

1-1-1982

Polymers from functionally-substituted cyclic ethers and cyclic acetals.

Donald Albert Bansleben
University of Massachusetts Amherst

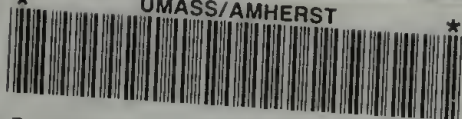
Follow this and additional works at: https://scholarworks.umass.edu/dissertations_1

Recommended Citation

Bansleben, Donald Albert, "Polymers from functionally-substituted cyclic ethers and cyclic acetals." (1982). *Doctoral Dissertations 1896 - February 2014*. 940.
<https://doi.org/10.7275/gnnb-1k82> https://scholarworks.umass.edu/dissertations_1/940

This Open Access Dissertation is brought to you for free and open access by ScholarWorks@UMass Amherst. It has been accepted for inclusion in Doctoral Dissertations 1896 - February 2014 by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.

UMASS/AMHERST



312066 0298 4214 5

**FIVE COLLEGE
DEPOSITORY**

POLYMERS FROM FUNCTIONALLY-SUBSTITUTED
CYCLIC ETHERS AND CYCLIC ACETALS

A Dissertation Presented

by

DONALD ALBERT BANSLEBEN

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

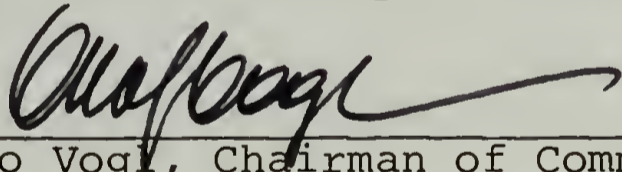
POLYMERS FROM FUNCTIONALLY-SUBSTITUTED
CYCLIC ETHERS AND CYCLIC ACETALS

A Dissertation Presented

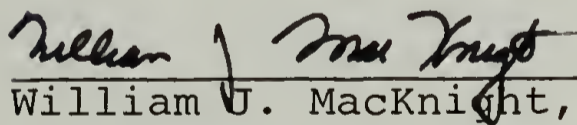
By

DONALD ALBERT BANSLEBEN

Approved as to style and content by:



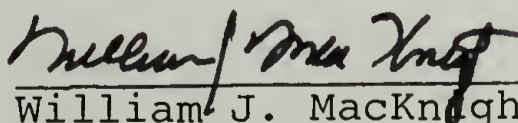
Otto Vogl, Chairman of Committee



William J. MacKnight, Member



C. Peter Lillya, Member



William J. MacKnight, Department Head
Polymer Science and Engineering

To My Parents
Who made all of this possible

and

To Janet
Whose love kept me going

ACKNOWLEDGEMENTS

The author would like to extend his sincerest appreciation and deepest gratitude to Professor Otto Vogl for his professional guidance, interest and personal support.

Appreciation is also expressed to Professor William J. MacKnight and Professor C. Peter Lillya for their suggestions and probing questions which were invaluable to the author's dissertation and professional development.

Many valued friendships were made during the course of these studies at the University of Massachusetts. In particular the author would like to thank Bill Harris, Paul Grosso, Mike Malanga and Lou Rosati for their unrelenting personal friendship and scientific cooperation.

The author also wishes to thank Dr. Shohei Yoshida of Japan for numerous stimulating scientific discussions and suggestions during his two year visit to these laboratories.

The efforts of Takeshi Kondo, a recent colleague in these laboratories, in the measurement of the thermal properties of a number of polymers prepared by the author is gratefully acknowledged. Similarly, appreciation is also expressed to Dr. David Schold at the DuPont Experi-

mental Station for kindly performing thermal analysis measurements of selected oxymethylene polymers prepared by the author.

ABSTRACT

Polymers from Functionally-Substituted Cyclic Ethers and Cyclic Acetals

(September 1982)

Donald Albert Bansleben

B.A., University of Connecticut,

M.S., University of Connecticut,

Ph.D., University of Massachusetts

Directed by: Professor Otto Vogl

Poly(alkylene oxides) containing pendant carboxylate groups separated from the main chain by a spacer-group of eight methylene units were synthesized from functionally-substituted epoxide and 1,3-dioxolane monomers.

Ester-substituted oxyethylene polymers of methyl 10,11-epoxyundecanoate and copolymers with various cyclic ethers were prepared in the presence of an aluminumalkyl-water coordination initiator system modified with acetylacetone. Poly(alkylene oxide) ionomers, polyelectrolytes and carboxylic acids were obtained by reactions on the pendant functional groups. The high molecular weight substituted poly(ethylene oxides) were characterized by spectral, thermal and dilute solution measurements.

Oxymethylene polymers containing 0.5-2 mole-percent pendant ester groups were synthesized by the cationic copolymerization of trioxane with methyl 10,11-epoxyundecanoate or 4-(1-carbomethoxynonyl)-1,3-dioxolane. A comparative study of the relative reactivities of the ester-substituted monomers with trioxane was made. The substituted 1,3-dioxolane monomer was shown to be more reactive than the substituted epoxide in ring-opening copolymerization with trioxane. Terpolymers of trioxane and 1,3-dioxolane with each of the two functional monomers were also prepared. The functional polyoxomethylenes were characterized by their spectral properties and thermal degradation behavior.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iv
ABSTRACT	vi
LIST OF TABLES	xiv
LIST OF FIGURES	xvi
Chapter	
I. INTRODUCTION	1
A. Poly(Alkylene Oxides)	3
1. General introductory remarks	3
2. Historical perspectives in epoxide polymerizations	6
3. Coordination polymerizations of functionally-substituted epoxides	13
a. Poly(alkylene oxides) with pendant halogen groups	14
b. Poly(alkylene oxides) with pendant unsaturation	18
c. Poly(alkylene oxides) with pendant nitrile groups	19
d. Poly(alkylene oxides) with pendant amino groups	21
e. Poly(alkylene oxides) with pendant hydroxyl groups	21
f. Poly(alkylene oxides) with pendant sulfone groups	22
g. Poly(alkylene oxides) with pendant amide groups	23
h. Poly(alkylene oxides) with pendant carboxylate groups	23
4. Functional poly(alkylene oxides) derived from epichlorohydrin elastomers	26
5. Oxymethylene polymers (POM)-- general introduction	27
6. Functional oxymethylene polymers	29
7. Concluding remarks on functional alkylene oxide polymers	35

B. Functional Polyolefins	36
1. General considerations	36
2. Polyolefins with pendant reactive groups	38

Chapter

II. EXPERIMENTAL SECTION	46
A. Materials	46
B. Purification of Solvents and Reagents . .	47
C. Preparation of Intermediates and Monomers	50
1. Methyl 10-undecenoate	50
2. Methyl 10,11-epoxyundecanoate . . .	52
3. 1-Dodecene oxide	53
4. 4-(1-Carbomethoxynonyl)-1,3- dioxolane (MEDOX)	55
a. 10-Formoxy-11- hydroxyundecanoic acid	55
b. 10,11-Dihydroxyundecanoic acid	56
c. Methyl 10,11- dihydroxyundecanoate	58
d. 4-(1-Carbomethoxynonyl)- 1,3-dioxolane	59
D. Coordination Polymerizations of Methyl 10,11-Epoxyundecanoate	61
1. General procedure for preparation of $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator	61
2. Polymerization of methyl 10,11- epoxyundecanoate with $\text{Al}(\text{C}_2\text{H}_5)_3/$ $\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator . .	62
a. Alternate work-up procedure for methyl 10,11- epoxyundecanoate polymeriza- tions	64
3. Copolymerizations of methyl 10,11- epoxyundecanoate with cyclic ethers using the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator	65
a. Copolymerization with ethylene oxide (EO)	65
b. Copolymerization with propylene oxide (PO)	67
c. Copolymerization with epichlorohydrin (ECH)	69
d. Copolymerization with 1-butene oxide (BO)	70

e.	Copolymerization with 4,4,4-trichloro-1-butene oxide (TCBO)	72
f.	Copolymerization with 1-hexene oxide (HO).	74
g.	Copolymerization with phenyl glycidyl ether (PGE).	76
h.	Copolymerization with oxetane (OX)	78
i.	Attempted copolymerization with tetrahydrofuran (THF)	80
E.	Polymerizations of Cyclic Ethers using the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) Initiator	81
1.	General procedure for polymerization	81
a.	Poly(ethylene oxide)	81
b.	Poly(propylene oxide)	82
c.	Poly(epichlorohydrin)	82
d.	Poly(butylene oxide)	83
e.	Poly(4,4,4-trichloro-1-butene oxide)	83
f.	Poly(1-hexene oxide)	83
g.	Poly(phenyl glycidyl ether)	84
h.	Oxetane polymerization	84
i.	Attempted tetrahydrofuran polymerization	84
F.	Modifications of Functionally-Substituted Poly(Alkylene Oxides)	84
1.	Preparation of poly(alkylene oxide) ionomers and poly-electrolytes	84
a.	Saponification of poly(methyl 10,11-epoxyundecanoate)	84
b.	Saponification of poly(methyl 10,11-epoxyundecanoate-co-ethylene oxide)	86
2.	Preparation of poly(alkylene oxide) carboxylic acids	88
a.	Poly(10,11-epoxyundecanoic acid)	88
b.	Poly(10,11-epoxyundecanoic acid-co-ethylene oxide)	89
G.	Preparation of Functional Oxymethylene Copolymers and Terpolymers	91

1.	Polymerization of 1,3,5-trioxane (TO) with (CF ₃ SO ₂) ₂ O as the initiator	91
2.	Copolymerization of trioxane (TO) and 1,3-dioxolane (DO) with (CF ₃ SO ₂) ₂ O as initiator	92
3.	Copolymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) and trioxane (TO) with (CF ₃ SO ₂) ₂ O as initiator	93
4.	Terpolymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane, trioxane and 1,3-dioxolane with (CF ₃ SO ₂) ₂ O as the initiator	95
5.	Copolymerization of methyl 10,11-epoxyundecanoate (MEU) and trioxane (TO) with (CF ₃ SO ₂) ₂ O as the initiator	96
6.	Terpolymerization of methyl 10,11-epoxyundecanoate (MEU), trioxane (TO) and 1,3-dioxolane (DO) with (CF ₃ SO ₂) ₂ O as the initiator	98
7.	Copolymerizability of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) and trioxane (TO) with (CF ₃ SO ₂) ₂ O as the initiator	99
8.	Copolymerizability of methyl 10,11-epoxyundecanoate (MEU) and trioxane (TO) with (CF ₃ SO ₂) ₂ O as the initiator	102
9.	Attempted copolymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) and 1,3-dioxolane (DO) with (CF ₃ SO ₂) ₂ O as the initiator	103
10.	Attempted polymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) with boron trifluoride etherate as the initiator	106
H.	Measurements	107
1.	General procedures and methods	107
2.	Determination of relative rates of polymerization of methyl 10,11-epoxyundecanoate (MEU) and 1-dodecene oxide (DDO) by ¹ H NMR spectroscopy	109
3.	Gravimetric determination of rate of polymerization of methyl 10,11-epoxyundecanoate (MEU) using Al(C ₂ H ₅) ₃ /H ₂ O/AcAc (1.0/0.5/1.0) as initiator	110

4.	Dilute solution viscometric measurements of poly(alkylene oxide) ionomers	111
a.	Determination of effect of added ionic solute on inherent viscosity	111
b.	Measurement of the effect of ionomer concentration on inherent viscosity	113
5.	Determination of copolymer composition for functional poly(oxymethylenes) by quantitative infrared analysis .	113
a.	Calibration of IR	113
b.	Copolymer samples	114

Chapter

III.	RESULTS AND DISCUSSION	115
A.	Objectives	115
B.	Preparation and Polymerization of Methyl 10,11-Epoxyundecanoate	116
1.	Synthesis of methyl 10-undecenoate and methyl 10,11-epoxyundecanoate .	116
a.	Characterization of 10-undecenoic acid and derivatives	123
2.	Choice of initiator for polymerization of function epoxide MEU	124
3.	Preparation of $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator	126
4.	Polymerization of methyl 10,11-epoxyundecanoate (MEU) with $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ as the initiator	130
5.	Polymerizability of methyl 10,11-epoxyundecanoate	141
C.	Copolymerization of Methyl 10,11-Epoxyundecanoate and Cyclic Ethers with $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) as the Initiator	148
1.	Preparation of poly(alkylene oxide) esters	148
2.	Characterization of methyl 10,11-epoxyundecanoate copolymers	161
3.	Homopolymerizations of cyclic ether monomers	166
4.	Characterization of cyclic ether polymers	173
D.	Modification Reactions of Poly(alkylene Oxide) Pendant Reactive Groups	177

1.	Modification reactions of poly(methyl 10,11-epoxyundecanoate)	180
2.	Characterization of poly(10,11-epoxyundecanoic acid sodium salt) and poly(10,11-epoxyundecanoic acid)	185
3.	Modification reactions of poly(methyl 10,11-epoxyundecanoate-co-ethylene oxide)	195
4.	Characterization of poly(10,11-epoxyundecanoic acid sodium salt-co-ethylene oxide) and poly(10,11-epoxyundecanoic acid-co-ethylene oxide)	201
5.	Dilute solution viscometric studies of poly(10,11-epoxyundecanoic acid sodium salt-co-ethylene oxide)	215
E.	Functionally-Substituted Oxymethylene Copolymers and Terpolymers	223
1.	Preparation of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX)	224
2.	Copolymerizations and terpolymerizations of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX)	231
3.	Attempted homopolymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane using BF ₃ etherate as the initiator	238
4.	Co- and terpolymerization of methyl 10,11-epoxyundecanoate (MEU) with trioxane	241
5.	Comparison of the copolymerization behavior of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) and methyl 10,11-epoxyundecanoate (MEU)	248
6.	Thermal analysis of functionally-substituted poly(oxymethylenes)	258
F.	Conclusions and Future Work	272
	REFERENCES	278
	APPENDIX A. INFRARED SPECTRA	292
	APPENDIX B. PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA	311
	APPENDIX C. ¹³ C NUCLEAR MAGNETIC RESONANCE SPECTRA	315

LIST OF TABLES

1.	Structures of Cyclic Oxides and Corresponding Polymers	4
2.	Copolymerizations of 4-(1-Carbomethoxynonyl)-1,3- Dioxolane (MEDOX) and Trioxane (TO) with Triflic Anhydride (TFA) as the Initiator	101
3.	Copolymerizations of Methyl 10,11-Epoxyundecanoate (MEU) and Trioxane (TO) with Triflic Anhydride (TFA) as the Initiator	104
4.	Polymerization of Methyl 10,11-Epoxyundecanoate with 5 Mole-% $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0)	112
5.	^{13}C NMR Chemical Shift Data for 10-Undecenoic Acid and Derivatives	125
6.	Polymerizations of Methyl 10,11- Epoxyundecanoate (MEU)	133
7.	Transition Temperatures of Poly(methyl 10,11- Epoxyundecanoate) Samples	142
8.	Copolymers of Methyl 10,11-Epoxyundecanoate with Cyclic Ethers	155
9.	^{13}C NMR Chemical Shift Data for Copolymers of Methyl 10,11-Epoxyundecanoate and Cyclic Ethers	163
10.	Transition Temperatures of Methyl 10,11- Epoxyundecanoate Copolymers	165
11.	Polymers of Cyclic Ethers	169
12.	^{13}C NMR Chemical Shift Data for Cyclic Ether Polymers	175
13.	Thermal Transition Temperatures for Cyclic Ether Polymers	176
14.	^{13}C NMR Chemical Shift Data for Functionally- Substituted Poly(Alkylene Oxides)	190
15.	Thermal Transition Temperatures of Functionally- Substituted Poly(Alkylene Oxide) Homopolymers	191
16.	^{13}C NMR Chemical Shift Data for Functionally- Substituted Poly(Alkylene Oxide) Copolymers	205
17.	Thermal Transition Temperatures of Functionally- Substituted Alkylene Oxide Copolymers	207
18.	Wide Angle X-Ray Diffraction Maxima of Functionally-Substituted Alkylene Oxide Copolymers	214
19.	Co- and Terpolymerizations of Functional Cyclic Acetal 4-(1-Carbomethoxynonyl)-1,3- Dioxolane	235

20.	Copolymerizability of 4-(1-Carbomethoxynonyl)- 1,3-Dioxolane (MEDOX) and Trioxane (TO)	239
21.	Co- and Terpolymerization of the Functional Cyclic Ether Methyl 10,11-Epoxyundecanoate (M ₂)	244
22.	Copolymerizability of Methyl 10,11- Epoxyundecanoate (MEU) with Trioxane (TO) . . .	246
23.	Transition Temperatures for Functionally- Substituted Oxymethylene Polymers	261

LIST OF FIGURES

1.	Synthesis of the functional epoxide methyl 10,11-epoxyundecanoate (MEU)	119
2.	Rate of epoxidation of methyl 10-undecenoate with m-chloroperbenzoic acid (m-ClPBA)	122
3.	Schematic illustration of preparation of $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator	128
4.	Polymerization of methyl 10,11-epoxyundecanoate	132
5.	^{13}C NMR spectrum of poly(MEU) backbone carbon atoms (expanded scale)	137
6.	Gel permeation chromatogram of high molecular weight poly(MEU), $\eta_{0.5\%} = 1.8$ dL/g	140
7.	DSC scans of poly(MEU) samples	143
8.	Comparative rates of polymerization for epoxides with long side chains, with and without carboxylate functional groups: (●) MEU and (▲) DDO	146
9.	Polymerization of methyl 10,11-epoxyundecanoate: polymer yield as a function of time	150
10.	Copolymerization of methyl 10,11-epoxyundecanoate (MEU) and cyclic ethers	153
11.	GPC trace of propylene oxide/methyl 10,11-epoxyundecanoate (78 mole-%/22 mole-%) copolymer	158
12.	Polymerizations of cyclic ethers with $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0).	168
13.	Preparation of poly(10,11-epoxyundecanoic acid sodium salt) from poly(methyl 10,11-epoxyundecanoate)	179
14.	Preparation of poly(10,11-epoxyundecanoic acid) by neutralization of poly(10,11-epoxyundecanoic acid sodium salt)	184
15.	Comparison of infrared spectra of functionally-substituted poly(alkylene oxides): (a) poly(methyl 10,11-epoxyundecanoate), (b) poly(10,11-epoxyundecanoic acid sodium salt) and (c) poly(10,11-epoxyundecanoic acid)	187
16.	DSC scans of poly(methyl 10,11-epoxyundecanoate) (curve a) and poly(10,11-epoxyundecanoic acid) (curve b)	195
17.	Preparation of poly(alkylene oxide) ionomer	197

18.	Preparation of poly(ethylene oxide-co-10,11-epoxyundecanoic acid)	200
19.	Comparison of infrared spectra of functionally-substituted poly(alkylene oxide) copolymers: (a) poly(ethylene oxide-co-methyl 10,11-epoxyundecanoate), (b) poly(ethylene oxide-co-10,11-epoxyundecanoic acid sodium salt) and (c) poly(ethylene oxide-co-10,11-epoxyundecanoic acid)	203
20.	DSC scans of functionally-substituted alkylene oxide copolymers: (a) poly(ethylene oxide-co-methyl 10,11-epoxyundecanoate), (b) poly(ethylene oxide-co-10,11-epoxyundecanoic acid sodium salt) and (c) poly(ethylene oxide-co-10,11-epoxyundecanoic acid)	210
21.	Wide angle x-ray diffraction (WAXD) scans of functional alkylene oxide copolymers: (a) poly(ethylene oxide-co-methyl 10,11-epoxyundecanoate) and (b) poly(ethylene oxide-co-10,11-epoxyundecanoic acid sodium salt)	212
22.	Effect of alkylene oxide ionomer concentration on dilute solution viscosity	219
23.	Effect of added ionic solute (NaCl) on dilute solution viscosity of poly(alkylene oxide) ionomer	222
24.	Preparation of the functional dioxolane monomer: 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX)	226
25.	Rate of the acetalization of methyl 10,11-dihydroxyundecanoate (MDHU)	236
26.	Copolymerization and terpolymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX)	234
27.	Preparation of functionally-substituted poly(oxymethylenes) based on methyl 10,11-epoxyundecanoate	243
28.	Yield of ester-substituted poly(oxymethylene) as a function of comonomer feed composition: (▲) 4-(1-carbomethoxynonyl)-1,3-dioxolane, (●) methyl 10,11-epoxyundecanoate	250
29.	Comparison of solution viscosities for functional oxymethylene copolymers prepared from (▲) 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) and (●) methyl 10,11-epoxyundecanoate (MEU)	253
30.	Observed induction times in the preparation of functional oxymethylene copolymers: (▲) TO/MEDOX and (●) TO/MEU	256
31.	Comparison of DSC scans of modified oxymethylene co- and terpolymers: (a) TO/DO, (b) TO/MEDOX, (c) TO/MEU/DO and (d) TO/MEDOX/DO	260

32.	TGA and derivative curves of untreated TO/DO copolymer	265
33.	TGA and derivative curves of untreated TO/MEDOX copolymer	267
34.	TGA and derivative curves of untreated TO/MEU/DO terpolymer	269
35.	TGA curves of untreated TO/DO copolymer (—), TO/MEDOX copolymer (----), and TO/MEU/DO terpolymer (-·-·-).	271

C H A P T E R I

INTRODUCTION

This dissertation describes the synthesis and ring-opening polymerizations of a functionally-substituted cyclic ether, methyl 10,11-epoxyundecanoate and cyclic acetal, 4-(1-carbomethoxynonyl)-1,3-dioxolane. The thrust of this research, therefore, was in the preparation and characterization of alkylene oxide polymers, in particular those based on an oxyethylene or oxymethylene backbone, containing pendant ester, carboxylate or carboxylic acid groups. The functional groups were separated from the backbone by a flexible spacer-group containing eight methylene units. This work was intended to build upon previous investigations¹⁻³ of functionally-substituted poly(alkylene oxides) within this research group. Earlier studies were concerned with the preparation and properties of alkylene oxide polymers where the pendant functional groups were attached directly to the polymer backbone. The underlying interest of this research group in functionally-substituted poly(alkylene oxides) lay in their potential as novel ionomer, polyelectrolyte and drug carrier systems.

The general area of functional polymers is one of rapidly growing interest. The recognition that properties intrinsic to a certain polymer structure can be modified, enhanced or tailored to meet specific and specialized end uses has spurred much research in the preparation of new functional monomers and their polymerization as well as in the area of reactions on polymers. Accordingly, it is the expressed intent of this introduction to review areas pertinent to the theme of this dissertation.

Beginning in Section A.1, the important members in the alkylene oxide family are briefly introduced. Section A.2 highlights the key developments and advances in the polymerization of epoxide monomers, paying particular attention to the evolution of initiator systems useful for the preparation of high molecular weight polyethers. In Section A.3, a comprehensive review of the coordination polymerization of functional epoxide monomers is presented, including previous studies emanating from these laboratories. Section A.4 concludes the review of functional oxyethylene polymers by focusing on the modification reactions of epichlorohydrin (ECH) elastomers.

A general introduction to oxymethylene polymers, or polyacetals, the second class of alkylene oxide polymers investigated in this dissertation, is given in Section A.5. Studies concerned with the preparation of

functional polyoxymethylenes (POM) are reviewed in Section A.6.

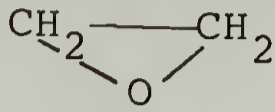
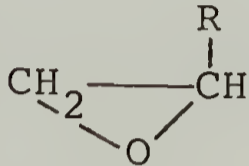
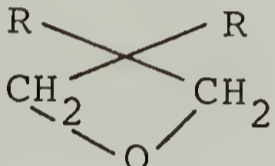
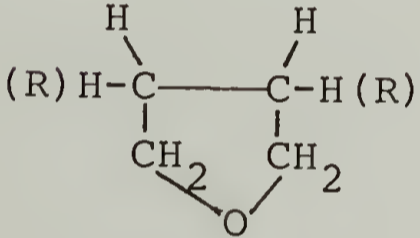
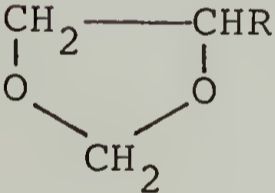
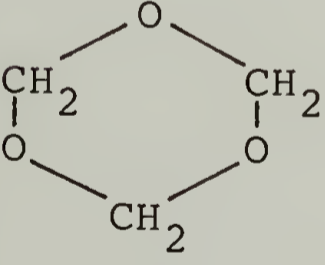
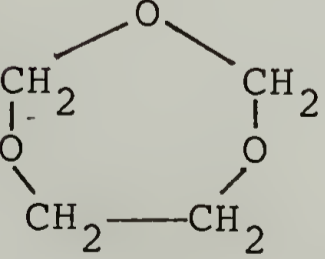
Section B is devoted entirely to a discussion and review of efforts to polymerize polar-substituted olefinic monomers. Both terminally unsaturated and internal olefin monomers are considered. In many respects, problems in the coordination polymerization of functionally-substituted olefins, the precursors to the corresponding epoxide monomers, are not unlike those encountered with the cyclic ethers. It was of interest therefore to include such a review as the final chapter in the Introduction.

A. Poly(Alkylene Oxides)

1. General introductory remarks. A considerable body of knowledge exists concerning the polymerization of cyclic ether and cyclic acetal monomers. Poly(alkylene oxides), prepared by the ring-opening polymerization of small and medium-sized oxygen heterocycles, continue to be of both academic interest and industrial importance.

Much of the interest in these polymers stems from the flexibility in the range of structures and properties which are possible. To illustrate the first point, Table 1 depicts the important categories of monomers and polymers in the alkylene oxide family. The range of proper-

TABLE 1
STRUCTURES OF CYCLIC OXIDES AND CORRESPONDING POLYMERS

Monomer	Polymer
	$-\text{CH}_2-\text{CH}_2-\text{O}-$
	$-\text{CH}_2-\underset{\text{R}}{\text{CH}}-\text{O}-$
	$-\text{CH}_2-\underset{\text{R}}{\text{C}}(\text{R})-\text{CH}_2-\text{O}-$
	$-\text{CH}_2-\text{CHR}-\text{CHR}-\text{CH}_2-\text{O}-$
	$-\text{CH}_2\text{O}-\text{CH}_2-\text{CHR}-\text{O}-$
	$-\text{CH}_2-\text{O}-$
	$-(\text{CH}_2-\text{O})_2-\text{CH}_2\text{CH}_2-\text{O}-$

ties encompassed by the structures in Table 1 is quite impressive, spanning the gamut from those of low molecular weight oils to high molecular weight amorphous rubbers or crystalline thermoplastics.

Considerable variation also exists in the ease of monomer and polymer synthesis. In general, the ease of polymerizability for a given heterocyclic monomer is determined by four factors:⁴ (i) ring-size, (ii) electron density at the heteroatom, (iii) the number, position and nature of substituents, and (iv) the type of initiator.

Much of the ensuing discussions in the next few sections will be devoted primarily to various aspects of substituted epoxide (3-membered rings), substituted-1,3-dioxolane (5-membered cyclic acetal, DO) and trioxane (6-membered cyclic acetal, TO) polymers and polymerizations. This approach was chosen in order to provide the necessary background information relevant to the overall theme of this investigation, while keeping the discussions of alkylene oxide polymers within manageable limits.

A number of books⁶⁻¹² and reviews^{5,13-17} may be consulted which offer more comprehensive discussions of cyclic ether and acetal polymerizations and poly(alkylene oxides) in general.

2. Historical perspectives in epoxide polymerizations.

Low molecular weight polymers of epoxides have been known for many years; these are readily obtained using ordinary acid and base initiators. Ethylene oxide (EO) and propylene oxide (PO), still perhaps the most important members of the 1,2-epoxide family, were first polymerized by Wurtz^{18,19} in 1863 and Levine and Waliti²⁰ in 1927, respectively. Since those disclosures, many other substituted epoxides have been synthesized and reported to undergo ring-opening polymerization with a variety of cationic and anionic initiators.

Among the categories of cyclic ether monomers shown in Table 1, the epoxides are unique in terms of their overall reactivity--no other cyclic ether monomer can be polymerized by both a cationic or anionic mechanism.²¹ It is by virtue of a large ring-strain energy of 13 kcal/mole²² that epoxides are very reactive.

The high reactivity of epoxides toward acid or base-initiated ring-opening polymerization is usually balanced, however, by an assortment of molecular weight limiting side-reactions. The latter can include chain transfer processes, cyclic oligomer formation (cationic polymerization only)²³ and/or chain-termination reactions of propagating species with initiator fragments. Nevertheless, low molecular weight poly(alkylene oxides)

have been well-suited for applications in the surfactant,²⁴ lubricant, pharmaceutical, cosmetic and polyurethane industries.

In 1933, Staudinger²⁵ was the first to demonstrate that an epoxide, specifically EO, could be polymerized to high molecular weight with oxides of calcium, strontium or zinc. Perhaps even more importantly, the dependence of polymer properties on molecular weight was first demonstrated in this study.²⁶ Nearly 25 years passed, however, before a high molecular weight poly(alkylene oxide) was commercialized. That polymer was poly(EO), commercialized by the Union Carbide Corp.²⁷ in 1957, after Hill and Bailey²⁸ developed highly active initiators based on carbonates and amides of calcium.

The development of a new generation of initiators for the polymerization of epoxides to high molecular weight began with the report by Pruitt and Baggett,^{29,30} who found that the reaction product of ferric chloride (FeCl_3) with PO could be used to polymerize PO to both a crystalline stereoregular (isotactic) form of high molecular weight and an amorphous, rubbery elastomer. The disclosures by Pruitt and Baggett prompted Price and Osgan³¹ to investigate the mechanism and stereochemistry of (1-)PO polymerization with the iron

system and solid potassium hydroxide. Salient features of Price's proposed mechanism with the $\text{FeCl}_3\text{-PO}$ initiator included: (1) coordination of the epoxide with a single metal atom and growth of the polymer through a 4-membered transition state, (2) ring-opening at the secondary carbon atom of the epoxide ring, (3) front-side attack of the propagating chain on a newly coordinated monomer, resulting in retention of configuration at the ring-opening asymmetric carbon and (4) possible racemization of the asymmetric center during ring-opening under some conditions due to carbonium ion formation (cationic polymerization). The latter claim was made to account for an optically inactive poly(PO) fraction. Elegant mechanistic studies by Vandenberg³²⁻³⁵ and subsequent studies by Price³⁶⁻³⁸ have since shown most of the details of the proposed mechanism to be incorrect. Despite the shortcomings of the mechanism described above, Price is credited as the first to recognize the ability of cyclic ethers to undergo coordination-type polymerization.

The greatest advances in the development of coordination initiators for the preparation of high molecular weight epoxide polymers are largely attributed to Vandenberg³⁴, Furukawa and Tsuruta.^{42,43} Novel organometallic initiators based on the reaction products of aluminum,^{39,40} zinc⁴¹⁻⁴³ or magnesium⁴⁴ alkyls with water

or alcohols were found to be highly active and effective for the polymerization and copolymerization of a variety of epoxide monomers. Of particular significance was the ability of these modified organometallic compounds to initiate the stereospecific and/or stereoelective polymerization of substituted epoxides. Examples of effective initiator compositions included $\text{AlEt}_3\text{-}0.5\text{H}_2\text{O}$, $\text{ZnEt}_2\text{-}1.0\text{H}_2\text{O}$, and $\text{MgEt}_2\text{-}1.0\text{H}_2\text{O}$.

In another independent study, Colclough⁴⁵ also found that $\text{Al}(\text{CH}_3)_3$ must be reacted with water in order to produce an initiator of high activity for PO polymerization, particularly for the preparation of crystalline poly(PO).

The non-activated alkyls of aluminum, zinc and magnesium were also reported⁴⁶⁻⁴⁹ to polymerize EO and PO. However, the poly(alkylene oxides) are generally obtained in significantly lower yields and molecular weights using organometallic compounds alone.³⁴

Vandenberg also found that the activity of the partially-hydrolyzed aluminumalkyls could be improved further by additional modification with a stoichiometric amount or less of a chelating agent.^{35,50} Acetylacetone⁵¹ (2,5-pentanedione, AcAc) has been the most widely studied and versatile of the chelating agents, which preferably are capable of forming five or six-

membered rings by coordination of unshared electrons with aluminum. The list of other possible chelating agents, generally difunctional, is long and includes: diketones, ketoacids, hydroxyketones, hydroxyaldehydes, hydroxyesters, dicarboxylic acids and esters, dialdehydes, ketoximes, dialdehyde monooximes, dioximes, nitro and dinitroso compounds.⁵⁰ The modified aluminumalkyl initiators have since been recognized as the most versatile initiator systems for the polymerization of epoxides, cyclic ethers and lactones to polymers of high molecular weight.

Despite the technological success and widespread use of partially-hydrolyzed organometallic initiators, significant gaps remain in understanding the nature of the active site and details of the mechanism by which epoxides (and other cyclic ethers) are polymerized. Certain common features, however, have been found in all of these initiators and are considered essential for good activity.

Vandenberg³⁵ has noted that the partially hydrolyzed aluminum, zinc and magnesium initiators contain metal-oxygen-metal groupings⁵²⁻⁵⁵ as well as residual metal-alkyl bonds. The presence of metal-oxygen-metal groupings is a key feature of a mechanism³⁵ for epoxide polymerization by the modified aluminum initiators which

has been proposed by Vandenberg. Equally important was his finding that all monosubstituted and symmetrically disubstituted epoxides polymerize with inversion of configuration at the ring-opening carbon atom, regardless of the propagation mechanism (cationic, anionic, or coordination). In the case of coordination polymerization, the latter finding suggested that a coordination mechanism involves more than one metal atom in the active site. The true identity of the active initiator is, however, still unknown.⁵⁶

The partially-hydrolyzed aluminumalkyls and their chelate-modified counterparts have received a great deal of attention because of their general versatility. Interestingly, but perhaps not unexpected, the $\text{AlR}_3\text{-H}_2\text{O}$ and AcAc-modified $\text{AlR}_3\text{-H}_2\text{O}$ initiators are believed to operate by different mechanisms. Studies by Furukawa^{57,58} and Vandenberg³⁵ have indicated that polymerizations initiated by the aluminumalkyl-water system may involve propagation by both a simple cationic mechanism as well as a coordination mechanism. In subsequent investigations, Saegusa presented evidence that both mechanisms were operative in the polymerization of ECH with $\text{AlR}_3\text{-H}_2\text{O}$,⁵⁹ while Price concluded from his copolymerization studies on aryl-substituted glycidyl ethers and cyclic ethers that the $\text{AlR}_3\text{-0.5H}_2\text{O}$ system exhibited a considerable degree of

Lewis acid character.⁶⁰ The partially hydrolyzed aluminum-alkyls thus appear to exhibit a "dual nature."⁶¹

By their modification with chelating agents, the partially-hydrolyzed aluminumalkyls are claimed to polymerize epoxides through a coordinated-anionic mechanism.^{34,35} One proposed function of the chelating agent was to block the fourth coordinate site of aluminum, thus minimizing the possibility of cationic polymerization and allowing the fifth and/or sixth coordinate positions of aluminum to function in a coordination propagation step.^{35,61}

Although many questions are at present still unresolved, efforts have continued in the development of new generations of modified organometallic initiators. Prominent examples include binary metal compositions of the general formula $[(RO)_2Al-O-M_t-O-Al(OR)_2]_n$,⁶²⁻⁶⁴ where M_t is a bivalent metal such as zinc, cobalt, or other transition metals and a chelate type initiator of the general formula $AlR_2AcAc-0.5H_2O-ZnR_2$,⁶⁵ where AcAc is the chelating agent. The first initiator composition mentioned, i.e., the bimetallic μ -oxo-alkoxides, was developed by Teyssié and coworkers, and has also been shown to give living polymers from lactones.

In the coordination polymerizations using the initiator systems already described, the concentration of

active sites must be small.⁶¹ Chain transfer reactions which plague ordinary cationic and anionic polymerizations of epoxides appear to be insignificant. The most convincing evidence in support of the two foregoing conclusions is the fact that many alkylene oxide polymers and copolymers can be prepared in high molecular weight. Of the specific systems reviewed, however, no evidence has been found to suggest that these are living polymerizations.

The interesting and useful properties of high molecular weight poly(alkylene oxides) have undoubtedly contributed to continuing efforts to elucidate the mechanisms of epoxide polymerization, to determine the nature and identity of active sites, and in the development of new initiators and epoxide monomers.

3. Coordination polymerizations of functionally-substituted epoxides. The majority of reports in the literature dealing with the coordination polymerization of epoxide monomers have focused on EO, PO, and ECH.

ECH is perhaps the best-known functionally-substituted epoxide. It can be polymerized in high molecular weight to a crystalline thermoplastic^{66,67} or an amorphous rubber⁶⁸ and has a reactive chlorine substituent. Amorphous poly(ECH) is particularly

interesting as it can be vulcanized (crosslinked) to a solvent-resistant elastomer. The copolymer of epichlorohydrin and ethylene oxide, prepared with an AcAc modified $\text{AlR}_3\text{-H}_2\text{O}$ initiator; has also been prepared commercially.⁶⁹ The copolymer can also be vulcanized and offers excellent low temperature resiliency.⁷⁰

In anticipation of preparing new polyether elastomers or thermoplastics with useful mechanical and physical properties, polymerizations of other functionally-substituted epoxides by coordination initiators have been gaining in number. A review of such efforts is presented in the remainder of this Section, including past and ongoing research in these laboratories.

a. Poly(alkylene oxides) with pendant halogen groups. ECH remains the most widely investigated and only monomer of the epihalohydrin family to achieve commercial importance. The remaining members, however, have also been polymerized in both random or stereoregular configurations by coordination initiators and were also copolymerized.

Epifluorohydrin has been polymerized to a highly crystalline material^{61,67} which melts at 68°C with the $\text{FeCl}_3\text{-PO}$ initiator, or to an amorphous polymer with the Vandenberg initiator.⁶⁸ Attempts to polymerize epichlorohydrin stereospecifically with the $\text{FeCl}_3\text{-PO}$ initiator or

an analagous complex prepared from FeCl_3 and epichlorohydrin were unsuccessful.⁷⁰ No mention was made in Vandenberg's original patent on epihalohydrin polymers about the polymerizability of epiodohydrin with modified aluminumalkyl initiators. The remaining member in the halomethyl epoxide family, epibromohydrin, was reportedly polymerized to a mixture of crystalline and amorphous polymer fractions with the $\text{Al}(\text{i-Bu})_3 \cdot 0.5\text{H}_2\text{O}$ initiator.

Kambara and Takahashi⁷² studied the coordination polymerization of 2-chloromethylpropylene oxide and 1,1-bis-chloromethylethylene oxide, analogs of isobutylene oxide. Various aluminumalkyl/transition metal acetylacetonate systems as well as the $\text{AlEt}_3 \cdot 0.5\text{H}_2\text{O}$ initiator were employed. The high molecular weight polymer obtained from 1,1-bis-chloromethylethylene oxide was found to be highly crystalline, with physical properties similiar to those of the next higher homologue, poly(3,3-bis-chloromethyloxacyclobutane). Surprisingly, the less symmetric 2-chloromethylpropylene oxide could also be polymerized to a crystalline polyether with 4 mole-% of a AlEt_3 /oxovanadium bis-AcAc initiator. The nature of the initiator systems such as the latter is also of interest here. Vandenberg has proposed³⁵ that the AlR_3 /metal-AcAc mixture may react and form the chelated aluminumalkyl type initiators described in Section 2, especially if adven-

titious traces of moisture were present.

The copolymerization of ECH with THF using the $\text{AlEt}_3\text{-H}_2\text{O}$ initiator has been studied by Furukawa and coworkers.⁷³ Specifically, copolymerization reactivity ratios r_1 and r_2 were determined. The results ($r_{\text{ECH}}=0.5\pm.3, r_{\text{THF}}=20\pm5$) indicated that the THF-ECH copolymer was blocky in nature, and contained long blocks of poly(THF). In addition, ECH homopolymer was also found. On that basis it was concluded that two different propagation sites may exist in the initiator: i.e. one which favors propagation of ECH monomer, and the other favoring THF monomer.

The polymerizability of several ring-substituted phenylglycidyl ethers, including o-chlorophenyl-, p-chlorophenyl-, and 2,4,6-trichlorophenylglycidyl ether has been examined.⁷⁴ Readily crystallizable polyethers were obtained from the $\text{FeCl}_3\text{-PO}$ initiated polymerization of the monochloro derivatives. The bulkier 2,4,6-trichlorophenylglycidyl ether derivative was successfully polymerized to high molecular weight with an organozinc-water initiating system, but showed a reduced ability to crystallize and was lower melting.

Gurgiolo and McAda of Dow Chemical have synthesized several halomethylvinylglycidyl ether monomers⁷⁵ and prepared vulcanizable elastomeric homopolymers and

copolymers⁷⁶ using the AcAc-modified $\text{AlR}_3/\text{H}_2\text{O}$ initiator. Particularly interesting was the fact that the elastomeric compositions could be vulcanized using the zinc oxide-magnesium oxide (ZnO-MgO) method often utilized for vulcanization of Neoprene (or poly(2-chloro-1,3-butadiene)). Such a system is ineffective in the crosslinking of poly(ECH) because of the sluggish reactivity of the primary chlorine atoms. All of the aforementioned polymers were readily vulcanized without the use of sulfur or the need for highly reactive crosslinking agents such as diamines.

Halogenated epoxides such as 4,4,4-trichloro-1,-butene oxide and the dehydrochlorinated analog, 1,1-dichloro-3,4-epoxy-1-butene have also been polymerized in the presence of the $\text{Al}(\text{i-Bu})_3/\text{H}_2\text{O}/\text{AcAc}$ (1/0.5/1) initiator system.⁷⁷ Both monomers were found to be considerably less reactive than ECH with the coordinate-anionic initiator, and could not be vulcanized through the pendant chlorine atoms. The functional haloepoxides were found to be quite reactive in copolymerizations with PO. Terpolymerization with PO and allylglycidyl ether gave compositions which could be vulcanized through the pendant unsaturated units.

More recently, Vandenberg has described^{78,79} the preparation of polymers and copolymers derived from the

cis- and trans-isomers of 1,4-dichloro-2,3-epoxybutane. The cis-isomer produced a crystalline (racemic) diisotactic polymer (m.p. 235°C, $T_g=95^\circ\text{C}$) when polymerized cationically with $\text{Al}(\text{i-Bu})_3 \cdot 0.7\text{H}_2\text{O}$ at -78°C . The diisotactic polyether from the cis-isomer was shown to crystallize in a helical chain conformation, whereas the trans-isomer, although crystalline, did not. The former cis-ditactic polyether is of potential commercial interest due to a combination of attractive properties and the relatively inexpensive raw materials from which it is derived, i.e. chlorine, butadiene, and oxygen.

b. Poly(alkylene oxides) with pendant unsaturation. Butadiene monoxide, the simplest epoxide monomer with pendant olefinic unsaturation can be polymerized in high molecular weight to stereoregular or amorphous form, using modified aluminumalkyl initiators.⁵⁰ The stereoregular, crystalline poly(butadiene monoxide) reportedly has properties similar to low density polyethylene.³⁴ Polymerization was shown by IR analysis to have occurred solely through the epoxide ring.

Of greater importance, however, has been the copolymerization of unsaturated epoxide monomers with other alkylene oxides, in particular PO. Sulfur-curable elastomeric copolymers of PO and allylglycidyl ether (5 mole-%) have been commercially available since 1972.⁸⁰⁻⁸² The

copolymer, prepared in the presence of an $\text{AlR}_3/\text{H}_2\text{O}/\text{AcAc}$ initiator, is amorphous and has the same composition as the comonomer charge. Excellent low temperature properties combined with good heat-aging resistance have led to the use of the cured elastomer in specialty applications such as automotive engine-mounts.⁸³

Fundamental studies of the copolymerizability of PO with butadiene oxide and diallyl monoxide in the presence of AlEt_3 have also been reported.⁸⁴ New poly(alkylene oxides) structures containing pendant side-chain unsaturation have been prepared by the coordination polymerization of 3,3-dimethyl-4,5-epoxy-1-pentene,⁸⁵ and copolymerization⁸⁶ of THF with diallyl monoxide. Both olefinic-substituted elastomers were reportedly suitable for vulcanization, while the unsaturated side groups on the homopolymer were also used as sites for grafting reactions.

c. Poly(alkylene oxides) with pendant nitrile groups. A number of epoxide monomers containing pendant nitrile groups have been prepared and their polymerization reactions investigated. The general aim of such efforts was to prepare alkylene oxide elastomers with properties which are superior to those of the well-known nitrile rubber (copolymers of butadiene and acrylonitrile). Unfortunately these efforts have met with mixed success.

Wei and Butler⁷⁷ have attempted the homopolymerizations of glycidonitrile, dimethylglycidonitrile, tetracyanoethylene oxide and epicyanohydrin using the $\text{Al}(\text{i-Bu})_3/0.5\text{H}_2\text{O}/\text{AcAc}$ initiator. The polymerizations of the polar epoxides were reported to be unsuccessful in all cases. No attempts were made to try and explain the inability of the α -epoxynitriles to polymerize, although the authors concluded that the method^{87,88} used to prepare the epicyanohydrin monomer had in fact yielded an unpolymerizable cyclic dimer.

A group of researchers at Uniroyal successfully homo-, co- and terpolymerized various cyanoepoxides in which the polar nitrile group was not directly substituted on the epoxy ring.⁸⁹ Substituted epoxy monomers investigated included β -cyanoethyl glycidyl ether, cyanomethyl glycidyl ether, β -chloro- β -cyanomethyl glycidyl ether, and 3,4-epoxyvaleronitrile. An attempted homopolymerization of epicyanohydrin failed to yield any polymer. It was noted that polymerizations of the polar monomers required larger quantities of the $\text{Al}(\text{i-Bu})_3/0.5\text{H}_2\text{O}/0.5\text{AcAc}$ initiator as compared to polymerizations of other alkylene oxides such as ECH or PO. In view of the recognized ability of nitrile groups to complex with available coordination sites on aluminumalkyls,⁹⁰ it was then proposed that similar interactions were responsible for the

reduced activity of the modified organometallic initiator. Copolymerizations of several of the epoxynitriles with ECH produced elastomers which were readily vulcanized through the pendant chloromethyl groups. Terpolymerization with EO or PO and allyl glycidyl ether gave elastomeric compositions which could be cured with a metal oxide system.

At present, no successful polymerizations of epicyanohydrin have been reported in the literature.

d. Poly(alkylene oxides) with pendant amino groups. Vandenberg has described⁹¹ the preparation of polymers of amino-epoxides and their copolymers with other alkylene oxides. Quaternization of the pendant amine groups gave cationic polyelectrolytes which were reported to be useful as flocculating agents.

e. Poly(alkylene oxides) with pendant hydroxyl groups. Poly(glycidol), an alkylene oxide polymer with pendant hydroxy groups, cannot be prepared in high molecular weight by the ring-opening polymerization of 2,3-epoxy-1-propanol. An attempt to polymerize the hydroxy-substituted epoxide with the $\text{AlR}_3\text{-H}_2\text{O}$ initiator gave a polymer with a molecular weight less than 2000.⁹²

An interesting method has been described in the patent literature,⁹³ however, for the preparation of high molecular weight homo- and copolymers of glycidol. The

method involves the polymerization (or copolymerization) of the trimethylsilylether of glycidol with the $\text{AlEt}_3\text{-0.5 H}_2\text{O}$ initiator, followed by acid-catalyzed hydrolysis of the silylether protecting group.⁹² The corresponding hydroxyl-substituted poly(alkylene oxides) are particularly interesting because of their high hydrophilic character.

Tsuruta and coworkers,⁹⁴ while studying the asymmetric selective polymerization of epoxyethyltrimethylsilane and (2,3-epoxypropoxy)trimethylsilane with a diethyl zinc/1-menthol system,⁹⁵ have prepared poly(glycidol). Very little stereoelective polymerization was found to have occurred, however, the poly(glycidol) obtained after the hydrolysis of the silylether group was found to have a viscosity-average molecular weight of 28,000.

f. Poly(alkylene oxides) with pendant sulfone groups. Epoxy cyclic sulfones have been polymerized in the presence of modified organoaluminum or organomagnesium initiators.⁹⁶ Polymers and copolymers have been prepared from 3,4-epoxysulfolane, 7-oxa-3-thiabicyclo[4.1.0]-heptane-3,3-dioxide and 8-oxa-4-thiabicyclo[5.1.0]-octane-4,4-dioxide. The polar sulfone groups in these alkylene oxide compositions were found to enhance the hydrophilic character of the polymers over unmodified polyethers.

g. Poly(alkylene oxides) with pendant amide groups. Several reports can be found in the recent literature which describe the synthesis of amide-substituted poly(alkylene oxides).

Acrylamide oxide or glycidamide was polymerized in 57% yield using a partially-hydrolyzed aluminumalkyl initiator.⁹⁷ The acidity of the initiator used was apparently further modified by the addition of a small amount of pyridine.

Interesting copolymers of N,N-disubstituted glycidamide and EO, prepared with a $\text{AlR}_3/\text{H}_2\text{O}$ initiator, have been prepared by a group of Soviet researchers.⁹⁸ These novel copolymers are reportedly being studied as a potential plasma-substitute.

h. Poly(alkylene oxides) with pendant carboxylate groups. Vandenberg⁹⁹ reported that alkyl glycidates, in particular ethyl glycidate (EG), could be polymerized to the corresponding linear polyethers with pendant ester groups. Using the $\text{AlEt}_3\text{-}0.6 \text{ H}_2\text{O}$ initiator system, crystalline homopolymers of EG having a reduced specific viscosity of ca. 0.2 dL/g were obtained from reactions conducted at -78°C . No characterization other than the melting point were cited. Copolymerization of the alkyl glycidate monomers with other alkylene oxides was not described.

Until recently, only scattered reports of the polymerizations of carboxyl-substituted epoxides have appeared. For example, a somewhat unusual copolymerization study has been reported in a Russian article.¹⁰⁰ The relative reactivity of a highly substituted epoxy-ester, methyl β,β -dimethyl glycidate, with a substituted oxetane was studied in the presence of a partially-hydrolyzed aluminumalkyl initiator.

In these laboratories, a number of recent investigations^{1-3,101-109} have been concerned with the preparation of alkylene oxide polymers and copolymers containing pendant carboxylate groups. Carboxyl-substituted polymer chains with heteroatoms in the backbone have become of interest as ionomer systems as well as for their potentially useful new properties. Since these polymers have been relatively unknown, a broad research program was initiated in these laboratories to study various aspects of their preparation and properties.

One early study focused on the incorporation of the simplest carboxyl-substituted epoxide, EG, into a polyoxymethylene backbone and led to the preparation of novel POM ionomers.^{1,101-104} The ion-containing POM investigation will be considered in the next Section in this Chapter, which deals specifically with functional oxymethylene polymers.

The cationic homopolymerization of EG and its copolymerization with THF were also examined, using triethyloxonium tetrafluoroborate (TEOFB) and superacid ester initiators.^{2,105} Relatively low molecular weight polymers were obtained in each case. Interestingly, a 1:2 EG/THF copolymer was consistently obtained for both initiator systems, even under conditions which precluded THF homopolymerization. This rather unusual behavior was explained on the basis of a reaction mechanism involving a penultimate effect during propagation.

Ester-substituted alkylene oxide copolymers of EG and cyclic ethers were also prepared in high molecular weight using the $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.3/0.5) initiator.^{2,3} Elastomeric copolymers were obtained with PO, BO, and Ox. EG was found to be relatively unreactive, however, as levels of incorporation were low (1-4 mole-%) and copolymer molecular weights and yields decreased when the concentration of EG in the feed was increased. The homopolymerization of EG with several other organometallic initiator systems, including $\text{AlEt}_3/\text{H}_2\text{O}$, $\text{ZnEt}_2/\text{CH}_3\text{NO}_2$, $\text{Al}(\text{O-iPr})_3$ and $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$, was unsuccessful. Conversion of the pendant ester groups of a PO/EG copolymer to the sodium carboxylate and carboxylic acid forms produced the first oxyethylene-based ionomers and carboxylic acids.

More recently, studies on the preparation and characterization of poly(alkylene oxide) esters in which the pendant ester groups are separated from the backbone by methylene spacer-groups were reported.^{106,107,109}

Homopolymerization of a homologous series of methyl ω -epoxyalkanoates¹⁰⁸ with the $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator revealed that polymerizability of the epoxide monomers became constant with a spacer-group length of three or more methylene units between the epoxy ring and ester group.

4. Functional poly(alkylene oxides) derived from epichlorohydrin. Nucleophilic displacement reactions on the chloromethyl groups of poly(ECH) have been studied extensively and provide another method for side-chain functionalization of alkylene oxide polymers. This method falls into the category of reactions on polymers. As some of our efforts have been concerned with the modification of poly(alkylene oxides), it appears appropriate to briefly outline the scope and diversity of other investigations.

Functional side-groups introduced on ECH elastomers via nucleophilic displacement reactions include: amino, diamino and quaternary ammonium;¹¹¹⁻¹²¹ imide;¹¹⁷ azide;¹²² carboxyl, carboxylate, sulfoxide and phosphorus

ester;¹²³ cinnamic ester^{124,125}; hydroxyl;^{93,126} phosphinyl;¹²⁷ thioether;¹²⁸ aminothioether;¹²⁹ thiosulfate;¹³⁰ isothiuronium,^{131,132} dithiocarbamate¹³³ and biologically active molecules.¹³⁴

Despite the apparent versatility of poly(ECH) for modification reactions, base-induced degradation of the polymer can be an important side-reaction. Degradation is known to occur in the presence of strong bases or weak nucleophiles,¹³⁵ and can result in difficulties in purification and polymers of lower molecular weight.

Difficulties may also be encountered when attempting substitution of all chlorine atoms. Nevertheless, a number of interesting new polymers have been prepared.

5. Oxymethylene polymers (POM)--general introduction. Polymers containing recurring oxymethylene units ($-\text{OCH}_2-$) have been known since 1859,¹³⁶ however it has only been in the last 30 years that polyoxymethylene of high molecular weight and which possessed good thermal stability was first prepared.¹³⁷⁻¹³⁹

As the linear polymer of formaldehyde, high molecular weight POM is generally prepared by two methods, each of which has achieved commercial success. The polymerization of anhydrous formaldehyde, a chain-growth reaction which propagates by an ionic mechanism through the

carbon-oxygen double bond, constitutes one method. Polyacetal formation was found to be quite facile using a variety of anionic or cationic initiators, many of these have been recently reviewed by Vogl.^{140,141} The best results are usually obtained with anionic polymerization initiators.

The second method of general utility for the preparation of high molecular weight POM, and the method most relevant to this investigation, involves the ring-opening polymerization of trioxane (TO), the cyclic trimer of formaldehyde.^{142,143} TO can be obtained in pure anhydrous form, but can only be polymerized by a cationic mechanism.

Polymerizations of anhydrous formaldehyde or trioxane are usually accompanied by the formation of considerable amounts of hemiacetal ($\text{HO}-\text{CH}_2-\text{O}-$) end-groups. The hemiacetal end-groups were recognized as a major source of the poor thermal stability of POM,¹⁴⁴ and are formed by chain transfer reactions of the growing polymer with adventitious traces of moisture or other protic impurities. Unmodified POM depolymerizes significantly when heated at temperatures above 90°C by an "unzipping" mechanism.¹⁴⁵ The hemiacetal endgroups are particularly labile and serve as the weak link in the chain where depropagation can begin.

Thermal stabilization of POM has been achieved

commercially by converting the labile end-groups to stable derivatives such as ester groups (by base-catalyzed esterification with acetic or propionic anhydride¹⁴⁶⁻¹⁴⁹), or by incorporating stabilizing comonomer units ("zipper-jammers") into the oxymethylene backbone.¹⁵⁰

Most often the latter is accomplished by the copolymerization of TO with about 2 mole-% of cyclic ethers such as EO or cyclic acetals like 1,3-dioxolane (DO). Statistical copolymers are usually obtained by this method. Studies in several laboratories have shown that polymerization of the more basic cyclic ether or cyclic acetal takes place before any significant consumption of trioxane.¹⁵¹⁻¹⁵⁵

Incorporation of the comonomer units in the POM chain then occurs by transacetalization reactions.

As will be seen in the next section, copolymerization of either formaldehyde or TO with functional comonomers has been the most prominent method for preparing functional oxymethylene polymers. At the same time, copolymerization provides a means to introduce oxyethylene "zipper-jammer" units in the polyacetal backbone.

6. Functional oxymethylene polymers. Relatively few reports in the literature have dealt with the preparation of polyacetals containing polar reactive groups.

Nevertheless, five different routes are known: (i) homo-

polymerization of functional aldehyde monomers, (ii) reaction of -OH endgroups with suitable reagents, (iii) chain transfer reactions during polymerization, (iv) copolymerization of TO or formaldehyde with functional monomers and (v) reactions on POM co- or terpolymers.

The reactions of -OH (hemiacetal) endgroups as well as chain transfer during polymerization will not be considered further; these are most often performed for purposes of end-group blocking, the concept of which was described in the preceding section. An excellent review by W. Vickers¹⁵⁶ has treated these two approaches in detail.

Interestingly, the homopolymerization of functional aldehyde monomers has received little attention. The polymerization of glycidaldehyde, an epoxy-aldehyde, has been studied by Furukawa and Saegusa.¹⁵⁷ At -78°C in the presence of $\text{Al}(\text{C}_2\text{H}_5)_3$ or aluminum isopropoxide, glycidaldehyde yielded the corresponding polyacetal with pendant oxirane groups. However, the course of the polymerization was also found to be strongly temperature dependent--at room temperature ring-opening polymerization of the epoxide occurred and the product obtained was the linear poly(ethylene oxide) with pendant aldehyde groups. More recently, Jedlinski has shown the course of this polymerization^{237,238} to be very different than reported

by Furukawa. A Tischenko reaction was found to produce a dimeric species which then polymerized through one of its epoxy groups.

Kobayashi and Sumitomo have reported the polymerization of nitrile-containing aldehydes, in particular β -cyanopropionaldehyde.¹⁵⁸ Using various initiators which included BF_3 -etherate, diethylzinc, triethylaluminum and Ziegler-types complexes of triethylaluminum-titanium tetrachloride, poly(cyanoethyl)oxymethylene was successfully prepared at -78°C . The polymerizations with AlEt_3 were considered to be initiated by a Grignard-adduct of β -cyanopropionaldehyde and AlEt_3 .⁹⁰

As mentioned previously, copolymerizations of formaldehyde or TO with functional cyclic ethers represent the most widely investigated route to functional POM. The best results have been achieved with trioxane. Nevertheless, preparation of functional POM by the copolymerization of formaldehyde with glycidaldehyde or EG has been claimed in a DuPont patent.¹⁵⁹

Since TO copolymerizes more readily with cyclic ether monomers than does formaldehyde, the majority of efforts describing the preparation of substituted POM have focused on reactions of suitable functional monomers with trioxane.

For example, several reports in the patent litera-

ture have described processes for enchainment of functional cyclic ethers such as glycidaldehyde;^{159,160} alkyl glycidates and glycidonitrile;^{159,161-164} or epichlorohydrin^{165,166} in the POM backbone. Each of the corresponding functional oxymethylene copolymers can be obtained by the solution copolymerization of trioxane with the appropriate cyclic ether. Vogl and Martin also demonstrated a particularly effective method for the intimate mixing of the comonomers in the gas phase.¹⁶¹⁻¹⁶⁴ Upon quenching in the presence of a suitable initiator (BF_3 or its complex with alkyl ethers), copolymerization readily occurred. Base stabilities of the TO/glycidonitrile and TO/alkyl glycidate copolymers prior to endcapping were generally less than 60 weight percent, however after endcapping the copolymers yielded thermoplastic resins with good mechanical properties.

The TO/ECH copolymers synthesized by Wissbrun and coworkers are also interesting. Nucleophilic substitution reactions on the pendant chloromethyl groups with disodium thioglycolate ($\text{Na}^+ \text{SCH}_2\text{COO}^- \text{Na}^+$) produced POM ionomers.^{166,167} Copolymers were prepared which ranged in ECH content from ca. 1.6 - 9 mole percent, however molecular weights tended to decrease as the fraction of ECH in the feed increased. After conversion to the ion-containing polyacetal, the properties of the POM ionomers

were studied as a function of ionic group content. Properties characterized included: percent crystallinity, optical clarity, melting and recrystallization behavior, tensile strength, water sensitivity and flow behavior.

More recently, investigations in these laboratories have been concerned with the preparation of POM ionomers.^{1,101-104} Oxymethylene copolymers and terpolymers containing pendant carboxylate groups were prepared by the copolymerization of EG with TO or terpolymerization of EG with TO and DO. The various ester-substituted POM polymers were converted to the ionomer form by saponification of the pendant ester groups with sodium hydroxide. Characterization of the various POM derivatives, which contained up to 2 mole-percent comonomer units, included measurement of their dynamic mechanical, dielectric and calorimetric properties.¹⁰⁴ Physical properties of the EG-modified POM were also studied. It was noted that the fraction of TO/EG copolymer stable to base was relatively low, indicating perhaps a blocky copolymer composition. Terpolymerization of TO and EG with DO was found to increase the fraction of material stable to base.

New approaches to improving the reactivity of functional cyclic ethers in copolymerizations with TO have also been undertaken in these laboratories. An investigation of the co- and terpolymerization of methyl

ω -epoxyalkanoates with TO was recently begun.^{109,168}

These efforts have since been expanded considerably and form a portion of the studies undertaken in this dissertation.

Polyacetals containing pendant aldehyde, ester, metal carboxylate, nitro, and amine functional groups have also been prepared by the terpolymerization of TO, EO (or DO), and substituted phenyl glycidyl ethers.¹⁶⁹ Ionomeric and amine-substituted POM were obtained by polymer reactions on the ester- and nitro-substituted oxymethylene terpolymers, respectively.

Polar-substituted vinyl compounds have also been copolymerized with TO, although very few examples can be found. Nevertheless, copolymers of divinyl sulfone,¹⁶¹⁻¹⁶³ allyl esters, acrylonitrile, alkyl acrylates and vinyl esters with trioxane have been claimed.

In contrast to the numerous reports in the literature detailing various aspects of the copolymerization of TO with DO, studies of the preparation of functionally-substituted POM by the reactions of TO with functional cyclic acetals are largely unknown. Only one such study has in fact been reported previously. Novel ester-substituted 1,3-dioxolanes¹⁷⁰ were synthesized

($\overline{\text{OCH}_2\text{OCH}_2\text{CH-R}}$, $\text{R} = -\text{CO}_2\text{CH}_3$, $-\text{CO}_2\text{C}_2\text{H}_5$ and $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCOCH}_3$) and copolymerized with trioxane using

BF_3 -dibutyletherate as initiator.¹⁷¹ Although levels of incorporation of the functional DO were not disclosed, the resultant copolymers were reported to show good thermal stability (weight loss at 222°C averaged 0.01-0.3 percent per minute) and were suggested to be cross-linkable through the pendant functional groups.

Interestingly, claims of the successful cationic homopolymerization of the functional dioxolane monomers were also made.¹⁷⁰ However, no details or examples were cited in support of that report.

7. Concluding remarks on functional alkylene oxide polymers. The discussions in the preceding sections have reviewed exclusively aspects and developments in the preparation of reactive polymers characterized by a polar backbone. In this respect, polyether and polyacetals are by far the most important members of the polar-chain variety usually prepared by a chain-growth mechanism. Many of the studies cited were undertaken with the recognition that some properties of the polymers could be modified, while other desirable properties characteristically associated with the backbone were retained. Investigations have also been undertaken with the sole intent of determining the ability of a particular functional monomer to polymerize or copolymerize.

B. Functional Polyolefins

Parallel efforts have also emerged in the preparation of functional hydrocarbon polymers or reactive polyolefins. As the final chapter in this introduction, the status of functional olefin polymerizations by coordination type initiators will be reviewed. This last category has been included in order to bring to light certain limitations encountered when the polymerizable group of the functional monomer is a double bond, as compared to the epoxy group.

1. General considerations. Certain polar functional groups are known to have a particularly adverse effect on coordination initiators frequently used in olefin polymerizations.¹⁸⁵ Yet the functionalization of linear hydrocarbon polymers is considered highly desirable from the standpoint of enhancing their adhesion characteristics and dyeability, influencing their rheological properties and solid-state morphology, and the possibility of introducing reactive groups.

Often the polar groups interact with one or each component of the initiator and thereby reduce or destroy the activity of the initiator.¹⁷² A common interaction is complexation of the reactive functional group with the organometallic constituent, generally through a non-bonded

pair of electrons on a heteroatom present in the functional group.

A survey of the literature reveals that many polar monomers have been claimed to be polymerized by Ziegler-Natta type initiators, but only a few have been shown to be polymerized at the same active centers (transition metal-carbon bonds) that polymerize ethylene and α -olefins. The Ziegler-Natta system in effect may serve as another source of cationic, radical or anionic centers which can initiate polymerization. For that reason, polymerizations of α , β -unsaturated polar monomers will not be considered, as interpretation of the actual mode of polymerization is often ambiguous and lacks supporting evidence.

Several strategies have emerged in efforts to enhance the ability of unsaturated polar compounds to be polymerized at the same centers that are active for non-polar olefins. In general, the more closely the polar monomer resembles an α -olefin, the greater the probability that destructive interactions can be minimized and polymerization at the active metal centers promoted.¹⁷³

In practice, this can be accomplished by: (i) isolating the double bond from the heteroatom by a spacer-group; (ii) increasing steric hindrance about the heteroatom; (iii) decreasing the electron-donating

character of the heteroatom by choosing a particular heteroatom or attaching an electron-withdrawing substituent to it; (iv) utilizing initiator components with a reduced tendency or ability to interact with the functional group and (v) lowering or modifying the reactivity of the organometallic component by complexing it with a suitable donor. Unfortunately, systematic studies of this total design are unknown.

2. Polyolefins with pendant reactive groups. The earliest report detailing the coordination polymerization of an olefin with a pendant reactive group was that by Natta and coworkers.¹⁷⁴ Allylsilane and trimethylallylsilane were polymerized to the corresponding poly(allylsilanes) with an isotactic configuration in the presence of violet titanium trichloride and AlEt_3 . Owing to the presence of labile Si-H bonds, the polymer of allylsilane could be crosslinked by reaction with oxygen, water or alcohols under suitable conditions. Copolymers with propylene and 1-hexene were subsequently reported.¹⁷⁵ In contrast, substitution of the silyl group directly on the double bond drastically reduced its ability to polymerize; vinyl ethylsilane polymerized only in low yield with $\text{AlEt}_3/\text{VCl}_3$.¹⁷⁶ Thus the presence or absence of one methylene unit was sufficient to alter the poly-

merizability of the polar monomer.

