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Synthesis And Polymerization Of Bifunctional Five-membered Cyclic Dithiocarbonates And Their Use As Stabilizers For Magnetic Nan

Mohammed Daoudi
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SYNTHESIS AND POLYMERIZATION OF BIFUNCTIONAL FIVE-MEMBERED CYCLIC DITHIOCARBONATES AND THEIR USE AS STABILIZERS FOR MAGNETIC NANOPARTICLES

by

MOHAMMED DAOUDI
B.S. Damascus University, 1976

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Chemistry in the College of Arts and Sciences at the University of Central Florida Orlando, Florida

Fall Term
2004
ABSTRACT

Novel bifunctional five-membered cyclic dithiocarbonates (1,3-oxathiolane-2-thione)s were synthesized by the reactions of the corresponding bifunctional oxiranes (epoxides) with carbon disulfide at room temperature with lithium bromide as catalyst. Full characterization of these monomers was performed including elemental analysis, proton and carbon nuclear magnetic resonance (NMR) spectroscopy, gas chromatography-mass spectroscopy, and Fourier transmission infrared (FTIR) spectroscopy.

The polyaddition polymerization of 1,3-oxathiolane-2-thione with 1,4-diaminobutane at room temperature resulted in a poly(thiourethane) material. The latter undergoes crosslinking due probably to the autooxidation of the product and formation of disulfide linkages.

The five-membered cyclic dithiocarbonate, 5-decyl-1,3-oxathiolane-2-thione, was used a model to demonstrate the usefulness of five-membered cyclic dithiocarbonates for the preparation of compounds bearing thiol and thiocarbamate groups. This functionality was desired for use as metallic nanoparticle stabilizers. A thermal decomposition oxidation method was used to synthesize the magnetic iron nanoparticles. The stabilized magnetic nanoparticles were characterized by transmission electron microscopy (TEM) to determine the shape and the size of the nanoparticles. Energy dispersive spectroscopy (EDS) was used to analyze the composition of the magnetic nanoparticles.
ACKNOWLEDGEMENTS

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Finally I extend my deepest gratitude to my wife for her patience, understanding, full support, and love.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>BA</td>
<td>Butylamine</td>
</tr>
<tr>
<td>BDGE</td>
<td>1,4-Butanediol diglycidyl ether</td>
</tr>
<tr>
<td>BEMBOT</td>
<td>Bis[5,5’-ethoxymethyl]-bis[1,3-oxathiolane-2-thione]</td>
</tr>
<tr>
<td>BPGRE</td>
<td>Bisphenol F diglycidyl ether</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>Deuterated chloroform</td>
</tr>
<tr>
<td>(CH$_3$)$_3$NO</td>
<td>Trimethylamine oxide</td>
</tr>
<tr>
<td>CI</td>
<td>Chemical Ionization</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>Carbon disulfide</td>
</tr>
<tr>
<td>DAB</td>
<td>1,4-Diaminobutane</td>
</tr>
<tr>
<td>DGRE</td>
<td>Diglycidyl resorcinol ether</td>
</tr>
<tr>
<td>DOT</td>
<td>5-Decyl-[1,3]oxathiolane-2-thione</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EB</td>
<td>1,2-Epoxybutane</td>
</tr>
<tr>
<td>EDD</td>
<td>1,2-Epoxydodecane</td>
</tr>
<tr>
<td>EI</td>
<td>Electronic Ionization</td>
</tr>
<tr>
<td>EOT</td>
<td>5-Ethyl-(1,3)oxathiolane-2-thione</td>
</tr>
<tr>
<td>EP</td>
<td>Epoxy resins</td>
</tr>
<tr>
<td>Fe(CO)$_5$</td>
<td>Iron pentacarbonyl</td>
</tr>
<tr>
<td>γ-Fe$_2$O$_3$</td>
<td>Iron (III) oxide</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Magnetite</td>
</tr>
</tbody>
</table>
FTIR  Fourier Transform Infrared
GC-MS  Gas chromatography-Mass Spectroscopy
GPC  Gel Permeation Chromatography
HMDA  Hexamethylene diamine
HPLC  High Performance Liquid Chromatography
LiBr  Lithium bromide
MBPMBOT  $5,5'$-[Methylene-bis(4,1phenyleneoxymethylene)-bis[1,3-oxathiolane-2-thione]]
ml  Milliliter
mmol  Milimole
MW  Molecular Weight
MWD  Molecular Weight Distribution
NaOH  Sodium hydroxide
NMR  Nuclear Magnetic Resonance
PMBOT  $5,5'$-Phenoxyethyl]-bis[1,3-oxathiolane-2-thione]
PT  Phenolic resins
PUR  Polyurethanes
RT  Room Temperature
TAEA  Tris(2-aminoethyl)-amine
TGA  Thermogravimetric Analysis
$T_g$  Glass Transition Temperature
THF  Tetrahydrofuran
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TLC</td>
<td>Thin Layer Chromatography</td>
</tr>
<tr>
<td>TP</td>
<td>Thermoplastics</td>
</tr>
<tr>
<td>TS</td>
<td>Thermosets</td>
</tr>
<tr>
<td>UF</td>
<td>Urea formaldehyde resin</td>
</tr>
<tr>
<td>UP</td>
<td>Unsaturated Polyester</td>
</tr>
</tbody>
</table>
CHAPTER ONE: INTRODUCTION

1.1 Magnetic Nanoparticles

A substantial amount of work was done in the last two decades or so in the synthesis, study, and applications of metallic particles having dimensions on the nanometer scale. These so-called nanomaterials are gaining more and more importance because their properties differ from those of the counterpart bulk materials. Magnetic nanoparticles have demonstrated potential for many applications such as high-density magnetic recording and storage media, energy storage, catalysts, sensors, along with pharmaceutical and biomedical applications.¹

