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SYNTHESIS AND CHARACTERIZATION OF
HEAD-TO-HEAD POLYISOBUTYLENE AND
RELATED POLYMERS

A Dissertation Presented

By

MICHAEL THOMAS MALANGA

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

September 1982

Polymer Science and Engineering

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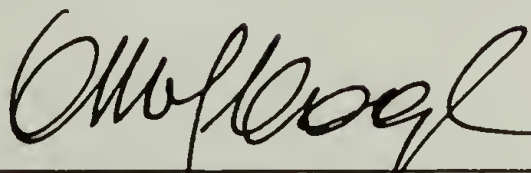
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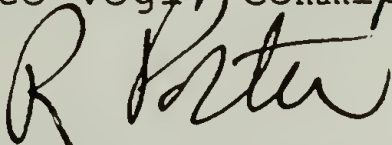
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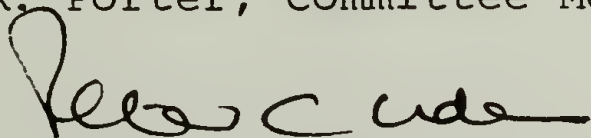
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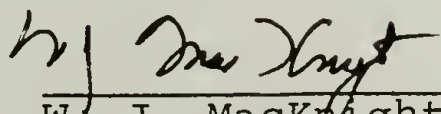
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To Patti

For the life of love and companionship
past, present and future

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The author must thank Professor Otto Vogl for everything he has done through the years. I can hope only to bring a small part of his influence with me wherever I go. I would also like to thank Professor Roger Porter and Professor Peter Uden for the time and effort they put forth while serving on my committee.

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ABSTRACT

Synthesis and Characterization of Head-to-Head Polyisobutylene and Related Polymers

September, 1982

Michael Malanga, B.S., University of Vermont

M.S., Ph.D., University of Massachusetts

Directed by: Professor Otto Vogl

Head-to-head (H-H) polyisobutylene was prepared by a Grignard/alkylbromide coupling polymerization using 2,2,3,3-tetramethyl-1,4-dibromobutane as the monomer. The coupling polymerization was carried out at -5 to -10°C in a mixture of benzene and tetrahydrofuran solvent using copper (I) salts as catalysts. The H-H polyisobutylene obtained was found to have bromine end groups and number-average molecular weights of 3,000 to 10,000.

The polymer showed interesting crystalline and thermal properties especially in comparison to head-to-tail (H-T) polyisobutylene. H-H polyisobutylene was found to be approximately 50% crystalline under normal conditions, with a melting point of 185-189°C and a glass transition at 85°C. H-H polyisobutylene thermally degrades at 315°C which is some 65°C lower than H-T polyisobutylene

under inert atmosphere. Initial studies show that the bond between the two quaternary carbons of the H-H link is the first to break.

Blending of the H-H and H-T polyisobutylene was found to yield a two-phase incompatible system as determined by DSC studies.

Poly(1,1-dimethylpropane) was prepared from 2,2-dimethyl-1,3-dibromopropane by a sodium Wurtz polymerization. The Grignard/alkylbromide coupling polymerization was determined to be ineffective for this dibromide. The polymer obtained had a glass transition temperature of -17°C and melted between 70 and 90°C . The thermal properties of poly(1,1-dimethylpropane) were compared to those of H-H and H-T polyisobutylene and found to be intermediate between the two.

The copolymerization of 3,4-dimethyltetrahydrofuran with selected cyclic ethers was also studied. It was found that although 3,4-dimethyltetrahydrofuran did not homopolymerize under the conditions used in this study, it did readily copolymerize with propylene oxide and epichlorohydrin. The initiator used was PF_5 and 1:1 copolymers of 3,4-dimethyltetrahydrofuran and either epoxide were obtained.

The reactivity ratios for the copolymerization of 3,4-dimethyltetrahydrofuran and epichlorohydrin were found

to be $r_1 = 0.22 \pm 0.05$ and $r_2 = 0.11 \pm 0.01$ respectively.
This gave strong indication of an alternating copolymer.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	v
ABSTRACT	vi
LIST OF TABLES	xix
LIST OF FIGURES	xxi
Chapter	
I. INTRODUCTION	1
A. Synthesis and Characterization of Head-to-Head Polyisobutylene	1
1. Objectives	1
2. Historical Development of Head-to-Head vs. Head-to- Tail Structure in Polymers	4
a. Head-to-head links in polymers	4
b. Methods developed for preparing head-to-head polymers	12
i. Alternating copolymerizations	13
ii. Halogenation of 1,4- polybutadienes	14
iii. Hydrogenation of sub- stituted 1,4-poly- butadienes	16
iv. Coupling polymeriza- tion of properly substituted monomers	18
c. Physical properties of head- to-head polymers and compari- son to head-to-tail	20
3. Coupling Reactions and Their Use in Polymerization	28
a. Wurtz coupling	28
b. Grignard reagent coupling with alkylhalides	32
4. Polymer Hydrogenation	39

a.	Catalytic hydrogenation of polymers	39
b.	Chemical hydrogenation of polymers	42
B.	Synthesis of Poly(1,1-dimethylpropane)	45
1.	Objectives	45
2.	Historical Development of poly(1,1-dimethylpropane)	46
a.	Low temperature, cationic polymerization of 3- methylbutene-1	46
b.	Cationic polymerization of 1,1-dimethylcyclopropane	48
3.	Physical properties of poly(1,1-dimethylpropane)	48
C.	Copolymerization of 3,4-Dimethyltetra- hydrofuran with Cyclic Ethers	50
1.	Objectives	50
2.	Consideration of Cationic Ring- Opening polymerization of cyclic ethers	51
a.	Mechanism for cationic polymerization of cyclic ethers	51
b.	Initiators for cationic ring-opening polymeriza- tion of cyclic ethers	53
c.	Kinetics and thermodynamics of cationic ring-opening polymerizations for cyclic ethers	55
3.	Cationic Ring-Opening Polymeriza- tions for Substituted Tetrahydro- furans	57

Chapter

II.	EXPERIMENTAL SECTION	61
A.	Materials	61
B.	Purification of Solvents and Reagents	62
C.	Measurements	64
D.	Synthesis of Head-to-Head Polyiso- butylene	67
1.	Monomer Synthesis	67
a.	Diethyl-2,2,3,3-tetra- methylsuccinate	67
b.	2,2,3,3-Tetramethylbutane- diol-1,4	68

c.	2,2,3,3-Tetramethyl- butanediosylate	70
d.	Tetra-n-butylammonium bromide	71
e.	2,2,3,3-Tetramethyl-1,4- dibromobutane	72
f.	2,5-Dimethyl-2,5-dibromo- hexane	73
2.	Head-to-Head Polyisobutylene Preparation Using Wurtz Coupling . .	75
a.	Polymerization of 2,2,3,3- tetramethyl-1,4-dibromobutane with sodium metal in cyclo- hexane	75
b.	In bulk	76
c.	Under vacuum	77
d.	Attempted polymerization of 2,5-dimethyl-2,5-dibromohexane with Wurtz coupling	78
3.	Preparation of Head-to-Head Poly- isobutylene by hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexa- diene)	78
a.	Preparation of 2,5-poly(2,5- dimethyl-2,4-hexadiene)	78
b.	Preparation of cobalt ^{II} /tri- isobutyl aluminum hydrogenation catalyst	80
c.	Preparation of cobalt ^{II} /n- butyl lithium hydrogenation catalyst	81
d.	Attempted hydrogenation of 2,5-poly(2,5-dimethyl-2,4- hexadiene) using cobalt ^{II} /tri- isobutyl aluminum catalyst . .	81
e.	Chemical hydrogenation of 2,5- poly(2,5-dimethyl-2,4-hexa- diene) using diimide	83
i.	in mesitylene	84
ii.	in o-xylene	84
iii.	in p-xylene	84
f.	Chemical hydrogenation of 2,5- poly(2,5-dimethyl-2,4-hexadiene) by repeated addition of diimide	85
g.	Chemical hydrogenation of 2,5- poly(2,5-dimethyl-2,4-hexa- diene by repeated reactions with diimide	86

4.	Attempted Preparation of Head-to-Head Polyisobutylene by Alternating Copolymerization of Ethylene with Tetramethylethylene	87
5.	Preparation of Head-to-Head polyisobutylene using Grignard/Alkylbromide Coupling Polymerization	88
	a. Preparation of $\text{CuBr}(\text{PPh}_3)_3$	88
	b. Polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane via Grignard coupling: benzene/tetrahydrofuran solvent	89
	i. in tetrahydrofuran, room temperature	91
	ii. triethylamine/benzene solvent, 60°C	91
	iii. in tributylamine/benzene, 60°C	91
	iv. in tributylamine/benzene, 60°C, CuCl_2 catalyst	92
	v. in tetrahydrofuran/triethylamine/benzene, -5°C	92
	vi. in triethylamine/benzene, -5°C, CuCl_2 catalyst	92
	c. Grignard polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane at -25°C	94
	d. Recovery of volatile products	95
	e. Attempted polymerization of 2,5-dimethyl-2,5-dibromohexane via Grignard/alkylbromide coupling	97
E.	Synthesis of Poly(1,1-dimethylpropane)	97
	1. Monomer Preparation	97
	a. 2,2-Dimethylpropaneditosylate-1,3	97
	b. 2,2-Dimethyl-1,3-dibromopropane	98
	2. Preparation of Poly(1,1-dimethylpropane) by Wurtz Coupling Polymerization	99
	a. Using sodium metal	99
	b. Second procedure using sodium metal	100

c.	Recovery of volatile products	102
d.	Using sodium metal under vacuum	102
e.	Using sodium/potassium alloy	103
3.	Grignard Polymerization Attempts for 2,2-dimethyl-1,3-dibromopropane	103
a.	In benzene/tetrahydrofuran	
b.	Recovery of volatile products	104
F.	Copolymerization of 3,4-Dimethyltetrahydrofuran with Cyclic ethers	105
1.	Monomer Preparation (DMTHF)	
a.	Diethyl-2,3-dimethylsuccinate	105
b.	2,3-Dimethylbutanediol-1,4	105
c.	3,4-Dimethyltetrahydrofuran	106
2.	Homopolymerization Attempts for 3,4-Dimethyltetrahydrofuran	107
a.	BF ₃ ·etherate initiator	107
b.	PF ₅ initiator	108
c.	AlEt ₃ /H ₂ O initiator	109
d.	AlEt ₃ /AcAc/H ₂ O initiator	110
3.	Copolymerization of 3,4-Dimethyltetrahydrofuran with Cyclic Ethers	111
a.	With THF, BF ₃ ·etherate initiator	111
b.	With THF, PF ₅ initiator	112
c.	With THF, AlEt ₃ /H ₂ O initiator	112
d.	With propylene oxide, PF ₅ initiator	112
e.	With epichlorohydrin, PF ₅ initiator	113
f.	Reactivity ratios for 3,4-dimethyltetrahydrofuran and epichlorohydrin during copolymerization	114

Chapter

III.	RESULTS AND DISCUSSION	116
A.	Synthesis of Head-to-Head Poly- isobutylene	116
1.	Monomer Preparations	116
a.	Preparation of 2,2,3,3- tetramethyl-1,4-dibromo- butane	116
b.	Preparation of 2,5-di- methyl-2,5-dibromohexane	119
2.	Wurtz Polymerization of 2,2,3,3- tetramethyl-1,4-dibromobutane or 2,5-dimethyl-2,5-dibromo- hexane	119
3.	Preparation and Attempted Hy- drogenation of 2,5-poly(2,5- dimethyl-2,4-hexadiene)	130
a.	Polymerization of 2,5- dimethyl-2,4-hexadiene	130
b.	Catalytic hydrogenation attempts for 2,5-poly- (2,5-dimethyl-2,4-hexa- diene)	135
c.	Chemical reduction of 2,5-poly(2,5-dimethyl- 2,4-hexadiene) with diimide	117
d.	Discussion of attempted hydrogenation of 2,5- poly(2,5-dimethyl-2,4- hexadiene)	149
4.	Attempted Alternating Copolymeriza- tion of ethylene with tetramethyl- ene	150
5.	Grignard/Alkylbromide coupling Polymerization of 2,2,3,3-tetra- methyl-1,4-dibromobutane	152
a.	Solvent effects	155
b.	Temperature effects	156
c.	Molecular weight of H-H polyisobutylene	159
d.	Cyclization vs. polymeriza- tion	159
e.	Discussion of Grignard poly- merization	161

B.	Physical Characterization of Head-to-Head Polyisobutylene and Comparison of Head-to-Head and Head-to-Tail Polyisobutylene	165
1.	Spectral analysis	165
a.	Infrared	165
b.	¹ H NMR	169
c.	¹³ C NMR	169
2.	The Crystalline Nature of Head-to-Head Polyisobutylene	177
a.	Wide angle X-ray scattering studies of head-to-head polyisobutylene	178
b.	Differential scanning calorimetry studies of the melting and crystallization for head-to-head polyisobutylene	182
c.	Light microscope examination of crystalline head-to-head polyisobutylene	185
d.	Discussion of the crystallinity of head-to-head polyisobutylene	188
3.	Thermal properties of head-to-head polyisobutylene	192
a.	The T _g of head-to-head polyisobutylene as observed by DSC	192
b.	Thermal degradation of head-to-head polyisobutylene by thermal gravimetric analysis	198
4.	Blending and compatibility of head-to-tail polyisobutylene	208
a.	DSC investigation of blends of H-H and H-T polyisobutylene	208
b.	TGA of H-H and H-T polyisobutylene blends	214
c.	Discussion of the incompatibility of H-H with H-T polyisobutylene	219
5.	Conclusions and Future Work	220
C.	Synthesis and Characterization of Poly(1,1-dimethylpropane)	221
1.	Polymerization of 2,2-dimethyl-1,3-dibromopropane	221

a.	Attempted Grignard polymerization of 2,2-dimethyl-1,3-dibromopropane	221
b.	Wurtz polymerization of 2,2-dimethyl-1,3-dibromopropane	225
2.	Characterization of poly(1,1-dimethylpropane)	227
a.	Spectral analysis of poly(1,1-dimethylpropane)	227
b.	DSC analysis of poly(1,1-dimethylpropane)	228
D.	Copolymerization of 3,4-Dimethyltetrahydrofuran with Cyclic Ethers	235
1.	Preparation of 3,4-dimethyltetrahydrofuran	235
a.	Stereochemistry	238
2.	Homopolymerization attempts of 3,4-dimethyltetrahydrofuran	244
3.	Copolymerization of 3,4-dimethyltetrahydrofuran with substituted epoxides	248
a.	Copolymerization of 3,4-dimethyltetrahydrofuran with epichlorohydrin	248
b.	Copolymerization of 3,4-dimethyltetrahydrofuran with propylene oxide	256
c.	Reactivity ratios for 3,4-dimethyltetrahydrofuran and epichlorohydrin during copolymerization	260
d.	Discussion of copolymerization	263
4.	Conclusions and Future Work	266
REFERENCES	268
APPENDIX A:	IR SPECTRA	279
APPENDIX B:	¹ H NMR SPECTRA	294
APPENDIX C:	¹³ C NMR SPECTRA	304

LIST OF TABLES

1.	Thermal degradation behavior of head-to-head and head-to-tail polymers	21
2.	Glass transition temperatures of head-to-head and head-to-tail polymers	24
3.	Hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexadiene) by repeated additions of diimide . .	86
4.	Hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexadiene) by repeated reactions with diimide	86
5.	Effect of solvent on Grignard/alkylbromide polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane	93
6.	Grignard/alkylbromide polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane. Yield, temperature, η_{inh} and M_n data	96
7.	Copolymerization of 3,4-dimethyltetrahydrofuran with epichlorohydrin	115
8.	Attempted Wurtz polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane or 2,5-dimethyl-2,5-dibromohexane	125
9.	^{13}C NMR chemical shift values for Wurtz polymerized H-H polyisobutylene	127
10.	Catalytic hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexadiene)	136
11.	Hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexadiene) using diimide	142
12.	^{13}C NMR chemical shift values for 50% hydrogenated 2,5-poly(2,5-dimethyl-2,4-hexadiene) . . .	148
13.	Number-average molecular weights and elemental analyses of H-H polyisobutylenes	160
14.	IR peak assignments for H-H and H-T polyisobutylene	168
15.	^{13}C NMR chemical shift values for H-H polyisobutylene	176
16.	Wide angle X-ray scattering data for H-H polyisobutylene	178
17.	Percent crystallinity of H-H polyisobutylene as determined by WAXS	181
18.	Thermal gravimetric analysis data for H-H and H-T polyisobutylene	202
19.	Glass transition data for blends of H-H and H-T polyisobutylene	211
20.	Wurtz polymerization data for 2,2-dimethyl-1,3-dibromopropane	226

21.	Spectral analyses of poly(1,1-	
	¹³ C dimethylpropane)	229
22.	¹³ C NMR chemical shift values for 3,4-	
	dimethyltetrahydrofuran	243
23.	Attempted homopolymerizations of 3,4-	
	dimethyltetrahydrofuran	247
24.	Bulk copolymerization of 3,4-dimethyltetra-	
	hydrofuran with epoxides	249
25.	¹³ C NMR chemical shift data for poly(3,4-	
	dimethyltetrahydrofuran-co-epichbrohydrin) . . .	253
26.	¹³ C NMR chemical shift data for poly(3,4-	
	dimethyltetrahydrofuran-co-propylene oxide) . .	259

LIST OF FIGURES

1.	Catalytic process for the Grignard/alkylbromide coupling reaction as catalyzed by nickel II complexes	36
2.	Preparation of 2,2,3,3-tetramethyl-1,4-dibromobutane	118
3.	^1H NMR and ^{13}C NMR spectra of 2,2,3,3-tetramethyl-1,4-dibromobutane	121
4.	Wurtz coupling polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane and 2,5-dimethyl-2,5-dibromohexane	123
5.	IR spectra of $-\text{CH}_2\text{-Br}$ stretching region for; (a) Wurtz polymer of H-H polyisobutylene (b) Strating 2,2,3,3-tetramethyl-1,4-dibromobutane	128
6.	Branching points for Wurtz polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane to H-H polyisobutylene	132
7.	Polymerization of 2,5-dimethyl-2,4-hexadiene with cationic initiator at low temperature to give trans-2,5-poly(2,5-dimethyl-2,4-hexadiene)	134
8.	IR spectra of gem-dimethyl stretching (A, A') and trans $-\text{CH}=\text{CH}-$ stretching (B, B') absorbances for (a) 2,5-poly(2,5-dimethyl-2,4-hexadiene), (b) partially hydrogenated 2,5-poly(2,5-dimethyl-2,4 hexadiene)	140
9.	Percent hydrogenation vs. time for diimide reduction of 2,5-poly(2,5-dimethyl-2,4-hexadiene) by repeated addition of diimide	144
10.	Percent hydrogenation vs. time for diimide reduction of 2,5-poly(2,5-dimethyl-2,4-hexadiene) by repeated reaction with diimide	146
11.	Preparation of H-H polyisobutylene by Grignard polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane	154
12.	Yield and inherent viscosity vs. temperature for Grignard polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane	158
13.	Polymerization vs. cyclization reaction during Grignard polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane	163

14.	IR spectra for H-H and H-T polyisobutylene	167
15.	^1H NMR spectra of H-H and H-T polyisobutylene . . .	171
16.	^{13}C NMR spectra of H-H and H-T polyisobutylene . . .	173
17.	Off-resonance decoupled ^{13}C NMR spectra for H-H and H-T polyisobutylene	175
18.	WAXS powder diagram for H-H polyisobutylene. Relative intensity vs. diffraction angle	180
19.	DSC scans of H-H polyisobutylene near its crystalline melting point. (a) virgin polymer as precipitated; (b) quenched, re- scanned; (c) annealed at 175°C for 12 hr and rescanned (heating rate 20°/min)	184
20.	Optical light micrograph, between crossed polars, of H-H polyisobutylene (400 X). The sample was melted and cooled at 2°/min through its crystallization	187
21.	Effect of H-H placement of gem-dimethyl groups on bond rotation along the chain backbone of H-H polyisobutylene	191
22.	DSC scan of H-H polyisobutylene (heating rate 20°/min) from 27-207°C. Sample: $\bar{M}_n = 4,000$, melt quenched prior to scan	194
23.	T_g vs scan rate for H-H polyisobutylene as determined by DSC. Sample: $\bar{M}_n = 10,000$	
24.	TGA for; (a) H-H polyisobutylene ($\bar{M}_n = 4,000$); (b) H-T polyisobutylene ($M_w \sim 5,000$). Heating rate of 20°/min, flow rate of 40 ml/min helium	200
25.	G.C. analysis of trapped products from the TGA of; (a) H-T polyisobutylene; (b) H-H polyisobutylene	204
26.	Proposed degradation scheme for H-H polyiso- butylene based on TGA and G.C. data	210
27.	DSC scans for blends of H-H with H-T polyiso- butylene; (a) 100% H-H; (b) 80:20, H-H:H-T; (c) 60:40, H-H:H-T; (d) 40:60, H-H:H-T; (e) 20:80, H-H:H-T; (f) 100% H-T. Scans from -90 to +130°C at 20°/min	213
28.	T_g vs. weight percent H-H polyisobutylene in the blend. ■ 100% H-H; □ 80:20, H-H:H-T; △ 60:40, H-H:H-T; ▲ 40:60, H-H: H-T; ○ 20:80, H-H:H-T; ● 100% H-T -----Experimental Calculated	216
29.	TGA for blends of H-H with H-T polyisobutylene. (a) 80:20, H-H:H-T; (b) 60:40, H-H:H-T; (c) 40:60, H-H:H-T; (d) 20:80, H-H:H-T. Heating rate, 20°/min, flow rate of 40 ml/min helium . . .	218

30.	IR spectra of 1,1-dimethylcyclopropane. (a) As prepared from Grignard coupling of 2,2-dimethyl-1,3-dibromopropane; (b) reproduced from Sadtler Index number 11831	224
31.	DSC scan for poly(1,1-dimethylpropane) from -50 to +100°C. Heating rate 20°/min	232
32.	Structure-property relationship for T _g s of H-T polyisobutylene, poly(1,1-dimethylpropane), and H-H polyisobutylene	234
33.	Preparation of 3,4-dimethyltetrahydrofuran	237
34.	G.C. analysis of 3,4-dimethyltetrahydrofuran showing; (a) cis- and (b) trans-isomers	240
35.	¹³ C NMR spectrum of 3,4-dimethyltetrahydrofuran	242
36.	Ring-closure of erythro and threo 2,3-dimethylbutanediol-1,4 to give cis- and trans-3,4-dimethyltetrahydrofuran	246
37.	¹³ C NMR spectrum of poly(3,4-dimethyltetrahydrofuran-co epichlorohydrin	252
38.	Stereochemistry of 3,4-dimethyltetrahydrofuran ring-opening during incorporation into copolymer	255
39.	¹³ C NMR spectrum of poly(3,4-dimethyltetrahydrofuran-co-propylene oxide)	258
40.	Copolymerization curve: 3,4-dimethyltetrahydrofuran with epichlorohydrin	262

C H A P T E R I

INTRODUCTION

A. Synthesis and Characterization of Head-to-Head Polyisobutylene

1. Objectives

The primary objective of this work was the preparation of polyisobutylene in a strictly head-to-head (H-H) structure for the purpose of studying the physical properties of this new polymer and comparing those properties to those of head-to-tail (H-T) polyisobutylene.

To date, the H-H polyolefins which have been studied have all been the derivatives of monosubstituted olefins such as styrene, propylene, and vinyl chloride. Except for some attempts to prepare H-H poly(α -methyl styrene) and poly(vinylidene chloride), 1,1-disubstituted H-H polyolefins have not been investigated. This dissertation is part of a continuing effort to explore the structure-property relationships between H-T and H-H placement in polymers. The major goals for this work included:

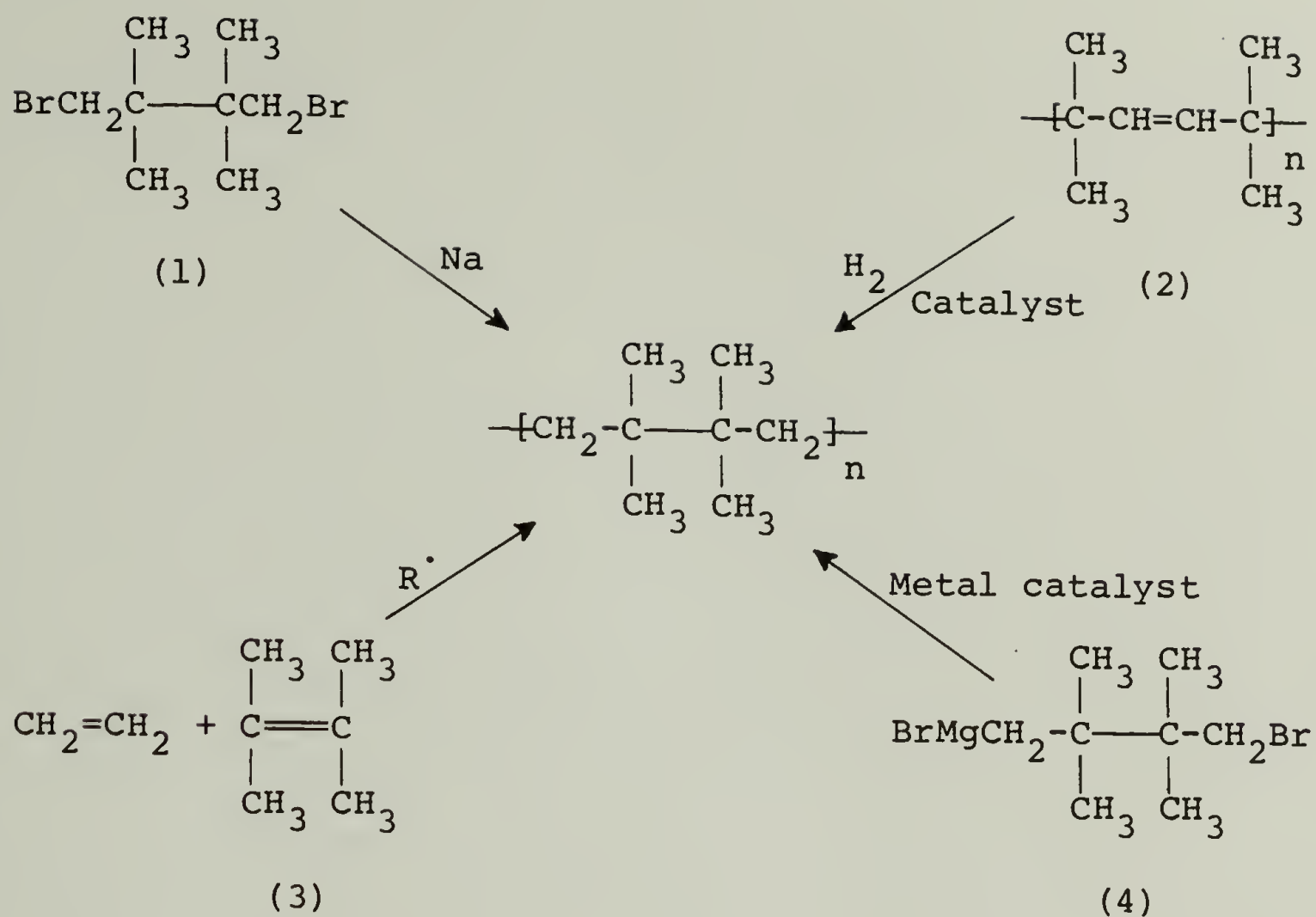
- Preparation of the correct structure for head-to-head polyisobutylene
- Basic characterization of the head-to-head polyisobutylene polymer

- Comparison of physical properties between head-to-head and head-to-tail polyisobutylene

The choice to study polyisobutylene stems from the fact that it is the simplest basic structure of the 1,1-disubstituted polyolefins, containing only methyl groups as substituents. Aside from this, polyisobutylene enjoys a relatively important niche in the polymer industry, and its physical properties are of great interest.

One of the primary areas of interest was how the differing placement of the gem-dimethyl groups along the polymer backbone would affect the thermal properties. This included the glass transition temperature (T_g), the crystalline melting point (T_m), and the thermal degradation temperature of the new polymer.

The preparation of the correct structure of H-H polyisobutylene was proposed along four separate routes. These routes are outlined in Equations (1), (2), (3), and (4).



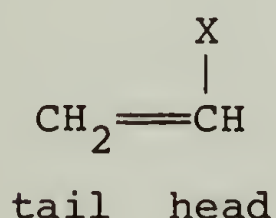
It should be apparent that each of these routes is an indirect means of attaining the desired structure. No workable direct means of polymerizing head-to-head polyisobutylene from isobutylene monomer is known nor has one as yet been proposed.

In the following section the background for each of these routes is examined. An examination of all the work on H-H polymers done to date is used as background to the study of the physical characteristics of H-H polyisobutylene, and a comparison of H-H and H-T polymer properties is also given.

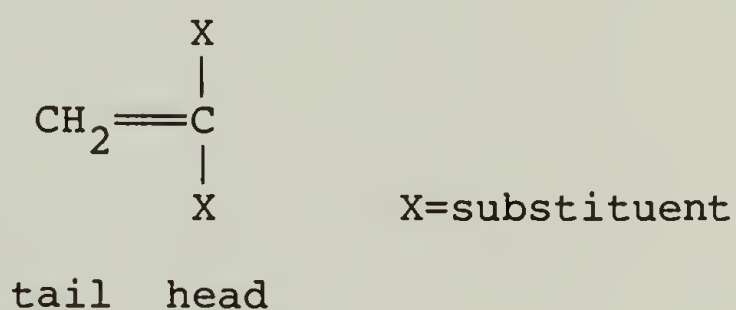
2. Historical Development of Head-to-Head vs Head-to-Tail Structure in Polymers

a. Head-to-head links in polymers

The placement of the substituents along the chain backbone of a polymer develops from the manner in which each polymerization step takes place. The accepted nomenclature for a vinyl monomer is such that the "head" of the monomer is considered the substituted end, while the "tail" of the monomer refers to the unsubstituted end.¹ This terminology is good for both monosubstituted and 1,1-disubstituted vinyl monomers (I, II).

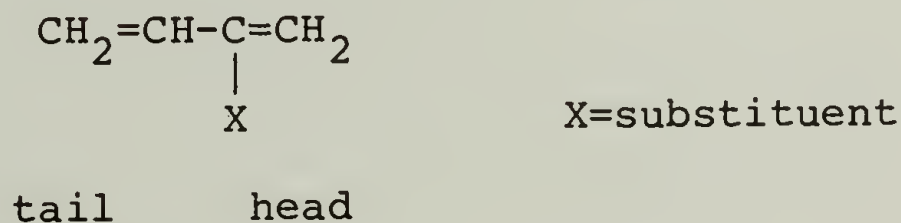


I



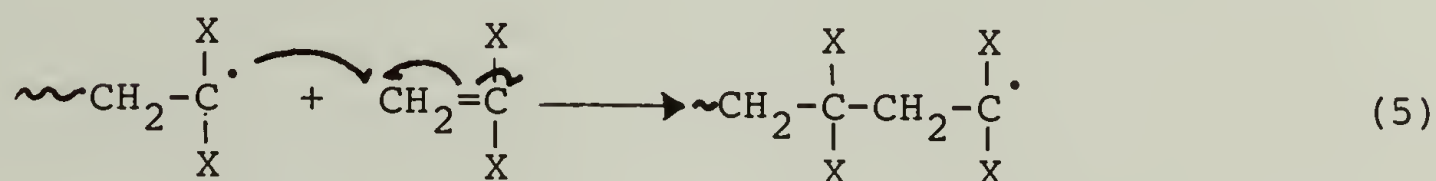
II

The terminology of H-H polymers has also been applied to monosubstituted butadienes such as chloroprene and isoprene where the "head" of the monomer is toward the substituted end of the monomer and the "tail" the opposite side (III).



III

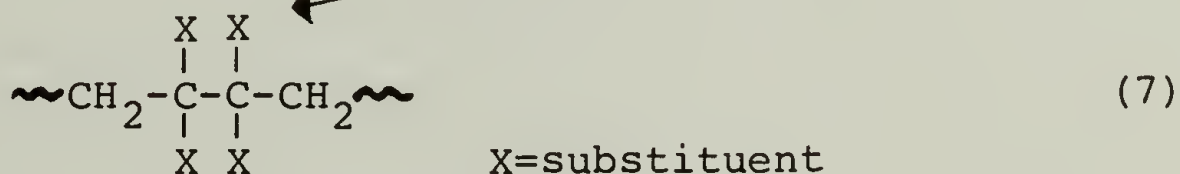
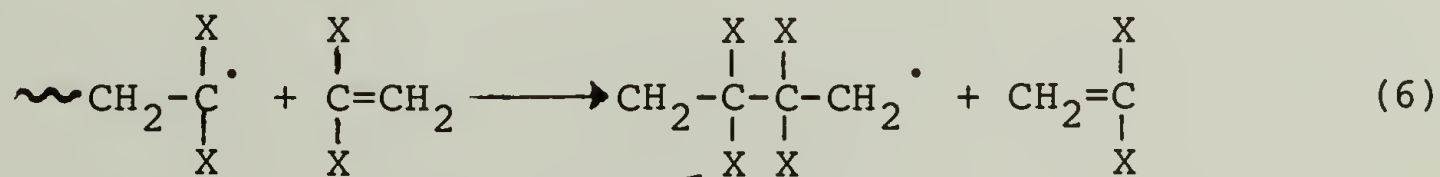
In terms of the monosubstituted and 1,1-disubstituted olefins it is of course well established that most chain growth polymerizations proceed in a H-T addition sequence (Equation 5).



X=substituent

This type of addition leads to the normal H-T polymer structure where the substituent (or substituents) is found on every other carbon atom along the backbone chain with a methylene group between each substituted carbon. This placement also provides a structure where every bond in the chain is the same as the next bond all the way along the polymer chain.

It has long been realized that flaws can develop in this structure if an occasional reverse addition occurs, as illustrated in Equations (6) and (7).



X=substituent

Reverse addition of this sort gives rise to a H-H structure in the polymer. If this type of reverse addition at each step were to continue, H-H then tail-to-tail (T-T),

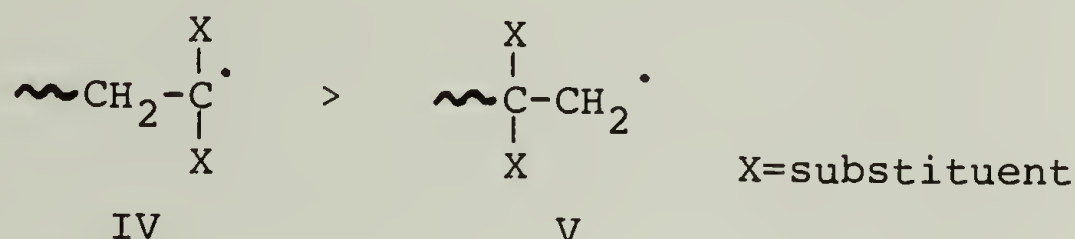
etc., a strictly H-H polymer would result. This H-H structure has two adjacent substituted carbon atoms separated by two methylene groups. This structure can vary for 1,2-disubstituted olefins such as poly(methyl crotonate) or poly(methyl cinnamate).

At one time it was held that polystyrene polymerized in a H-H fashion as evidenced by the structure of the decomposition volatiles.² Staudinger argued that H-T placement for polystyrene occurred when he found that destructive distillation of the polymer yielded products with phenyl groups on alternate carbon atoms.³ Marvel was one of the first to use condensation reactions on polymers to determine H-H or H-T structure.^{4,5} The classic example involves the treatment of poly(vinyl chloride) with zinc and the removal of chlorine.⁶ This work, in conjunction with statistical analysis by Flory^{7,8} and Wall,^{9,10,11} which calculated the amount of chlorine which would be left if the placement were H-H or H-T, showed that poly(vinyl chloride) polymerized predominantly in a H-T fashion.

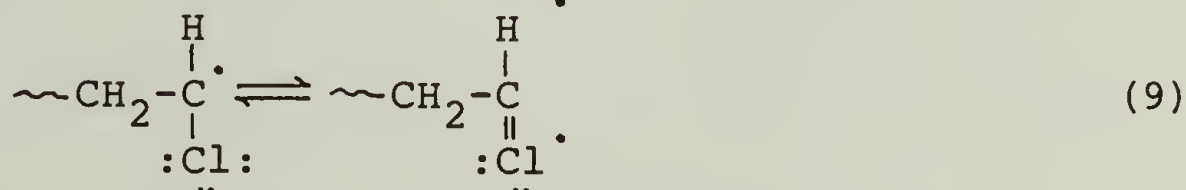
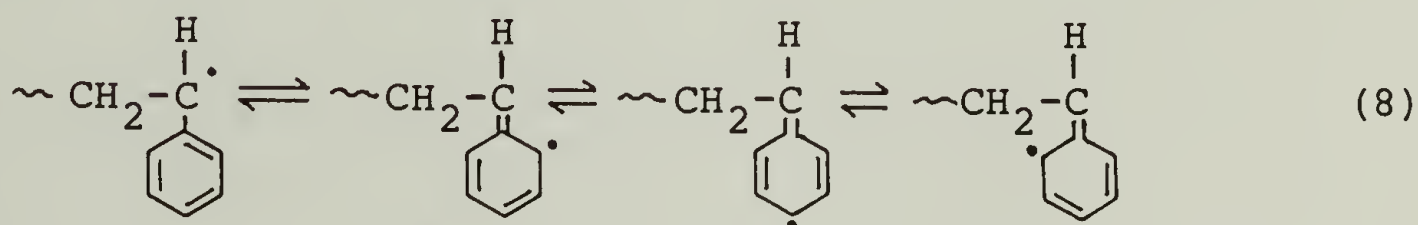
Although there are no known cases of 100% H-H polymerization for any α -olefin, monosubstituted or 1,1-disubstituted, there are now many reported cases of some incorporation of H-H linkages in polymers.

Reverse addition does not occur often in these polymerizations for a variety of very sound reasons. These include steric considerations, and inductive and resonance

effects. In most cases a secondary or tertiary radical is more stable than a primary radical due to the inductive influence of the substituent¹² (IV is favored over V).



It is also true that resonance stabilization occurs for a number of different monomers.¹³ Equations (8) and (9) show examples of resonance stabilization for growing polymer radicals.



These types of considerations, coupled with the steric effect found when adding a substituted carbon to another substituted carbon, favor addition of a substituted carbon to a non-substituted carbon. This leads to an overwhelming preference for H-T polymerization.

The illustrations given thus far have shown only radical chain growth mechanisms but the same principles apply as well to anionic and cationic mechanisms.

As mentioned, some reverse addition still does

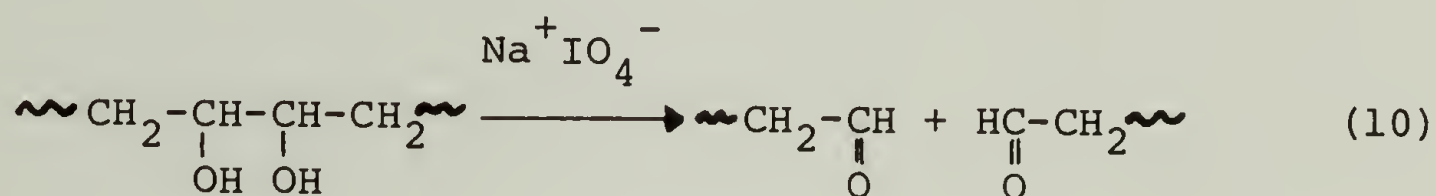
occur in chain growth polymerizations. Most notable are the examples of the fluorine substituted α -olefins. Poly(vinylidene fluoride) has been studied by several authors using high resolution ^{19}F NMR to determine structure. Ferguson first showed evidence of H-H structures for poly(vinylidene fluoride)¹⁴ and Naylor¹⁵ reported 8-10% H-H linkages in 1960. This work was supported by Wilson^{16,17} who found 10-12% H-H linkage for this polymer, and up to 32% H-H linkages for poly(vinyl fluoride) (PVF). In the same study Wilson also found a temperature dependence for the amount of H-H linkages which developed in PVF. The percent H-H varied 26-32% over a 155°C range when polymerizations were carried out from 25°C to 180°C. This indicated that up to 1 out of 6 monomer units was adding in reverse.

It is generally accepted that the small size of the fluorine atom can account best for this ease of reverse addition.¹ The small steric influence and the relatively poor resonance ability presumably combine to allow the H-H linkages to form.

For the same reasons, but to a lesser degree, chlorinated olefins also exhibit the ability to add in reverse. Otsu et al.¹⁸ have shown that isopropenyl chloride can occasionally perform an addition step in reverse and form H-H linkages. They also studied the addition mechanism of cis- and trans-propenyl chloride and inferred that 1-2% of a vinyl chloride polymerization will take place in

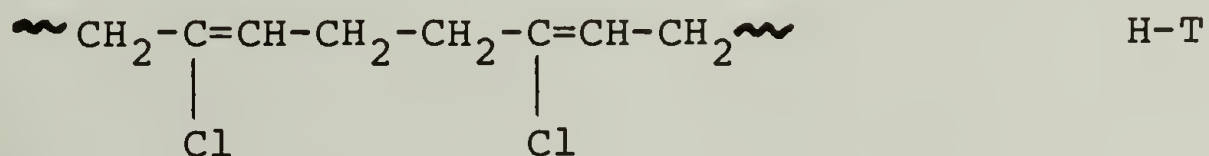
a H-H fashion.

The temperature of the polymerization has been found to affect the addition sequence. Friedlander, Harris and Pritchard¹⁹ found that the polymerization of vinyl acetate gave about 1 to 2% H-H links. This was demonstrated by first hydrolyzing poly(vinyl acetate) to poly(vinyl alcohol) and then studying the periodate oxidation (Equation 10).

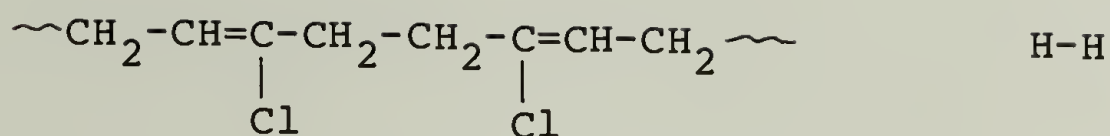


The periodate ion will selectively cleave the H-H links and leave the H-T unchanged. The resulting polymer can be studied by IR²⁰ or viscosity loss²¹ to determine the amount of H-H polymer in the original poly(vinyl acetate). The influence of polymerization temperature is not large, in this case a 60°C increase from 30°C to 90°C only changed the amount of H-H from 1.30% to 1.98%.

High resolution NMR has also been used to show that general purpose polychloroprene is formed in 75% H-T fashion and 25% H-H, T-T.²² (VI and VII)

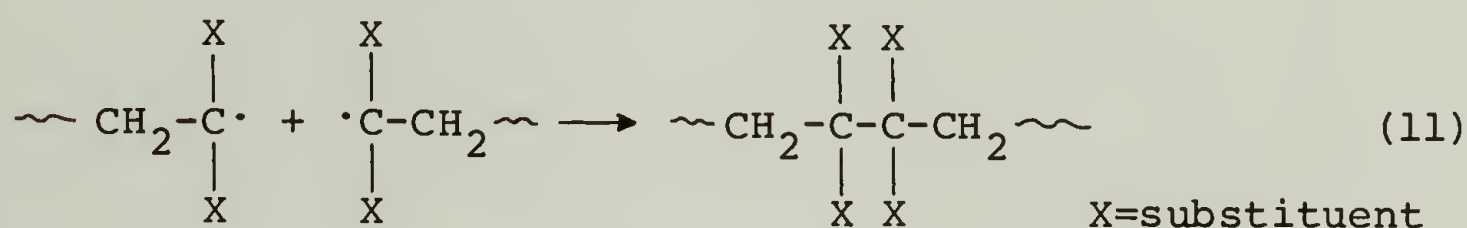


VI



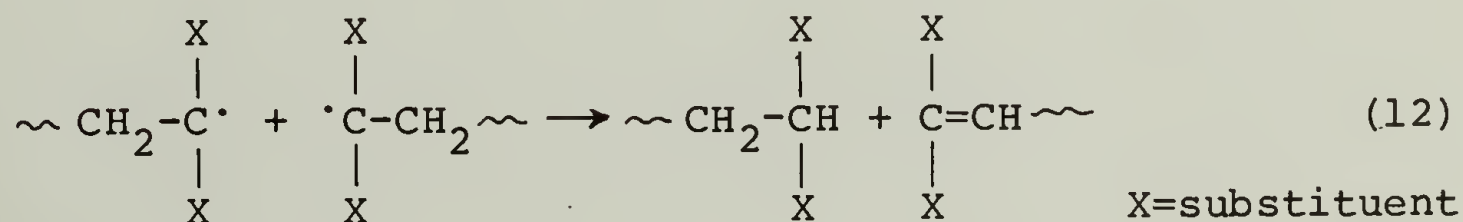
VII

Reverse addition of the monomer is not, however, the only means of forming H-H links in radical polymerizations. Termination reactions can occur by recombination of two growing chains as shown in Equation 11.



This type of bimolecular termination reaction not only "kills" two radical growing sites, it also forms a H-H placement somewhere in the midst of the polymer chain.

Since recombination is not the only possible termination reaction, its importance in forming H-H links can vary with the system. Disproportionation, for example, is a second mechanism for termination. This does not lead to a H-H link (Equation 12).



The type of monomer, the solvent, and the polymerization temperature all play a role in which termination

reaction predominates. Some examples of this include work done by Bevington, Melville and Taylor^{23,24} who determined, using ^{14}C labeled initiators, that the main form of termination for polystyrene is recombination. The same authors found that at 25°C poly(methyl methacrylate) (PMMA) radicals will disproportionate twice as often as they will combine, but that temperature severely affects this ratio. At 0°C the PMMA radicals show only 1.5 times the tendency to disproportionation over recombination, while at 60°C this increases to 6 times. The lower temperatures favor recombination in this case, and therefore favor more H-H links. Other authors have done studies to support this claim.²⁵

Bailey and Jenkins²⁶ used radioactive tracer techniques to indicate unambiguously that recombination is the exclusive means of bimolecular termination for radically polymerized acrylonitrile. Disproportionation is negligible at 60°C.

It was primarily due to the fact that these H-H links occasionally formed in normal chain growth polymerizations that the study of pure H-H polymers became of interest. Several authors had suggested that weak links in polymers may result from these H-H linkages,^{27,28} and that degradation properties may be adversely affected. After the initial studies, H-H polymers have come to be studied more and more for their own sake. H-H polymers

also afford a unique possibility for the study of structure-property relationships because only the placement of the substituents in the polymer structure is changed. The substituents themselves remain the same. Therefore one has the possibility of observing structure-property relationships strictly from a structural change point of view.

b. Methods developed for preparing head-to-head polymers

The concept of preparing 100% H-H polymers has become of quite some interest in recent years.^{29,30} The synthesis of H-H polymers is complicated by two factors. First, there are no direct polymerization methods to reach strictly H-H polymers starting from monomer. Second, it is essential to prepare as nearly a 100% H-H polymer as possible in order to properly study physical properties. Therefore, research groups involved in investigation of H-H polymers are constantly seeking so-called indirect methods of synthesis. The essence of this concept is to examine the desired structure of the H-H polymer and consider routes which will lead to that structure via other polymerization techniques, alternating copolymerization, and/or reactions on polymers.

These methods have so far fallen into four basic categories:

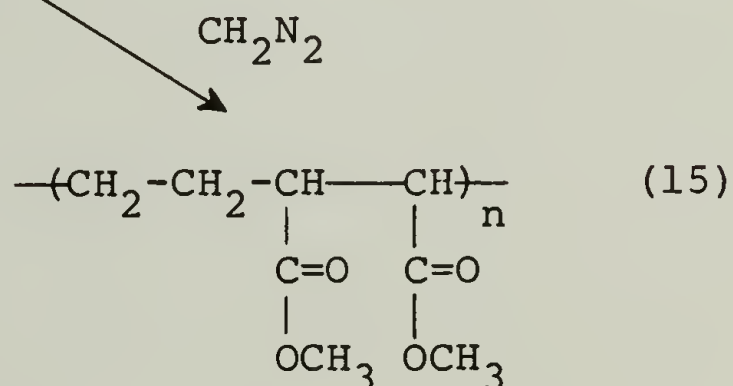
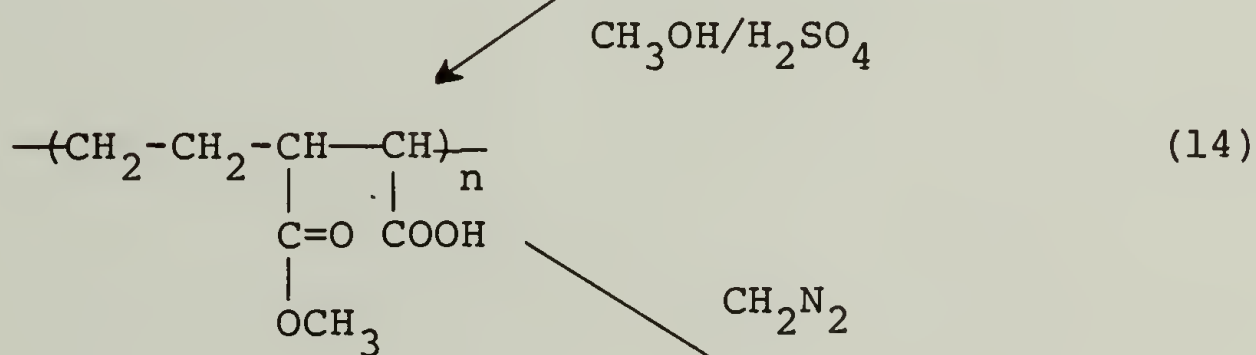
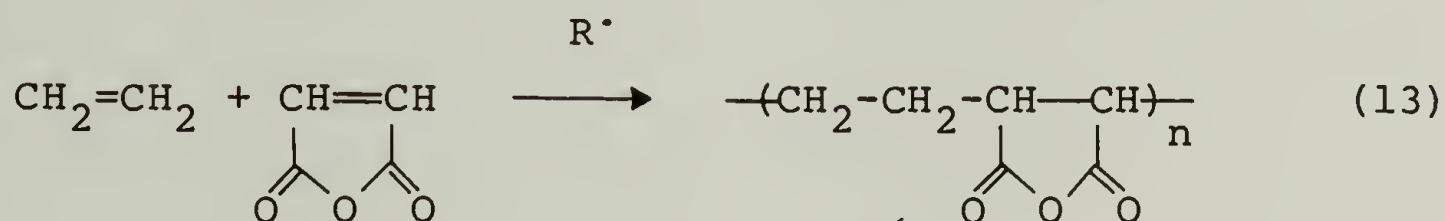
- Alternating copolymerizations (with or without subsequent reaction on polymer)

- Halogenation of 1,4-polybutadienes
- Hydrogenation of substituted 1,4-polybutadienes
- Coupling polymerizations of properly substituted monomers

(i) Alternating copolymerizations

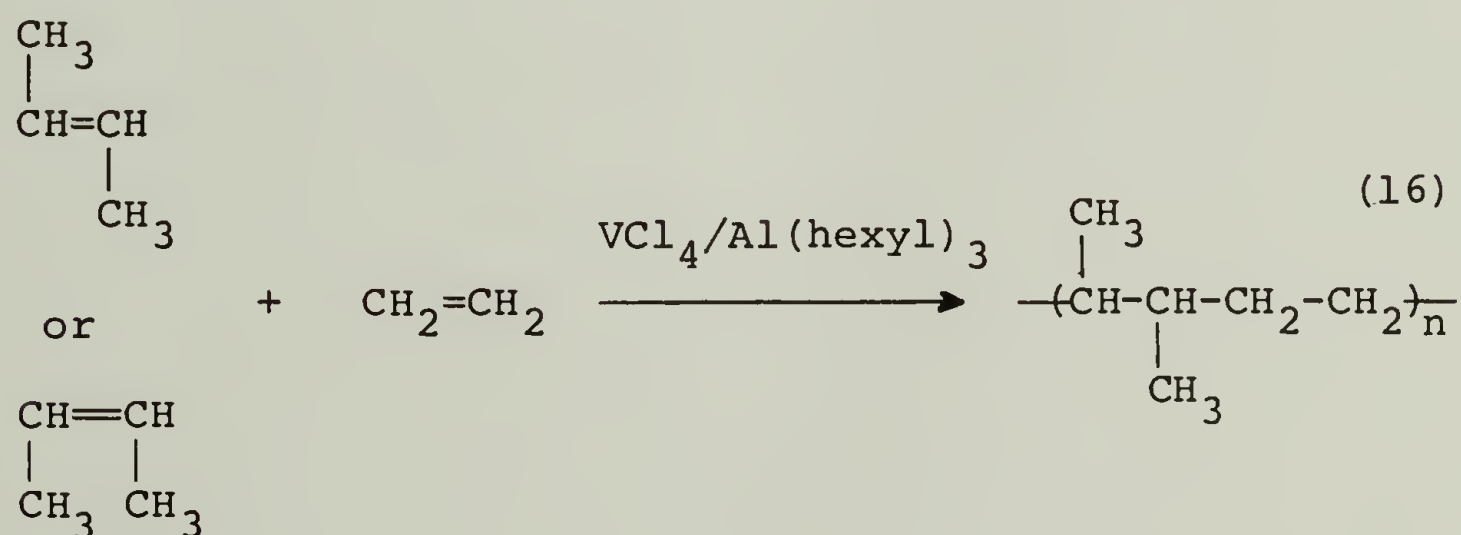
Alternating copolymerization was one of the first techniques to be used in preparing strictly H-H polymers. The method took advantage of the exclusively alternating copolymerization which occurs between substituted or unsubstituted ethylene and maleic anhydride.^{31,32}

H-H poly(methyl acrylate) was first prepared by Otsu, Auki and Nakatani³³ and by Tanaka and Vogl³⁴ who studied its properties more in depth. The reaction scheme followed in Equations (13), (14), and (15) was used.



The same general reaction scheme affords a route to H-H poly(methyl cinnamate),³⁵ and H-H poly(methyl crotonate)³⁶ if 1,2-diphenylethylene and 1,2-dimethylethylene, respectively, are used in place of ethylene.

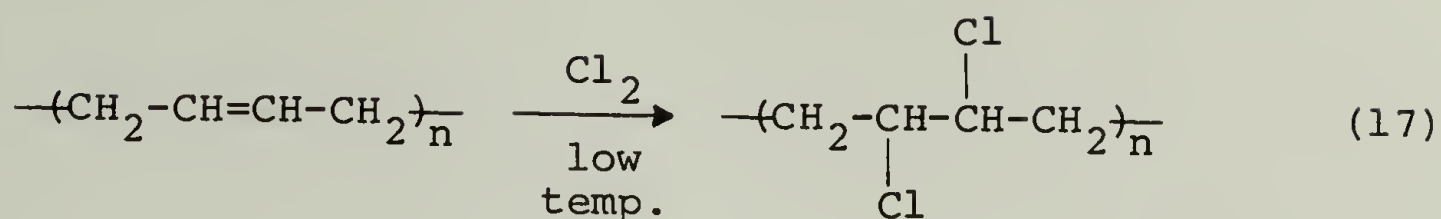
Attempts have also been made to copolymerize 2-butene with ethylene (in a strictly alternating manner) in order to directly obtain H-H polypropylene. Natta et al.³⁷ found that using vanadium/aluminum alkyl catalysts at low ethylene pressures an apparently very alternating copolymer could be isolated in low yield. This form of H-H polypropylene appeared very stereoregular owing to the coordination catalyst and the fact that cis-2-butene was used as starting material. Zambelli et al.³⁸ used a similar method (Equation 16) to study the stereochemistry of the polymers developed from the cis and trans isomers.



(ii) Halogenation of
1,4-polybutadienes

H-H poly(vinyl chloride) and H-H poly(vinyl bromide) have been prepared by the reaction of the halogen

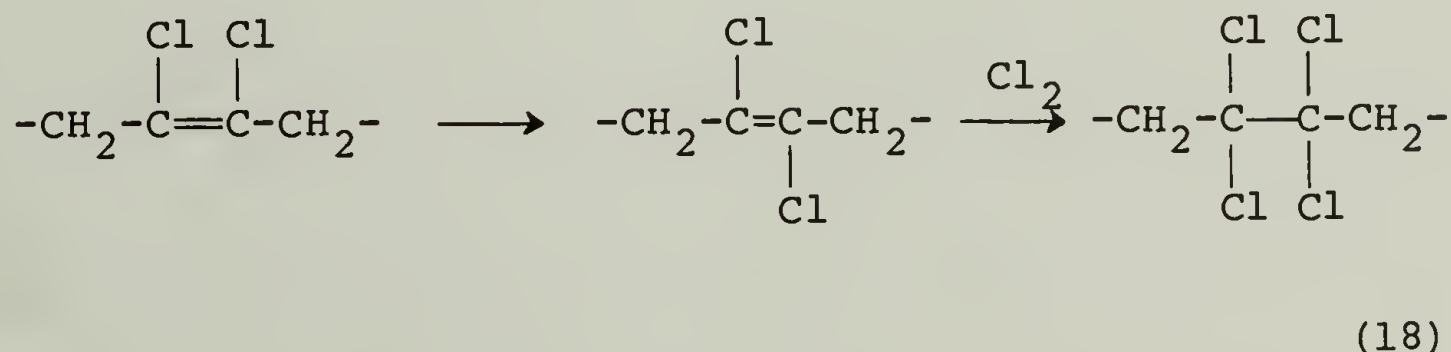
on the unsaturation in 1,4-polybutadiene (Equation 17).



This work has been done by several groups.³⁹⁻⁴³ Each group describes problems developed with cross-linking reactions. The total exclusion of oxygen, the proper choice of solvent, and the use of FeCl_2 have all been used to help eliminate this problem.

Kawaguchi, Sumida, and Vogl have also used this method to prepare H-H poly(vinyl bromide) from nearly 100% cis-1,4-polybutadiene and bromine.⁴⁴

The preparation of H-H poly(vinylidene chloride) was done by the chlorination of 1,4-poly(2,3-dichlorobutadiene).⁴⁰ The initial polybutadiene was claimed to be a highly 1,4 mixture of cis and trans. Evidence was given for the claim that the trans polymer gave direct chlorination, while the cis polybutadiene underwent cis-trans isomerization before adding chlorine (Equation 18).

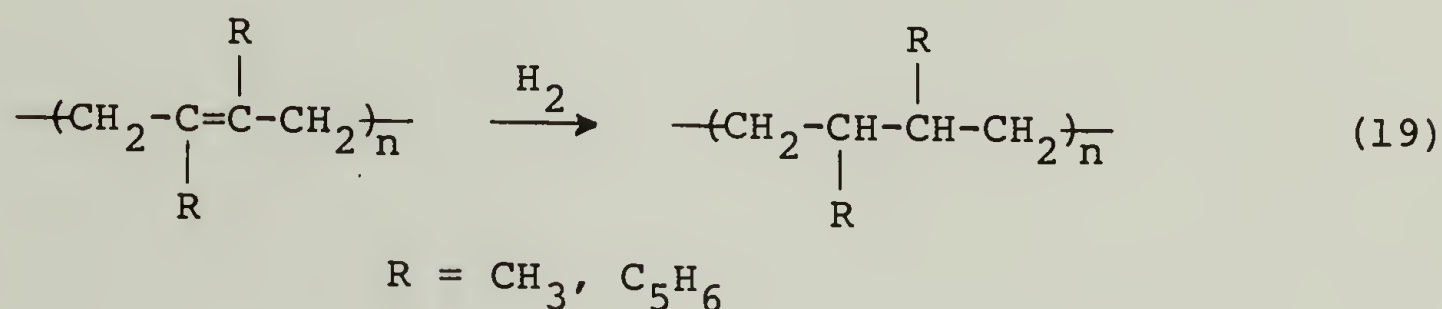


No investigations into physical properties for this polymer

were reported.

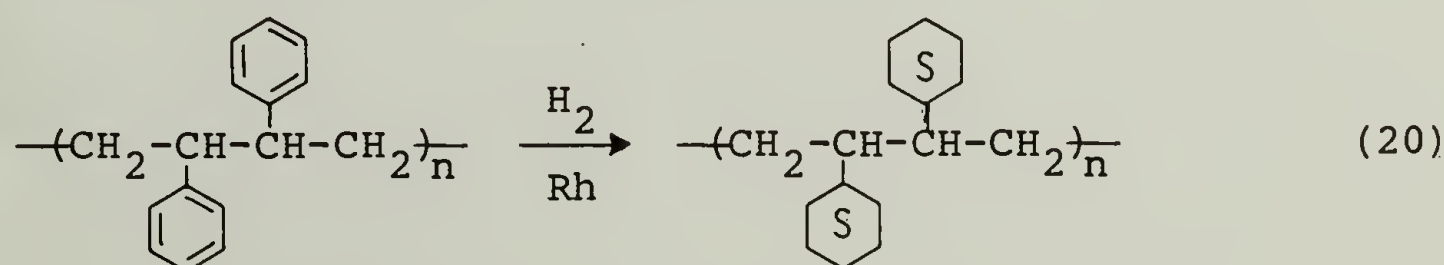
(iii) Hydrogenation of substituted
1,4-polybutadienes

One of the most successful means of preparing H-H polyolefins is to reduce the double bond of the appropriately substituted 1,4-polybutadiene (Equation 19).

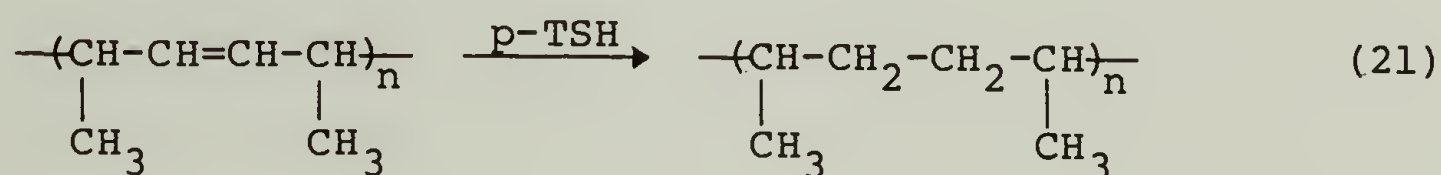


Inoue, Helbig and Vogl⁴⁵ have synthesized H-H polystyrene (PSt) by the chemical reduction of a radically polymerized 2,3-diphenylbutadiene-1,3. This reduction proceeds by an anionic mechanism with potassium and ethanol in tetrahydrofuran (THF). Since the monomer was polymerized by a radical mechanism and the reduction is stereospecific, the H-H polystyrene produced is 50/50 erythro/threo.

These same authors were able to hydrogenate the phenyl ring of the H-H PSt polymer under elevated hydrogen pressure with rhodium catalyst in order to prepare H-H poly(vinyl cyclohexane)⁴⁶ (Equation 20).



H-H polypropylene was also made by a similar route. First by Khlok, Pedram, and Prudhomme⁴⁷ who hydrogenated a 97% 1,4-poly(2,3-dimethylbutadiene-1,3) (75% trans, 23% cis) with a cobalt/aluminum alkyl catalyst to an amorphous elastomeric polymer. Then by Arichi, Pedram and Cowie⁴⁸ who used p-toluenesulfonylhydrazide (p-TSH) to hydrogenate 1,4-poly(2,3-dimethylbutadiene-1,3) as well as 2,5-poly(2,4-hexadiene) (Equation 21).



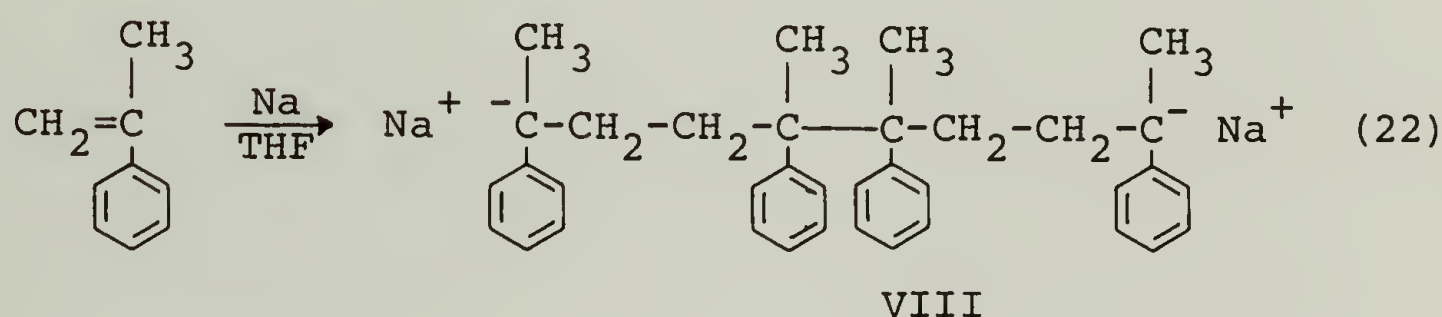
The authors describe some problems with this method for preparing strictly H-H polypropylene however. They were unable to fully reduce the unsaturation for their 1,4-poly(2,3-dimethylbutadiene-1,3), leaving an estimated 6% of the double bonds, also the 2,5-poly(2,4-hexadiene). was only about 89% 2,5 polymer with some 2,3 and 4,5 polymerization occurring. Therefore the physical characterization of these H-H polypropylenes was somewhat wanting.

Grossman and Vogl used this method for preparing H-H polypropylene by carefully synthesizing high cis and high trans-1,4-poly(2,3-dimethylbutadiene-1,3) with carefully selected aluminum/titanium ratios in the initiator system.⁴⁹⁻⁵¹ This enabled them to study the stereochemistry of the resulting H-H polypropylene on hydrogenation.

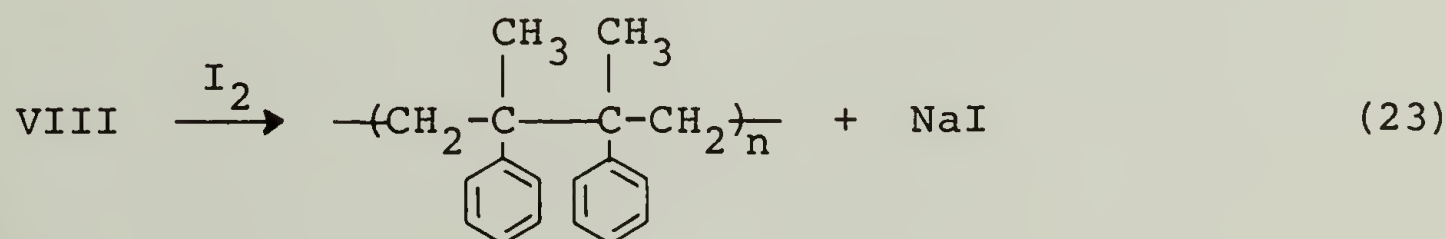
tion. They report a tendency toward cis addition of hydrogen since erythro and threo predominating structures in the H-H polymer were identified.

(iv) Coupling polymerization of properly substituted monomers

The use of coupling reactions for preparing H-H polymers was pioneered by D.H. Richards and coworkers. They first reported the preparation of low molecular weight H-H poly(α -methyl styrene) using what they believed to be the correct structure of the tetramer formed with α -methyl styrene and sodium metal in THF⁵² (Equation 22).

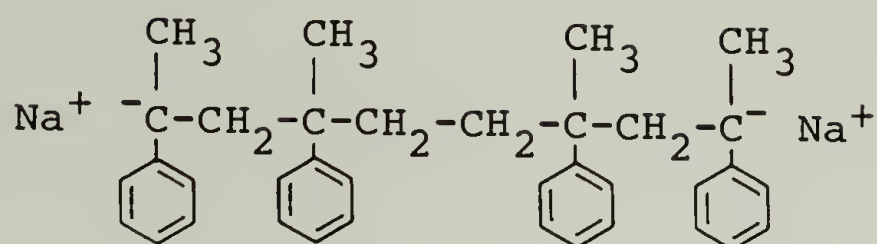


When the dianion was treated with iodine, a smooth coupling reaction proceeded (Equation 23), which was believed to give H-H poly(α -methyl styrene) of molecular weight $\sim 3,000$.