In some instances one methylene group is not enough. For example, allyl halides readily react with Ziegler initiators, producing hydrogen halides which subsequently deactivate the polymerization sites.¹⁷⁷

ω -Halo-1-alkenes, like iodo- and bromo-1-undecene were more readily polymerized or copolymerized with 4-methyl-1-pentene with $\text{AlEt}_2\text{Cl-TiCl}_3$ as initiator.¹⁷⁸

ω -Chloro-1-alkenes could only be copolymerized. The latter study also showed that the relative ease of polymerization was related to the size of the halogen group, increasing as the halogen atom became larger.

Recognizing the Lewis acid character of Ziegler-Natta initiators, Backsai prepared modified initiators by the addition of Lewis bases (ethers or amines) which were found to be suitable for producing copolymers of α -olefins and ω -halo-1-alkenes.¹⁷⁹ Tertiary phosphines have also been claimed as a modifier for Ziegler-Natta initiators and were used in α -olefin/ ω -halo-1-alkene copolymerizations.¹⁸⁰ Polyolefins containing reactive halogen atoms in the side chain are considered to be useful for grafting, cross-linking or displacement (substitution) reactions.

In 1967, Giannini and coworkers reported a study in which the polymerizations of nitrogen and oxygen con-

taining monomers such as amines and alcohols were investigated.¹⁸¹ Several effects were examined which included: (a) the polymerizability of unsaturated amines and alcohols in which the heteroatom and/or aluminumalkyl initiator component were sterically hindered, (b) the use of polar monomers already complexed with the organometallic component of the initiator, and (c) polymerizability of the polar monomer after delocalization of the electron-donating character of the heteroatom by bonding it to a more electropositive atom such as silicon (Si). Thus, crystalline polyolefins containing branched tertiary amine groups were prepared in the presence of Ziegler-Natta initiators in which the organometallic component was also sterically hindered. When the N-alkyl group was not branched, polymerization only occurred after complexation of the amine group with a reactive organometallic compound such as diethylaluminum chloride. In such cases, however, only amorphous polymers were obtained. O- and N-silylated 5-hydroxy-1-pentene, 11-hydroxy-1-undecene and 5-N-isopropylamino-1-pentene were also polymerized and subsequently de-silylated to yield the corresponding high molecular weight crystalline polyolefins containing pendant hydroxyl groups or amorphous polymer with pendant amine groups.

Olefin copolymers containing pendant carboxylate

groups are usually prepared by high pressure, free radical processes; these modified low density polyethylenes constitute an important class of materials. Partial neutralization of the pendant carboxylic acid groups produces thermoplastic resins known as ionomers,¹¹⁰ which contain thermally-reversible ionic crosslinks. These polymers are not linear, however, since they contain both short and long-chain branches.

Several studies have been concerned with the preparation of carboxyl-substituted polyolefins by low pressure, coordination polymerization processes. Functional olefin derivatives such as aliphatic or aromatic esters were normally employed in such cases. The free acid groups are prone to irreversible reactions with the organometallic component and cannot be used unless an excess of metal alkyl is present.

High molecular weight linear copolymers of ethylene or propylene which contained up to 5 mole-percent pendant ester groups have been claimed in a patent issued to Farbwerke-Hoechst.¹⁸² The relatively unhindered ethyl ester of 10-undecenoic acid, as well as the more bulky 2,6-dimethylphenyl ester were employed as functional monomers. A variety of copolymerization conditions and the use of heterogeneous or homogeneous coordination initiators were examined. The highest levels of incorporation of the

functional monomers were generally achieved with soluble vanadium initiator systems which were further modified by the addition of a Lewis base (dibutyl ether).

Vulcanizable ethylene or propylene copolymers containing pendant unsaturation have also been reported.¹⁸³ Allyl octadecenoate, a non-conjugated functional diene, was incorporated at very low levels into an ethylene copolymer using an initiator derived from the reaction of diethylaluminum chloride and a VCl_3 -THF complex. The copolymer contained 0.8% functional monomer. An ethylene-propylene rubber incorporating the same functional fatty-acid derivative was also prepared.

In patents issued to ICI, Clark claimed a method for producing functional olefin copolymers using polar comonomers which were first complexed with a suitable aluminumalkyl compound (Et_2AlCl).^{172,184} Olefins containing functional groups with active hydrogens such as carboxyl, hydroxyl or amide as well as ester, keto or cyano groups were complexed, and then copolymerized with ethylene and α -olefins. This technique was applied in one example to prepare a copolymer of 4-methyl-1-pentene and 10-undecenoic acid.

Similar results have been obtained in cases where the initiator was prepared using an excess of aluminum-alkyl to transition metal halide or alkoxyhalide

(Al/Ti,V,Cr>1). Thus olefin-alkenoic acid copolymers or olefin-alkenyl ester copolymers were reportedly prepared in this fashion.¹⁸⁵⁻¹⁸⁷ In some instances, Al/Ti ratios of 30:1 were used for copolymerizations of 10-undecenoic acid derivatives with α -olefins.¹⁸²

Many of the studies mentioned have been concerned with 10-undecenoic acid derivatives, largely due to the availability of this unsaturated acid. Several high yield synthetic routes to unsaturated carboxylic acids with fewer than eight methylene units in the spacer-group are now known which could make these functional α -olefins more accessible. These include Bailey's method for the pyrolysis of lactones¹⁸⁸ and Ogibin's oxidative decarboxylation of dicarboxylic acids.¹⁸⁹

Copolymers of propylene with unsaturated monomers containing pendant succinic anhydride, phthalic anhydride or norbornyl anhydride groups have been claimed using a $\text{TiCl}_3\text{-AlEt}_2\text{Cl}$ initiator.¹⁹⁰ Typically, copolymerizations were carried out using a 5-fold molar excess of aluminum-alkyl to the functional comonomer.

In a comprehensive patent issued to the Shell Oil Co., the coordination polymerization and copolymerization of a large number of functional olefins were disclosed.¹⁸⁵ This study is probably the most broad-ranging to date, and employed many of the criteria outlined earlier in this sec-

tion regarding methods to improve the polymerizability of functional alkenes. The categories of polar alkenes whose polymerizabilities were investigated included:

alkenamines, phenoxyalkenes, alkyl alkenoates, aluminum tris-(alkenoxides), alkenamides, alkenylphosphonates, alkenylphosphines and alkenylthiophosphonates.

Coordination polymerizations of polar-substituted monomers containing internal double bonds have largely been restricted to functional norbornene derivatives. In that regard, a number of polar norbornene monomers have been successfully polymerized using the well-known metathesis initiator systems. Metathesis initiators^{191,192} are generally prepared from tungsten or molybdenum halides and an organometallic compound. Polymerization occurs by ring-opening at the double bond and yields the corresponding cyclopentanylvinylene backbone.

Functional polyalkenamer-type polymers prepared with metathesis initiators were first described in two independent studies published in 1973. Hepworth^{193,196,197} and Ueshima^{194,195} disclosed the ring-opening polymerization of norbornenes which contained polar substituents such as acetate, alkanoate, halide or cyano groups. No polymerization was observed with noble metal catalysts such as hydrated ruthenium trichloride or

with the usual type of Ziegler-Natta initiators ($\text{AlEt}_3\text{-TiCl}_4$).¹⁹⁵ Polar-substituted norbornenes had previously been reported to undergo polymerization in the presence of noble metal salts (ruthenium, osmium, iridium).¹⁹⁸

Additional studies have since been disclosed in which norbornenes substituted with amide, imide,^{199,200} pyridyl or anhydride¹⁹⁷ groups were polymerized to the functionally-substituted polyalkenamers.

One report in the patent literature claimed the copolymerization of ethylene with a norborene derivative using a Ziegler-Natta type initiator.²⁰¹ The copolymerization of 5-norbornene-2-methoxychloroethylaluminum with ethylene in the presence of TiCl_4 and $\text{Et}_3\text{Al}_2\text{Cl}_3$ was reported to give resins useful for molding or adhesives.

CHAPTER II

EXPERIMENTAL SECTION

A. Materials

The following chemicals were obtained from the sources indicated:

acetic acid	F	ethylene oxide	M
acetylacetone	T	formic acid, 88%	F
benzene	MCB	1-hexene	A
benzophenone	E	hydrogen peroxide, 30%	F
boron trifluoride etherate	A	magnesium sulfate, anhydrous	B
1-butene oxide	A	methanol	MCB
calcium hydride	F	nitrogen, prepurified	M
m-chloroperoxybenzoic acid, technical	A	oxetane	A
p-chlorophenol	A	paraformaldehyde	MK
1,2-dichloroethane	A	phenyl glycidyl ether	T
dichloromethane	MCB	dl- α -pinene	A
diethyl ether, anhydrous	F	potassium hydroxide	MCB
1,4-dioxane	F	potassium metal	B
1,3-dioxolane	T	propylene oxide	E
1-dodecene		sodium hydroxide	MCB
epichlorohydrin	E	sodium metal	B

tetrahydrofuran	F	triethylaluminum, neat	ET
toluene	F	trioxane	C
p-toluenesulfonic acid, monohydrate	E	trifluoromethane- sulfonic acid anhydride	A
4,4,4-trichloro-1- butene oxide	PS	10-undecenoic acid	E

Sources: A = Aldrich Chemical Co.; B = J.T. Baker Chemical Co.; C = Celanese Plastics and Specialties Co.; E = Eastman Organic Chemicals; ET = Ethyl Corp.; F = Fisher Scientific Co.; M = Matheson; MCB = Matheson, Coleman and Bell; MK = Mallinckrodt Chemical Works; PS = Polysciences, Inc.; T = Tridom Chemical Co.

B. Purification of Solvents and Reagents

Distillations were carried out using either a 15 or 30 cm Vigreux column equipped with a variable reflux ratio distillation head. All distillations, either at atmospheric or reduced pressure, were carried out with magnetic stirring and under a nitrogen atmosphere.

Acetylacetone (2,4-pentanedione) was distilled (b.p. 133-134°C) and stored under nitrogen in the absence of light.

Benzene was washed successively with conc. sulfuric acid, distilled water, 5% aqueous sodium hydroxide, distilled water and then dried over anhydrous magnesium sulfate. A center cut of benzene (b.p. 80°C) was collected by distillation from a sodium/potassium alloy (50/50 by

weight) and stored under nitrogen.

Boron trifluoride etherate was distilled (b.p. 122.5-124°C) immediately before use.

1-Butene oxide was refluxed for 12 hours over calcium hydride, then distilled (b.p. 63°C) and stored under nitrogen.

m-Chloroperoxybenzoic acid (80-90%, technical) was purified by a procedure slightly modified from the method of Kennedy.²⁰² The crude peracid was washed in a sintered glass funnel with a phosphate buffer of pH 7.5 (prepared from 35.5g sodium orthophosphate, mono-H and 34.0g potassium orthophosphate, di-H in one liter distilled water) and with distilled water. After partial drying at 20mm over anhydrous calcium sulfate, the solid was further dried at 0.01 mm and room temperature over phosphorus pentoxide for 7 hours. Purified m-ClPBA was stored at 0°C in a plastic container.

1,2-Dichloroethane (DCE) was washed successively with conc sulfuric acid, distilled water, 5% aqueous sodium hydroxide, distilled water and then dried over anhydrous calcium chloride. DCE was refluxed over LAH for 2 days, distilled (b.p. 82°C) and stored under nitrogen.

Dichloromethane (DCM) was washed in the same manner as described for 1,2-dichloroethane (DCE), distilled (b.p. 40°C) from calcium hydride and stored under nitrogen.

1,4-Dioxane was heated under reflux over sodium

metal for 12 hours, then fractionally distilled (b.p. 100°C) and stored under nitrogen.

1,3-Dioxolane (DO) was refluxed over LAH for 12 hours, fractionally distilled and the fraction boiling at 72-75°C was collected. The fraction was redistilled (b.p. 74°C) from fresh LAH after refluxing overnight and was stored under nitrogen.

Epichlorohydrin (ECH) was distilled (b.p. 113.0-113.5°C) from calcium hydride and stored under nitrogen.

Oxetane (trimethylene oxide, Ox) was refluxed for 12 hours over calcium hydride, then distilled (b.p. 50°C) and stored under nitrogen.

Phenyl glycidyl ether (PGE) was distilled (b.p. 70°C/1 mm) and stored under dry nitrogen.

Propylene oxide (PO) was refluxed for 30 minutes over calcium hydride, then distilled (b.p. 34°C) and stored at 5°C under nitrogen.

Tetrahydrofuran (THF) was distilled (b.p. 62.5°C) from lithium aluminum hydride immediately before use.

Toluene was washed in the same manner as described for benzene, pre-dried over phosphorus pentoxide, distilled (b.p. 110°C) from sodium/potassium alloy (50/50 by weight) and stored under dry nitrogen.

4,4,4-Trichloro-1,2-butylene oxide (TCBO) was distilled (b.p. 78-81°C/90-91 mm) from calcium hydride and stored under nitrogen. A fore-cut of ca. 25% (b.p. 60-

80°C/91 mm) was discarded.

Trioxane (TO) was fractionally distilled (b.p. 109.5-112°C) from potassium hydroxide, then re-distilled (b.p. 115-116°C) from a sodium-benzophenone complex. Immediately prior to use TO was once again distilled (b.p. 115°C) from a sodium-benzophenone complex directly into pre-tared polymerization reaction vessels.

Trifluoromethanesulfonic acid anhydride (TFA) was used as received, but was transferred in a nitrogen-filled glove bag to a flame-dried Schlenk tube equipped with a 3-way teflon stopcock. TFA was stored under nitrogen.

All other solvents and reagents were used as received.

C. Preparation of Intermediates and Monomers

1. Methyl 10-undecenoate. A 2 liter, 3-neck round-bottomed flask fitted with a reflux condenser, nitrogen inlet and outlet tubes, and magnetic stirring bar was charged with 10-undecenoic acid (250 g, 1.36 mole) and absolute methanol (510 ml, 13 mole). Concentrated sulfuric acid (7.2 ml) was then added, causing a mild exothermic reaction to occur. The homogeneous mixture was heated and held at reflux for 22 hours, then cooled to room temperature. After cooling of the yellow solution, excess methanol was removed under reduced pressure (ca. 35 mm) on a rotary

evaporator. The remaining yellow oil was transferred to a large separatory funnel and 500 ml distilled water was added. Two immiscible layers formed; and after gentle shaking the lower aqueous layer was decanted and discarded. The yellow oil was then diluted with anhydrous diethyl ether (1 l) and washed with 2 x 500 ml portions of distilled water, 5% aqueous sodium bicarbonate and distilled water. The ethereal solution was dried overnight with anhydrous magnesium sulfate and filtered. Removal of the solvent on the rotary evaporator gave essentially a quantitative yield of crude product. Vacuum distillation (b.p. 116.5-118°C/5 mm) afforded 246 g (91%) of clear, colorless methyl 10-undecenoate (lit.²⁰³ b.p. 124°/10 mm) which was stored under nitrogen. The infrared spectrum (neat) showed absorptions at 1740 cm^{-1} (C=O stretch, ester) and 1640 cm^{-1} (C=C stretch, monosubstituted olefin) (see p. 293). The ^1H NMR spectrum (CDCl_3) showed δ : 1.2-1.8 ppm ($-\text{CH}_2-$, 12H), 1.9-2.2 ppm ($=\text{CHCH}_2-$, 2H), 2.2-2.5 ppm ($-\text{CH}_2\text{CO}-$, 2H), 3.7 ppm ($-\text{OCH}_3$, 3H, singlet), 4.8-5.2 ppm ($\text{CH}_2=$, 2H), and 5.5-6.1 ppm ($=\text{CH}-$, 1H) (see p. 312). The ^{13}C NMR spectrum (CDCl_3) showed peaks at 25.07 ppm ($-\text{CH}_2\text{CH}_2\text{CO}-$), 29.07 and 29.31 ppm ($=\text{CH}-\text{CH}_2-(\text{CH}_2)_5$), 33.91 ppm ($=\text{CH}-\text{CH}_2-$), 34.11 ppm ($-\text{CH}_2\text{CO}-$), 51.26 ppm ($-\text{OCH}_3$), 114.25 ppm ($\text{CH}_2=$), 139.02 ppm ($=\text{CH}-$) and 173.95 ppm ($-\text{C=O}$) (see p. 316).

2. Methyl 10,11-epoxyundecanoate. A 2-liter, 3-neck round-bottomed flask was equipped with a mechanical stirrer, reflux condenser, Claisen adapter, pressure-equalizing addition funnel, and gas inlet and outlet tubes. The assembled apparatus was flushed with nitrogen and flamed out. Under a positive pressure of nitrogen, the reaction vessel was then charged with purified m-chloroperoxybenzoic acid (66 g, 0.38 mole) and one liter of DCM. After the peracid had completely dissolved, the contents of the reaction vessel were chilled to 0-5°C. A solution of methyl 10-undecenoate (75 g, 0.38 mole) in DCM (180 ml) was placed in the dropping funnel, and dropwise addition was carried out for 2 hours. The contents of the flask were maintained at 0-5°C during addition and for 1 hour after. A white precipitate (m-chlorobenzoic acid) began to separate from the reaction mixture during the latter stages of addition. The reaction was allowed to proceed for 15 hours at room temperature, refluxed for 5 hours and finally chilled to 5°C. The precipitated m-chlorobenzoic acid (obtained in nearly quantitative yield) was collected by filtration and washed with fresh, chilled DCM. The filtrate and washings were combined and the solvent was removed on the rotary evaporator. The remaining colorless oil was dissolved in anhydrous diethyl ether (600 ml); the ethereal solution was washed with 2 x 200 ml portions of 5% aqueous sodium bicarbonate, 3 x 300 ml portions of distilled water, dried

over anhydrous magnesium sulfate and filtered. Removal of the ether on the rotary evaporator gave 81 g (99%) of crude methyl 10,11-epoxyundecanoate. Polymerization-grade methyl 10,11-epoxyundecanoate (MEU) was obtained in 74% yield (60 g) by distillation (b.p. 109.0-109.5°C/0.6 mm) from calcium hydride and was stored under nitrogen. The purity of MEU was determined by gas chromatography to be > 99.5%. The infrared spectrum (neat) showed absorptions at 1735 cm^{-1} (C=O stretch, ester), 910 cm^{-1} and 830 cm^{-1} (epoxide ring-stretching modes) (see p. 293). The ^1H NMR spectrum (CDCl_3) showed δ : 1.3-1.8 ppm ($-\text{CH}_2-$, 14H), 2.2-2.4 ppm ($-\text{CH}_2\text{CO}_2-$, 2H), 2.3-2.8 ppm ($\text{CH}_2-\overset{\text{O}}{\text{C}}-$, 2H), 2.7-3.0 ppm ($-\text{CH}-\overset{\text{O}}{\text{C}}-$, 1H) and 3.7 ppm ($-\text{OCH}_3$, 3H, singlet) (see p. 312). The ^{13}C NMR spectrum (CDCl_3) showed peaks at 25.00 ppm ($-\text{CH}_2\text{CH}_2\text{COOCH}_3$) 26.04 ppm ($-\overset{\text{O}}{\text{C}}-\text{CH}_2\text{CH}_2-$), 29.21 and 29.43 ppm ($(\text{CH}_2)_4$), 32.58 ppm ($-\overset{\text{O}}{\text{C}}-\text{CH}_2-$), 34.07 ppm ($-\text{CH}_2-\text{COO}-$), 46.90 ppm ($\text{CH}_2-\overset{\text{O}}{\text{C}}-$), 51.30 ppm ($-\text{OCH}_3$), 52.20 ppm ($-\overset{\text{O}}{\text{C}}-$), and 174.03 ppm ($-\overset{\text{O}}{\text{C}}-$) (see p. 316).

3. 1-Dodecene oxide. A 500 ml 3-neck round-bottomed flask was equipped with a mechanical stirrer, reflux condenser, Claisen adapter, pressure-equalizing funnel, and gas inlet and outlet tubes. The assembled apparatus was flushed with nitrogen and flamed-out. Under a positive pressure of nitrogen, the reactor was then charged with purified m-chloroperoxybenzoic acid (35 g, 0.21 mole) and

150 ml of DCM (spectral grade). The contents of the reactor were gently heated, with mixing, until a clear colorless solution was obtained, and then cooled to room temperature. A solution of 1-dodecene (35 g, 0.21 mole) in DCM (20 ml) was placed in the dropping funnel and added dropwise to the peracid solution over a period of 90 minutes. The contents of the reaction flask were maintained at room temperature during addition and for 2 hours thereafter, then heated under reflux for 4 hours, stirred at room temperature for 11 hours, chilled to 5°C and filtered. The insoluble, m-chlorobenzoic acid collected was rinsed with chilled DCM (50 ml); the filtrate and washings were combined and the solvent was removed on the rotary evaporator. The oily residue was dissolved in diethyl ether (250 ml). The ethereal solution was washed successively with 5% aqueous sodium bicarbonate (2 x 100 ml) and distilled water (3 x 100 ml), dried over anhydrous magnesium sulfate and filtered. The yield of crude 1-dodecene oxide after removal of the solvent on the rotary evaporator was 36 g (94%). Distillation (b.p. 126-128°C/10 mm) gave 22 g (63%) of 1-dodecene oxide (DDO), a clear and colorless liquid (lit.²⁰⁴ b.p. 106-109°C/6 mm). The infrared spectrum (neat) showed absorptions at 925 and 835 cm^{-1} (epoxide ring stretching modes) (see p. 294). The ^1H NMR spectrum (d_6 -benzene) showed δ : 0.7-1.1 ppm ($-\text{CH}_3$, 3H), 1.1-1.5 ppm

($-\text{CH}_2-$, 18H), 2.1-2.5 ppm ($\text{CH}_2-\overset{\text{O}}{\text{C}}$, 2H) and 2.5-2.7 ppm ($\overset{\text{O}}{\text{C}}-\text{CH}-$, 1H) (see p. 313). The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 14.33 ppm ($-\text{CH}_3$), 23.11 ppm ($-\text{CH}_2\text{CH}_3$), 26.42 ppm ($-\overset{\text{O}}{\text{C}}\text{CHCH}_2-\text{CH}_2-$), 29.86 and 30.04 ppm ($-(\text{CH}_2)_5-$), 32.35 ppm ($-\text{CH}_2\text{CH}_2\text{CH}_3$), 32.94 ppm ($-\text{CH}_2\overset{\text{O}}{\text{C}}\text{H}-$), 46.32 ppm ($\overset{\text{O}}{\text{C}}\text{H}_2-$), and 51.75 ppm ($-\overset{\text{O}}{\text{C}}\text{H}-$) (see p. 317).

4. 4-(1-Carbomethoxynonyl)-1,3-dioxolane (MEDOX).

a. 10-Formoxy-11-hydroxyundecanoic acid. The procedure described is a modification of the method of Swern et al.²⁰² A clean, dry 250 ml 4-neck round-bottomed flask was charged with 10-undecenoic acid (25 g, 0.13 mole). The flask was fitted with a nitrogen inlet and exit tube, reflux condenser, thermometer, 125 ml side-arm addition funnel and magnetic stirring bar. The assembled apparatus was purged with nitrogen for 15 minutes. Formic acid (75 ml, 88% solution in water) was then added, and two immiscible layers formed immediately. A standard 30% aqueous hydrogen peroxide solution (18 g, 0.14 mole) was placed in the addition funnel and added dropwise to the acid mixture over 3 minutes. Following an induction period of 5 minutes, the reaction became exothermic. The temperature of the reaction was not allowed to rise above 40°C; temperature control was achieved by the intermittent use of a cold water bath. At the end of 30 minutes the milky reaction mixture had transformed into a clear, nearly colorless solution.

The reaction began to subside after another 15 minutes (temperature began to drop) but was subsequently maintained at 40°C an additional 4 hours using a warm water bath. After cooling to room temperature the solution was poured into 200 ml of cold distilled water, whereupon two phases formed. The lower organic phase was decanted and dissolved in anhydrous diethyl ether (100 ml). The aqueous phase was extracted with 3 x 100 ml portions of diethyl ether and discarded. The four ethereal fractions were combined and washed with distilled water until the washings were neutral. The ethereal solution was dried over anhydrous calcium sulfate for 12 hours, filtered and the solvent removed on the rotary evaporator. The yield of a light yellow oil was 28 g (83%). An infrared spectrum (neat) of the crude product showed absorptions at 3650-2480 cm^{-1} (O-H stretch, carboxylic acid and alcohol), 1730 cm^{-1} (C=O stretch, formate ester), 1710 cm^{-1} (C=O stretch, carboxylic acid) and 1180 cm^{-1} (C-O stretch, formate ester) (see p. 294). No additional characterization or purification of this intermediate was performed. On the basis of infrared evidence it was concluded that the expected oxidation product, 10-formoxy-11-hydroxyundecanoic acid, had been obtained.

b. 10,11-Dihydroxyundecanoic acid. A 250 ml round-bottomed flask containing 10-formoxy-11-hydroxyundecanoic acid (28 g, 0.11 mole) was fitted with a reflux condenser and magnetic stirring bar. Addition of a

1N aqueous sodium hydroxide solution (125 ml, 0.250 mole OH^-) caused an immediate but mild exothermic reaction. The resulting clear yellow solution was heated at reflux for 1 hour, then cooled to room temperature. A water-immiscible oil separated out. Upon standing for several hours, the oil solidified to a wax-like cake. The relatively small amount of solid present, however, indicated that a considerable quantity of the saponified product remained in solution. The reaction mixture was acidified by pouring into a chilled solution of 3N hydrochloric acid (100 ml, 0.30 mole H^+). A large amount of precipitate formed; the acidified mixture was maintained at 5°C and stirred overnight. The finely-divided, off-white precipitate was collected by filtration and washed with cold distilled water until the washings were slightly acidic (completely neutral washings could not be obtained due to slight solubility of the product in water). The yield of crude product, after air-drying overnight, was 21 g (87%), m.p. $62-70.5^\circ\text{C}$. A small portion of the product was recrystallized from isopropanol-water, m.p. $66.0-67.5^\circ\text{C}$ (lit.²⁰⁵ m.p. $84-85^\circ\text{C}$). The infrared spectrum (KBr wafer) showed absorptions at 3380 cm^{-1} (O-H stretch, alcohol), $3500-2300\text{ cm}^{-1}$ (O-H stretch, carboxylic acid), 1695 cm^{-1} (C=O stretch, carboxylic acid), 1190 cm^{-1} (O-H bending, secondary alcohol) and 1150 cm^{-1} (O-H bending, primary alcohol). See p. 295. The ^1H NMR spectrum (d_8 -dioxane) showed δ : 1.1-1.7 ppm ($-\text{CH}_2-$, 14H), 2.1-2.4

ppm ($-\text{CH}_2-\text{CO}_2\text{H}$, 2H), 3.1-3.6 ppm ($-\text{CH}_2\text{OH}$ and $-\overset{|}{\text{CHOH}}$, 3H) and 5.1-5.9 ppm ($-\text{OH}$, 2H). See p. 313. The ^{13}C NMR spectrum (d_6 -DMSO) showed peaks at 26.40 ppm ($-\text{CH}_2\text{CH}_2\text{COOH}$); 26.94 ppm ($-\text{CH}_2\text{CH}_2\overset{\text{OH}}{\text{CH}}-$); 30.48 ppm, 30.74 ppm and 31.06 ppm ($(\text{CH}_2)_4$); 35.32 ppm ($-\overset{\text{OH}}{\text{CH}}-\text{CH}_2-$); 35.64 ppm ($-\text{CH}_2\text{COOH}$); 68.00 ppm ($-\text{CH}_2\text{OH}$); 73.18 ppm ($-\overset{|}{\text{CHOH}}$) and 176.04 ppm ($-\overset{\text{O}}{\text{C}}-$). See p. 317.

c. Methyl 10,11-dihydroxyundecanoate. In a clean, dry 100 ml round-bottomed flask was placed 10,11-dihydroxyundecanoic acid (5.0 g, 23 mmole), p-toluenesulfonic acid monohydrate (0.087 g, 0.46 mmole) and absolute methanol (40 ml, 1 mole). The flask was equipped with a magnetic stirring bar and reflux condenser fitted with a T-adaptor which was connected to a source of nitrogen. The reaction was heated at reflux in an oil bath for 27 hours. After cooling to room temperature, the solution was then concentrated on the rotary evaporator. The residual pale yellow oil was dissolved in diethyl ether (165 ml), washed with one 50 ml portion of 2% (w/w) aqueous sodium carbonate, 4 x 75 ml portions of distilled water, dried over anhydrous sodium sulfate and filtered. The ether was evaporated, leaving a pale yellow oil which crystallized upon standing. The yield of crude product was 4.4 g (83%), m.p. 44-46.5°C. The low melting solid was recrystallized from a petroleum ether/anhydrous diethyl ether mixture (1:1 v/v), washed with cold petroleum ether

and dried at 0.05 mm and room temperature over phosphorus pentoxide. The yield of pure methyl 10,11-dihydroxyundecanoate was 3.8 g (91% recovery), m.p. 46-48°C (lit.²⁰⁶ m.p. 45-46°C). The infrared spectrum (neat) showed absorptions at 3630-3040 cm^{-1} (O-H stretch, alcohol) and 1740 cm^{-1} (C=O stretch, ester). See p. 295. The ^1H NMR spectrum (CDCl_3) showed δ : 1.1-1.8 ppm ($-\text{CH}_2-$, 14H), 2.1-2.45 ppm ($-\text{CH}_2\text{COOCH}_3$, 2H), 2.75-3.0 ppm ($-\text{OH}$, 2H), 3.3-3.8 ppm ($\text{CH}_2-\text{CH}-$, 3H) and 3.65 ppm ($-\text{OCH}_3$, 3H, singlet). See p. 314. The ^{13}C NMR spectrum (CDCl_3) showed peaks at 24.93 ppm ($-\text{CHOHCH}_2\text{CH}_2-$); 25.57 ppm ($-\text{CH}_2\text{CH}_2\text{COOCH}_3$); 29.15, 29.32 and 29.59 ppm ($-(\text{CH}_2)_4$); 33.14 ppm ($-\text{CH}-\text{CH}_2-$); 34.11 ppm ($-\text{CH}_2-\text{COOCH}_3$); 51.50 ppm ($-\text{OCH}_3$); 66.82 ppm ($-\text{CH}_2\text{OH}$), 72.35 ppm ($-\text{CHOH}$) and 174.45 ppm ($-\overset{\text{O}}{\text{C}}-$). See p. 318.

d. 4-(1-Carbomethoxynonyl)-1,3-dioxolane. A one liter round-bottomed flask was charged with methyl 10,11-dihydroxyundecanoate (50 g, 0.21 mole), paraformaldehyde (6.7 g, 0.22 mole), p-toluenesulfonic acid monohydrate (0.82 g, 4.3 mmole) and reagent-grade benzene (400 ml). The flask was fitted with a Dean-Stark trap, reflux condenser topped with a T-adaptor which was connected to a nitrogen source, and magnetic stirring bar. The turbid reaction mixture was heated at reflux whereupon a homogeneous solution was obtained. The theoretical quantity of water (3.9 ml) was collected in ca. 2 hours by azeotropic distillation, but the reaction was maintained at reflux over-

night. After cooling to room temperature, the pale yellow solution was transferred to a one liter separatory funnel and washed successively with distilled water (3 x 200 ml), 5% aqueous sodium carbonate (1 x 200 ml) and distilled water (5 x 200 ml). The benzene solution was dried over anhydrous magnesium sulfate, filtered and concentrated on the rotary evaporator. Purity of the crude 4-(1-carbomethoxynonyl)-1,3-dioxolane, as determined by gas chromatography (SE 30 column), was ca. 93%. The yield of viscous yellow oil, which could be solidified by cooling, was 52 g (99%). Fractional distillation (b.p. 142.0-143.0°C/0.28 mm) gave 38 g (73%) of pure-white 4-(1-carbomethoxynonyl)-1,3-dioxolane, m.p. 29.5-31.5°C. Monomer purity was determined by gas chromatographic analysis to be 99.5%. The infrared spectrum (neat) showed absorptions at 3100-2600 cm^{-1} (C-H stretch); 1740 cm^{-1} (C=O stretch, ester); 1240, 1195 and 1170 cm^{-1} (C-O stretch, methyl ester) and 1090 cm^{-1} (O-C-O stretch, cyclic formal). See p. 296. The ^1H NMR spectrum (CDCl_3) showed δ : 1.1-1.9 ppm ($-\text{CH}_2-$, 14H), 2.1-2.4 ppm ($-\text{CH}_2\text{COOCH}_3$, 2H), 3.3-3.5 ppm ($\overset{\text{O}}{\text{CH}_2}-$, 2H), 3.6 ppm ($-\text{OCH}_3$, 3H, singlet), 3.8-4.15 ppm ($\overset{\text{O}}{\text{CH}}-$, 1H) and 4.8-4.9 ppm ($\overset{\text{O}}{\text{CH}_2}$, 2H, doublet). See p. 314. The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 25.41 ppm ($-\text{CH}_2\text{CH}_2\text{COOCH}_3$); 26.32 ppm ($-\overset{\text{O}}{\text{CH}}-\text{CH}_2\text{CH}_2-$); 29.61, 29.69, 29.83, and 29.97 ppm ($\{\text{CH}_2\}_4$); 33.55 ppm

$(-\overset{\text{O}}{\underset{|}{\text{CH}}}-\text{CH}_2\text{CH}_2-)$; 34.25 ppm $(-\text{CH}_2\text{COOCH}_3)$; 51.10 ppm $(-\text{OCH}_3)$; 69.89 ppm (CH_2-O) ; 76.52 ppm $(-\overset{|}{\text{CH}}-\text{O})$; 95.17 ppm (CH_2O) and 173.49 ppm $(-\overset{\text{O}}{\underset{||}{\text{C}}}-)$. See p. 318.

ANAL. calcd. for $\text{C}_{13}\text{H}_{24}\text{O}_4$: C, 63.90%; H, 9.90%.
 Found: C, 63.73%; H, 10.07%.

D. Coordination Polymerizations of Methyl 10,11-Epoxyundecanoate

1. General procedure for preparation of $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator. A large side-armed Schlenk tube, equipped with a 3-way pressure stopcock and teflon-coated magnetic stirring bar, was evacuated to a pressure of 0.01 mm and then carefully flamed-out. After cooling to room temperature, the apparatus was alternately filled with nitrogen and evacuated (3 times total). Triethylaluminum (7.0 ml, 51 mmole) was carefully transferred to the Schlenk tube via a nitrogen-purged gas-tight syringe. A heavy counter-flow of nitrogen was maintained through the tube during addition of the aluminumalkyl. The tube was then partially immersed in an ice-water bath (5°C), fitted with a clean, dry side-arm addition funnel (with teflon stopcock) and the entire apparatus was purged with nitrogen for 5 minutes. Using nitrogen-purged gas-tight syringes, the addition funnel was charged with anhydrous diethyl ether (40 ml) and freshly distilled acetylacetone (5.3 ml, 51 mmole). The AcAc solution was added dropwise to the well-stirred, neat triethylaluminum over a period of 3

hours. A slight positive pressure of nitrogen was maintained through the apparatus in order to sweep away ethane gas formed as a by-product in the reaction. After the addition was completed, the pale yellow solution was stirred for 1.5 hours to allow completion of the reaction. Freshly distilled water (0.46 ml, 26 mmole) was then carefully added, dropwise, to the ethereal solution over a 5 minute interval using a nitrogen-purged, gas-tight syringe. The $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$ initiator solution (0.97 molar in aluminum) was stirred under a slight positive pressure of nitrogen for an additional 2 hours, then stored under nitrogen at 5°C prior to use.

2. Polymerization of methyl 10,11-epoxyundecanoate with $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator. A 125 x 20 mm polymerization tube, fitted with a 3-way pressure stopcock, was evacuated to a pressure of 0.01 mm and then carefully flamed-out. After cooling to room temperature, the vessel was alternately (3 times) filled with nitrogen and evacuated to 0.01 mm. Under a strong counter-flow of nitrogen, the tube was then charged with MEU (2.9 g, 13 mmole) and benzene (12 ml) using nitrogen-purged syringes. The contents of the tube were then degassed by the usual freeze-thaw technique (3 freeze-thaw cycles). The $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ initiator solution (2.1 ml, 0.68 mmole aluminum, 5 mole-% based on epoxide monomer) was added with a

nitrogen-purged syringe and the contents of the tube were mixed thoroughly. The tube was sealed under vacuum (0.01 mm) after freezing its contents with a liquid nitrogen bath. Polymerization was allowed to proceed for 7 days at room temperature in the absence of light. During this period, the nearly colorless solution gradually increased in viscosity, finally becoming an immobile, transparent plug after 4 days. After the tube was opened, the rubbery plug was removed and dissolved in a mixture of benzene (200 ml), 1,4-dioxane (50 ml) and anhydrous methanol (5 ml). The polymer solution was filtered through a fritted funnel (coarse grit) and the volume of the filtrate was reduced to ca. 75 ml on the rotary evaporator. Poly(MEU) was precipitated by dropwise addition into acidified methanol (600 ml methanol, 2 ml conc. hydrochloric acid), collected by filtration and washed with absolute methanol (300 ml). The polymer was dried for 48 hours at 0.01 mm and room temperature over phosphorus pentoxide. Yield of the white, elastomeric poly(MEU) was 1.4 g (48%). The inherent viscosity of the polymer (0.5% in CHCl_3 , 30°C) was 1.8 dL/g; this corresponds to average molecular weights $\bar{M}_n = 248,000$ and $\bar{M}_w = 578,000$ (based on polystyrene calibration standards) as determined by gel permeation chromatographic analysis of poly(MEU) in THF solution (0.15 w/v %). The infrared spectrum (thin film) showed absorptions centered at 1740 cm^{-1} (C=O stretch, ester); 1240

1198 and 1170 cm^{-1} (C-O stretch, methyl ester); and 1105 cm^{-1} (C-O-C stretch, ether). See p. 296. The ^{13}C NMR spectrum (CDCl_3) showed peaks at 25.06 ppm ($-\text{CH}_2\text{CH}_2\text{COOCH}_3$), 25.59 ppm ($-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$); 29.32 ppm, 29.40 ppm, 29.60 ppm and 29.94 ppm ($\{\text{CH}_2\}$); 32.31 ppm ($-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$); 34.14 ppm ($-\text{CH}_2\text{COOCH}_3$); 51.33 ppm ($-\text{OCH}_3$); 71.76 and 73.14 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-$); 79.39 and 79.83 ppm ($-\text{O}\overset{|}{\text{CH}}-$) and 174.07 ppm ($-\overset{\text{O}}{\text{C}}-$). See p. 319.

ANAL. calcd. for $\{\text{C}_{12}\text{H}_{22}\text{O}_3\}_n$: C, 67.25%; H, 10.35%. Found: C, 67.28%; H, 10.58%; ash < 0.05%.

a. Alternate work-up procedure for methyl 10,11-epoxyundecanoate polymerizations. An improved method for work-up of the polymerization was developed and is described here. Polymerizations of methyl 10,11-epoxyundecanoate with the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (5 mole-%) were carried out by the method described previously, however, reaction times were arbitrarily varied. 1,4-Dioxane containing several percent absolute methanol was found to reduce substantially the time required for dissolution of the rubbery polymer plugs and was adopted as the solvent medium of choice for the work-up of subsequent polymerizations. This eliminated the need to use additional aromatic hydrocarbon (benzene or toluene) as diluent. Another practice adopted was to cut the elastic polymer plug into numerous smaller chunks prior to dissolution. This increased the surface area exposed to diluent

and usually eliminated problems in maintaining effective magnetic stirring of the mixture. Precipitation, washing and drying of the polymer were performed according to the method described.

3. Copolymerizations of methyl 10,11-epoxyundecanoate with cyclic ethers using the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator.

a. Copolymerization with ethylene oxide (EO). A thick-walled polymerization tube fitted with a 3-way pressure stopcock was dried in the manner described previously. The nitrogen-filled vessel was charged with MEU (4.8 g, 23 mmole) and toluene (35 ml). The contents of the tube were degassed by three freeze-thaw cycles. Ethylene oxide (3.0 atm, 5.6 g, 130 mmole) was condensed at liquid nitrogen temperature into an evacuated one-liter gas bulb (with attached cold finger) and then was degassed by three freeze-thaw cycles. The EO was distilled through a vacuum line directly into the polymerization vessel. The tube, which contained 15 mole-% MEU in the frozen comonomer charge, was then partially immersed in an icewater bath (ca. 5°C). After thawing, the contents of the tube were thoroughly mixed and maintained at 0-5°C (below the boiling point of EO). The $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ initiator solution (5.6 ml, 5.4 mmole aluminum, 3.6 mole-% based on epoxide monomers) was injected with a gas-tight syringe, and the reaction

solution was immediately and thoroughly mixed. The tube was sealed at 0.01 mm after freezing its contents at liquid nitrogen temperature. Polymerization was allowed to proceed for 3 days at 5°C (an immobile plug was formed after 1 day at 5°C) and an additional 24 days at room temperature. At the end of this time the tube was opened; the highly elastic copolymer plug was removed and was dissolved in 1,4-dioxane (500 ml) which contained 3% absolute methanol (15 ml). The resulting moderately viscous solution was filtered through a coarse grit sintered glass funnel. The copolymer was precipitated by pouring the filtrate into three liters of acidified n-hexane (containing 4 ml methanol/1 ml conc. HCl). After decanting the hexane solution, the rubbery copolymer was stirred overnight in diethyl ether (2 l). Poly(EO-co-MEU) was collected by filtration, washed with fresh anhydrous ether (300 ml) and dried for 2 days at 0.05 mm and room temperature over phosphorus pentoxide. The yield of tough, white elastomeric copolymer was 9.6 g (92%). The inherent viscosity of the copolymer (0.5% in 1,4-dioxane, 30°C) was 1.64 dL/g. The infrared spectrum (thin film) showed absorptions at 1735 cm^{-1} (C=O stretch, ester) and 1105 cm^{-1} (C-O-C stretch, ether). See p. 297. The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 25.45 ppm ($-\text{CH}_2\text{CH}_2\text{COOCH}_3$); 25.94 ppm ($-\text{OCHCH}_2\text{CH}_2-$); 29.62 ppm, 29.78 ppm, 29.98 ppm

and 30.31 ppm ($\text{-(}\underline{\text{CH}_2}\text{)}_4$); 32.75 ppm ($\text{-O}\overset{|}{\text{CH}}\text{-}\underline{\text{CH}_2}\text{-}$); 34.30 ppm ($\text{-}\underline{\text{CH}_2}\text{-COOCH}_3$); 51.11 ppm ($\text{-O}\underline{\text{CH}_3}$); 70.01, 71.17, 72.10 and 72.33 ppm ($\text{-O-}\underline{\text{CH}_2}\underline{\text{CH}_2}\text{-}$); 74.61 ppm ($\text{-O}\underline{\text{CH}_2}\overset{|}{\text{CH}}\text{-}$); 79.61 ppm ($\text{-OCH}_2\text{-}\overset{|}{\text{CH}}\text{-}$) and 173.4 ppm ($\text{-}\overset{\text{O}}{\underset{||}{\text{C}}}\text{-}$). See p. 319.

The relative composition of the copolymer was 4 mole-% MEU and 96 mole-% EO.

ANAL. calcd. for $\text{(C}_{12}\text{H}_{22}\text{O}_3\text{)}_{.04}\text{(C}_2\text{H}_4\text{O)}_{.96}$:
C, 56.67 %; H, 9.35%. Found: C, 55.40%; H, 9.06%;
ash, 2.2%.

b. Copolymerization with propylene oxide (PO). A polymerization tube, fitted with a 3-way pressure stopcock, was dried in the manner described previously. The tube was charged with MEU (1.7 g, 8.0 mmole, 30 mole-% of comonomer feed), benzene (13 ml), propylene oxide (1.9 g, 30 mmole) and the $\text{Al(C}_2\text{H}_5)_3/\text{H}_2\text{O/AcAc}$ (1.0/0.5/1.0) initiator (6.0 ml, 1.9 mmole aluminum, 5 mole-% based on epoxide monomers). The contents of the vessel were de-gassed by three freeze-thaw cycles and the tube was sealed at 0.01 mm. The clear yellow reaction solution, initially of very low viscosity, formed a soft immobile plug after 17 hours. Polymerization was allowed to proceed a total of 13 days at room temperature. The tube was opened, the elastic yellow plug obtained was dissolved in a mixture of 1,4-dioxane (150 ml), benzene (150 ml) and absolute methanol (3 ml). The syrupy solution was filtered and the volume reduced to ca. 150 ml on the rotary evaporator. The copolymer was precipitated

by pouring the viscous residue into three liters of acidified methanol-water (5 parts methanol to 1 part water by volume, plus 3 ml conc. hydrochloric acid), collected by filtration, washed with a methanol-water mixture (500 ml, 1:1 v/v) and dried for 2 days at 0.01 mm and room temperature over phosphorus pentoxide. Yield of the semi-transparent, gum-like PO copolymer was 2.1 g (58%). The inherent viscosity of the copolymer (0.5% in CHCl_3 , 30°C) was 1.0 dL/g; this corresponded to average molecular weights $\bar{M}_n = 106,000$ and $\bar{M}_w = 215,000$ (based on polystyrene calibration standards) as determined by GPC analysis of the copolymer in THF solution (0.15 w/v %). The infrared spectrum (thin film) showed absorptions at 1740 cm^{-1} (C=O stretch, ester) and 1100 cm^{-1} (C-O-C stretch, ether). See p. 297. The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 18.16 and 19.07 ppm ($-\text{CH}_3$); 25.63 ppm ($-\text{CH}_2\text{CH}_2\text{COOCH}_3$); 26.20 ppm ($-\text{OCHCH}_2\text{CH}_2-$); 29.83, 29.98, 30.20 and 30.56 ppm ($\text{-(CH}_2\text{)}_4$); 33.04 ppm ($-\text{OCHCH}_2-$); 34.46 ppm ($-\text{CH}_2\text{COOCH}_3$); 51.23 ppm ($-\text{OCH}_3$); 73.49, 74.22, 74.79 and 74.99 ppm ($-\text{OCH}_2\text{CHCH}_3$); 74.61 ppm ($-\text{OCH}_2\text{CH}-$); 76.17 and 76.78 ppm ($-\text{OCH}_2\text{CHCH}_3$); 79.93, 80.26 ppm ($-\text{OCH}_2\text{CH}-$) and 173.58 ppm ($-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$). See p. 320.

The relative composition of the copolymer was 22 mole-% MEU and 78 mole-% PO.

ANAL calcd. for $\text{-(C}_{12}\text{H}_{22}\text{O}_3\text{)}_{.22}\text{-(C}_3\text{H}_6\text{O)}_{.78}$: C,

64.70%; H, 10.38%. Found: C, 64.65%; H, 9.76%; ash, 0.26%.

c. Copolymerization with epichlorohydrin (ECH). A polymerization tube fitted with a 3-way pressure stopcock was dried in the manner described previously, then was charged under positive nitrogen pressure with MEU (1.4 g, 6.5 mmole, 30 mole-% of comonomer feed), toluene (14 ml) and epichlorohydrin (2.0 g, 22 mmole). The contents of the tube were de-gassed by three freeze-thaw cycles. The tube was charged with the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ initiator (1.4 ml of initiator solution 0.97 molar in aluminum, 5 mole-% based on epoxide monomers) and sealed at 0.01 mm. Polymerization was allowed to proceed for 40 days at room temperature. During this period the contents of the tube underwent gradual changes: transforming from a clear yellow solution to a soft, semi-transparent gel (ca. 3.5 days), and finally becoming a soft translucent elastic plug. The tube was opened and its contents were dissolved in 400 ml of a benzene-dioxane (1:1 v/v) mixture whose pH was previously adjusted to 5 by the addition of 2% methanolic HCl. The resulting turbid solution was clarified by centrifugation; this procedure removed minute white particles dispersed throughout the solution. Precipitation of the copolymer as white, crumb-like particles was accomplished by pouring the solution into 2.5 liters of acidified methanol (pH was adjusted to ca. 4 using anhydrous

hydrochloric acid). The copolymer was collected, washed with fresh methanol, stirred overnight in absolute methanol (one liter) and filtered. Final drying was performed over phosphorus pentoxide for 1 day at 0.05 mm and room temperature. The yield of extremely tough, elastomeric poly-(ECH-co-MEU) was 2.0 g (60%). The inherent viscosity of the copolymer (0.1% in CHCl_3 , 30°C) was 2.6 dL/g. The infrared spectrum (thin film) showed absorptions at 1740 cm^{-1} (C=O stretch, ester); 1255 , 1195 and 1175 cm^{-1} (C-O stretch, methyl ester); 1120 cm^{-1} (C-O-C stretch, ether) and 745 cm^{-1} (C-Cl stretch). See p. 298. The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 25.43 ppm ($-\text{CH}_2\text{CH}_2\text{COOCH}_3$); 25.96 ppm ($-\text{OCHCH}_2\text{CH}_2-$); 29.66, 29.71 and 30.21 ppm ($\{\text{CH}_2\}_4$); 32.36 ppm ($-\text{OCHCH}_2-$); 34.27 ppm ($-\text{CH}_2\text{COOCH}_3$); 44.12 ppm ($-\text{CH}_2\text{Cl}$); 51.11 ppm ($-\text{OCH}_3$); 69.91 ppm ($-\text{OCH}_2\text{CHCH}_2\text{Cl}$); 73.39 and 73.46 ppm ($-\text{OCH}_2\text{CH}-$); 79.45 ppm ($-\text{OCH}_2\text{CHCH}_2\text{Cl}$); 80.01 ppm ($-\text{OCH}_2\text{CH}-$) and 173.53 ppm ($-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$). See p. 320.

The relative composition of the copolymer was 16 mole-% MEU and 84 mole-% ECH.

ANAL. calcd. for $\{\text{C}_{12}\text{H}_{22}\text{O}_3\}_{.16}\{\text{C}_3\text{H}_5\text{ClO}\}_{.84}$:
 C, 47.61%; H, 6.95%; Cl, 26.59%. Found: C, 47.54%; H, 6.93%; Cl, 24.45%; ash < 0.5%.

d. Copolymerization with 1-Butene Oxide (BO). A polymerization tube fitted with a 3-way pressure stopcock was dried in the manner described previously. The tube was

charged under positive nitrogen pressure with MEU (1.7 g, 7.8 mmole, 30 mole-% of comonomer feed), toluene (12 ml) and BO (1.9 g, 26 mmole). The contents of the tube were de-gassed by three freeze-thaw cycles. The tube was then charged with the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (1.7 ml of initiator solution 0.97 molar in aluminum, 5 mole-% based on epoxide monomers) and sealed at 0.01 mm. After 1 day at room temperature the contents of the tube formed a clear yellow plug, nevertheless the polymerization was allowed to proceed a total of 49 days. The tube was opened and the contents were dissolved in 1,4-dioxane (150 ml) which also contained 3 ml of acidified methanol (5 drops conc. hydrochloric acid in 3 ml absolute methanol). The resulting turbid solution was filtered through a fine grit sintered glass funnel and the copolymer was precipitated by pouring the filtrate into 2.5 liters of acidified methanol (5 drops conc. hydrochloric acid). The rubbery mass of poly(BO-co-MEU) was collected by filtration, washed with absolute methanol (one liter) and dried for 18 hours at 40°C and 0.01 mm over phosphorus pentoxide. Yield of the snappy, white elastomer was 3.2 g (89%). The inherent viscosity of the copolymer (0.5% in CHCl_3 , 30°C) was 2.7 dL/g. The infrared spectrum (thin film) showed absorptions at 1740 cm^{-1} (C=O stretch, ester); 1240, 1195 and 1170 cm^{-1} (C-O stretch, methyl ester) and 1100 cm^{-1} (C-O-C

stretch, ether). See p. 298. The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 10.12 ppm ($-\underline{\text{CH}}_3$); 25.45 ($-\underline{\text{CH}}_2\text{CH}_3$ and $-\underline{\text{CH}}_2\text{CH}_2\text{COOCH}_3$); 26.10 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-\text{CH}_2\underline{\text{CH}}_2-$); 29.65, 29.84, 30.06 and 30.41 ppm ($\{\underline{\text{CH}}_2\}_4$); 32.92 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\underline{\text{CH}}_2-$); 34.27 ppm ($-\underline{\text{CH}}_2\text{COOCH}_3$); 51.02 ppm ($-\text{OCH}_3$); 72.24, 72.40 and 73.04 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2\text{CH}_3$); 73.56 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-$); 80.19 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-$); 80.77, 81.24 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2\text{CH}_3$) and 173.43 ppm ($-\overset{\text{O}}{\text{C}}-$). See p. 321.

The relative composition of the copolymer was 25 mole-% MEU and 75 mole-% BO.

ANAL. calcd. for $\{\text{C}_{12}\text{H}_{22}\text{O}_3\}_{.25}\{\text{C}_4\text{H}_8\text{O}\}_{.75}$: C, 66.94%; H, 10.76%. Found: C, 66.55%; H, 11.21%.

e. Copolymerization with 4,4,4-trichloro-1-butene oxide (TCBO). A polymerization tube fitted with a 3-way pressure stopcock was dried in the usual manner, then charged under positive nitrogen pressure with MEU (0.93 g, 4.4 mmole, 30 mole-% of comonomer feed), toluene (13 ml) and TCBO (2.5 g, 15 mmole). The contents of the tube were de-gassed by three freeze-thaw cycles. The tube was then charged with the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ initiator (1.0/0.5/1.0) (1.0 ml, 0.05 mmole aluminum, 5 mole-% initiator based on epoxide monomers) and was sealed at 0.01 mm. A clear yellow plug formed after 2 weeks reaction at room temperature. The tube was opened after standing a total of 30 weeks at room temperature. The soft elastic plug was removed and was partially dissolved in 1,4-dioxane (175 ml)

containing acidified methanol (5 ml of 1% hydrochloric acid). The 1,4-dioxane-insoluble portion was removed by centrifugation, washed with fresh 1,4-dioxane and soaked in absolute methanol. The rubbery solid was collected by filtration, washed with methanol, and dried for one day at 56°C and 0.01 mm over phosphorus pentoxide. Yield of the elastomeric copolymer was 0.3 g (8%). The relative composition of the copolymer was 41 mole-% MEU and 59 mole-% TCBO.

ANAL. calcd for $(C_{12}H_{22}O_3)_{.41}(C_4H_5Cl_3O)_{.59}$:
C, 45.69%; H, 6.30%; Cl, 32.79%. Found: C, 45.41%; H, 6.54%; Cl, 30.45%.

The 1,4-dioxane solution decanted after centrifugation was poured into 2.5 liters of acidified methanol (5 drops conc. hydrochloric acid). A white precipitate formed and was collected by filtration, washed with methanol and dried for one day at 56°C and 0.01 mm over phosphorus pentoxide. The yield of dioxane-soluble copolymer was 0.5 g (15%). The inherent viscosity of the copolymer (0.5% in 1,4-dioxane, 30°C) was 0.15 dL/g. The infrared spectrum (thin film) showed absorptions at 1740 cm^{-1} (C=O stretch, ester); 1250 , 1195 and 1170 cm^{-1} (C-O stretch, methyl ester); 1120 cm^{-1} (C-O-C stretch, ether); 775 and 700 cm^{-1} (C-Cl stretch). See p. 299. The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 25.44 ppm ($-\underline{\text{CH}}_2\text{CH}_2\text{COOCH}_3$);

26.12 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-\text{CH}_2\text{CH}_2-$); 29.68, 29.90 and 30.06 ppm ($(\text{CH}_2)_4$); 32.66 and 32.92 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2\text{CH}_2-$); 34.26 ppm ($-\text{CH}_2\text{COOCH}_3$); 51.13 ppm ($-\text{OCH}_3$); 57.72 and 57.94 ppm ($-\text{CH}_2\text{CCl}_3$); 72.07, 72.33, 72.56 and 72.68 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2\text{CCl}_3$); 73.65, 73.95 and 74.13 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-$); 77.75 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2\text{CCl}_3$); 79.94 and 80.17 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-$); 97.60 ppm ($-\text{CCl}_3$) and 173.75 ppm ($-\overset{\text{O}}{\underset{|}{\text{C}}}-$). See p. 321.

The relative composition of the dioxane-soluble copolymer fraction was 41 mole-% MEU and 59 mole-% TCBO.

ANAL. calcd. for $(\text{C}_{12}\text{H}_{22}\text{O}_3)_{.41}(\text{C}_4\text{H}_5\text{Cl}_3\text{O})_{.59}$:
C, 45.69%; H, 6.30%; Cl, 32.79%. Found: C, 45.95%; H, 6.38%; Cl, 33.27%.

f. Copolymerization with 1-hexene oxide (HO). A polymerization tube fitted with a 3-way pressure stopcock was dried in the usual manner, then charged under positive nitrogen pressure with MEU (1.3 g, 6.0 mmole, 30 mole-% of comonomer feed), toluene (11 ml) and HO (2.0 g, 20 mmole). The contents of the tube were then de-gassed by three freeze-thaw cycles. The comonomer solution was charged with the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (1.3 ml, 1.3 mmole aluminum, 5 mole-% based on epoxide monomers) and the tube was sealed at 0.01 mm. The contents of the tube formed a soft and transparent yellow plug after ca. one day. Polymerization was allowed to proceed a total of 31 days at room temperature. The tube was opened, the clear elastic plug was removed and dissolved in a benzene/

1,4-dioxane mixture (3/2 by volume) containing 30 ml of methanolic HCl (1% HCl). The resulting clear solution was filtered through a sintered glass funnel (coarse grit). The filtrate was poured into methanol (three liters) and the MEU/HO copolymer precipitated as a rubbery, white solid. After decanting of the supernatant mixture, the copolymer was then stirred overnight in fresh methanol (one liter), filtered and washed with absolute methanol. Poly(HO-co-MEU) was dried for one day at room temperature and 0.05 mm over phosphorus pentoxide. Yield of the semi-transparent, gum-like copolymer was 2.7 g (83%). The inherent viscosity of the copolymer (0.5% in CHCl_3 , 30°C) was 0.45 dL/g. The infrared spectrum (thin film) showed absorptions at 1745 cm^{-1} (C=O stretch, ester); 1250, 1198 and 1170 cm^{-1} (C-O stretch, methyl ester) and 1110 cm^{-1} (C-O-C stretch, ether). See p. 299. The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 14.42 ppm ($-\underline{\text{CH}}_3$); 23.38 ppm ($-\underline{\text{CH}}_2\text{CH}_3$); 25.33 ppm ($-\underline{\text{CH}}_2\text{CH}_2\text{COOCH}_3$); 26.04 ppm ($-\text{OCH}_2\overset{|}{\text{CHCH}}_2\underline{\text{CH}}_2-$); 28.19 ppm ($-\underline{\text{CH}}_2\text{CH}_2\text{CH}_3$); 29.56, 29.76, 30.00 and 30.34 ppm ($\text{-(}\underline{\text{CH}}_2\text{)}_4$); 32.53 ppm ($-\text{OCH}_2\overset{|}{\text{CHCH}}_2\text{C}_3\text{H}_7$ and $-\text{OCH}_2\overset{|}{\text{CHCH}}_2-$); 34.14 ppm ($-\underline{\text{CH}}_2\text{COOCH}_3$); 50.90 ppm ($-\text{OCH}_3$); 72.56, 72.81, 73.77 and 74.66 ppm ($-\text{OCH}_2\overset{|}{\text{CHC}}_4\text{H}_9$); 74.66 ($-\text{OCH}_2\overset{|}{\text{CH}}-$); 77.48, 77.97 and 80.13 ppm ($-\text{OCH}_2\overset{|}{\text{CHC}}_4\text{H}_9$); 80.13 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-$) and 173.21 ppm ($-\overset{\text{O}}{\text{C}}-$). See p. 322.

The relative composition of the copolymer was 25 mole-% MEU and 75 mole-% HO.

ANAL. calcd. for $(C_{12}H_{22}O_3)_{.25}(C_6H_{12}O)_{.75}$: C, 69.99%; H, 11.36%. Found: C, 69.90%; H, 11.37%; ash, 0.2%.

g. Copolymerization with phenyl glycidyl ether (PGE). A polymerization tube equipped with a 3-way pressure stopcock was dried in the manner described previously, then charged under positive nitrogen pressure with MEU (1.0 g, 4.7 mmole, 30 mole-% of comonomer feed), toluene (13 ml) and PGE (2.3 g, 15 mmole). The contents of the tube were de-gassed by three freeze-thaw cycles and the $Al(C_2H_5)_3/H_2O/AcAc$ (1.0/0.5/1.0) initiator (1.0 ml, 1.0 mmole aluminum, 5 mole-% initiator based on epoxide monomers) was added. The tube was sealed at 0.01 mm. The reaction mixture, initially a clear and fluid solution, formed a soft yellow gel (semi-transparent) after 12 hours, and became a rigid plug after 2 days. The tube was allowed to stand at room temperature for 30 weeks and then was opened. Attempts to dissolve the contents at room temperature in a 1,4-dioxane (175 ml)/acidified methanol (5 ml, 1% HCl) mixture were unsuccessful. The tough rigid plug was fractured into small pieces after immersing in liquid nitrogen. The small fragments were slurried overnight in absolute methanol, collected by filtration and dried for 24 hours at 56°C and 0.01 mm over phosphorus pentoxide. Yield of the hard rubbery MEU/PGE copolymer was 1.9 g (57%).

A portion of the copolymer was subsequently found

to be soluble in hot 1,4-dioxane. Thus 1.9 g of copolymer was slurried (under nitrogen) in 1,4-dioxane (50 ml) and heated to ca. 100°C. The hot mixture was centrifuged and the supernatant liquid poured into acidified methanol (250 ml, containing 1% hydrochloric acid). A light-yellow rubbery precipitate formed. The solid was collected by filtration, washed with methanol, and dried for one day at 61°C and 0.01 mm over phosphorus pentoxide. The yield of dioxane-soluble MEU/PGE copolymer was 0.5 g (26%). The inherent viscosity (0.5% in 1,4-dioxane, 30°C) was 1.1 dL/g. The infrared spectrum (thin film) showed absorptions at 3100-3000 cm^{-1} (aromatic C-H stretch), 2990-2720 cm^{-1} (aliphatic C-H stretch), 1470 cm^{-1} (C=O stretch, ester), 1250 cm^{-1} (asymmetric C-O-C stretch, aralkyl ether), 1150-1080 cm^{-1} (C-O-C stretch, ether), 750 and 690 cm^{-1} (aromatic ring out-of-plane bending). See p. 300. The ^{13}C NMR spectrum (d_2 -dichloromethane) showed peaks at 26.07 ppm ($-\underline{\text{CH}}_2\text{CH}_2\text{COOCH}_3$); 26.57 and 26.64 ppm ($-\text{OCH}_2\overset{|}{\text{CHCH}}_2\underline{\text{CH}}_2-$); 30.33, 30.45, 30.55 and 30.85 ppm ($(+\underline{\text{CH}}_2)_4$); 32.91, 33.05 and 33.18 ppm ($-\text{OCH}_2\overset{|}{\text{CHCH}}_2-$); 35.06 ppm ($-\underline{\text{CH}}_2\text{COOCH}_3$); 52.27 ppm ($-\text{OCH}_3$); 69.08 and 69.40 ppm ($-\underline{\text{CH}}_2\text{OPh}$); 70.66, 70.81 and 71.03 ppm ($-\text{OCH}_2\overset{|}{\text{CHCH}}_2\text{OPh}$); 74.0 and 74.5 ppm ($-\text{OCH}_2\text{CH}-$); 79.05, 79.50 and 80.09 ppm ($-\text{OCH}_2\underline{\text{CHCH}}_2\text{OPh}$); 80.82, 80.95 and 81.03 ppm ($-\text{OCH}_2\underline{\text{CH}}-$); 115.69 ppm (ortho-aromatic C); 121.87 ppm (para-aromatic C); 130.53 ppm (meta-aromatic C); 160.01 ppm (C_1 -aromatic C) and 175.05

ppm ($-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-$). See p. 322.

The relative composition of the dioxane-soluble copolymer fraction was 28 mole-% MEU and 72 mole-% PGE.

ANAL. calcd. for $(\text{C}_{12}\text{H}_{22}\text{O}_3)_{.28}(\text{C}_9\text{H}_{10}\text{O}_2)_{.72}$:

C, 70.29%; H, 8.01%. Found: C, 70.28%; H, 8.04%.

The copolymer fraction insoluble in hot dioxane and collected by centrifugation was slurried in acidified methanol (250 ml, containing 1% hydrochloric acid), filtered and washed with fresh methanol. The white elastomer was dried for one day at 61°C and 0.01 mm over phosphorus pentoxide. Yield of the insoluble MEU/PGE copolymer was 0.75 g (39%).

The relative composition of the copolymer was 26 mole-% MEU and 74 mole-% PGE.