Magnetic particle containing fluids are composed of three components. The liquid base or carrier component is chosen to conform with its field of application. Water-based, silicone-based, and hydrocarbon-based liquids are often used. The second component is the magnetic particles which must be in colloidal size because their stability is ensured by their thermal motion. The particles should possess a high magnetizability. Finally, the stabilizers of the magnetic nanoparticles play a crucial role in the fabrication of magnetic materials and fluids as they prevent particles from aggregation. The stabilizers (surfactants) are composed of long-chains that could be a polymer or an aliphatic molecule and a polar functional group. The stabilizers interact with the magnetic nanoparticles through the functional group to form a tightly associated or bonded monolayer around the particles. The long-chain part of the stabilizer should resemble the
carrier liquid in order not to inhibit the thermal motion of the particles. The magnetic 
nanoparticle fluids are stabilized when the thermal motion of the fluids is higher than the 
attractive forces between particles. When magnetic nanoparticles are coated with a layer 
of surfactant, the long-chain molecules are close to each other and a repulsive or steric 
force is created. In this case, a simple model describes a magnetic fluid as a system that is 
homogeneously dispersed. The non-interacting particles, which generally have spherical 
shape, are coated with a surfactant layer and placed in a liquid medium². 

The magnetic fluids materials were first synthesized in mid-1960s and were called 
ferrofluids, and ferromagnetic or magnetizable fluids.²³ Since then, a variety of physical 
and chemical methods have been developed and used to fabricate magnetic nanoparticles, 
including grinding mechanical method,² metal evaporation/condensation,²⁴ reduction of 
metal salts,⁵ laser pyrolysis, thermal decomposition.⁶ and sonochemical methods⁷. 

The fist fabricating method that was developed in mid-1960s involves the 
mechanical grinding of magnetite (Fe₃O₄) in the presence of oleic acid as stabilizer and 
kerosene as carrier liquid. This method is time consuming and too expensive.² 

The chemical precipitation method of preparing magnetic fluids involves the 
precipitation of magnetite from iron(II)-iron(III) salt solution in the presence of 
concentrated alkaline solution according to the following chemical equations.²³: 

\[ 8 \text{NaOH} + 2\text{FeCl}_3.6\text{H}_2\text{O} + \text{FeSO}_4.7\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4\downarrow + \text{Na}_2\text{SO}_4 + 6\text{NaCl} + 23 \text{H}_2\text{O} \]

Or 

\[ 8 \text{NaOH} + 2\text{FeCl}_3.6\text{H}_2\text{O} + \text{FeCl}_2.4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4\downarrow 8\text{NaCl} + 20 \text{H}_2\text{O} \]
The growth of particles is restricted by vigorous agitation of the solution.

The thermal decomposition oxidation method involves the decomposition of a volatile precursor such as iron pentacarbonyl, Fe(CO)$_5$, in the presence of a stabilizer and using a mild oxidant such as trimethylamine oxide, (CH$_3$)$_3$NO. This method provides iron oxide (maghemite) nanoparticles ($\gamma$-Fe$_2$O$_3$) that are chemically stable in contrast to pure iron nanoparticles.$^1$

The applicability of magnetic nanoparticles in various technological fields depends on their physical properties, each particular application requiring certain properties. However, the magnetization, which is the ability of the magnetic fluid to interact with a magnetic field is an important property and should have a high value.$^2$ Paramagnetic materials are materials that have a small susceptibility to external magnetic fields. So, their atomic magnetic dipoles are aligned with the external magnetic field. When the external field is removed, paramagnetic materials lose their magnetic property. In contrary, ferromagnetic materials have large susceptibility to external magnetic fields. These materials retain their magnetic property when the external field is removed, thus exhibiting a spontaneous magnetization.

1.2 Polymeric Surfactants

Surfactants are amphipathic compounds consisting of hydrophobic and hydrophilic portions. Thus, the surfactants have dual character. This means the surfactant has the tendency to accumulate at the interface between polar and nonpolar phases. The
surfactants or surface active agents are essential material for the preparation of magnetic nanoparticles.\textsuperscript{9,10}

Dispersed nanoparticles in fluids are in constant movement and collide with each other. The van der Waals attraction between those particles can lead to particle coagulation. So, it is compulsory to provide the particle with a repulsive force that is higher than the attractive force. This stabilization can be achieved, e.g., with polymeric surfactants. Polymeric surfactants provide dispersion stabilization by the interaction of the chains on the adjacent particles. The concentration of stabilizing chains in the interaction zone will increase considerably upon contact. So, the free energy of the system is increased due to mixing of polymeric segments. The latter gives rise to the repulsive force, which results in stability of the nanoparticles. This stabilization is usually referred to as steric stabilization. In order for this steric stabilization to be effective, the nanoparticles should be completely covered by the polymeric surfactant, the chains should be strongly adsorbed (anchored) to particles surfaces, and the chains should have good solvency by the dispersion medium. On other hand, the amphiphillic polymers create a layer of polymeric chains or stabilizing moieties around the surface of colloidal particles. This layer prevents two approaching particles from coming in direct contact and aggregate.\textsuperscript{9,10}

It has been found that the most convenient and effective polymeric surfactants are amphiphillic block copolymers of the type A-B, A-B-A, and AB graft copolymers. The B portion, referred to as anchoring chain, should have high affinity for the surface of particles, while the A portion, referred to a stabilizing chain, should have low affinity for
the surface and should be highly solvated in the continuous medium. Various polymeric surfactants have been developed and used to stabilize magnetic particles such as polyesters and polyvinylalcohol (PVA).\textsuperscript{9,10}

1.3 Thermosets and Epoxy Resins

Thermosets are plastic materials that are formed by polycondensation polymerization. When two thermoset components (monomers) or more are mixed together, they undergo a chemical reaction and are converted into a hard solid. This process is called curing or hardening, an irreversible process. That means the thermoset material cannot go back into being two separate components again. In other words, after curing, these materials cannot be softened on heating, they are infusible and insoluble. The chemistry of curing involves the formation and growth of linear chains that soon begin to branch and then crosslink. As the crosslinking reaction proceeds, the polymer molecular weight (MW) increases rapidly and several chains are linked together to form a network of infinite molecular weight. This transformation from viscous liquid to an elastic gel is referred to as the gel point, and the process is gelation, which is a characteristic of thermosets. Beyond the gel point, the polymer does not flow any more and is no longer processable. The crosslinking process creates links between the polymer chains which limits their mobility and possibility of relative displacements.\textsuperscript{11,12,13}