However, Richards later retracted his idea on what the structure of the tetramer was,⁵³ and disputed the validity of Swarc's description of the tetramer.⁵⁴ Instead

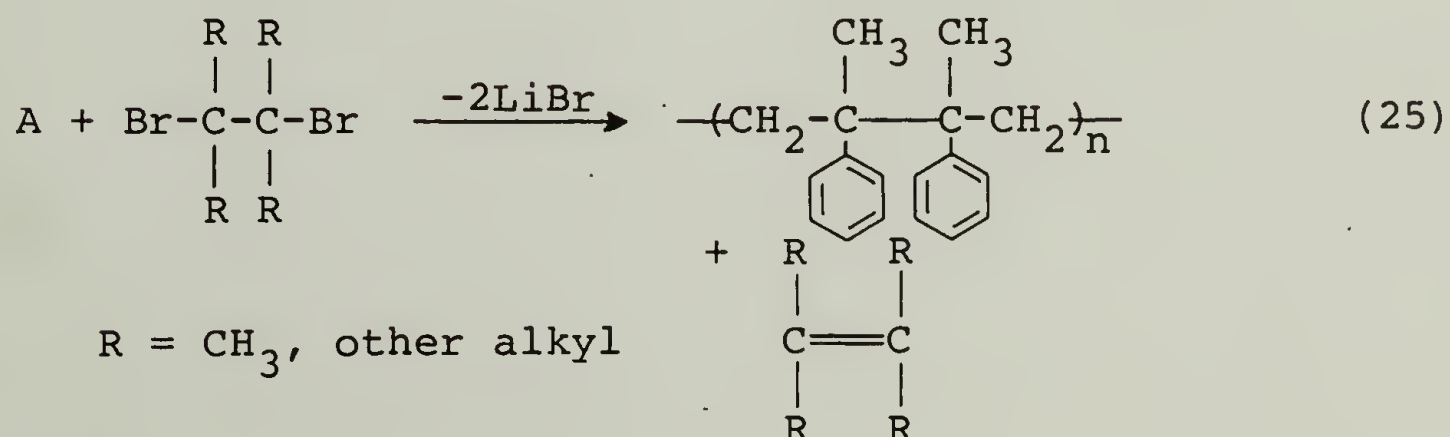
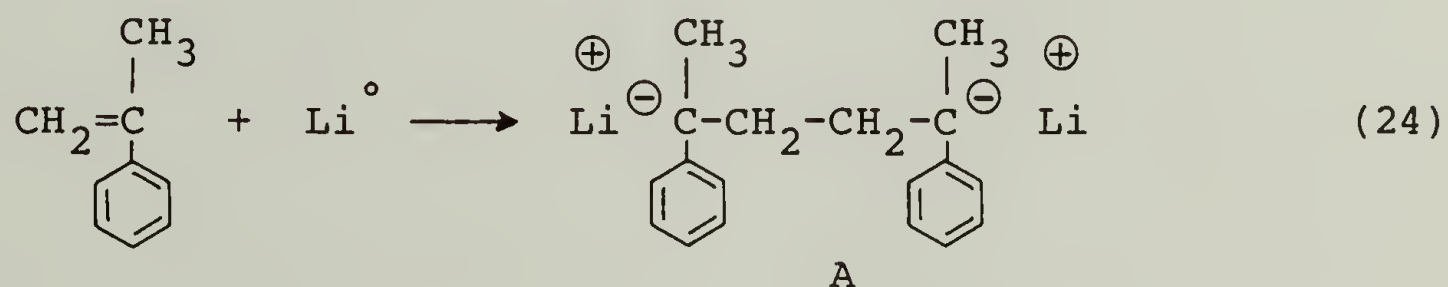
he found the tetramer to be of the structure IX.



IX

The linking reaction of this moiety was found then to yield only about 50% H-H linkages of poly(α -methyl styrene).⁵⁵

However, in 1968 Richards and Scilly did report the synthesis of H-H poly(α -methyl styrene) by a slightly different coupling reaction.⁵⁶ Low molecular weight H-H polymer could be achieved for styrene or α -methyl styrene by first reacting the monomer with lithium metal in THF then adding a vicinal dibromide to the solution⁵⁷ (Equations 24 and 25).



In this type of coupling reaction one really must consider the dimer or tetramer to be the true monomer of the polymerization since it is that structure which undergoes the coupling to higher molecular weight.

c. Physical properties of head-to-head polymers and comparison to head-to-tail polymers

The characterization of the pure H-H polymers has been, for the most part, carried out by the same research group which synthesized the new polymer. Thermal properties are some of the most extensively studied due to the fact that the H-H link has been singled out as a possible weak link in the polymer chain. An example of this claim is the work by Grassie and Kerr²⁸ in 1959, who found that if the temperature of polymerization is increased when making PSt the polymer produced degrades faster. This was explained by proposing that at higher polymerization temperatures more H-H links are formed, and that these H-H links are less thermally stable. However, it was clearly shown⁴⁵ that pure H-H PSt has the same maximum rate of degradation temperature as H-T PSt under the same conditions. See Table 1. Although this does not explain Grassie's results, it does tend to eliminate H-H links as a cause. Luderwald and Vogl later showed that although H-H and H-T PSt degrade at the same temperature they do so through entirely different mechanisms.⁵⁸ The H-T PSt

TABLE 1

THERMAL DEGRADATION BEHAVIOR OF HEAD-TO-
HEAD AND HEAD-TO-TAIL POLYMERS

Polymer	Maximum Degradation Rate Temperature in °C (a)		
	H-H	H-T	Source
Polypropylene	468	479	ref. 49
Polystyrene	397	398	ref. 48, 59
Poly(vinyl cyclohexane)	433	441	ref. 58
Poly(methyl acrylate)	418	419	ref. 34
Poly(methyl crotonate)	383	410	ref. 35
Poly(methyl cinnamate)	376	410	ref. 36

(a) Samples run at 20°/min heating rate

predominately unzips to monomer, while the H-H polymer statistically degrades into oligomeric materials.⁵⁹

In general, there has not been a great deal of difference in the maximum rate of degradation temperature between H-H and H-T polymer analogs (Table 1). However, whenever the mechanism of degradation has been studied, it does appear that the first bond to break in a H-H polymer is the carbon-carbon bond between the two substituted carbons. It was found in the case of H-H poly(α -methyl styrene) that the polymer degrades to monomer after the initial bond scission occurs at this relatively weak bond.⁶⁰

Other polymers, such as H-H poly(vinyl cyclohexane), have been found to degrade in a more similar manner to their H-T polymer counterparts. It was found (by pyrolysis-mass spec) that, like H-T poly(vinyl cyclohexane) (H-T PVCH), H-H PVCH would degrade primarily by first losing cyclohexane rings. Random cleavage of the polymethylene chain occurs thereafter.⁵⁸ However, some characteristic fragments were found which arise from the favored thermal cleavage between, or next to, the two tertiary carbon atoms of the polymer backbone chain.

Also, H-H polypropylene was reported as having a ten degree lower degradation temperature than H-T polypropylene although the molecular weights of the two polymers was not exactly specified.⁴⁹

It seems that each polymer has to be taken on an

individual basis in terms of comparing H-H and H-T degradation. A general proposal has been suggested²⁹ which indicates that the H-H polymers have a lower degradation temperature than the H-T polymers if hydrogen is the fourth substituent on the highly substituted carbon atom and no group larger than hydrogen is substituted in the beta position. This theory empirically fits all the data gathered to date.

Another interesting comparative study involves the change in glass transition temperatures found between H-H polymers and their H-T analogs. See Table 2. Initially it was believed by some that for any polymer the H-H placement would create a more flexible chain by virtue of the fact that it contains two methylene groups linked together in the chain. During the polymerization of H-T poly(vinyl chloride) (PVC) it was shown that increased polymerization temperatures gave decreasing glass transition temperatures (T_g s).⁶¹ Speculation was that increased polymerization temperature gave increased H-H PVC units. Since H-H PVC has a lower T_g than H-T PVC the results could be rationalized. However, with the preparation of pure H-H PVC this theory was discredited when the T_g s of H-H and H-T PVC were found to be very close.^{39,62}

Thus far it has been shown generally that it is not the influence of the increased methylene linkages which predominates in the T_g of H-H polymers, but rather the nature of the substituents which controls chain flexibility.

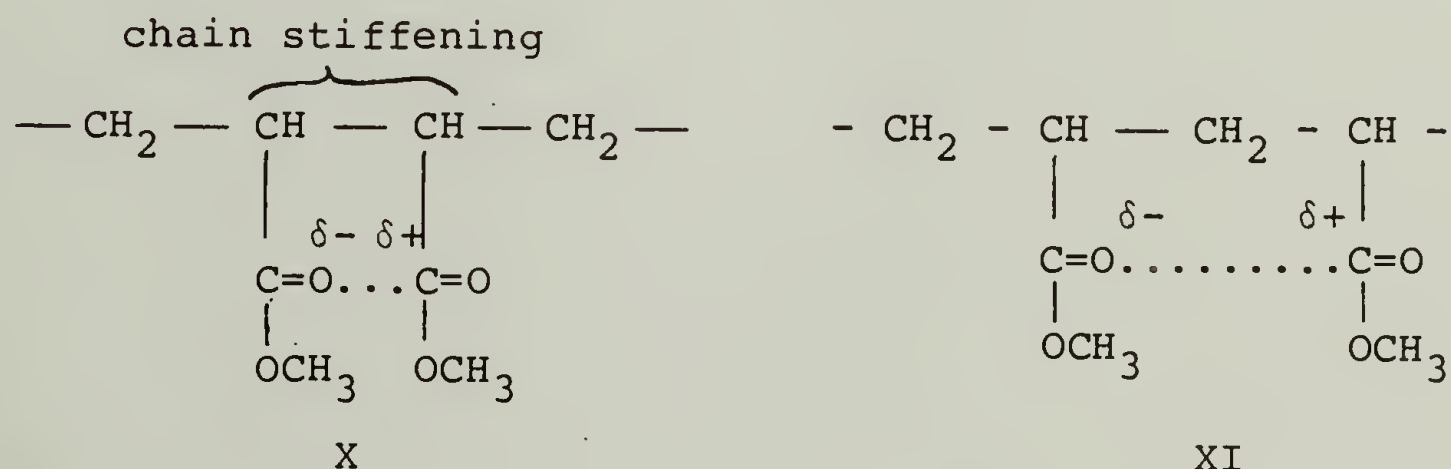
TABLE 2

GLASS TRANSITION TEMPERATURES OF HEAD-TO-HEAD
AND HEAD-TO-TAIL POLYMERS

Polymers	T_g in °C		Source
	H-H	H-T	
Polypropylene	-39	-17	ref. 49
Polystyrene	97	98	ref. 45
Poly(vinyl cyclohexane)	88	138	ref. 46
Poly(methyl acrylate)	40	12	ref. 34
Poly(methyl crotonate)	107	80	ref. 35
Poly(methyl cinnamate)	210	190	ref. 36
Poly(vinyl chloride)	91	83	ref. 39, 41
Poly(vinyl bromide)	76	85	ref. 62

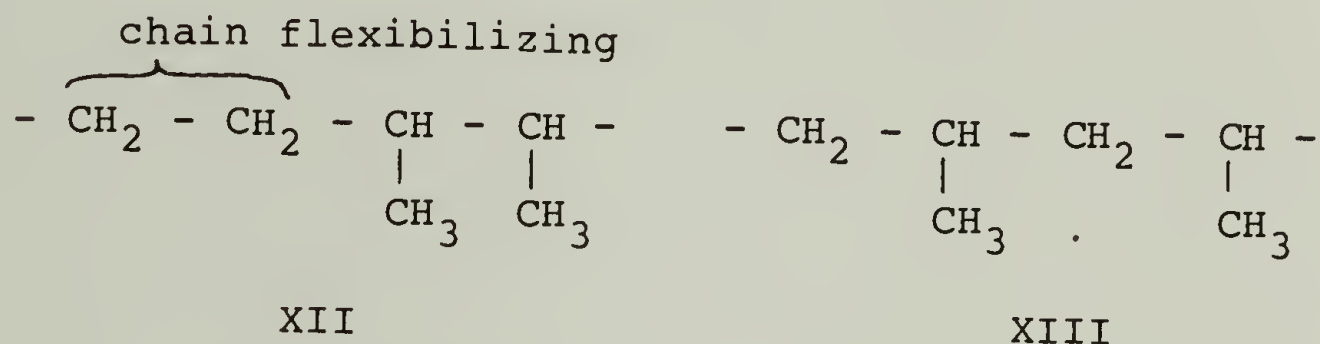
Again, an empirically substantiated rule has been suggested which deals with the polarity of the substituents.⁴⁶ If there is some polar interaction between the substituents the H-H placement tends to increase the interaction because the groups are brought closer together. This has an overall chain stiffening effect which leads to an increase in T_g . On the other hand if the substituent groups are non-polar, and have no inductive influence on one another, placement in the H-H position produces an increased chain flexibility because of the two methylene links produced for every linkage.

This is illustrated by the examples of poly(methyl acrylate) and polypropylene. H-H poly(methyl acrylate) (H-H PMAc) has a T_g of 40°C as compared to H-T PMAc which shows a T_g of 12°C. The increased proximity of the methyl acrylate groups has stiffened the chain as pictured in X and XI.



In contrast to this H-H polypropylene (H-H PP) has a T_g of 39°C which is about 22°C lower than that of H-T PP.

In this example no polar chain stiffening occurs between the methyl substituents and thus the amount of flexibility derived from the methylene spacers is the major influence (XII and XIII).



Arichi, Pedram and Cowie⁶³ also studied the dilute solution properties of H-H PP and found a decrease in the unperturbed dimensions of the chain as compared to H-T PP, and a higher theta temperature for H-H PP than for H-T PP in isoamylacetate. These results can also be attributed to an increased flexibility in the chain due to $-\text{CH}_2-\text{CH}_2-$ groups in the backbone.

One anomaly to this scheme is the case of polystyrene. The T_g of H-H PSt is the same as that of H-T PSt, but dilute solution studies,⁶⁴ and ^{13}C NMR spectroscopy⁶⁵ show that the radius of gyration of H-H PSt is greater than that of H-T PSt. This indicates a stiffening of the chain for H-H PSt over H-T PSt, and is probably due to the bulky nature of the phenyl group. The rheological behavior of atactic H-H and H-T PSt also supports this data.⁶⁶

In most cases only the atactic H-H polymers have been prepared due to the nature of the indirect synthesis.

These atactic polymers are generally amorphous. Natta et al.³⁷ did find a highly crystalline H-H PP when it was prepared by the copolymerization of ethylene with cis-2-butene using coordination catalysts. This is in sharp contrast to the entirely amorphous atactic H-H polypropylene described by Grossman⁴⁹ prepared through the hydrogenation of 1,4-poly(2,3-dimethylbutadiene).

Some work on the NMR of H-H polymers has been done. Initially this type of study was used to determine the amount of H-H polymer in normal chain growth polymerizations.^{14,15} More recently Weil and Vogl have used ¹³C NMR to show the influence of long range order on chemical shift values for H-H and H-T polymer pairs.^{67,68} Marchal, Benoit and Vogl have also published a study on the dielectric properties of H-H PSt using thermally stimulated discharge techniques.⁶⁹

Recently studies on how the H-H arrangement of a polymer affects its compatibility with other polymers and with its own H-T polymer have been initiated. The manner in which the H-H polymer acts in situations where the H-T polymer is known to show miscibility can produce insights into the nature of polymer-polymer interactions.

Kryszewski, Jachowicz, Malanga and Vogl⁷⁰ showed that H-H PSt is compatible with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) as judged by a single T_g for the polymer blend. The T_g was observed both by differential scanning

calorimetry (DSC) and dilatometry measurements. This indicates that the interaction between the phenyl groups on the polymer backbone and the phenylene oxide is independent of the position of the phenyl groups on the chain. This leads one to speculate that the chemical interaction between PSt and PPO is not based upon adjacent polystyrene phenyl groups.

Similar results have been found for the blends of PVC with poly(ϵ -caprolactone). The H-H PVC appears to be miscible with poly(ϵ -caprolactone) to the same degree as H-T PVC is.⁷¹

It becomes apparent also that systems which would allow the study of compatibility between the H-H and H-T analogs of a polymer would also be of interest.

3. Coupling Reactions and Their Use in Polymerization

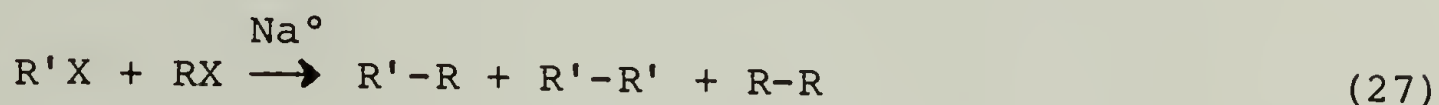
a. Wurtz coupling

The Wurtz coupling reaction involves the coupling of alkyl halides by treatment with sodium. Generally the term is extended to include other metals as well such as lithium. See Equation (26).



The Wurtz reaction, although well known, is not widely used for synthetic purposes due to a number of side reactions which occur including disproportionation,

elimination and various rearrangements.⁷² Mixed Wurtz reactions (Equation 27) are even less desirable because of the number of different products which one obtains.



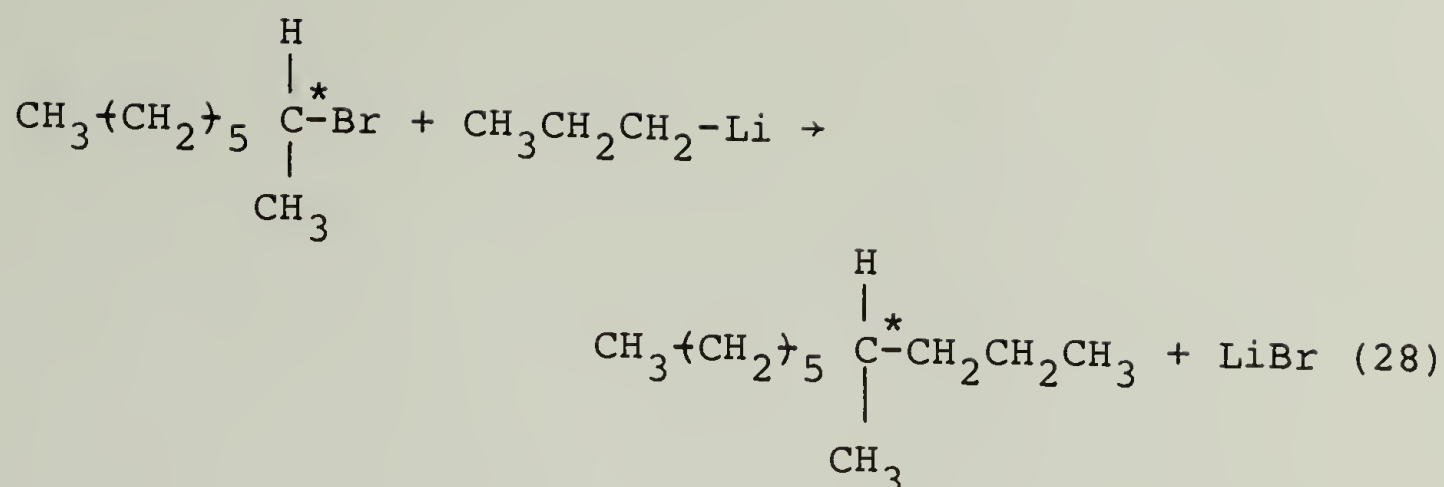
Wurtz couplings are therefore only worthwhile if one can eliminate the majority of side reactions and use symmetrical halides as starting materials.

Mixed aryl and alkyl halide reactions are so-called Wurtz-Fittig reactions. These tend to be somewhat better synthetically and can be of use in preparing alkylated aromatic compounds.

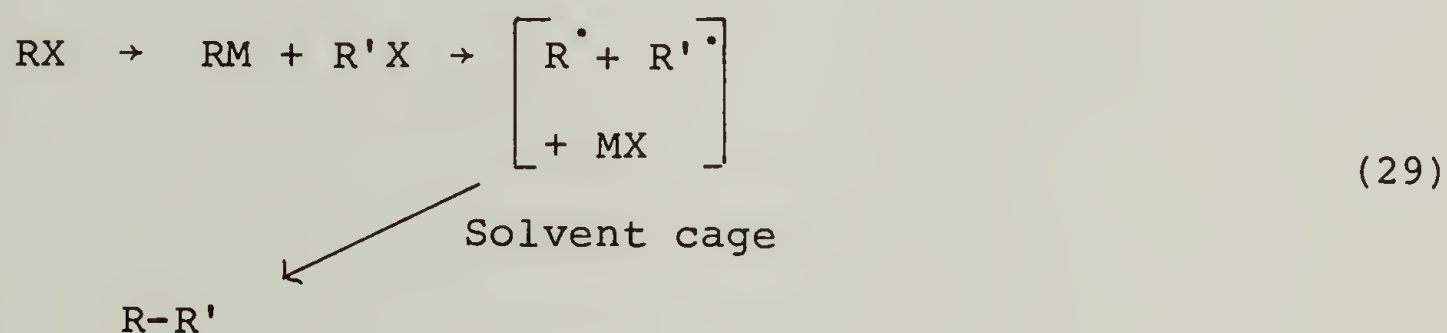
Besides sodium and lithium, iron⁷³ and zinc⁷⁴ have also come into use in Wurtz type reactions, although not with good success.

The mechanism of the Wurtz reaction has been under dispute for some time. Evidence for both a nucleophilic substitution process of an SN_2 type and a free-radical mechanism has been cited.

The general rationale for the SN_2 reaction has been the inversion of configuration at R. An example is the work by Saver and Braig⁷⁵ showing that the reaction between 2-bromo-n-octane and n-propyl lithium went with inversion (Equation 28).



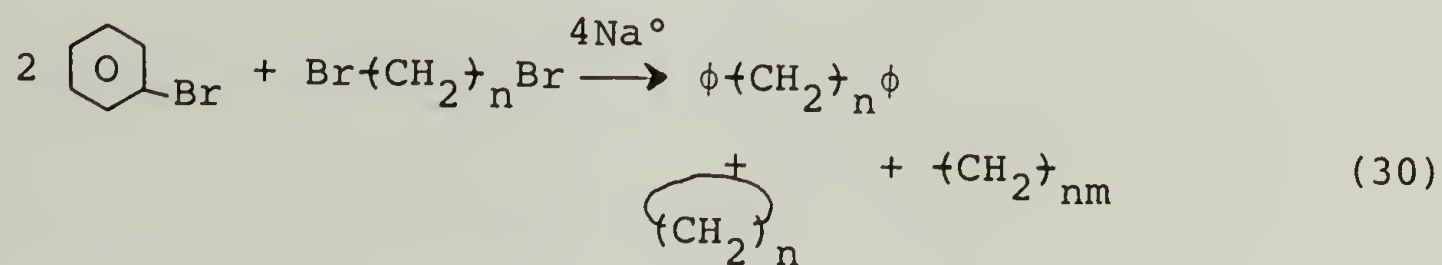
Strong evidence for free-radical mechanism has also been found and is probably still considered the favored mechanism.⁷⁶⁻⁷⁸ The free-radical mechanism is believed to be very much dependent on a solvent cage (Equation 29) because if the radicals were entirely "free" the products of a mixed reaction would be exactly 50% RR', 25% R'R' and 25% RR. This statistical breakdown is rarely found, and in most examples RR' is the predominant product.



The coupling of dibromides or other dihalides was first described by Goldschmiedt⁷⁹ long before polymers were understood to consist of long linear chains. Descriptions of waxy or oily residues were not uncommon in older papers when this fraction was not the desired product and often

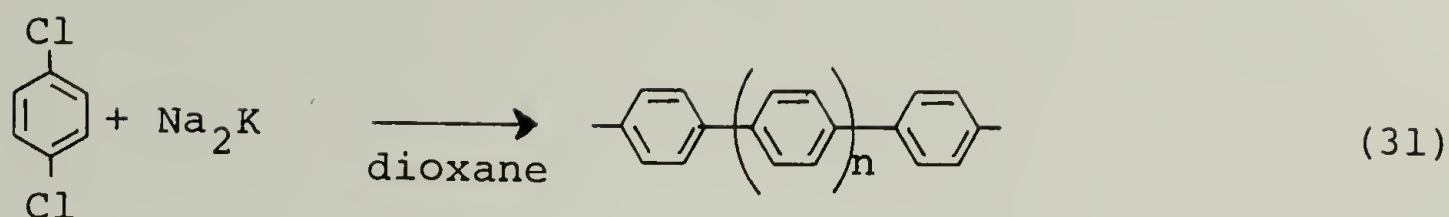
discarded.⁸⁰

The Wurtz-Fittig reaction has also been used between α,ω -dibromoparaffins and bromobenzene.^{81,82} The reaction was used to make phenyl end-capped polymethylene chains, but the authors report sticky resins and evidence of cyclization for chains of lengths favoring cyclization. See Equation (30).



Carothers, Hill, Kirby and Jacobson⁸³ reported on the successful polymerization of 1,10-dibromodecane using sodium. The Wurtz reaction was carried out first in diethyl ether then in bulk with $\overline{\text{DP}}_n$ of up to 10 found. This indicates a polymethylene chain of about 100 carbon atoms. Cyclization was not found to be a problem in this case where an unfavored ten-membered ring would have to be formed. Some insoluble product was reported which is expected to be a cross-linked material indicating abstraction and disproportionation reactions.

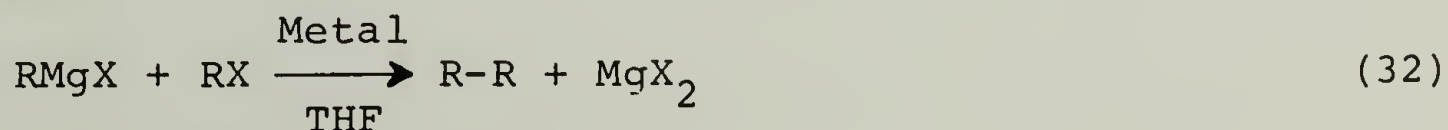
Edwards and Goldfinger⁸⁴ prepared polyphenylene using para-dichlorobenzene in reaction with a sodium-potassium alloy (Equation 31).



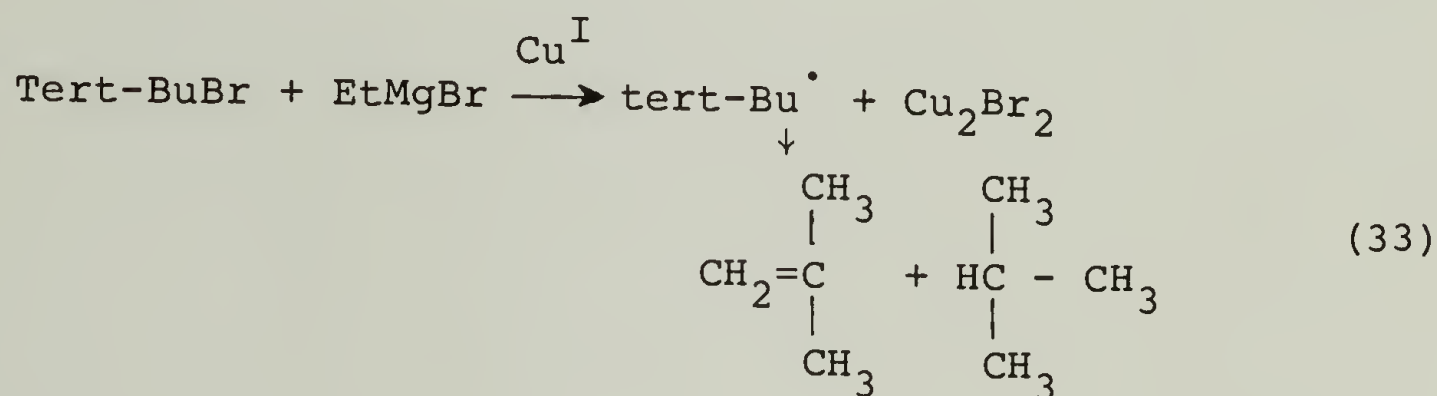
The reaction was carried out in 1,4-dioxane and gave a polymer with a $\overline{\text{DP}}_n$ of approximately 34 (as determined by chlorine analysis).

b. Grignard reagent coupling with alkylhalides

A reaction of greater synthetic practicality in general, and of more value in terms of polymerization applications involves the transition metal catalyzed coupling of Grignard reagents with alkyl and aryl halides. The coupling between Grignard reagents and allylic and benzylic halides has been known for some time and will proceed without catalyst.⁷² The reaction of alkyl Grignard reagents with alkylhalides is now known to occur with the formation of a carbon-carbon bond and the loss of magnesium dihalide salt in the presence of the proper transition metal. Tamura and Kochi first reported the use of so-called "soluble transition metal catalysts" which were easy to use and were extremely effective.⁸⁵⁻⁸⁷ Their reactions were normally performed in tetrahydrofuran solution using soluble silver, copper, and iron metal catalysts (Equation 32).



A specific example is the coupling of 1-bromohexane with butyl magnesium bromide. The reaction was carried out at 0°C in the presence of a soluble dilithium tetrachlorocuprate (I) solution. The yields were generally near 90%. These authors also report that secondary and tertiary bromides do not couple in an analogous manner but instead disproportionate (Equation 33).



Onuma and Hashimoto⁸⁸ showed that amine ligands for the copper catalyst can also be effective in the coupling reaction. Here N, N, N', N'-tetramethylenediamine was used in conjunction with CuCl₂ to catalyze reactions between aryl Grignard reagents and alkyl and aryl halides with good success.

The introduction of nickel-phosphine complexes as catalysts for this type of coupling was reported independently by two groups. Tamao, Sumitani and Kumada⁸⁹ showed how dichloro(1,2-bis(diphenylphosphino)ethane)nickel(II) could be employed to couple many types of alkyl magnesium bromides with alkyl and allyl halides. Curriu and Masse made similar claims.⁹⁰ After this initial work a wide

variety of transition metals and different ligands were reported as catalysts for the coupling reaction. Murahashi et al.⁹¹ described palladium based catalysts along with Sekiya and Ishikawa.⁹² Platinum, cobalt and chromium compounds were also shown to be at least somewhat reactive.⁹³ However, the Cu and Ni catalysts were generally found to be the most effective and were the broadest based.

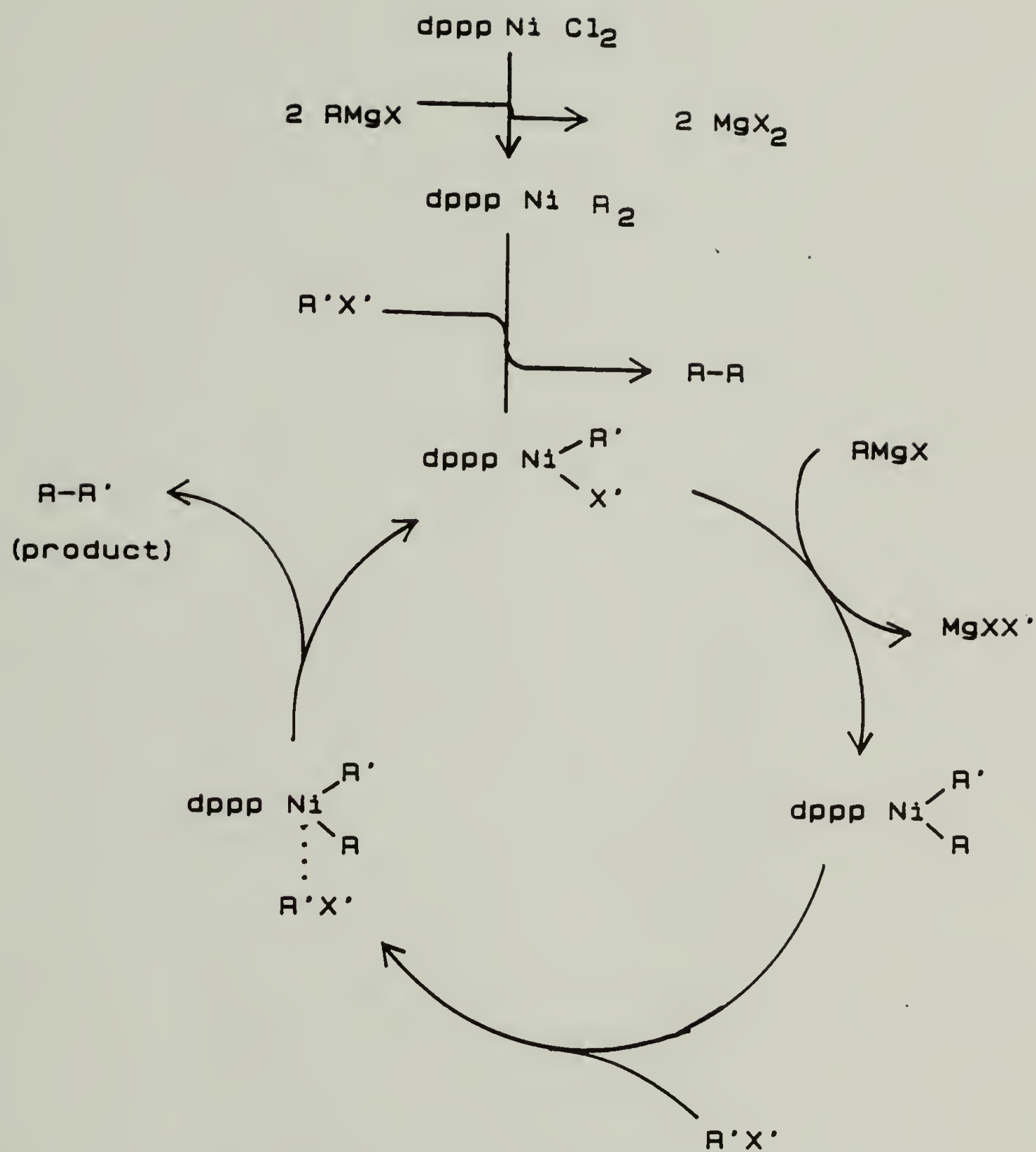
The mechanism for the coupling reaction between an alkylhalide and a Grignard reagent has been examined with some degree of detail by Morrell and Kochi.⁹⁴ They used nickel (II) complexes for their study, but the general mechanism can also be applied to other metals as well. They isolated the intermediate complexes by using stoichiometric amounts of catalyst to Grignard reagent and alkylhalide. In this way they provide a rationale for the cyclic mechanism which is outlined in Figure 1.

The only use to date of this coupling reaction for the polymerization of dihalides has been reported by Yamamoto.⁹⁵⁻⁹⁷ The reaction of a dihalide with one equivalent of magnesium metal to form the mono-Grignard/monobromide reagent provides a new monomer (Equation 34).



This new monomer can be generated in situ and need not be isolated, rather it is simply subjected to a

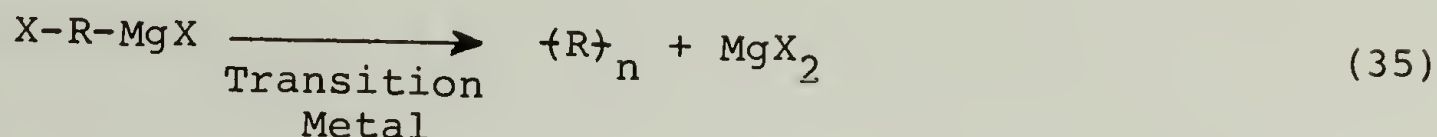
Figure 1. Catalytic process for the Grignard/alkylbromide coupling reaction as catalysed by nickel II complexes.



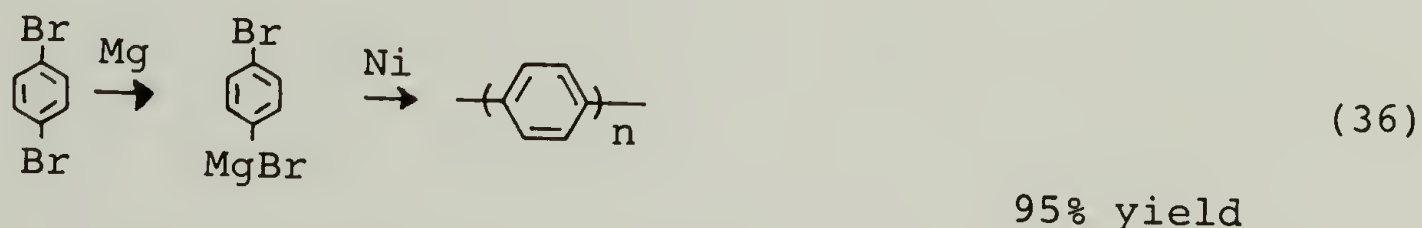
X = halogen

$\text{dppp} = \text{Ph}_3\text{P}[\text{CH}_2]_3\text{PPh}_3$

polycondensation with the addition of transition metal catalyst (Equation 35).



Yamamoto et al. first used this polymerization scheme to prepare polyphenylene from para-dibromobenzene⁹⁵ (Equation 36).

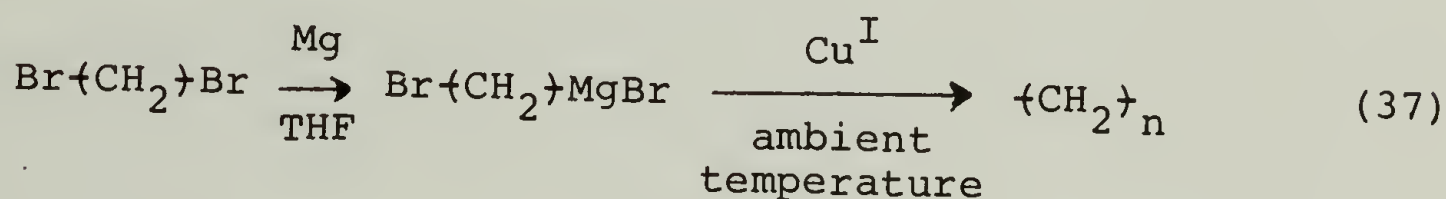


They report the preparation of poly(m-phenylene), poly(oxybiphenylene) and poly(phenylenemethylene) from m-dichlorobenzene, bis(p-bromophenyl)ether and 1-chloromethyl-4-chlorobenzene respectively. The polymers obtained are described as having a "high degree of polymerization" but no accurate molecular weights are reported.

This paper also describes the use of a large variety of catalysts on the condensation. In terms of yield the order of catalytic effect was found to be Ni > Pd > Co > Fe > Cr for the reaction with p-dibromobenzene. Tetrahydrofuran, dibutyl ether, and diglyme were used as solvent with little difference in results.

Yamamoto, Senechika, Hayashi and Yamamoto⁹⁶ went on to

report the preparation of polymethylene from α,ω -dibromo- n -alkanes using the same Grignard coupling technique. In this case, where aliphatic halides are coupled with aliphatic Grignards, copper compounds were shown to be the most effective. When copper(I)-(tri-triphenylphosphino) bromide was employed as catalyst a yield of 99% was reported for the coupling of 1-bromododecyl-12-magnesium bromide (Equation 37).



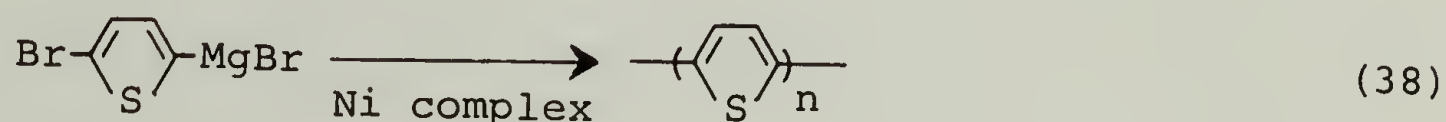
The molecular weights, based on viscosity, were calculated as high as 7,000. The polymethylene precipitated from the THF solution at these molecular weights, which was cited as a controlling factor in the final $\overline{\text{DP}}_n$ obtained.

For α,ω -dibromo- n -alkanes having 5 or more methylene units the polycondensation appeared to proceed smoothly. However, some of the 1,5-dibromopentane was found to cyclize even at -20°C . This ring closure side reaction was also shown for α,ω -dibromoalkanes which can form 3 and 4 membered rings. In fact the 1,4-dibromobutane, 1,3-dibromopropane and 1,2-dibromoethane were found not to give polymer at all.

Other copper compounds such as CuBr, CuCl, and

CuBr_2 also acted as good catalysts but Ni and Pd complexes appeared only to produce low molecular weight materials, specifically cycloalkanes.

Yamamoto has also described the use of the same coupling reaction to prepare poly(2,5-thienylene)⁹⁷ (Equation 38).



A number-average molecular weight of 1370 was found by osmometry.

The versatility of this coupling polymerization has therefore been demonstrated by Yamamoto, although certainly its full potential has not yet been explored. The possibilities for synthesizing new polymer structures is very exciting with limitations only for monomers which contain groups reactive toward Grignard reagents. Esters, amines, and ketones would need to be blocked before the coupling reaction, and the blocking groups removed after the polymerization.

4. Polymer Hydrogenation

a. Catalytic hydrogenation of polymers

The catalytic reduction of unsaturated polymers has been extensively investigated. Catalysts have come to be broken down into two categories:

- Heterogeneous metal catalysts
- Homogeneous metal catalyst complexes

The heterogeneous hydrogenation catalysts are generally supported on some form of charcoal or other inert material. Wicklatz⁹⁸ gives a good review of these heterogeneous catalysts. His discussion includes the factors which affect hydrogenation such as reaction temperature, reaction pressure, catalyst, and polymer structure. For nondestructive hydrogenations of polymers platinum, palladium, and nickel provide the most effective results. However, the use of these insoluble metal catalysts present practical problems where most polymeric materials are concerned. The problems occur due to the tendency of polymers to absorb to the metal catalyst and its support. This will block reactive sites and reduce the ability of the catalyst to perform. To compensate for this it is necessary to use high catalyst concentrations and high pressure, which results in further problems of chain cleavage and difficulty in removing all the catalyst residues from the system. One final problem which makes heterogeneous catalysis unattractive is the increased difficulty of reaction with substituted polymers where steric factors at the unsaturation site play a large role in hydrogenation.

The introduction of homogeneous metal catalysts (also known as soluble or coordination hydrogenation catalysts) for the hydrogenation of olefins in the early

sixties provided an answer to many of these problems when they were applied to polymers around 1970. The advantages of this new catalytic system include low catalyst concentration, lower temperature and pressure during the reaction, a shorter reaction time, and an easier removal of catalyst.⁹⁹

Sloan et al.¹⁰⁰ first described the use of cobalt aluminum catalysts for use in hydrogenation of olefins. They found that $\text{Co(III)} > \text{Fe(III)} > \text{Cr(III)}$ appeared to be the sequence of activity for the metals. The catalysts were prepared from mixtures of triisobutylaluminum and acetylacetonates of the metals. Also mentioned are Mn, Mo, Ni, Pd, Ru, V, Zn and Cu as having some effect in the reduction of olefins when put into soluble complex form.

In a series of papers Falk goes on to describe the use of soluble cobalt catalysts for the hydrogenation of polymers.¹⁰¹⁻¹⁰⁴ The catalysts were prepared by reacting cobalt(II)-ethylhexanoate with either n-butyl-lithium or triisobutylaluminum usually in a decalin solution. This gave either the Co/Li or the Co/Al catalyst solution. The catalyst activity was found to be a function of the ratio of lithium or aluminum to cobalt. The conditions of catalyst concentration, temperature and hydrogen pressure were all discussed in terms of optimum reactivity. The proper selection of these conditions was shown to produce hydrogenation catalysts which could discriminate

between different unsaturation sites on the polymer.

The aluminum to cobalt ratio was generally in the range of 3 to 1 or 4 to 1 and lithium to cobalt ratios from 2 to 1 up to 6 to 1 were found to be most reactive. However, for specific polymer systems this ratio might be different. Falk optimized conditions for the hydrogenations of 1,4-polybutadiene, 1,4-polyisoprene and PSt.

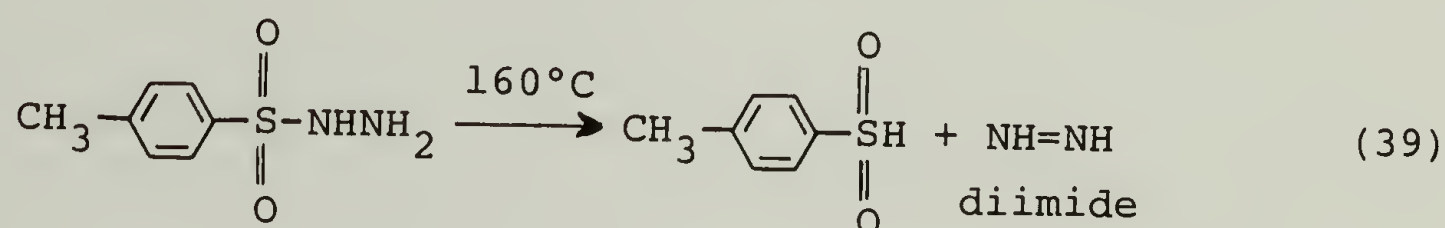
Grossman and Vogl used an Al/Co catalyst in the preparation of H-H PP from 1,4-poly(2,3-dimethylbutadiene).⁵¹ They found a ratio of 4 to 1, Al to Co was necessary at a 30 mole % concentration of catalyst to hydrogenate this double bond. This high catalyst concentration was probably necessary due to the two methyl groups on the double band.

b. Chemical hydrogenation of polymers

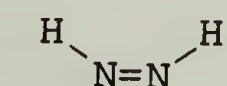
One form of chemically induced reduction which has already been discussed is the use of potassium and ethanol on 1,4-poly(2,3-diphenylbutadiene).⁴⁵ This was used to prepare H-H PSt. As mentioned this reaction proceeds by an anionic intermediate which is stabilized by the resonance effects of the phenyl rings. This kind of chemical reduction is limited in scope therefore to stilbene type structures.

More recently the use of highly reactive diimide (N_2H_2) species has been extensively studied as a

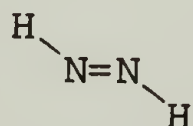
general means of hydrogenating low molecular weight polyolefins.^{105,106} The application of diimide hydrogenation has been greatly improved through the introduction of arylsulfonylhydrazides. These materials produce diimides when heated to their decomposition temperature. A widely used arylsulfonylhydrazide is p-toluenesulfonylhydrazide due to its good solubility in aromatic solvents (Equation 39).



The mechanism by which diimide reacts with double bonds has been studied. The diimide is formed in both the syn and anti form (XIV and XV), however only the syn form reacts to reduce the double bond.¹⁰⁷

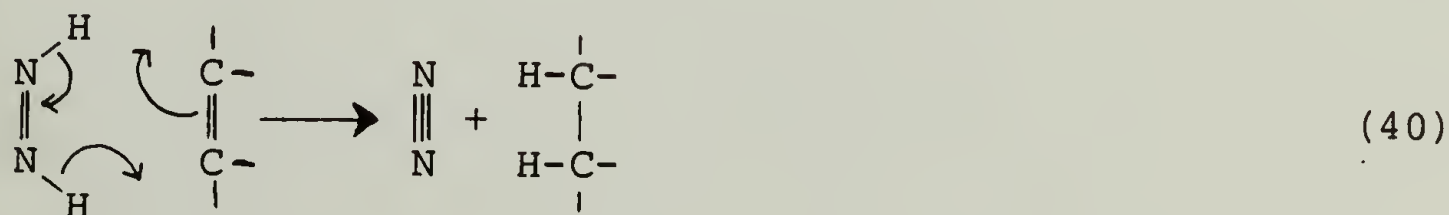


XIV, syn



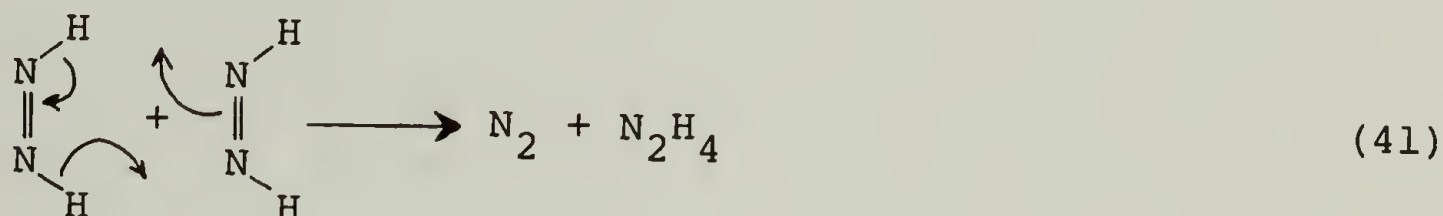
XV, anti

The reaction takes place by a cyclic mechanism according to equation 40.¹⁰⁸



For this reason the attack usually comes from the less hindered side of the double bond and therefore a double bond of cis geometry is more easily reduced than trans. Also bulky groups near the unsaturation will reduce the efficiency of the reaction.

The side reaction of diimides involves the self-disproportionation to give off nitrogen and form hydrazine (Equation 41).



The first report of diimide reduction on polymers was by Nakagawa and Okawara¹⁰⁹ who employed it to hydrogenate residual unsaturation in PVC.

Mango and Lenz¹¹⁰ along with Harwood et al.¹¹¹ published simultaneously on the use of diimide for the hydrogenation of unsaturated polymers. They reported the complete hydrogenations of cis- and trans-1,4-polybutadiene, styrene-butadiene copolymers, polycyclohexadiene, and cis-polyisoprene. However, the more substituted polymers such as 1,4-poly-(2,3-dimethylbutadiene), 2,5-poly(2,5-dimethyl-2,4-hexadiene) and 1,4-poly(2-chlorobutadiene) were only partially reduced. It should be noted however that these authors did not attempt to force hydrogenation by repeated reaction but simply report one attempt with two equivalents

of p-toluenesulfonylhydrazide.¹¹²

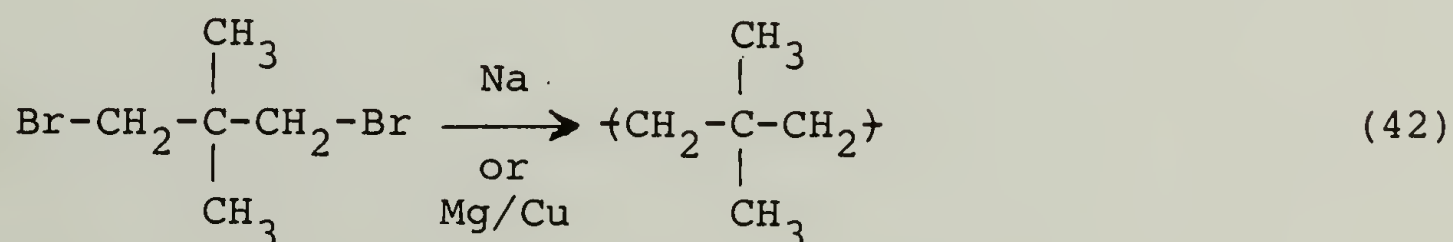
As previously mentioned Cowie et al.⁴⁸ did use p-toluenesulfonylhydrazide (p-TSH) to hydrogenate 1,4-poly(2,3-dimethylbutadiene) and 2,5-poly(2,4-hexadiene). However they found that several reductions with excess quantities of p-TSH were necessary to affect hydrogenation, and they still report residual amounts of unsaturation which could not be reduced.

It appears obvious that the use of homogeneous and chemical hydrogenation methods has much to offer in reducing polymers, and that further study is needed.

B. Synthesis of Poly(1,1-dimethylpropane)

1. Objectives

The synthesis of poly(1,1-dimethylpropane) by a coupling polymerization of 2,2-dimethyl-1,3-dibromopropane was an effective means of modeling the preparation of H-H polyisobutylene. The monomer was more easily accessible from the diol and the attempted polymerizations were proposed through Wurtz coupling and Grignard/alkylbromide coupling (Equation 42).



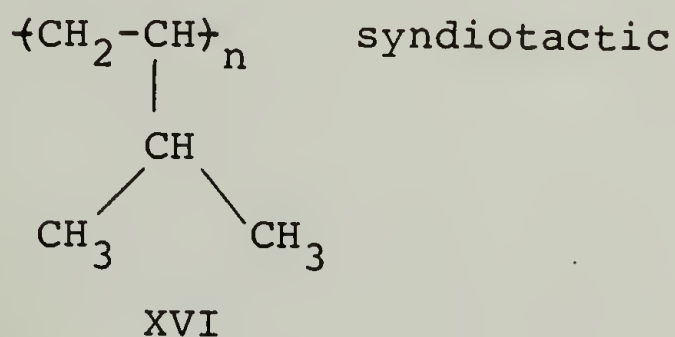
The structure of the polymer obtained from this polymerization was also of interest. Each gem-dimethyl group is separated from the next by two methylene groups. It can be viewed as a polymer with a structure somewhat between normal H-T polyisobutylene and H-H polyisobutylene.

2. Historical Development of poly(1,1-dimethylpropane)

a. Low temperature, cationic polymerization of 3-methylbutene-1

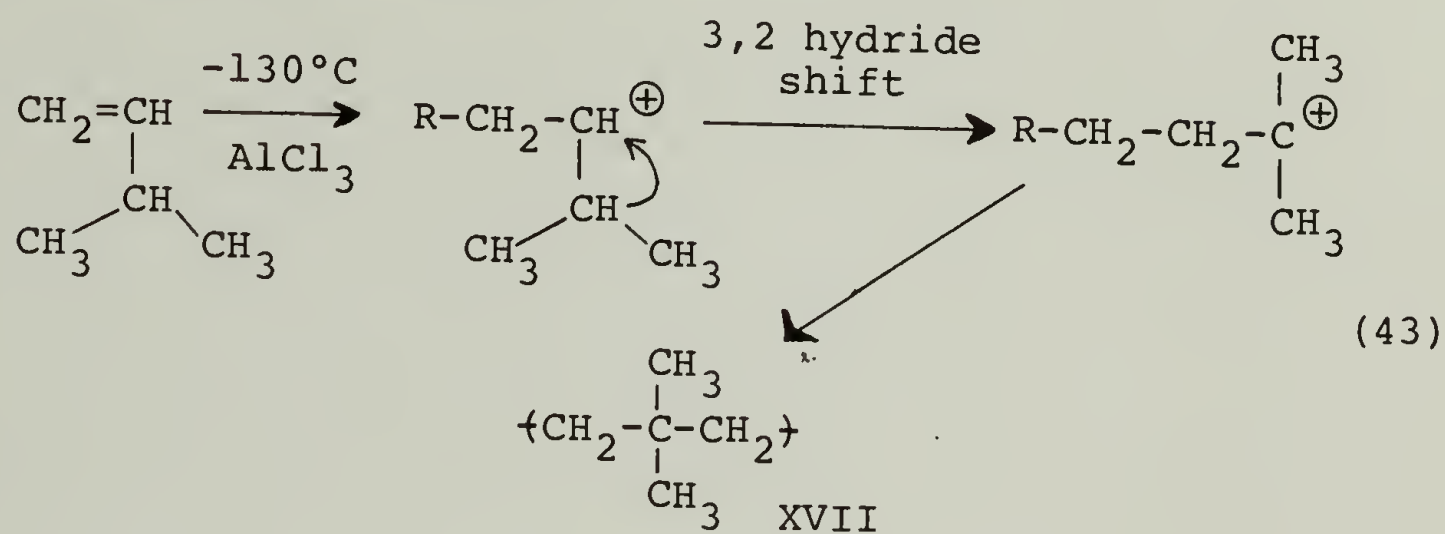
The structure of poly(1,1-dimethylpropane) was first realized by Kennedy and Thomas in 1962.¹¹³ They found that the temperature at which 3-methylbutene-1 was polymerized had a direct effect on the crystallinity of the polymer obtained. At temperatures down to approximately -100°C a colorless, amorphous, tough semi-solid was observed. At polymerization temperatures near -130°C a white crystalline polymer was formed.

Initially it was believed that a highly syndiotactic 1,2 structure had been prepared. (See XVI.)



3-Methylbutene-1 is known to be highly crystalline in its isotactic form if a coordination catalyst system is used.

However, after careful NMR study the structure of the polymer obtained at -130°C with cationic initiators appeared to be that of a 1,3 polymer which was postulated by a 3,2 hydride shift (Equation 43).



This structure was based on the assumption that the low temperature of polymerization allowed sufficient time for the carbenium ion to rearrange from the less stable secondary to the more stable tertiary form at each propagation step.

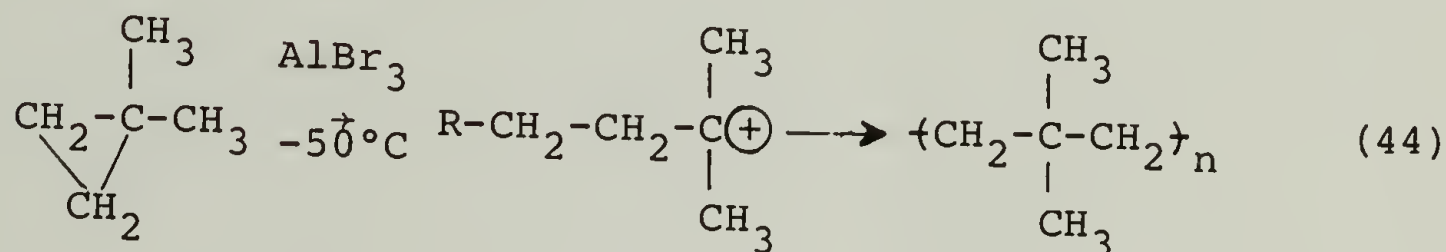
Further work was conducted by Edwards and Chamberlain¹¹⁴ as well as Kennedy¹¹⁵ to elucidate this polymer structure by spectroscopic techniques. Evidence is cited in both studies which differentiates between XVI and XVII, however, only indirect identification of poly(1,1-dimethylpropane) was obtained.

Pyrolysis of the two polymers and fragment analysis was also used with some success to show that poly(1,1-dimethylpropane) had been formed and the 3,2 hydride shift had taken place.¹¹⁶

b. Cationic polymerization of 1,1-dimethylcyclopropane

In an effort to help show the 3,2 hydride shift was the mechanism for the low temperature cationic polymerization of 3-methylbutene-1, Ketley¹¹⁷ performed a ring-opening polymerization of 1,1-dimethylcyclopropane.

When 1,1-dimethylcyclopropane was subjected to cationic initiators (Lewis acids) at -50°C it polymerized presumably with the cation carried on the tertiary carbon (Equation 44).



The molecular weights were relatively low (about 1,000) but sufficient for a comparison with Kennedy's polymer by spectroscopic work.

Indeed, the infrared spectra of the two polymers were very similar. No further characterization of this ring-opened polymer was carried out by Ketley so the results were not definitive.

3. Physical Properties of poly(1,1-dimethylpropane)

Kennedy and coworkers^{118,119} carefully observed the change in molecular weight for the cationic polymerization of 3-methylbutene-1 from $+10$ to -130°C . A sharp change

with an increase in molecular weight was observed at approximately -100°C . This temperature is the transition point from 1,2 polymerization to 1,3. The 1,2 polymer was generally of low molecular weight with the 1,3 polymer reported to have a molecular weight of 50,000.

Poly(1,1-dimethylpropane) is described as a white powder or crumb. The crystallinity of the polymer was studied both with x-ray diffraction¹²⁰ and by differential thermal analysis (DTA).¹²¹ The polymer appears to be polymorphous with what is described as an α and a β form of crystal structure. Depending on the preparation and handling the "d" values from the x-ray diffraction experiments were slightly different.

This polymorphism manifests itself in the DTA as well with two reported melting peaks. The α crystal structure melted at 65 to 66°C while the β had an endotherm at 49°C . The α form appears to be the more stable of the two. When the β polymer was melted and then rescanned only the α polymer melt was observed.

The poly(1,1-dimethylpropane) is only semicrystalline and it shows a T_g of -15°C .

This polymer has very sharp differences in its physical properties from H-T polyisobutylene, yet it is only different by the insertion of one methylene group in the polymer repeat structure. The structure-property relationships between the three polymers (H-H polyisobutylene, H-T

polyisobutylene and poly(1,1-dimethylpropane)) is of great interest.

C. Copolymerization of 3,4-
Dimethyltetrahydrofuran
with Cyclic Ethers

1. Objectives

The cationic polymerization of cyclic ethers, including tetrahydrofuran (THF), and cyclic acetals has been extensively studied and described in numerous papers and reviews.¹²²⁻¹²⁹ The cationic polymerizations of substituted cyclic ethers have also been investigated. These have been studied both in homopolymerization and in copolymerization with other cyclic ethers.

In our laboratory the synthesis of 3,4-dialkyltetrahydrofuran by the dehydration of 2,3-dialkylbutanediol-1,4 has been studied in connection with the synthesis of 2,3-dialkylbutadienes.¹³⁰

It was the purpose of this part of the dissertation to investigate the homo- and copolymerizability of one of these 3,4-substituted tetrahydrofurans, namely 3,4-dimethyltetrahydrofuran (DMTHF). The objectives were to prepare this monomer from the 2,3-dimethylbutanediol-1,4, and to attempt to homopolymerize it using available techniques. The polymerization of this monomer has not been investigated previously. Also the possibility of copolymerization of DMTHF with other cyclic ethers was a prime

objective.

The following section of the introduction will briefly review the cationic polymerization of substituted cyclic ethers as a background for this work, with some emphasis on the copolymerization of substituted cyclic ethers.

2. Consideration of Cationic Ring-opening Polymerizations for Substituted Cyclic Ethers and Acetals

In any ring-opening polymerization (as well as most polymerization mechanisms) there are two conditions which necessarily must be met for a monomer to polymerize:

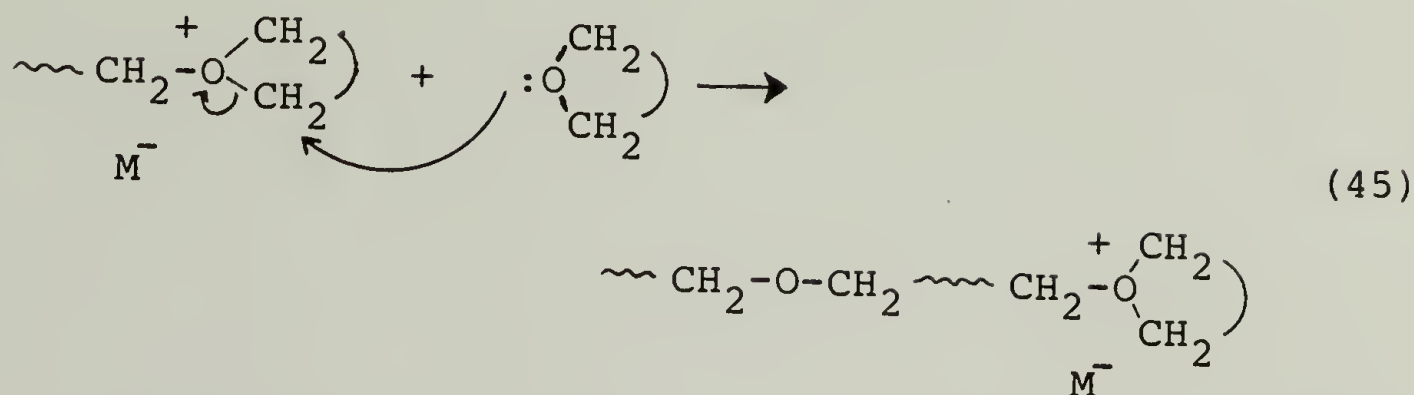
- There must be a mechanism available to the monomer to allow it to go to polymer at a detectable rate
- Under prevailing experimental conditions there must be a negative free energy of polymerization

If only one criterion is met the monomer will not polymerize. Both are needed for successful polymerization.

a. Mechanism for cationic polymerization of cyclic ethers

It is now very well established that for most cationic ring-opening polymerizations of cyclic ethers and acetals the cation is carried on the oxygen atom.¹²⁵ This requires that after the initiation and formation of the oxonium ion the propagation occurs by the nucleophilic attack by the oxygen atom of the monomer onto the carbon atom

α to the oxonium ion (Equation 45).



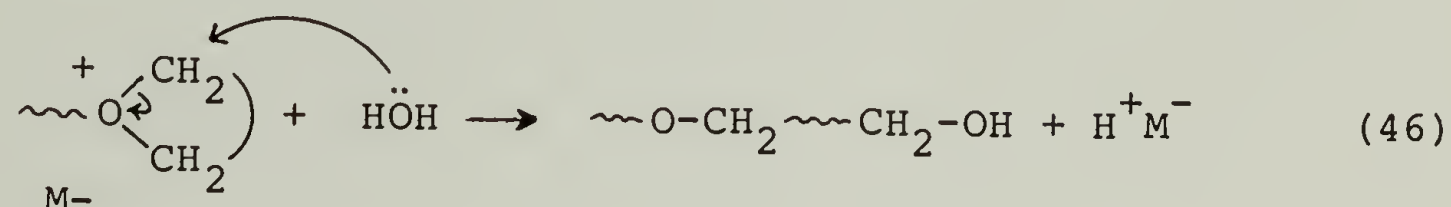
The oxonium ion is always associated with a gegen-ion (M^-). The extent of this association is dependent upon solvent, temperature, initiator, and other considerations.

Termination reactions are also closely related to the polymerization conditions. With proper attention to detail, reaction conditions can be found which create so called "living polymers."^{131,132} The main factors are conditions which favor long-lived and stable oxonium species. As a result polymers are obtained with narrow molecular weight distributions.¹³³ Chain transfer to polymer is quite common for polyethers and polyacetals. This reaction does not result in a change in the kinetic chain length, however, it does terminate the original growing end. The reaction involves the nucleophilic attack by an oxygen on the polymer backbone onto the propagating end. The overall effect is a broadening of molecular weight distribution.¹³⁴

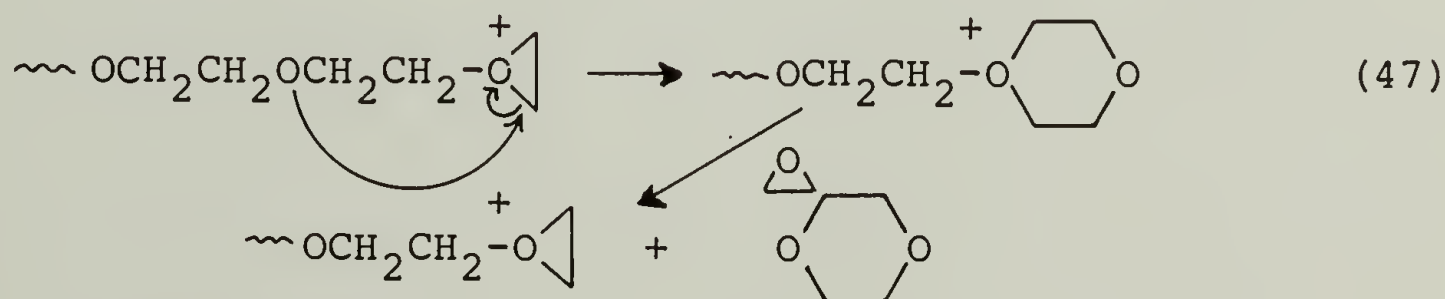
Combination may also occur between the gegen-ion, or some anionic fraction of the gegen-ion, and the oxonium

ion. This is of course a function of the stability of the gegen-ion. $(\text{PF}_6)^-$, $(\text{SbF}_6)^-$ and $(\text{SbCl}_6)^-$ are considered to be the most stable gegen-ions with little combination ever occurring with the oxonium. $(\text{BF}_4)^-$ and $(\text{FeCl}_4)^-$ are examples of somewhat less stable gegen-ions.¹³⁵

Termination is also possible by chain transfer to impurities such as water or other anion donating species. These types of termination definitely "kill" the growing end (Equation 46).



Finally the formation of stable rings via back-biting reactions can also occur.¹³⁶ An example is the formation of 1,4-dioxane, a rather stable 6-membered ring, which is known to occur during the cationic polymerization of ethylene oxide.¹³⁷ This is pictured in Equation 47.



b. Initiators for cationic ring-opening polymerization of cyclic ethers

The initiation of cationic ring-opening polymerizations is accomplished by a variety of systems:

- Lewis Acids
- Proton Acids
- Carbenium Ions
- Oxonium Ions
- Organometallic (Coordinate Cationic) Catalysts

The Lewis acids include BF_3 , SnCl_4 , SbCl_5 and PF_5 along with others. These acids, in combination with some protonic species, form the coinitiator-initiator complex. This complex does the actual initiating by donation of a proton to form the oxonium, with the anion becoming the gegen-ion (Equation 48).



