise to a solution of dodecanoic acid (1.60 g, 8.00 mmol) in tetrahydrofuran (15 mL) at -78 °C. The solution was allowed to warm to 25 °C and stirred for a further 6 h. The solid was filtered and washed twice as Parry et al.[220] Volatiles were removed in vacuo to yield a fine, white powder (0.382 g, 1.31 mmol, 16%).

$^1$H NMR ($C_6D_6$): $\delta = 2.53$ (t, 2 H, $J = 7.6$ Hz, OOCCH$_2$(CH$_2$)$_9$CH$_3$), 1.70 (t, 4 H, $J = 8.0$ Hz, -CH$_2$CH$_3$ and OOCCH$_2$CH$_2$(CH$_2$)$_8$CH$_3$), 1.29 (m, 16 H, OOCCH$_2$CH$_2$(CH$_2$)$_8$CH$_3$), 0.93 (t, 3 H, $J = 7.2$ Hz, OOCCH$_2$CH$_2$(CH$_2$)$_8$CH$_3$), 0.79 (q, 1.4 H, $J = 8.0$ Hz, -CH$_2$CH$_3$), 0.09 (q, 0.4 H, $J = 8.0$ Hz, EtZn-CH$_2$CH$_3$) ppm;

Elemental analysis (%): C 57.29 H 9.52 (calculated for C$_{14}$H$_{28}$O$_2$Zn: C 57.24 H 9.61).

6, EtZn(OOCH)·(C$_5$H$_5$N). Diethylzinc (1.0 M in toluene, 2.30 mL, 2.30 mmol) was added to a suspension of zinc bis(formate) (0.355 g, 2.28 mmol) in toluene (3 mL). Pyridine (0.37 mL, 4.60 mmol) was added, forming a yellow solution. The mixture was stirred for 2 h, giving a clear, colourless solution with no particulates. Volatiles were removed in vacuo to yield a clear, colourless liquid (0.284 g, 57%).

$^1$H NMR ($C_6D_6$): $\delta = 8.73$ (s, 1 H, -OOCH), 8.44 (m, 2 H, pyridine ortho), 6.85 (tt, 1 H, $J_1 = 1.6$ Hz, $J_2 = 7.7$ Hz, pyridine para), 6.58 (m, 2 H, pyridine meta), 1.64 (t, 3 H, $J = 8.0$ Hz, -CH$_2$CH$_3$), 0.73 (q, 2 H, $J = 8.0$ Hz, -CH$_2$CH$_3$) ppm.

$^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta = 170.60$ (-C=O), 149.15 (pyridine ortho), 138.90 (pyridine para), 125.11 (pyridine meta), 13.89 (-CH$_2$CH$_3$), 1.84 (-CH$_2$CH$_3$) ppm;

Elemental analysis (%): C 43.88 H 5.00 N 6.43 (calculated for C$_8$H$_{11}$O$_2$NZN Zn C 43.96 H 5.07 N 6.41).

IR (Nujol mull): $\nu = 1609$ (br), 1489 (sh), 1451 (sh), 1447 (sh), 1377 (br), 1262, 1219, 1156, 1071, 1014, 986, 951, 918, 800, 758, 705, 686, 636, 610 cm$^{-1}$.
6.2.1.3 NMR experiments

In general, solutions were prepared by either (1) adding an appropriate volume of a 0.15 M solution of diethylzinc in deuterated solvent to the respective zinc \( \text{bis} \) (carboxylate), or (2) the respective zinc \( \text{bis} \) (carboxylate) was suspended in an appropriate volume of deuterated solvent and diethylzinc (neat) was added via microsyringe to the suspension. Once prepared, the solutions were stirred in a glovebox for 16 h or until clear, before being transferred to Young’s tap NMR tubes for analysis. The ethylzinc stearate and ethylzinc dodecanoate samples required gentle warming, after the incubation period, to aid full dissolution. The relative quantities are given in Table 6.1.

Table 6.1 Relative quantities of reagents used in NMR experiments.