Thermosetting materials provide high thermal and dimensional stability, good resistance to creep and deformation under load, good chemical resistance, and excellent
electrical insulation. These properties provide advantages for their widespread use in applications such as aerospace, automotive, appliances, building and housing, medical and dental, and clothing. Polyurethanes, amino resins, phenolic resins (PT), unsaturated polyesters (UP), and epoxy resins (EP) are examples of well-developed and established thermoset materials.\textsuperscript{11,12}

Epoxy or epoxide resins are a class of polymers that possess reactive groups, which can be converted to thermoset resins by reacting with curing agents or hardeners. The first epoxy resins were prepared in the 1930s in Switzerland, but the first commercial production facility was commenced only in the late 1940s by Devoe-Raynolds Company in the United States.\textsuperscript{14,15} The chemistry of epoxy resins is unique among the thermoset resins. No volatiles are released during the curing process since it involves an addition reaction during curing. The shrinkage is much less than that encountered in other thermoset resins. They also can be cured or hardened over a wide range of temperatures.\textsuperscript{15}

Epoxy resins should be cured or hardened before they can be used. They need to be converted, through crosslinking reactions, into a three-dimensional network held together by covalent bonds.\textsuperscript{16} The curing chemistry involves the ring opening of the epoxide ring upon the addition of reagents. This reaction proceeds by an ionic mechanism. The highly polar carbon-oxygen bond is broken. Many reactions and reagents are used to cure epoxy resins. The most common curing reaction is the polyaddition reaction and the most common curing reagents are polyamines, polyacids,
polymercaptans, and polyphenols.\textsuperscript{15} The curing reaction of an epoxy resin with polyamines curing agents is presented in Scheme 1.\textsuperscript{16}

![Scheme 1](image)

Epoxy resins offer excellent electrical properties, high chemical and thermal resistance, dimensional stability, high strength, and low moisture absorption. They perform well at elevated temperature and in corrosive environments. These properties make the epoxy resins an excellent material in many technological applications. They are used in encapsulation or casting of various electrical and electronic components and in the surface coating of various metal substrates. Another important application is the coating field where pipes, containers, appliances, marine parts, car bodies and parts are coated with epoxy resins for corrosion protection. Composites of epoxy resins with glass fibers are typical materials in aircraft components, tanks, and pressure vessels. One of
their major applications is in the adhesive field where two-part systems cure with minimal shrinkage and without emitting volatiles.\textsuperscript{14-17} The epoxy resins possess very good processability. They can be molded at relatively low pressure and short cycles.\textsuperscript{17}

### 1.4 Dithiocarbonate Chemistry

The reaction of oxiranes (epoxides) with carbon disulfide provides analogues of the epoxy resins (1,3-oxathiolane-2-thione).\textsuperscript{18,19} These compounds can be cured by means of common curing agents used for epoxy resins.\textsuperscript{19,20} The introduction of the thiostructure provides the polymer produced from these monomers with some superior properties over their epoxy resin precursors which give them advantages in some important applications such as subambient temperature, efficient polyelectrolytes, thermal stabilizers and metal scavengers in aqueous polymeric dispersions.\textsuperscript{20}

K. Pielichowski, P., Czub, and J. Pielichwski reported that some of the dithiocarbonate derivatives (1,3-oxathiolane-2-thione) have higher thermal stability than their epoxy precursors.\textsuperscript{21} There have been many reports in the literature on the reaction of epoxides (oxiranes) with carbon disulfide in different reaction conditions. Depending on those conditions and type of catalyst used, five-membered cyclic dithiocarbonates, its regioisomers, trithiocarbonates and episulfides could be formed \textsuperscript{22,23,24}.

Takeshi Endo \textit{et al.} reported recently that five-membered cyclic dithiocarbonates can be selectively synthesized by the reaction of oxiranes with \( \text{CS}_2 \) in presence of LiBr as catalyst and THF as solvent. This reaction takes place under mild conditions (room
temperature and atmospheric pressure). A selectivity of 90% and a yield of more than 70% have been achieved (Scheme 2).\textsuperscript{18}

![Scheme 2](image)

There are two possible mechanisms for the reaction of epoxides with carbon disulfide. At high pressure and high temperature, the reaction proceeds via nucleophilic attack of the halide ion at the less substituted position of the epoxide. Then the resulting carbonate ion undergoes cyclization to produce the dithiocarbonate (Scheme 3).\textsuperscript{18,24}

However, at room temperature and atmospheric pressure, the reaction proceeds via formation of xanthate anion that is formed from lithium bromide and carbon disulfide. This anion reacts with oxirane to form the carbonate anion, which undergoes cyclization to generate the five-membered cyclic dithiocarbonate (Scheme 4).\textsuperscript{18,24}
Scheme 3

\[
\text{R} \overset{\text{O}}{\text{O}} \text{Li}^+ \text{Br}^- + \text{S} = \text{C} = \text{S} \rightarrow \text{R} \overset{\text{O}}{\text{O}} \text{Br}
\]

Scheme 4

\[
\text{Li}^+ \text{Br}^- + \text{S} = \text{C} = \text{S} \rightarrow \text{R} \overset{\text{C}}{\text{C}} \text{SLi}
\]
Five-membered cyclic dithiocarbonates can be polymerized to obtain sulfur-containing polymers. Sulfur containing polymers possess interesting optical (high refractive index) and good thermal stability properties. The polymerization proceeds by a cationic ring opening mechanism. First, the five-membered cyclic dithiocarbonate is cationically isomerized in the presence of Lewis acids, such as ZnCl$_2$ and SnCl$_4$. Protonic acids such, as CF$_3$SO$_3$H (TfOH) and CH$_3$SO$_3$H can also be used as catalysts. The resulting product is then polymerized in presence of CF$_3$SO$_3$Me (TfOMe) or CF$_3$SO$_3$Et (TfOEt) to obtain the corresponding polydithiocarbonates (Scheme 5).