Many times a promoter is used along with this complex to aid in initiating relatively stable cyclic ethers.¹³⁸ The promoters used are often very reactive cyclic ethers such as epichlorohydrin (ECH) which will readily form oxonium ions with the coinitiator-initiator complex, and can then act to start the propagation of the less reactive monomer.¹³⁹

The protonic acid initiators include very strong acids such as trifluoroacetic and fluorosulfonic acids. The effectiveness of these initiators is a function of their electrophilic nature. If the anion is too strong a nucleophile, compared to the cyclic ether, it will compete for the oxonium ion formed. This will terminate the

polymerization.

Carbenium ions are also used to initiate the cationic ring-opening polymerization of cyclic ethers. Species such as $\text{Ph}_3\text{C}^+ (\text{SbCl}_6)^-$ are thought to initiate the polymerization of monomers such as THF by a hydride abstraction from the α -carbon.¹³⁸ This new carbenium ion formed goes on to form the tertiary oxonium ion and initiate propagation.

Also metal catalysts such as aluminum alkyl-water systems have been found to be quite effective for cyclic ether polymerizations.^{140,141} These are sometimes also used in conjunction with promoters and the nature of the polymerization is dependent upon reaction conditions.

c. Kinetics and thermodynamics of cationic ring-opening polymerizations for cyclic ethers

Kinetically the ring-opening polymerization is very similar to the kinetics of step-growth polymerization. The main difference between the kinetics of step-growth and ring-opening is that the latter has termination reactions whereas the former does not. This leads to the fact that ring-opening polymerizations may not continue to increase in molecular weight throughout the entire polymerization.

The rates of polymerization for ring-opening and step-growth are very similar as well. Both fall into the range of $\sim 10^{-2}$ or $\sim 10^{-3}$ L/Mole sec,¹⁴² while chain growth rates of $\sim 10^3$ L/mole sec.

As previously mentioned, not only is a mechanism needed for the polymerization to occur but also a free energy decrease during the polymerization must be realized in order for the reaction to proceed. The classic equation (49) describes this.

$$\Delta G = \Delta H - T\Delta S \quad (49)$$

This states that for most polymerizations both the enthalpy (ΔH) and the entropy (ΔS) of polymerization will be negative in order for the free energy (ΔG) term to be negative. In terms of ring-opening polymerizations both ΔH and ΔS can be important. ΔH is a function of angle strain, crowding of eclipsed adjacent protons or substituents and strain due to crowding of protons or substituents across the ring. ΔH ranges from near 0 to -20 Kcals for most polymerizations. ΔS is comparatively constant but is affected more by conformational considerations of the ring.¹⁴⁴

Thus the thermodynamics of ring-opening does play an enormous role in the polymerizability of cyclic ethers. 3 and 4 membered rings have ΔG 's of the order of -20 Kcal/mole leading to relatively reactive monomers, while 5 membered rings have ΔG 's closer to -5 Kcal/mole and are therefore less reactive. Six membered rings are found to be unpolymerizable with ΔG 's which are positive, owing in part to conformational considerations which decrease ΔS .¹⁴⁵

It has been shown both empirically and by

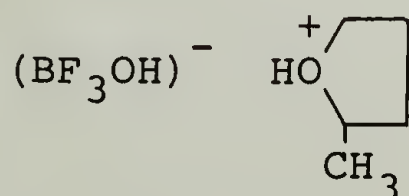
theoretical calculations that substitution on most rings will decrease the likelihood of ring-opening. Small¹⁴⁶ makes the general statement that substituents appear always to decrease polymerizability in all cases where data exists.

3. Cationic Ring-opening Polymerizations for Substituted Tetrahydrofurans

Due to the thermodynamic difficulties involved there has not been a great deal of investigation surrounding the polymerization of substituted tetrahydrofurans.

For the case of 2-methyltetrahydrofuran (2-MTHF) it was reported by Rose¹⁴⁷ that this monomer along with 3-methyl- and 2-chloromethyltetrahydrofuran (3-MTHF and 2-CMTHF) was not polymerizable with any cationic initiator.

Hamermesh and Houry¹⁴⁸ reported that 2-MTHF and 2,5-dimethyltetrahydrofuran (2,5-DMTHF) could not be polymerized using either $\text{BF}_3 \cdot \text{etherate}$ or SbCl_5 at or below room temperature. They did, however, show evidence that the secondary oxonium ion (XVIII) was formed when a 1:1 ratio of $\text{BF}_3 \cdot \text{etherate}$ to 2-MTHF was combined to yield an exothermic value very close to that which was calculated for a 1:1 adduct.



(XVIII)

Five-membered rings when substituted generally tend to favor ring closure over chain formation. Brown and Van Gulick¹⁴⁹ used the ring-closure of 1-bromo-3,3-dimethylbutylamine-4 by dehydrobromination as a model for THF and other 5-membered rings. The reaction goes in quantitative yield with the ring being largely favored over the chain. This was attributed to entropy effects due to the fact that substituents reduce the number of conformations the chain can exist in as a result of non-bonded interactions. This restricts the chain in such a way that the coiled conformations are favored over the normally energetically favored extended chain conformations. To this end the entropy approaches zero in going to the cyclized product and ring-closure is favored. Similar arguments can be made for 5-membered cyclic ethers as well.

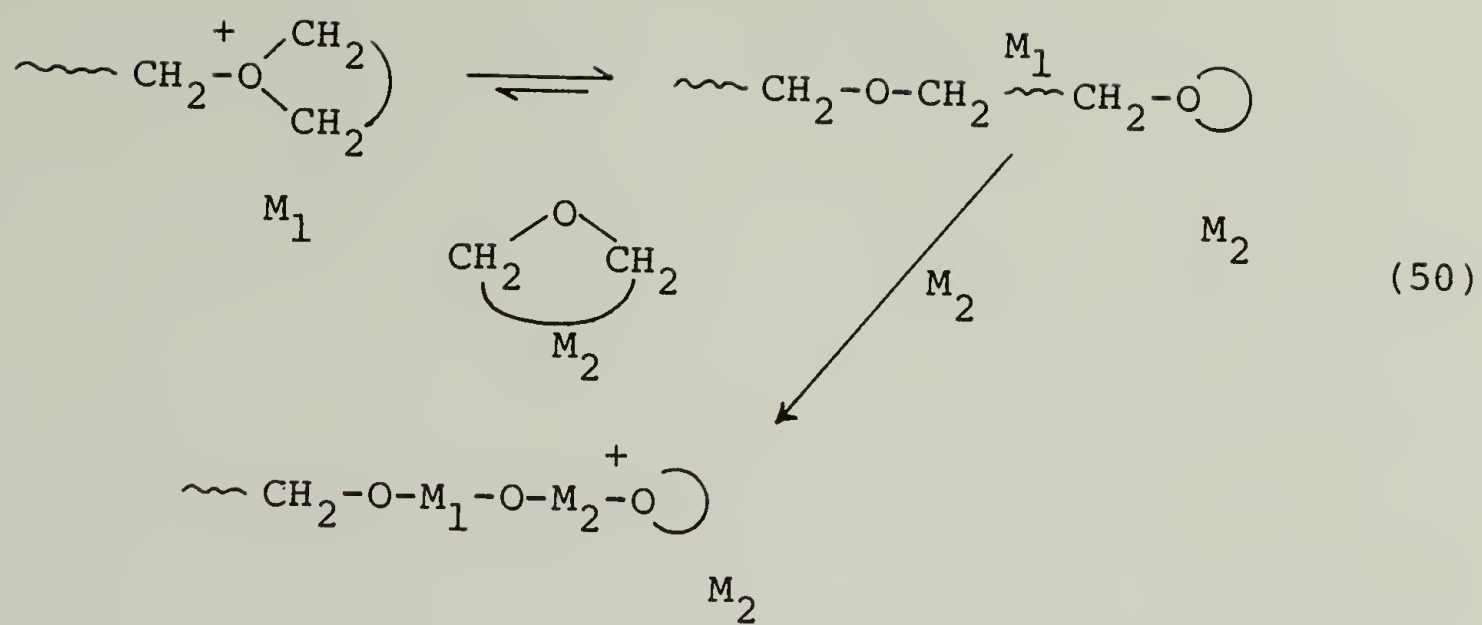
More recently Chaing and Rhodes¹⁵⁰ have shown that PF_5 initiated 3-MTHF effectively gave poly(3-MTHF) at temperatures between 0 and -30°C . They report intrinsic viscosities of 0.5 dL/g under the best conditions.

Dreyfuss and Dreyfuss¹³⁴ reported that no homopolymer of 2-MTHF was obtainable with PF_5 initiator, however, Pruckmayer and Wu¹⁵¹ showed that this monomer does at least have some ability to ring-open. Using high resolution proton NMR these authors found that an average degree of polymerization of 3 could be identified. But no high polymer for 2-MTHF has yet been reported.

Most of these substituted THFs can be copolymerized with more reactive cyclic ethers. Ishigaki, Shono and Hachiama¹⁵² showed that both 2-MTHF and 2-CMTHF could be copolymerized with 3,3-Bis(chloromethyl)oxacyclobutane (BCMO) ethylene oxide (EO), propylene oxide (PO) and ECH. These authors used $\text{BF}_3 \cdot \text{etherate}$ initiator and carried out the polymerizations in the bulk. The reactivity toward copolymerization for several comonomers was found to be $\text{ECH} > \text{PO} > \text{EO}$.

When the reactivity ratios for 2-MTHF and ECH were calculated experimentally Ishigaki et al.¹⁵² found r_1 (2-MTHF) = 0.27 ± 0.05 and r_2 (ECH) = 0.04 ± 0.05 . This copolymerization was shown to proceed in a highly alternating sense, and when a 1:1 comonomer mixture was used 50% of the copolymer was made up of 2-MTHF. Copolymers of 2-MTHF and THF have also been reported.¹³⁴

Yamashita et al.¹⁵³ compiled much of the copolymerization data for cyclic ethers and made the suggestion that the reason for these unreactive 5 and 6-membered rings entering into copolymerizations is that the propagation step can proceed before the depropagation occurs. This is illustrated in Equation 50 where M_1 is the relatively unreactive monomer and M_2 is the reactive cyclic ether.



C H A P T E R I I

EXPERIMENTAL SECTION

A. Materials

The following chemicals were obtained from the sources indicated.

acetone	F	2,5-dimethyl-2,5-	
acetonitrile	A	hexanediol	A
acetylacetone	T	2,2-dimethyl 1,4-	
ammonium chloride	F	propanediol	A
benzene	F, A	dimethylsulfoxide (DMSO)	F
benzoyl peroxide	Ma	epichlorohydrin (ECH)	E
boron trifluoride		ethyl acetate	A
(gas)	M	ethyl-2-bromo-2-methyl-	
boron trifluoride·		propionate	A
etherate	A	ethyl-2-bromopropionate	
n-butyl bromide	E	ethylene	A
n-butyl lithium	A	n-hexane	F
calcium chloride	F	hydrobromic acid (48%)	MCB
carbon tetrachloride	F	hydrochloric acid	
p-chlorobenzene		(conc.)	F
diazonium hexa-		hydrogen (gas)	M
fluorophosphate	A	isopropanol	F
cobalt(II)-		lithium aluminum	
ethylhexanoate	PB	hydride (LAH)	Alp
copper(II)bromide	Allied	lithium bromide	Ma
copper(II)chloride	F	magnesium (turnings)	F
copper(I)chloride	F	magnesium sulfate	MCB
cyclohexane	F	mercuric bromide	F
decalin	F	mesitylene	E
denatured ethanol	F	methanol	F
o-dichlorobenzene	E	methyl ethyl ketone	E
diethyl ether		methyl propyl ketone	E
(anhydrous)	F	paraffin oil	F
N,N-dimethyl		petroleum ether	F
acetamide	A	phosphorous pentoxide	
2,3-dimethyl-2-		(P ₂ O ₅)	MCB
butene	A	polyisobutylene (H-T)	P
2,5-dimethyl-2,4-		potassium hydrogen	
hexadiene	A	sulfate	Ma

potassium metal	F	p-toluene sulfonyl	
propylene oxide	A	hydrazide	A
pyridine	E	tributylamine	A
sodium bisulfite	F	triethyl aluminum	
sodium hydroxide	VWR	(10% in heptane)	Et
sodium metal	A	triethylamine	E
sulfuric acid	F	triisobutyl aluminum	Et
tetrahydrofuran (THF)	B	triphenyl phosphine	A
tetralin	E	m-xylene	E
p-toluene sulfonyl		o-xylene	E
chloride	F	p-xylene	E
		zinc powder	F

Sources: A=Aldrich Chemical Co.; Allied=Allied Chemical Corp.; Alp=Alpha Research Chemicals and Materials; B=J. T. Baker Reagents and Laboratory Products; E=Eastman Organic Chemicals; Et=Ethyl Corporation; F=Fisher Scientific Co.; M=Matheson; MCB=Matheson, Coleman and Bell; Ma=Mallincrodt Chemicals Inc.; P=Polysciences Inc.; PB=Pfaltz and Bauer Research Chemicals; T=Tridom Chemical Inc.; VWR=VWR Scientific Inc.

B. Purification of Solvents and Reagents

Distillations were generally carried out using a 30 cm Vigreux column equipped with a variable reflux ratio distillation head. Reduced pressure distillations were carried out with magnetic stirring and a nitrogen capillary inlet tube.

Acetonitrile was distilled (bp 81.5°C) from P_2O_5 and stored under nitrogen.

Benzene was distilled (bp 80°C) from a sodium-potassium alloy (approx. 50/50 by wt.) and stored under nitrogen.

n-Butyl bromide was distilled (bp 102°C) from calcium chloride just before use.

Copper(II) chloride was obtained as the hydrate and

dehydrated at 100°C for 48 hours in a vacuum oven just prior to use.

Cyclohexane was distilled (bp 81°C) from a sodium-potassium alloy (approx. 50/50 by wt.) and stored under argon.

Decalin was distilled (bp ~ 190°C) at reduced pressure from LAH and stored under nitrogen.

N,N-Dimethyl acetamide was dried over barium oxide for several days then distilled (bp 166°C) before use.

2,5-Dimethyl-2,4-hexadiene was purified by a zone melting procedure. It was placed in an ice-bath until all but 10% was frozen. The unfrozen liquid was poured off and the frozen core was distilled (bp 133°C).

Dimethylsulfoxide (DMSO) was distilled (bp 189°C) under reduced pressure from potassium hydroxide just prior to use.

Epichlorohydrin (ECH) was distilled (bp 115.2°C) under reduced pressure from LAH and stored over molecular sieves.

Ethyl-2-bromo-2-methylpropionate (bp 66°C) and ethyl-2-bromopropionate (bp 157°C) were distilled before use.

Propylene oxide (PO) was distilled (bp 34°C) from LAH and stored under nitrogen.

Pyridine was distilled (bp 116°C) under reduced

pressure from potassium hydroxide and stored under nitrogen.

Tetrahydrofuran (THF) was refluxed for several days with excess LAH and then distilled (bp 66°C) and stored under nitrogen.

Tetralin was distilled (bp 206°C) under reduced pressure from sodium-potassium alloy (approx. 50/50 by wt.) and stored under nitrogen.

Zinc powder was activated by washing with a 2.5% hydrochloric acid solution for about one minute then collected and washed with several portions of distilled water, two portions of ethanol and one portion of diethyl ether. The powder was then dried at 100°C/1 mm pressure before use.

All other solvents and reagents were used as received.

C. Measurements

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer with a 12 minute scan rate. Solid samples were measured as KBr pellets, liquid samples as smears between NaCl plates, and gaseous samples in a 10 cm gas cell with NaCl windows. The infrared spectra of some polymers were measured as films cast from solution directly onto a NaCl plate. The peak assignments were made to the nearest 5 cm^{-1} .

The ^1H NMR spectra were recorded on either a Varian T-60, 60 MHz, or a Perkin-Elmer Model R-24, 60 MHz spectrometer. Solutions were made in either CDCl_3 , d-benzene, D_2O or CD_3OD and were generally 10 to 15% concentration. Chemical shift values were measured as δ (ppm) relative to TMS as an internal standard.

All ^{13}C NMR spectra were recorded on a Varian CFT-20, 100 MHz spectrometer generally fully proton decoupled. The measurements were carried out in a variety of solvents (CDCl_3 , d-benzene, benzene, D_2O , CD_3OD , o-dichlorobenzene). When a nondeuterated solvent was used D_2O was employed as an external lock. At room temperature TMS was used as an internal standard. At elevated temperatures the chemical shifts were calculated in ppm from TMS using a solvent peak standard. Polymer samples were generally measured at elevated temperatures.

Gas chromatographic analyses were carried out on either a Varian Aerograph 920, or a Varian Aerograph 1400 gas chromatograph. A 5 ft. x 1/4 inch column was used with various packings (100/120 mesh Varaport 30, diisodecyl phthalate, and an Se-30).

Thermogravimetric analyses were performed on a DuPont 900 and 950 analyzer thermobalance. The samples were run under helium atmosphere with a flow rate of 40 ml/min. Heating rates were 20 deg/min and generally 2.5 to 3.0 mg of samples was used.

The thermal transitions in the polymer samples and blends were investigated on a Perkin-Elmer Model DSC-II differential scanning calorimeter. The temperature scale of the instrument was calibrated at the desired heating rate by adjusting the direct dial average temperature readout of the programmer to correspond with the transition temperature of indium (mp 429.78°K) and tin (mp 505.06°K). Low temperature calibration was done with acetone (mp 178.70°K). The weight of each sample, typically 10-30 mg, was measured on a Perkin-Elmer AD-2 Autobalance to a precision of 0.01 mg. A heating rate of 20 deg/min and a range of 2 mcal/sec were generally employed.

The DSC scans were used to calculate the glass transition temperatures (T_g) by finding the mid-point of the transition. Melting transitions (T_m) are generally reported as maximum peak temperatures in the endotherms.

Wide angle X-ray scattering was performed on a Siemens model D-500 X-ray diffractometer with a 40 KV copper source. Nickel filtration was used with a sensitivity of 4000 counts/sec and a scan speed of 1 deg/min.

Light microscopy was carried out with a standard Model 18 Zeiss light microscope. The instrument was equipped with adjustable strain free polarization and a variable analyzer. Photography was done with a MDA Leica 35 mm camera using Kodak Ektachrome film and a first order red shift filter.

D. Synthesis of Head-to-Head
Polyisobutylene

1. Monomer Synthesis

a. Diethyl-2,2,3,3-tetramethylsuccinate¹⁵⁴

Into a 5 liter 3-neck roundbottom Morton flask equipped with a mechanical stirrer, reflux condenser and dropping funnel freshly distilled THF (3.0 liters) was added under dry N₂ flow. Anhydrous copper(II) chloride (344 g, 2.16 mole) was added to the flask with vigorous stirring of the THF. The copper(II) chloride crystals rapidly changed color from brown to orange and swelled in size. Activated Zn powder (167 g, 2.6 mole) and a catalytic amount of mercuric bromide (0.1 g) were added into the mixture. Distilled ethyl-2-bromo-2-methylpropionate (253 g, 1.3 mole) was placed in the dropping funnel and slowly added to the mixture over 1.5 hr time. Some heat is evolved during the addition. After complete addition of the ethyl-2-bromo-2-methylpropionate the mixture was brought to reflux for 2 hr then left overnight at room temperature to allow the solids to settle to the bottom. The clear orange supernatant liquid was decanted from the flask and concentrated by removing most of the THF under reduced pressure using a rotary evaporator. A white solid salt, zinc bromide, precipitated from the solution as it was concentrated. The solution was decanted from the salts and transferred to a separatory funnel. All the solids were

washed with ethyl ether and added to the liquid in the separatory funnel. The ether solution was first washed with dilute HCl and then with a 5% NaHCO₃ solution. This immediately precipitated a thick white salt which was re-dissolved by addition of a saturated NH₄Cl solution. The aqueous phase was discarded and the washing procedure repeated until all the salts were removed and the aqueous wash tested to basic pH. The ether layer was collected, dried with anhydrous magnesium sulfate, filtered and concentrated on a rotary evaporator under reduced pressure. The residue was distilled under reduced pressure and the major fraction removed at bp 98-102°C/9.0 mm (lit. 119-121°C/15 mm)¹⁵⁵ was collected. The yield was 27% (39.8 g, 0.16 mole). IR (neat): 1735 cm⁻¹ (ν C=O). See p. 280 ¹H NMR (CDCl₃), δ = 3.9-4.3 ppm (-CH₂-), 1.2-1.45 ppm (-CH₂-CH₃), 1.3 ppm (-CH₃). See p. 295. ¹³C NMR (CDCl₃), δ = 175.9 ppm (C=O), 60.4 ppm (-CH₂-), 47.3 ppm (-C[|]-), 22.1 ppm (-C[|]-CH₃), 14.2 ppm (-CH₂-CH₃). See p. 305.

b. 2,2,3,3-Tetramethylbutanediol-1,4

LAH (31.2 g, 0.82 mole) was placed in a 2 liter, 3 neck roundbottom flask equipped with a mechanical stirrer, a condenser and a dropping funnel. The apparatus was also equipped with a nitrogen inlet and outlet and was kept well flushed with dry nitrogen. Anhydrous diethyl ether (800 ml) was charged into the flask with stirring. Diethyl-

2,2,3,3-tetramethylsuccinate (94.7 g, 0.41 mole) was dissolved in 100 ml of anhydrous diethyl ether and placed in the dropping funnel. This solution was added dropwise to the LAH solution over a period of 2 hr with constant stirring of the reaction and cooling with an ice bath. After the addition was complete the reaction mixture was heated to reflux for 1 hr. The mixture was allowed to cool to room temperature and the flask was further cooled in an ice bath. A 15% NaOH solution (35 ml) followed by 35 ml of water was added dropwise to the cooled mixture with vigorous stirring. The mixture was stirred further for 1 hr and the white precipitate was filtered off and washed with several portions of ether. The ether solutions were collected, dried with anhydrous magnesium sulfate, filtered and concentrated on a rotary evaporator. The 2,2,3,3-tetramethylbutanediol-1,4 was collected as a yellow solid after all the ether was removed. Recrystallization from petroleum ether yielded 56.0 g (94%, 0.38 mole) of a granular white crystalline solid with a melting point of 220-221°C (Lit. 224°C).¹⁵⁶ IR (neat): 3300 cm⁻¹ (ν OH). See p. 281. ¹H NMR (CD₃OD), δ = 4.85 ppm (O-H), 3.39 ppm (-CH₂-), 0.89 ppm (CH₃). See p. 296. ¹³C NMR (D₂O), δ = 70.3 ppm (-CH₂-O), 40.9 ppm (-C-), 21.9 ppm (CH₃). See p. 306.

c. 2,2,3,3-Tetramethylbutaneditosylate-1,4

The preparation of 2,2,3,3-tetramethylbutaneditosylate-1,4 was carried out by placing 500 ml of freshly distilled pyridine into a clean 2 liter Erlenmeyer flask and dissolving 2,2,3,3-tetramethylbutanediol-1,4 (47.8 g, 0.33 mole) in the pyridine. The flask was placed in an ice-rocksalt bath at -5°C and allowed to cool for 1 hr. A magnetic stirring bar was placed in the solution and the mixture was stirred while p-toluenesulfonyl chloride (128.2 g, 0.66 mole) was slowly added over a 1 hr period. The solution was kept well agitated for the next 12 hr and held at -5°C in the ice-salt bath. Distilled water (50 ml) was added slowly to the reaction flask with continued cooling and stirring. The contents of the reaction flask were not allowed to warm to greater than $+5^{\circ}\text{C}$. Distilled water (500 ml) was then added to precipitate the ditosylate. The solid white flakey crystals were collected on a fritted glass funnel and washed with several portions of water. The product was then dried overnight at $60^{\circ}\text{C}/0.1$ mm pressure over P_2O_5 . 130.4 g (87%, 0.29 mole) of crude 2,2,3,3-tetramethylbutaneditosylate-1,4 was collected. To ensure all the hydroxyl groups were reacted, the crude product was put through a second reaction sequence as described above with 29.1 g (0.15 mole) of p-toluenesulfonyl chloride. The product, collected by filtration, was recrystallized twice from methanol and gave 83.0 g (55%, 0.18 mole) of pure

ditosylate after drying in vacuo. The melting point of the flat white crystals was 105-106°C. IR (KBr): 1600 cm^{-1} (ν S-O-CH₂). See p. 282. ¹H NMR (CDCl₃), δ = 7.3-7.8 ppm (aromatic), 3.8 ppm (-CH₂-O), 2.4 ppm (aromatic-CH₃), 0.8 ppm (- $\underset{\text{|}}{\underset{\text{|}}{\text{C}}}$ -CH₃). See p. 297. ¹³C NMR (CHCl₃), δ = 144.9, 132.9, 129.9, 127.9 ppm (aromatic), 75.9 ppm (-CH₂-O), 38.7 ppm (- $\underset{\text{|}}{\underset{\text{|}}{\text{C}}}$ -), 21.7 ppm (aromatic-CH₃), 20.5 ppm (- $\underset{\text{|}}{\underset{\text{|}}{\text{C}}}$ -CH₃). See p. 307. Analysis: Calculated for C₂₂H₃₀S₂O₆; C, 58.15%; H, 6.61%. Found; C, 57.82%; H, 6.06%.

d. Tetra-n-butylammonium bromide

To a clean dry 2 liter, 1 neck roundbottom flask tri-n-butylamine (185.3 g, 1 mole) and n-butylbromide (137.0 g, 1 mole) were added. A magnetic stirring bar was placed in the flask and the mixture was agitated. Acetonitrile (90 ml) was charged into the system, and a reflux condenser fitted to the roundbottom. A heating mantel was placed under the roundbottom and the mixture was refluxed under nitrogen for 24 hr. After the reaction was complete the acetonitrile was removed through evaporation by attaching an aspirator to the flask. The reaction mixture was allowed to cool to room temperature and ethyl acetate (400 ml) was poured into the flask. The tetra-n-butylammonium bromide began to crystallize out when the mixture was transferred to a large Erlenmeyer flask. The Erlenmeyer was cooled for several hours in an ice bath and the

product was collected as a flakey, white crystalline solid on a fritted glass funnel. The product was washed with six 50 ml portions of ethyl acetate and dried for 5 hr in vacuo followed by 18 hr at 60°C/0.1 mm pressure over P_2O_5 . The yield of tetra-n-butylammonium bromide was 234.0 g (73%, 0.73 mole). The crystals melted at 102-103°C (Literature value 103-104°C).¹⁵⁷

e. 2,2,3,3-Tetramethyl-1,4-dibromobutane (TMDBB)

Dried and distilled N,N-dimethyl acetamide (DMAc) (500 ml) was placed in a 2 liter, 3 neck roundbottom flask equipped with a magnetic stirring bar, condenser, thermometer and nitrogen inlet and outlet. 2,2,3,3-Tetramethylbutanediosylate-1,4 (83 g, 0.18 mole) was added to the DMAc along with tetra-n-butylammonium bromide (234 g, 0.73 mole). The system was kept under nitrogen and stirred while it was slowly heated to $110 \pm 1^\circ\text{C}$. A thermowatch temperature monitor was used in conjunction with an oil bath to keep the temperature within one degree of 110°C . Other experiments showed this temperature to be optimum for the reaction. The temperature was maintained for 24 hr. After allowing the reaction mixture to cool to room temperature the solution was poured into 2 liters of distilled water. The 2,2,3,3-tetramethyl-1,4-dibromobutane (TMDBB) precipitated from the water-DMAc mixture and was collected by filtration on a Buchner funnel. The product

was then washed with several portions of distilled water and collected. To purify the product it was first dissolved in a minimum amount of dry benzene and freeze dried carefully. Following this the TMDBB was sublimed at 80°C/0.1 mm pressure, and a final sublimation was performed through a bed of P_2O_5 . The white powdery product obtained was 32.6 g (65%, 0.12 mole). It melted at 48-50°C and was a volatile solid. IR (KBr): 1250, 645 cm^{-1} (ν CH_2-Br). See p. 283. 1H NMR ($CDCl_3$), δ = 3.6 ppm ($-CH_2-Br$), 1.1 ppm ($-CH_3$). See p. 298. ^{13}C NMR ($CDCl_3$), δ = 44.5 ppm ($-CH_2-Br$), 39.8 ppm ($-\overset{|}{C}-$), 22.2 ppm ($-CH_3$). See p. 308. Analysis: Calculated for $C_8H_{16}Br_2$; C, 35.29%; H, 4.88%; Br, 58.82%. Found: C, 35.40%; H, 5.77%; Br, 59.09%.

Note: Attempts to use lithium bromide as the brominating agent for the ditosylate were carried out in acetone, methyl ethyl ketone and methyl propyl ketone. These reactions were done under refluxing conditions for 24 hr. Work-up of the reaction yielded only starting material in each case.

f. 2,5-Dimethyl-2,5-dibromohexane (DMDBH)

A clean 3 neck, 250 ml roundbottom flask was equipped with a condenser, thermometer and ground glass stopper. A 48% aqueous solution of hydrobromic acid (70 ml, 0.68 mole) was carefully poured into the roundbottom and a magnetic stirring bar was added. The hydrobromic

acid was cooled in an ice bath to 0°C and 40 ml of concentrated sulfuric acid was added dropwise to the flask. The addition of the sulfuric acid was done slowly enough so the temperature of the solution remained below 30°C at all times. 2,5-Dimethyl-2,5-hexanediol (25.0 g, 0.17 mole) was added slowly to the acid solution over a period of 30 min. while maintaining the solution temperature below 30°C. The reaction mixture was stirred overnight for 12 hr at room temperature, and the solution was slowly poured with stirring into 1 liter of ice water to precipitate the 2,5-dimethyl-2,5-dibromohexane (DMDBH). The fluffy white solid was collected on a Buchener funnel and washed with several portions of distilled water. The DMDBH was redissolved in 200 ml of diethyl ether, dried with anhydrous magnesium sulfate and filtered. All the ether was removed on a rotary evaporator and the white solid DMDBH collected. The DMDBH was purified by freeze-drying from benzene followed by sublimation at 90°C/0.1 mm pressure through a bed of P₂O₅. The white powdery product had a melting point of 70-72°C (Lit. 67-68°C).¹⁵⁸ ¹H NMR (CDCl₃), δ = 2.0 ppm (-CH₂-) 1.8 ppm (-CH₃). See p. 298. ¹³C NMR (CDCl₃), δ = 66.6 ppm ($\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$), 44.0 ppm (-CH₂-) 34.4 ppm (-CH₃). See p. 308.

2. Head-to-Head Polyisobutylene
Preparation Using Wurtz
Coupling

a. Polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane
with sodium metal in cyclohexane

A clean dry 50 ml, 3 neck roundbottom flask with 14/20 ground glass joints was fitted with a mechanical stirrer, a reflux condenser and an addition funnel. A nitrogen inlet and outlet was also provided for the system and the glassware was flamed out under nitrogen flow for several minutes. After the flask cooled to room temperature 5 ml of fresh paraffin oil was placed in the roundbottom. Freshly cut sodium metal (0.68 g, 29.6 mmole) was added to the oil. With vigorous stirring the flask was heated carefully with a flame until the sodium melted. After several moments the metal became well dispersed and the stirring was discontinued while the flask and its contents were allowed to cool. The oil was washed from the sodium by repeated addition and removal of dry, distilled cyclohexane. Finally, 5 ml of cyclohexane was left over the sodium as the polymerization solvent. 2,2,3,3-Tetramethyl-1,4-dibromobutane (TMDBB) (2.0 g, 7.4 mmole) was dissolved in 5 ml of cyclohexane and added to the addition funnel with a syringe. Several drops of the TMDBB solution were added to the sodium metal and the mixture heated gently to reflux with a small flame. The remainder of the TMDBB solution was added slowly over 30 minutes to

maintain a gentle reflux. Stirring was continued for 24 hr. The polymer was precipitated by pouring the solution into 100 ml of methanol, however only a trace amount of white powder was obtained.

b. Polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane with sodium metal in the bulk

A clean 10 ml, 1 neck, roundbottom flask was fitted with a condenser and a nitrogen "T" tube. The "T" tube was extended in such a way that it reached through the condenser to the flask and nitrogen was passed through. The glassware was then flamed-out with a gentle flame and allowed to cool with nitrogen flow. Sodium metal (0.34 g, 14.8 mmole) was cut under mineral oil and washed with several portions of diethyl ether. The sodium was transferred to the reaction flask and TMDBB (2.0 g, 7.4 mmole) was added along with a small magnetic stirring bar. The monomer was melted with a gentle flame and heated until the sodium metal began to melt. The reaction became exothermic for several minutes and the flask was placed in an oil bath at 100°C. With stirring, and under nitrogen, the reaction was kept at 100°C for 24 hr. The polymer was collected by washing the system with several portions of cyclohexane and collecting the washings. The solvent was removed at reduced pressure on a rotary evaporator and the H-H polyisobutylene was collected and dried overnight at 80°C/0.1 mm pressure over P_2O_5 . The yield was 0.16 g (20%, 1.5 mmole).

IR (neat): 2962, 2926, 2872 cm^{-1} ($\nu_{\text{as}}\text{CH}_3$, $\nu_{\text{as}}\text{CH}_2$, $\nu_{\text{s}}\text{CH}_3$); 1375, 1365 cm^{-1} ($\delta_{\text{s}}\text{CH}_3$, gem-dimethyl). See p. 284.

^{13}C NMR (CDCl_3), δ = 40.6 ppm (branch $-\overset{\text{I}}{\underset{\text{T}}{\text{C}}}-$), 38.9 ppm ($-\overset{\text{I}}{\underset{\text{T}}{\text{C}}}-$), 31.5 ppm ($-\text{CH}_2-$), 24.1 ppm (endgroup $-\text{CH}_3$), 23.0 ppm (branch $-\text{CH}_2-$), 21.38 ppm ($-\overset{\text{I}}{\underset{\text{T}}{\text{C}}}-\text{CH}_3$). See p. 309.

Analysis: Calculated for C_8H_{16} ; C, 85.71%; H, 14.29%.

Found: C, 85.24%; H, 14.80%.

c. Attempted polymerization of 2,2,3,3 tetramethyl-1,4-dibromobutane with sodium metal under vacuum

A polymerization tube was built by attaching a 19/38 ground glass female joint to a standard 25 ml vacuum sealable polymerization tube. The tube was cleaned with a hot chromic acid solution, then rinsed with dilute sodium hydroxide solution and distilled water. After drying, a 3-way, male, 19/38 vacuum stopcock was fitted to the polymerization tube. A Firestone valve¹⁵⁹ used in conjunction with a vacuum line ($< .05$ mm), was used to alternately fill the tube with nitrogen and evacuate it. The tube was flamed-out once under vacuum and allowed to cool. Sodium metal (0.40 g, 17.8 mmole) was cut under n-hexane, placed under the 3-way stopcock in the top of the polymerization tube, and the tube was again evacuated. The sodium was heated slowly until it melted and flowed down the narrow section of the polymerization tube and into the bulb. The slightly oxidized outer layer of sodium was left behind during the melting. The clean sodium formed a sodium

mirror in the polymerization bulb. TMDBB (2.0 g, 7.4 mmole) was dissolved in 5 ml of distilled benzene and syringed into the polymerization tube with the metal. The solution was put through several freeze/thaw cycles under vacuum to remove dissolved oxygen. Finally the polymerization tube was sealed with a flame and the mixture heated in an oil bath at 60°C with shaker agitation. After four days the tube was opened and the solution poured into methanol. No precipitation of polymer was observed.

d. Attempted polymerization of 2,5-dimethyl-2,5-dibromohexane (DMDBH) with Wurtz coupling

The polymerization of DMDBH was attempted using procedures similar to those described for TMDBB with sodium metal. In spite of several experimental variations all polymerization attempts with DMDBH by Wurtz techniques were unsuccessful. There was however significant reaction of the sodium with DMDBH in several cases with evolution of volatiles and liquids.

3. Preparation of Head-to-Head
Polyisobutylene by Hydrogenation
of 2,5-Poly(2,5-Dimethyl-2,4-
Hexadiene)

a. Preparation of 2,5-Poly(2,5-dimethyl-2,4-hexadiene)¹⁶⁰

A clean dry 2 liter resin kettle with a four neck top was sealed and equipped with a mechanical stirrer, addition funnel, thermometer and a gas inlet and outlet tube. The apparatus was thoroughly flushed with nitrogen before

525 ml of petroleum ether was added through the addition funnel. The petroleum ether was cooled to -70°C by placing the reaction vessel in a Dry Ice/isopropanol bath. A small lecture bottle of boron trifluoride (BF_3) gas was attached to the gas inlet tube and carefully opened to allow a gentle flow of BF_3 to fill the vessel. As fumes started to escape from the outlet the BF_3 was shut-off. 2,5-Dimethyl-2,4-hexadiene (30 g, 0.27 mole) was placed in the addition funnel and dissolved in 45 ml of petroleum ether. The monomer solution was then introduced to the reaction vessel with vigorous stirring over a period of about five minutes. The temperature of the reaction mixture was kept below -60°C and the mixture became a yellow slush which was difficult to stir. After several more minutes of stirring the resin kettle was removed from the cold bath and 50 ml of denatured ethanol was added followed by 375 ml of acetone. At this time a thick white precipitate was obtained and the yellow color disappeared. The polymer was collected by filtration on a fritted glass funnel and washed several times with acetone. The white powdery polymer was placed in 500 ml of very dilute ammonium hydroxide solution, stirred for 30 minutes and filtered again. It was washed with several portions of distilled water followed by acetone and dried in vacuo at $60^{\circ}\text{C}/0.1$ mm pressure over P_2O_5 for 24 hr. The powdery white 2,5-poly(2,5-dimethyl-2,4-hexadiene) was obtained in 70% yield (21.0 g). I.R. (KBr):

1377, 1367 cm^{-1} ($\delta_{\text{s}}\text{CH}_3$, gem-dimethyl); 1000, 987 cm^{-1} (trans-diene). See p. 285. ^{13}C NMR (o-dichlorobenzene) (120°C); 135.5 ppm ($-\text{CH}=\text{}$), 41.4 ppm ($-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-$), 23.9 ppm ($-\text{CH}_3$). See p. 312. M.P., 263°C. The inherent viscosity (0.5 g/100 ml, decalin, 130°C) was 1.5 dl/g. The polymer was soluble only at elevated temperatures in saturated hydrocarbon or chlorinated aromatic solvents.

b. Preparation of cobalt^{II}/triisobutyl aluminum hydrogenation catalyst

A clean dry Schlenk tube with 2 sidearms was equipped with a 3-way stopcock and flamed out under vigorous nitrogen flow. After allowing the glass to cool a magnetic stirbar was placed in the tube and 40 ml of dry, distilled decalin was syringed into the tube. Triisobutyl aluminum (3.9 ml, 15.6 mmole) was slowly syringed into the stirring decalin. Cobalt(II)-ethylhexanoate (6% Co, w/w) (3.8 g, 3.9 mmole) was dissolved in 10 ml of decalin and placed into a dropping funnel attached to the Schlenk tube. The tube was cooled in an ice bath while the cobalt solution was slowly added over a 30 minute period with constant stirring. The catalyst ratio was 4:1, Al:Co. It could be stored for some weeks under nitrogen and remain active. A large bore syringe needle was used to transfer the catalyst solution to the hydrogenation equipment for each experiment.

Note: A catalyst solution with a ratio of 3.3:1,

Al:Co was also prepared in a similar manner using 3.9 ml (15.6 mmole) of $\text{Al}(\text{i-Bu})_3$ and 4.6 g (4.7 mmole) cobalt(II)-ethylhexanoate.

c. Preparation of cobalt^{II}/n-butyl lithium hydrogenation catalyst

To prepare the Co/Li catalysts a similar procedure to that used for the preparation of the Co/Al catalysts was used. n-butyl lithium (1.0 g, 15.6 mmole) was combined with cobalt(II)-ethylhexanoate (6% Co, w/w) (3.8 g, 3.9 mmole based on Co) (Li:Co ratio of 4:1) in 50 ml of dry decalin.

d. Attempted hydrogenation of 2,5-Poly(2,5-dimethyl-2,4 hexadiene) using cobalt^{II}/triisobutyl aluminum catalyst

A 600 ml Parr Autoclave equipped with a sealed stirring unit and a heating furnace was cleaned and dried. 2,5-Poly(2,5-dimethyl-2,4-hexadiene) (1.0 g, 9.1 mmole based on monomer units) was introduced into the autoclave and the system was sealed. Nitrogen was flushed through the autoclave for 30 minutes to remove oxygen. Distilled decalin (100 ml) was syringed into the autoclave and nitrogen was passed through it for an additional 30 minutes. The cobalt^{II}/triisobutyl aluminum solution (4:1, Al:Co, 1.17 ml, 0.091 mmole of Co) 1.0 mole % was added by syringe to the mixture and the final seals made to the autoclave. A cylinder of high grade hydrogen (99.9%) was attached to the autoclave and the system was brought to 200 psi pressure then released slowly to 0 psi. This cycle was carried

out twice and the hydrogen pressure was finally brought to 170 psi. While stirring, the temperature of the autoclave and its contents was brought to $180 \pm 5^\circ\text{C}$. The pressure increased to 210 psi and remained stable. The autoclave was stirred and heated for 6 hr after which the temperature was allowed to drop to ambient and the hydrogen pressure was released. The autoclave was opened and the decalin solution was poured into 400 ml of isopropanol to precipitate the polymer. The white powdery polymer was collected on a fritted glass funnel, washed with methanol then dried at $60^\circ\text{C}/0.1$ mm pressure over P_2O_5 for 24 hr. The recovered polymer was obtained in 78% yield (0.78 g) after a reprecipitation from hot decalin into isopropanol. The polymer recovered was identified as starting material. M.P., 261°C . IR (KBr): $1377, 1367\text{ cm}^{-1}$ ($\delta_s\text{CH}_3$, gem-dimethyl); $1000, 987\text{ cm}^{-1}$ (trans-diene).

Note: Catalytic hydrogenations were carried out under a variety of conditions and with a number of different catalysts. All the experiments were done in a similar way to that described in D.3.d. A summary of these experiments is given in Table 10. See p. 136.

In experiments carried out above 190°C no polymer was recovered when the solution was poured into isopropanol. In these cases the starting monomer, 2,5-dimethyl-2,4-hexadiene, was identified from the decalin solution by distilling the monomer from the mother liquor. The bp of

2,5-dimethyl-2,4-hexadiene was 133°C. ^{13}C NMR (CDCl_3); δ = 18.0 ppm ($-\underline{\text{CH}}_3$, trans), 26.3 ppm ($-\underline{\text{CH}}_3$ cis), 121.8 ppm ($-\underline{\text{CH}}=$), 131.7 ppm ($-\overset{\text{I}}{\text{C}}=$). See p. 313.

e. Chemical hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexadiene) using diimide

A 250 ml, 3 neck roundbottom flask was equipped with a reflux condenser, a thermometer, a nitrogen inlet and outlet and a magnetic stirbar. The apparatus was thoroughly flushed with nitrogen and 2,5-poly(2,5-dimethyl-2,4-hexadiene) (2.5 g, 22.7 mmole based on repeat unit) was introduced along with 75 ml of decalin and 25 ml of m-xylene. While stirring the mixture, p-Toluenesulfonylhydrazide (p-TSH) (8.4 g, 45.4 mmole) was added and the temperature of the solution was increased slowly to 160°C using an oil bath equipped with a thermowatch. The solution was stirred at this temperature for 12 hr before allowing it to cool to room temperature. The solution was then poured into 400 ml of isopropanol to precipitate the polymer. The white solid precipitate was collected on a fritted glass filter funnel by suction filtration and washed with several portions of methanol. After reprecipitation from hot decalin into isopropanol and drying 12 hr at 60°C/0.1 mm pressure over P_2O_5 the yield of white powdery polymer was 2.2 g (88%). The polymer recovered was found to be partially hydrogenated (estimated at 4%) by infrared

analysis.

i. Hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexadiene) with diimide in 1,3,5-trimethylbenzene (mesitylene)

The general procedure described above was used with the solvent being mesitylene in place of decalin/m-xylene. The temperature was reflux for mesitylene at 130°C and a reaction time of 16 hr was used. The yield was 2.4 g (94%) of 8% hydrogenated polymer based on IR analysis.

ii. Hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexadiene) with diimide in 1,2-dimethylbenzene (σ -xylene)

The general procedure described in D.3.e. was used with o-xylene as solvent. Four equivalents of p-toluene-sulfonylhydrazide (p-TSH) (16.8 g, 90.8 mmole) were used at a reflux temperature of 145°C for 20 hr. The yield of recovered polymer was 2.3 g (93%). Partial hydrogenation was estimated at 18% by IR.

iii. Hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexadiene) with diimide in 1,4-dimethylbenzene (p-xylene)

The general procedure described in D.3.e. was used with p-xylene as solvent. Four equivalents of p-TSH (16.8 g, 90.8 mmole) were used at a reflux temperature of 139°C for 22 hr. The yield of recovered polymer was 2.4 g (95%). Partial hydrogenation was estimated at 28% by IR.

f. Hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexadiene) by repeated additions of diimide

A 250 ml, 3 neck roundbottom flask was equipped with a reflux condenser, thermometer, nitrogen inlet and outlet and a magnetic stirbar. The apparatus was thoroughly flushed with nitrogen and 2,5-poly(2,5-dimethyl-2,4-hexadiene) (2.5 g, 22.7 mmole based on repeat unit) was introduced along with 75 ml decalin and 25 ml m-xylene. While stirring the mixture, p-TSH (8.4 g, 45.4 mmole) was added and the temperature of the solution brought to 160°C using an oil bath equipped with a thermowatch. The solution was stirred at 160°C for 12 hr. A 10 ml aliquot was removed by pipette, worked-up by precipitation into isopropanol, followed by filtration and washing with methanol. The sample was dried at 60°C/0.1 mm pressure over P₂O₅. The IR spectroscopic analysis (KBr pellet) showed 11% hydrogenation after 12 hr. The reaction was continued with an addition of 2 equivalents of p-TSH (8.4 g, 45.4 mole) every 24 hr. Aliquots of 10 ml were removed and worked-up after 24, 48, 96, 126, 174 hours. IR analysis showed the percent hydrogenation given in Table 3.

Analysis after 174 hr: Calculated for C₈H₁₆; C, 85.71%; H, 14.29%. Found: C, 80.40%; H, 13.79%; N, 0.38%; S, 0.70%.

TABLE 3

HYDROGENATION OF 2,5-poly(2,5-DIMETHYL-
2,4-HEXADIENE) BY REPEATED ADDITIONS
OF DIIMIDE

hrs	12	24	48	96	126	174
% hydrogenation	11%	21%	39%	44%	48%	49%

g. Hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexadiene)
by repeated reactions with diimide

The general procedure used was that which was described in D.3.f. In this experiment however, 4 equivalents of p-TSH (16.8 g, 90.8 mmole) were added every 24 hr and the entire polymer was worked-up, dried, and placed into fresh reagents after each 24 hr. In this experiment the reaction was repeated six times. The percent hydrogenation was determined after each experiment by IR analysis. Table 4 shows the data obtained.

TABLE 4

HYDROGENATION OF 2,5-poly(2,5-DIMETHYL-
2,4-HEXADIENE) BY REPEATED REACTIONS
WITH DIIMIDE

Number of reactions	1	2	3	4	5	6
Percent Hydrogenation	37%	60%	64%	68%	69%	70%
Yield (g)	2.31	2.15	2.05	1.94	1.89	1.88

The polymer became insoluble after six reactions. Analysis after 6 hydrogenation experiments. Calculated for C_8H_{16} ; C, 85.71%; H, 14.29%. Found; C, 80.51%; H, 13.94%; N, 0.51%; S, 0.83%.

4. Attempted Preparation of Head-to-Head Polyisobutylene by Alternating Copolymerization of Ethylene with Tetramethylethylene

a. Copolymerization of ethylene with tetramethylethylene with benzoyl peroxide initiator

A 600 ml Parr autoclave with a packed stirring unit and a variable temperature heating furnace was cleaned and assembled. The top was sealed and 100 ml of dry benzene was charged into the autoclave. The vessel was flushed with argon for 15 minutes. Under positive argon pressure recrystallized benzoyl peroxide (0.15 g, 0.62 mmole) was charged into the autoclave along with 2,3-dimethyl-2-butene (Tetramethylethylene) (1.0 g, 12.0 mmole) via syringe. The final seals were made to the autoclave and a cylinder of polymerization grade ethylene (99.9%) was attached to the autoclave. The pressure vessel was charged to 200 psi with ethylene and the pressure was reduced to 0 psi. The pressure was again brought to 220 psi with ethylene and the furnace was programmed to slowly bring the internal temperature of the reaction to 70°C. Vigorous stirring of the reaction mixture was employed throughout the procedure. As the contents reached 70°C the pressure

increased to 320 psi and after 4 hr of heating dropped to 310 psi. The reaction was carried out for 22 hr at which time the internal pressure was down to 300 psi. The autoclave was permitted to cool to room temperature before venting to release the excess ethylene pressure. After opening the vessel the benzene solution was poured directly into 300 ml of methanol with stirring. The white fluffy precipitate was collected on a fritted glass funnel and washed with several portions of methanol. The polymer was dried overnight at 60°C/0.1 mm pressure over P_2O_5 to yield 0.31 g (23% based on 1:1 copolymer). 1H NMR (d-benzene), 1.3 ppm ($-CH_2-CH_2-$) (6.8^1H), 1.0 ppm ($-CH_3$) (1.0^1H) shows 5% tetramethylethylene and 95% ethylene. See p. 299. ^{13}C NMR (d-benzene), 36.3 ppm ($-\overset{|}{C}-$), 30.1 ppm ($-\overset{|}{CH_2}-CH_2-$), 23.8 ppm ($-\overset{|}{CH_3}$). See p. 315. Analysis: Calculated for $\{C_2H_4\}(\{C_6H_{12}\})$; C, 85.71%; H, 14.29%. Found; C, 83.03%; H, 13.61%.

5. Preparation of Head-to-Head Polyisobutylene Using Grignard/Alkylbromide Coupling Polymerization

a. Preparation of copper(I)(tri-phenylphosphino) bromide $[CuBr(PPh_3)_3]$ 161

To a clean dry 100 ml, 1 neck roundbottom flask equipped with a magnetic stirbar and a reflux condensor triphenylphosphine (PPh_3) (12.2 g, 46.7 mmole) was added. To this copper(II) bromide ($CuBr_2$) (3.0 g, 13.4 mmole) was added giving a 7:2, $PPh_3:CuBr_2$ ratio. Pure ethanol (60 ml)

was poured into the mixture and the solution was brought to reflux for 2 hr. As the reaction proceeded a white precipitate formed which was the $\text{CuBr}(\text{PPh}_3)_3$ salt. After the reaction was complete the product was collected by filtration and washed with four 20 ml portions of diethyl ether. Drying was accomplished at $60^\circ\text{C}/0.1$ mm pressure over P_2O_5 for 12 hr. The yield of white powder crystals was 8.9 g (99%). M.P., 72°C (Lit. 69°C).¹⁶² Analysis: Calculated for $\text{C}_{54}\text{H}_{45}\text{P}_3\text{CuBr}$; C, 69.72%; H, 4.84%. Found; C, 69.32%; H, 4.89%.

b. Polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane via Grignard coupling: benzene/tetrahydrofuran solvent

A 100 ml, 3 neck, 14/20 roundbottom flask was equipped with a reflux condenser, an addition funnel, and a nitrogen inlet and outlet. The glassware was flushed with nitrogen for several minutes then flamed-out to dryness. After cooling, magnesium turnings (0.447 g, 18.4 mmole) which had been ground to expose fresh surfaces were charged into the reaction vessel. The turnings were flushed with nitrogen then flamed-out under nitrogen flow to assure all the moisture was removed. After allowing the magnesium to cool, 30 ml of dry benzene was syringed into the flask along with a magnetic stirbar. 5 ml of dry THF was placed in the addition funnel and TMDBB (5.0 g, 18.4 mmole) was dissolved in the benzene. The Grignard reaction was started by adding the THF to the solution and heating the

flask gently with a flame. A smooth exothermic reaction began and the temperature was kept low using a water bath as the magnesium was consumed. After approximately 2 hr all of the magnesium metal had reacted and the Grignard formation assumed complete. The temperature of the solution was lowered to -5°C with an ice/salt bath and $\text{CuBr}(\text{PPh}_3)_3$ (100 mg) was added to the grey solution. After 1 hr a white solid precipitate was apparent in the flask and the temperature was kept at -5°C for 3 hr more before being allowed to warm to room temperature. The reaction was stirred for a further 13 hr at ambient temperature before the vessel was opened and the solution poured into 200 ml of methanol. A fine white precipitate formed which was collected on a fritted glass funnel and washed with methanol. To purify the polymer it was dissolved in hot tetralin and hot filtered with a steam jacketed Buchner funnel before being reprecipitated into methanol/isopropanol. The filtered polymer was dried at $60^{\circ}\text{C}/0.1$ mm pressure over P_2O_5 for 1 day to give a white powder polymer in 0.55 g (28%) yield. M.P. $\sim 190^{\circ}\text{C}$ (DSC). IR (film): 2962, 2872, 2926 cm^{-1} ($\nu_{\text{as}}\text{CH}_3$, $\nu_{\text{s}}\text{CH}_3$, $\nu_{\text{as}}\text{CH}_2$); 1375, 1365 cm^{-1} ($\delta_{\text{s}}\text{CH}_3$, gem-dimethyl). See p. 167. ^1H NMR (σ -dichlorobenzene), 1.4 ppm ($-\text{CH}_2-$), 0.9 ppm ($-\text{CH}_3$). See p. 171. ^{13}C NMR (σ -dichlorobenzene) (80°C), 38.8 ppm ($-\overset{\text{i}}{\underset{\text{i}}{\text{C}}}-$), 31.4 ppm ($-\text{CH}_2-$), 21.7 ppm ($-\text{CH}_3$). See p. 316. Inherent viscosity (0.5 g/100 ml) 0.25 dl/g (in o-dichloro-

benzene at 60°C).

i. Grignard/alkylbromide coupling of TMDBB with tetrahydrofuran as solvent at room temperature

The procedure described previously in D.5.b. was followed for this experiment. The solvent for this reaction was 30 ml of dry THF. All other reagent quantities remained the same. In this experiment the temperature at which the coupling was performed was room temperature ($\sim 27^{\circ}\text{C}$). No polymer was recovered from this reaction.

ii. Grignard/alkylbromide coupling of TMDBB with triethylamine/benzene solvent system at 60°C

The general procedure described in D.5.b. was used in this experiment. The reagent quantities were the same. The solvent was changed to 3 ml triethylamine and 30 ml dry benzene. The coupling polymerization was carried out at 60°C. After the standard work-up 0.10 g (5%) of H-H polyisobutylene was recovered.

iii. Grignard/alkylbromide coupling of TMDBB with tributylamine/benzene solvent system at 60°C

The general procedure described in D.5.d. was used in this experiment. The reagent quantities were the same. The solvent system was changed to 3 ml tributylamine and 30 ml dry benzene. The coupling polymerization was carried out at 60°C. After the standard work-up 0.18 g (9%) of H-H polyisobutylene was isolated.

iv. Grignard/alkylbromide coupling of TMDBB with tri-butylamine/benzene solvent system at 60°C; CuCl_2 as catalyst

The general procedure described in D.5.b. was used in this experiment. The reagent quantities were the same. In place of $\text{CuBr}(\text{PPh}_3)_3$, CuCl_2 was used (100 mg). The solvent system was changed to 3 ml tri-n-butylamine and 30 ml benzene. The coupling polymerization was carried out at 60°C. Standard work up yielded 0.10 g (5%) of H-H polyisobutylene.

v. Grignard/alkylbromide coupling of TMDBB with tetrahydrofuran/triethylamine/benzene solvent system at -5°C

The general procedure described in D.5.b. was used in this experiment. The solvent system was changed to 2.5 ml THF, 2.5 ml triethylamine, and 25 ml benzene. The coupling polymerization was carried out at -5°C. All other reagents and quantities remained the same. The yield of H-H polyisobutylene was 0.49 g (24%).

vi. Grignard/alkylbromide coupling of TMDBB with triethylamine/benzene solvent system at -5°C; CuCl_2 catalyst

The procedure described in D.5.b. was used in this experiment. The solvent system was a mixture of 5 ml triethylamine and 20 ml of benzene. The catalyst for the coupling was CuCl_2 (100 mg). The coupling was carried out at -5°C. The reaction with the magnesium appeared incomplete, and no polymer was recovered from this reaction. Table 5 is a summary of solvent effect on polymer yield.

TABLE 5

EFFECT OF SOLVENT ON GRIGNARD/ALKYLBROMIDE
POLYMERIZATION

Grignard Solvent	Polymer Solvent	Catalyst	Polymerization temp.	yield
THF	none	$\text{CuBr}(\text{PPH}_3)_2$	R.T.	0
Triethylamine	1/10 Benzene	$\text{CuBr}(\text{PPH}_3)_2$	60°C	5%
Tributylamine	1/10 Benzene	CuCl_2	60°C	5%
Tributylamine	1/10 Benzene	$\text{CuBr}(\text{PPH}_3)_2$	60°C	9%
THF/TEA	1/5 Benzene	$\text{CuBr}(\text{PPH}_3)_2$	- 5°C	24%
THF	1/4 Benzene	$\text{CuBr}(\text{PPH}_3)_2$	- 5°C	28%
TEA	1/4 Benzene	CuCl_2	- 5°C	0

c. Grignard/alkylbromide coupling polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane carried out at -25°C with degassed solvent

A Schlenk tube equipped with a three-way vacuum stopcock sidearm, a "U" tube sidearm and a reflux condenser was flushed with nitrogen for 15 minutes and then flamed-out to remove any moisture on the glassware. After allowing the apparatus to cool, freshly ground magnesium turnings (0.447 g, 18.4 mmole) were added to the Schlenk tube. The turnings were then thoroughly flushed with nitrogen and dried with a flame. After permitting the glassware to cool again 20 ml of freshly distilled benzene was syringed into the Schlenk tube and the solvent was degassed by three freeze/thaw cycles under vacuum. A small magnetic stirbar was added and 5 ml of dry THF was syringed into the benzene. TMDBB (5.0 g, 18.4 mmole) which had been previously placed in the "U" tube sidearm was then added to the reaction vessel with stirring. The system was heated but no reaction started with the magnesium. Two additional 5 ml portions of THF were added and with further heating the reaction became exothermic. After 1.5 hr the magnesium was completely consumed. The temperature of the reaction was lowered to -25°C with a Dry Ice/carbon tetrachloride bath. With continued stirring $\text{CuBr}(\text{PPh}_3)_3$ (50 mg) was added to the cooled solution. The temperature was maintained for 10 hr then the solution was slowly heated with an oil bath to 60°C for another 3 hr. The solution was then cooled and

the polymer precipitated by addition to isopropanol. After filtration and methanol washing the H-H polyisobutylene was redissolved in hot tetralin and filtered hot on a steam jacketed Buchner funnel. The polymer was reprecipitated into methanol, collected, washed and dried at 60°C/0.1 mm for 24 hr. The yield was 0.15 g (7.5%). ^{13}C NMR (o-dichlorobenzene) (80°C), 38.91 ppm ($-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-$), 31.51 ppm ($-\text{CH}_2-$), 21.78 ppm ($-\text{CH}_3$). See p. 173. Analysis: Calculated for $\{\text{C}_8\text{H}_{16}\}_n$; C, 85.71%; H, 14.29%. Found; C, 83.27%; H, 14.50%; Br, 1.63%. \bar{M}_n (as calculated by bromine endgroups), 1.0×10^4 .

Note: Table 6 shows the temperature, \bar{M}_n , and yield data for several experiments.

d. Recovery of volatile products produced during the Grignard polymerization of 2,2,3,3-tetramethyl 1,4-dibromobutane


The procedure described in D.5.b. was used to perform this experiment. The apparatus was modified to include a trap adjacent to the nitrogen outlet. This trap was cooled with a Dry Ice/isopropanol bath to -78°C and any volatiles from the reaction were recovered. After removing benzene and THF residues the clear liquid weighed 1.2 g (~60% of starting material based on bromine loss). ^{13}C NMR (benzene), 44.5 ppm ($\text{CH}_2\text{-Br}$), 39.8 ppm ($-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-$), 21.9 ppm ($-\text{CH}_3$). This shows recovered monomer present, but major peaks, 36.3 ppm ($-\overset{\text{I}}{\text{C}}-$), 31.4 ppm (CH_2-), 24.8, 24.1,

TABLE 6
GRIGNARD POLYMERIZATION DATA

Catalyst CuBr (PPH ₃) ₃	Temp.	Yield	η_{inh} (a)	\bar{M}_n (b)
0.4 mol%	70°C	Trace		
0.8	50°C	5%	0.09	
0.4	- 5°C	24%	0.21	3.2×10^3
0.4	-25°C	7%	0.32	1.0×10^4
0.8	- 5°C	28%	0.20	3.0×10^3
0.8	- 5°C	24%	0.19	2.7×10^3
0.8	- 5°C	31%	0.25	3.6×10^3

(a) In o-Dichlorobenzene at 60°C.

(b) Calculated from bromine end groups.

25.9 ppm ( CH₃) were assigned to a cyclobutane derivative. See p. 310.

e. Attempted polymerization of 2,5-dimethyl-2,5-dibromohexane (DMDBH) via Grignard/alkylbromide coupling

The general procedure described in D.5.b. was used substituting DMDBH for TMDBB. All quantities remained the same. The preparation of the Grignard was very smooth, however no polymer was recovered after normal work-up.

Note: A variety of condition changes were made in a number of experiments, however, in no case was any polymer obtained.

E. Synthesis of Poly(1,1-dimethylpropane)

1. Monomer Preparation

a. 2,2-Dimethylpropaneditosylate-1,3

The preparation of 2,2-dimethylpropaneditosylate-1,3 was carried out in the same manner as in the preparation of 2,2,3,3-tetramethylbutaneditosylate-1,4 (D.1.c.). In this experiment 2,2-dimethylpropanediol-1,3 (50.0 g, 0.48 mole) was reacted first with p-toluenesulfonyl chloride (p-TsCl) (186.6 g, 0.96 mole) then with a second quantity of p-TsCl (46.6 g, 0.12 mole) to yield 180.5 g (91.4%) of 2,2-dimethylpropaneditosylate-1,3. The product was a white flakey crystal with a melting point of 124-125°C. ¹H NMR (CDCl₃), δ = 7.25-7.8 ppm (aromatic-H), 3.7 ppm (-O-CH₂-), 2.45 ppm (aromatic-CH₃), 0.85 ppm

($-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3$). See p. 300. IR (KBr); 1600 cm^{-1} ($\nu_{\text{S}}\text{ S-O-CH}_2$). See p. 286. ^{13}C NMR (CDCl_3), $\delta = 145.0, 132.4, 130.0, 127.8$ ppm (aromatic carbons), 73.7 ppm ($-\text{CH}_2-\text{O}-$), 35.3 ppm ($-\overset{|}{\underset{|}{\text{C}}}-$), 21.6 ppm (aromatic- CH_3), 20.9 ppm ($-\overset{|}{\underset{|}{\text{C}}}-\text{CH}_3$). See p. 317. Analysis: Calculated for $\text{C}_{19}\text{H}_{24}\text{S}_2\text{O}_6$; C, 55.34%; H, 5.83%. Found; C, 55.12%; H, 5.59.

b. 2,2-Dimethyl-1,3-dibromopropane

2,2-Dimethylpropaneditosylate-1,3 (150.0 g, 0.36 mole) was used to prepare 2,2-Dimethyl-1,3-dibromopropane (DMDBP) in the same way as 2,2,3,3-tetramethyl-1,4-dibromobutane was prepared (see D.1.d.). Tetra-n-butylammonium bromide (322.0 g, 1.0 mole) was used in 750 ml of DMAc. The temperature was critical and was held at 105°C for 36 hr. The crude product was separated by pouring the DMAc solution into an excess of water and collecting the organic phase. The DMDBP was dried by heating it over CaCl_2 12 hr and distilling at reduced pressure using a spinning band column. The product was collected at bp $31-32^\circ\text{C}/0.05\text{ mm}$ pressure (approximately 190°C at 760 mm) (Lit. $185-190^\circ\text{C}$).¹⁶³ The clear liquid gave 56.7 g (69%) yield and G.C. showed $> 99.9\%$ purity. IR (neat); $1245, 666\text{ cm}^{-1}$ ($\nu\text{CH}_2-\text{Br}$). See p. 287. ^1H NMR (CDCl_3), $\delta = 3.4$ ppm (CH_2-Br), 1.2 ppm ($-\text{CH}_3$). See p. 301. ^{13}C NMR (d-benzene) $\delta = 43.0$ ppm (CH_2-Br), 35.6 ppm ($-\overset{|}{\underset{|}{\text{C}}}-$), 24.3 ppm ($-\text{CH}_3$). See p. 318. Note: The temperature at which this bromina-

tion reaction is carried out is critical. Other experiments showed that 80°C-100°C was not a high enough temperature for the nucleophilic substitution to take place. At temperatures above 115°C a significant amount of n-butylbromide side product was formed as determined by ^{13}C NMR spectroscopy.

2. Preparation of Poly(1,1-Dimethylpropane) by Wurtz Coupling Polymerization

a. Wurtz polymerization of 2,2-dimethyl-1,3-dibromopropane using sodium metal

A 10 ml, 2 neck, pear shaped, flask was equipped with a condenser and a nitrogen inlet and outlet. The glassware was well flushed with nitrogen and subsequently flamed-out with a gentle blue flame then allowed to cool to room temperature. Sodium metal (0.34 g, 15.0 mmole) was freshly cut under n-hexane, rinsed with diethyl ether and placed in the reaction vessel under nitrogen. The metal was heated with a flame until it melted and flowed to expose new surfaces. Upon cooling a small magnetic stirbar was added and DMDBP (0.85 g, 3.7 mmole) was syringed into the flask. The Wurtz reaction was started by heating the flask with a gentle flame until the reaction became exothermic. A great deal of heat was evolved and the system was cooled with a water bath. The reaction exotherm volatilized some of the monomer and the reaction became deep blue in color. As the reaction slowed 2.0 ml of dry

cyclohexane was added and the temperature of the reaction was brought to reflux (81°C) in an oil bath. After 30 min. the solution became viscous and difficult to stir, consequently, another 1.0 ml of cyclohexane was added. After 5 hr the mixture was allowed to cool to room temperature. To work-up the polymer a large excess of dry cyclohexane was added and the solution was filtered. The filtrate containing the polymer was dried with magnesium sulfate, filtered and evaporated to dryness under reduced pressure. The poly(1,1-dimethylpropane) was collected, redissolved in benzene and precipitated into methanol. After drying at 60°C/0.1 mm pressure over P_2O_5 the yield was 0.11 g (43%) of a crystalline polymer. M.P. (by DSC), 71 and 87°C shows polymorphism. IR (film); 1385, 1375 cm^{-1} ($\delta_s CH_3$, gem-dimethyl doublet). See p. 288. 1H NMR (d-benzene), $\delta = 1.3$ ppm ($-CH_2-$), 1.0 ppm ($-CH_3$). See p. 302. ^{13}C NMR (d-benzene) (45°C), $\delta = 35.7$ ppm ($-CH_2-$), 32.5 ppm ($-\overset{|}{C}-$) 27.9 ppm ($-CH_3$). See p. 319.

b. Second procedure for polymerizing 2,2-dimethyl-1,3-dibromopropane with sodium metal

A 250 ml Schlenk tube was fitted with a "U" tube sidearm and a 3-way vacuum stopcock. To the top of this vacuum stopcock a second 3-way vacuum stopcock was fitted through the use of a connecting ground glass joint. A Firestone valve¹⁵⁹ was connected between the reaction apparatus and a vacuum line and the Schlenk tube was alter-

nately filled with argon and evacuated. The glassware was then flamed dry under vacuum and allowed to cool. The system was pressurized with argon and removed to a glovebag. A piece of freshly cut sodium metal (0.35 g, 15.2 mmole) under n-hexane was placed into the connection between the two 3-way vacuum stopcocks. The polymerization vessel was removed from the glovebag and reconnected to the Firestone valve. It was evacuated to < 0.025 mm pressure and (using a gentle flame) the sodium metal was melted; sodium flowed into the Schlenk tube leaving the oxidized metal behind. The pure metal was made into a sodium mirror by heating under vacuum with a soft blue flame. The Schlenk tube was cooled in a liquid nitrogen bath and the system again brought under argon pressure. DMDBP (1.7 g, 7.4 mmole) was syringed into the tube and quickly frozen. A small magnetic stirring bar was added through the "U" tube sidearm, and the mixture was allowed to warm to room temperature with stirring. When the mixture was gently warmed with a soft blue flame the reaction became exothermic immediately, and turned a dark blue color. After approximately 30 minutes the reaction mixture became too viscous to stir and 20 ml of dry cyclohexane was added. The system was heated to 60°C and allowed to stir for an additional 12 hr. The polymer was then collected and purified by the method already described in E.2.a. The yield of white crystalline polymer was 0.20 g (55%). The material showed a dual

melting point at 70-74°C and 85-90°C by DSC. It also gave a glass transition temperature at -17°C. IR, ^1H NMR, and ^{13}C NMR were all similar to the product described in E.2.a. as poly(1,1-dimethylpropane).

c. Recovery of volatile products produced during the sodium Wurtz polymerization of 2,2-dimethyl-1,3-dibromopropane

The same procedure which was used in E.2.a. was used in this experiment with the addition of a liquid nitrogen cooled trap which was attached between the reaction vessel and the vacuum line. The quantities of reagents were increased also: sodium metal (1.0 g, 43.5 mmole), DMDBP (5.0 g, 21.7 mmole), cyclohexane (40 ml). After the polymerization reaction a gas IR cell (KBr windows, 10 cm path length) was attached to the vacuum line and evacuated. The trap was opened to the cell and the contents allowed to warm to room temperature. The IR cell was closed and the spectrum of the gas taken. IR (gas): 1019, 936, 847 cm^{-1} ($\text{CH}_3-\text{C}-\text{CH}_3$ scissoring) (see p. 224). The liquid material remaining in the trap was identified as a mixture of cyclohexane and starting monomer.

d. Polymerization of 2,2-dimethyl-1,3-dibromopropane under vacuum with sodium metal

The procedure which is described in E.5.c. for the sealed polymerization of TMDBB was used to attempt the Wurtz polymerization of DMDBP. The quantities and solvent

were changed as follows; sodium metal (0.68 g, 29.6 mmole), DMDBP (1.7 g, 7.4 mmole), cyclohexane (5 ml). Some blue color formed on the surface of the metal but no polymer was recovered.

e. Polymerization of 2,2-dimethyl-1,3-dibromopropane using the Wurtz reaction with sodium/potassium alloy

A procedure similar to that described in E.2.b. was used with some modifications. A 250 ml, 3 neck, roundbottom flask was used in place of a Schlenk tube, and both sodium and potassium metal were melted into the flask. The alloy was formed by stirring the two metals together while heating. The following quantities were used; sodium metal (0.25 g, 10.9 mmole), potassium metal (0.25 g, 6.4 mmole), DMDBP (1.7 g, 7.4 mmole), cyclohexane (25 ml). The reaction between the dibromide and the metal alloy was very exothermic and most of the product seemed to volatilize. On precipitation the amount of polymer was negligible.