<table>
<thead>
<tr>
<th>Carboxylate</th>
<th>Solvent</th>
<th>Ratio (OOCR:Et)</th>
<th>Zn(OOCR)(_2) /mmol</th>
<th>ZnEt(_2) /mmol</th>
<th>Total volume /mL</th>
<th>[Zn] /M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate</td>
<td>C(_6)D(_6)</td>
<td>2:1</td>
<td>0.180</td>
<td>0.091</td>
<td>0.70</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:1</td>
<td>0.081</td>
<td>0.082</td>
<td>0.50</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:2</td>
<td>0.152</td>
<td>0.304</td>
<td>1.00</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>THF-(d_8)</td>
<td>3:2</td>
<td>0.196</td>
<td>0.131</td>
<td>0.87</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:1</td>
<td>0.078</td>
<td>0.078</td>
<td>0.53</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3:2</td>
<td>0.097</td>
<td>0.064</td>
<td>0.55</td>
<td>0.30</td>
</tr>
<tr>
<td>Hexanoate</td>
<td>C(_6)D(_6)</td>
<td>1:1</td>
<td>0.075</td>
<td>0.076</td>
<td>0.50</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3:2</td>
<td>0.100</td>
<td>0.068</td>
<td>0.45</td>
<td>0.37</td>
</tr>
<tr>
<td>Dodecanoate</td>
<td>C(_6)D(_6)</td>
<td>1:1</td>
<td>0.064</td>
<td>0.064</td>
<td>0.42</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3:2</td>
<td>0.127</td>
<td>0.087</td>
<td>0.57</td>
<td>0.38</td>
</tr>
<tr>
<td>Stearate</td>
<td>C(_6)D(_6)</td>
<td>1:1</td>
<td>0.004</td>
<td>0.008</td>
<td>0.53</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3:2</td>
<td>0.053</td>
<td>0.038</td>
<td>0.54</td>
<td>0.17</td>
</tr>
<tr>
<td>Formate</td>
<td>C(_6)D(_6)</td>
<td>1:1</td>
<td>0.283</td>
<td>0.282</td>
<td>0.93</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:2</td>
<td>0.193</td>
<td>0.382</td>
<td>1.26</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:5</td>
<td>0.090</td>
<td>0.439</td>
<td>1.45</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:4</td>
<td>0.102</td>
<td>0.408</td>
<td>1.37</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:2</td>
<td>0.121</td>
<td>0.241</td>
<td>1.21</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:1</td>
<td>0.084</td>
<td>0.080</td>
<td>0.84</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4:3</td>
<td>0.092</td>
<td>0.069</td>
<td>0.92</td>
<td>0.18</td>
</tr>
</tbody>
</table>
6.2.1.4 Copolymerisation of CO$_2$ and cyclohexene oxide

In a typical experiment, a Schlenk tube was charged with the ethylzinc carboxylate catalyst (0.66 mmol Zn) and cyclohexene oxide (20 mL, 198 mmol) and stirred for 15 min. The solution was transferred to an oven-dried Parr reaction vessel under nitrogen, degassed, and placed under CO$_2$ atmosphere. The reactor was brought to 80 °C under 3 atm. CO$_2$, before increasing the pressure to 15 bar and stirring for 7.5 h. The resulting polymer mixture was removed from the reactor using dichloromethane, and the solvent removed under reduced pressure. The polymeric product was obtained as a clear solid. No further purification was carried out.

Percentage monomer conversion, polymer molecular weight, and polydispersity index (PDI) were determined as described in Chapter 2.
6.2.2 Zinc oxide nanoparticle synthesis

In general, the nanoparticle precursor solutions were prepared such that the total concentration of zinc species was 0.15 M; for the rapid hydrolysis method, the total concentration of zinc species was 0.15 M after the addition of the water solution. For both the rapid and slow hydrolysis methods, two precursor stock solutions were prepared: A) 1.0 M ZnEt₂ in toluene; B) 1.0 M [Zn] in toluene.