ANAL. calcd. for $(\text{C}_{12}\text{H}_{22}\text{O}_3)_{.26}(\text{C}_9\text{H}_{10}\text{O}_2)_{.74}$:

C, 70.40%; H, 7.93%. Found: C, 70.38%; H, 7.98%.

h. Copolymerization with oxetane (Ox). A polymerization tube equipped with a 3-way pressure stopcock was dried in the manner described previously, then charged under positive nitrogen pressure with MEU (1.9 g, 8.8 mmole, 30 mole-% of comonomer feed), toluene (12 ml) and Ox (1.7 g, 29 mmole, 70 mole-% of comonomer feed). The contents of the tube were de-gassed by three freeze-thaw cycles and the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (2.0 ml, 1.9 mmole aluminum, 5 mole-% initiator based on epoxide monomers) was added. The tube was sealed at 0.01 mm and

allowed to stand at room temperature for 7 weeks. The viscosity of the solution increased gradually; a semi-transparent immobile plug was formed after ca. 5 days reaction. The tube was opened, the highly elastic plug was removed and dissolved in 1,4-dioxane (250 ml) which also contained acidified methanol (6 drops conc. hydrochloric acid in 3 ml methanol). The turbid solution, moderately viscous, was filtered through a sintered glass funnel (medium grit) and further clarified by centrifugation. Precipitation of the copolymer was accomplished by pouring the supernate into 2.5 liters of methanol. The pure-white elastomeric solid was collected by filtration, washed with methanol, and dried for 2 days at room temperature and 0.01 mm over phosphorus pentoxide. Yield of the MEU-Ox copolymer, a tough gum-like rubber, was 3.1 g (87%). The inherent viscosity of the copolymer (0.5% in CHCl_3 , 30°C) was 2.2 dL/g. The infrared spectrum (thin film) of the copolymer showed absorptions at 1740 cm^{-1} (C=O stretch, ester); 1240 , 1195 and 1170 cm^{-1} (C-O stretch, methyl ester), and 1115 cm^{-1} (C-O-C stretch, ether). See p. 300. The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 25.61 ppm ($-\text{CH}_2\text{CH}_2\text{COOCH}_3$); 26.15 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2\text{CH}_2-$); 29.87, 30.03 and 30.54 ppm (CH_2); 31.15 and 31.71 ppm ($-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-$); 33.03 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2-$); 34.45 ppm ($-\text{CH}_2\text{COOCH}_3$); 51.14 ppm ($-\text{OCH}_3$); 67.48, 68.43 and 69.03 ppm ($-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-$); 74.05 and 74.39 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-$); 79.47, 79.92, 80.32 and 80.53 ppm

$(-\text{OCH}_2\text{CH}-)$ and 173.52 ppm $(-\text{C}(=\text{O})-)$. See p. 323.

i. Attempted copolymerization with tetrahydrofuran (THF). A polymerization tube equipped with a 3-way pressure stopcock was dried in the manner described previously, then charged under positive nitrogen pressure with MEU (1.6 g, 7.4 mmole, 30 mole-% of comonomer feed), toluene (11 ml) and freshly distilled THF (1.8 g, 25 mmole, 70 mole-% of comonomer feed). The contents of the tube were de-gassed by three freeze-thaw cycles and the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (1.7 ml, 1.6 mmole aluminum, 5 mole-% based on epoxide monomers) was added. The tube was sealed at 0.01 mm and allowed to stand at room temperature for 29 days. The viscosity of the yellow solution increased gradually and a clear plug was formed after ca. 4 days reaction. The tube was opened, the elastic yellow plug was removed and dissolved in 1,4-dioxane (130 ml) which had been acidified (pH 4) with methanolic HCl. The turbid solution was filtered through a sintered glass funnel (medium grit) and poured into two liters of methanol. The finely divided white solid that precipitated was collected by filtration, slurried overnight in absolute methanol. (200 ml), filtered and dried for one day at 40°C and 0.01 mm over phosphorus pentoxide. Yield of the white elastomeric solid was 1.3 g (38%). The inherent viscosity of the polymer (0.5% in 1,4-dioxane, 30°C) was 0.8 dL/g. The polymer was identified from its infrared spectrum and

^{13}C NMR spectrum as poly(MEU), not the copolymer of MEU and THF. The infrared spectrum (thin film) showed absorptions at 1740 cm^{-1} (C=O stretch, ester); 1240 , 1195 and 1145 cm^{-1} (C-O stretch, methyl ester); and 1110 cm^{-1} (C-O-C stretch, ether). See p. 301. The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 25.36 ppm ($-\text{CH}_2\text{CH}_2\text{COOCH}_3$); 26.04 ppm ($-\text{OCH}_2\text{CH}(\text{CH}_2\text{CH}_2-)$); 29.60 , 29.79 , 30.03 and 30.39 ppm ($(\text{CH}_2)_4$); 32.96 ppm ($-\text{OCH}_2\text{CHCH}_2-$); 34.17 ppm ($-\text{CH}_2\text{COOCH}_3$); 50.89 ppm ($-\text{OCH}_3$); 73.80 ppm ($-\text{OCH}_2\text{CH}-$); 80.22 ppm ($-\text{OCH}_2\text{CH}-$) and 173.19 ppm ($-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$). See p. 323.

E. Polymerizations of Cyclic Ethers using
the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0)
Initiator

1. General procedure for polymerization. Polymerizations of cyclic ether monomers were also carried out in the absence of the ester-substituted epoxide MEU for comparative purposes. Experimental procedures and techniques used for each individual cyclic ether listed below were identical to those used (and already described) for their copolymerization with MEU. The information provided below is therefore presented in a highly condensed form. This format was adopted in order to minimize redundancy with the detailed descriptions given in Section D.3 of this chapter.

a. Poly(ethylene oxide). EO (3.3 g, 75 mmole), toluene (10 ml), $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (3.8 ml, 3.7 mmole aluminum, 5 mole-%). Reaction time: 7

days; yield: 3.0 g (92%); inherent viscosity (0.1% in CHCl_3 , 30°C): 9.9 dL/g. Infrared spectrum (thin film): $3020\text{--}2680\text{ cm}^{-1}$ (C-H stretch), 1110 cm^{-1} (C-O-C stretch, ether). See p. 301. ^{13}C NMR spectrum (CDCl_3): 71.94 ppm ($-\text{CH}_2\text{CH}_2\text{O}-$). See p. 324.

b. Poly(propylene oxide). PO (1.9 g, 30 mmole), benzene (10 ml), $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (4.7 ml, 1.5 mmole aluminum, 5 mole-%). Reaction time: 13 days; yield: 1.9 g (98%); inherent viscosity (0.1% in CHCl_3 , 30°C): 6.7 dL/g. Infrared spectrum (thin film): $3020\text{--}2680\text{ cm}^{-1}$ (C-H stretch), 1105 cm^{-1} (C-O-C stretch, ether). See p. 302. ^{13}C NMR spectrum (benzene, D_2O external lock): 18.01 and 18.88 ppm ($-\text{CH}_3$); 73.79 and 74.08 ppm ($-\text{CH}_2\overset{|}{\text{CHO}}-$) and 76.01 ppm ($-\text{CH}_2\overset{|}{\text{CHO}}-$). See p. 324.

c. Poly(epichlorohydrin). ECH (3.0 g, 32 mmole), toluene (11 ml), $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (1.7 ml, 1.6 mmole aluminum, 5 mole-% initiator). Reaction time: 40 days; yield: 0.59 g (20%) of a benzene-soluble fraction, 2.1 g (70%) of a benzene-insoluble fraction; inherent viscosity (0.5% in CHCl_3 , 30°C) of benzene-soluble fraction: 0.13 dL/g. Infrared spectrum (thin film): $3060\text{--}2680\text{ cm}^{-1}$ (C-H stretch), 1730 cm^{-1} (C=O stretch), 1110 cm^{-1} (C-O-C stretch, ether) and 745 cm^{-1} (C-Cl stretch). See p. 302. ^{13}C NMR spectrum (d_6 -benzene): 43.98 ppm ($-\text{CH}_2\text{Cl}$), 69.80 ppm ($-\text{CH}_2\overset{|}{\text{CHO}}$) and 79.40 ppm ($-\text{CH}_2\overset{|}{\text{CHO}}-$). See p. 325.

d. Poly(butylene oxide). BO (3.0 g, 42 mmole), toluene (9.3 ml), and $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (2.1 ml, 2.1 mmole aluminum, 5 mole-% initiator). Reaction time: 29 days; yield: 2.8 g (93%); appearance: gum-like rubber; inherent viscosity (0.1% in CHCl_3 , 30°C): 11 dL/g. Infrared spectrum (thin film): 3040-2660 cm^{-1} (C-H stretch), 1105 cm^{-1} (C-O-C stretch, ether). See p. 303. ^{13}C NMR spectrum (d_6 -benzene): 9.96 ppm ($-\text{CH}_3$); 25.31 ppm ($-\text{CH}_2\text{CH}_3$); 72.16, 72.35 and 72.88 ppm ($-\text{CH}_2\text{CHO}-$); 80.63 and 81.07 ppm ($-\text{CH}_2\text{CHO}-$). See p. 325.

e. Poly (4,4,4-trichloro-1-butene oxide). TCBO (3.1 g, 17 mmole), toluene (11 ml), $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (0.9 ml, 0.9 mmole aluminum, 5 mole-% initiator). Reaction time: 68 days; yield: 3.0 g (97%), insoluble in benzene or boiling acetone; appearance: crumb-like white elastomer. Infrared spectrum (KBr): 3020-2720 cm^{-1} (C-H stretch), 1190-1000 cm^{-1} (C-O-C stretch, ether), 775 and 695 cm^{-1} (C-Cl stretch). See p. 303.

f. Poly(1-hexene oxide). HO (3.0 g, 30 mmole), toluene (10 ml) and $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (1.5 ml, 1.5 mmole aluminum, 5 mole-% initiator). Reaction time: 31 days; yield: 2.8 g (92%); appearance: semi-transparent elastomer; inherent viscosity (0.1% in CHCl_3 , 30°C): 11 dL/g. Infrared spectrum (thin film): 3060-2600 cm^{-1} (C-H stretch), 1110 cm^{-1} (C-O-C stretch,

ether). See p. 304. ^{13}C NMR spectrum (d_6 -benzene): 14.54 ppm ($-\underline{\text{C}}\text{H}_3$); 23.61 ppm ($-\underline{\text{C}}\text{H}_2\text{CH}_3$); 28.44 ppm ($-\underline{\text{C}}\text{H}_2\text{CH}_2\text{CH}_3$); 32.83 ppm ($-\underline{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2\text{CH}_3$); 73.00, 73.19, 73.98 and 75.09 ppm ($-\underline{\text{C}}\text{H}_2\overset{|}{\text{C}}\text{HO}-$); and 80.52 ppm ($-\text{CH}_2\overset{|}{\text{C}}\text{HO}-$). See p. 326.

g. Poly(phenyl glycidyl ether). PGE (3.3 g, 22 mmole), toluene (13 ml), and $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (1.1 ml, 1.1 mmole aluminum, 5 mole-% initiator). Reaction time: 32 days; yield: quantitative; appearance: hard white plug. Insoluble and non-swellable in common organic solvents.

h. Oxetane polymerization. Not attempted.

i. Attempted tetrahydrofuran polymerization. THF (2.7 g, 37 mmole), toluene (9.5 ml), and $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (1.9 ml, 1.8 mmole aluminum, 5 mole-% initiator). Reaction time: 68 days; appearance: clear yellow solution, no increase in viscosity. No precipitate formed when the reaction mixture was poured into acidified methanol.

F. Modifications of Functionally-Substituted Poly(Alkylene Oxides)

1. Preparation of poly(alkylene oxide) ionomers and poly-electrolytes.

a. Saponification of poly(methyl 10,11-epoxyundecanoate). A clean 4-neck 250 ml round-bottomed flask was equipped with a mechanical stirring apparatus,

reflux condenser, 3-way adapter, and nitrogen inlet and outlet tubes. The flask was charged with poly(MEU) (5.0 g 0.023 mole) and then was purged with nitrogen for 5 minutes. Purified 1,4-dioxane (120 ml) was added and the flask was partially immersed in a 100°C oil bath. Poly(MEU) dissolved rapidly and produced a slightly turbid solution. A 4N aqueous sodium hydroxide solution (15 ml, 0.060 mole OH^-) was added, causing formation of two immiscible phases. The mixture was stirred vigorously. After 10 minutes the reaction mixture became very milky in appearance and the viscosity started to increase rapidly. Shortly thereafter a white solid began to precipitate. The reaction was stopped after one hour and the contents of the flask were cooled to room temperature. The highly swollen, granular mass of precipitated polymer was collected by filtration and washed with methanol until the washings were neutral. The pure-white polymer, a free-flowing powder, was dried for one day at room temperature and 0.01 mm over phosphorus pentoxide. The yield of poly(10,11-epoxyundecanoic acid sodium salt) was 4.6 g (89%). The inherent viscosity of the polymer (0.5% in water, 30°C) was 0.41 dL/g. The infrared spectrum (KBr wafer) showed absorptions centered at 1565 cm^{-1} (CO_2^- stretch, carboxylate anion) and 1100 cm^{-1} (C-O-C stretch, ether). See p. 304. The ^{13}C NMR spectrum (D_2O) showed peaks at 26.57 ppm ($-\text{OCH}_2\overset{|}{\text{CHCH}_2\text{CH}_2}-$), 27.38 ppm ($-\text{CH}_2\text{CH}_2\text{COO}^-\text{Na}^+$), 29.73 and 30.63 ppm ($(\text{CH}_2)_4$), 32.80 ppm

$(-\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2-)$, 38.98 ppm $(-\text{CH}_2\text{COO}^-\text{Na}^+)$, 73.63 ppm
 $(-\text{OCH}_2\overset{|}{\text{CH}}-)$, 80.62 ppm $(-\text{OCH}_2\overset{|}{\text{CH}}-)$ and 184.59 ppm $(-\text{COO}^-\text{Na}^+)$.
 See p. 326.

ANAL. calcd. for $(\text{C}_{11}\text{H}_{19}\text{NaO}_3)_n$: C, 59.44%; H, 8.32%; Na, 10.34%. Found: C, 59.34%; H, 8.53%; Na, 10.1%.

b. Saponification of poly(methyl 10,11-epoxyundecanoate-co-ethylene oxide). A 4-neck 250 ml round-bottomed flask was equipped with a mechanical stirring apparatus, reflux condenser, 3-way adapter, and nitrogen inlet and outlet tubes. The flask was charged with poly(MEU-co-EO) (6.0 g, 4 mole-% ester groups) and then was purged with nitrogen for 5 minutes. Purified 1,4-dioxane (150 ml) was added with a syringe and the flask was partially immersed in a 100°C oil bath. Poly(MEU-co-EO) dissolved after ca. 4 hours; the resulting solution was turbid and moderately viscous. A solution of 4N aqueous sodium hydroxide (10 ml, 0.040 mole OH^-) was added. The turbidity of the reaction mixture immediately began to increase, reached a maximum after ca. 25 minutes, then decreased rapidly until the solution was nearly transparent. The reaction was stopped after 1.5 hours and the contents of the flask were cooled to room temperature. The solution was divided into two portions of equal volume (75 ml). One portion was set aside for reaction with glacial acetic acid, see Sec. F.2.b. in this chapter (p. 89). The remaining 75 ml aliquot was poured into one liter of an ether/

methanol solution (4/1 by volume). The poly(alkylene oxide) ionomer precipitated as a fluffy white solid. After decanting the supernatant liquid, the copolymer was then soaked for one day in 800 ml of ether/methanol (3/1 by volume) solution, the supernate was again decanted and the soaking procedure repeated one final time. The ionomer was collected by filtration, washed with fresh ether-methanol solution (3/1 by volume) and finally anhydrous diethyl ether. Drying of the fluffy white copolymer was performed over phosphorus pentoxide, at room temperature and 0.01 mm for two days. The yield of poly(alkylene oxide) ionomer was 1.4 g (47%). The inherent viscosity of the ionomer (0.5% in H_2O , $30^\circ C$) was 4.0 dL/g. The infrared spectrum (thin film from methanol) showed absorptions at $3020-2660\text{ cm}^{-1}$ (C-H stretch), 1567 cm^{-1} (C=O stretch, carboxylate anion) and 1110 cm^{-1} (C-O-C stretch, ether). See p. 305. The ^{13}C NMR spectrum (D_2O) showed peaks at 25.73 ppm ($-OCH_2\overset{|}{CH}CH_2CH_2-$); 27.15 ppm ($-\underline{CH}_2CH_2COOCH_3$); 29.89 and 30.01 ppm ($\{CH_2\}_4$); 31.59 ppm ($-OCH_2\overset{|}{CH}CH_2-$); 38.87 ppm ($-\underline{CH}_2COO^-Na^+$); 69.28, 69.92, 70.05 and 71.63 ppm ($-\underline{CH}_2CH_2O-$); 73.77 and 74.00 ppm ($-OCH_2\overset{|}{CH}-$); 80.06 ppm ($-OCH_2\overset{|}{CH}-$) and 185.03 ppm ($-\underline{COO}^-Na^+$). See p. 327.

The relative composition of the ionomer was 4 mole-% 10,11-epoxyundecanoate sodium salt (EUA^-Na^+) and 96 mole-% EO.

ANAL. calcd for $\{C_{11}H_{19}NaO_3\}_{.04}\{C_2H_4O\}_{.96}$: C, 55.38%; H, 9.06%; Na, 1.80%. Found: C, 54.15%; H, 9.06%; Na, 1.8%.

2. Preparation of poly(alkylene oxide) carboxylic acids.

a. Poly(10,11-epoxyundecanoic acid). A 3-neck 100 ml round-bottomed flask was equipped with a mechanical stirring apparatus, reflux condenser, and nitrogen inlet and outlet tubes. The flask was charged with poly(10,11-epoxyundecanoic acid sodium salt) (1.0 g, 4.6 mmole carboxylate groups), and flushed with nitrogen for 10 minutes. The polymer was dissolved in distilled water (30 ml) and gave a turbid solution of moderately low viscosity. Glacial acetic acid (6.0 ml, 105 mmole) was added. Precipitation of a highly swollen solid occurred almost immediately. The mixture was stirred vigorously for 2 hours, and then was poured into acetone (600 ml) and filtered. The white granular solid collected by filtration was washed successively with acetone, methanol and then air-dried. An infrared spectrum (KBr wafer) showed two carbonyl absorptions, at 1705 cm^{-1} (C=O stretch, carboxylic acid) and at 1565 cm^{-1} (C=O stretch, carboxylate anion) indicating that some unreacted carboxylate salt groups remained. Complete neutralization was achieved by slurrying the polymer overnight in distilled water (25 ml) whose pH had been adjusted to 4 with glacial acetic acid. The polymer was again collected by filtration, washed with water and dried in a desiccator for 1 hour over anhydrous calcium sulfate at 35 mm. Final drying was performed for 12 hours at 56°C and 0.01 mm over phosphorus pentoxide. The yield of wax-like poly(EUA)

was 0.98 g (96%). The inherent viscosity of the polymer (0.5% in 1,4-dioxane, 30°C) was 0.17 dL/g. The infrared spectrum (thin film) displayed prominent absorptions at 3540-2350 cm^{-1} (O-H stretch, carboxylic acid), 1710 cm^{-1} (C=O stretch, carboxylic acid), 1110 cm^{-1} (C-O-C stretch, ether) and 925 cm^{-1} (O-H out-of-plane bending). See p. 305. The ^{13}C NMR spectrum (d_8 -dioxane) showed peaks at 25.71 ppm ($-\underline{\text{CH}}_2\text{CH}_2\text{COOH}$), 26.09 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2\underline{\text{CH}}_2-$), 30.15 ppm ($\{\underline{\text{CH}}_2\}_4$), 32.93 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\underline{\text{CH}}_2-$), 34.05 ppm ($-\underline{\text{CH}}_2\text{COOH}$), 73.70 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-$), 80.22 ppm ($-\text{OCH}_2\underline{\text{CH}}-$) and 175.17 ppm ($-\underline{\text{COOH}}$). See p. 327.

ANAL. calcd. for $\{\text{C}_{11}\text{H}_{20}\text{O}_3\}_n$: C, 65.97%; H, 10.07%. Found: C, 65.71%; H, 10.25%; Na, 0.1%.

b. Poly(10,11-epoxyundecanoic acid-co-ethylene oxide). A 75 ml aliquot of poly(10,11-epoxyundecanoic acid sodium salt-co-ethylene oxide) (3.0 g) in aqueous 1,4-dioxane had been prepared as previously described in Section F.1.b. of this chapter. The turbid solution of poly(alkylene oxide) ionomer was stirred (mechanically) at room temperature in a 250 ml round-bottomed flask equipped with a reflux condenser, and nitrogen inlet and outlet tubes. Glacial acetic acid (3.2 ml, 56 mmole) was added. The reaction mixture immediately became very opaque and was allowed to stir for one day under nitrogen. The mixture was poured into distilled water (400 ml), the resulting aqueous suspension of poly(alkylene oxide) carboxylic acid

was centrifuged and the supernatant liquid decanted. The sticky, rubbery copolymer was repeatedly washed by re-suspending in distilled water, centrifuging and decanting the supernatant liquid. Washings remained slightly acidic, even after the odor of acetic acid was no longer detected, indicating a slight solubility of the copolymer. The highly swollen copolymer was pre-dried for one day at 0.01 mm in a dessicator, then dried to constant weight at room temperature and 0.01 mm over phosphorus pentoxide. Yield of the spongy, white poly(EUA-co-EO) was 1.0 g (33%). The inherent viscosity of the poly(alkylene oxide) carboxylic acid was 1.8 dL/g (0.5% in 1,4-dioxane, 30°C). The infra-red spectrum (thin film) showed absorptions at 3650-2500 cm^{-1} (O-H stretch, carboxylic acid), 1730 cm^{-1} (C=O stretch, carboxylic acid) and 1110 cm^{-1} (C-O-C stretch, ether). See p. 306. The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 25.27 ppm ($-\text{CH}_2\text{CH}_2\text{COOH}$); 25.80 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2\text{CH}_2-$); 29.48, 29.64, 29.83 and 30.15 ppm ($\{\text{CH}_2\}_4$); 32.55 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}\text{CH}_2-$); 34.31 ppm ($-\text{CH}_2\text{COOH}$); 69.91, 71.00, 71.40 and 72.98 ppm ($-\text{OCH}_2\text{CH}_2-$); 74.44 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-$); 79.53 ppm ($-\text{OCH}_2\overset{|}{\text{CH}}-$) and 170.82 ($-\text{COOH}$). See p. 328.

ANAL. calcd. for $\{\text{C}_{11}\text{H}_{20}\text{O}_3\}_{.04}\{\text{C}_2\text{H}_4\text{O}\}_{.96}$:
 C, 56.35%; H, 9.30%. Found: C, 54.37%; H, 8.95%; Na, 0.09%; ash, 5.4%.

G. Preparation of Functional Oxymethylene
Copolymers and Terpolymers

1. Polymerization of 1,3,5-trioxane (TO) with $(\text{CF}_3\text{SO}_2)_2\text{O}$ as the initiator. TO (2.1 g, 23 mmole) was distilled under nitrogen from a blue sodium metal-benzophenone complex into a tared, flamed-out 6-inch polymerization tube. The tube was equipped with a 3-way adapter (with teflon stopcock) and a magnetic stirring bar. Purified DCE (4.6 ml) was added with a nitrogen-purged syringe and the tube was partially immersed in a 65°C oil bath. A period of 15 minutes was allowed for the TO to dissolve and for the solution to attain thermal equilibrium. The tube was then charged with a stock 0.035 molar TFA/DCE initiator solution (0.11 ml, 3.7×10^{-3} mmole TFA) using a nitrogen-purged gas-tight syringe. The reaction mixture became turbid after 40 seconds; several minutes afterwards the entire volume of solution was filled with the snow-white precipitate of polyoxymethylene. The tube was kept in the 65°C oil bath for 33 hours and then was cooled to room temperature. The polymer was collected by filtration and washed successively with 5% aqueous sodium bicarbonate (200 ml), distilled water (100 ml) and absolute methanol (100 ml). Polyoxymethylene was dried in a dessicator at 0.05 mm and room temperature over anhydrous calcium sulfate. The yield of white, powdery POM was 2.0 g (96%). The infrared spectrum (KBr wafer) of the polymer showed absorptions at 3180-2760

cm^{-1} (C-H stretch) and two broad, intense absorptions centered at 1105 cm^{-1} (C-O stretch, asymmetric) and 960 cm^{-1} (C-O stretch, symmetric). A weak absorption in the O-H stretching region of the infrared spectrum ($3660\text{--}3240 \text{ cm}^{-1}$) indicated the concentration of hydroxyl end groups to be quite low. See p. 306.

2. Copolymerization of trioxane (TO) and 1,3-dioxolane (DO) with $\text{CF}_3\text{SO}_2\text{H}$ as initiator. TO (1.7 g, 19 mmole) was distilled under nitrogen from a blue sodium-benzophenone diketyl complex into a tared, flamed-out 6-inch polymerization tube. The tube was equipped with a 3-way adapter (with teflon stopcock) and magnetic stirring bar. Under positive nitrogen pressure, the tube was charged with DCE (4.2 ml), DO (0.14 g, 2 mmole, 10 mole-% of comonomer feed) and then partially immersed in a 65°C oil bath. A period of ca. 15 minutes was allowed for the TO to dissolve and for the solution to attain thermal equilibrium. A stock 0.035 molar TFA/DCE initiator solution (0.1 ml, 3.5×10^{-3} mmole TFA) was added with a nitrogen-purged, gas-tight syringe. The clear, colorless solution became turbid after ca. 2-3 minutes. Rapid precipitation of a finely-divided white solid began soon after the onset of turbidity. The tube was kept in the 65°C oil bath for 33 hours and then was cooled to room temperature. The copolymer was collected by filtration and washed successively with 5%

aqueous sodium bicarbonate (200 ml), distilled water (100 ml), and absolute methanol (100 ml). The copolymer was dried for 12 hours at 0.05 mm and room temperature over anhydrous calcium sulfate. The yield of white, powdery TO/DO copolymer was 1.7 g (91%). The inherent viscosity of the copolymer (0.1% in 98 weight-% p-chlorophenol/2 weight-% α -pinene, 60°C) was 0.97 dL/g. The infrared spectrum (KBr wafer) showed absorptions at 3660-3300 cm^{-1} (O-H stretch, moderately weak), 3140-2750 cm^{-1} (C-H stretch), 1120 cm^{-1} (C-O-C stretch, asymmetric) and 940 cm^{-1} (C-O-C stretch, symmetric). See p. 307. The melting point of the copolymer (as determined by DSC) was 162.5°C.

3. Copolymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) and trioxane (TO) with $(\text{CF}_3\text{SO}_2)_2\text{O}$ as initiator. TO (2.5 g, 28 mmole) was distilled under nitrogen from a blue sodium-benzophenone diketyl complex into a tared, flamed-out 6-inch polymerization tube. The tube was equipped with a 3-way adapter (with teflon stopcock) and magnetic stirring bar. The assembled apparatus was transferred to a nitrogen dry box where MEDOX (0.34 g, 1.4 mmole, 5 mole-% of comonomer feed) was added. After removal from the dry box, the tube was charged under positive nitrogen pressure with purified DCE (5.8 ml), and then was partially immersed in a 65°C oil bath. A period of ca. 15 minutes was allowed for the monomers to dissolve and the

solution to reach thermal equilibrium. A stock 0.035 molar TFA/DCE initiator solution (0.14 ml, 4.9×10^{-3} mmole TFA) was added using a nitrogen-purged gas-tight syringe. The reaction mixture turned pale orange after 2 to 3 minutes. The change in color was soon followed by the development of turbidity in the solution and precipitation of an off-white solid. The tube was kept in the 65°C oil bath for 33 hours and then cooled to room temperature. The precipitated solid was collected by filtration and washed successively with 5% aqueous sodium bicarbonate (200 ml), distilled water (100 ml) and absolute methanol (100 ml). The oxy-methylene copolymer was dried for 12 hours at 0.05 mm and room temperature over anhydrous calcium sulfate. The yield of chalky, white TO/MEDOX copolymer was 2.2 g (75%). The inherent viscosity of the copolymer (0.1% in 98 weight-% p-chlorophenol/2 weight-% α -pinene, 60°C) was 0.51 dL/g. The infrared spectrum (KBr wafer) showed the following absorptions: 3660-3300 cm^{-1} (O-H stretch, moderately weak), 3080-2760 cm^{-1} (C-H stretch), 1740 cm^{-1} (C=O stretch, ester, weak), 1100 cm^{-1} (C-O-C stretch, asymmetric) and 940 cm^{-1} (C-O-C stretch, symmetric). See p. 307.

Relative composition of the copolymer, determined by quantitative infrared analysis, was 1 mole-% MEDOX and 99 mole-% TO.

4. Terpolymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane, trioxane and 1,3-dioxolane with $(\text{CF}_3\text{SO}_2)_2\text{O}$ as the initiator. TO (3.1 g, 35 mmole) was distilled under nitrogen from a blue sodium-benzophenone diketyl complex into a tared, flamed-out 6-inch polymerization tube. The tube was equipped with a 3-way adapter (with teflon stop-cock) and magnetic stirring bar. The assembled apparatus was transferred to a nitrogen dry box where MEDOX (0.43 g, 1.7 mmole, 5 mole-% of termonomer feed) was added. After removal from the dry box, the tube was charged under positive nitrogen pressure with DCE (7.8 ml) and DO (0.26 g, 3.5 mmole, 10 mole-% of termonomer feed). The polymerization vessel was partially immersed in a 65°C oil bath; a period of 15 minutes was allowed for the monomers to dissolve and the solution to reach thermal equilibrium. The clear, colorless solution was then charged with a stock 0.035 molar TFA/DCE initiator solution (0.18 ml, 6.3×10^{-3} mmole TFA). The reaction mixture turned pale-orange after 2 to 3 minutes; the change in color was soon followed by the development of turbidity in the solution. An off-white solid slowly began to precipitate from the solution. The tube was kept in the 65°C oil bath for 33 hours and then was cooled to room temperature. The precipitated solid was collected by filtration and washed successively with 5% aqueous sodium bicarbonate (200 ml), distilled water (100 ml) and absolute methanol. The terpolymer was dried for 12

hours at 0.05 mm and room temperature over anhydrous calcium sulfate. The yield of chalky, white TO/MEDOX/DO terpolymer was 3.0 g (79%). The inherent viscosity (0.1% in 98 weight-% p-chlorophenol/2 weight-% α -pinene) was 0.66 dL/g. The melting point of the terpolymer was 163°C (measured by DSC). The infrared spectrum (KBr wafer) showed absorptions at 3640-3320 cm^{-1} (O-H stretch, moderately weak), 3060-2760 cm^{-1} (C-H stretch), 1735 cm^{-1} (C=O stretch, ester, weak), 1110 cm^{-1} (C-O-C stretch, asymmetric) and 940 cm^{-1} (C-O-C stretch, symmetric). See p. 308.

The terpolymer was found by quantitative infrared analysis to contain 0.5 mole-% MEDOX.

5. Copolymerization of methyl 10,11-epoxyundecanoate (MEU) and trioxane (TO) with $(\text{CF}_3\text{SO}_2)_2\text{O}$ as the initiator. TO (2.0 g, 24 mmole) was distilled under nitrogen from a blue sodium-benzophenone diketyl complex into a tared, flamed-out 6-inch polymerization tube. The tube was equipped with a 3-way adapter (with teflon stopcock) and magnetic stirring bar. MEU (0.24 g, 1.1 mmole, 5 mole-% of comonomer feed) and DCE (4.5 ml) were added by nitrogen-purged gas-tight syringes. The tube was then partially immersed in a 65°C oil bath; a period of 15 minutes was allowed for the TO to dissolve and the solution to reach thermal equilibrium. The clear, colorless solution was then charged with a stock

0.035 molar TFA/DCE initiator solution (0.11 ml, 3.8×10^{-3} mmole TFA). After 15 hours the contents of the tube became light orange; soon afterwards the solution became turbid and an off-white solid began to precipitate slowly. The tube was kept in the 65°C oil bath for 33 hours and then was cooled to room temperature. The precipitated solid was collected by filtration and washed successively with 5% aqueous sodium bicarbonate (200 ml), distilled water (100 ml) and absolute methanol (100 ml). The functional oxymethylene copolymer was dried for 12 hours at 0.05 mm and room temperature over anhydrous calcium sulfate. The yield of chalky, white TO/MEU copolymer was 2.1 g (94%). The inherent viscosity (0.1% in 98 weight-% p-chlorophenol/2 weight-% α -pinene, 60°C) was 0.27 dL/g. The melting point of the TO/MEU copolymer (determined by DSC) was 166.4°C. The infrared spectrum (KBr wafer) showed the following absorptions: 3640-3270 cm^{-1} (O-H stretch, moderately weak), 3140-2750 cm^{-1} (C-H stretch), 1740 cm^{-1} (C=O stretch, ester, moderately weak), 1105 cm^{-1} (C-O-C stretch, asymmetric) and 940 cm^{-1} (C-O-C stretch, symmetric). See p. 308.

The copolymer was found to contain 1.6 mole-% MEU by quantitative infrared analysis.

6. Terpolymerization of methyl 10,11-epoxyundecanoate (MEU), trioxane (TO) and 1,3-dioxolane (DO) with $(\text{CF}_3\text{SO}_2)_2\text{O}$ as the initiator. TO (2.5 g, 27 mmole) was distilled under nitrogen from a blue sodium-benzophenone diketyl complex into a tared, flamed-out 6-inch polymerization tube. The tube was equipped with a 3-way adapter (with teflon stopcock) and a magnetic stirring bar. MEU (0.29 g, 1.4 mmole), DCE (6.1 ml) and DO (0.20 g, 2.7 mmole) were added by nitrogen-purged gas-tight syringes. The polymerization vessel was then partially immersed in a 65°C oil bath; a period of 15 minutes was allowed for the TO to dissolve and for the solution to reach thermal equilibrium. The clear, colorless solution was then charged with a stock 0.035 molar TFA/DCE initiator solution (0.14 ml, 4.9×10^{-3} mmole TFA). After 19 hours the reaction mixture became light orange; soon afterwards the solution became turbid and an off-white solid began to precipitate. The tube was kept in the 65°C oil bath for 33 hours and then was cooled to room temperature. The precipitated solid was collected by filtration and washed successively with 5% aqueous sodium bicarbonate (200 ml), distilled water (100 ml) and absolute methanol (100 ml). The terpolymer was dried for 12 hours at 0.05 mm and room temperature over anhydrous calcium sulfate. The yield of chalky, white TO/MEU/DO terpolymer was 1.4 g (46%). The inherent viscosity (0.1% in 98 weight-% p-chlorophenol/2 weight-%

α -pinene, 60°C) was 0.32 dL/g. The melting point of the TO/MEU/DO terpolymer (determined by DSC) was 166.5°C. The infrared spectrum showed the following absorptions: 3630-3320 cm^{-1} (O-H stretch, moderately weak), 3060-2760 cm^{-1} (C-H stretch), 1740 cm^{-1} (C=O stretch, ester), 1105 cm^{-1} (C-O-C stretch, asymmetric) and 940 cm^{-1} (C-O-C stretch, symmetric). See p. 309.

The terpolymer was found to contain 0.5 mole-% MEU by quantitative infrared analysis.

7. Copolymerizability of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) and trioxane (TO) with $(\text{CF}_3\text{SO}_2)_2\text{O}$ as the initiator. Five polymerization tubes, equipped with magnetic stirring bars and 3-way adapters with teflon stopcocks, were flamed-out under nitrogen, cooled to room temperature and weighed. TO was then distilled, under nitrogen, from a blue sodium-benzophenone diketyl complex into each tube. Immediately after charging with TO and reweighing the tubes were transferred to a nitrogen dry-box. Each successive tube was charged with the appropriate amount of MEDOX so that comonomer mixtures with 5, 10, 15, 25 and 40 mole-% MEDOX were prepared. After removal from the dry box, the tubes were charged under positive nitrogen pressure with purified DCE. The volume of DCE added to each tube was that required for the concentration of comonomers to be 5 mole-lit $^{-1}$. The tubes were partially

immersed in a 65°C oil bath; a period of 15 minutes was allowed for the solids to dissolve and the solutions to reach thermal equilibrium. Each tube was then charged with the required amount of a stock initiator solution, 0.035 molar TFA/DCE. The time for onset of turbidity was recorded for each reaction. The tubes were kept in the 65°C oil bath for 34 hours, removed and cooled to room temperature. Precipitated solids were collected by filtration in pre-tared sintered glass funnels. Each copolymer was washed successively with 5% aqueous sodium bicarbonate (200 ml), distilled water (100 ml) and absolute methanol (100 ml). Samples were dried for one day at 0.05 mm and room temperature over anhydrous calcium sulfate. The yields and inherent viscosities (0.1% in 98 weight-% p-chlorophenol/2 weight-% α -pinene, 60°C) were determined. Infrared spectra (KBr wafers) were recorded and showed the following absorptions: 3660-3320 cm^{-1} (O-H stretch), 3130-2750 cm^{-1} (C-H stretch), 1740 cm^{-1} (C=O stretch, ester, variable intensity), 1110 cm^{-1} (C-O-C stretch, ether) and 940 cm^{-1} (C-O-C stretch, symmetric). See p. 309.

Refer to Table 2, p. 101, for quantities of individual chemicals used in the series of experiments described as well as for copolymer yields and inherent viscosities.

TABLE 2

COPOLYMERIZATIONS OF 4-(1-CARBOMETHOXYNONYL)-1,3-DIOXOLANE (MEDOX) AND
TRIOXANE (TO) WITH TRIFLIC ANHYDRIDE (TFA) AS THE INITIATOR^a

Tube	TO		MEDOX			Copolymer Yield			η^b in dL/g	Comonomer ^c units, in mole-%
	in g	in mmole	in g	in mmole	mole-% in comonomer feed	DCE, in ml	Initiator Solution in ml	in g	in %	
1	2.7	31	0.37	1.5	5	5.8	0.15	2.5	79	0.68 0.70
2	2.7	31	0.75	3.1	10	5.8	0.15	2.5	73	0.44 1.1
3	2.9	33	1.2	4.9	15	6.2	0.17	2.6	63	0.43 1.4
4	2.9	32	2.0	8.1	25	6.1	0.18	2.8	57	0.31 1.8
5	1.7	19	1.9	7.8	40	3.6	0.12	1.6	45	0.33 1.8

^aReaction conditions--temp.: 65°C; time: 33 hours; initiator: (CF₃SO₂)₂O, 0.016 mole-% based on comonomers; solvent: 1,2-dichloroethane (DCE).

^bMeasured at 60°C on 0.1% solution in 98 wt.-% p-chlorophenol/2 wt.-% α -pinene.

^cDetermined by infrared spectroscopy.

8. Copolymerizability of methyl 10,11-epoxyundecanoate (MEU) and trioxane (TO) with $(\text{CF}_3\text{SO}_2)_2\text{O}$ as the initiator.

Five polymerization tubes, equipped with magnetic stirring bars and 3-way adapters with teflon stopcocks, were flamed-out under nitrogen, cooled to room temperature and individually weighed. TO was then distilled, under nitrogen, from a blue sodium-benzophenone diketyl complex into each tube. The tubes were tightly stoppered with the 3-way adapters and reweighed. The desired amounts of MEU (5-40 mole-% of comonomer feed) and purified DCE were added to each vessel using nitrogen-purged gas-tight syringes. After partial immersion of the tubes in a 65°C oil bath, ca. fifteen minutes was allowed for TO to dissolve and the solutions to reach thermal equilibrium. Each tube was then charged with the desired amount of a stock 0.035 molar TFA/DCE initiator solution. The time for onset of turbidity was recorded for each reaction. Four of the polymerization tubes (initially containing 5, 10, 15 and 25 mole-% MEU in the feed) were removed from the 65°C oil bath after 3.5 days; each contained an off-white solid suspended in orange liquid. The last tube was removed from the bath after 5.5 days. Each of the precipitated solids was collected by filtration in pre-tared sintered glass funnels and washed successively with 5% aqueous sodium bicarbonate (200 ml), distilled water (100 ml) and absolute methanol (100 ml). Samples were then dried for one day at 0.05 mm and room

temperature over anhydrous calcium sulfate. The yield and inherent viscosity (0.1% in 98 weight-% p-chlorophenol/2 weight-% α -pinene, 60°C) of each copolymer were determined. Infrared spectra (KBr wafers) were recorded and showed the following absorptions: 3650-3320 cm^{-1} (O-H stretch, moderately weak), 3120-2750 cm^{-1} (C-H stretch), 1740 cm^{-1} (C=O stretch, ester, variable intensity depending on sample), 1110 cm^{-1} (C-O-C stretch, ether) and 940 cm^{-1} (C-O-C stretch, symmetric). See p. 310.

Refer to Table 3, p. 104 for quantities of individual chemicals used in the series of experiments described as well as for copolymer yields and inherent viscosities.

9. Attempted copolymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) and 1,3-dioxolane (DO) with $(\text{CF}_3\text{SO}_2)_2\text{O}$ as the initiator. A 6-inch polymerization tube equipped with a magnetic stirring bar and 3-way adapter (with teflon stopcock) was flamed-out under nitrogen and placed in a nitrogen dry-box. The tube was charged with MEDOX (0.33 g, 1.3 mmole, 5 mole-% of comonomer feed) and then removed from the dry-box. DO (2.0 g, 27 mmole) and DCE (5.5 ml) were added by nitrogen-purged gas-tight syringes. The contents of the tube formed a clear, colorless solution. The polymerization vessel was partially immersed in a 65°C oil bath; ca. 15 minutes was allowed for the comonomer solution to reach thermal equilibrium. The

TABLE 3

COPOLYMERIZATIONS OF METHYL 10,11-EPOXYUNDECANOATE (MEU) AND TRIOXANE (TO) WITH TRIFLIC ANHYDRIDE (TFA) AS THE INITIATOR^a

Tube	TO		MEU			Copolymer Yield			^b η in dL/g	^c Comonomer units, in mole-%
	in g	in mmole	in g	in mmole	mole-% in comonomer feed	DCE, in ml	Initiator Solution in ml	in g	in %	
1	3.3	37	0.40	1.9	5	7.5	0.18	2.6	69	1.0
2	3.0	33	0.71	3.3	10	7.0	0.17	1.8	49	1.1
3	2.9	32	1.0	4.7	15	7.1	0.17	1.2	31	0.9
4	3.3	37	2.0	9.3	25	8.7	0.21	0.72	13	1.1
5	2.9	32	2.7	13	40	8.5	0.21	0.12	2.1	1.9

^aReaction conditions--temp.: 65°C; time: 33 hours; initiator: (CF₃SO₂)₂O, 0.016 mole-% based on comonomers; solvent: 1,2-dichloroethane (DCE).

^bMeasured at 60°C on 0.1% solution in 98 wt.-% p-chlorophenol/2 wt.-% α -pinene.

^cDetermined by infrared spectroscopy.

tube was then charged with a stock 0.035 molar TFA/DCE initiator solution (0.13 ml, 4.5×10^{-3} mmole TFA). After 15 hours the reaction mixture was still of low viscosity but gray in color. The tube was removed from the oil bath after 33 hours and allowed to stand at room temperature an additional 5 days. The gray solution was poured into anhydrous diethyl ether (150 ml). A yellow oil that separated out slowly crystallized to an off-white solid. After soaking overnight in ether, the wax-like solid was collected by filtration and washed successively with ether, 5% aqueous sodium bicarbonate (30 ml), distilled water and absolute methanol (50 ml). The waxy polymer was dried for 12 hours at 0.05 mm and room temperature over anhydrous calcium sulfate. The yield of polymer was 0.27 g (12%), the inherent viscosity (0.5% in CHCl_3 , 30°C) was 0.34 dL/g, and the melting point was 56-60°C.

Identification of the polymer by spectroscopic methods (IR and ^{13}C NMR) showed conclusively the product to be the homopolymer of DO. The infrared spectrum (thin film) showed absorptions at $3020\text{-}2720\text{ cm}^{-1}$ (C-H stretch), 1115 cm^{-1} and 1035 cm^{-1} (C-O stretch). See p. 310. The ^{13}C NMR spectrum (d_6 -benzene) showed peaks at 67.31 ppm ($-\text{OCH}_2\text{CH}_2-\text{O}-$) and 95.85 ppm ($-\text{OCH}_2-\text{O}-$). See p. 328.

10. Attempted polymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) with boron trifluoride etherate as the initiator. A polymerization tube fitted with a 3-way pressure stopcock was evacuated to 0.01 mm, flamed-out, cooled to room temperature and filled with nitrogen. The tube was charged with MEDOX (0.65 g, 2.7 mmole) and DCM (2.5 ml). The resulting clear, colorless solution was degassed by three freeze-thaw cycles. The contents of the tube were chilled to 5°C using an ice-water bath and boron trifluoride etherate (0.02 ml, 5 mole-%) was added using a nitrogen-purged gas-tight syringe. The tube was sealed at 0.01 mm and kept at room temperature for 6 days. During this period the reaction mixture turned golden brown, however, no increase in viscosity was observed. The tube was then kept at -20°C (dry ice/CCl₄ bath) for one day and at -78°C (dry ice/acetone bath) for 1 hour. The contents of the tube were allowed to thaw and kept at room temperature an additional 18 days. The tube was opened and the fluid brown solution was poured into a vial and washed with 5% aqueous sodium bicarbonate (5 ml) and distilled water (3 x 8 ml portions). The dichloromethane layer was analyzed by gas chromatography. A single product was observed in the gas chromatogram; it was identified as MEDOX by comparison with an authentic sample.

H. Measurements

1. General procedures and methods. Infrared spectra were recorded on Perkin-Elmer Model 727 or Model 283 spectrophotometers. Solid samples were measured as KBr pellets, and liquid samples were analyzed between NaCl plates. The infrared spectra of most of the polymers were measured from thin films cast directly onto a single NaCl plate from CHCl_3 or dioxane solution. The peak assignments were made to the nearest 5 cm^{-1} .

The ^1H NMR spectra of intermediates, monomers and polymers were measured on a 60 MHz T-60 Perkin-Elmer NMR spectrometer.

The ^{13}C NMR spectra were measured on a 22.6 MHz Varian CFT-20 spectrometer. Solution concentrations were generally 20-40% (w/v) in deuterated benzene, chloroform or 1,4-dioxane. Common instrument parameters used during the acquisition of spectral data included a pulse width (PW) of 13 to 19 microseconds, a pulse delay (PD) of 0 to 5 seconds and an acquisition time (AT) of 1.023 seconds.

Inherent viscosity measurements were run at 30° or 60°C using Ubbelohde or Ostwald-type viscometers. Values reported are an average of 3 to 5 determinations. Solution concentrations were 0.1 or 0.5 g/dl in a suitable solvent.

The glass transition temperatures (T_g) and melting temperatures (T_m) of the polymers were determined on a

Perkin-Elmer DSC-2 Differential Scanning Calorimeter or DuPont Model 951 Thermal Analyzer at a heating rate of 20°C/minute. The instruments were calibrated against a cyclohexane standard for low temperature measurements and against an indium standard for high temperature measurements.

Melting points of low molecular weight solids were measured on a MEL-TEMP capillary melting point apparatus and are uncorrected.

Thermogravimetric analysis (TGA) of polymers was performed on a DuPont Model 951 Thermal Analyzer at a heating rate of 15°C/minute in a nitrogen atmosphere.

Gel permeation chromatography (GPC) was performed on a Waters Associates Model 201 liquid chromatograph, employing a set of 5 MicroStyragel[®] columns (nominal pore size 500, 10^3 (two), 10^4 and 10^5 Å). THF was employed as solvent, at a flow rate of 1.5 ml/minute. Solutions were ca. 0.15% (w/v) in THF. Columns were calibrated using narrow-distribution polystyrene standards.

Wide-angle X-ray diffraction (WAXD) measurements of bulk polymer samples were obtained using a Siemens Model D-500 Diffractometer. A copper cathode radiation source was employed; the wavelength of Cu-K α radiation was 1.5418 Å. The X-rays were filtered by a monochromator located before the detector.

Gas chromatography (GC) was performed on a Varian

Aerograph Model 1420 temperature-programmable gas chromatograph, using an SE 30 column and helium as the carrier gas. The column was generally programmed from 100-225°C at a heating rate of 4 or 6°C/minute.

Microanalyses were done by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

2. Determination of relative rates of polymerization of methyl 10,11-epoxyundecanoate (MEU) and 1-dodecene oxide (DDO) by ^1H NMR spectroscopy. Two thin-walled NMR tubes (with constricted necks) were fitted with 3-way pressure stopcocks, evacuated to 0.01 mm and carefully flame-dried with a Bunsen burner. The tubes were refilled with nitrogen, and for the sake of convenience labeled A and B, respectively. Tube A was charged with the appropriate quantities of MEU and purified benzene so that the concentration of MEU was $1.8 \text{ mole} \cdot \text{lit}^{-1}$. Tube B was charged with the appropriate quantities of DDO and purified benzene so that the concentration of DDO was $1.8 \text{ mole} \cdot \text{lit}^{-1}$. The contents of each tube were degassed by three freeze-thaw cycles. Each tube was charged under nitrogen with 5 mole-% $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator and sealed at 0.01 mm. The ^1H NMR spectrum was recorded for each reaction mixture immediately after sealing and allowing the contents of each tube to thaw. Both tubes were kept at

room temperature for the duration of the experiment (ca. 3 weeks). ^1H NMR spectra were recorded at random intervals during this time. The solutions remained relatively mobile for 1 to 2 days, thereafter spectra were obtained from gelled polymer solutions.

The relative rate of polymerization for each monomer was determined by following the change (decrease) in the integrated signal intensity of the epoxy group methine and methylene protons ($\text{-}\overset{\text{O}}{\underset{|}{\text{CH}}}\text{-}$ and $\text{CH}_2\overset{\text{O}}{\underset{|}{-}}$, δ : 2.3-3.0 ppm) as a function of time.

3. Gravimetric determination of rate of polymerization of methyl 10,11-epoxyundecanoate (MEU) using $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) as initiator. Each of six polymerization tubes was equipped with a 3-way pressure stopcock, evacuated to 0.01 mm and flame-dried using a Bunsen burner. The tubes were cooled to room temperature and purged with nitrogen. Each tube was charged with MEU (0.97 g, 4.5 mmol) and purified benzene (3.9 ml); concentration of the monomer solutions was 20% (w/v). The contents of each tube were degassed by three freeze-thaw cycles. Under positive nitrogen pressure, tubes 1-6 were successively charged with the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (0.23 ml, 0.22 mmol aluminum, 5 mole-% based on epoxide monomer) and sealed at 0.01 mm. Each polymerization reaction was allowed to proceed at room temperature for a specified

period of time. The standard work-up procedure for each reaction was to dissolve the contents of the tube in a benzene (35 ml)-acidified methanol (5 ml, 1% HCl) mixture, followed by precipitation of the polymer into methanol (250 ml). Each polymer was collected by filtration in a tared sintered glass funnel, rinsed with fresh methanol and dried to a constant weight. The yield of poly(MEU) was then determined and recorded. See Table 4, p. 112.

4. Dilute solution viscometric measurements of poly(alkylene oxide) ionomers.

a. Determination of the effect of added ionic solute on inherent viscosity. An aqueous solution of an ethylene oxide copolymer which contained 4 mole-% 10,11-epoxyundecanoic acid sodium salt units was prepared (see p. 86 for origin of copolymer). Thus 0.050 g of the poly(alkylene oxide) ionomer was weighed into a 10 ml volumetric flask, and distilled water was added to the fiducial mark. The resulting ionomer solution was filtered through a coarse fritted funnel. The inherent viscosity of the soapy solution was then determined at 30°C in a Ubbelohde-type viscometer. The desired quantity of sodium chloride (NaCl) was added directly to the copolymer solution, and the inherent viscosity was re-measured. This procedure was used for the following four concentrations (weight-% based on ionomer) of added sodium chloride: 1,

TABLE 4

POLYMERIZATION OF METHYL 10,11-EPOXYUNDECANOATE
 WITH 5 MOLE-% $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$
 (1.0/0.5/1.0)^a

Tube	Polymerization Time in Days	Yield of Poly (MEU) in grams	Yield of Poly (MEU) in %
1	1.3	0.063	6.6
2	3.0	0.14	14
3	7.1	0.27	28
4	12.1	0.41	43
5	30	0.37	38
6	54	0.83	86

^aReaction conditions--solvent: benzene, monomer
 concentration: 20 w/v %, room temperature polymerization.

1.5, 3.5 and 5%.

b. Measurement of the effect of ionomer concentration on inherent viscosity. An aqueous solution of an ethylene oxide copolymer which contained 4 mole-% 10,11-epoxyundecanoic acid sodium salt units was prepared (see p. 86 for origin of copolymer). Thus 0.100 g of poly(alkylene oxide) ionomer was weighed into a 10 ml volumetric flask, and distilled water was added to the fiducial mark. The ionomer solution was filtered through a fritted glass funnel (10-20 μ). The inherent viscosity of a known volume of the one g/dL solution was then determined at 30°C in an Ubbelohde dilution viscometer (size 75). Four successive dilutions of the ionomer solution were performed; a known volume of distilled water being added each time. The inherent viscosity was remeasured after each dilution. Solution concentrations after dilution were 0.75, 0.50, 0.25 and 0.125 g/dL, respectively.

5. Determination of copolymer composition for functional poly(oxymethylenes) by quantitative infrared analysis.

a. Calibration of IR. Blends of methyl 10,11-dihydroxyundecanoate (MDU) and polyoxymethylene (POM) in varying proportions were prepared in the form of KBr pellets (average thickness 0.015 mm) and their infrared spectra were recorded. While the concentration of MDU in the blends was varied from 0 to 21% by weight; the overall

concentration of the KBr solid solutions was held constant at 10% by weight. The absorbance of the carbonyl (C=O) peak at 1740 cm^{-1} was measured for each sample. A calibration plot of Absorbance (1740 cm^{-1}) vs moles C=O in the sample was constructed.

b. Copolymer samples. Infrared spectra for ester-substituted POM samples were measured from KBr pellets (average thickness 0.015 mm). The pellets were prepared as 10% by weight solutions of the appropriate co- or terpolymer in KBr. The carbonyl (C=O) absorbance at 1740 cm^{-1} was measured and the moles C=O present in the sample were then determined from the calibration curve. The mole-% functional monomer incorporated in each co- or terpolymer was calculated using the relation:

$$\text{Mole-\% functional monomer incorporated} = \frac{(\text{moles C=O in sample})}{\frac{\text{sample weight in g}}{30^*}}$$

*Formula weight of repeating unit ($-\text{OCH}_2-$).

CHAPTER III

RESULTS AND DISCUSSION

A. Objectives

The objectives of this research were: (1) to prepare two categories of poly(alkylene oxides), containing pendant ester groups separated from an elastomeric oxyethylene or crystallizable oxymethylene backbone by a flexible hydrocarbon spacer-group; (2) to convert by polymer reactions selected members in the ester-substituted polyether family to novel poly(alkylene oxide) ionomers, polyelectrolytes and polyacids; and (3) to perform both qualitative and quantitative characterization of the resultant polymers.

In order to achieve these objectives, polymerization studies of two difunctional heterocyclic monomers, methyl 10,11-epoxyundecanoate (MEU) and 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX), were undertaken. Both of these monomers were prepared from 10-undecenoic acid, a relatively inexpensive and readily available intermediate. Consequently, the two functional groups in each monomer are separated by an eight carbon spacer-group. The long spacer group was intended to allow the polymerizable functional groups to react independent of any effects of the ω -ester

groups while at the same time ensuring optimal accessibility and reactivity of the pendant ester moieties for subsequent polymer modification reactions.

The functional epoxide, MEU, was successfully homopolymerized and copolymerized with common cyclic ethers using a modified aluminumalkyl initiator system. Polymer reactions including saponification and neutralization of the pendant carboxyl groups were readily carried out.

Functionally-substituted oxymethylene copolymers were successfully prepared by two routes--cationic polymerization of trioxane with MEU or with the functional 1,3-dioxolane monomer MEDOX.

The characterization of the two categories of functional poly(alkylene oxides) was successfully carried out using techniques such as infrared and ^{13}C NMR spectroscopy, gel permeation chromatography, and differential scanning calorimetry. The functional oxymethylene polymers, due to their limited solubility characteristics, were characterized primarily by IR spectroscopy and dilute solution viscometry.

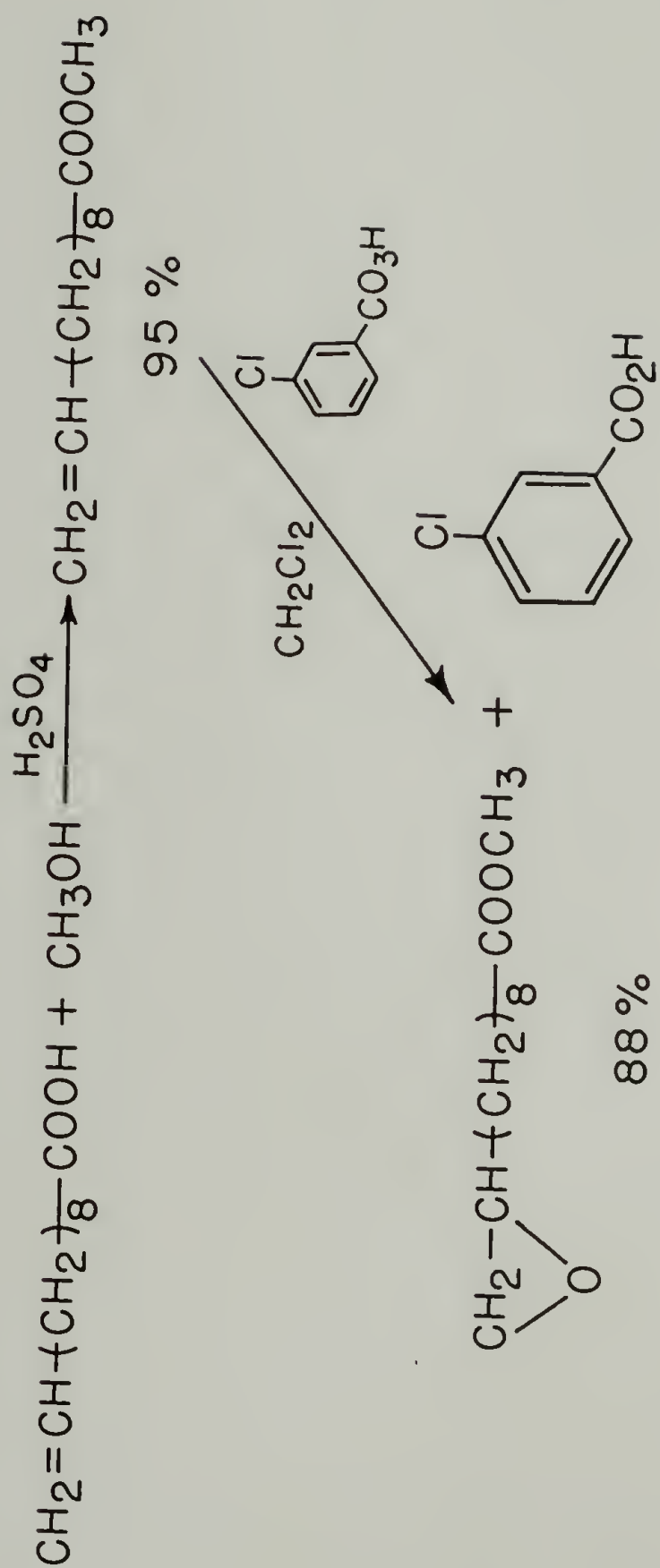
B. Preparation and Polymerization of Methyl 10,11-Epoxyundecanoate

1. Synthesis of methyl 10-undecenoate and methyl 10,11-epoxyundecanoate. The synthesis of the functional epoxide monomer, methyl 10,11-epoxyundecanoate (MEU), was accom-

plished in two steps, starting from 10-undecenoic acid. Figure 1 illustrates the reaction sequence used to prepare MEU. 10-Undecenoic acid, a pyrolysis product of castor oil,²⁰⁷ is readily available and of sufficiently high purity (95%) to be used without additional purification. Methyl 10-undecenoate, the first product shown in Figure 1, was prepared in over 90% yield by an acid-catalyzed esterification of 10-undecenoic acid in a 10-fold excess of methanol. Despite the presence of a strong acid catalyst, sulfuric acid, isomerization of the terminal double bond to a more thermodynamically stable internal olefin did not occur. Spectroscopic techniques including infrared and ¹³C NMR spectroscopy provided clear and conclusive evidence that no rearrangement had taken place. Isomerization of the terminal double bond could have been potentially troublesome; separation of isomeric esters of 9- and 10-undecenoic acid would have been extremely difficult under the best of conditions. More serious would have been the problem of polymerization of an internal versus terminal epoxide group; significant differences exist in the respective rates of their polymerization by modified organometallic initiator systems employed in this study. Internal epoxy groups polymerize only sluggishly due to steric crowding at the polymerization site.⁷

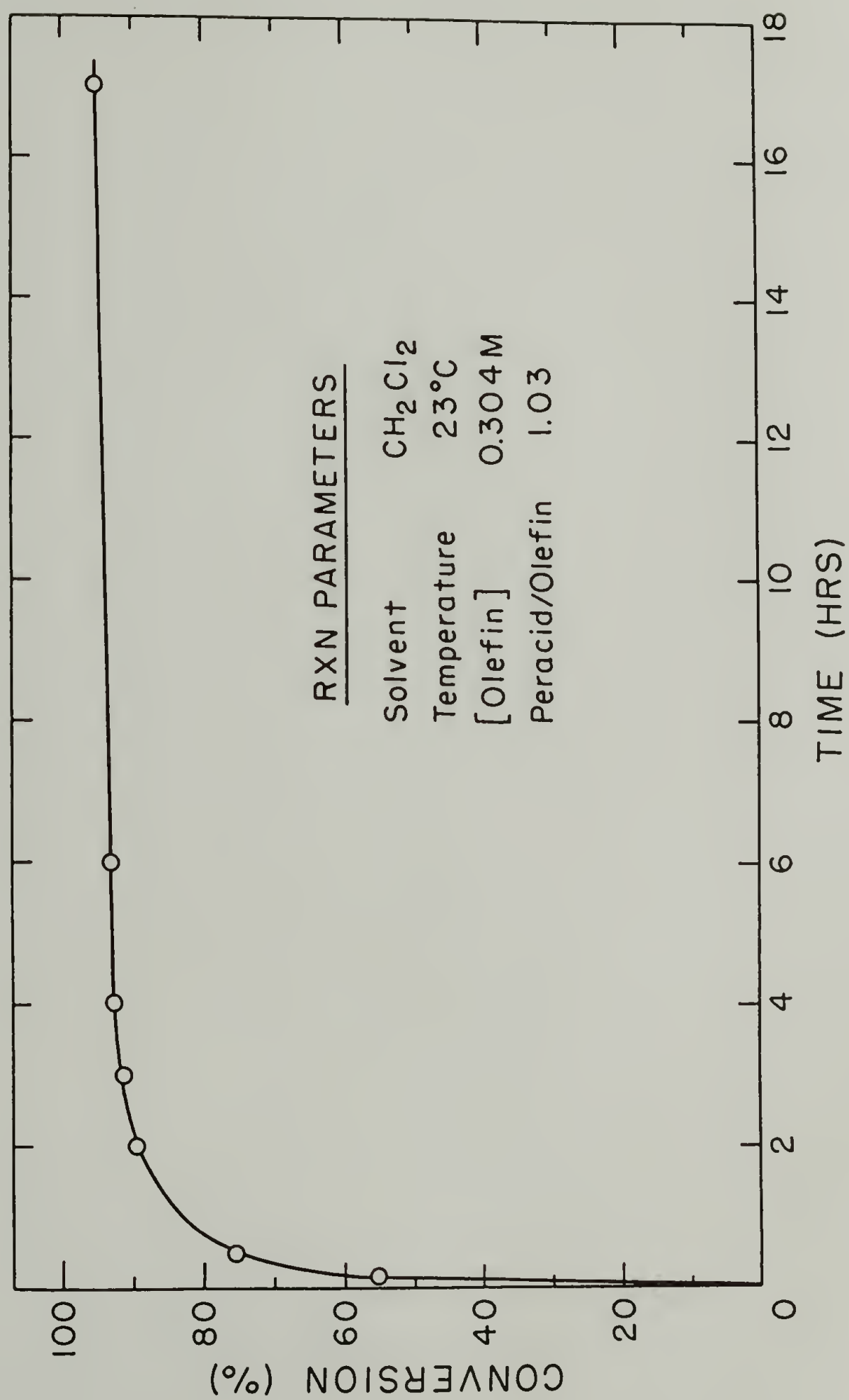
Methyl 10,11-epoxyundecanoate (MEU) was obtained in 74% yield by the epoxidation of methyl 10-undecenoate with

Figure 1. Synthesis of functional epoxide methyl 10,11-epoxyundecanoate (MEU).



m-chloroperbenzoic acid (m-ClPBA). The use of this peracid over other epoxidation agents²⁰⁸ such as performic, peracetic or trifluoroperacetic acid was desirable for several reasons. m-ClPBA is quite stable,²⁰⁹ is readily available, and perhaps most important, can be used under mild experimental conditions.¹⁰⁷ In addition, work-up of the reaction mixture is simplified greatly by the poor solubility of m-chlorobenzoic acid, the by-product of the oxidation, in the reaction medium. The need for a stronger oxidant from among those already mentioned, often required for the epoxidation of α,β -unsaturated alkenoates,¹⁰⁵ was not necessary. Unlike α,β -unsaturated acid esters such as methyl acrylate or even esters of l-propenoic acid,¹⁰⁸ the double bond of methyl 10-undecenoate is not rendered electron deficient by the electron-withdrawing carboxyl group. The presence of the long methylene spacer group (eight carbons in methyl 10-undecenoate) made oxidation of the double bond quite facile, and as will be discussed in more detail later in this chapter, had a positive effect on ease of polymerizability of MEU. The relative ease of oxidation of the double bond by m-ClPBA can be seen by inspection of Figure 2, which depicts the rate of epoxidation of methyl 10-undecenoate. Aliquots of an epoxidation reaction conducted at room temperature in dichloromethane solution were periodically removed and analyzed by gas chromatography; their composition was then determined as a

Figure 2. Rate of epoxidation of methyl 10-undecenoate with m-chloroperbenzoic acid (m-ClPBA).



function of time. Thus, within two hours the functional epoxide MEU could be obtained in high conversion (>90%). As expected, these results are in excellent agreement with the relative ease of epoxidation of other members within the same homologous series by m-ClPBA.^{108,109} The latter study showed that members with a spacer-group length greater than two undergo rapid epoxidization.

In summary, the reaction route for the preparation of MEU was convenient and provided the desired products in high yield. It is important to recognize, however, that the esterification step must precede the epoxidation reaction. While it is expected that 10-undecenoic acid could be readily epoxidized by m-ClPBA, it is readily apparent that serious side reactions would be encountered in any ensuing attempt at acid-catalyzed esterification. Likely side reactions would be protonation of the epoxide ring followed by a nucleophilic, ring-opening attack by HSO_4^- or water generated by the esterification reaction. The stability of a carboxylic acid substituted epoxide ring prior to esterification is also questionable since epoxides are known to undergo cationic polymerization in the presence of organic acids.⁹

a. Characterization of 10-undecenoic acid and derivatives. ¹³C NMR spectroscopy was a very useful and important method for the characterization of intermediates, monomers and polymers throughout this investigation. Table

5 compiles the chemical shift data for 10-undecenoic acid, methyl 10-undecenoate and methyl 10,11-epoxyundecanoate relative to tetramethylsilane (TMS).

