

THE UNIVERSITY OF CALGARY

**SYNTHESIS OF BENZENEPOLYTHIOLS AND THEIR REACTIONS WITH
ELEMENTAL SULFUR**

by

HONG YAO

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

CALGARY, ALBERTA

MARCH 1998

© Hong Yao 1998



National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-34713-3

Canada

Abstract

The overall objective of this research was to examine the reaction of benzenepolythiols with elemental sulfur to determine the properties of the resultant polysulfides and their effect on the physical properties of elemental sulfur.

Benzenepolythiols are not readily accessible on a large scale, but have been prepared by nucleophilic substitution of chlorobenzene under forcing conditions. Consequently, a new method for C-S bond formation in aromatic substrates was developed using dimethyl disulfide activated by acidic mesoporous clays. This method worked well for alkylbenzenes affording a variety of methylthiolated benzene derivatives. Birch reduction of these compounds gave the desired benzenethiols in good yields.

It was found that benzene di- and trithiols reacted rapidly with liquid sulfur forming linear and network polymers respectively. Even when present in low concentrations (10^{-3} molar fraction), the polysulfides had significant effects on the physical properties of sulfur causing increased viscosity and a very substantial depression of freezing point ($>50^{\circ}\text{C}$). This last effect is of considerable industrial importance as it could be applied to mitigate sulfur deposition in natural gas wells and pipelines and allow transport of liquid sulfur at a low cost.

Linear and network polysulfides were also prepared in organic solvent solution. Elemental and Raman spectroscopic analysis indicated that, on average, sulfur couplings between aromatic units consisted of tri- and tetrasulfide linkages. Polysulfides isolated from liquid sulfur were elastomeric in nature but were unstable and were contaminated with polymeric sulfur.

ACKNOWLEDGMENT

I would like to acknowledge and express my gratitude to the following people:

My husband Wei, my parents and my grandma for all their love, encouragement and support throughout the years.

My supervisor, Dr. Peter D. Clark, for his guidance, patience and sense of humor which made this work a very enjoyable experience for me.

My friends and colleagues with whom I have been working for the past five years, in particular, Dr. Shaun Mesher, Dr. Andrew Kirk and Alex Primak.

All the management and staff of Alberta Sulphur Research Ltd. (ASRL) for allowing me to use all their facilities and instrumentation. In particular, Kathy Almond and Joana Simion for helping me with the polymeric content measurement. Kevin Lesage for his advice concerning GC-MS analyses. Ed Fitzpatrick for his expertise and help with the autoclave reactions. Dr. Clement Lau for his help and advice concerning the thermal stability study on polysulfides which I did not have the opportunity to finish. Ms. Dianne Jorgenson for her general advice and kindness. A special thanks to Krysl Ciesluk for her help with the formatting of this dissertation.

Greta Prihodko for her kindness and administrative expertise.

Dr. R. Yamdagni, Qiao Wu, Dorothy Fox for their technical assistance and Dr. M. Parvez for conducting the X-ray structure analysis.

The Department of Chemistry, University of Calgary for the research facilities and Graduate Teaching Assistantship (GAT) funding.

Natural Sciences and Engineering Research Council of Canada and Alberta Sulphur Research Ltd. (ASRL) for funding of this project.

In memory of my grandma, Zhenyin Xu

TABLE OF CONTENTS

	Page
Approval Page.....	ii
Abstract.....	iii
Acknowledgments.....	iv
Dedication.....	vi
Table of Contents.....	vii
List of Tables	xiii
List of Schemes.....	xv
Abbreviations.....	xx

CHAPTER ONE : INTRODUCTION

1.	General Objective of Thesis Research.....	1
1.1	Present Methods of Removing Sulfur Deposits in Sour Gas Well: Advantages and Drawbacks	3
1.2	Thermal Stability of Organic Polysulfides Under H ₂ S Pressure	9
1.3	Current Methods of Synthesis of Aromatic Thiols.....	11
1.4	New Methods for Synthesis of Aromatic Thiols: Clay-Catalyzed C-S Bond Formation	14
1.4.1	The Structure of Montmorillonite Clay	14
1.4.2	Surface Areas and Porosities of K10 Montmorillonite	15
1.4.3	Surface Areas and Porosities of Cation-Exchanged K10	16
1.4.4	Lewis and Brønsted Acidity of “Clayzic”	20
1.4.5	Organic Reactions Using K10 and Cation-Exchanged K10 as Catalysts	21
1.4.5.1	Reactions due to the Lewis Acidity	21
1.4.5.1.1	Friedel-Crafts Reactions Catalyzed by Cation-Exchanged K10.....	21

	Page
1.4.5.1.2 Diels-Alder Reactions.....	23
1.4.5.1.3 Michael Reactions	25
1.4.5.2 Reactions due to Brönsted Acidity	26
1.4.5.2.1 Protonation of Alkenes	26
1.4.5.3 Reactions Catalyzed by Clay-supported Metallic Nitrates	27
1.4.5.3.1 Nitration.....	27
1.4.5.3.2 Oxidation	28
1.4.5.3.3 Carbonyl Group Deprotection	29
1.5 Preparation and Properties of Polysulfides.....	31
1.5.1 Synthesis of Poly(phenylene sulfide).....	32
1.5.1.1 Electrophilic Substitution Reactions	32
1.5.1.2 Nucleophilic Substitution Reactions	33
1.5.2 Characterization of Poly(phenylene sulfide)	35
1.5.2.1 Molecular Weight Distribution.....	35
1.5.2.2 Micro-analysis of Poly(phenylene sulfide)	36
1.5.2.3 Thermal Characterization of Poly(phenylene sulfide)	36
1.5.2.4 Raman Spectroscopy	37

CHAPTER TWO: OBJECTIVES OF THE RESEARCH WORK

2.1	Development of New Methods for the Synthesis of Poly(alkylthio)benzenes with Clay Catalysts	39
2.2	Investigation of Reactions of Benzenepolythiols with Elemental Sulfur	42

	Page
2.2.1 Kinetics of the Reactions	42
2.2.2 Physical Properties of Elemental Sulfur/Polysulfide Mixtures	43
2.3 Characterization of Polysulfides Isolated from Reactions of Benzenepolythiols with Elemental Sulfur	45
2.3.1 Elemental Analysis	45
2.3.2 Raman Spectroscopy	45
2.3.3 Average Molecular Weight.....	46
<u>CHAPTER THREE</u> : NEW METHODS FOR SYNTHESIS OF BENZENETHIOLS	48
3.1 Mechanism and General Considerations	48
3.2 Results and Discussions	53
3.2.1 Reactions with Monosubstituted Aromatics.....	53
3.2.1.1 Reactions with Toluene	53
3.2.1.2 Reactions with Anisole	57
3.2.1.3 Reactions with Thioanisole	61
3.2.2 Reactions with Xylenes	66
3.2.2.1 Reactions with <i>p</i> -Xylene.....	69
3.2.2.2 Reactions with <i>o</i> -Xylene.....	69
3.2.2.3 Reactions with <i>m</i> -Xylene.....	70
3.2.3 Reactions with Trisubstituted Aromatics - Mesitylene	71
3.3 Characterization of the Catalysts	77

	Page
3.3.1 Pore Size and Surface Area	77
3.3.2 ²⁷ Al and ²⁹ Si NMR of the Catalysts.....	78
3.4 Conclusions	81

CHAPTER FOUR: FORMATION OF LINEAR AROMATIC POLYSULFIDES FROM REACTION OF BENZENE-THIOLS WITH ELEMENTAL SULFUR.....82

4.1 Chemistry of Sulfur	83
4.2 Reaction of 1,4-Benzenedithiol with Sulfur	86
4.2.1 Polymeric Content Measurement	89
4.2.2 Viscosity Measurement	92
4.2.3 Depression of Freezing Point	94
4.3 Reaction with 2,5-Dimethyl-1,4-benzenedithiol	96
4.3.1 Polymeric Content Measurement	96
4.3.2 Viscosity Measurement	97
4.3.3 Freezing Point Depression.....	98
4.4 Summary.....	99

CHAPTER FIVE: FORMATION OF NETWORK AROMATIC POLYSULFIDES FROM REACTION OF BENZENETRITHIOLS WITH ELEMENTAL SULFUR.....100

5.1 Reaction of 1,3,5-Benzenetrithiol with Sulfur.....	101
--	-----

	Page
5.1.1 Polymeric Content Measurements after Reaction with 1,3,5-Benzenetrithiol	101
5.1.1.1 Polymeric Content of Aged Solid Samples	103
5.1.2 Viscosity Measurements	106
5.1.3 Depression of Freezing Point	107
5.2 Reaction with 2,4,6-Trimethylbenzenetrithiol.....	110
5.2.1 Polymeric Content Measurements	110
5.2.2 Viscosity Measurement	112
5.2.3 Freezing Point Depression.....	114
5.3 Summary.....	115

CHAPTER SIX: ISOLATION AND CHARACTERIZATION OF POLYSULFIDES.....117

6.1 Isolation and Characterization of Linear Polysulfides.....	118
6.1.1 Average Molecular Weight Measurements	118
6.1.2 Raman Spectroscopy Study	122
6.1.3 Elemental Analysis	127
6.2 Isolation and Characterization of Network Polysulfides	128
6.2.1 Raman Spectroscopy Study	128
6.2.2 Elemental Analysis	131
6.3 Summary.....	132

	Page
<u>CHAPTER SEVEN: EXPERIMENTAL</u>	134
7.1 Instruments	134
7.2 Experimental Procedures Pertaining to Chapter 3	137
7.2.1 Chemicals and Reagents	137
7.2.2 Catalysts Preparation	137
7.2.3 Alkylthiolation Procedures	138
7.2.4 Literature Procedures for the Preparation of 1,3,5-Benzenetrithiol.....	144
7.2.5 Birch Reduction Procedures	145
7.3 Experimental Procedures Pertaining to Chapter 4 and 5	146
7.3.1 Polymeric Content Measurement	146
7.3.2 Viscosity Measurement	147
7.3.3 Freezing Point Measurement	147
7.4 Experiment Procedures Pertaining to Chapter 6.....	148
7.4.1 Chemicals and Reagents	148
7.4.2 Preparation of Linear Polysulfides from 2,5-Dimethyl-1,4-benzenedithiol.....	148
7.4.3 Molecular Weight Measurement by VPO	149
 <u>CHAPTER EIGHT: CONCLUDING COMMENTS</u>	151
 APPENDIX.....	154
 REFERENCES	169

LIST OF TABLES

Table		Page
1	Sulfur Carrying Power for Different Sulfur Solvents	4
2	Comparison of Specific Surface Area (a) and Total Pore Volume (V_p) for Untreated Montmorillonite Clay and K10	16
3	Comparison of Specific Surface Area (a) and Total Pore Volume (V_p) for Clayzic and K10	17
4	Results of Reactions of Toluene with DMDS in the Presence of Clay Catalysts	56
5	Results of Reactions of Anisole with DMDS in the Presence of Clay Catalysts	60
6	Results of Reactions of Thioanisole with DMDS in the Presence of Clay Catalysts	62
7	Results of Reactions of Xylenes with DMDS in the Presence of Clay Catalyst(s)	67
8	Bond Lengths of $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3\text{-ZnCl}_2$ (Å)	74
9	Bond Angles of $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3\text{-ZnCl}_2$ (°)	74
10	Results of Reactions of Mesitylene with DMDS in the Presence of Clay Catalyst.....	75
11	Specific Surface Area and Maximum Pore Size of K10, K10/ H^+ and K10/ H_2SO_4	77
12	^{29}Si NMR Chemical Shifts (ppm) of the Clay Catalysts.....	79
13	^{27}Al NMR Chemical Shifts (ppm) of the Clay Catalysts	80
14	Preparation Conditions of the Samples for VPO Measurements	121
15	Preparation Conditions of the Samples for Raman Spectroscopy Studies.....	123

	Page
16	Raman Spectra of Polysulfides Formed from the Reaction of 2,5-Dimethyl-1,4-Benzenedithiol and Elemental Sulfur 123
17	Elemental Analysis of Linear Polysulfides from the Reaction of 2,5-Dimethyl-1,4-Benzenedithiol and Elemental Sulfur 127
18	Preparation Conditions of the Samples for Raman Spectroscopy Studies 128
19	Raman Spectra of Network Polysulfides 130
20	Reaction Conditions and Elemental Analysis of Network Polysulfides from the Reaction of 2,4,6-Trimethylbenzene- trithiol and Elemental Sulfur..... 131

LIST OF SCHEMES

Scheme	Page
1 Formation of Dialkyl Polysulfides From Organic Disulfides Catalyzed by Amines.....	5
2 Dissolution of Sulfur by Polysulfides	6
3 Regeneration of Dialkyl Disulfides.....	7
4 Formation of 1,2-Benzenedithiol from Benzenethiol	11
5 Formation of 1,2-Benzenedithiol from 2-Aminobenzenethiol.....	12
6 Formation of Benzenethiols from Polychlorobenzenes	12
7 Synthesis of Polythiobenzenes Using Clay Catalysts.....	13
8 Structure of Montmorillonite Clay	15
9 Comparison of Pore Size Distribution for Clayzic and non-Acid Treated Clay	18
10 Comparison of Cumulative Pore Volumes for K10 and non-Acid Treated Clay	18
11 Comparison of Pore Size Distributions for Clayzic and K10	19
12 Comparison of Cumulative Pore Volumes for Clayzic and K10	19
13 Porous Structure of K10/ZnCl ₂ (Clayzic)	19
14 FTIR Spectra of Pyridine Adsorbed on K10(a) and Clayzic (b) (R = % Reflectance)	21
15 Comparison of the Conversions Achieved with a Clay-Based Catalyst and with Standard Lewis Acids	22
16 Comparison of the Conversions Achieved with a Clay-Based Catalyst and with Standard Lewis Acids	23
17 Diels-Alder Reactions Catalyzed by K10-Fe(III).....	24

	Page
18	Diels-Alder Reactions with Unactivated Dienes Catalyzed by K10-Fe(III)25
19	Michael Addition Catalyzed by K10-Ni(II)/FeCl ₃26
20	Cation-Exchanged K10 Used in the Reactions of Protonating Alkenes27
21	Nitration of <i>t</i> -Butylbenzene Using Clayfen as Catalyst28
22	Nitration of Estrone Using Clayfen as Catalyst28
23	Oxidation of Secondary Alcohols Using Clayfen as Catalyst.....29
24	Oxidation of Benzenethiol Using Clayfen as Catalyst.....29
25	Carbonyl Group Deprotection Using Clayfen as Catalyst.....30
26	Conversion of Thiocarbonyl to Carbonyl Group Using Clayfen as Catalyst.....30
27	Reactions of Benzene with Sulfur Sources (S ₈ , S ₂ Cl ₂ or SCl ₂) by Friedel and Crafts32
28	Synthesis of Poly(arylene sulfide) through Nucleophilic Substitution of Dichlorobenzene by Macallum.....33
29	Mechanism through Nucleophilic Substitution for the Formation of Poly(phenylene sulfide).....34
30	Mechanism through Single Electron Transfer (SET) for the Formation of Poly(phenylene sulfide).....35
31	Reaction Pathway of DMDS with Arene on the Surface of Clayzic40
32	Formation of Polythiobenznes by Birch Reduction41
33	Reaction of Benzenedithiol with Molten Sulfur in a Sealed FT-IR Cell.....42
34	Cyclization of Phenylthioacetal over K10/ZnCl ₂48

	Page
35	Formation of Benzo[b]thiophene by Intramolecular Cyclization49
36	Formation of Diphenyl Disulfide by Intermolecular Attack50
37	Formation of Alkylthiolated Aromatics on the Surface of Clayzic51
38	Formation of Dimethyl Polysulfide on the Surface of Clayzic52
39	Reaction of Toluene with DMDS in the Presence of Clay Catalyst(s)53
40	Brönsted Acid-Catalyzed Methylthiolation on the Clay Surface55
41	Reaction of Anisole with DMDS in the Presence of Clay Catalyst(s)57
42	Possible Reaction Pathway Involving Nucleophilic Substitution on the Surface of K10/MnCl ₂59
43	Reaction of Thioanisole with DMDS.....61
44	Co-ordination between Polyalkylthiolated Arenes with Acid Sites on the Clay Surface.....65
45	Reactions of Xylenes with DMDS in the Presence of Clay Catalyst(s)66
46	Reactions of Mesitylene with DMDS in the Presence of Clay Catalyst(s)72
47	ORTEP Diagram of CH ₃ SCH ₂ CH ₂ SCH ₃ -ZnCl ₂73
48	The Effect of Acid-treatment on Clay Catalysts78
49	Formation of Polymeric Sulfur83
50	Removal of Polymeric Sulfur by Degassing Processes.....85
51	Re-establishment of Polymeric Sulfur at 140°C86

	Page
52	Formation of Polysulfide Polymer from 1,4-Benzenedithiol and Elemental Sulfur88
53	Polymeric Content in Liquid Sulfur (200 g) after Reaction with 1,4-Benzenedithiol (0.1 g, 0.70 mmol) at 140°C91
54	Reduced Viscosity of Sulfur (4.1 g) after Reaction with 1,4-Benzenedithiol (0.1 g, 0.70 mmol) at 120°C93
55	Freezing Point of Sulfur after Reaction with 1,4-Benzenedithiol95
56	Polymeric Content of Liquid Sulfur (200 g) after Reaction with 2,5-Dimethyl-1,4-benzenedithiol (0.1 g, 0.59 mmol) at 140°C97
57	Reduced Viscosity of Sulfur (4.0 g) after Reaction with 2,5-Dimethyl-1,4-benzenedithiol (0.12 g, 0.71 mmol) at 120°C98
58	Freezing Point of Sulfur after Reaction with 2,5-Dimethyl-1,4-benzenedithiol99
59	Polymeric Content in Liquid Sulfur (un-degassed, 200 g) after Reaction with 1,3,5-Benzenetrithiol (0.1 g, 0.575 mmol) at 140°C102
60	Polymeric Content in Liquid Sulfur (initially degassed, 200 g) after Reaction with 1,3,5-Benzenetrithiol (0.1 g, 0.575 mmol) at 140°C103
61	Decomposition of Polysulfides in Solid Sulfur from the Reaction of 1,3,5-Benzenetrithiol with Sulfur over 18 h at 140°C104
62	Decomposition of Polysulfides from the Reaction of 1,3,5-Benzenetrithiol with Sulfur after Quenched at 1.5 h106
63	Reduced Viscosity of Sulfur (4.0 g) after Reaction with 1,3,5-Benzenetrithiol (0.01 g, 0.0575 mmol) at 140°C107
64	Freezing Point of Sulfur with 1,3,5-Benzenetrithiol108
65	Polymeric Content in Liquid Sulfur (200 g) after Reaction with 2,4,6-Trimethylbenzenetrithiol (0.1 g, 0.463 mmol) at 140°C111

	Page
66	Solid ^{13}C NMR Spectrum of Network Polysulfides Recovered from CS_2 Extraction112
67	Reduced Viscosity of Sulfur (4.0 g) after Reaction with 2,4,6-Trimethylbenzenetrithiol (0.01 g, 0.046 mmol) at 140°C113
68	Freezing Point of Sulfur after Reaction with 2,4,6-Trimethylbenzenetrithiol.....115
69	Anionic Polymerization of 2,5-Dimethyl-1,4-benzenedithiol with Elemental Sulfur in the Presence of Et_3N120
70	Attempted Termination Using Dialkyl Disulfides121
71	Raman Spectrum of the Linear Polysulfides (c) Formed from the Reaction of 2,5-Dimethyl-1,4-benzenedithiol with Elemental Sulfur124
72	Raman Spectrum of the Linear Polysulfides (d) Formed from the Reaction of 2,5-Dimethyl-1,4-benzenedithiol with Elemental Sulfur.....124
73	Disulfide Linkages in Linear Polysulfides125
74	Raman Spectrum of the Network Polysulfides (f) Formed from the Reaction of 2,4,6-Trimethylbenzenetrithiol with Elemental Sulfur (24 equiv.)129
75	Raman Spectrum of the Network Polysulfides (g) Formed from the Reaction of 2,4,6-Trimethylbenzenetrithiol with Elemental Sulfur (4 equiv.)129

ABBREVIATIONS

bp	boiling point
Bu	butyl
°C	degree Celsius
CHCl ₃	chloroform
CH ₂ Cl ₂	dichloromethane
cm ⁻¹	wavenumbers
CS ₂	carbon disulfide
DMDS	dimethyl disulfide
Et ₃ N	triethylamine
eq.	equation
equiv.	equivalent
g	grams
h	hours
HMPA	hexamethylphosphoramide
Hz	Hertz
<i>m</i> -	meta
M ⁺	molecular ion
Me	methyl
<i>m/e</i>	mass-to-charge ratio
MHz	megaHertz
min	minutes
mL	milliliters
mmol	millimoles
mp	melting point
MS	Mass Spectroscopy
NMR	nuclear magnetic resonance
<i>o</i> -	ortho
p	page
<i>p</i> -	para

PhCl	chlorobenzene
s	strong
TFAA	trifluoroacetic acid
THF	tetrahydrofuran
w	weak

CHAPTER ONE

INTRODUCTION

1. General Objective of Thesis Research

Sulfur deposition occurs frequently in natural gas wells producing sour gas (a mixture of CH_4 , H_2S and CO_2)^[1,2]. This phenomenon sometimes causes a serious problem since the deposited sulfur can severely restrict the gas flow or even stop it completely. Since the early 1970's, various solvents have been used to remove the sulfur deposits in sour gas wells, among which, dialkyl disulfide mixtures and pure dimethyl disulfide (DMDS) have proved to be the most effective^[3]. However, such chemicals are relatively expensive compared to other industrial materials and they have a strong, unpleasant odor. It is the objective of research described in this thesis to examine a new approach by using benzenethiols $[\text{Ar}(\text{SH})_x]$ as a means of preventing sulfur deposition. It is believed that this type of compound will react with elemental sulfur dissolved in the gas forming network polysulfides as the products. However, instead of dissolving sulfur, it is projected that the polysulfide products will delay sulfur deposition by promoting supercooling such that the sulfur will remain as liquid at least until it can flow to the surface and be removed. Also, it is anticipated that a depression in the melting point of the sulfur will extend the temperature range over which sulfur can be kept in the liquid phase.

The current methods of synthesis of benzenethiols utilize multi-step procedures and result in low isolated yields^[25,26]. One objective of this thesis was to develop a

simple and cheap method of synthesizing aromatic polythiols by using montmorillonite clays to promote C-S bond formation in benzene derivatives.

Another major objective of the research described in this thesis was to study the reactions of elemental sulfur with aromatic thiols and characterize the products of these reactions. The following sections give a detailed introduction to these topics.

1.1 Present Methods of Removing Sulfur Deposits in Sour Gas Wells:

Advantages and Drawbacks

Sour gas is a mixture of methane and other hydrocarbons containing hydrogen sulfide (H_2S) and carbon dioxide (CO_2). The amount of H_2S varies in the range of a few parts per million (ppm) to 97% depending on the locations of the reservoirs^[1].

Elemental sulfur deposition is often found in reservoirs with high H_2S content^[1,2,5]. The sulfur occurs either in physical solution or in chemical equilibrium with hydrogen polysulfides^[2]. The solubility of sulfur in sour gas depends on temperature, pressure and the H_2S content^[4]. The formation and subsequent decomposition of hydrogen polysulfide to sulfur and H_2S plays an important role in sulfur transportation and deposition in sour gas production systems. The equilibrium between sulfur and hydrogen polysulfide in the presence of H_2S is illustrated in eq. 1. As the temperature and pressure drops when sulfur saturated gases flow from reservoir to wellhead, the hydrogen polysulfide equilibrium is driven to left releasing elemental sulfur in the production pathway. In many cases, sulfur is deposited in the wellstring such that gas flow is either severely restricted or is stopped completely.



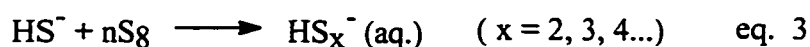
The current solution to the sulfur deposition is to inject sulfur solvents into sour gas wells in which deposition is occurring^[3,6]. Solvents currently available can be classified as either physical solvents, which do not chemically react with the sulfur or chemical solvents, which combine with sulfur in order to increase their sulfur carrying capacity.

Table 1. Sulfur Carrying Power for Different Sulfur Solvents^[1]

Physical Solvents	% S (W/W) at 20°C
Aliphatic	0.28
Thioether (RSR)	1.5
Aromatic	1.7
CS ₂	30
Chemical Solvents	% S (W/W) at 20°C
Amines	~25
Merox (RSSR)	~60
CH ₃ SSCH ₃	~150

The data in Table 1 show that the sulfur carrying power of physical solvents, in general, is less than that of the chemical solvents, with one exception, carbon disulfide (CS₂), whose sulfur carrying power rivals that of the chemical solvents^[1]. However, carbon disulfide is highly toxic and flammable, its auto-ignition temperature being only slightly above the boiling point of water^[1]. Another drawback of physical solvents is that in order to handle modest levels of sulfur deposition, unacceptably large amounts of solvent have to be used. Therefore, the sulfur carrying capacity of the chemical solvents makes them particularly attractive for use under heavy deposition conditions.

Amine solvents have been used extensively in sulfur deposit mitigation, despite the fact that they can cause corrosion of carbon steel^[7]. The chemistry of sulfur uptake is believed to be^[8]:



In the presence of amine, hydrogen sulfide forms the hydrosulfide ion (HS⁻) which is capable of attacking the sulfur ring to give hydropolysulfide ion (HS₉⁻). Thus, the

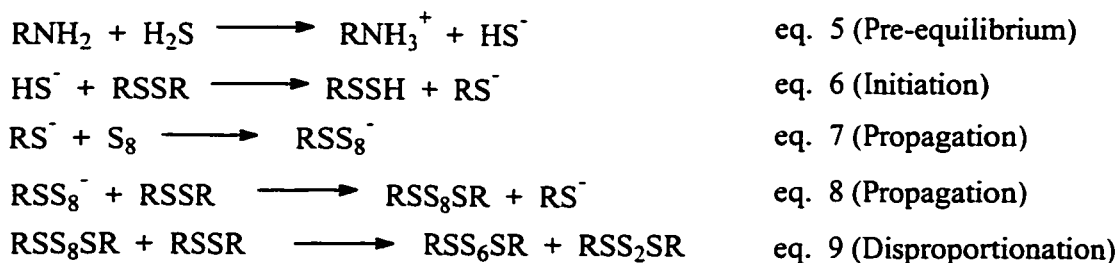
elemental sulfur is solublized in the aqueous solution of amine by being converted into the water soluble hydropolysulfide ion. The hydrosulfide ion and elemental sulfur in the presence of water are known to be highly corrosive^[9].

At present, the most extensively used sulfur carrying solvents are dialkyl disulfide mixtures, commonly referred to as Mercox^[3], the composition of which depends on the chemical composition of crude oil feedstocks from which they originate. Among the various components in Mercox mixtures, DMDS was identified as the most active disulfide. Under the influence of basic substances such as amines, dialkyl disulfides dissolve sulfur by the formation of polysulfides.



The following mechanism is proposed for the formation of dialkyl polysulfides^[1]:

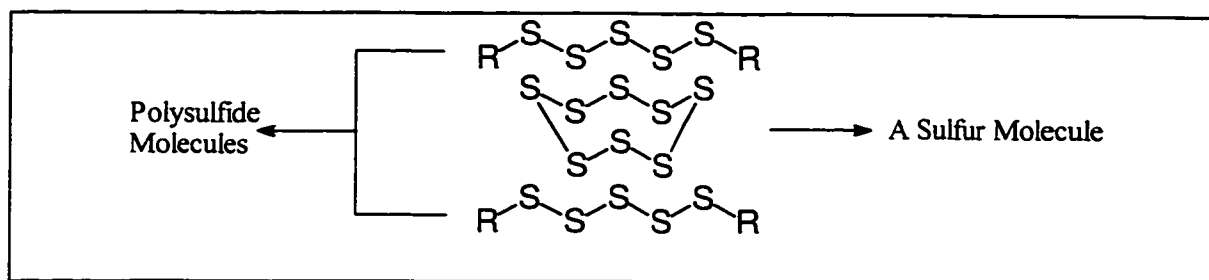
**Scheme 1. Formation of Dialkyl Polysulfides From Organic Disulfide
Catalyzed by Amines**



The catalytic amount of amine reacts with H_2S to give hydrosulfide ion (HS^-) (eq. 5), which can cleave the disulfide to yield RS^- species which in turn initiate the sulfur uptake reaction. The RS^- anion opens the S_8 ring and forms an alkyl polysulfide ion (eq. 7). As this propagation reaction proceeds, more and more elemental sulfur is incorporated into the organic structure by forming longer and longer polysulfide chains. The propagation reaction (eq. 8) gives dialkyl polysulfides and a new RS^- species which can

restart the propagation chain (eq. 7). The final product is dialkyl polysulfide RS_xR , where the value of x varies according to the amount of sulfur available. For DMDS, HPLC evidence for polysulfides containing up to 17 sulfur atoms has been obtained^[10]. However, these long chain polysulfides are not very stable and tend to disproportionate to give shorter chain polysulfides unless excess sulfur is present^[11]. The ability of dialkyl disulfides to open up and incorporate elemental sulfur is the basis of their remarkable power to carry sulfur. In addition, the produced polysulfide mixture is also a good physical solvent for sulfur since it can dissolve sulfur even without chemically reacting with it. This ability is likely a result of the similarities in their molecular structures (Scheme 2). Another important feature of sulfur uptake by disulfides is its reversible nature which is particularly important when disulfides are used in large volumes in super sour gas wells where solvent regeneration and re-circulation are necessary.

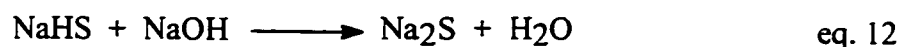
Scheme 2. Dissolution of Sulfur by Polysulfides



Attempts have been made to regenerate and re-circulate disulfide solvents, especially when sulfur deposition is extensive^[2]. The regeneration of sulfur-loaded dimethyl disulfide may be achieved by a chemical wash technique using aqueous sodium sulfide (Na_2S) solution. The dialkyl polysulfides are re-converted to disulfides and Na_2S_x by the process shown in Scheme 3. Sodium hydroxide is also added to regenerate Na_2S

which can be reused^[12]. This technique may enable the large volumes of dialkyl disulfides which are needed in super sour gas wells to be regenerated economically and re-circulated many times through the production system.

Scheme 3. Regeneration of Dialkyl Disulfides

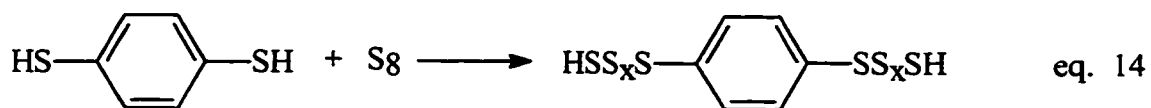


Dimethyl disulfide is by far the most powerful sulfur-uptake solvent with up to 250 wt% sulfur carrying capacity^[13]. However, it is relatively expensive in comparison to other industrial materials and has a strong, unpleasant odor.

Previously, mixtures of aryl disulfides have been considered as downhole sulfur solvents since they also react to form aryl polysulfides^[14] (eq. 13). These mixtures also arise as by-products of the refining of sour crude and thus their composition depends on the nature of the oil. It has been found that in the presence of a catalyst (NaHS and H₂S), that the rate of sulfur uptake by commercial diaryl disulfide mixtures is rapid and comparable to the rate of uptake by dialkyl disulfides. It is very dependent on temperature^[14].



Since diaryl disulfides are formed from oxidation of thiols, another possibility is to use aromatic di- and polythiols as sulfur “solvents”. Sulfur uptake could be achieved by the formation of polysulfides as shown below:



It is believed that this type of reaction could be used to prevent sulfur deposition rather than be applied in the sense of dissolving sulfur. In many cases, sulfur deposition only occurs in the upper part of the wellstring. When it occurs in the surface pipelines, sulfur can be removed by mechanical means. Thus, one way of minimizing the problem associated with sulfur deposition is to add an agent which can delay sulfur deposition. Addition of arylthiols could achieve this objective by two mechanisms:

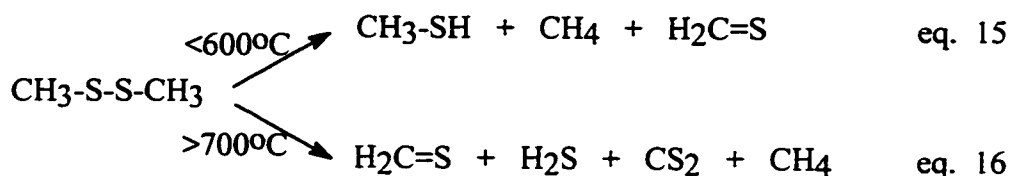
1. Depression of freezing point of sulfur such that it remains liquid in the wellstring, enabling it to flow to the surface. It is useful to note that gas temperatures often fall in the 100-70°C range as they flow from the reservoir to the wellhead.
2. By forming network polysulfides which could prevent crystallization of sulfur by a kinetic effect, i.e., promote supercooling of liquid sulfur.

1.2 Thermal Stability of Organic Polysulfides Under H₂S Pressure

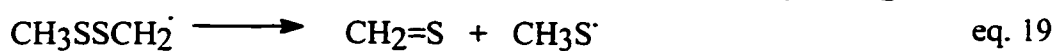
The thermal decomposition of organic polysulfides has been an area of interest in connection with their use in deep sour gas wells as decomposition products can lead to corrosion of steel and produce unwanted by-products (CH₃SH) in the gas. Studies have shown that polysulfide linkages are weaker than the disulfide linkages such that the energy required per homolytic cleavage of the S-S bond decreases with the increasing number of sulfur atoms per chain^[15,16]. This accounts for the instability of organic polysulfides containing greater than 3 sulfur atoms.

In the case of diphenyl tetrasulfide at temperatures around 140°C, it was suggested^[17] that the polysulfide decomposition involved the rupture of the S-S bonds. The initial products may then recombine to regenerate the original polysulfide or disproportionate to give a mixture of polysulfides containing higher and lower sulfur atoms per chain length. Also, it was observed that dimethyltetrasulfide disproportionated rapidly into a mixture of dimethyl di-, tri-, tetra-, penta- and hexasulfides when heated at 80°C for 40 hours^[15,18,19]. However, the decomposition of dimethyl trisulfide under the same conditions gave only dimethyl di-, tri- and tetrasulfides at a much slower rate, possibly a reflection of the greater stability of the S-S bonds in the trisulfide linkage as compared to the S-S bonds in the tetrasulfide linkage.

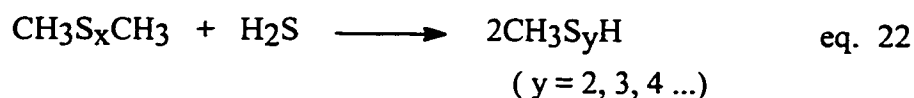
Böck and co-workers investigated the decomposition of a number of dialkyl disulfides flowing through a heated tube^[20]. High temperature pyrolysis of dimethyl disulfide (>700°C) gave thioformaldehyde, hydrogen sulfide, carbon disulfide and methane as major products. At lower temperature, the formation of methanethiol, thioformaldehyde and methane was favored^[20].



A free radical mechanism involving the cleavage of S-S bonds in the disulfide was proposed to account for the various products formed^[21]:



The rate of formation of CH_3SH from dimethyl polysulfide in the open system has been determined and it was found that all data fitted the first order rate expression^[22]. The addition of hydrogen sulfide inhibits the decomposition of dimethyl polysulfide in a closed system while extensive decomposition of dimethyl polysulfide was observed under the same condition without H_2S ^[22]. Although the method used in these experiments provided useful information, it did not duplicate conditions actually found in a deep sour gas well. The major difficulty in the experiments was that the act of taking samples disturbed the equilibrium of interest, e.g.:

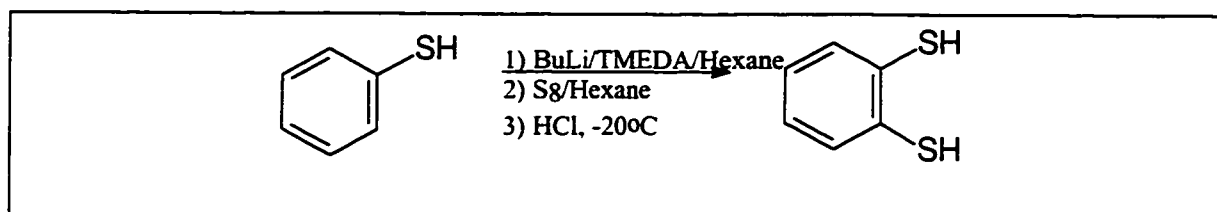


Due to the interaction of H_2S and S_8 with sulfur solvents and effects of pressure and species concentrations on the equilibrium, non-invasive methods are required to determine the “true” chemistry of sulfur solvent- S_8 - H_2S interactions under down-hole conditions.

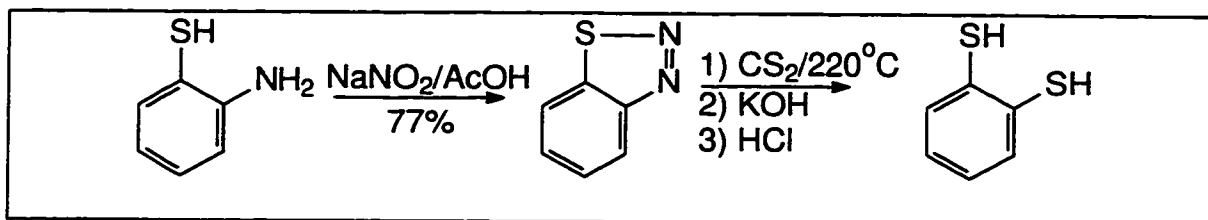
1.3 Current Methods of Synthesis of Aromatic Thiols

As mentioned before, aromatic polythiols are considered as potentially useful materials for preventing sulfur deposition in sour gas wells. If such compounds are to be used industrially, a simple, efficient synthesis of these compounds is important. Di-, tri- and tetra- substituted benzenethiols can be synthesized by using procedures described in the literature^[23-25]. One literature synthesis of 1,2-benzenedithiol^[23] is described in Scheme 4.

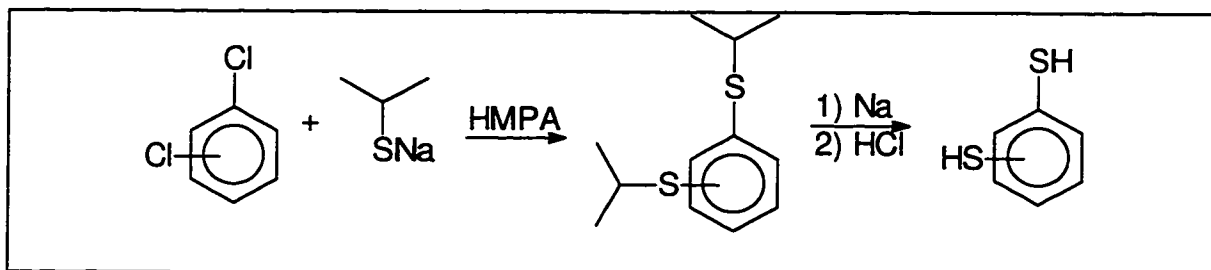
Scheme 4. Formation of 1,2-Benzenedithiol from Benzenethiol^[23]



This method utilized lithiation at the *ortho* position of benzenethiol in solution with N,N,N',N'-tetramethylethylenediamine (TMEDA) and hexane^[23]. Upon addition of elemental sulfur to the reaction mixture, the 1,2-benzenedithiolate was formed which, after direct acidification, gave the 1,2-benzenedithiol in reasonable yield (~75%). This compound can also be obtained by diazotization of 2-aminobenzenethiol. Reaction of the resultant 1,2,3-benzothiadiazole with carbon disulfide in an autoclave and hydrolysis of the 2-thioxo-1,3-benzodithiole product gave the desired 1,2-benzenedithiol^[26] (Scheme 5).

Scheme 5. Formation of 1,2-Benzenedithiol from 2-Aminobenzenethiol

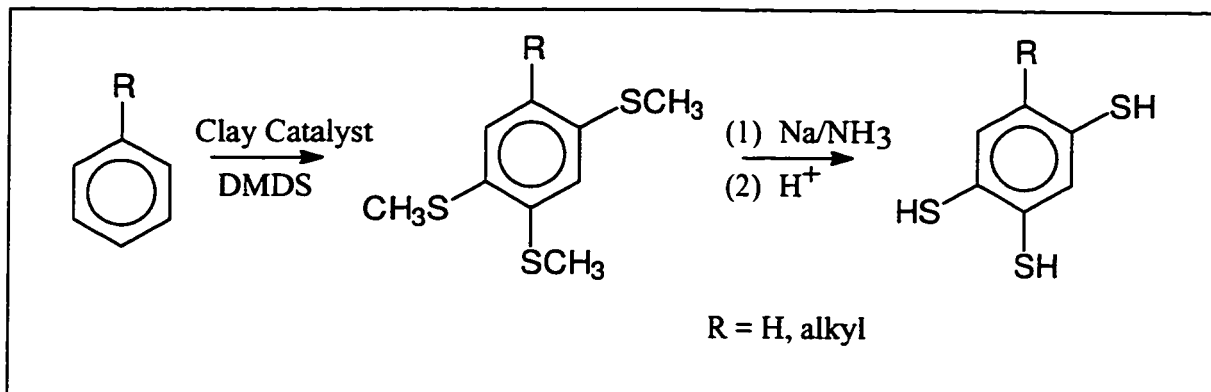
A more general method of preparing benzenethiols from polychlorobenzenes was developed by Testaferri and Tiecco in 1980^[24,25]. Nucleophilic substitution of deactivated aryl halides by the sodium salt of *iso*-propylthiol can be achieved by working in hexamethylphosphoramide (HMPA) solution. The reaction mixtures, containing the poly(*iso*-propylthio)benzenes, were treated directly with excess sodium to produce aromatic thiolates, which upon acidification, gave the corresponding thiols. According to this method, polythiolated products, including benzenehexakisthiol, can be obtained (Scheme 6).