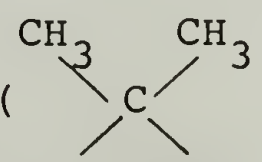
3. Grignard Polymerization Attempts for
2,2-Dimethyl-1,3-Dibromopropane

a. Polymerization of 2,2-dimethyl-1,3-dibromopropane via Grignard coupling: benzene/tetrahydrofuran solvent

The general procedure described in D.5.b. to polymerize TMDBB was used in an attempt to polymerize DMDBP. The only modifications were in the monomer and magnesium quantities. Magnesium metal (0.53 g, 21.8 mmole) and DMDBP (5.0 g, 21.8 mmole) were used to form the Grignard reagent. The formation of the mono-Grignard proceeded smoothly,

however, after the coupling step no polymer was isolated.

b. Recovery of volatile products produced during the Grignard polymerization of 2,2-dimethyl-1,3-dibromopropane

The same procedure as that which is described in D.5.b. was used in this experiment with the following modifications. The apparatus was equipped with a trap adjacent to the nitrogen outlet. This trap was cooled with a Dry Ice/isopropanol bath to -78°C and as the reaction was run any volatiles given off were recovered. DMDBP (5.0 g, 21.8 mmole) and magnesium metal turnings (0.53 g, 21.8 mmole) were used to make the mono-Grignard reagent. After the reaction was complete a gas IR cell (KBr windows, 10 cm path length) was connected to a vacuum line and evacuated. The trap containing the volatiles from the reaction was also connected to the line and opened to the IR cell. The temperature of the trap was permitted to rise to room temperature and the gaseous products transferred to the IR cell. No liquid remained in the trap at room temperature indicating all the side products of the coupling reaction were gaseous under ambient conditions. The IR of the products showed the following; IR (gas); 3101, 3019, 2995, 2985, 2905 cm^{-1} ($\nu_{\text{s}}\text{CH}_3$, CH_2 and $\nu_{\text{as}}\text{CH}_3$, CH_2); 1470, 1441, 1400, 1392 cm^{-1} ($\delta_{\text{s}}\text{CH}_3$, CH_2 and $\delta_{\text{as}}\text{CH}_3$, CH_2); 1019, 936, 847 cm^{-1} ( scissoring). The product was identified as 1,1-dimethylcyclopropane. See p. 224

F. Copolymerization of 3,4-Dimethyl-
tetrahydrofuran with Cyclic Ethers

1. Monomer Preparation of 3,4-Dimethyltetrahydrofuran (DMTHF)

a. Diethyl-2,3-dimethylsuccinate

Diethyl-2,3-dimethylsuccinate was prepared from ethyl-2-bromopropionate in an analogous procedure to that described in D.1.a. for the preparation of diethyl-2,2,3,3-tetramethylsuccinate. The diethyl-2,3-dimethylsuccinate was prepared in 3.5 L of dry THF with copper(II) chloride (297.3 g, 2.21 mole), zinc powder (144.5 g, 2.21 mole) and ethyl-2-bromopropionate (200 g, 1.11 mole). Distillation of the product gave the succinate at bp 75-80°C/2 mm pressure (Lit. 108°C/15 mm).¹⁶⁴ The yield was 18.5 g (17%). IR (neat); 1731 cm^{-1} ($\nu\text{C=O}$). See p. 219.

b. 2,3-Dimethylbutanediol-1,4

2,3-Dimethylbutanediol-1,4 was prepared from the reduction of diethyl-2,3-dimethylsuccinate by the method described in D.1.b. for the preparation of 2,2,3,3-Tetramethylbutanediol-1,4. Anhydrous diethyl ether (330 ml) was used with LAH (11.4 g, 0.30 mole) to reduce diethyl-2,3-dimethylsuccinate (30.0 g, 0.15 mole). Yield of distilled 2,3-dimethylbutanediol-1,4 was 17.2 g (96%) with a bp of 130°C/12 mm pressure (Lit. 137-138°C/17 mm).¹⁶⁵ IR (neat); 3320 cm^{-1} (νOH), 1030 cm^{-1} ($\nu\text{C-O}$). See p. 290.

c. Preparation of 3,4-dimethyltetrahydrofuran

Two methods were used to prepare the 3,4-dimethyltetrahydrofuran (DMTHF).^{166,130}

(1) A 100 ml, 2 neck roundbottom flask was equipped with a thermometer, Dean Stark trap and a nitrogen inlet and outlet. The glassware was flamed-out under nitrogen flow and allowed to cool. 3,4-Dimethylbutanediol-1,4 (1.5 g, 12.7 mmole) was added to the flask along with 50 ml of dry DMSO. A magnetic stirring bar was added and the solution was heated with stirring to 155°C. After one hour a mixture containing DMTHF began to collect in the receiver, and after one day, 5.2 ml of a clear liquid had been collected. The liquid fraction was a mixture of water, DMSO, and DMTHF as shown by G.C. The mixture was fractionally distilled from LAH and gave 1.12 g (88%) yield of 3,4-dimethyltetrahydrofuran. Bp 39-41°C/50 mm (Lit. 108°C/760 mm).¹⁶⁷ IR (neat); 1040 cm^{-1} ($\nu_{\text{C-O-C}}$). See p. 291. ^1H NMR (CDCl_3), δ = 3.15-4.0 ppm ($\text{CH}_2\text{-O}$), 1.25-2.2 ppm ($-\overset{|}{\text{CH}}-$), 0.65-0.9 ppm ($-\text{CH}_3$). See p. 303.

(2) A 50 ml, 3 neck, roundbottom flask equipped with a 10 cm vacuum Vigreux column, condenser, receiver flask, dropping funnel and a nitrogen inlet and outlet was flamed-out under nitrogen flow. A magnetic stirbar was added and the system was repeatedly evacuated to 0.1 mm pressure and then refilled with dry nitrogen. Powdered potassium hydrogen sulfate (KHSO_4) (1.0 g, 5.2 mmole) was

added to the flask and the system was attached to a vacuum line and brought to 50 mm pressure with nitrogen gas. 2,3-Dimethylbutanediol-1,4 (8.0 g, 68 mmole) was placed in the dropping funnel. The receiver was cooled with a Dry Ice/acetone bath and the reaction flask with the KHSO_4 was heated to 190°C with stirring. The 2,3-dimethylbutanediol-1,4 was then added dropwise to the hot KHSO_4 while maintaining the flask temperature at $180\text{--}200^\circ\text{C}$. After the addition was completed and no further reaction products were distilling over, the reaction apparatus was evacuated to 10 mm pressure to assure complete removal of all volatile products from the reaction mixture. The yield of DMTHF after distillation from LAH was 5.1 g (75%). Bp $40^\circ\text{C}/50$ mm pressure (Lit. $108^\circ\text{C}/760$ mm).¹⁶⁷ IR (neat); 1040 cm^{-1} ($\nu\text{C-O-C}$). See p. 291. ^1H NMR (CDCl_3); $\delta = 3.15\text{--}4.0$ ppm ($\text{CH}_2\text{-C-}$), $1.25\text{--}2.2$ ppm (-CH-), $0.65\text{--}0.9$ ppm (-CH_3). See p. 303. ^{13}C NMR (benzene); 75.3 ppm ($\text{cis-CH}_2\text{-O}$), 74.5 ppm ($\text{trans-CH}_2\text{-O}$), 42.0 ppm (cis-CH-), 36.9 ppm (trans-CH-), 15.9 ppm (cis-CH_3), 12.6 ppm (trans-CH_3). See p. 320. G.C. also shows a 50/50 mixture of cis-trans isomers. See p. 240.

2. Homopolymerization attempts for 3,4-dimethyltetrahydrofuran

a. Attempted polymerization of 3,4-dimethyltetrahydrofuran with boron·trifluoride etherate

A small bulb type polymerization tube was oven dried at 200°C overnight. The tube was fitted with a serum

cap and two syringe needles for nitrogen inlet and outlet. The tube was flamed-out under nitrogen to ensure dryness. DMTHF (1.0 g, 10 mmole) was injected into the tube followed by $\text{BF}_3 \cdot \text{etherate}$ (5 ml, 0.4 mmole) and ECH (0.2 μl , 0.06 mmole). The contents of the tube were then frozen in a liquid nitrogen bath and the tube was evacuated. The tube was sealed under vacuum and kept at -22°C in a cryostat bath for several weeks with no increase in viscosity. Addition of the solution to methanol yielded no polymer. Note: A control tube run with unsubstituted THF to show catalyst reactivity gave poly(tetrahydrofuran).

b. Attempted polymerization of 3,4-dimethyltetrahydrofuran with phosphorous pentafluoride gas

A 10 ml, 2 neck, pear shaped flask was equipped with a capillary nitrogen inlet tube and a small condenser. The condenser was equipped to allow nitrogen to pass through to the bottom of a small polymerization tube. The apparatus was flamed-out under nitrogen and permitted to cool. DMTHF (0.9 g, 9.0 mmole) was syringed into the polymerization tube along with ECH (0.2 μl , 0.06 mmole). *p*-Chlorobenzenediazonium hexafluorophosphate (97 mg, 0.36 mmole) was charged into the pear shaped flask. With a steady flow of nitrogen over the diazonium salt and through the polymerization tube, the flask was heated to $150\text{--}160^\circ\text{C}$ to decompose the diazonium salt. The resulting PF_5 gas was swept into the polymerization tube. After several minutes

all of the p-chlorobenzenediazonium hexafluorophosphate was decomposed and the heating was discontinued. The polymerization tube was sealed and placed in a cryostat bath at -30°C . After several days no change in viscosity had occurred. No polymer could be precipitated in methanol.

G.C. of the mixture showed only monomer still present.

Note: Control polymerizations with unsubstituted THF gave high polymer.

c. Attempted polymerization of 3,4-dimethyltetrahydrofuran with triethyl aluminum/water (1:1) initiator¹⁶⁸

i. Preparation of $\text{AlEt}_3/\text{H}_2\text{O}$ (1:1) initiator

A small Schlenk tube was equipped with a 3-way stopcock and a small magnetic stirbar, after having been oven dried at 200°C for 12 hr and flamed-out under vacuum. The Schlenk tube was purged with nitrogen and cooled in an ice water bath. A 10% solution of AlEt_3 in heptane (by weight) 10.0 ml, 7.0 mmoles of Al) was added by syringe to the tube and cooled down. Distilled water (0.13 ml, 7.0 mmole) was slowly added dropwise to the stirred AlEt_3 solution. The initiator mixture was stirred at 0°C for 2 hr before use. Under nitrogen it remained active for several weeks.

ii. Attempted polymerization of 3,4-dimethyltetrahydrofuran

A small bulb type polymerization tube was flamed out under vacuum. The tube was purged with dry argon by

means of a 3-way stopcock and cooled. ECH (0.2 μ l, 0.06 mmole) was added by syringe followed by DMTHF (0.60 g, 6.3 mmole) and the $\text{AlEt}_3/\text{H}_2\text{O}$ initiator solution (0.25 ml, 0.2 mmole). The tube and contents were degassed by four freeze/thaw cycles and sealed under vacuum. The tube was kept at -22°C for several weeks without any evidence of polymerization. G.C. of the polymerization mixture showed only monomer.

Note 1: An identical polymerization tube was prepared with 4.0 ml of dry benzene as solvent. No polymer was found.

Note 2: Control polymerizations with unsubstituted THF gave high polymers.

d. Polymerization attempt for 3,4-dimethyltetrahydrofuran with triethyl aluminum/acetylacetone/water (1:1:0.5) initiator¹⁶⁹

i. Preparation of $\text{AlEt}_3/\text{AcAc}/\text{H}_2\text{O}$ (1:1:0.5) initiator

A Schlenk tube fitted with a 3-way vacuum stopcock was flamed-out under vacuum. The tube was flushed with nitrogen (a magnetic stirbar added) and allowed to cool. With positive nitrogen pressure AlEt_3 (100%) (7.0 ml, 51.3 mmole) was injected into the Schlenk tube which was equipped with a dropping funnel and cooled with an ice water bath to 0°C . 30 ml of anhydrous diethyl ether was syringed into the addition funnel followed by acetylacetone (5.2 ml, 51.3 mmole). With stirring, the ethereal solution

was slowly added to the AlEt_3 . After total addition, 10 ml of ether was used to rinse the addition funnel. The solution was stirred for 3 hr at 0°C , then distilled water (0.46 ml, 25.6 mmole) was added dropwise over a five minute period. The final orange solution was kept at 0°C and away from light. It remained active for several days under nitrogen.

ii. Attempted polymerization of 3,4 dimethyltetrahydrofuran

A polymerization method similar to that described in F.2.c.ii. was used for this experiment. All quantities remained the same except for the change in initiator solution. $\text{AlEt}_3/\text{AcAc}/\text{H}_2\text{O}$ (1:1:0.5) (0.2 ml, 0.25 mmole) was used for initiation. After several weeks no increase in viscosity or other sign of polymerization was observed. G.C. showed only monomer and solvent present.

Note: Control reactions carried out with unsubstituted THF also showed no tendency to form high polymer. However control experiments with ECH did polymerize very well with this system.

3. Copolymerization of 3,4-Dimethyl-tetrahydrofuran with Cyclic Ethers

a. Copolymerization attempt of 3,4-dimethyltetrahydrofuran with tetrahydrofuran using boron trifluoride

The same procedure as described in F.2.a. was used to attempt the copolymerization of DMTHF with THF. The bulk polymerization was carried out with DMTHF (1.0 g, 10

mmole) and THF (0.72 g, 10 mmole) and ECH (0.4 μ l, 0.12 mmole). $\text{BF}_3 \cdot \text{etherate}$ (10 μ l, 0.8 mmole) was used as initiator. No copolymer was obtained. A control polymerization with unsubstituted THF gave low molecular weight poly(tetrahydrofuran).

b. Attempted copolymerization of 3,4-dimethyltetrahydrofuran with tetrahydrofuran using phosphorus pentafluoride gas.

The same procedure as described in F.2.b. was used for this experiment. The bulk copolymerization was carried out with a 1:1 mole ratio of DMTHF to THF and with 2 mole % of initiator. Here again no copolymer was found.

c. Attempted copolymerization of 3,4-dimethyltetrahydrofuran with tetrahydrofuran using triethyl aluminum/water (1:1) initiator

The same procedure as described in F.2.c.ii. was used to attempt the copolymerization of DMTHF with THF. Again a 1:1 mole ratio of the two comonomers was used but no copolymer was found. A control polymerization with only THF gave high molecular weight poly(tetrahydrofuran).

d. Copolymerization of 3,4-dimethyltetrahydrofuran with propylene oxide using phosphorous pentafluoride gas.

A 10 ml, 2 neck, pear shaped flask was equipped with a capillary nitrogen inlet tube and a small condenser. The condenser was equipped to allow nitrogen to pass through to the bottom of a small polymerization tube. The apparatus was flamed-out under nitrogen and permitted to

cool. DMTHF (0.4 g, 4.0 mmole) and propylene oxide (PO) (0.29 ml, 4.0 mmole) were charged into the polymerization tube. The initiator, PF_5 gas, was generated from p-chlorobenzenediazonium hexafluorophosphate (97 mg, 0.36 mmole) which was placed in the pear shaped flask and heated to 150-160°C. As the diazonium salt decomposed the PF_5 gas was swept through the condenser (to trap out volatiles) and into the polymerization tube. After the addition of the initiator was complete, the tube was sealed and kept at -22°C for two weeks during which time a highly viscous material formed. The sticky polymer was purified by re-precipitation from methanol into water and dried at 60°C/0.1 mm pressure overnight. The yield of clear viscous polymer was 0.20 g (32%). IR (film); 1030, 1110 cm^{-1} ($\nu\text{C-O-C}$) doublet. See p. 293. The inherent viscosity was 0.13 dl/g (0.5 g/100 ml benzene at 30°C). ^{13}C NMR (benzene), 75.5, 74.9 ppm ($\text{CH}_2\text{-O-CH}_2$); 73.2, 72.2 ppm ($-\text{CH}-$, CH_3), PO); 36.5, 35.1, 36.2, 34.8 ppm ($-\text{CH}-\text{CH}-$, CH_3); 17.9 ppm ($-\text{CH}_3$, CH_3 , PO); 15.0, 12.6 ppm ($-\text{CH}_3$, DMTHF). See p. 258.

c. Bulk copolymerization of 3,4-dimethyltetrahydrofuran with epichlorohydrin using phosphorous pentafluoride gas

The same general procedure was used for the copolymerization of DMTHF with ECH as is described in F.3.d. for the copolymerization of DMTHF with PO. The polymerization tube was charged with DMTHF (0.43 g, 4.3 mmole) and ECH

(0.5 ml, 5.4 mmole). p-Chlorobenzenediazonium hexafluorophosphate (76 mg, 0.28 mmoles) was used for initiation. After the PF_5 gas was swept through the polymerization tube, the tube was sealed and kept at -20°C for one week. A viscous plug of polymer formed. The polymer plug was soaked in methanol for several hours to extract residual monomer, followed by reprecipitation from benzene into methanol. After several washings with methanol the polymer was dried at $60^\circ\text{C}/0.1$ mm pressure for 24 hr. The yield was 0.72 g (70%) of a viscous, semi-solid, clear polymer. IR (neat): 1034, 1110 cm^{-1} ($\nu\text{C-O-C}$, doublet). See p. 292. The inherent viscosity was 0.11 dl/g (0.5 g/100 ml benzene at 30°C). ^{13}C NMR (benzene), 79.5, 79.1 ppm ($-\text{CH}-\text{O}-$);
 CH_2Cl
 75.6, 75.3, 74.3, 73.9 ppm ($-\text{CH}_2-\text{O}-$, DMTHF); 70.8, 69.9 ppm ($-\text{CH}_2-\text{O}-$, ECH); 44.3 ppm ($-\text{CH}_2-\text{Cl}$); 36.5, 36.1, 35.2
 CH_3
 34.7 ppm ($-\text{CH}-$); 14.8, 12.5 ppm ($-\text{CH}_3$). Analysis: Calculated for $\{(\text{C}_6\text{H}_{12}\text{O})_{0.4}(\text{C}_3\text{H}_5\text{OCl})_{0.6}\}$; C, 52.81%; H, 8.17%; Cl, 22.25%. Found; C, 52.66%; H, 8.02%; Cl, 21.80%.

f. Reactivity ratios for 3,4-dimethyltetrahydrofuran and epichlorohydrin during copolymerization

The phosphorous pentafluoride initiator system described in F.3.d. was used for the polymerization of various mole ratios of DMTHF and ECH. The copolymerizations were not permitted to go beyond 10% and the polymers were isolated by precipitation into methanol and dried at $60^\circ\text{C}/$

0.1 mm pressure for 16 hr. Elemental analyses were carried out for C, H and Cl and from the results the copolymer compositions were calculated. See Table 7.

TABLE 7
COPOLYMERIZATION OF 3,4-DIMETHYLTETRA-
HYDROFURAN WITH EPICHLOROHYDRIN

Monomer Feed Ratio		Copolymer Yield	Analyses		
ECH	DMTHF		C	H	Cl
90	10	9.9%	41.95	6.18	33.93
82.5	17.5	8.2%	52.97	8.20	20.93
75	25	7.4%	55.07	9.01	17.97
60	40	8.4%	55.98	9.20	17.10
40	60	7.2%	57.89	9.51	16.06

CHAPTER III

RESULTS AND DISCUSSION

A. Synthesis of Head-to-Head Polyisobutylene

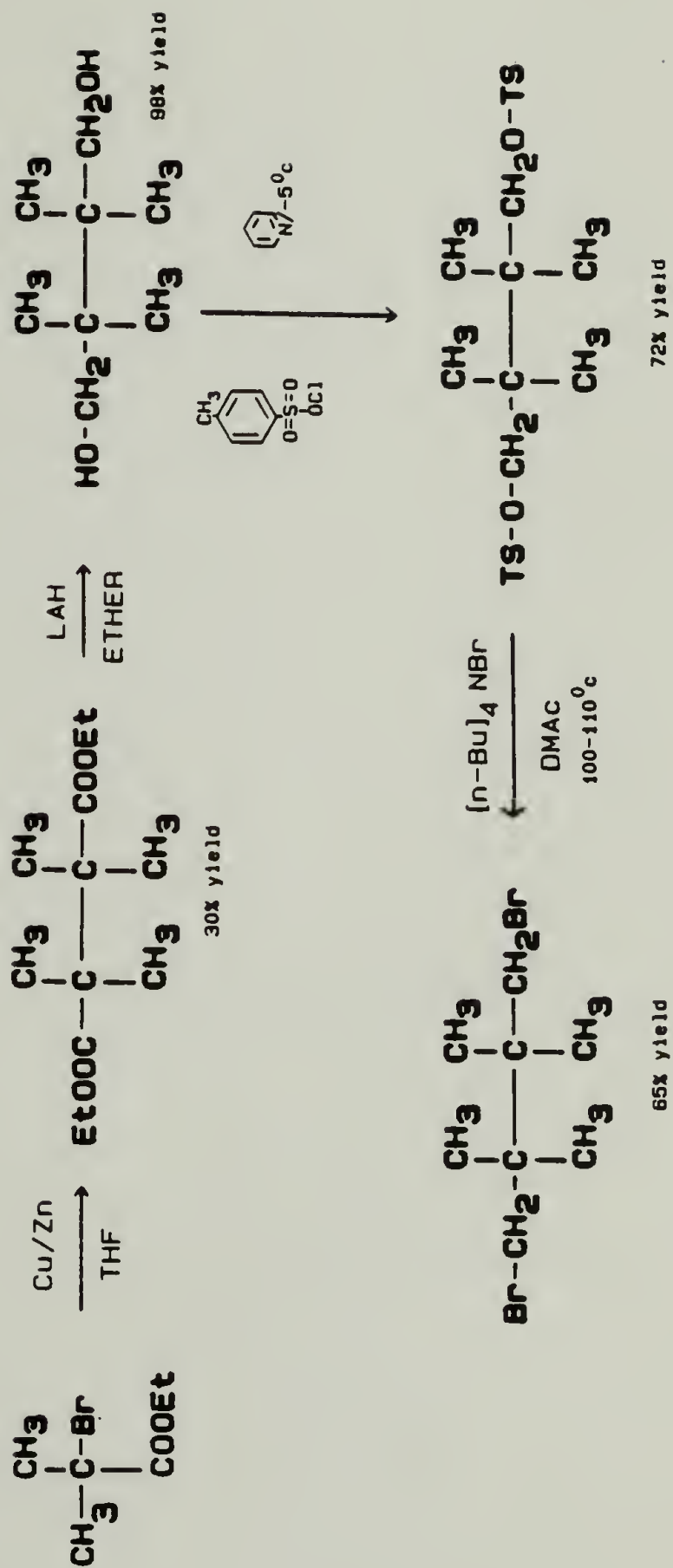
1. Monomer Preparations

a. Preparation of 2,2,3,3-tetramethyl-1,4-dibromobutane (TMDBB)

The synthesis of this dibromide has not yet been described in either Chemical Abstracts or Beilstein. Initially the bromination of 2,2,3,3-tetramethylbutanediol-1,4 (TMBD) was attempted using hydrobromic acid and sulfuric acid which yielded only 3,3,4,4-tetramethyltetrahydrofuran (TMTHF). Apparently dehydration and ring-closure is favored over bromination for this diol. This is not too surprising when one considers the fact that this is a primary alcohol which is not as reactive as a secondary or tertiary alcohol in nucleophilic substitutions. TMTHF is a relatively stable tetrahydrofuran due to its substitution and reduction of ring strain. For these reasons the alternative route was developed of first forming the ditosylate of the diol and then reacting the sulfonate with tetra-n-butylammonium bromide salt. The synthetic route to TMDBB is outlined in Figure 2. It generally required two reactions of TBD with p-toluenesulfonyl chloride to obtain the

Figure 2. Preparation of 2,2,3,3-tetramethyl-1,4-dibromobutane.

PREPARATION OF 2,2,3,3-TETRAMETHYL-1,4-DIBROMOBUTANE



ditosylate in 70% yield. The quaternary ammonium bromide salt was found to be a good brominating reagent. Lithium bromide was shown to be of no value in brominating the tosylate when the reaction was carried out in acetone, methyl ethyl or methyl propyl ketone.

The temperature at which the reaction is done is also important. The optimum temperature was found to be between 100 and 110°C. Below this the activation energy for the substitution is apparently not reached and above this temperature the tetra-n-butylammonium bromide begins to disproportionate to form n-butyl bromide. Both elemental analysis and spectral data are consistent with the structure of TMDBB. The ^1H and ^{13}C NMR are shown in Figure 3.

b. Preparation of 2,5-dimethyl-2,5-dibromohexane (DMDBH)

This monomer was prepared by the nucleophilic substitution reaction of bromide ion on 2,5-dimethylbutane-1,3-diol-2,5. DMDBH was obtained in 87% yield and its structure identified by spectral analysis.

2. Wurtz polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane or 2,5-dimethyl-2,5-dibromohexane

The initial effort to prepare H-H polyisobutylene was by the reaction of sodium metal with TMDBB or DMDBH (Figure 4). The Wurtz reaction, as discussed in the introduction, forms carbon-carbon σ -bonds from two alkyl

Figure 3. ^1H NMR and ^{13}C NMR spectra of 2,2,3,3-tetramethyl-1,4-dibromobutane.

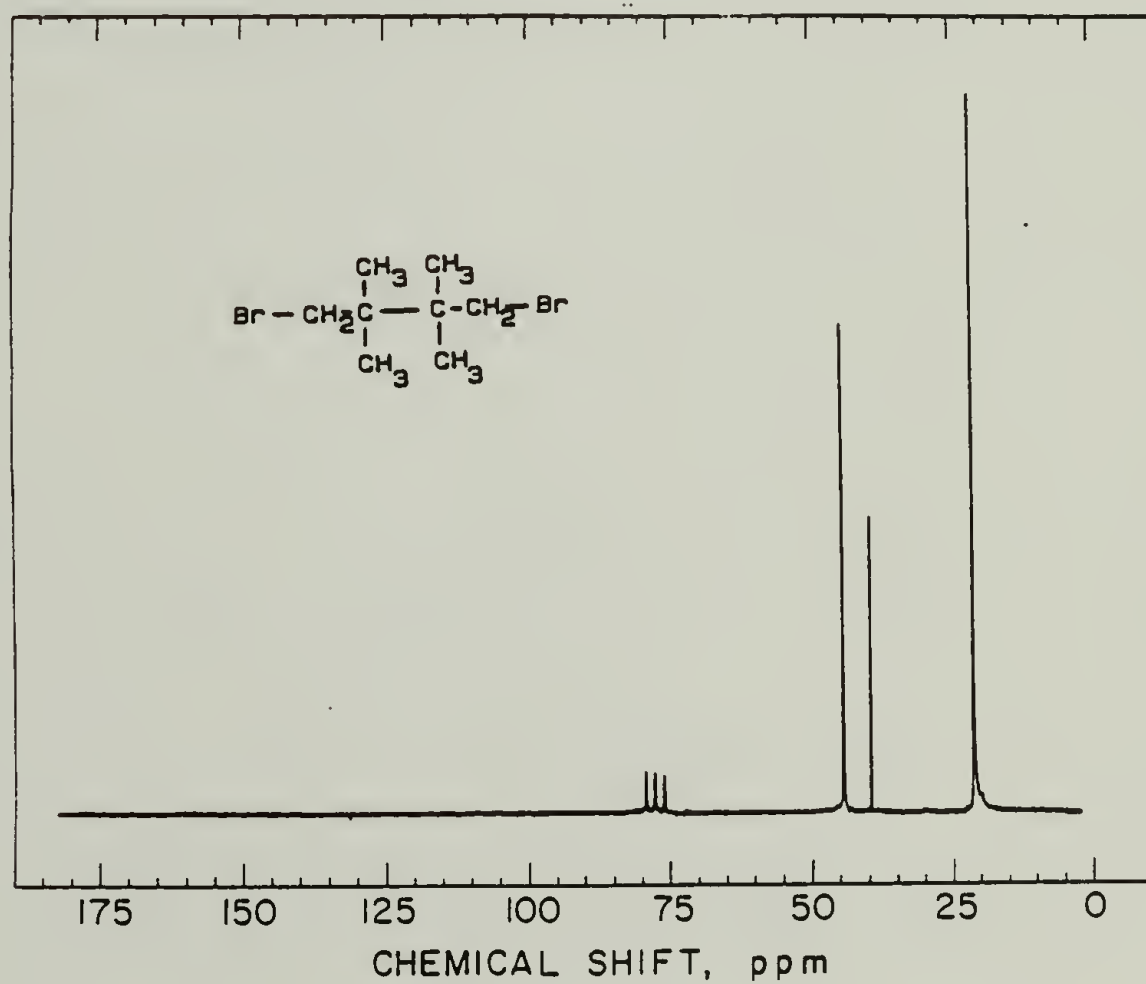
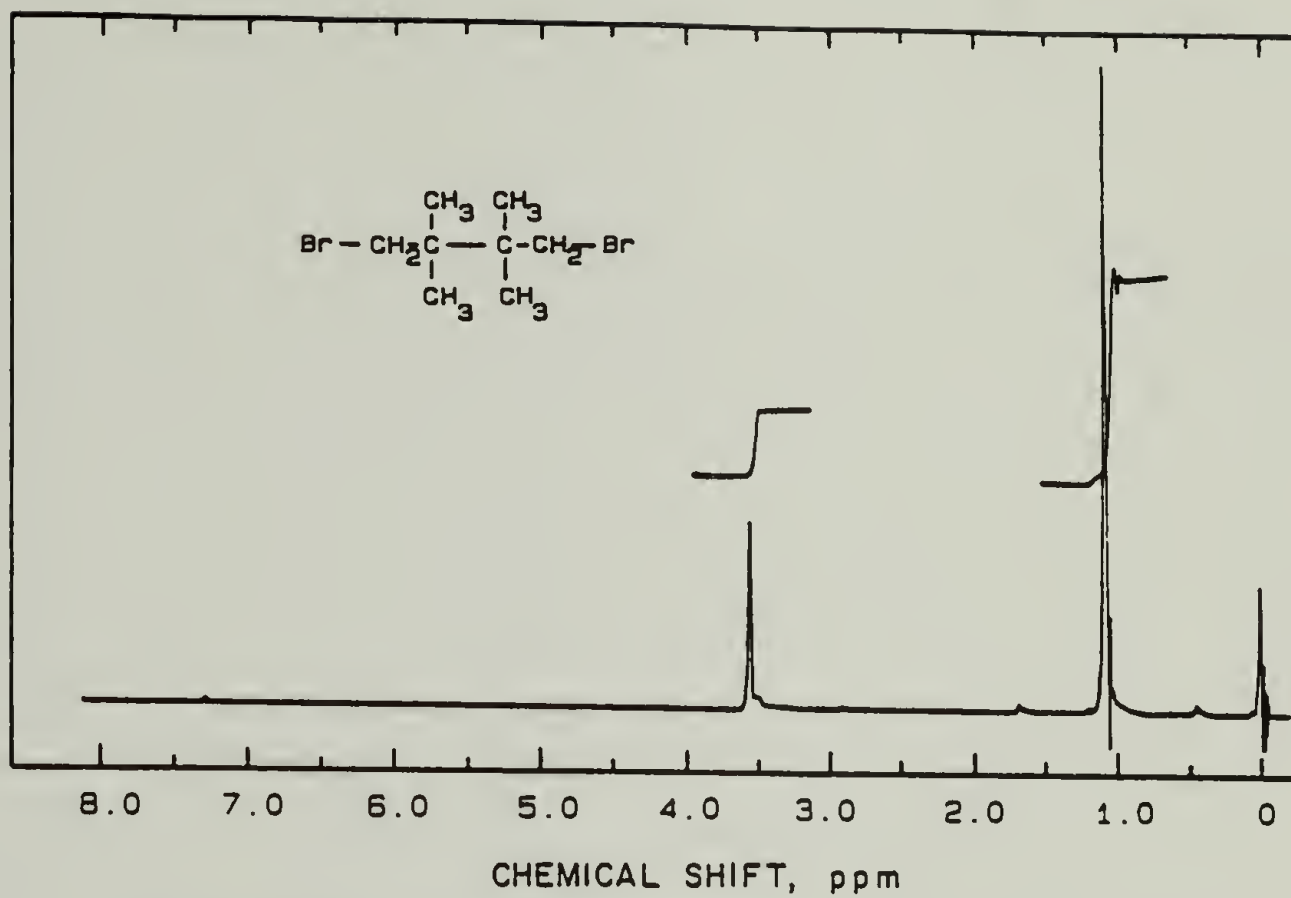
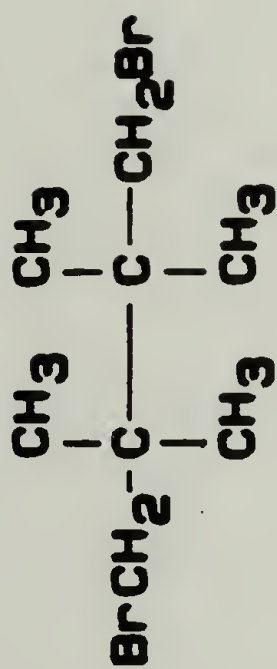
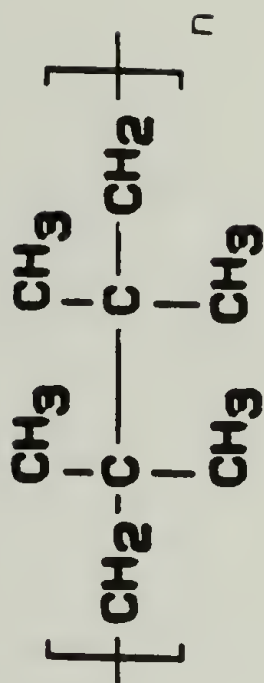
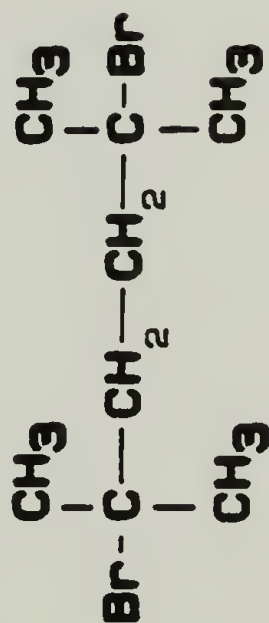


Figure 4. Wurtz coupling polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane and 2,5-dimethyl-2,5-dibromohexane.

WURTZ POLYMERIZATION



Na/heat



- LMW
- BRANCHED

bromides. However, the reaction is generally believed to proceed through the formation of free radicals, which can lead to a variety of side reactions.

When DMDBH was reacted with sodium or sodium/potassium alloy in the bulk or in solution no coupling reaction was found to occur. There was, however, an exothermic reaction with evolution of volatiles. Although the reaction products were not isolated, it is believed that the reaction proceeded by a dehydrohalogenation with formation of 2,5-dimethyl-1,5-hexadiene and other unsaturated compounds. In the case of DMDBH there are 8 α -hydrogens available for dehydrohalogenation.

2,2,3,3-tetramethyl-1,4-dibromobutane (TMDBB) has no α -hydrogens which can leave with the bromine. When TMDBB was heated in the presence of sodium metal, the reaction became very exothermic with the formation of a deep blue color. There were some volatile materials obtained in the reaction, however, after 1 day 10 to 20% of the starting dibromide was found to have formed polymer. The reactions carried out in solvents were not successful probably due to dilution of TMDBB which encourages side reactions. Table 8 is a summary of Wurtz reactions for TMDBB and DMDBH.

The H-H polyisobutylene obtained by the reaction of sodium with TMDBB was found to have an inherent viscosity of 0.13 dL/g in benzene, and gel permeation chromatography

TABLE 8

ATTEMPTED WURTZ POLYMERIZATION OF 2,2,3,3-TETRAMETHYL-1,4-DIBROMOBUTANE (TMDBB) OR 2,5-DIMETHYL-2,5-DIBROMOHEXANE (DMDBH)

Monomer	Metal	Solvent	Temp.	Time	Polymer Yield
TMDBB	Na	cyclohexane	81°C	1 day	trace
TMDBB	Na	bulk	100°C	1 day	20%
TMDBB	Na	bulk	100°C	1 day	10%
TMDBB	Na/K	benzene/vacuum	60°C	4 days	0
TMDBB	Na	bulk/vacuum	60°C	4 days	0
DMDBH	Na	cyclohexane	81°C	10 hrs	0
DMDBH	Na/K	bulk	100°C	1 day	0
DMDBH	Na	benzene	100°C	1 day	0

(GPC) showed a molecular weight of 1,000 to 2,000. This would indicate a degree of polymerization (\overline{DP}_n) of about 8 to 16.

Both the elemental analysis and the IR data of the polymer indicated that no bromine endgroups remained. The IR spectra of the polymer and the monomer in the region of $\text{CH}_2\text{-Br}$ stretching absorption are given in Figure 5. The absorption at 650 cm^{-1} had almost completely disappeared in the H-H polyisobutylene.

The ^{13}C NMR spectrum for H-H polyisobutylene showed that the polymer contained some branch points as well as a significant amount of $-\text{CH}_3$ endgroups. The ^{13}C NMR spectrum can be found on p. 309 of the appendix.

Three major carbon atoms can be identified; the methyl groups on the backbone, the methylene carbons and the quarternary carbons. However, there are several extraneous peaks which have been assigned to methyl end groups and branch point carbon atoms.

Table 9 shows the ^{13}C NMR chemical shifts for the Wurtz polymerized H-H polyisobutylene. The calculated chemical shift values were determined by the method of Lindeman and Adams.¹⁷⁰ The branch point carbon atoms were also assigned through the use of model compounds from the Sadtler Index.¹⁷¹ Hexamethylethane was employed as a model compound in the identification of $-\text{CH}_3$ end groups (see p. 311).

Figure 5. IR spectra of $\text{-CH}_2\text{-Br}$ stretching region for; (a) Wurtz polymer of H-H polyisobutylene; (b) Starting 2,2,3,3-tetramethyl-1,4-dibromobutane.

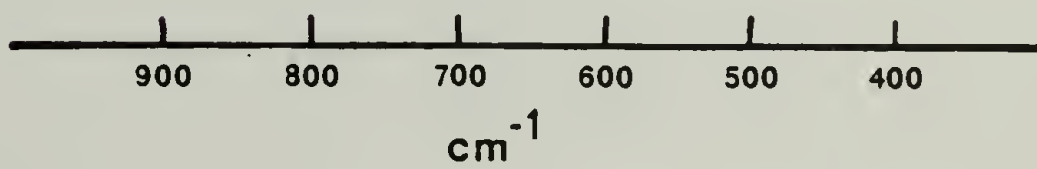
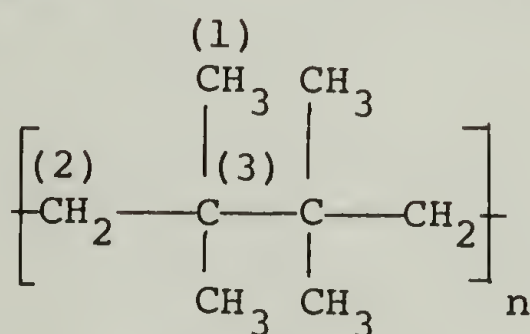


TABLE 9
 ^{13}C NMR CHEMICAL SHIFT VALUES FOR WURTZ
 POLYMERIZED HEAD-TO-HEAD
 POLYISOBUTYLENE

Carbon Atom	Chemical Shifts (ppm)	
	Found	Calculated
$-\text{CH}_3$ (1)	21.8	21.3
$-\text{CH}_2-$ (2)	31.5	31.4
$\begin{array}{c} \\ -\text{C}- \\ \end{array}$ (3)	38.9	38.7
branch $-\text{CH}_2-$	23.0	22.9
end group $-\text{CH}_3$	24.1	23.8
branch $\begin{array}{c} \\ -\text{C}- \\ \end{array}$	40.6	39.5
Minor unassigned peaks	22.5, 34.7	



The branching which occurs during the reaction is assumed to be due to the free radical nature of the polymerization. The radicals generated are primary carbon radicals and if these do not react immediately to form carbon-carbon bonds they can abstract a proton from the polymer backbone. The abstraction of either a methyl proton or a methylene proton leads to the formation of methyl end groups and the branch points illustrated in Figure 6. Back-biting reactions are also a possibility in the presence of such radical species.

This manner of preparing H-H polyisobutylene, although interesting, does not meet the original objectives for preparation. First, the molecular weight and \overline{DP}_n of the polymer formed are too low to properly be compared to normal H-T polyisobutylene. Second, branch points tend to change both the crystalline and amorphous parts of the polymer and influence both the T_g and T_m .

3. Preparation and Attempted Hydrogenation of 2,5-poly(2,5-dimethyl-2,4- hexadiene) (PDMHD)

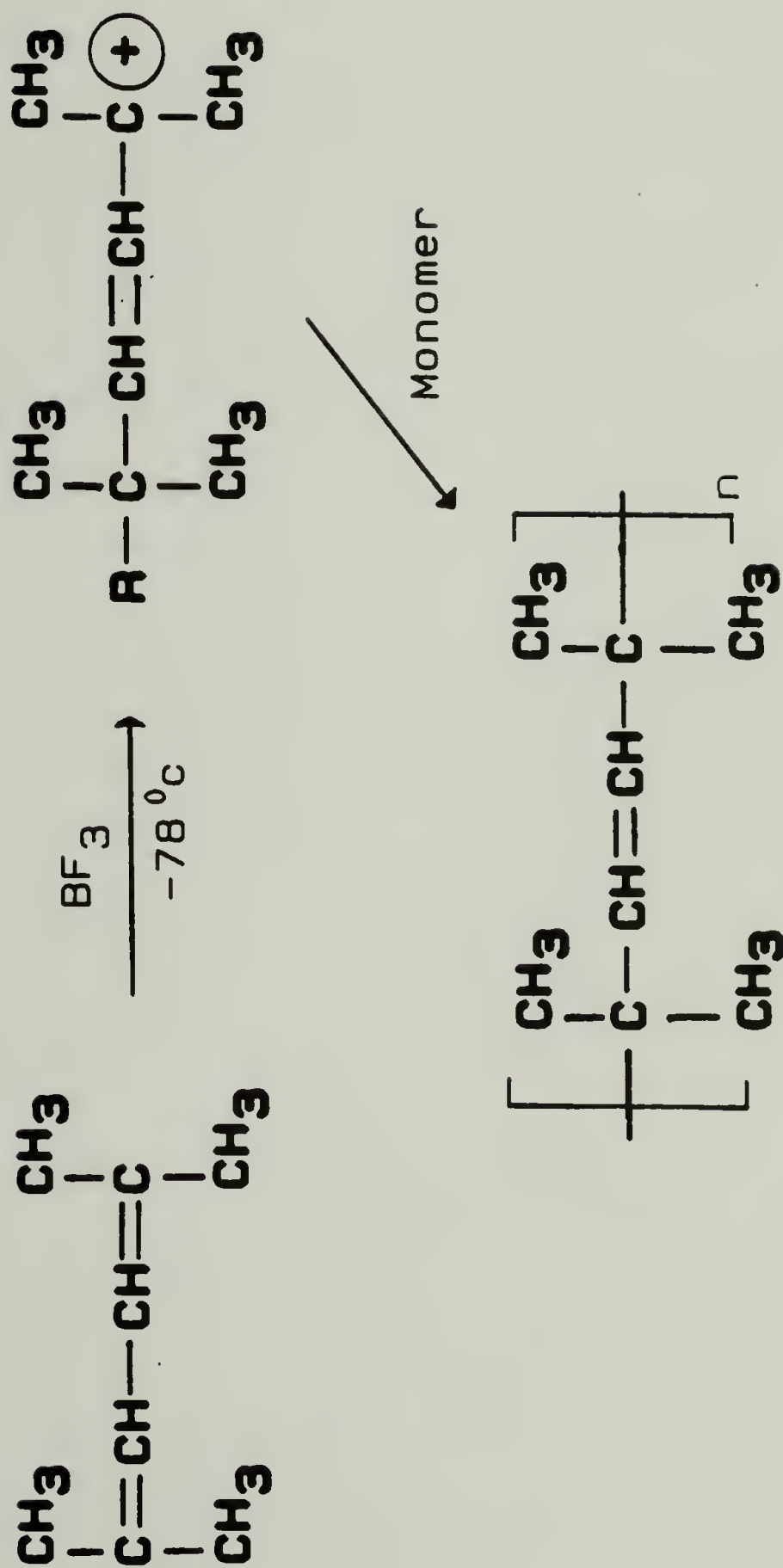
a. Polymerization of 2,5-dimethyl-2,4-hexadiene (DMHD)

The polymerization of DMHD was carried out as described previously by Moody¹⁷² and outlined in Figure 7. The polymer (PDMHD) was found to be a strictly 2,5-polyhexadiene by ^{13}C NMR spectroscopy which showed only the three carbons $-\underline{\text{CH}}_3$, $-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-$ and $-\underline{\text{CH}}=$. No indication of 2,3 or 4,5 polymer was evident in either the ^{13}C NMR or the IR.

Figure 6. Branching points for Wurtz polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane to H-H polyisobutylene.

Figure 7. Polymerization of 2,5-dimethyl-2,4-hexadiene with cationic initiator at low temperature to give trans-2,5-poly(2,5-dimethyl-2,4-hexadiene).

POLYMERIZATION OF 2, 5-DIMETHYL-2, 4-HEXADIENE



PDMHD is a highly crystalline polymer as previously described¹⁷² and has a rigid trans geometry as evidenced by WAXS and IR. The polymer is also only completely soluble above 160°C in solvents such as decalin and trichlorobenzene. It has a melting point at 260°C, however it begins to decompose at approximately 190°C by an unzipping mechanism to give back the monomer DMHD.¹⁷²

b. Catalytic hydrogenation attempts for 2,5-poly(2,5-dimethyl-2,4-hexadiene) (PDMHD)

The hydrogenation of PDMHD was attempted using both heterogeneous and homogeneous catalysts which have proven to be successful in polymer hydrogenations in the past. The reactions were carried out under a variety of conditions varying catalyst, catalyst concentration, hydrogen pressure and temperature. (See Table 10 for a summary of results.)

The temperatures were chosen above 160°C to allow for solution of the polymer, and decalin was used as the solvent. Hydrogenation of the polymer was measured by IR spectroscopy by using the absorbance of the internal standard of the gem-dimethyl bending modes at 1365 cm^{-1} and 1375 cm^{-1} . The ratio of the intensity of this doublet and the intensity of the trans $-\text{CH}=\text{CH}-$ absorption at 1000 cm^{-1} provides a quantitative means of measuring the percent hydrogenation.

In no case using catalytic techniques was the

TABLE 10

CATALYTIC HYDROGENATION OF 2,5 POLY(2,5-DIMETHYL-2,4-HEXADIENE)

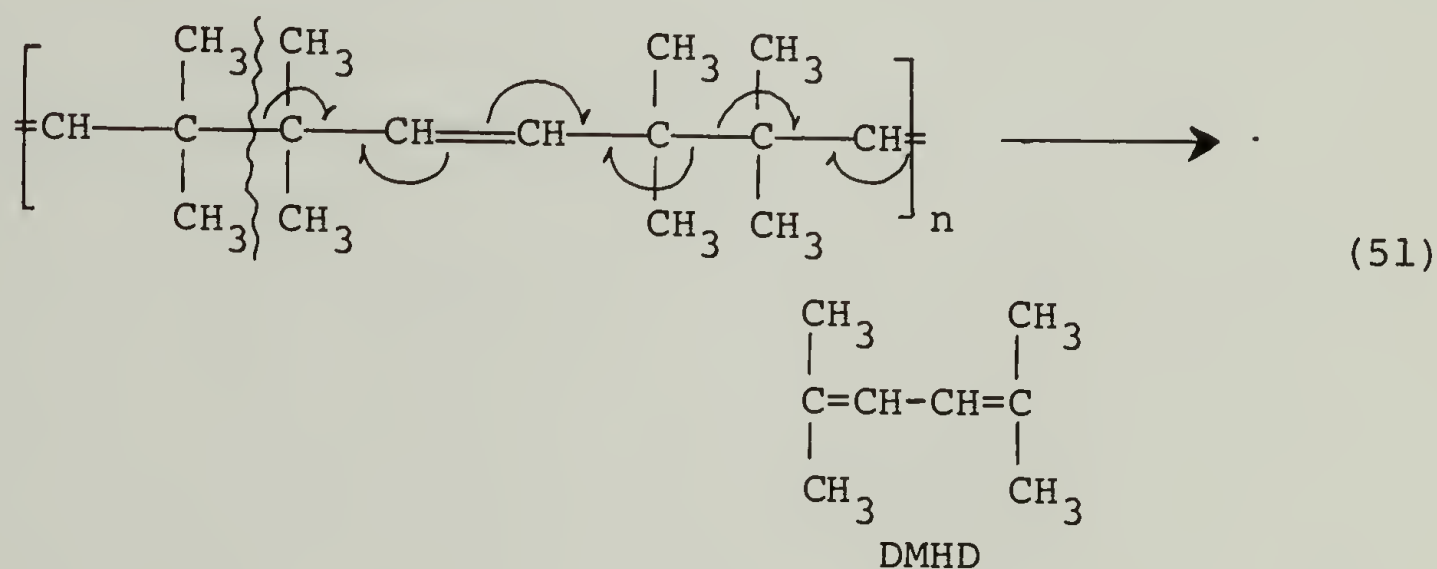
Polymer (b)	Temp.	Catalyst	H ₂	Catalyst Conc.	Yield	Recovered
1.0 gm	180°C	Co/Al(i-Bu) ₃ ^(a)	200 psi	1 mole %	0.78 gm	UNREACTED
2.0 gm	190°C	Co/Al(i-Bu) ₃ ^(a)	200 psi	30 mole %	1.56 gm	UNREACTED
1.0 gm	180°C	Co/Li(n-Bu)	200 psi	1 mole %	0.89 gm	UNREACTED
1.0 gm	180°C	Co/Li(n-Bu)	200 psi	10 mole %	0.79 gm	UNREACTED
2.0 gm	200°C	Co/Al(i-Bu) ₃	1400 psi	2 mole %	0	MONOMER
1.0 gm	200°C	Pd/charcoal	1400 psi	10 mole %	0	MONOMER
1.0 gm	200°C	Rh/charcoal	1200 psi	10 mole %	0	MONOMER

(a) The same reaction was carried out with Al/Co ratios of 4:1 and 3.3:1 with similar results.

(b) 1-2% solution in decalin.

hydrogenation of the unsaturation shown to occur to any degree. The PDMHD remained unreacted according to IR and ^{13}C NMR analysis.

When the conditions of the hydrogenation were made more severe by raising the temperature and pressure the polymer was degraded. The monomer, DMHD, was found after the hydrogenation attempt by distilling it from the decalin reaction mixture. This indicates an unzipping reaction has occurred as outlined in Equation (51).



This is consistent with the degradation that other workers have found for this polymer when heated near 200°C .^{160,172}

c. Chemical reduction of 2,5-poly(2,5-dimethyl-2,4-hexadiene (PDMHD) with diimide

The hydrogenation of PDMHD was also attempted using diimide chemistry under a variety of conditions. The diimide moiety was generated in situ by decomposition of p-toluenesulfonylhydrazide (p-TSH) at 120°C .

Several different solvents and solvent combinations were explored. The requirement for the solvent was that it dissolve both the p-TSH and at least swell PDMHD above 120°C. The solvents used were decalin/m-xylene, decalin/mesitylene, σ -xylene, p-xylene and m-xylene.

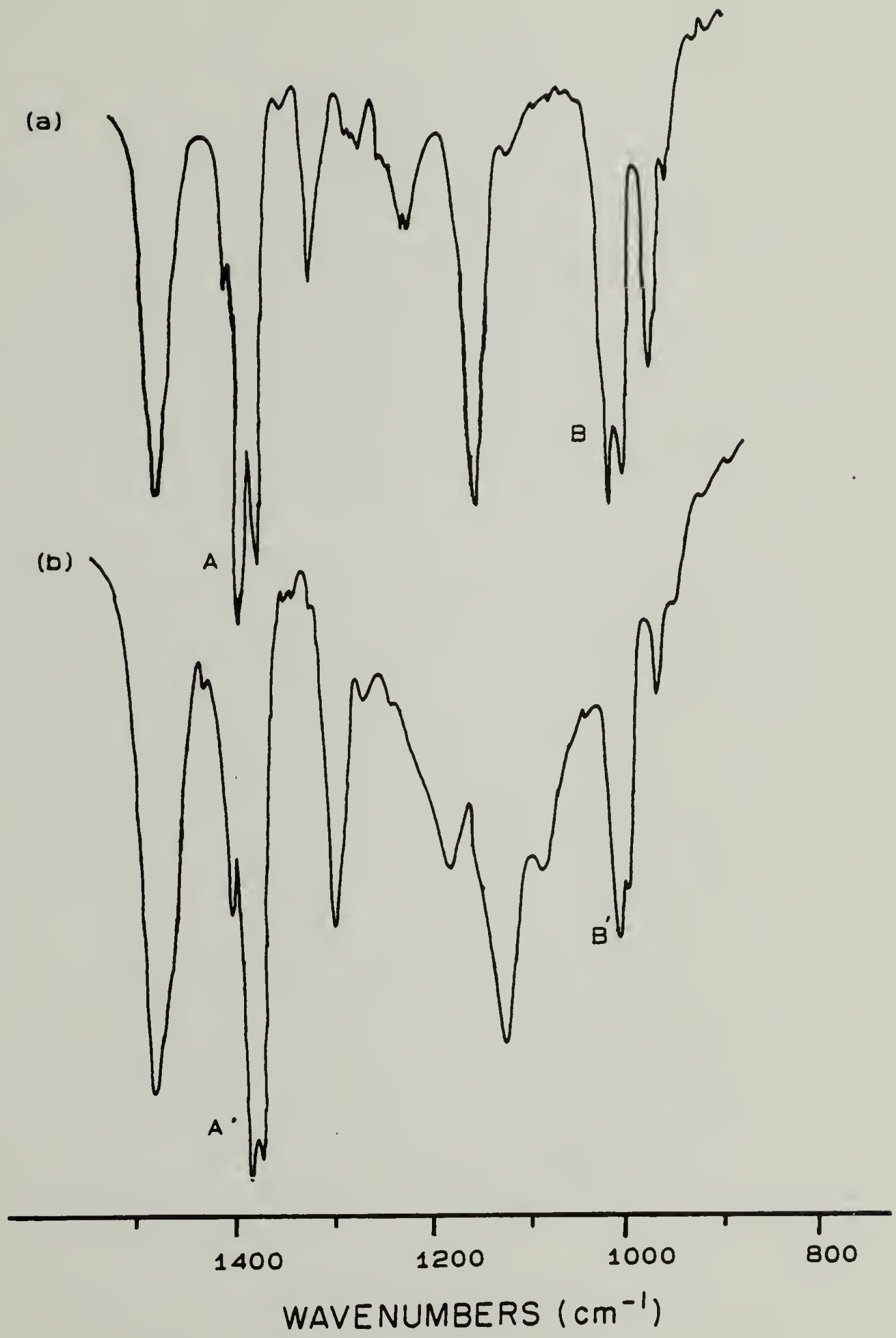
The amount of hydrogenation was again measured with IR spectroscopy by the same method as described previously for catalytic hydrogenation attempts. An example is given in Figure 8, where the top spectrum is for PDMHD and the bottom for the hydrogenation of PDMHD using 4 equivalents of diimide and p-xylene as solvent. The reaction is described on p. 84 of the experimental chapter.

To determine percent hydrogenation for this example the absorbances labeled A and A' in Figure 8, are the internal standards of the gem-dimethyl bending, and B and B' are the -C=CH- stretching bands for trans PDMHD. Equation (52) was used to calculate the percent hydrogenation of the PDMHD from the intensities of A, A', B, and B'.

$$\% \text{ Hydrogenation} = 100 - \left[\frac{A \cdot B' \cdot 100}{A' \cdot B} \right] \quad (52)$$

Most hydrogenations of polymers using diimide as the reducing agent require only 2 equivalents of p-TSH and 4-5 hr for quantitative hydrogenation.^{108,109} However, more substituted polymers tend to be more difficult to react upon. In this work it was determined that single

Figure 8. IR spectra of gem-dimethyl stretching (A, A') and trans -CH=CH- stretching (B, B') absorbances for; (a) 2,5-poly(2,5-dimethyl-2,4-hexadiene), (b) partially hydrogenated 2,5-poly(2,5-dimethyl-2,4-hexadiene).



reactions were not sufficient to hydrogenate PDMHD. Generally the first reaction gave from 5 to 37% reduction of the unsaturation (Table 11). The solvent and temperature did not appear to have a large effect on the progress of this hydrogenation. The time and amount of diimide seemed to be of more importance. For this reason two experiments were done to attempt to fully saturate the polymer and prepare 100% H-H polyisobutylene.

The first experiment involved repeated addition of p-TSH to a single-pot reaction. In this way fresh diimide was added to the polymer at intervals of 24, 48, 96, 126 and 174 hrs. Prior to each addition a small sample of the polymer was worked-up to determine the amount of hydrogenation which had occurred. Figure 9 is a graph of hydrogenation as a function of time as compiled by this experiment. The reaction was terminated after 6 days when the degree of hydrogenation appeared to have reached a limit near 50%.

A second experiment was conducted in which the hydrogenated PDMHD was isolated after each 24 hr of reaction time and then subjected to fresh solvent and diimide for further reaction. This procedure was repeated 6 times with 4 equivalents of diimide each time. The results are found in Figure 10 where the percent hydrogenation is plotted against the number of hydrogenation experiments. In this case the polymer became completely insoluble in the

TABLE 11

HYDROGENATION OF 2,5-POLY(2,5-DIMETHYL-2,4-HEXADIENE) USING DIIMIDE

Solvent (a)	Temperature	Time	Equivalents of Diimide	Percent Hydrogenation
decalin/m-xylene 75:25	160°C	12 hr	2.0	4%
mesitylene	130°C	16 hr	2.0	8%
o-xylene	145°C	20 hr	4.0	18%
p-xylene	139°C	22 hr	4.0	28%
decalin/m-xylene 75:25	160°C	24 hr	2.0	21%
decalin/m-xylene 75:25	160°C	24 hr	4.0	37%

(a) 2.5 g of polymer in 100 ml of solvent.

Figure 9. Percent hydrogenation vs. time for diimide reduction of 2,5-poly(2,5-dimethyl-2,4-hexadiene) by repeated addition of diimide.

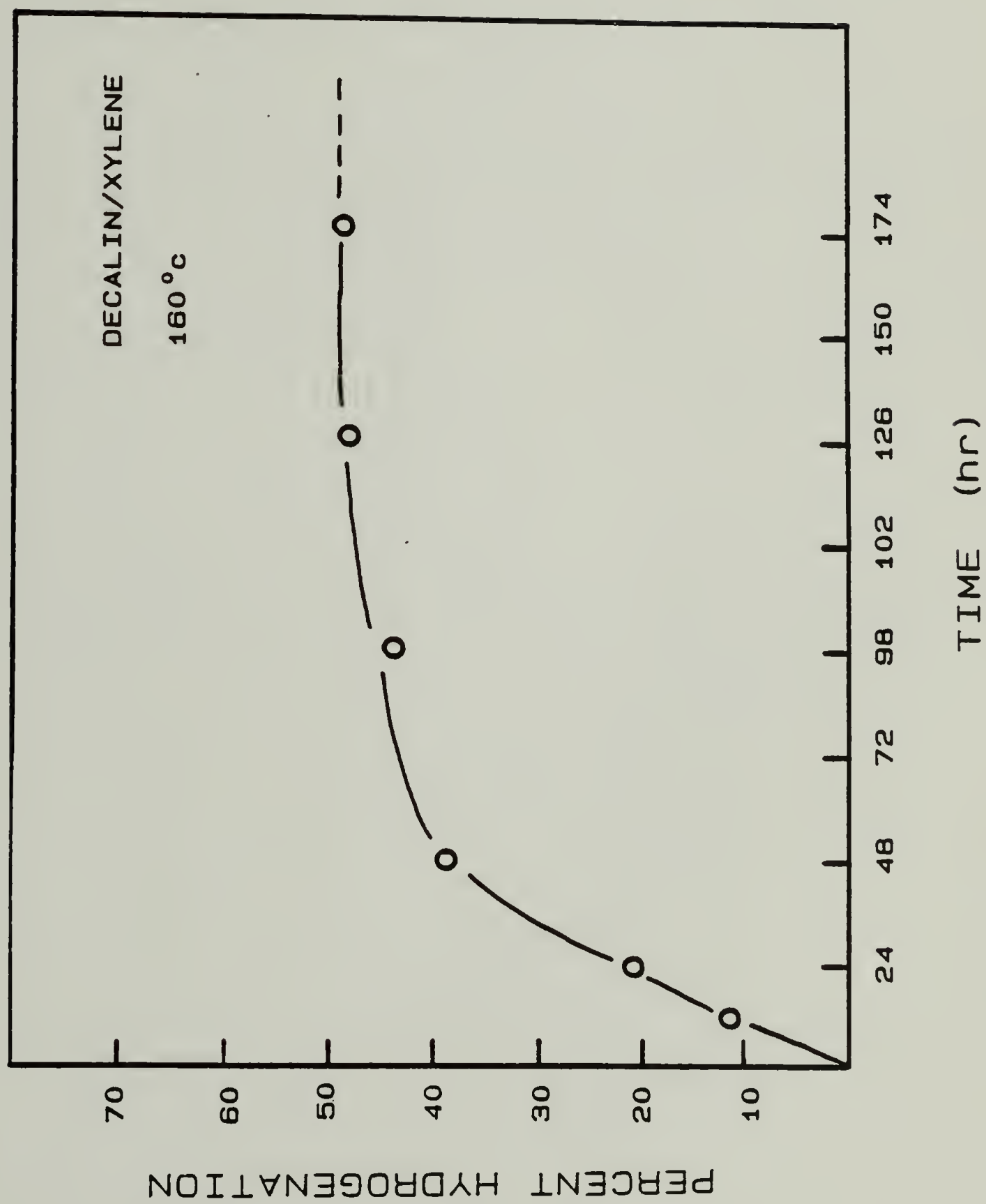
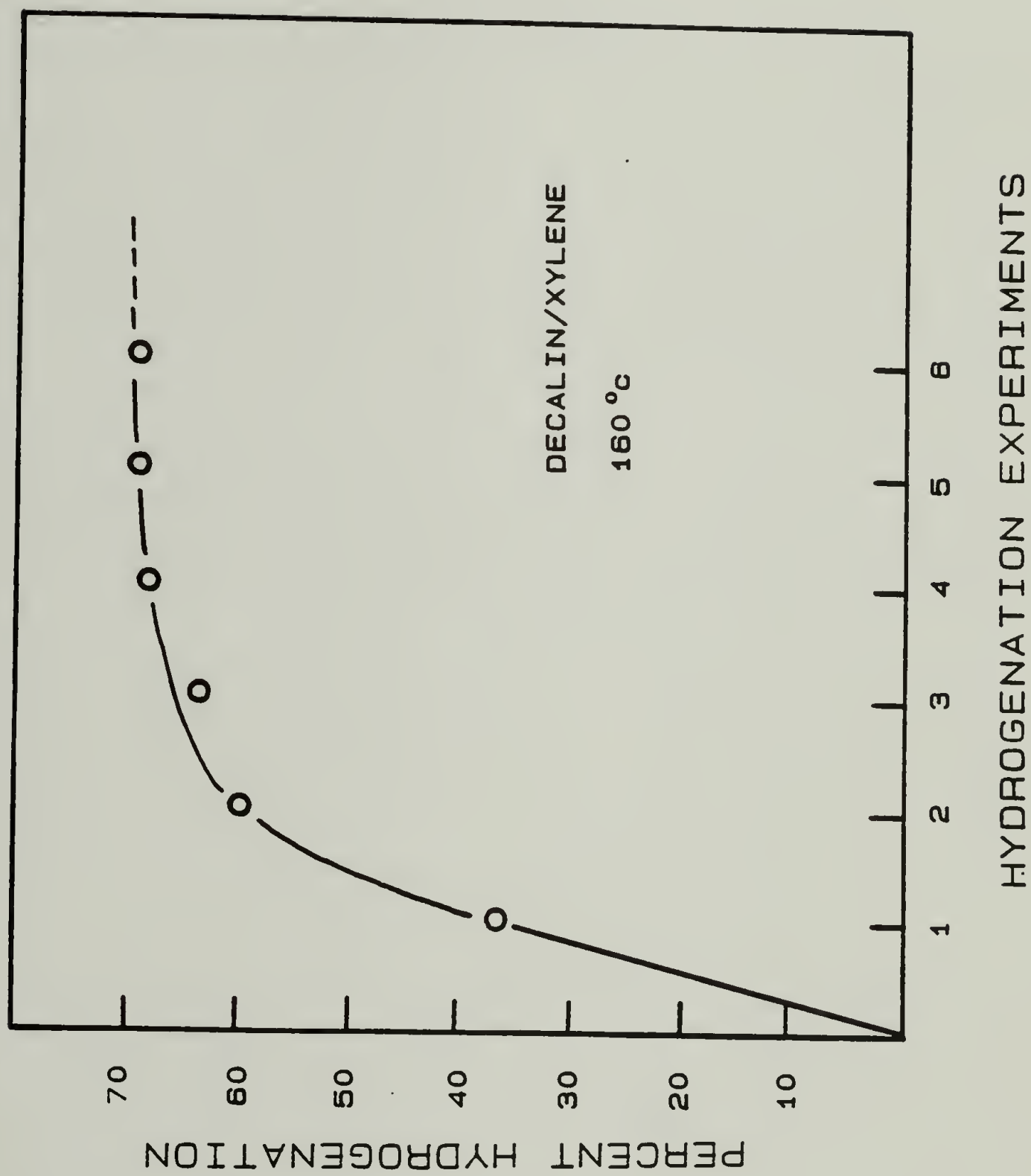


Figure 10. Percent hydrogenation vs. time for diimide reduction of 2,5-poly(2,5-dimethyl-2,4-hexadiene) by repeated reaction with diimide.