2. Choice of initiator for polymerization of functional epoxide MEU. The polymerization of MEU was investigated with the objective of preparing the corresponding ester-substituted poly(alkylene oxide) of high molecular weight. The latter requirement substantially narrowed the choice of possible initiator systems. Excluded from the list of potential initiators were typical cationic initiators, including protonic and Lewis acids, and anionic initiators such as potassium hydroxide. While it is well known that epoxides can be polymerized by initiators of either the cationic or anionic type,⁷ the resultant polyethers generally are of low molecular weight (<5,000) due to the frequent occurrence of undesirable chain-transfer reactions. Consequently, these initiator systems were not investigated in this work.

One of the most useful initiator systems for the polymerization of many epoxides to high molecular weight are those based on the reaction products of an aluminum-alkyl with water and a chelating agent.³⁴ Such modified organoaluminum oxide compositions are easy to prepare, but still remain at present poorly characterized and often exhibit complicated behavior. A wide range of activity is

TABLE 5

¹³C NMR CHEMICAL SHIFT DATA FOR 10-UNDECENOIC ACID AND DERIVATIVES^a

Compound	C Atoms of Functional Groups				C Atoms of Spacer-Group ^b							
	$\underline{\text{CH}}_2$ -	$\text{-}\underline{\text{CH}}\text{-}$	$\underline{\text{C=O}}$	-OCH_3	1	2	3	4	5	6	7	8
10-Undecenoic Acid	114.27	138.98	180.62	-	33.94	—	—	29.23/29.38	—	—	24.79	34.23
Methyl 10-Undecenoate	114.25	139.02	173.95	51.26	33.91	—	—	29.07/29.31	—	—	25.07	34.11
Methyl 10,11-Epoxyundecanoate	46.90	52.20	174.03	51.30	32.58	26.04	—	29.21/29.43	—	—	25.00	34.07

^aIn ppm downfield from TMS.^bC atom nearest olefin or epoxy group designated C₁ of spacer group.

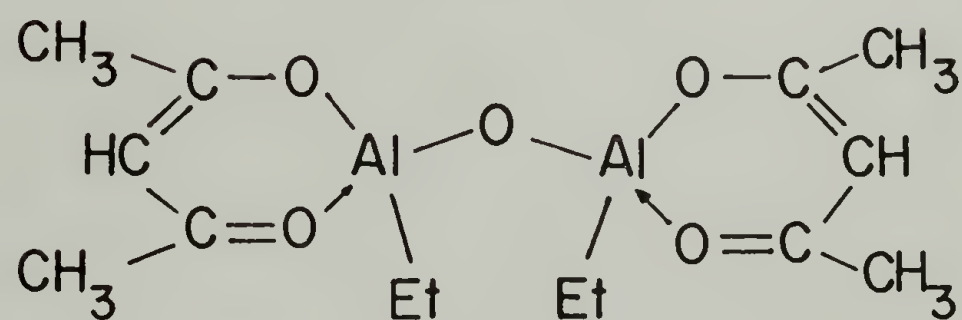
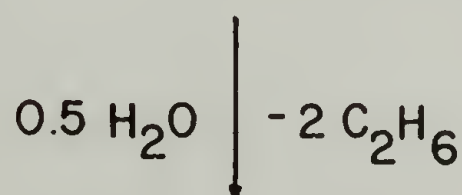
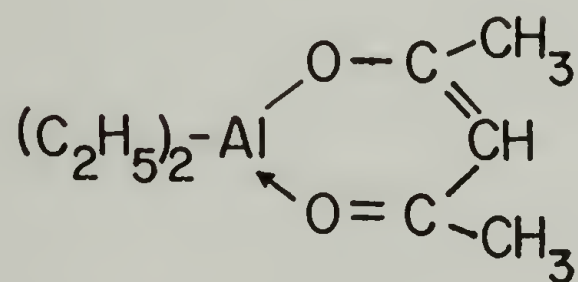
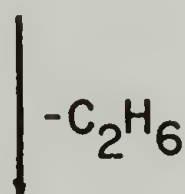
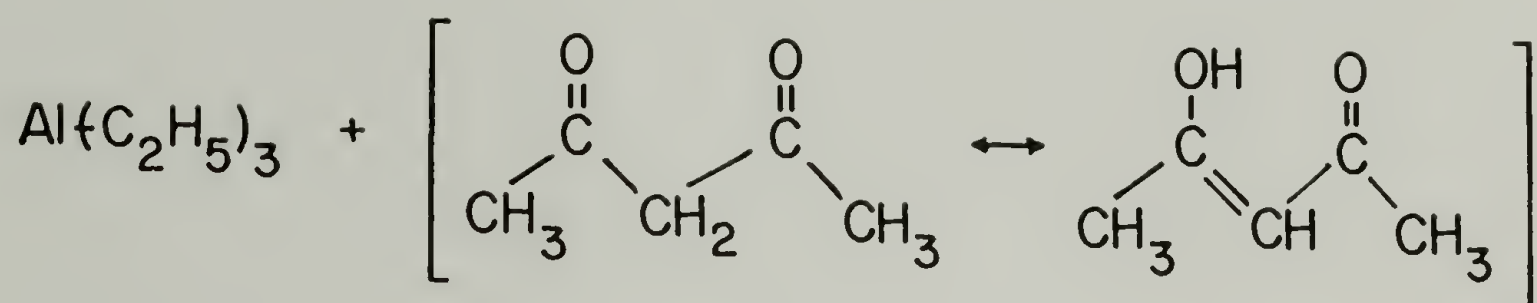
possible depending on the identity of the organoaluminum compound, the chelating agent, and the ratio of each component (including water).³⁵ In no instance however has the structure of the "active" initiator been clearly established.

In this research the polymerization of MEU and its copolymerization with other common cyclic ethers was successfully carried out using $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) as the initiator. Previous reports in the literature have described similar organoaluminum oxide compositions to be active for the polymerization of several cyclic ethers with ester-substituted epoxides.^{2,3}

3. Preparation of $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator. Triethylaluminum (TEA), a reactive organometallic compound and acidic in the Lewis sense, was converted in two steps to an active initiator composition useful for the preparation of functionally-substituted alkylene oxide polymers and copolymers. Figure 3 schematically illustrates the basic reactions involved in the preparation of the coordination initiator as well as the most probable fundamental units of the initiator as proposed by Vandenberg.³⁵

It was established under the experimental conditions used that the sequence in which the polyreactive additive (water) and the chelating agent (AcAc) were

Figure 3. Schematic illustration for preparation of the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator.



reacted with TEA largely influenced both the nature of the initiator and its ability to initiate polymerizations.

Briefly, it was found that chelation of the triethylaluminum (1 mole) with acetylacetone (1 mole) should precede the hydrolytic reaction with water (0.5 mole). The initiator prepared by this sequence was completely soluble in diethyl ether and was active in all epoxide polymerizations attempted.

The reverse sequence yielded starkly different results, although Vandenberg has claimed both methods to be equally satisfactory.³⁵ When an ethereal solution of TEA (1 mole) was first reacted with water (0.5 mole), a large amount of white solid formed. Addition of acetylacetone (1 mole) failed to solubilize the partially hydrolyzed aluminumalkyl. The "heterogeneous" initiator obtained was subsequently found to be completely inactive in the polymerization of epichlorohydrin (ECH) or copolymerization of ECH and MEU. It is now believed that the insoluble white solid formed was the polymeric aluminum oxide having the general formula $(C_2H_5AlO)_n$.²¹⁰ Difficulties in obtaining the homogeneous initiator by this route were likely due to the instantaneous but highly localized reaction that occurred when drops of water were added directly to the solution of triethylaluminum in ether. Alternative, but less convenient, procedures for avoiding the formation of insoluble polymeric aloxanes involve the contacting of water vapor

with the aluminumalkyl²¹⁰ or by the addition of the appropriate amount of an organic diluent (e.g., ether) that is saturated with water. These refined methods were not investigated.

4. Polymerization of methyl 10,11-epoxyundecanoate (MEU) with $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) as the initiator.

MEU was polymerized in benzene or toluene solution (20-25 w/v%) with 5 mole-% of the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator (Figure 4). The polymerizations were carried out in sealed tubes in order to exclude the possibility of introducing moisture or oxygen from the atmosphere or other sources which would be expected to alter the activity of the coordination initiator. The rather sizable amount of initiator used is within the usual limits of concentration (0.2-10 mole%) reported for polymerizations of other substituted epoxides.⁵⁰

The results of three separate polymerization experiments of MEU, conducted at room temperature, are given in Table 6. In each instance a different batch of the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator was used. The time allowed before work-up of each polymerization varied considerably (7, 54 and 71 days). Polymerizations of MEU were found to occur rather sluggishly: a 48% yield of polymer was obtained after 7 days reaction, 67% after 54 days and 73% after 71 days. All three experiments

Figure 4. Polymerization of methyl 10,11-epoxyundecanoate (MEU).

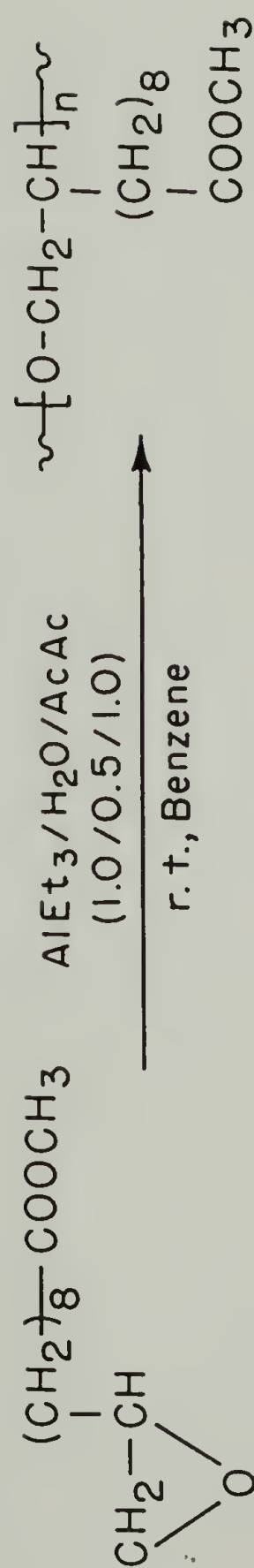


TABLE 6

POLYMERIZATIONS OF METHYL 10,11-EPOXYUNDECANOATE (MEU)

Experiment	Charged Monomer in g	Solvent	Solution Conc in w/v %	Al(C ₂ H ₅) ₃ /H ₂ O/AcAc ^a			Polymn. Time in Days	Polymer Yield in %	η_{INH} ^c in dL/g
				Age in Days	Initiator	mL Charged ^b			
1	2.9	benzene	21	1		2.1	7	48	1.8
2	13.	benzene	25	1		2.9	54	67	1.3
3	10.	toluene	20	3		2.4	71	73	2.8 ^d

^aInitiator composition: 1 mole Al(C₂H₅)₃/0.5 mole H₂O/1 mole AcAc.^b5 mole-% initiator based on MEU.^c0.5% solutions in CHCl₃, 30°C unless noted otherwise.^d0.5% solution in 1,4-dioxane, 30°C.

yielded poly(MEU) of high molecular weight. The polymers were snappy white elastomers with inherent viscosities ranging from 1.3-2.8 dL/g. The range of inherent viscosities may indeed reflect subtle differences in the activity of the different batches of initiator. The purity of MEU was in all cases nearly identical ($\geq 99.5\%$ by gas chromatographic analysis). It has been proposed that monomer impurities and other adventitious reactive species introduced are scavenged by coordination initiators of the type used.⁵⁰ This may be a factor in the number of active sites available for initiating polymerization.

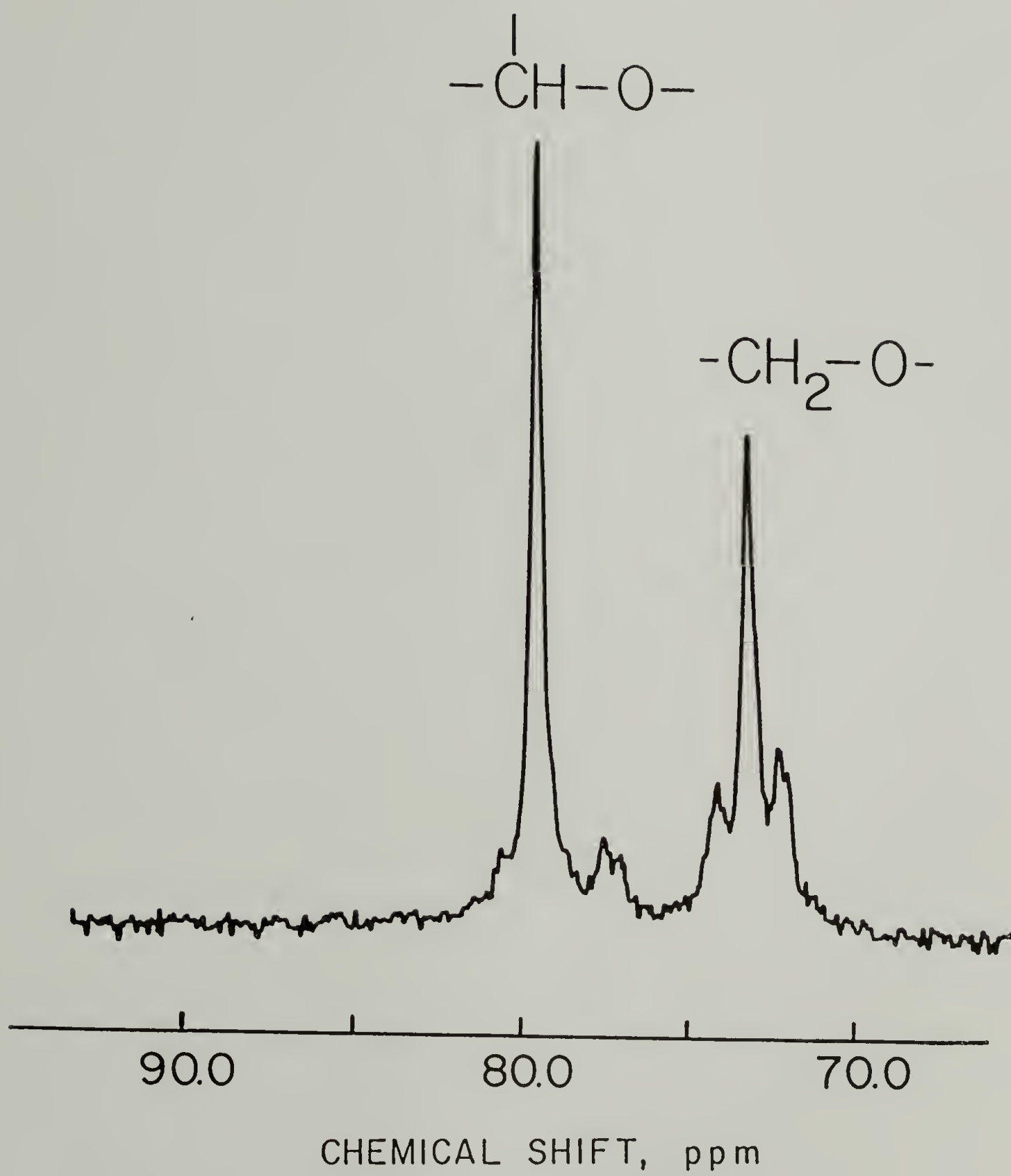
Spectroscopic techniques such as IR and ^{13}C NMR spectroscopy were used to characterize the various poly(MEU) elastomers. The results obtained were consistent with those expected for a substituted poly(ethylene oxide) structure. The IR spectra showed a strong ester carbonyl absorption at 1740 cm^{-1} and the characteristic C-O stretching mode of the poly(alkylene oxide) backbone centered near 1105 cm^{-1} .

The ^{13}C NMR spectra provided some interesting insight into the polymerizations of MEU by the modified aluminumalkyl initiator. The ring-opening polymerization of a substituted cyclic ether by a coordination initiator can give rise to regular (head-to-tail) placements, irregular placements (head-to-head, tail-to-tail), and/or stereoregular placements of monomer in the polyether chain.³⁵

Different steric environments about the backbone carbon atoms thus are reflected by the number of chemical shifts observed in the ^{13}C NMR spectrum for the methine and methylene atoms of the backbone chain.²¹¹

For poly(MEU), the chemical shifts for the methylene and methine carbon atoms of the poly(alkylene oxide) backbone appear in the region of 74 ppm and 80 ppm, respectively. Figure 5 shows the backbone region (in expanded scale) of a typical poly(MEU) elastomer prepared by the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator. Clearly evident are multiple absorptions for each type of carbon atom. It was concluded that stereorandom polymerization had occurred; stereoregular polymerization would produce a single chemical shift for each type of backbone carbon atom. The poly(alkylene oxide) backbone appears to consist largely of regular head-to-tail placements; a more complicated chemical shift pattern is generally observed for polyethers (e.g., polypropylene oxide) which are known to contain significant proportions of irregular placements.²¹² The occurrence of a small proportion of irregular placements cannot be completely ruled out. Methods have been reported for chemically cleaving polyether chains and analyzing the fragments by gas chromatography in order to determine relative proportions of head-to-tail and head-to-head placements.^{35,36} Such a study was beyond the scope of this investigation, but would appear to offer an added

Figure 5. ^{13}C NMR spectrum of poly(MEU) backbone carbon atoms (expanded scale).

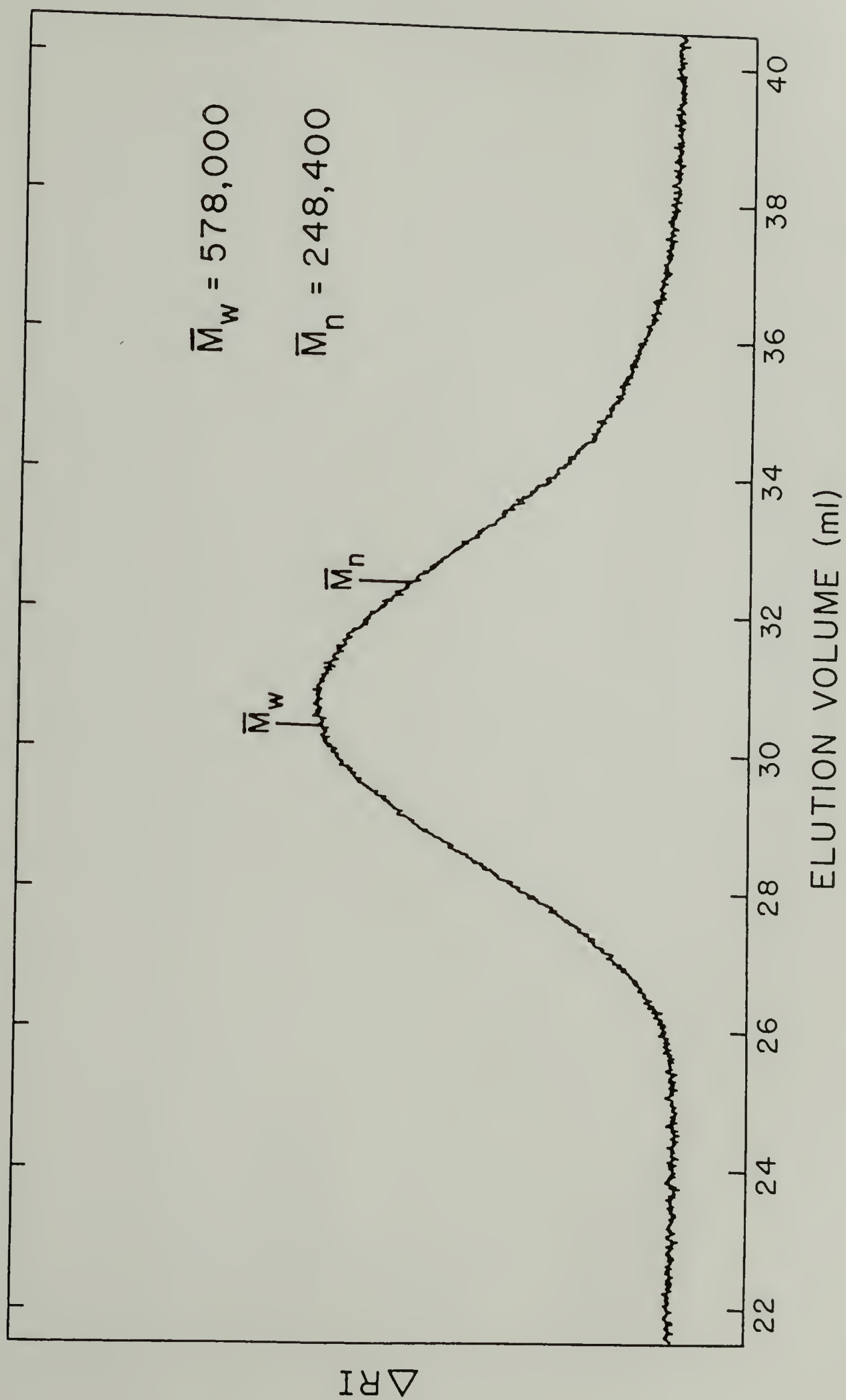


degree of sensitivity to the presence of low proportions of irregular chain placements.

Relative number-average (\bar{M}_n) and weight-average (\bar{M}_w) molecular weights were determined by gel permeation chromatography (GPC) for the poly(MEU) sample whose inherent viscosity was measured to be 1.8 dL/g (0.5% in CHCl_3 , 30°C). The GPC trace is reproduced in Figure 6. Relative to polystyrene calibration standards, the calculated molecular weight averages were: $\bar{M}_n = 248,000$ and $\bar{M}_w = 578,000$. The molecular weight distribution (MWD) was close to the most probable MWD; the ratio of \bar{M}_w/\bar{M}_n was 2.3.

The thermal properties of the various poly(MEU) samples were measured by differential scanning calorimetry (DSC). Detection of the glass transition temperature (T_g) for the elastomeric poly(alkylene oxides) was complicated by a low temperature endothermic transition occurring over a fairly broad temperature range (-35 to -5°C). The maximum in this transition occurs in the region of -7 to -8°C for all samples. The exact origin of this transition has not been established. A plausible explanation would appear to be melting of the C_8 side chains. Assignment of the glass transition (T_g) was therefore unambiguous in only one instance. Thus, a T_g of -40°C was found for the poly(MEU) sample with an inherent viscosity of 2.3 dL/g (0.5% in 1,4-dioxane, 30°C). Quenching of the other poly(MEU) samples in liquid nitrogen after annealing at temperatures above

Figure 6. Gel permeation chromatogram of high molecular weight poly(MEU), $\eta_{0.5\%} = 1.8$ dL/g.



100°C (i.e., above the temperature of other melting transitions found) did not aid in detection of T_g . A large endothermic melting transition was also found to occur above room temperature in two of the samples and may be associated with melting of the polymer backbone. Table 7 lists the values of the transition temperatures (T_g and T_m) for the poly(MEU) samples. The latter two samples were of lower molecular weight ($\eta < 0.2$ dL/g). Apparently some degradation of these polymers had occurred before their thermal properties were measured. It was concluded that poly(MEU) is a semi-crystalline elastomer exhibiting rather complicated thermal behavior. Figure 7 shows the DSC scans for the first two poly(MEU) samples listed in Table 7.

5. Polymerizability of methyl 10,11-epoxyundecanoate.

Studies were undertaken in an attempt to more fully investigate the rate of polymerization of MEU. Figure 8 schematically illustrates the results of the first study, a comparative rate study for the polymerizations of MEU and 1-dodecene oxide (DDO). The experiment was designed to measure the influence of the ester functional groups of MEU on its polymerizability using 5 mole-% of the coordination initiator $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$. DDO, a monofunctional epoxide, has a long side chain ($\text{C}_{10}\text{H}_{21}$) and was considered a good standard of comparison for the MEU polymerization as well as convenient check on the activity of the initiator.

TABLE 7

TRANSITION TEMPERATURES OF POLY(METHYL 10,11-EPOXYUNDECANOATE) SAMPLES

Sample	T_g in °C	T_m in °C	η_{inh}^a in dL/g
1	b	-7, 81	1.8
2	-40	-7, 45	0.10 ^c
3	b	-7, 43	0.12 ^d

^a0.5% solution, 30°C: sample 1 measured in chloroform, samples 2 and 3 measured in 1,4-dioxane.

^bNot detected.

^cViscosity of polymer when first isolated measured to be 2.3 dL/g.

^dViscosity of polymer when first isolated measured to be 1.3 dL/g.

Figure 7. DSC scans of poly(MEU) samples.

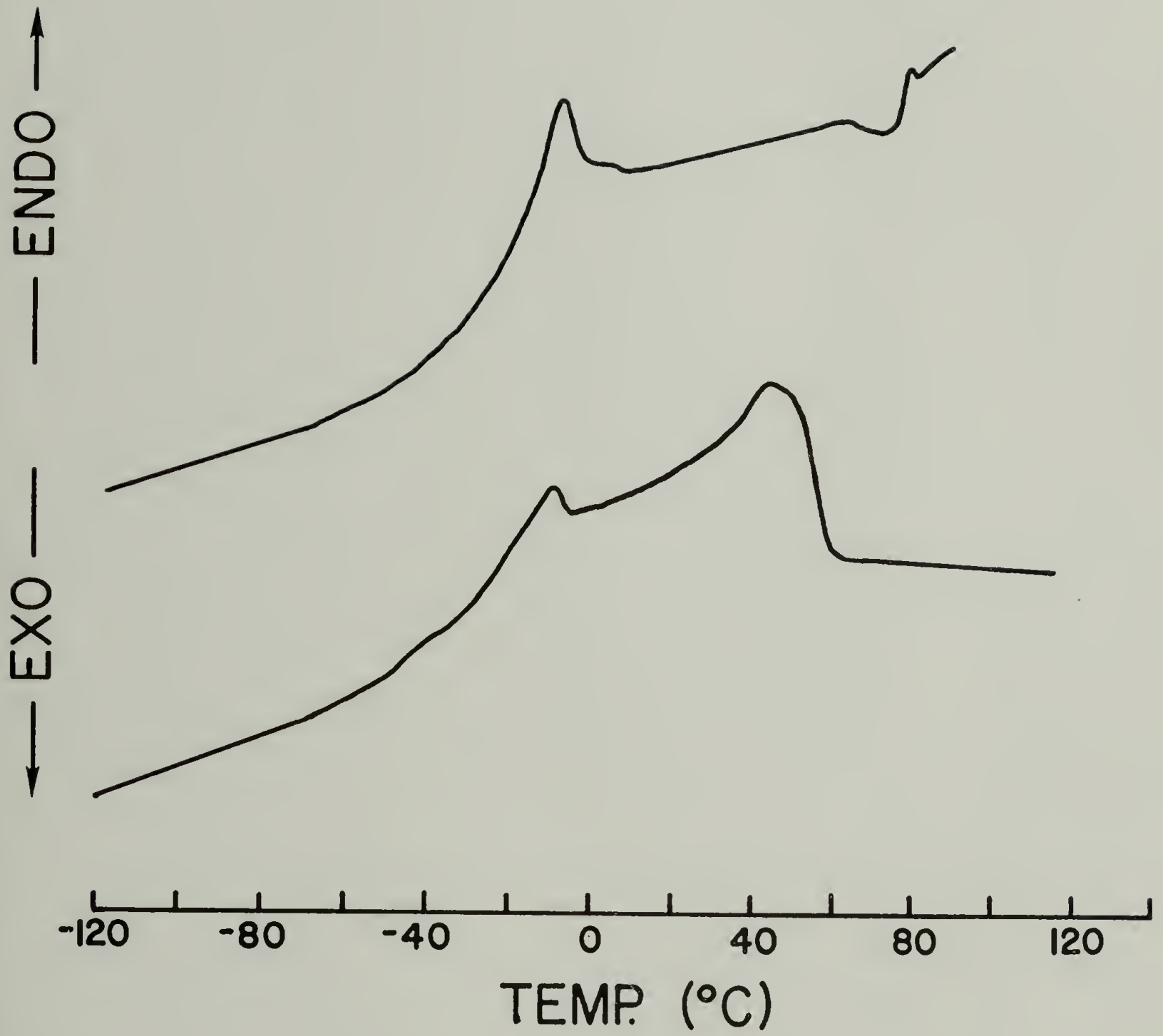
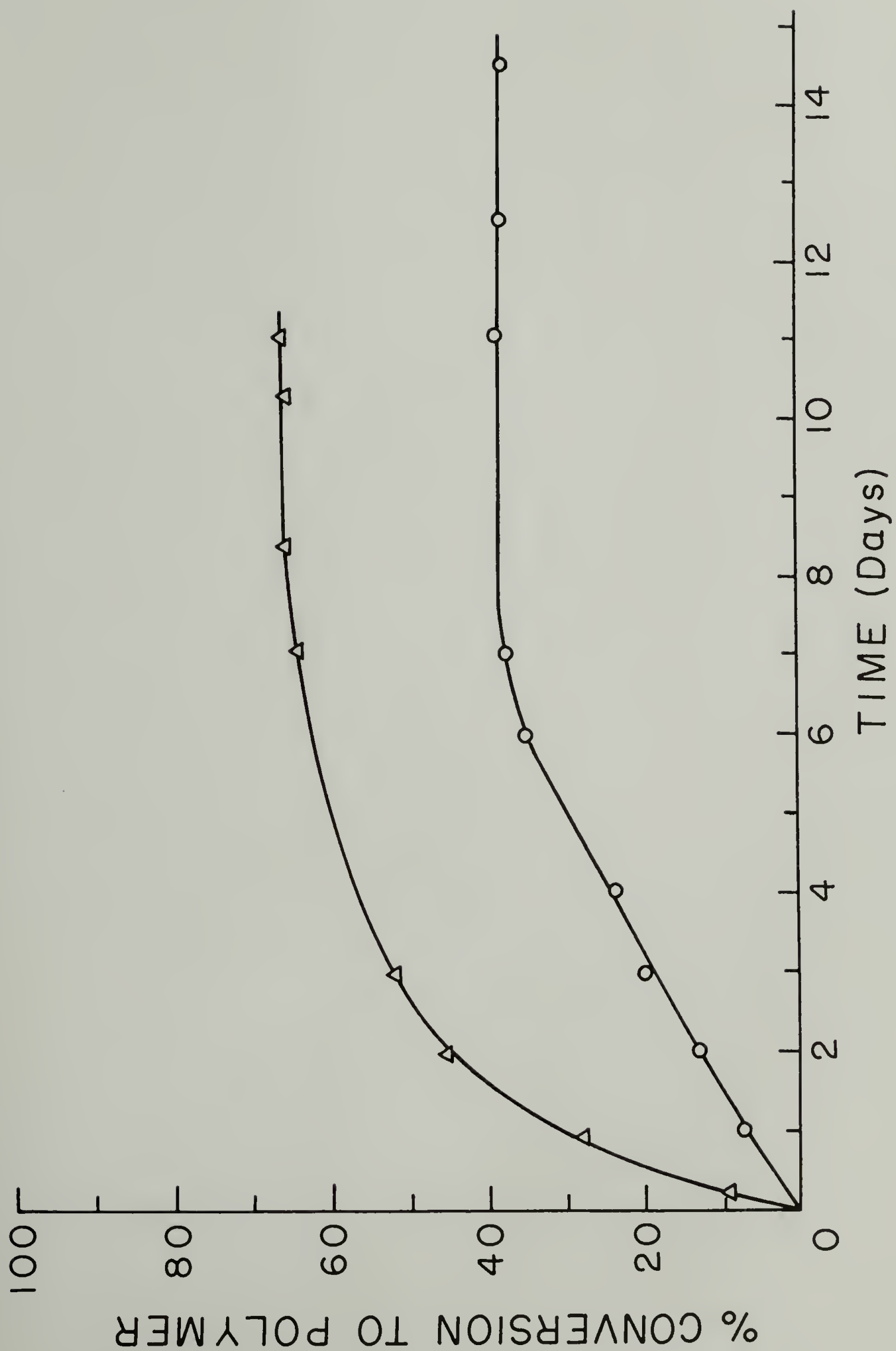


Figure 8. Comparative rates of polymerization for epoxides with long side chains, with and without carboxylate functional groups: (o) MEU and (Δ) DDO.



^1H NMR spectroscopy was used to follow the respective polymerization reactions. The polymerization of MEU was found to level off after 2 weeks, with ca. 40% of the monomer converted to polymer. Over the same 2 week period a 60% conversion of DDO to the corresponding poly(alkylene oxide) was observed. The initial rates of polymerization differed markedly, as seen in Fig. 8. DDO was polymerized to ca. 45% conversion within 2 hr, while 17% of MEU polymerized in that time. Differences observed in the rates of polymerization cannot be attributed to grossly dissimilar steric environments about the oxirane ring or deactivation of the epoxide ring of MEU by the electron-withdrawing carboxyl groups. The results shown in Fig. 8 clearly suggest an active participation of the ester functional groups in the modification of initiator activity over a period of time. It appears likely that the ester groups begin to compete ever more effectively with the epoxy groups of MEU for coordination sites on the initiator as the concentration of polymerizable groups decreases. Nevertheless, despite a large excess of ester groups as compared to the amount of initiator used (and active initiator sites) high polymer is obtained.

In an independent but related set of experiments, the rather slow conversion of MEU monomer to poly(MEU) was observed once again by a different method. Six polymerization reactions of MEU were conducted at room temperature in

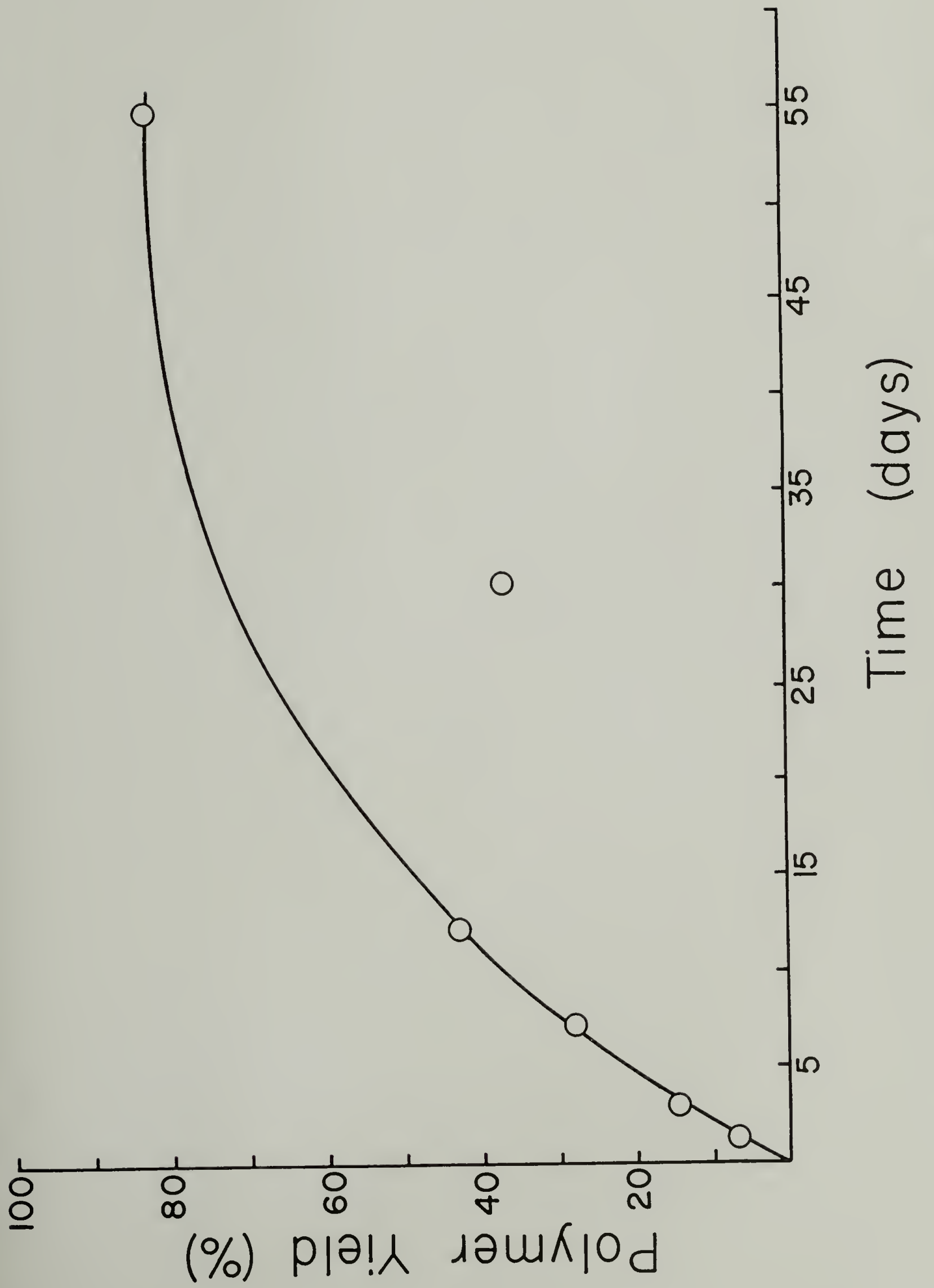
benzene solution (20 w/v%) with 5 mole-% of the coordination initiator $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0). The batch of initiator was different from that used for the rate of polymerization experiments monitored by ^1H NMR spectroscopy. Each polymer was isolated after an arbitrary period of time and the conversion of monomer to polymer was determined gravimetrically. The results are shown in Figure 9. As expected, the yield of poly(MEU) was found to increase slowly as a function of reaction time. Isolated yields were: 7% after 1 day, 14% after 3 days, 28% after 7 days, 43% after 12 days, 37% after 30 days and 83% after 54 days.

Both sets of experiments showed qualitatively the same overall general trend for the polymerization of MEU, i.e., the polymerization was found to be relatively sluggish. Some caution, however, must be exercised when attempting to compare absolute magnitudes of conversion at various stages in each study. It is likely that the two batches of initiator differed in their activity.

C. Copolymerization of Methyl 10,11-Epoxy-
undecanoate and Cyclic Ethers With
 $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0)
as the Initiator

1. Preparation of poly(alkylene oxide) esters. Copolymerization of methyl 10,11-epoxyundecanoate (MEU) was carried out with a number of cyclic ether monomers using

Figure 9. Polymerization of methyl 10,11-epoxyundecanoate: polymer yield as a function of time.



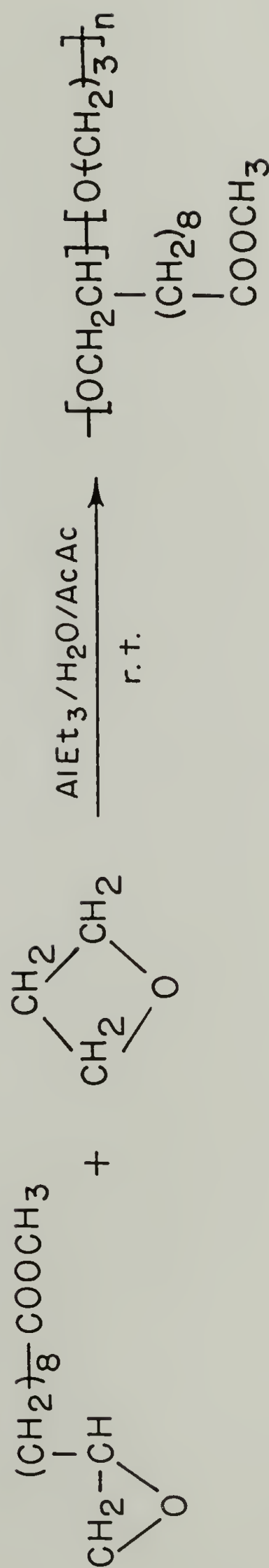
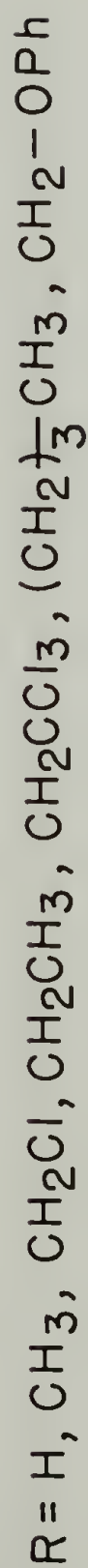
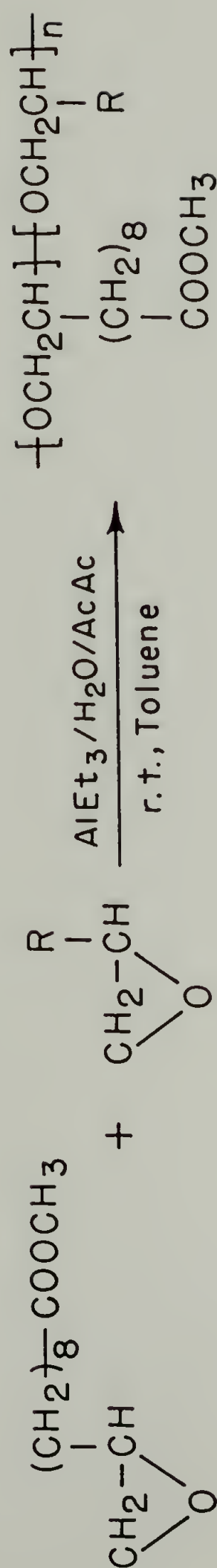
the coordination initiator $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$. Comonomers used were ethylene oxide (EO), propylene oxide (PO), epichlorohydrin (ECH), 1-butene oxide (BO), 4,4,4-trichloro-1-butene oxide (TCBO), 1-hexene oxide (HO), phenyl glycidyl ether (PGE), oxetane (Ox) and tetrahydrofuran (THF).

Figure 10 illustrates the general copolymerization reactions and structure of the corresponding poly(alkylene oxide) esters.

The copolymerizations were generally carried out at room temperature in benzene or toluene solution (16-20 w/v %) with 5 mole-% of the modified aluminumalkyl initiator. Comonomer feeds usually contained 30 mole-% MEU and 70 mole-% of the desired cyclic ether comonomer. Copolymerizations of MEU with EO required slightly different procedures. EO/MEU copolymerizations were carried out at ca. 5°C for several days before being allowed to continue at room temperature (25°C). This procedure was necessary to avoid build-up of excessive pressure in the sealed tube reactor during the early part of the reaction because of the low boiling point (11°C) of EO. After much of the EO was consumed, the polymerization was continued at the higher temperature.

The copolymerizations were allowed to proceed for periods ranging from 1 to 7 weeks; although the choice of reaction time was purely arbitrary, in nearly all instances the comonomer mixture had formed a solid plug after 1 week.

Figure 10. Copolymerization of methyl 10,11-epoxyundecanoate (MEU) and cyclic ethers.



Optimization of the polymerization time was not the foremost purpose of this study.

As the results shown in Table 8 indicate, MEU was found to copolymerize with all 3- or 4-membered cyclic ethers selected for this investigation. The yields of functional alkylene oxide copolymers, percent MEU incorporated, and inherent viscosities of the copolymers differed markedly in many instances and reflect differences in the relative reactivity of the functional epoxide with other cyclic ethers, slightly varying polymerization conditions and possible variations in initiator activity.

Results from the copolymerizations of MEU with EO are particularly interesting and significant. In two independent experiments, EO was copolymerized with 30 mole-% MEU and 15 mole-% MEU. The resultant EO/MEU copolymers were obtained in 57% and 92% yields and were found to contain 15 mole-% and 4 mole-% MEU comonomer units, respectively. Both copolymers were of high molecular weight, their respective inherent viscosities were 4.8 dL/g (0.5% in CHCl_3 , 30°C) and 1.6 dL/g (0.5% in 1,4-dioxane, 30°C). In one respect these results indicate the difficulty of reproducibility in the copolymerization of MEU with a highly reactive cyclic ether like EO.

More important is the significance of the successful copolymerizations of MEU and EO, particularly when comparisons are made with previous efforts to incorporate the

TABLE 8

COPOLYMERS OF METHYL 10,11-EPOXYUNDECANOATE WITH CYCLIC ETHERS



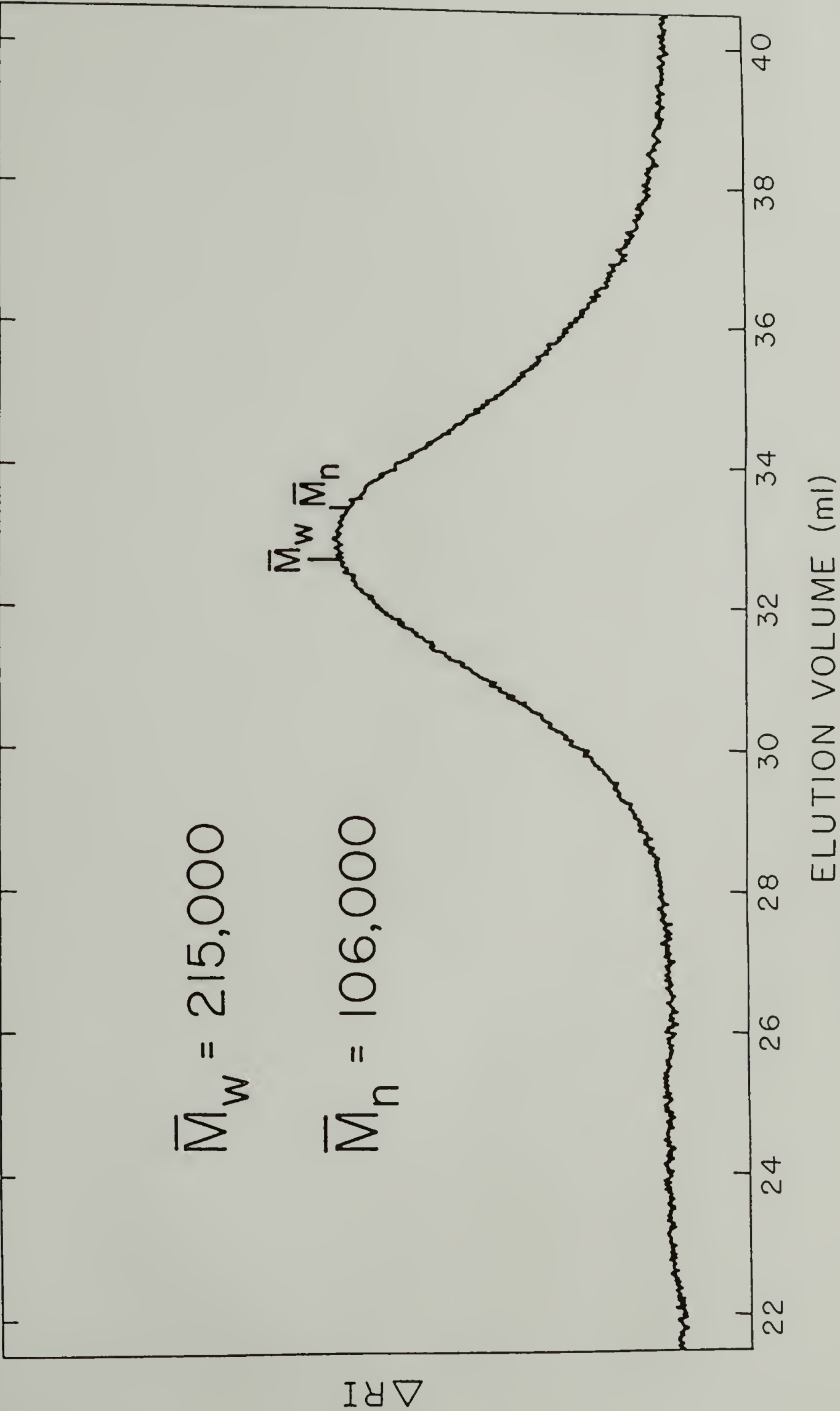
Comonomer	m	R	Yield, in %	η_{INH}^a in dL/g	Mole-% MEU ^b in Copolymer
Ethylene oxide	1	H	57 92	4.8 1.6 ^c	15 4 ^d
Propylene oxide	1	CH ₃	90	1.0	20
Epichlorohydrin	1	CH ₂ Cl	60	2.6	17
1-Butene oxide	1	CH ₂ CH ₃	90	2.7	25
4,4,4-Trichloro- 1-butene oxide	1	CH ₂ CCl ₃	35	0.2	40
1-Hexene oxide	1	(CH ₂) ₃ CH ₃	83	0.5	25
Phenyl glycidyl ether	1	CH ₂ OPh	26 ^e 39 ^f	1.1 —	28 26
Oxetane	2	H	87	2.2	25

^a0.5% in CHCl₃, 30°C.^dComonomer feed contained 15 mole-% MEU.^bComonomer feed contained 30 mole-% MEU.^eDioxane-soluble fraction.^c0.5% in 1,4-dioxane, 30°C.^fDioxane-insoluble fraction.

functional epoxide ethyl glycidate (EG) into copolymers^{2,3} with EO using coordination initiators. Only EO homopolymer was obtained under all circumstances. The poor reactivity of the α -carboxyl substituted epoxide with EO, the most reactive member in the cyclic ether family, has been attributed to the strong deactivating effect of the carboxyl group on the oxirane ring. EG was therefore unable to compete with EO (a stronger Lewis base) for active sites of the coordination initiator; once polymerization began the growing polyether chain continued to react exclusively with EO monomer. In contrast, the spacer group of MEU is long enough to remove any inductive effects of the carboxyl group, thereby allowing the functional epoxide to compete with EO for coordination sites, with subsequent insertion into the poly(alkylene oxide) chain.

The copolymerizations of MEU (30 mole-%) with cyclic ethers less reactive than EO gave poly(alkylene oxide) esters with higher levels of functional monomer incorporation. Copolymers of MEU with PO or BO were obtained in 90% yields and were found to incorporate 22 mole-% and 25 mole-% MEU, respectively. The PO/MEU copolymer had an inherent viscosity of 1.0 dL/g, this corresponds to GPC average molecular weights $\bar{M}_n = 106,000$ and $\bar{M}_w = 215,000$. The GPC curve for the copolymer is shown in Figure 11. The polydispersity of the sample is 2.0, indicating a statistical copolymer composition. The BO/MEU

Figure 11. GPC trace of propylene oxide/methyl 10,11-epoxyundecanoate (78 mole-%/22 mole-%) copolymer.



copolymer, a gum-like rubber, had an inherent viscosity of 2.7 dL/g (0.5% in CHCl_3 , 30°C). MEU gave an extremely tough elastomer in copolymerization with ECH. The ECH/MEU copolymer had an inherent viscosity of 2.6 dL/g (0.5% in CHCl_3 , 30°C), ca. 17 mole-% MEU had been incorporated (slightly greater than 50% of the methyl ω -epoxyalkanoate). Copolymerization of MEU with TCBO gave two fractions; a 1,4-dioxane insoluble crystalline fraction, in 8% yield, and an amorphous copolymer fraction, in 15% yield, which was soluble in 1,4-dioxane. The soluble TCBO/MEU copolymer fraction was found to be of relatively low molecular weight; the inherent viscosity was 0.2 dL/g (0.5% in 1,4-dioxane, 30°C). Both fractions, however, incorporated a higher level of MEU (ca. 40 mole-%) than was present in the comonomer feed (30 mole-%). This is the only copolymerization of MEU where this phenomenon was observed. These results indicate that MEU was the more reactive comonomer; the strong inductive effect of the trichloromethyl group undoubtedly reduces the Lewis basicity of the oxirane ring in TCBO and consequently its ability to coordinate readily with the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ initiator.

MEU was copolymerized in 83% yield with HO. The copolymer contained 25 mole-% MEU and was of moderately low molecular weight, the inherent viscosity of the HO/MEU copolymer was 0.5 dL/g (0.5% in CHCl_3 , 30°C). The resulting copolymer was a sticky, semi-transparent gum rubber,

which possessed little green strength, unlike most of the other MEU copolymers already described. It would appear, however, that the HO/MEU copolymer does possess potentially interesting adhesive properties due to its extremely sticky nature and noticeably strong affinity for substances like glass.

Like the copolymerization of MEU and TCBO, the copolymerization of MEU and PGE produced two fractions. The overall yield of copolymer was 65%. The two MEU/PGE copolymer fractions were separated by heating the entire copolymer to 100°C in 1,4-dioxane: 39% of the copolymer was insoluble and was recovered in the form of a tough, white elastomer. The insoluble MEU/PGE copolymer fraction was found to contain 26 mole-% MEU, was moderately crystalline and may have stereoregularity. The fraction soluble in hot 1,4-dioxane amounted to 26% of the copolymer; its composition was 28 mole-% MEU and 72 mole-% PGE. The soluble PGE/MEU copolymer had an inherent viscosity of 1.1 dL/g (1,4-dioxane, 30°C) and although soluble may have a lower level of crystallinity.

MEU was also found to copolymerize readily with oxetane (Ox), the simplest cyclic ether with a 4-membered ring. The Ox/MEU copolymer was obtained in high yield (87%), had an inherent viscosity of 2.2 dL/g (0.5% in CHCl_3 , 30°C) and was found to contain ca. 25 mole-% MEU.

The attempted copolymerization of MEU and THF by

the coordination initiator $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) gave only MEU homopolymer in 38% yield. These results are not surprising as THF polymerizations can only be carried out with cationic initiators;¹¹ propagation is known to occur through an oxonium ion intermediate. It is generally believed that partially hydrolyzed aluminum alkyls, when further modified with chelating agents such as acetylacetone, initiate polymerization by a coordinate anionic mechanism.³⁴ ^{13}C NMR spectroscopy clearly showed the absence of any chemical shifts that could be assigned to tetramethylene oxide units. THF probably acted as a non-reactive diluent in the polymerization which may have served, however, to solvate the propagating MEU centers. Poly(MEU) obtained from this reaction had an inherent viscosity of 0.8 dL/g. Analysis of the polymer by DSC showed identical thermal transitions as described previously for poly(MEU) (see p. 138), indicating no unusual effects of the polar diluent on the polymerization reaction.

2. Characterization of methyl 10,11-epoxyundecanoate copolymers. Infrared spectra of the various copolymers had features typical of the MEU units in the polyether chain and showed as well prominent absorptions assignable to the alkylene oxide comonomer units. All spectra exhibited an intense band centered at ca. 1100 cm^{-1} , the characteristic stretching frequency for the polyether

backbone, and a strong carbonyl (C=O) stretch at 1740 cm^{-1} .

^{13}C NMR spectra were obtained for all the poly(alkylene oxide) esters prepared. Assignments of individual carbon chemical shifts were made after comparison with the spectra of poly(MEU) and homopolymerization control samples run for each of the cyclic ether monomers. The chemical shift data are compiled in Table 9. The spectra and data were consistent with those expected for substituted poly(ethylene oxide) structures, or for the Ox/MEU copolymer, a poly(trimethylene oxide/substituted ethylene oxide) structure. The carbon atoms of the poly(alkylene oxide) backbone showed chemical shifts in the region of 70-82 ppm. The chemical shifts of the methylene carbon atoms in the copolymer backbone were found in the region of 70-75 ppm; the methine chemical shifts appeared at lower field or in the region of 77-82 ppm. As expected, multiple chemical shifts were generally observed for each type of backbone carbon as a result of the sensitivity of the ^{13}C method to triad or dyad structures in the chain. Pentad structures are usually not detected for polymers with hetero-atoms in the main chain.²¹³ It is expected that the copolymer backbone consists predominantly of regular head-to-tail placements, but may also contain abnormal placements (head-to-head and tail-to-tail) or even configurational isomers. No attempts were made in this work to determine quantitatively the relative

TABLE 9
 ^{13}C NMR CHEMICAL SHIFT DATA FOR COPOLYMERS OF METHYL 10,11-EPOXYUNDECANOATE AND CYCLIC ETHERS^a

$$\text{---} \left(\text{CH}_2 \right)_m \text{---} \underset{\text{R}}{\underset{|}{\text{CH}}} \text{---} \underset{\text{R}}{\underset{|}{\text{CH}}} \text{---} \left(\text{CH}_2 \right)_n \text{---} \underset{\text{R}}{\underset{|}{\text{CH}}} \text{---} \text{OCH}_2 \text{CH} \text{---} \left(\text{CH}_2 \right)_8 \text{---} \text{COOCH}_3$$

Copolymer ^b	m	R	$\text{---OCH}_2\text{---}$	$\text{R} \text{---OCH}_2\text{---}$	$\text{---OCH}_2\text{CH---}$	$\text{---OCH}_2\text{---}$
EO-MEU	1	H	70.01, 71.17, 72.10, 72.33	70.01, 71.17, 72.10, 72.33	74.61	79.61
PO-MEU	1	CH ₃	73.49, 74.22, 74.79, 74.99	76.17, 76.78	74.61	79.93, 80.26
ECH-MEU	1	CH ₂ Cl	69.91	79.45	73.39, 73.45	80.01
BO-MEU	1	CH ₂ CH ₃	72.24, 72.40, 73.04	80.77, 81.24	73.56	80.19
TCBO-MEU	1	CH ₂ CCl ₃	72.07, 72.33, 72.56, 72.68	77.75	73.65, 73.95, 74.13	79.94, 80.17
HO-MEU	1	(CH ₂) ₃ CH ₃	72.56, 72.81, 73.77, 74.66	77.48, 77.97, 80.13	74.66	80.13
PGE-MEU	1	CH ₂ OC ₆ H ₅	70.66, 70.81, 71.03	79.05, 79.50, 80.09	74.0, 74.5	80.82, 80.95, 81.03
Ox-MEU	2	H	67.48, 68.43, 69.03	67.48, 68.43, 69.03	74.05, 74.39	79.92, 80.32, 80.53

^aIn ppm downfield from TMS, only carbon atoms in backbone are listed.

^bEO: ethylene oxide, PO: propylene oxide, ECH: epichlorohydrin, BO: 1-butene oxide, TCBO: 4,4,4-trichloro-1-butene oxide, HO: 1-hexene oxide, PGE: phenyl glycidyl ether, Ox: oxetane.

proportions of each type of placement.

The thermal transition temperatures of the poly(alkylene oxide) esters were measured by differential scanning calorimetry (DSC). The results are given in Table 10. The values reported for the glass transition temperatures (T_g) and the melting temperatures (T_m) of the various copolymer samples were obtained at a heating rate of 20°C/min (in a nitrogen atmosphere). In addition, the transition temperatures reported in Table 10 were those measured after 3 scans of the sample over the temperature range of interest. As indicated in Table 10, the copolymers of MEU with ethylene oxide; 4,4,4-trichloro-1-butene oxide, and phenyl glycidyl ether were semi-crystalline elastomers. The two EO copolymers, which contained 15 mole-% and 4 mole-% MEU, had T_g 's of -63°C and -58°C and T_m 's of 43°C and 56°C, respectively. The values of T_g and T_m for the copolymer incorporating 15 mole-% MEU are significantly lower than those of the EO rich copolymer. These results are believed to be consistent with an expected decrease in the level of crystallinity, degree of crystalline region perfection and lowering of T_g due to the higher level of bulkier MEU comonomer units incorporated. The unusual MEU/TCBO copolymer, prior to fractionation, was also found to exhibit a low level of crystallinity: the copolymer softened at -35°C and showed a small melting endotherm at 41°C. The last semi-crystalline copolymer listed,

TABLE 10
TRANSITION TEMPERATURES OF METHYL 10,11-EPOXYUNDECANOATE COPOLYMERS^a

$$\text{-(OCH}_2\text{CH)}_n\text{-(OCH}_2\text{CH)}_m\text{-(CH}_2)_8\text{COOCH}_3$$

Comonomer	R	Mole-% MEU in Copolymer	T _g ^b in °C	T _m ^c in °C
Ethylene oxide	H	4 15	-58 -63	56 43
Propylene oxide	CH ₃	22	-61	-
Epichlorohydrin	CH ₂ Cl	17	-45	-
l-Butene oxide	CH ₂ CH ₃	25	-58	-
4,4,4-Trichloro- l-butene oxide	CH ₂ CCl ₃	41	-35	-
l-Hexene oxide	(CH ₂) ₃ CH ₃	25	-68	-
Phenyl glycidyl ether	CH ₂ OPh	26	d	DEC ^e

^a Determined by DSC.

^b Mid-point in ΔCp curve.

^c Maximum of melting endotherm.

^d Not observed.

^e Decomposition over broad temperature range.

unfractionated PGE/MEU, melted over a broad temperature range (158-220°C) and appeared to decompose during melting. A check of the sample later showed that it had turned brown. In addition, T_g could not be detected despite repeated scans. Reasons for this behavior, particularly decomposition upon melting, have not been established. All remaining copolymers of MEU were found to be amorphous as no melting transitions were detected.

3. Homopolymerizations of cyclic ether monomers. The polymerizations of cyclic ether monomers (Fig. 12) were carried out with 5 mole-% of the coordination initiator $Al(C_2H_5)_3/H_2O/AcAc$ (1.0/0.5/1.0). These polymerizations were conducted in order to gain further insight into what effects the ester-substituted epoxide MEU had on initiator activity. In addition the poly(alkylene oxides) provided valuable samples for comparing (qualitatively) their bulk properties with the corresponding MEU copolymers and were essential for the interpretation of copolymer infrared and ^{13}C NMR spectra, and DSC scans. Table 11 gives the results of these experiments. As can be seen by inspection of these results, the homopolymers of EO, PO, BO, ECH, HO and TCBO were all obtained in yields of 90% or more. In addition, as indicated by the relative magnitudes of their inherent viscosities, the polymers of EO, PO, BO and HO were of very high molecular weight. The inherent viscosity

Figure 12. Polymerizations of cyclic ethers with $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0).

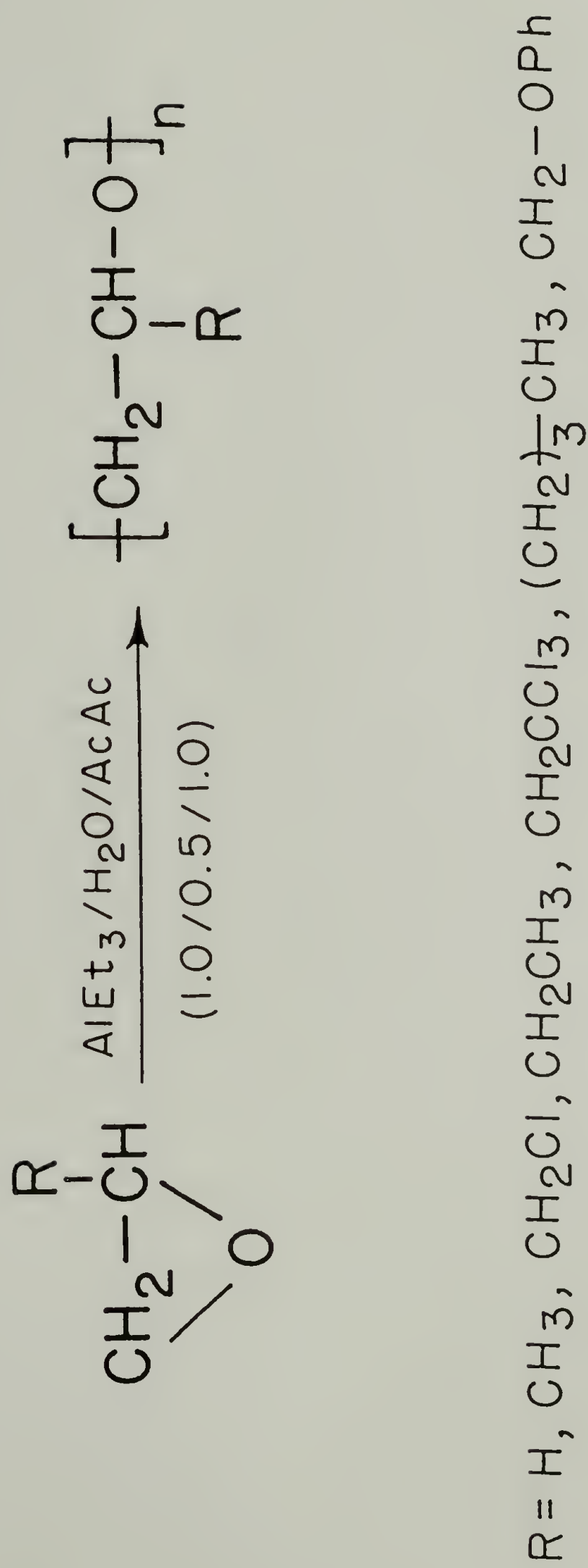


TABLE 11
POLYMERS OF CYCLIC ETHERS^a

Polymer ^b	Reaction Time in Days	Yield in %	$\eta_{0.1\%}^e$ in dL/g
EO	8	92	9.9
PO	13	98	6.7
BO	29	93	10.7
ECH	40	20 ^c 70 ^d	0.13 -
TCBO	68	97	-
HO	31	92	10.8
THF	70	0	-

^aPolymerization conditions: toluene solution (20% w/v), room temp., 5 mole-% $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator.

^bEO: ethylene oxide, PO: propylene oxide, BO: 1-butene oxide, ECH: epichlorohydrin, TCBO: 4,4,4-trichloro-1-butene oxide, HO: 1-hexene oxide and THF: tetrahydrofuran.

^cBenzene-soluble fraction.

^dBenzene-insoluble fraction.

^eChloroform solution, 30°C.

for poly(PO) was 6.7 dL/g (0.1% in CHCl_3 , 30°C), this corresponded to a GPC number-average molecular weight (\bar{M}_n) of 530,000 and a weight-average molecular weight (\bar{M}_w) of 774,000 (polystyrene equivalent molecular weights). The polymer from ECH gave crystalline and amorphous fractions in 70% and 20% yields, respectively. The soluble, amorphous poly(ECH) was of relatively low molecular weight; the inherent viscosity was only 0.13 dL/g (0.1% in CHCl_3 , 30°C). This was not totally unexpected as descriptions of experiments in the patent literature for the preparation of poly(ECH) with modified aluminumalkyl initiators frequently cite multiple additions of the initiator.⁶⁸ This suggests possible side reactions of the pendant chloromethyl groups with the initiator, thereby decreasing or destroying initiator activity. Poly(TCBO) was obtained in 97% yield, however the polymer was found to be insoluble in common organic solvents and could not be dissolved for a viscosity measurement. The attempted polymerization of THF with the coordination initiator was unsuccessful. The latter results were not surprising and strongly suggest that the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator contains no sites for cationic polymerization nor does it act as a proton source to initiate cationic polymerization, a theory suggested by Kennedy.²¹⁴

With the exception of poly(EO), the poly(alkylene oxides) were tough, snappy elastomers. Poly(EO) was a

tough, leathery polymer. These leathery properties are attributed to and manifestations of a substantial amount of crystallinity, a fact later verified by DSC.