Scheme 6. Formation of Benzenepolythiol from Polychlorobenzenes

A drawback of the above method is that it involves the use of the fairly expensive aprotic polar solvent (HMPA). Due to its high boiling point and miscibility with water and most other organic solvents, getting rid of the solvent becomes a tough task. In addition, the polyhalogenated benzene derivatives must also be available. One objective of the work described herein was to develop a new method of synthesizing

polyalkylthiobenzenes using DMDS and environmentally friendly catalysts based on montmorillonite clays. Dealkylation of these products should then afford the desired thiols as shown in Scheme 7.

Scheme 7. Synthesis of Benzenepolythiols Using Clay Catalysts



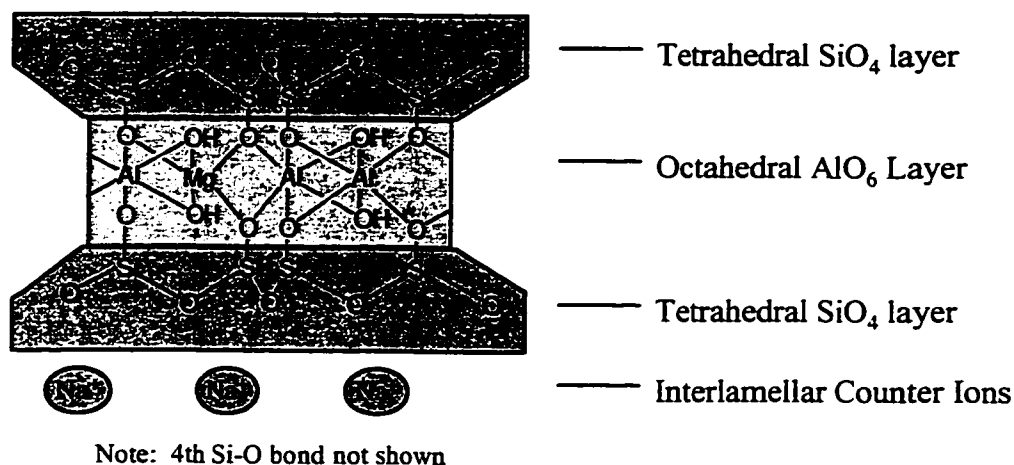
1.4 New Methods for Synthesis of Aromatic Thiols: Clay-Catalyzed C-S Bond Formation

K10 is a commercially available acid-treated montmorillonite clay which was used in this study for the preparation of catalysts designed to promote C-S bond formation in aromatics^[27]. Previous work in our laboratories has used this support material for the synthesis of thio-substituted thiophenes and benzothiophenes^[28]. An objective of this work was to extend its use to less reactive aromatic hydrocarbons.

1.4.1 The Structure of Montmorillonite Clay

Montmorillonite clay particles are organized parallel plates stacked one upon another^[29]. Those parallel layers are made of tetrahedral silicate and octahedral aluminate sheets. The octahedral aluminate layer is comprised of three sheets of atoms which, in turn, are sandwiched between two tetrahedral silicate sheets. A number of metallic cations, usually divalent, such as Mg^{2+} , Fe^{2+} , Zn^{2+} and Ni^{2+} , substitute for Al^{3+} in the octahedral sheets. Similarly, aluminum can be substituted for silicon in the tetrahedral layer, to a maximum of about 15%. The result of this substitution by other atoms is charge deficiencies among the layers causing the layers to be negatively charged. The negative charge is counter balanced by interlamellar cations, such as Na^+ , K^+ and Ca^{2+} , which occur as freely moving ions between the negatively charged plates. The general structure of montmorillonite clay is illustrated in Scheme 8.

Scheme 8. Structure of Montmorillonite Clay



The diversity of clays as catalysts in organic reactions arises from the fact that the tetravalent silicon can be replaced by Al^{3+} or the trivalent aluminum by a divalent metal cation. The resulting negative charges are balanced by Na^+ , K^+ , Ca^{2+} and Mg^{2+} , but these ions can be exchanged with other ions, such as Zn^{2+} , Fe^{2+} , Cu^{2+} , Fe^{3+} , Al^{3+} , Ti^{4+} , which give a variety of active sites for promoting chemical synthesis.

1.4.2 Surface Areas and Porosities of K10 Montmorillonite

K10 is the commercial trade name for an acid-treated montmorillonite clay. According to powder X-ray diffraction analysis, significant 2:1 layer structure appears to have been retained suggesting that the acid treatment conditions used in producing K10 are relatively mild^[30,31]. The most significant transformation resulting from acid treatment is the formation of mesopores. The porous structure of K10 consists of a broad distribution of pore diameters, the majority occurring in the 60-100 Å diameter range^[31], while untreated montmorillonite clay possesses very little porosity in the mesopore range^[32] (Scheme 9). It seems reasonable to assume that the mesoporous structure of K10

may result from a random stacking of plate-like particles and that these plate-like particles are likely the remnants of the 2:1 layers of the parent clay. Scheme 10 shows that the cumulative pore volume for K10 is considerably greater than that for untreated clay. In both cases, the majority of the total pore volume is derived from mesopores in the 50-150 Å diameter range. These data are consistent with the specific surface area and total pore volume measurements for K10 and untreated montmorillonite clay (see Table 2)^[32]. Both the surface area and total pore volume for K10 are considerably greater than that of the untreated montmorillonite clay.

Table 2. Comparison of specific surface area (a) and total pore volume (V_p) for untreated montmorillonite Clay and K10^[32]

Material	a (m^2g^{-1})	V_p (cm^3g^{-1})
Untreated-Montmorillonite Clay	47	0.06
K10	230	0.36

1.4.3 Surface Areas and Porosities of Cation-Exchanged K10

Clay-based materials have been used as catalysts in liquid phase organic reactions for many years. Early attempts to develop active clay-based catalysts for Friedel-Crafts reactions had limited success^[33,34]. In 1989, the emergence of zinc chloride supported on K10, ‘clayzic’, was a breakthrough in the search for environmentally friendly Friedel-Crafts catalysts^[35,36]. As mentioned before, the interlamellar cations in the montmorillonite clay can be exchanged by other cations, such as Zn^{2+} , Fe^{2+} , Cu^{2+} , Al^{3+} , Fe^{3+} and Ti^{4+} . Among these cation-exchanged K10 catalysts, “clayzic” has been studied most thoroughly^[32]. It has been found that there are significant differences between the pore size distribution for K10 and “clayzic” in the 50-150 Å diameter range (Scheme

11)^[32]. The sharp maximum at about 60 Å in the K10 distribution is now at a much lower intensity in “clayzic” appearing only as a shoulder. The broad distribution in the K10 plot between 70-150 Å has been almost totally lost. It seems likely that these changes are a result of zinc incorporated into the pores. This dramatic decrease of the number of pores in the 70-150 Å diameter range together with decrease of pore volume can be explained by the assumption that zinc chloride, when supported on K10, occupies both the surface of the clay and the mesopores within the clay and that the number of pores and pore volume (and thus the surface area) of those occupied pores is not measured when using dinitrogen as the adsorbate^[37]. The explanation seems reasonable since the surface covered with zinc ions will be too polar to allow the non-polar nitrogen molecules to adsorb. This would also imply that mesopores containing zinc ions are very polar in nature.

Table 3. Comparison of specific surface area (a) and total pore volume (V_p) for clayzic and K10^[32]

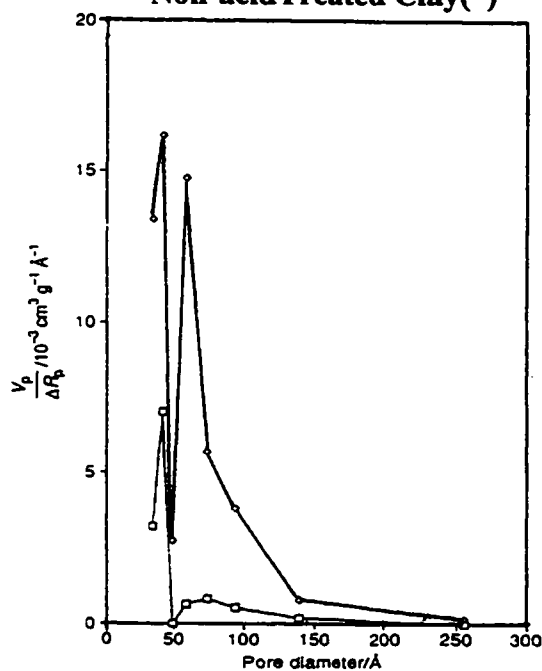
Material	a (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)
K10	230	0.36
Clayzic	132	0.28

The cumulative pore volume plots shown in Scheme 12 show that the measured pore volume for “clayzic” is much smaller than that of K10 and that a significant decrease occurs in the mesopores for the 50-150 Å diameter range^[32]. From Table 3, one can see that the measured specific surface area decreases from 230 m²g⁻¹ for K10 to 132 m²g⁻¹ for “clayzic” and the measured total pore volume drops from 0.36 cm³g⁻¹ for K10 to 0.28 cm³g⁻¹ for “clayzic”. In conclusion, it seems likely that when zinc chloride is supported

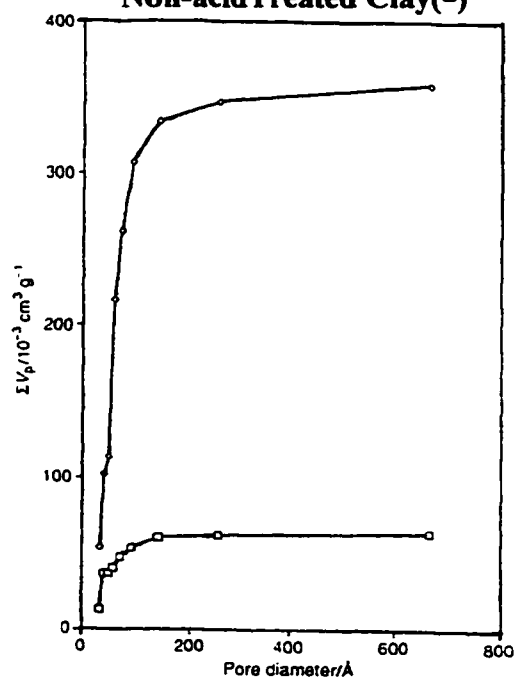
on K10, it occupies both the surface of the clay and mesopores within the clay as illustrated in Scheme 13.

It is believed that the organic reactions catalyzed by cation-exchanged clay take place both inside the mesopores and at the interlayer region. The great enhancement of catalytic activities towards many types of organic reactions after the acid treatment suggests that the porous structure has considerable effect on catalytic activity.

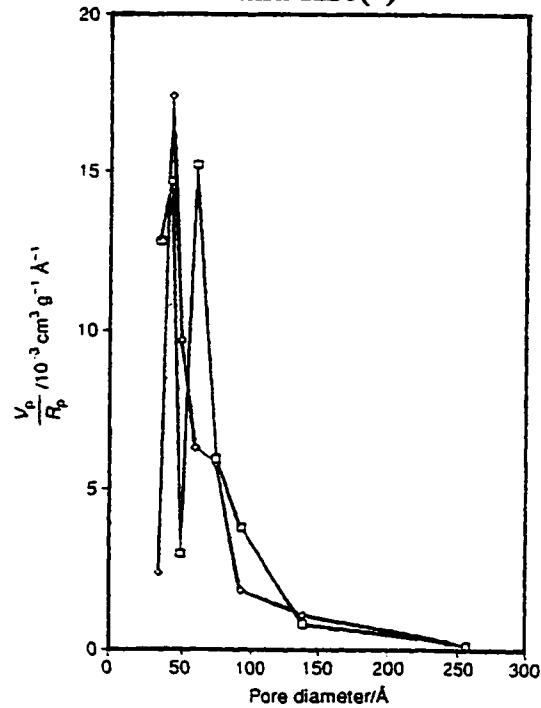
Scheme 9. Comparison of Pore Size Distribution for K10 (◇) and Non-acidTreated Clay(□)



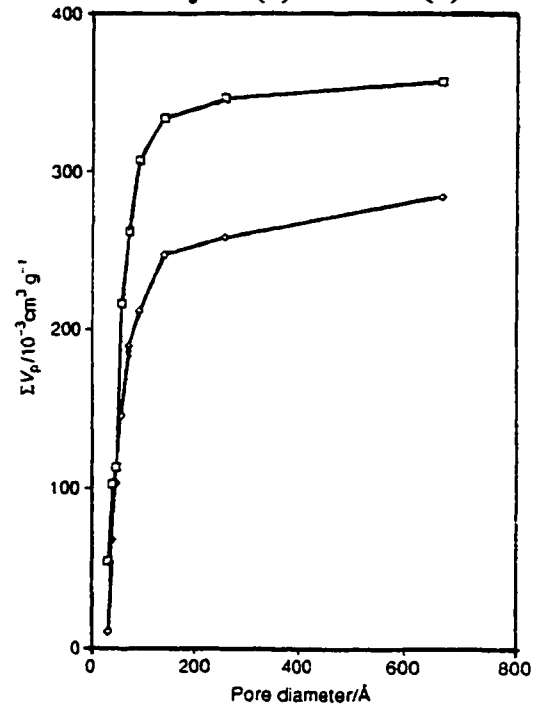
Scheme 10. Comparison of Cumulative Pore Volumes for K10 (◇) and Non-acidTreated Clay(□)



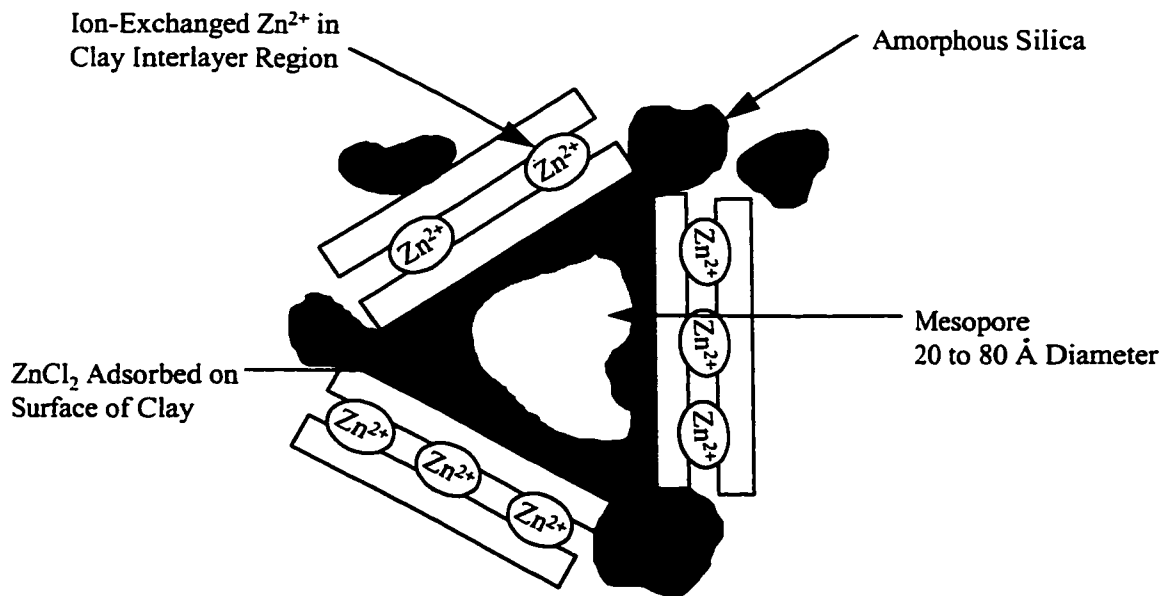
Scheme 11. Comparison of Pore Size Distribution for Clayzic (◇) and K10(□)



Scheme 12. Comparison of Cumulative Pore Volumes for Clayzic (◇) and K10(□)



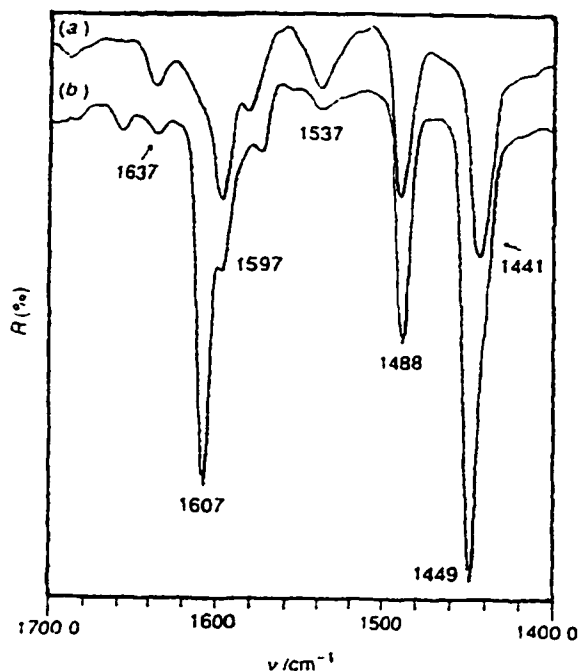
Scheme 13. Porous Structure of K10/ZnCl₂ (Clayzic)



1.4.4 Lewis and Brønsted Acidity of “Clayzic”

Surface Brønsted and Lewis acid sites can be differentiated through the well resolved infrared bands of adsorbed pyridine^[38]. Some studies have been carried out by recording the FTIR spectra of the adsorbed pyridine molecule on “clayzic”^[32]. The experiments were carried out by absorbing pyridine vapor onto the K10 and clayzic samples under vacuum until they were saturated and then recording diffuse reflectance FTIR (DRIFT) spectra (Scheme 14)^[32]. The bands at 1537 and 1637 cm^{-1} are due to the formation of pyridinium ions produced when pyridine molecules are protonated by Brønsted acid sites. The bands at 1449 and 1607 cm^{-1} are caused by the vibration of pyridine molecules coordinated to Lewis acid sites. The relative intensities of these bands represent the strength of Lewis and Brønsted acidity. It can be seen from Scheme 14 that K10 has more Brønsted acid sites than clayzic, while clayzic possesses significant Lewis acidity. The absence of the bands 1449 cm^{-1} and 1607 cm^{-1} in K10 suggests that K10 only has very limited Lewis acidity. Hence, the catalytic capability clayzic has towards many types of organic reactions is associated with its Brønsted and Lewis acidity as well as its pore structure.

Scheme 14. FT-IR Spectra of Pyridine Adsorbed on K10 (a) and Clayzic (b) (R = % Reflectance)



1.4.5 Organic Reactions Using K10 and Cation-Exchanged K10 as Catalysts

1.4.5.1 Reactions due to the Lewis Acidity

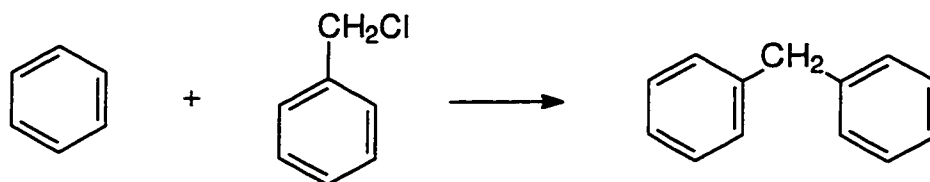
1.4.5.1.1 Friedel-Crafts Reactions Catalyzed by Cation-Exchanged K10

The Friedel-Crafts reaction is one of the most important ‘named’ reactions in organic chemistry. It includes aryl alkylations, acylations, benzoylations and sulfonylations^[32]. Traditional Friedel-Crafts reactions usually use mineral acids such as H_2SO_4 and HF or Lewis acids such as AlCl_3 and BF_3 . Among these catalysts, AlCl_3 is probably the most widely used^[39]. Although it is fairly cheap and readily available, it has a few drawbacks which include: i) it reacts violently with water and liberates HCl ; ii) it is

corrosive; iii) poor selectivity in alkylation reactions (polyalkylation and isomerization is observed); iv) greater than stoichiometric amounts of catalyst are required due to its complexation with product molecules; and v) isolation of product requires addition of water which liberates large amounts of HCl and creates an organic-contaminated, acidic aqueous solution which is increasingly expensive and difficult to dispose of. Since AlCl_3 is not an environmentally friendly catalyst, many alternatives to AlCl_3 have been examined^[32].

It has been found that in the use of cation-exchanged K10 as catalysts, Friedel-Crafts reactions proceed with greater selectivity and under milder conditions than for analogous homogeneous reactions^[34,40]. The reaction conditions and results of benzylation of benzene using benzyl chloride are listed in Scheme 15^[34].

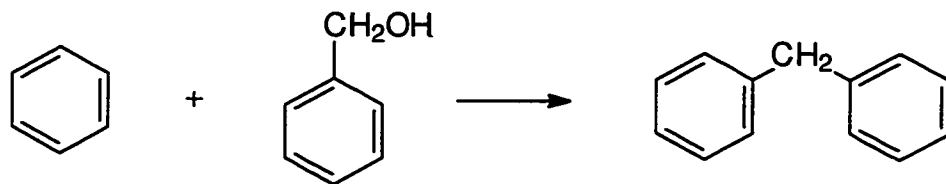
Scheme 15. Comparison of the Conversions Achieved with a Clay-Based Catalyst and with Standard Lewis Acids^[34]



Clay-based Catalyst	Reaction Time (h)	Conversion of PhCH_2Cl (%)	Corresponding Lewis-acid Catalyst	Reaction Time (h)	Conversion of PhCH_2Cl (%)
K10	15	98			
K10/ ZnCl_2	1.5	100	ZnCl_2	24	45
K10/ AlCl_3	9	84	AlCl_3	-	45
K10/ TiCl_4	5	90	TiCl_4	-	40
K10/ FeCl_3	0.25	100	FeCl_3	0.25	100
K10/ CoCl_2	11	70	CoCl_2	24	2

The overall reactivity of Lewis acids towards Friedel-Crafts reactions is generally considered to be: AlBr_3 , $\text{AlCl}_3 > \text{FeCl}_3 > \text{SbCl}_3 > \text{ZrCl}_4 > \text{BCl}_3$, $\text{BF}_3 > \text{SbCl}_5$. However, as can be seen from Scheme 15, clay-based catalysts are, in most cases, much more reactive than the unsupported compounds. Obviously, K10/AlCl_3 is a weaker Lewis acid than K10/ZnCl_2 , although AlCl_3 is usually considered as a much stronger Lewis acid than ZnCl_2 . The significant improvement of the activity of clay-based catalysts with respect to the unsupported catalysts is also observed. It takes ZnCl_2 alone 24 h to achieve 45% conversion of benzyl chloride, while for ZnCl_2 supported onto K10, 100% conversion of benzyl chloride is achieved after 1.5 h. The same trend can be also found in the reactions of benzylation of benzene by benzyl alcohol as illustrated in Scheme 16^[34].

Scheme 16. Comparison of the Conversions Achieved with a Clay-Based Catalyst and with Standard Lewis Acids^[34]



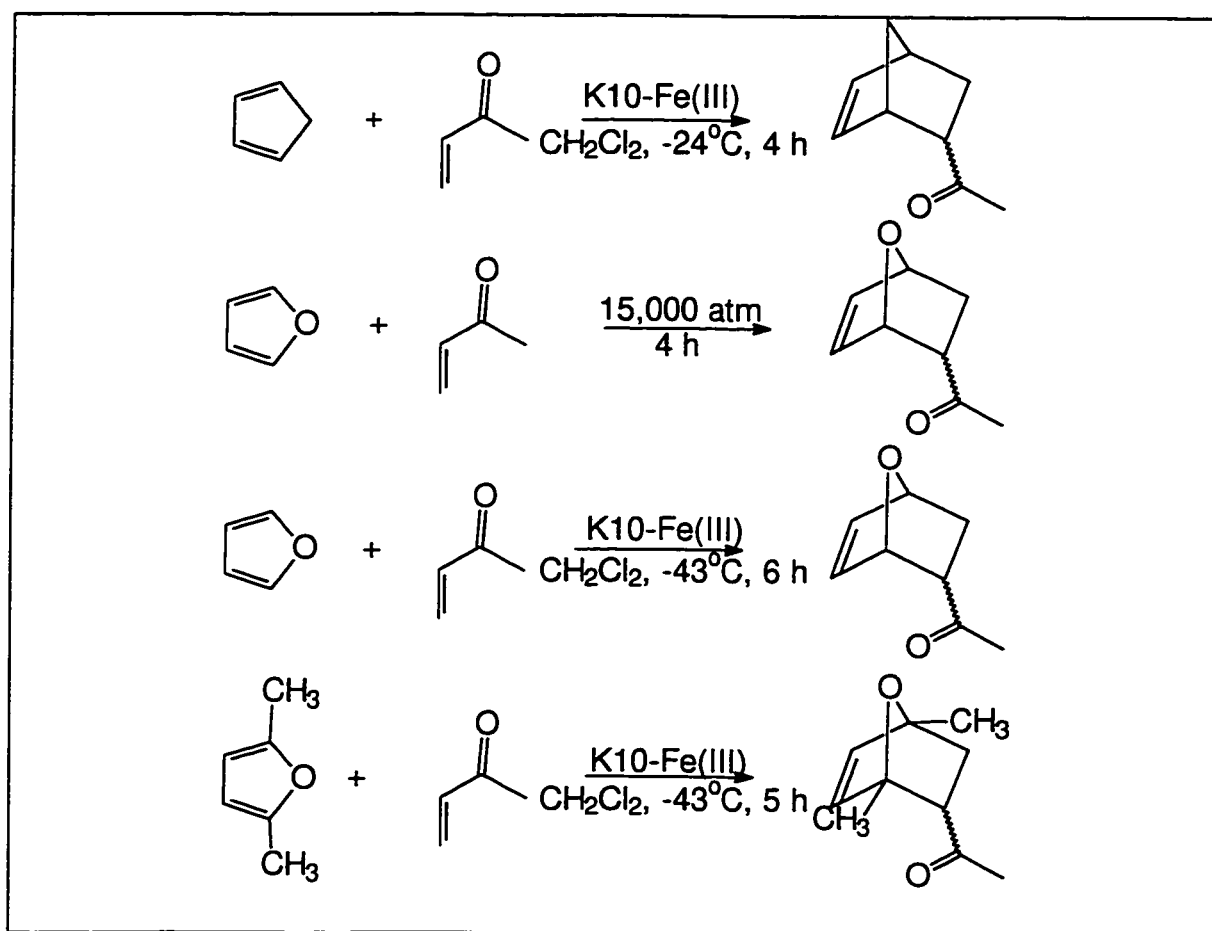
Clay-based Catalyst	Reaction Time (h)	Conversion of PhCH_2OH (%)	Corresponding Lewis-acid Catalyst	Reaction Time (h)	Conversion of PhCH_2OH (%)
K10/ TiCl_4	1	100	TiCl_4	24	0
K10/ AlCl_3	1.2	100	AlCl_3	24	3
K10/ NbCl_5	1.2	100	NbCl_5	24	5

1.4.5.1.2 Diels-Alder Reactions

Some Diels-Alder reactions which are catalyzed by Lewis acids can also be catalyzed by clay-based catalysts^[41-43]. The reactions usually proceed under extremely

mild conditions with good yields and selectivities. For example, the reaction of cyclopentadiene and methyl vinyl ketone catalyzed by Fe(III)-exchanged montmorillonite clay at -24°C for 4 h gave 96% of the product with an endo:exo ratio of 21:1^[42]. The facile reactions under the catalysis of ion-exchanged K10 is, presumably, due to the stabilization of the dienophile on the clay surface, thus, reducing the HOMO(diene)-LUMO(dienophile) energy gap.

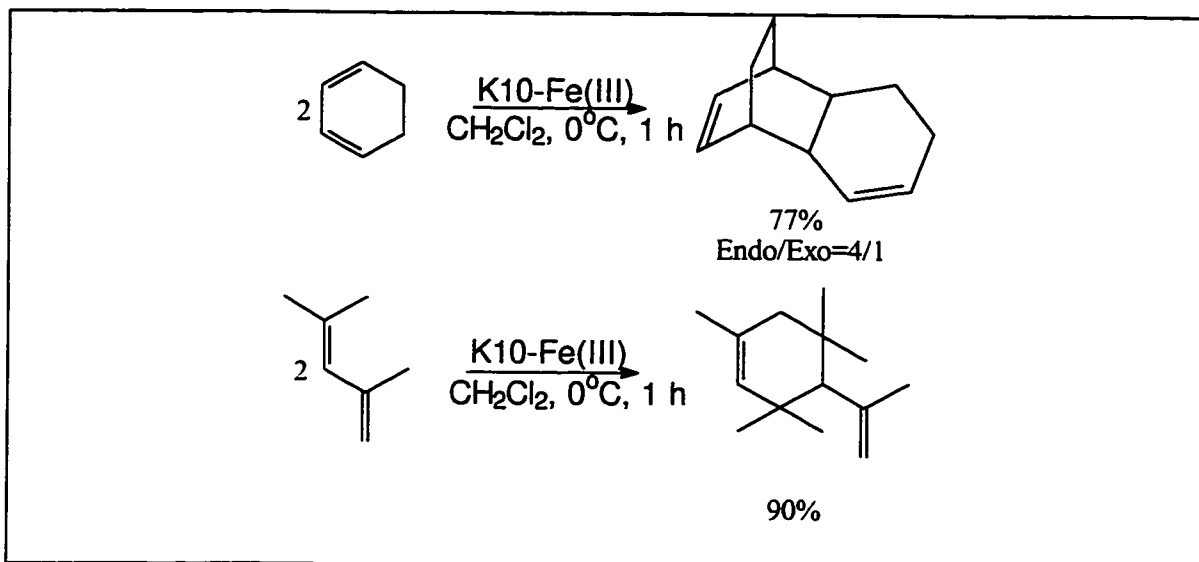
Scheme 17. Diels-Alder Reactions Catalyzed by K10-Fe(III)^[42]



Furans are notorious for their reluctance to undergo Diels-Alder cycloadditions since the aromaticity is destroyed as the reaction proceeds^[44,45]. The traditional reaction conditions (1520 MPa or 15,000 atm) for furan reacting with methyl vinyl ketone gave

the corresponding adduct in 48% yield with no selectivity^[44]. However, the use of K10-Fe(III) under mild conditions in dichloromethane at -43°C gave the product in 60% yield with an exo:endo ratio of 2.2^[43]. This catalyst also works well for substituted furans. 2,5-Dimethylfuran reacts with methyl vinyl ketone under the same reaction conditions, giving 65% of the adduct^[43] (Scheme 17). Also, it has been shown that clays exchanged with transition metal cations, such as Cr^{3+} and Fe^{3+} , are also effective in catalyzing Diels-Alder reactions with un-activated dienes (Scheme 18)^[41].

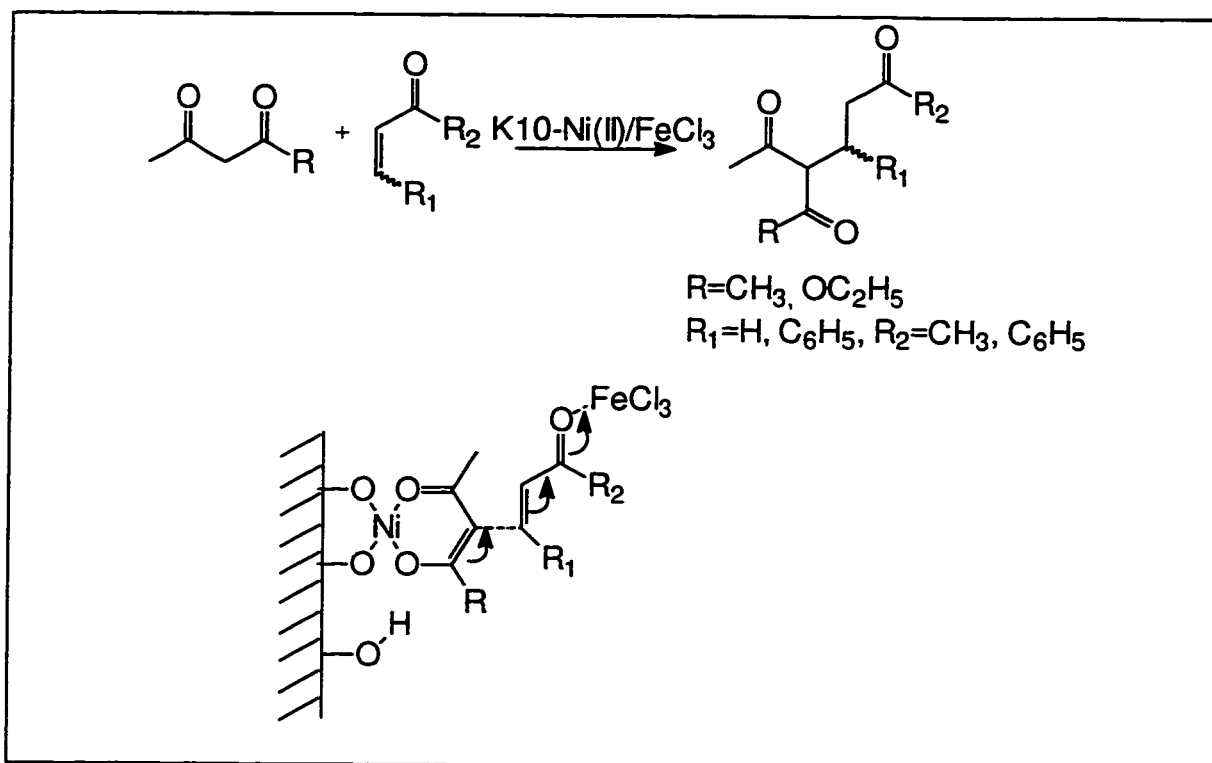
Scheme 18. Diels-Alder Reactions with Un-activated Dienes Catalyzed by K10-Fe(III)^[41]



1.4.5.1.3 Michael Reactions

Instead of using a base to produce a carbanion, a solid acid may be used to stabilize the conjugated base on the surface^[46]. Nickel bromide was chosen to facilitate this reaction as it complexes strongly with the Michael donor. Ferric chloride was introduced as a homogeneous catalyst to stabilize the Michael acceptor. Thus, the reaction system can be described as in the Scheme 19.

Scheme 19. Michael Addition Catalyzed by K10-Ni(II)/FeCl₃^[46]

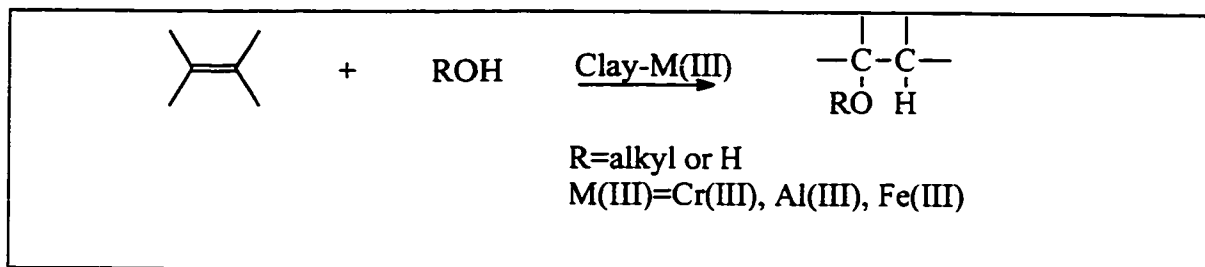


1.4.5.2 Reactions Due to Brønsted Acidity

1.4.5.2.1 Protonation of Alkenes

Cation-exchanged K10 produces both Lewis and Brønsted acidity on its surface. Thus, clays can be used as solid acids for a number of reactions normally catalyzed by mineral acids in aqueous solutions^[47,48]. For example, they can be used in the reactions of protonating alkenes as illustrated in Scheme 20.

Scheme 20. Cation-Exchanged K10 Used in the Reactions of Protonating Alkenes^[47,48]



Esters can be formed by the direct addition of carboxylic acids to alkenes using ion-exchanged clay catalysts^[49,50]. The reaction of ethene and acetic acid requires 200°C to produce an efficient yield (96%) of ethyl acetate whereas substituted alkenes such as 2,2-dialkylalkenes give high yields of *t*-alkyl esters with acids at temperatures below 30°C. The advantages of using clay-based catalysts in these reactions are: i) interlamellar reactions are not restricted only to formation of highly stable carbocations as intermediates; ii) they proceed efficiently with terminal alkenes; iii) they are more selective; and iv) product isolation is simple.

Other types of reactions which can also use clay-based catalysts are: esterification of carboxylic acids^[51,52], formation of lactones^[53], formation of enamines from ketones^[54] and formation of acetals^[55]. The reaction usually gives clean products in high yields.

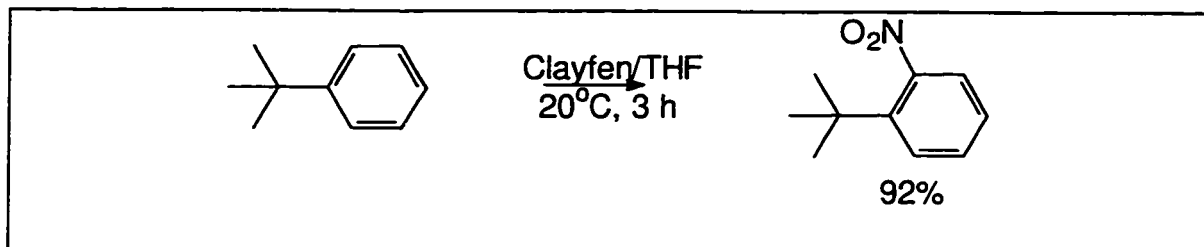
1.4.5.3 Reactions Catalyzed by Clay-supported Metallic Nitrates

1.4.5.3.1 Nitration

Nitration of aromatic substrates is traditionally performed with mixtures of nitric acid and sulfuric acid, giving predominantly *ortho* and *para* products with their

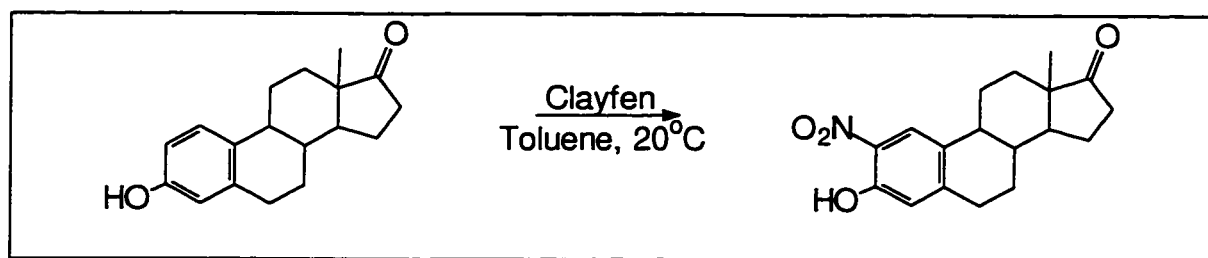
distribution close to the statistical 2:1 ratio. It has been found that activated aromatic compounds can be nitrated with iron(III) nitrate deposited on K10 montmorillonite (Clayfen) at room temperature in organic solvents to give mono-nitrated compounds, with very high regioselectivity and yield^[56] (Scheme 21).

Scheme 21. Nitration of *t*-Butylbenzene Using Clayfen as Catalyst



The nitration of estrone in the 2-position provides potentially biologically active estrone derivatives functionalized in ring A^[57]. The classical procedure gave a mixture of 2- and 4-nitroestrone^[57]. The use of clayfen as catalyst in toluene at room temperature gave 2-nitroestrone as the only product in 55% isolated yield as illustrated in Scheme 22^[58].

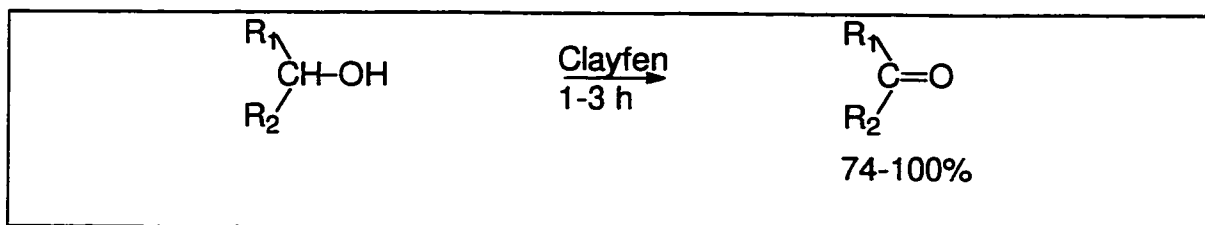
Scheme 22. Nitration of Estrone Using Clayfen as Catalyst^[58]



1.4.5.3.2 Oxidation

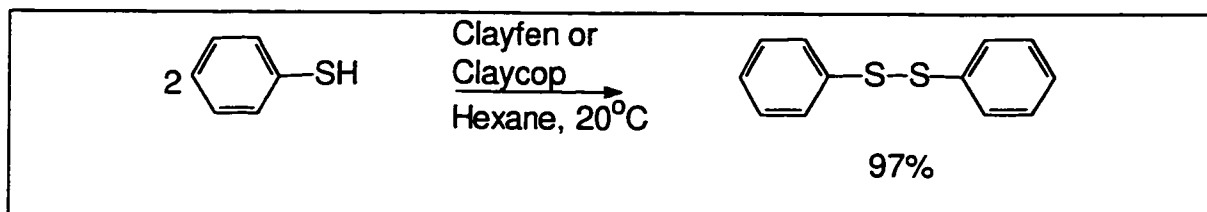
Secondary alcohols can readily be oxidized in high yields at moderate temperatures by simply adding Clayfen to a solution in hexanes. Yields in the range 74-100% are reported^[59] (Scheme 23).

Scheme 23. Oxidation of Secondary Alcohols Using Clayfen as Catalyst^[59]



Clayfen and Claycop are also excellent agents for the oxidative coupling of thiols to disulfides. Reaction is usually complete within 1 min at room temperature giving yields up to 97%^[60] (Scheme 24).