Stock solution B was prepared by mixing ZnEt₂ and Zn(OOCR)₂ in toluene in the appropriate ratio to give a carboxylate loading [OOCR]/[Zn] of 0.20 or 0.33, and equilibrating for 2-4 h (OOCR = hexanoate and dodecanoate) or 16 h (OOCR = stearate). The hexanoate and dodecanoate solutions were clear after 2 h; the stearate solutions required gentle heating to achieve full dissolution ([OOCR]/[Zn] = 0.33 was not achievable for stearate at this concentration). After the equilibration period, the solutions were made up to volume using a volumetric flask.

Example synthesis, Stock Solution B Diethylzinc (0.517 g, 4.19 mmol) in toluene (2 mL) was added to zinc bis(dodecanoate) (0.387 g, 0.83 mmol) and stirred for 4 h. The clear solution was made up to 5 mL with toluene ([Zn] = 1.0 M; [OOCR]/[Zn] = 0.33).

Proportions of each stock solution were then mixed and made up to the correct volume with the appropriate solvent in an inert atmosphere glovebox (hexane or toluene; see Table 6.2).

For both types of nanoparticle synthesis (see 6.2.2.1 and 6.2.2.2), after the required reaction time, the particles were precipitated using excess acetone, centrifuged (10000 rpm.; 15 min) and the liquid decanted. The particles were washed by re-suspending in a small amount of fresh toluene and re-precipitating with excess acetone. Centrifugation was repeated and the wet product paste dried in vacuo for 16 h. The liquid decanted from the centrifuge tubes was collected, evaporated, and the residue measured and analysed.

6.2.2.1 Typical synthesis, rapid hydrolysis method

A solution of water in HPLC grade acetone (0.86 M, 2.30 mL, 1.98 mmol H₂O) was added dropwise to the precursor solution (total addition time 4 min); a gel stage was observed after approximately 75% of the water solution was added, lasting 5-10 seconds. The solution was stirred for a further 2 h.
Low temperature reactions: the solutions were maintained at either 0 ±1 °C or 
-78 ±2 °C during the water addition and for the 2 h reaction time. The solutions were allowed 
to warm to 20 °C without stirring (30 min) before isolation of the particles.

Time studies: (1) Analysis by UV-vis spectroscopy: the precursor solution was 
prepared on a 2 mmol scale and aliquots (0.2 mL) were taken at various time points after the 
final water addition, i.e. a 1 min sample is taken 1 min after water addition is complete but 
5 min after water addition commenced (total water addition time 4 min); (2) Bulk analysis: 
the precursor solution was prepared on a 5 mmol scale and aliquots (6.5 mL) were taken at 
various time points after the final water addition. Each aliquot was isolated and treated as 
described above.

6.2.2.2 Slow hydrolysis method

The precursor solutions were prepared and sealed in vials. The vials were brought out 
of the glovebox, the lids removed, and the vials placed in the controlled humidity chamber. 
The solutions were allowed to equilibrate for 15 min before stirring for a further 24 h. No gel 
stage was observed.

Table 6.2 Relative proportions of stock solution and solvent used in preparation of 
nanoparticle precursor solutions.

<table>
<thead>
<tr>
<th>[OOCR]/[Zn]</th>
<th>Stock solution /mL</th>
<th>Solvent /mL</th>
<th>[Zn]† /M</th>
<th>[Et] /M</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>Rapid hydrolysis</td>
<td>Slow hydrolysis</td>
<td></td>
</tr>
<tr>
<td>0.33</td>
<td>-</td>
<td>1.00</td>
<td>3.4</td>
<td>5.7</td>
</tr>
<tr>
<td>0.20</td>
<td>0.40</td>
<td>0.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.14</td>
<td>0.57</td>
<td>0.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.70</td>
<td>0.30</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>0.07</td>
<td>0.80</td>
<td>0.20</td>
<td></td>
<td>5.7</td>
</tr>
<tr>
<td>0.05</td>
<td>0.85</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>1.00</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† total concentration of zinc after addition of water (for rapid hydrolysis)
6.2.2.3 Impurity investigation: Hydrolysis of ethylzinc carboxylate species

Diethylzinc and solvent were added to the respective zinc bis(carboxylate) and the suspension stirred for 2 h, yielding hazy solutions which cleared on heating. A solution of distilled water in HPLC grade acetone was added dropwise (4 min addition time) and the mixture stirred for 2 h under N₂. Volatiles were removed in vacuo to yield a white powder. Reagent quantities are given in Table 6.3.