Scheme 5

The polyaddition of bifunctional five-membered cyclic dithiocarbonates with diamine compounds leads to the corresponding poly(thiourethane)s (Scheme 6).
This polymer may be used as reactive polymer bearing a thiol group. Thiol groups play an important role in various chemistries, such as metal thiolate chemistry, and are also important in biological chemistry.\textsuperscript{28}

The five-membered cyclic dithiocarbonates have limited reactivity. They react with amines to produce compounds containing a thiol group. In fact, they have high reactivity and very high selectivity with amines. Their reaction with primary amines takes place at mild conditions at ambient temperature in seconds (Scheme 7).\textsuperscript{28,29,30} This reaction results in formation of SH group and thiourethane bond.
Thiol groups have high reactivity and good affinity to metals.\textsuperscript{28,29,31} It has been reported that long-chain thiols can be absorbed from solution to coat gold particles and formed oriented monolayers.\textsuperscript{32} Thus, we have great interest in exploring the chemistry of five-membered cyclic dithiocarbonates, and their amine adducts, in the stabilization of magnetic nanoparticles. This chemistry can open the door to magnetic thermosets and elastomers. In addition, these studies will provide a new metal nanoparticle surfactant, adding to the tools available to nanoscientists and technologists worldwide.

1.5 Research Objectives

The purpose of this study was to synthesis compounds bearing five-membered cyclic dithiocarbonates using a very selective method then to explore the chemistry of these dithiocarbonates, and their amine adducts, in the stabilization of magnetic nanoparticles. The polymerization of five-membered cyclic dithiocarbonates was also targeted in order to synthesis linear and crosslinked polymers. To explore the possibility of using crosslinked polymeric materials for stabilization of magnetic nanoparticles was demonstrated using a model system.
CHAPTER TWO: EXPERIMENTAL

2.1 Characterization

The characterization of starting materials, monofunctional, bifunctional five-membered cyclic dithiocarbonates, polymers, and magnetic nanoparticles were performed using the following techniques and equipment:

2.1.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

$^1$H NMR and $^{13}$C NMR spectra were obtained using a Gemini Varian NMR spectrometer at 300 MHz. and 75 MHz, respectively. Deuterated chloroform (CDCl$_3$) was used as solvent and tetramethylsilane as internal standard.

2.1.2 Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectra were obtained using Perkin-Elmer Spectrum One and VERTEX 70 Bruker Fourier transform infrared spectrometers (32 scans with a resolution of 4 cm$^{-1}$ were used). NaCl cells were used for liquid samples. The absorption range was established from 4000-400 cm$^{-1}$.

2.1.3 Gas Chromatography-Mass Spectroscopy (GC-MS)

GC-MS spectra were recorded on Trace GC/Trace DQC from Thermo-FINNIGAN. A capillary column of RTX-5MS (15 m length and 0.25 mm ID) was used.
The oven temperature was initially set to 80 °C for five min. then programmed to reach 250 °C at rate of 30 °C/min.

2.1.4 Differential Scanning Calorimetry (DCS)

DSC analysis was carried out using a DSC model 2920 from TA Instruments. The sample (10-29 mg) was heated at a rate of 20 °C from – 40 °C to 275 °C.

2.1.5 Thermogravimetric Analysis (TGA)

TGA analysis was carried out using a TGA model 2050 from TA Instruments. The heating rate was 20 °C from room temperature to 700 °C.

2.1.6 Transmission Electron Microscopy (TEM)

The shape and size of the magnetic nanoparticles were obtained on FEI Tecnai F30 TEM Transmission Electron Microscopy (TEM). The resolution is 0.2 nm with a magnification of 10,000,000X.

2.2 Materials

Carbon disulfide (CS₂) was dried over calcium chloride (CaCl₂) then distilled over calcium hydride (CaH₂) under nitrogen gas atmosphere. THF was distilled over lithium aluminum hydride (LiAlH₄) under nitrogen, dried over metallic sodium and redistilled. LiBr was dried overnight at 100 °C. 1,4-Butanediol diglycidyl ether (BDGE),
diglycidyl resorcinol ether (DGRE), bisphenol F diglycidyl ether (BPDGE), 1,2-epoxydodecane (EDD), 1,2-epoxybutane (EB), butylamine (BA), 1,4-diaminobutane (DAB), hexamethylenediamine (HMDA), and tris(2-aminoethyl)-amine (TAEA) were obtained from Aldrich and used without further purification. Their purities were checked by GC-MS spectroscopy and NMR spectroscopy.

2.3 Synthesis of Monomers

2.3.1 5-Ethyl-[1,3]oxathiolane-2-thione (1)

The monofunctional five-membered cyclic dithiocarbonate monomer (1) was prepared following the method developed by Endo, T. et al.\textsuperscript{22,24} 1,2-Epoxybutane (10 g, 139 mmol) was dissolved in 25 mL of distilled and dried THF. LiBr (0.2 g, 2.3 mmol) was added to the mixture and stirred under N\textsubscript{2} for about 10 min. to completely dissolve all the catalyst. CS\textsubscript{2} (12 mL, 220 mmol) was added to the mixture through a syringe. Upon addition of carbon disulfide, the solution changed from colorless to light yellow in coloration. The mixture was stirred overnight under N\textsubscript{2} at room temperature. The monitoring of the reaction was performed by TLC technique. Upon completion the product was concentrated under reduced pressure to obtain a yellow liquid. This crude product was purified by column chromatography using silica gel as absorbent and a solvent system of hexane/methylene chloride in 1:3 ratio. A bright yellow liquid was obtained with a yield of about 60%. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ: 5.08 (m, 1H), 3.60 (m, 2H), 2.05 (m, 2H), 1.10 (m, 3H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) δ: 212.3, 93.0, 38.9,
26.7, and 9.6. GC retention time: 7.81 min. MS (EI, 70 eV) m/z: 148 (M), 91 (M-C,H), 75 (M-CHSC,H), 55 (M-C,H). FTIR (NaCl): 1190 cm⁻¹ (C=S), 1050 cm⁻¹ (C-O), and 646 cm⁻¹ (C-S).