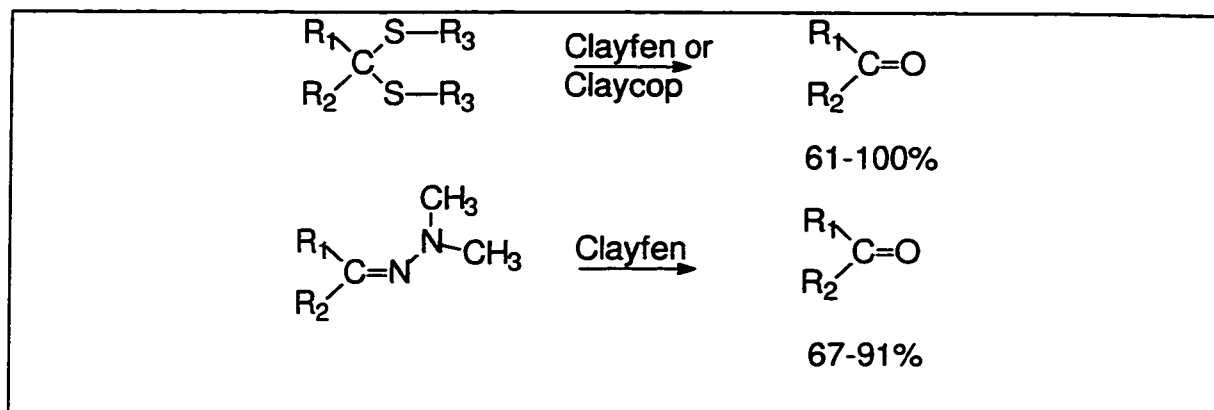
Scheme 24. Oxidation of Benzenethiol Using Clayfen as Catalyst^[60]



1.4.5.3.3 Carbonyl Group Deprotection

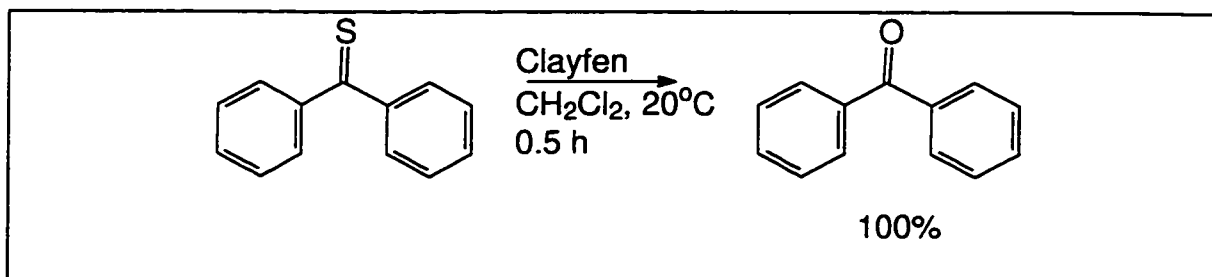
Clayfen and Claycop can be used for the cleavage of protecting groups and regeneration of the carbonyl compounds. For example, they have found use in cleavage of thioacetals to give the corresponding ketones in very high yields at room temperature^[61]. Also, Clayfen catalyzes the cleavage of N, N-dimethylhydrazones at low temperature to give the corresponding carbonyl compounds in yields of 67-91%^[62] (Scheme 25).

Scheme 25. Carbonyl Group Deprotection Using Clayfen as Catalyst^[62]



Clayfen has also been used to catalyze the oxidative conversion of thiobenzophenones to the corresponding benzophenones at room temperature in yields of 77-100%^[63] (Scheme 26).

Scheme 26. Conversion of Thiocarbonyl to Carbonyl Group Using Clayfen as Catalyst^[63]



As may be seen from this brief overview of clay-catalyzed chemistry, a variety of organic reactions has been accomplished and improved with clay-based catalysts. As will be seen later in this thesis, similar catalysts have been applied to achieve a one-step method for C-S bond formation in alkylbenzenes.

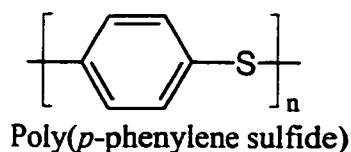
Ultimately, the objective of the work described in this thesis was to make network polysulfides from various benzenethiols. Consequently, the following sections review previous work on polysulfide synthesis.

1.5 Preparation and Properties of Polysulfides

Polysulfide polymers have the general structure $(-R-S_x-)_n$ where x is referred to as the “rank” and represents the average number of sulfur atoms in the polysulfide unit. The rank of polysulfide polymers usually ranges from slightly more than two to about four^[64]. The discovery of polysulfide polymers dates back more than 100 years. In 1838, there were reports of rubbery, intractable, high sulfur, semi-solid products from the reaction of potassium sulfides with a halogenated material designated “chloraetherin”, which was a mixture of products obtained from the addition of chlorine to ethene in aqueous suspension^[65,66]. However, it was not until 1927 that the first useful product was developed by Patrick from the reaction of sodium polysulfide and 1,2-dichloroethane^[67]. Shortly after, the first synthetic elastomer ethylene tetrasulfide, sold under the trade name Thiokol A^[64], was manufactured commercially in the United States. However, these original polymers were difficult to process, evolved irritating fumes during compounding and possessed some undesirable physical properties. Over the years, there have been significant improvements in the products and in methods of processing. Polysulfide rubbers have unusually good resistance to solvents and the environment and possess good low temperature properties. Due to their unique properties, they have found uses in a variety of industrial applications^[68,69].

Poly(phenylene sulfide), PPS was developed commercially in 1973^[70]. Its structure consists of a series of alternating di-substituted aromatic rings (*p*-phenylene units) and divalent sulfur atoms as shown below. It is a semi-crystalline, thermoplastic polymer which has excellent mechanical, electrical, thermal and chemical resistance properties. It has found uses in applications such as coatings, injection molding, film,

fiber and advanced composites. New applications are being discovered as engineers are becoming more familiar with these materials^[70].



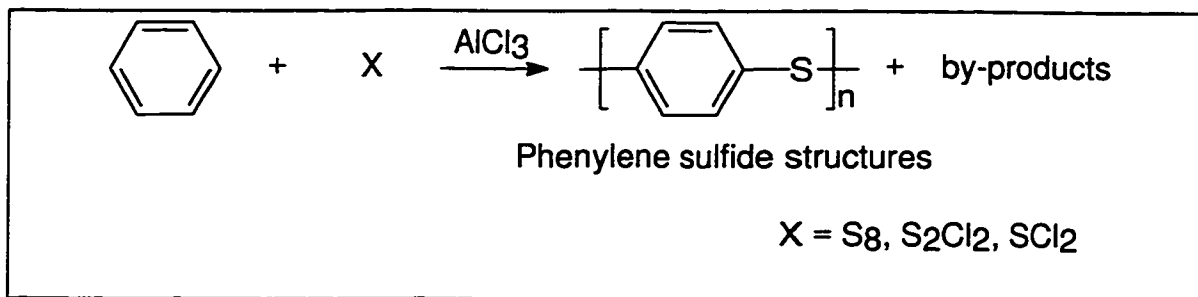
1.5.1 Synthesis of Poly(phenylene sulfide)

The synthesis of PPS can be classified as either: (1) electrophilic substitution^[71,72], or (2) nucleophilic substitution-based processes^[73].

1.5.1.1 Electrophilic Substitution Reactions

The earliest reference to making the poly(phenylene sulfide) structure is by Friedel and Crafts in 1888^[71] when they studied the reactions of benzene with sulfur sources such as S₈, S₂Cl₂, SCl₂. These reactions were moderate yielding (50-80%) and produced crude products containing other materials such as thianthrene (Scheme 27)

Scheme 27. Reactions of Benzene with Sulfur Sources (S₈, S₂Cl₂ or SCl₂) by Friedel and Crafts^[71]



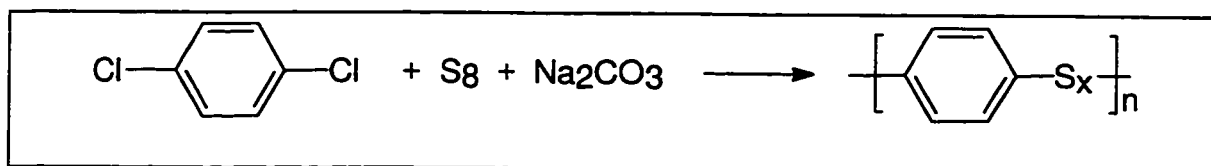
The products produced were very poorly characterized by today's standards. In 1984, the electrophilic substitution reactions of benzene and sulfur in the presence of aluminum chloride were reinvestigated^[72]. Improved analytical methods allowed the

detection of structures which contained thianthrylene sulfide linkages, phenylene sulfide linkages and polysulfides. Typical molecular weights for polymers produced from the reaction of benzene and sulfur in the presence of aluminum chloride were only 3,500^[72]. It was concluded that the formation of high molecular weight poly(arylene sulfides) in the presence of aluminum chloride is, therefore, highly unlikely.

1.5.1.2 Nucleophilic Substitution Reactions

In 1948, A. D. Macallum discovered the first nucleophilic displacement route to poly(arylene sulfide)^[73]. The process involves the reaction of elemental sulfur, sodium carbonate and dichlorobenzene at 275-300°C in a sealed vessel (Scheme 28). Elemental analysis of polymers produced by this method shows that they generally contain more sulfur than is predicted. The rank of sulfur is in the range of 1.2-2.3. Over the years, several modifications were reported^[74,75] and people started to recognize the unusual thermal stability of the polymer and its potential to be a high performance engineering plastic. However, despite these efforts, initial problems associated with severe reaction conditions, control of the exothermic reaction and unpredictable polymer yields and properties remained unsolved^[76].

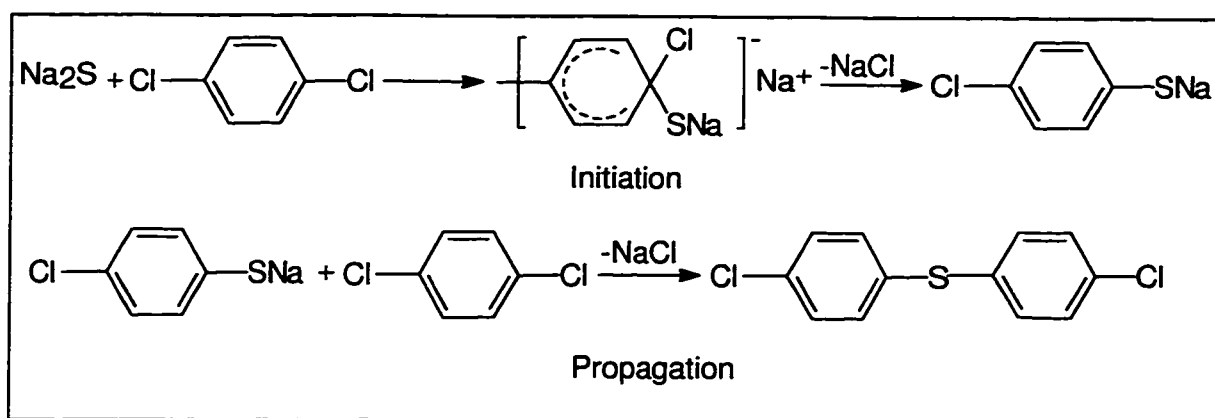
Scheme 28. Synthesis of Poly(arylene sulfide) through Nucleophilic Substitution of Dichlorobenzene by Macallum^[73]



A modified procedure was developed by researchers at the Phillips Petroleum Company^[77]. The new process involved the reaction of *p*-dichlorobenzene and sodium

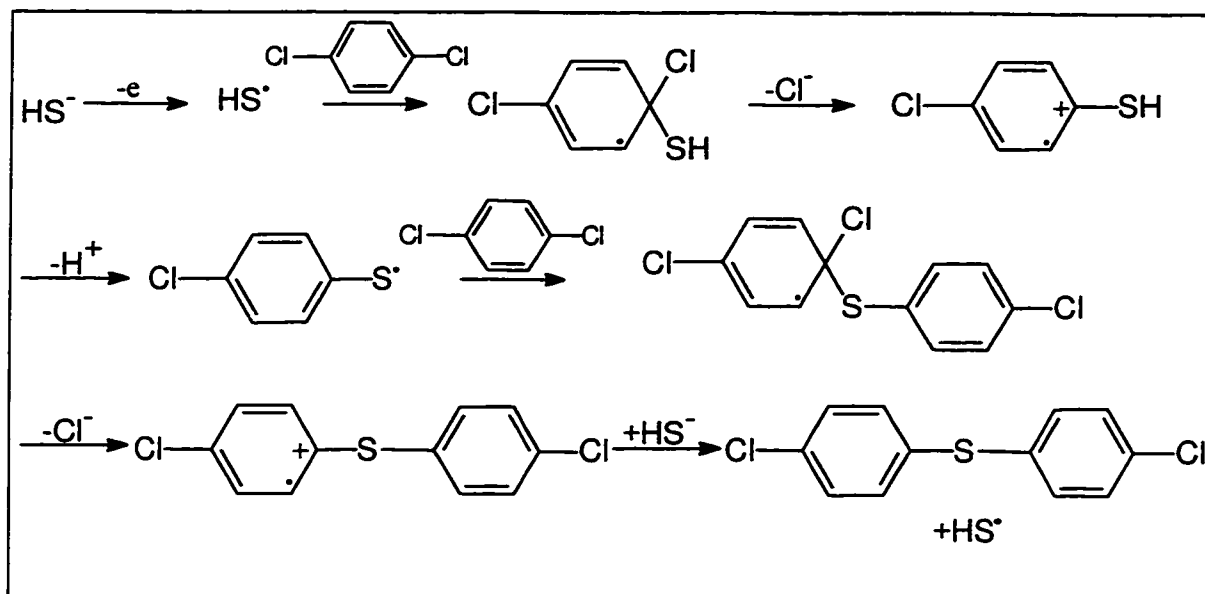
sulfide in N-methyl pyrrolidone at 260°C under pressure of 1110 KPa (~11 atm). The typical molecular weight obtained by this method is in the range of 15,000-20,000. It eventually lead to the commercial production of PPS in 1973 under the trade name of Ryton® Polyphenylene Sulfide. The mechanism of the reaction is illustrated in Scheme 29.

Scheme 29. Mechanism through Nucleophilic Substitution for the Formation of Poly(phenylene sulfide)^[77]



An alternative mechanism involving radical cations and single electron transfer (SET) was also proposed⁷⁸. Initiation is believed to occur via oxidation of hydrosulfide via SET to a hydrosulfenyl radical which reacts with *p*-chlorobenzene leading to 4-chlorophenylsulfenyl radical. Sulfenyl radicals can then react with additional dichlorobenzene in chain propagation reactions as shown in Scheme 30. However, whether the PPS polymerization proceeds by purely nucleophilic substitution ($\text{S}_{\text{N}}2$) or by a single electron transfer (SET) process has not been established.

Scheme 30. Mechanism through Single Electron Transfer (SET) for the Formation of Poly(phenylene sulfide)^[78]



An improved procedure for synthesis of PPS with molecular weight in the range of 35,000-65,000 was developed by Campbell^[79]. The reaction mixture consists of heating a mixture of p -dichlorobenzene and Na_2S in N -methylpyrrolidone with an alkaline metal salt of acetic acid, propanoic acid, benzoic acid, or phenol at 245°C under 547 -963 KPa (5.4-9.5 atm) pressure.

1.5.2 Characterization of Poly(phenylene sulfide)

1.5.2.1 Molecular Weight Distribution

Due to their high crystalline melting temperature ($T_m=285^\circ\text{C}$) and excellent solvent resistance, molecular weight characterization of poly(phenylene sulfide) is very difficult^[80]. In 1986, a gel permeation chromatographic system (GPC) capable of determining molecular weights and molecular weight distribution of poly(phenylene

sulfide) was developed^[81]. The GPC measurement was carried out at 250°C using chloronaphthalene as solvent in order to maintain poly(phenylene sulfide) in solution. The typical molecular weight of poly(phenylene sulfide) synthesized by the method of Edmonds and Hill is 15,000-20,000.

1.5.2.2 Micro-analysis of Poly(phenylene sulfide)

The average number of sulfur atoms per polymer linkage is measured by elemental analysis. The rank of sulfur is found to be between 1.2-2.3 for poly(phenylene sulfide) synthesized by Macallum's process^[73].

1.5.2.3 Thermal Characterization of Poly(phenylene sulfide)

Glass transition temperature (T_g), which is defined as the temperature at which the polymer undergoes the transformation from a rubber to a glass state, is useful for polymer characterization as its value is dependent on polymer structure. These effects are observed empirically^[82]:

1. T_g increases with increasing chain length but for chain length greater than 500 atoms, T_g reaches a limiting value independent of chain length.
2. T_g of a polymer is higher the greater the size of the carrier restricting internal rotation around the chain links of the polymer backbone. (e.g. measurement of degree of crosslinking)

Therefore, the T_g measurement can give rough information on how large the polymer molecules are and their degree of crosslinking. T_g is usually measured by differential scanning calorimetry (DSC). It measures the difference in energy input into

the substances and a reference material as they are subjected to a controlled temperature program. At the glass transition temperature, the polymer slowly transforms from a glassy state to an amorphous state and there are abrupt changes in physical properties such as heat capacity and thermal expansion coefficient. These changes are observed as an endothermic jump in the heating curve in DSC measurement.

It has been found that poly(*p*-phenylene sulfide) has a glass transition temperature (T_g) at about 85°C and a melting point (T_m) at 285°C^[70].

1.5.2.4 Raman Spectroscopy

Raman spectroscopy may be used to detect highly polarizable S-H, C-S and S-S-S groups, while IR usually is only effective for thiols^[83]. Raman spectral data can yield useful structural clues, especially for networks which have limited solubility in organic solvents^[83]. It allows differentiation between thiols, mono-, di- and trisulfide linkages^[83]. Thus, the type of sulfur bonding in poly(phenylene sulfide) polymers can be deduced from their Raman vibrational spectra.

Spectral data for various thiols usually show a strong Raman band at 2560±20cm⁻¹. In addition to this S-H stretching frequency, a moderate to strong C-S stretching band is observed between about 625-725 cm⁻¹. For aromatic sulfides, a stretching band is observed at about 700 cm⁻¹ for the phenyl-S stretch. For example, the phenyl-S stretch of diphenyl disulfide is observed at 695 cm⁻¹^[83].

For acyclic disulfides, two strong bands can be observed in Raman spectra: C-S stretch at about 600-725 cm⁻¹ and S-S stretch at about 450-550 cm⁻¹. The C-S-S-C group should give rise to two S-S stretching vibrations, namely, symmetric and asymmetric. If

the dihedral angle around the S-S bond is not 180° , both are Raman active, but the symmetric and asymmetric frequencies are essentially equal if the dihedral angle is approximately 90° ^[84]. The appearance of two closely lying bands near 500 cm^{-1} might be ascribed to these two vibrational modes^[85]. In the case of trisulfides, the C-S stretch has essentially the same spectral location and ρ values as in the corresponding disulfides. The S-S-S stretch appears as a symmetric band at $500\text{--}480\text{ cm}^{-1}$ ^[83].

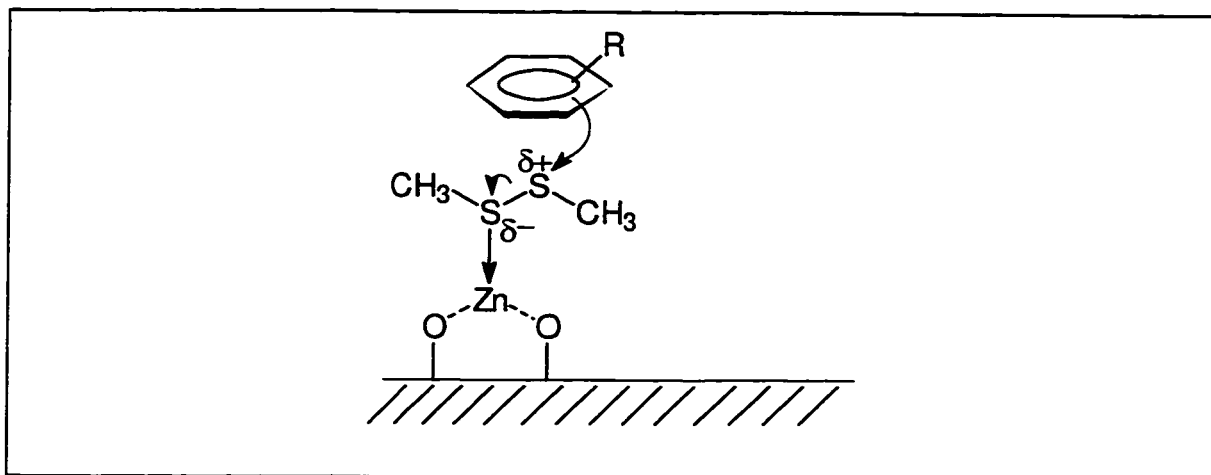
CHAPTER TWO

OBJECTIVES OF THE RESEARCH WORK

2.1 Development of New Methods for the Synthesis of Poly(thioalkyl)benzenes With Clay Catalysts

The current methods of synthesizing polyalkylthiobenzenes involve the use of HMPA as solvent. HMPA is miscible with water and most organic solvents. It also has a high boiling point (230°C). Therefore, the separation of the products from HMPA is a difficult task. In addition, it is carcinogenic and expensive. As mentioned in the Introduction, benzenepolythiols may be used as potential reagents for preventing sulfur deposition in sour gas wells. The first objective of this research was to develop a new approach to synthesize this type of compound using montmorillonite clay as a catalyst. Previous studies in our laboratory showed that ‘clayzic’ can promote C-S formation with thiophene and benzothiophene when DMDS is used as the thiolating agent^[27]. It is believed that the same catalysts will promote the same reactions on aromatic substrates as well. The reaction pathway is shown in Scheme 31.

Scheme 31. Reaction Pathway of DMDS with An Arene on the Surface of Clayzic



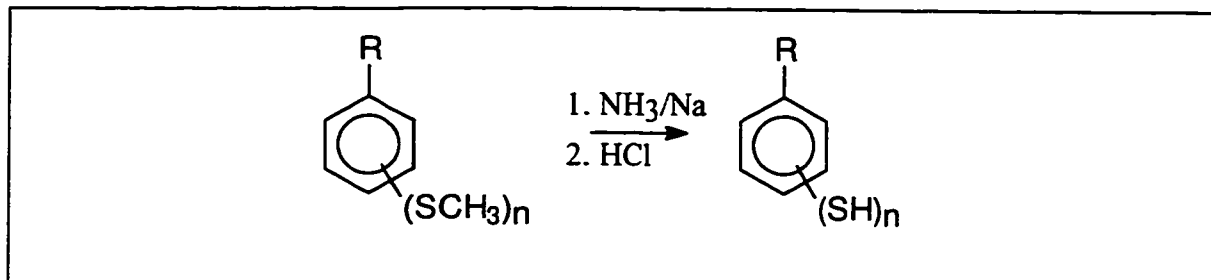
The Brønsted or Lewis acid sites on the clay surface coordinate with one sulfur atom of DMDS, polarizing the S-S bond and making the adjacent sulfur atom readily available for the electrophilic attack by the aromatics. The S-S bond of dimethyl disulfide breaks and eventually leads to alkylthiolated aromatics.

To date, only activated aromatics such as thiophene and benzothiophene have been alkylthiolated using clay catalysts^[27]. In this study, toluene, xylenes, mesitylene, anisole and thioanisole in addition to benzene were reacted with DMDS and montmorillonite clays. The catalytic activities of the catalysts depend on the exchangeable cations impregnated onto the clay surface. Therefore, the catalysts were modified either by acid-treatment (Brønsted acid) or by cation-exchange (Lewis acid) to optimize the reaction conditions.

The conversion of polyalkylthiobenzenes to benzenepolythiols can be achieved by reductive cleavages of the S-alkyl bond using alkali metals in liquid amines^[24,25,86]. The combinations of metals and amines that have been reported in the literature including Na/NH₃^[86], Na/pyridine^[87] and Li/CH₃NH₂^[88], among which, the Birch reduction

(Na/NH₃) is probably the one most commonly used. It has the advantage of product isolation by simply evaporating ammonia.

Scheme 32. Formation of Benzenepolythiols by Birch Reduction



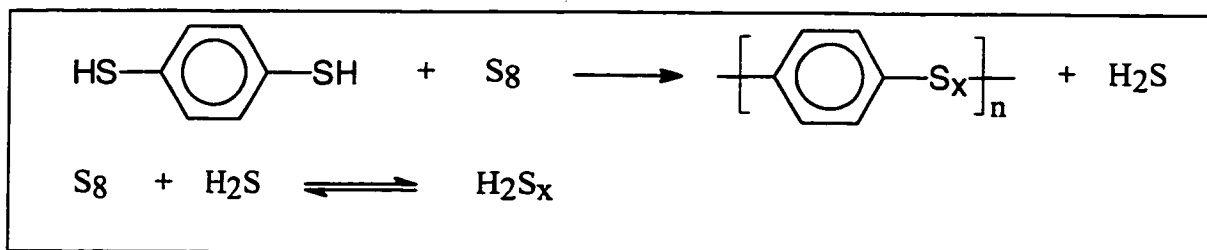
2.2 Investigation of Reactions of Benzenepolythiols with Elemental Sulfur

2.2.1 Kinetics of the Reactions

How the reactions of benzenepolythiols with elemental sulfur proceed is very important from the industrial point of view. The reactions have to proceed at reasonable rates for the benzenepolythiols to have industrial value. Thus, the second objective of the research was to investigate the kinetics of these reactions in order to have a better understanding of how they react with sulfur under the conditions usually found in sour gas wells.

The methods which can be used to monitor the reactions involve FT-IR, viscosity and polymeric content measurements. The FT-IR method measures the absorption of H-S and H-S_x stretches of H₂S and H₂S_x formed during the reaction. If the reaction is carried out in a sealed FT-IR cell, an equilibrium between H₂S and elemental sulfur will be established (Scheme 33). The absorptions of H-S and H-S_x stretches are found at 2571 cm⁻¹ and 2479 cm⁻¹^[89]. A quantitative analysis of H₂S and H₂S_x has been established previously using the intensities of these two peaks^[108]. Thus, by following the development of H₂S and H₂S_x, it may be possible to follow the formation of polysulfide indirectly.

Scheme 33. Reaction of Benzenedithiol with Molten Sulfur in a Sealed FT-IR Cell



The other two methods which can be used to follow the reactions are polymeric content measurement and viscosity measurement. As reactions proceed, the polysulfides are expected to grow longer with more sulfur becoming incorporated into the chains. The viscosity measurement will show this process since it is expected to increase as the chains grow longer. The $-S-S_x-S-$ bonds are unstable and tend to disproportionate. Once the formation and breakage of S-S bonds are in equilibrium, the viscosity increase will stop and a plateau should be observed. This same effect should also be observed from the polymeric content measurement. As the reaction proceeds and more polysulfides form, the polymeric content in the liquid sulfur is expected to increase. Since S_8 dissolves readily in CS_2 while the polysulfides formed from the reaction are insoluble, the polymeric content measurement can be determined by CS_2 extraction. However, the general instability of polysulfides may result in only semi-quantitative data being obtained by these methods.

2.2.2 Physical Properties of Elemental Sulfur/Polysulfide Mixtures

The purpose of this research is to examine the reactions of benzenepolythiols with elemental sulfur in hopes that they can be used as potential reagents for preventing sulfur deposition in sour gas wells. Therefore, the physical properties of elemental sulfur/polysulfide mixtures, especially its freezing point, have to be investigated in order to demonstrate that there is indeed a delay in terms of sulfur deposition after the reactions.

Freezing points of mixtures depend only on the number of solute particles present, not on their identities. The freezing point of sulfur is, therefore, expected to be lowered

by addition of benzenepolythiols /polysulfides as mentioned in the Introduction. Also, it is expected that, if we make the assumption that the benzenepolythiols do not react with sulfur at 140°C, the freezing point depression can be calculated according to the following equation:

$$T^* - T = \left(\frac{RT^{*2}}{\Delta H_{\text{melting}}} \right) \chi_B \quad \text{eq. 23}$$

$\Delta H_{\text{melting}}$:	Enthalpy of melting
T^* :	Usual freezing point of monoclinic sulfur
R :	8.314 J/mol
χ_B :	Molar fraction of benzenepolythiols

However, benzenepolythiols do react with sulfur at 140°C and form polysulfides. It is these compounds which may cause supercooling of the sulfur/polysulfide mixture.

The freezing point depression determination was accomplished by mixing benzenepolythiols with molten sulfur at 140°C. When the reactions had finished (usually after 24 h), the freezing points were measured with agitation in order to limit the effect caused by supercooling. Some measurements were also made without stirring.

2.3 Characterization of Polysulfides Isolated from Reactions of Benzene-polythiols with Elemental Sulfur

One interesting question is how much sulfur can be incorporated into the polysulfide chains. The question can be answered by examining two aspects of the polysulfides: (1) the average number of sulfur atoms per repeat unit, and (2) the average number of repeat units per molecule. The former can be achieved by elemental analysis (quantitatively) as well as Raman spectroscopic analysis (qualitatively), while the second aspect can be resolved by molecular weight measurement using vapor pressure osmometry (VPO).

2.3.1 Elemental Analysis

The elemental analysis will give the percentages of C and H in the polysulfides. Since sulfur is the only other element present in the polysulfides, its percentage can be calculated from the percentages of C and H. Therefore, the empirical molecular formula can be derived and the average number of sulfur atoms per molecule can be determined. From this number, one can extrapolate the average sulfur linkage, i.e., disulfide, trisulfide, tetrasulfide or even higher polysulfide linkages.

2.3.2 Raman Spectroscopy

As mentioned in the Introduction, Raman spectroscopy is used to detect highly polarizable S-H, C-S and S-S-S groups. It can yield useful structural clues, especially for network polymers which have limited solubility in organic solvents. It can also differentiate thiols, mono-, di-, and trisulfides. Thus, the type of sulfur bonding in

polysulfides can be deduced from their Raman vibrational spectra. For diaryl disulfides, two strong bands are observed in Raman spectra: C-S stretch at about 620-715 cm^{-1} and S-S stretch at about 520-540 cm^{-1} . Raman spectra have been reported for dimethyl trisulfide and diethyl trisulfide^[83]. The S-S stretching frequencies for these polysulfides occur in the Raman as strong bands in the range 510-480 cm^{-1} . For the higher polysulfides, the S-S stretching frequencies usually can be found in the range of 450-500 cm^{-1} as a strong un-resolvable band.

2.3.3 Average Molecular Weight

VPO measures the average molecular weight of a solute on the principle that the vapor pressure of a solution is lower than that of the pure solvent at the same temperature. Thus, by raising the solution temperature, the vapor pressure of the solution can be raised to match that of the solvent. The average molecular weight of a solute can be calculated according to the following equation:

$$\Delta V = \frac{KC_2}{m_2} \quad \text{eq. 24}$$

C_2 = solute concentration in gram/kilogram

m_2 = solute molecular weight

ΔV = observed voltage change on Vapor Pressure Osmometer which is proportional to the temperature difference ΔT .

The calibration factor K is determined for each set of experimental conditions by measuring ΔV and C_2 for one or more materials of known molecular weight m_2 . By

reversing the procedure, unknown molecular weights are determined using that value of K.

All of the above characterization methods require the separation of the polysulfides from the reaction mixtures. However, the presence of polymeric sulfur in molten sulfur under the reaction temperature (140°C) makes the isolation of "pure" polysulfides extremely difficult. In order to isolate the polysulfides, the reactions of benzenepolythiols with sulfur are carried out in a solvent (THF or toluene). The advantage is that the reactions can proceed at a much lower temperature and no polymeric sulfur will be present. The disadvantage is that the polysulfides isolated from these reactions may not be the same as those from the reactions in molten sulfur. However, it should still yield some useful information on the nature of these polysulfide polymers which can be extrapolated to polysulfides formed in molten sulfur.

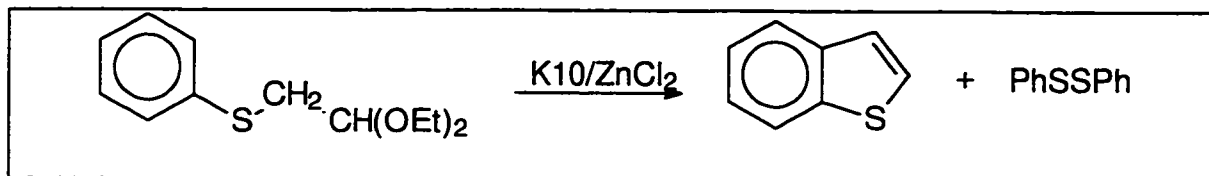
CHAPTER THREE

NEW METHODS FOR SYNTHESIS OF BENZENETHIOLS

3.1 Mechanism and General Considerations

The rationale for using K10/ZnCl₂ to catalyze alkylthiolation of aromatics by disulfides is based on the observation of diphenyl disulfide formation during the attempted cyclization of a phenylthioacetal to benzo[*b*]thiophene over K10/ZnCl₂ (Scheme 34)^[90].

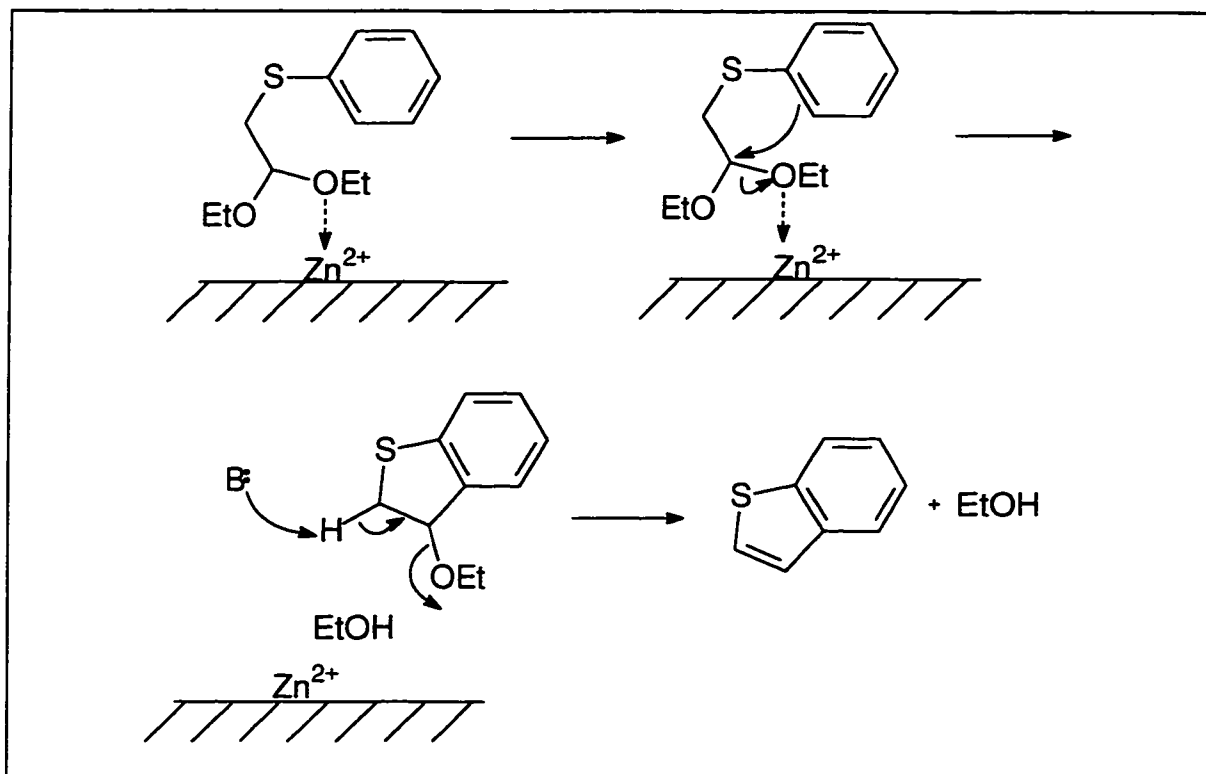
Scheme 34. Cyclization of Phenylthioacetal over K10/ZnCl₂

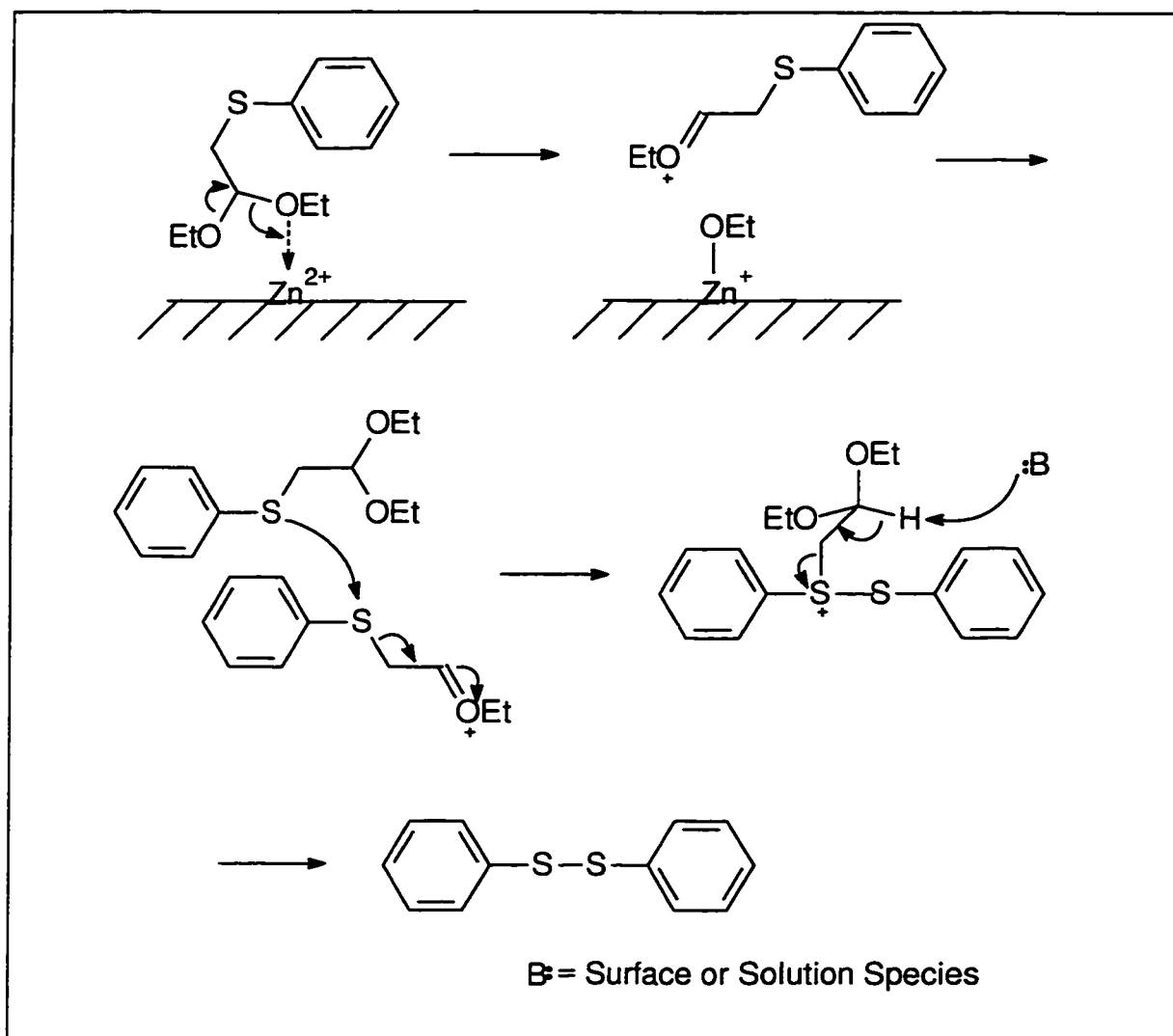


The cyclization of phenylthio-acetaldehyde diethylacetal over K10/ZnCl₂ was expected to give benzo[*b*]thiophene as the sole product. The proposed mechanism for the formation of benzo[*b*]thiophene is shown in Scheme 35^[90]. The co-ordination between the oxygen and the Zn(II) sites makes the adjacent carbon electrophilic and facilitates the cyclization process. However, significant amounts of diphenyl disulfide were also formed. The yield of the by-product depends on the reaction conditions. It was observed that diphenyl disulfide was formed in approximately 50% yield in chlorobenzene solution using a low catalyst/reagent ratio (0.1). Under these conditions, the number of active catalytic sites to co-ordinate the acetal would be limited and the chance of bi-molecular processes leading to diphenyl disulfide would be enhanced (Scheme 36). The attack of a sulfur atom of another phenylthio-acetaldehyde diethylacetal on a reactant molecule

which has already undergone elimination of an ethoxy group would, eventually, yield diphenyl disulfide. Under low catalyst/reagent ratio conditions, more acetal would be available in solution and the chance for intermolecular attack would be increased.