Comparison of the inherent viscosities of the corresponding poly(alkylene oxide) esters (Table 8) with those for the cyclic ether homopolymers (Table 11) gave further indications that MEU interacts strongly with the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0) initiator. It is unlikely that the lower molecular weights of the copolymers are due to decreased polymerizability of the oxirane ring in MEU by the electron-withdrawing carboxyl group. The long spacer-group removes any inductive effects. Chain transfer by the methyl ester groups would also appear to be insignificant or absent since the ester groups were present in far excess of the added initiator and copolymers obtained were still of moderately high molecular weight. Polymerization work-up procedures for poly(MEU) and the poly(alkylene oxide) esters provided indirect evidence for the existence of strong but reversible interactions between the ester groups of the functional epoxide monomer and the initiator. It was found that acidified diluents (either 1,4-dioxane or benzene) were effective and essential for dissolving the elastomeric plugs produced during the polymerizations. In contrast, similar plugs obtained from the cyclic ether control polymerizations did not require acidification in order for dissolution to occur.

Without acidification, the elastic copolymer plugs generally swelled to ca. 2-5 times their original volume but did not dissolve. Methanol was generally used in all work-ups (dissolution) to deactivate the coordination initiator but was of minimal effectiveness alone for work-up and isolation of the poly(alkylene oxide) esters. These observations appear to be consistent with the hypothesis that specific interactions are occurring between the ester groups and the initiator. The most likely form of such interactions would appear to be coordination of the non-bonded electron pair of the ester carbonyl oxygen with aluminum. Vandenberg has claimed in an early patent that ester-containing compounds are among the class of suitable modifiers for initiators of the type used throughout much of this work.⁵⁰ It is known that initiator activity is a function of the amount of reactive additives (e.g., H_2O) and chelating agents.³⁵ It is conceivable that the ester groups of MEU function in a fashion as suggested above, competing with acetylacetone (2,4-pentanedione) for coordination sites of aluminum. However, it should be recognized that coordination of aluminum with AcAc is highly favored because of the resultant 6-membered ring formed.

It can be reasonably concluded from this work that interactions (reversible) do occur between the functional groups and initiator. Most important from the standpoint

of the success of this work was the fact that activity of the coordination initiator remained high. This, in effect, has allowed access to this new family of ester-substituted poly(alkylene oxides).

4. Characterization of cyclic ether polymers. Fundamental characterization of the cyclic ether homopolymers listed in Table 11 was also carried out and included analysis by infrared spectroscopy, ^{13}C NMR spectroscopy and differential scanning calorimetry.

The dominant absorption in the infrared spectra of the various poly(alkylene oxides) was the C-O stretching mode of the chain backbone. This characteristic absorption was generally centered near 1100 cm^{-1} . The IR spectrum of poly(EO) was quite unlike that of the EO/MEU copolymers, reflecting the substantial differences in crystallinity of the homo- and copolymers. As expected, poly(ECH) exhibited a strong absorption at 745 cm^{-1} , characteristic of C-Cl stretching in the pendant chloromethyl groups. In addition, a small carbonyl (C=O) absorption at 1730 cm^{-1} was also observed in the spectrum of poly(ECH). It appears some oxidation of the polymer had occurred. Poly(TCBO) exhibited two C-Cl stretching bands, at 775 and 695 cm^{-1} . An IR spectrum could not be obtained for poly(PGE) as the polymer was extremely hard, insoluble and intractable. The infrared spectra of the various poly(alkylene oxides)

are found in Appendix A, pp. 301-304.

Table 12 compiles the ^{13}C NMR chemical shift data for the poly(alkylene oxides) prepared with the coordination initiator $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0). ^{13}C NMR spectra could not be obtained for poly(TCBO) or poly(PGE); these polymers were insoluble and non-swellable. Chemical shifts for the carbon atoms in the backbone were found in the region of 70-81 ppm. The methylene carbons generally were found at the lower end of this range: 70-75 ppm. The methine carbons appeared at 76-81 ppm. Poly(PO), poly(BO), and poly(HO) exhibited multiplets in these regions, indicative of a complex microstructure in these polymers. The ^{13}C NMR spectra of the poly(alkylene oxides) are reproduced in Appendix C, pp. 324-326.

The glass transition temperatures (T_g) and melting temperatures (T_m) of the cyclic ether polymers were measured by DSC. The thermal transition temperatures are reported in Table 13 (values reported are from the third scan of the sample; all samples were heated under nitrogen at 20°C/min). As expected, poly(EO) and poly(TCBO) were semi-crystalline in nature. T_g of the high molecular weight EO homopolymer was -59°C and T_m was 63°C. The glass transition temperature for poly(TCBO) could not be detected despite several attempts to quench the sample from the melt. Interestingly, poly(TCBO) prepared in this work was found to be semi-crystalline, the rubbery polymer

TABLE 12
 ^{13}C NMR CHEMICAL SHIFT DATA FOR CYCLIC ETHER POLYMERS^{a,b}

Polymer ^c	$-\text{OCH}_2-$	$-\text{OCH}-$	C Atoms in Side Chain			
			$\text{-(CH}_2\text{)}_n$			$-\text{CH}_2\text{Cl}$
			n=1	2	3	
EO	71.94					
PO	71.45, 71.72, <u>73.79, 74.08</u>	76.01, 77.18, <u>78.42</u>			15.67, 16.87, <u>18.01, 18.88</u>	
BO	72.16, 72.35, <u>72.88</u>	80.63, <u>81.07</u>	25.31		9.96	
ECH	69.80	79.40				43.98
HO	73.00, 73.19, <u>73.98, 75.09</u>	77.89, 78.38, <u>80.52</u>	32.83	28.44	23.61	14.54

^aIn ppm downfield from TMS in benzene solution.

^bChemical shift values underlined represent dominant peak in multiplet.

^cEO: Ethylene oxide, PO: propylene oxide, BO: 1-butene oxide, ECH: epichlorohydrin and HO: 1-hexene oxide.

TABLE 13
THERMAL TRANSITION TEMPERATURES FOR
CYCLIC ETHER POLYMERS^a

Polymer ^b	T _g in °C	T _m in °C
EO	-59	63
PO	-67	-
BO	-63	-
ECH	-31 ^c -24 ^d	- 123
TCBO	e	170
HO	-66	-

^aDetermined by DSC: heating rate 20°C/min.

^bEO: ethylene oxide, PO: propylene oxide, BO: 1-butene oxide, ECH: epichlorohydrin, TCBO: 4,4,4-trichloro-1-butene oxide, HO: 1-hexene oxide.

^cBenzene-soluble fraction.

^dBenzene-insoluble fraction.

^eNot detected.

exhibited a large melt endotherm at 170°C (T_m). Wei and Butler have also prepared the "polymer of TCBO" with a modified triisobutylaluminum initiator, $\text{Al}(\text{i-Bu})_3/\text{H}_2\text{O}/\text{AcAc}$ (1.0/0.5/1.0), but reported the polymer to be completely amorphous after analysis by x-ray and DTA.⁷⁷ However, the TCBO monomer used was reported to contain ca. 22% of 1,1-dichloro-3,4-epoxy-1-butene (DCB) and the polymer obtained showed a C=C stretch in the IR spectrum. In effect, Wei and Butler prepared a copolymer of TCBO and DCB; thus it is not surprising that differences exist in the microstructures of the TCBO/DCB copolymer and the TCBO homopolymer prepared in this work.

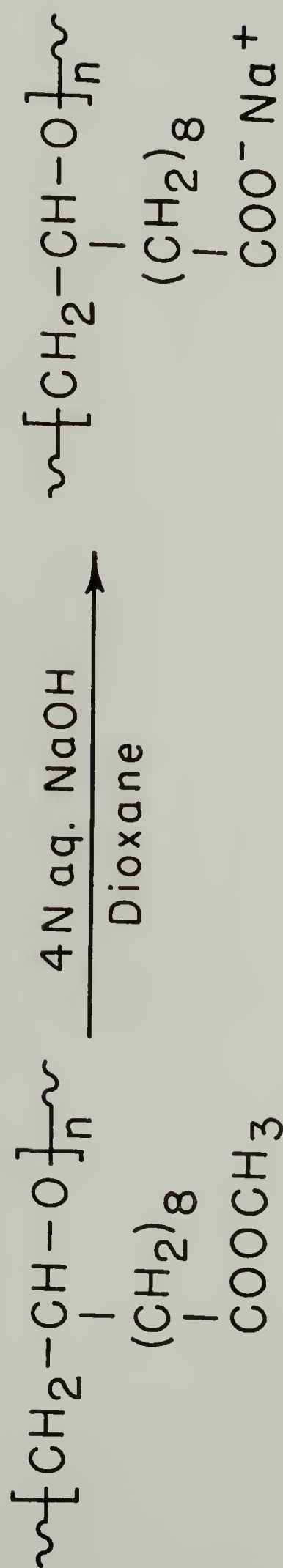
The two fractions of poly(ECH) showed differences in their thermal properties. The relatively low molecular weight benzene-soluble fraction had a T_g of -31°C and was amorphous. The benzene-insoluble fraction of poly(ECH) exhibited a T_g of -24°C and a melting transition at 123°C .

All the remaining poly(alkylene oxides) listed in Table 13 were found to be amorphous.

D. Modification Reactions of Poly(Alkylene Oxide) Pendant Reactive Groups

One of the objectives in this research, as stated at the outset of this chapter, was the conversion of pen-

Figure 13. Preparation of poly(10,11-epoxyundecanoic acid sodium salt) from poly(methyl 10,11-epoxyundecanoate).



dant ester groups on the functional poly(alkylene oxides) to metal carboxylate and carboxylic acid functionalities. The resultant poly(alkylene oxides) are of interest as a new family of ion-containing polyethers, including polyelectrolytes, ionomers, and polymeric acids. Two poly(alkylene oxide) esters prepared in this work were selected for such modification reactions: poly(MEU) and poly(EO-co-MEU). The polymer of MEU was chosen for investigation because of its high concentration of pendant reactive groups (one ester group per repeating unit), while the EO/MEU copolymer was particularly attractive for modification because of its hydrophilic properties. The following three sections are therefore devoted exclusively to the work carried out in this area.

1. Modification reactions of poly(methyl 10,11-epoxyundecanoate). Poly(alkylene oxide) ester copolymers derived from ethyl glycidate have previously been shown to be readily converted to the corresponding poly(alkylene oxide) ionomers by reaction with strong base.¹⁻³ The conversion of the pendant ester groups of poly(MEU) to the sodium carboxylate form was accomplished under analogous reaction conditions (Figure 13).

Poly(MEU) with an inherent viscosity of 0.12 dL/g (0.5% in 1,4-dioxane, 30°C) was dissolved in 1,4-dioxane.

Following the addition of a 4N sodium hydroxide solution (3 fold excess of OH^- to ester), two immiscible solutions resulted which were stirred for 1 hr at 100°C .

Poly(10,11-epoxyundecanoic acid sodium salt) (abbreviated as $\text{poly}(\text{EUA}^-\text{Na}^+)$), the product of the saponification, precipitated from the mixture, making recovery quite simple. Excess base (OH^-) was readily removed from the polymer by washing with methanol. The recovered yield of $\text{poly}(\text{EUA}^-\text{Na}^+)$ was 89%.

As expected, the presence of metal carboxylate groups along the entire length of the polyether backbone (one carboxylate salt group/repeating unit) influenced considerably the properties of the polymer. In contrast to the ester-substituted poly(alkylene oxide), $\text{poly}(\text{EUA}^-\text{Na}^+)$ was not elastomeric at room temperature. The polyelectrolyte retained none of the adhesive properties (tackiness) of its ester-substituted precursor and behaved instead like a free-flowing powder. Elemental analysis of the polymer found 10.1% Na, indicating that nearly 99% of the ester groups had been hydrolyzed.

The solubility characteristics of $\text{poly}(\text{EUA}^-\text{Na}^+)$ were also markedly different from its esterified precursor $\text{poly}(\text{MEU})$. The poly(alkylene oxide) carboxylate salt was found to be completely insoluble in all organic solvents. The only suitable solvent was water, although solubility

of the polymer in cold water was limited to ca. 10 percent by weight. The inherent viscosity of poly(EUA⁻Na⁺) was 0.41 dL/g (0.5% in H₂O, 30°C). The lack of a significantly larger effect on the dilute solution behavior can probably be attributed to the inability of the polymer chains to assume conformations that completely minimize electrostatic repulsions between the negatively charged carboxylate groups. This inability is related to the high concentration and proximity of carboxylate groups. It is conceivable that the poly(alkylene oxide) backbone solvates the pendant ion-pairs, producing favorable polymer-polymer interactions. The effect of ionic group concentration on the dilute-solution behavior of polyelectrolytes is a well-known and interesting phenomenon.²¹⁵ Poly(EUA⁻Na⁺) prepared in this work represents the first member in a new family of polyelectrolytes.

In previous studies mentioned, the transformation of ion-containing poly(alkylene oxides) derived from EG to the corresponding poly(alkylene oxide) acids was also described.¹⁻³ Neutralization of the pendant carboxylate salt groups was accomplished using glacial acetic acid, a weak organic acid. The procedure worked equally well in a solution or slurry process. The use of stronger inorganic or organic acids was avoided in these cases because of the

Figure 14. Preparation of poly(10,11-epoxyundecanoic acid) by neutralization of poly(10,11-epoxyundecanoic acid sodium salt).

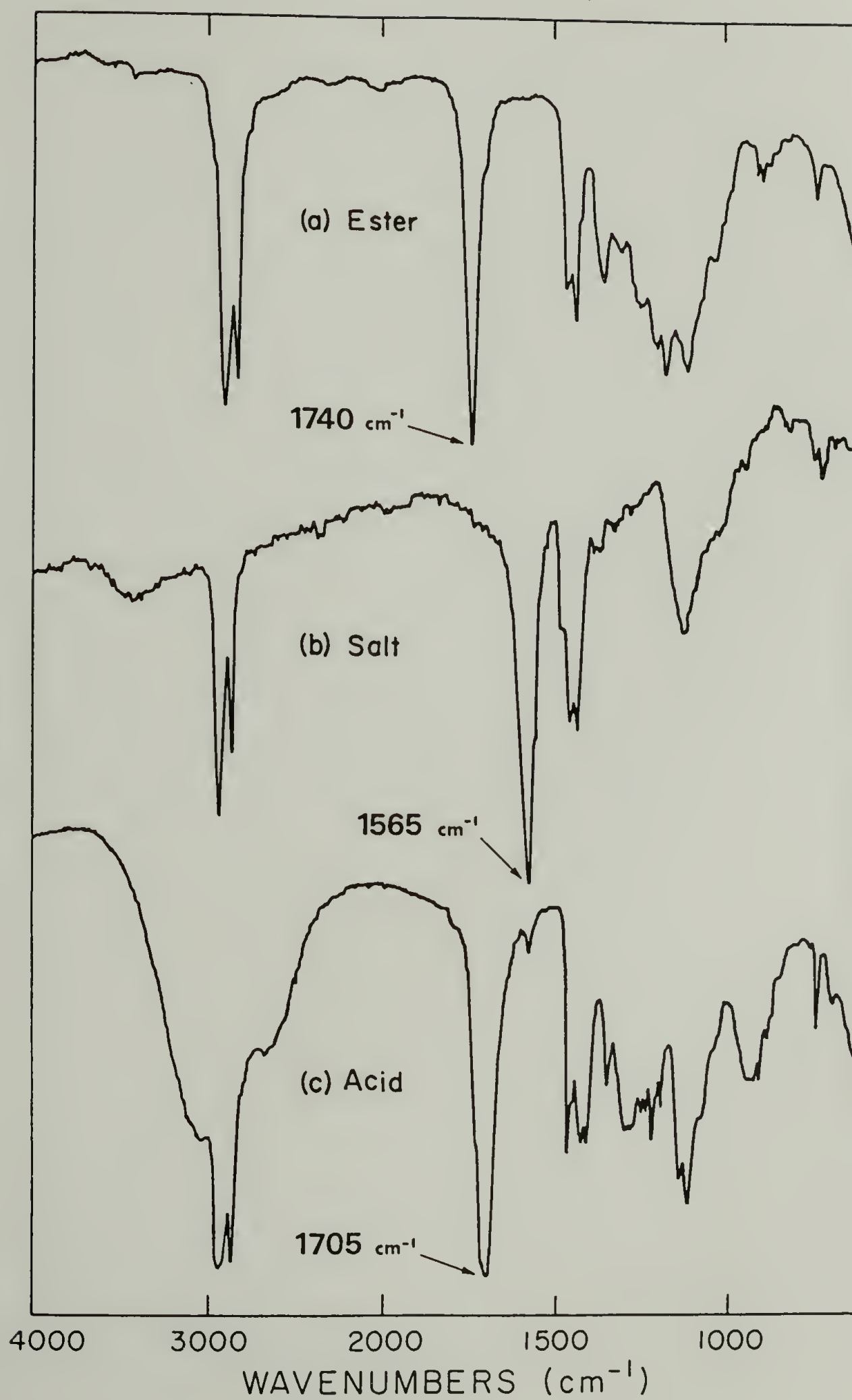


well-known sensitivity of polyethers and polyacetals to strong acids.⁷

In a slightly modified procedure, poly(EUA⁻Na⁺) was converted to the polyacid form as shown by the reaction in Figure 14. It was found to be convenient to carry out the acidification in aqueous solution since the polyelectrolyte was insoluble or did not readily swell in organic media. The neutralization with a 20-fold excess of glacial acetic acid was carried out at room temperature. Granular white polymer precipitated almost immediately and was collected after 2 hr, washed and dried. The IR spectrum of the polymer recovered, however, revealed the presence of unreacted -COO⁻Na⁺ groups (C=O stretch at 1565 cm⁻¹). The partially-neutralized poly(EUA) was slurried overnight in aqueous acetic acid (pH ca. 4) and the polymer was recovered in 96% yield. The IR spectrum of the waxy poly(EUA) showed no -COO⁻Na⁺ groups. The inherent viscosity of the polymer was 0.17 dL/g (0.5% in 1,4-dioxane, 30°C).

2. Characterization of poly(10,11-epoxyundecanoic acid sodium salt) and poly(10,11-epoxyundecanoic acid). The IR spectra of poly(EUA⁻Na⁺) and poly(EUA) differed substantially from each other and also from the IR spectrum of their ester-substituted precursor poly(MEU).

Figure 15. Comparison of infrared spectra of functionally-substituted poly(alkylene oxides): (a) poly(methyl 10,11-epoxyundecanoate), (b) poly(10,11-epoxyundecanoic acid sodium salt) and (c) poly(10,11-epoxyundecanoic acid).



The IR spectra of the three functionally-substituted poly(alkylene oxides) are reproduced for purposes of comparison in Figure 15. The characteristic stretching mode for the poly(alkylene oxide) backbone, i.e. the C-O stretch, is found near 1100 cm^{-1} in all three IR spectra shown in Figure 15. The carbonyl (C=O) stretching frequency of poly(MEU) appears at 1740 cm^{-1} in spectrum a. Poly(EUA⁻Na⁺), obtained by saponification of poly(MEU), shows a strong carboxylate anion stretch at 1565 cm^{-1} (spectrum b). Poly(EUA), obtained by neutralization of poly(EUA⁻Na⁺), shows the carboxylic acid C=O stretch at 1710 cm^{-1} (spectrum c) in addition to the broad O-H stretch in the region of $3540\text{--}2350\text{ cm}^{-1}$.

Poly(EUA⁻Na⁺) and poly(EUA) were also characterized by ^{13}C NMR spectroscopy and the results were compared with those obtained previously for poly(MEU). As expected, the most prominent difference in the spectra of the three functional poly(alkylene oxides) was in the chemical shift of the carbonyl carbon. Saponification of the pendant methyl ester groups of poly(MEU) resulted in a substantial downfield shift of ca. 11.5 ppm for the carbonyl carbon of poly(EUA⁻Na⁺). Conversion of the pendant carboxylate anions ($-\text{COO}^-\text{Na}^+$) of poly(EUA⁻Na⁺) to the carboxylic acid form of poly(EUA) once again produced a large change, ca. 9 ppm upfield, in the carbonyl carbon chemi-

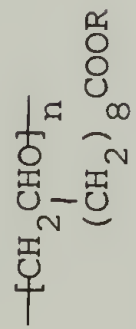
cal shift. The chemical shifts of the oxyethylene backbone carbons were relatively unchanged, although substantial broadening of the methine and methylene carbon signals was observed in the spectrum of poly(EUA⁻Na⁺), indicating a change in the relaxation behavior of the poly(alkylene oxide) backbone. The longer relaxation time for the backbone of poly(EUA⁻Na⁺) is probably due to the influence of the ionic groups on the conformation of the molecules in solution. The chemical shift data for the three functionally-substituted poly(alkylene oxides) are compiled in Table 14.

The thermal transition temperatures (T_g and T_m) of the functionally-substituted poly(alkylene oxides) were determined by DSC. Results of DSC studies are given in Table 15 (values reported were those determined on the third scan of the sample; all samples were heated in a nitrogen atmosphere at 20°C/min). Despite repeated attempts, the T_g of poly(EUA⁻Na⁺) could not be detected. In addition, no melting endotherms were observed at temperatures up to ca. 225°C (500°K). Heating of the ion-containing poly(alkylene oxide) to higher temperatures was not attempted; sample degradation, including decarboxylation was expected.

Poly(EUA) exhibited a T_g of 11°C (284°K). Thus, ultimate conversion of the pendant ester groups of

TABLE 14

¹³C NMR CHEMICAL SHIFT DATA FOR FUNCTIONALLY-SUBSTITUTED POLY (ALKYLENE OXIDES)^a



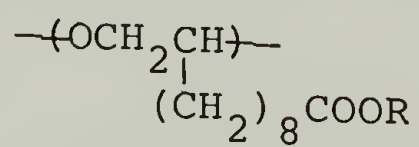
Polymer	R	Solvent	-OCH ₂ -	-OCH- 	$\begin{array}{c} \text{O} \\ \\ \text{-CO-} \end{array}$	-OCH ₃	Carbon Atoms of Spacer-Group ^b							
							1	2	3	4	5	6	7	8
MEU	OCH ₃	C ₆ D ₆	71.76, 73.14	79.39, 79.83	174.07	51.33	32.31	25.59	—	29.60/29.94	—	25.06	34.14	
EUA ⁻ Na ⁺	Na ⁺	D ₂ O	73.63	80.62	184.59	-	32.80	26.57	—	29.73/30.63	—	27.38	38.98	
EUA	H	dioxane- d ₈	73.70	80.22	175.17	-	32.93	26.09	—	30.13	—	25.71	34.05	

^aIn ppm downfield from TMS.

^bCarbon atom nearest polymer backbone designated as C-1 of spacer group.

TABLE 15

THERMAL TRANSITION TEMPERATURES OF FUNCTIONALLY-SUBSTITUTED POLY(ALKYLENE OXIDE) HOMOPOLYMERS^a



Polymer	R	T _g in °C	T _m in °C
MEU	CH ₃	-40	16-53
EUA	H	11	105-118, 115-134
EUA ⁻ Na ⁺	Na ⁺	b	b

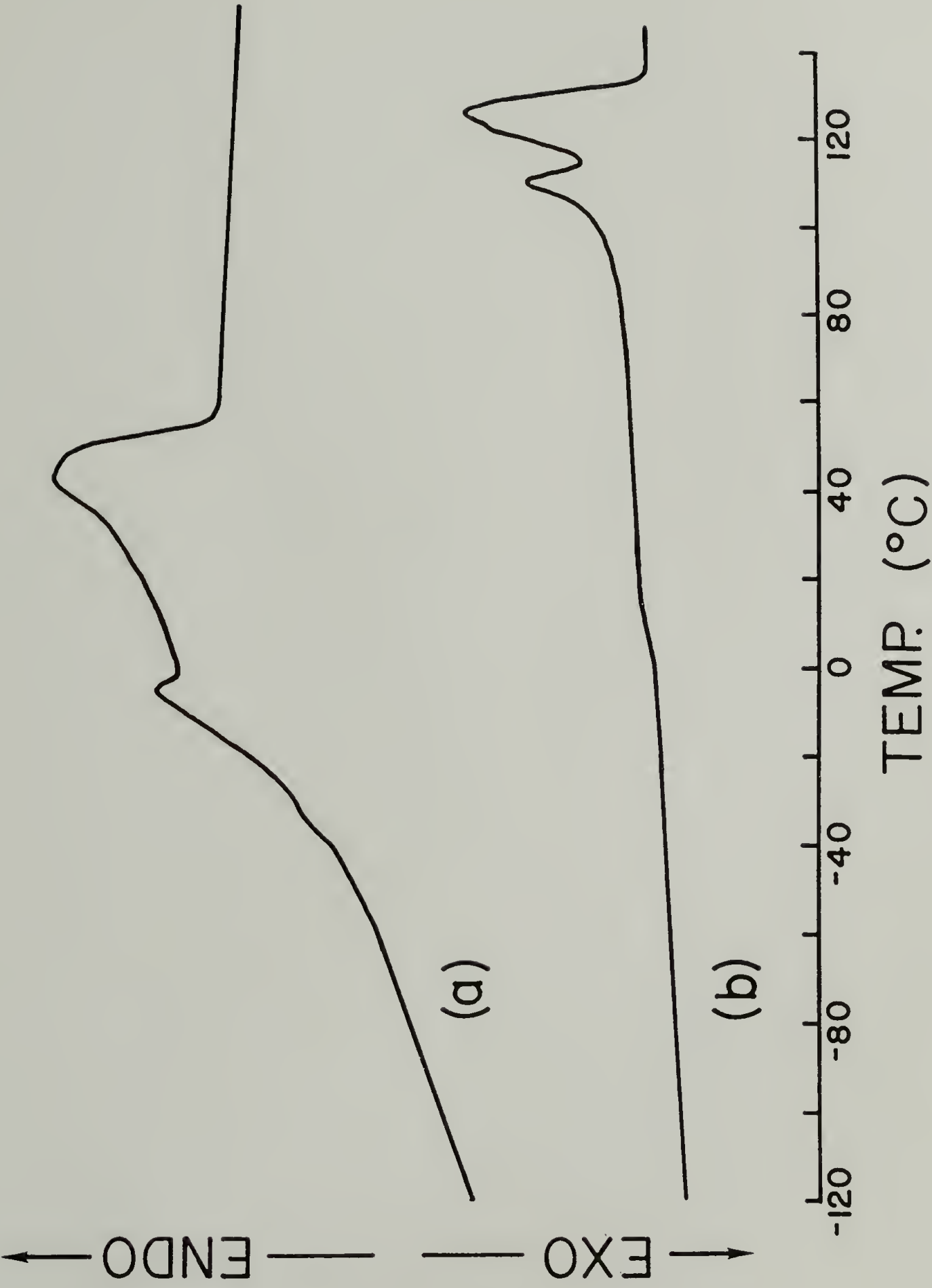
^aDetermined by DSC, heating rate 20°C/min.

^bNot detected over temperature range -120 to 225°C.

poly(MEU) to the carboxylic acid form resulted in an increase in T_g of ca. 50°C. One important factor which affects the T_g of a polymer is the occurrence of specific inter- or intramolecular interactions such as hydrogen bonding.²¹⁶ Conversion of the pendant ester groups of poly(MEU) to the carboxylic acid form opens the possibility of both modes of hydrogen bonding. Two distinct possibilities exist: inter- and intramolecular hydrogen bonding between carboxylic acid groups and/or H-bonding (inter- and intramolecular) between carboxylic acid groups and the poly(alkylene oxide) backbone. Interactions of either or both type can account for the large increase in T_g .

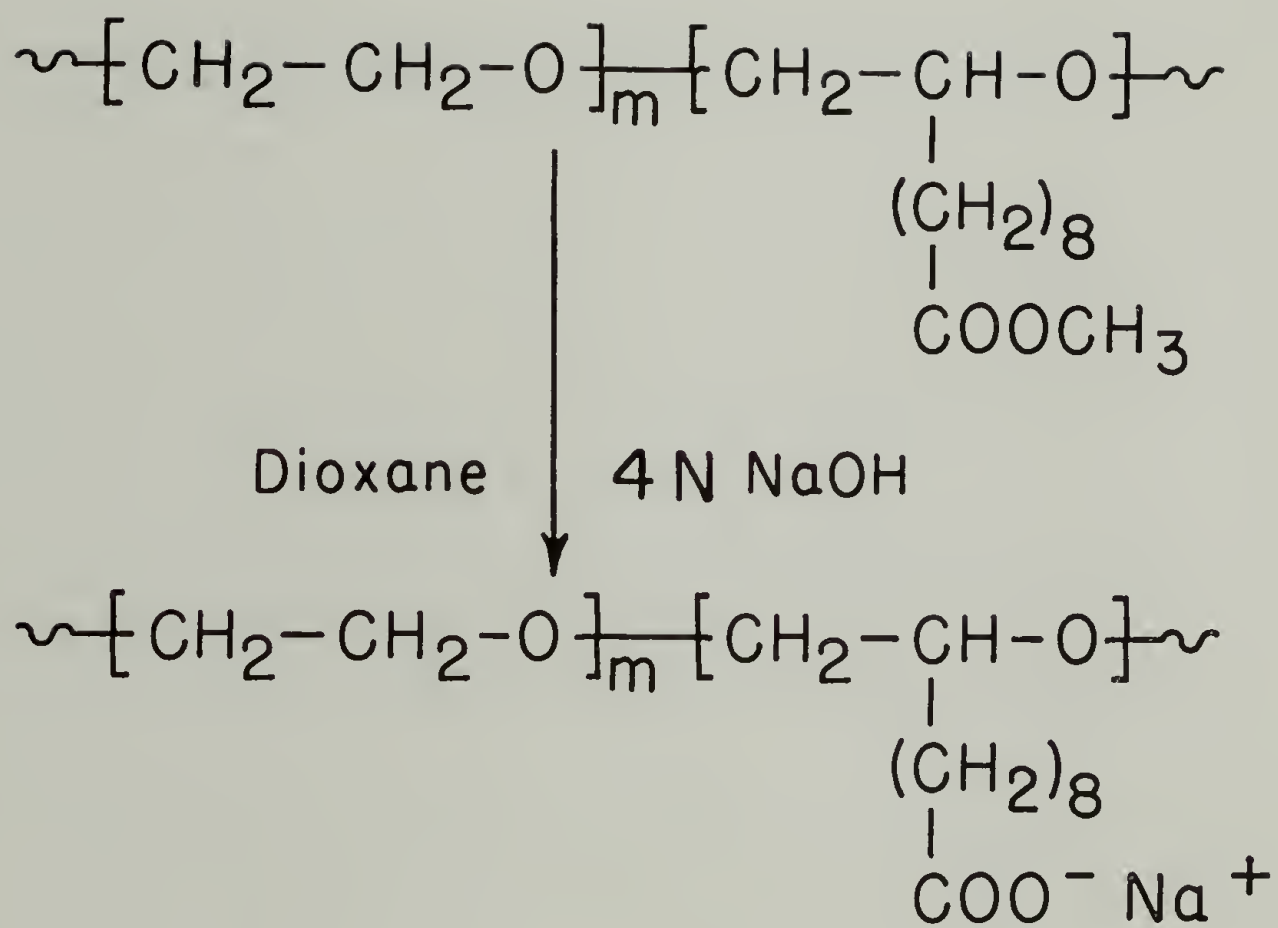
Poly(EUA) and the poly(MEU) elastomer from which it was derived were shown to be semi-crystalline, exhibiting broad melt endotherms. Poly(MEU) melted over a 37°C range in temperature (16-53°C or 289-326°K). Poly(EUA) exhibited two overlapping endothermic transitions: melting occurred at 103-118°C (377-391°K) and 115-134°C (388-407°K). The origin of these first order phase transitions has not been established, i.e. whether the crystallinity is of the polyethylene oxide type or is due to side-chain crystallization. The DSC scans for poly(MEU) and poly(EUA) are reproduced in Figure 16.

Figure 16. DSC scans of poly(methyl 10,11-epoxyundecanoate) (curve a) and poly(10,11-epoxyundecanoic acid) (curve b).



3. Modification reactions of poly(ethylene oxide-co-methyl 10,11-epoxyundecanoate). The copolymer of MEU and EO was converted to the corresponding poly(alkylene oxide) ionomer by cleavage of the pendant ester groups with 4N sodium hydroxide. The reaction, shown in Figure 17, was carried out in an analogous fashion to the saponification of poly(MEU). The EO/MEU copolymer used for the reaction had an inherent viscosity of 1.6 dL/g (0.5% in 1,4-dioxane, 30°C) and contained 4 mole-% pendant ester groups. A 4 percent by weight solution of the poly(alkylene oxide) ester in 1,4-dioxane was stirred vigorously with 4N sodium hydroxide solution (8 molar excess OH^- to ester groups) for 1 hr at 100°C. Unlike the saponification of poly(MEU), the ion-containing poly(alkylene oxide) copolymer did not precipitate from the reaction mixture. The turbid reaction mixture was divided into two equal portions, one portion was poured into a large volume of diethyl ether, causing precipitation of the poly(alkylene oxide) ionomer as a fluffy white solid. The ionomeric copolymer, purified by repeated soakings in methanol-ether mixtures, was isolated in 47% yield. Elemental analysis of the ionomer found 1.8% sodium, indicating quantitative conversion of the ester groups (4 mole-%) to the sodium carboxylate form. The inherent viscosity of the ionomer (0.5% in water, 30°C)

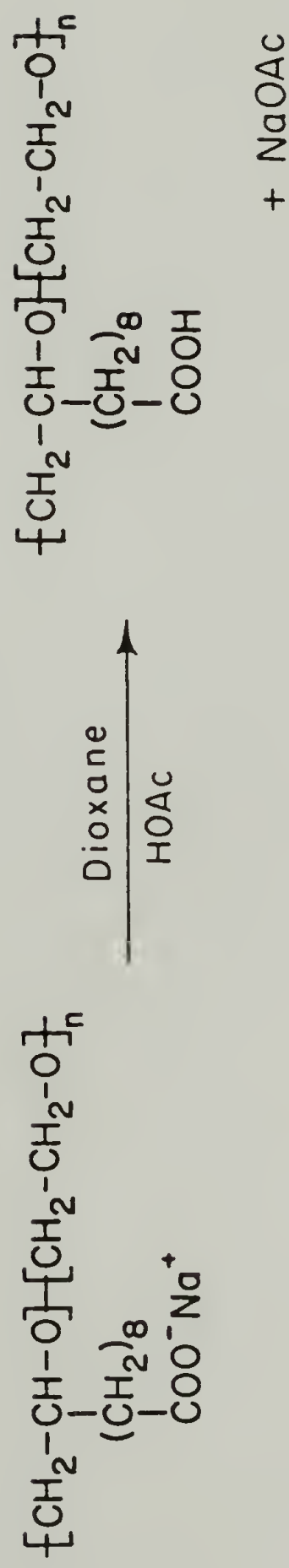
Figure 17. Preparation of poly(alkylene oxide) ionomer.



was 4.0 dL/g. The behavior of the ionized copolymer at room temperature was notably different from the starting EO/MEU copolymer. The poly(alkylene oxide) ionomer, abbreviated as poly(EO/EUA⁻Na⁺) for poly(ethylene oxide-co-10,11-epoxyundecanoic acid sodium salt) exhibited neither the property of tackiness nor the elasticity (snappiness) found in the ester-substituted copolymer. Presumably, changes in these properties can be attributed to the presence of the ionic groups.

Preparation and isolation of the poly(alkylene oxide) acid, poly(EO/EUA), was also carried out. The remaining poly(EO/EUA⁻Na⁺)/dioxane solution mentioned previously was utilized for this purpose. The neutralization reaction is depicted in Figure 18. Excess glacial acetic acid was added to the ionomer solution. The EO/EUA copolymer was isolated by precipitation into water; the yield after washing and drying was 33%. Elemental analysis of the copolymer found ca. 0.1% sodium, this corresponded to 0.2 mole-% residual sodium carboxylate ($\text{-COO}^-\text{Na}^+$) groups in the copolymer (indicating 95% of the pendant ionic groups had been neutralized). The inherent viscosity of the spongy, white poly(alkylene oxide) acid was 1.8 dL/g (0.5% in 1,4-dioxane, 30°C). The relatively low recovered yield of the copolymer following neutralization and precipitation is probably due to some solubility

Figure 18. Preparation of poly(ethylene oxide-co-10,11-epoxyundecanoic acid).

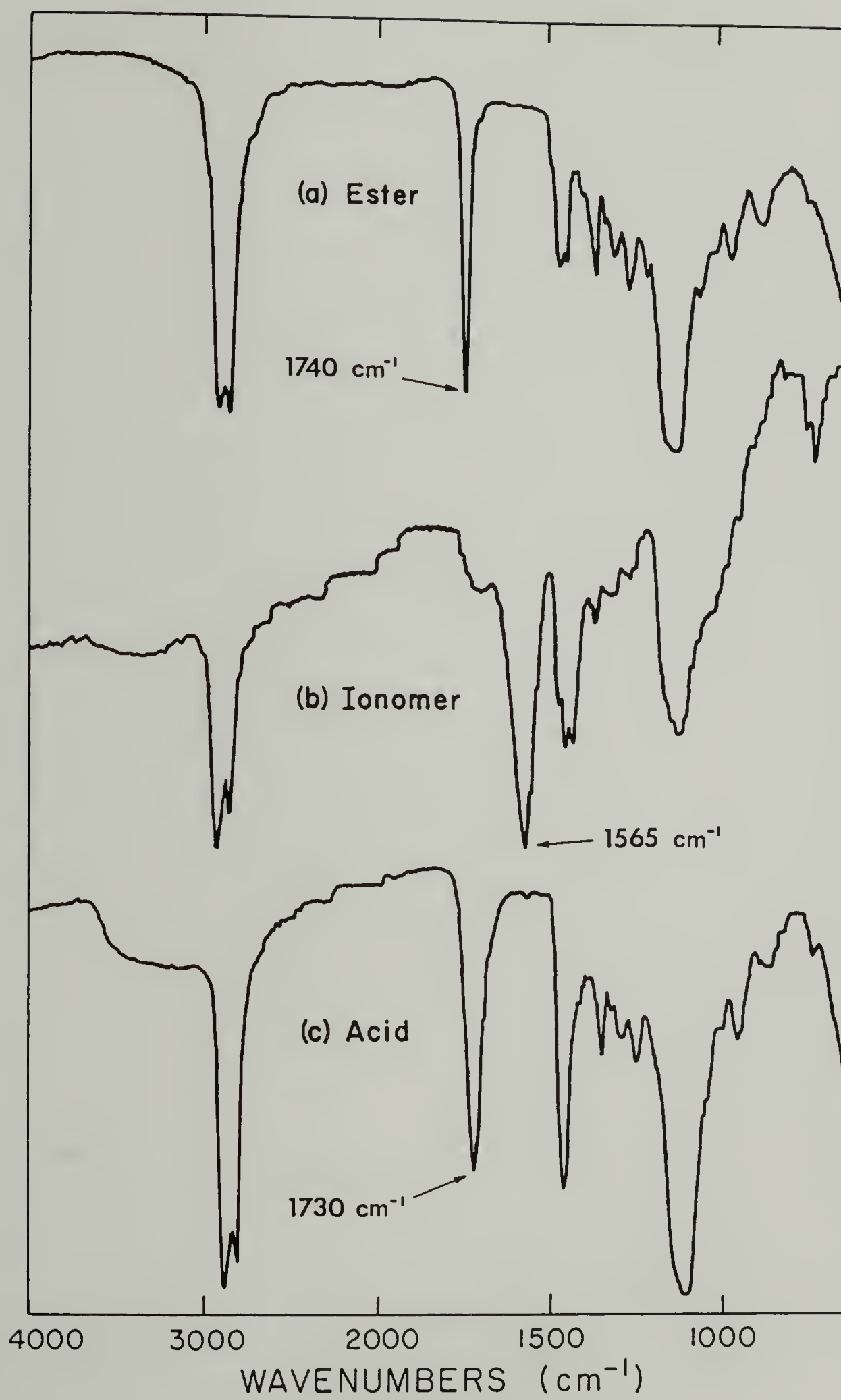


of the material in water. This is not surprising as the copolymer contained a large proportion of EO. On the other hand, water was found to be the most suitable medium for precipitation.

As expected, the comonomer composition in the poly(alkylene oxide) carboxylic acid was unchanged from the ester and ionomer forms. The relative composition of the copolymer was 4 mole-% EUA and 96 mole-% EO.

4. Characterization of poly(ethylene oxide-co-10,11-epoxyundecanoic acid sodium salt) and poly(ethylene oxide-co-10,11-epoxyundecanoic acid). The IR spectra of the poly(alkylene oxide) ionomer and poly(alkylene oxide) carboxylic acid are shown in Figure 19. Also shown for comparative purposes is the IR spectrum of the ester-substituted copolymer of MEU and EO. The characteristic C-O stretching frequency for the poly(alkylene oxide) backbone is found near 1110 cm^{-1} in all three infrared spectra of Fig. 19. Large differences in the frequency of the carbonyl stretch (C=O) can also be observed by comparing the spectra. The carbonyl stretching frequency of the starting poly(alkylene oxide) ester elastomer, poly(EO/MEU), appears at 1735 cm^{-1} in spectrum a. Poly(EO/EUA⁻Na⁺), obtained by the saponification of poly(EO/MEU), shows a strong carboxylate anion stretch at 1565 cm^{-1} (spectrum b). Poly(EO/EUA), prepared

Figure 19. Comparison of infrared spectra of functionally-substituted poly(alkylene oxide) copolymers: (a) poly(ethylene oxide-co-methyl 10,11-epoxyundecanoate), (b) poly(ethylene oxide-co-10,11-epoxyundecanoic acid sodium salt), and (c) poly(ethylene oxide-co-10,11-epoxyundecanoic acid).



by neutralization of poly(EO/EUA⁻Na⁺), shows the carboxylic acid C=O stretch at 1730 cm⁻¹ (spectrum c) and a weak absorption at 1610 cm⁻¹ assigned to residual (0.2%) carboxylate anions.

Poly(EO/EUA⁻Na⁺) and poly(EO/EUA) were also characterized by ¹³C NMR spectroscopy; the results were compared with those previously obtained for poly(EO/MEU). As expected, the most prominent difference in the spectra of the three functional poly(alkylene oxides) was the chemical shift of the carbonyl carbon. Saponification of the pendant ester groups of the alkylene oxide copolymer EO/MEU resulted in a substantial downfield shift of ca. 11.6 ppm for the carbonyl carbon of poly(EO/EUA⁻Na⁺). Following neutralization of the ionomer's pendant carboxylate anions (-COO⁻Na⁺) to the carboxylic acid form of poly(EO/EUA), a large upfield shift of ca. 14.2 ppm was observed for the carbonyl carbon. Signals for the oxyethylene backbone carbons were relatively unchanged. The chemical shift data for the three functionally-substituted poly(alkylene oxides) are compiled in Table 16.

The thermal transition temperatures (T_g and T_m) of the functionally-substituted alkylene oxide copolymers were determined by DSC. Results of the DSC studies are given in Table 17. The reported values of T_g and T_m are

TABLE 16
 ^{13}C NMR CHEMICAL SHIFT DATA FOR FUNCTIONALLY-SUBSTITUTED POLY(ALKYLENE OXIDE) COPOLYMERS^a

$\text{---}\{\text{CH}_2\text{CH}_2\text{O}\}_n\text{---CH}_2\underset{\text{(CH}_2)_8\text{COOR}}{\text{CHO}}\text{---}$											
Copolymer	R	EO $\text{---OCH}_2\text{CH}_2\text{---}$	$\text{---OCH}_2\text{---}$	---OCH--- 	$\text{O}=\text{C---}$	---OCH_3	Carbon Atoms of Spacer Group				
							1	2	3-6 ^b	7	8
EO/MEU	CH ₃	70.01, 71.17, 72.10, 72.33	74.61	79.61	173.4	57.11	32.75	25.94	29.62/29.78/ 29.98/30.31	25.45	34.30
EO/EUA ⁻ Na ⁺	Na ⁺	69.28, 69.92, 70.05, 71.63	73.37, 74.00	80.06	185.03	-	31.59	25.73	29.89/30.01	27.15	38.87
EO/EUA	H	69.91, 71.00, 71.40, 72.98	74.44	79.53	170.82	-	32.55	25.80	29.48/29.64/ 29.83/30.15	25.27	34.31

^aIn ppm downfield from TMS. Solvent: d₆-benzene.

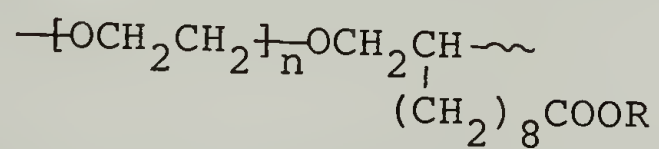
^bAssignment of individual carbon chemical shifts could not be accurately determined.

those determined on the third scan of each sample. All samples were heated in a nitrogen atmosphere at 20°C/min. Inspection of the data in Table 17 shows that conversion of the 4 mole-% ester groups of poly(EO/MEU) to the corresponding carboxylate salt groups was accompanied by a 6°C rise in the glass transition temperature. The T_g of the poly(alkylene oxide) ester and ionomer were -58°C and -52°C, respectively. The effect of ionic groups on the T_g of polymers has been studied extensively and is well documented.^{217, 218} The results given in Table 17 are in agreement with the general tendency for T_g to increase when ionic groups are present in a polymer matrix. The increase in T_g has been ascribed to a reduction in segmental mobility due to electrostatic forces between boundions in the polymer chain and the counterions.²¹⁹ Similarly, the acid form of the alkylene oxide copolymer showed a higher T_g than the ester-substituted copolymer. The respective glass transition temperatures of poly(EO/EUA) and poly(EO/MEU) are -50°C and -58°C. Presumably, strong interchain attractive forces due to hydrogen bonding (dimer formation) between pendant carboxylic acid groups or with the polyether backbone reduces segmental motion and serve to raise T_g .

As indicated by the results in Table 17, each of the functionally-substituted alkylene oxide copolymers was

TABLE 17

THERMAL TRANSITION TEMPERATURES OF FUNCTIONALLY-SUBSTITUTED ALKYLENE OXIDE COPOLYMERS^a



Copolymer ^b	R	T _g in °C	T _m in °C
EO/MEU	CH ₃	-58	56
EO/EUA ⁻ Na ⁺	Na ⁺	-52	52
EO/EUA	H	-50	23

^aDetermined by DSC, heating rate 20°C/min.

^bContained 4 mole-% pendant functional groups
-COOR.

semi-crystalline in nature. The trend found in the melting temperatures (T_m) of the functional polyethers was opposite to that seen for T_g as the pendant functional groups were changed from ester to carboxylate salt to carboxylic acid. Substantial lowering of the melt temperatures is probably due to a reduction in perfection of crystalline regions. Annealing of samples was not carried out and so a more precise explanation for the observed melting behavior cannot be put forward. The DSC scans for three functionally-substituted alkylene oxide copolymers are reproduced in Figure 20.

Wide angle x-ray diffraction patterns were obtained for poly(EO/MEU) and the sodium ionomer, poly(EO/EUA⁻Na⁺). The latter copolymer, as mentioned previously, contained 4 mole-% salt groups by virtue of complete saponification of the ester-substituted alkylene oxide copolymer. The x-ray diffraction scans are reproduced in Figure 21. Samples were scanned over a range of Bragg angles, from $2\theta \approx 2^\circ$ to $2\theta \approx 40^\circ$. The presence of poly(EO) backbone crystallinity in both samples was readily apparent from the scattering maxima at $2\theta = 19.2^\circ$ and $2\theta = 23.4^\circ$. These scattering maxima arise from the monoclinic poly(ethylene oxide) unit cell.²²⁰ Qualitative comparison of the relative areas beneath the two scattering maxima indicated that the ester-substituted copo-

Figure 20. DSC scans of functionally-substituted alkylene oxide copolymers: (a) poly(ethylene oxide-co-methyl 10,11-epoxyundecanoate), (b) poly(ethylene oxide-co-10,11-epoxyundecanoic acid sodium salt), and (c) poly(ethylene oxide-co-10,11-epoxyundecanoic acid).

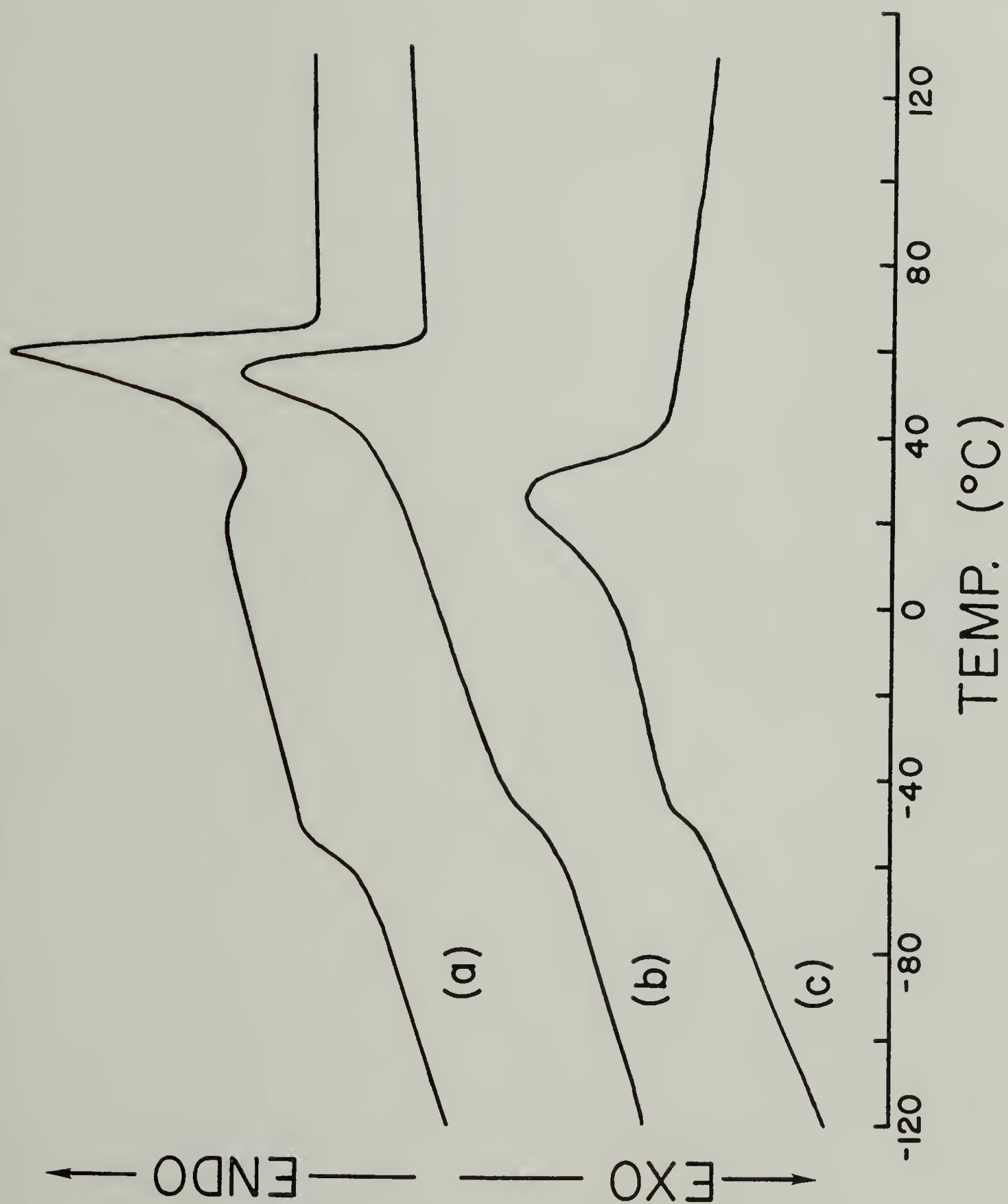
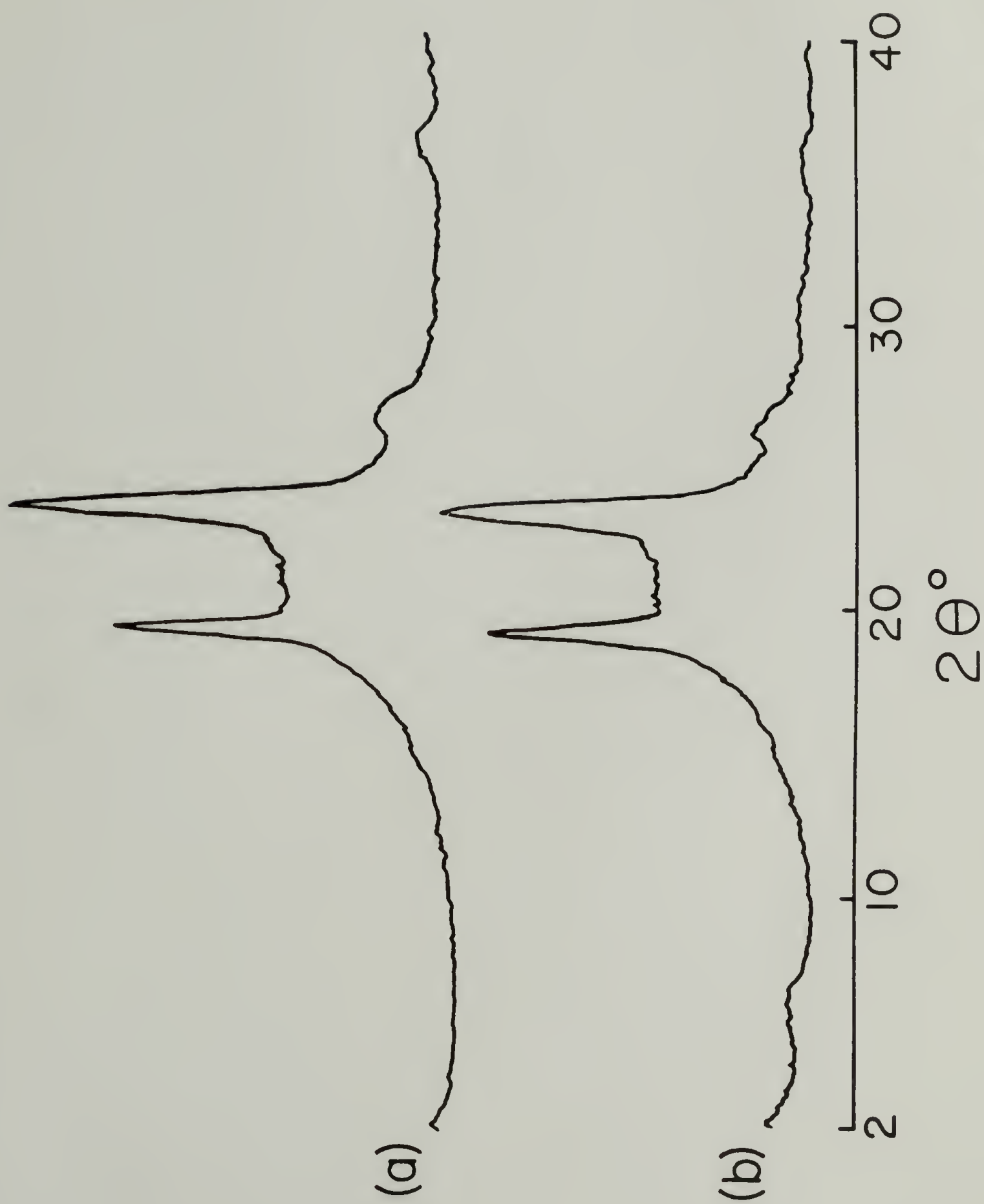


Figure 21. Wide angle x-ray diffraction (WAXD) scans of functional alkylene oxide copolymers: (a) poly(ethylene oxide-co-methyl 10,11-epoxyundecanoate) and (b) poly(ethylene oxide-co-10,11-epoxyundecanoic acid sodium salt).



lymer and the ionomer have a similar level of crystallinity. The most interesting feature in Fig. 21 is the appearance of a new and relatively weak peak centered near $2\theta = 6.5^\circ$ in the scattering pattern of the alkylene oxide ionomer. This peak is a common feature of all ionomers examined by wide-angle x-ray and has been termed the "ionic" peak by MacKnight and Earnest.²²¹ The nature of the polymer backbone and the presence or absence of backbone crystallinity have no effect on the presence or absence of the ionic peak.²²¹ The occurrence of this ionic or "low-angle" peak is evidence¹¹⁰ that the solid-state structure of the ionomer is significantly different from that of the esterified copolymer. Wilson, Longworth and Vaughan¹¹⁰ were the first to observe the "low-angle" peak and suggested it arises from the presence of a second phase in ionomers. Much controversy still exists, however, over the distribution of salt groups in ionomers and it is outside the scope of this discussion to critically review this subject. What can be emphasized is that the finding of the ionic peak for the alkylene oxide copolymer is the first such observation for an ionomer based on a poly(ethylene oxide) backbone. A complete listing of all the scattering peaks in Fig. 21 is given in Table 18. Wide angle x-ray diffraction measurements were not performed on the carboxylic acid substituted alkylene oxide copolymer, poly(EO/EUA).

TABLE 18

WIDE ANGLE X-RAY DIFFRACTION MAXIMA OF FUNCTIONALLY-SUBSTITUTED ALKYLENE OXIDE COPOLYMERS

Copolymer	Mole-% Functionality, and Type	Angular Position of Peak in degrees 2θ
EO/MEU	4, ester	19.2 [*] , 23.4 [*] , 26.3 and 36.0
EO/EUA ⁻ Na ⁺	4, carboxylate salt	6.5, 19.2 [*] , 23.4 [*] , 26.4 and 35.9

* Major peaks in WAXD scan.

5. Dilute-solution viscometric studies of poly(ethylene oxide-co-10,11-epoxyundecanoic acid sodium salt). The behavior of ionomers in solution is an area of research that has as yet received little attention.²²¹ Dilute solution properties of polyelectrolytes on the other hand have been widely investigated. The important distinction which has been made between materials classified as ionomers and polyelectrolytes will be considered briefly because of its relevance to the studies presented in this section. Ionomers generally contain less than 10 mole-% salt groups, polyelectrolytes usually contain one charged group per repeating unit and are water-soluble. The term ionomer usually refers to a partially-ionized polymer with a nonpolar backbone (e.g. hydrocarbon).²²² However, since the early studies on ionic POM polymers the term has included backbones of the polyether type.^{101-104,167,169}

Two features common to ionomers of the polyethylene (non-polar) backbone variety are also present in the ethylene oxide based material prepared in this investigation. The ionic alkylene oxide copolymer, poly(EO/EUA⁻Na⁺), contains a low level of ionic comonomer units (4 mole-%) and shows an ionic peak at low angles in x-ray scattering. Classification of the ion-containing alkylene oxide copolymer as an ionomer has been made on that basis. On the other hand, it is also well known that

poly(ethylene oxide) exhibits polyelectrolyte behavior in aqueous solution.²²³ Holliday has suggested that the difference between polyelectrolytes and other ionic polymers is one of degree.²²⁴ The difference is due to the hydrophilic nature of polyelectrolytes, which is the result of the existence of a large proportion of ionic and/or hydrophilic groups in the chain. The results of the viscometric studies of poly(EO/EUA⁻Na⁺) to be presented in the following discussion also show expected polyelectrolyte behavior of the copolymer in aqueous media. However, for the reasons cited earlier, the ion-containing alkylene oxide copolymer will be classified in the ionomer family.

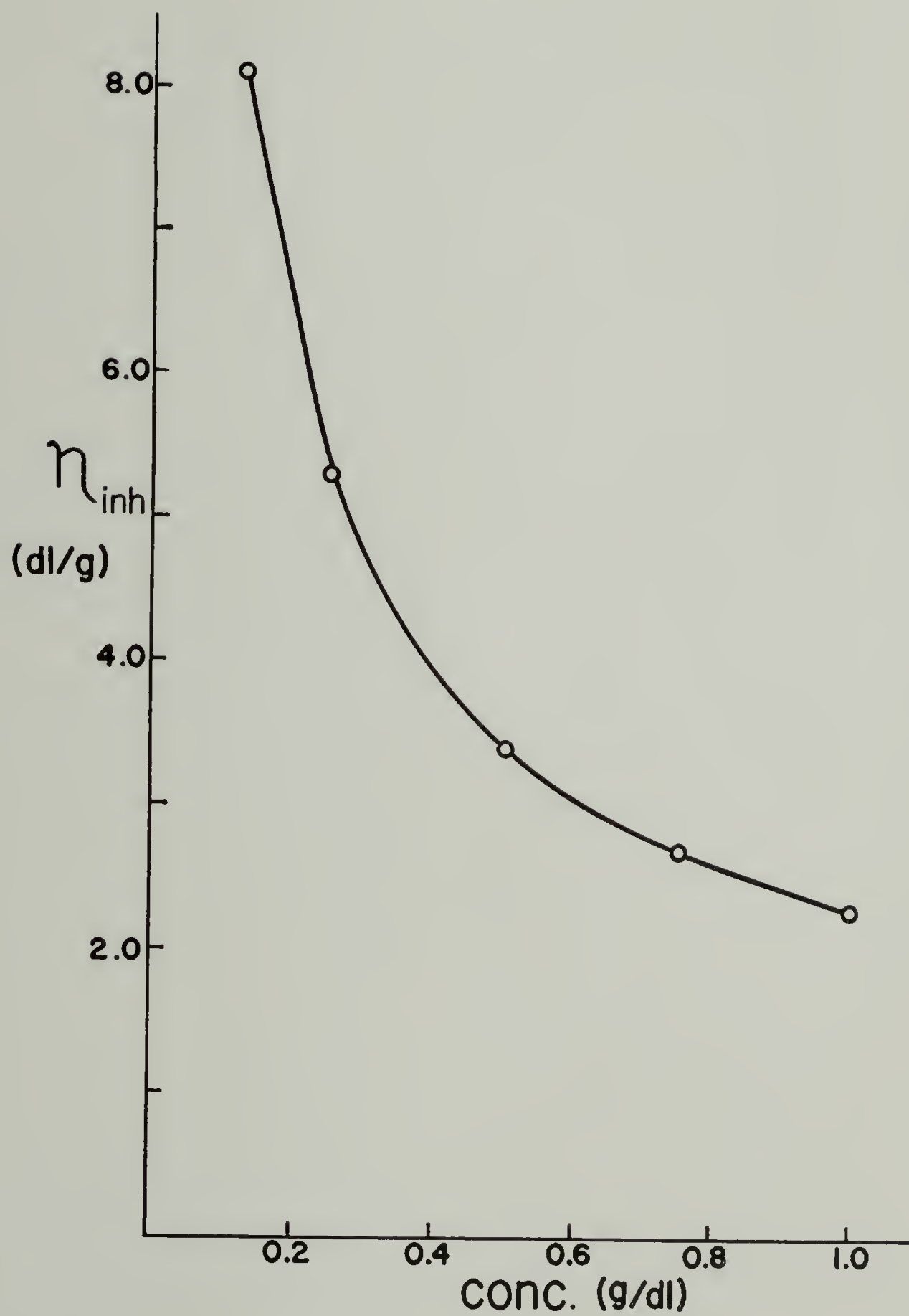
The results of two independent studies of the dilute-solution behavior of poly(EO/EUA⁻Na⁺) in water will now be given. Two separate effects were examined: a) the effect of ionomer concentration on the inherent viscosity of aqueous solutions and b) the effect of added ionic solute (NaCl) on the inherent viscosity of the ionomer in aqueous solution.

The inherent viscosity of the poly(alkylene oxide) ionomer in aqueous solution was determined at 30°C over the concentration range 0.13 g/dL-1.0 g/dL. A stock 1.0 g/dL ionomer solution was prepared and its viscosity was determined. Viscosity measurements were also made

following dilution of the stock ionomer solution with the desired amount of water. The results of these measurements are shown graphically in Figure 22. A near-exponential increase in the viscosity occurred over the concentration range examined as the copolymer concentration decreased. Thus at ionomer concentrations approaching 0.1 g/dL the inherent viscosity of the copolymer solution was measured to be greater than 8 dL/g. At a near 10-fold higher concentration the inherent viscosity was 2.3 dL/g. As expected, the observed inverse relationship between concentration and viscosity is that typical of polyelectrolytes in solution.