2.3.2 Bis[5,5'-ethoxymethyl]-bis[1,3]oxathiolane-2-thione (BEMBOT) (2)

The bifunctional five-membered cyclic dithiocarbonate monomer (2) was prepared following the method developed by Endo, T. *et al.* Butanediol diglycidyl ether (BDDE) (5 g, 25 mmol) was dissolved in 15 mL dried THF. LiBr (0.35 g, 4 mmol) was added to the mixture and stirred under N₂ for about 10 min. to completely dissolve all catalyst. CS₂ (15 mL, 275 mmol) was added to the mixture through a syringe. Upon addition of carbon disulfide, the solution changed from colorless to light yellow in coloration. The mixture was then stirred overnight under N₂ at room temperature. The monitoring of the reaction was performed by TLC technique. The product was concentrated under reduced pressure to obtain a yellow liquid. This crude product was purified by column chromatography using silica gel as absorbent and a solvent system of hexane/ethyl acetate in 1:1 ratio. A dark yellow liquid was obtained with a yield of about 65%. ¹H NMR (300 MHz, CDCl₃) δ: 5.26 (m, 2H), 3.60-3.84 (m, 12H), 1.71 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ: 211.7, 89.4, 71.3, 69.1, 35.3, and 26.3. FTIR (NaCl): 1182 cm⁻¹ (C=S), 1043 cm⁻¹ (C-O), and 649 cm⁻¹ (C-S).
### 2.3.3 5,5′-Phenoxyethyl-bis[1,3-oxathiolane-2-thione] (3)

The bifunctional five-membered cyclic dithiocarbonate monomer (3) was synthesized following the method developed by Endo, T. et al.\textsuperscript{22,23} LiBr (0.3 g, 3.5 mmol) was dissolved in 40 mL dried THF. Then 10 g (45 mmol) of diglycidyl resorcinol ether (DGRE) was added to the mixture. The mixture was stirred under N\textsubscript{2} for about 10 minutes to completely dissolve the starting material and catalyst. To the clear solution, 20 mL (360 mmol) of distilled and dried carbon disulfide (CS\textsubscript{2}) was added to the mixture through a syringe. Upon addition of carbon disulfide, the color of the solution turned to light yellow. The mixture was then stirred overnight under N\textsubscript{2} at room temperature. TLC was used for the monitoring of the reaction. The product was concentrated under reduced pressure to obtain a yellow liquid. This crude product was purified by column chromatography using silica gel as absorbent and a solvent system of hexane/ethyl acetate in 1:1 ratio. A viscous yellow liquid was obtained, which was dried under vacuum, resulting in a sticky solid with a yield of about 70%. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\): 7.20 (t, 1H), 6.54 (d, 2H) 6.49 (s, 1H), 5.43 (m, 2H), 4.27 (m, 4H), and 3.74 (m, 4H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\): 211.3, 158.7, 130.4, 107.5, 101.7, 87.9, 66.5 and 36.0. FT-IR (NaCl): 1169 cm\textsuperscript{-1} (C=S), 1047 cm\textsuperscript{-1} (C-O), and 649 cm\textsuperscript{-1} (C-S).
The bifunctional five-membered cyclic dithiocarbonate monomer (4) was prepared following the method developed by Endo, T. et al.\textsuperscript{22,24} LiBr (0.4 g, 4.5 mmol) was dissolved in 40 mL of dried THF. Then 12 g (38 mmol) of bisphenol F diglycidyl ether (BPDGE) was added to the mixture. The mixture was stirred under N\textsubscript{2} to completely dissolve the starting material, after which CS\textsubscript{2} (20 mL, 368 mmol) was added through a syringe. Upon addition of carbon disulfide, the color of the solution changed from colorless to very light yellow. The mixture was then stirred overnight under N\textsubscript{2} at room temperature. The reaction was monitored using TLC. The product was concentrated under reduced pressure to obtain a yellow liquid. This crude product was purified by column chromatography using silica gel as absorbent and a solvent system of hexane/ethyl acetate in 1:1 ratio. A viscous yellow liquid was obtained and after drying under vacuum resulted in pale yellow crystals with a yield of about 70%. The melting point of this product is 75-78 °C. \textsuperscript{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3})} δ: 7.07 (d, 4H), 6.84 (m, 4H), 5.41 (m, 2H), 4.26 (m, 4H), 3.92 (s, 2H), and 3.75 (m, 4H). \textsuperscript{\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3})} δ: 211.4, 155.8, 134.4, 129.7, 114.3, 87.5, 66.1, and 35.6. FT-IR (microscope): 1179 cm\textsuperscript{-1} (C=S), 1041 cm\textsuperscript{-1} (C-O), and 652 cm\textsuperscript{-1} (C-S).
2.3.5 5-Decyl-[1,3]oxathioline-2-thione (5)

The five-membered cyclic dithiocarbonate monomer (5) was prepared following the method developed by Endo, T. et al.22,24 1,2-Epoxydodecane ((EDD) (10 g, 54 mmol) was dissolved in 15 mL dried THF. Lithium bromide (0.4 g, 4.6 mmol) was added, and the mixture stirred under N₂ for about 10 min. to completely dissolve all catalyst. Distilled and dried carbon disulfide (15 mL, 276 mmol) was added to the mixture through a syringe. Upon addition of carbon disulfide, the color of the solution changed from colorless to yellow. The mixture was then stirred overnight under N₂ at room temperature. The product was concentrated under reduced pressure to obtain a yellow liquid. This crude product was purified by column chromatography using silica gel as absorbent and a solvent system of hexane/ethyl acetate in 6:1 ratio. A bright yellow liquid was obtained with a yield of about 75%. GC retention time: 11.16 min. MS (EI, 70 eV) m/z: 260 (M), 227 (M-SH), 199 (M-CH₂CH₂SH). FT-IR (NaCl): 1192 cm⁻¹ (C=S), 1046 cm⁻¹ (C-O), and 646 cm⁻¹ (C-S). ¹H NMR (300 MHz, CDCl₃) δ: 5.12 (m, 1H), 3.39-3.59 (m, 2H), 1.84-2.01 (m, 1H), 1.26 (m, 17H), and 0.88 (t, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 212.2, 92.3, 39.7, 34.0, 32.1, 29.6, 25.6, 23.0, and 14.5.