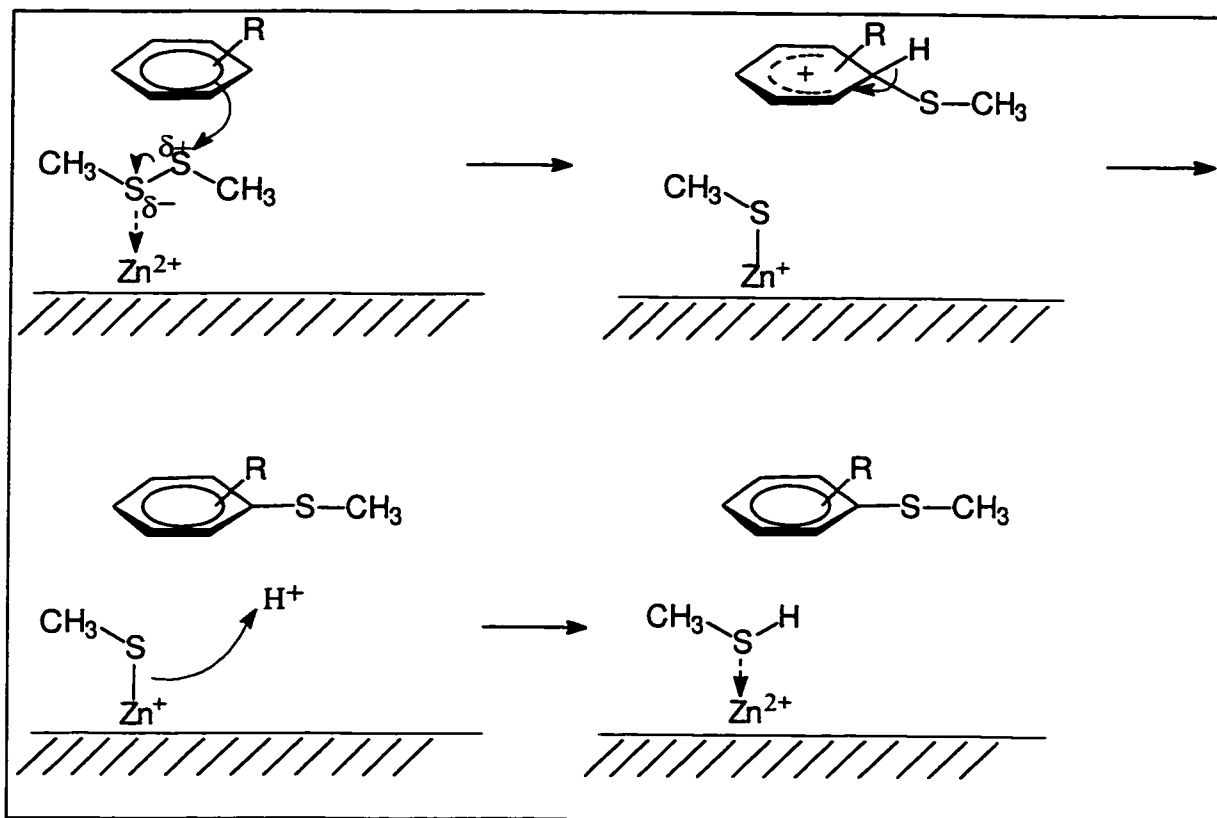
Scheme 35. Formation of Benzo[b]thiophene by Intramolecular Cyclization^[90]



Scheme 36. Formation of Diphenyl Disulfide by Intermolecular Attack^[90]

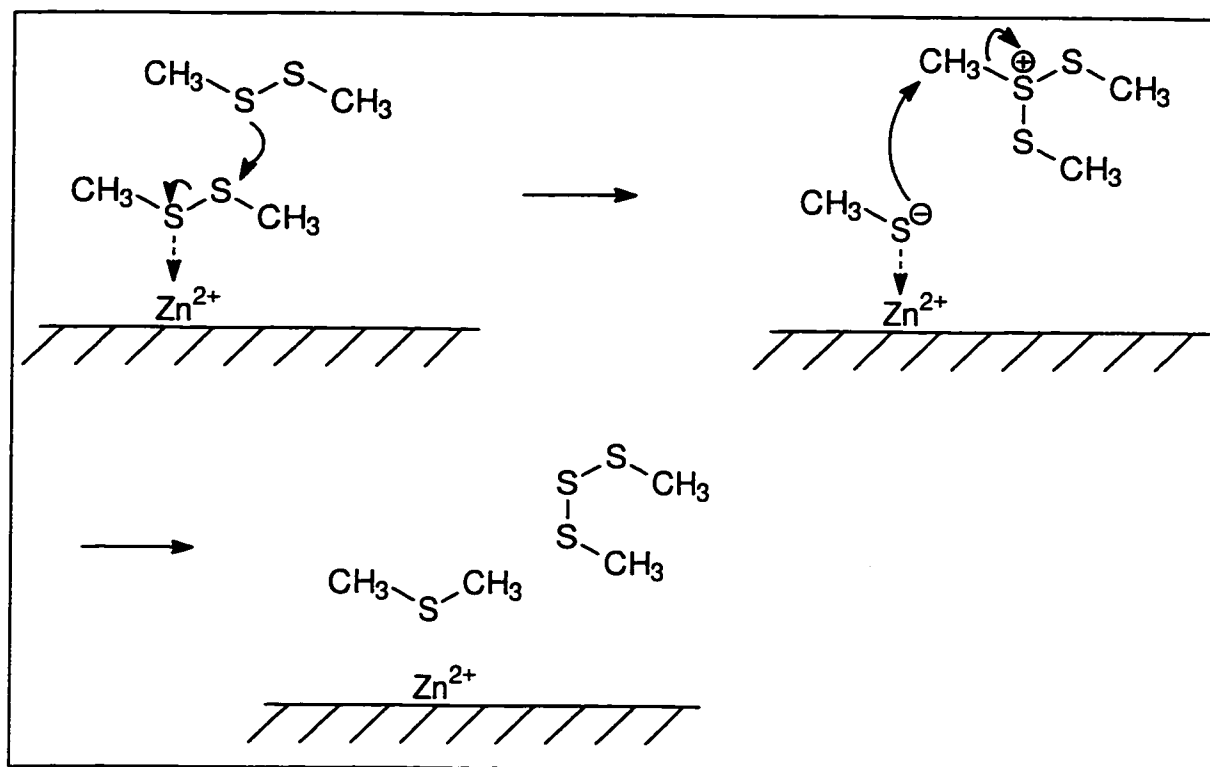
Consequently, it was anticipated that dimethyl disulfide (DMDS) would coordinate to Zn(II) on a clay surface rendering the adjacent S-atom electrophilic. A possible route to the formation of alkylthiolated aromatics by clay catalysts is illustrated in Scheme 37.

Scheme 37. Formation of Alkylthiolated Aromatics on the Surface of Clayzic



The by-product of this reaction is CH_3SH , whose S-atom would also co-ordinate to the acid sites as shown in Scheme 37. An oxidizing agent (eg. O_2) is needed for the reaction since CH_3SH can be easily oxidized back to dimethyl disulfide and thus regenerate the reactant and the active sites. The other by-product often found in the reaction is dimethyl polysulfides (mostly dimethyl trisulfide and tetrasulfide), which are the disproportionation products of dimethyl disulfide. Their formation on the clay surface is illustrated in Scheme 38.

Scheme 38. Formation of Dimethyl Polysulfide on the Surface of Clayzic



The solvents used in the reactions are either 1,2-dichloroethane or chlorobenzene. It is found that the solvents have to be reasonably polar, so they can help polarize the S-S bond, although they cannot have the carbonyl functional group since it may interact strongly with the Lewis or Brønsted acid sites on the clay surface and thus block the active sites of the catalyst.

3.2 Results and Discussions

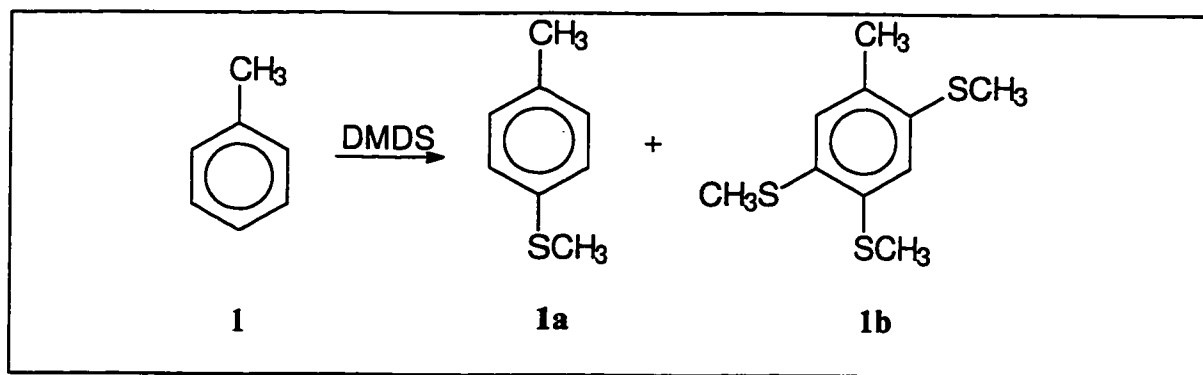
Benzene was among the first few aromatics with which reactions with dimethyl disulfide were carried out using modified clay catalysts such as K10/ ZnCl_2 , K10/ MnCl_2 and K10/ H_2SO_4 . However, no reaction was observed with benzene using these catalysts. The alkylthiolation reaction is believed to be an electrophilic substitution of the aromatic ring (Scheme 37). Since benzene is a relatively electron-poor benzenoid aromatic in comparison to alkylbenzenes, we conclude that the DMDS-catalyst complex is only weakly electrophilic and, as a consequence, is unable to promote reaction with benzene. Consequently, a series of reactions with more reactive arenes was carried out.

3.2.1 Reactions with Monosubstituted Aromatics

3.2.1.1 Reactions with Toluene

Chlorobenzene (PhCl) was chosen as the solvent for reactions with toluene in order to carry out the reactions at both moderate and high temperatures. The products formed from the reactions of toluene with various catalysts are shown in Scheme 39. The results are summarized in Table 4.

Scheme 39. Reaction of Toluene with DMDS in the Presence of Clay Catalyst(s)



Entries 1 and 2 in Table 4 show that when K10/ZnCl₂ and K10/MnCl₂ were used as catalysts, the reactions gave 4-methylthioanisole **1a** as the only isolable product, although in poor yield. The methyl group is an *o*- and *p*-directing group but the *p*-position may be favored because it is less hindered sterically. When K10 was used, a mixture of **1a** and 5-methyl-1,2,4-tris(methylthio)benzene **1b** was obtained (entry 3, Table 4) in low yield. The formation of **1b** can be explained by the fact that after the formation of **1a**, the 2- and 5-positions became activated to further reaction with DMDS. The highest yield (11%) of **1b** obtained in this series of reactions resulted when K10/H₂SO₄ was used as a catalyst (entry 4, Table 4). In this case, it is probable that the reaction was catalyzed by the Brönsted acid sites on the clay surface. The reaction pathway of the alkylthiolation catalyzed by the Brönsted acid sites on the clay surface is shown in Scheme 41. It was mentioned in the Introduction that Brönsted acidity was only present in K10 and K10/H₂SO₄. Results in Table 5 show that reaction of toluene with DMDS was catalyzed most effectively by the Brönsted acid sites on the clay surface. However, overall, all reactions of toluene with DMDS resulted in only poor yields of useful products. All attempts to improve the yields of the reaction by increasing the amount of the catalysts and extending the reaction time gave similar yields and sometimes more complex reaction mixtures often with increased quantities of CH₃S_xCH₃.

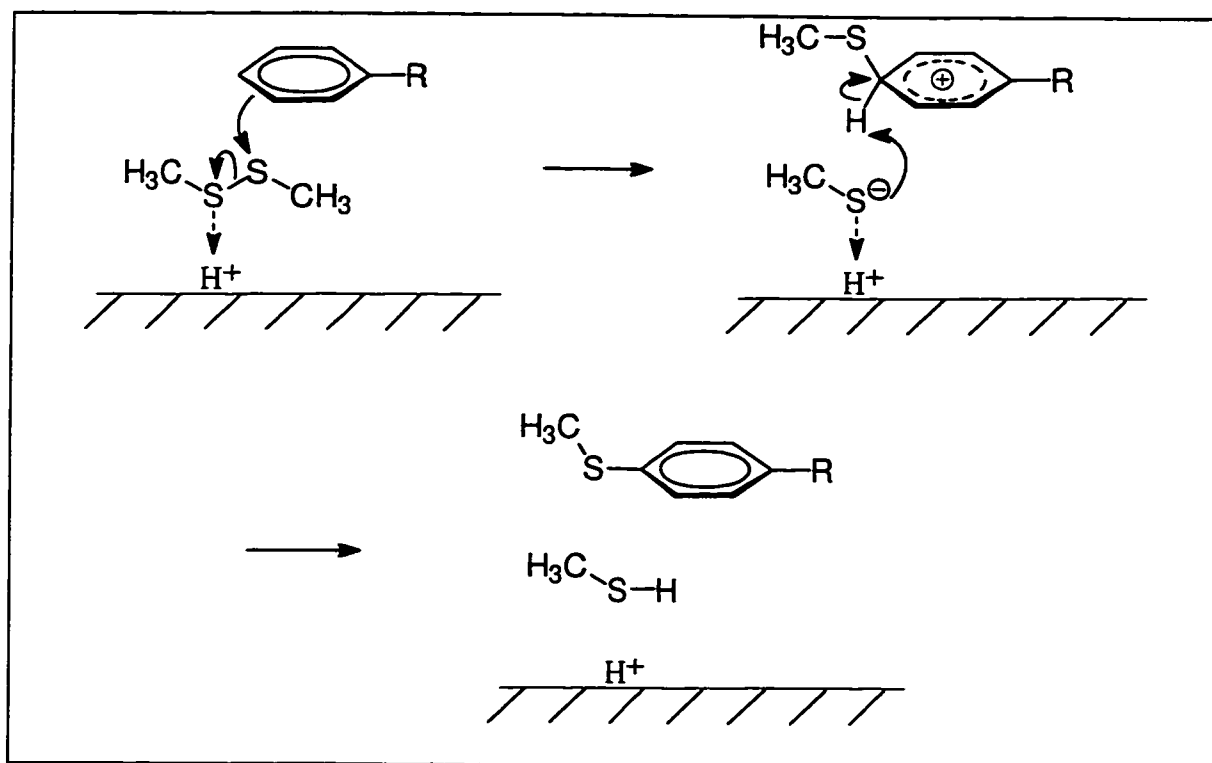
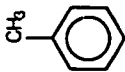
Scheme 40. Brønsted Acid Catalyzed Methylthiolation on the Clay Surface

Table 4. Results of Reactions of Toluene with DMDS in the Presence of Clay Catalysts

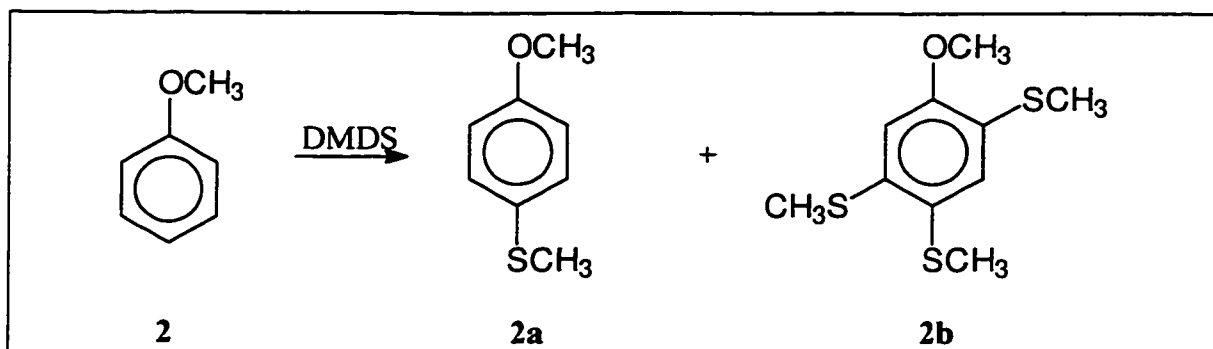
Arenes	Entry	Catalyst(s)	Molar Ratio ^a ArH:DMDS:H ₂ SO ₄	Clay (g/K10 or mmol/M ^{III})	Solvent	Product(s)	Yield (%)
	1	K10/ZnCl ₂	0.1:0.2	40 mmol	PhCl	1a	4
	2	K10/MnCl ₂	0.1:0.2	40 mmol	PhCl	1a	<5
	3	K10	0.1:0.2	30 g	PhCl	1a, 1b (1%, 3%)	4
	4	K10/H ₂ SO ₄	0.1:0.2:0.2	30 g	PhCl	1b	11

^a. H₂SO₄ is only present in entry 4.

3.2.1.2 Reactions with Anisole

Reaction of anisole with DMDS using various catalysts gave products analogous to those formed with toluene. However, much improved yields were obtained for the reactions of anisole with DMDS (Table 5) most likely a consequence of anisole being more activated than toluene towards the electrophilic substitution.

Scheme 41. Reaction of Anisole with DMDS in the Presence of Clay Catalyst(s)



When using K10/ZnCl₂ and K10/FeCl₃ as catalysts, monoalkylthiolated anisole **2a** was the only product obtained (entries 10 and 11). The use of K10/H₂SO₄ as catalyst gave a mixture of 1-methoxy-4-methylthiobenzene **2a** and 1-methoxy-2,4,5-tris(methylthio)benzene **2b**. It was observed that the use of more H₂SO₄ did not necessarily improve the yield of the reaction (entries 7 and 8). When a 1:1 ratio of DMDS and H₂SO₄ was used, an overall yield of 24% was obtained with 15% of **2a** and 9% of **2b** (entry 7). However, when a 2:1 DMDS/H₂SO₄ ratio was used, the yield went up to 54% with 36% of **2a** and 18% of **2b** (entry 8). At least two explanations can be proffered to rationalize these results. Excess H₂SO₄ may dissolve some aluminum and, hence cause collapse of the porous structure of the clay, forming amorphous silica. This would dramatically reduce the surface area of the catalyst and thus reduce its catalytic

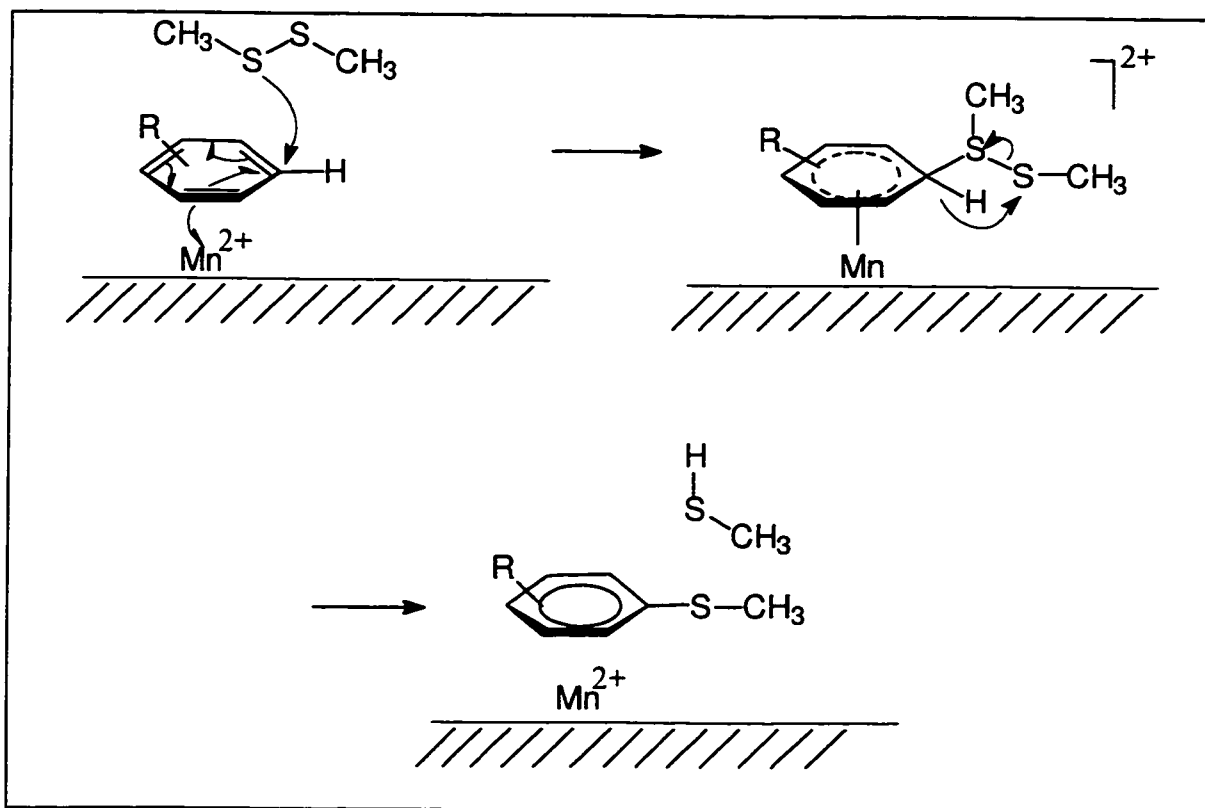
activity. Secondly, acid-catalyzed polymerization could cause loss of reagent and products.

It was also observed that the use of chlorobenzene as solvent favored the formation of polysubstituted methylthiolated aromatics and resulted in higher product yields (entries 6 and 8). Under the same catalytic conditions, the use of dichloroethane as solvent gave 36% overall yield with a **2a:2b** ratio of 6:1 (entry 6) while the use of chlorobenzene gave 54% yield with a 2:1 ratio of **2a:2b** (entry 8). All the reactions were carried out at the reflux temperature of the solvent. Since chlorobenzene boils at a much higher temperature than dichloroethane, increased formation of **2b** may be a temperature effect. However, under these more vigorous reaction conditions, formation of $\text{CH}_3\text{S}_x\text{CH}_3$ was observed, especially with prolonged reactions.

Previous work in our laboratories has shown^[28] that K10/ MnCl_2 catalyzes the alkylthiolation of benzothiophene very efficiently. High yields were obtained with very little $\text{CH}_3\text{S}_x\text{CH}_3$ formed as by-product. Since the formation of $\text{CH}_3\text{S}_x\text{CH}_3$ is believed to occur via co-ordination of the S-atom of the disulfide to the active acid sites, the absence of $\text{CH}_3\text{S}_x\text{CH}_3$ suggested that such co-ordination did not take place. Thus, a probable explanation for the catalytic activity of $\text{MnCl}_2/\text{K10}$ is that it is the aromatic substrate which is activated by co-ordination at the Mn^{2+} site (Scheme 42). It is proposed that co-ordination occurs by interaction of the π electrons of the aromatics with a d orbital of Mn^{2+} . Nucleophilic attack by the S-atom of the disulfide on this polarized species would eventually lead to the formation of methylthio-substituted aromatics. In this study, $\text{K10}/\text{MnCl}_2$ was shown to be a very active catalyst for promoting alkylthiolation as in the

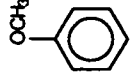
reactions of anisole with DMDS, the use of K10/MnCl₂ achieved the highest yield (77%, entry 9).

Scheme 42. Possible Reaction Pathway Involving Nucleophilic Substitution on the Surface of K10/MnCl₂



Note: Charges on top right structure do not infer reduction of Mn²⁺.

Table 5. Results of Reactions of Anisole with DMDS in the Presence of Clay Catalyst(s)

Arenes	Entry	Catalyst(s)	Molar Ratio Ar:DMDS:H ₂ SO ₄	Clay (g/K10 or mmol/M ^{nt})	Solvent	Product(s)	Yield (%)
	5	K10/H ₂ SO ₄	0.1:0.6:0.3	50 g	Cl(CH ₂) ₂ Cl	2a, 2b (36%:5%)	41
	6	K10/H ₂ SO ₄	0.1:0.6:0.3	100 g	Cl(CH ₂) ₂ Cl	2a, 2b (31%:5%)	36
	7	K10/H ₂ SO ₄	0.1:0.6:0.6	100 g	PhCl	2a, 2b (15%:9%)	24
	8	K10/H ₂ SO ₄	0.1:0.6:0.3	100 g	PhCl	2a, 2b (36%:18%)	54
	9	K10/MnCl ₂	0.1:0.6	200 mmol	PhCl	2a, 2b (65%, 12%)	77
	10	K10/FeCl ₃	0.1:0.6	60 mmol	Cl(CH ₂) ₂ Cl	2a	32
	11	K10/ZnCl ₂	0.1:0.6	100 mmol	PhCl	2a	46

3.2.1.3 Reactions with Thioanisole

With the success achieved from the reactions of anisole and DMDS under various conditions, the research was extended to reaction with thioanisole. Scheme 43 shows that in addition to 1,4-bis(methylthio)benzene **3a**, 1,2,4,5-tetrakis(methylthio)benzene **3b** was also formed. The reaction conditions and results of a series of reactions are listed in Table 6. One of the expected products of this reaction is 1,4-bis(methylthio)benzene. This compound is of particular interest in this study as it is a precursor of 1,4-benzenedithiol, one of the compounds that could be used to make linear polysulfides in mixture with elemental sulfur.

Scheme 43. Reaction of Thioanisole with DMDS

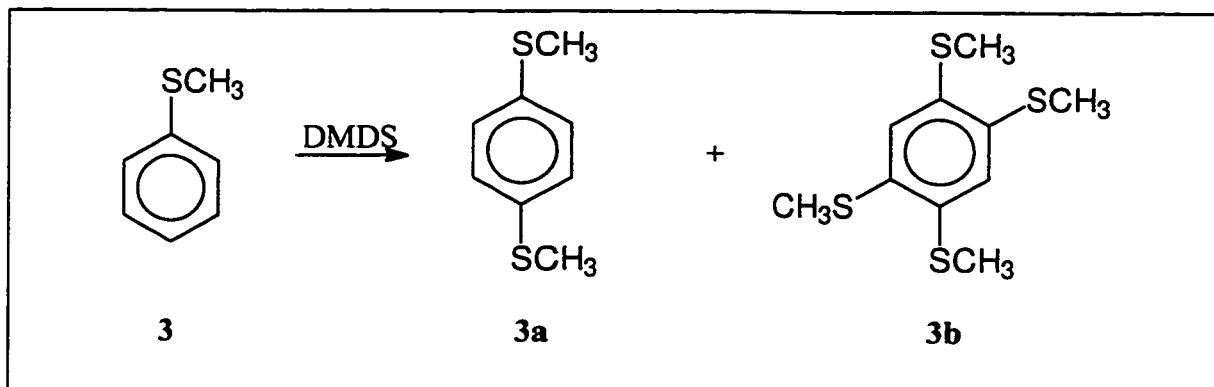
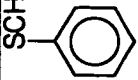


Table 6. Results of Reactions of Thioanisole with DMDS in the Presence of Clay Catalyst

Arenes	Entry	ArH:DMDS:H ⁺	Clay(g/K10 or mmol/M ^{nt})	Catalyst(s)	Solvent	Product(s)	Yield (%)
	12	0.1:0.6	100 mmol	K10/ZnCl ₂	PhCl	3a	<5
	13	0.1:0.6	50 g	K10/H ⁺	PhCl	3a	26
	14	0.1:0.6:0.45	120 g	K10/H ₂ SO ₄	PhCl	3a	25
	15	0.1:0.6:0.6	120 g	K10/H ₂ SO ₄ ^a	PhCl	3a	33
	16	0.1:0.6:0.6	120 g	K10/H ₂ SO ₄	Cl(CH ₂) ₂ Cl	3a, 3b (15%:5%)	20
	17	0.1:0.6:0.6	120 g	K10/TFAA ^b	PhCl	3a, 3b (46%:6%)	52
	18	0.1:0.6:0.3	120 g	K10/TFAA ^b	PhCl	3a, 3b (49%:14%)	63
	19	0.1:0.6	200 mmol	K10/MnCl ₂	PhCl	3a, 3b (43%:12%)	55

^a The reaction was done in an autoclave at 150°C with an air pressure of 1000 psi.

^b Trifluoroacetic acid instead of sulfuric acid was added as a co-catalyst.

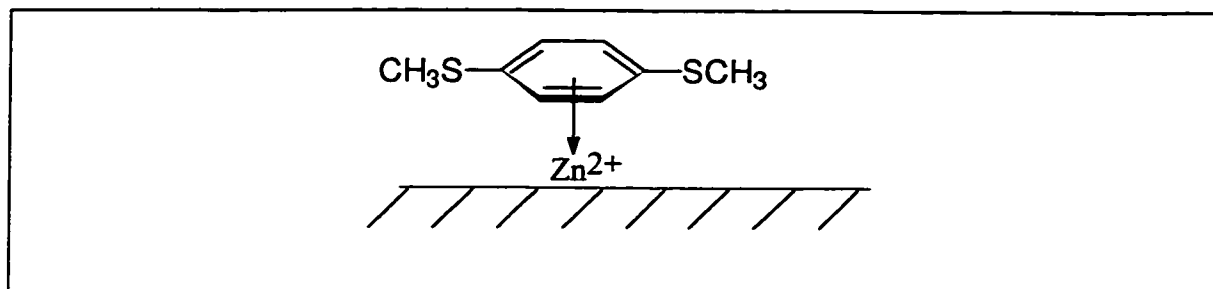
As was observed with toluene and anisole, the use of K10/ZnCl₂ as catalyst gave extremely poor yields of the 1,4-product (entry 12, Table 6). Although K10/ZnCl₂ has been proven to be a good catalyst for some Friedel-Crafts reactions, obviously it was not a good catalyst for alkylthiolation of aromatics. The catalyst designated as K10/H⁺ was a proton exchanged clay. It was prepared by adding H₂SO₄ (98%) to a slurry of K10 and water. The mixture was stirred and kept at 80°C for 16 h, and then a large amount of cold water was added to terminate the activation. The solid was filtered and washed with hot water, then dried in oven at 100°C and, subsequently, was ground to a powder^[118]. The reaction using this catalyst gave **3a** in 26% yield (entry 13). Most probably, the reaction was catalyzed exclusively by Brönsted acid sites on the clay surface since free H₂SO₄ should have been filtered out during catalyst preparation. Very little by-product CH₃S_xCH₃ was found. Although the product yield was quite low, the reaction was very clean with product being easy to isolate. Similar results were obtained when K10/H₂SO₄ was used as catalyst (entries 14-16). When equal amounts of DMDS and H₂SO₄ were used, **3a** was isolated in 33% yield (entry 15), a slight improvement from 25% obtained when 0.75 equivalent of H₂SO₄ was used (entry 14). One disadvantage of using H₂SO₄ as co-catalyst was that large amounts of dimethyl polysulfides were formed, especially when prolonged reaction times were required. The products and by-products were sometimes complex mixtures making it difficult to isolate the desired compounds.

In both cases mentioned above, the formation of **3b** was observed from GC-MS analysis. It was not isolated because it was present in only minor quantities amongst a large amount of by-products. When ClCH₂CH₂Cl was used as solvent, reaction mixtures were less complex allowing the isolation of **3b** (entry 16) in lower yield in comparison to

when PhCl was used as solvent (20% versus 25%). The other disadvantage of using H_2SO_4 as co-catalyst was that the small amount of water associated with the concentrated H_2SO_4 caused the clay particles to coalesce making the stirring of the reaction mixture extremely difficult. Some experiments were conducted using trifluoroacetic acid (CF_3COOH) in place of H_2SO_4 . These experiments resulted in much improved yields (entries 17 and 18). The amount of CF_3COOH used also affected the product yields. The best yield was obtained when a DMDS/ CF_3COOH ratio of 0.5 was used (entry 18). A mixture of **3a** and **3b** was isolated (ratio being determined by ^1H NMR) with **3a** as the major product.

Many attempts were made to further direct the reaction to a tetrakis-thiolated benzene product. Some experiments were conducted using isolated **3a** and mixing it with fresh clay catalyst, H_2SO_4 and DMDS. However, no reaction was detected and only starting material was recovered. Interestingly, it was observed that the clay catalyst changed color on addition of **3a** to the reaction mixture, indicating that co-ordination between **3a** and the clay surface may have occurred as shown in Scheme 44. This type of co-ordination may be favoured over co-ordination of DMDS to the active sites as with two -S-methyl groups and the π system, **3a** would be electron-rich in comparison to DMDS. Consequently, only a very low concentration of activated DMDS would be available to alkylthiolate **3a**, explaining the very low degree of reaction observed in these experiments.

Scheme 44. Co-ordination between Polyalkylthiolated Arenes with Acid Sites on the Clay Surface



It is also possible that methanethiol, a by-product of the reaction of DMDS with an aromatic, could also block the active sites of the catalyst. However, if the reaction is done under air pressure, it is anticipated that the O_2 could quickly react with methanethiol, regenerating DMDS and the acid site. In practice, only a slight improvement was observed in terms of isolated yield (entry 15). However, the reaction usually gave more complex product mixtures which made isolation of products more difficult.

As was the case with anisole, K10/ $MnCl_2$ proved to be a very active catalyst for promoting alkylthiolation of thioanisole (entry 19). The reaction was very clean with little by-products formation and a satisfactory yield (55%). Since $MnCl_2$ is not considered to be a Lewis acid, it is suggested that the reaction was catalyzed through the co-ordination between Mn^{2+} and the aromatic substrate as illustrated in Scheme 42.

3.2.2 Reactions with Xylenes

With two methyl groups to enhance the π -electron density of the aromatic ring, xylenes are expected to be more activated towards electrophilic substitution than toluene. The reactions of DMDS with *o*-xylene, *p*-xylene and *m*-xylene were carried out using the same series of catalysts as employed in the methylthiolation of mono-substituted aromatics. The general reactions are described in Scheme 45 with reaction conditions and yields summarized in Table 7.

Scheme 45. Reactions of Xylenes with DMDS in the Presence of Clay Catalyst(s)

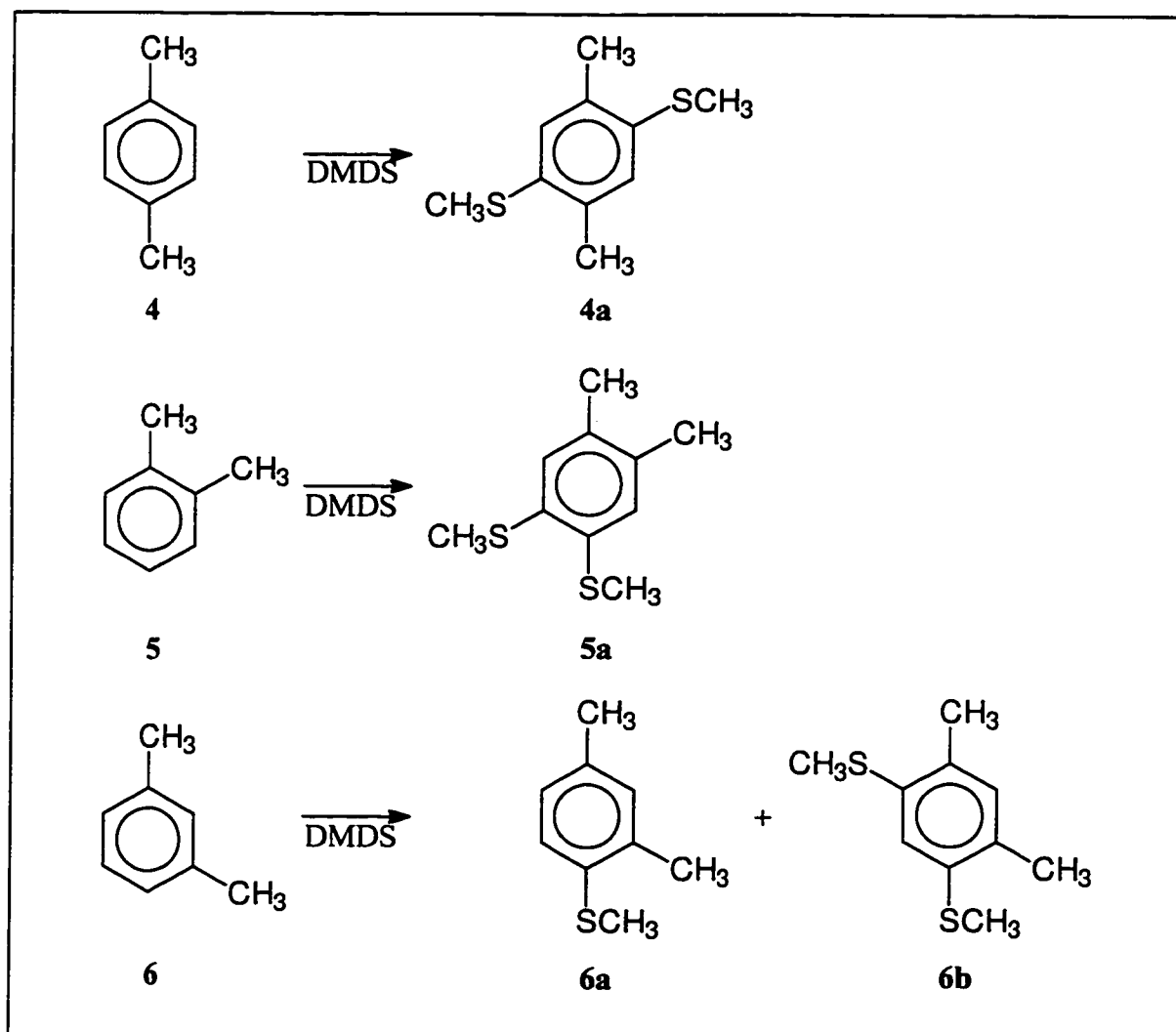


Table 7. Results of Reactions of Xylenes with DMDS in the Presence of Clay Catalyst(s)

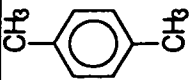
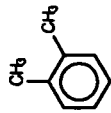
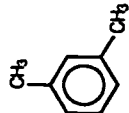
Arenes	Entry	Catalyst(s)	Molar Ratio ArH:DMDS:H ⁺	Clay(g/K10 or mmol/M ⁿ⁺)	Solvent	Product(s)	Yield (%)
	20	K10/ZnCl ₂	0.1:0.4	200 mmol	PhCl	4a	10
	21	K10/H ⁺ ^a	0.1:0.2	10 g	Neat	4a	8
	22	K10/H ₂ SO ₄	0.1:0.8:0.32	30 g	Cl(CH ₂) ₂ Cl	4a	20
	23	K10/H ₂ SO ₄	0.1:0.4:0.1	50 g	Cl(CH ₂) ₂ Cl	4a	14
	24	K10/H ₂ SO ₄	0.1:0.4:0.2	50 g	Cl(CH ₂) ₂ Cl	4a	25
	25	K10/H ₂ SO ₄	0.1:0.4:0.2	100 g	Cl(CH ₂) ₂ Cl	4a	29
	26	K10/H ₂ SO ₄	0.1:0.4:0.2	100 g	PhCl	4a	42
	27	K10/H ₂ SO ₄	0.1:0.4:0.1	100 g	PhCl	4a	17
	28	K10/MnCl ₂	0.1:1.0	200 mmol	PhCl	4a	33

Table 7. (cont.)

Arenes	Entry	Catalyst(s)	Molar Ratio ArH:DMS:H ⁺	Clay(g/K10 or mmol/M ^{tt})	Solvent	Product(s)	Yield (%)
	29	K10	0.1:0.4	50 g	PhCl	5a	14
	30	K10/H ₂ SO ₄	0.1:0.6:0.6	100 g	Cl(CH ₂) ₂ Cl	5a	23
	31	K10/H ₂ SO ₄	0.1:0.6:0.6	100 g	PhCl	5a	23
	32	K10/ZnCl ₂	0.1:0.6	100 mmol	PhCl	No Reaction	-
	33	K10/MnCl ₂	0.1:0.6	200 mmol	PhCl	5a	38
	34	K10/H ⁺ ^a	0.1:0.2	10 g	Neat	6a	14
	35	K10/H ₂ SO ₄	0.1:0.4:0.2	100 g	PhCl	6a, 6b (60%, 9%)	69
	36	K10/H ₂ SO ₄	0.1:0.8:0.32	30 g	Cl(CH ₂) ₂ Cl	6a, 6b (19%, 29%)	48

^a K10/H⁺ is an acid-washed K10 catalyst, the preparation of which is described in detail in Chapter 7.

3.2.2.1 Reactions with *p*-xylene

The reactions of *p*-xylene with DMDS using various catalysts gave 1,4-dimethyl-2,5-bis(methylthio)benzene **4a** as the only product (Table 7). Although alkylthiolation of toluene could not be accomplished with K10/ZnCl₂, the more reactive *p*-xylene gave **4a** in 10% yield (entry 20). Product yields were improved by changing the DMDS/acid ratio as well as solvent. In general, the use of PhCl as solvent gave higher yields (entries 26-28) and reactions catalyzed by Brønsted acids yielded better results in comparison to reactions catalyzed by Lewis acid catalysts. The best yield of **4a** was obtained with a DMDS/acid ratio of = 0.5 (entry 26). Further increasing the amount of sulfuric acid did not improve the yield, possibly a result of loss of some of the porous structure of K10 as a result of acid digestion of the clay. Use of K10/MnCl₂ gave **4a** in 33% isolated yield. Like all the reactions catalyzed by K10/MnCl₂, this reaction was very clean and no polysulfides were formed. Increasing the severity of the reaction conditions failed to increase the degree of thiosubstitution, perhaps due to the steric hindrance or co-ordination of the initial products to the active sites.

3.2.2.2 Reactions with *o*-xylene

The reactions of *o*-xylene with DMDS were carried out using the same series of catalysts used in the reactions of *p*-xylenes. The 4,5-disubstituted product **5a** was isolated as the only product under all reaction conditions. The mono-alkylthiolated product was not detected by GC-MS. All of the four unsubstituted positions of *o*-xylene are activated by the methyl groups, the 4,5 positions being favored somewhat because they are sterically less hindered than 3,6 positions. It is reasonable to assume that the first

substitution occurs at either the 4- or 5-positions giving a mono-methylthiolated product. This product is, likely, more active than *o*-xylene due to the extra SCH₃ group and reacts quickly with second molecule of DMDS giving **5a**. It is probable that steric factors direct the second molecule of DMDS to 5-position because it is less hindered than 3-position. The second substitution must be much faster than the first as the mono-alkylthiolated product was not observed.

It was noticed that K10 alone catalyzed the reaction to some degree giving **5a** in 14% yield (entry 29), mostly probably via Brönsted acid sites on the clay surface. K10/ZnCl₂, containing mostly Lewis sites, was a poor catalyst for methylthiolation of *o*-xylene (entry 32, Table 7). Addition of H₂SO₄ to K10 resulted in slightly higher yields (entries 30 and 31). The highest yield of **5a** was obtained when K10/MnCl₂ was used as catalyst (entry 33).

3.2.2.3 Reactions with *m*-xylene

Reactions of *m*-xylene with DMDS resulted in better yields of products in comparison to reactions with *p*- and *o*-xylenes. When the reaction was carried out with a DMDS/H₂SO₄ ratio of 0.5, a mixture of mono-methylthiolated product **6a** and bis(methylthiolated) product **6b** was isolated in total yield of 69% (entry 35). The use of ClCH₂CH₂Cl as solvent in place of PhCl gave slightly lower yields (48%, entry 36) as was observed in the reactions of *p*- and *o*-xylenes. Use of the K10/H⁺ catalyst gave **6a** as the only product. Obviously, this catalyst is a much milder catalyst than K10/H₂SO₄. The 4- and 6-positions are equivalent in *m*-xylene and should be more susceptible to electrophilic attack than the 2-position. Consequently, the initial product formed was

mono-methylthiolated product **6a**. Since position 6 is doubly activated by the two methyl groups, whereas position 5 is only activated by the -S-methyl group, the second substitution yields **6b**. Consequently, with more active catalysts e.g., the use of H₂SO₄ as co-catalyst with K10, mixed products **6a** and **6b** were obtained.