Two factors are believed responsible for the anomalous shape of the $(\ln \eta)/c$ versus concentration curve.²²⁵ In the absence of added low molecular weight ionic solute, as the macro-ion concentration is decreased the ionic strength of the medium also falls, allowing expansion of the chain dimensions. Secondly, in the absence of added salt, the polyelectrolyte chains are expanded to a degree such that an increase in concentration causes the macromolecules to interfere with one another. Thus an influence of concentration on configuration is also possible. The results of the experiments conducted in this work with poly(EO/EUA⁻Na⁺) showed its remarkable "thickening" capabilities at low

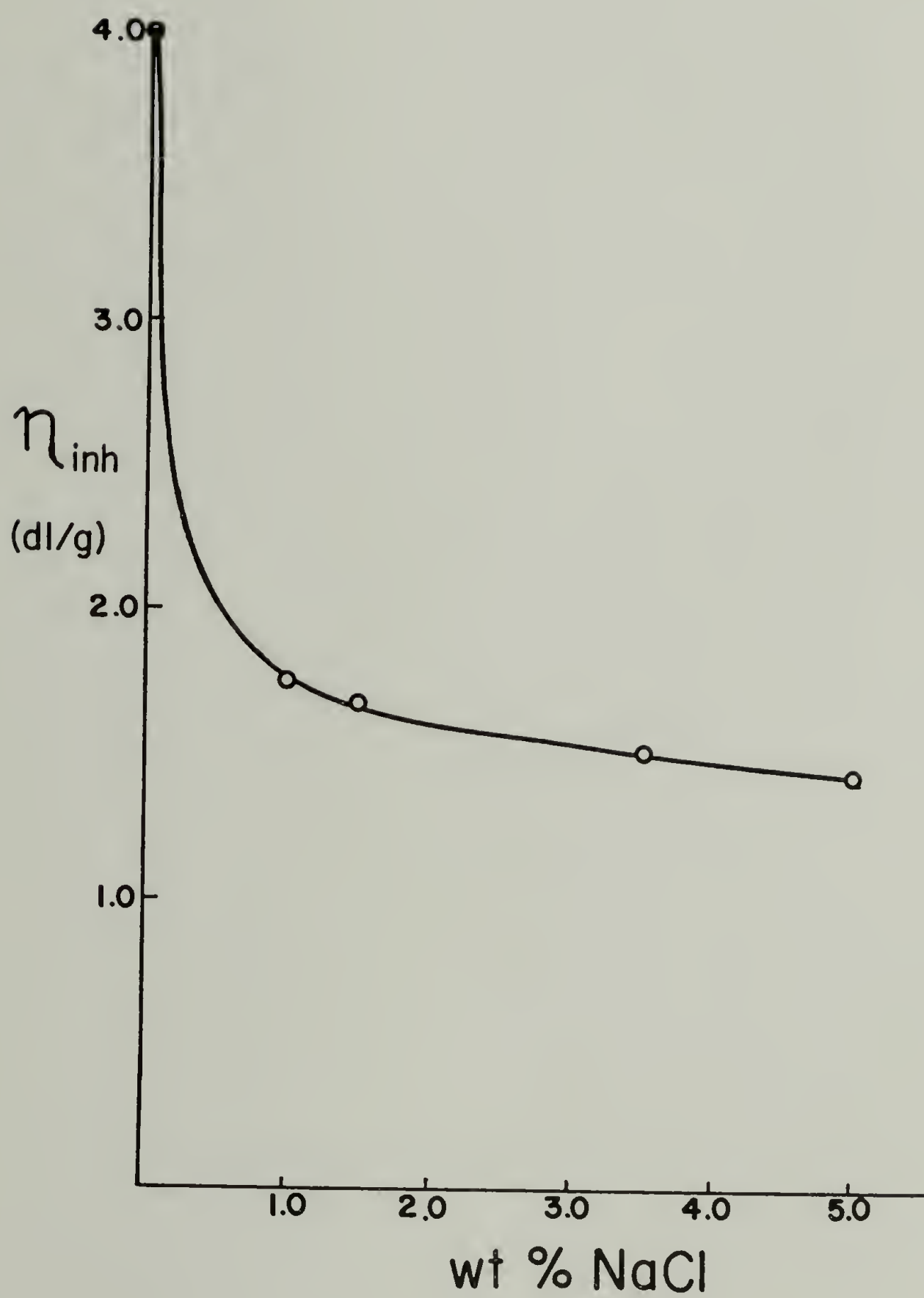
Figure 22. Effect of alkylene oxide ionomer concentration on dilute solution viscosity.



concentrations. One further observation of interest made for the aqueous ionomer solutions was their soap-like character. It is conceivable this behavior may result from the dual hydrophilic/hydrophobic nature of the alkylene oxide ionomer. The hydrophilic nature arises from the polar polymer backbone and pendant carboxylate groups, while the hydrophobic character is imparted by the eight carbon spacer-group.

The influence of added low molecular weight ionic solute, sodium chloride, on the inherent viscosity of the ionomer in water was also studied. The concentration of ionomer was held constant at 0.5 g/dL while the salt concentration was systematically increased. The results of this investigation are shown graphically in Figure 23. The concentration range of sodium chloride investigated was one to five percent by weight (based on the amount of polymer in solution). The net effect of adding a neutral salt such as sodium chloride was to change the ionic strength of the solution. As can be seen by inspection of Figure 23, a substantial reduction (47%) in solution viscosity occurred with the addition of just one percent NaCl. Increasing the salt concentration five-fold resulted in an additional 17% reduction in the inherent viscosity. It was also noted that as the sodium chloride concentration was increased the "soap-like" behavior of

Figure 23. Effect of added ionic solute (NaCl) on dilute solution viscosity of alkylene oxide ionomer.



the ionomer solution gradually decreased. Although not investigated, at still higher salt concentrations (>5%) one would expect the inherent viscosity to reach a lower limiting value. This trend is in fact evident in Figure 23. At this point the copolymer would behave as an uncharged molecule, reflecting the hypothetical dimensions of the ionomer in solution in the absence of electrostatic interactions. These higher concentrations could not be achieved in this work without precipitation of the copolymer from solution.

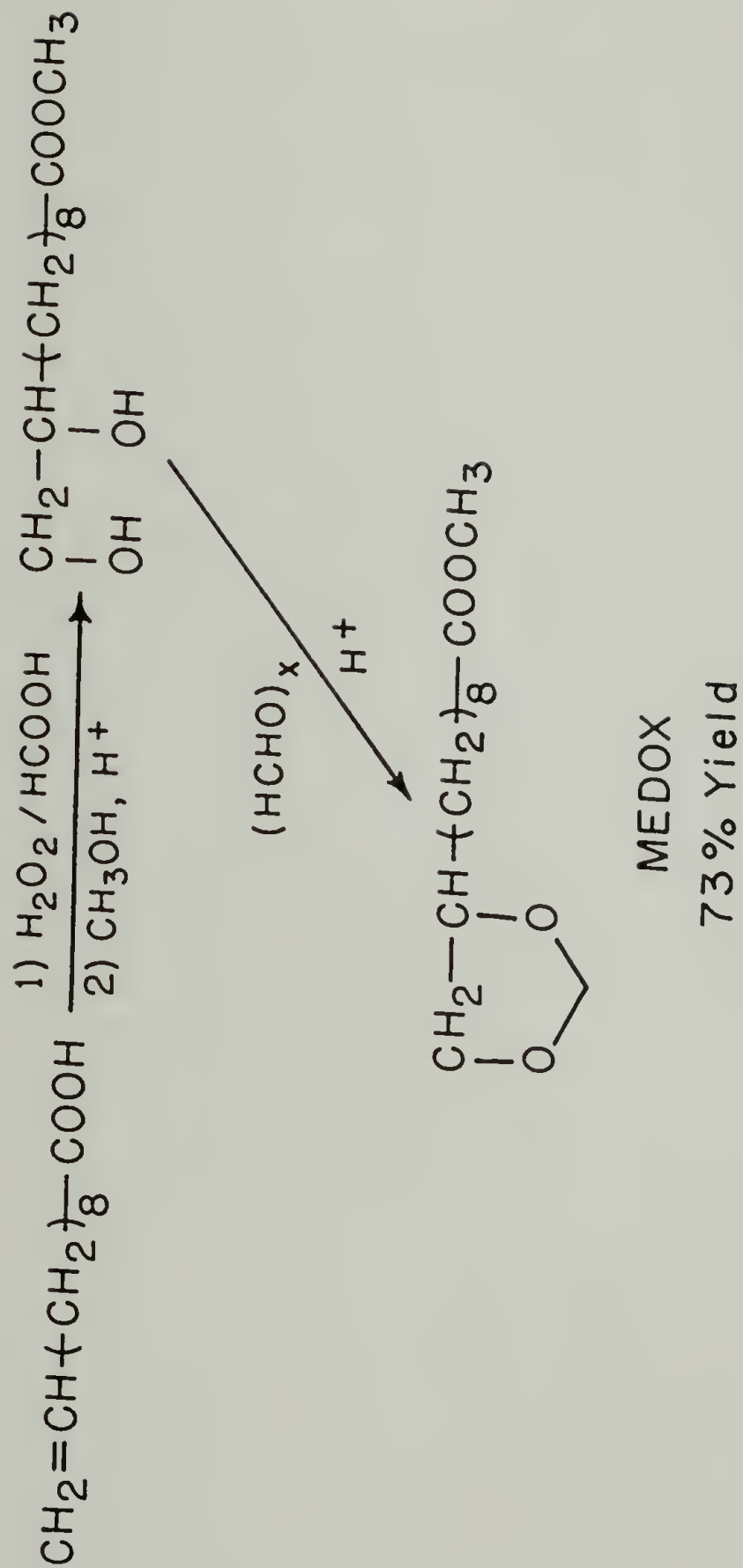
E. Functionally-Substituted Oxymethylene Copolymers and Terpolymers

Among the objectives defined at the beginning of this chapter was the preparation of ester-substituted polymers based on an oxymethylene backbone. The discussion up to this point had focused on functional oxyethylene polymers and copolymers. The success in incorporating the difunctional cyclic ether MEU, where the functional groups are separated from one another by means of a spacer-group, into a polyether chain prompted a parallel investigation into the use of MEU as a comonomer in cationic polymerizations with trioxane (TO), the cyclic trimer of formaldehyde. The direction taken in the preparation of functional POM largely evolved from the early

work on POM-based ionomers^{1,161-163} involving copolymerization of TO and ethyl glycidate (EG) and the terpolymerization of TO with EG and 1,3-dioxolane (DO). An alternative synthetic route to ester-substituted POM was also developed simultaneously in this work. The synthesis of a novel ester-substituted 1,3-dioxolane monomer, 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX), was accomplished and subsequent copolymerizations with TO and terpolymerizations with TO and DO were carried out. The results and discussions presented in the following sections focus on the preparation and basic characterization of ester-substituted POMs in which the ester groups are separated from the polymer backbone by long (C₈) spacer-groups. The advantages of using a spacer-group to separate the two reactive functional groups have already been described.

1. Preparation of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX). The synthesis of the functional 1,3-dioxolane monomer MEDOX was carried out in four steps starting from 10-undecenoic acid (Figure 24). The first compound shown in Figure 24, 10,11-dihydroxyundecanoic acid (DHU), was obtained in an overall yield of 87% by the oxidation of 10-undecenoic acid with excess performic acid.²⁰⁵ Since performic acid is relatively unstable, it was prepared in

Figure 24. Preparation of the functional dioxolane monomer: 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX).



situ by reaction of 30% aqueous hydrogen peroxide with formic acid. The reaction of performic acid with the ω -unsaturated acid was exothermic. The mechanism by which the hydroxylation proceeds is quite interesting and is worthy of mention. The first product formed in the oxidation reaction is the functional epoxide 10,11-epoxyundecanoic acid.²⁰⁵ Due to the rapid regeneration of formic acid upon oxidation of the double bond, the epoxide group reacts instantly with the strong acid to yield 10-formoxy-11-hydroxyundecanoic acid. The latter was readily hydrolyzed by two equivalents of strong base to the sodium salt of 10,11-dihydroxyundecanoic acid. Neutralization of the carboxylate salt with concentrated HCl yielded the desired dihydroxy-acid DHU. The recrystallized product (isopropanol-water) melted at 66-67.5°C, ca 20°C below the melting point reported in the literature²⁰⁵ (85-86°C, needles from water). Nevertheless, the IR, ^1H NMR and ^{13}C NMR spectra indicated conclusively that DHU had been obtained.

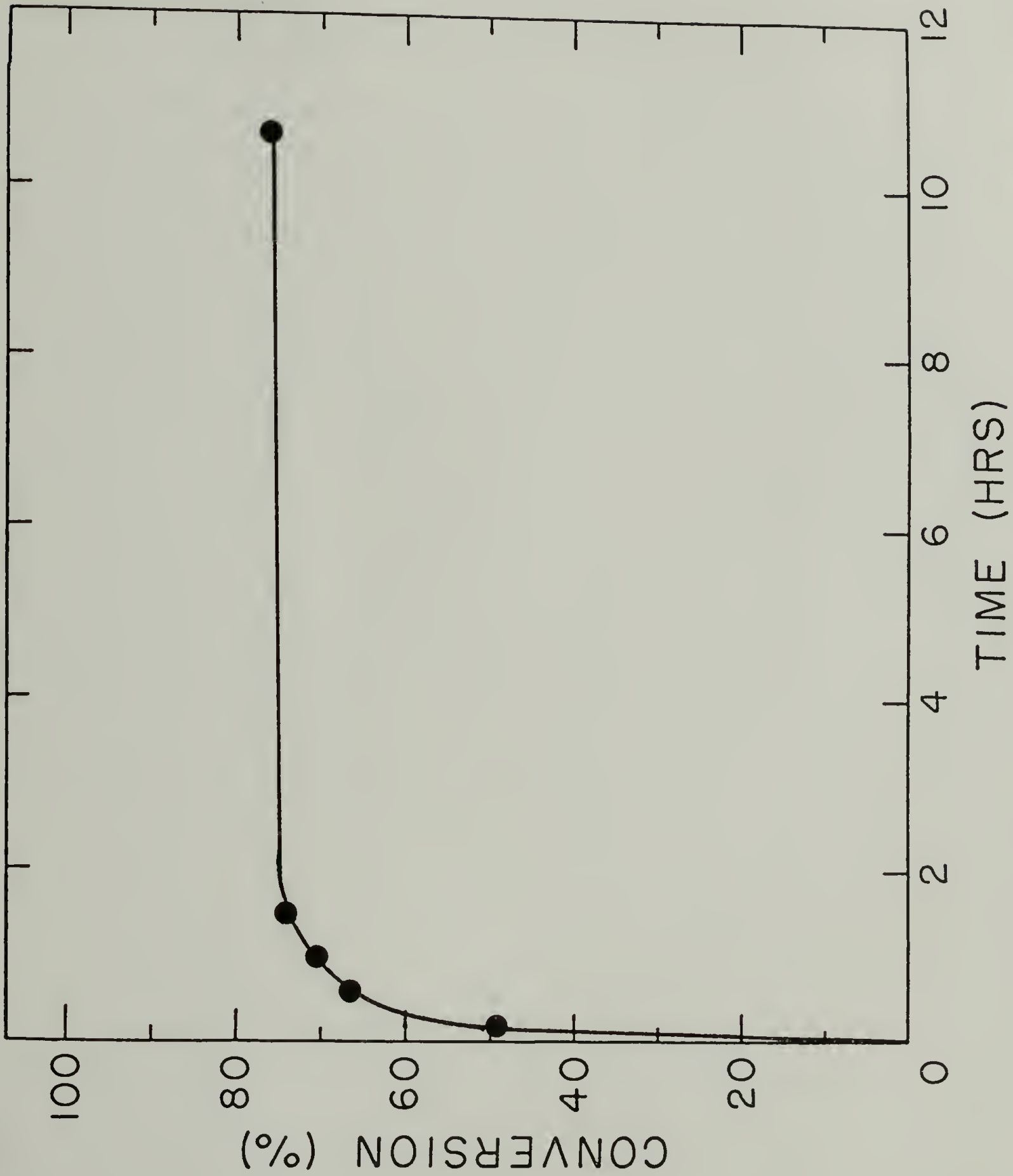
Crude DHU was converted to the methyl ester by an acid-catalyzed esterification with methanol. The second product shown in Figure 24, methyl 10,11-dihydroxyundecanoate (MDHU), was recovered in 91% yield after recrystallization from petroleum ether/diethyl ether (1:1). The esterification proceeded smoothly, no polycon-

densation side-reactions occurred. The melting point of the glycol-ester was 46-48°C (lit.²⁰⁶ 45-46°C).

Formation of the functionally-substituted cyclic acetal MEDOX was accomplished by the acetalization reaction of MDHU with paraformaldehyde, catalyzed by para-toluenesulfonic acid (p-TsOH). The water of reaction was removed by azeotropic distillation with benzene. The functional monomer was a low melting solid, m.p. 29.5-31.5°C, which was obtained in 73% yield after purification by distillation (b.p. 142-143°C/0.3mm).

A study of the relative rate of dioxolane ring formation in the preparation of MEDOX was also carried out. Aliquots of a reaction mixture were periodically removed and their composition was analyzed by gas chromatography. The conversion of MDHU to MEDOX as a function of time was conveniently monitored in this fashion. The results are shown graphically in Figure 25. Reaction of the glycol with paraformaldehyde was initially very rapid as ca. 50% of the -OH groups were cyclized after 10 minutes. Within 1 hour ca. 70% of the glycol had been consumed, after this time the rate of conversion rapidly tailed off. An ultimate conversion of 76% was attained after 10 hr reaction. IR analysis of the product after work-up confirmed the presence of unreacted hydroxyl groups. Hydroxylic-containing starting material was

Figure 25. Rate of the acetalization of methyl 10,11-dihydroxyundecanoate (MDHU).



easily removed by distillation.

Several attempts were also made to prepare MEDOX employing a slight change in the sequence of steps depicted in Figure 24. Following the preparation of DHU (first product in Figure 24), acetalization of the glycol-acid was attempted prior to esterifying the carboxylic acid group. A complicated mixture of products was obtained, thus indicating that serious side-reactions had occurred. Analysis of the mixture by IR spectroscopy showed two types of carbonyl absorptions, the cyclic acetal ring stretch (indicating that some of the desired carboxyl-substituted DO had been formed) and unreacted OH groups. The carbonyl absorption of the carboxylic acid starting material DHU was still present (1700 cm^{-1}), however, a second carbonyl appeared at 1740 cm^{-1} . The latter absorption was located in the region where aliphatic ester groups absorb, suggesting the possibility that a side-reaction involving the formation of methyol esters may have occurred.²²⁶ As the distribution of products appeared to be nearly equal and problems in purification were anticipated, this route to MEDOX was not pursued further.

2. Copolymerizations and terpolymerizations of
4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX). The copolymerization of MEDOX with TO and terpolymerization with TO

and DO were investigated using trifluoromethanesulfonic acid anhydride (TFA) as the initiator (Figure 26). TFA is known to copolymerize TO and DO (cationically) at high rates and to high conversions, requires a short induction period and produces levels of unstable fractions comparable with those of other initiators.²²⁷ Consideration of the aforementioned characteristics suggested that the use of TFA as the initiator for preparing functionally-substituted polyoxymethylenes was highly desirable.

Two series of experiments were therefore conducted in order to determine the co- and terpolymerizability of MEDOX. All reactions were run in 1,2-dichloroethane (DCE) at 60°C using 0.016 mole-% TFA (based on an initial monomer concentration of 5 mole-lit⁻¹).

The first series of experiments, whose results are shown in Table 19, were designed to determine whether or not MEDOX could be readily incorporated into the POM chain. Co- and termonomer feeds which contained 5 mole-% MEDOX were prepared for that purpose. A TO homopolymerization control was also carried out for comparison as was an attempted copolymerization of MEDOX and DO. All polymers isolated from these experiments were characterized by IR spectroscopy and dilute solution viscometry. Viscosity-average molecular weights (\bar{M}_v) reported in Table 19 were calculated from the inherent viscosity-molecular

Figure 26. Copolymerization and terpolymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX).

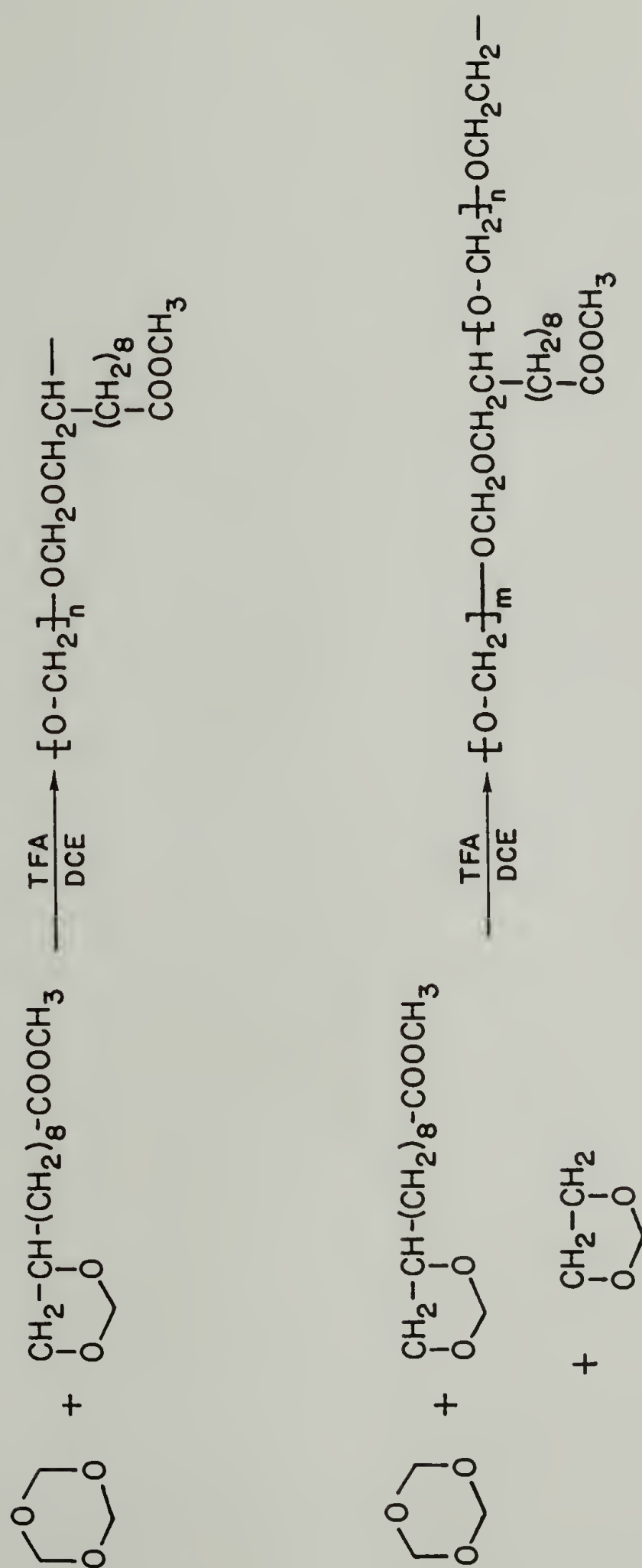


TABLE 19

CO- AND TERPOLYMERIZATIONS OF FUNCTIONAL CYCLIC ACETAL
4-(1-CARBOMETHOXYNONYL)-1,3-DIOXOLANE^a

M ₁	M ₂ (mole-%)	M ₃ (mole-%)	Induction Time for Precipitation in min.	Yield in %	η_{inh}^b in dL/g	$\bar{M}_v \times 10^{-4}$	Mole-% M ₂ in Polymer ^c
TO			0.5	96	-	-	-
TO	MEDOX(5)		3.	75	0.51	1.9	1.2
TO		DO(10)	3.	91	0.97	4.5	-
TO	MEDOX(5)	DO(10)	3.	79	0.66	2.7	0.5
-	MEDOX(5)	DO	No ppt.	12	0.34 ^d	-	-

TO: 1,3,5-trioxane, MEDOX: 4-(1-carbomethoxynonyl)-1,3-dioxolane, DO: 1,3-dioxolane

^aReaction conditions-solvent: 1,2-dichloroethane; temp.: 60°C; initiator: (CF₃SO₂)₂O, 0.016 mole-%; [M]_{total} = 5 mol·lit⁻¹; reaction time: 33 hr.

^b0.1% in 98 wt-% p-chlorophenol/2 wt-% α -pinene, 60°C.

^cDetermined by IR spectroscopy.

^d0.5% in CHCL₃, 30°C.

weight relationship derived by Wagner and Wissbrun.²²⁸

As can be seen by inspection of Table 19, the control polymerization of TO proceeded rapidly and gave a 96% yield of bright-white POM. Similarly, copolymerization of TO and 10 mole-% DO gave the corresponding oxyethylene stabilized POM in high yield (91%) and reasonably high molecular weight ($\bar{M}_V=45,000$). MEDOX was successfully incorporated into a POM copolymer and terpolymer in yields of 75% and 79%, respectively. The TO/MEDOX copolymer was found by IR analysis to contain 1.2 mole-% ester groups, indicating that ca. 20% of the functional dioxolane present in the feed had been consumed. The TO/MEDOX/DO terpolymer contained ca. 0.5 mole-% ester functionality but was of considerably lower molecular weight ($\bar{M}_V=27,000$) than the TO/DO copolymer ($\bar{M}_V=45,000$). Two possible explanations for the differences in molecular weight can be put forward. Chain transfer processes are known to govern the average degree of polymerization in TO/DO copolymers prepared when TFA is used as initiator.²²⁷ Conceivably, MEDOX may be more prone to chain transfer than DO. Secondly, if the incorporation of MEDOX was not truly random, functionally-substituted POMs of reduced thermal and hydrolytic stability would be obtained. Since viscosity solutions were prepared by dissolving samples at 110°C in an acidic solvent

(p-chlorophenol);²²⁸ it would be reasonable to assume that more chain degradation is likely to occur if these samples were not truly statistical polymers. The poly-(oxymethylenes) prepared and listed in Table 19 were not end-capped or heat-treated and should be considered more labile to degradation under the conditions cited due to the presence of unstable hemiacetal end groups.

The attempted copolymerization of MEDOX and DO gave only poly(DO) in 12% yield with an inherent viscosity of 0.34 dL/g (0.5% in CHCl_3 at 30°). ^{13}C NMR spectroscopy showed conclusively that MEDOX had not been incorporated. Only two signals appeared in the ^{13}C NMR spectrum (p. 328); the chemical shift of the oxyethylene carbon atoms in the poly(DO) backbone appeared at 67.3 ppm while the oxymethylene carbon chemical shift appeared at 95.9 ppm. In addition, the infrared spectrum was identical to a spectrum of poly(DO) obtained from the literature.²²⁹

The second series of experiments carried out was designed to examine more fully the copolymerizability of MEDOX and trioxane. Five copolymerization reactions in which the comonomer feeds contained 5, 10, 15, 25 and 40 mole-% MEDOX were conducted simultaneously. Reaction conditions were identical to those described previously. That is, copolymerizations were conducted in DCE solution (5 mole-lit⁻¹ in comonomers) at 60°C with TFA (0.016

mole-%) as the initiator. The results of these experiments are given in Table 20. Overall it was concluded from the results that the reactivity of MEDOX with TO was low. The highest level of incorporation of MEDOX was 1.8 mole-%. Furthermore, as the proportion of MEDOX in the comonomer feed was increased, the yields and molecular weights of the functionally-substituted POMs were found to decrease. The difference in induction times, which ranged from 2 min for the lower MEDOX feed ratios to 4 min for the highest feed ratio, was not considered to be highly significant. Explicit reasons for the low reactivity of MEDOX have not been determined, although thermodynamic considerations are believed to be important and are discussed below.

3. Attempted homopolymerization of 4-(1-carbomethoxynonyl)-1,3-dioxolane using BF_3 -etherate as the initiator. The ring-opening polymerization of MEDOX using BF_3 -etherate as the initiator was examined briefly. Successful polymerization of MEDOX would yield a structure which corresponded to an alternating copolymer of TO and MEU. The reaction was conducted in dichloromethane solution (1 molar in MEDOX) using 5 mole-% BF_3 -diethyl etherate. Six days at room temperature failed to produce any observable change in the viscosity of the solution,

TABLE 20

COPOLYMERIZABILITY OF 4-(1-CARBOMETHOXYNONYL)-1,3-DIOXOLANE (MEDOX) AND TRIOXANE (TO)

Mole-% MEDOX in Comonomer Feed	Induction Time in min.	Copolymer Yield in %	η_{inh}^a in dL/g	$\bar{M}_v^b \times 10^{-4}$	Mole-% MEDOX in Copolymer ^c
5	2.0	79	0.68	2.8	0.70
10	2.0	73	0.44	1.5	1.1
15	2.7	63	0.43	1.5	1.4
25	2.9	57	0.31	0.93	1.8
40	3.9	45	0.33	1.0	1.8

^a0.1% in 98 wt-% p-chlorophenol/2 wt-% α -pinene, 60°C.^bEquation for calculations from Ref. 228.^cDetermined by IR spectroscopy.

although the reaction mixture did become golden brown in color. The sealed tube reaction was subsequently maintained at -20°C for 1 day, -78°C for 1 hr and at room temperature for an additional 18 days. Analysis of the reaction mixture after this time by gas chromatography showed only one product, which was identified as MEDOX by comparison with an authentic sample. These results were not totally unexpected. Sumitomo has cited the reluctance of 4-alkylsubstituted-1,3-dioxolanes to undergo ring-opening homopolymerization and has shown that polymerizability decreases as the substituent size increases.²³⁰ The bulkiest alkyl substituent examined was the isopropyl group. 4-Isopropyl-1,3-dioxolane was reported to be very reluctant to polymerize at temperatures above -78°C . Polymerizations of substituted dioxolanes are reportedly dominated by a monomer-polymer equilibrium reaction; the reluctance of 1,3-dioxolanes with bulky substituents to homopolymerize has been explained on the basis of unfavorable thermodynamic properties arising from conformational isomers of high energy in both the monomeric and polymeric states.²³¹⁻²³³

The low reactivity of MEDOX in copolymerizations with TO is therefore not surprising in view of its apparent inability to homopolymerize under the conditions investigated.

4. Co- and terpolymerization of methyl 10,11-epoxyundecanoate (MEU) with trioxane. TFA initiated copolymerizations of MEU with trioxane, and terpolymerizations with TO and DO were also investigated under conditions identical to those used when the functional monomer was MEDOX. The copolymerization reaction and structure of the functionally-substituted POM prepared from MEU are shown in Figure 27. In Table 21 are shown the results of two experiments which established that the functional epoxide could be incorporated into the POM backbone under the reaction conditions of interest. The copolymerization of 5 mole-% MEU with TO gave the corresponding ester-substituted POM in 94% yield, but of a relatively low viscosity-average molecular weight ($\bar{M}_V=7,700$). The TO/MEU copolymer was shown by IR spectroscopy to contain 1.6 mole-% ester groups, indicating that 32% of the MEU in the comonomer feed had been incorporated into the POM chain. Terpolymerization of TO, MEU (5 mole-%) and DO (10 mole-%) unexpectedly gave a 46% yield of the functional POM which was, however, of slightly higher molecular weight ($\bar{M}_V=9,800$) than the TO/MEU copolymer. The terpolymer contained 0.5 mole-% MEU, or about 10% of the functional monomer in the original feed.

Induction periods of 15 hr and 19 hr were observed for the copolymerization and terpolymerization reactions,

Figure 27. Preparation of functionally-substituted poly(oxymethylenes) based on methyl 10,11-epoxyundecanoate.

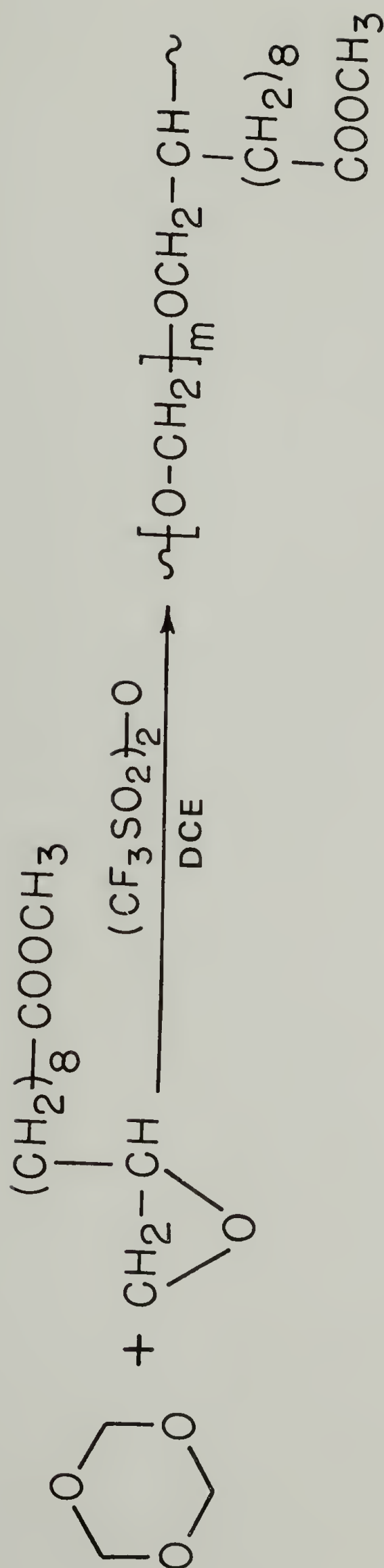


TABLE 21

CO- AND TERPOLYMERIZATION OF THE FUNCTIONAL CYCLIC ETHER
METHYL 10,11-EPOXYUNDECANOATE (M₂)

M ₁	M ₂ (mole-%)	M ₃ (mole-%)	Induction Time in hr.	Yield in %	η_{inh}^b in dL/g	\bar{M}_v^c $\times 10^{-4}$	Mole-% M ₂ ^d in Polymer
TO	MEU(5)	-	15	94	0.27	0.77	1.6
TO	MEU(5)	DO(10)	19	46	0.32	0.98	0.5

^aReaction conditions-solvent: 1,2-dichloroethane; temp.: 60°C; initiator: (CF₃SO₂)₂O, 0.016 mole-%; [M]_{total} = 5 mole·lit⁻¹; reaction time: 35 hr.

^b0.1% in 98 wt-% p-chlorophenol/2 wt-% α-pinene, 60°C.

^cCalculated using equation from Ref. 228.

^dDetermined by IR spectroscopy.

respectively. Precipitation of solid polymer did not occur before this time. Shortly before the onset of cloudiness and precipitation each reaction solution changed from colorless to light orange. The long induction times, levels of MEU incorporated into the POM chain and color changes reported here agree well with earlier findings by Z. Janović.¹⁶⁸

A more detailed and systematic study of the copolymerizability of MEU with TO was also carried out, analogous to the copolymerization experiments of MEDOX and TO which were described in Section 1 of this Chapter. Thus, TO/MEU comonomer solutions (5 molar) which contained 5-40 mole-% MEU were prepared in DCE, and their copolymerization was carried out at 60°C using 0.016 mole-% TFA as initiator. The results of these experiments are shown in Table 22. Induction times for the copolymerization reactions, shown in the second column of Table 22, were long and increased as the proportion of MEU in the comonomer feed increased. Copolymerization of MEU and TO was found to occur only reluctantly at the higher feed ratios of MEU, e.g. a 2% yield of copolymer was obtained after ca. 5.5 days reaction when the comonomer feed contained 40 mole-% MEU. In general, the yield of copolymer was found to decrease as the proportion of functional comonomer in the feed increased. Inherent viscosities and the

TABLE 22

COPOLYMERIZABILITY OF METHYL 10,11-EPOXYUNDECANOATE (MEU) WITH TRIOXANE (TO)

Mole-% MEU in Comonomer Feed	Induction Time in min.	Copolymer Yield in %	η_{inh}^a in dL/g	$\bar{M}_v^b \times 10^{-4}$	Mole-% MEU ^c in Copolymer
5	15	69	0.24	0.66	1.0
10	22	49	0.29	0.85	1.1
15	25	31	0.27	0.77	0.9
25	45	13	0.19	0.48	1.1
40	88	2.1	0.17	0.41	1.9

^a0.1% in 98 wt-% p-chlorophenol/2 wt-% α -pinene, 60°C.

^bEquation for calculations from Ref. 228.

^cDetermined by IR spectroscopy.

corresponding viscosity-average molecular weights reported in Table 22 were for untreated (or unstabilized) MEU-modified POM. The MEU-modified oxymethylene copolymers were all of relatively low molecular weight as M_v was less than 10,000 in all cases. Determination of each copolymer composition was accomplished by quantitative IR analysis. On the average, the functional POMs contained 1 mole-% MEU. These results indicated that MEU was relatively unreactive in copolymerizations with TO, and that to a first approximation the level of incorporation was independent of the functional monomer concentration.

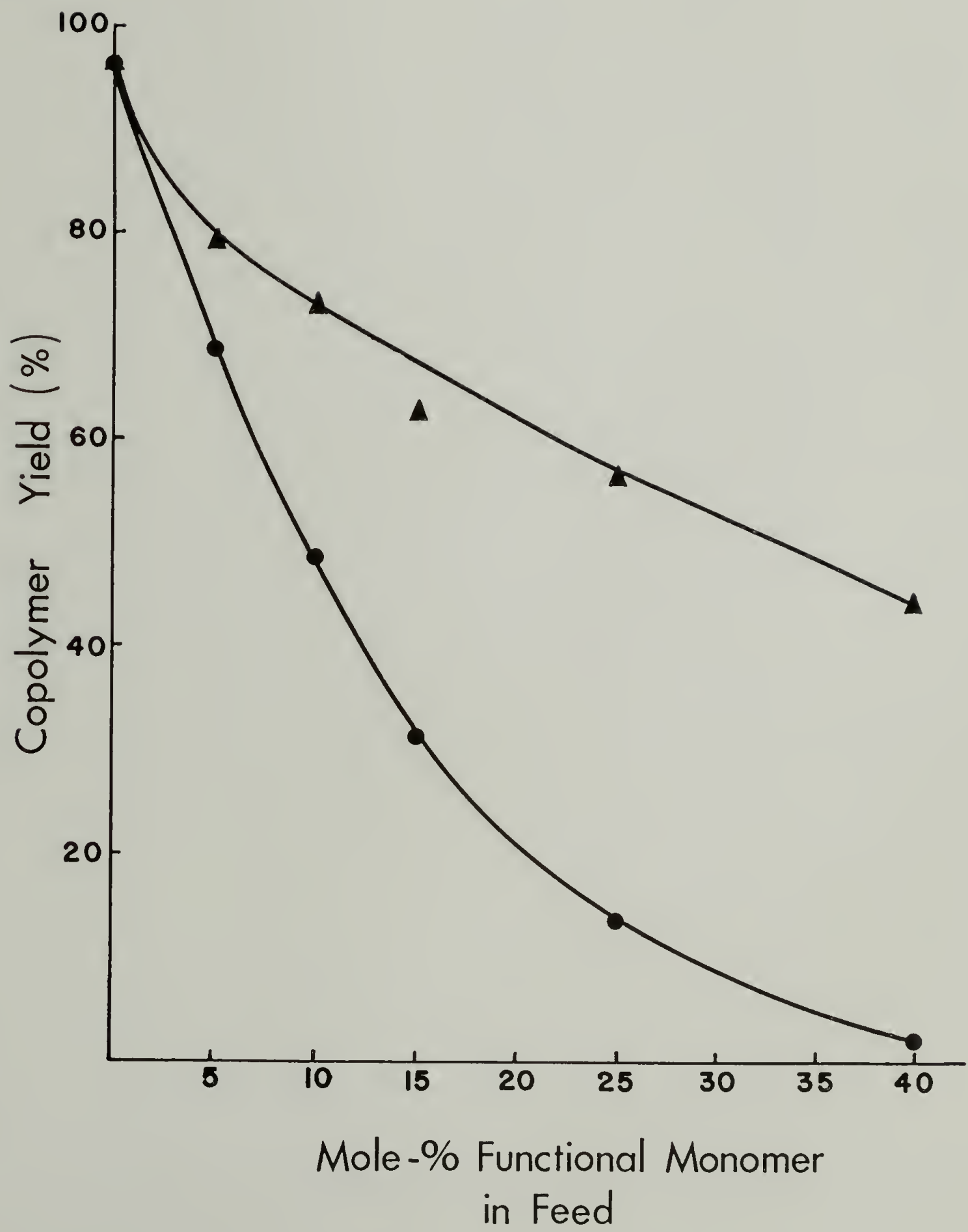
Similar findings have been made in the polymerization of ethyl glycidate (EG) with TO and DO when triflic acid was used as the initiator.¹ The range of EG concentration studied in the investigation was 5-15 mole-%. EG was found to be relatively unreactive as only 2 mole-% could be incorporated in the POM chain. Furthermore, these levels of incorporation were achieved by the addition of EG to the polymerization reaction after the polymerization had started. When DO was added as a termonomer in the polymerization of EG and TO, considerably higher yields of the EG-modified POM were obtained. In attempted "one-step" copolymerizations of EG and TO, no polymer was obtained after 3 hr at 40°C. The latter results are now more readily understood based on the long induction times

observed in copolymerization experiments of TO and MEU. Explicit reactions for the long induction times have not been established.

5. Comparison of the copolymerization behavior of 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) and methyl 10-11-epoxyundecanoate (MEU). Since the copolymerizations of both MEDOX and MEU with TO were conducted under analogous reaction conditions, the copolymerizability of each functional monomer can be contrasted with the other. The discussion which follows is intended for that purpose.

Figure 28 compares the yield of ester-substituted POM as a function of the mole-% functional monomer in the initial comonomer feeds. The curves were constructed from data taken from Tables 20 and 22. The upper curve in Figure 28 depicts functional POM yields for copolymerizations of TO with MEDOX, while the lower represents the corresponding copolymerizations with MEU. The yield which corresponds to 0 mole-% functional monomer in the feed (y-intercept) was that obtained from the homopolymerization of TO. Comparison of the two curves shows that MEDOX gave consistently higher yields of ester-substituted POM than did MEU over the entire range of functional monomer concentration investigated (5-40 mole-%). Both functional monomers, however, produced the same overall trend in copolymer yields. That is,

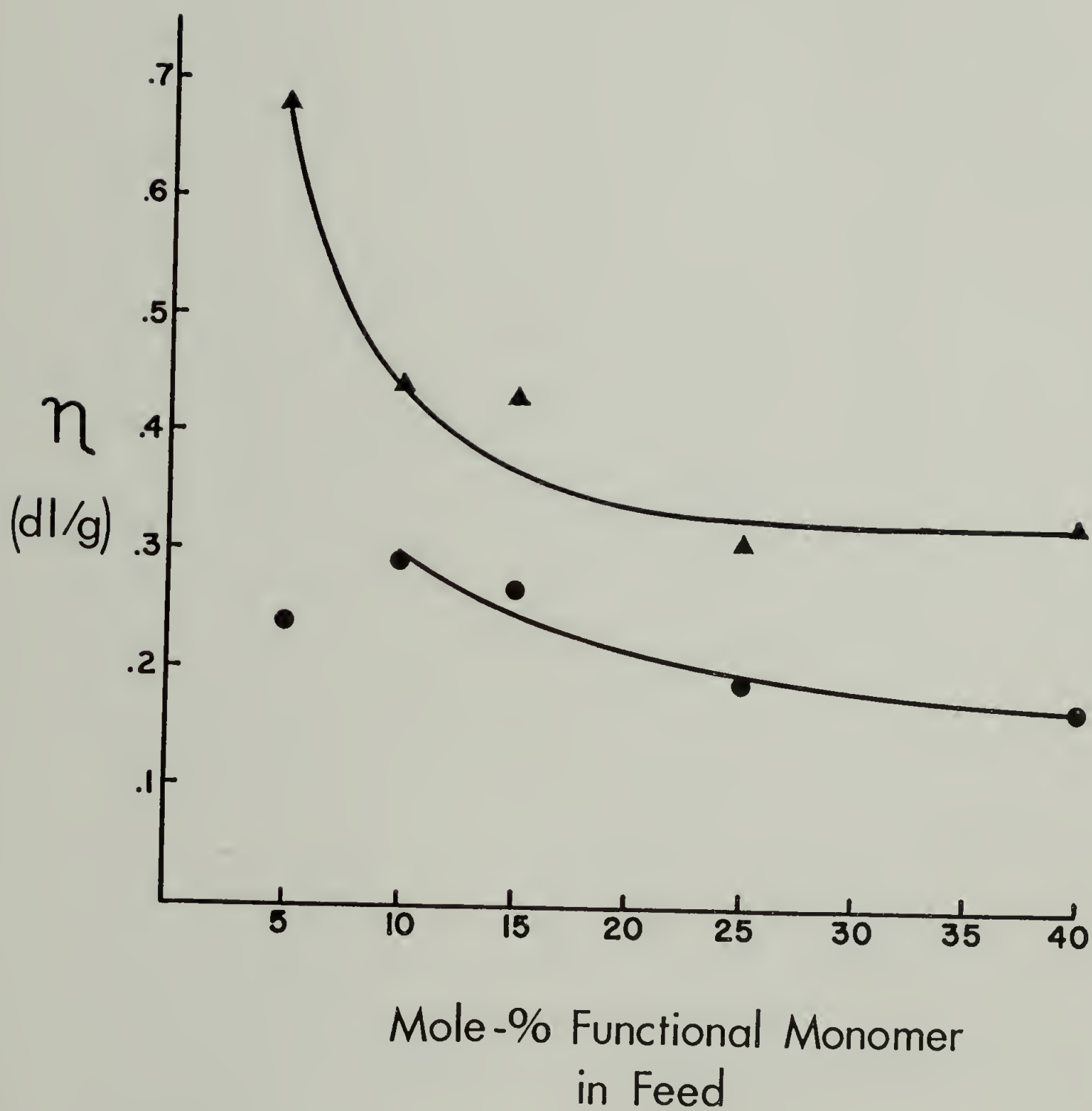
Figure 28. Yield of ester-substituted poly(oxy-methylene) as a function of comonomer feed composition: (▲) 4-(1-carbomethoxynonyl)-1,3-dioxolane, (●) methyl 10,11-epoxyundecanoate.



increasing the proportion of functional monomer in the feed resulted in a reduction of the copolymer yield.

Figure 29 is a plot of the inherent viscosity (η) of the TO/MEDOX and TO/MEU copolymers as a function of the amount of each functional monomer present in the initial copolymerization charges. The inherent viscosities for each copolymer were determined at 60°C on 0.1 g/dL solutions in p-chlorophenol/ α -pinene (98/2 wt %). The viscosities were measured on unfractionated and untreated copolymers. Although levels of incorporation of MEDOX and MEU in the copolymers were found to be similar (1-2 mole-%), comparison of the two curves indicates that the functional POMs obtained were generally higher in molecular weight when MEDOX was the comonomer. This conclusion is also supported by comparison of the O-H stretching region (3660-3300 cm^{-1}) in the infrared spectra of the TO/MEDOX and TO/MEU copolymers. For example, see p. 309 and p. 310 in Appendix A. MEU-modified POM generally exhibited an absorption of slightly greater intensity in the O-H stretching region than did TO/MEDOX copolymers. The O-H absorption arises from the presence of hemiacetal ($\text{HO-CH}_2\text{O-}$) end-groups, indicating that the concentration of endgroups is higher (hence the molecular weight lower) for copolymers derived from MEU. However, molecular weights of the functional POMs were significantly lower

Figure 29. Comparison of solution viscosities for functional oxymethylene copolymers prepared from (▲) 4-(1-carbomethoxynonyl)-1,3-dioxolane (MEDOX) and (●) methyl 10,11-epoxyundecanoate (MEU).

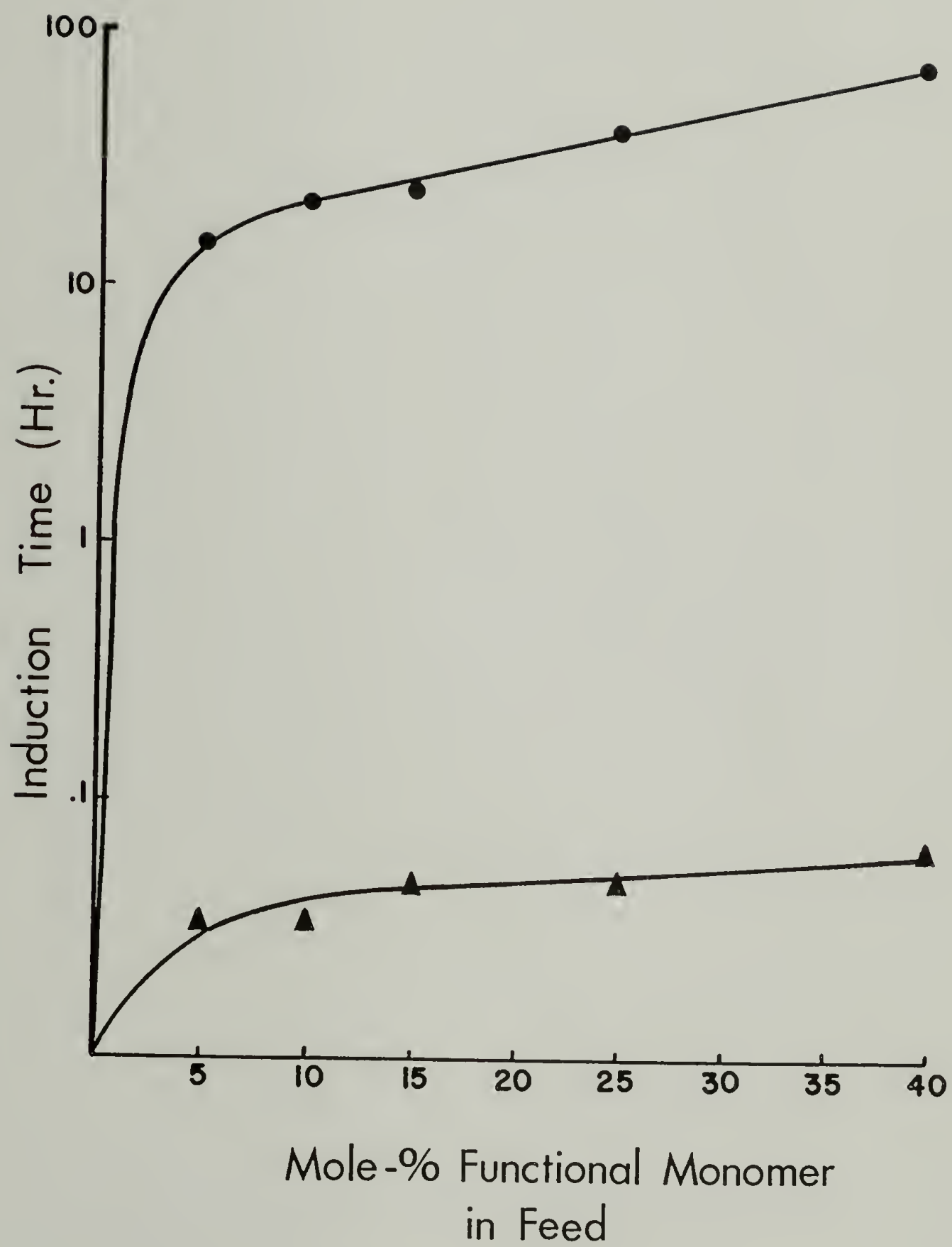


than the molecular weight ($\bar{M}_v=45,000$) of the TO/DO copolymer standard.

Perhaps the most striking differences observed in the preparation of ester-modified POMs using MEDOX or MEU were the widely different induction periods associated with both types of monomers. This behavior is most easily seen by referring to Figure 30, a semi-logarithmic plot of the induction times observed for each copolymerization reaction as a function of the concentration of functional monomer in the initial feed. The induction time corresponded to the onset of cloudiness in each reaction solution, which preceded the rapid precipitation of copolymer from solution. The ordinate intercept in Figure 30 corresponds to the induction period measured for the homopolymerization of TO. Thus it can be seen by comparing the two curves that throughout the feed composition examined (5-40 mole-%) functionally-substituted POM was formed ca. 1000 times slower when the comonomer was MEU. Yet despite the large differences in induction times both MEU and MEDOX were incorporated in similar amounts (1-2 mole-%) into the POM chain.

Although the mechanisms of these reactions were not studied, it appears appropriate to comment on the observed behavior from the standpoint of mechanistic features of related systems as reported in the literature.

Figure 30. Observed induction times in the preparation of functional oxymethylene copolymers: (▲) TO/MEDOX and (●) TO/MEU.



Penczek and co-workers have studied the copolymerization of TO and DO by TFA initiation. It was proposed that the first step in the initiation was the ring-opening of DO, producing a diester adduct of DO and TFA.²²⁷ Ensuing chain growth was envisioned to occur by "cationation" of TO and/or DO in a macroester-macroion equilibrium process (a process similar to the accepted mechanism of THF polymerization by triflic acid and its derivatives¹¹). The mechanism of $\text{BF}_3 \cdot \text{dibutyletherate}$ initiated copolymerization of TO with ethylene oxide (EO) has also been reviewed recently.¹⁵¹ It has been shown that EO is almost completely consumed before any significant TO consumption occurs.¹⁵³ DO and 1,3,5-trioxepane are formed as by-products in the solution stage of TO copolymerizations and are consumed during the heterogenous stage.¹⁵³ It is conceivable that initiation in copolymerizations of TO and MEU may proceed through some rate-determining step which could involve MEDOX. Formation of MEDOX may occur by the insertion reaction of MEU and free formaldehyde. Yamashita and coworkers have shown that substituted 1,3-dioxolanes are formed as products in the cationic oligomerization of substituted epoxides in the presence of triflic acid derivatives.^{234,235}

At present, however, reasons for the observed behavior remain unknown.

6. Thermal analysis of functionally-substituted poly-(oxymethylenes). Representative samples of the ester-substituted POMs were selected for thermal analysis studies. The focus of these studies were the melting behavior and thermal degradation of the functional oxymethylene polymers. In addition, the high molecular weight TO/DO copolymer was similarly evaluated.

The melting behavior of the DO, MEDOX and MEU-modified POMs was examined after samples were heat-treated to give a constant thermal history. Thus, all samples were heated to 200°C (at 20°C/min), annealed at 200°C for 3 minutes and cooled to room temperature (20°C/min). The DSC scans for four of the POMs are reproduced in Figure 31, and represent the second heating cycle for each sample. In all cases, a fraction of the sample vaporized during the heat-treating procedure. Since the POMs had not been end-capped, volatilization was probably due to some thermal unzipping of the polymers due to the presence of unstable hemiacetal end-groups.¹⁴² A complete list of the melting (T_m) and onset of recrystallization temperatures (T_{REXSTL}) for the oxymethylene co- and terpolymers analyzed are given in Table 23. Also listed are the heats of fusion as measured on the DSC and the percent crystallinity of each sample. The calculation of percent crystallinity was made on the basis of initial sample

Figure 31. Comparison of DSC scans of modified oxymethylene co- and terpolymers: (a) TO/DO, (b) TO/MEDOX, (c) TO/MEU/DO and (d) To/MEDOX/DO.

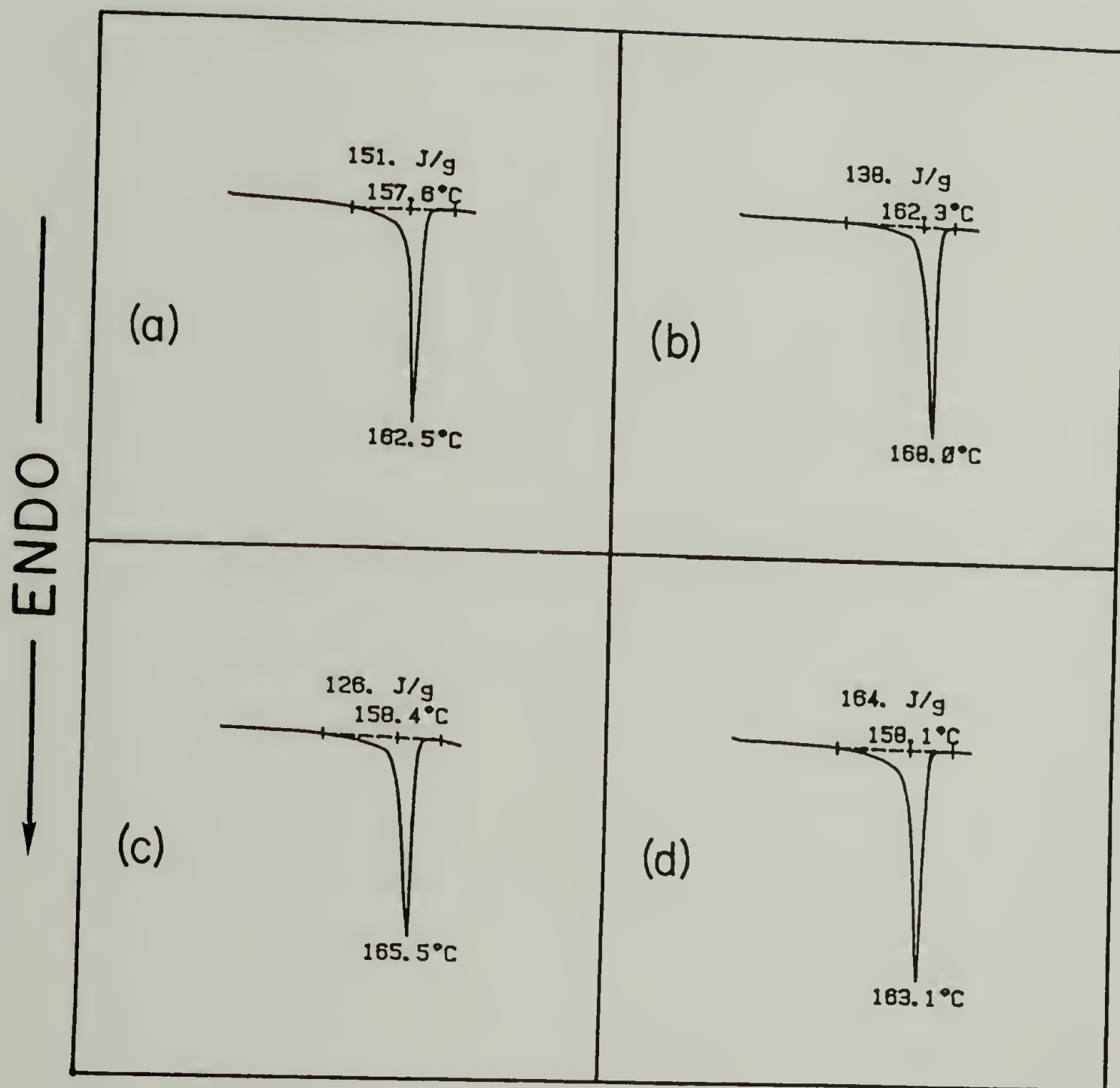


TABLE 23

TRANSITION TEMPERATURES FOR FUNCTIONALLY-SUBSTITUTED OXYMETHYLENE POLYMERS^a

Polymer	Mole-% Oxyethylene Units in Polymer	\bar{M}_v^b	T_m in °C	T_{REXSTL}^c in °C	ΔH_c in cal/g	Crystallinity in %
TO/DO	-	45,000	162.5	141.5	36	72
TO/MEDOX	1.8	9,300	168.0	147.5	33	66
TO/MEU	1.6	7,700	166.4	146.9	13	25
TO/MEDOX/DO	0.5	27,000	163.1	143.2	39	78
TO/MEU/DO	0.5	9,800	163.5	144.9	30	60

^aDetermined by DSC analysis, heating rate 20°C/min. Cooling rate 20°C/min.^bCalculated using equation in Ref. 228.^cTemperature at onset of crystallization.

weights and assumed ΔH_c of 100% crystalline POM is 50 cal/g.¹⁶⁷ Since portions of the samples invariably volatilized during analysis, values of ΔH_c and percent-crystallinity in the last two columns of Table 23 must be interpreted with some caution.

Unlike the results from calorimetric studies of TO/EG/DO terpolymers,¹ only one melting endotherm was observed for all modified POMs analyzed in this work. In addition, peak melting temperatures for the functional POMs derived from MEDOX and MEU were, on the average, 3-9°C higher than T_m for EG-modified POM.¹ The latter results are consistent with a higher level of crystal perfection in the MEDOX- and MEU-modified POM, since the comonomer content and average molecular weights are similar to those reported for the TO/EG/DO polymers studied previously. Such differences may be due to complete exclusion of oxyethylene units with the long side chain from the crystalline regions. Wegner has shown that a low level of oxyethylene units do incorporate into the crystalline regions of POM.²³⁶ This possibility appears much less likely for MEDOX and MEU than for EG.

Differences found in the percent crystallinity of the MEDOX-modified and MEU-modified POM are also of interest. Higher levels of crystallinity were found in the substituted POMs which were prepared with the functional

comonomer MEDOX. The reason for the very low level of crystallinity (25%) in the TO/MEU copolymer has not been established. The results in Table 23 do show a similar trend in percent-crystallinity as a function of comonomer content observed in previous studies of substituted POMs.^{1,167} That is, POM crystallinity was found to decrease as the comonomer content increased.

Thermogravimetric analysis of the TO/DO and TO/MEDOX copolymers as well as the TO/MEU/DO terpolymer provided some insight into the relative thermal stabilities of the untreated oxymethylene polymers prepared in this work. The TGA curves are reproduced in Figures 32-34 along with the corresponding derivative curve, the latter being a profile of the rate of degradation. For purposes of easier comparison, the three TGA curves are also collectively reproduced in Figure 35. The relative order of thermal stabilities, as seen by referring to Figure 35, is TO/DO > TO/MEDOX > TO/MEU/DO. Both functional POM samples showed some degradation before the TO/DO copolymer, although it should also be pointed out that the functionally-substituted POMs are of considerably lower molecular weight than the unsubstituted copolymer.

The approximate temperatures at which degradation began in untreated TO/DO, TO/MEDOX and TO/MEU/DO were 120°C, 95°C and 85°C, respectively. Maximum rates of

Figure 32. TGA and derivative curves of untreated TO/DO copolymer.

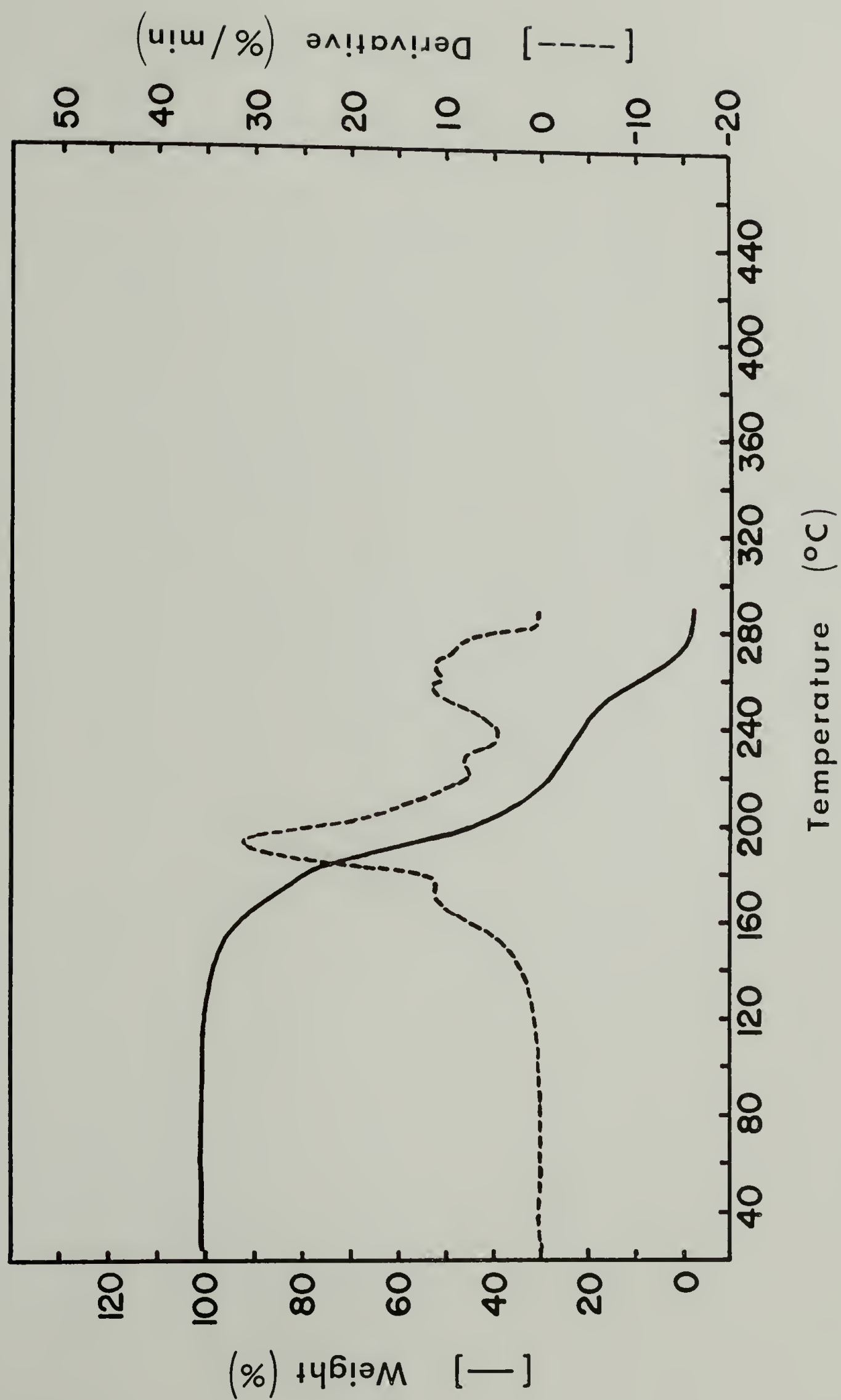


Figure 33. TGA and derivative curves of untreated TO/MEDOX copolymer.

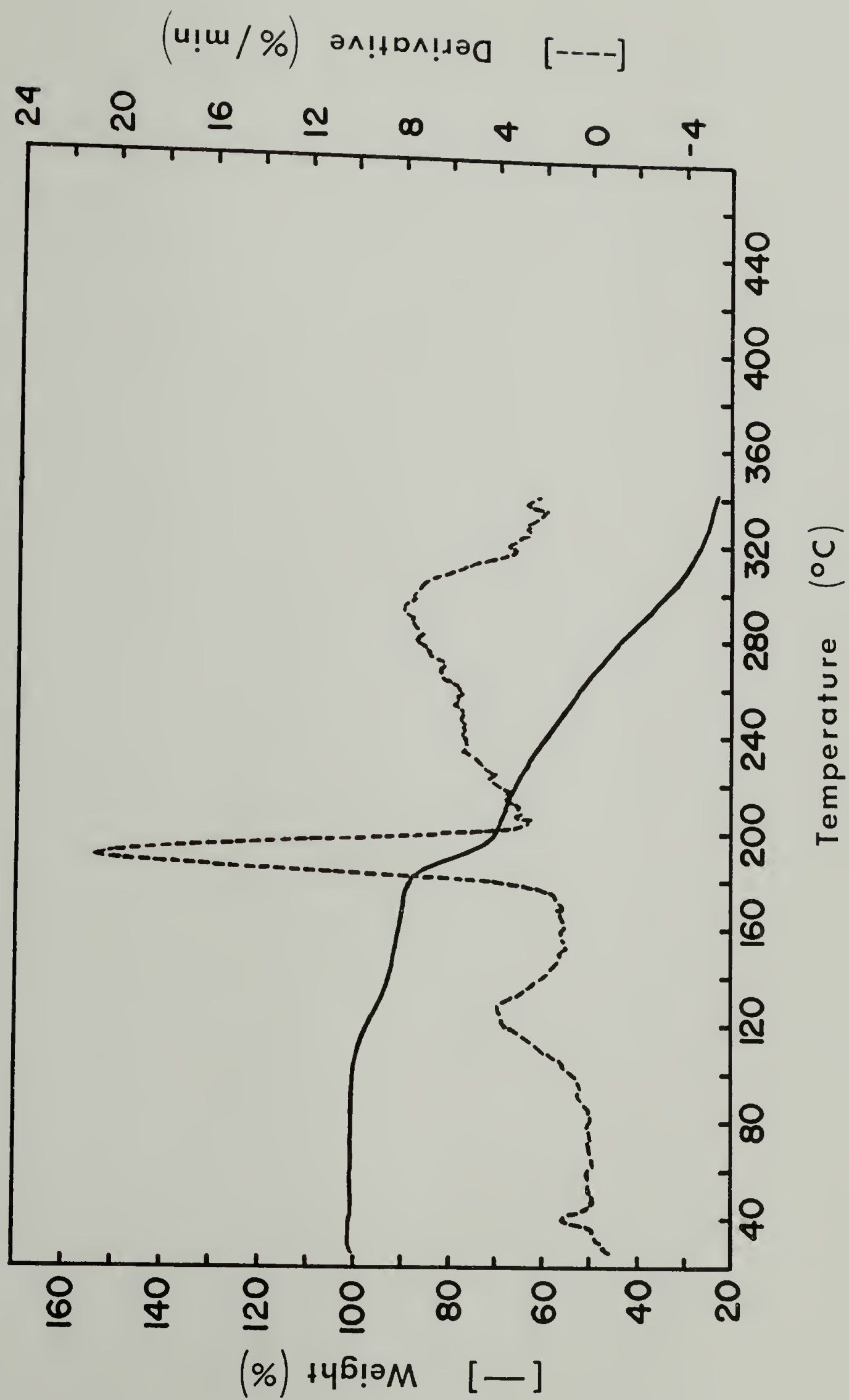


Figure 34. TGA and derivative curves of untreated TO/MEU/DO terpolymer.