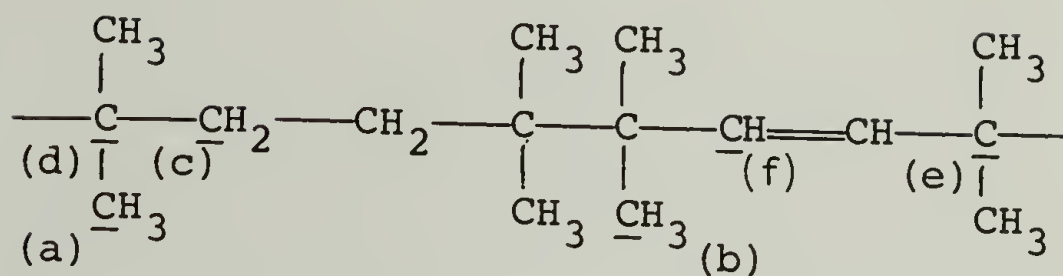
reaction solvent as well as in decalin up to 180°C. The percent hydrogenation was, however, 70% at this point according to IR analysis. The insolubility is due most probably to cross-linking reactions. The elemental analysis showed a lower than calculated carbon content, and sulfur and nitrogen contents of 0.8% and 0.5% respectively which indicates some incorporation of the toluenesulfonyl group. The exact nature of the cross-link which develops has not been explored. However, with the unsaturation of the PDMHD, and with the temperatures involved cross-linking reactions are not surprising.

The ^{13}C NMR spectrum of the 50% hydrogenated PDMHD is given on p. 314 of the appendix. The data for the chemical shifts is shown in Table 12. From this one can observe that the partially hydrogenated polymer is a 50:50 copolymer of H-H polyisobutylene and PDMHD since all of the carbon atoms in the spectrum can be assigned to these two components. This spectrum indicates that the new copolymer may be blocky in nature because the methyl and quaternary carbon shifts are well defined for each comonomer.

It might be expected that the hydrogenation would proceed in a somewhat blocky manner because once several adjacent diene units are saturated, the symmetry of the molecule is changed in that local environment. This disruption of the symmetry would then allow for better

TABLE 12

HYDROGENATED 2,5-POLY(2,5-DIMETHYL-2,4-HEXADIENE)



Carbon	Chemical Shift (ppm)	H-H Polyiso-butylene* (ppm)	PDMHD
(a)	21.9	21.7	
(b)	23.6		23.9
(c)	32.1	31.4	
(d)	38.5 (39.1)	38.8	
(e)	42.1		41.4
(f)	135.5		135.5

*Conditions are described on p. 169.

hydrogenation in that vicinity, hence an apparently blocky copolymer.

d. Discussion of attempted hydrogenation of 2,5-poly(2,5-dimethyl-2,4-hexadiene)

The reasons for the lack of success in obtaining complete hydrogenation for 2,5-poly(2,5-dimethyl-2,4-hexadiene) (PDMHD) by either catalytic or chemical means are thought to be a combination of several different problems:

- The bulky substitution of 4 methyl groups surrounding each double bond.
- The high degree of crystallinity and molecular order in PDMHD.
- The completely trans structure of the unsaturation.
- The unzipping mechanism available for degradation.

All of these factors play some role in inhibiting the hydrogenation of the polymer and thereby blocking this route as a method for obtaining H-H polyisobutylene.

The substitution of the 4 methyl groups on the β carbons appear to act to "block" the approach of the metal hydride moiety toward the double bond. It is well known that highly substituted dienes are more difficult to react upon than unsubstituted.⁹⁹

The fact that the PDMHD is very crystalline in the

solid state means it may retain some of its molecular order even in solution. This conformational order might impede hydrogenation by making the double bond again less accessible.

The trans configuration of the diene polymer is also a negative factor in terms of hydrogenation. Cis dienes are normally easier to reduce since cis addition of hydrogen is the addition pathway in most cases.¹⁰⁰

Finally, the fact that the polymer degrades by unzipping at temperatures near 200°C precludes using very forceful conditions to increase catalytic hydrogen uptake.

4. Attempted Alternating Copolymerization of Ethylene with Tetramethylethylene

The copolymerization of ethylene with tetramethylethylene was attempted using benzoyl peroxide as initiator. The ethylene pressure was held at approximately 300 psi and the temperature at 70°C for 22 hr.

The copolymer obtained was a solid waxy material. Elemental analysis was somewhat low for both carbon and hydrogen indicating low molecular weight and the incorporation of end groups from the initiator.

If the copolymerization had proceeded in a completely alternating manner the structure of the polymer would have been that of H-H polyisobutylene. The ¹³C and ¹H NMR spectra of the copolymer clearly show that only a small amount of tetramethylethylene was incorporated into

the copolymer.

The ^{13}C NMR spectrum showed one peak at 30.1 ppm which is directly identifiable as the polyethylene carbon (see p. 315 of the appendix). Two other peaks are located at 23.8 ppm and 36.3 ppm and have been assigned to the methyl carbon and quarternary carbon respectively for the tetramethylethylene units incorporated. These are both shifted by ~ 2 ppm from the resonances found for pure H-H polyisobutylene (CH_3 - 21.7 ppm, $-\text{C}-$ 38.8 ppm). Since the tetramethylethylene groups are essentially scattered randomly throughout a polyethylene backbone and are not adjacent to one another this shift is not surprising.

Integration of the ^1H NMR spectrum was used to determine the copolymer composition (see p. 299 of the appendix). The ^1H resonance found at 1.3 ppm is due to the methylene protons of the polyethylene. The peak found at 1.0 ppm is the methyl ^1H of the tetramethylethylene units.

The integration ratio of CH_2 to CH_3 protons gave a copolymer composition of 95% ethylene and 5% tetramethylethylene.

It is interesting that a small amount of tetramethylethylene was copolymerized under our reaction conditions. The only other report of tetramethylethylene polymerization was given by Vogl,¹⁷³ where an oily viscous homopolymer was obtained.

However, the objective of this experiment was to

prepare H-H polyisobutylene, which would require a strictly alternating 1:1 copolymer of ethylene and tetramethylethylene. This was not possible under the conditions used.

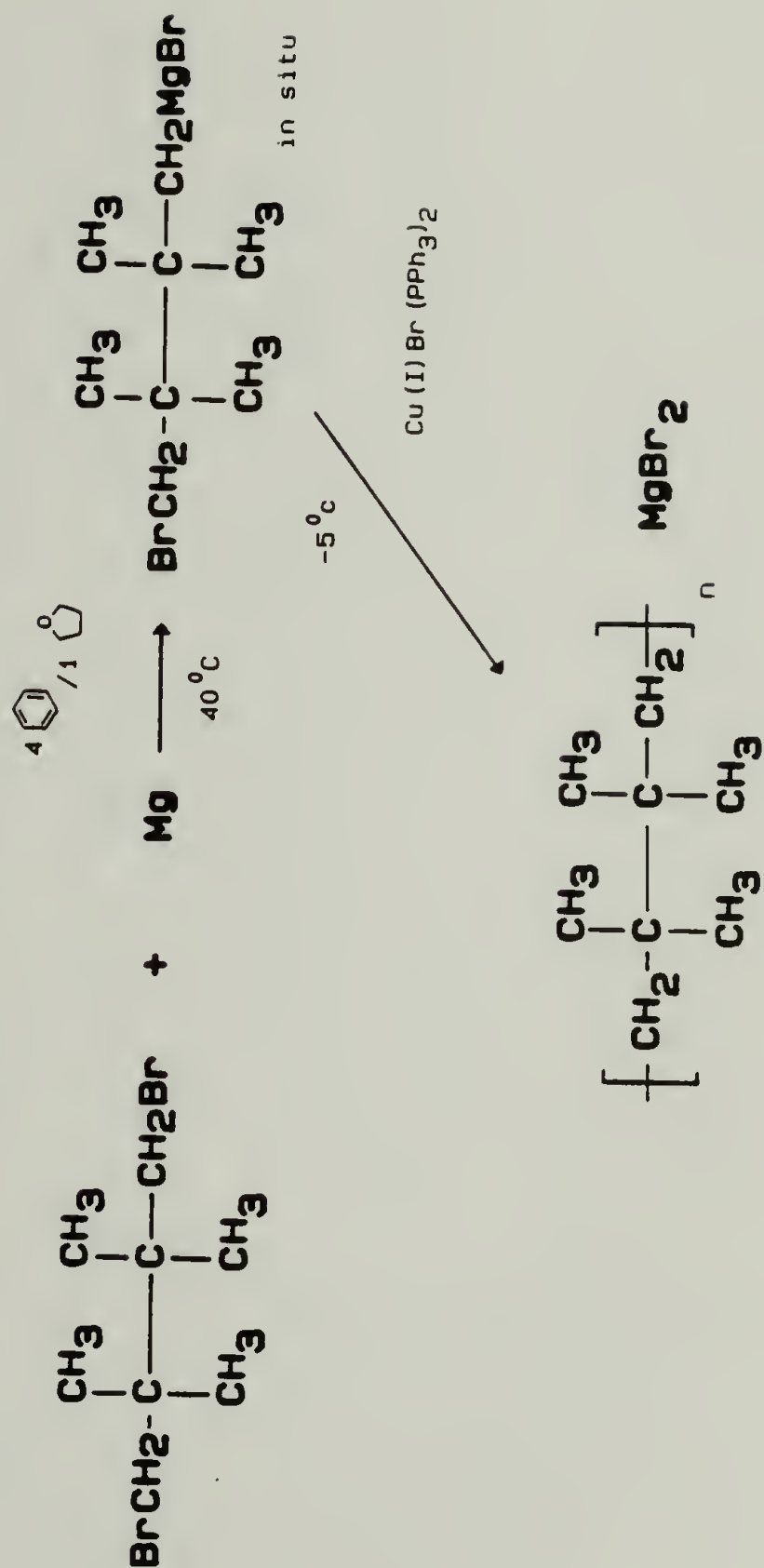
It is not surprising that ethylene and tetramethylethylene do not copolymerize by an alternating mechanism. Generally alternating copolymers require some special interaction between the comonomers usually due to some electronic effect (i.e., 1:1 charge-transfer complexes between comonomers). In this case there are no polar interactions between tetramethylethylene and ethylene. This coupled with the steric inhibition toward propagation exhibited by tetramethylethylene leads to only a small amount of incorporation.

5. Grignard/Alkylbromide Coupling Polymerization of 2,2,3,3- Tetramethyl-1,4- Dibromobutane

TMDBB was polymerized to H-H polyisobutylene by first forming the mono-Grignard/mono-bromide of TMDBB followed by catalytic coupling of the reactive ends (Figure 11). It should be noted again that the monomer for this polymerization is not the TMDBB, but the mono-Grignard/mono-bromide of TMDBB which is the species actually polymerized. The polymerization is from here on referred to as the Grignard polymerization. It was found that the success of this Grignard polymerization was dependent upon the solvent, and the coupling temperature.

Figure 11. Preparation of H-H polyisobutylene by Grignard polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane.

**GRIGNARD POLYMERIZATION OF
2, 2, 3, 3-TETRAMETHYL-1, 4-DIBROMOBUTANE**



YIELD: 30%

a. Solvent effects

Previously, the Grignard polymerization was carried out by Yamamoto exclusively in ether solvents such as THF, dibutyl ether or diglyme. There are no reports of using mixed solvents or amine ligands for these polymerizations.

When the mono-Grignard reagent of TMDBB was prepared in THF the Grignard formation proceeded smoothly. However, the coupling step was found not to yield polymer in any appreciable amount. It is believed that the reason for this is the lack of solubility of H-H polyisobutylene in THF. When an amine ligand such as triethylamine (TEA) or tri-n-butylamine (TBA) was used in conjunction with benzene as a solvent the formation of the Grignard was much more difficult to carry out, but the coupling reaction yielded some polymer.

H-H polyisobutylene is most soluble in aromatic solvents at elevated temperatures and for this reason it is desirable to carry out the polymerization in benzene or some other aromatic solvent. However, it is not possible to form the mono-Grignard/mono-bromide reagent of TMDBB in benzene alone. An ether is necessary to polarize the carbon-bromine bond for the insertion of the magnesium. It was empirically found that by using a 4:1 ratio of benzene:THF as the solvent system that a good polymerization could be obtained. The solvent conditions were not, however, optimized any further. The mixed solvent system appears to

be necessary, but the best ratio and the best solvents should be studied further.

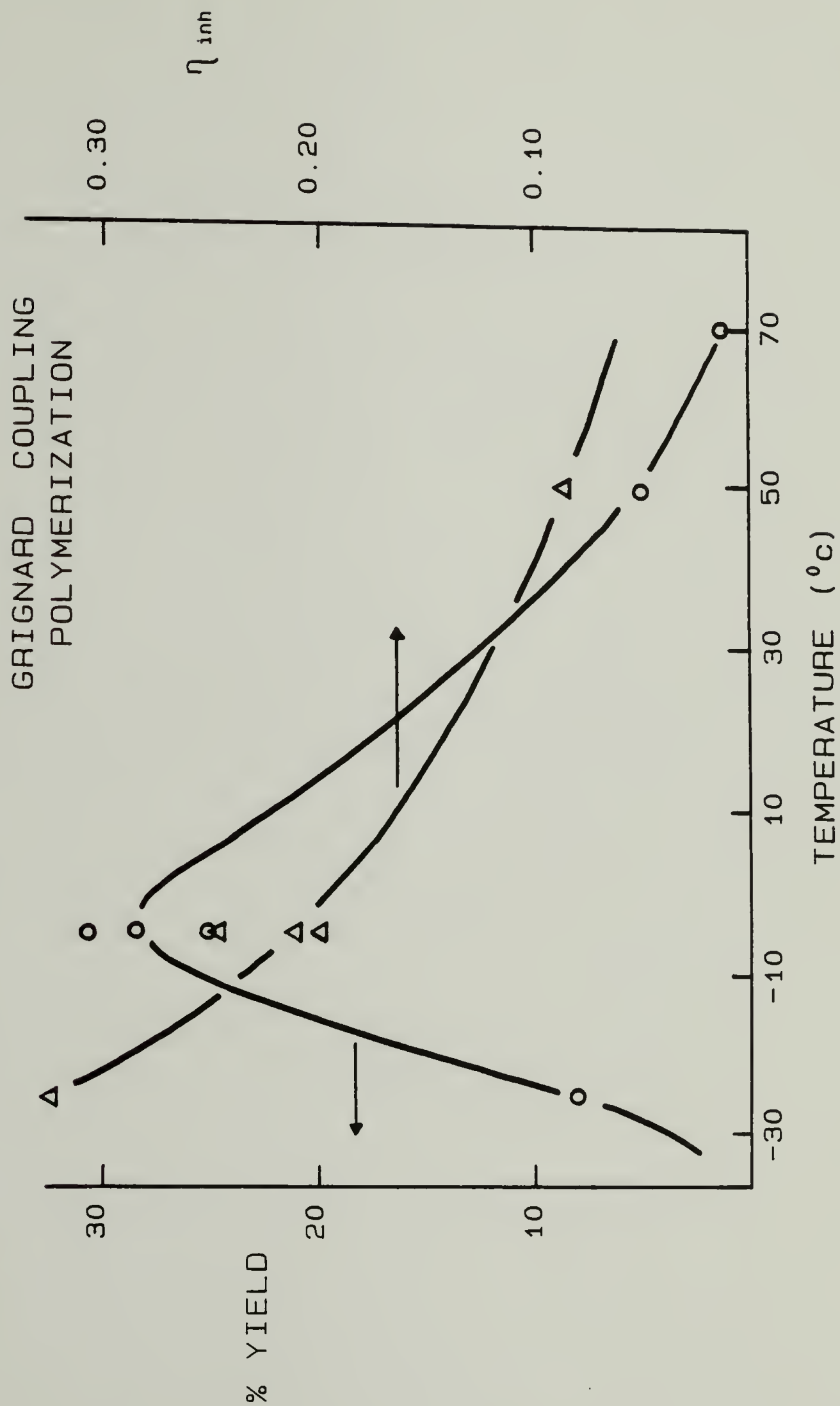
b. Temperature effects

The yield and molecular weight of H-H polyisobutylene were studied as a function of the temperature at which the coupling reaction was performed. The reactions were conducted in a 4:1/benzene:THF solvent system. All other reaction conditions were kept consistent, and only the coupling temperature was varied. The yields were based on mole percent, and the inherent viscosity of the polymer was used as an indication of molecular weight. Figure 12 shows the plots of yield and η_{inh} as a function of temperature on the same graph.

The yield goes through a maximum between -10 and $+10^{\circ}\text{C}$ with a significant drop in yield of polymer to either side of that temperature range. The inherent viscosity however appears to increase as the temperature of polymerization is decreased.

These observations are not entirely in line with what should be expected from a normal step-growth polymerization. In the first place the yields of the polymerization under the best conditions were only 25-30% which in a normal step-growth polymerization would give rise to only a very low \overline{DP}_n . Yet the viscosity data indicates a moderate \overline{DP}_n for the coupling reaction. Secondly the fact that at

Figure 12. Yield and inherent viscosity vs. temperature for Grignard polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane.



-25°C a decrease in yield is observed with an increase in viscosity implies that other factors are involved in the production of higher molecular weight polymers.

c. Molecular weight of H-H polyisobutylene

The number-average molecular weights (\bar{M}_n) of the H-H polyisobutylenes obtained through the Grignard polymerizations were calculated from end group analysis. The elemental analysis for C, H and Br gave total compositions of $100 \pm 0.6\%$. This was taken as evidence (along with spectral analysis) that only bromine groups were present as end groups to the polymer. Using the analysis to count the number of Br end groups \bar{M}_n was determined (Table 13).

The \bar{M}_n s were consistent with the inherent viscosity results. The highest molecular weight was found for the H-H polyisobutylene prepared at -25°C. A broad molecular weight distribution is expected since this is still basically a step-growth reaction. Normal weight-to-number-average molecular weights (\bar{M}_w/\bar{M}_n) for step-growth polymerizations is 2.0. Assuming that ratio, \bar{M}_w is estimated at between 6,000 and 20,000.

d. Cyclization vs. polymerization

The major side reaction which occurs for the Grignard polymerization is believed to be the ring-closure of TMDBB to 1,1,2,2-Tetramethylcyclobutane (TMCB). This

TABLE 13
NUMBER-AVERAGE MOLECULAR WEIGHTS AND
ELEMENTAL ANALYSES OF HEAD-TO-HEAD
POLYISOBUTYLENES

Temperature of Polymerization	C %	H %	Br %	Total %	\bar{M}_n
-5°C	79.92	14.12	5.31	99.4	3,000±400
-5°C	80.40	14.07	5.97	100.4	2,700±400
-5°C	81.61	14.50	4.50	100.6	3,600±400
0°C	80.95	14.03	5.00	100.0	3,200±400
-25°C	83.27	14.50	1.63	99.4	10,000±400

takes place when the Grignard-end of the monomer couples in an intramolecular reaction with its own alkylbromide end.

TMCB has been identified as part of the volatiles which escape from the polymerization along with some TMDBB. The product was identified by ^{13}C NMR analysis (see p. 310 of appendix). The calculated chemical shifts¹⁷⁴ for TMCB are; $-\text{CH}_3$, 24.4 ppm; $-\text{CH}_2$, 32.1 ppm; $-\text{C}-$, 32.8 ppm. Found; $-\text{CH}_3$, 24.8 ppm; $-\text{CH}_2$, 31.4 ppm; $-\text{C}-$, 36.3 ppm.

The weight of the residual volatiles after THF and benzene were removed was about 60% of the starting material which accounts in part for the low yield of the polymerization.

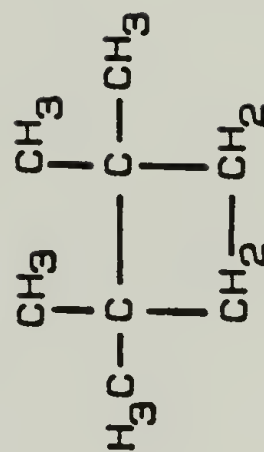
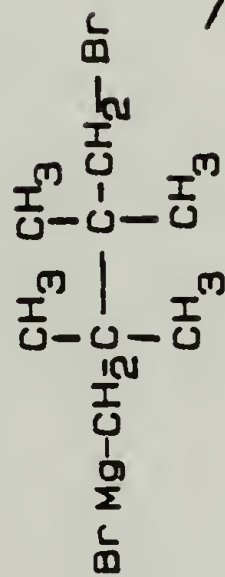
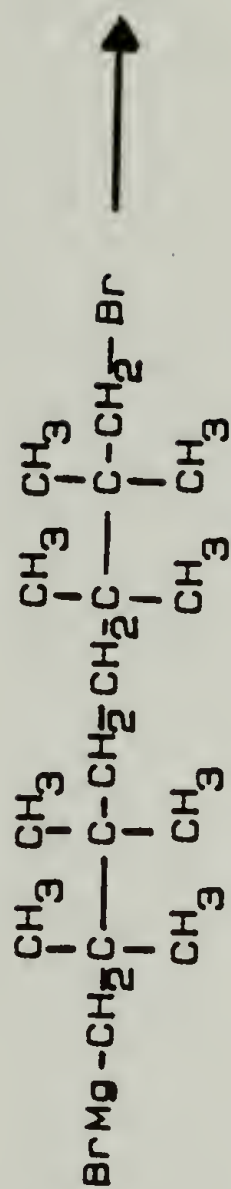
e. Discussion of Grignard polymerization

All the results which have been discussed in this section can be explained by consideration of the cyclization vs polymerization of the mono-Grignard of TMDBB (Figure 13).

It is thought that the first coupling reaction determines whether polymerization will occur. If the first coupling is intramolecular then cyclization takes place. The temperature of polymerization dramatically affects this initial step. The higher the temperature the more likely the ring-closure reaction will occur at the expense of the intermolecular coupling. However, if the initial coupling reaction is intermolecular an eight carbon chain is

Figure 13. Polymerization vs. cyclization reaction during Grignard polymerization of 2,2,3,3-tetramethyl-1,4-dibromobutane.

POLYMERIZATION VS CYCLIZATION



FURTHER COUPLING

NO CYCLIZATION

formed. Thermodynamic considerations do not favor the formation of eight-membered rings consequently only further linearization will proceed after the first coupling of two TMDBB molecules.

This reasoning can account for the formation of relatively high molecular weight polymer at such low yields for a step-growth polymerization. That is, once a cyclization has occurred that monomer is removed from the polymerization, and it does not in any way interfere with the remainder of the reaction. If half of the monomers cyclize in the first step, then 50% of the yield is lost however, the remaining 50% of eight-membered chains will go on to polymerize.

Finally, at -25°C the highest molecular weight was found but at a very low yield. This may be due to the difference in reactivity between the Grignard-end of the initial monomer and the Grignard-end of the dimer. The polarity of the Grignard-end is effectively the reverse of the alkylbromide-end and in the monomer these are only separated by two carbons. This may reduce the reactivity somewhat of the Grignard/alkylbromide reagent and at lower temperatures this becomes more important. However, once the dimer has formed the two ends are now separated by 6 carbons and are no longer influencing each other to a marked degree. This might allow for faster coupling once the dimer is formed and higher molecular weights are

resulted.

B. Physical Characterization of Head-to-Head Polyisobutylene and Comparison of Head-to-Head and Head-to-Tail Polyisobutylene

The H-H polyisobutylene described throughout the remainder of this dissertation is the polymer obtained by the Grignard polymerization of TMDBB.

1. Spectral Analysis

a. Infrared

The IR spectra for H-H and H-T polyisobutylene are shown together in Figure 14. There is very little difference between the two in terms of strong absorbances. The assignments for the major peaks are given in Table 14. One point of interest is the difference in the gem-dimethyl C-H bending region. When the gem-dimethyl group is at an internal position, a doublet is observed due to the interaction between the in-phase and out-of-phase symmetrical CH_3 bending of the two methyl groups bonded to a common carbon atom.¹⁷⁵ This is apparently effected by the proximity of the two gem-dimethyl groups for H-H polyisobutylene. The doublet absorbs at 1365 cm^{-1} and 1375 cm^{-1} for H-H and at 1368 cm^{-1} and 1390 cm^{-1} for H-T polyisobutylene.

A peak due to the residual $\text{CH}_2\text{-Br}$ end groups is also found at 645 cm^{-1} for the H-H polyisobutylene made from

Figure 14. IR spectra for H-H and H-T polyisobutylene.

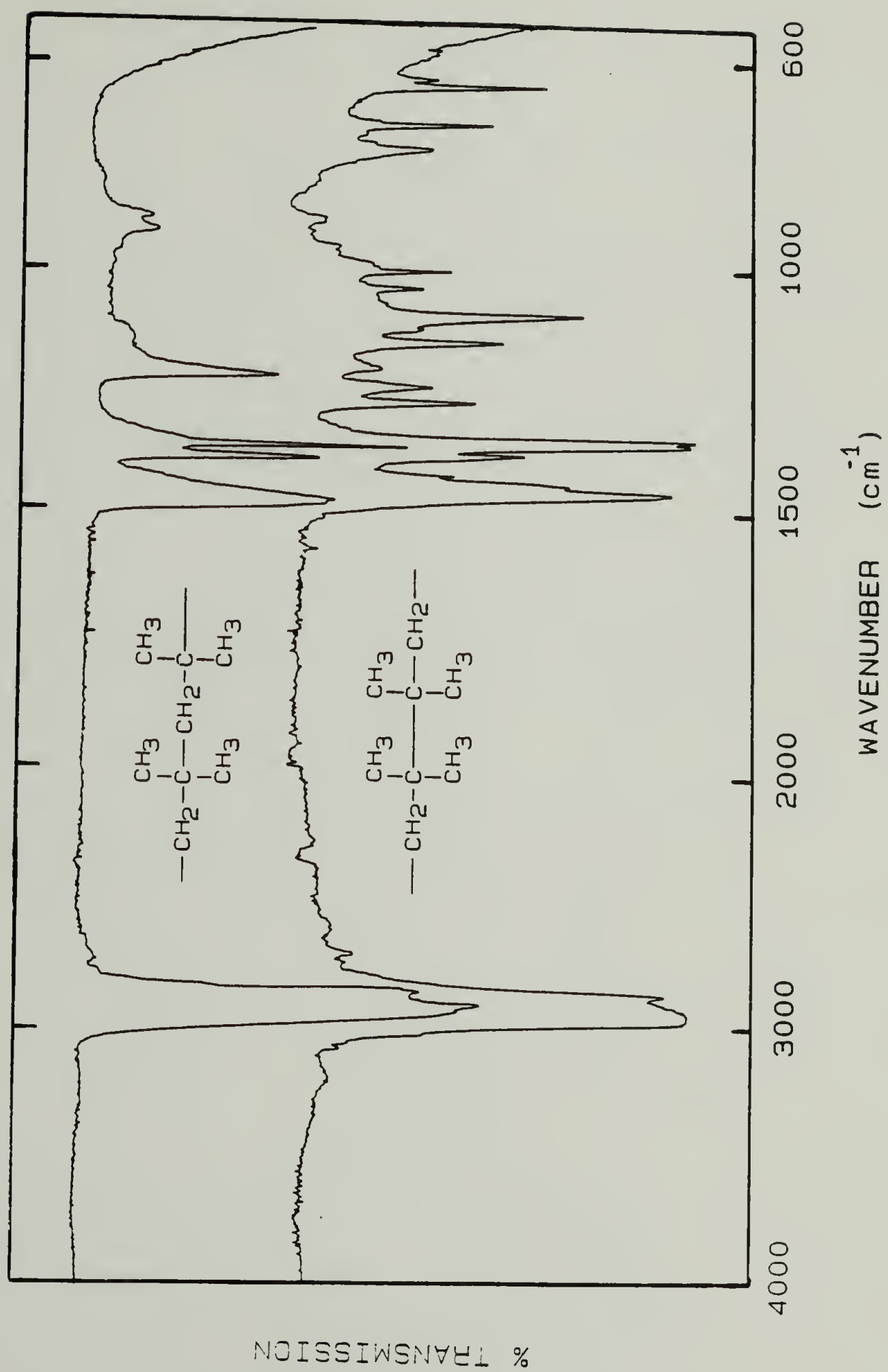



TABLE 14
IR PEAK ASSIGNMENTS FOR H-H
AND H-T POLYISOBUTYLENE

H-H polyisobutylene peaks	H-T polyisobutylene peaks	Assignments
2962 cm^{-1}	2960 cm^{-1}	ν_{as} -CH ₃
2872 cm^{-1}	2885 cm^{-1}	ν_{s} -CH ₃
1450 cm^{-1}	1455 cm^{-1}	δ_{as} -CH ₃
1365, 1375 cm^{-1}	1368, 1392 cm^{-1}	δ_{s} -CH ₃ (gem-dimethyl)
2926 cm^{-1}	2926 cm^{-1}	ν_{as} -CH ₂ -
2905 cm^{-1}	2900 cm^{-1}	ν_{s} -CH ₂ -
1395 cm^{-1}	--	δ_{as} -CH ₂ -
1465 cm^{-1}	1470 cm^{-1}	δ_{s} -CH ₂ -
740 cm^{-1}	--	p -CH ₂ -
1289 cm^{-1}	1230 cm^{-1}	 $\begin{array}{c} \text{CH}_3 \\ \\ \textcircled{\text{R}} - \text{C} - \textcircled{\text{R}} \\ \\ \text{CH}_3 \end{array}$
1256 cm^{-1}	1160 cm^{-1}	
1171 cm^{-1}		
1120 cm^{-1}		
		stretching

TMDBB by Grignard polymerization.

b. ^1H NMR

The ^1H NMR spectra for H-H and H-T polyisobutylene are given in Figure 15. Both spectra are relatively simple since only two protons are observable for each and splitting is not a factor due to the nature of the structures.

The chemical shift values for H-H polyisobutylene protons were 1.3 and 0.9 ppm for $-\text{CH}_2-$ and $-\text{CH}_3$ respectively, while for H-T polyisobutylene 1.4 and 1.2 ppm were found for the same two protons. It should be noted that the molecular weight of the H-T polyisobutylene was determined by GPC peak maximum as 5,000.

c. ^{13}C NMR

The ^{13}C NMR spectra of similar molecular weight samples of H-H and H-T polyisobutylene in o-dichlorobenzene at 80°C are given in Figure 16. The spectra are again very simple and can be readily assigned. Figure 17 shows the off-resonance decoupled spectra of H-H and H-T polyisobutylene under the same conditions.

Table 15 is a compilation of the data from this study with the calculated values for the chemical shifts of the carbon atoms in the two polymers shown as well.

The methyl and methylene carbons of the H-H polyisobutylene are shifted further upfield than their analog carbon atoms in H-T polyisobutylene. However, the quarter-

Figure 15. ^1H NMR spectra of H-H and H-T polyisobutylene.

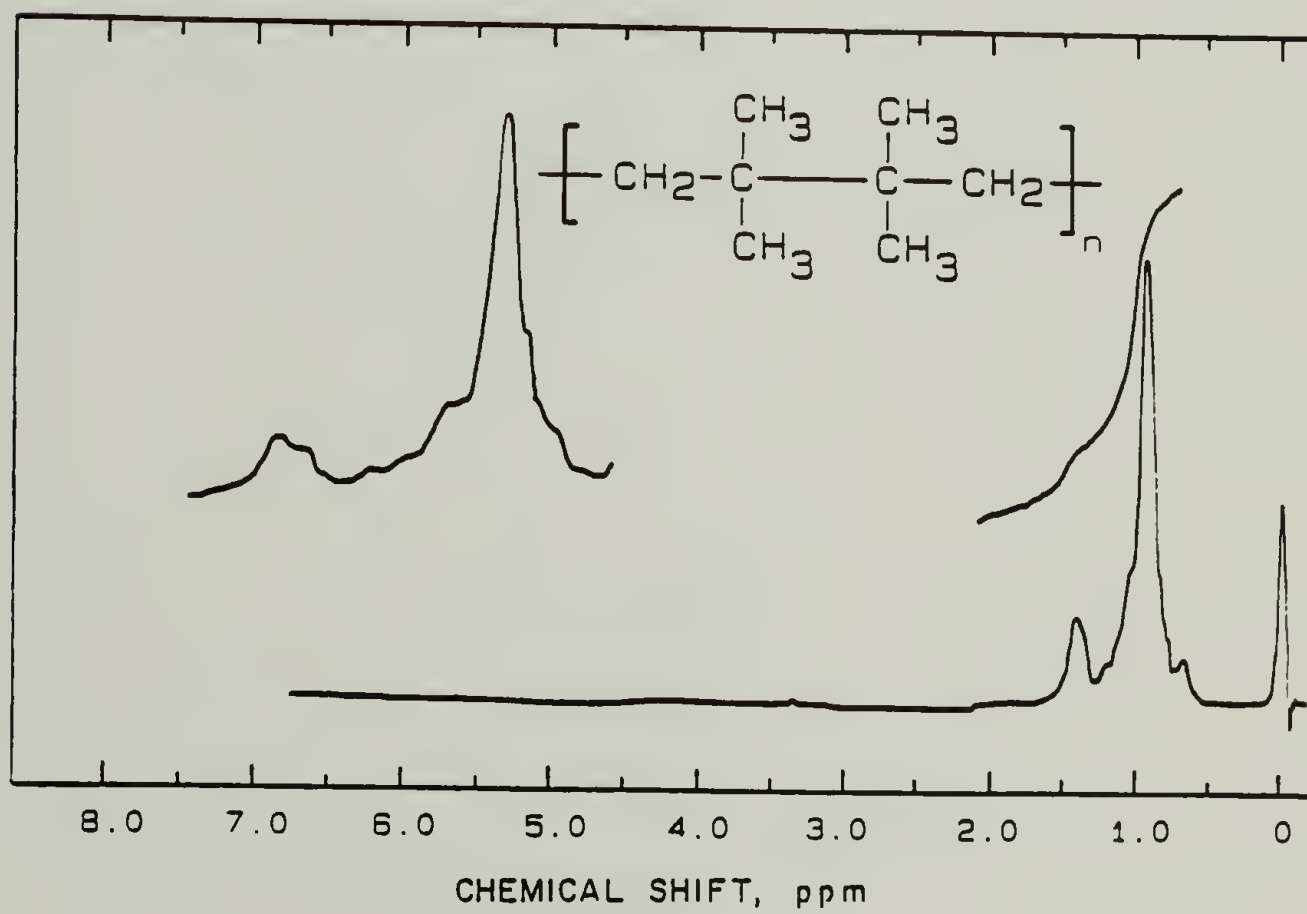
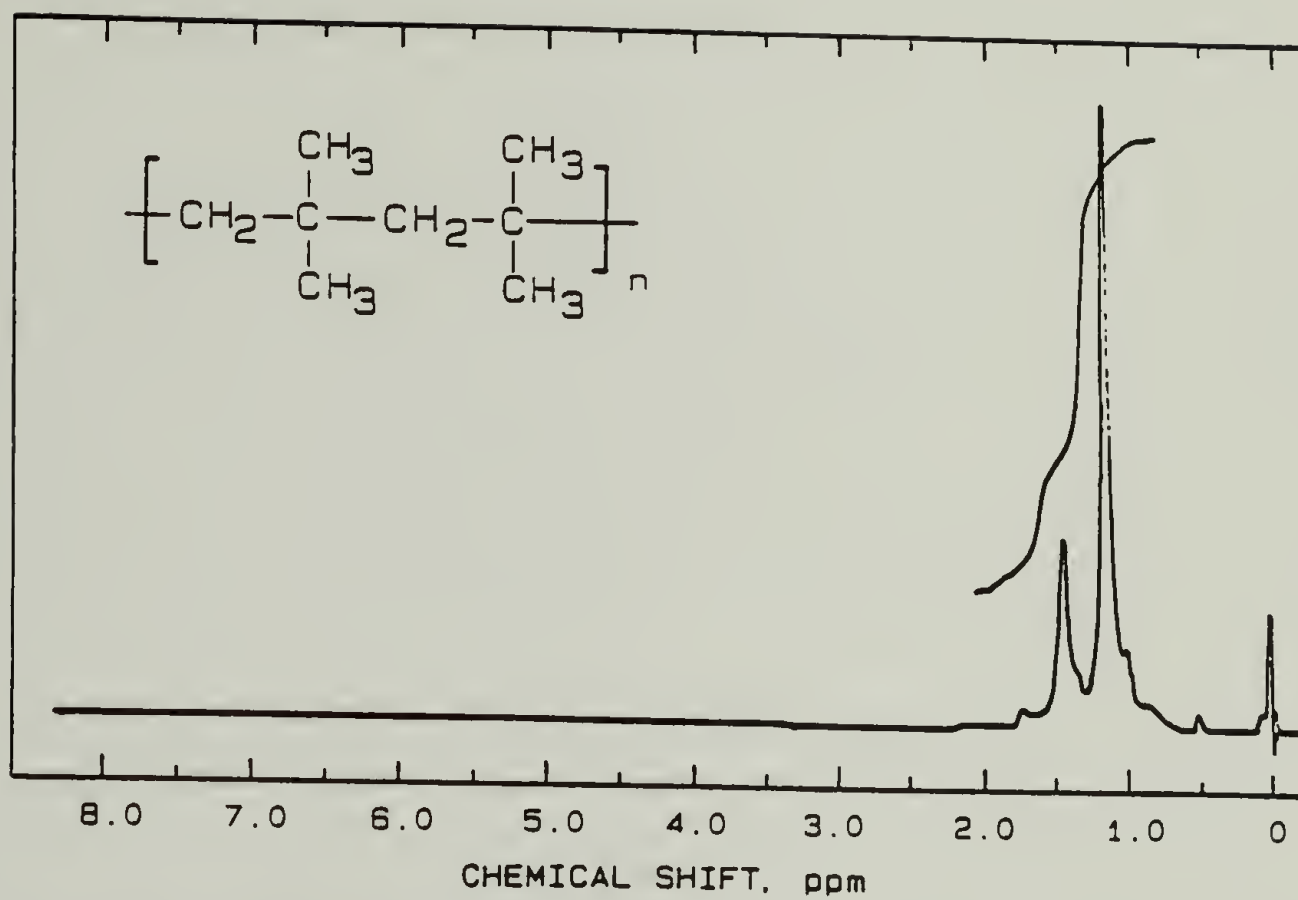


Figure 16. ^{13}C NMR spectra of H-H and H-T poly-isobutylene.

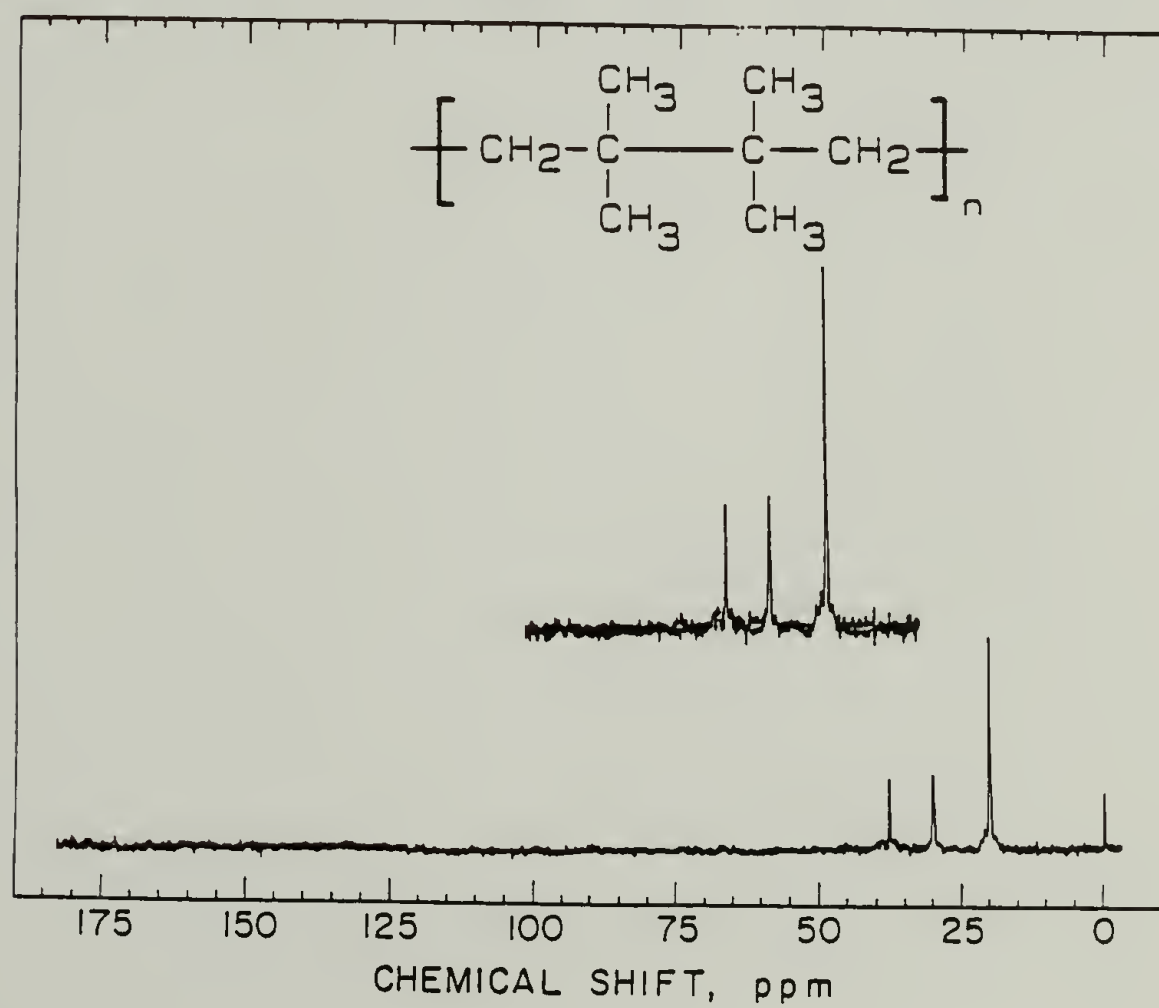
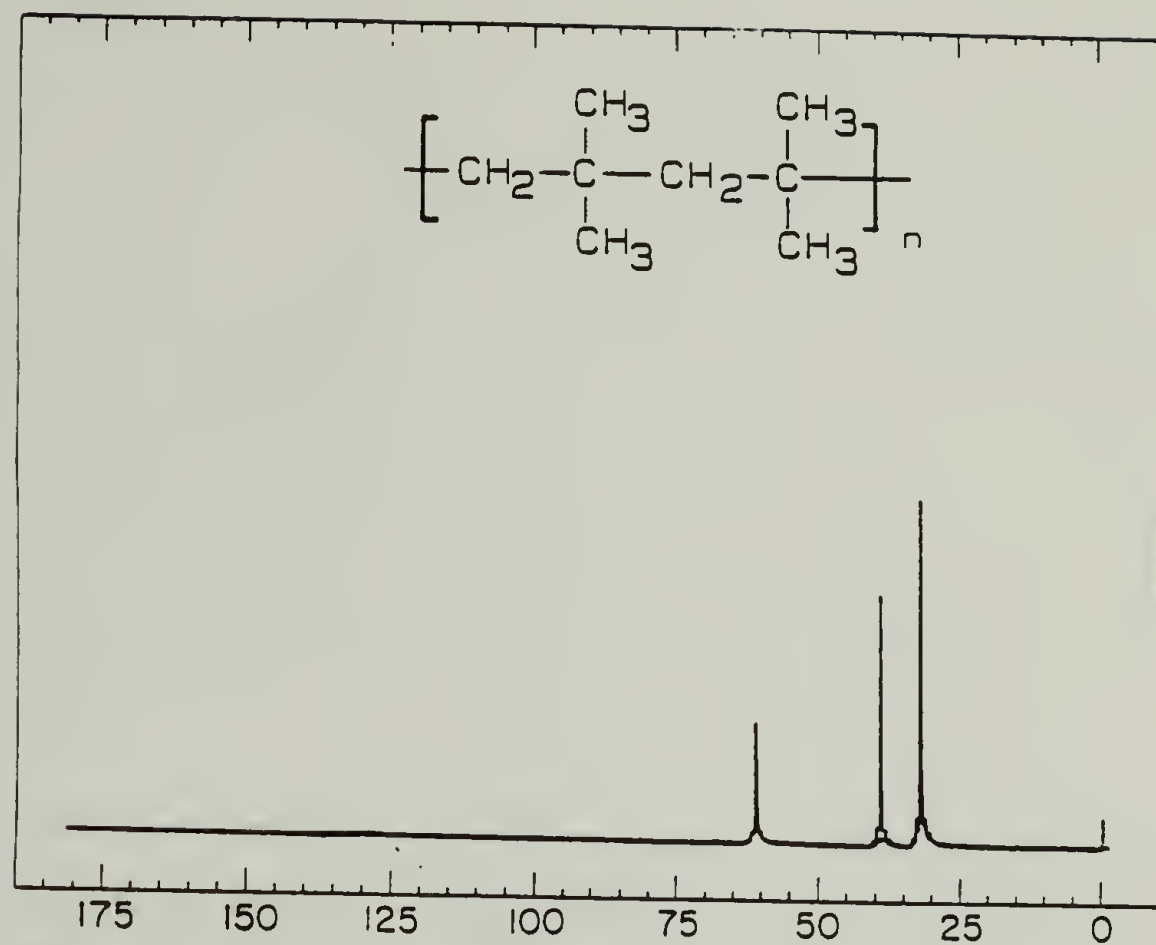


Figure 17. Off-resonance decoupled ^{13}C NMR spectra for H-H and H-T polyisobutylene.

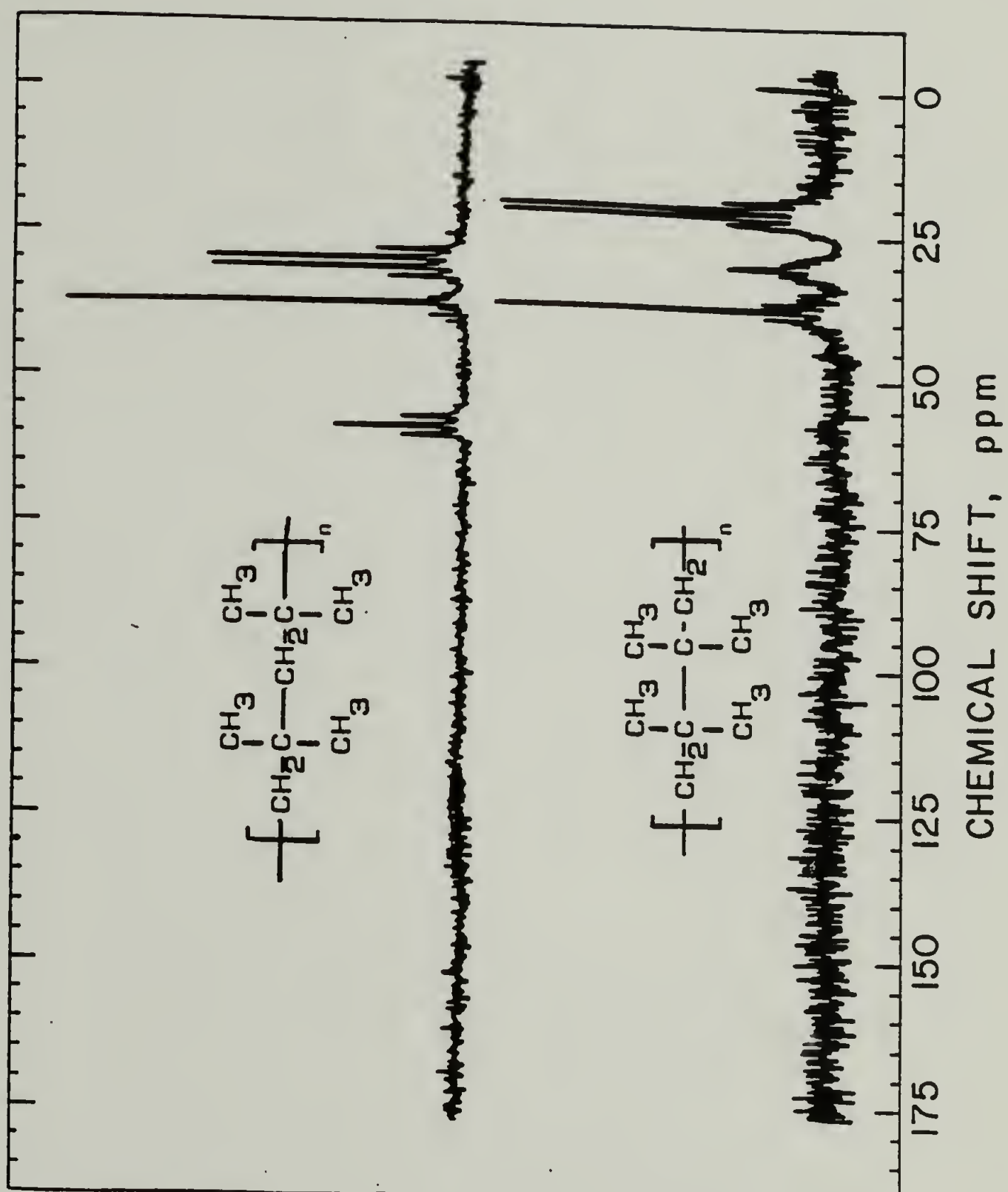


TABLE 15

^{13}C NMR CHEMICAL SHIFT VALUES FOR HEAD-TO-HEAD
AND HEAD-TO-TAIL POLYISOBUTYLENE

Carbon	Chemical Shift Found (ppm)	Chemical Shift Calculated		Splitting of Off-Resonance Decoupled Spectra
		¹⁷⁴ (Grant/Paul)	(Adams/ Lindeman) ¹⁷⁰	
<u>H-T polyisobutylene</u>				
-CH ₃	31.6	29.1	29.3	quadruplet
CH ₂ -	60.0	57.0	54.3	triplet
-C- 	38.5	36.2	36.4	singlet
<u>H-H polyisobutylene</u>				
-CH ₃	21.7	22.7	21.3	quadruplet
-CH ₂	31.4	33.4	31.4	triplet
-C- 	38.8	36.9	38.7	singlet

nary carbon chemical shift is the same in H-H as it is essentially in H-T polyisobutylene.

One interesting point is the change in position of the methylene carbon resonance relative to the quarternary carbon resonance for the two polymers. In H-H polyisobutylene the methylene carbon is shifted upfield from the quarternary carbon at 31.4 ppm, while for H-T polyisobutylene the methylene carbon is shifted downfield from the quarternary carbon at 60.0 ppm. A change of 30 ppm for this carbon due only to its placement in the chain. Off-resonance decoupled ^{13}C NMR experiments support this assignment along with the calculated values.

No end groups were found in either the ^1H or the ^{13}C NMR spectra. Neither is sensitive enough to detect such a small concentration of $-\text{CH}_2\text{-Br}$ groups under the conditions described.

2. The Crystalline Nature of Head-to-Head Polyisobutylene

H-T polyisobutylene is an amorphous rubber and when properly cross-linked it finds commercial value due to its low T_g and good impermeability to gases. The H-T polymer exhibits a complete lack of crystallinity in its unstressed state. The crystallinity of H-H polyisobutylene was therefore of great interest in comparison and the results of its initial study are presented.

a. Wide angle X-ray scattering studies of head-to-head polyisobutylene

H-H polyisobutylene as prepared by the Grignard polymerization of TMDBB was a white powder when precipitated from tetralin into methanol. The wide angle X-ray scattering (WAXS) experiments of several samples were carried out on a Siemens Model D-500 instrument as described in the experimental chapter. The relative intensity of the diffraction pattern as plotted against the diffraction angle (2θ) is given in Figure 18 for a typical sample.

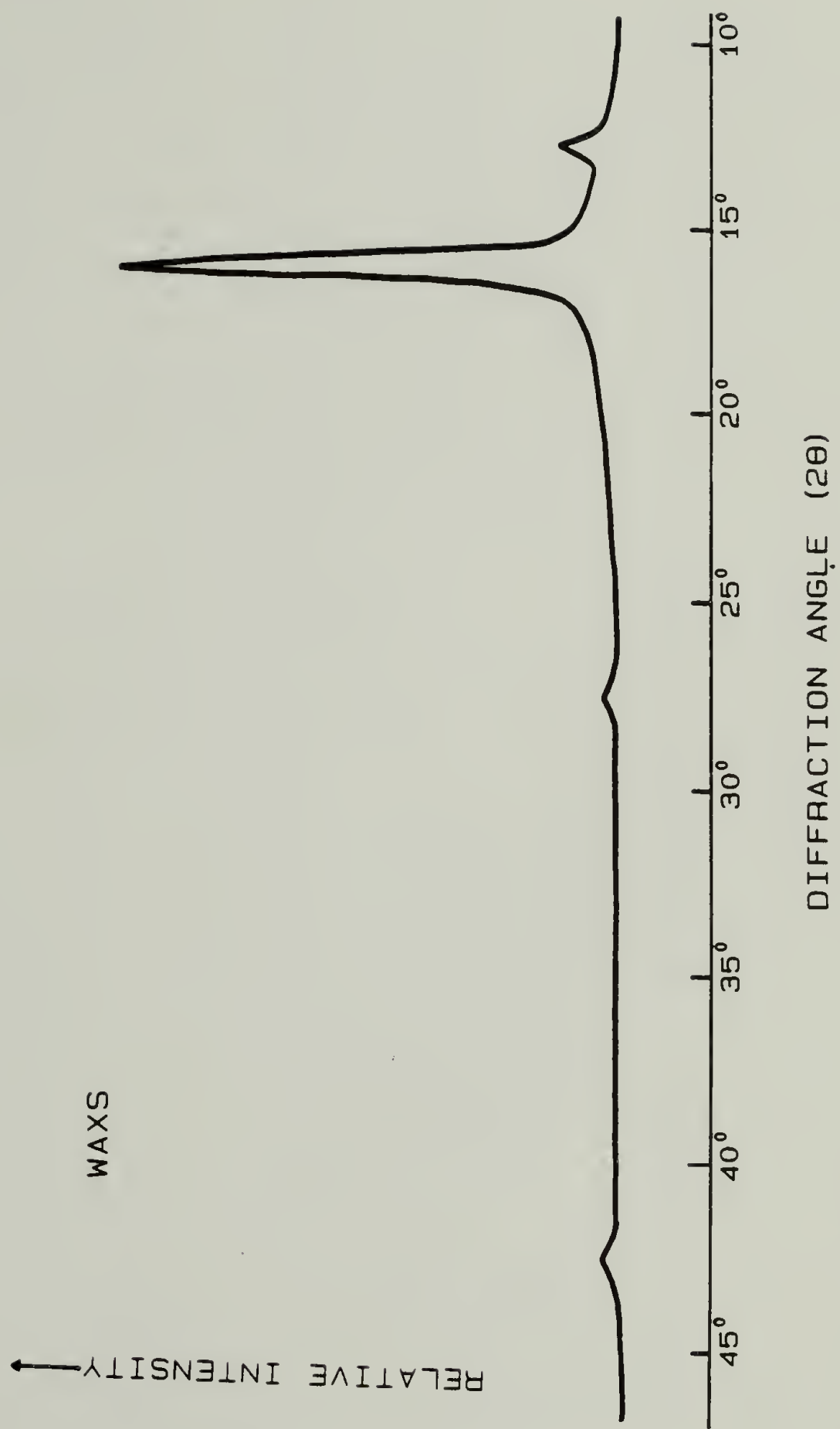
The pattern shows a very crystalline material with one very strong peak at 16.00° and at least 3 other weaker points (see Table 16).

TABLE 16
WIDE ANGLE X-RAY SCATTERING DATA FOR
HEAD-TO-HEAD POLYISOBUTYLENE

Diffraction Angle (2θ)	Intensity	Calculated "d-spacings"
12.75°	Medium	6.94 \AA
16.00°	Very strong	5.54 \AA
27.60°	Weak	3.23 \AA
42.50°	Weak	2.13 \AA

This strongest peak corresponds to a d-spacing of 5.54 \AA . The crystal structure itself was not determined

Figure 18. WAXS powder diagram for H-H polyisobutylene. Relative intensity vs. diffraction angle.



due to an inability to obtain an oriented sample of polymer film. The film which was formed from the melt of H-H polyisobutylene was too brittle for proper handling. Attempts to prepare melt pressed films were also unsuccessful due to decomposition of the polymer at temperatures above T_m (see p. 198).

The WAXS studies did, however, provide an estimation of the percent crystallinity of H-H polyisobutylene samples by peak area analysis (Table 17).

TABLE 17
PERCENT CRYSTALLINITY OF HEAD-TO-HEAD
POLYISOBUTYLENE AS DETERMINED
BY WAXS

Sample \overline{M}_n	Sample Preparation	Estimated Percent Crystallinity
3200	Precipitated and dried, 60°C/24 hrs	46%
3000 (a)	Annealed @ 70°C/12 hrs	59%
3000 (a)	Quenched from the melt into liquid N ₂	54%

(a) Same sample of H-H polyisobutylene.

The study showed that H-H polyisobutylene was approximately 50% crystalline. It also indicated that this crystallinity could not be influenced to any great extent by quenching.

b. Differential scanning calorimetry (DSC)
studies of the melting and crystallization
for head-to-head polyisobutylene

The melting of H-H polyisobutylene was first observed in a capillary melt indicator at 175-195°C. More careful study of the melting behavior was conducted by DSC.

Figure 19 shows the melting of the virgin polymer has two peaks in the endotherm arising from the melt transition. The two peaks occur at 185 and 189°C respectively. However, when the sample was quickly quenched from the melt and then rescanned only the peak at 185°C remained though the endotherm was broadened somewhat.

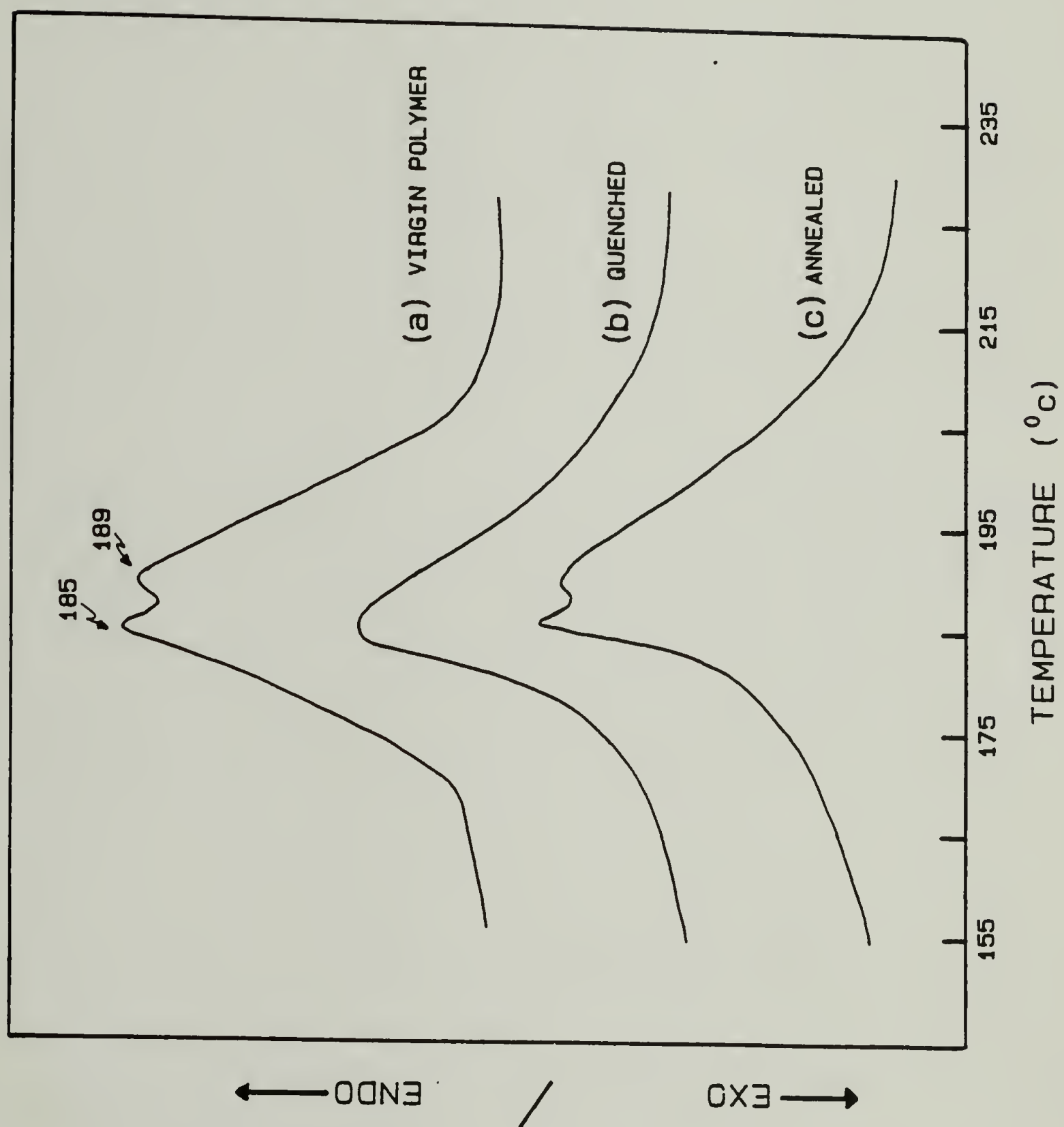
Upon annealing the sample at 175°C for 12 hr and subsequent rescanning both peaks could again be observed.

This melting phenomenon could be repeated over again by remelting and annealing.

Apparently there may be two possible crystal structures for head-to-head polyisobutylene which the chain can enter into. An α form which melts at 185°C and a β form which melts at 189°C. The β crystal apparently requires more time to form from the melt than the α crystal.

From the WAXS studies, the samples which were melt quenched showed the loss of only one diffraction maximum at 12.75° which was present prior to melting the virgin polymer. More information about the nature of the crystal structure may be gained when oriented films of H-H polyisobutylene are prepared and studied.

Figure 19. DSC scans of H-H polyisobutylene near its crystalline melting point (T_m). (a) virgin polymer as precipitated; (b) quenched, rescanned; (c) annealed at 175°C for 12 hr and rescanned. (heating rate 20°/min)



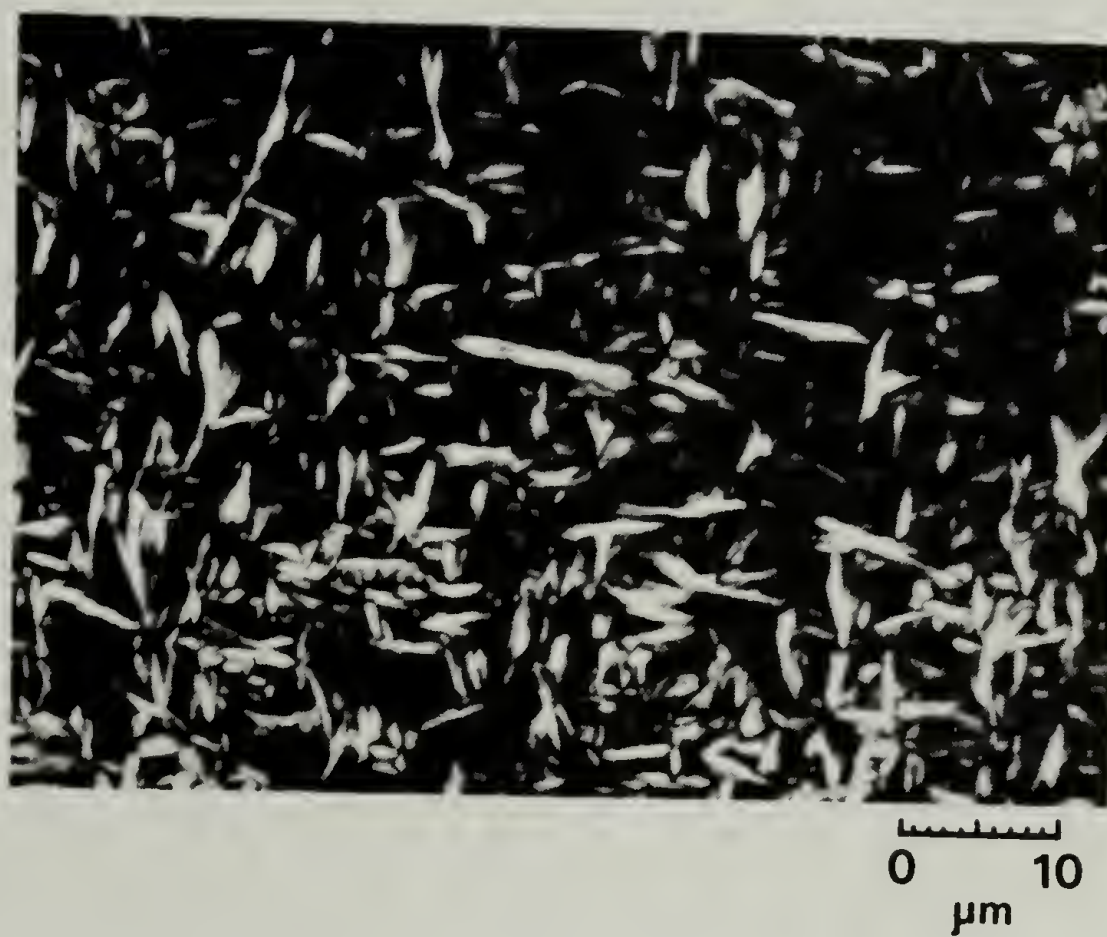
c. Light microscope examination of crystalline head-to-head polyisobutylene

The optical morphology of H-H polyisobutylene was observed by viewing the crystalline birefringence of the polymer. A hot stage used in combination with a cross polarized microscope allowed for observation of the melt at 187°C. The samples were then slowly cooled at 2°C/min and recrystallization was observed.

The typical optical appearance of a sample of H-H polyisobutylene is shown in Figure 20 as viewed between crossed polars. The field is of a coarse spiky microstructure. This spike like appearance is very similar to that of chain-extended polyethylene which is crystallized anabarically at pressures greater than 5 Kbar.¹⁷⁶ Bassett^{177,178} has shown that light microscopy can be used to observe the change over from orthorhombic spherulitic crystalline structure to chain-extended hexagonal structure in polyethylene.

The similarities between the two microscope pictures gives initial evidence that H-H polyisobutylene might crystallize in a chain-extended fashion. This implies a very stiff symmetric polymer backbone which does not fold back on itself readily.

Figure 20. Optical light micrograph, between crossed polars, of H-H polyisobutylene (400 x). The sample was melted and cooled at 2°/min through its crystallization.



d. Discussion of the crystallinity of head-to-head polyisobutylene

The relatively high percent crystallinity found for H-H polyisobutylene is of great significance when compared with amorphous H-T polyisobutylene. The fundamental question to be considered is why the simple change in the arrangement of the gem-dimethyl groups influences the crystallization of the two polymers to such an extent?

Flory¹⁷⁹ offers a discussion of H-T polyisobutylene in terms of conformational energy considerations in which he states that the energy minima in going from one chain conformation to another for this polymer are probably not sharply defined despite large steric factors. This is due to the fact that there is so much non-bonded repulsion between carbon atoms along the chain that constant bond angles can no longer be assumed and intrinsic bond torsional potentials are completely removed. Flory states that these are perhaps the reasons that H-T polyisobutylene is found to be an amorphous polymer of low T_g , as the chain becomes flexible by its ability to easily change through conformations. This is something which is not necessarily expected due to the large amount of steric interaction. The overall conformation of the H-T polyisobutylene chain is viewed as being randomly twisting and irregular.