Table 6.3 Reagent quantities used in hydrolysis of ethylzinc carboxylate species

<table>
<thead>
<tr>
<th>OOOCR</th>
<th>Zn(OOCR)₂ /g (mmol)</th>
<th>ZnEt₂ /g (mmol)</th>
<th>Solvent (mL)</th>
<th>H₂O soln. /mL (mmol H₂O)</th>
<th>Yield /g</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetate</td>
<td>0.567 (3.09)</td>
<td>0.255 (2.06)</td>
<td>toluene (10)</td>
<td>5.0 (4.00)</td>
<td>0.712</td>
</tr>
<tr>
<td>hexanoate</td>
<td>0.366 (1.24)</td>
<td>0.102 (0.83)</td>
<td>hexane (10)</td>
<td>2.0 (8.00)</td>
<td>0.367</td>
</tr>
<tr>
<td>dodecanoate</td>
<td>0.582 (1.25)</td>
<td>0.107 (0.87)</td>
<td>toluene (10)</td>
<td>2.0 (8.00)</td>
<td>0.618</td>
</tr>
<tr>
<td>stearate</td>
<td>0.353 (0.56)</td>
<td>0.046 (0.37)</td>
<td>toluene (5)</td>
<td>1.0 (4.00)</td>
<td>0.333</td>
</tr>
</tbody>
</table>
6.2.3 ZnO/Epoxy composite preparation

The epoxy resin system used was produced by Huntsman Advanced Materials, and consisted of a diglycidyl ether of bisphenol A (DGEBA) and an amine hardener, thermally cured. The DGEBA resin (CY219), was donated by Moldlife Ltd. The hardener (XB3473) was purchased from Robnor Resins.

The composites were cured in silicone moulds, prepared using Elastosil M4641 (Amber Composites) Parts A and B, mixed in a ratio of 10:1 A:B and cured at room temperature for 12 h.

After preparation, the uncured resins were transferred to the PTFE coated silicone moulds and heated under vacuum to 100 °C (approximately 30 min). The vacuum was then released and the samples cured at 120 °C (2 h) and 140 °C (2 h).

The submicron ZnO particles were sourced from Strem Chemicals.

6.2.3.1 Nanocomposite synthesis (see Table 6.4 for reagent quantities)

Epoxy resin was dried under vacuum at 65 °C for 6 h. The ZnO precursor solution was added and stirred to form a homogeneous solution. A solution of distilled water (2 equiv.) in acetone (2-4 mL) was added dropwise and the mixture stirred for 2 h. Volatiles were removed in vacuo for 10 min at 25 °C and a further 30 min at 65 °C. Hardener was then added, mixed well and degassed at 65 °C for 15 min.

6.2.3.2 Microcomposite synthesis (see Table 6.5 for reagent quantities)

DGEBA and submicron ZnO were mixed and degassed under vacuum at 65 °C for 15 min. Hardener was added and the mixture degassed at 65 °C for a further 15 min before transferring to the moulds.
Table 6.4 Reagent quantities and TGA results for nanocomposites