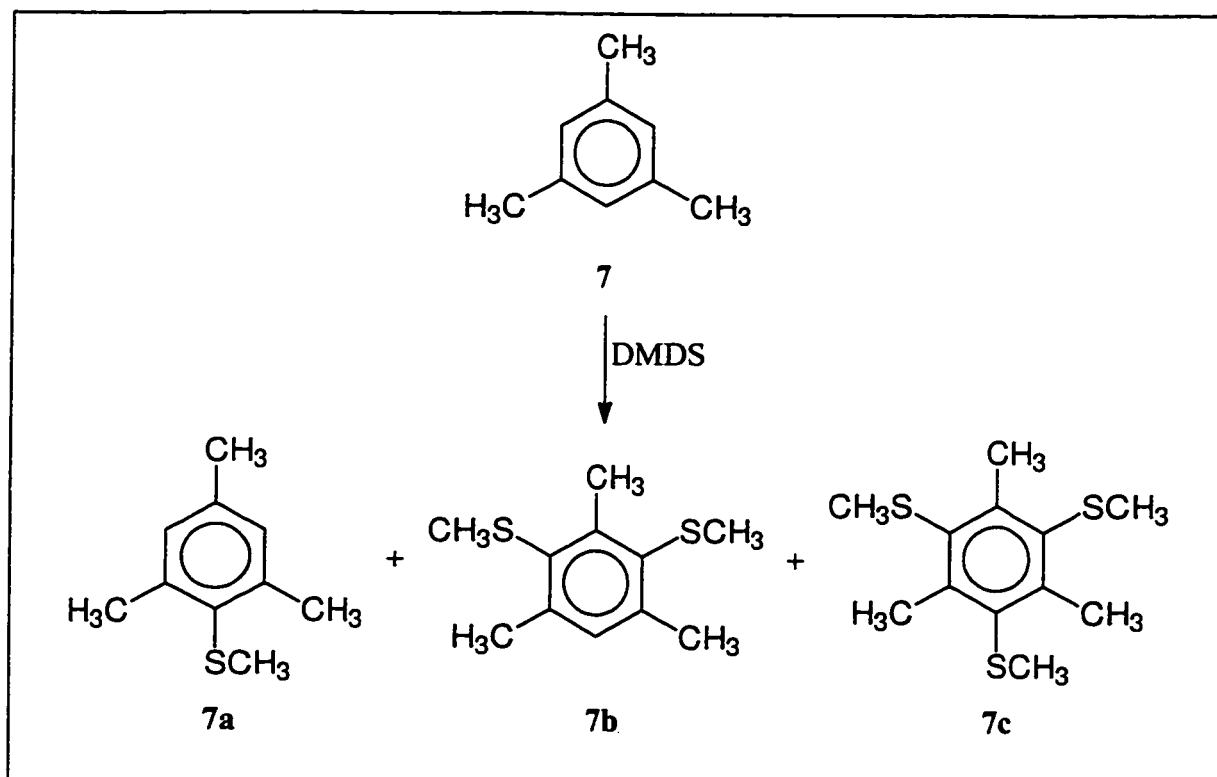
3.2.3 Reactions with Trisubstituted Aromatics - Mesitylene

Reaction of mesitylene with DMDS using the catalysts described previously gave monomethylthio- **7a**, bis(methylthio)- **7b** or tris(methylthio)- **7c** mesitylenes (Scheme 46). The structures of these products were determined by standard spectroscopic techniques (see Experimental Section, p. 138) The reaction conditions, products, as well as isolated yields, are listed in Table 10.

Various catalysts were used in the reaction of mesitylene with DMDS and their catalytic activities were compared. Mesitylene has three activating methyl groups, and, as a consequence, is more active than toluene and the xylenes. Indeed, much improved yields were observed for all the reactions using K10-based catalysts. K10/ZnCl₂, which was found to be a poor catalyst for methylthiolation of toluene and xylenes, gave an excellent yield (entry 36, Table 10) using PhCl as solvent. A mixture of mono-methylthiolated product **7a** and bis(methylthiolated) mesitylene **7b** was obtained but no trace of tris(methylthio)mesitylene **7c** was detected in the crude reaction mixture (GC-MS). When this catalyst was used in dichloroethane solution, a white solid was recovered from the reaction mixture. The compound has a mass of 122 and singlets at δ 2.70 and δ 2.12, corresponding to four and six protons in its ¹H NMR spectrum. The solid was recrystallized from ether and its molecular structure was determined by X-ray

crystallography (Scheme 47). Obviously, this complex was the product of the solvent 1,2-dichloroethane reacting with DMDS with the resulting substitution product chelating with ZnCl_2 . The mass of 122 is then only that of the dichloroethane substitution product. Thus, in this case, it was found that solvent was even more reactive than the aromatic substrate mesitylene. Therefore, for the reactions promoted by K10/ZnCl_2 , 1,2-dichloroethane was avoided due to its interaction with the catalyst. The experimental data on bond lengths and bond angles of this complex are listed in Tables 8 and 9.

Scheme 46. Reactions of Mesitylene with DMDS in the Presence of Clay Catalyst(s)



Scheme 47. ORTEP Diagram of $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3\text{-ZnCl}_2$

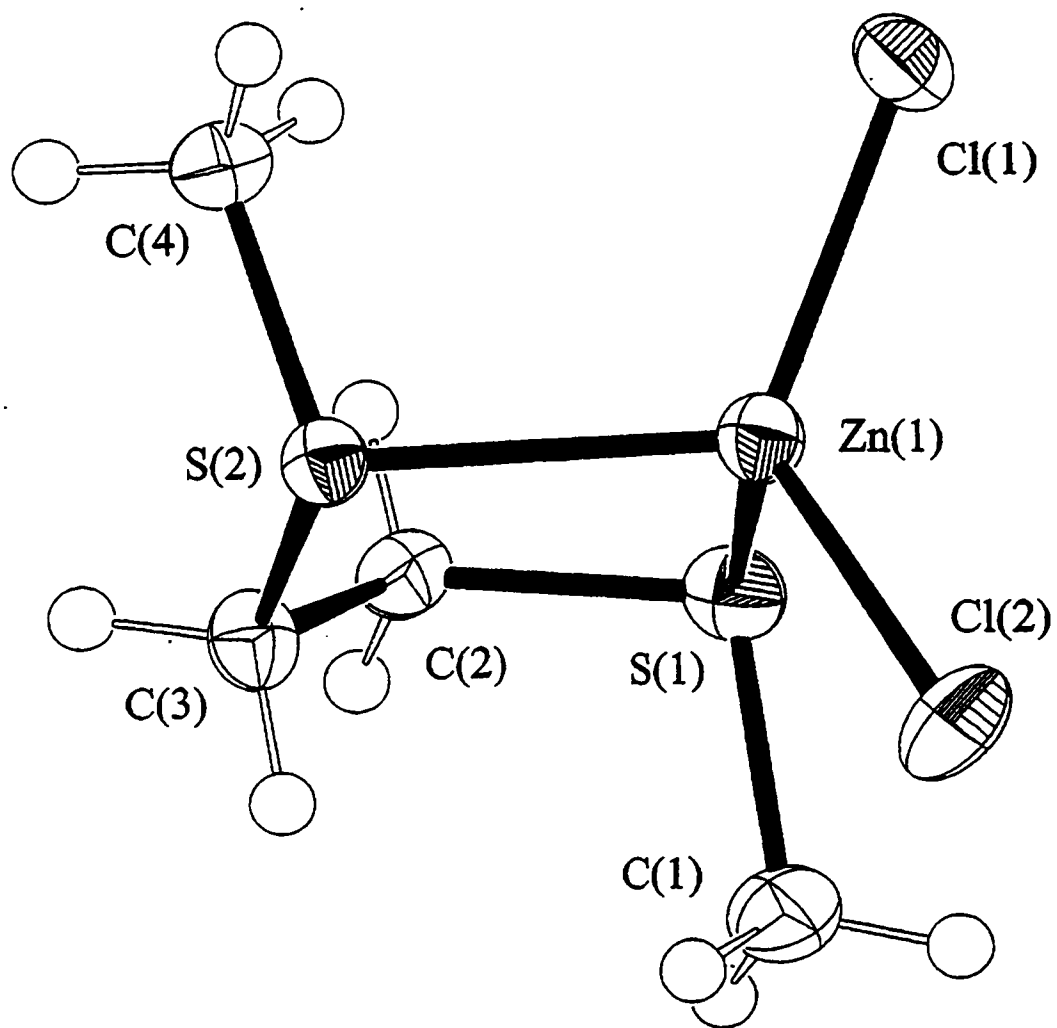


Table 8. Bond Lengths (Å)^a

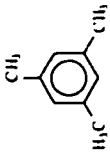
atom	atom	distance	atom	atom	distance
Zn(1)	Cl(1)	2.209(2)	Zn(1)	Cl(2)	2.203(2)
Zn(1)	S(1)	2.460(2)	Zn(1)	S(2)	2.391(2)
S(1)	C(1)	1.812(7)	S(1)	C(2)	1.823(6)
S(2)	C(3)	1.808(6)	S(2)	C(4)	1.802(6)
C(2)	C(3)	1.520(7)			

Table 9. Bond Angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
Cl(1)	Zn(1)	Cl(2)	123.29(7)	Cl(1)	Zn(1)	S(1)	106.11(6)
Cl(1)	Zn(1)	S(2)	112.66(6)	Cl(2)	Zn(1)	S(1)	106.11(7)
Cl(2)	Zn(1)	S(2)	112.26(6)	S(1)	Zn(1)	S(2)	90.70(6)
Zn(1)	S(1)	C(1)	103.4(2)	Zn(1)	S(1)	C(2)	97.7(2)
C(1)	S(1)	C(2)	102.6(3)	Zn(1)	S(2)	C(3)	99.2(2)
Zn(1)	S(2)	C(4)	104.2(2)	C(3)	S(2)	C(4)	102.2(3)
S(1)	C(2)	C(3)	115.2(4)	S(2)	S(3)	C(2)	115.4(4)

^a The data were obtained by Dr. Masood Parvez. The complete experimental data on this complex are listed in the Appendix.

Table 10. Results of Reaction of Mesitylene with DMDS in the Presence of Clay Catalyst(s)

Arenes	Entry	Catalyst(s)	ArH:DMDS:H ⁺	Clay(g/K10 or mmol/M ⁿ⁺)	Solvent	Product(s)	Yield (%)
	36	K10/ZnCl ₂	0.1:0.6	120 mmol	PhCl	7a, 7b (14%, 76%)	90
	37	K10/H ⁺ ^a	0.1:0.6	50 g	Cl(CH ₂) ₂ Cl	7a	72
	38	K10/H ₂ SO ₄	0.1:0.6:0.3	30 g	Cl(CH ₂) ₂ Cl	7b	63
	39	K10/H ₂ SO ₄	0.1:0.6:0.6	30 g	Cl(CH ₂) ₂ Cl	7b, 7c (37%, 29%)	66
	40	K10/H ₂ SO ₄ (fuming)	0.1:0.6:0.3	30 g	Cl(CH ₂) ₂ Cl	7b, 7c (52%, 4%)	56
	41	K10/MnCl ₂	0.1:0.6	200 mmol	PhCl	7a, 7b (39%, 57%)	96

^a. K10/H⁺ is an acid-washed catalyst, the preparation of which is described in Chapter 7.

When concentrated H_2SO_4 was used as a co-catalyst, (DMDS/ H_2SO_4 ratio 0.5) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ solution, bis(methylthio)mesitylene **7b** was isolated as the sole product in 63% yield (entry 39). The use of DMDS/ H_2SO_4 in a 1:1 ratio gave a similar total yield (66%) with the formation of **7c** in 29% yield (entry 39). Since the small amount of water in concentrated H_2SO_4 caused clay particles to coalesce, making stirring of the reaction mixture extremely difficult, an experiment was conducted using fuming H_2SO_4 (entry 40, Table 10). Overall, this reaction resulted in a similar total product yield (56%) with **7b** as the major product.

The crude mixture of products isolated from the reaction in entry 39 was mixed with fresh K10/ H_2SO_4 catalyst and DMDS and the reaction was continued for another 18 h. **7c** was isolated as the only product with combined yield of 35%. Although this reaction produced large amounts of by-product dimethyl polysulfides, it allowed a facile synthesis of 1,3,5-trimethyl-tris(methylthio)benzene **7c** which, otherwise, is difficult to obtain. **7c** is the precursor of 2,4,6-trimethylbenzenetrithiol which was used to investigate the formation of network polysulfides by reaction with sulfur (see Chapter 5).

K10/ MnCl_2 clay was again proven to be an excellent catalyst for promoting C-S bond formation of aromatics. The reaction catalyzed by K10/ MnCl_2 in PhCl gave 96% of **7a** and **7b** with **7b** as the major product (entry 41, Table 10). The formation of polysulfides was not detected by GC-MS and the work-up only involved simple filtration and evaporation of the solvent.

3.3 Characterization of the Catalysts

3.3.1 Pore Size and Surface Area

K10, K10/H⁺ and K10/H₂SO₄ were used in the reactions of aromatic substrates with DMDS. Some of these reactions were likely catalyzed by the Brönsted acid sites on the clay surface as illustrated in Scheme 40. The catalytic activity of these catalysts was found to be: K10/H₂SO₄>K10/H⁺>K10. In an attempt to rationalize their activities in the thiolation reactions, pore size distributions and surface areas were measured (Table 11).

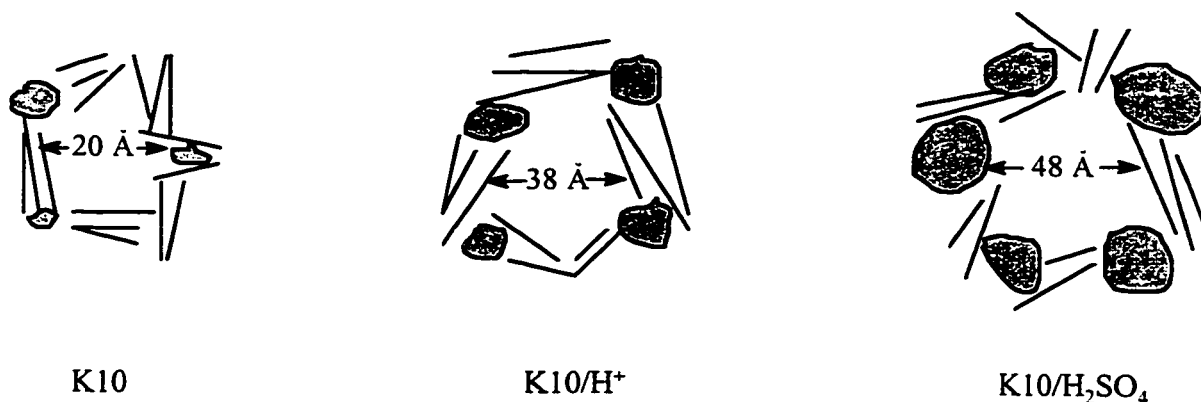
Table 11. Specific Surface Area and Maximum Pore Size of K10, K10/H⁺ and K10/H₂SO₄

	Specific Surface Area (m ² /g)	Maximum Pore Diameter (Å)
K10	272	20
K10/H ⁺	161	38
K10/H ₂ SO ₄	54	48

These data show that commercial K10 has very large surface area of 272 m²/g, which, upon further acid treatment, is reduced significantly to ~161 m²/g. As illustrated in Scheme 48, the acid treatment dissolves some of the alumina layer, leaving amorphous silica behind. Thus, some small pores would collapse forming larger pores. These changes might explain why the maximum pore distribution shifted to larger diameter with additional acid treatment (Table 11). Specifically, for K10/H₂SO₄, the maximum pore size was found to be at 48 Å while that of K10 occurred at 20 Å. Overall, the activity of these catalysts towards the alkylthiolation of aromatics increased as large pores were formed. Thus, despite the loss of surface area, it seems that pore size might determine the catalyst's activity. The K10/H₂SO₄ had the largest pores with a maximum at 48 Å. It is

suggested that these large pores effectively accommodate the transition state of the alkylthiolation reactions. In addition, larger pores should increase diffusion of reactants and products throughout the catalyst structure increasing the reaction rates. Untreated K10 has relatively small pores (maximum at ~ 20 Å) which may not be able to accommodate the solvated transition states of the thiolation reactions.

Scheme 48. The Effect of Acid-treatment on Clay Catalysts



3.3.2 ^{27}Al and ^{29}Si NMR Spectra of the Catalysts

High resolution magic angle spin (MAS) solid-state ^{27}Al and ^{29}Si NMR spectroscopic techniques have been used to study a number of inorganic solids, such as clays^[91] and zeolites^[92,93]. The studies have shown that separate signals are observed for the ^{29}Si nucleus in the basic SiO_4 unit depending on the environment given by the four atoms attached to the oxygens^[94]. Since the chemical shift is affected mainly by the electron density on the oxygen atoms of the silicon tetrahedron, the nature of the neighboring atoms, linked or coordinated to these oxygens, is expected to influence the shift.

Table 12. ^{29}Si NMR Chemical Shifts (ppm) of the Clay Catalysts

Catalyst	δ_1	δ_2	δ_3
K10	-93.16	-103.03	-
K10/H ⁺	-92.61	-103.15	-
K10/H ₂ SO ₄	-92.42	-103.55	-113.65

The ^{29}Si NMR chemical shifts of the clay catalysts used in the alkylthiolation reactions of the aromatics are reported in Table 12. K10 and K10/H⁺ showed two different resonances, at -93 ppm and -103 ppm. Magi et al.^[95] assigned the signal at -93 ppm to Si atoms in the tetrahedral layer of the clay, linked to three other Si atoms and to an Al atom in the tetrahedral layer. The peak at -103 ppm, according to Engelhardt^[96], was characteristic of the dehydroxylated phases. It may be explained by the presence of Q⁴ (1Al) structural units in three-dimensionally connected aluminosilicate-like structures formed by SiOAl linkages between the silicate sheet and the gibbsite sheet during dehydroxylation. This interpretation is supported by the observation of the ^{27}Al NMR signal at 65-74 ppm which is typical of tetrahedral Al in aluminosilicates (see later). For K10/H₂SO₄, a new peak was found at -113.65 ppm, which Magi^[95] assigned as siliceous impurities associated with the clay. With stronger acid treatment, it was expected that more amorphous silica would form as was discussed in Chapter 1. The observation of the signal at -113 ppm in the case of K10/H₂SO₄ is likely a result of formation of amorphous silica.

MAS ^{29}Al NMR can be used to distinguish tetrahedrally and octahedrally coordinated aluminum^[97]. An intense peak at about 2 ppm for K10 and K10/H⁺ is characteristic of octahedral Al. In both cases, a small peak was observed at about 68

ppm, showing traces of tetrahedral Al^[98] (Table 13). However, the signals corresponding to tetrahedral and octahedral Al were not found for K10/H₂SO₄. It was likely that the strong acid treatment depleted most of the aluminum from its octahedral Al layer, leaving very little crystalline Al to be detected by ²⁷Al NMR. This was consistent with the surface area and pore size distribution measurements which showed a significantly lower surface area and a larger pore size distribution due to the dissolution of Al upon acid treatment.

Table 13. ²⁷Al NMR Chemical Shifts (ppm) of the Clay Catalysts

Catalyst	δ_1 tetrahedral	δ_2 tetrahedral	δ_3 tetrahedral	δ_4 octahedral
K10	67.21	-	-	1.87
K10/H ⁺	68.82	-	-	2.56
K10/H ₂ SO ₄	-	-	-	-

It can be concluded that K10/H₂SO₄ had only limited crystallinity and that its ability towards methylthiolation reactions was mainly caused by the presence of mesopores. This would not only accommodate the transition state more effectively, but also facilitate the diffusion of the reactants and products to and from the surface of the catalyst.

3.4 Conclusions

It has been demonstrated that modified clay catalysts can be used to promote C-S bond formation on aromatic substrates, such as toluene, anisole, thioanisole, xylenes and mesitylene. The method allowed a one-step, facile synthesis of sulfur-functionalized arenes which, otherwise, are difficult to obtain.

Among the catalysts used, K10/MnCl₂ was the most active, giving high yields and clean reactions. The reaction pathway is believed to involve co-ordination of aromatic substrates with Mn(II) on the clay surface and subsequent nucleophilic attack by DMDS molecules.

It was also found that the activity of the remaining catalysts was in the order: K10/H₂SO₄>K10/H⁺>K10>K10/ZnCl₂. The reaction pathway for these catalysts is likely via co-ordination of a S-atom of DMDS with acid sites on the clay surface and subsequent electrophilic substitution on the aromatic substrates. However, a competitive reaction involving formation of dimethyl polysulfides reduced product yields and complicated the isolation of products.

In general, modified clay catalysts promote direct alkylthiolation of aromatics giving sulfur-functionalized aromatics. These reactions are one of the few examples of direct C-S bond formation in aromatic systems (see references [27,28] for other examples).

CHAPTER FOUR

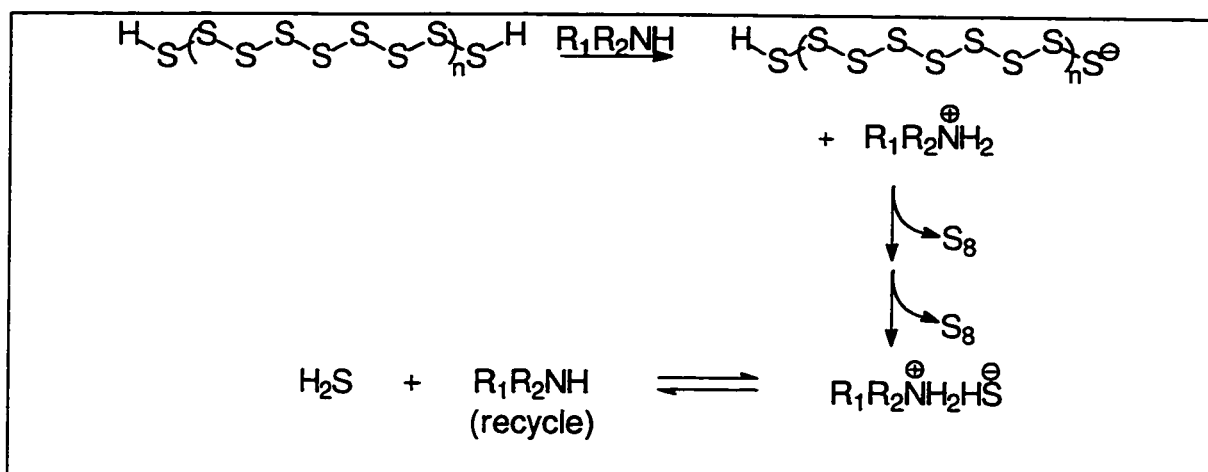
FORMATION OF LINEAR AROMATIC POLYSULFIDES FROM REACTION OF BENZENETHIOLS WITH ELEMENTAL SULFUR

The reaction of thiols with elemental sulfur has been reported as early as 1871 when Müller^[99] observed the formation of diethyl disulfide from the reaction of ethanethiol with sulfur at 150°C. The reaction of an aromatic thiol with sulfur was first reported by Wuyts^[100] in 1909 who observed the formation of diphenyl disulfide from the reaction of benzenethiol and sulfur. For *p*-substituted aromatic dithiols, the formation of a linear polysulfide polymer is expected. In this study, both reactions of 1,4-benzenedithiol and 2,5-dimethyl-1,4-benzenedithiol with elemental sulfur will be examined. The former was initially synthesized by the reaction of dichlorobenzene and sodium *iso*-propylthiolate in HMPA at 100°C followed by reductive cleavage of the S-*iso*-propyl bond using Na. The thiol is formed by the addition of HCl^[24,25]. In addition, the newly developed method reported in Chapter 3 makes both compounds readily accessible.

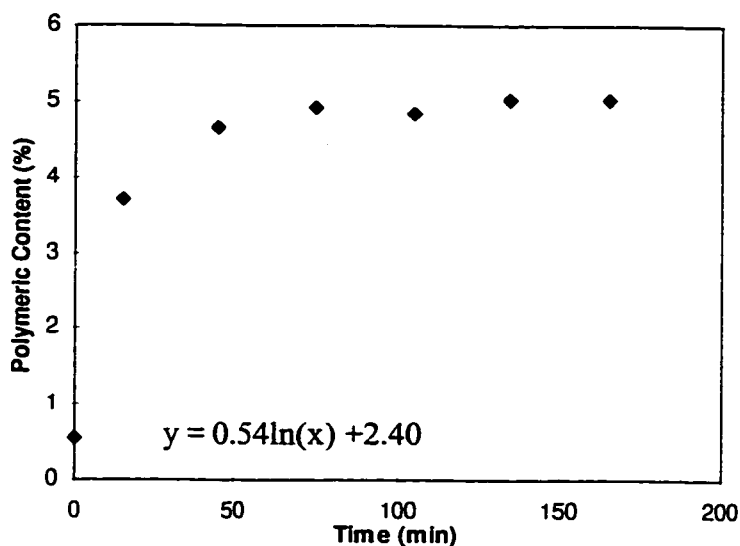
In this study, the reaction rates of aromatic thiols with sulfur were monitored by viscosity measurement and by polymeric content measurement. As will be discussed later, both methods may give only qualitative data as the presence of polymeric sulfur complicates interpretation of the results.

The molar concentration of free radicals was calculated theoretically by Tobolsky and Eisenberg^[69] and the result was in excellent agreement with esr measurements made over the whole liquid range. At 140°C, it was calculated that the concentration of sulfur radicals was about 10^{-11} M. In studies conducted at 120°C, only a very small radical population was present. These radicals are very reactive and quickly consume more S_8 to form polymeric sulfur (S_x) (Scheme 49). At a temperature below 150°C, bond homolysis is quite slow such that relatively little polymeric sulfur is formed. Liquid sulfur usually contains 2-5 weight % of polymeric sulfur at 140°C^[107].

Polymeric sulfur can be removed temporarily through a “degassing” process^[107] if the liquid contains traces of H_2S . The degassing process is normally catalyzed by the addition of a base, such as ammonia, urea or amines. In the presence of H_2S , some of the S_x may be capped by H_2S to form H_2S_x . The basic catalysts speed up the decomposition of H_2S_x through an acid-base reaction mechanism. In this process, H_2S is released which can be purged from liquid sulfur by a sparge gas or by efficient agitation of the sulfur. The mechanism of removal of polymeric sulfur through the ‘degassing’ process is shown in Scheme 50.

Scheme 50. Removal of Polymeric Sulfur by Degassing Process

The following is a typical procedure for degassing sulfur. Sulfur was melted and the stirred liquid was heated to 170°C to generate polymeric sulfur diradicals. H₂S was then bubbled through the liquid to cap the sulfur diradicals with hydrogen and form H₂S_x. An amine base (morpholine) was added at this point to decompose H₂S_x, followed by N₂ purging to eliminate H₂S and morpholine. The disappearance of H₂S, H₂S_x and morpholine could be monitored by FT-IR due to their distinct absorptions at 2571 cm⁻¹, 2479 cm⁻¹ and 2900-3000 cm⁻¹. It was found that the moment when all three were eliminated, the amount of polymeric sulfur was 0% (see Section 4.2.1 for comments of polymeric sulfur content determination). However, it was also found that polymeric sulfur re-established to its normal level after the morpholine was removed. The rate of re-establishment of polymeric sulfur is illustrated in Scheme 51. It reached almost 5% in less than 1 h after morpholine was removed from the system and remained at about 5% as long as the temperature was kept at 140°C.

Scheme 51. Re-establishment of Polymeric Sulfur at 140°C

4.2 Reaction of 1,4-benzenedithiol with sulfur

The formation of a linear polysulfide in molten elemental sulfur was initiated by the sulfur diradicals. Suggested initiation, propagation and termination reactions are shown in Scheme 52. The sulfur diradicals extract hydrogen radicals from the thiol, giving thio-radicals, which can attack S_8 , breaking the S_8 ring and incorporating the elemental sulfur as polythio radicals. The two polythio radicals can then couple giving a linear polysulfide polymer. The polymerization process may then be terminated by the polythio radicals extracting the hydrogen from the starting dithiol or the products H_2S_x/H_2S . It is believed that the long chain polysulfides are not stable and that they break down to shorter sulfur linkages (disproportionation). The other product found (FT-IR) in this reaction was H_2S_x which eventually decomposed to form H_2S and S_8 .

Unfortunately, a quantitative determination of H_2S and H_2S_x by FT-IR measurements as discussed in Chapter 1.2.2 was not possible due to the fact that the S-H stretching band of the thiols in molten sulfur overlapped with those of the S-H of H_2S .

Therefore, the exact concentration of H_2S could not be determined accurately and, hence, could not be used as a method for determining the rate of reaction of aromatic thiols with sulfur.

4.2.1 Polymeric Content Measurement

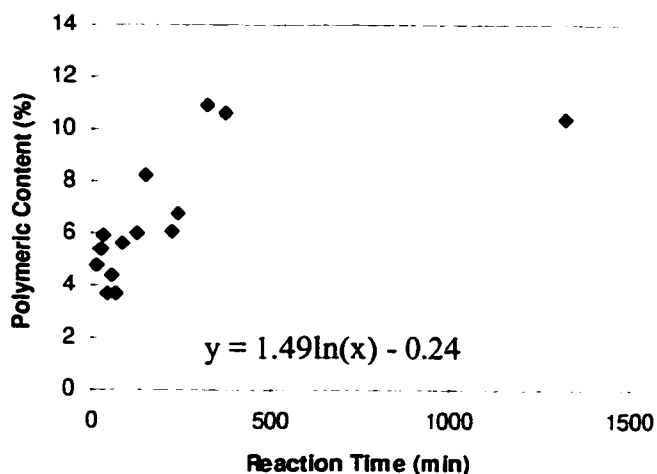
In this experiment, 1,4-benzenedithiol (0.1 g) was added to degassed sulfur (200 g) at the moment when no H_2S , H_2S_x or morpholine could be detected by FT-IR. These quantities were chosen to allow detection and analysis of the polymer as well as simulate condition that might be applied in commercial application. The reaction mixture was maintained at $140 \pm 1^\circ\text{C}$ with stirring. Samples were taken at regular intervals after the reaction started and were quenched in dry ice to freeze the equilibrium established in liquid sulfur. After the samples had warmed up to room temperature, they were ground to 10 mesh and were weighed (~ 2 g) in a pre-weighed medium porous crucible (W_0 : weight of the crucible, W_1 : weight of the crucible + weight of the sample). They were then washed by CS_2 (~ 75 mL) with the aid of suction to dissolve and thus remove all soluble sulfur. The weight of the residue was measured (W_2) and the polymeric content (p.c.) was calculated [$\text{p.c.} = (W_2/W_1 - W_0) \times 100\%$]. Due to the re-establishment of polymeric sulfur during the experiment (in addition to polymer formation), the insoluble pale yellow solid recovered after the extraction was a mixture of aromatic polysulfides and polymeric sulfur (S_x).

The re-establishment of polymeric sulfur during these experiments makes the data interpretation more difficult. Due to the structural similarity between the polymeric sulfur and polysulfide polymer, it is impossible to separate them from one another. Therefore, the exact polymeric content resulting from the formation of polysulfides cannot be ascertained accurately. In the study of the reaction of 1,3,5-benzenetrithiol with elemental sulfur, experiments using degassed and non-degassed sulfur were both carried out. No noticeable difference was found in terms of the reaction rates as well as the final

polymeric contents in spite of the fact that the initial polymeric content was ~0% when degassed sulfur was used. It was therefore assumed that the polymeric sulfur was reformed in the normal fashion in these systems and reached its normal level as the reactions proceeded. Therefore, removal of the polymeric sulfur prior to carrying out an experiment may make little difference to the final results.

The results summarized in Scheme 53 show that the polymeric content increased rapidly at the beginning of the reaction and then leveled-off after about 2 h. When the reaction was finished, the polymeric content was about 11%. Based on the assumption that the amount of polymeric sulfur was ~ 5% in this system as in pure liquid sulfur, the average length of the polysulfides linkage can be estimated. Taking into consideration the polymeric sulfur present in the reaction mixture, polysulfide polymer consisted of about 6% (weight) of the total sulfur. The initial concentration of 1,4-benzenedithiol added into the liquid sulfur is 0.05% (weight). The difference (5.95%) was attributed to elemental sulfur incorporated into the polysulfide chains. Hence, the average length of the polysulfide chains was estimated to be ~500. The molecular weight of the polysulfides could not be determined due to the difficulties of separating the linear polysulfides from polymeric sulfur. In addition, due to the extreme mobility of the equilibrium, attempts to isolate the aromatic polymer would disturb the reaction and the product would not have the 'real' identity of the polysulfides under the reaction conditions. [Note: attempts to synthesize and isolate the polymer are described in a later section.]

Scheme 53. Polymeric Content in Liquid Sulfur (200 g) after Reaction with 1,4-Benzenedithiol (0.1 g, 0.70 mmol) at 140°C



The major problem associated with the total polymeric content measurement is that it is relatively insensitive and does not necessarily give the actual polymeric content under the reaction conditions because it is not an 'in situ' measurement. The determination involves sample quenching, warming and CS₂ extraction. In all of these steps, the equilibrium may be disturbed to some extent. Upon quenching in dry ice, the exposed sulfur can be frozen quickly to dry ice temperature thus retaining its equilibrium. However, the poor heat conductivity of sulfur prevents the inner layers of sulfur from being frozen as quickly as the exposed sulfur and hence, the equilibrium might be shifted. In addition, all the sulfur samples were warmed up to room temperature for the CS₂ extraction. This warming process may also result in some adjustment of the equilibrium. However, efforts were made to carry out sample analysis for all experiments using the exact same procedure and keeping the amount of time the same in each step during the sample preparations. However, it is concluded that these results can be treated only

qualitatively as to how the reaction proceeds. Overall, the rapid rise in polymer content at the beginning of the reaction indicated that the reaction proceeded quickly.

The formation of polymeric polysulfides in liquid sulfur affects its physical properties such as viscosity and freezing point. These factors are of prime importance with regards to production of sour gas and the transportation of liquid sulfur and are discussed in the following sections.

4.2.2 Viscosity Measurement

In the viscosity measurements, all the results are expressed as ‘reduced viscosity’, which is defined to be^[108]:

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{C}$$

$$\eta_{\text{sp}} = \frac{\eta}{\eta_0} - 1$$

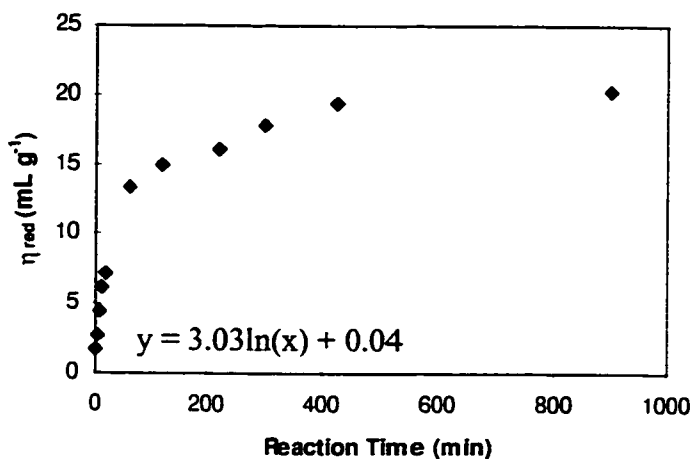
C: concentration of the solute (g/mL)

η_{sp} : specific increase in viscosity

η_0 : viscosity of the pure solvent

The advantages of using reduced viscosity is that it eliminates the solvent viscosity and only shows the viscosity change caused by the formation of polysulfides. It also takes into consideration the amount of solute added to the solvent. Thus, the use of reduced viscosity allows a direct comparison of the data obtained from different reactions.

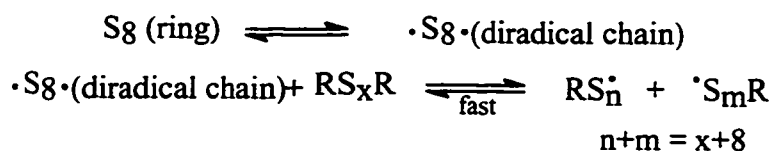
Scheme 54. Reduced Viscosity of Sulfur (4.1 g) after Reaction with 1,4-Benzenedithiol (0.1 g, 0.70 mmol) at 120°C



The measurements were carried out using a Brookfield Digital Viscometer. The temperature of the sampling cup was maintained at 120°C by flowing a thermostatted liquid through the inside of the device. Sulfur was introduced as a solid to the sampling cup and was melted. The viscosity of this “blank” sulfur was then taken before addition of the thiol. Measurements were carried out regularly as the reaction proceeded. The results showed that the viscosity of sulfur increased rapidly in the first 1.5 h and reached a plateau after about 8 h. These observations may be interpreted in terms of rapid formation of aromatic polysulfides resulting in a rapid increase of the viscosity over the first 1.5 h of the reaction. After 1.5 h, the increase in viscosity started to slow down once the rate of S-S bonds breaking became comparable to that of S-S bonds forming. According to the viscosity measurement (Scheme 54), the system reached equilibrium after about 8 h.

4.2.3 Depression of Freezing Point

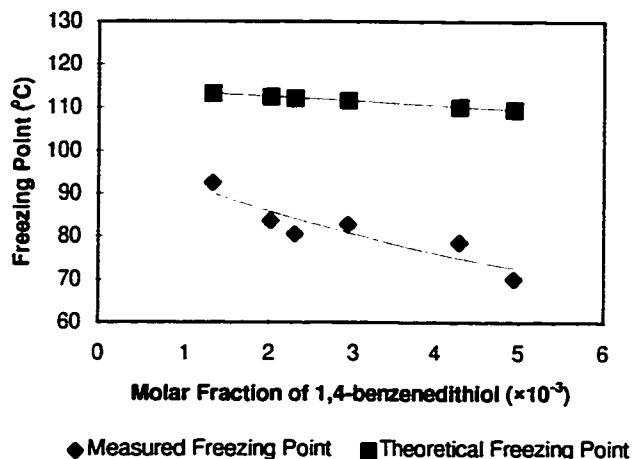
One of the goals of this study is to examine methods to prevent the deposition of solid sulfur in sour gas wells by lowering its freezing point. The addition of benzenepolythiols to elemental sulfur can achieve this goal by two means: (1) the formation of polysulfides in pre-deposited sulfur thus lowering its freezing point and, (2), by forming polymeric polysulfides which could prevent crystallization of sulfur by a kinetic effect, i.e., promote supercooling of liquid sulfur. Supercooling in the presence of polysulfide polymers may be explained by assuming that the elemental sulfur interchanges with the polysulfide linkages. The process must be a dynamic one, because at any given moment the elemental sulfur is completely extractable. However, the dynamic interchange may promote the supercooling of the elemental sulfur. The following scheme, which shows the regeneration of elemental sulfur by reversible reactions, is proposed^[69]:



Experiments were carried out by mixing known amounts of sulfur and thiol with different thiol concentrations in the range of 1×10^{-3} to 5×10^{-3} molar fraction. The mixtures were left in the oven at 140°C for 18 h to ensure the completion of the reactions. Since sulfur can be supercooled easily, agitation would help to prevent the supercooling. Therefore, all the measurements were carried out with stirring in order to eliminate supercooling, unless specified otherwise. The theoretical freezing point can be calculated

according to the amount of thiol added (eq. 23). The experimental results (◆) are presented in Scheme 55 together with the theoretical calculations (■).

Scheme 55. Freezing Point of Sulfur after Reaction with 1,4-benzenedithiol



The addition of 1,4-benzenedithiol substantially lowered the freezing points of sulfur with the depression increasing at higher concentrations. The bigger gap between the calculated and the measured freezing points at higher concentrations might be due to an enhancement of the supercooling effect. The sulfur rank of the polysulfides would probably remain similar in all experiments as sulfur was always in great excess. As will be discussed later in the case of reaction with 1,3,5-benzenetrithiol, the freezing points were further lowered in the absence of agitation, presumably a consequence of supercooling.

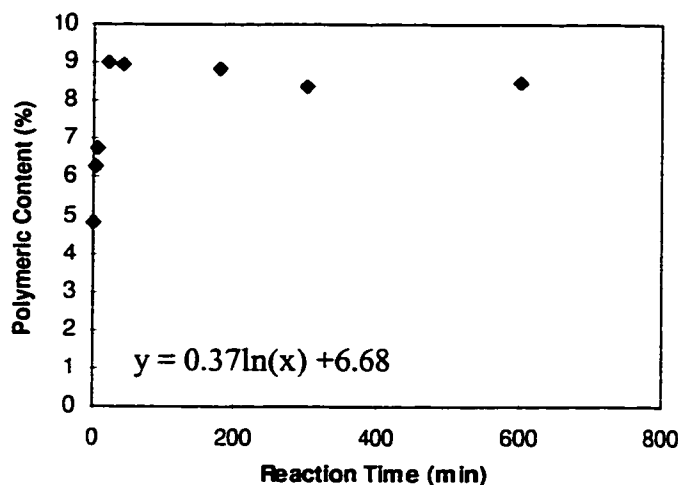
4.3 Reaction with 2,5-Dimethyl-1,4-benzenedithiol

The precursor of 2,5-dimethyl-1,4-benzenedithiol, 1,4-dimethyl-2,5-bis(methylthio)benzene, was synthesized by methylthiolation of *p*-xylene using montmorillonite clay catalysts (Chapter 3). The method is simple and can produce 2,5-dimethyl-1,4-benzenedithiol in large quantity at low cost. Therefore, its reaction with elemental sulfur was studied in order to evaluate its usefulness in terms of preventing sulfur deposition in sour gas wells.

4.3.1 Polymeric Content Measurement

The experiments were carried out using the same procedure as was employed in the reactions of 1,4-benzenedithiol with sulfur. The result is shown in Scheme 56. The rise in the polymeric content was similar to that obtained from the reaction of 1,4-benzenedithiol. In this experiment, the sulfur was not degassed prior to use. The initial polymeric content of 4.8% rose quickly to about 9% in the first hour after addition of the dithiol. In contrast, the viscosity of the reaction mixture continued to increase for 8 h after the reaction began (Scheme 57). This continued rise in viscosity is likely due to gradual loss of H_2S from the reaction mixture since $\text{H}_2\text{S}/\text{H}_2\text{S}_x$ is known to lower the viscosity of liquid sulfur^[109]. A maximum polymeric content of ~9% was observed for this reaction. This equates to about 450 sulfur atoms sandwiched between the two aromatic groups, a result consistent with that obtained from the reaction of 1,4-benzenedithiol.