2.4 Preparation of Mercaptan (6)

The mercaptan derivative of 5-decyl-(1,3)oxathioline-2-thione (5) was synthesized according to the literature²⁹. 5-Decyl-(1,3) oxathioline-2-thione (5) (1.5 g, 6 mmol) previously synthesized was dissolved in 10 mL of dried THF. The mixture was
stirred under N\textsubscript{2} until complete dissolution. n-Butylamine (BA) (0.8 g, 11 mmol) was added to the mixture. The mixture was stirred under nitrogen overnight. The color of the solution changed gradually from slightly yellow to colorless or slight white color. The product was concentrated by vaporizing the solvent under vacuum to obtain white crystals in 55% yield. The melting of this product is 74-75 °C. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta: 4.61\) (s, 1H), 3.74 (m, 1H), 3.17 (m, 2H), 2.81 (m, 2H), 1.88 (m, 2H), 1.28-1.5 (m, 21H), and 0.92 (t, 6H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta: 158.2, 71.1, 41.1, 40.2, 31.8, 29.6, 24.9, 22.7, 19.9\) and 14.1).

2.5 Polymers

2.5.1 Linear Polymers

The polyaddition of five-membered cyclic dithiocarbonates with diamines compounds produces polythiourethane materials (Scheme 14). 5,5′-Phenoxyethyl]-bis[1,3-oxathiolane-2-thione] (3) (1 g, 2.7 mmol) was dissolved in 10 mL of THF followed by addition of 0.8 g (7 mmol) of hexamethylene diamine. The mixture was stirred under N\textsubscript{2} at room temperature for 20 h. Some solid materials were noticed. The solution was poured into ethanol to precipitate the polymer. A white product was obtained after filtration and drying. The solubility test showed that this polymer is not soluble in all solvents available in the lab. The burning test indicated that this polymer does not melt but it burns with a characteristic smell (like burning hair).
2.5.2 Crosslinked Polymers

Bis[5,5′-ethoxymethyl]-bis[1,3]oxathiolane-2-thione (2) was dissolved in THF and tris(2-aminoethyl)-amine was added to the mixture (Scheme 15). A rubbery solid was formed. The solvent was separated and the product was dried to obtain a white rubbery product. The TGA analysis (Figure 20) showed that this thermoset decomposes at around 150 °C. The DSC thermogram showed a transition ~ 140 °C corresponding to decomposition for this crosslinked polymer.

2.6 Fabrication of nanoparticles

Magnetic nanoparticles (γ-Fe₂O₃) were synthesized according to the thermal decomposition and oxidation method reported in literatures.¹,⁷,⁸ Monodispersed iron nanoparticles were prepared by dissolving 1.5 g of mercaptan (6), a derivative of the five-membered cyclic dithiocarbonate (5), in 15 mL 1,4-dioxane. The mixture was heated to reflux then 0.3 mL of iron pentacarbonyl, Fe(CO)₅, was injected into the mixture. The mixture was then heated to reflux and kept at that temperature for 2 h. The color of the mixture changed gradually during this process from orange to dark black. After that, the mixture was cooled to room temperature and 0.4 g of dehydrated (CH₃)₃NO was added to the mixture. The temperature of the mixture was increased gradually to reflux and kept there for 2 h. The black mixture was then cooled to room temperature. A first part was drawn from the mixture with the reaction solvent. A second part was precipitated in ethanol, separated by centrifugal force, and then redispersed in toluene. The third part
was precipitated in ethanol, separated by centrifugal force, and then redispersed in octane.
CHAPTER THREE: RESULTS AND DISCUSSION

3.1 Five-membered cyclic dithiocarbonates

The mono- and bifunctional five-membered cyclic dithiocarbonate monomers were synthesized according to the literature method that involving the reaction of oxiranes with carbon disulfide (CS$_2$) at room temperature and using THF as solvent. The reaction is catalyzed by lithium bromide (LiBr).

First, it was demonstrated that this chemistry works by using a simple oxirane such as 1,2-epoxybutane (Scheme 8). The resulted product, 5-ethyl-(1,3)-oxathiolane-2-thione (1), was characterized by GC-MS, NMR, and FTIR. The NMR and FTIR data are in good agreement with the data published in the literature. The chromatogram (Figure 1) shows a large peak indicating a pure product. The MS spectrum of this peak shows an m/z of 148 that corresponds to the molecular weight of this product. The FTIR spectrum (Figure 2) shows characteristic absorption frequencies at 646 cm$^{-1}$ (C-S stretching vibration), 1050 cm$^{-1}$ (C-O), and 1190 cm$^{-1}$ (C=S stretching).

![Scheme 8](image-url)
The bifunctional dithiocarbonate, bis[5,5′-ethoxymethyl]-bis[1,3]oxathiolane-2-thione (2) was prepared in a similar manner as (1) (Scheme 9) to obtain a yellow liquid. The procedure worked well and provided a good yield. The obtained monomer was characterized by NMR and FTIR. The $^1$H NMR data (Figure 5) indicated a pure product with characteristic peaks at 5.26 ppm (m, 2H) one proton in each cyclic dithiocarbonate and 3.66 (m, 4H) two protons in each cyclic dithiocarbonate. The $^{13}$C NMR data (Figure 6) showed characteristic peaks, which are related to the cyclic dithiocarbonate moiety of the compound, at 211.6 ppm (C=S), 89.4 ppm (CH), and 35.3 ppm (CH$_2$). The FTIR spectrum (Figure 7) includes three characteristic absorption frequencies at 648 cm$^{-1}$ (C=S stretching vibration), 1043 cm$^{-1}$ (C-O stretching vibration), and 1182 cm$^{-1}$ (C=S stretching).