<table>
<thead>
<tr>
<th>Capping agent</th>
<th>Intended wt%</th>
<th>Epoxy /g</th>
<th>Hardener /g</th>
<th>Precursor solution</th>
<th>Measured content /wt%</th>
<th>Vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ZnEt&lt;sub&gt;2&lt;/sub&gt; /mmol&lt;sup&gt;a&lt;/sup&gt;</td>
<td>XA /mmol&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Stearate</td>
<td>5</td>
<td>7.961</td>
<td>1.842</td>
<td>5.94</td>
<td>0.68</td>
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<tr>
<td>Stearate</td>
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<td>5.009</td>
<td>1.172</td>
<td>8.37</td>
<td>0.93</td>
<td>9.8</td>
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<tr>
<td>Benzoate</td>
<td>10</td>
<td>4.057</td>
<td>0.933</td>
<td>4.76</td>
<td>1.00</td>
<td>6.4</td>
</tr>
<tr>
<td>-</td>
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<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>-</td>
<td>5</td>
<td>4.494</td>
<td>1.046</td>
<td>3.6</td>
<td>-</td>
<td>5.1</td>
</tr>
<tr>
<td>-</td>
<td>10</td>
<td>4.173</td>
<td>0.967</td>
<td>7.0</td>
<td>-</td>
<td>9.6</td>
</tr>
<tr>
<td>-</td>
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<td>1.111</td>
<td>18.3</td>
<td>-</td>
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<td>-</td>
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<td>3.492</td>
<td>0.803</td>
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<td>-</td>
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<td>-</td>
<td>40</td>
<td>2.948</td>
<td>0.678</td>
<td>29.7</td>
<td>-</td>
<td>40.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> 1 M solution in toluene.

<sup>b</sup> for stearate-capped, XA = ZnSA<sub>2</sub>; for benzoate-capped, XA = benzoic acid.

Table 6.5 Example reagent quantities and TGA results for microcomposites

<table>
<thead>
<tr>
<th>Intended wt%</th>
<th>Epoxy /g</th>
<th>Hardener /g</th>
<th>ZnO /g</th>
<th>Measured content /wt%</th>
<th>Vol. fraction /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.363</td>
<td>1.233</td>
<td>0.069</td>
<td>1.2</td>
<td>0.3</td>
</tr>
<tr>
<td>5</td>
<td>6.148</td>
<td>1.439</td>
<td>0.397</td>
<td>3.5</td>
<td>0.7</td>
</tr>
<tr>
<td>10</td>
<td>3.848</td>
<td>0.885</td>
<td>0.528</td>
<td>9.4</td>
<td>2.1</td>
</tr>
<tr>
<td>20</td>
<td>4.663</td>
<td>1.079</td>
<td>1.442</td>
<td>19.3</td>
<td>4.7</td>
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<tr>
<td>30</td>
<td>6.212</td>
<td>1.428</td>
<td>3.284</td>
<td>31.0</td>
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<td>40</td>
<td>4.263</td>
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<tr>
<td>50</td>
<td>3.003</td>
<td>0.691</td>
<td>3.699</td>
<td>50.5</td>
<td>17.3</td>
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</table>
6.2.3.3 Hierarchical (micro + nano) composite synthesis (see Table 6.6 for reagent quantities)

Epoxy resin (4.970 g) was dried under vacuum at 65 °C for 6 h. ZnEt$_2$ (1.0 M in toluene, 18.7 mL) was added and stirred to form a homogeneous solution. A solution of distilled water (0.68 mL, 37.8 mmol) in acetone (4 mL) was added dropwise and the mixture was stirred for 2 h. Volatiles were removed under high vacuum for 10 min at 25 °C and a further 30 min at 65 °C. Hardener (1.143 g) was added and mixed well (15 min). Portions of the nano-ZnO/epoxy resin mixture were removed and mixed with submicron ZnO particles and extra epoxy resin to achieve a total volume of 1 mL. The mixtures were stirred manually before transferring to the silicone moulds.

Table 6.6 Reagent quantities and TGA results for hierarchical composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nano/Epoxy /g</th>
<th>Epoxy /g</th>
<th>µ-ZnO /g</th>
<th>Measured content /wt%</th>
<th>Total Vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.565</td>
<td>0.478</td>
<td>0.951</td>
<td>55.3</td>
<td>20.2</td>
</tr>
<tr>
<td>B</td>
<td>0.848</td>
<td>0.242</td>
<td>0.951</td>
<td>57.6</td>
<td>21.7</td>
</tr>
<tr>
<td>C</td>
<td>1.130</td>
<td>-</td>
<td>0.951</td>
<td>a</td>
<td>a</td>
</tr>
</tbody>
</table>

*a* sample was very brittle and dry when cured, therefore was not analysed.
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Morphology from a Novel Family of Structurally Characterized Zinc Alkoxy Alkyl
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precipitation of doped zinc sulfide nanocrystals for photonic applications.' J. Mater. Res.