Scheme 56. Polymeric Content of Liquid Sulfur (200 g) after Reaction with 2,5-Dimethyl-1,4-benzenedithiol (0.1 g, 0.59 mmol) at 140°C

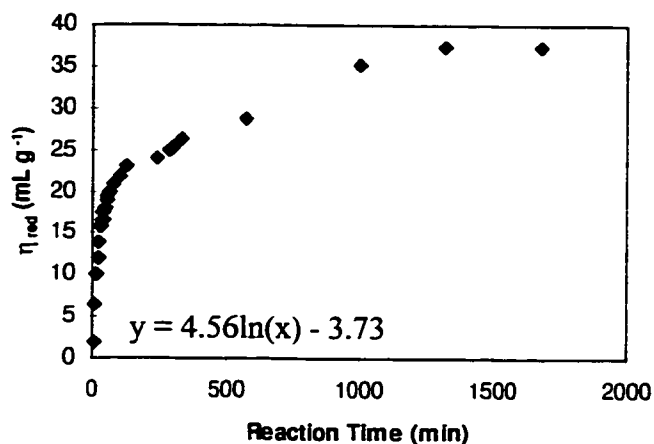


4.3.2 Viscosity Measurement

As was discussed previously, the measured viscosity, taken at various times, was converted to reduced viscosity (Scheme 57). These results demonstrated that the viscosity increase was similar to that obtained in the reaction of 1,4-benzenedithiol. The rapid increase which occurred in the first 2 h of the reaction was likely due to polymer formation and the very slow increase after about 8 h of the reaction could be due to the release of H₂S from the reaction mixture. Overall, viscosity behaviour of sulfur reacted with either 1,4-benzenedithiol or its dimethyl derivative was similar. However, the maximum reduced viscosities of the two liquid sulfur products were different with the maximum reduced viscosity for 2,5-dimethyl-1,4-benzenedithiol (~37 mL g⁻¹) being greater than that of 1,4-benzenedithiol (~20 mL g⁻¹). This difference might be due to either or both of the following aspects: (1) the methyl groups on the benzene rings make the polysulfides more rigid and less flexible, restricting the flow of S₈ and increasing the viscosity and/or (2) the polysulfides with methyl groups on the aromatic rings have higher

molecular weight or longer polysulfide chains. Note, however, that experimental data suggested that the polymers were of similar size in each case.

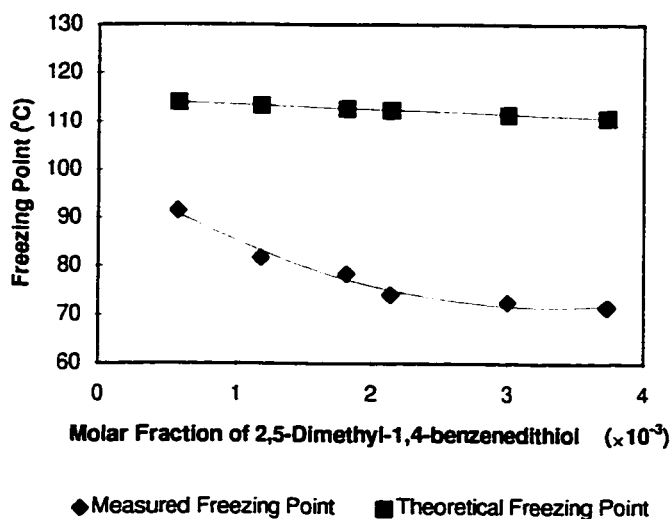
Scheme 57. Reduced Viscosity of Sulfur (4.0 g) after Reaction with 2,5-Dimethyl-1,4-benzenedithiol (0.12 g, 0.71 mmol) at 120°C



4.3.3 Freezing Point Depression

Both viscosity and polymeric content measurements suggested that 2,5-dimethyl-1,4-benzenedithiol reacted with sulfur reasonably quickly and formed long chain polysulfides. Whether this compound is suitable for industrial use depends on the effectiveness of the polysulfides in terms of lowering the freezing point of sulfur. Freezing point depression measurements (Scheme 58) show a similar magnitude of freezing point depression in comparison to that obtained with 1,4-benzenedithiol. As observed before, the gap between the calculated freezing points (■) and the measured freezing points (◆) was larger at higher concentrations. Overall, at a molar concentration of 3.74×10^{-3} , a depression of close to 50°C was observed. This is very significant from an industrial view point.

Scheme 58. Freezing Point of Sulfur after Reaction with 2,5-Dimethyl-1,4-benzenedithiol



4.4 Summary

Polymeric content measurements suggested that both types of polymers consisted of long chain polysulfide linkages in the range of 400-500. It was the formation of these long chain polymeric polysulfides that caused the freezing point depression of sulfur. The freezing point depression measured from the reaction of 2,5-dimethyl-1,4-benzenedithiol with sulfur was very similar to that from the reaction of 1,4-benzenedithiol, most likely, due to the structural similarities between the two types of polymers. The presence of the methyl groups in the case of 2,5-dimethyl-1,4-benzenedithiol increased the viscosity of the reaction mixture but had no effect on the freezing point or the reaction rates.

CHAPTER FIVE

FORMATION OF NETWORK AROMATIC POLYSULFIDES FROM REACTION OF BENZENETRITHIOLS WITH ELEMENTAL SULFUR

The reactions of benzenedithiols with sulfur give linear polysulfides. As discussed in the previous Chapter, their presence in liquid sulfur significantly lowers its freezing point. Logically, the use of trithiols should give the similar reactions, except, in this case, network polysulfides will be formed. Since network polysulfides may further enhance the “supercooling” effect, it was of interest to determine both the rate of reaction of trithiols with sulfur and the effect of the products on sulfur properties. Reactions of two trithiols will be discussed in this Chapter: 1,3,5-benzenetrithiol and 2,4,6-trimethylbenzenetrithiol. The first compound was synthesized by the reaction of 1,3,5-trichlorobenzene with sodium *iso*-propyl thiolate in HMPA followed by the addition of sodium and acidification with dilute HCl^[24,25]. This method involves the use of HMPA as solvent which is difficult to work with due to the reasons stated in Chapter 2. The newly developed method for C-S bond formation reported in Chapter 3 makes the tri-methyl derivative readily accessible.

5.1 Reaction of 1,3,5-benzenetrithiol with sulfur

The mechanism of the formation of network polysulfide polymers in molten sulfur is presumed to be the same as described for the formation of linear polysulfides (Scheme 52). In the case of trithio-functionalized aromatics, cross-linked network polysulfides are likely to be formed.

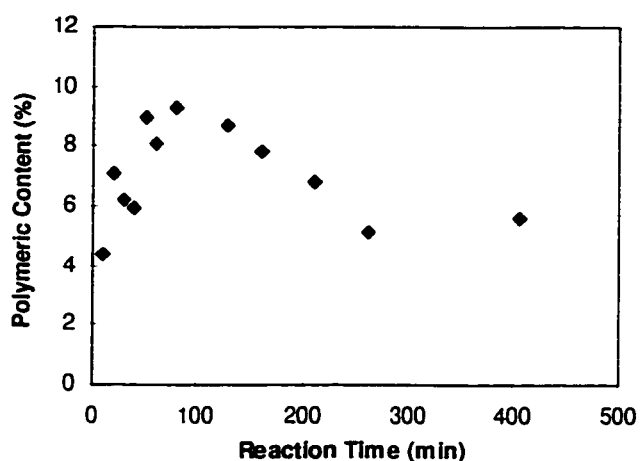
5.1.1 Polymeric Content Measurements after Reaction with 1,3,5-Benzenetrithiol

As was discussed previously, the polymeric content experiments were considered as qualitative measurements as to how the reactions proceeded. The qualitative aspect of these experiments is due to the complication introduced by the presence of polymeric sulfur in molten sulfur as well as the extreme mobility of the reaction equilibrium. The effects caused by the presence of polymeric sulfur were also studied in this case by carrying out two experiments, one using 'degassed' sulfur and the other using 'untreated' sulfur in which the 'degassing' process was not applied. The purpose was to compare the data obtained from both experiments and determine whether the 'degassing' process (i.e. removal of polymeric sulfur) had any effect on the rates of the reactions and on the total polymeric contents after the completion of the reactions.

The result of the experiment in which the 'untreated' sulfur was used is illustrated in Scheme 59. The initial polymeric content was 4%. Upon the addition of 1,3,5-benzenetrithiol, the amount of polymer in the liquid sulfur increased rapidly and reached 9 % after about 1 h. A gradual decrease in polymeric content was observed after the maximum had been reached. These results can be explained by disproportion of large polysulfides formed from polymeric sulfur to smaller species. However, analytical

procedures may be also be important since the solubility of large and small aromatic polysulfides in CS₂ may be different. Interestingly, the same decrease in polymeric content was not observed in the reactions of dithiols with elemental sulfur, possibly because the formation and decomposition of linear polysulfides was much slower in comparison to network polysulfide reactions. The decomposition of the network polysulfides was also observed in the viscosity measurements. (see p. 106)

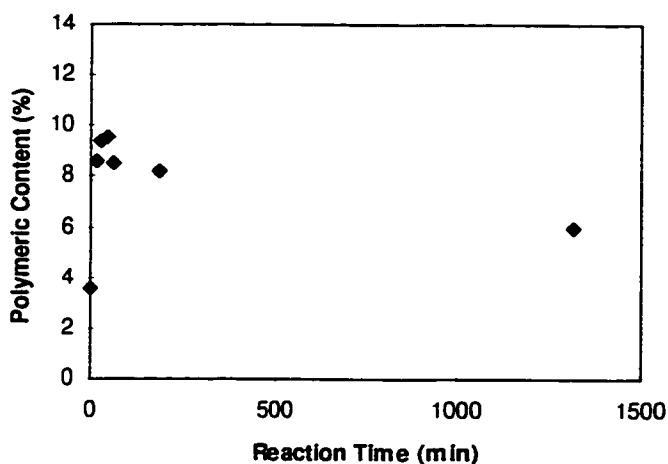
Scheme 59. Polymeric Content in Liquid Sulfur (un-degassed, 200 g) after Reaction with 1,3,5-Benzenetrithiol (0.1 g, 0.575 mmol) at 140°C



Very similar polymeric content values were measured in the experiment in which 'degassed' sulfur was used; the data are illustrated in Scheme 60. The highest polymeric content, 9.4 %, was reached 0.5 h after the reaction had started. After this, a slow decrease of the polymeric content was also observed to about 6 % after 24 h. Thus, overall, it is concluded that the initial network polysulfides formed from the reaction of 1,3,5-benzenetrithiol with sulfur are not stable under the reaction conditions (140°C in molten sulfur) and disproportionate to smaller species. There was no significant difference between the two experiments in which 'degassed' and 'un-degassed' sulfur were used. In both cases, a maximum polymeric content of about 9% was observed

followed by a slow decrease due to the instability of the network polysulfides. The polymeric content dropped to about 5.5-6% after about 20 hours of the reaction regardless of the type of sulfur used in the experiment.

Scheme 60. Polymeric Content in Liquid Sulfur (initially degassed, 200 g) after Reaction with 1,3,5-Benzenetrithiol (0.1 g, 0.575 mmol) at 140°C

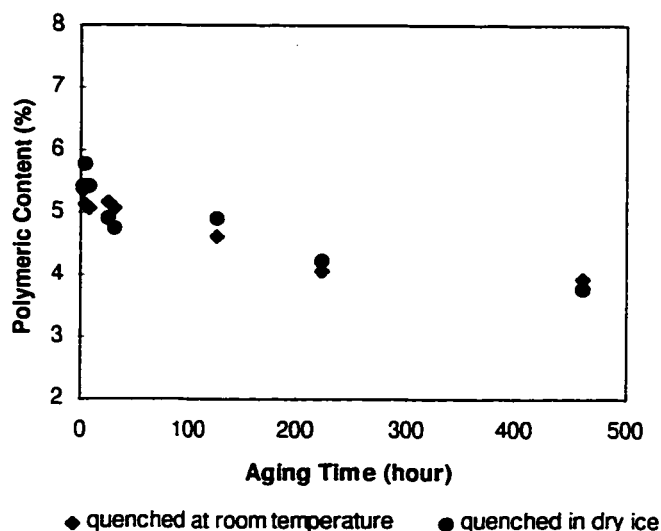


5.1.1.1 Polymeric Content of Aged Solid Samples

Another important aspect of this research was to study the stability of network polysulfides in solid sulfur since it is known that polymeric content, in general, has a significant effect on the properties of the solid^[110]. This aspect of polysulfide content was studied by measuring the polymeric quantity in quenched samples over a period of time as the samples aged at either room temperature or dry ice temperature.

1,3,5-Benzenetrithiol was added to liquid sulfur and the mixture was stirred at 140°C for 18 hours. One portion was allowed to solidify slowly at room temperature and the other portion was quenched at dry ice temperature. The two samples were kept at their respective quench temperatures and were subjected to polymeric content analysis at various time intervals. Scheme 61 illustrates the decomposition of the network polysulfides aged at room temperature and dry ice temperature.

Scheme 61. Decomposition of Polysulfides in Solid Sulfur after the Reaction of 1,3,5-Benzenetrithiol with Sulfur over 18 h at 140°C

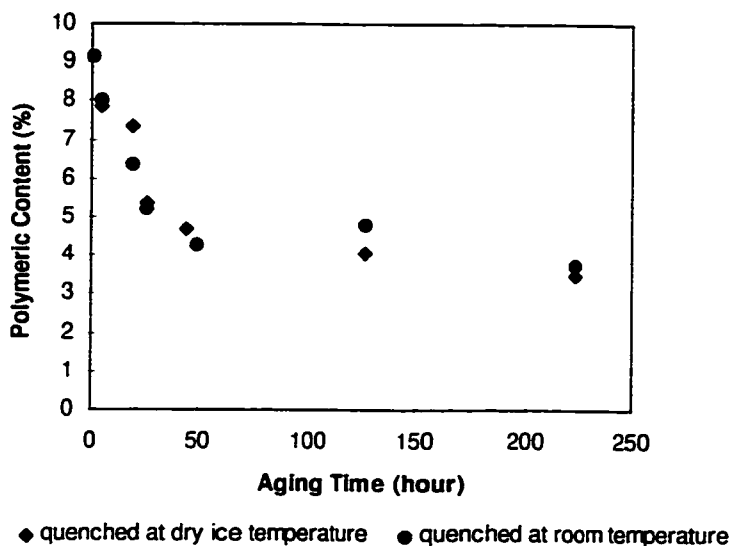


After the reaction mixture was quenched, the polymeric content was about 5.5%. A decrease in the polymeric content over a period of 18 days indicates that network polysulfides are not stable in the solid state and tend to lose sulfur (Scheme 61). Surprisingly, the decomposition rates of the network polysulfides at the two temperatures were almost identical indicating that polysulfides are unstable at both room and dry ice temperatures. The samples were allowed to stand for 18 days before the final measurements were taken. It was found that at this point, the polymeric content of both samples dropped to about 3.8%, a value similar to that found immediately after quenching of sulfur held at 140°C containing no aromatic thiols. In general, these observations show that network polysulfides are not stable in solid sulfur but undergo gradual decomposition to sulfur. However, as discussed previously, small network polysulfides may have some solubility in CS₂ and hence, may have been removed by the extraction process.

The stability of the larger polysulfides formed immediately after reaction with 1,3,5-benzenetrithiol was also investigated. The purpose was to determine how long large network polysulfides survive within solid sulfur. The reaction mixture was quenched 1.5 h after the reaction was started. Again, the reaction mixture was divided into two portions, one being quenched at room temperature and the other in dry ice. The polymeric content measurements obtained at both temperatures are shown in Scheme 62.

In the solid state, both at dry ice and at room temperature, the polysulfides were extremely unstable in the first stage of the aging, as a drop of the polymeric contents from over 9% to about 4.5% were obtained in 48 hours in both cases. A much slower decrease was observed in the second stage. At the end of 10 days, the polymeric content was found to be about 3.5%. By comparing Scheme 59 and 60 to Scheme 62, it seems that the decomposition rate of network polysulfides was faster in molten sulfur than in the solid state. Data shown in Scheme 59 show that it took less than 3 h for the polymeric content to drop from 9% to 6%, while in solid sulfur, it took almost 24 h. This is expected since the homolytic scission of S-S bond is much slower at room temperature and dry ice temperature than at 140°C. The decomposition rates of the polysulfides were about the same at the two different temperatures studied in the solid state (Schemes 61 and 62). The reason for this may be that it is not the rate of S-S bond breaking which controls polymer decomposition in the solid state, but the “conformational mobility” within the crystal lattice.

Scheme 62. Decomposition of Polysulfides from the Reaction of 1,3,5-Benzenetrithiol with Sulfur after Quenching at 1.5 h



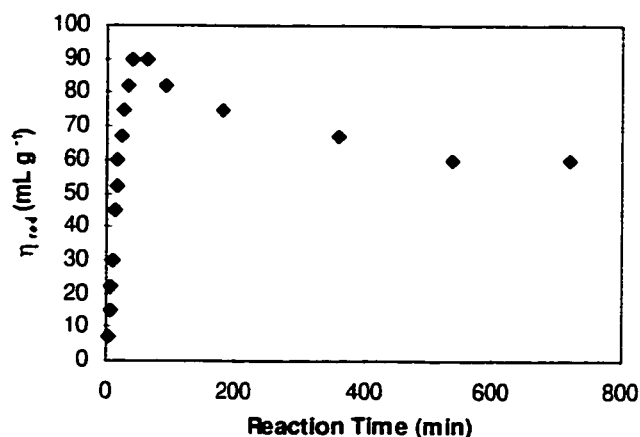
The formation of network polysulfides had a tremendous impact on the physical properties (viscosity and freezing point) of liquid sulfur. These issues are discussed in the following sections.

5.1.2 Viscosity Measurements

1,3,5-Benzenetrithiol (0.01 g, 0.0575 mmol) was added directly to liquid sulfur (4.0 g) in the viscosity measuring cup heated at 140°C with measurements being taken at regular intervals. These data (Scheme 63) show that the reduced viscosity rose quickly to 89.6 mL g⁻¹ in 1 h and then decreased slowly over the following 8 h before stabilizing at 74.7 mL g⁻¹. This behavior is somewhat different to that observed from the reactions of dithiols with sulfur where the viscosity increased and maintained a constant value (Scheme 54 and 57). The increase and gradual decrease in viscosity with trithiol is consistent with the result obtained from the polymeric content measurement which also

showed a decrease after about 1 h of the reaction. As suggested earlier (p. 105), these observations may be explained by large network polysulfides disproportionating to smaller species.

Scheme 63. Reduced Viscosity of Sulfur (4.0 g) after Reaction with 1,3,5-Benzenetrithiol (0.01 g, 0.0575 mmol) at 140°C



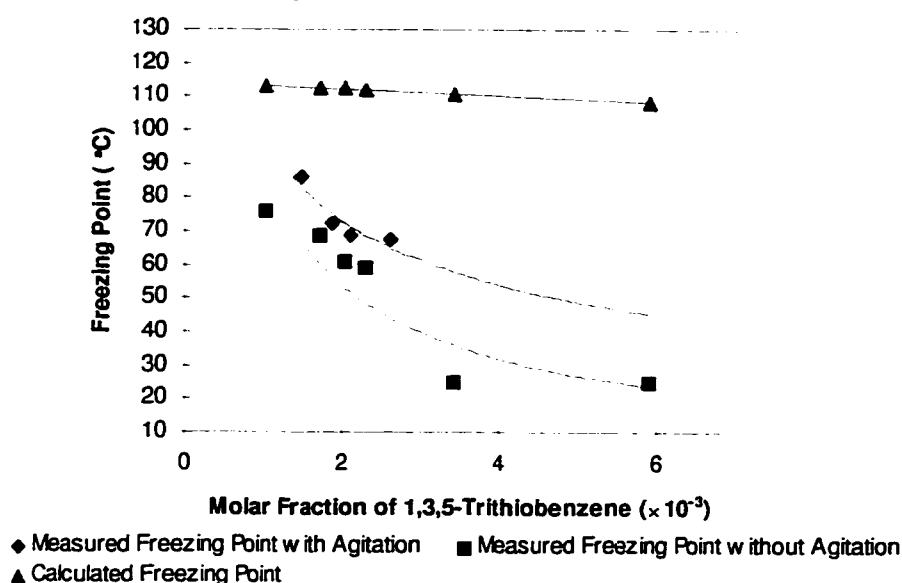
On comparing the reaction rates of dithiols and trithiols with liquid sulfur, it was clear that the reaction of trithiol was much faster than that of the dithiols. The maximum viscosity was reached within 1.5 h after addition of the thiol compared to 10 h in the case of 2,5-dimethyl-1,4-benzenedithiol. The final stabilized viscosity of 74.7 mL g⁻¹ measured after reaction with the trithiol was much higher than the final viscosity obtained from the reaction of 1,4-benzenedithiol with sulfur (~20 mL g⁻¹). This higher value, most likely, reflects the formation of the network polysulfides which more effectively restrict the flow of S₈ molecules in the liquid state.

5.1.3 Depression of Freezing Point

Another physical property of liquid sulfur which was affected by the formation of network polysulfides was the freezing point. This parameter is of considerable

importance to this research as a lowering of sulfur freezing point should facilitate gas production from the sour gas reservoirs. A series of samples, with different concentrations of thiol, was prepared for the freezing point measurements. These samples were kept at 140°C for 48 h. This reaction time was used in these experiments to allow equilibration of the network polysulfides as observed in the viscosity and polymeric content measurements. The measurements were carried out with and without agitation in order to eliminate, as much as possible, the effect of supercooling.

Scheme 64. Freezing Point of Sulfur with 1,3,5-Benzenetrithiol



Overall, a significant depression of the freezing point was obtained both with and without agitation (Scheme 64). When a trithiol molar fraction of about 2×10^{-3} was used, a freezing point depression of $>50^\circ\text{C}$ was obtained. However, at a concentration higher than 3×10^{-3} (molar fraction), the reaction mixture became so viscous that it was difficult to maintain continuous stirring and reliable determinations were difficult to obtain. Experiments conducted at concentrations of 3.39×10^{-3} and 5.9×10^{-3} (molar fraction) resulted in dark brown viscous liquids which solidified slowly at room temperature. As

can be seen from Scheme 64, agitation did limit the freezing point depression indicating that supercooling was a factor in these measurements. This super-cooling phenomenon is probably a kinetic effect which is caused by the dynamic interchanges between elemental sulfur and the polysulfides (see Chapter 4.2.3 for further comments).

The other conclusion that can be deduced from these experiments is that freezing point depression was greater in the case of network polysulfides than for the linear polysulfides. In experiments with agitation, the difference between the calculated and the measured freezing points in the case of network polysulfides was 45°C at a trithiol molar fraction of 2.62×10^{-3} . For the same concentration of 1,4-benzenedithiol, a difference of about 35°C was obtained. This larger depression of the freezing point is probably caused by the network polysulfides which increase the viscosity of the reaction mixture beyond that possible with linear species thus slowing down the crystallization of S₈ molecules. In summary, the network polysulfides are more effective species in terms of preventing or delaying solidification of sulfur.

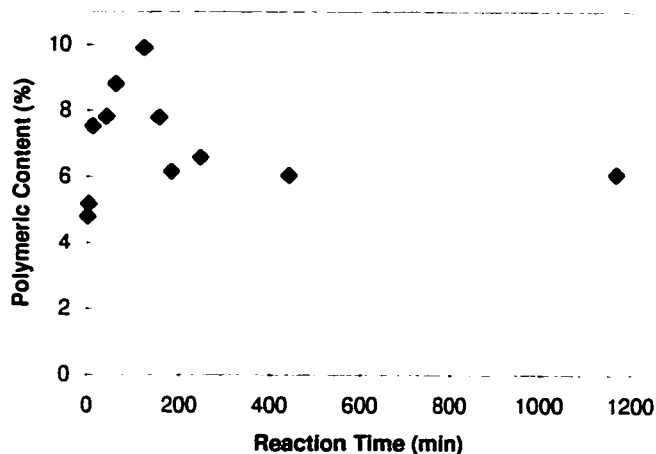
5.2 Reaction with 2,4,6-Trimethylbenzenetrithiol

2,4,6-Trimethylbenzenetrithiol is much easier to obtain than 1,3,5-benzenetrithiol. Its synthesis involves the direct C-S bond formation catalyzed by modified montmorillonite clay as reported in Chapter 3 and is expected to react with elemental sulfur in the same fashion as did 1,3,5-benzenetrithiol. Consequently, its reaction with elemental sulfur and the physical properties of the sulfur after the reaction were studied.

5.2.1 Polymeric Content Measurements

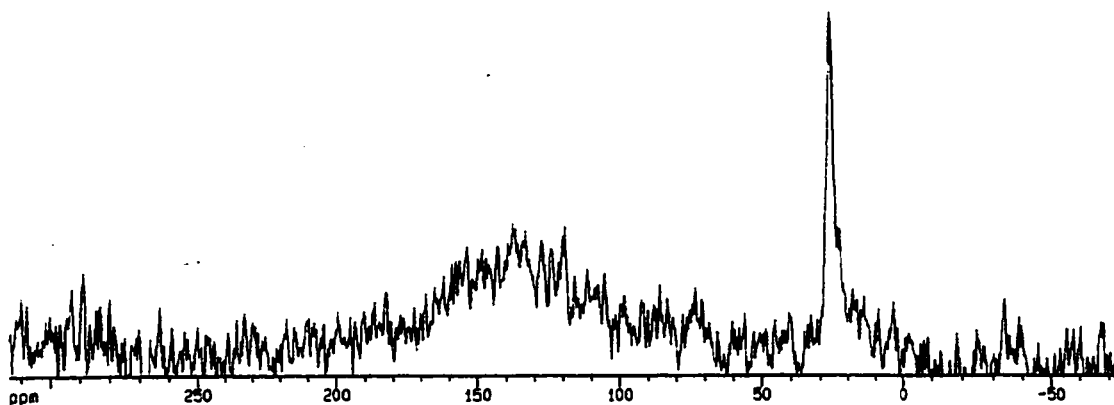
Because the use of 'degassed' and 'un-degassed' sulfur had little impact on either reaction rate or polymeric content, for the reaction of 1,3,5-benzenetrithiol with sulfur, un-degassed' sulfur was used. Polymeric content data (Scheme 65) show very similar results to those obtained from the reaction of 1,3,5-benzenetrithiol with sulfur. The rapid rise of the polymeric content at the beginning of the reaction indicated that the formation of network polysulfides was very fast. A decrease in polymeric content after 150 min was observed again indicating that equilibration of large network polysulfides to smaller species was occurring. However, as suggested previously, this decrease could also be due to loss of H_2S from solution. Regardless of the actual reason for the decrease, both trithiols resulted in a maximum polymeric content after about 1.5 - 2 h of the reaction followed by a gradual decrease over 2-10 h. Reactions of both trithiols was much faster than the reactions between dithiols and sulfur. In the case of dithiols, the maximum polymeric contents in the reaction mixture were reached 8 - 10 h after the reactions started.

Scheme 65. Polymeric Content in Liquid Sulfur (200 g) after Reaction with 2,4,6-Trimethylbenzenetrithiol (0.1 g, 0.463 mmol) at 140°C



The solid ^{13}C NMR spectrum of the network polysulfides isolated from the polymeric content measurement was recorded and is shown in Scheme 66. The aromatic carbons can be found at $\delta 100\text{--}170$ ppm as a very broad peak. This peak likely represents both the tertiary and the quaternary carbons due to its broad nature. The methyl group can be found at $\delta 26.70$ ppm as a quite sharp peak.

**Scheme 66. Solid ^{13}C NMR Spectrum of Network Polysulfides
Recovered from CS_2 Extraction**

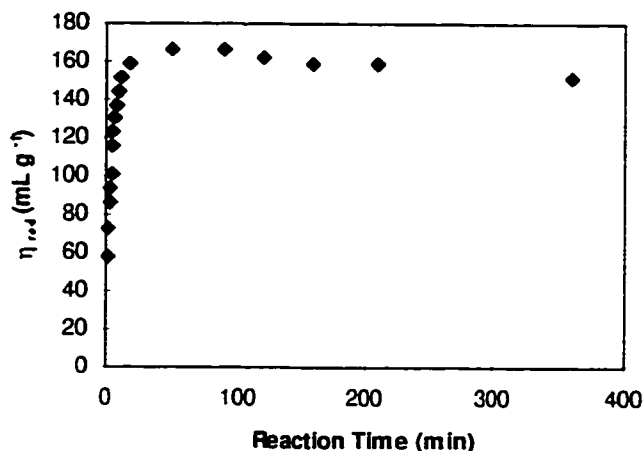


5.2.2 Viscosity measurement

The viscosity of liquid sulfur (4.0 g) after reaction with 2,4,6-trimethylbenzenetrithiol (0.01 g, 0.046 mmol) at 140°C was measured following the same procedure as described in the previous section. The results are shown in Scheme 67.

Viscosity measurements from the reaction of 2,4,6-trimethylbenzenetrithiol with sulfur were quite different from those obtained from the reaction of 1,3,5-benzenetrithiol. The most obvious difference was that the rapid drop of the viscosity observed in the reaction of 1,3,5-benzenetrithiol with sulfur was not observed. However, the maximum viscosity, 166.2 mL g⁻¹ reached after 90 min of reaction, was the same as in the reaction of 1,3,5-benzenetrithiol (Scheme 63). Therefore, it can be concluded that the two trithiols reacted with elemental sulfur at about the same rate. The reduced viscosity obtained from reaction with the trimethyl derivative dropped only slightly to 159.0 mL g⁻¹.

Scheme 67. Reduced Viscosity of Sulfur (4.0 g) after Reaction with 2,4,6-Trimethylbenzenetrithiol (0.01 g, 0.046 mmol) at 140°C



It is interesting that the reduced viscosity measured from the reaction of 2,4,6-trimethylbenzenetrithiol with sulfur was much higher than that obtained from the reaction with 1,3,5-benzenetrithiol (159 mL g⁻¹ and 75 mL g⁻¹ respectively). Besides steric effects resulting from the methyl substituents, it is probable that larger polysulfides were present in case of the trimethyl derivative, possible as a result of stabilization by the methyl groups.

There is some discrepancy between the polymeric content measurements and viscosity measurements for reactions with the trimethyl-derivative. In the polymeric content measurements, a decrease was observed 2 h after the maximum value had been reached. However, the viscosity measurements showed only a slight drop after the maximum viscosity was reached. This inconsistency may be explained by two factors. One is the nature of the polymeric content analysis where some errors might be introduced as explained in the previous section (p. 91). The other reason might be because of the size of the polysulfides. The network polysulfides are likely to be highly cross-linked. As the long polysulfide chains decompose to more stable, shorter

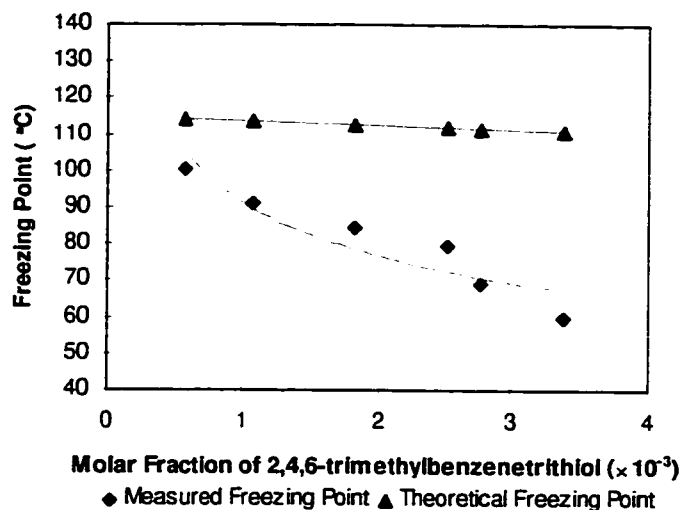
polysulfide species, some of them might become small enough to be extracted by CS₂ during the polymeric content analysis. However, their presence in the reaction mixture would still contribute to its viscosity. Therefore, only a small viscosity decrease was observed.

5.2.3 Freezing Point Depression

The freezing points of the mixtures obtained after reaction of 2,4,6-trimethylbenzenetrithiol with sulfur at 140°C for 24 h were measured. These results are shown in Scheme 68 along with the calculated freezing points.

Despite the observed decomposition of the network polysulfides, a significant freezing point depression was observed. The measurements were all carried out with agitation in order to eliminate, as much as possible, the effect caused by supercooling, as discussed in the previous section. Overall, the magnitude of the depression obtained was similar to that obtained with 1,3,5-benzenetrithiol. The difference between the calculated and measured freezing points was again larger at higher concentrations. Using a thiol molar fraction of 3.38×10^{-3} , a depression of 51°C was obtained. However, the measurements became extremely difficult to do accurately using higher concentrations of thiol due to the very high viscosity of the liquid. At molar fraction of 5×10^{-3} , the reaction mixture was completely immobile and slowly crystallized at room temperature.

Scheme 68. Freezing Point of Sulfur after Reaction with 2,4,6-Trimethylbenzenetrithiol



5.3 Summary

According to the viscosity and polymeric content measurements, trithiols reacted with sulfur faster than dithiols. In general, the reactions with dithiols were complete in about 10 h while the reactions with trithiols usually finished in 2 h followed by an equilibration of the network polysulfides to smaller species. The presence of the methyl groups in 2,4,6-trimethylbenzenetrithiol did not affect either the reaction rates or the freezing points of the reaction mixtures as was observed in 2,5-dimethyl-1,4-benzenedithiol. Compared to reactions with dithiols, the formation of the network polysulfides from the reactions of trithiols with elemental sulfur more effectively lowered the freezing point of sulfur. The network polysulfides were not only acting as good sulfur ‘solvents’ but also the high viscosity caused by the network polysulfides slowed down the crystallization process of the sulfur molecules.

In summary, trithiols are better reagents than dithiols in terms of preventing sulfur from solidifying under the normal conditions. Between the two trithiols investigated in

this research, 2,4,6-trimethylbenzenetrithiol is considered as a better choice than 1,3,5-benzenetrithiol. The effects on the freezing point of sulfur exerted by the polysulfides formed from both trithiols are very similar. The advantage of 2,4,6-trimethylbenzenetrithiol is that its synthesis involves simple methods and common chemicals.

CHAPTER SIX

ISOLATION AND CHARACTERIZATION OF POLYSULFIDES

In order to fully characterize the polysulfide polymers formed from the reactions of benzene thiols and molten sulfur, they must be separated from the reaction mixtures. However, due to the following two reasons, it is impossible to isolate the polysulfides from the reaction mixtures using elemental sulfur as the solvent and preserve their true identities: (1) the structural similarities between the aromatic polysulfides formed from the reactions and polymeric sulfur, which is always present in molten sulfur under the reaction conditions, prevents efficient separation; (2) the polysulfides are only stable under the reaction conditions when excess elemental sulfur is present. This would be particularly true for large aromatic polysulfides and any attempt to isolate them from sulfur would disturb such equilibria.

Despite the above two reasons, it is still of interest to characterize the polysulfides formed from these reactions in order to get some general information on their structures such as average number of sulfur linkages and molecular weight distribution. To avoid the problem caused by the polymeric sulfur present in molten sulfur, the reactions were carried out in a solvent at a much lower temperature. Hence, conditions are chosen such that polymeric sulfur would not be present. The solvents used in this study were toluene and THF, both materials being reasonably good solvents for sulfur. Toluene was distilled over CaH_2 and THF was purified by distilling over Na/K just before use.

6.1 Isolation and Characterization of Linear Polysulfides

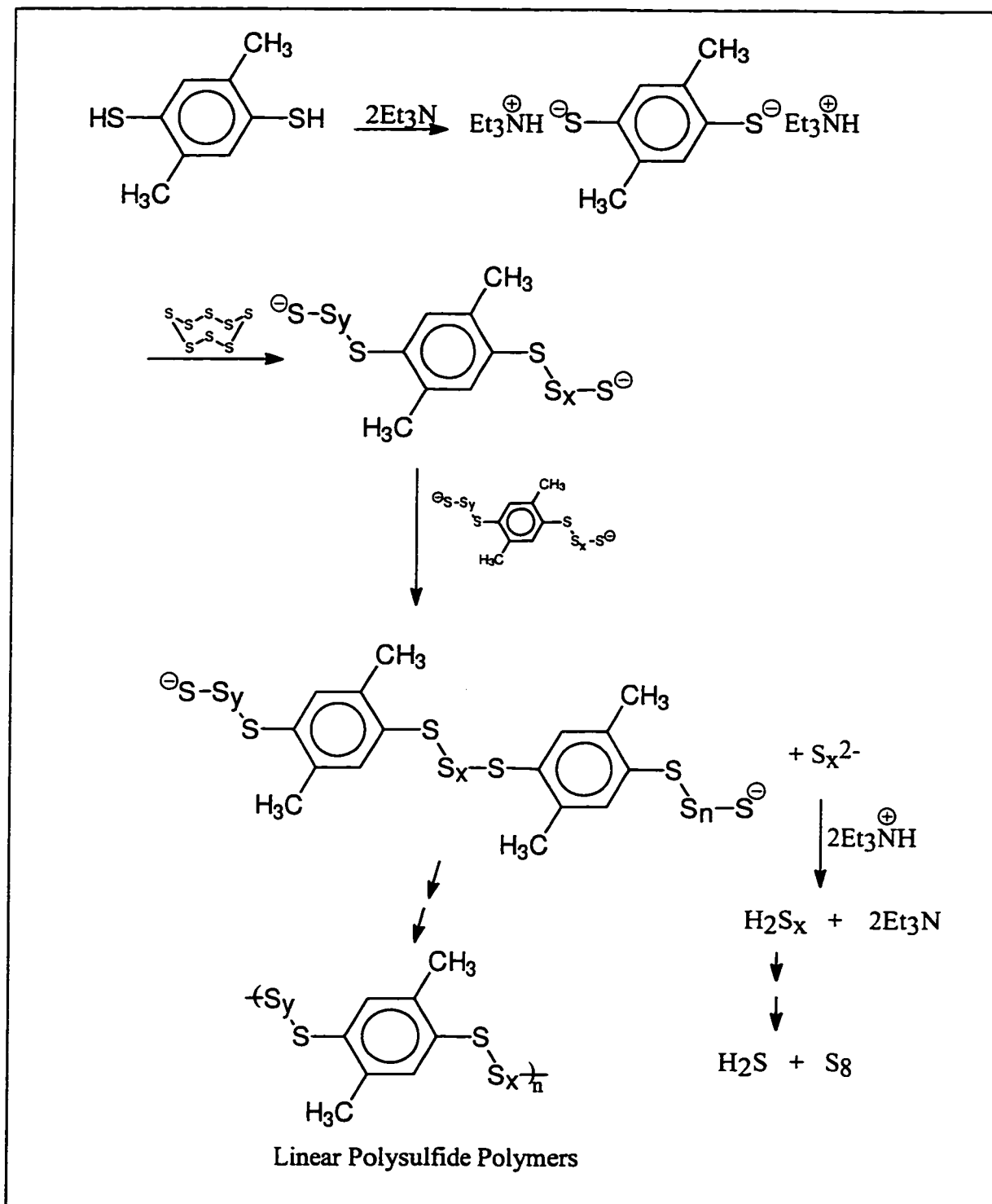
The linear polysulfides formed from the reactions of 2,5-dimethyl-1,4-benzenedithiol with elemental sulfur were studied because of the easy access of this thiol. The reaction was carried out in refluxing toluene under argon with the catalysis of a base [Et₃N or (n-Bu)₃NH⁺HS⁻]. The addition of a base catalyst was necessary in order to initiate the reaction at low temperature. Hence, the reaction was an anionic copolymerization following the type of mechanism illustrated in Scheme 69. Overall, the base extracts acidic protons from the thiol giving aromatic thiolates which then attack elemental sulfur to form aromatic polythiolates. These aromatic polythiolates can couple with each other and release S_x²⁻ ions, which react with alkyl ammonium ions (Et₃NH⁺), forming H₂S_x and regenerating the catalyst. H₂S_x eventually decomposes to H₂S and is released from the reaction mixture. After the reaction had finished (usually after 18 h), the reaction mixture was concentrated and the linear polysulfide polymers were precipitated in methanol. The polysulfides were recovered as pale yellow powders.

6.1.1 Average Molecular Weight Measurements

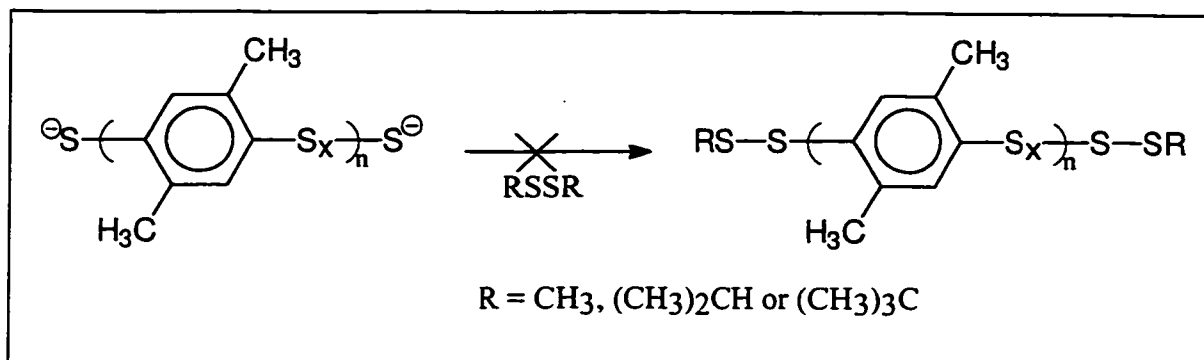
Average molecular weight data give information on the size of the polymer and the number of repeat units. Some attempts were made to measure the average molecular weight by a standard ¹H NMR technique. The theory of this type of determination is as follows. If the anionic polymerization of sulfur and aromatic thiols is terminated by the addition of dialkyl disulfides such as DMDS (CH₃SSCH₃), di-*iso*-propyl disulfide [(CH₃)₂CHSSCH(CH₃)₂] or di-*t*-butyl disulfide [(CH₃)₃CSSC(CH₃)₃], the expected polysulfides would be capped by an S-alkyl group, as shown in Scheme 70. Examination

of these polysulfides by ^1H NMR would give the information on their molecular weight. It is known that the areas under ^1H NMR signals represent the concentration of the corresponding groups if a long enough delay time is given during the data acquisition. Thus, the ratio of the integration of terminal -R groups to the methyl groups on the aromatic ring or aromatic protons would give the number of repeat units of the aromatic group present in the polysulfide chains. Unfortunately, the reactions did not proceed as expected. ^1H NMR spectra of the products precipitated in methanol after termination by the disulfides revealed no signals corresponding to the S-alkyl groups. Hence, it is likely that the terminal thiolates were capped by hydrogens originating from the thiol groups and present in the reaction mixture as H_2S (see Scheme 69).