**Scheme 9**

![Scheme 9 diagram](image)
The bifunctional dithiocarbonate 5,5'-phenoxyethyl-bis[1,3-oxathiolane-2-thione] (3) was prepared in a similar manner as (1) (Scheme 10). The drying under vacuum yielded a hard yellow solid with a good yield. It was noticed that this product showed some difficulties for complete drying of the solvents used for purification. The monomer (3) was characterized by NMR and FTIR spectroscopy. The $^1$H NMR data (Figure 8) indicated a pure product but with presence of traces of solvent used for the purification. Two peaks are characteristic for this compound, at 5.43 ppm (m, 2H) and at 3.73 ppm (d, 4H). The $^{13}$C NMR data (Figure 9) showed characteristic peaks at 211.3 ppm (C=S), 87.9 ppm (CH), and 36.0 ppm (CH$_2$). The FTIR spectrum (Figure 10) includes three characteristic absorption frequencies at 648 cm$^{-1}$ (C-S stretching vibration), 1047 cm$^{-1}$ (C-O stretching vibration), and 1169 cm$^{-1}$ (C=S stretching).

Scheme 10
The bifunctional dithiocarbonate 5,5′-[methylene-bis (4,1-phenyleneoxymethylene)-bis[1,3-oxathiolane-2-thione] (4) was prepared in a similar manner as (1) (Scheme 11). The purification and drying generated pale yellow crystals with a reasonable yield. The characterization of this monomer was performed using NMR and FTIR spectroscopy. The $^1$H NMR data (Figure 11) showed the presence of traces of the solvent along with the product. This product is difficult to dry. Like other cyclic dithiocarbonate compounds, $^1$H NMR data for product (4) showed two characteristic peaks at 5.41 ppm (m, 2H) and at 3.74 ppm (d, 4H) and the $^{13}$C NMR data (Figure 12) showed characteristic peaks at 211.4 ppm (C=S), 87.5 ppm (CH), and 35.6 ppm (CH$_2$). The FTIR result includes three characteristic absorption frequencies at 652 cm$^{-1}$ (C=S stretching vibration), 1041 cm$^{-1}$ (C-O stretching vibration), and 1179 cm$^{-1}$ (C=S stretching).

Scheme 11
5-Decyl-[1,3]oxathiolane-2-thione (5) (Scheme 12) was also synthesized by the same method, to obtain a yellow liquid, to be used as a model surfactant for the preparation of magnetic nanoparticles. It was characterized using NMR, GC-MS, and FTIR spectroscopy. The chromatogram showed a major peak with small peaks associated with MS spectrum showing a mass of 260 of the mentioned peak (the molecular mass of this compound) indicating a quite high purity of the synthesized compound. The FTIR spectrum includes three characteristic absorption frequencies at 646 cm\(^{-1}\) (C-S stretching vibration), 1046 cm\(^{-1}\) (C-O stretching vibration), and 1192 cm\(^{-1}\) (C=S stretching). \(^1\)H NMR data for product (5) also showed the two characteristic peaks at 5.21 ppm (m, 1H) and at 3.40-3.59 ppm (d, 2H), like bifunctional compounds, but those protons are slightly shifted upfield, and the \(^{13}\)C NMR data (Figure 17) showed characteristic peaks at 212.2 ppm (C=S), 92.3 ppm (CH), and 39.2 ppm (CH\(_2\)), which are slightly shifted downfield.

Scheme 12
3.2 Synthesis of thiol-containing compounds

Five membered cyclic dithiocarbonates react with high reactivity and selectively with amines to generate compounds with the thiol functional group. This reaction occurs at room temperature without any catalyst and in a very short time if primary amines are used. The model compound (5), 5-decyl-[1,3]oxathiolane-2-thione (DOT), was reacted with n-butylamine, a primary amine, (Scheme 13) to give (6) a white crystalline product. This product had a low melting point (74-75 °C). It was characterized using NMR spectroscopy. The obtained data are in fair agreement with that predicted by the ChemDraw software program. The $^1$H NMR analyses showed two characteristic peaks, the first one at 1.5-1.8 ppm that is assigned to SH, while the peak at 4.6 ppm is assigned to NH. The $^{13}$C NMR data two characteristic chemical shifts at 158 ppm (C=S) and at 71.1 (CH).

Scheme 13
3.3 Polymerization

The intent was to synthesize a linear polymer by the addition polymerization of the bifunctional cyclic dithiocarbonate monomers with diamines. It turned out that the reaction of bis[5,5′-ethoxymethyl]-bis[1,3]oxathiolane-2-thione (BEMBOT) (3) with hexamethylene diamine (HMDA) (Scheme 14) led to an insoluble polymer. Solubility tests were conducted and showed that this polymer is not soluble in any solvent available in the lab. The burning test was performed to check if this polymer is a thermoplastic material or a thermoset material. The polymer burned, with a characteristic smell (similar to that generated when a piece of hair is burnt), but it did not melt. These tests confirm that this material is a crosslinked polymer. Two possibilities could lead to this result. The monomer, bifunctional dithiocarbonates, may react with the generated product bearing thiol groups leading to crosslinked polymer. This possibility was eliminated by conducting a reaction between five-membered cyclic dithiocarbonates with 1-butane thiol. This reaction does not occur at room temperature. The second possibility for crosslinking may be that the produced thiol groups undergoing autooxidation to form disulfide linkages.27
A rubbery crosslinked polymer was prepared by curing bis[5,5'-ethoxymethyl]-bis[1,3]oxathiolane-2-thione (2) with tris(2-aminoethyl)-amine (TAEA) (Scheme 15). The TGA thermogram (Figures 20) of this thermoset material showed that this crosslinked polymer decomposes at about 150 °C and the DSC thermogram (Figure 21) showed that this material has a transition ~ 140 °C corresponding to decomposition, consistent with TGA results.
3.4 Magnetic Nanoparticles

Magnetic nanoparticles (γ-Fe₂O₃) were prepared according to the thermal decomposition and oxidation procedure reported in literatures.¹,⁷,⁸ The thiol-containing compound (6) was dissolved in 1,4-dioxane. Iron pentacarbonyl, Fe(CO)₅, was injected into the mixture. The mixture was then heated to reflex. The color of the mixture changed gradually during this process from orange to dark black. After that, the mixture was
cooled to room temperature and dehydrated (CH\textsubscript{3})\textsubscript{3}NO was added to the mixture. The temperature of the mixture was increased gradually to reflux. The black mixture was then cooled to room temperature. The magnetic nanoparticles were precipitated in ethanol, separated by centrifugal force, and then redispersed in octane.