## Appendix 1

### A1 Crystal Structure Data

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<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
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<tbody>
<tr>
<td>Molecular formula</td>
<td>C_{20}H_{38}O_{12}Zn_5</td>
<td>C_{8}H_{13}NO_2Zn</td>
<td>C_{9}H_{16}O_{2}Zn</td>
</tr>
<tr>
<td>Formula weight, $M$</td>
<td>797.35</td>
<td>232.57</td>
<td>306.95</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
<td>monoclinic</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\overline{1}$</td>
<td>$P2_1/c$</td>
<td>$Pca2_1$</td>
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<tr>
<td>Unit cell parameters, Å</td>
<td>$a = 10.9551(2)$</td>
<td>$a = 7.6301(3)$</td>
<td>$a = 13.4868(5)$</td>
</tr>
<tr>
<td></td>
<td>$b = 12.9319(2)$</td>
<td>$b = 16.0551(6)$</td>
<td>$b = 9.2244(4)$</td>
</tr>
<tr>
<td></td>
<td>$c = 22.0224(2)$</td>
<td>$c = 9.2431(3)$</td>
<td>$c = 9.2241(3)$</td>
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<tr>
<td>Unit cell volume, Å³</td>
<td>3106.24(9)</td>
<td>1068.69(7)</td>
<td>1147.55(8)</td>
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<tr>
<td>Calculated density, g cm⁻³</td>
<td>1.705</td>
<td>1.445</td>
<td>1.777</td>
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<tr>
<td>Absorption coefficient, mm⁻¹</td>
<td>4.754</td>
<td>2.953</td>
<td>5.063</td>
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<tr>
<td>Crystal colour / morphology</td>
<td>colourless platy needles</td>
<td>Colourless blocks</td>
<td>Colourless plates</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
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<td>0.35 x 0.22 x 0.14</td>
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<td>5.77 to 72.46°</td>
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<td>Reflns collected / unique</td>
<td>24305 / 24305</td>
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<td></td>
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<td>[R(int) = 0.0287]</td>
<td>[R(int) = 0.0448]</td>
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<td>Reflns observed [F&gt;4σ(F)]</td>
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<td>CCDC entry</td>
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<td>799383</td>
<td>799384</td>
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Figure A1 The molecular structure of one (A) of the two crystallographically independent complexes present in the crystals of 1 (30% probability ellipsoids).
Figure A2 (a) The molecular structure of the asymmetric unit (50% probability ellipsoids), and (b) chain structure of 2.
Figure A3 (a) The molecular structure of the asymmetric unit (50% probability ellipsoids) and (b) part of one of the herringbone sheets in the ac plane present in the crystals of 3.
Table A1  Selected bond lengths (Å) for the two crystallographically independent complexes (A and B) present in the crystals of 1.

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<th>Bond Lengths</th>
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<td>2.0432(19)</td>
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<td>Table A2.</td>
<td>Selected bond lengths (Å) and angles (°) for 2.</td>
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<td>---</td>
<td>---</td>
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<td>O(1)–Zn(2)–O(5)</td>
<td>77.0(3)</td>
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<td>O(1)–Zn(2)–O(3B)</td>
<td>92.5(3)</td>
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<tr>
<td>O(5)–Zn(2)–O(3B)</td>
<td>94.6(3)</td>
</tr>
<tr>
<td>Zn(1)–O(1)–Zn(2)</td>
<td>102.1(3)</td>
</tr>
</tbody>
</table>
A2 Description of Hydrolysable Ethyl Content Apparatus