Scheme 69. Anionic Polymerization of 2,5-Dimethyl-1,4-benzenedithiol with Elemental Sulfur in the Presence of Et₃N



Scheme 70. Attempted Termination Using Dialkyl Disulfides



Another method of measuring molecular weight is to utilize vapor pressure osmometry (VPO). As was mentioned in Chapter 2.3.3, VPO measures the molecular weight of a solute based on the principle that the vapor pressure of a solution is lower than that of the pure solvent at the same temperature. By raising the solution temperature the vapor pressure of the solution can be raised to match that of the solvent. This temperature difference can be used to calculate the molecular weight of the solute. The measurement was carried out in toluene at 50°C using conditions listed in Table 14.

Table 14. Preparation Conditions of the Samples for VPO Measurements

Sample	Catalyst	Catalyst Amount	Sulfur Amount	Solvent
(a)	(n-Bu) ₃ NH ⁺ HS ⁻	8.5×10 ⁻² equiv.	6 equiv.	THF
(b)	(n-Bu) ₃ NH ⁺ HS ⁻	2.8×10 ⁻² equiv.	6 equiv.	THF

It should be noted from the above Table that different amounts of catalyst were used. The original thought was that with different concentrations of catalyst, polysulfides might be produced with different molecular weights since with lower concentrations of catalyst, higher molecular weight polymer should be favored. It was found, however, that the average molecular weights for samples (a) and (b) were quite similar. Sample (a) had

an average molecular weight of 390 and the average molecular weight for sample (b) was 430. It was obvious that the molecular weights of the polysulfides prepared by the method were not very high and no significant difference was observed using different concentrations of catalyst. One of the reasons for limited polymerization may be that terminal thiolate ions were capped by hydrogens in the reaction mixture, thus limiting the propagation reactions. HPLC analysis of the samples (a) and (b) showed that they consisted of a series of compounds, possibly disulfide, trisulfide and tetrasulfide or higher polysulfides. The existence of polysulfide linkages were further confirmed by Raman spectroscopy study, as described below.

6.1.2 Raman Spectroscopy Study

Raman spectroscopy can be used to detect highly polarizable S-H, C-S and S-S-S groups. Among the various possible absorptions, the S-S stretch was the one of most interest since the frequency of the S-S absorption can be used to differentiate between S-S or S-S-S or even higher polysulfide linkages^[83]. Hence, Raman spectroscopic studies were carried out on some of the aromatic thiol-sulfur polymers.

Four linear polysulfides samples formed from the reactions of 2,5-dimethyl-1,4-benzenedithiol with sulfur were prepared. The reaction conditions are listed in Table 15.

Table 15. Preparation Conditions of the Samples for Raman Spectroscopy Studies

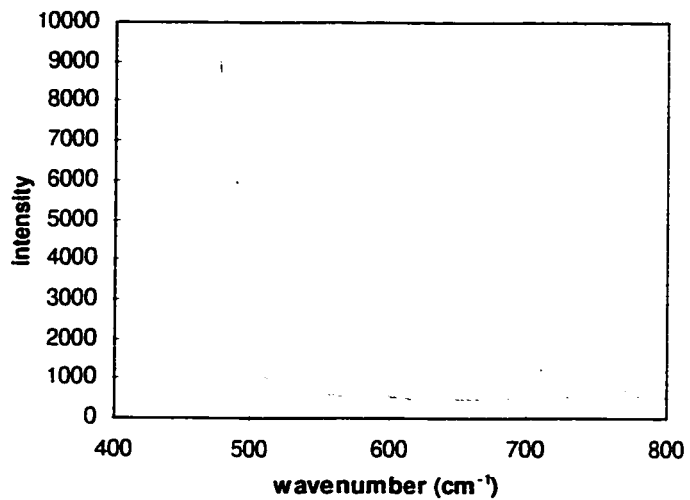
Sample	Catalyst	Catalyst Amount	Sulfur Amount	Solvent
(a)	(n-Bu) ₃ NHHS ⁺	8.7×10 ⁻² equiv.	6 equiv.	THF
(c)	Et ₃ N	1.0×10 ⁻³ equiv.	10 equiv.	Toluene
(d)	Pyridine	2.1×10 ⁻¹ equiv.	10 equiv.	Toluene
(e)	Na	2 equiv.	4 equiv.	THF

All the polysulfide polymers were precipitated in methanol and were collected as pale yellow powders. They were packed into the bottom of capillary tubes and their Raman spectra were recorded. The spectra of (c) and (d) are shown in Scheme 71 and 72 and the results are listed in Table 16.

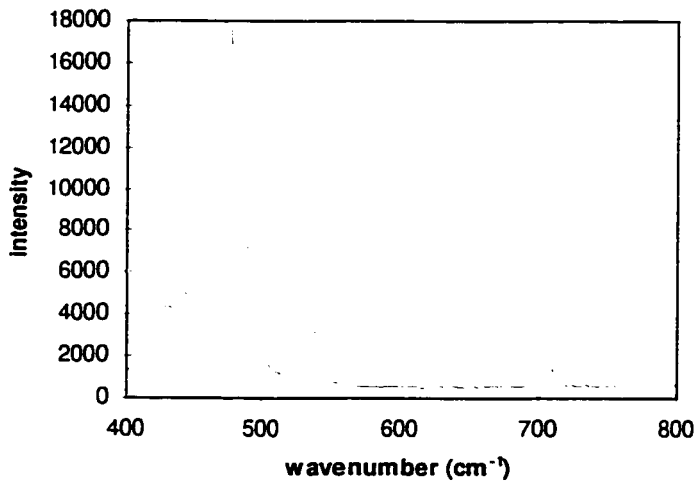
Table 16. Raman Spectra of Polysulfides formed from the reactions of 2,5-dimethyl-1,4-benzenedithiol and elemental sulfur

Sample	C-S (cm ⁻¹)	S-S (cm ⁻¹)
(a)	709 (w)	539 (w); 490 (s); 482 (s) 442 (w); 430 (w); 424 (w)
(c)	709 (w)	539; 523 490 (s); 478 (s) 440 (w); 424 (w)
(d)	708 (w)	529 (w); 523 (w) 490(s), 478 (s) 442 (w); 430 (w), 424(w)
(e)	708 (w)	540 (w); 524 (w) 492 (s); 482 (s); 476 (s)

Scheme 71. Raman Spectrum of the Linear Polysulfides (c) Formed from the Reaction of 2,5-Dimethyl-1,4-benzenedithiol with Elemental Sulfur

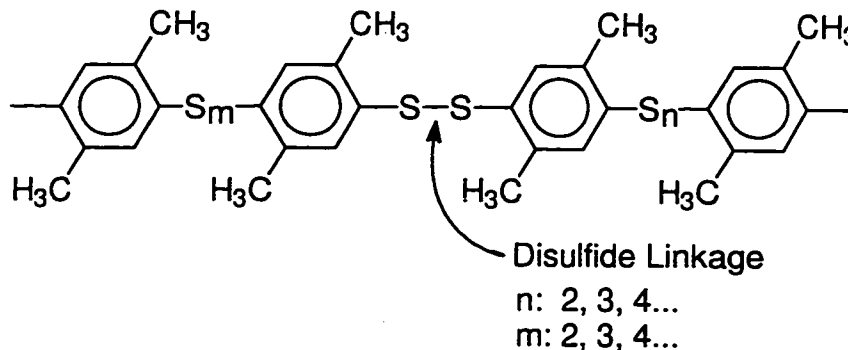


Scheme 72. Raman Spectrum of the Linear Polysulfides (d) Formed from the Reaction of 2,5-Dimethyl-1,4-benzenedithiol with Elemental Sulfur



The results showed that C-S stretching in all four samples could be found at about the same position $708\text{--}709\text{ cm}^{-1}$. However, the S-S stretches showed up in different regions as broad peaks. Generally, the S-S stretching bands could be found in three different regions. One was in the area of $540\text{--}520\text{ cm}^{-1}$. The other was in the area of $460\text{--}490\text{ cm}^{-1}$. The last could be found in the area of $420\text{--}440\text{ cm}^{-1}$. It is known^[83] that for a diaryl disulfide, the S-S stretch band occurs at about $520\text{--}540\text{ cm}^{-1}$. The position of the disulfide S-S stretching band is also affected by substituents on the aromatic ring. As illustrated in Scheme 73, the two adjacent polysulfide linkages could be any combinations of disulfide, trisulfide, tetrasulfide or even higher polysulfides. As a result, the S-S stretches appeared as broad peaks in the area of $520\text{--}540\text{ cm}^{-1}$.

Scheme 73. Disulfide Linkages in Linear Polysulfides



According to the literature^[83], as the sulfur chain elongates, the position of the S-S stretching bands shifts to lower wavenumber. For trisulfides, the symmetric S-S-S stretching bands occur in the region of $480\text{--}510\text{ cm}^{-1}$. For the higher polysulfides, the S-S stretching frequencies are usually found in the range of $450\text{--}500\text{ cm}^{-1}$ ^[83]. The S-S stretching bands of the polysulfide polymer found in the range of $460\text{--}490\text{ cm}^{-1}$ falls in the range of trisulfide stretching wavenumber. The last group of bands was in the range of

420-440 cm^{-1} which, likely can be assigned to the stretching bands of the higher polysulfides. These bands could not be resolved and appeared as broad absorptions.

The Raman spectra of samples (a), (c) and (d) were quite similar. All three groups of bands were observed with similar relative intensities. The bands in the range of 460-490 cm^{-1} appeared to be very strong, possibly indicating that the majority of the polysulfide linkages in linear polysulfides existed as trisulfides. The bands in the ranges of 520-540 cm^{-1} and 420-440 cm^{-1} were relatively weak which indicated that the number of disulfide and higher polysulfide linkages were much less compared to trisulfide linkages. In the case of sample (e), the bands in the range of 420-440 cm^{-1} were not observed. Since only 4 equivalent of elemental sulfur was used during the sample preparation of (e), compared to 6 equivalent and 10 equivalent in samples (a), (c) and (d), it was reasonable to assume that the higher polysulfide content was low such that the S-S stretching bands were not observed. No significant difference was observed in terms of positions and intensities of the bands when 6 equivalents and 10 equivalents of sulfur were used as in the cases of sample (a), (c) and (d).

The Raman spectra clearly confirmed the existence of di-, tri- and higher polysulfide linkages in the polysulfide polymer prepared from the reaction of dithiol with elemental sulfur in a solvent. From the intensities of the different stretching bands, it was possible to conclude that the majority of the S-S linkage were trisulfides, with a small number of sulfur linkages existing as disulfides and higher polysulfides.

6.1.3 Elemental Analysis

As mentioned in Chapter 2.3.1, elemental analysis data for the polysulfides should enable the average number of sulfur atoms per molecule to be determined. This information can then be extrapolated to give the average number of atom per sulfur linkage. Since sulfur was the only other element present in the polysulfides besides carbon and hydrogen, its percentage was calculated according to the percentages of C and H obtained from the elemental analysis. With the percentages of C, H and S, the empirical molecular formula could be calculated. The results are shown in Table 17.

Table 17. Elemental Analysis of Linear Polysulfides from the Reaction of 2,5-Dimethyl-1,4-benzenedithiol and Elemental Sulfur

Sample	Empirical Formula
(a)	$C_8H_{7.7}S_{3.6}$
(c)	$C_8H_{6.5}S_{3.7}$
(d)	$C_8H_{6.5}S_{3.8}$
(e)	$C_8H_{6.3}S_{3.6}$

The results showed that the average number of sulfur atoms per molecule was about 3.7. If all the sulfur linkages were trisulfide, the empirical molecular formula should have been $C_8H_8S_3$. Therefore, the average number of sulfur atoms per linkage in these polysulfides was slightly higher than three. This result is consistent with the Raman spectroscopy result which showed that the majority of the polysulfides contained trisulfide linkages with lesser amounts of disulfides and higher polysulfides. In the case of sample (e), although the stretching bands of higher polysulfides were not observed in Raman spectra, the average number of sulfur per molecule (3.6 as determined from elemental analysis) indicated that higher polysulfide linkages were present. The inability

to observe these polysulfides by Raman spectroscopy may be a consequence of the broad absorptions for these functional groups.

6.2 Isolation and Characterization of Network Polysulfides

The network polysulfides formed from the reactions of 2,4,6-trimethyl-1,3,5-benzenetrithiol and elemental sulfur were isolated and characterized. The reactions were carried out in refluxing toluene with the catalysis of Et_3N . The network polysulfides precipitated out when reaction finished and were isolated by filtration. Due to their insolubility in all solvents, their molecular weights could not be determined by VPO. Thus, the network polysulfides were characterized by Raman spectroscopy and elemental analysis.

6.2.1 Raman Spectroscopy Study

Two samples were prepared for the Raman spectroscopy study. The reaction conditions are listed in Table 18.

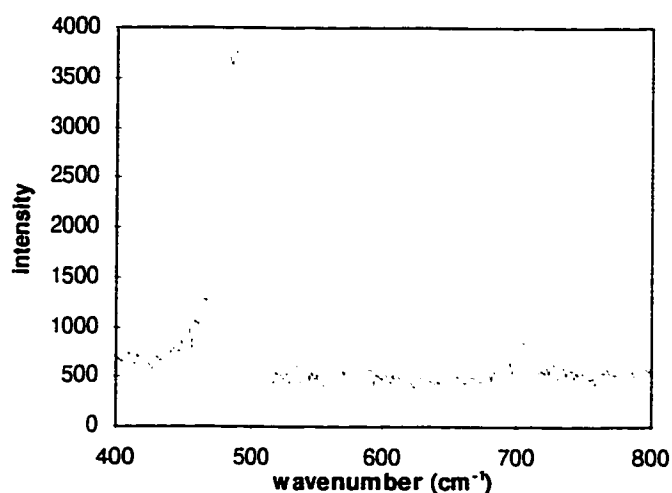
Table 18. Preparation conditions of the samples for Raman spectroscopy studies

Sample	Catalyst	Catalyst Amount	Sulfur Amount	Solvent
(f)	Et_3N	6.3×10^{-2} equiv.	24 equiv.	Toluene
(g)	Et_3N	6.3×10^{-2} equiv.	4 equiv.	Toluene

Unlike the linear polysulfide polymers discussed in the previous section, the network polysulfides had only limited solubility in toluene under the refluxing condition. When they reached certain sizes, they dropped out from the solution and the reaction stopped. Therefore, the size of the network polysulfides as well as the S-S linkages

should depend on their solubility in toluene. The two samples prepared for the Raman study used different amount of sulfur in order to examine the effect of sulfur amount on the types of S-S linkages. In sample (f), 24 equivalents of sulfur was used, while only 4 equivalents was used in sample (g). Their Raman spectra were recorded and are shown in Scheme 74 and 75. The results are listed in Table 19.

Scheme 74. Raman Spectrum of the Network Polysulfides (f) Formed from the Reaction of 2,4,6-Trimethylbenzenetrithiol with Elemental Sulfur (24 equiv.)



Scheme 75. Raman Spectrum of the Network Polysulfides (g) Formed from the Reaction of 2,4,6-Trimethylbenzenetrithiol with Elemental Sulfur (4 equiv.)

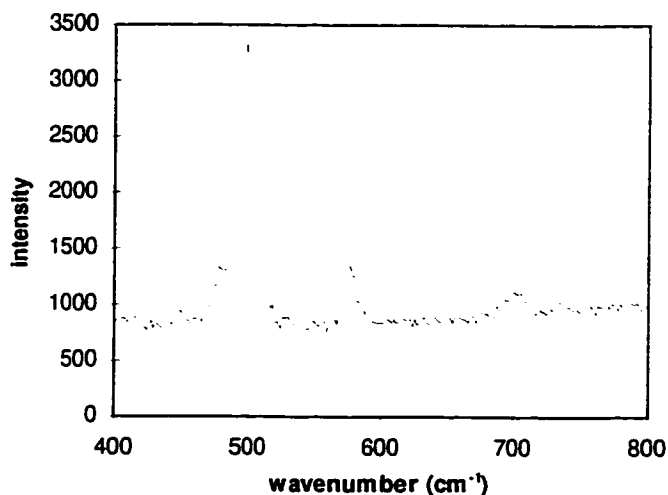


Table 19. Raman Spectra of Network Polysulfides

Sample	C-S (cm^{-1})	S-S (cm^{-1})
(f)	704 (w)	580 (w); 488 (s); 484 (s), 464(w)
(g)	709 (w)	578 (w) 498 (s); 476 (w)

The results showed that they have very similar Raman spectra. The C-S stretching was found to be a weak band at about 705 cm^{-1} . Two groups of S-S stretching bands were found. One appeared at about 580 cm^{-1} , which was probably the stretching band for disulfides. The intensities of these bands were fairly weak, indicating that the number of disulfide linkages in the network polysulfides was probably low. For both samples, the other stretching bands could be found at $480\text{-}500 \text{ cm}^{-1}$. For sample (f), two strong bands at 488 cm^{-1} and 484 cm^{-1} were observed. These were likely the stretching bands for trisulfides. Due to the adjacent polysulfide linkages, these bands were very broad but their strong intensity indicated that the majority of the polysulfide linkages in the polymer were trisulfides. For sample (g) where only 4 equivalent of sulfur was used, the stretching bands for the trisulfide linkages were found at a slight higher wavenumber 497 cm^{-1} . Another band at 476 cm^{-1} was weak appearing as a shoulder of the stretching band of 497 cm^{-1} . A higher wavenumber shift indicated a shorter polysulfide linkage. It was reasonable to assume that on average, the polysulfide linkages in sample (g) were shorter than those in sample (f). This was expected since much less sulfur was used during the sample preparation.

6.2.2 Elemental Analysis

As discussed in the previous section, the elemental analysis will give average number of sulfur atoms per unit. It was very useful in the case of network polysulfides since they have very limited solubility in organic solvents and the molecular weight measurement could not be performed. The samples prepared for elemental analysis used different amounts of elemental sulfur in order to determine if different lengths of the sulfur linkage could be produced in the network polysulfides. The conditions of the reactions, as well as the results of the elemental analysis, are listed in Table 20.

Table 20. Reaction Conditions and Elemental Analysis of Network Polysulfides from the Reaction of 2,4,6-Trimethylbenzenetrithiol and Elemental Sulfur

Sample	Catalyst	Catalyst Amount	Sulfur Amount	Empirical Formula
(h)	Et ₃ N	6.3×10 ⁻² equiv.	3 equiv.	C ₉ H _{9.5} S _{4.7}
(g)	Et ₃ N	6.3×10 ⁻² equiv.	4 equiv.	C ₉ H _{8.4} S _{5.1}
(j)	Et ₃ N	6.3×10 ⁻² equiv.	6 equiv.	C ₉ H _{8.7} S _{5.0}
(k)	Et ₃ N	6.3×10 ⁻² equiv.	9 equiv.	C ₉ H _{9.5} S _{5.1}
(l)	Et ₃ N	6.3×10 ⁻² equiv.	12 equiv.	C ₉ H _{8.7} S _{5.2}
(m)	Et ₃ N	6.3×10 ⁻² equiv.	18 equiv.	C ₉ H _{10.3} S _{5.2}
(n)	Et ₃ N	6.3×10 ⁻² equiv.	21 equiv.	C ₉ H _{9.0} S _{5.2}
(f)	Et ₃ N	6.3×10 ⁻² equiv.	24 equiv..	C ₉ H _{7.6} S _{5.2}
(o)	Et ₃ N	6.3×10 ⁻² equiv.	27 equiv.	C ₉ H _{9.4} S _{5.4}

It was observed that with increasing amount of sulfur, the average number of sulfur atoms per molecule increased from 4.6, when only 1 equivalent of sulfur was used, to 5.4 when 27 equivalent sulfur was used. If all the S-S linkages in the network polysulfides were trisulfide linkages, an average number of sulfur atoms of 4.5 should be obtained. The elemental analysis showed that in the presence of excess of sulfur, the average number of sulfur atoms per molecule was about 5.2, indicating that the average polysulfide linkage was slightly higher than three. This result was consistent with the result obtained from the linear polysulfides experiments, which also showed that the average polysulfide linkage was slightly longer than three sulfur atoms. Therefore, it was reasonable to assume that in the case of network polysulfides, the majority of the polysulfide linkages existed in the form of trisulfides with small amount of disulfides and higher polysulfides. The S-S stretching bands for the higher polysulfides were not observed in the Raman spectroscopy study, probably due to the weak intensity of broad bands.

6.3 Summary

Both linear and network polysulfides were prepared from the reactions of 2,5-dimethyl-1,4-benzenedithiol or 2,4,6-trimethyl-1,3,5-benzenetrithiol with elemental sulfur in a solvent with the catalysis of a base. The polysulfides were isolated and characterized by VPO (for linear polysulfides only), Raman spectroscopy and elemental analysis in order to determine the nature of the sulfur linkages. Although the polysulfides isolated from these reactions would not necessarily represent the polysulfides formed from the reactions of polythiols in molten sulfur, some general information could be

deduced from these results. For both linear and network polysulfides, it was found that the majority of the polysulfide linkages were trisulfides, with lesser amounts of disulfides and higher polysulfides. These trisulfides appeared to be very stable under the reaction conditions. Thus, the polysulfides synthesized in toluene solution were much smaller than the polysulfides formed in liquid sulfur. Very likely, the large polysulfides formed in liquid sulfur are only stable in the presence of excess elemental sulfur which drives the equilibrium towards larger species.

CHAPTER SEVEN

EXPERIMENTAL

7.1 Instruments

GC-MS

A Hewlett Packard 5890 gas chromatograph fitted with a SPB-5 capillary column (0.25 mm×30 m) was used to monitor the progress of the methylthiolation reactions. Temperature was programmed to hold at 100°C for 2 minutes followed by a rise of 10°C/minute to 300°C. Mass spectra of eluting species were recorded using a HP5970 mass selective detector.

Elemental Analysis

Samples were analyzed for C, H and N content at the Instrument Laboratory in Department of Chemistry at the University of Calgary using a Control Equipment Corporation (CEC) 440 Elemental Analyzer. The absolute precision of the instrument is within ± 0.3 wt%.

Mass Spectrometry

Low resolution mass spectra were recorded on a VG 7070F instrument operated by staff of the Instrument Laboratory in Department of Chemistry at the University of Calgary.

NMR Spectroscopy

Bruker ACE-200 (^1H : 200 MHz; ^{13}C : 50 MHz) and Bruker AM-400 (^1H : 400 MHz; ^{13}C : 100 MHz) instruments were used for acquiring ^1H and ^{13}C NMR spectra. Deuteriochloroform was used as the solvent and chloroform as the internal standard (^1H , $\delta 7.27$, ^{13}C , $\delta 77.0$), unless otherwise stated. ^1H NMR spectra listed have the following format: chemical shift (in ppm), (multiplicity, number of protons). Abbreviations used are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = undefined multiplet. ^{13}C NMR spectra listed have the following format: chemical shift (in ppm), (assignment). Abbreviations used are as follows: (C_q) = quaternary carbons, (C_t) = aromatic tertiary carbons, (CH_3) = methyl. A Bruker AMX 300 MHz instrument was used for ^{29}Al and ^{27}Si NMR analysis of clay catalysts as well as for the solid ^{13}C NMR analysis of the polysulfides. $\text{Al}(\text{NO}_3)_3$ in H_2O was used as external standard for ^{29}Al NMR (^{29}Al , 0 ppm). Sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as external standard for ^{27}Si NMR (^{27}Si , 0 ppm). Glycine was used as external standard for solid ^{13}C NMR (^{13}C , 176.03 ppm).

Viscosity Measurement

A Brookfield Digital Viscometer was used for the viscosity measurements. The instrument was calibrated by viscosity standards No. S2000 (8132 mPa. s at 20°C , 1486 mPa. s at 40°C) and No. S600 (2184 mPa. s at 20°C , 470 mPa. s at 40°C). The temperature of the measuring cup was maintained by flowing liquid from a circulating bath maintained at constant temperature ($\pm 0.1^\circ\text{C}$).

Vapor Pressure Osmometry

A Jupiter Instrument Model 833 Vapor Pressure Osmometer was used to determine the molecular weights of linear polysulfides. This system has a detection limit of 5×10^{-5} mol/L when used with toluene or chloroform. The molecular weight range was 100-25,000 when toluene was used. The factor K in eq. 24 was determined using sucrose octaacetate (mol. wt. 678.6) in toluene at 50°C.

Melting Point

The melting points were measured with Fisher-Johns Melting Point Block and were uncorrected.

Raman Spectroscopy

Raman spectra were recorded with a Jarrell-Ash model 25-100 double-grating monochromator, scattering at 90°. Slit widths were set at 60, 90, 90 in order to achieve 2 cm^{-1} resolution at 1000 cm^{-1} . The incident radiation 19440 cm^{-1} (argon-ion laser, by Coherent Radiation) and 450 mW power at the sample were used. The observed frequencies were calibrated against those of liquid CCl_4 .

7.2 Experimental Procedures Pertaining to Chapter 3

7.2.1 Chemicals and Reagents

Toluene, anisole, thioanisole, xylenes, mesitylene, chlorobenzene, 1,2-dichloroethane and other chemicals were obtained from the Aldrich Company and were used without further purification. Dimethyl disulfide was washed with sulfuric acid and water, dried with MgSO_4 and distilled over CaCl_2 . K10 montmorillonite clay was obtained from the Fluka Chemical Company and was activated in the oven under vacuum at 150°C for two hours before use.

7.2.2 Catalysts Preparation

ZnCl_2 , FeCl_3 and MnCl_2 -impregnated K10 were prepared by adding a solution of ZnCl_2 , FeCl_3 and MnCl_2 (60 mmol) in methanol (45 mL) to K10 (30 g), stirring the resultant slurry for 24 h at room temperature, removing methanol by rotary evaporation and heating the clay at 150°C at reduced pressure (15 mmHg) for 24 h. It was subsequently ground to particles and calcinated at 150°C under vacuum for 2 h before use.

The sulfuric acid-treated K10 was prepared^[118] by adding concentrated sulfuric acid (68.7 g, 98%) to a suspension of K10 (100 g) in water (500 g), stirring the suspension for 16 h at 90°C , removing the excess water and acid by filtering and washing the filter cake with hot water. The wet clay was dried in an oven at 100°C and later ground to particles. It was then calcinated in a vacuum oven at 150°C for 2 h before use. The catalyst prepared by this method is abbreviated as K10/ H^+ in Chapter 3.

7.2.3 Alkylthiolation Procedures

5-Methyl-1,2,4-tris(methylthio)benzene (1b)

A stirred suspension of toluene (0.92 g, 0.01 mol), dimethyl disulfide (1.88 g, 0.02 mol) and modified clay (K10, 3 g, K10/ZnCl₂ or K10/MnCl₂, 2 g) in chlorobenzene (40 mL) was heated under reflux for 18 h. For Entry 4 of Table 4, concentrated sulfuric acid (1.96 g, 0.02 mol) was used as co-catalyst and was added while the rest of the reaction mixture was heated under reflux. The progress of the reactions was monitored by GC-MS. After the reaction was complete, the clay was filtered through Celite and was washed with dichloromethane. A pale yellow oil was obtained after drying the organic phase with MgSO₄ and evaporating off the solvent. By-product dimethyl polysulfides were removed by distillation using a Krugelrohr apparatus at 100°C under 15 mmHg vacuum. (1a) was distilled from the crude product at 25°C/0.1 mmHg. The distillation residue crystallized at room temperature and (1b) was recrystallized from ethanol as white crystals. Yield: see Table 4. ¹H NMR: δ2.33(s, 3H), δ2.46(s, 3H), δ2.47(s, 3H), δ2.48(s, 3H), δ7.02(s, 1H), δ7.09(s, 1H). ¹³C NMR: δ135.49(C_q), δ135.25(C_q), δ134.83(C_q), δ134.75(C_q), δ128.86(C_i), δ125.65(C_i), δ19.61(CH₃), δ16.98(CH₃), δ16.67(CH₃), δ16.04(CH₃). Mass: m/z 230(100, M⁺); mp 87-88°C. High resolution mass calcd. for C₁₀H₁₄S₃: 230.0258, found: 230.0239

1-Methoxy-4-methylthiobenzene (2a) and 1-Methoxy-2,4,5-tris(methylthio)benzene (2b)

A stirred suspension of anisole (1.08 g, 0.01 mol), dimethyl disulfide (5.64 g, 0.06 mol) and modified clay (K10, 5-10 g, K10/ZnCl₂, 5 g or K10/MnCl₂, 10 g or K10/FeCl₃, 3 g) in chlorobenzene or 1,2-dichloroethane (40 mL) was heated under reflux for 18 h. For entries 5, 6 and 8 in Table 5, concentrated sulfuric acid (2.94 g, 0.03 mol) was added as co-catalyst. For entry 7, concentrated sulfuric acid (5.88 g, 0.06 mol) was added. The progress of the reactions were monitored by GC-MS. After the reaction had finished, the clay was filtered through Celite and was washed with dichloromethane. A pale yellow oil was obtained after drying the organic layer with MgSO₄ and evaporating off the solvent. By-product dimethyl polysulfides were removed by distillation using a Krugelrohr apparatus at 100°C under 15 mm Hg vacuum. **(2a)** was distilled from the crude product at 58°C/0.5 mm Hg. The residue crystallized at room temperature and **(2b)** was recrystallized from ethanol as white crystals. The product distributions and yields are recorded in Table 5. ¹H NMR **(2a)**: δ2.45(s, 3H), δ3.80(s, 3H), δ6.86(d, 2H), δ7.28(d, 2H). ¹³C NMR: δ158.22(C_q), δ130.23(C_i), δ128.80(C_q), δ114.60(C_i), δ55.31(CH₃), δ18.04(CH₃). Mass: m/z 154 (80, M⁺), 139 (100, -CH₃); bp 58°C/0.05mmHg (lit. 99°C/4 mmHg)^[111]. ¹H NMR **(2b)**: δ2.44(s, 6H), δ2.48(s, 3H), δ3.92(s, 3H), δ6.71(s, 1H), δ7.18(s, 1H). ¹³C NMR: δ155.94(C_q), δ138.01(C_q), δ129.14(C_i), δ127.66(C_q), δ108.93(C_i), δ55.93(CH₃), δ17.85(CH₃), δ16.29(CH₃), δ15.18(CH₃). Mass: 246 (100, M⁺) mp 93-94°C. Anal. Calcd. for C₁₀H₁₂OS₃: C, 48.77; H, 5.54. Found: C, 48.78; H, 5.69.

1,4-Bis(methylthio)benzene (3a) and 1,2,4,5-Tetrakis(methylthio)benzene (3b)

A stirred suspension of thioanisole (1.24 g, 0.01 mol), dimethyl disulfide (5.64 g, 0.06 mol) and modified clay (K10, 12 g, K10/ZnCl₂, 5 g or K10/MnCl₂, 10 g or K10/H⁺, 5 g) in chlorobenzene or 1,2-dichloroethane (40 mL) was heated under reflux for 18 h. For entry 14 of Table 6, concentrated sulfuric acid (4.41 g, 0.045 mol) was added as co-catalyst. For entries 15 and 16, concentrated sulfuric acid (5.88 g, 0.06 mol) was added. Reaction 15 in Table 6 was carried out in an autoclave pressurized with air at 1000 psi (6.69 Mpa) and held at 150°C. In reactions 17 and 18, trifluoroacetic acid (6.84 g, 0.06 mol and 3.42 g, 0.03 mol respectively) instead of H₂SO₄ (conc.) was used as a co-catalyst. The progress of the reactions was monitored by GC-MS. After the reactions had finished, the clay was filtered through Celite and was washed with dichloromethane. Pale yellow oils were obtained by drying the organic phase with MgSO₄ and evaporating the solvent. By-product dimethyl polysulfides were removed by distillation using a Krugelrohr apparatus at 100°C under 15 mmHg vacuum. (3a) and (3b) were separated by fractional crystallization from ethanol. (3a) was obtained as white flakes and (3b) as pale yellow solid. The product yields are summarized in Table 6. ¹H NMR (3a): δ2.47(s, 6H), δ7.21(s, 4H). Mass: m/z 170 (84, M⁺), 155 (100, -CH₃); mp 82-84°C, lit. 85°C^[112]. ¹H NMR (3b): δ2.49(s, 12H), δ7.11(s, 2H). ¹³C NMR: δ135.70(C_q), δ126.47(C_t), δ16.70(CH₃). Mass: m/z 262 (100, M⁺); mp 126-128°C, lit. mp 127-129°C^[25].

1,4-Dimethyl-2,5-bis(methylthio)benzene (4a)

A stirred suspension of *p*-xylene (1.06 g, 0.01 mol), dimethyl disulfide (1.88 g,

0.02 mol - 9.4 g, 0.10 mol) and modified clay (K10, 3-10 g, K10/ZnCl₂, 10 g or K10/MnCl₂, 10 g or K10/H⁺, 1 g) in chlorobenzene or 1,2-dichloroethane (40 mL) was heated under reflux for 18 h. Concentrated sulfuric acid (0.98 g, 0.01 mol - 3.14 g, 0.032 mol) was added as co-catalyst in entries 22 -27 of Table 7. The progress of the reactions was monitored by GC-MS. After the reaction had finished, the clay was filtered through Celite and was washed with dichloromethane. The organic solution was dried with MgSO₄ and the solvent was evaporated. By-product dimethyl polysulfides were removed by distillation using a Krugelrohr apparatus at 100°C under 15 mmHg vacuum. (4a) was obtained as white solid. It was purified by recrystallization from ethanol. See Table 7 for yields. ¹H NMR: δ2.34(s, 6H), δ2.45(s, 6H), δ6.99(s, 2H). ¹³C NMR: δ134.58(C_q), δ133.94(C_q), δ127.53(C_i), δ19.63(CH₃), δ16.04(CH₃). Mass: m/z 198 (100, M⁺), 183 (52, -CH₃); mp 90-92°C. lit. 83-85°C^[113].

1,2-Dimethyl-4,5-bis(methylthio)benzene (5a)

A stirred suspension of *o*-xylene (1.06 g, 0.01 mol), dimethyl disulfide (3.76 g, 0.04 mol - 5.64 g, 0.06 mol) and modified clay (K10, 5-10 g, K10/ZnCl₂, 5 g or K10/MnCl₂, 10 g) in chlorobenzene or 1,2-dichloroethane (40 mL) was heated under reflux for 18 h. Concentrated sulfuric acid (5.88 g, 0.06 mol) was added as co-catalyst in experiments 30 and 31 of Table 7. The progress of the reactions was monitored by GC-MS. After the reaction was complete, the clay was filtered through Celite and was washed with dichloromethane. A thick yellow oil was obtained after the dried (MgSO₄) solvent and dimethyl polysulfides were removed. It slowly crystallized at 20°C. (5a) was obtained as pale yellow crystals after recrystallization from ethanol. See Table 7 for yields. ¹H

NMR: δ 2.36(s, 6H), δ 2.43(s, 6H), δ 7.09 (s, 2H). ^{13}C NMR: δ 135.37(C_q), δ 134.80(C_q), δ 124.41(C_t), δ 16.82(CH_3), δ 16.53(CH_3). Mass: m/z 198 (100, M^+); mp 85-88°C. High resolution mass calcd. for $\text{C}_{10}\text{H}_{14}\text{S}_2$: 198.0537, found: 198.0532

1,3-Dimethyl-4-methylthiobenzene (6a) and 1,5-Dimethyl-2,4-bis(methylthio)-benzene (6b)

A stirred suspension of *m*-xylene (1.06 g, 0.01 mol), dimethyl disulfide (1.88 g, 0.02 mol - 7.52 g, 0.08 mol) and modified clay (K10, 3-10 g, $\text{K10}/\text{H}^+$, 1 g) in chlorobenzene or 1,2-dichloroethane (40 mL) was heated under reflux for 18 h. Concentrated sulfuric acid (1.96 g, 0.02 mol - 3.14 g, 0.032 mol) was added as co-catalyst in experiments 35 and 36 of Table 7. The progress of the reactions was monitored by GC-MS. After the reaction had finished, the clay was filtered through Celite and was washed with dichloromethane. A thick yellow oil was obtained after the dried (MgSO_4) solvent and dimethyl polysulfides were removed. **(6a)** was obtained by distillation at 70°C/0.5 mmHg. The distillation residue slowly crystallized at 20°C. **(6b)** was obtained from this solid by recrystallization from ethanol. The product distributions and yields are recorded in Table 7. ^1H NMR **(6a)**: δ 2.31(s, 3H), δ 2.34(s, 3H), δ 2.45(s, 3H), δ 7.00-7.13(m, 3H). Mass: m/z 152 (100, M^+), 137 (52, $-\text{CH}_3$), 105 (71, $-\text{SCH}_3$); bp 70°C/0.5 mmHg, lit. 100-115°C^[114]. ^1H NMR **(6b)**: δ 2.31(s, 6H), δ 2.47(s, 6H), δ 6.97(s, 1H), δ 7.07(s, 1H). ^{13}C NMR: δ 135.0(C_q), δ 133.6(C_q), δ 131.6(C_t), δ 124.5(C_t), δ 19.3(CH_3), δ 16.2(CH_3). Mass: m/z 198 (100, M^+), 183 (54, $-\text{CH}_3$); mp 80-81°C. Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{S}_2$: C, 60.61; H, 7.01. Found: C, 60.43; H, 7.31.

2-Methylthiomesitylene (7a), 1,3,5-trimethyl-bis(methylthio)benzene (7b) and 1,3,5-trimethyl-tris(methylthio)benzene (7c)

A stirred suspension of mesitylene (1.2 g, 0.01 mol), dimethyl disulfide (5.64 g, 0.06 mol) and modified clay (K10, 3g, K10/H⁺, 5 g) in chlorobenzene or 1,2-dichloroethane (40 mL) was heated under reflux for 18 h. Concentrated sulfuric acid (2.94 g, 0.03 mol - 5.88 g, 0.06 mol) was added as co-catalyst in experiments 38 and 39 of Table 10. Fuming sulfuric acid (2.94 g, 0.03 mol) was used in reaction 40. The progress of the reactions was monitored by GC-MS. After the reaction had finished, the clay was filtered through Celite and was washed with dichloromethane. The solvent and dimethyl polysulfides were removed as described previously and (7a) and (7b) were separated by fractional distillation under vacuum. The distillation residue solidified at 20°C. (7c) was obtained by recrystallization of the solid from ethanol. The product yields are summarized in Table 10. ¹H NMR (7a): δ6.96(s, 2H), δ2.54(s, 6H), δ2.29(s, 3H), δ2.23(s, 3H). ¹³C NMR: δ142.55(C_q), δ137.93(C_q), δ131.82(C_q), δ128.92(C_i), δ21.58(CH₃), δ20.93(CH₃), δ18.43(CH₃). Mass: m/z 166 (100, M⁺), 151 (80, -CH₃); bp 64°C/0.5 mmHg, lit. 74°C/1 mmHg^[115]. ¹H NMR (7b): δ7.06(s, 1H), δ2.90(s, 3H), δ2.52(s, 6H), δ2.22(s, 6H). ¹³C NMR: δ147.06 (C_q), δ142.83(C_q), δ133.70(C_q), δ129.82(C_i), δ21.89(CH₃), δ20.39(CH₃), δ18.48(CH₃). Mass: m/z 212 (100, M⁺); b.p. 75°C/0.005 mmHg. lit. 110-115°C/0.5 mmHg^[113]. ¹H NMR (7c): δ2.93(s, 9H), δ2.23(s, 9H). ¹³C NMR: δ147.60(C_q), δ134.90(C_q), δ21.60(CH₃), δ18.70(CH₃). Mass; m/z 258 (100, M⁺); mp 68-68.5°C. Anal. Calcd. for C₁₂H₁₈S₃: C, 55.82; H, 6.98. Found: C, 55.34; H, 6.60.

7.2.4 Literature Procedures for the Preparation of 1,3,5-Benzenetrithiol^[24,25]

Preparation of sodium *iso*-propylthiolate

Sodium (6 g, 0.26 mol) was dissolved in ethanol (abs., 150 mL). 2-Propanethiol (19.8 g, 0.26 mol) was added dropwise to the stirred sodium ethoxide solution at 0°C. The thiolate was obtained after evaporating the solvent and washing the residue with anhydrous diethyl ether. The solid product was collected by filtration and was dried in a vacuum. Yield: 96%

1,3,5-Benzenetrithiol

1,3,5-Trichlorobenzene (1.5 g, 0.0083 mol) in HMPA (40 mL) was added with stirring to sodium *iso*-propylthiolate (5.67 g, 0.058 mol) and the reaction mixture was left at 100°C for 3 h. The progress of the reaction was monitored by GC-MS. After the substitution reaction was completed, small pieces of sodium (1 g, 0.043 mol) were added and the reaction was continued for another 4 h until the reduction was completed. Ice water was then added followed by the addition of HCl (~7%). A brown solid precipitated and was collected and dried (Yield: 96%). The crude product was purified by steam distillation and was collected as an off-white solid. ¹H NMR: δ3.43(s, 3H), δ6.96(s, 3H). ¹³C NMR: δ133.00(C_q), δ126.3(C_t). Mass; m/z 174 (100, M⁺); mp 58-60°C. lit. 59-60°C^[24].

7.2.5 Birch Reduction Procedures

1,4-Benzenedithiol, 2,5-Dimethyl-1,4-benzenedithiol and 2,4,6-Trimethylbenzenetrithiol

To a suspension of 1,4-bis(methylthio)benzene (**3a**) or 1,4-dimethyl-2,5-bis(methylthio)benzene (**4a**) or 1,3,5-trimethyl-tris(methylthio)benzene (**7c**) in liquid NH_3 was added Na in small pieces (2 mols of Na to 1 mol of SCH_3 to be reduced). The stirring was continued for 6 h until all the Na was dissolved. The reaction mixture was then quenched by addition of saturated NH_4Cl solution. After all the NH_3 had evaporated, NaOH (5%) was added and the aqueous solution was extracted twice with diethyl ether. The aqueous layer was then acidified by addition of HCl (5%) until precipitation of the thiols was complete. The thiols were recovered by filtration and were purified by crystallization. 1,4-Benzenedithiol and 2,5-dimethyl-1,4-benzenedithiol were recrystallized from ethanol and 2,4,6-trimethyl-1,3,5-benzenetrithiol was crystallized from benzene. ^1H NMR (2,5-dimethyl-1,4-benzenedithiol): δ 2.25(s, 6H), δ 3.19(s, 2H), δ 7.09 (s, 2H). ^{13}C NMR: δ 134.53(C_q), δ 131.83(C_t), δ 127.96(C_q), δ 20.34 (CH_3). mp. 122-124°C, lit. 123-124°C^[116]. Yield: 87%. ^1H NMR (2,4,6-Trimethylbenzenetrithiol): δ 2.56(s, 9H), δ 3.29(s, 3H). ^{13}C NMR: δ 133.64(C_q), δ 129.61(C_q), δ 21.89(CH_3). Mass: 216 (100, M^+); mp. 205-208°C. High resolution mass calcd. for $\text{C}_9\text{H}_{12}\text{S}_3$: 216.0101, found: 216.0089. Yield: 78%.