By placing the gem-dimethyl groups on adjacent carbons and separating each set of highly substituted carbon

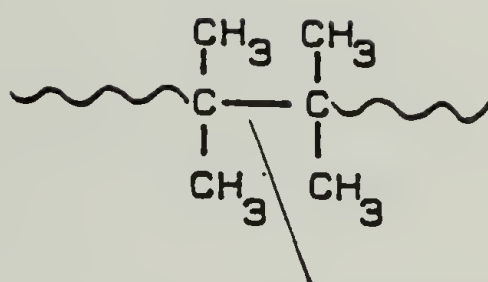
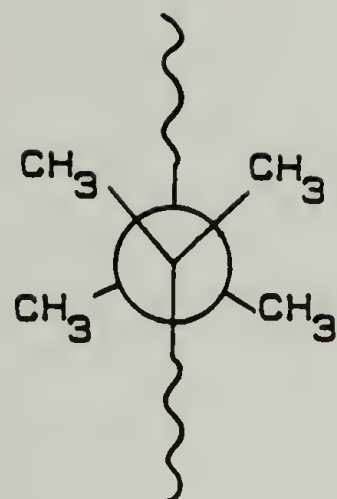
atoms by two methylenes the structure of H-H polyisobutylene is formed. It is argued on the basis of the evidence presented in this section that H-H polyisobutylene is a highly symmetric polymer which easily packs and allows for the formation of extended-chain crystals. Space-filling models of the H-H polyisobutylene structure indicate that rotation about the quarternary carbon-carbon bond is severely restricted as would be expected. Looking down the chain through this carbon-carbon bond where little rotation can occur is conceptualized in Figure 21. In a sense this section of the molecule is "locked" into a specific conformation, and can be considered a "hard" segment.

However, there are two methylene groups which act as flexible spacers between each "hard" segment of highly substituted carbon atoms (Figure 21). It is this combination of alternating hard and flexible segments that give the H-H polyisobutylene chain the ability to obtain a very symmetrical conformation.

It is reasoned that this is also why the polymer appears to crystallize in an extended-chain. That is, the chain can not easily fold back on itself due to the inability of the quarternary carbon-carbon bond to rotate.

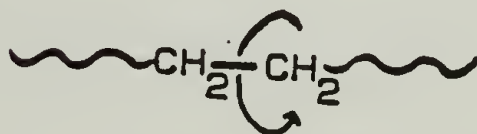
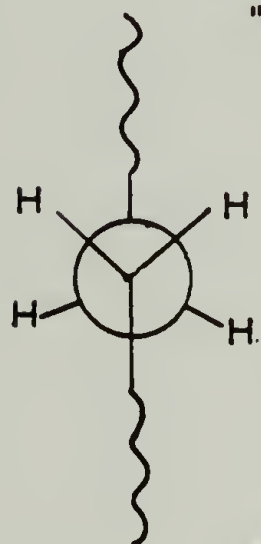
It is interesting that this argument fits so well with Flory's reasoning for the amorphous nature of H-T polyisobutylene. It is also the first time where such a drastic change in the crystalline nature has been reported

Figure 21. Effect of H-H placement of gem-dimethyl groups on the bond rotation along the chain backbone of H-H polyisobutylene.



LITTLE ROTATION
ABOUT THIS BOND

"HARD" SEGMENT



LOW ENERGY FOR
ROTATION

"FLEXIBLE" SEGMENT

(spacer)

between a H-H and H-T polymer. This is important because it is the only 1,1-disubstituted polyolefin which has so far been studied in its H-H configuration. It suggests that other 1,1-disubstituted H-H polymers may exhibit similar properties, and the study of H-H poly(α -methyl styrene) and H-H poly(vinylidene chloride) are two examples where this would apply.

3. Thermal Properties of Head-to-Head Polyisobutylene

The melting phenomenon of H-H polyisobutylene has been previously described and discussed in the crystallinity section. The glass transition temperature (T_g) and thermal degradation properties are discussed in this section.

a. The T_g of head-to-head polyisobutylene as observed by DSC

H-H polyisobutylene was found to be semi-crystalline with about 50% of the polymer still present in some amorphous phase. The T_g of the new polymer was shown by DSC technique. The sample was first melted and quickly quenched into liquid N_2 to trap as much of the polymer in the amorphous state as possible. Scanning at $20^\circ\text{C}/\text{min}$ the T_g was observed at 87°C as determined by the mid-point of the transition. A typical DSC trace for H-H polyisobutylene is shown in Figure 22, and in Figure 23 is given a

Figure 22. DSC scan of H-H polyisobutylene (heating rate 20°/min) from 27-107°C. Sample: $\bar{M}_n = 4,000$, melt quenched prior to scan.

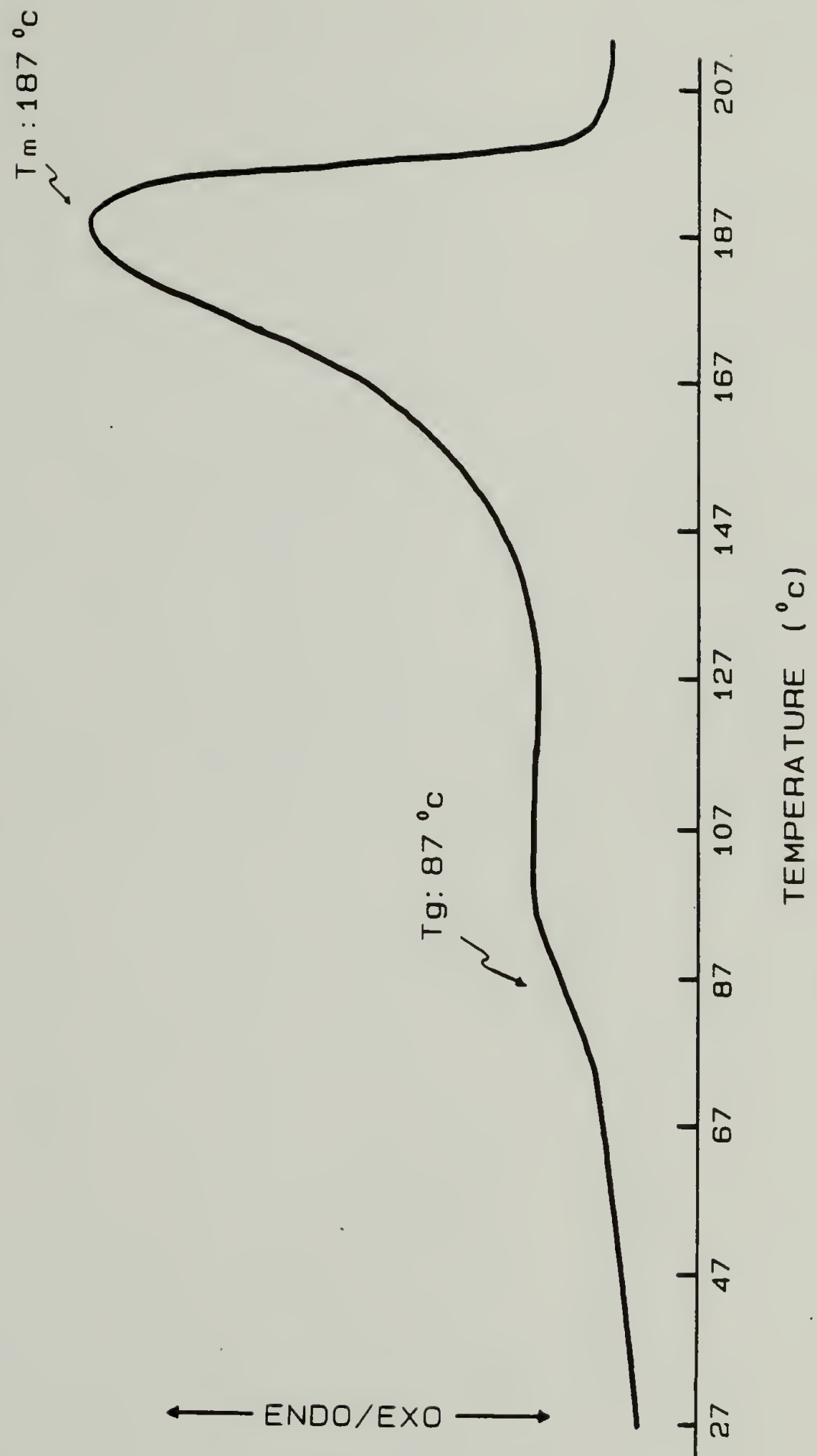
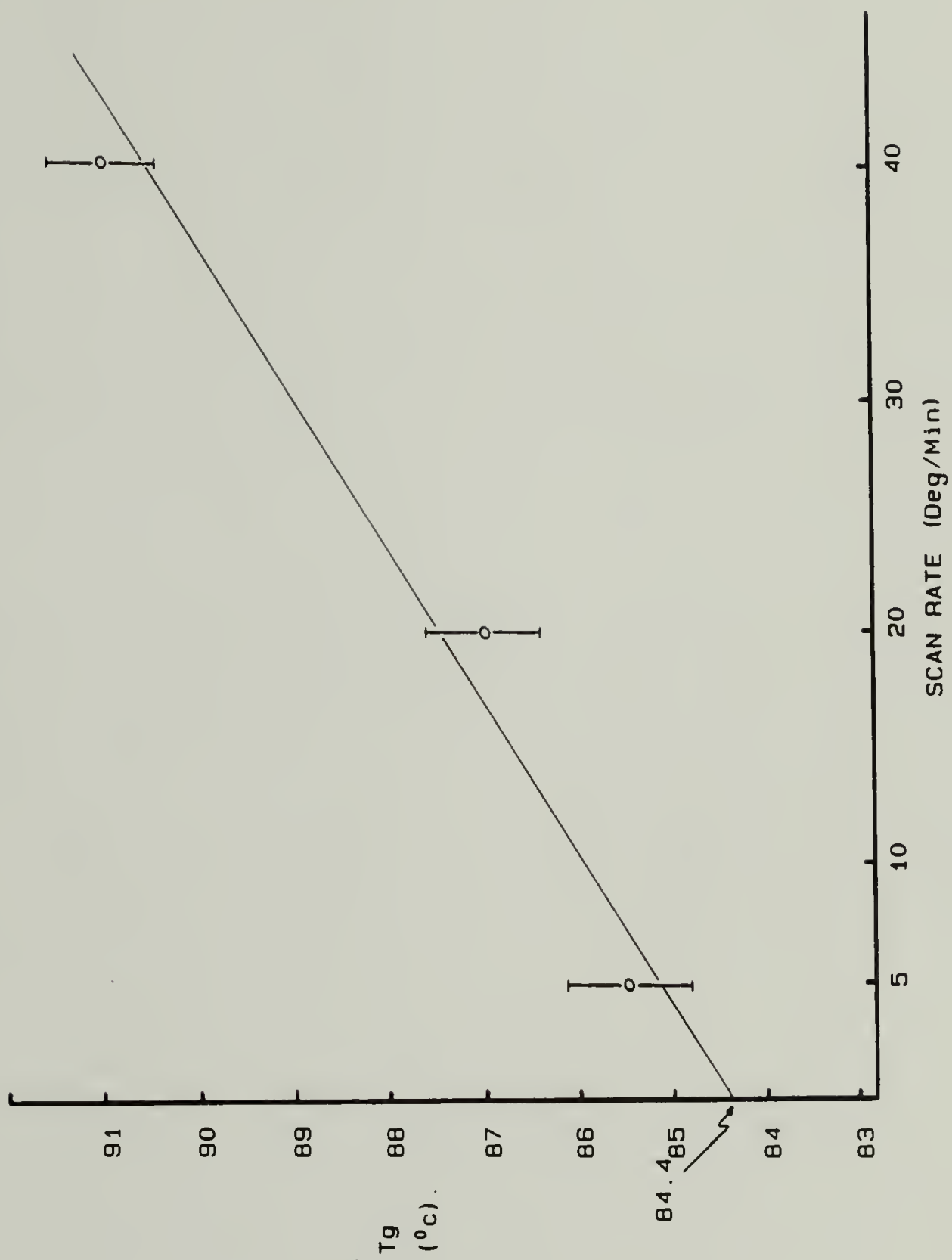


Figure 23. T_g vs. scan rate for H-H polyisobutylene as determined by^gDSC. Sample: $\bar{M}_n = 10,000$.



plot of T_g as a function of scan rate. The later figure provides a T_g extrapolated to zero scan rate of 84-85°C.

Subambient DSC studies revealed no other transitions down to -100°C.

Here again a drastic difference in the T_g of the H-H and H-T analogs has been found. Under the same DSC conditions H-T polyisobutylene of 5,000 MW gave a T_g of $\sim 61^\circ\text{C}$ (Lit. -70°C^{180}).

The rationale for this can be made along two argumentative routes. First, in terms of overall chain stiffness, H-H polyisobutylene must be a more rigid chain. The reason for this has been explained in more detail through the discussion of crystallinity. Although the H-H polymer has the added flexibility of the two methylene groups adjacent to one another the main affect of H-H placement is chain stiffening. This is consistent with previous results when comparing T_g s between H-H and H-T polymers for structures which have specific interactions between substituents. In this case, unlike the H-H polyacrylates, the interaction is not inductive in nature, rather it is steric interactions which significantly stiffen the polymer backbone for H-H polyisobutylene and increase T_g .

Secondly, the large difference in T_g can be explained by free volume considerations. The very crystalline H-H polyisobutylene will have a much lower free volume than the completely amorphous H-T polymer. Thus, with much

less free volume the T_g of H-H polyisobutylene is expected at a higher temperature.

In this respect it should be noted that the T_g of H-H polyisobutylene was also affected by its percent crystalline nature. In one example A T_g of 91°C was observed for a sample of H-H polyisobutylene which was $\sim 60\%$ crystalline as compared to a sample which was $\sim 45\%$ crystalline giving a T_g of 81°C .

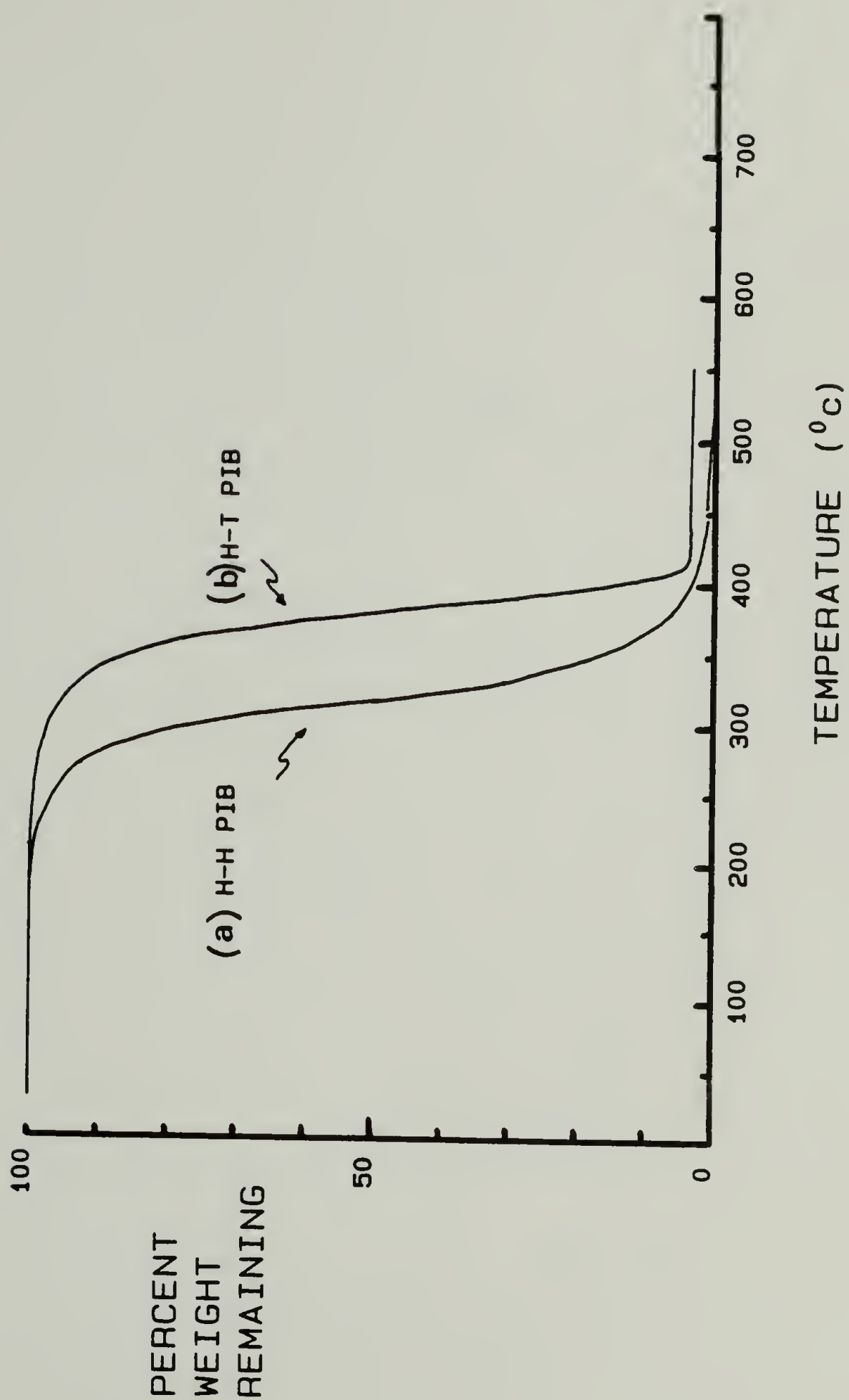
H-T polyisobutylene still remains an anomaly in the series of substituted polyolefins in terms of its T_g . The T_g s of polyethylene at -120°C ,¹⁸¹ and polypropylene at -20°C ¹⁸⁰ reflect the decrease in internal mobility of the chains due to the increasing energy barrier toward rotation about backbone carbon-carbon bonds. The T_g of H-H polyisobutylene is much more in line with what might be expected for such a highly substituted chain.

b. Thermal degradation of head-to-head polyisobutylene by thermal gravimetric analysis (TGA)

The TGA of H-H polyisobutylene was conducted under helium atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. Under identical conditions normal H-T polyisobutylene of several molecular weights was also investigated.

Typical TGA curves for H-H and H-T polyisobutylene are presented in Figure 24. Both polymers degrade in a smooth and uncomplicated manner under these conditions, and

Figure 24. TGA for; (a) H-H polyisobutylene ($\bar{M}_n = 4,000$); (b) H-T polyisobutylene (MW $\sim 5,000$). Heating rate of $20^\circ/\text{min}$, flow rate of 40 ml/min helium.



both degrade to less than 5% char.

Table 18 shows some of the data obtained for various molecular weights of both the H-H and H-T polyisobutylenes. This data indicates that the onset of degradation for H-T polyisobutylene is affected by the molecular weight (M_w) of the sample, however, the maximum rate of degradation temperature is not. The same observation was made for the H-H polyisobutylene samples studied.

The maximum rate of degradation temperature was estimated from the TGA curves by maximum slope midpoint. For H-H polyisobutylene this was determined to be $\sim 320^\circ\text{C}$ as compared to $\sim 385^\circ\text{C}$ for H-T polyisobutylene.

In conjunction with this study the volatiles of the TGA were trapped as they were released from the polymer and the trapped materials were gas chromatographed (G.C.). The results of the G.C. are shown in Figure 25 for both polymers indicating that the same product is obtained from the degradation of both H-H and H-T polyisobutylene.

H-T polyisobutylene is known to degrade by a mechanism which yields a large amount of isobutylene.^{182,183} The same product, as identified by G.C., was found to form in better than 90% yield when H-H polyisobutylene was thermally degraded. Assuming that the G.C. peak for the H-T degradation product is isobutylene then it is also isobutylene which H-H polyisobutylene degrades to.

When both pieces of data gained from the TGA are

TABLE 18

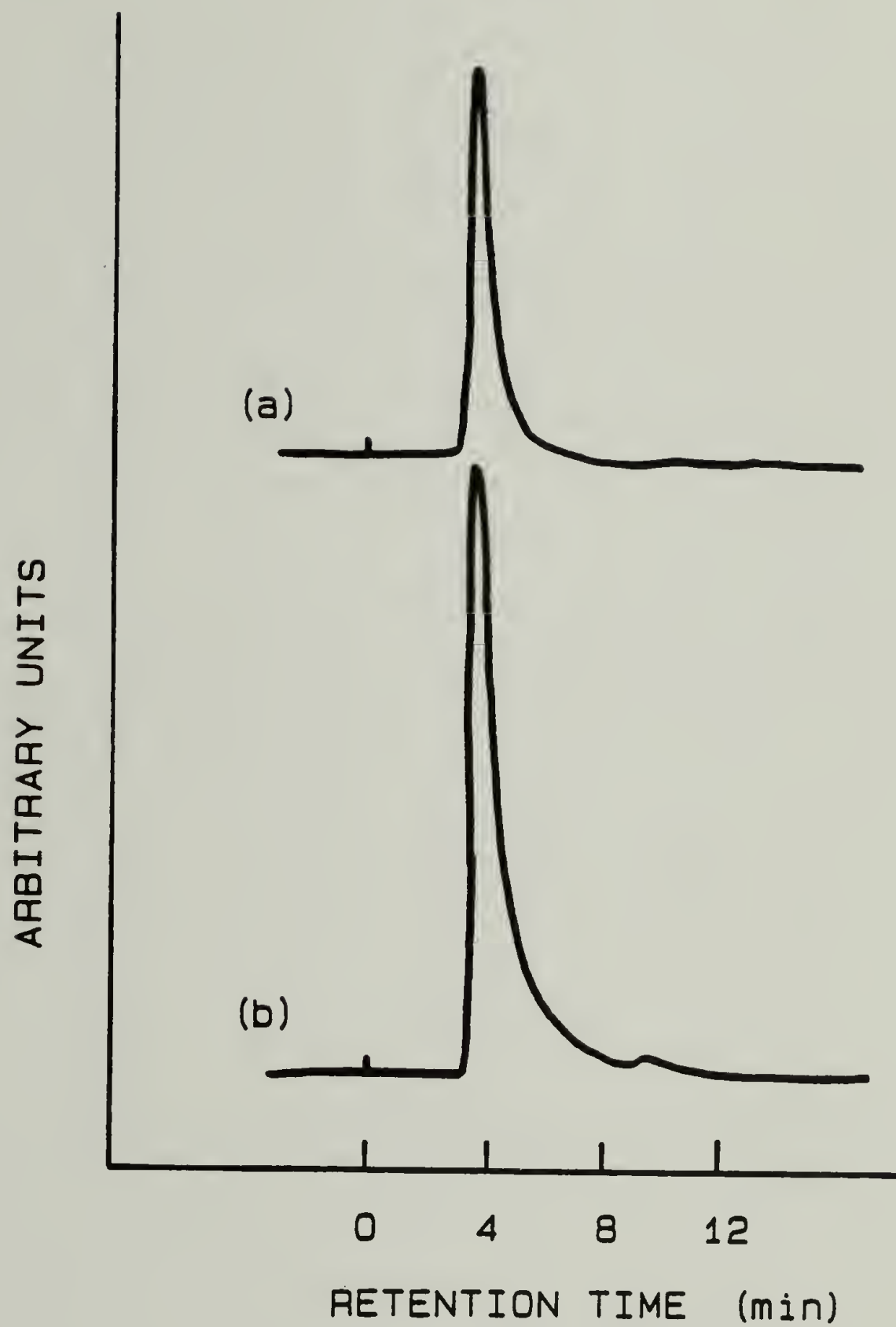
THERMAL GRAVIMETRIC ANALYSIS DATA FOR HEAD-TO-HEAD
AND HEAD-TO-TAIL POLYISOBUTYLENE

Structure	Molecular Weight	Onset	Degradation Temperature (°C) 5% loss	Maximum Rate
H-H	2700 (a)	220	260	312
H-H	3000	210	260	315
H-H	3700	225	270	319
H-T	5000 (b)	160	265	385
H-T	9300	200	315	385
H-T	10800	250	315	385

(a) \bar{M}_n by end group analysis.

(b) MW (reported by source) from GPC peak maximum.

Figure 25. G.C. analysis of trapped products from the TGA of; (a) H-T polyisobutylene; (b) H-H polyisobutylene.



examined together:

- H-H polyisobutylene degrades 65°C lower than H-T polyisobutylene
- H-H polyisobutylene degrades primarily to isobutylene

A rather clear picture for the degradation of H-H polyisobutylene arises.

When taken together this data signifies that the first bond to homolytically cleave in the H-H structure is the quarternary carbon-carbon bond. Then the unzipping mechanism can occur to degrade the polymer to isobutylene (Figure 26).

H-H polyisobutylene contains 3 different backbone carbon-carbon bonds; $\text{CH}_2\text{-CH}_2$, $\text{CH}_2\text{-C}(\text{CH}_3)_2$ and $(\text{CH}_3)_2\text{C-C}(\text{CH}_3)_2$. On the other hand H-T polyisobutylene has only one bond type ($\text{CH}_2\text{-C}(\text{CH}_3)_2$). Bond dissociation energy considerations imply that the more substituted the C-C bond the less energy is required to break it (i.e., bond dissociation energies for $\text{CH}_3\text{-CH}_3$ and $(\text{CH}_3)_3\text{C-C}(\text{CH}_3)_3$ are 88 and 68 kcal/mole respectively).¹⁸⁹ For this reason it is believed that the quarternary C-C bond breaks first in the H-H polymer. It is the weakest link. It is thought that this is why the H-H polymer degrades 65°C lower than the H-T under inert atmosphere. This is in agreement with degradation data of H-H and H-T polymers found in the past, however, it is the largest difference found to date.

The fact that mainly isobutylene is isolated as the degradation product of H-H polyisobutylene indicates that the $\text{CH}_2\text{-C}(\text{CH}_3)$ bond does not break first. If this were the case then significant quantities of ethylene and tetramethylethylene would have been found.

4. Blending and Compatibility of Head-to-Head and Head-to-Tail Polyisobutylene

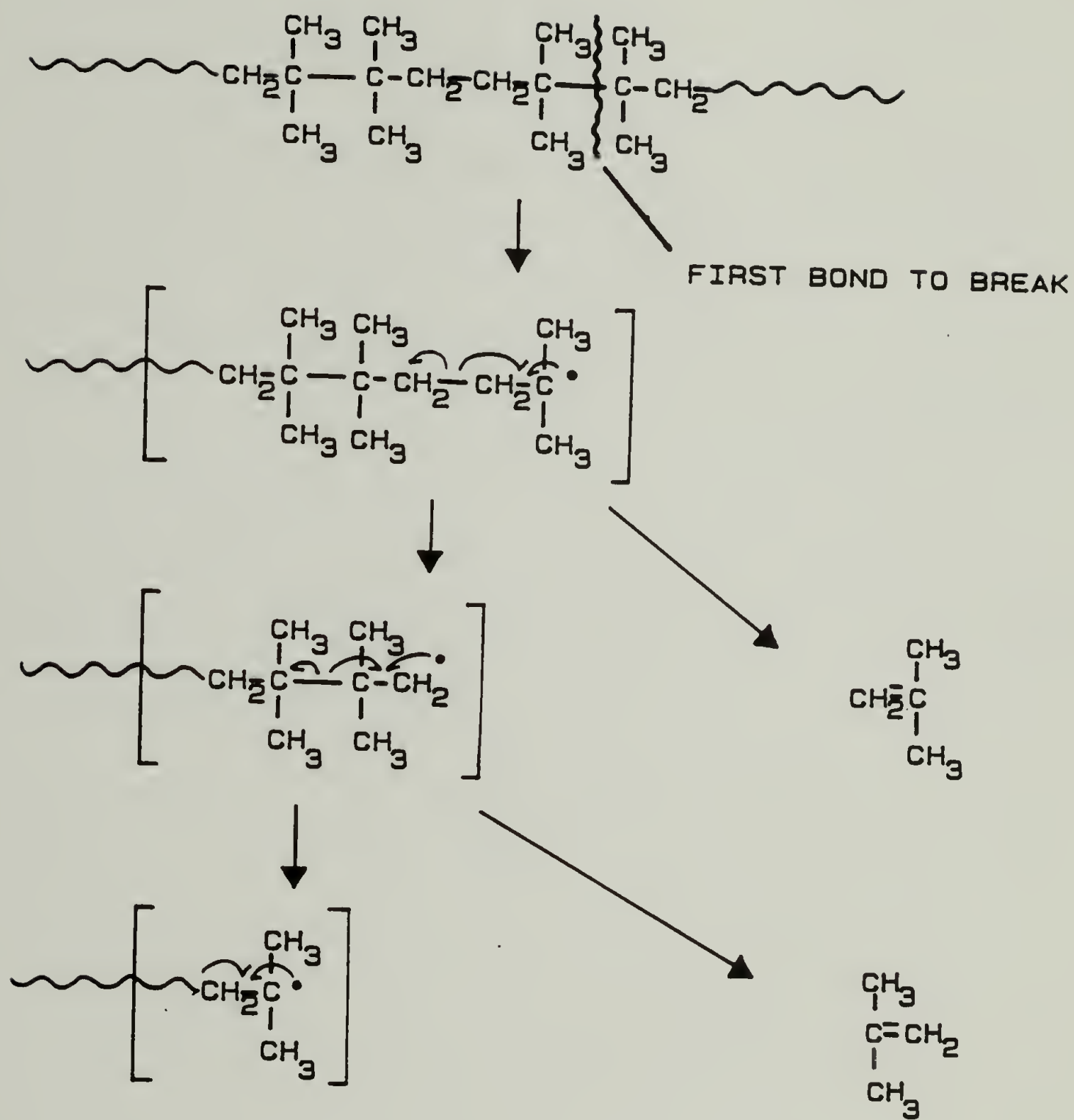
An intriguing possibility to explore polymer-polymer compatibility presented itself in this study. As has been stated throughout this dissertation the only chemical difference in the structures of H-H and H-T polyisobutylene is the relative positions of the gem-dimethyl groups along the backbone chain. The large difference in physical properties offers a unique opportunity to examine the blends of these two polymers.

a. DSC investigation of blends of H-H and H-H polyisobutylene

To prepare blends of H-H and H-T polyisobutylene both polymers (of $\sim 5,000$ MW) were first dissolved in a co-solvent (o-dichlorobenzene). The blends were then cast from the warm solvent taking precautions against the H-H polyisobutylene precipitating from solution. Once the films were cast they were washed with methanol and dried in vacuo. Weight-to-weight blends of 80/20, 60/40, 40/60, and 20/80, H-H/H-T polyisobutylene were prepared.

The DSC scans were conducted from -90 to $+130^\circ\text{C}$ for

Figure 26. Proposed degradation scheme for H-H polyisobutylene based on TGA and G.C. data.



the blends as well as for the pure components. It should be noted that H-H and H-T samples of the closest molecular weight were chosen for this study. The DSC traces are shown in Figure 27 and the T_g data presented in Table 19.

TABLE 19
GLASS TRANSITION DATA FOR BLENDS OF H-H
AND H-T POLYISOBUTYLENE

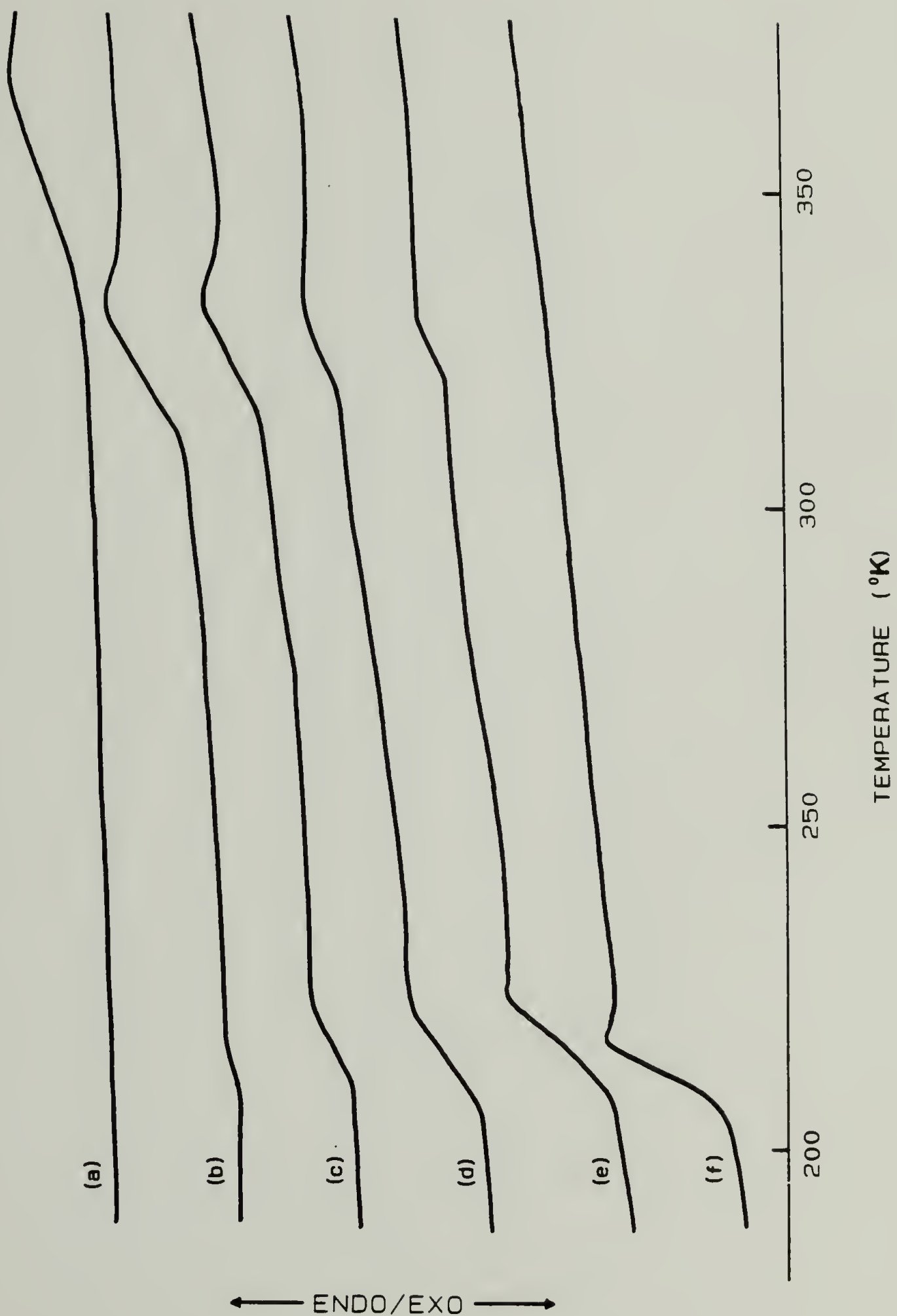
Blend Sample	T_{g1} (H-T) ($^{\circ}\text{C}$)	T_{g2} (H-H)
100% H-H	--	85
80%/20% (H-H/H-T)	-55	48
60%/40% (H-H/H-T)	-57	48
40%/60% (H-H/H-T)	-57	45
20%/80% (H-H/H-T)	-59	43
100% H-T	-61	--

The DSC traces show a classic dual T_g system which is symptomatic of an incompatible polymer-polymer blend.

There is some decrease in the value of T_{g2} for the H-H component when 20% H-T polyisobutylene is blended with it. This is explained as plastisization of the H-H polymer by the H-T probably caused by some low molecular weight H-T polyisobutylenes. After this initial decrease the T_{g2} of the H-H polyisobutylene levels off.

The Fox-Flory equation¹⁸⁴ predicts that for a totally compatible system a single T_g will be found for the

Figure 27. DSC scans for blends of H-H with H-T polyisobutylene; (a) 100% H-H; (b) 80:20, H-H:H-T; (c) 60:40, H-H:H-T; (d) 40:60, H-H:H-T; (e) 20:80, H-H:H-T; (f) 100% H-T. Scans from -90 to +100°C at 20°/min.



blend and the occurrence of the T_g is based on the weight percent of each component (Equation 53).

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (53)$$

Figure 28 shows the plot of T_g as a function of weight percent H-H polyisobutylene in the blend. The broken lines indicate the empirical results of the study, while the solid line is based on the calculations.

b. TGA of H-H and H-T polyisobutylene blends

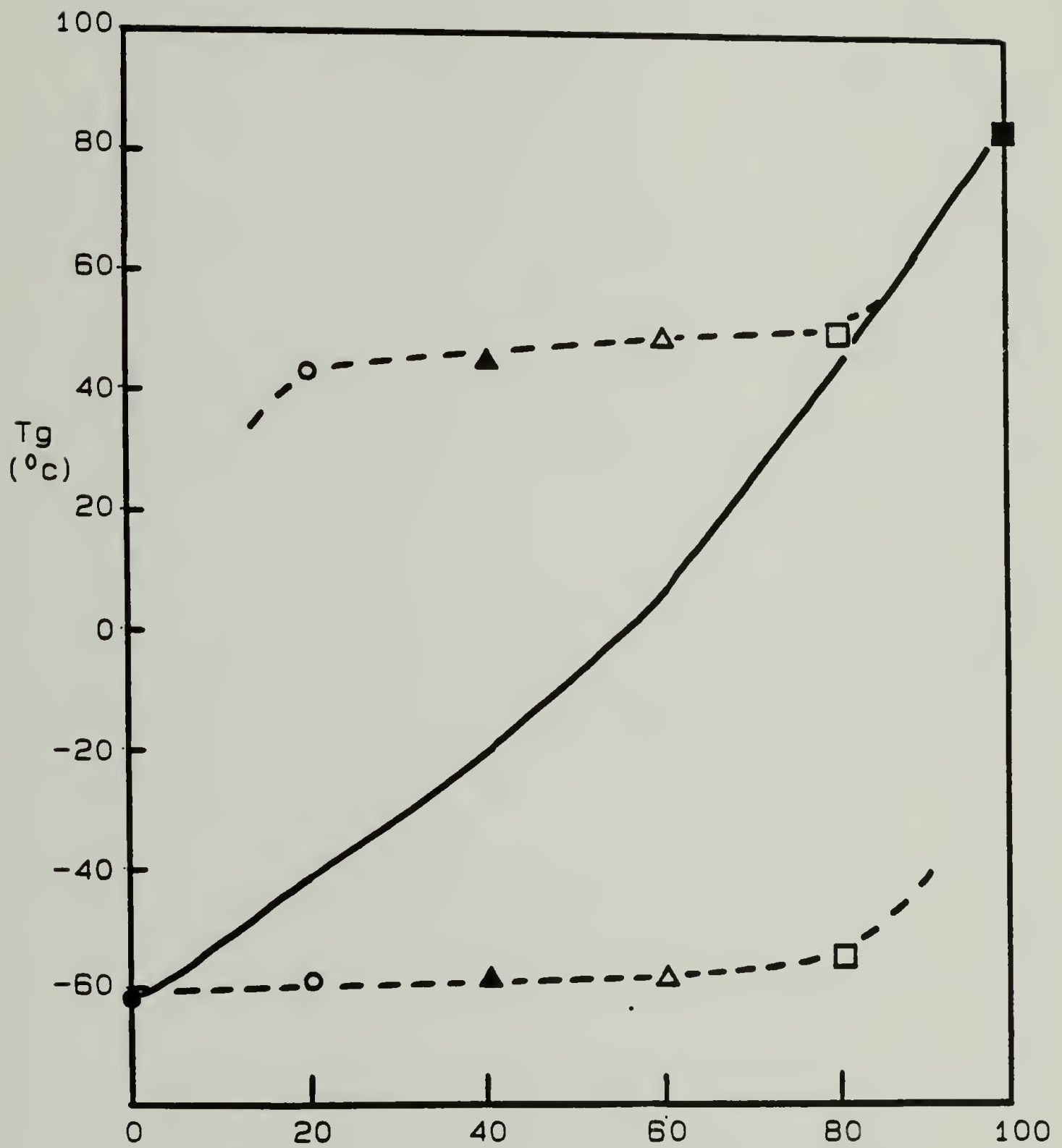
The same samples which were prepared for the DSC study were also used in investigating the codegradation of H-H and H-T polyisobutylene. Here again the large difference in the maximum rate of degradation temperatures was ideal for examining the codegradation of the two polymers.

In Figure 29 the TGA scans for these blends is presented. It is consistent with the DSC studies that each component of the blend degrades independently. This is generally true of incompatible polymers systems. Although it could not singularly be taken as proof of the incompatibility of the two polymers it does lend further credence to the DSC data.

Figure 28. T_g vs. weight percent H-H polyisobutylene in the blend: \blacksquare 100% H-H; \square 80:20, H-H:H-T; \triangle 60:40, H-H:H-T; \blacktriangle 40:60, H-H:H-T; \circ 20:80, H-H:H-T; \bullet 100% H-T.

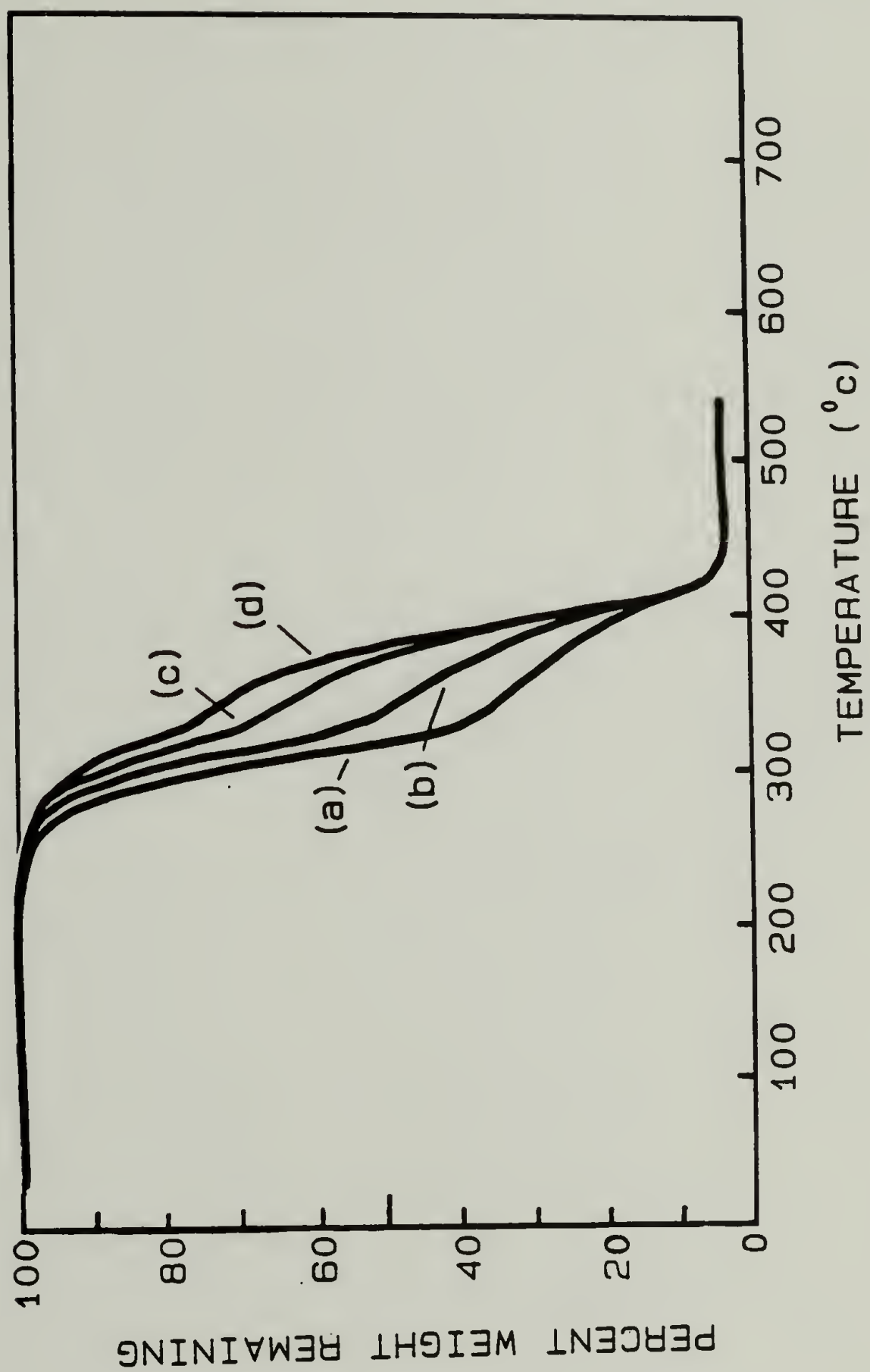
----- Experimental

_____ Calculated by Fox Flory equation¹⁸⁴



WEIGHT PERCENT H-H POLYISOBUTYLENE IN BLEND

Figure 29. TGA for blends of H-H with H-T polyisobutylene. (a) 80:20, H-H:H-T; (b) 60:40, H-H:H-T; (c) 40:60, H-H:H-T; (d) 20:80, H-H:H-T. Heating Rate, 20°/min, flow rate of 40 ml/min helium.



c. Discussion of the incompatibility
of H-H with H-T polyisobutylene

When both the DSC and TGA studies of the blends for H-H and H-T polyisobutylene are taken together a very strong case for the incompatibility, or non-miscibility, of the two polymers is made. It is interesting that an example is found where two polymers of identical chemical composition but with somewhat different chemical structure do not interact with each other favorably enough to form a single phase.

In general, for two high polymers of the same molecular weight but with different structures to form a compatible blend it is necessary from a thermodynamic point of view that the free energy of mixing be negative.¹⁸⁵ The entropy gain in mixing two large molecules is always small and the enthalpy term is only sufficiently negative enough if some specific chemical interaction is present between components of the two polymers on a molecular scale.

Apparently there is not a sufficient enough favorable interaction between H-H and H-T polyisobutylene to allow for a negative free energy of mixing.

This has some interesting implications as it is different from the "like dissolves like" axiom for small molecules. It is consistent with current beliefs that for macromolecules a much more polar interaction is needed to effectively produce homogeneous phases of two or more

components.

5. Conclusions and Future Work

The primary goals of this study as stated in the introductory remarks have been accomplished. The investigation into the successful synthesis of H-H polyisobutylene required the study of several different synthetic routes. The Grignard polymerization, which proved to be the most fruitful means of preparing H-H polyisobutylene, is exciting because it opens the way to the preparation of some new polymer structures. However, further study of this coupling polymerization is necessary in terms of metal catalyst, solvent, and temperature effects. It is also believed that the use of longer chain dibromides, perhaps eight carbons or more, would alleviate some of the problems of side reactions observed in this work.

The investigation into the physical properties of H-H polyisobutylene and the comparison of those properties with H-T polyisobutylene has given some unique insights into the structure-property relationships of polyolefins. Large differences in thermal properties and crystalline nature have been observed simply by arranging the substituents on the polymer backbone differently. These differences have carried over to the point that H-H polyisobutylene is incompatible with H-T polyisobutylene as shown by phase separation and individual T_g s for blends of the two

polymers.

Since this was the first thorough investigation into the physical properties of H-H 1,1-disubstituted polyolefins future work with polymers such as H-H poly(α -methyl styrene), poly(methyl methacrylate) and poly(vinylidene chloride) should bring continued insight to this family of polymers.

C. Synthesis and Characterization of Poly(1,1-dimethylpropane)

The preparation of the monomer for this section of the work was carried out in analogous fashion to TMDBB. 2,2-Dimethyl-1,3-dibromopropane (DMDBP) was prepared from 2,2-dimethylpropanediol-1,3 (which is commercially available) by tosylation and detosylation/bromination steps. As discussed in the introduction this study was done to model the monomer and polymer preparation of H-H polyisobutylene.

1. Polymerization of 2,2-dimethyl-1,3-dibromopropane

The polymerization of DMDBP was investigated with both the Wurtz and Grignard coupling reactions. For DMDBP the Wurtz reaction was found to be more successful for polymerization.

a. Attempted Grignard polymerization of 2,2-dimethyl-1,3-dibromopropane

The Grignard/alkylbromide coupling polymerization was attempted for DMDBP in the same manner that the

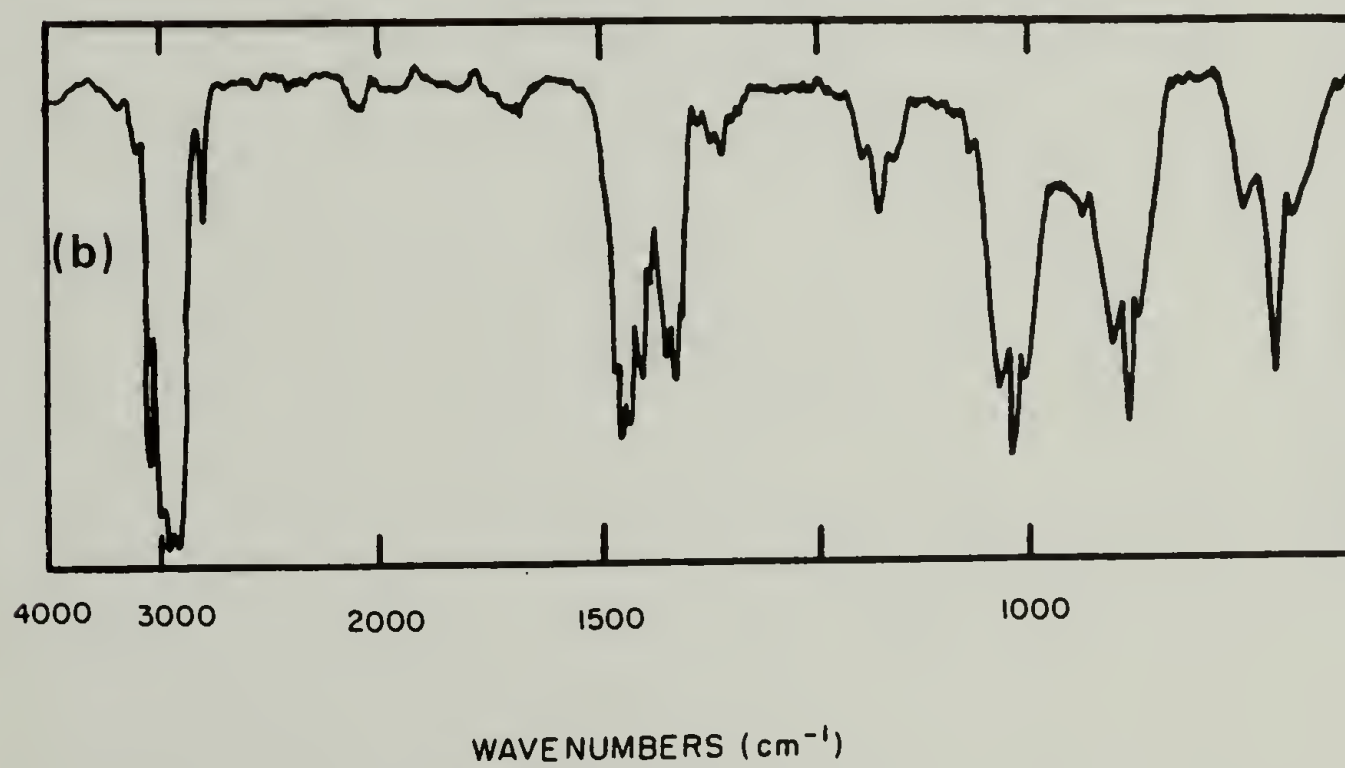
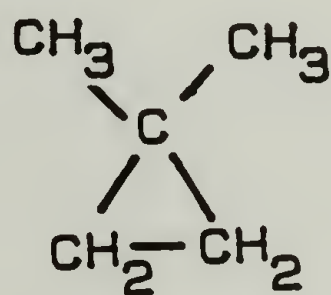
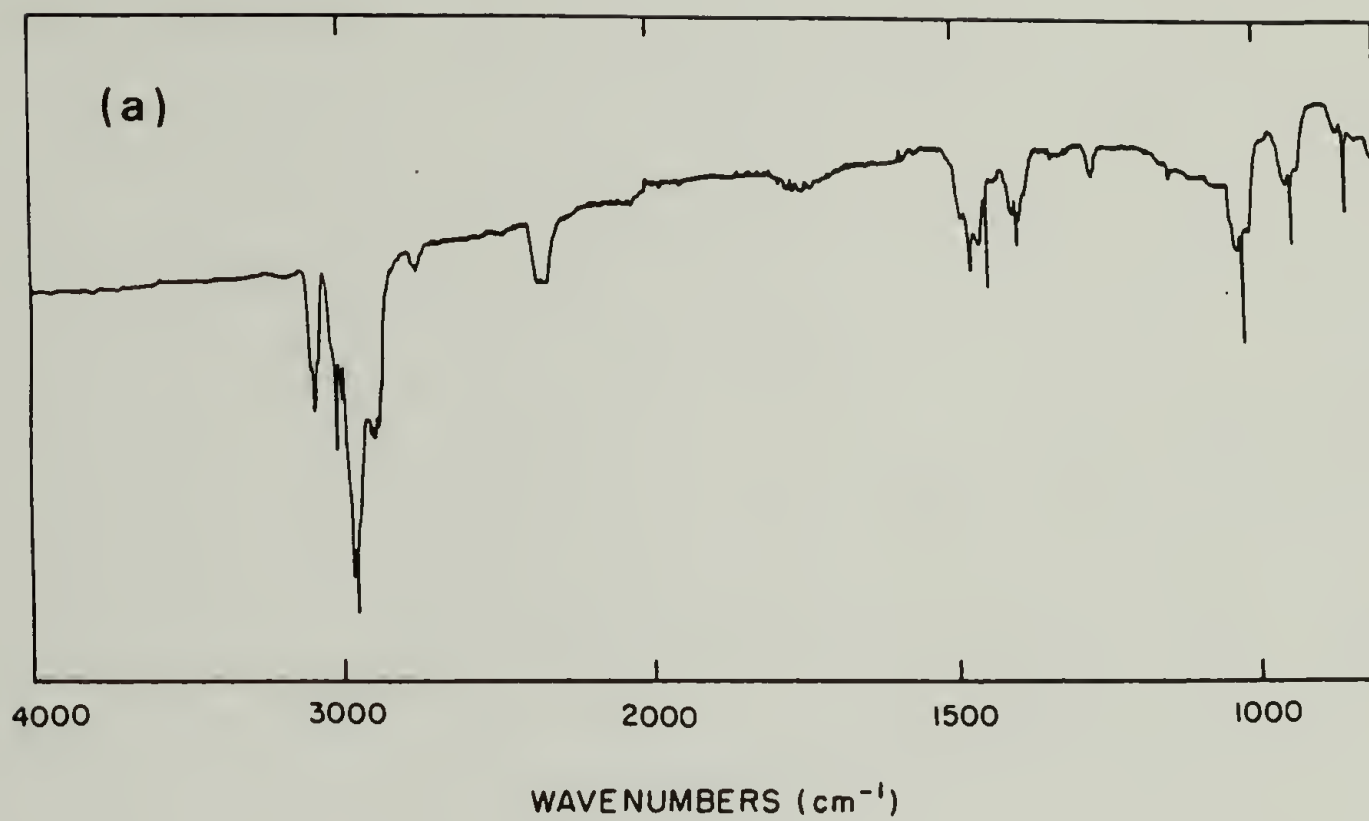
successful polymerization of TMDBB was carried out, however no polymer was isolated. It was apparent from the uptake of magnesium that the Grignard reagent was forming but no polymer was obtained regardless of the conditions of solvent, temperature and catalyst employed.

The volatiles from the reaction were isolated by trapping, and the IR spectrum of the product (all gas at room temperature) is given in Figure 30 (spectrum a). All the product given off by the attempted coupling polymerization was gaseous at room temperature and it was identified as 1,1-dimethylcyclopropane (DMCP). The IR spectrum of DMCP as given in the Sadtler Index¹⁷¹ is shown in Figure 30 (spectrum b) and is identical to the product found in our study in all major absorption bands.

The DMCP product isolated did not account for all of the starting monomer, only an estimated 5-10% of the starting material was trapped as volatiles. When the Grignard reaction mixture was poured into methanol at the end of the reaction some heat was evolved. This indicated that reactive Grignard ends were still present in the mixture and these reacted with the methanol.

It appears as though the separation of only one carbon atom between the Grignard-end and the alkylbromide-end of the monomer is not sufficient to allow for proper coupling. This is consistent with what was observed at very low temperatures (-25°C) during the Grignard

Figure 30. IR spectra of 1,1-dimethylcyclopropane.
(a) As prepared from Grignard coupling of 2,2-dimethyl-1,3-dibromopropane; (b) reproduced from Sadtler Index number 11831.



polymerization of TMDBB.

b. Wurtz polymerization of 2,2-dimethyl-1,3-dibromopropane

The polymerization of DMDBP was shown to proceed with much greater success under Wurtz reaction polymerization conditions. The polymerizations were carried out with sodium metal and sodium/potassium alloy in a variety of forms including mirrors and metal dispersions. Table 20 shows a summary of a few of the conditions which were used to polymerize DMDBP to poly(1,1-dimethylpropane).

In all cases where the polymerization was most successful the temperature of the coupling reaction was kept below 100°C. If the Wurtz reaction became too hot excessive volatilization occurred.

It was shown that some formation of cyclized monomer took place during the Wurtz reaction by volatile trapping. However, the yields of poly(1,1-dimethylpropane) were as high as 50% in this case.

The reason for success with the Wurtz coupling reaction for DMDBP is thought to be the lower temperature at which the reaction can be carried out. TMDBB does not melt until 50°C, where as DMDBP is liquid at room temperature. For this reason DMDBP can be kept cooler during the reaction with sodium, which keeps the cyclization reaction low as well as preventing a significant amount of branching. Both these problems were found to be substantial for the

TABLE 20

WURTZ POLYMERIZATION DATA FOR 2,2-DIMETHYL-
1,3-DIBROMOPROPANE

Metal	Solvent	Temperature	Time	Polymer Yield
Na	cyclohexane	81°C	5 hr	43%
Na	cyclohexane/vacuum	60°C	3 days	0
Na-dispersion	cyclohexane/vacuum	60°C	4 days	0
Na-mirror	bulk	80-100°C	1 day	55%
Na/K	cyclohexane	81°C	1 day	0

Wurtz polymerization of TMDBB.

In actual fact DMDBP turned out to be a poor model for the polymerization of TMDBB. The difference in coupling characteristics due to one carbon atom separation between reactive ends turns out to be important for the polymerization of the two monomers.

Future work in the area of coupling of branched dihalides should take into account that the further the separation of the alkylhalide-end from the Grignard-end the easier the Grignard polymerization can be carried out. This observation also supports work by Yamamoto on unbranched α,ω -dibromoalkanes where the same phenomenon was found.⁹⁶

2. Characterization of poly(1,1-dimethylpropane)

a. Spectral analysis of poly(1,1-dimethylpropane)

The spectral analyses including IR, ^1H NMR and ^{13}C NMR spectroscopy are all outlined in Table 21. The spectra for this data are located on p. 288, 302, and 319, respectively of the appendix.

The IR spectrum shows that the characteristic gem-dimethyl doublet due to symmetric out-of-plane bending occurs at 1375 and 1385 cm^{-1} which is shifted from the doublet in H-H polyisobutylene by $\sim 10 \text{ cm}^{-1}$ (1365, 1375 cm^{-1}).

The IR spectrum for poly(1,1-dimethylpropane) appears to have the same major absorption bands whether

prepared by low temperature cationic polymerization of 3-methylbutene-1, cationic ring-opening polymerization of 1,1-dimethylpropane, or Wurtz coupling polymerization of DMDBP.¹¹⁷

The ^1H NMR spectrum shows two singlets, one at 1.0 ppm and one at 1.3 ppm which is similar to previous ^1H NMR studies of poly(1,1-dimethylpropane) where chemical shifts of 0.8 ppm and 1.1 ppm were found for the $-\text{CH}_3$ and $-\text{CH}_2-$ protons respectively. The integration of the peaks is very close to the calculated proton ratio as shown in Table 21.

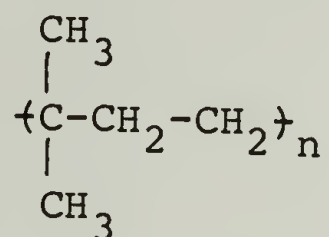
The ^{13}C NMR spectrum for poly(1,1-dimethylpropane) shows the three major carbon atom peaks at values very close to those calculated by the Lindeman and Adams technique.¹⁷⁰ The one substantial extraneous peak occurs at 29.8 ppm and is probably due to $-\text{CH}_3$ end groups which seem to be the major end groups for this polymer since elemental analysis shows only 0.3% Br in the polymer.

Several small peaks are present at 28.5, 33.2 and 38.5 ppm which are most likely the result of branching carbon atoms. However, in this case, unlike TMDBB polymerization, these peaks are very small indicating minimal amounts of branching in the final polymer.

b. DSC analysis of poly(1,1-dimethylpropane)

Poly(1,1-dimethylpropane) was studied by DSC to reveal a semi-crystalline polymer. The scan is given in

TABLE 21
SPECTRAL ANALYSES OF POLY(1,1-DIMETHYLPROPANE)



IR Data

$\text{CH}_3, \text{CH}_2; \nu_{\text{as}}, \nu_{\text{s}}$	2872, 2962, 2926, 2910 cm^{-1}
$\text{CH}_3, \text{CH}_2; \delta_{\text{as}}, \delta_{\text{s}}$	1480, 1459, 1400, 1375, 1385 cm^{-1}
$\text{R}-\underset{\text{ }}{\overset{\text{ }}{\text{C}}}-\text{R}$	1100, 1020, 1265 cm^{-1}

^1H NMR Data

^1H	Chemical Shift (ppm)	<u>Integration</u>	
		found	calculated
$-\text{CH}_3$	1.0 (singlet)	5.7	6.0
$-\text{CH}_2-$	1.3 (singlet)	3.4	4.0

^{13}C NMR Data

Carbon Atom	Chemical Shift (ppm)	Calculated ¹⁷⁰
		Chemical Shift (ppm)
$-\text{CH}_3$	27.9	27.3
$-\text{CH}_2-$	35.7	36.3
$-\underset{\text{ }}{\overset{\text{ }}{\text{C}}}-$	32.5	33.6

Figure 31 from -50 to +100°C.

The T_g of the polymer was found to be -17°C as calculated from the midpoint of the step transition (ΔC_p). This is in excellent agreement with the T_g found by Kennedy¹¹³ for poly(1,1-dimethylpropane) as prepared by low temperature cationic polymerization of 3-methylbutene-1 which was reported as -12°C. It is interesting that this T_g falls almost precisely between the T_g s of H-H and H-T polyisobutylene since the structures of the three polymers are all related (Figure 32). The insertion of one methylene group into the polymer backbone in going from H-T polyisobutylene to poly(1,1-dimethylpropane) is thought to allow for enough space between the gem-dimethyl groups to decrease the tremendous amount of non-bonded interaction between methyl groups. This makes for a more regular structure in the backbone and lowers free volume thereby increasing T_g .

When an additional $-C(CH_3)_2-$ group is inserted into the chain in going from poly(1,1-dimethylpropane) to H-H polyisobutylene the effect is to stiffen the chain further and again increase T_g . This explanation is given more fully in sections A.2.d. and A.3.a. of the results and discussion.

The melting endotherms (T_m) for poly(1,1-dimethylpropane) occur at somewhat higher temperatures than seen previously. Two peaks were observed, (Figure 31), one at

Figure 31. DSC scan for poly(1,1-dimethylpropane) from -50 to +100°C. Heating rate 20°/min.

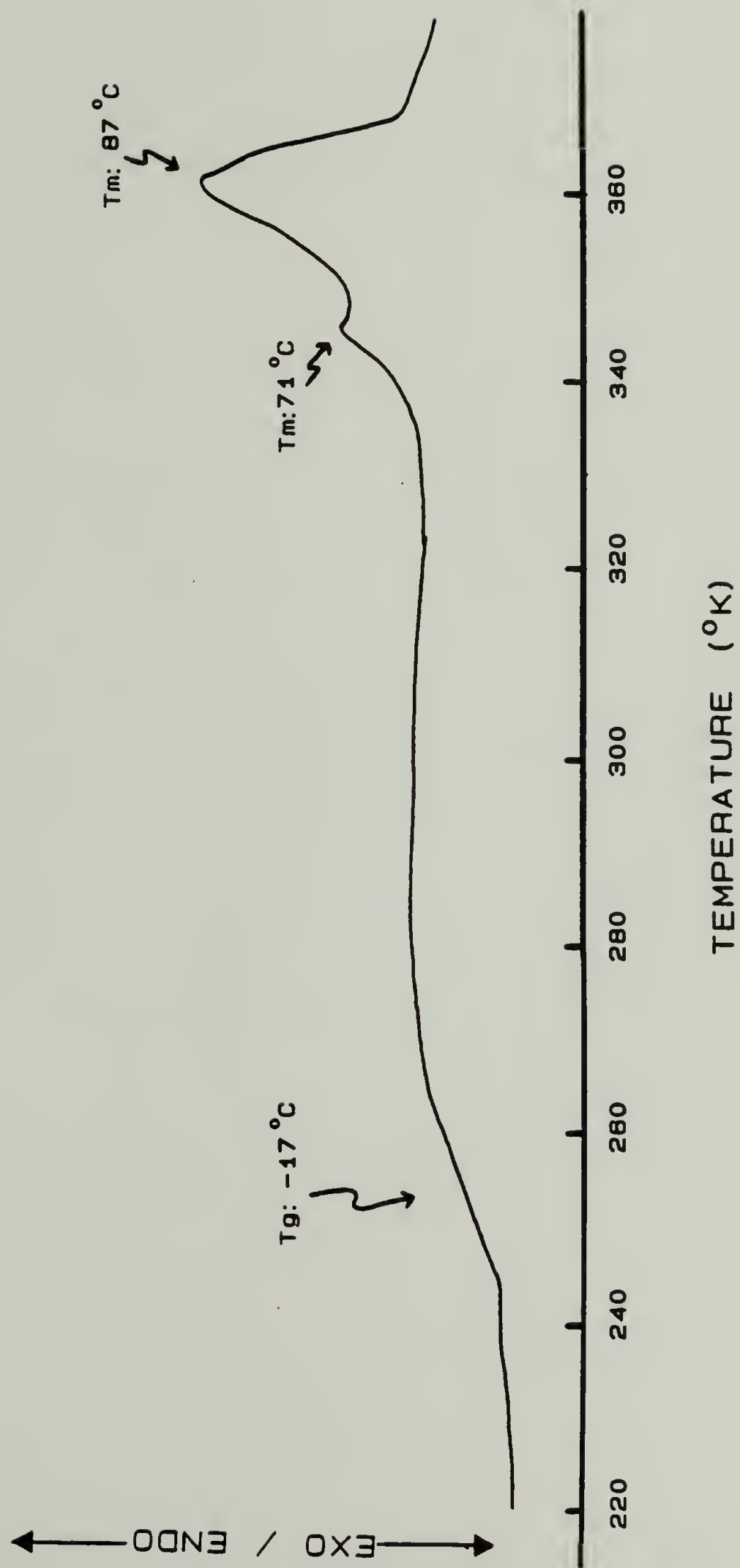
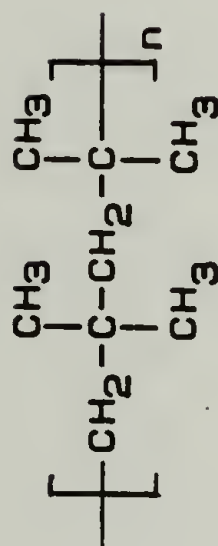
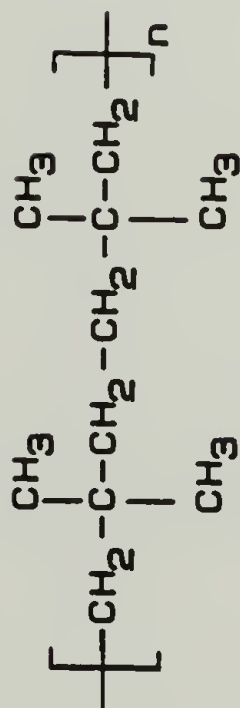


Figure 32. Structure-Property relationship for T_g of H-T polyisobutylene, poly(1,1-dimethylpropane), and H-H polyisobutylene.