Iron oxide magnetic nanoparticles were prepared for the TEM analysis by dropping a drop of the magnetic fluid on a very thin piece, and then the dispersing solvent was evaporated to obtain a thin layer of the particles.

Figures 22-24 showed the TEM images of the mercaptan-stabilized prepared iron oxide magnetic nanoparticles at high and low resolution (different magnifications). These analyses showed that the size of the particles is around 5-7 nm and the size is quite uniform. It also showed that the magnetic nanoparticles are generally spherical in shape. In addition, it was demonstrated that cyclic dithiocarbonates can effectively facilitate and stabilize formation of magnetic nanoparticles with reasonably uniform size and shape.

EDS results (Figure 25) showed the presence of carbon (C), iron (Fe), oxygen (O), copper (Cu), silicone (Si), and sulfur (S). Carbon comes from the surfactant, iron from iron oxide nanoparticles, oxygen from the surfactant and from the iron oxide nanoparticles, copper and silicone from the sample holder, and finally sulfur from the surfactant.
Figure 1. GC-MS spectra of 5-ethyl-(1,3)-oxathiolane-2-thione (1).
Figure 2. FTIR spectrum of 5-ethyl-(1,3)oxathiolane-2-thione) (1).
Figure 3. $^1$H NMR spectrum of 5-ethyl-(1,3)oxathiolane-2-thione (1).
Figure 4. $^{13}$C NMR spectrum of 5-ethyl-(1,3)oxathilane-2-thione (1).
Figure 5. $^1$H NMR spectrum of bis[5,5′-ethoxymethyl]-bis[1,3-oxathiolane-2-thione] (2).
Figure 6. $^{13}$C NMR Spectrum of bis[5,5'-ethoxymethyl]-bis[1,3-oxathiolane-2-thione] (2).
Figure 7. FTIR Spectrum of bis[5,5′-ethoxymethyl]-bis[1,3-oxathiolane-2-thione] (2).
Figure 8. $^1$H NMR spectrum of 5,5'-phenoxyethyl-bis[1,3-oxathiolane-2-thione] (3).
Figure 9. $^{13}$C NMR spectrum of 5,5′-phenoxyethyl-bis[1,3-oxathiolane-2-thione] (3).
Figure 10. FTIR spectrum of 5,5′-phenoxymethyl-bis[1,3-oxathiolane-2-thione] (3).
Figure 11. $^1$H NMR spectrum of 5,5'-[methylene-bis(4,1-phenyleneoxymethylene)-bis[1,3-oxathiolane-2-thione] (4).
Figure 12. $^{13}$C NMR spectrum of 5,5$'$-methylene-bis(4,1phenyleneoxymethylene)-bis[1,3-oxathiolane-2-thione] (4).
Figure 13. FTIR spectrum of 5,5′-[methylene-bis(4,1phenyleneoxymethylene)-bis[1,3-oxathiolane-2-thione] (4).
Figure 14. GC-MS spectrum of 5-decyl-[1,3]oxathiolane-2-thione (5).
**Figure 15.** FTIR spectrum of 5-decyl-[1,3]oxathiolane-2-thione (5).
Figure 16. $^1$H NMR spectrum of 5-decyl-(1,3)-oxathiolane-2-thione (5).
Figure 17. $^{13}$C NMR spectrum of 5-decyl-(1,3)oxathiolane-2-thione (5).
Figure 18. $^1$H NMR spectrum of the mercaptan compound.
Figure 19. $^{13}$C NMR spectrum of the mercaptan compound.
Figure 20. TGA thermogram of resin prepared from monomer (2) and TAEA.
Figure 21. DSC thermogram of thermoset resin of monomer (2) and TAEA.
Figure 22. TEM micrograph of magnetic nanoparticles (2 nm).
Figure 23. TEM micrograph of magnetic nanoparticles (10 nm).
Figure 24. TEM micrograph of magnetic nanoparticles (50 nm).
Figure 25. EDS spectrum of magnetic nanoparticles.
CHAPTER FOUR: CONCLUSION

Mono- and bifunctional cyclic dithiocarbonates (1,3-oxathiolane-2-thione)s were synthesized using a method involving reaction of the corresponding oxiranes with carbon disulfide and lithium bromide as catalyst. Some of these products were synthesized for the first time.

The monomer, 5-decyl-[1,3]oxathiolane-2-thione (5), containing a hydrophobic tail, can be easily dispersed in hydrocarbons such as octane. The hydrophilic head was generated from this cyclic dithiocarbonate by reacting it with n-butylamine, yielding product (6) that bears a polar and head thiol group. This group has high affinity toward metals.

A decomposition/oxidation method was used to synthesize iron oxide magnetic nanoparticles in the presence of model surfactant (6), resulting in the formation of magnetic nanoparticles.

In this work we demonstrated that cyclic dithiocarbonates are an excellent candidate for the generation of stabilized magnetic nanoparticles. This is achieved by generating thiol functional groups. The creation of those groups is a result of the selective reaction of five-membered cyclic dithiocarbonates with amines. This could be in the form of linear polymers or thermoplastics or in the form of films of thermosets.

In the future, we will explore attaching five-membered cyclic dithiocarbonates to other moieties, such as norbornene derivatives, that may be polymerized by ring-opening
metathesis polymerization to obtain narrow molecular weight distribution polymer surfactants.
LIST OF REFERENCES