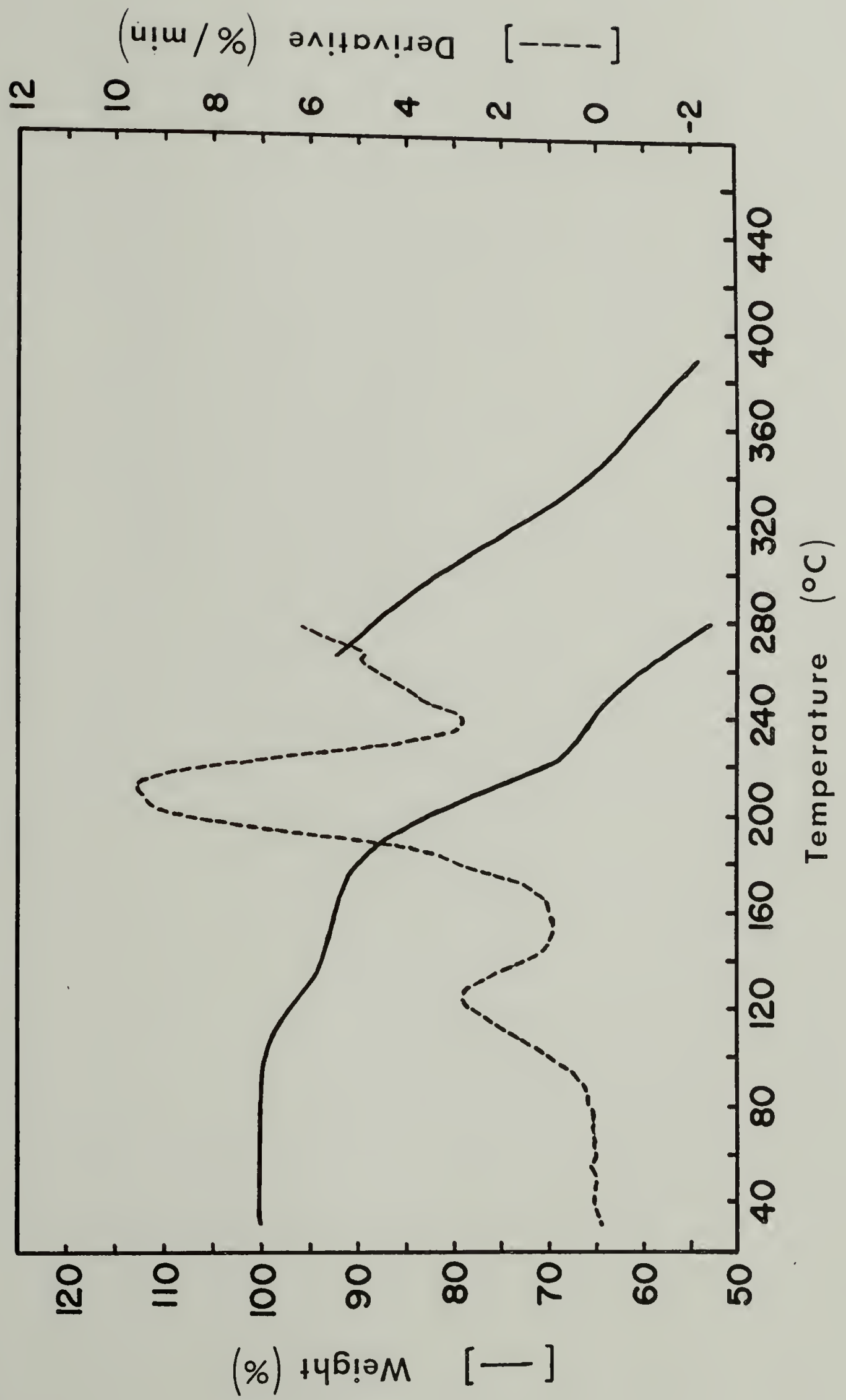
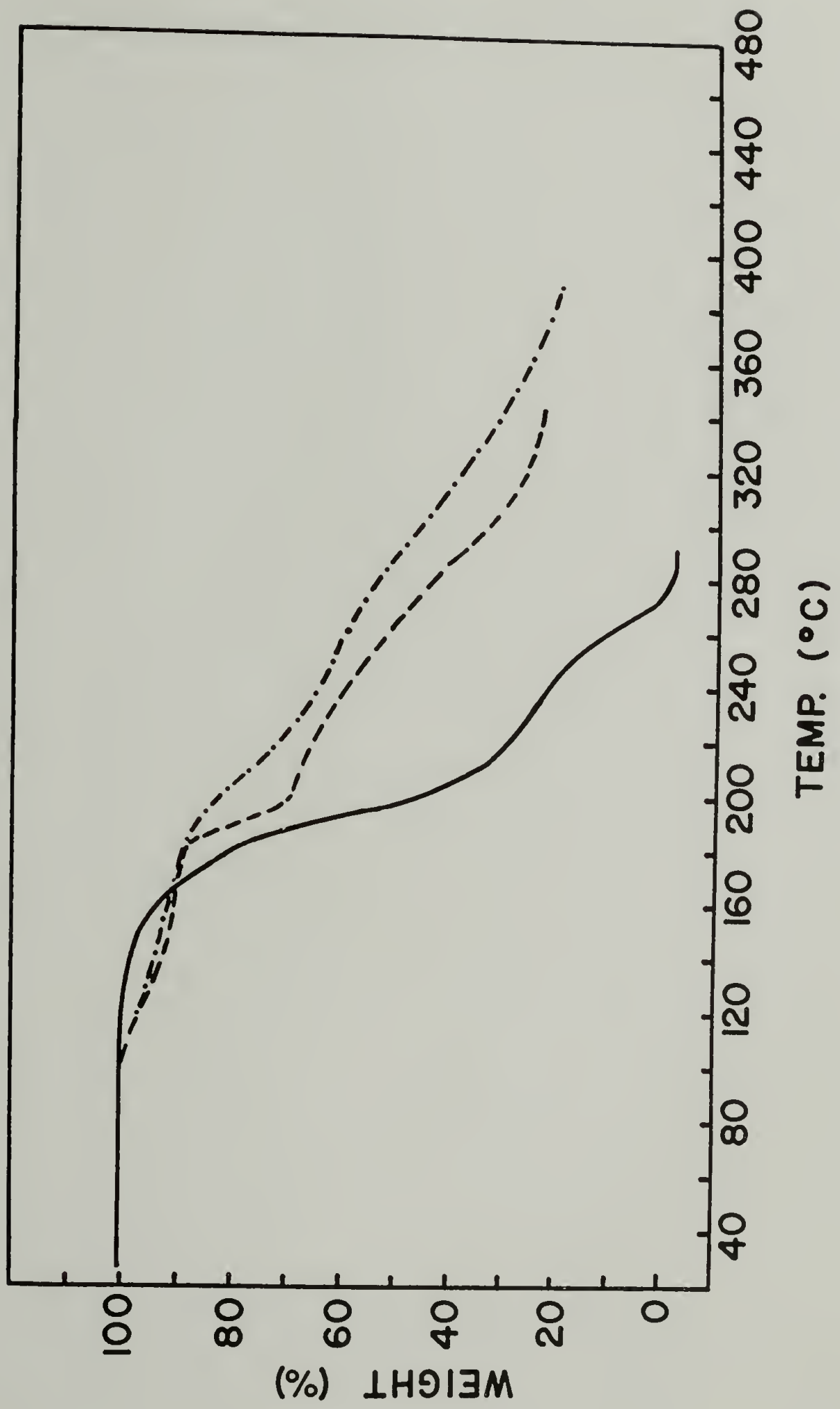


Figure 35. TGA curves of untreated TO/DO copolymer (—), TO/MEDOX copolymer (----), and TO/MEU/DO terpolymer (-.-.-).



degradation occurred at 193°C, 189°C and 210°C, respectively. The TO/DO copolymer was completely degraded (100% weight loss) by 275°C. The two ester-substituted POMs, however, were completely degraded only at higher temperatures, suggesting the possibility that thermally-induced crosslinking through the ester groups may occur. Crosslinking conceivably could occur through anhydride formation between ester groups. Approximately 20% of the initial TO/MEDOX copolymer mass remained at 350°C, while nearly 20% of the TO/MEU/DO terpolymer remained at 370°C. If the lower-temperature degradation processes which accounted for ca. 8-10% weight loss in the functionally-substituted POMs can be overcome, it appears likely that polyoxymethylenes of improved thermal stability can indeed be prepared.

F. Conclusions and Future Work

The major objectives which formed the basis of this dissertation have been successfully accomplished. High molecular weight functional polymers based on an oxyethylene backbone were prepared by the homopolymerization of an ester-substituted epoxide, methyl 10,11-epoxyundecanoate, and its copolymerization with a number of cyclic ether monomers. The high polymerizability of the functional epoxide was primarily ascribed to

the development of an optimal modified aluminumalkyl initiator composition and removal of intramolecular interactions in the difunctional monomer by a long, flexible hydrocarbon spacer-group.

Representative examples of the ester-substituted poly(alkylene oxides) were converted to poly(alkylene oxide) ionomers and carboxylic acids. An ion-containing poly(alkylene oxide) derived from an EO-MEU copolymer was shown by wide-angle x-ray diffraction to exhibit evidence of microphase separation previously observed in ionomers based on hydrocarbon polymers. The highly polar poly(alkylene oxide) ionomer was also water-soluble and exhibited behavior in solution typical of polyelectrolytes.

New advances were made in the preparation of functionally-substituted poly(alkylene oxides) based on a predominantly oxymethylene backbone. Incorporation of a functional cyclic ether or cyclic acetal monomer into POM was studied under analogous reaction conditions. The interest in carboxylated POM lay in its potential as ionomers with a highly polar and crystallizable backbone. Based on the results obtained in this work, the preferred functional comonomer for preparing functional POM by copolymerization with trioxane is the 4-substituted cyclic acetal, 4-(1-carbomethoxynonyl)-1,3-dioxolane or MEDOX.

Both MEDOX and MEU, however, were found to be relatively unreactive in cationic copolymerizations with trioxane or in terpolymerizations with trioxane and 1,3-dioxolane.

While much was accomplished, numerous possibilities also exist for future studies in the area of functionally-substituted poly(alkylene oxides). Studies of both fundamental and practical interest can be pursued. For example, an investigation seeking to establish the kind and nature of interactions that undoubtedly occurred between the aluminum coordination catalyst and the functional epoxide should, in the opinion of this author, be carried out. A better understanding of such processes could be used to influence the kinetics of the polymerization reaction and perhaps ultimately the properties of the poly(alkylene oxides). The possibility of producing optically-active functional poly(alkylene oxides) by stereoelective polymerization is also quite intriguing. This would involve the preparation of optically-active initiating species, which should be possible if chiral modifiers are employed.

The major thrust of future efforts, however, should focus on the poly(alkylene oxide) ionomers. In particular, a detailed investigation of solid-state properties and solution behavior of the elastomeric ionomers should be undertaken. The fundamental question is whether

or not the polar backbone interacts with the pendant ionic groups and if so, then how are the properties of the polymer affected. At present, a single piece of evidence (wide-angle x-ray) obtained in this work suggested that ionic domains do exist in the solid-state. More conclusive and definitive evidence is still needed.

Of considerable interest is the preparation of ion-containing poly(alkylene oxides) neutralized with divalent or trivalent metal cations. Conceivably, a new family of elastomeric network polymers based on a polyether backbone would result. This would also provide a means of influencing the solubility behavior of the highly polar polymers in aqueous media. One potential application of water-swellaible poly(alkylene oxide) ionomers, pseudo-crosslinked by multivalent cations, would be as a new family of hydrogels.

An area which may prove to be very fruitful is the potential of the ester- or carboxylic acid substituted oxyethylene polymers as carriers for controlled drug release. Drugs could be covalently bound to the polyether chain through the pendant carboxyl groups. Lower molecular weight functional copolymers based largely on ethylene oxide could be used. It is expected that such materials would be water-soluble and exhibit a good potential solubility in the bloodstream. Poly(ethylene glycols) have

been used extensively as food thickeners and extenders and exhibit no known deleterious effects in the body.

Stabilization of the functional polyethers against oxidation in any future studies is considered to be a key to preventing degradation of these materials.

Susceptibility of the alkylene oxide polymers to oxidation was a problem at times in this work.

Many interesting questions also arose from the author's efforts in the preparation of functionally-substituted oxymethylene copolymers. Foremost is the peculiar difference in induction times observed in preparing ester-substituted POM using a functional epoxide versus functional dioxolane as comonomer. Gas chromatographic analysis of reaction aliquots from the solution phase of trioxane/ethylene oxide copolymerizations¹⁵⁸ has provided valuable insight into the latter copolymerization process and should prove to be equally useful in this work. Major emphasis should also be placed on increasing the molecular weights of the functionally-substituted POM as well as determining if the copolymers produced are truly random. Indications were obtained in this work that endcapping or heat-treatment of the ester-substituted POM would result in POMs of improved thermal stability as compared with TO/EO or TO/DO copolymers. If molecular weight deficiencies can be overcome, the use of

a functional dioxolane comonomer like MEDOX in the preparation of POM may prove to be an attractive method for improving the thermal stability of the commercially important thermoplastic.

Conversion of the pendant ester groups to the metal carboxylate form should also be carried out and the solid-state properties of the ion-containing POMs studied in a fashion similar to earlier work on POM ionomers.

R E F E R E N C E S

1. L. DeMejo, Ph.D. Dissertation, University of Massachusetts, 1977.
2. D. Tirrell, O. Vogl, T. Kobayashi, S. Kobayashi and T. Saegusa, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, 20(1), 794 (1979).
3. D. Tirrell, O. Vogl, T. Saegusa, S. Kobayashi and T. Kobayashi, *Macromolecules*, 13, 1041 (1980).
4. G. Odian, Principles of Polymerization, First Edition, McGraw-Hill, Inc., New York, 1970, p. 451.
5. G.B. Butler and K.F. O'Driscoll, Eds., Reviews in Macromolecular Chemistry, 1(1), Marcel Dekker, Inc., New York, 1967, p. 39.
6. N.G. Gaylord and H.F. Mark, Linear and Stereoregular Addition Polymers, Wiley-Interscience, New York, 1959.
7. J. Furukawa and T. Saegusa, Polymerization of Aldehydes and Oxides, Wiley-Interscience, New York, 1963.
8. N.G. Gaylord, Polyethers, Part I, Wiley-Interscience, New York, 1963.
9. P.H. Plesch, The Chemistry of Cationic Polymerization, Macmillan, New York, 1963.
10. E.J. Vandenberg, Ed., Polyethers, ACS Symposium Series No. 6, Am. Chem. Soc., Washington, D.C., 1975.
11. S. Penczek, P. Kubisa, and K. Matyjaszewski, Advances in Polymer Science, Vol. 37, Springer-Verlag, Berlin, 1980.
12. T. Saegusa and E. Goethals, Eds., Ring-Opening Polymerization, ACS Symposium Series No. 59, Am. Chem. Soc., Washington, D.C., 1977.
13. W. Cooper, *Rept. Progr. Appl. Chem.*, 48, 230 (1963).

14. L.A. Bakalo and B.A. Krentsel, *Usp. Khim*, 31, 657 (1962); *Chem. Abstr.* 58: 4402 (1963).
15. S. Penczek, *Wiadomosci Chem.*, 16, 643, 717 (1962); *Chem. Abstr.* 60: 6932 (1964).
16. S. Onogi, and K. Uno, Eds., Progress in Polymer Science--Japan, Vol. 6, Halsted Press, New York, 1973.
17. N.M. Bikales, Ed., Encyclopedia of Polymer Science and Technology, Vol. 6, Wiley-Interscience, New York, 1967, p. 103.
18. A. Wurtz, *Ann. Chim. et Phys.*, 69, 330 (1863).
19. A. Wurtz, *Ann. Chim. et Phys.*, 69, 334 (1863).
20. P.A. Levine and A. Walti, *J. Biol. Chem.*, 75, 325 (1927).
21. G. Odian, Principles of Polymerization, Second Edition, Wiley-Interscience, New York, 1981, p. 511.
22. R.A. Nelson and R.S. Jessup, *J. Research Natl. Bur. Standards*, 48, 206 (1972).
23. E.J. Goethals, *Pure and Appl. Chem.*, 48, 335 (1976).
24. L.G. Lundsed and I.R. Schmolka, in Block and Graft Copolymerization, R.J. Ceresa, Ed., Wiley, New York, 1976, Vol. 2, Ch. 1, 2.
25. H. Staudinger and A. Lehmann, *Ann.*, 505, 41 (1933).
26. Ref. 7, p. 126.
27. Union Carbide and Carbon Corp., Australian Pat. Appl. 27792 (May 14, 1957).
28. F.N. Hill, F.E. Bailey, Jr. and J.T. Fitzpatrick, *Ind. Eng. Chem.*, 50, 5 (1958).
29. M.E. Pruitt and J.M. Baggett, U.S. Pat. 2,706,181 (1955).
30. M.E. Pruitt and J.M. Baggett, U.S. Pat. 2,706,189 (1955).
31. C.C. Price and M. Osgan, *J. Am. Chem. Soc.*, 78, 4787 (1956).

32. E.J. Vandenberg, J. Am. Chem. Soc., 83, 3538 (1961).
33. E.J. Vandenberg, J. Polym. Sci., Pt. B, 2, 1085 (1964).
34. E.J. Vandenberg, J. Polym. Sci., 47, 486 (1960).
35. E.J. Vandenberg, J. Polym. Sci., Pt. A-1, 7, 525 (1969).
36. C.C. Price and R. Spector, J. Am. Chem. Soc., 87, 2069 (1965).
37. C.C. Price and R. Spector, J. Am. Chem. Soc., 88, 4171 (1966).
38. C.C. Price, M.K. Akkapeddi, B.T. DeBona and B.C. Furie, J. Am. Chem. Soc., 94(11), 3964 (1972).
39. E.J. Vandenberg, U.S. Pat. 3,135,705 (1964).
40. E.J. Vandenberg, U.S. Pat. 3,219,591 (1965).
41. E.J. Vandenberg, Belg. Pat. 601,793 (1961); Brit. Pat. 927,817 (1963).
42. J. Furukawa, T. Tsuruta, R. Sakata, T. Saegusa and A. Kawasaki, Makromol. Chem., 32, 90 (1959).
43. J. Furukawa, T. Tsuruta, T. Saegusa, R. Sakata, G. Kakogawa, A. Kawasaki and I. Harada, J. Chem. Soc.--Ind. Chem. Sec., 62, 1269 (1959).
44. E.J. Vandenberg, Italian Pat. 648,581 (1962); Brit. Pat. 952,898 (1964).
45. R.O. Colclough, G. Gee, W.C.E. Higginson, J.B. Jackson and M. Litt, J. Polym. Sci., 34, 171 (1959).
46. D.G. Stewart, D.Y. Waddan, and E.T. Borrowes, U.S. Pat. 2,870,100 (1959).
47. P.E. Ebert and C.C. Price, J. Polym. Sci., 34, 157 (1959).
48. R.A. Miller and C.C. Price, J. Polym. Sci., 34, 162 (1959).
49. S. Kambara and M. Hatano, J. Polym. Sci., 27, 584 (1958).

50. E.J. Vandenberg, Brit. Pat. 898,306 (1962).
51. Hercules Powder Company, Belg. Pat. 579,074 (1959).
52. R. Sakata, T. Tsuruta, T. Saegusa, and J. Furukawa, Makromol. Chem., 40, 64 (1960).
53. C. Booth, W.C.E. Higginson, and E. Powell, Polymer, 5, 479 (1964).
54. R.J. Herold, S.L. Aggarwal, and V. Neff, Can. J. Chem., 41, 1368 (1963).
55. M. Ishimori, O. Nakasugi, N. Takeda and T. Tsuruta, Makromol. Chem., 115, 103 (1968).
56. C.C. Price, in Polyethers, E.J. Vandenberg, Ed., ACS Symposium Series No. 6, Am. Chem. Soc., Washington, D.C., 1975, p. 9.
57. H. Imai, T. Saegusa, and J. Furukawa, Makromol. Chem., 81, 92 (1965).
58. T. Saegusa, H. Imai, and J. Furukawa, Makromol. Chem., 65, 60 (1963).
59. T. Saegusa, T. Ueshima, and S. Tomita, Makromol. Chem., 107, 131 (1967).
60. C.C. Price and L.R. Brecker, J. Polym. Sci., A-1, 7, 575 (1969).
61. P. Sigwalt, Angew. Makromol. Chem., 94, 161 (1981).
62. T. Ouhadi, A. Hamitou, R. Jérôme, and Ph. Teyssié, Macromolecules, 9, 927 (1970).
63. Ph. Teyssié, T. Ouhadi and J.P. Bioul, Int. Rev. Sci., Phys. Chem., Ser. Two, 8, 191 (1975).
64. Ph. Teyssié, J.P. Bioul, A. Hamitou, J. Heuschen, L. Hocks, R. Jérôme and T. Ouhadi, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 18, 65 (1977).
65. I. Kuntz and W.R. Kroll, J. Polym. Sci., Pt. A-1, 8, 1601 (1970).
66. J.M. Baggett and M.E. Pruitt, U.S. Pat. 2,871,219 (1959).

67. S. Ishida and S. Murahashi, *J. Polym. Sci.*, 50, 571 (1959).
68. E.J. Vandenberg, U.S. Pat. 3,158,580 (1964).
69. W.D. Willis, L.O. Amberg, A.E. Robinson and E.J. Vandenberg, *Rubber World*, 153, 88 (1965).
70. E.J. Vandenberg, in *Kirk-Othmer Encyclopedia of Chemical Technology*, M. Grayson and D. Eckroth, Eds., 3rd Ed., Wiley, New York, 1979, Vol. 8, p. 568.
71. S. Ishida, *Bull. Chem. Soc. Japan*, 33, 727 (1960).
72. S. Kambara and A. Takahashi, *Makromol. Chem.*, 58, 226 (1962).
73. T. Saegusa, T. Ueshima, H. Imai and J. Furukawa, *Makromol. Chem.*, 79, 221 (1964).
74. T.B. Gibb, Jr., R.A. Clendinning and W.D. Niegisch, *J. Polym. Sci., Pt. A-1*, 4, 917 (1966).
75. A.E. Gurgiolo and R.W. McAda, U.S. Pat. 3,799,947 (1974).
76. A.E. Gurgiolo and R.W. McAda, U.S. Pat. 3,590,009 (1971).
77. P.E. Wei and P.E. Butler, *J. Polym. Sci., Pt. A-1*, 6, 2461 (1968).
78. E.J. Vandenberg, *Pure and Appl. Chem.*, 48, 295 (1976).
79. E.J. Vandenberg, U.S. Pat. 3,065,188 (1962).
80. E.J. Vandenberg, U.S. Pat. 3,728,320 (1973).
81. E.J. Vandenberg, U.S. Pat. 3,728,321 (1973).
82. E.E. Gruber, D.A. Meyer, G.H. Swart and K.U. Weinstock, *Ind. Eng. Chem. Prod. Res. Develop.*, 3(3), 194 (1964).
83. E.J. Vandenberg and A.E. Robinson, in *Polyethers*, E.J. Vandenberg, Ed., ACS Symposium Series No. 6, Am. Chem. Soc., Washington, D.C., 1975, p. 101.

84. Yu. A. Gurin, S.G. Sokolova, G.S. Solodovnikova and A.K. Panteleeva, *Vysokomol. Soedin, Ser. B.*, 17(2), 135 (1975); *Chem. Abstr.* 83: 29471d (1975).
85. T.N. Baker III and G.A. Bonetti, U.S. Pat. 3,652,523 (1972).
86. Yu. A. Gorin, E.I. Rodina and N.K. Paskova, U.S.S.R. Pat. 379,593 (1973); *Chem. Abstr.* 79: 106004a (1973).
87. F.O. Pazschke, *J. Prakt. Chem.*, [2], 1, 97 (1873).
88. W. Hartenstein, *J. Prakt. Chem.*, [2], 7, 297 (1873).
89. S.E. Cantor, G.D. Brindell and T.J. Brett, Jr., *J. Macromol. Sci.-Chem.*, A7(7), 1483 (1973).
90. K. Kobayashi and H. Sumitomo, *J. Polymer Sci., Pt. A-1*, 7, 1287 (1969).
91. E.J. Vandenberg, U.S. Pat. 3,403,114 (1964).
92. H.L. Cohen, *J. Polym. Sci.-Chem.*, 13, 1993 (1975).
93. E.J. Vandenberg, U.S. Pat. 3,446,757 (1969).
94. P.H. Khanh, H. Koinuma, S. Inoue and T. Tsuruta, *Makromol. Chem.*, 134, 253 (1970).
95. T. Tsuruta, S. Inoue and H. Koinuma, *Makromol. Chem.*, 112, 58 (1968).
96. E.J. Vandenberg, U.S. Pat. 3,476,718 (1969).
97. S. Saeki and H. Senda, Japan. Kokai 76 86,598 (1976); *Chem. Abstr.* 85: 160871t (1976).
98. T.N. Kuren'gina, L.V. Alferova, E.B. Toporkova and V.A. Kropachev, U.S.S.R. Pat. 663,698 (1979); *Chem. Abstr.* 91: 75115d (1979).
99. E.J. Vandenberg, U.S. Pat. 3,106,549 (1963).
100. N.M. Geller and V.A. Kropachev, *Vysokomol. Soedin., Ser. B*, 16(2), 103 (1974); *Chem. Abstr.* 81: 37899y (1974).
101. L. DeMejo, W.J. MacKnight and O. Vogl, *Polymer (London)*, 19(8), 856 (1978).

102. L. DeMejo, W.J. MacKnight and O. Vogl, Abstracts, SPE ANTEC, 1978, p. 5.
103. L. DeMejo, W.J. MacKnight and O. Vogl, Polymer J. (Japan), 11(1), 15 (1979).
104. L. DeMejo, W.J. MacKnight and O. Vogl, Acta Polymerica, 31, 617 (1980).
105. T. Saegusa, T. Kobayashi, S. Kobayashi, S. Lund-Couchman and O. Vogl, Polymer J. (Japan), 11(6), 463 (1979).
106. O. Vogl, D. Bansleben, J. Muggee, M. Malanga, D. Tirrell and T. Saegusa, Plenary Lectures, 5th Cationic Symposium, Kyoto, 1980, p. 86.
107. O. Vogl, J. Muggee and D. Bansleben, Polymer J. (Japan), 12(9), 677 (1980).
108. J. Muggee, Ph.D. Thesis, University of Massachusetts, 1982.
109. O. Vogl, P. Loeffler, D. Bansleben and J. Muggee, in press.
110. R.W. Rees and D.J. Vaughan, Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem., 6, 286 (1965).
111. E.J. Vandenberg, U.S. Pat. 3,403,114 (1968).
112. E. Pulkkinen and T. Petaja, Finn. Chem. Lett., 1, 22 (1977).
113. C.K. Riew and R.K. Schlatter, U.S. Pat. 3,864,288 (1975).
114. R.K. Schlatter, Jr. and H.A. Tucker, Ger. Offen. 2,540,310 (1976).
115. E. Bortel and R. Lamot, Roczn. Chem., 50, 1765 (1976).
116. W. Wrasidlo, U.S. Pat. 4,005,012 (1977).
117. T.V. Markman, N.A. Mukhitdinov and M.A. Askarov, Deposited Doc. 1974, VINITI 451-74; Chem. Abstr. 86: 121980d (1977).
118. C.K. Riew, Polym. Prep., Am. Chem. Soc. Div. Polym. Chem., 14(2), 940 (1973).

119. C.R. Dick and E.L. Ward, U.S. Pat. 3,746,678 (1973).
120. T.N. Kuren'gina, L.V. Alferova and V.A. Kropachev, Vysokomol. Soedin., Ser. B, 15, 885 (1973).
121. M.T. McDonald, U.S. Pat. 3,591,520 (1971).
122. E.J. Vandenberg, U.S. Pat. 3,645,917 (1972).
123. E.J. Vandenberg, U.S. Pat. 3,417,036 (1968).
124. H. Fukutomi and H. Ohotani, Ger. Offen. 2,124,686 (1971).
125. Mitsubishi Chemical Industries Co., Ltd., Brit. Pat. 1,404,927 (1975).
126. R.A. Hickner and H.A. Farber, U.S. Pat. 3,415,902 (1967).
127. E.J. Vandenberg, U.S. Pat. 3,660,314 (1972).
128. D.S. Breslow, U.S. Pat. 3,417,060 (1968).
129. R.A. Hickner and H.A. Farber, U.S. Pat. 3,804,900 (1974).
130. E.J. Vandenberg, U.S. Pat. 3,706,706 (1972).
131. E.J. Vandenberg and W.D. Willis, U.S. Pat. 3,594,355 (1971).
132. E.J. Vandenberg and W.D. Willis, U.S. Pat. 3,694,258 (1972).
133. T. Nakai and M. Okawara, Bull. Chem. Soc. Jpn., 41, 707 (1968).
134. W. Deits, Ph.D. Dissertation, University of Massachusetts, 1979.
135. E.J. Vandenberg, J. Polym. Sci.-Chem., 10, 2903 (1972).
136. A. Butlerov, Ann., 111, 242 (1859).
137. R.N. MacDonald, French Pat. 1,082,519 (1954).
138. R.N. MacDonald, Brit. Pat. 748,836 (1956); Chem. Abstr. 50: 13504d (1956).

139. R.N. MacDonald, U.S. Pat. 3,768,994 (1956); Chem. Abstr. 51: 2323 (1957).
140. O. Vogl, Makromol. Chem., 175, 1281 (1974).
141. O. Vogl, J. Macromol. Sci.-Rev., C12(1), 109 (1975).
142. D.L. Hammick and A.R. Boeree, J. Chem. Soc., 121, 2738 (1922).
143. A.K. Schneider, U.S. Pat. 2,795,571 (1957).
144. C.E. Schweitzer, R.N. MacDonald and J.O. Punderson, J. Appl. Polym. Sci., 1, 158 (1959).
145. W. Kern and H. Cherdron, Makromol. Chem., 40, 101 (1960).
146. E.I. duPont de Nemours and Company, Brit. Pat. 770,717 (1957).
147. E.I. duPont de Nemours and Company, French Pat. 1,131,939 (1956).
148. J.O. Punderson, Brit. Pat. 880,737 (1960).
149. S. Dal Nogare and J.O. Punderson, U.S. Pat. 2,998,409 (1961).
150. C. Walling, F. Brown and K.W. Bartz, U.S. Pat. 3,027,352 (1962).
151. G.L. Collins, R.K. Greene, F.M. Berardinelli and W.H. Ray, J. Polym. Sci.-Chem., 19, 1597 (1981).
152. C.S.H. Chen and A. DiEdwardo, Advan. Chem. Ser., 91, 359 (1969).
153. C.S.H. Chen and A. DiEdwardo, J. Macromol. Sci., A4, 349 (1970).
154. K. Weissermel, E. Fischer, K. Gutweiler and H.D. Hermann, Kunststoffe, 54, 410 (1964).
155. V. Jaacks, Makromol. Chem., 101, 33 (1967).
156. W.H.J. Vickers, Eur. Polym. J., 3, 199 (1967).
157. J. Furukawa and T. Saegusa, Special Lectures at the International Symposium on Macromolecular Chemistry, Butterworths, London, 1962, p. 401.

158. H. Sumitomo and K. Kobayashi, J. Polym. Sci., Pt. A-1, 4, 907 (1966).
159. E.I. duPont de Nemours and Company, Brit. Pat. 1,006,390 (1965); Chem. Abstr. 64: 2190h (1966).
160. Diamond Alkali Co., Neth. Appl. 6,503,906 (1965); Chem. Abstr. 64: 8396h (1966).
161. K.V. Martin and O.F.L. Vogl., Brit. Pat. 1,005,761 (1965).
162. K.V. Martin and O.F.L. Vogl, French Pat. 1,401,637 (1965).
163. K.V. Martin and O.F.L. Vogl, U.S. Pat. 3,284,411 (1966); Chem. Abstr. 66: 11321u (1967).
164. K.V. Martin, U.S. Pat. 3,316,218 (1967).
165. T.R. Steadman and F. Jaffee, U.S. Pat. 3,115,480 (1963).
166. K.F. Wissbrun, F.M. Berardinelli and M.B. Price, U.S. Pat. 3,488,322 (1970).
167. K.F. Wissbrun, Makromol. Chem., 118, 211 (1968).
168. Z. Janović and O. Vogl, unpublished results.
169. K. Weissermel, E. Fischer, K.H. Häfner and H. Cherdron, Angew. Makromol. Chem., 4/5, 168 (1968).
170. A.B. Perstorp, Brit. Pat. 1,272,509 (1972); Chem. Abstr. 78: 98248v (1973).
171. A.B. Perstorp, French Pat. 2,077,359 (1971); Chem. Abstr. 78: 44242v (1973).
172. K.J. Clark, U.S. Pat. 3,492,277 (1970).
173. J. Boor, Jr., Ziegler-Natta Catalysts and Polymerizations, Academic Press, New York, 1979, p. 532.
174. G. Natta, G. Mazzanti, P. Longi and F. Bernardini, J. Polym. Sci., 31, 181 (1958).
175. P. Longi, F. Greco and U. Rossi, Makromol. Chem., 116, 113 (1968).

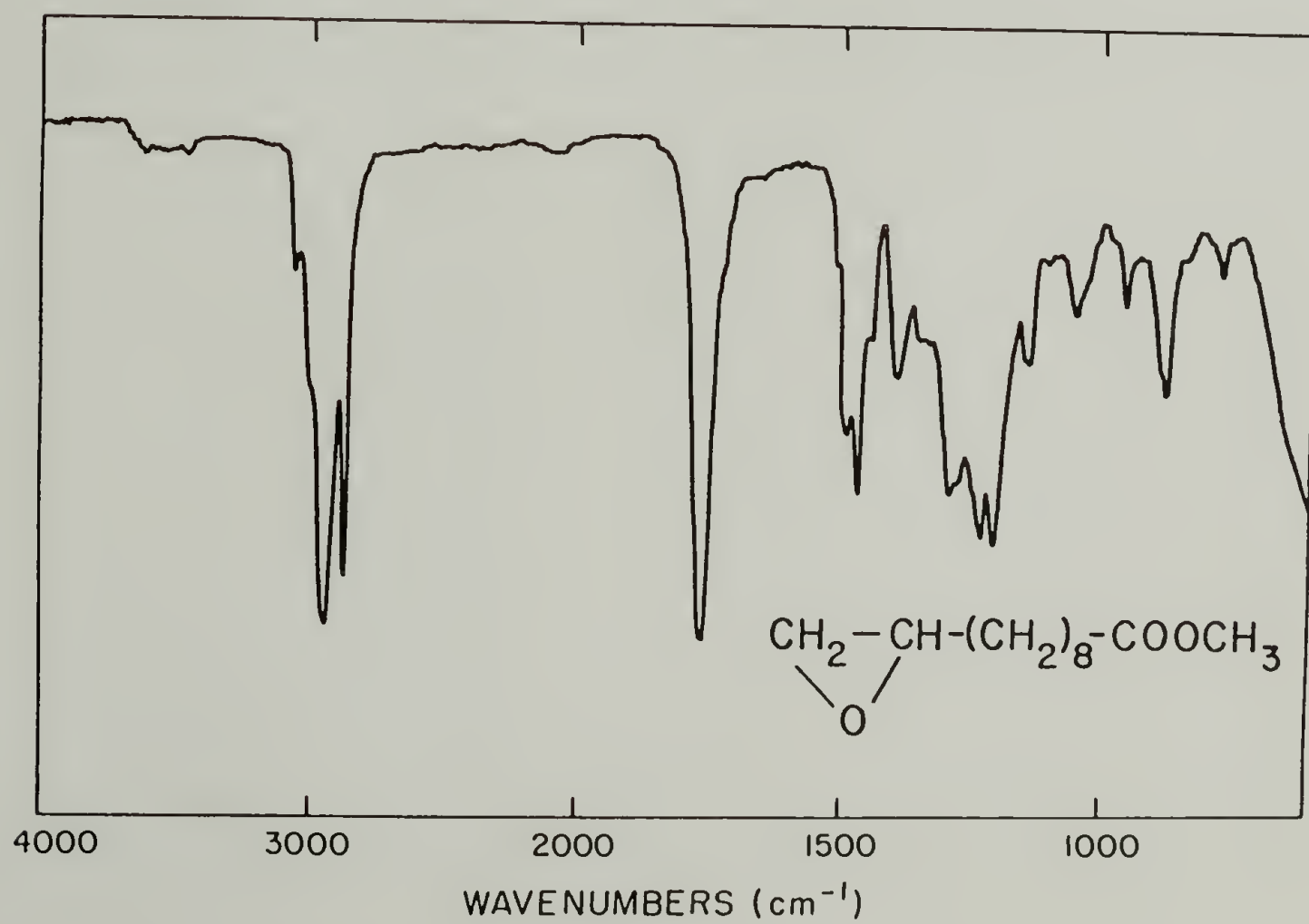
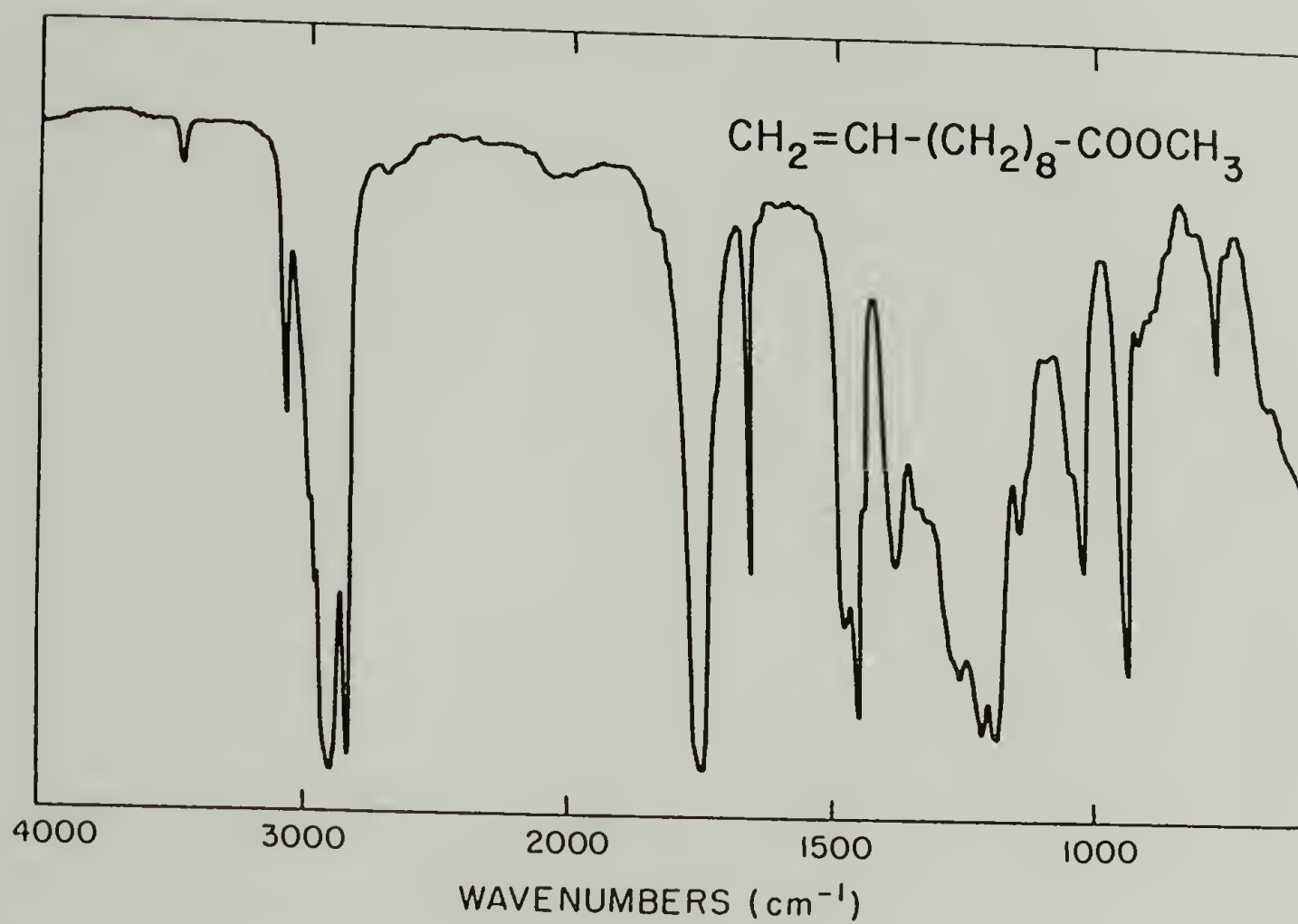
176. A. Carbonaro, A. Greco and I.W. Bassi, *Eur. Polym. J.*, 4, 445 (1968).
177. R. Backsai, *Chem. Engnrg. News*, 42, 55 (September 14, 1964).
178. K.J. Clark and T. Powell, *Polymer*, 6, 531 (1965).
179. R. Backsai, *Ger. Offen.* 1,301,085 (1969); *Chem. Abstr.* 71: 102435d (1969).
180. Farbwerke Hoechst A.-G., *Neth. Appl.* 6,517,178 (1966); *Chem. Abstr.* 66: 19046d (1967).
181. U. Giannini, G. Brückner, E. Pellino and A. Cassata, *J. Polym. Sci.-Letters*, 5, 527 (1967).
182. Farbwerke Hoechst A.-G., *French Pat.* 1,498,009 (1967); *Chem. Abstr.* 69: 67923w (1968).
183. Y. Amiard, J.P. Bellissent and G. Marie, *French Pat.* 2,087,215 (1972); *Chem. Abstr.* 77: 103036k (1972).
184. K.J. Clark, *S. African Pat.* 67 06,660 (1969); *Chem. Abstr.* 71: 102432a (1969).
185. H.V. Holler and E.A. Youngman, *U.S. Pat.* 3,761,458 (1974); *Chem. Abstr.* 80: 15684b (1974).
186. K. Tanaka, T. Iwata and J. Sasaki, *Japan Kokai* 73 37,755 (1974); *Chem. Abstr.* 81: 38135h (1974).
187. Y. Suzuki, K. Tanaka, T. Iwata, J. Sasaki, N. Ichikura and H. Maki, *Japan Kokai* 73 37,756 (1974); *Chem. Abstr.* 81: 38347d (1974).
188. W.J. Bailey and C.N. Bird, *J. Org. Chem.*, 42, 3895 (1977).
189. Yu. N. Ogibin, E. Troyanskii, G. Kishin, V. Kadentsev, E. Lubuzhi and O. Chizhov, *Izv. Akad. Nauk. SSR, Ser. Khim.*, 11, 2518 (1976); *Chem. Abstr.* 86: 105880r (1976).
190. T. Iwata and J. Sasaki, *Japan Kokai* 73 43,191 (1973); *Chem. Abstr.* 81: 153495n (1974).
191. H.C. Eleuterio, *U.S. Pat.* 3,074,918 (1963).

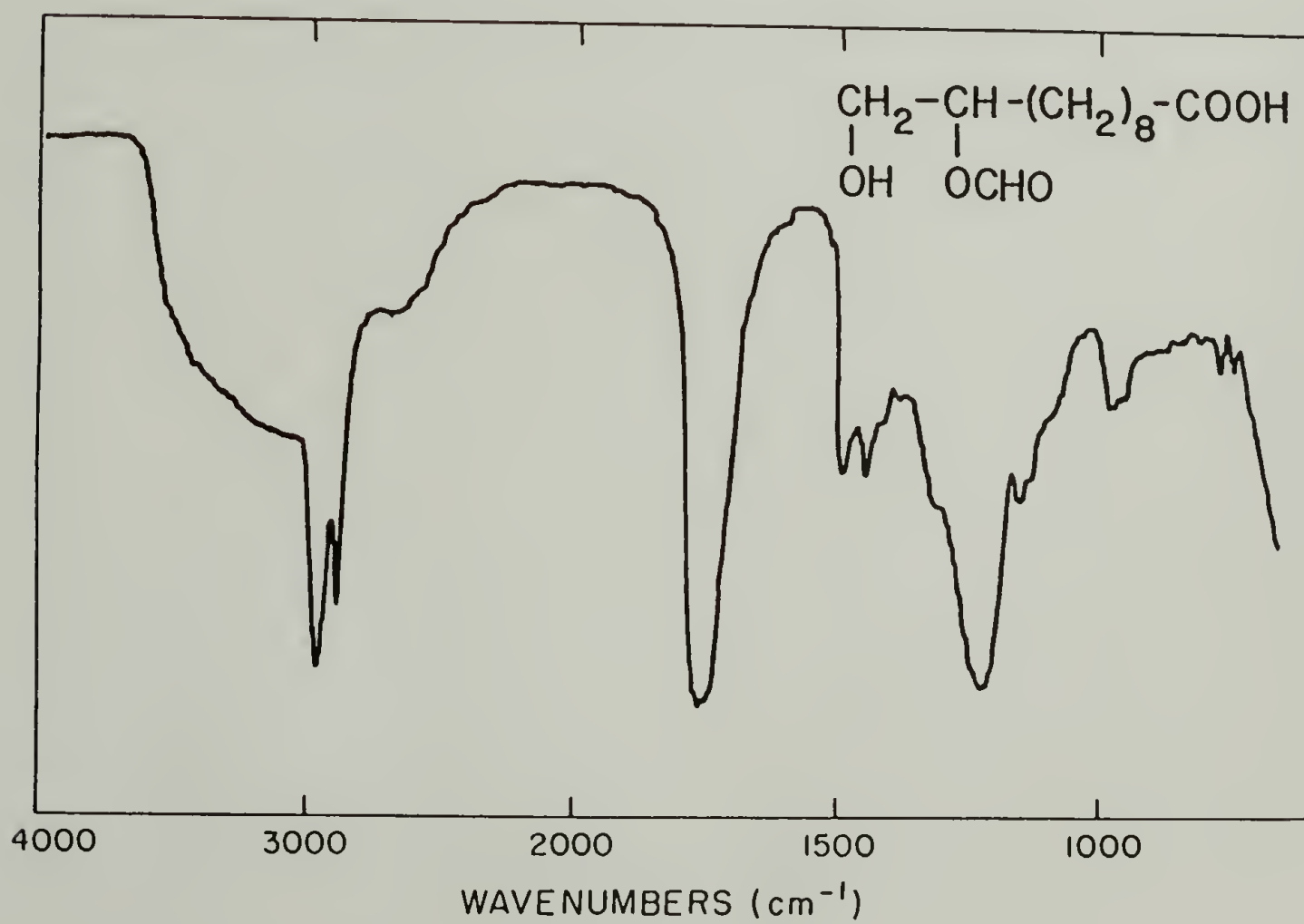
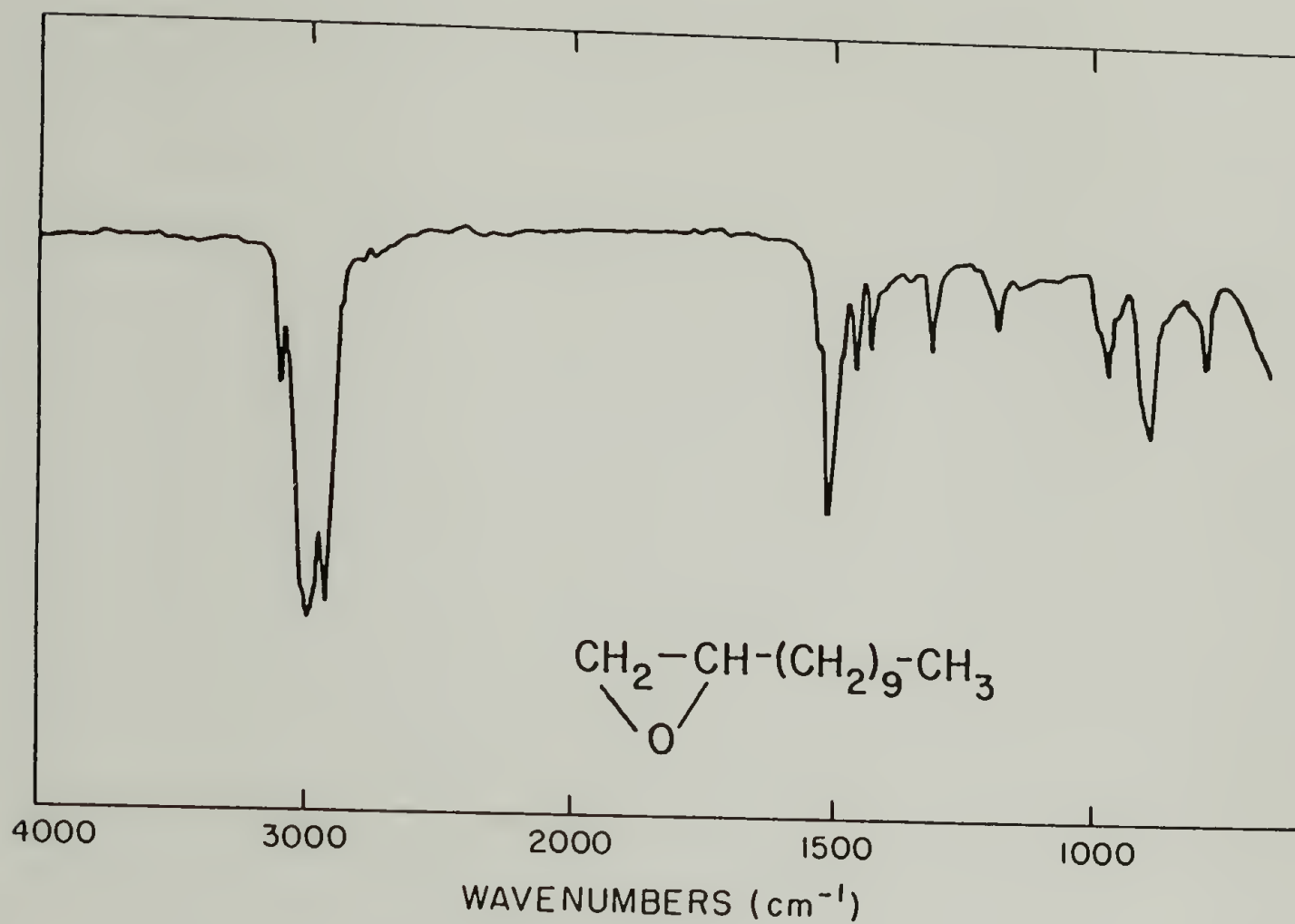
192. G. Natta, G. Dall'Asta and G. Mazzanti, *Angew. Chem.*, 76, 765 (1964).
193. P. Hepworth, *Ger. Offen.* 2,231,995 (1973); *Chem. Abstr.* 78: 98287g (1973).
194. T. Ueshima and S. Kobayashi, *Purasuchikkusu*, 24(10), 9 (1973); *Chem. Abstr.* 80: 83985a (1974).
195. T. Ueshima, S. Kobayashi and M. Matsuoka, *U.S. Pat.* 3,856,758 (1974).
196. P. Hepworth, *U.S. Pat.* 3,859,265 (1975).
197. P. Hepworth, *U.S. Pat.* 3,980,626 (1976).
198. R. Ichikura, T. Iwata and M. Saito, *Japan. Kokai* 72 05,101 (1972); *Chem. Abstr.* 77: 6076r (1972).
199. H. Ikeda, S. Matsumoto, K. Makino, R. Nakamura and S. Fukuhara, *Japan. Kokai* 75 56,493 (1975); *Chem. Abstr.* 83: 132335m (1975).
200. S. Matsumoto, K. Komatsu and K. Igarishi, *Ring-Opening Polymerization*, T. Saegusa and E. Goethals, Eds., *ACS Symposium Ser. No. 59*, Am. Chem. Soc., Washington, D.C. (1977), p. 303.
201. R. Ichikura, T. Iwata and M. Saito, *Japan. Kokai* 72 05,101 (1972); *Chem. Abstr.* 77: 6076r (1972).
202. P. Dreyfuss and J.P. Kennedy, *Anal. Chem.*, 47(4), 771 (1975).
203. H. Noerdlinger, *Chem. Ber.*, 23(2), 2357 (1890).
204. W.D. Emmons and A.S. Pagano, *J. Am. Chem. Soc.*, 77, 89 (1955).
205. D. Swern, G.N. Billen, T.W. Findley and J.T. Scanlan, *J. Am. Chem. Soc.*, 67, 1786 (1945).
206. S.M. Osman and G.A. Qazi, *Fette, Seifen, Anstrichmittel*, 78(8), 326 (1976).
207. K.S. Markley, Ed., *Fatty Acids, Part I*, Interscience Publ., New York, 1960, p. 121.
208. D. Swern, *Chem. Rev.*, 45, 1 (1949).
209. N.N. Schwartz and J.H. Blumbergs, *J. Org. Chem.*, 29, 1976 (1964).

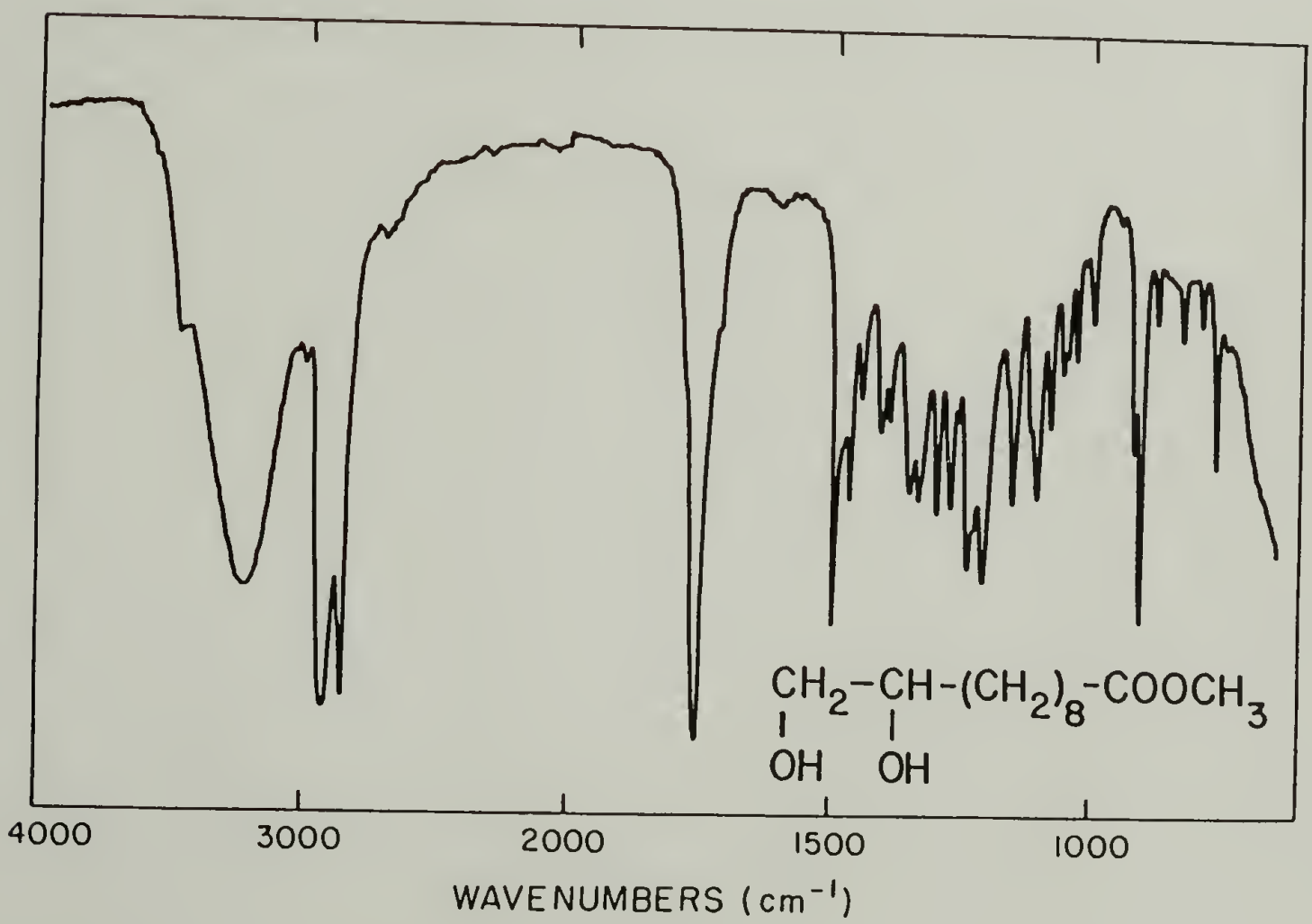
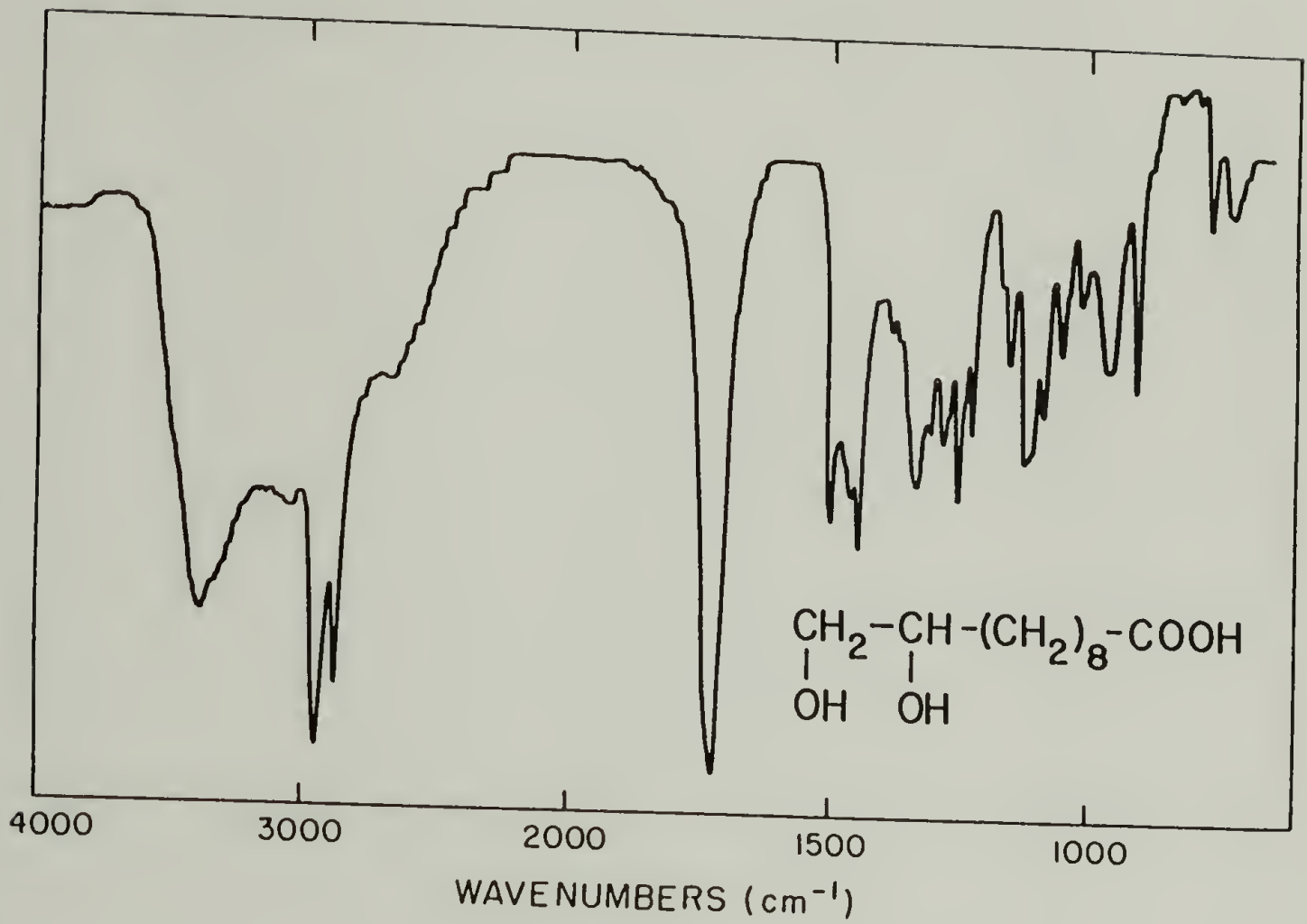
210. A. Storr, K. Jones and A.W. Laubengayer, *J. Am. Chem. Soc.*, 90(12), 3173 (1968).
211. J. Schaefer, *Macromolecules*, 2, 533 (1969).
212. N. Oguni, K. Lee and H. Tani, *Macromolecules*, 5(6), 819 (1972).
213. K.J. Ivin, *J. Polym. Sci., Pt.-C*, 62, 89 (1978).
214. J.P. Kennedy, Cationic Polymerization of Olefins: A Critical Inventory, Wiley-Interscience, New York, 1975.
215. C. Tanford, Physical Chemistry of Macromolecules, Wiley, New York, 1961.
216. L.E. Nielsen, Mechanical Properties of Polymers, Reinhold Publ. Corp., New York, 1962.
217. E.P. Otocka and T.K. Kwei, *Macromolecules*, 1, 401 (1968).
218. A. Eisenberg, *Macromolecules*, 4, 125 (1971).
219. L. Holliday, Ed., Ionic Polymers, Wiley, New York, 1975, p. 36.
220. H. Tadokoro, Y. Chatani, T. Yoshihara, S. Tahara and S. Murashi, *Makromol. Chem.*, 73, 109 (1964).
221. W.J. MacKnight and T.R. Earnest, Jr., *J. Polym. Sci.-Macromol. Rev.*, 16, 41 (1981).
222. Y. Tsujita, S.L. Hsu and W.J. MacKnight, *Macromolecules*, 14, 1824 (1981).
223. M.F. Hoover, *Polym. Prepr., Am. Chem. Soc. Div. of Polym. Chem.*, 10, 908 (1969).
224. Ref. 219, p. 9.
225. C. Tanford, Ed., Physical Chemistry of Macromolecules, Wiley, New York, 1961, p. 493.
226. J.F. Walker, Ed., Formaldehyde, 2nd Ed., Reinhold Publ. Corp., New York, 1953, p. 271.
227. S. Penczek, J. Feigin, P. Kubisa, K. Matyjaszewski and M. Tomaszewicz, *Makromol. Chem.*, 172, 243 (1973).