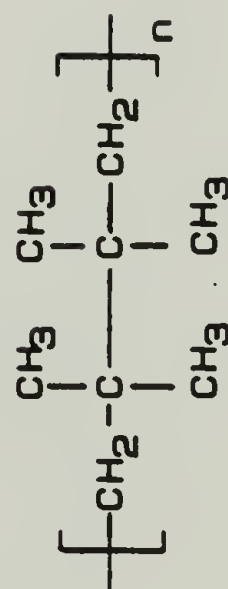
H-T POLYISOBUTYLENE

T_g= -81 °C



POLY (1, 1-DIMETHYLPROPANE)

T_g= -17 °C



H-H POLYISOBUTYLENE

T_g= +85 °C

71°C and a larger peak at 87°C. DTA studies of poly(1,1-dimethylpropane) prepared from 3-methylbutene-1 also showed two crystal forms, one melting at 49°C and the other at 66°C.¹²¹ The relative difference between the two peaks is the same, about 16°C. Therefore the discrepancy may be explained by the manner in which the data were obtained (DTA vs. DSC).

It is interesting to note that the difference between T_m and T_g for poly(1,1-dimethylpropane) is 104°C (87°C and -17°C) which is exactly the same difference found between T_m and T_g for H-H polyisobutylene (189°C and 85°C).

D. Copolymerization of 3,4-Dimethyltetrahydrofuran with Cyclic Ethers*

1. Preparation of 3,4-dimethyltetrahydrofuran (DMTHF)

DMTHF was prepared by the route outlined in Figure 33.

Two methods of ring closure for 2,3-dimethylbutane-1,4-diol (DMBD) were investigated. The dehydration of DMBD as carried out in DMSO at 155°C gave 88% yield of DMTHF, however, the monomer could not be purified to polymerization grade by normal distillation from LAH. The reason for this is believed to be sulfur impurities introduced by the thermal decomposition of DMSO at 155°C. Dehydration of DMBD with potassium hydrogen sulfate (KHSO_4) gave DMTHF in

*This work has been published in part.¹⁸⁶

Figure 33. Preparation of 3,4-dimethyltetrahydrofuran.

excess of 70% yield. The use of KHSO_4 became the method of choice even though lower yields were obtained because DMTHF made in this manner could be easily purified.

The relationship between this section of the dissertation and the rest of the work was the monomer synthesis. The initial coupling reaction in the route to prepare DMTHF is the same reaction used for the first step in the preparation of TMDBB except for a methyl substituent. The easy preparation of this DMTHF and the interest in its polymerizability led to this phase of the study.

a. Stereochemistry

DMTHF was found to be an equal mixture of the cis and trans isomers as determined by G.C. analysis as well as by integration of the ^{13}C NMR spectrum. Figure 34 shows the G.C. of DMTHF as carried out on a Carbowax 20 m column at 50°C . The assignments of cis and trans were made by trapping each fraction and using ^{13}C NMR to determine the isomer responsible for each peak.

The ^{13}C NMR chemical shift values of the two isomers of DMTHF for each carbon atom are well separated (Figure 35 and Table 22). From Figure 35 it is apparent that the carbon atom most affected by the stereochemistry is the methine carbon. The chemical shift values of the cis isomer are downfield from those of the DMTHF trans isomer.¹⁸⁷ The difference between the shifts for the cis

Figure 34. G.C. analysis of 3,4-dimethyltetrahydrofuran showing; (a) cis- and (b) trans-isomers.

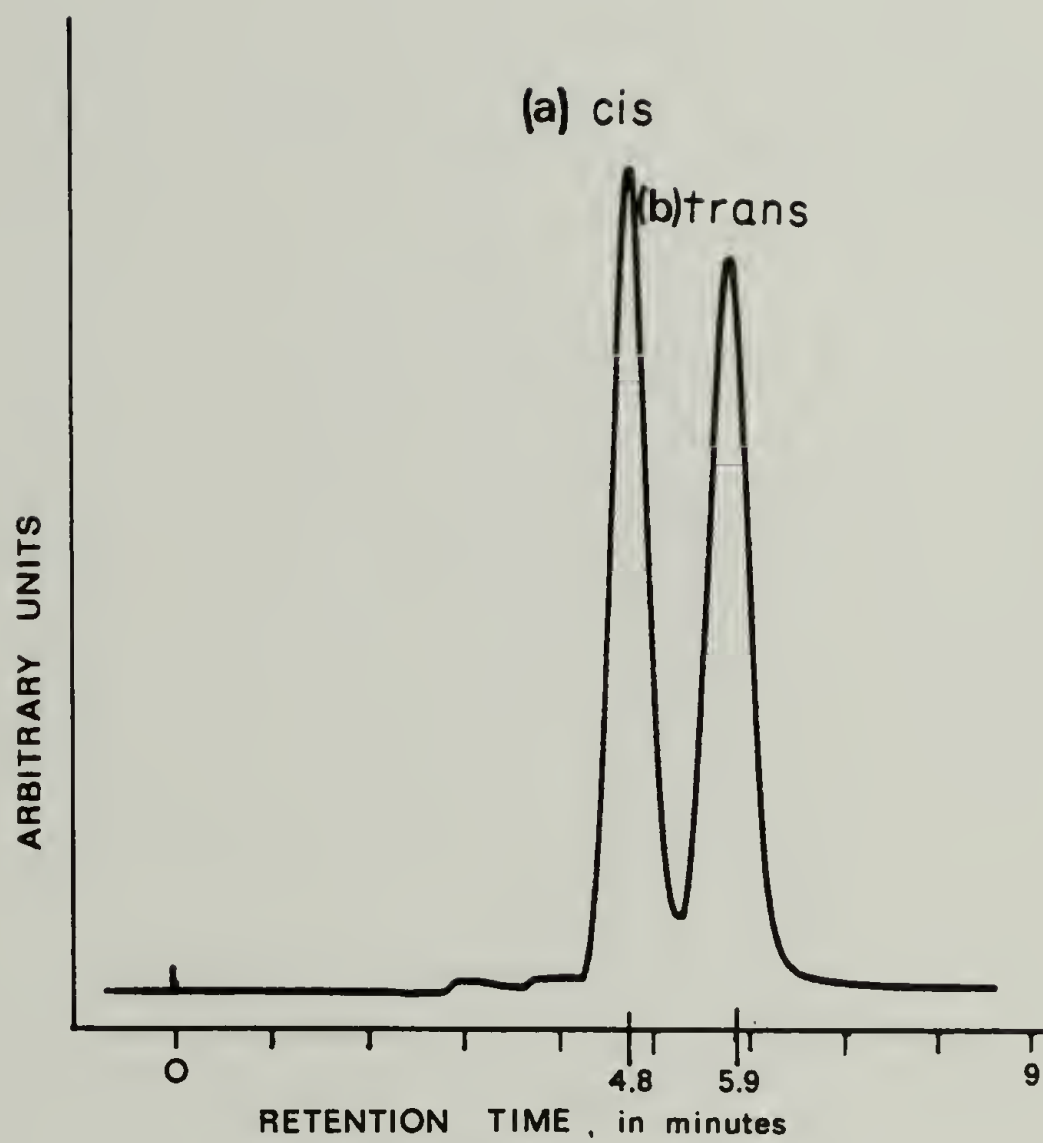


Figure 35. ^{13}C NMR spectrum of 3,4-dimethyltetrahydrofuran.

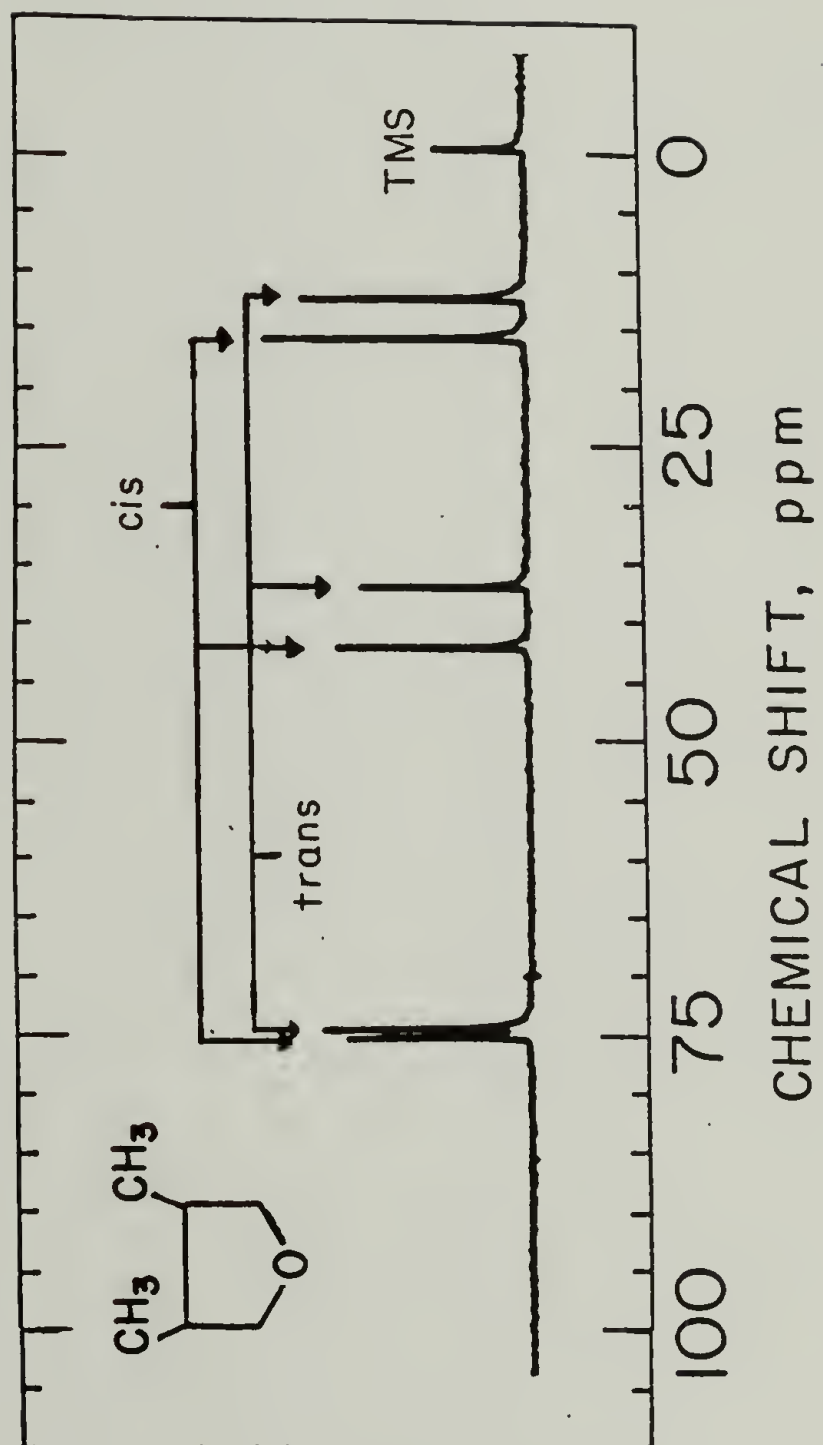


TABLE 22

^{13}C NMR CHEMICAL SHIFT VALUES FOR
3,4-DIMETHYLTETRAHYDROFURAN*

CIS	$\text{a}^{\text{I}}\text{CH}_3$		$\text{b}^{\text{I}}\text{CH}-$		$\text{c}^{\text{I}}\text{CH}_2-\text{O}$	
	Trans		Cis	Trans	Cis	Trans
15.9 (23)	12.6 (19)		42.0 (17)	36.9 (15)	75.3 (16)	74.5 (18)

*In PPM downfield from TMS, 30% solution in benzene. Numbers in parenthesis indicate relative peak intensities.

and trans methine carbon atoms is nerarly 5 ppm, while for the methyl carbon atom the difference is only about 3.4 ppm. The methylene carbon atom is the least affected with only 0.8 ppm difference between the cis and trans isomer carbon atoms. This is expected as the further removed from the stereochemical center a carbon atom is, the less it will be influenced by that stereochemistry.

The fact that cis and trans DMTHF were obtained in a 1:1 ratio indicated that the DMBD starting material used for ring closure had been a mixture of erythro and threo isomers in a 1:1 ratio because the erythro diol will close only to the cis DMTHF and the threo gives only the trans DMTHF (Figure 36). This leads back to the original coupling step in Figure 33 which is not stereospecific and gives the formation of both erythro and threo configurations. During the ring-opening polymerization of DMTHF this becomes important in terms of the stereochemistry of resulting polymers.

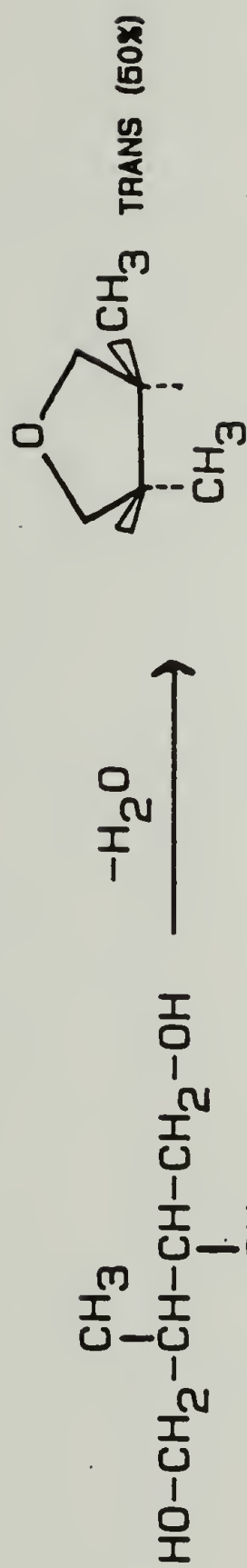
2. Homopolymerization Attempts of 3,4-Dimethyltetrahydrofuran

Several attempts were made to homopolymerize DMTHF with a variety of Lewis acids and other cationic initiatory systems. Table 23 gives a brief summary of these attempts.

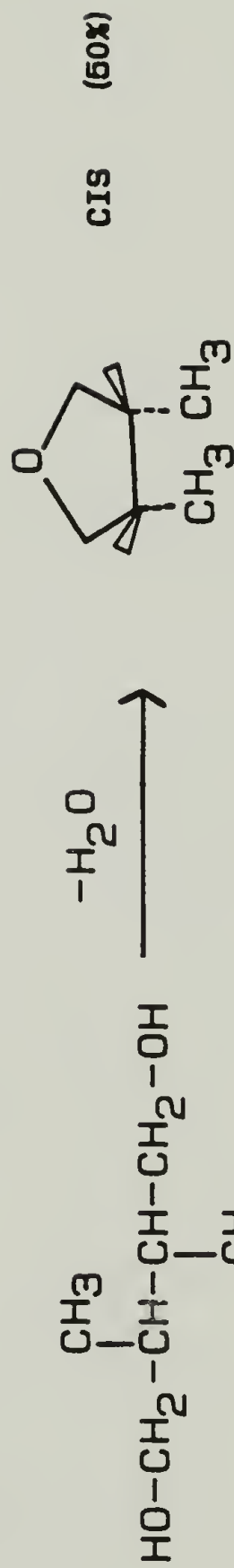
In each of these attempts 1.0 mole % epichlorohydrin was added as a coinitiator, and control polymerizations of unsubstituted THF were carried out in each

Figure 36. Ring-closure of erythro and threo 2,3-dimethyl-butanediol-1,4 to give cis- and trans-3,4-dimethyltetrahydrofuran.

CYCLIZATION OF DMTHF



THREO



ERYTHRO

TABLE 23

ATTEMPTED HOMOPOLYMERIZATION OF 3,4-DIMETHYLTETRAHYDROFURAN

Catalyst	Catalyst Concentration (mole percent)	Conditions
$\text{BF}_3 \cdot \text{etherate}$	4.0	-22°C/several weeks
PF_5	4.0	-30°C/one week
$\text{AlEt}_3/\text{H}_2\text{O}$ (1:1)	3.0	-22°C/several weeks In the Bulk
$\text{AlEt}_3/\text{H}_2\text{O}$ (1:1)	3.0	-22°C/several weeks In 20% benzene solution
$\text{AlEt}_3/\text{AcAc}/\text{H}_2\text{O}$ (1:1:0.5)	5.0	-22°C/several weeks

example.

As predicted from earlier thermodynamic calculations, homopolymerization of DMTHF did not occur to any measureable extent.^{144,145} This is in agreement with the observation that substitution in cyclic ethers decreases or even prevents their polymerizability.¹⁴⁶ It indicates that the free energy of polymerization is zero or positive for DMTHF.

Bulk copolymerization of equimolar mixtures of DMTHF with THF was also unsuccessful under similar conditions to those in Table 23 where THF was readily homopolymerized.

3. Copolymerization of 3,4-Dimethyltetrahydrofuran with Substituted Epoxides

The copolymerization of DMTHF with epichlorohydrin (ECH) and propylene oxide (PO) was successfully carried out at -20°C. Table 24 shows the results of these copolymerizations. The initiation of these copolymerizations was conducted using PF₅ gas.

a. Copolymerization of 3,4-dimethyltetrahydrofuran with epichlorohydrin

The copolymer between DMTHF and ECH was obtained in a yield of 70% as a semi-solid material of low molecular weight and was characterized by its IR and ¹³C NMR spectra. Chlorine analysis of the copolymer indicated that a 40/60 (DMTHF/ECH) copolymer ratio had been obtained.

TABLE 24

BULK COPOLYMERIZATION OF 3,4-DIMETHYLTETRAHYDROFURAN
WITH EPOXIDES

<u>Monomer</u>		<u>Copolymer Composition</u>			<u>Yield</u>	<u>Initiator</u>	<u>Remarks</u>	
<u>M₁</u>	<u>M₂</u>	<u>M₁</u>	<u>M₂</u>	<u>M₂</u>				
DMTHF	ECH	41.3	58.7 (a)		70%	PF ₅	Resinous semi-solid polymer (η)inh 0.11, 30°C/benzene.	
DMTHF	PO	49.8	50.2 (b)		32%	PF ₅	Resinous liquid polymer (η)inh 0.13 30°C benzene	

(a) Determined by Cl analysis (this comonomer mixture was 60/40:ECH/DMTHF)

(b) Determined by ¹³C NMR integration

The ^{13}C NMR spectrum is shown in Figure 37 for poly(DMTHF-co-ECH) with Table 25 giving the chemical shift data. The erythro/threo configurations of the DMTHF incorporated into the copolymer became apparent in the ^{13}C NMR. As discussed previously in the stereochemistry of the DMTHF monomer, the cis isomer of DMTHF can only open to the erythro configuration and the trans gives exclusively the threo configuration. Each carbon atom of the copolymer shows an erythro/threo splitting except for the $\underline{\text{CH}}_2\text{Cl}$ carbon atom which is too far removed from the stereochemical influence to be affected.

Figure 38 indicates how the erythro/threo linkages develop from the cis/trans DMTHF during the propagation step of the copolymerization. Note that this is a purely configurational phenomenon and it can not be altered by conformational changes.

From the integration of the peaks it was determined that an equal amount of erythro and threo linkages were present in the copolymer indicating that no preference was shown for the cis or trans isomer of DMTHF during propagation.

The fact that several of the carbon atoms show a double splitting is thought to possibly be due to H-H and H-T linkages for the two comonomers.

The spectrum has only a single peak for the $\underline{\text{CH}}_2\text{Cl}$ carbon. This is a direct indication that very little

Figure 37. ^{13}C NMR spectrum of poly(3,4-dimethyl-tetrahydrofuran-co-epichlorohydrin).

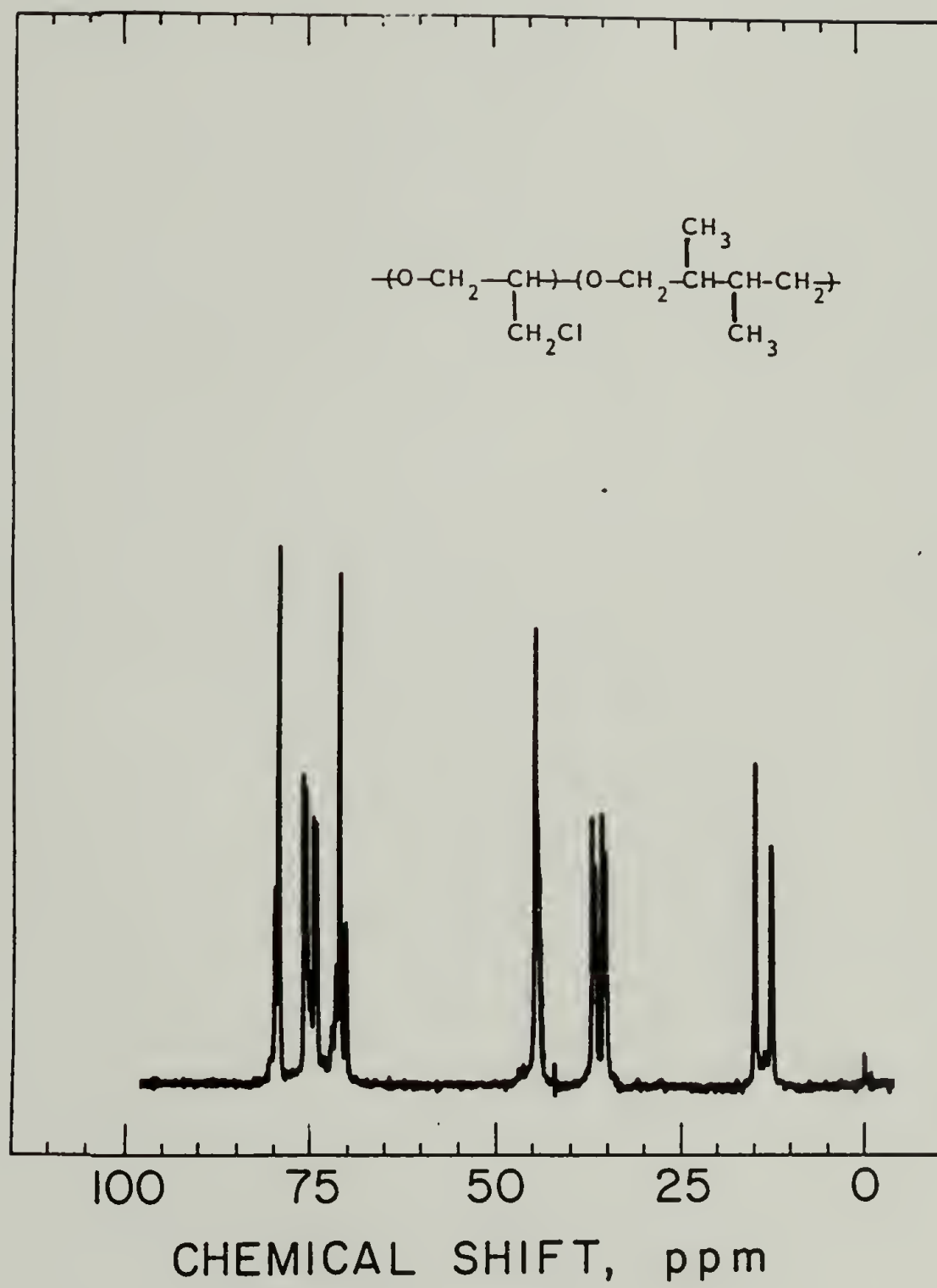
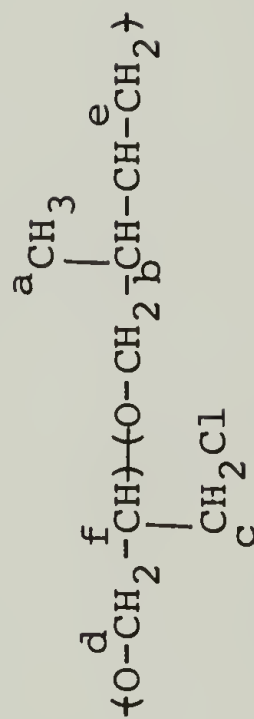


TABLE 25

^{13}C NMR CHEMICAL SHIFT DATA FOR POLY(3,4-DIMETHYLTETRA-
HYDROFURAN-CO-EPICHLOROHYDRIN)

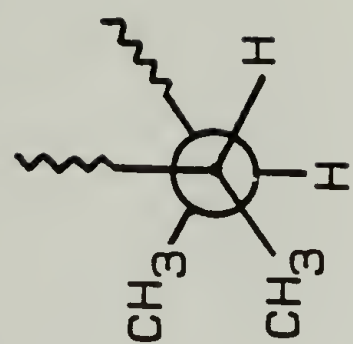
	(a)	(b)	(c)	(d)	(e)	(f)
THREO	12.6 (30)*	34.7 (31)	44.3 (80)	69.9 (21)	73.1 (34)	79.9 (71)
ERYTHRO	14.8 (43)	36.1 (29)		70.8 (87)	75.3 (39)	79.5 (26)
THREO		35.2 (36)			74.2 (35)	
ERYTHRO		36.5 (35)			75.6 (40)	



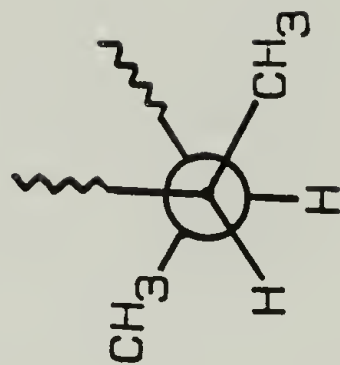
*In ppm downfield from TMS, 30% in benzene. Numbers in parenthesis are relative peak intensities.

Figure 38. Stereoregularity of 3,4-dimethyltetrahydrofuran ring-opening during incorporation into copolymer.

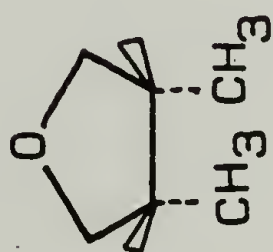
STEREOCHEMISTRY OF DMTHF RING-OPENING



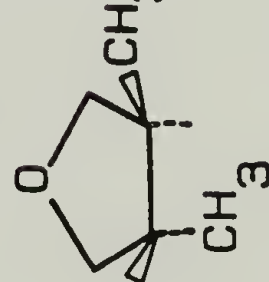
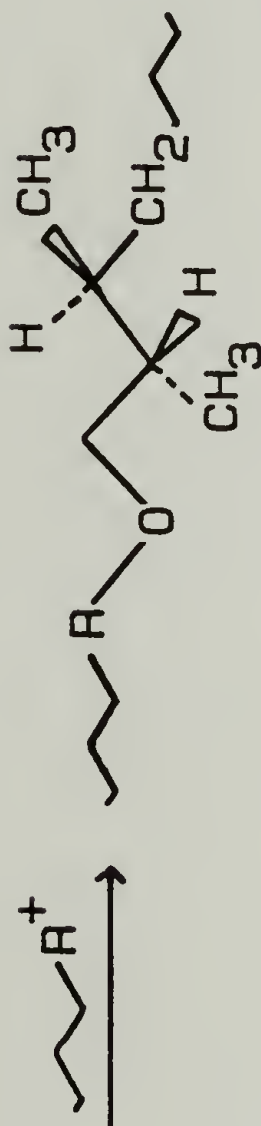
ERYTHRO



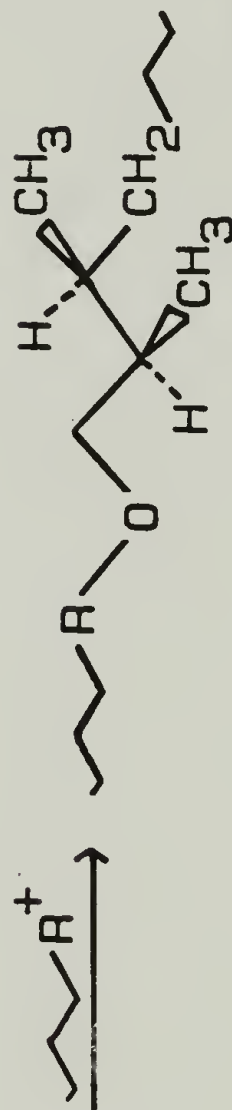
THREO



CIS



TRANS



homopolymer of ECH is present since the chemical shift for $\underline{\text{CH}_2}\text{Cl}$ in the homopolymer would be different from that of the alternating copolymer.

b. Copolymerization of 3,4-dimethyltetrahydrofuran with propylene oxide

Bulk copolymerization for an equimolar mixture of DMTHF and PO was also successful yet gave a lower yield than that of the copolymerization of DMTHF with ECH. The product was a clear viscous liquid which was soluble in methanol and was precipitated into water.

Apparently PO is less reactive as a comonomer with DMTHF than ECH, as evidenced by lower yield. This same trend was found by others for copolymerizations of 2-MTHF with either ECH or PO.¹⁵²

Integration of the ^{13}C NMR chemical shift peaks shows a nearly 1:1 copolymer composition of DMTHF and PO, and again the erythro/threo splitting of the DMTHF units was obtained (Figure 39 and Table 26). Here again, as with the poly(DMTHF-co-ECH), the methyl carbon atom of the PO unit is the only one not affected by the stereochemistry of the copolymer due to its distance from the site. Also the double splitting of the $\begin{array}{c} | \\ -\underline{\text{CH}}- \end{array}$ atom on the DMTHF unit indicates that H-H linkages may be present.

Figure 39. ^{13}C NMR spectrum of poly(3,4-dimethyl-tetrahydrofuran-co-propylene oxide).

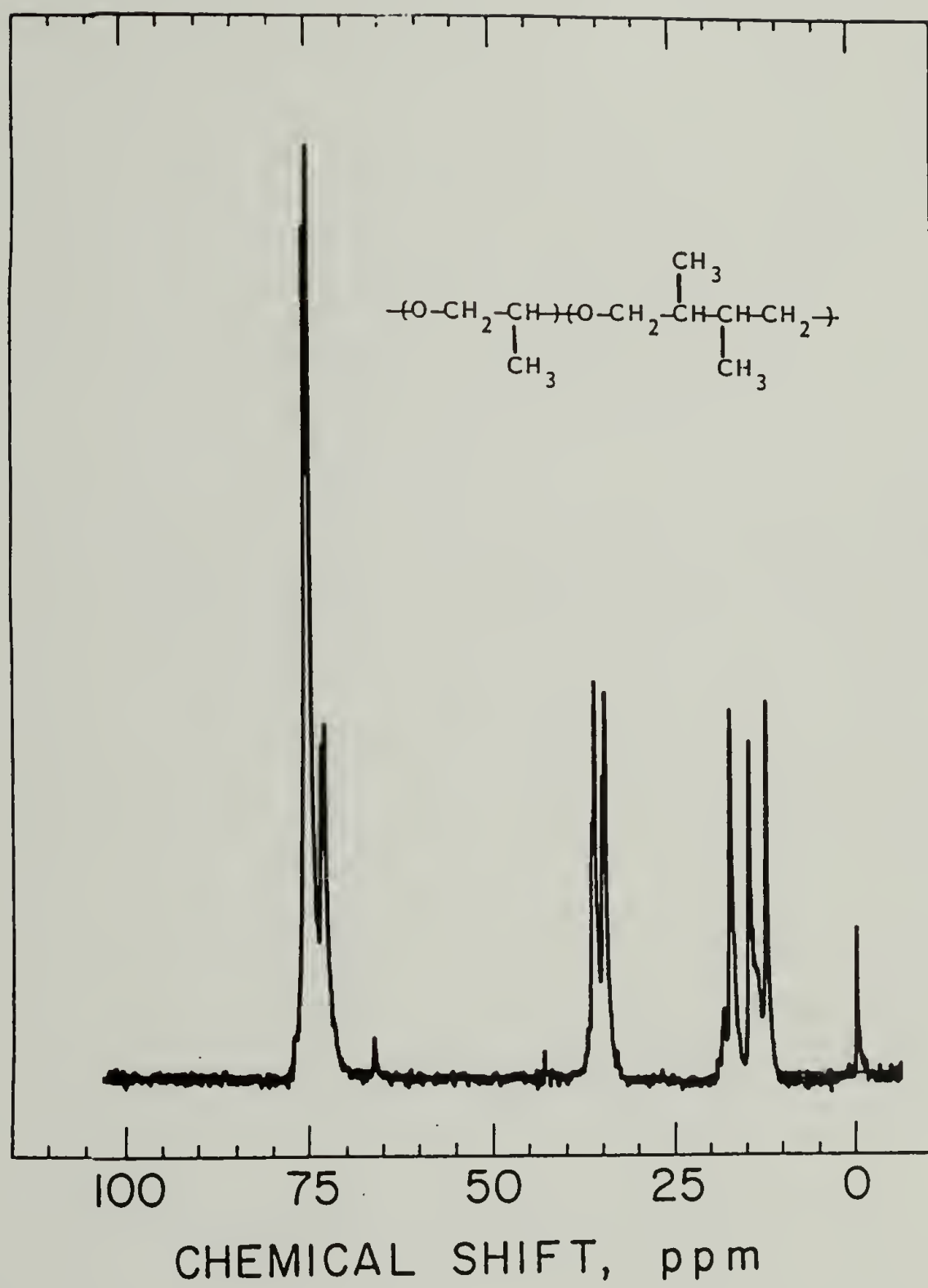
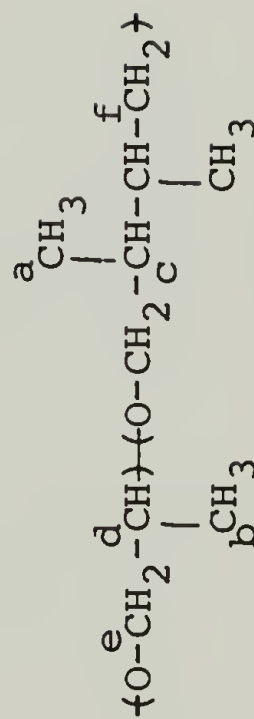


TABLE 26

^{13}C NMR CHEMICAL SHIFT DATA FOR POLY(3,4-DIMETHYL-
TETRAHYDROFURAN-CO-PROPYLENE OXIDE)

	(a)	(b)	(c)	(d)	(e) & (f)
THREO	12.8 (51)*	17.9 (50)	34.7 (52)	72.8 (47)	75.0 (125)
ERYTHRO	15.0 (48)		36.2 (41)	73.2 (44)	75.5 (114)
THREO			35.1 (41)		
ERYTHRO			36.5 (34)		



*In ppm downfield from TMS, 30% in benzene. Numbers in parenthesis are relative peak intensities.

c. Reactivity ratios for 3,4-dimethyltetrahydrofuran and epichlorohydrin during copolymerization

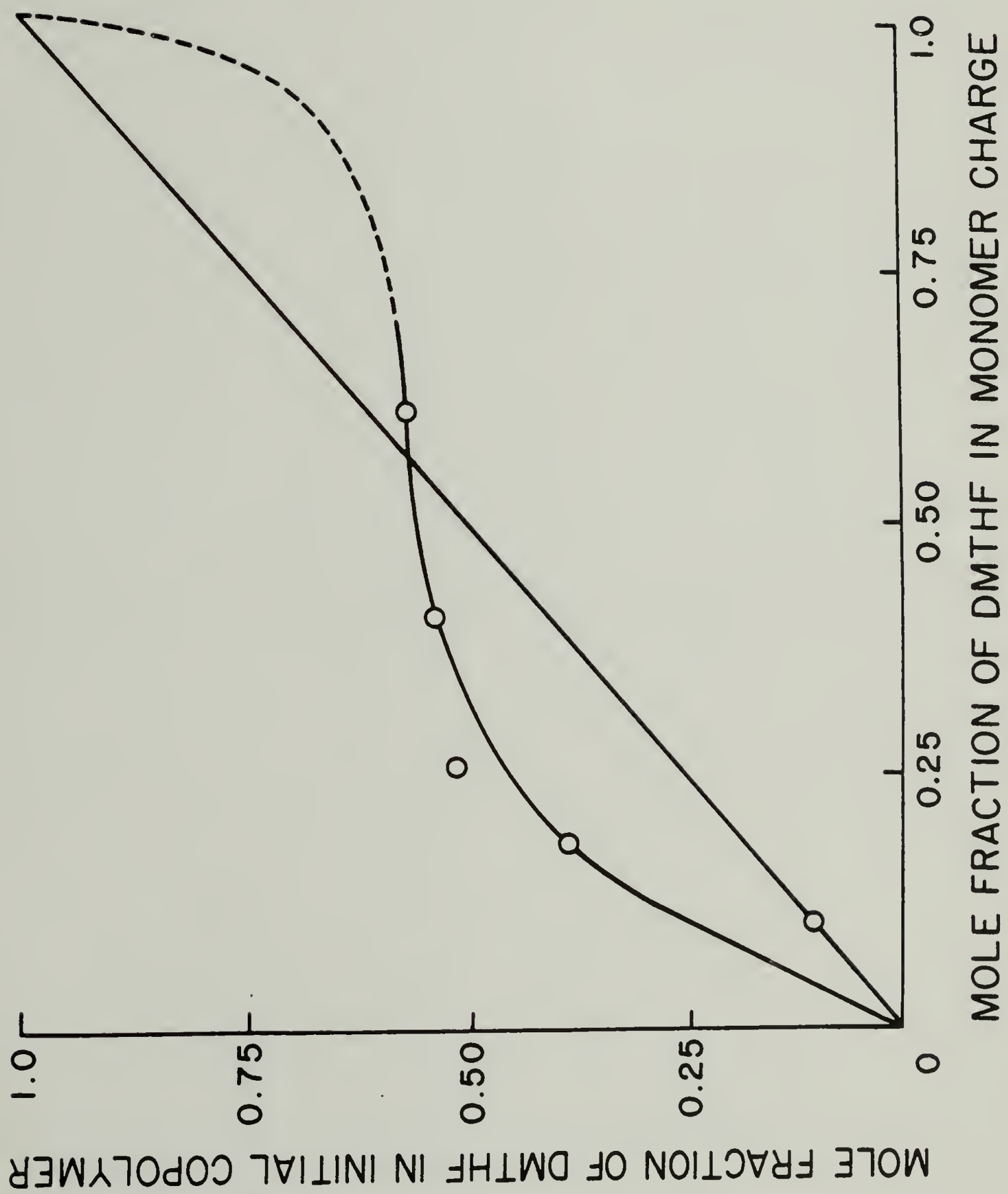
The fact that DMTHF would not homopolymerize to any appreciable extent yet it entered into a nearly 1:1 copolymer with both ECH and PO was somewhat surprising. At the time the copolymerizations were carried out, it was thought that some incorporation of DMTHF could be obtained due to the relatively high reactivity of the comonomers. The question was why DMTHF incorporated in a copolymer in 50%, yet showed no tendency to homopolymerize?

The nature of the copolymerization of DMTHF with ECH was selected for further investigation. The objective was to determine the reactivity ratios of the copolymerization in an effort to determine more about the manner in which the two monomers incorporated into the polymer. ECH was chosen due to its higher reactivity and because chlorine analysis could be used to determine copolymer composition accurately.

The reactivity ratios, r_1 and r_2 , were determined graphically according to the method of Kelen and Tudos¹⁸⁸ and showed values of $r_1 = 0.22 \pm 0.05$ for DMTHF and $r_2 = 0.11 \pm 0.01$ for ECH. The copolymer composition curve for these two monomers is given in Figure 40.

It should be noted that above a 60/40 mixture of DMTHF/ECH the copolymerization yield was too low for accurate measurement of the composition.

Figure 40. Copolymerization curve: 3,4-dimethyl-tetrahydrofuran with epichlorohydrin.



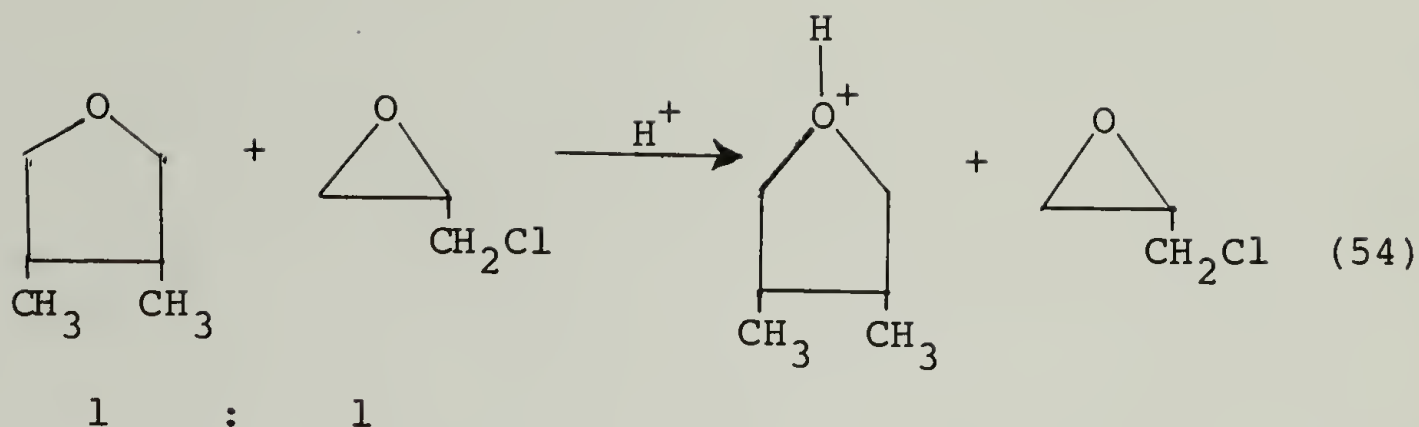
It is apparent from this data that the copolymerization proceeds in a nearly alternating fashion between DMTHF and ECH. This was consistent with the fact that so much DMTHF was found in the poly(DMTHF-co-ECH).

d. Discussion of copolymerization

To explain the fact that DMTHF and ECH enter into an alternating copolymerization, while DMTHF itself does not homopolymerize, a consideration of the mechanism of propagation is necessary.

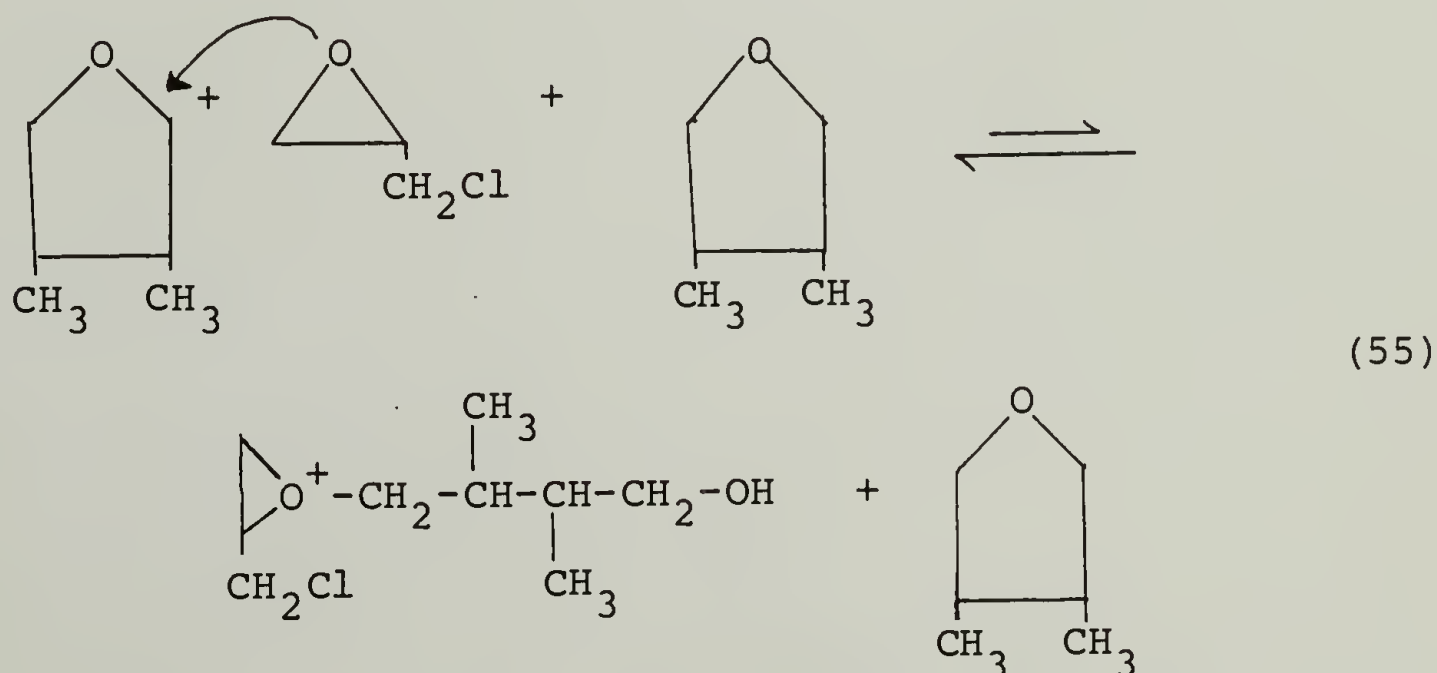
The initial step in the cationic ring-opening polymerization of cyclic ethers is the formation of the oxonium ion. The tendency for a cyclic ether to form an oxonium ion is based fundamentally on the basicity of the ether. The more basic the oxygen atom, the more easily the oxonium is formed.

It is known that unsubstituted THF is a better nucleophile than ECH¹⁵³ and that substitution of the THF ring increases the basicity of the oxygen. Therefore, it is believed that DMTHF is a much better nucleophile (more basic) than ECH and, consequently, will form the oxonium ion much more readily. Thus the first step in the copolymerization is the formation of the DMTHF oxonium ion as shown in Equation 54.



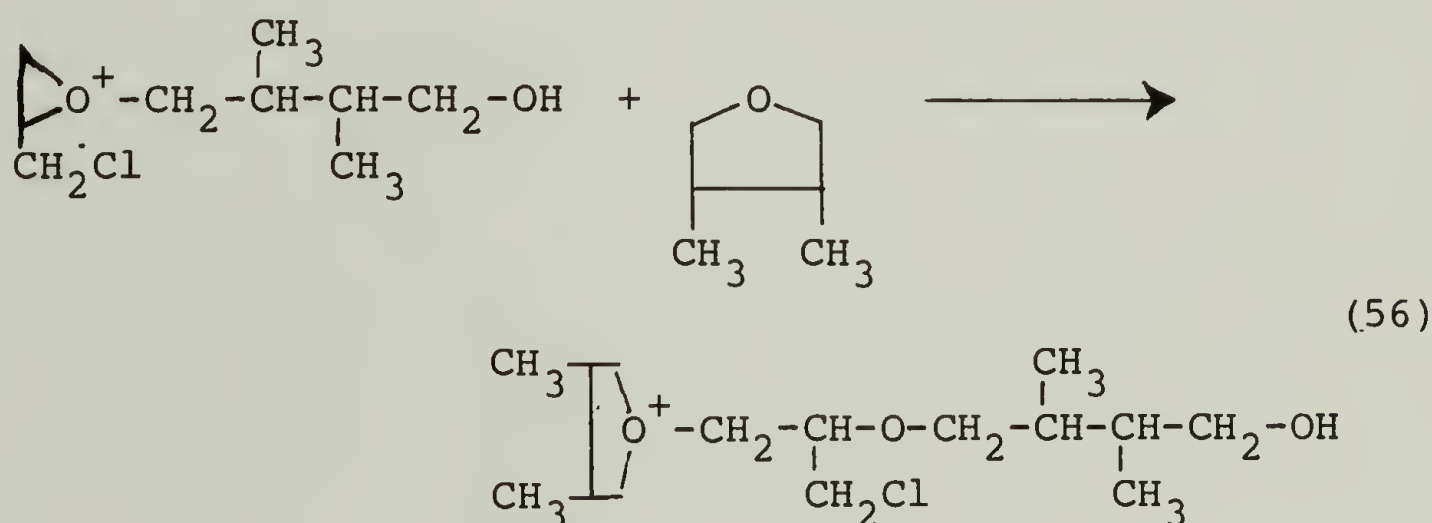
The fact that DMTHF does not homopolymerize does not preclude it from forming the initial oxonium ion. In fact, it has been shown that 2-MTHF forms a 1:1 adduct with $\text{BF}_3/\text{H}_2\text{O}$ systems although it is difficult to homopolymerize. However, once the DMTHF oxonium is formed it will not ring-open because of thermodynamic considerations already discussed.

The next step in the copolymerization is therefore the addition of an ECH monomer to the growing chain. This is presumed to be the rate determining step shown in Equation (55).



The product can ring close again to form the more stable DMTHF readily. Further evidence that this is the rate determining step is that the copolymerization between DMTHF and PO gives lower yields at longer reaction times than DMTHF and ECH due to a lower reactivity for PO in cationic polymerization systems.

Once the addition of the ECH has taken place it is now possible for propagation to occur if another DMTHF adds to the growing oxonium end (Equation 56).



The fact that the copolymerization was found to proceed in an alternating fashion indicates that the DMTHF is the next monomer to add (Equation 55) which is consistent with the suggestion that it is the more basic of the two monomers.

This sequence of steps apparently repeats itself again and again until ultimately an alternating copolymer is formed.

Finally, at high feed ratios of DMTHF to ECH

slightly more DMTHF is incorporated into the poly(DMTHF-co-ECH), which suggests that DMTHF must have some ability to add to its own oxonium ion to form at least two DMTHF units in succession.

4. Conclusions and Future Work

The objectives of this part of the dissertation were to initiate a study of the homo- and copolymerizability of 3,4-substituted THFs. This goal has been achieved and some rather intriguing results have been shown.

DMTHF was investigated under different polymerization conditions and found not to homopolymerize. This indicates that the free energy of polymerization for this ring-opening is positive or zero which is consistent with the calculations.

It was shown, however, that this same DMTHF which is so unreactive in homopolymerizations incorporates into copolymers with ECH and PO to a very substantial extent. DMTHF and ECH enter into an apparently alternating copolymerization, the nature of which has been speculated upon based on the relative basicity of the two comonomers.

Further investigations into the nucleophilicity of 3,4-disubstituted THFs in general could make this explanation more clear. Also, future work might include the study of reactive comonomers other than ECH and PO to determine if similar copolymerization results occur.

Finally, it would be interesting to study the effect of different substituents on the polymerizability of 3,4-disubstituted THFs.

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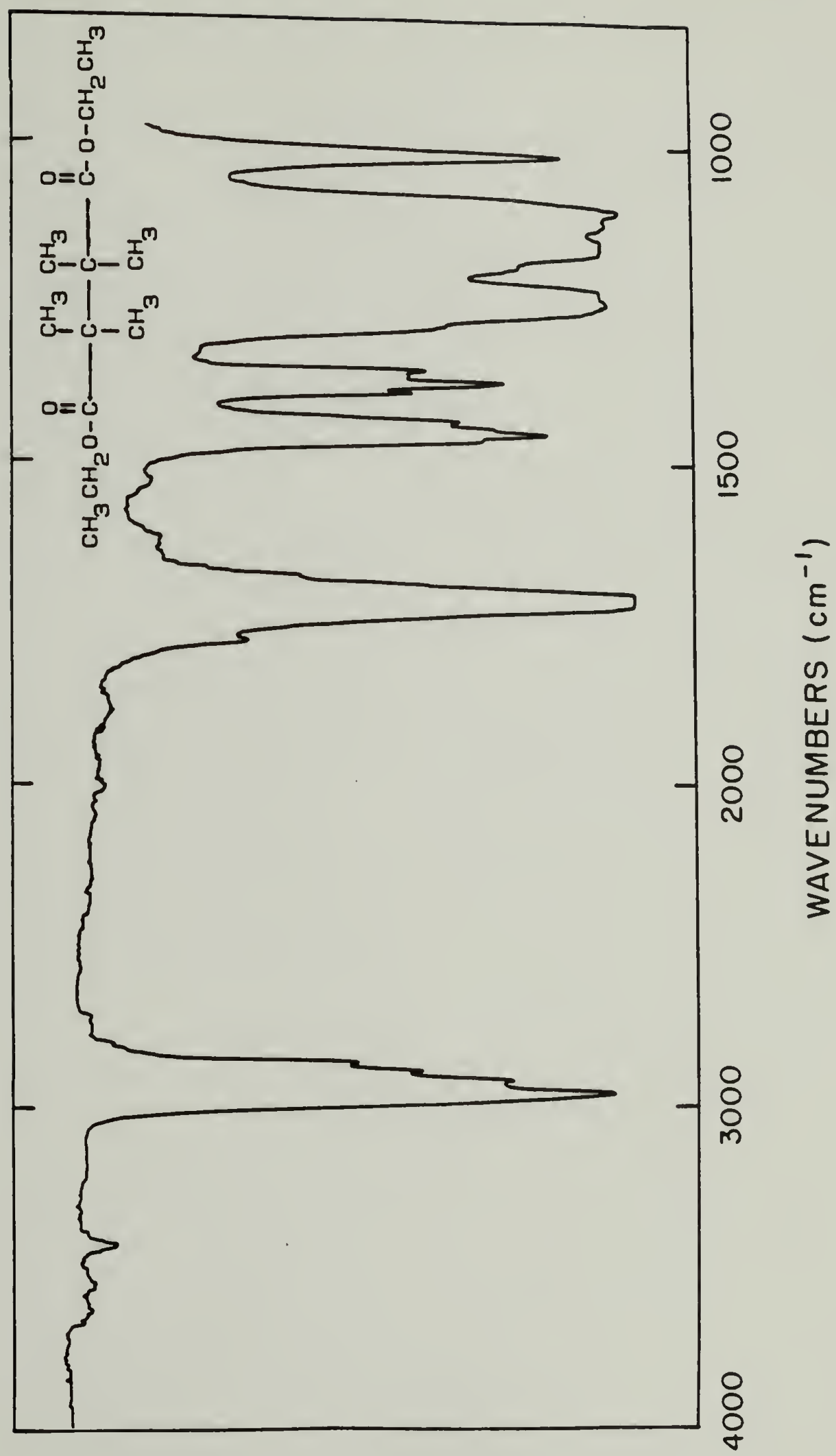
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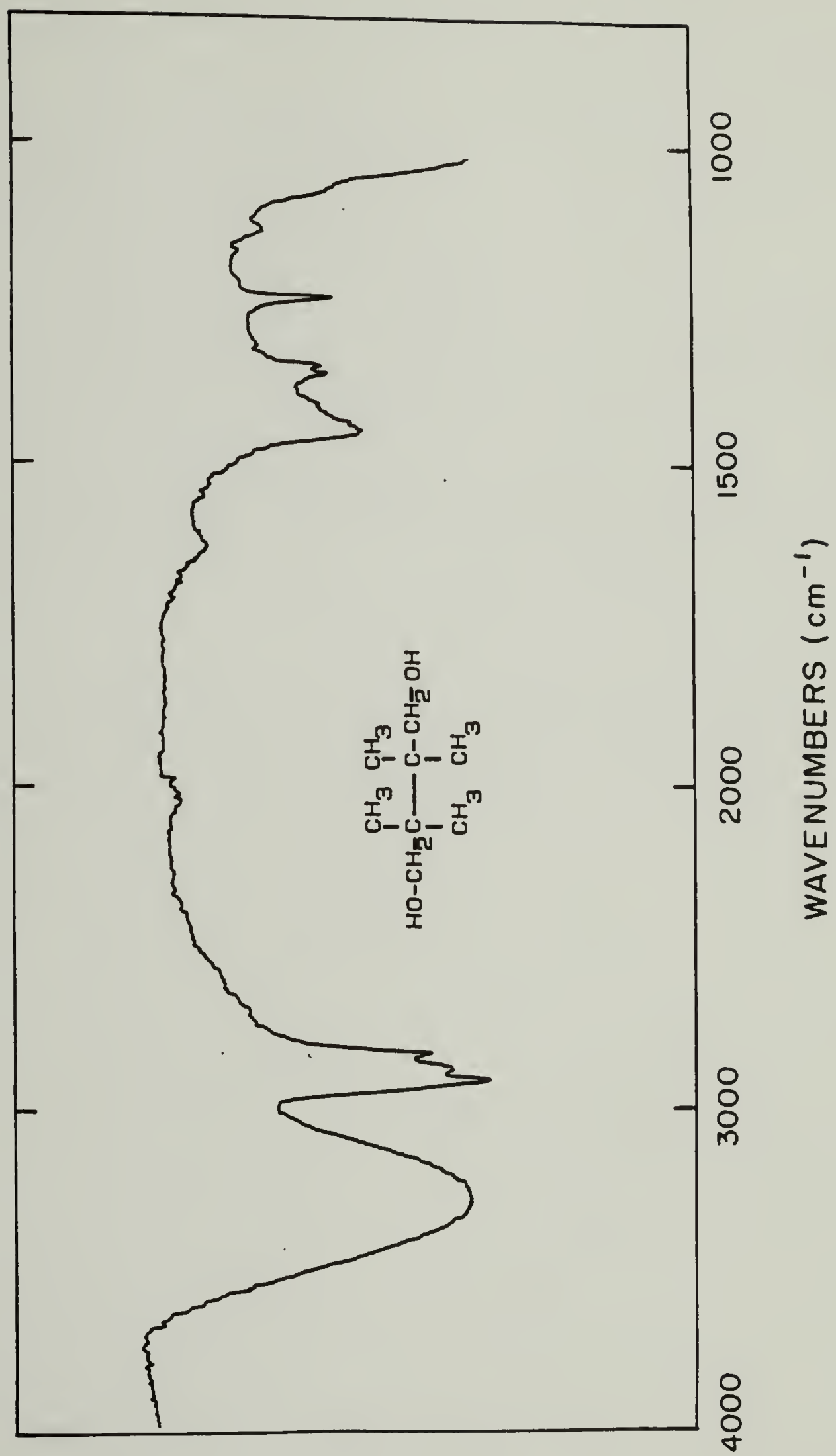
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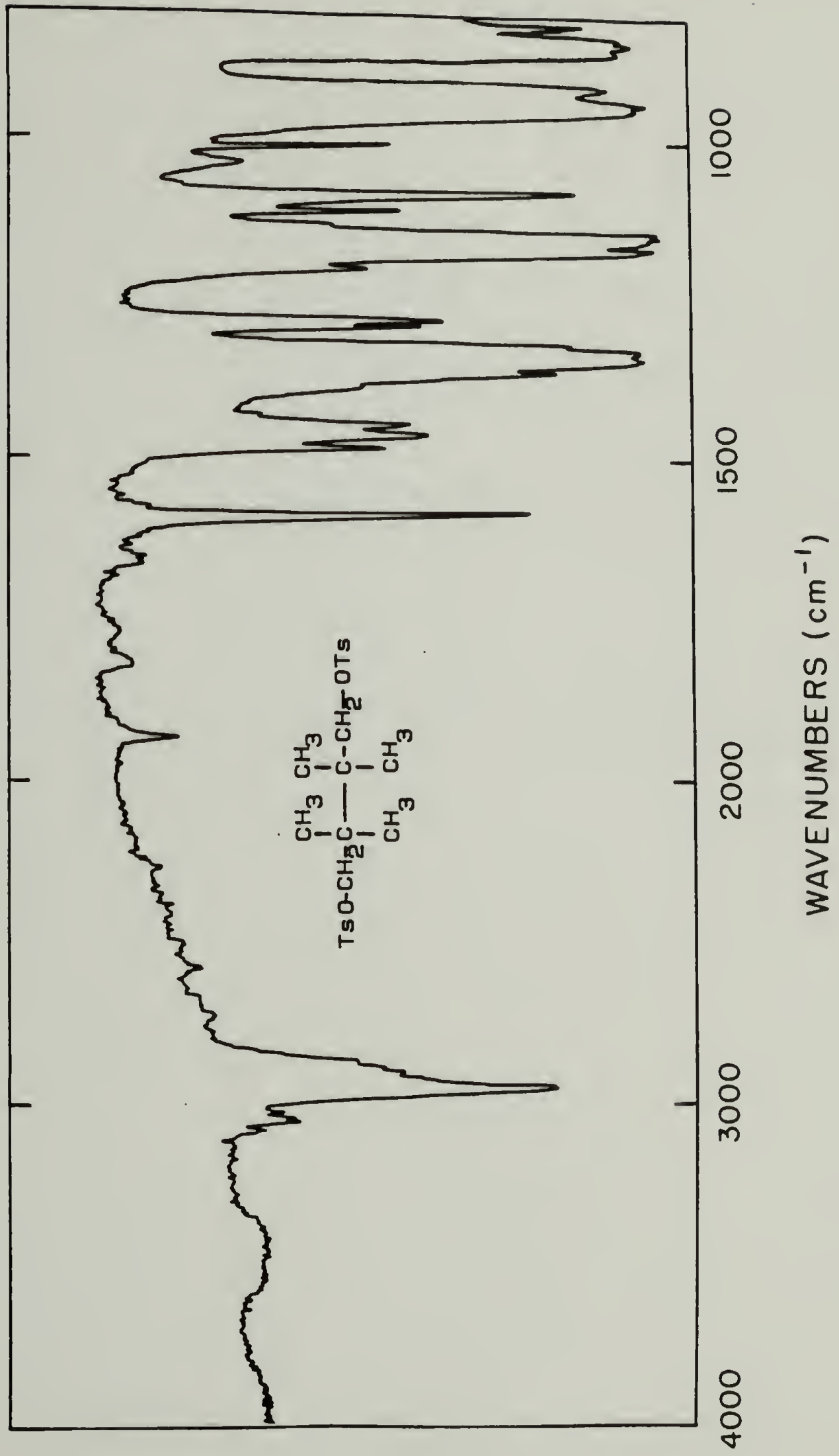
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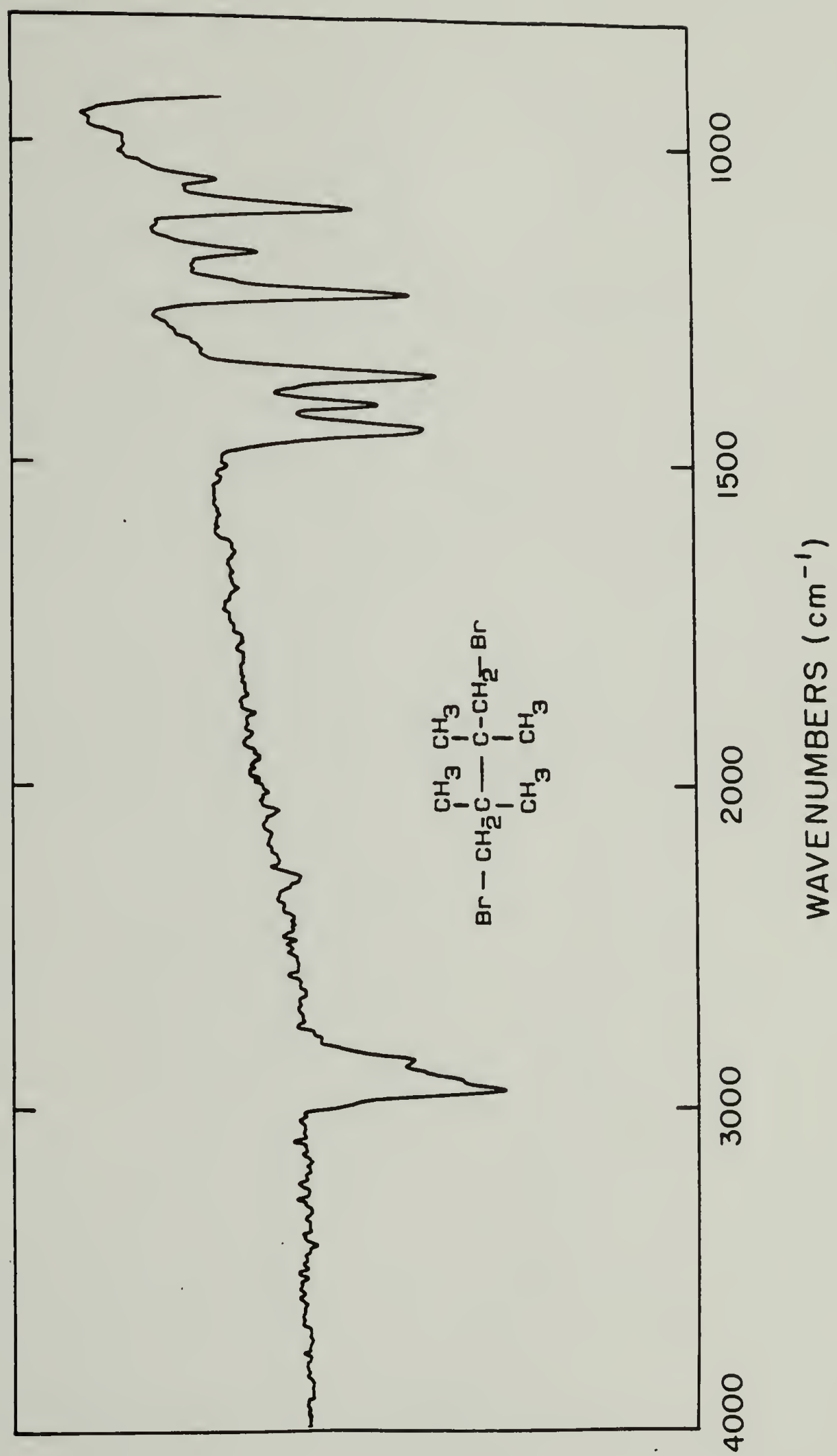
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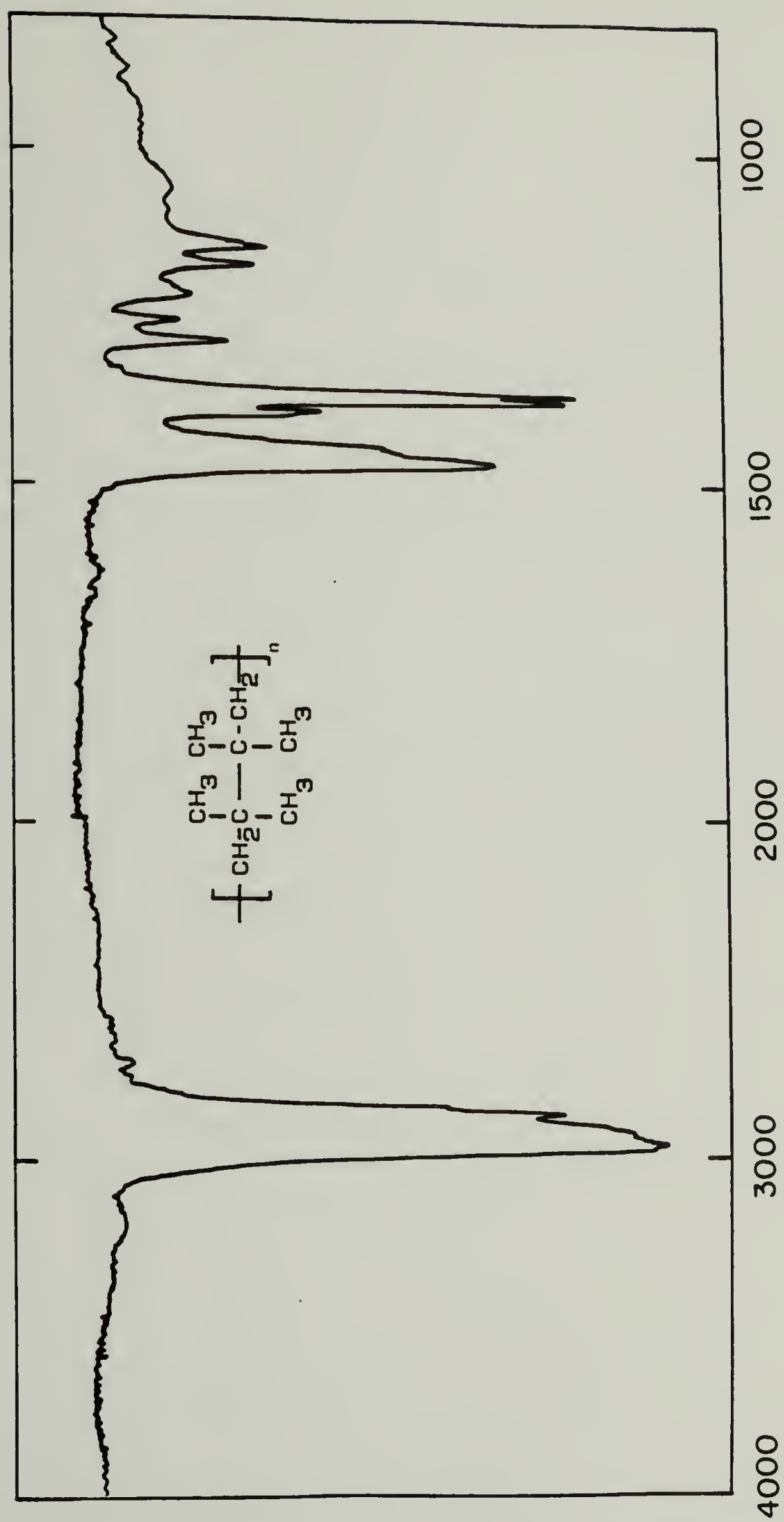
A P P E N D I X A
INFRARED SPECTRA