7.3 Experimental Procedures Pertaining to Chapter 4 and 5

7.3.1 Polymeric Content Measurement

Degas Procedure

Sulfur was melted in an oven at 140°C and was maintained at 140°C for 16 h to allow attainment of an equilibrium polymer and radical population. H₂S was bubbled through the liquid for about 30 minutes during which time the temperature of liquid sulfur reached about 185°C. The sulfur was kept at 140-180°C for 30 minutes to allow complete formation of H₂S_x and then was equilibrated to a reaction temperature 140°C. Morpholine (2 drops) was added to the sulfur and, after 5 minutes, the liquid was purged with N₂. FT-IR spectra of liquid samples were taken every 10-15 minutes to check for absorptions due to H-S, H-S_x and C-H, found at 2561 cm⁻¹, 2497 cm⁻¹ and 3000 cm⁻¹ respectively. T = 0 was defined as the time when absorptions due to H₂S and H₂S_x disappeared from the FT-IR spectra.

Procedure for the Polymeric Content Measurement

Elemental sulfur (200 g, degassed or untreated) was melted and the temperature was maintained at 140±2°C. A thiol (0.1 g) was added to the stirred sulfur and the timer was started. Liquid sulfur samples were taken regularly and were quenched in dry ice. The samples were kept in dry ice for 30 minutes before they were allowed to warm to 20°C. After 30 minutes at 20°C, the sulfur was ground to 10 mesh with a pestle and mortar. About 2 g (W₁) of ground sulfur sample was transferred to a pre-weighed coarse crucible (W₀). Elemental sulfur was removed from the formed polymer by addition of

CS₂ (~60 mL). The dissolved sulfur was removed by filtration with insoluble polymeric sulfur and polysulfide polymer remaining as a rubbery solid. The crucible, containing the insoluble solid, was weighed (W_2) and the polymeric content (p.c.) was calculated according to:

$$\text{p.c.} = (W_2 - W_0) / W_1 \times 100\%$$

For each experiment, the polymeric content measurements were carried out at least twice and the error was found to be about $\pm 20\%$. Likely, the errors were caused by the reasons discussed in p. 91.

7.3.2 Viscosity Measurement

The temperature of the measuring cup of the Brookfield digital viscometer was maintained at 120°C or 140°C by internal circulation of a thermostatted fluid. Elemental sulfur (~4.0 g) was introduced into the measuring cup and was melted. The rpm of the viscometer was set at 100 in all experiments, which means that viscosity (mPa. s) = reading \times 2.56. The motor was turned on and the initial reading was taken for the pure sulfur. The timer was started when thiols were introduced into the measuring cup. Viscosity readings were taken regularly until stable values were obtained.

7.3.3 Freezing Point Measurement

A series of samples were prepared by dissolving thiols in liquid sulfur at different molar fractions. The mixtures were kept at 140°C overnight for the reactions to go to completion. The sample vials were then transferred into an oil bath pre-heated to 140°C. The heat was removed and the temperature of the oil bath was allowed to drop. The

freezing point of the sulfur-thiol mixtures were taken by immersing a thermocouple in the liquid sulfur connected to a digital temperature read-out. The freezing points were recorded as the temperature at which an inflection was noted in the cooling curve, coupled with visual observations to confirm that solidification had taken place. The samples were then re-melted and the experiment was repeated. The data obtained from the two experiments were found to be $\pm 0.5^\circ\text{C}$.

7.4 Experimental Procedures Pertaining to Chapter 6

7.4.1 Chemicals and Reagents

Toluene was washed with H_2SO_4 (conc.) three times and then with H_2O until the aqueous layer was neutral. It was then dried by CaCl_2 and was distilled (from CaH_2) under argon directly into the reaction flask just before use. THF was heated under reflux with Na/K in the presence of benzophenone until a deep blue solution was obtained. It was then distilled and was transferred into the reaction flask under argon. Et_3N was distilled from CaH_2 under argon. Xylenes, pyridine and $(n\text{-Bu})_3\text{N}$ were obtained from the Aldrich Chemical Company and were used without further purification. $(n\text{-Bu})_3\text{NH}^+\text{HS}^-$ was prepared by saturating 1 M solution of $(n\text{-Bu})_3\text{N}$ in xylenes with H_2S .

7.4.2 Preparation of Linear Polysulfides from 2,5-Dimethyl-1,4-benzenedithiol

2,5-Dimethyl-1,4-benzenedithiol (0.1 g, 0.588 mmol) and sulfur (0.077g, 2.39 mmol - 0.188 g, 5.88 mmol) in THF or toluene (50 mL) was added to the catalyst [either Et_3N : 0.3 μL ($d = 0.726 \text{ g/mL}$), $2.16 \times 10^{-6} \text{ mol}$ or pyridine: 10 μL ($d = 0.978 \text{ g/mL}$),

1.24×10^{-4} mol or $(n\text{-Bu})_3\text{NH}^+\text{HS}^-$: 150 μL , 5.12×10^{-5} mol or Na: 0.027 g, 1.17 mmol]. The reactions were carried out in refluxing toluene under argon when Et_3N and pyridine were used and the reactions were done at 20°C when $(n\text{-Bu})_3\text{NH}^+\text{HS}^-$ was used and at -40°C (acetonitrile/dry ice) when Na was used^[117]. The reaction mixtures were stirred under argon for 18 h. The reaction mixtures (excluding the reaction catalyzed by Na) were concentrated and the polysulfides were precipitated in methanol and were collected as yellow powders. In the case when Na was used, the reaction mixture was warmed up to 20°C and HCl (~5%) was added dropwise to consume excess Na. The reaction mixture was then poured into HCl (5%, ~20 mL) and was extracted with diethyl ether. The diethyl ether layer was washed with water and dried with MgSO_4 . The polysulfides were obtained as pale yellow powders after evaporating off the ether.

7.4.3 Molecular Weight Measurement by VPO

Calibration of Vapor Pressure Osmometer

Consecutively diluted solutions of sucrose octaacetate (wt. 678.6) in toluene were used to determine the K value in eq. 24. A cell temperature of 50°C was used. Initially, both sample and reference syringes were filled with toluene. Exactly the same amount of solution was injected and the reading was taken as V_0 . The toluene in the sample syringe was replaced by sucrose octaacetate solutions with the reference syringe still filled with toluene. Following the same procedure, a series of readings were recorded (V) with different concentrations of sucrose octaacetate solution. $\Delta V/C$ was plotted against C (g/L) ($\Delta V = V - V_0$) and K was calculated as $678.6 \times \text{intercept}$. K was determined to be 4968.62.

Molecular Weight Measurement

A series of toluene solutions of the linear polysulfides made from the reaction of 2,5-dimethyl-1,4-benzenedithiol with elemental sulfur were prepared. The same procedure for the calibration was followed and a plot of $\Delta V/C$ vs. C (g/mL) was obtained. The molecular weight was calculated as $K/\text{intercept}$. For sample (a) and (b), intercepts of 12.79 and 11.56 were obtained respectively and the molecular weights of 390 and 430 were calculated.

CHAPTER EIGHT

CONCLUDING COMMENTS

Work described in this thesis has demonstrated that benzenepolythiols react readily with elemental sulfur and have a very significant effect on the freezing point and viscosity of liquid sulfur. Spectroscopic studies suggest that these changes in physical properties result from the formation of linear and network polysulfides.

Although benzenepolythiols are described extensively in the literature, they are not readily available in large quantities because of the elaborate and expensive methods required for their synthesis. New synthetic methods described herein have allowed a simple and, in some cases, high yield synthesis of benzenepolythiols. The initial C-S bond forming step by reaction of a benzene derivative with DMDS in the presence of a modified mesoporous clay is unusual in that it allows direct substitution of C-H by S in a benzene derivative. This reaction was found to be quite general as long as an electron donating substituent was already present on the benzene ring. Birch reduction of the methylthio-derivatives gave benzenepolythiols in good yield.

Study of the reaction of benzenepolythiols with liquid sulfur was complicated by the presence and formation of polymeric sulfur. When excess sulfur was present, there was clear evidence that very long chain linear and network polymers were formed initially but, most probably, these species equilibrated to shorter chain compounds. In situ spectroscopic measurements gave only limited information regarding the degree of

polymerization. Characterization of linear and network polymers made by reaction of benzenepolythiols with elemental sulfur in organic solvents showed that individual chain lengths were in the order of 2 - 4 sulfur atoms. Raman spectroscopy was particularly useful in identifying di, tri- and tetrasulfide linkages. One of the limitations of synthesizing the polymers in organic solvents was that the polymers precipitated from solution during the reaction. Thus, it could not be determined whether longer chain polysulfides were simply unstable or too insoluble to be formed.

Some information on linear and network polymer stability was ascertained by studying polymer stability in solid sulfur recovered from the reaction of a benzenepolythiol with liquid sulfur. In general, it was found that the polymers did decompose over time but that they were more stable than when present in the liquid state.

The use of benzenepolythiols to inhibit sulfur deposition in sour gas wellstrings and flowlines may be feasible as rates of reaction and changes in physical properties seem to be sufficient to meet the constraints of an industrial system, particularly with respect to the degree of freezing point depression that could be achieved. A major constraint in their use would be the economics of benzenepolythiol synthesis, despite the simpler and lower cost methods described in this thesis. Another application of the freezing point depression attainable by reaction of elemental sulfur with benzenepolythiols would be in transportation of liquid sulfur by rail and by ship. In particular, very large savings could be achieved by ship transportation of liquid sulfur if the cargo needed to be maintained only in the 70 - 80°C range instead of temperatures in excess of 130°C. A large part of

the energy saving derives from not having to re-melt the sulfur in the cases where solid sulfur is transported.

APPENDIX

I. X-ray Structure Report for $\text{C}_4\text{H}_{10}\text{S}_2\text{Cl}_2\text{Zn}$

A. Crystal Data

Empirical Formula	$\text{C}_4\text{H}_{10}\text{S}_2\text{Cl}_2\text{Zn}$
Formula Weight	258.53
Crystal Color, Habit	colourless, prism
Crystal Dimensions	0.35×0.26×0.15 mm
Crystal System	monoclinic
Cell Determination (2θ range)	25 (18.5 - 23.3°)
Omega Scan Peak Width at Half-height	0.28°
Lattice Parameters	$a=7.311(1) \text{ \AA}$ $b=17.553(2) \text{ \AA}$ $c=7.784(2) \text{ \AA}$ $\beta=104.98(1)^\circ$ $V=964.9(3) \text{ \AA}^3$
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.779 g/cm ³
F_{000}	520.00
μ (MoK α)	34.54 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku AFC6S
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$) graphite monochromated
Temperature	-103.0°C
Scan Type	ω -2 θ

Scan Rate	8.0°/min (in ω) (up to 4 scans)
Scan Width	$(1.26 + 0.34 \tan \theta)^\circ$
$2\theta_{\max}$	50.1°
No. of Reflections Measured	Total: 1923 Unique: 1784 ($R_{int} = 0.042$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.7800 - 1.0000) Decay (4.94%)

C. Structure Solution and Refinement

Structure Solution	Direct Method (SAPI91)
Refinement	Full-matrix least-squares
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00\sigma(I)$)	1096
No. Variables	82
Reflection / Parameter Ratio	13.37
Residuals: R; R_w	0.032; 0.031
Goodness of Fit Indicator	1.56
Max Shift / Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	$0.37 e^-/\text{\AA}^3$
Minumum peak in Final Diff. Map	$-0.47 e^-/\text{\AA}^3$

D. Atomic coordinates and B_{eq}

atom	x	y	z	B_{eq}
Zn(1)	0.4930(1)	0.1075(1)	0.1448(1)	1.98(2)
Cl(1)	0.7028(2)	0.0145(1)	0.2143(2)	2.51(4)
Cl(2)	0.4903(2)	0.1914(1)	-0.0661(2)	2.91(4)
S(1)	0.5220(2)	0.1812(1)	0.4194(2)	2.17(4)
S(2)	0.1812(2)	0.0677(1)	0.1483(2)	1.79(3)
C(1)	0.4519(9)	0.2764(4)	0.3388(8)	2.7(2)
C(2)	0.3099(8)	0.1453(3)	0.4740(7)	2.0(1)
C(3)	0.1407(8)	0.1322(4)	0.3158(7)	2.1(1)
C(4)	0.2174(9)	-0.0218(4)	0.2655(9)	2.5(2)
H(1)	0.5538	0.3006	0.3054	3.1847
H(2)	0.3455	0.2735	0.2381	3.1847
H(3)	0.4190	0.3051	0.4297	3.1847
H(4)	0.3409	0.0983	0.5345	2.3856
H(5)	0.2739	0.1812	0.5505	2.3856
H(6)	0.1036	0.1801	0.2609	2.5164
H(7)	0.0407	0.1121	0.3595	2.5164
H(8)	0.1081	-0.0343	0.3040	3.0486
H(9)	0.2400	-0.0608	0.1883	3.0486
H(10)	0.3237	-0.0180	0.3656	3.0486

E. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	0.0242(4)	0.0270(4)	0.0265(4)	0.0010(4)	0.0109(3)	0.0032(4)
Cl(1)	0.0267(8)	0.035(1)	0.0349(9)	0.0070(7)	0.0099(7)	0.0012(8)
Cl(2)	0.049(1)	0.034(1)	0.0282(9)	-0.0124(9)	0.0120(8)	0.0052(8)
S(1)	0.0251(9)	0.029(1)	0.0243(8)	-0.0001(7)	-0.0006(7)	-0.0023(7)
S(2)	0.0222(8)	0.0235(9)	0.0220(8)	-0.0012(7)	0.0052(6)	-0.0020(7)
C(1)	0.037(4)	0.026(4)	0.038(4)	-0.002(3)	0.009(3)	-0.005(3)
C(2)	0.034(4)	0.022(4)	0.023(3)	0.000(3)	0.011(3)	-0.002(3)
C(3)	0.027(3)	0.031(4)	0.025(3)	-0.002(3)	0.010(3)	-0.005(3)
C(4)	0.033(4)	0.024(4)	0.039(4)	0.001(3)	0.009(3)	0.002(3)

II. Table of Results Pertaining to Chapters 4 and 5

Polymeric Content Measurement of Liquid Sulfur (200 g) with
1,4-Benzenedithiol (0.1 g, 0.70 mmol) at 140°C (Scheme 53)

Time (minutes)	Polymeric Content (%)
10	4.8
20	5.4
30	5.9
40	3.7
50	4.4
60	3.7
80	5.6
120	6.0
140	8.2
215	6.1
320	10.9
235	6.8
370	10.6
1320	10.4

Polymeric Content Measurement of Liquid Sulfur (200 g) with
2,5-Dimethy-1,4-benzenedithiol (0.1 g, 0.59 mmol) at 140°C (Scheme 56)

Time (minutes)	Polymeric Content (%)
0	4.8
2	6.3
5	6.7
20	9.0
40	9.0
180	8.8
300	8.4
600	8.5

Polymeric Content Measurement of Liquid Sulfur (un-degassed, 200 g) with
1,3,5-Benzenetrithiol (0.1 g, 0.575 mmol) at 140°C (Scheme 59)

Time (minutes)	Polymeric Content (%)
10	4.4
20	7.1
30	6.2
40	5.9
50	9.0
60	8.1
80	9.3
130	8.7
160	7.8
210	6.8
260	5.1
405	5.6

Polymeric Content Measurement of Liquid Sulfur (degassed, 200 g) with
1,3,5-Benzenetrithiol (0.1 g, 0.575 mmol) at 140°C (Scheme 60)

Time (minutes)	Polymeric Content (%)
0	3.5
15	8.0
30	8.9
45	9.3
60	7.8
180	8.0
1320	6.6

Polymeric Content in Liquid Sulfur with 1,3,5-Benzenetrithiol
after 18 h of Reaction at 140°C (Scheme 61)

Aging Time (h)	Polymeric Content (%)	
	Quenched at 20°C	Quenched in dry ice (T=-78°C)
1.5	5.3	5.4
4	5.1	5.8
7	5.1	5.4
25	5.2	4.9
31	5.1	4.7
127	4.6	4.9
223	4.1	4.2
460	3.9	3.8

Polymeric Content in Liquid Sulfur with 1,3,5-Benzenetrithiol
after 1.5 h of Reaction at 140°C (Scheme 62)

Aging Time (h)	Polymeric Content (%)	
	Quenched at 20°C.	Quenched in dry ice (T=-78°C)
1	9.2	9.2
5	7.9	8.0
19	7.5	6.3
26	5.4	5.2
44	4.7	
49		4.3
127	4.1	4.8
223	3.5	3.7

Polymeric Content in Liquid Sulfur (200 g) with
2,4,6-Trimethylbenzenetrithiol (0.1 g, 0.463 mmol) at 140°C (Scheme 65)

Time (minutes)	Polymeric Content (%)
0	4.8
2	5.2
10	7.5
40	7.8
60	8.8
120	9.9
152	7.8
180	6.2
244	6.6
440	6.0
1165	6.1

Viscosity Measurement of Liquid Sulfur (4.1 g) with
1,4-Benzenedithiol (0.1 g, 0.70 mmol) at 120°C (Scheme 54)

Reaction Time (minutes)	Viscosity (mPa. s)
0	10.24
1	11.01
2	11.52
7	12.29
11	13.06
19	13.57
60	16.38
120	17.15
220	17.49
427	19.20
900	19.20

Viscosity Measurement of Liquid Sulfur (4.0 g.) with
2,5-Dimethyl-1,4-benzenedithiol (0.12 g, 0.71 mmol) at 120°C (Scheme 57)

Reaction Time (minutes)	Viscosity (mPa. s)
5	11.26
10	13.82
15	15.87
20	16.90
25	17.92
30	18.94
35	19.46
40	19.97
45	20.22
50	20.74
55	20.99
60	21.25
80	21.76
100	22.27
120	23.04
240	23.55
280	24.06
300	24.32
330	24.83
570	26.11
1000	29.79
1320	30.98
1680	30.98

Viscosity Measurement of Liquid Sulfur (4.0 g.) with
1,3,5-Benzenetrithiol (0.01 g, 0.058 mmol) at 140°C (Scheme 63)

Reaction Time (minutes)	Viscosity (mPa. s)
2	7.94
5	8.19
7	8.45
10	8.70
13	9.22
14.5	9.47
17.5	9.73
21	9.98
25	10.24
32	10.50
40	10.75
60	10.75
90	10.50
180	10.24
360	9.98
540	9.73
720	9.73

Viscosity Measurement of Liquid Sulfur (4.0 g.) with
2,4,6-Trimethylbenzenetrithiol (0.01 g, 0.046 mmol) at 140°C (Scheme 67)

Reaction Time (minutes)	Viscosity (mPa. s)
1.5	9.98
2	10.50
3	11.01
3.5	11.26
4	11.52
5	12.03
5.5	12.29
6.5	12.54
8	12.80
9	13.06
10.5	13.31
17	13.57
50	13.82
90	13.82
120	13.70
160	13.57

Freezing Point of Sulfur with 1,4-Benzenedithiol (Scheme 55)

Molar Fraction ($\times 10^{-3}$)	Measured Freezing Point (°C)	Calculated Freezing Point (°C)
1.32	92.5	113.16
2.01	83.7	112.45
2.30	80.5	112.06
2.93	82.8	111.52
4.29	78.5	110.13
4.94	70.1	109.47

Freezing Point of Sulfur with 2,5-Dimethyl-1,4-benzenedithiol (Scheme 58)

Molar Fraction ($\times 10^{-3}$)	Measured Freezing Point ($^{\circ}\text{C}$)	Calculated Freezing Point ($^{\circ}\text{C}$)
0.571	91.5	113.92
1.18	81.7	113.30
1.82	78.4	112.65
2.14	74.1	112.32
3.00	72.5	111.44
3.74	71.5	110.72

Freezing Point of Sulfur with 1,3,5-Benzenetrithiol (Scheme 64)

Molar Fraction ($\times 10^{-3}$)	Measured Freezing Point ($^{\circ}\text{C}$)		Calculated Freezing Point ($^{\circ}\text{C}$)
	With Agitation	Without Agitation	
1.01	-	76	113.47
1.48	86.3	-	-
1.72	-	69	112.75
1.89	72.3	-	-
2.04	-	61	112.43
2.11	68.8	-	-
2.31	-	59	112.15
2.62	67.4	-	-
3.39	-	25	111.05
5.9	-	25	108.49

Freezing Point of Sulfur with 2,4,6-Trimethylbenzenetrithiol (Scheme 68)

Molar Fraction ($\times 10^{-3}$)	Measured Freezing Point ($^{\circ}\text{C}$)	Calculated Freezing Point ($^{\circ}\text{C}$)
0.561	100.3	113.93
1.08	91.3	113.40
1.83	84.5	112.64
2.53	79.6	111.92
2.77	69.2	111.68
3.38	59.7	111.06

III. Table of Results Pertaining to Chapters 6

Elemental Analysis of Linear Polysulfides from the Reaction of 2,5-Dimethyl-1,4-benzenedithiol with sulfur (Table 16)

Sample	C (%)	H (%)
(a)	43.56	3.51
(c)	43.42	2.93
(d)	42.74	2.89
(e)	43.40	3.76

Elemental Analysis of Network Polysulfides from the Reaction of 2,4,6-Trimethylbenzenetrithiol with sulfur (Table 19)

Sample	C (%)	H(%)
(h)	40.34	3.55
(g)	38.51	2.99
(j)	39.08	3.13
(k)	38.40	3.39
(l)	38.72	3.13
(m)	38.17	3.66
(n)	38.26	3.17
(f)	38.42	2.71
(o)	37.18	3.22

REFERENCES

1. J. B. Hyne and G. D. Derdall, *How to handle sulfur deposited by sour gas*, World Oil, Oct. 1980, p111.
2. J. B. Hyne, *Super Sour Gas: A New Sulfur Source for Exploitation*, preprint; Sulfur 87 International Conference, Houston TX 1987; pp.25
3. U. S. Patent 3,531,600, Sept. 29, 1970. H. B. Fisher to Phillips Petroleum Company, "Production of Sour Gas-Sulfur Wells Employing a Sulfur Solvent."
4. J. B. Hyne, *Alberta Sulphur Res. Ltd. (ASRL) Q. Bull.*, **3**, 15 (1966)
5. J. B. Hyne, C. S. C. Lau, N. I. Dowling, P. Davis and K. L. Lesage, *Alberta Sulphur Res. Ltd. (ASRL) Q. Bull.*, **22**, 25 (1985)
6. U. S. Patent 4,033,410. July 5, 1977. D. Kauffman to Shell Oil Company, "Monoethanolamine Process for Sulfur Removal from Circulating Oil used in Sour Gas Wells"
7. H. Ockelmann and F. E. Blount, "Ten Years Production Experience with Sour Gas Production in Germany" Proceedings of the 48th Annual Fall meeting of Society of Petroleum Engineers of AIME, Las Vegas, Sept. 30, 1973, Paper No. SPE 4663
8. S. P. Sharp and L. F. Sudduth, US Patent 3,846,311, Sep. 07 1971 "Methods for Removing Elemental Sulphur from Wells and Flowlines"
9. D. Macdonald, *Alberta Sulphur Res. Ltd. (ASRL) Q. Bull.*, **11**, 28 (1974-1975)
10. P. D. Clark; K. L. Lesage and J. B. Hyne, *Alberta Sulphur Res. Ltd. Q. Bull.*, **20**, 1-11 (1984)

11. P. D. Clark and K. L. Lesage, *Alberta Sulphur Res. Ltd. Q. Bull.*, **18**, 44 (1982)
12. N. I. Dowling, K. L. Lesage and J. B. Hyne, *Alberta Sulphur Res. Ltd. Q. Bull.*, **21**, Nos. 3-4, 30 (1984-5)
13. P. D. Clark, K. L. Lesage and J. B. Hyne, *Alberta Sulphur Res. Ltd. Q. Bull.*, **19**, 63 (1983)
14. P. D. Clark, K. L. Lesage and P. Sarkar, *Energy & Fuels*, **3**, 315 (1989)
15. T. L. Pickering and A. V. Tolbosky, *Inorganic and Organic Polysulfides* in "Sulfur Organic and Inorganic Chemistry", (S. Senning Ed.) Vol. **111**, Marcell Dekker, New York (1972), pp.19
16. L. Field, *Disulfides and Polysulfides*, in "Organic Chemistry of Sulfur", (S. Oae Ed.) Plenum Press (1977), pp. 303
17. G. F. Bloomfield, *J. Chem. Soc., Part 2*, 1547 (1947)
18. T. L. Pickering, K. J. Saunder and A. V. Tobolsky, *Cleavage and Disproportionation Reaction of Organic Polysulfides*, in "The Chemistry of Sulfides", Interscience, New York (1968), pp. 61
19. T. L. Pickering, K. J. Saunder and A. V. Tobolsky, *J. Am. Chem. Soc.*, **89**, 2364 (1967)
20. T. Hirabayashi, S. Mohamad and H. Böck, *Chem. Ber.*, **115**, 483 (1982)
21. E. H. Farmer and F. W. Shipley, *J. Chem. Soc. Part 2*, 1519 (1947)
22. C. O. Oriakhi, "Thermal Decomposition of Organic Polysulfanes" M.Sc. Thesis, University of Calgary, 1991
23. D. M. Giolands and K. Kirschbaum; *Synth.*, 451 (1992)

24. L. Testaferri, M. Tingoli and M. Tiecco; *J. Org. Chem.*, **45**, 4376 (1980)
25. F. Maiolo, L. Testaferri, M. Tiecco and M. Tingoli; *J. Org. Chem.*, **46**, 3070 (1981)
26. S. Hunig and E. Fleckenstein, *Justus Liebigs Ann. Chem.*, **738** 192 (1970)
27. P. D. Clark, S. T. E. Mesher, A. Primak, *Phosphorus, Sulfur and Silicon*, **114**, 99 (1996)
28. P. D. Clark, S. T. E. Mesher, A. Primak and H. Yao, *Catal. Lett.* **48**, 79 (1997)
29. P. Laszlo; *Science*, 1474 (March 1987)
30. C. Pesquera, F. Gonzalez, I. Benito, C. Blanco, S. Mendioroz and J. Pajones; *J. Mol. Chem.*, **2**, 907 (1992)
31. J. P. Butrille and T. J. Pinnavaia; *Catal. Today*, **14**, 141 (1992)
32. J. H. Clark, S. R. Cullen, S. J. Barlow and T. W. Bastock; *J. Chem. Soc. Perkin Trans. 2*, 1117 (1994)
33. B. E. M. Hassan, E. A. Sultan, F. M. Tawfik and S. M. Sappah; *Egypt J. Chem.*, **28**, 93 (1985)
34. P. Laszlo and A. Mathy; *Helv. Chim. Acta.*, **70**, 577 (1987)
35. J. H. Clark, A. P. Kybett, D. J. Macquarrie, S. J. Barlow and P. Landon; *J. Chem. Soc., Chem. Commun.*, 1353 (1989)
36. J. H. Clark, S. R. Cullen, S. J. Barlow and T. W. Bastock; *J. Chem. Soc. Perkin Trans. 2*, 411 (1994)
37. F. Krachenbuhl, W. I. Stoeckli, J. Brunner, G. Kahr and M. Mueller-Von Mous, *Clay Miner.*, **32**, 1 (1989)
38. G. P. Parry; *J. Catal.*, **2**, 371 (1963)

39. T. W. Bastock and J. H. Clark, in "*Speciality Chemicals*". ed. B. Pearson, Elsevier, London, 1992
40. A. Cornelis, P. Laszlo and S. Wang; *Tetrahedron Lett.*, **34**, 3849 (1993)
41. P. Laszlo and J. Lucchetti; *Tetrahedron Lett.*, **25**, 1567 (1984)
42. P. Laszlo and J. Lucchetti; *Tetrahedron Lett.*, **25**, 2147 (1984)
43. P. Laszlo and J. Lucchetti; *Tetrahedron Lett.*, **25**, 4387 (1984)
44. W. G. Dauben and H. O. Krabbenhoft; *J. Am. Chem. Soc.*, **98**, 1992 (1976)
45. H. Kotsuki, H. Noshizawa, M. Ochi and K. Matsuoka; *Bull. Chem. Soc. Japan*, **55**, 496 (1982)
46. P. Laszlo, M. Montaufier and S. L. Randriamahefa; *Tetrahedron Lett.*, **34**, 4867 (1990)
47. S. Hoyer, P. Laszlo, M. Orlovic and E. Polla; *Synth.*, 655 (1986)
48. A. Ballantine, W. Jones, J. H. Purnell, D. T. B. Tennakoon and J. M. Thomas, *Chem. Lett.*, 763 (1985)
49. A. Ballantine, M. Davies, R. M. O'Neil, I. Patel, J. H. Purnell, K. J. Williams and J. M. Thomas, *J. Mol. Catal.*, **26**, 57 (1984)
50. A. Ballantine, M. Davies, J. H. Purnell, M. Payanakoon, J. M. Thomas and K. J. Williams, *J. Chem. Soc. Chem. Commun.*, 8 (1981)
51. H. Solisarkova and S. Micik, *Conf. Clay Mineral Petrol.*, (Proc.), 67 (1984)
52. Mitsui Petroleum Industries, *Japan Kokai Tokyo Toho*, JP 60,025,946 (1985)
53. J. M. Adams, S. E. Davies, S. H. Graham and J. M. Thomas, *J. Catal.*, **78**, 197 (1982)

54. S. Hunig, E. Benzing and E. Lucke, *Chem. Ber.*, **95**, 926 (1962)
55. T. Vu Boc, H. Petit and P. Mactti, *Bull. Soc. Chim. Belg.*, **15**, 264 (1979)
56. A. Cornélis, P. Laszlo and P. Pennetreau, *Bull. Soc. Chim. Belg.*, **93**, 961 (1984)
57. H. Werbin and C. J. Holoway, *J. Biol. Chem.*, **223**, 651 (1956)
58. A. Cornélis, P. Laszlo and P. Pennetreau, *J. Org. Chem.*, **48**, 4771 (1983)
59. A. Cornélis and P. Laszlo, *Synth.*, 849 (1980)
60. A. Cornélis, N. Depaye, A. Gerstmans and P. Laszlo, *Tetrahedron Lett.*, **24**, 3103 (1983)
61. M. Balogh, A. Cornélis and P. Laszlo, *Tetrahedron Lett.*, **25**, 3313 (1984)
62. P. Laszlo and E. Polla, *Tetrahedron Lett.*, **25**, 3309 (1984)
63. S. Chalais, A. Cornélis, P. Laszlo and A. Mathy, *Tetrahedron Lett.*, **26**, 2327 (1985)
64. D. E. Vietti, "Polysulfides" in "Comprehensive Polymer Science - The Synthesis, Characterization, Reactions and Applications of Polymers" Vol. 5, Ed. G. Allen and J. C. Bevington, Pergamon Press, 1989
65. C. Lowig and S. Weidman, *Ann. Chem. Pharm.*, **36**, 320 (1840)
66. C. Lowig and S. Weidman, *Pogg. Ann. Physik.*, **49**, 123 (1842)
67. C. Patrick and N. M. Mnookin, *Br. Pat.*, 302 270 (1927) (*Chem. Abstr.*, 1929, **23**, 4307)
68. M. Ellerstein, in "Encyclopedia of Polymer Science and Engineering", ed. J. I. Kroschwitz, Wiley, New York, 1988, vol. 13, p. 186
69. A. V. Tobolsky and W.J. MacKnight, "Polymeric Sulfur and Related Polymers", Wiley, New York, 1965

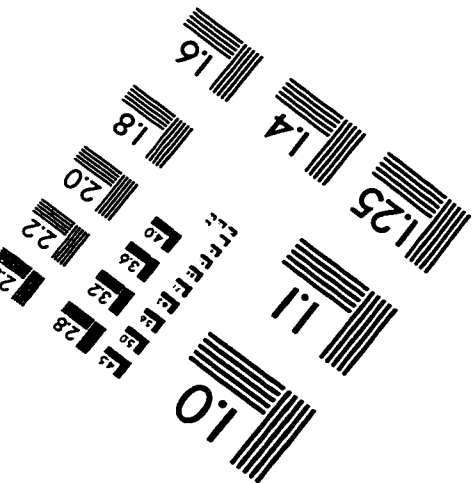
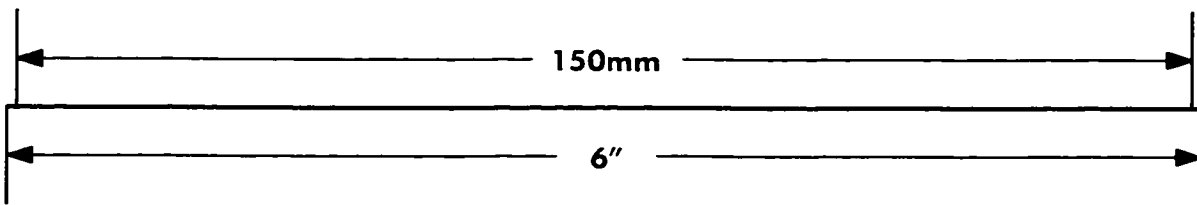
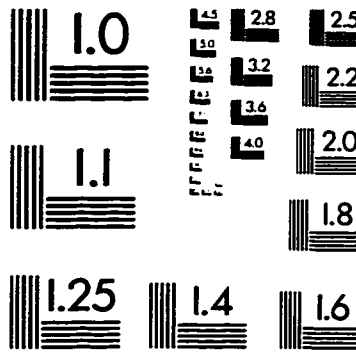
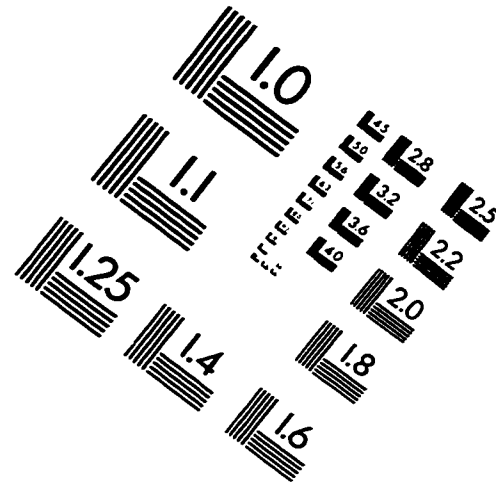
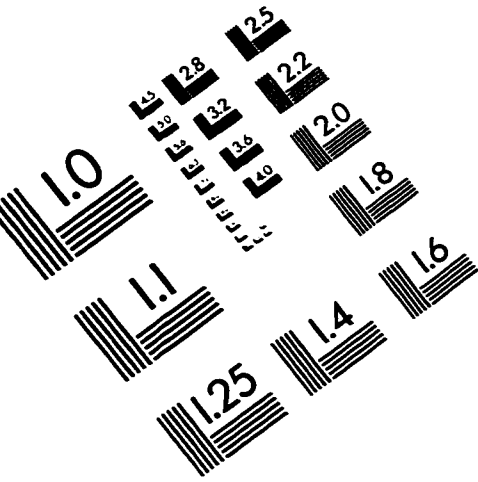
70. J. F. Geibel and R. W. Campbell, "Poly(phenylene sulfide)s" in "Comprehensive Polymer Science - The Synthesis, Characterization, Reactions and Applications of Polymers" Vol. 5, Ed. G. Allen and J. C. Bevington, Pergamon Press, 1989
71. C. Friedel and J. M. Crafts, *Ann. Chim. Phys.*, **14(6)**, 433 (1888)
72. J. W. Cleary, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **25(2)**, 36, (1984)
73. A. D. Macallum, *J. Org. Chem.*, **13**, 154 (1948)
74. R. W. Lenz and C. E. Handlovits, *J. Polym. Sci.*, **43**, 167 (1960)
75. R. W. Lenz, C. E. Handlovits and H. A. Smith, *J. Polym. Sci.*, **58**, 351 (1962)
76. H. A. Smith and C. E. Handlovits, ASD-TDR-62-372, Report on Conference on High Temperature Polymer and Fluid Research, Dayton, Ohio, 1962, p. 123
77. T. Edmonds, Jr. & H. W. Hill, Jr. (Phillips Petroleum Co.), *US Pat.* 3 354 129 (1967) (*Chem. Abstr.*, 1951, **45**, 5193c)
78. W. Koch and W. Heitz, *Makromol. Chem.*, **184**, 779 (1983)
79. R. W. Campbell, U.S. Patent 3,919,177 to Phillips Petroleum Company (November 1975).
80. G. Kraus and W. M. Whitte, *28th Macromolecular Symposium of the IUPAC*, Amherst, MA, July 12, 1982
81. C. J. Stacy, *J. Appl. Polym. Sci.*, **32**, 3959 (1986)
82. M. Richardson, "Thermal Analysis" in "Comprehensive Polymer Science - The Synthesis, Characterization, Reactions and Applications of Polymers" Vol. 1, Ed. G. Allen and J. C. Bevington, Pergamon Press, 1989
83. S. K. Freeman, in "Application of Laser Raman Spectroscopy" John Wiley & Sons, New York (1974), pp. 202

84. S. G. Frandiss, *J. Mol. Str.*, **3**, 89 (1969)
85. S. K. Freeman and D. W. Mayo, Paper Presented at the Eastern Analytical Symposium, Atlantic City, N. J., November 1972
86. W. Reifschneider, U. S. Patent #3,399,239 (1968)
87. J. L. Reddinger and J. R. Reynolds, *J. Org. Chem.*, **61**, 4833 (1996)
88. W. Truce and D. P. Tate, *Abstracts of papers, 132nd Meeting, Am. Chem. Soc.*, September, 1957, p. 43
89. T. K. Wiewiorowski and F. J. Touro, *J. Phys. Chem.*, **70**, 234 (1966)
90. A. Kirk, "Mesoporous Supports for the Catalysis of Friedel-Crafts Alkylation and Cyclalkylation Reactions with Sulfur-Containing Aromatics" Ph.D Thesis, University of Calgary, 1997
91. T. Cseri, S. Bekassy, F. Figueras, E. Cseke, L. Menorval and R. Dutartre., *Appl. Catal. A: General*, **132**, 141 (1995)
92. E. Lippmaa, M. Magi, A. Samoson, M. Tarmak, G. Engelhardt, *J. Am. Chem. Soc.*, **103**, 4992 (1981)
93. J. Klinowski, *Progr. NMR Spectrosc.*, **16**, 237 (1984)
94. E. Lippmaa, M. Magi, A. Samoson, G. Engelhardt and A. R. Grimmer, *J. Am. Chem. Soc.*, **102**, 4889 (1980)
95. M. Magi, E. Lippmaa, A. Samonson, G. Engelhardt and A. R. Grimmer, *J. Phys. Chem.*, **88**, 1518 (1984)
96. G. Engelhardt and D. Michel, "High Resolution Solid States NMR of Silicates and Zeolites", Wiley, Chichester, 1987

97. J. M. Thomas, *Proc. Int. Congr. Catal., 8th. Berlin*, **1**, 31 (1984)
98. C. Cativiela, F. Figueras, J. M. Fraile, J. I. Garcia, J. A. Mayoral, L. C. De Menoroal and E. Pires, *Appl. Catal. A*, **101**, 253 (1993)
99. N. Müller, *J. Prakt. Chem.*, **2(4)**, 39 (1871)
100. H. Wuyts, *Bull. Soc. Chim. France*, **4(5)**, 405 (1909)
101. A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.*, **81**, 780 (1959)
102. D. M. Gardner and G. K. Fraendel, *J. Am. Chem. Soc.*, **78**, 3279 (1956)
103. J. E. Van Aken, *Physika*, **39**, 107 (1968)
104. D. C. Koningsberger and T. De Neef, *Chem. Phys. Lett.*, **4**, 615 (1970)
105. J. A. Poulis, C. H. Massen and P. Leeden, *Trans. Faraday Soc.*, **58**, 474 (1962)
106. F. Fairbrother, G. Gee and G. Merrall, *J. Polymer Sci.*, **16**, 459 (1955)
107. P. D. Clark, K. L. Lesage, T. McDonald, A. Mason and A. K. Neufeld, *Alberta Sulphur Res. Ltd. (ASRL) Q. Bull.*, **31**, 23 (1994)
108. P. A. Lovell, "Dilute Solution Viscometry" in "Comprehensive Polymer Science - The Synthesis, Characterization, Reactions and Applications of Polymers" Vol. 1, Ed. G. Allen and J. C. Bevington, Pergamon Press, 1989
109. R. Fanelli, *Ind. Eng. Chem.* **38**, 38 (1946)
110. M. Dale and A. C. Ludwig, "Elemental Sulfur, Chemistry and Physics", B. Meyer, Ed., Chapter 8, p. 161, Interscience (1965)
111. C. M. Suter and H. L. Hansen, *J. Am. Chem. Soc.* **54**, 4100 (1932)
112. A. Alemagna, P. Cremonesi, P. Del Buttero, E. Licandro and S. Maiorana, *J. Org. Chem.* **48**, 3114 (1983)

113. J. K. Bosscher, E. W. A. Kraak and H. Kloosterziel, *Chem. Comm.* 1365 (1971)
114. U.S. Patent: 2,923,-743 Feb, 2 1960
115. G. Illuminati, *J. Am. Chem. Soc.* **80**, 4945 (1958)
116. P. Beimling and G. Kobmehl, *Chem. Ber.* **119(10)**, 3198 (1986)
117. J. M. Catala and M. Clauss, *Macromolecules*, **24**, 2663 (1991)
118. R. Mokaya and M. Jones, *J. Catal.*, **153**, 76 (1995)

IMAGE EVALUATION TEST TARGET (QA-3)



APPLIED IMAGE, Inc.
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989

© 1993, Applied Image, Inc., All Rights Reserved