Hydrolysable ethyl was estimated from the displacement of toluene by evolved gas on hydrolysis of \([\text{Zn}_5(\text{OAc})_6(\text{Et})_4]\). The apparatus is detailed in Figure A4. Initially, the cannula (E) was filled with toluene by introducing nitrogen at a high pressure into flask B. The nitrogen supply was ceased and the system allowed to settle until no more toluene was transferred. A fresh, tared flask (D) was then attached to the collection device (C). A solution of 1 (0.049 g, 0.06 mmol) in dry toluene (1.5 mL), in flask A, was attached by cannula to flask B. A solution of water in acetone (0.1 mL, 5 M, 0.50 mmol water) was added to flask A. After liquid transfer was complete, flask D was weighed and the total volume calculated (5.51 mL), taking into account the 0.1 mL water solution added. The total ethyl content of 1 was then calculated using the density of ethane (1.253 × 10^{-3} \text{ gmL}^{-1}) to be 0.231 × 10^{-3} moles, or 13.7 wt%. The expected volume of ethane from 0.049 g of 1, given the proposed structure, is 5.86 mL (14.6 wt%), implying a ethane yield of 94%. The accuracy of the method was estimated by injecting air from a 10 mL syringe into a clean flask (A) and calculating the collected volume. The measured volumes were lower than the volume injected (estimated from the mass of an equivalent volume of toluene measured from the syringe) by an average of 0.29 ± 0.13 mL, suggesting that systematic measurement error accounts for much of the (still minor) deviation between the measured and predicted value.
Figure A4 Schematic of hydrolysable ethyl apparatus: Flask A contains a solution of the compound to be tested and is connected by cannula to flask B, containing toluene; Flask B is connected via cannula E to collecting device C and collecting flask D. Cannula E is filled with toluene prior to testing. Flask A is then connected and the compound decomposed with water. The ethane evolved displaces liquid from flask B which is then collected in flask D.

Flasks A and B and collecting device C are all sealed with rubber septa during the experiment.
A3  Nanocomposite Characterisation Details

A3.1  Heat Capacity Measurement

A3.1.1 Values of $C_p$ measured by DSC

Figure A5 Comparison of ZnO/epoxy composite heat capacities, measured by DSC. Error bars represent the standard deviation of at least three measurements. The “Pure” series (open triangles) refers to the heat capacities of pure epoxy resin and ZnO microparticles (powder), respectively, measured in the same way.
A3.1.2 Calculation of heat capacity by Laser Flash Method:

The precise equation used by the NETZSCH LFA Analysis software (Version 4.8.4) is:

\[
\frac{C_p^{\text{sample}}}{T_{\infty}^{T}} = \frac{T_{\infty}^{T_{\text{ref}}} \times Q^{\text{sample}}}{Q^{T_{\text{ref}}} \times V^{\text{sample}} \times V_{\text{ref}}^{T_{\text{ref}}} \times \frac{\rho^{\text{ref}}}{\rho^{\text{sample}}} \times \frac{l^{\text{ref}}}{l^{\text{sample}}} \times C_p^{T_{\text{ref}}} (T)}
\]

where \( T_{\infty} \) is the extrapolated voltage increase across the sample (proportional to the adiabatic temperature increase), \( Q \) is the energy applied to the sample (the integral of the laser pulse), \( V \) is the signal amplification factor, \( \rho \) is the sample density, and \( l \) is the sample thickness (source: NETZSCH LFA Analysis (Version 4.8.4, 30.07.2007) Supplementary Information, available via the software Help Menu © Copyright 1999-2007 NETZSCH-Geraetebau GmbH).

A3.2 Fitting of Density Data

![Graph showing the fitting of density data.](image)

**Figure A6** Fitting of the nanocomposite density data. The gradient of the line represents the difference between the densities of the ZnO filler and pure epoxy \((\rho_{\text{ZnO}} - \rho_{\text{epoxy}})\), giving the ZnO density as 5.64 gcm\(^{-3}\).
Figure A7 Fitting of the microcomposite density data. The gradient of the line represents the difference between the densities of the ZnO filler and pure epoxy ($\rho_{ZnO} - \rho_{epoxy}$), giving the ZnO density as 5.20 gcm$^{-3}$. 

$$y = 4.0573x + 1.145$$

$R^2 = 0.9962$