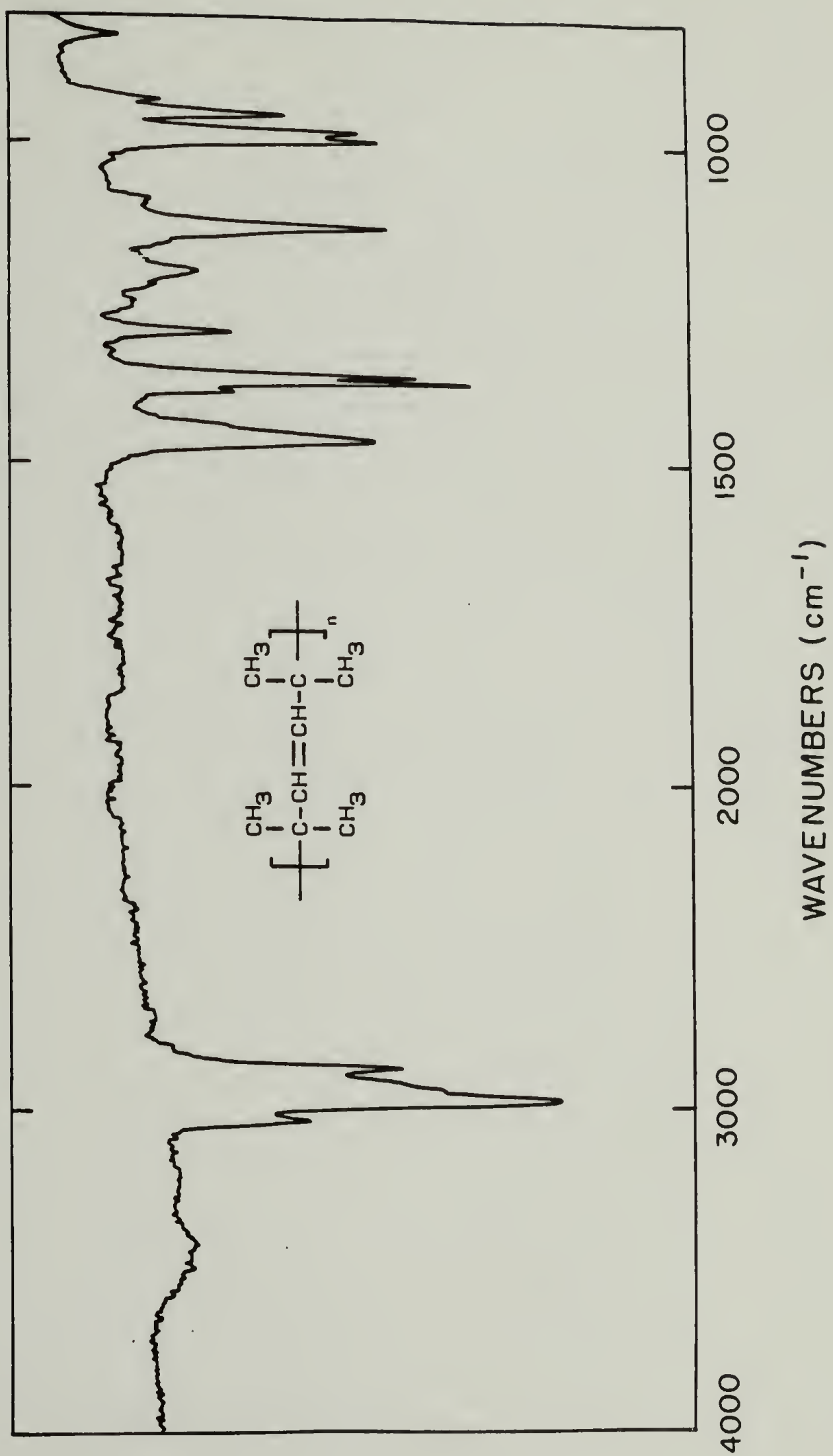


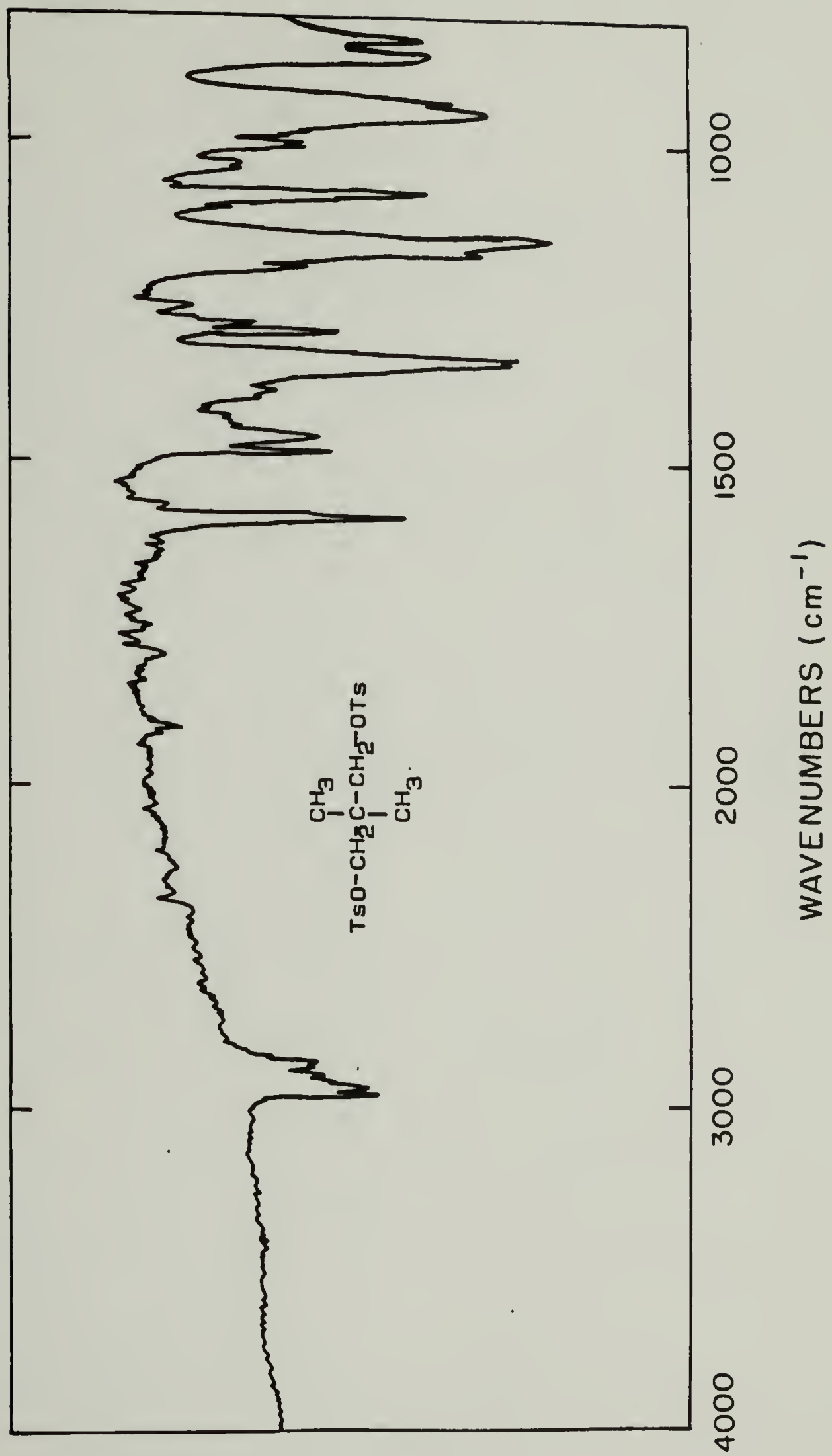


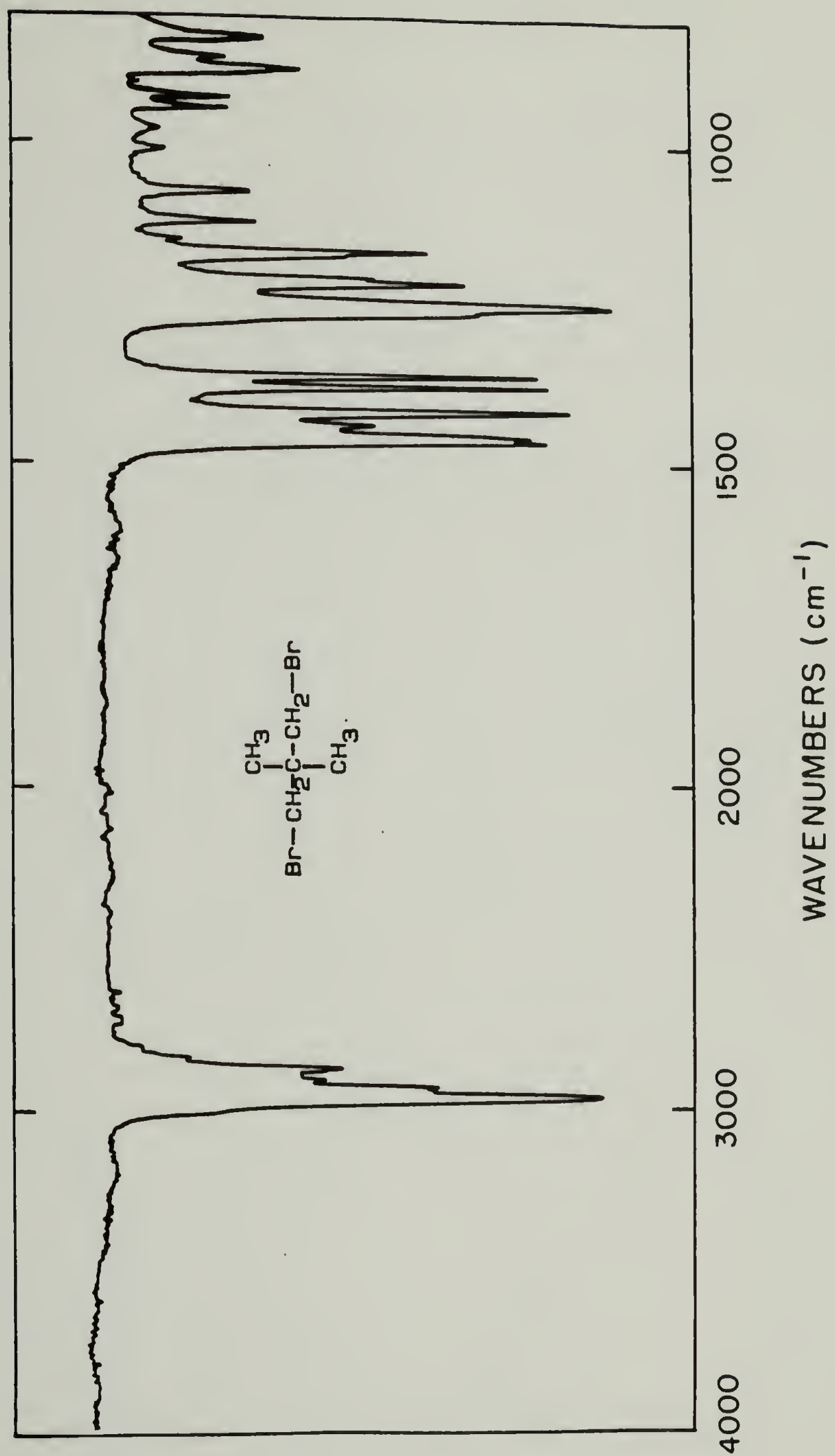


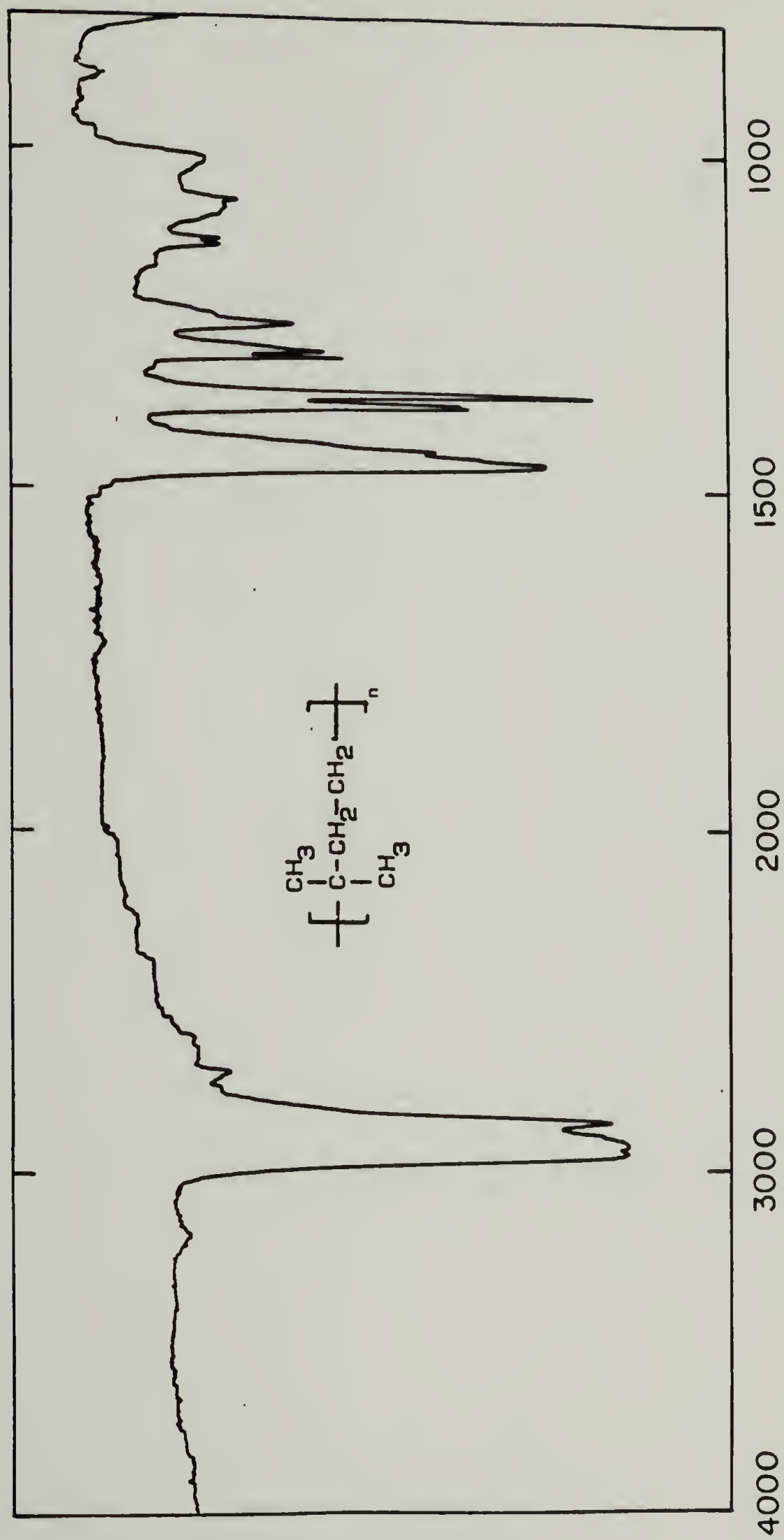


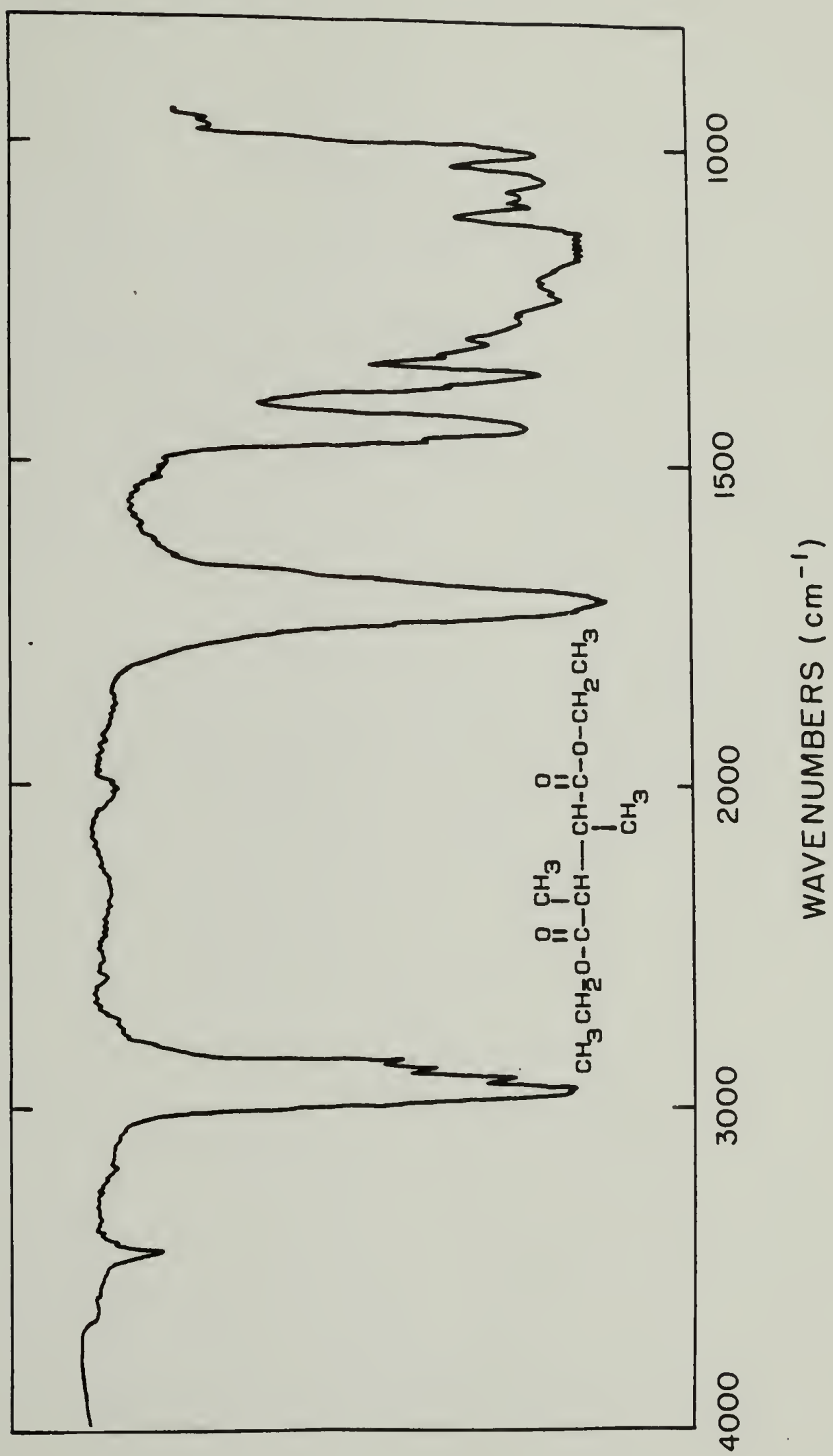


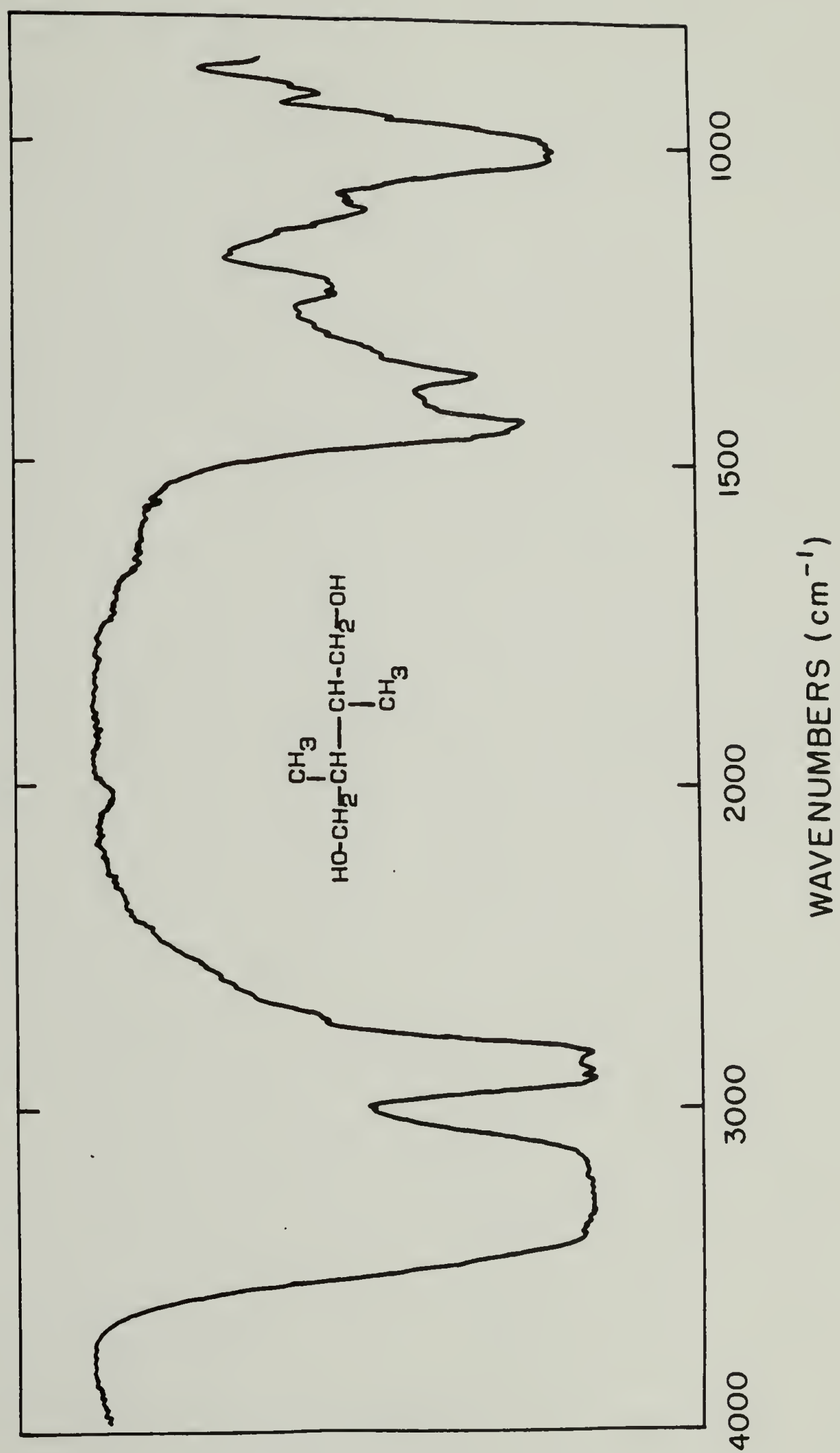


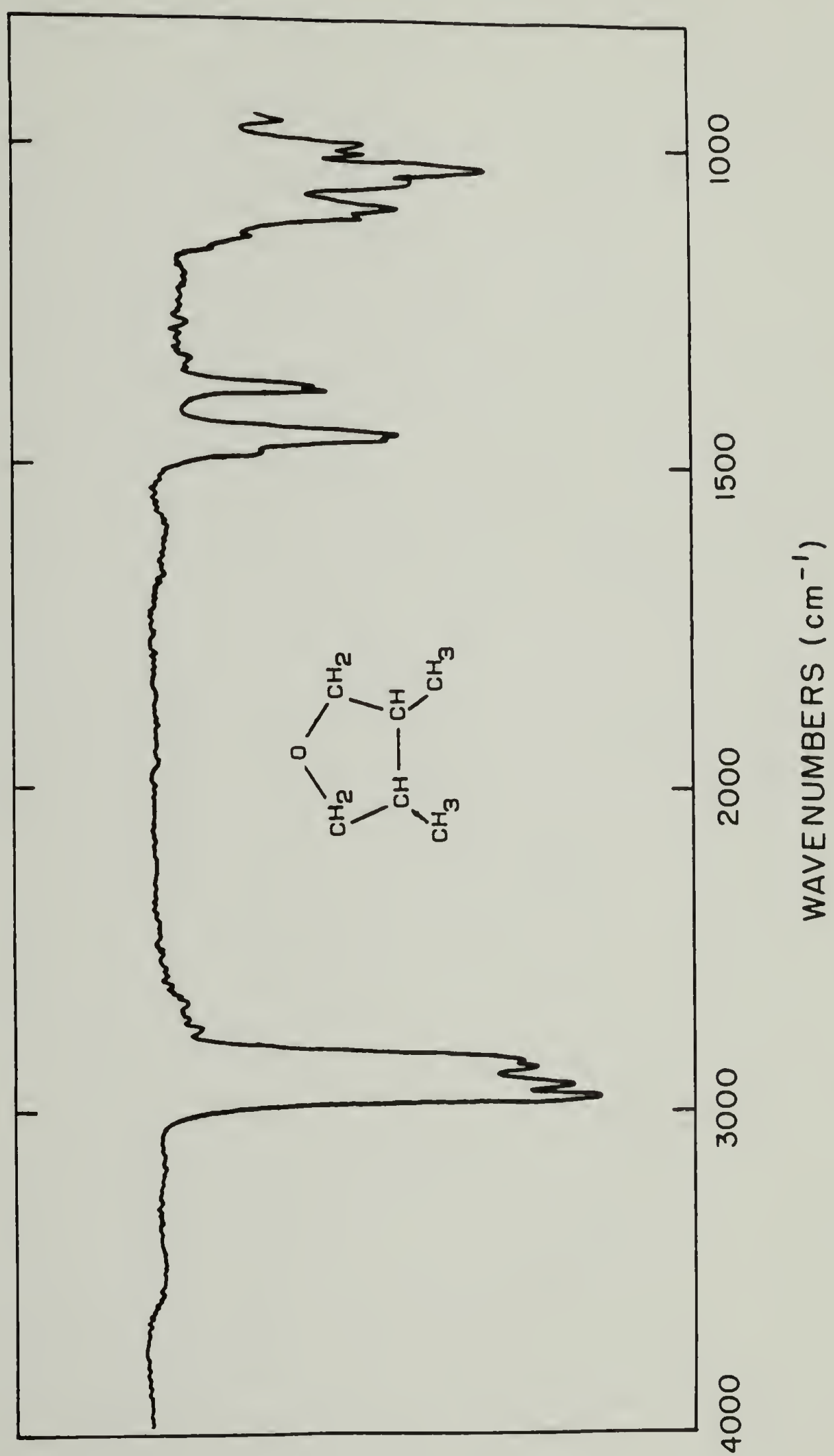


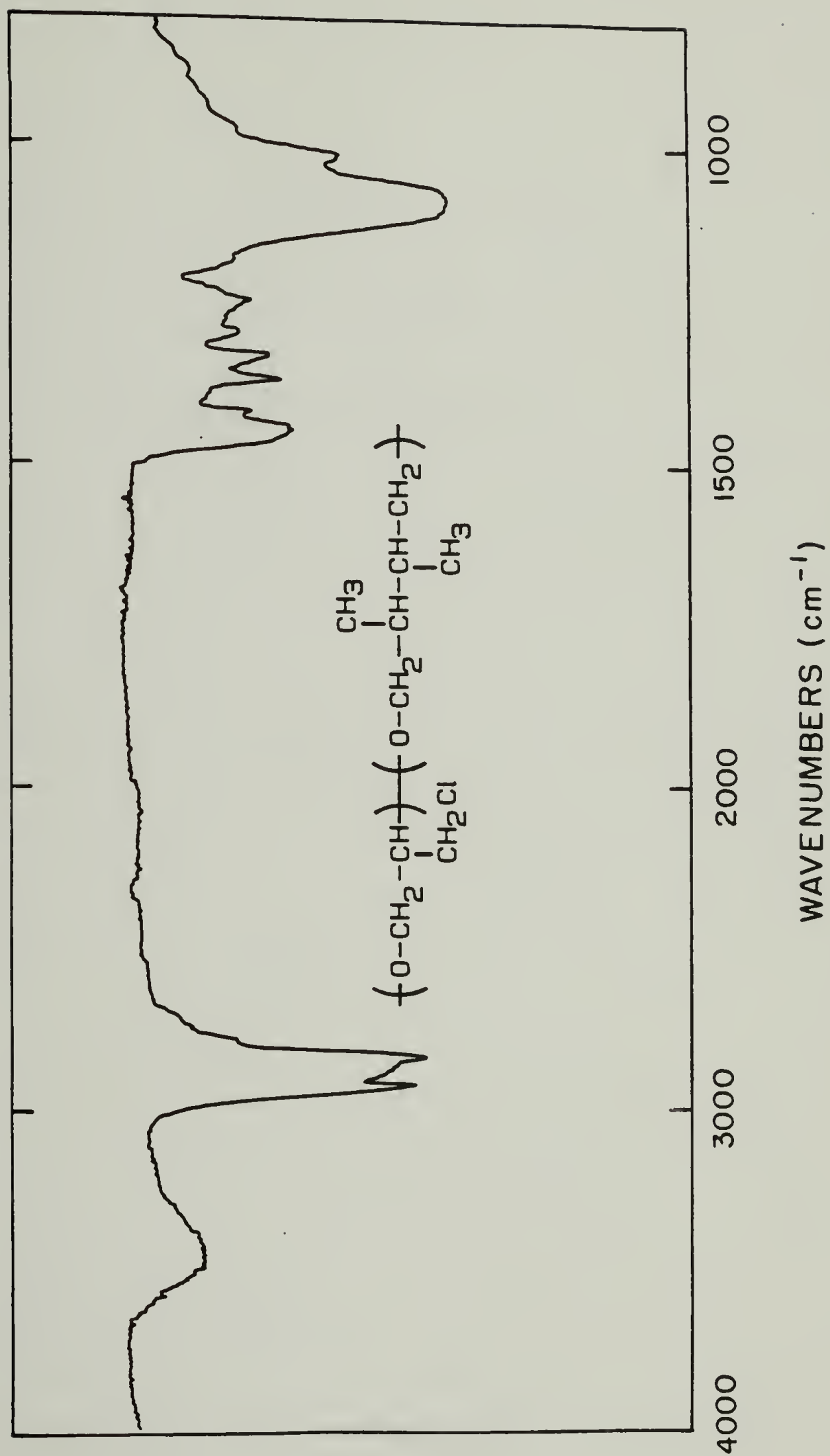


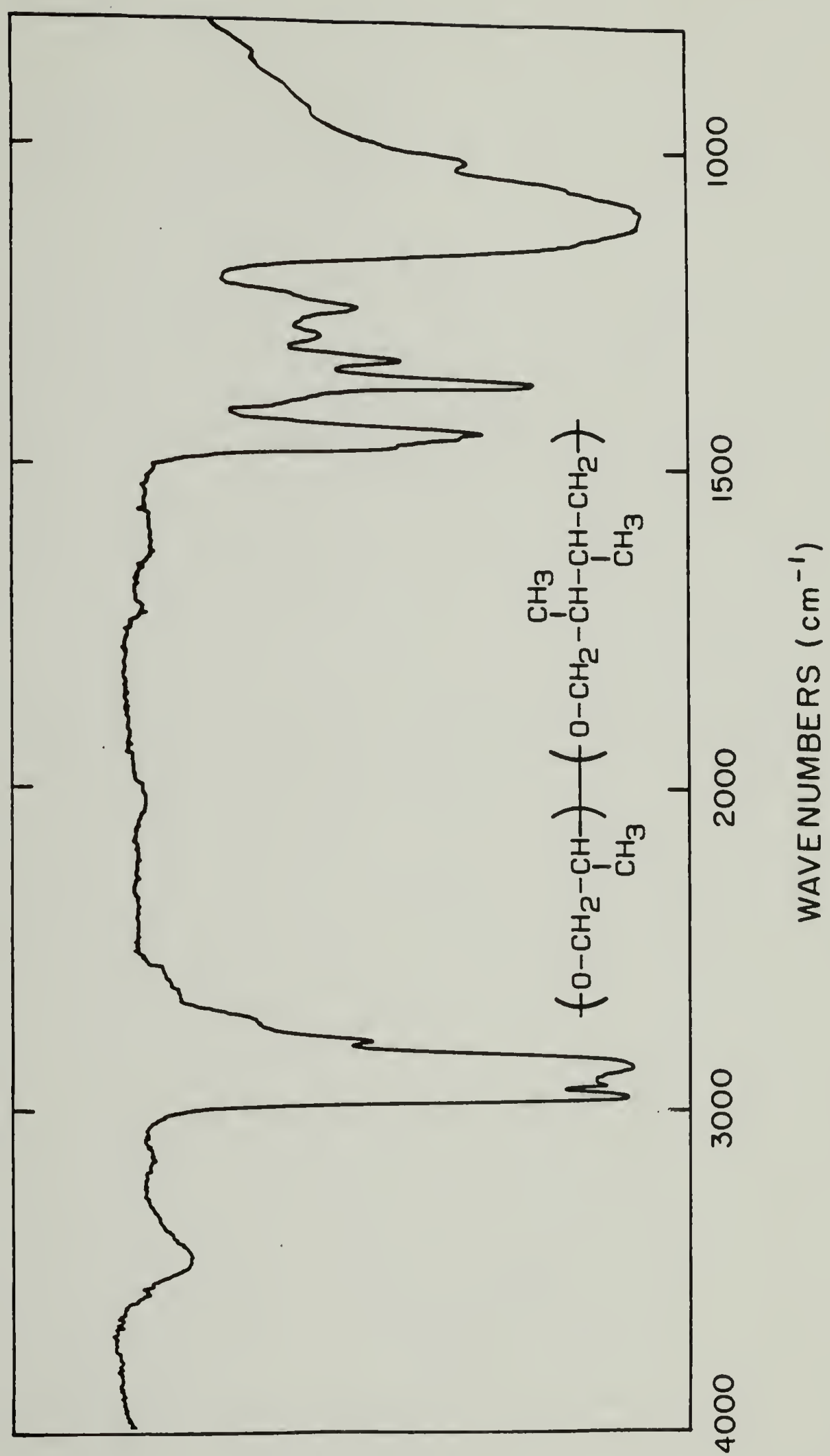






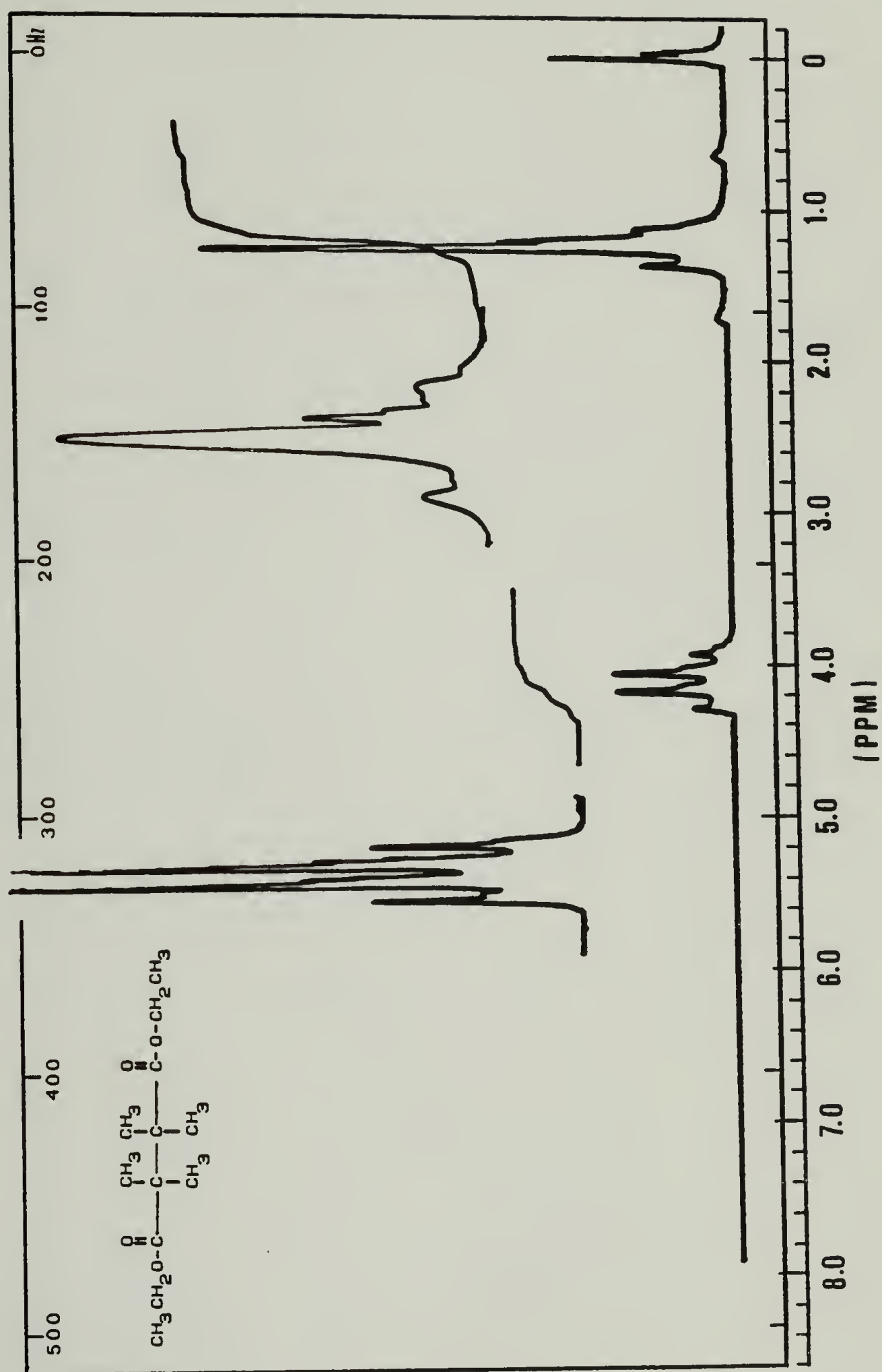


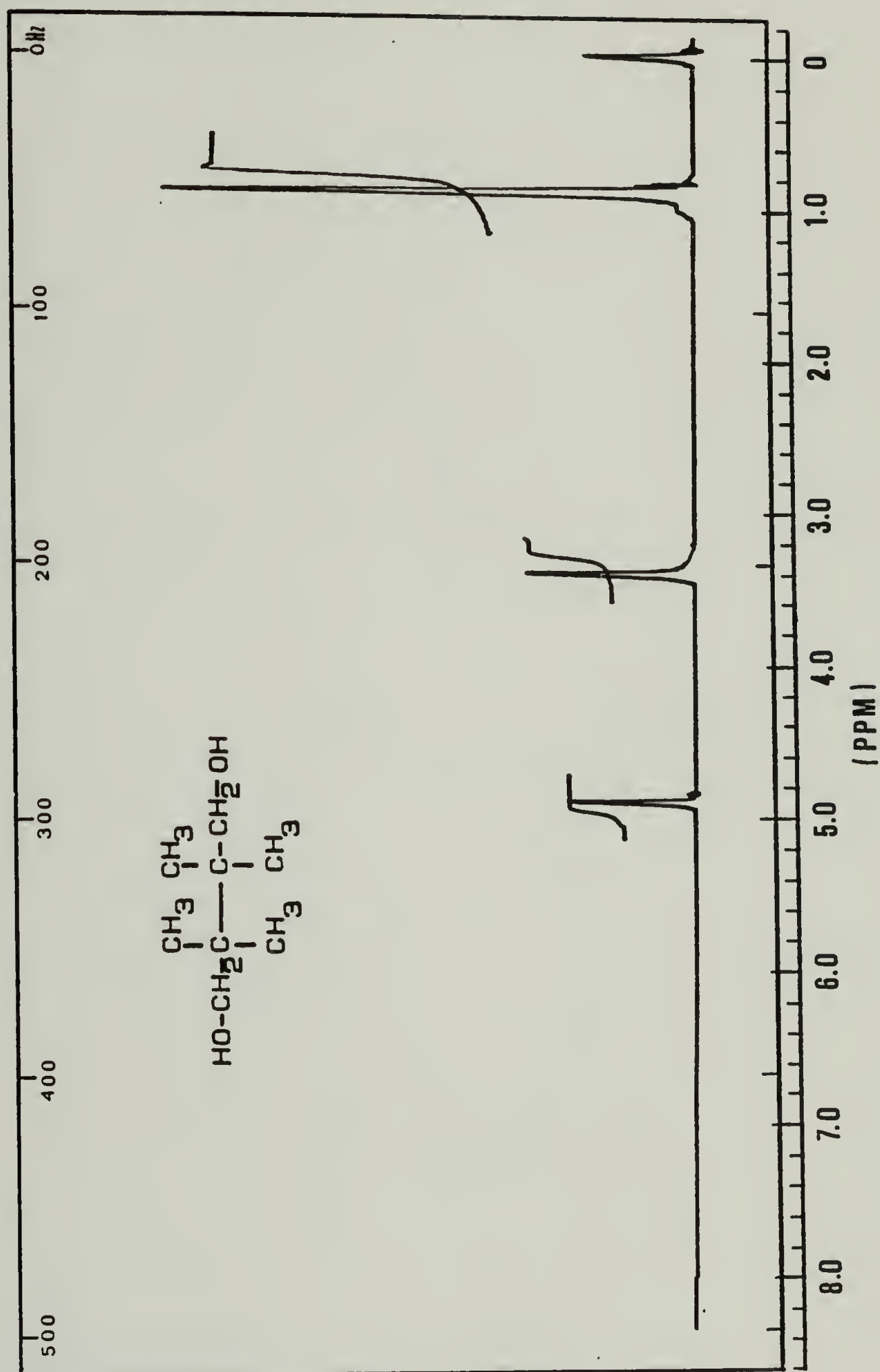


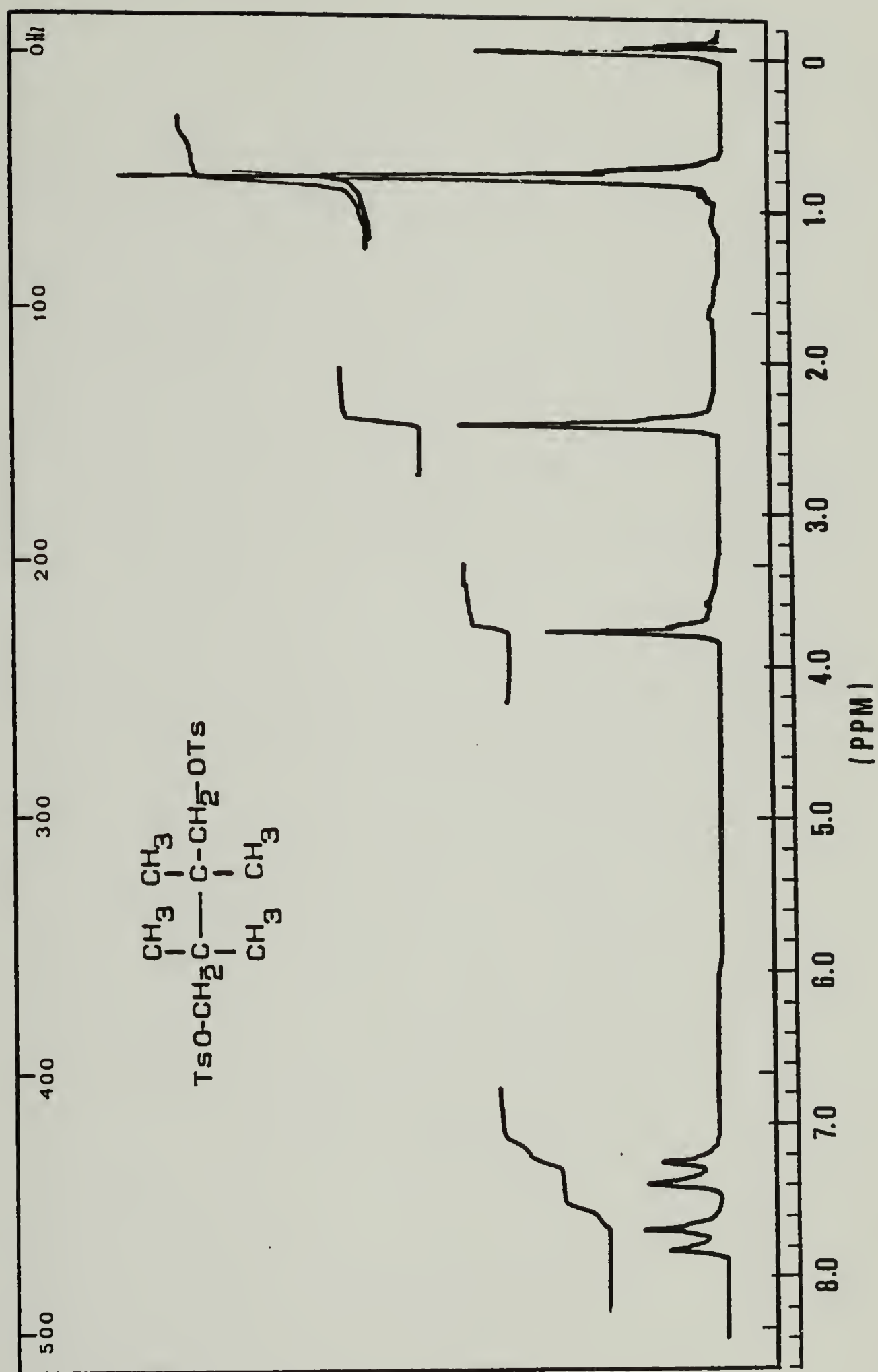


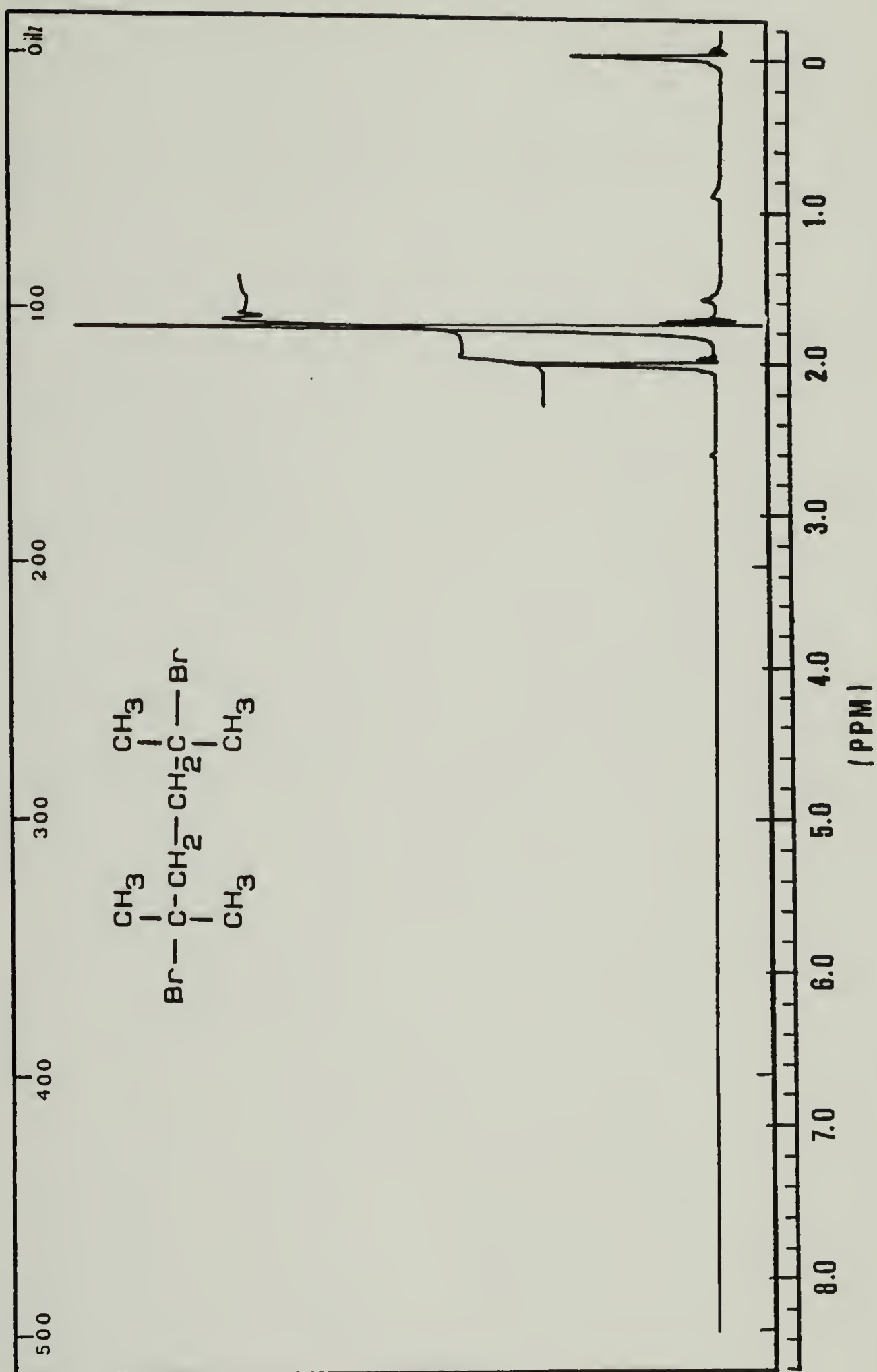
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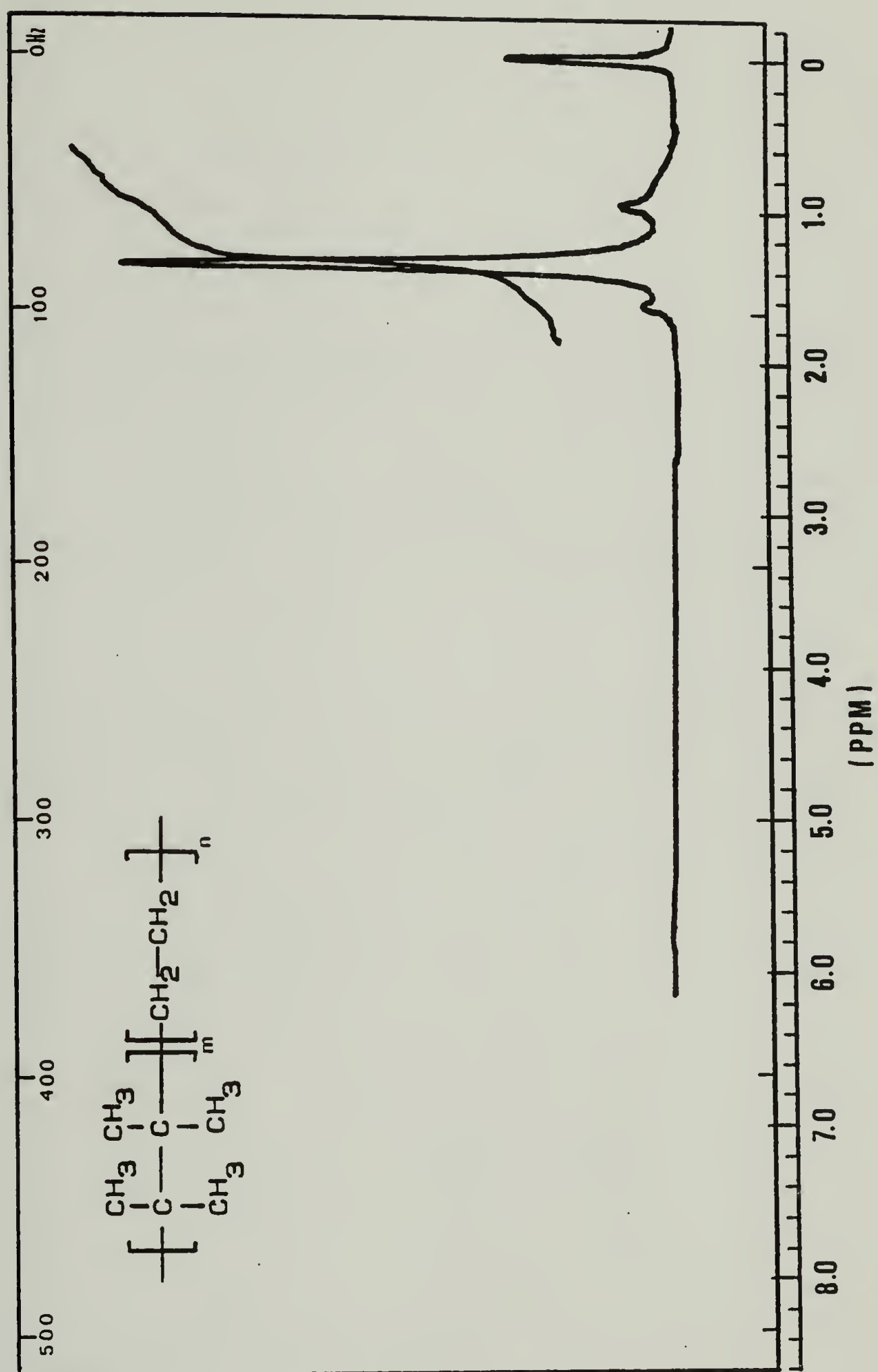
¹H NMR SPECTRA

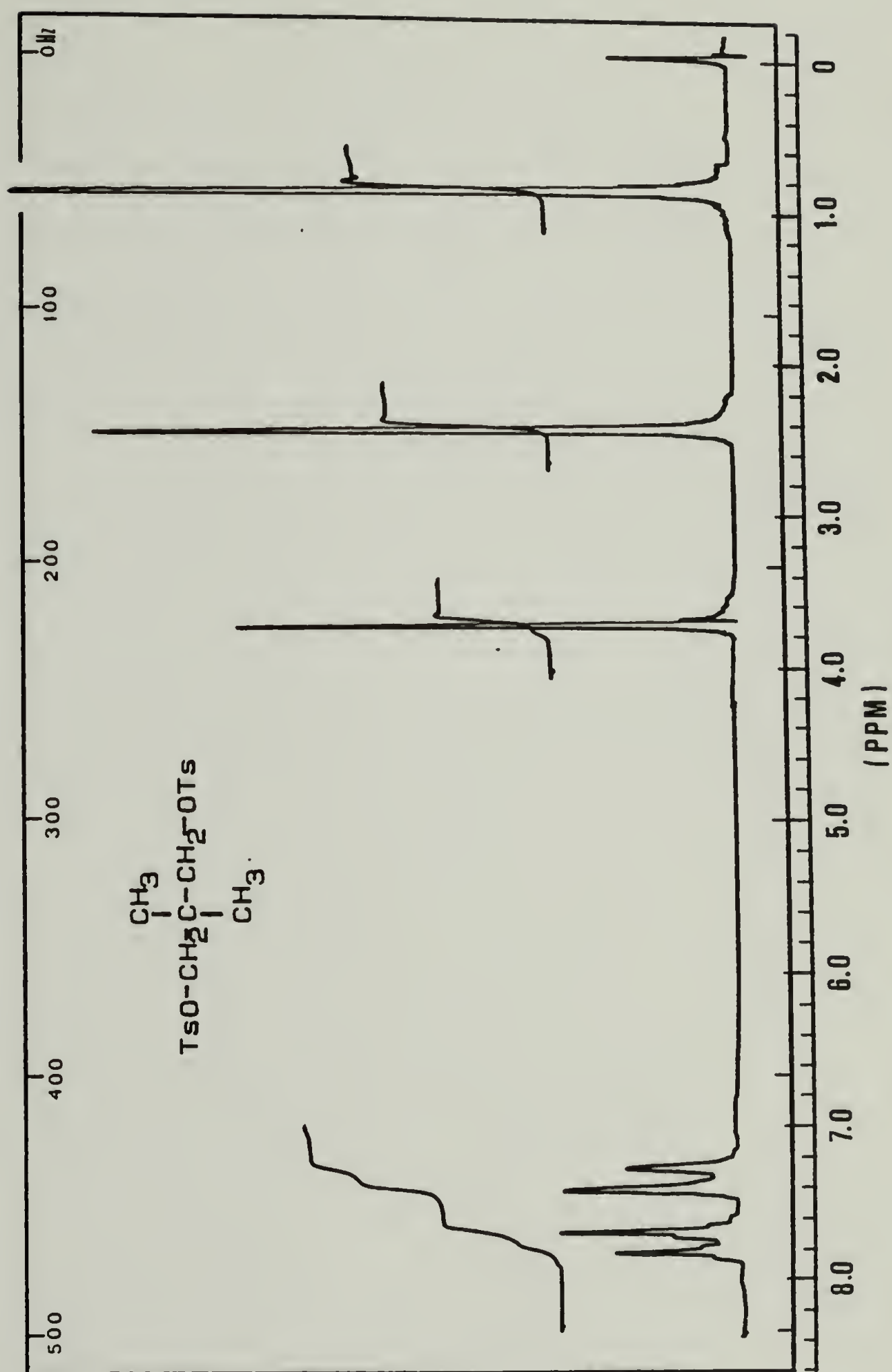


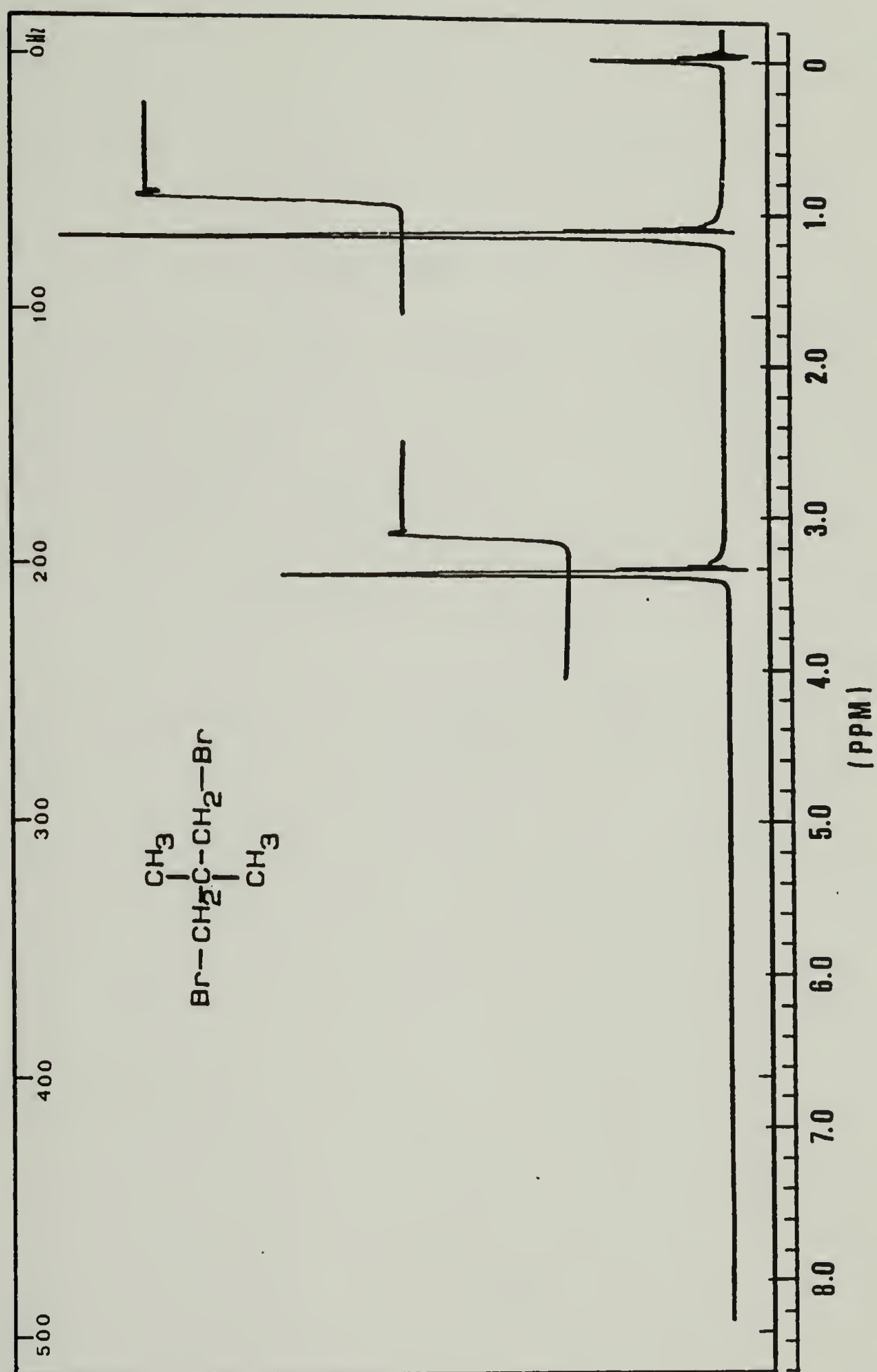


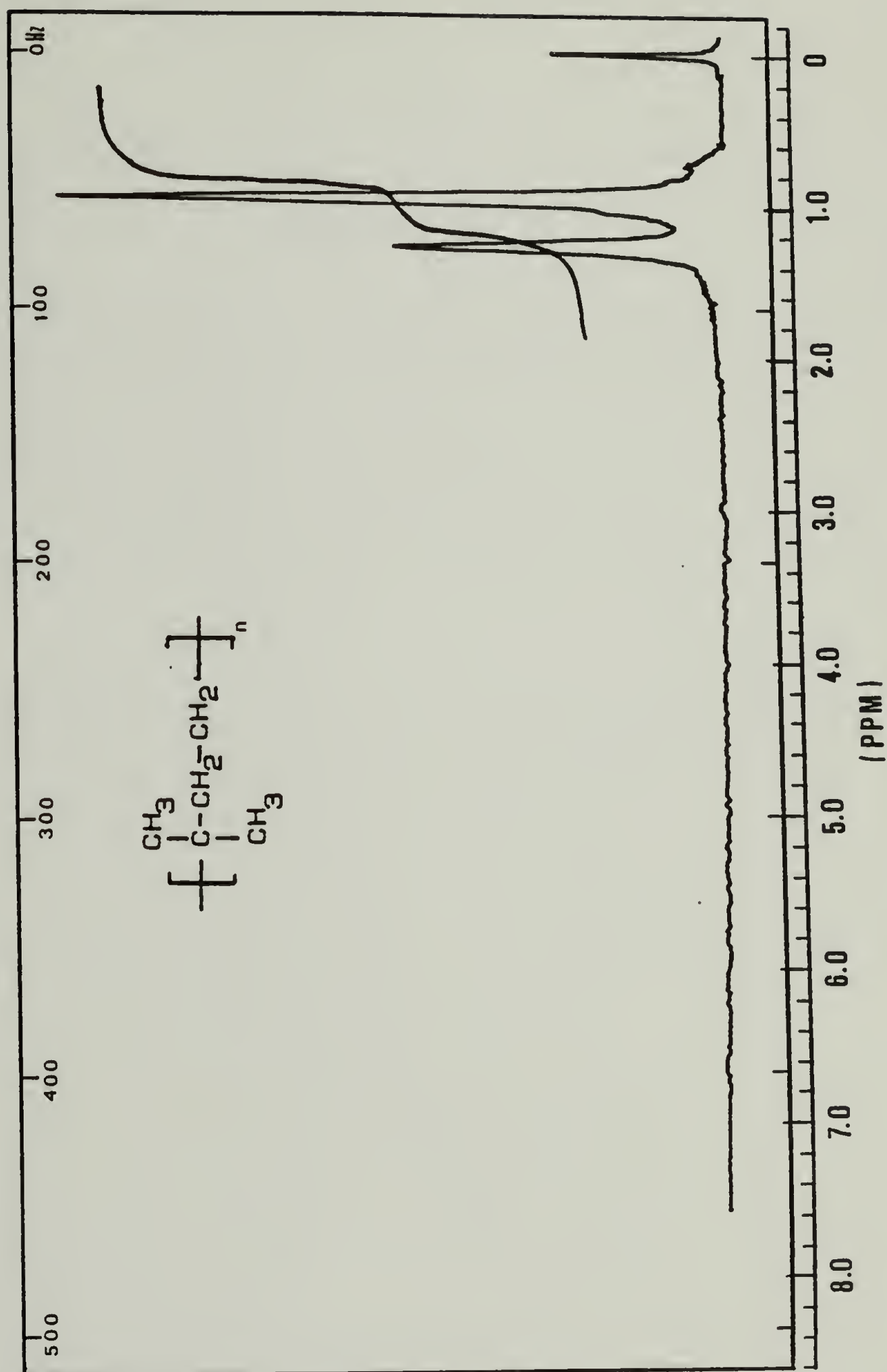


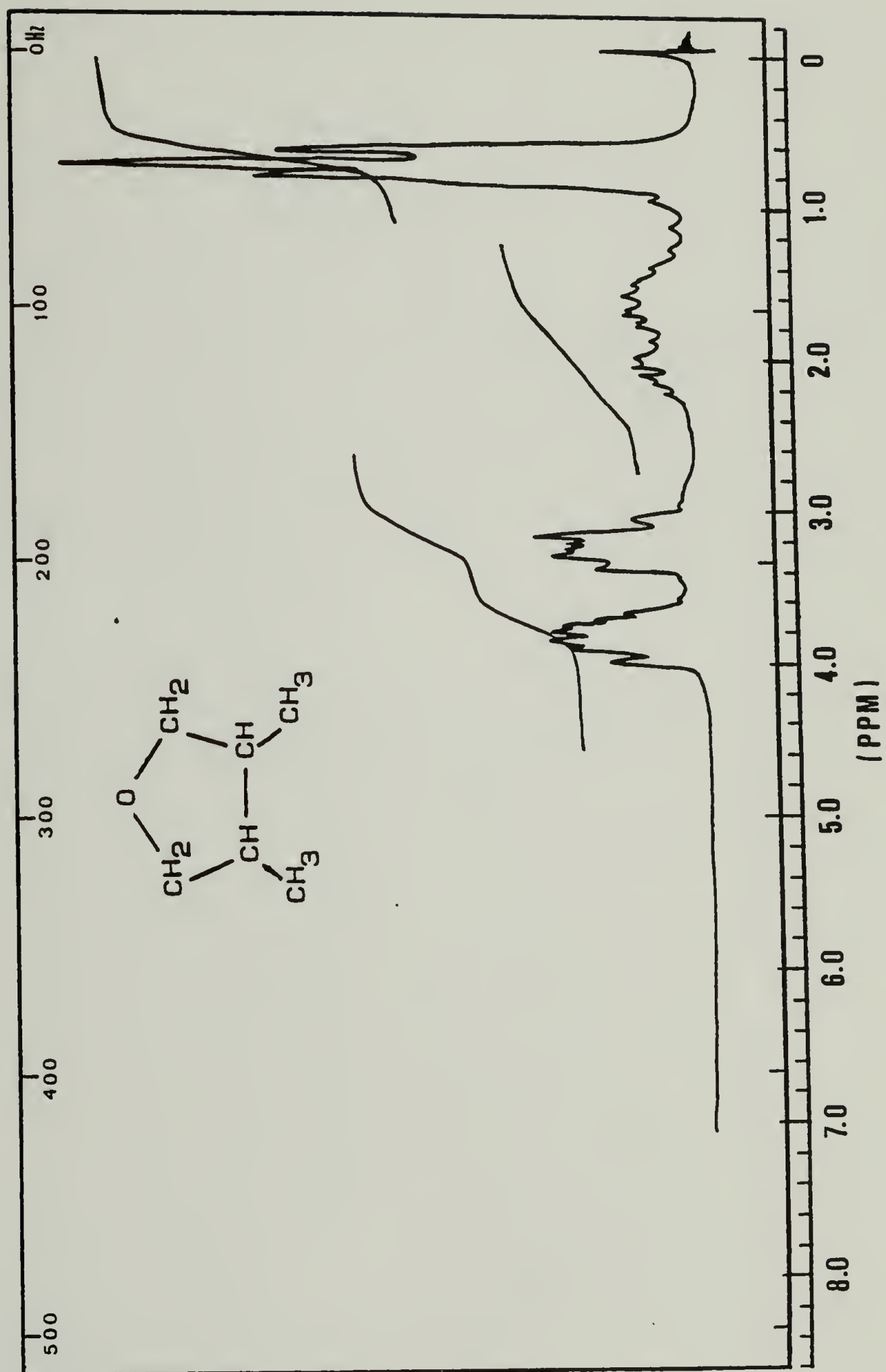












A P P E N D I X C

^{13}C NMR SPECTRA