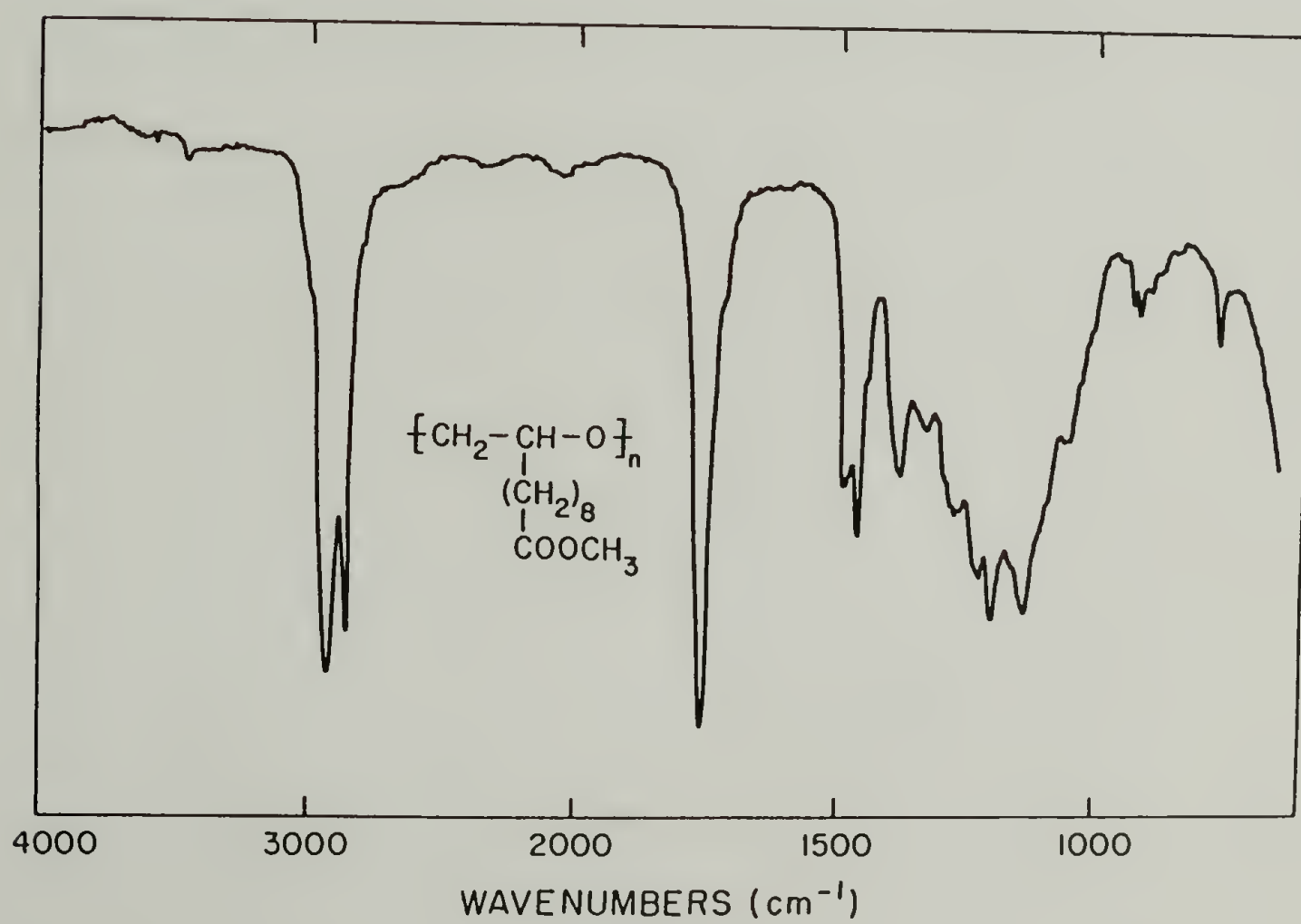
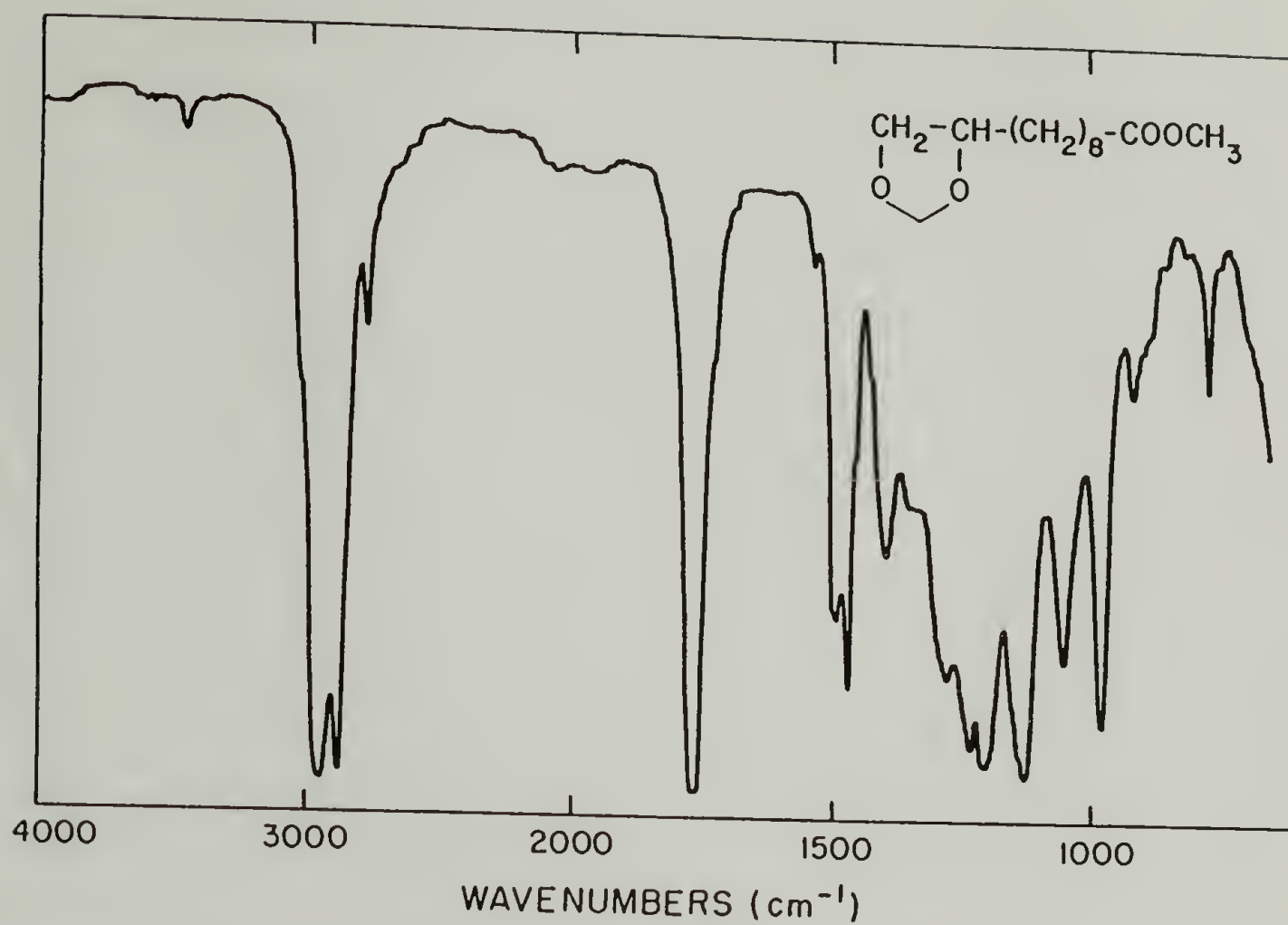
228. H.L. Wagner and K.F. Wissbrun, Makromol. Chem., 81, 14 (1965).
229. M. Okada, Y. Yamashita and Y. Ishii, Makromol. Chem., 80, 196 (1964).
230. M. Okada, K. Mita and H. Sumitomo, Makromol. Chem., 177, 895 (1976).
231. M. Okada, K. Mita and H. Sumitomo, Makromol. Chem., 176, 859 (1975).
232. M. Okada, K. Mita and H. Sumitomo, Makromol. Chem., 177, 2055 (1976).
233. M. Okada, T. Hisada and H. Sumitomo, Makromol. Chem., 179, 959 (1978).
234. Y. Kawakami, A. Ogawa and Y. Yamashita, J. Org. Chem., 44, 441 (1979).
235. Y. Kawakami, A. Ogawa and Y. Yamashita, J. Polym. Sci.-Chem., 17, 3785 (1979).
236. M. Droscher, G. Lieser, H. Riemann and G. Wegner, Polymer, 16, 497 (1975).
237. Z. Jedlinski and J. Majnusz, Makromol. Chem., 155, 111 (1972).
238. Z. Jedlinski, M. Rybezyk, J. Majnusz and S. Janik, Makromol. Chem., 176, 905 (1975).

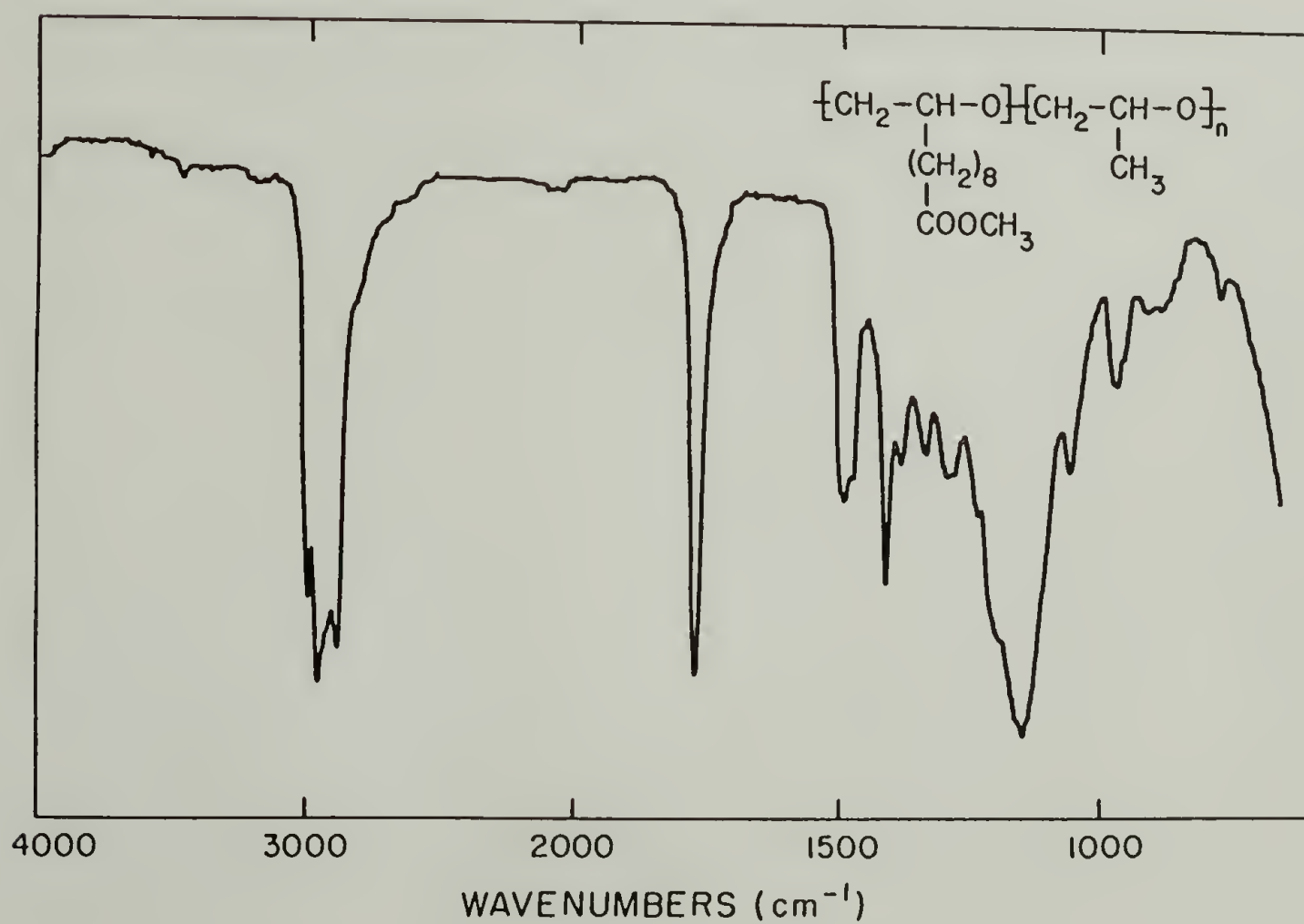
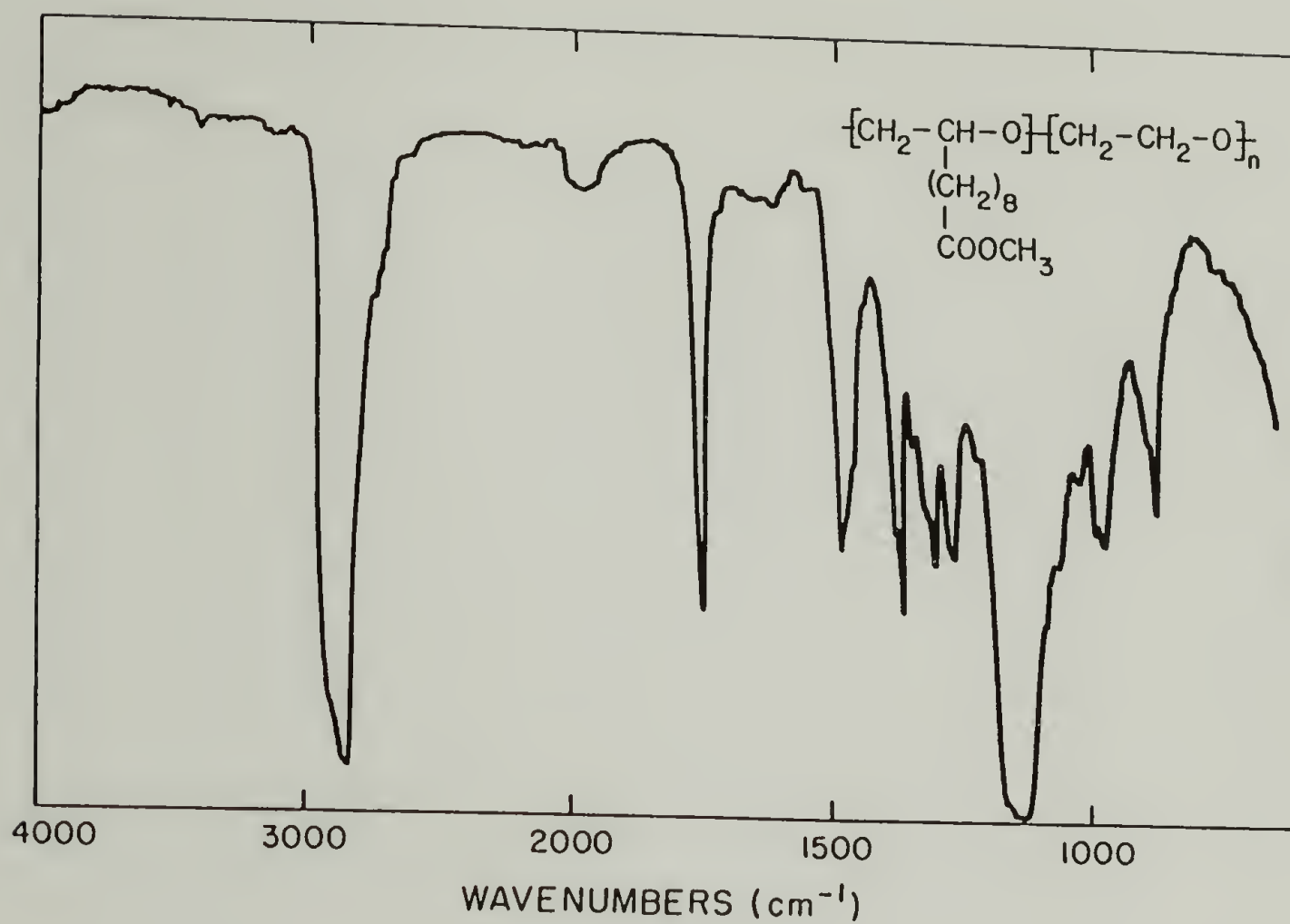
A P P E N D I X A
INFRARED SPECTRA

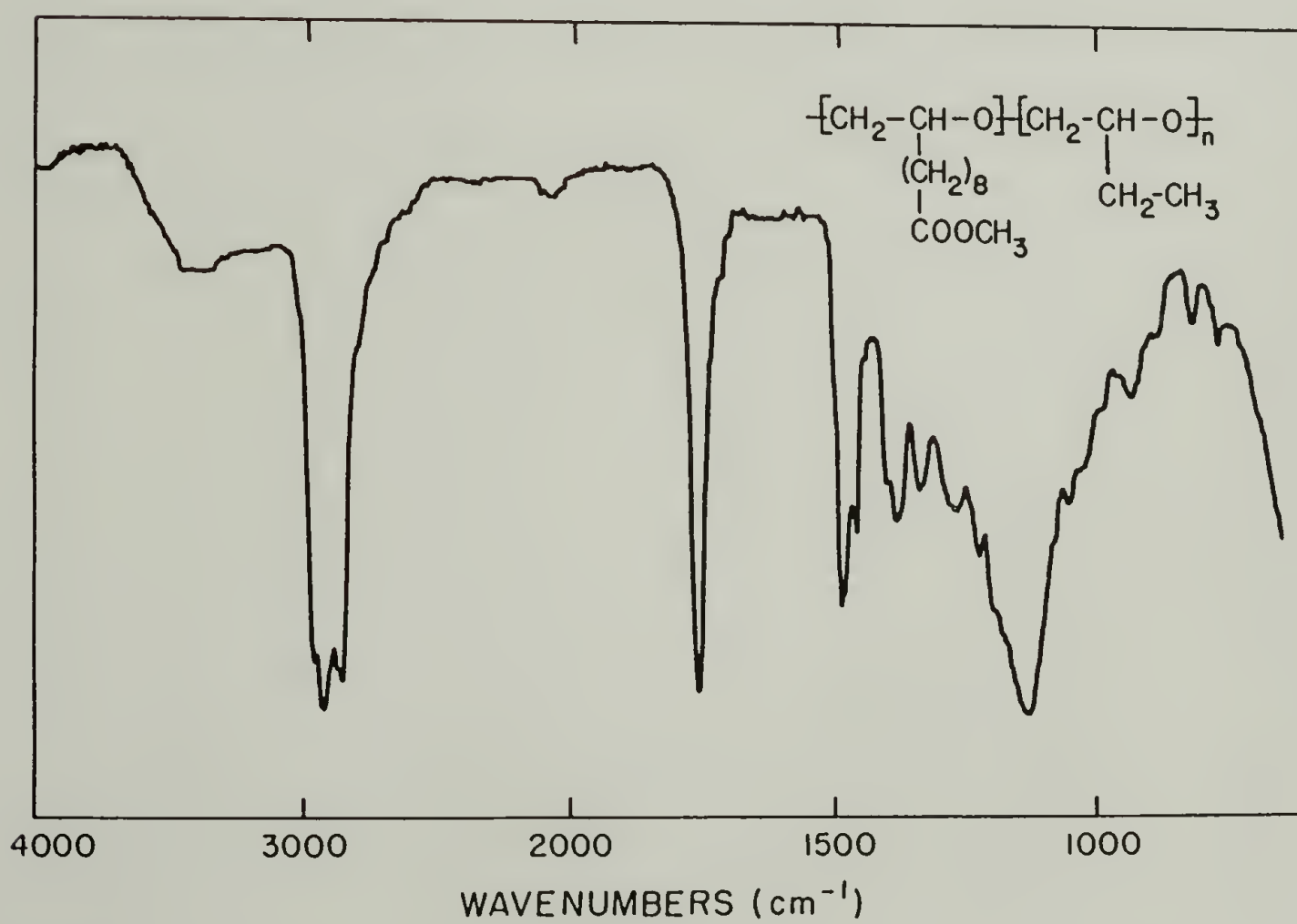
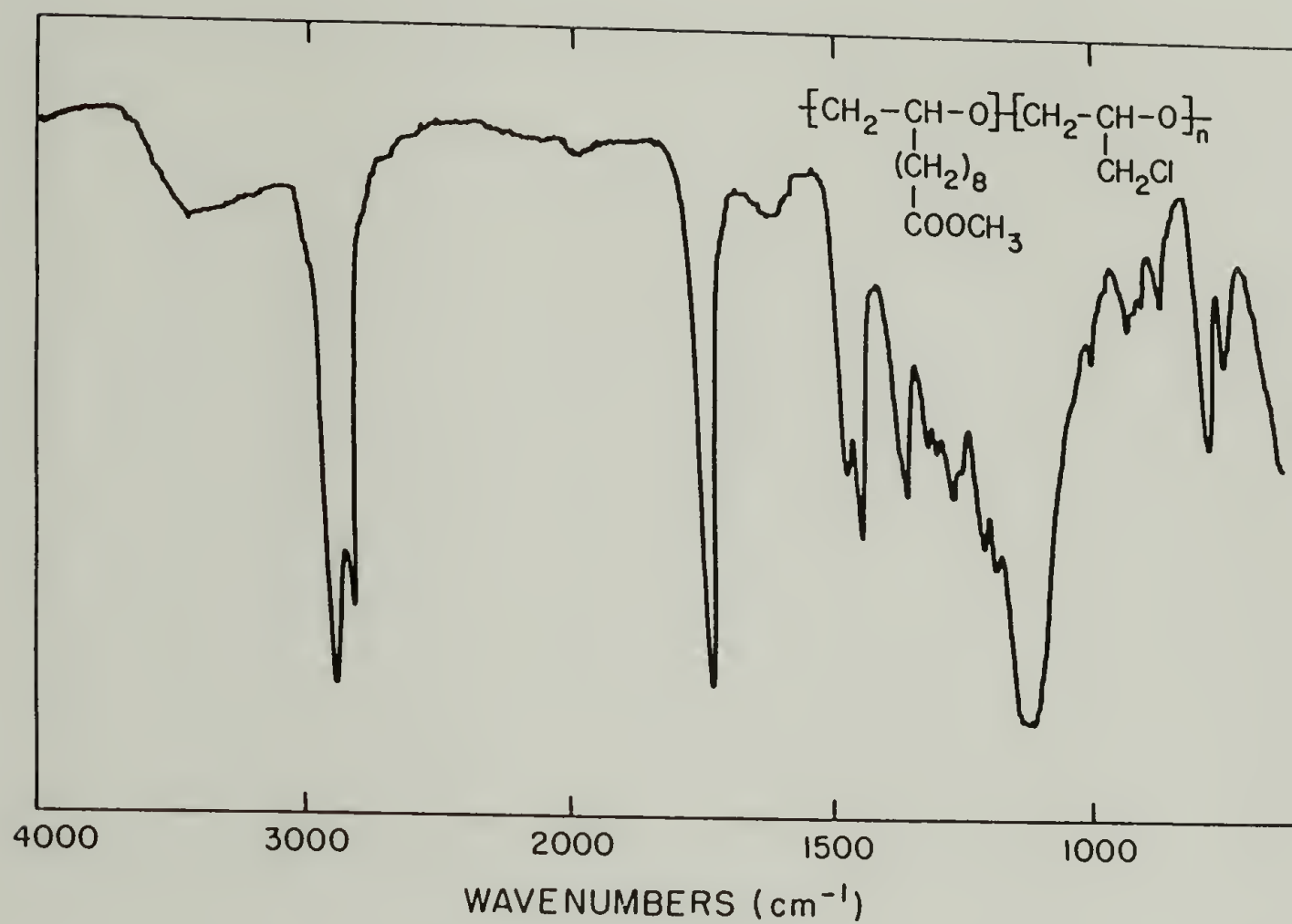


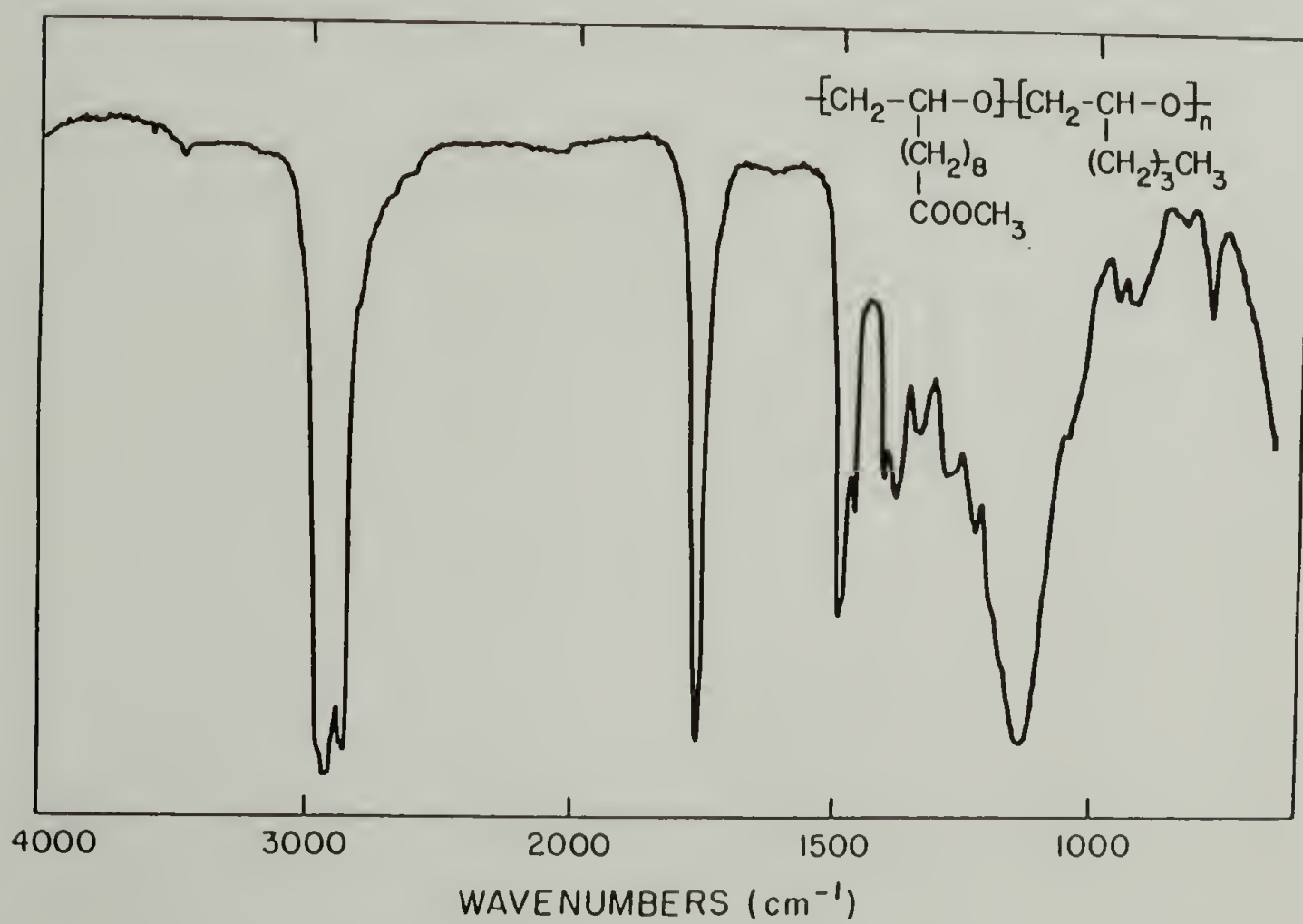
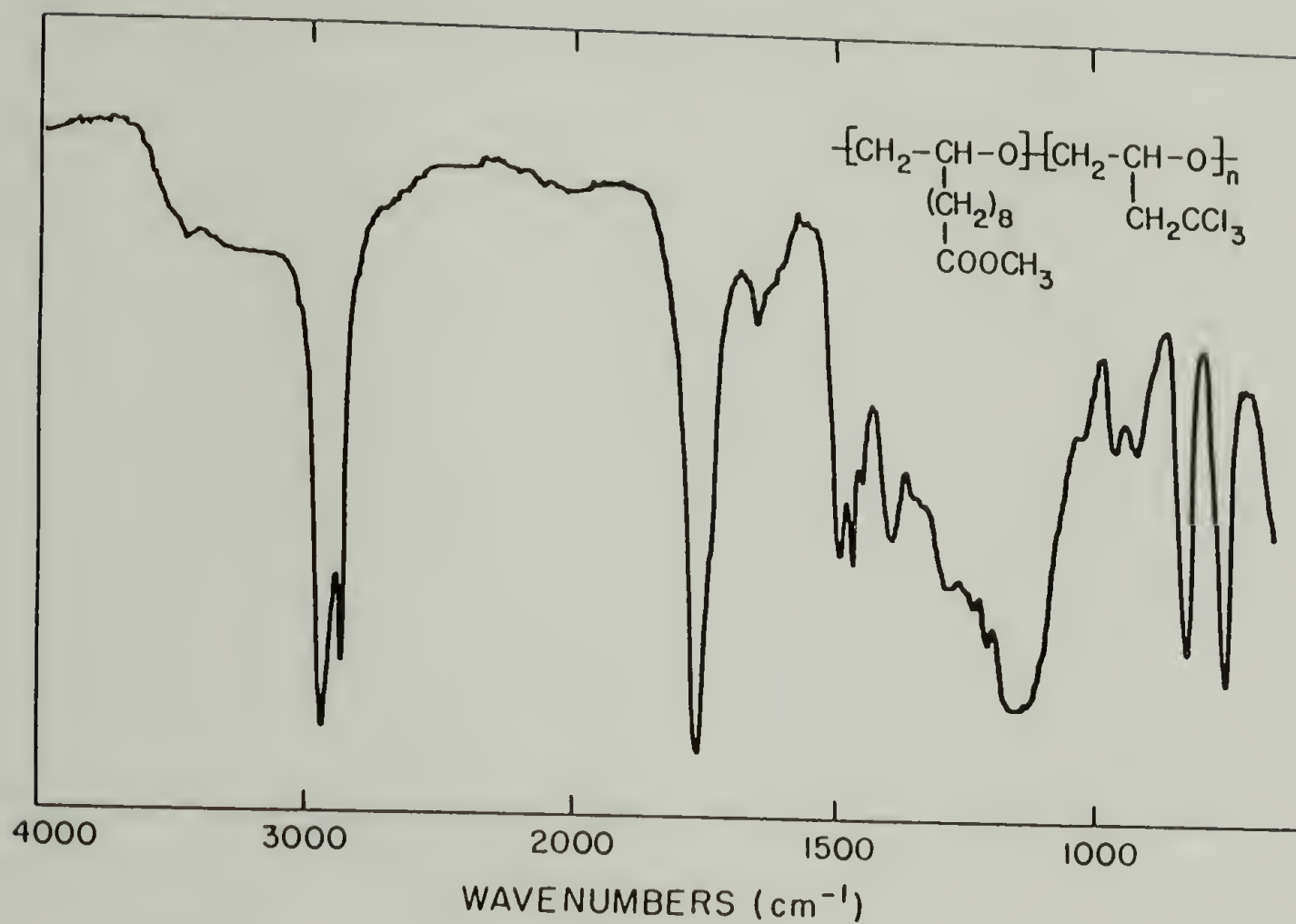


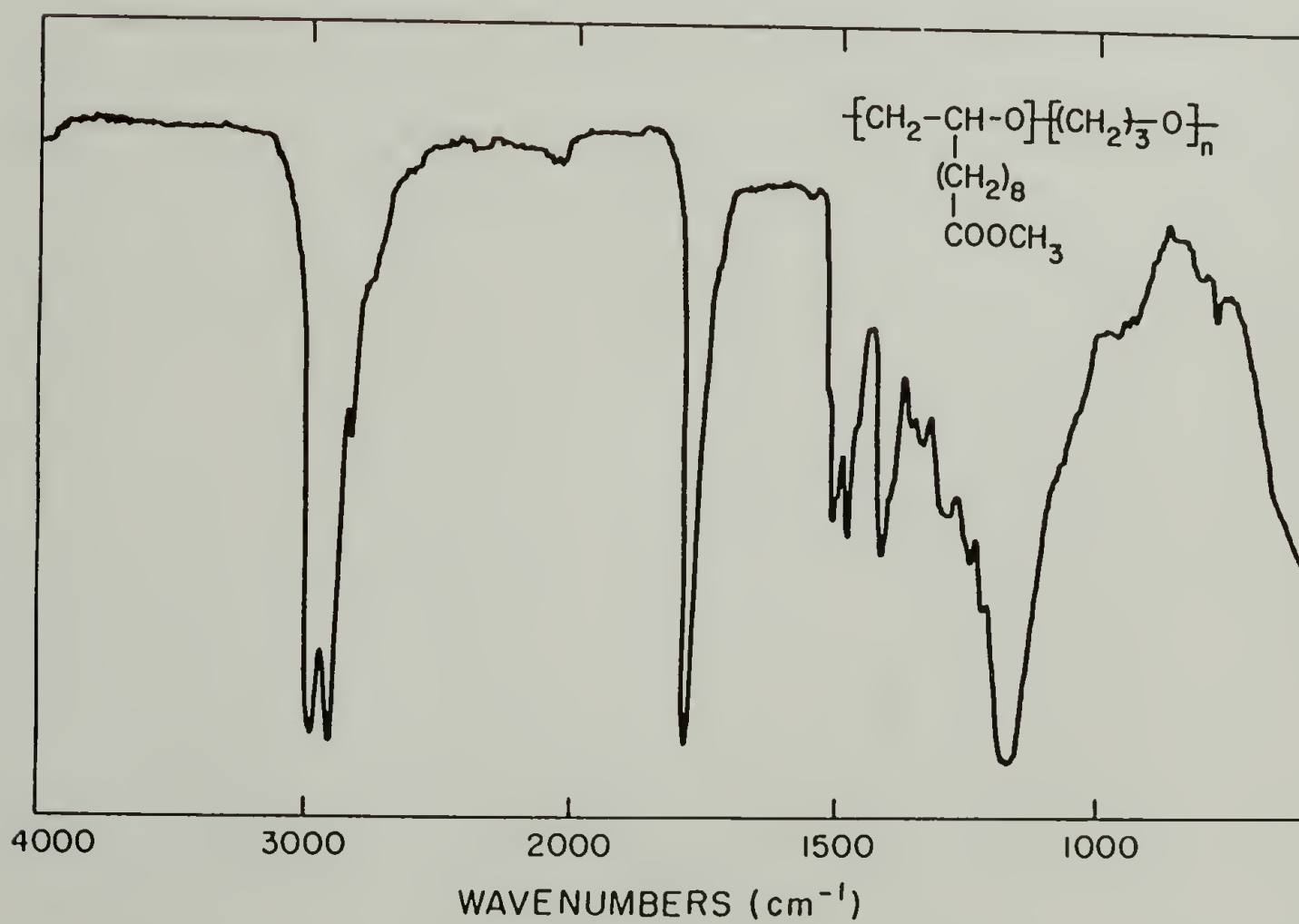
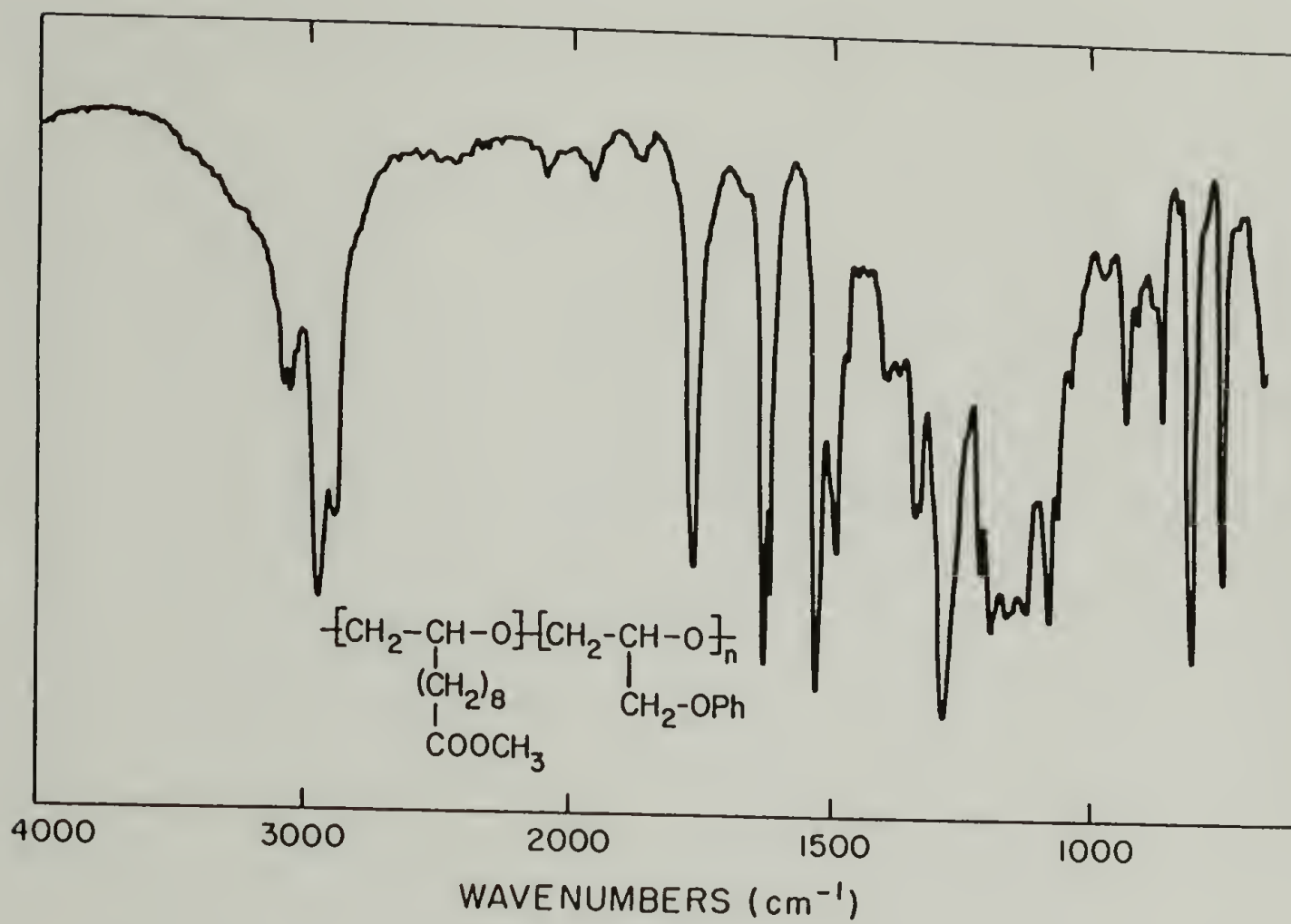


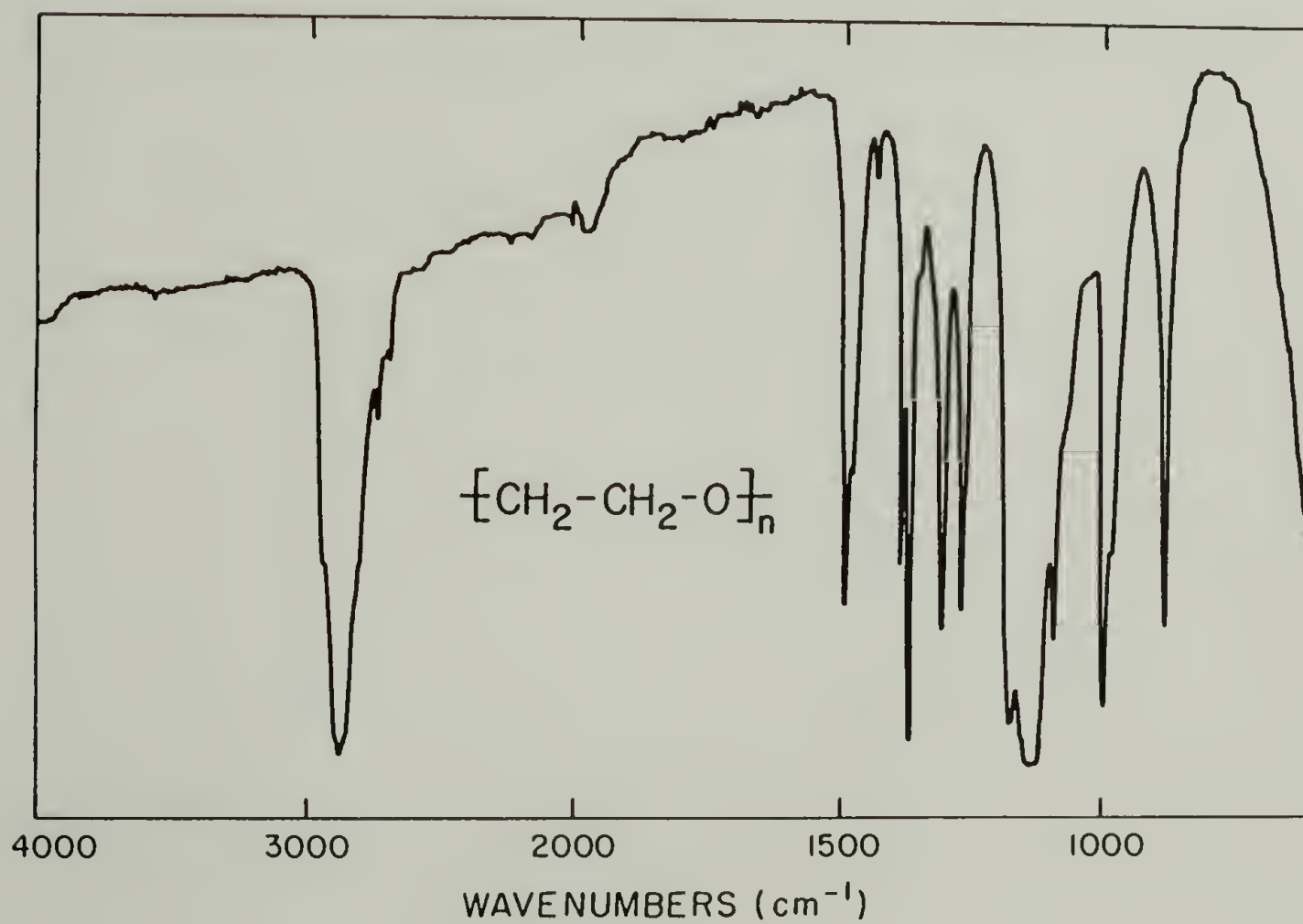
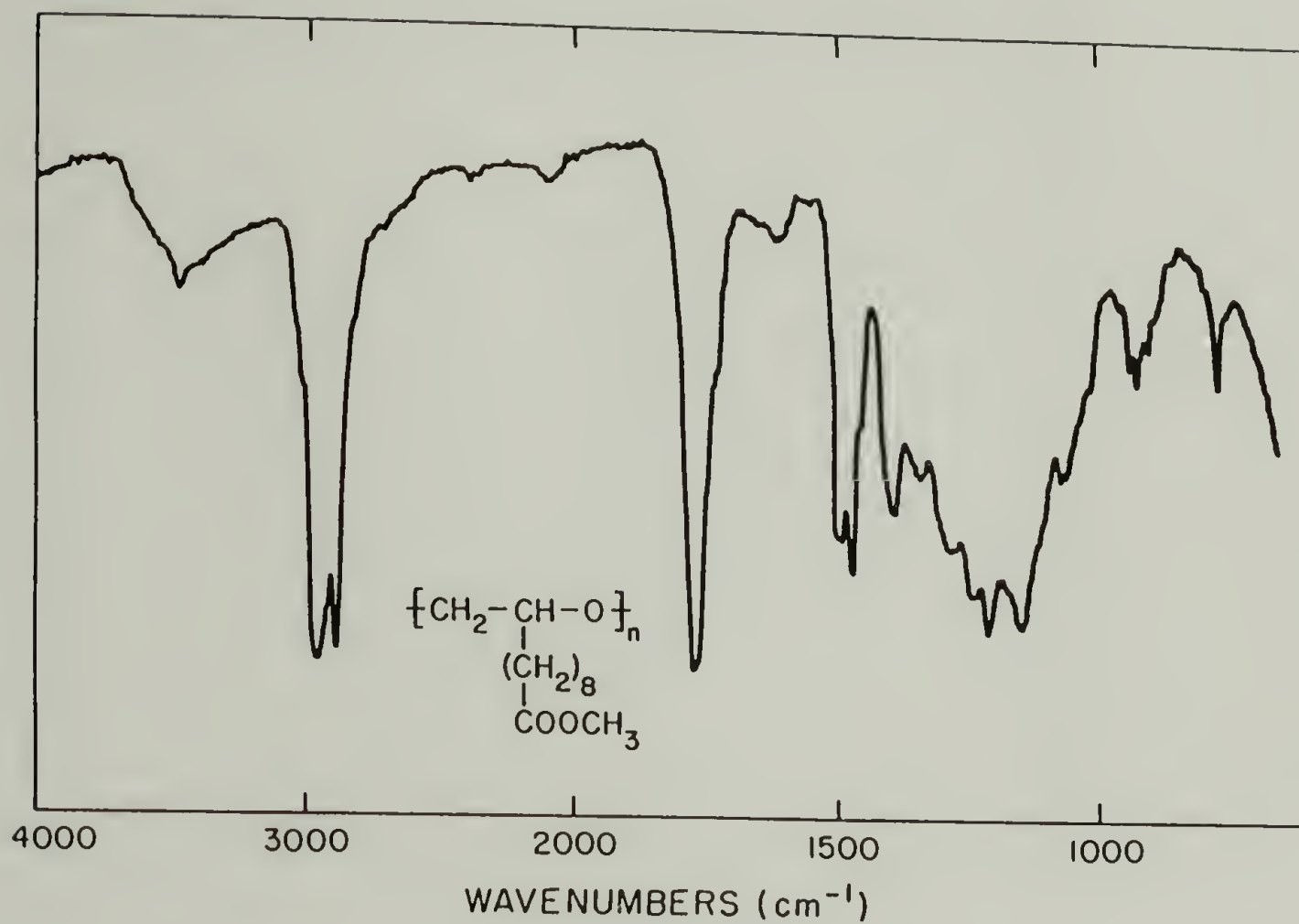


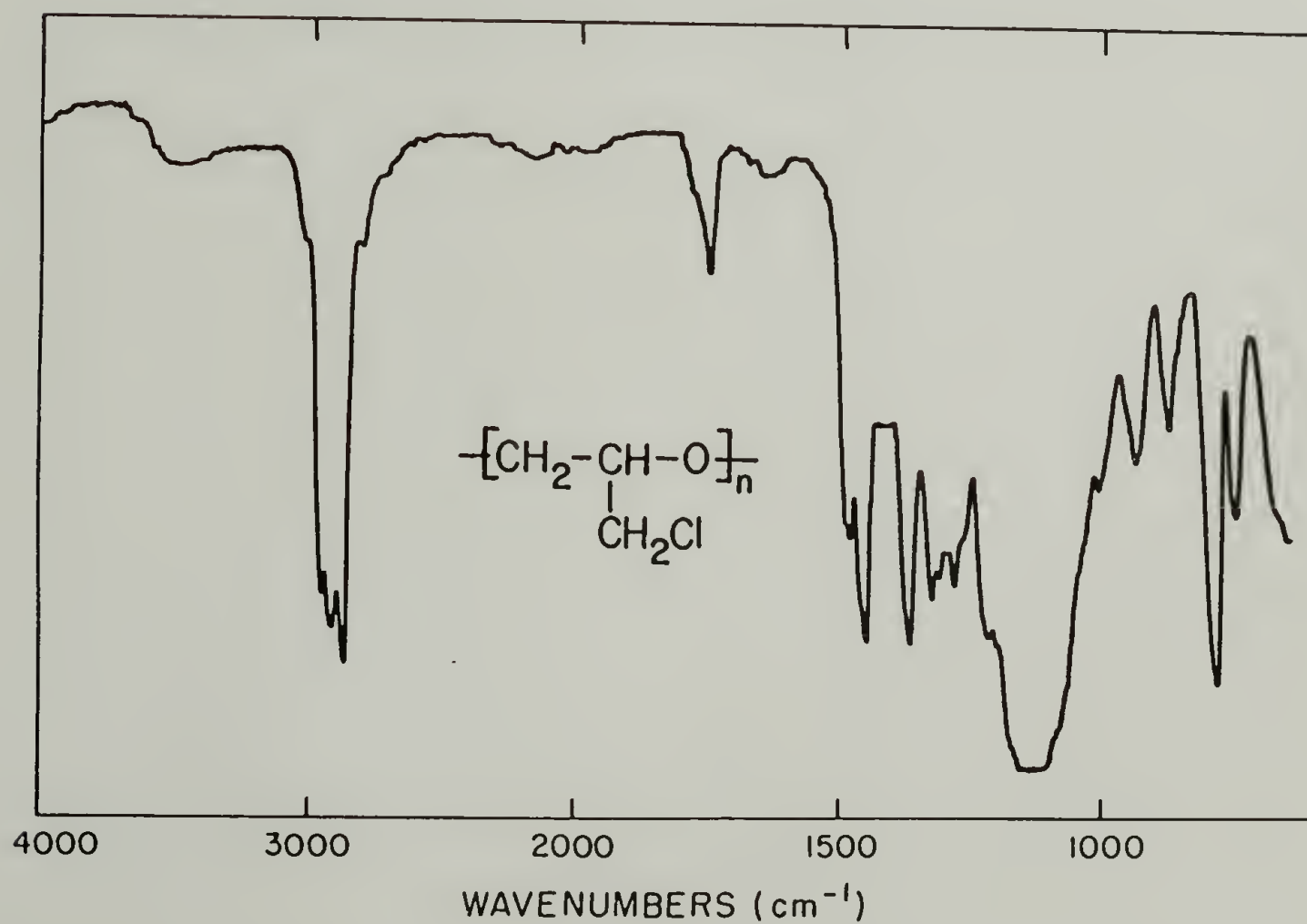
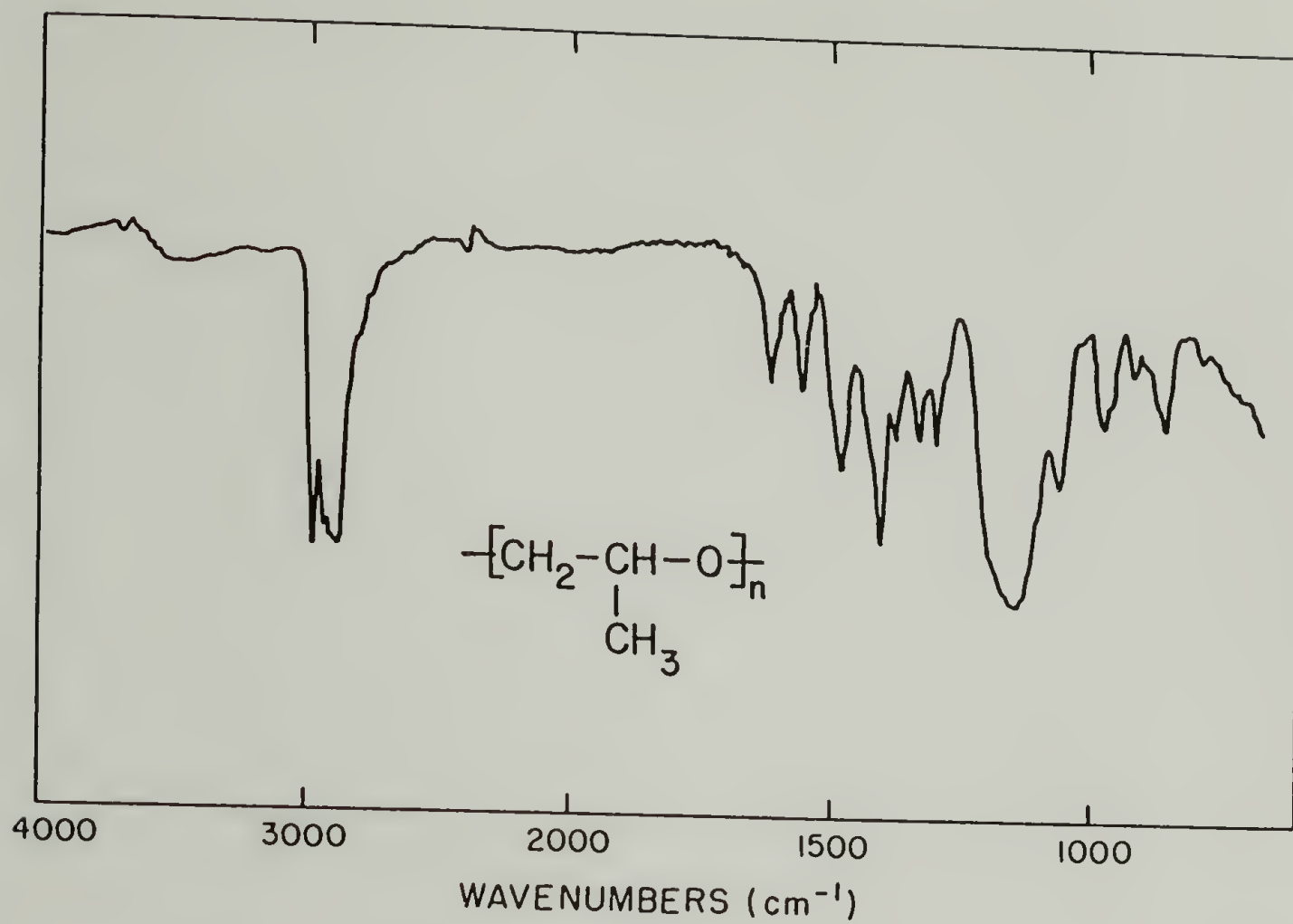


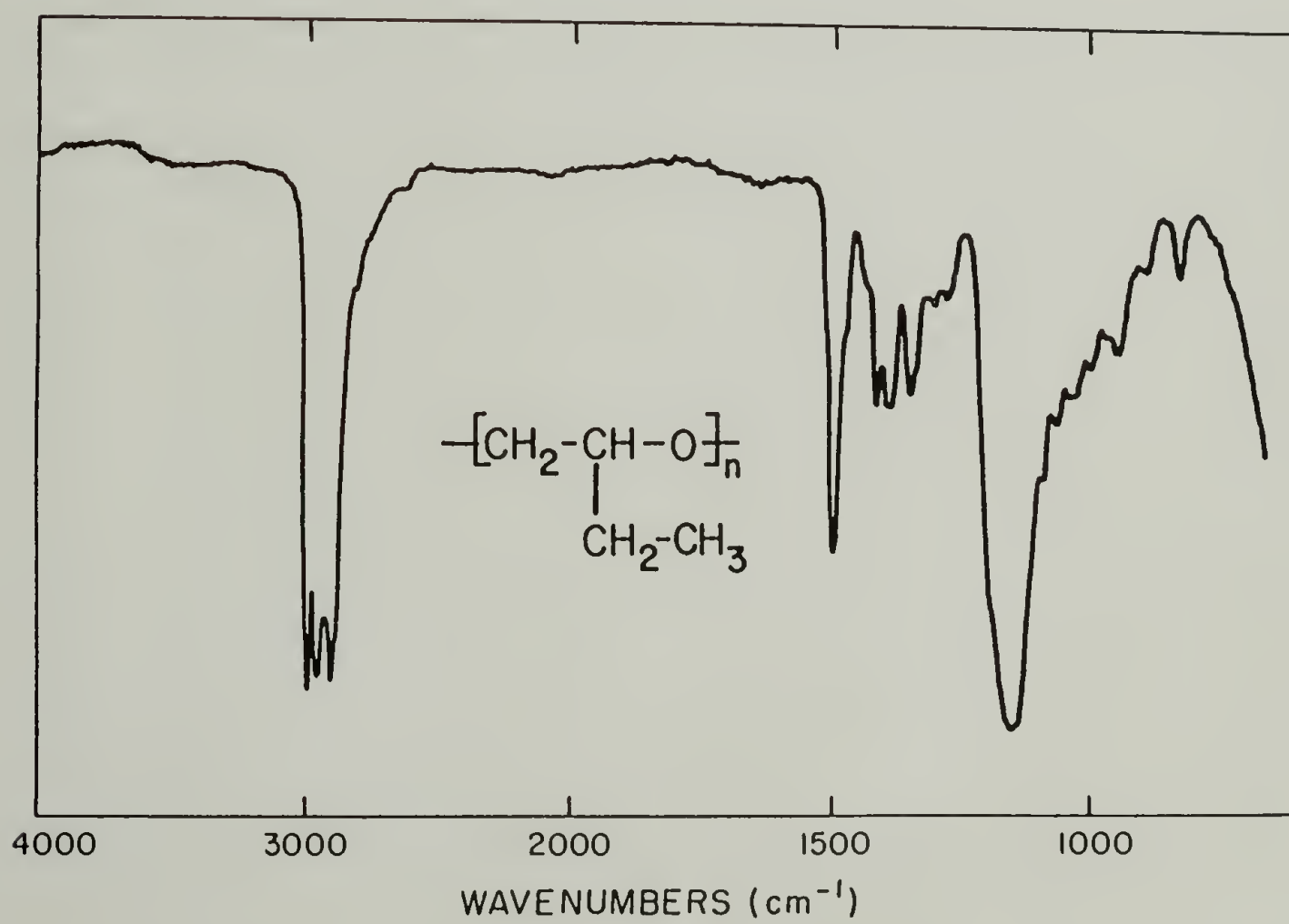
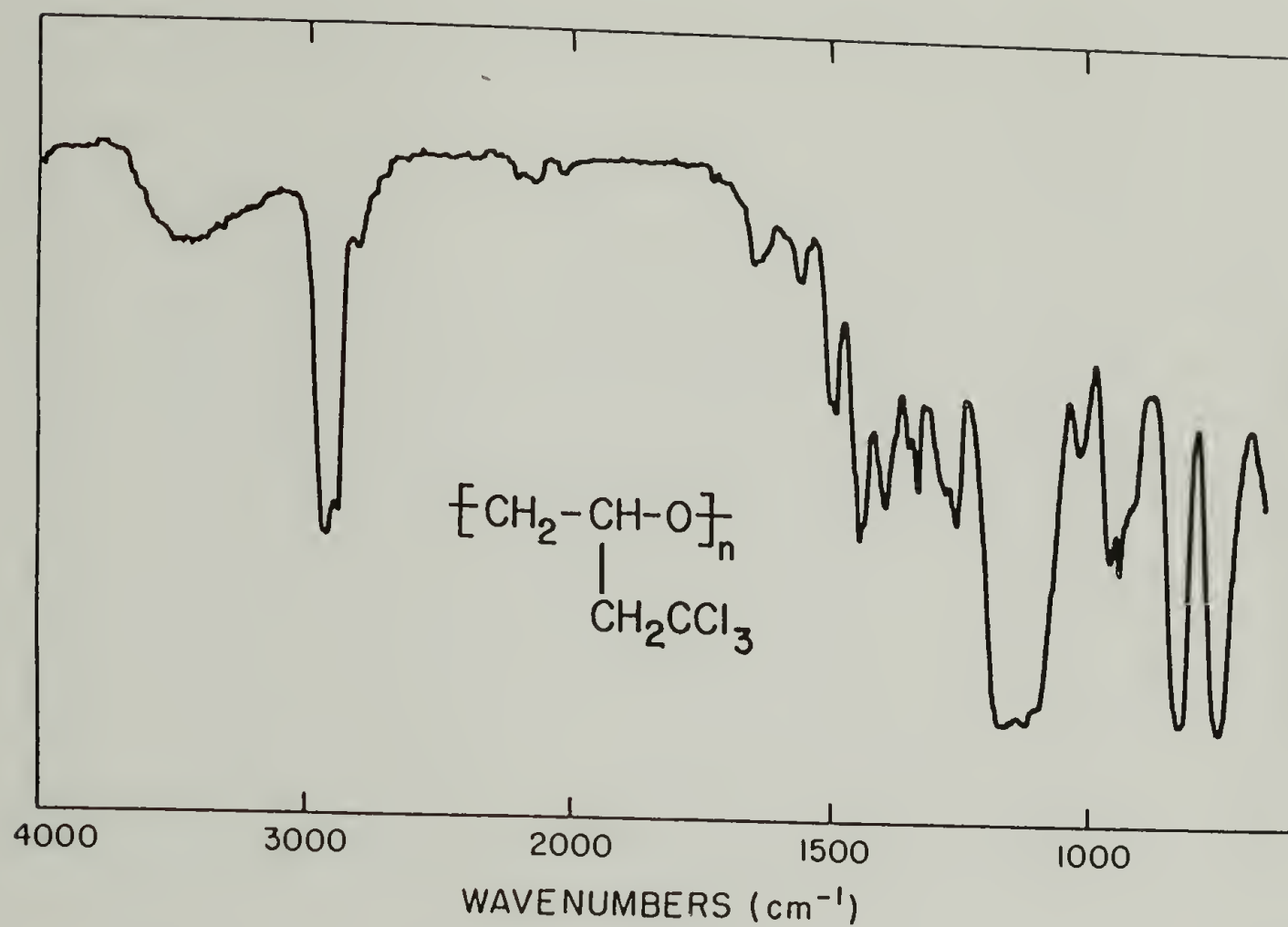


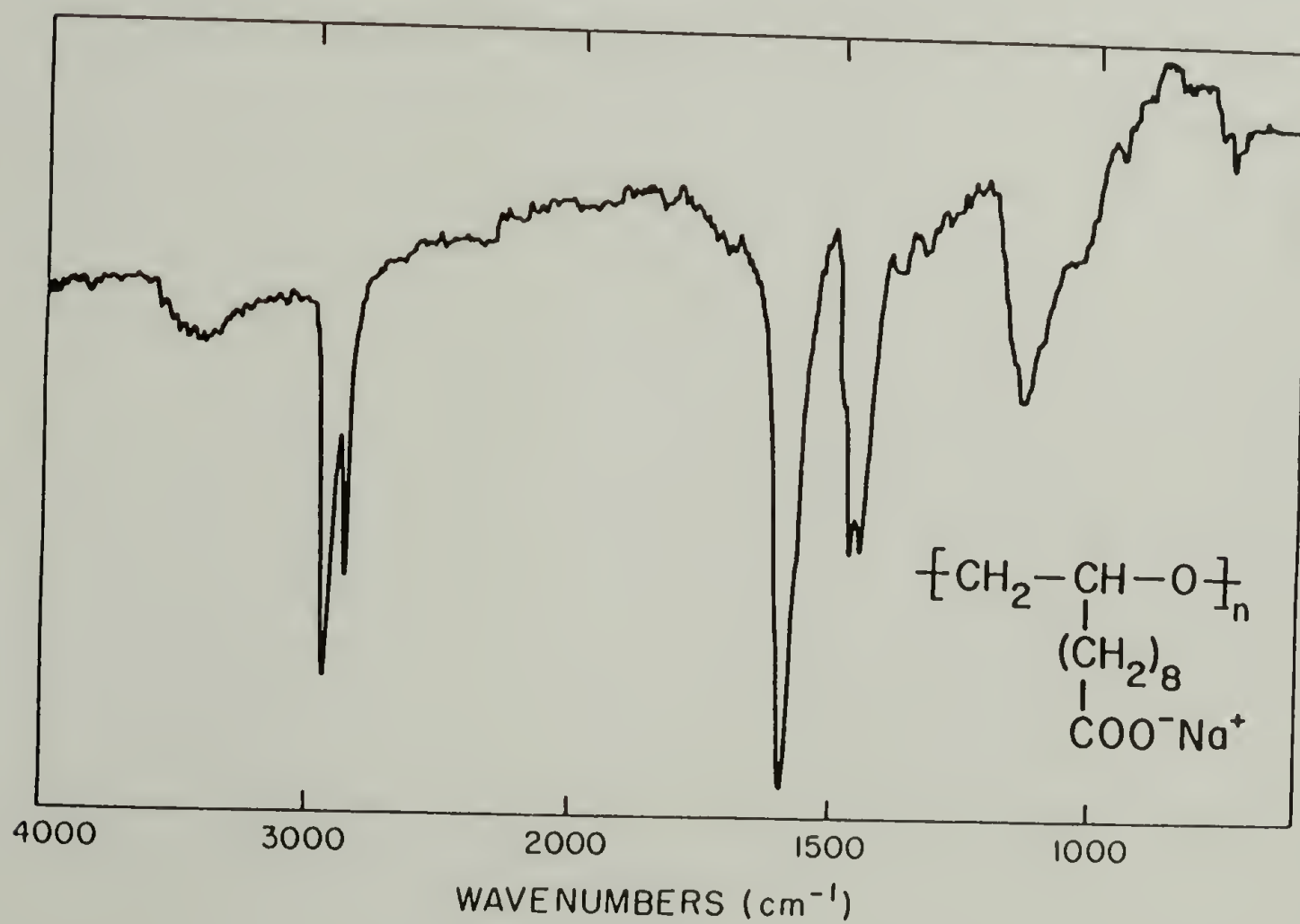
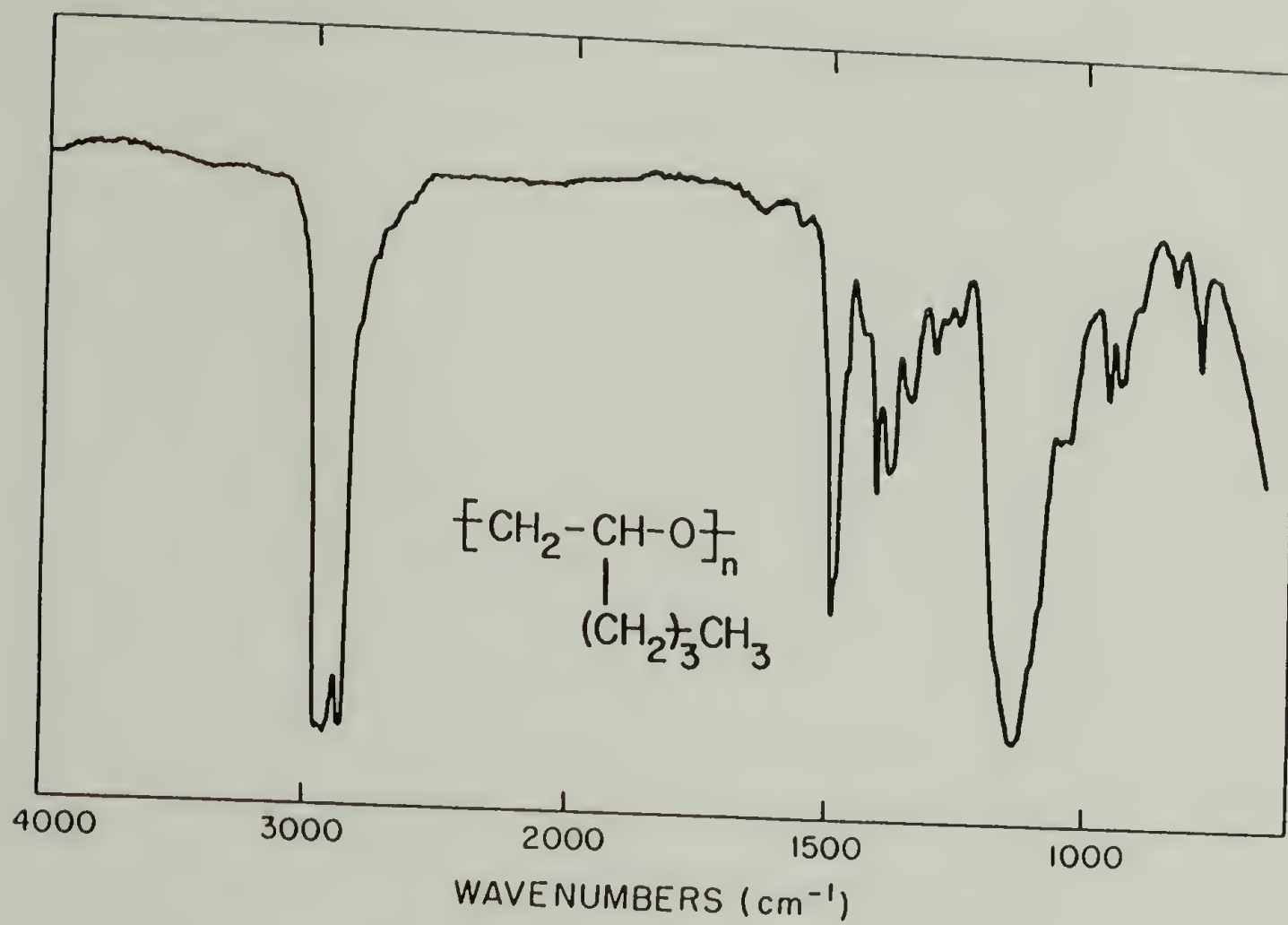


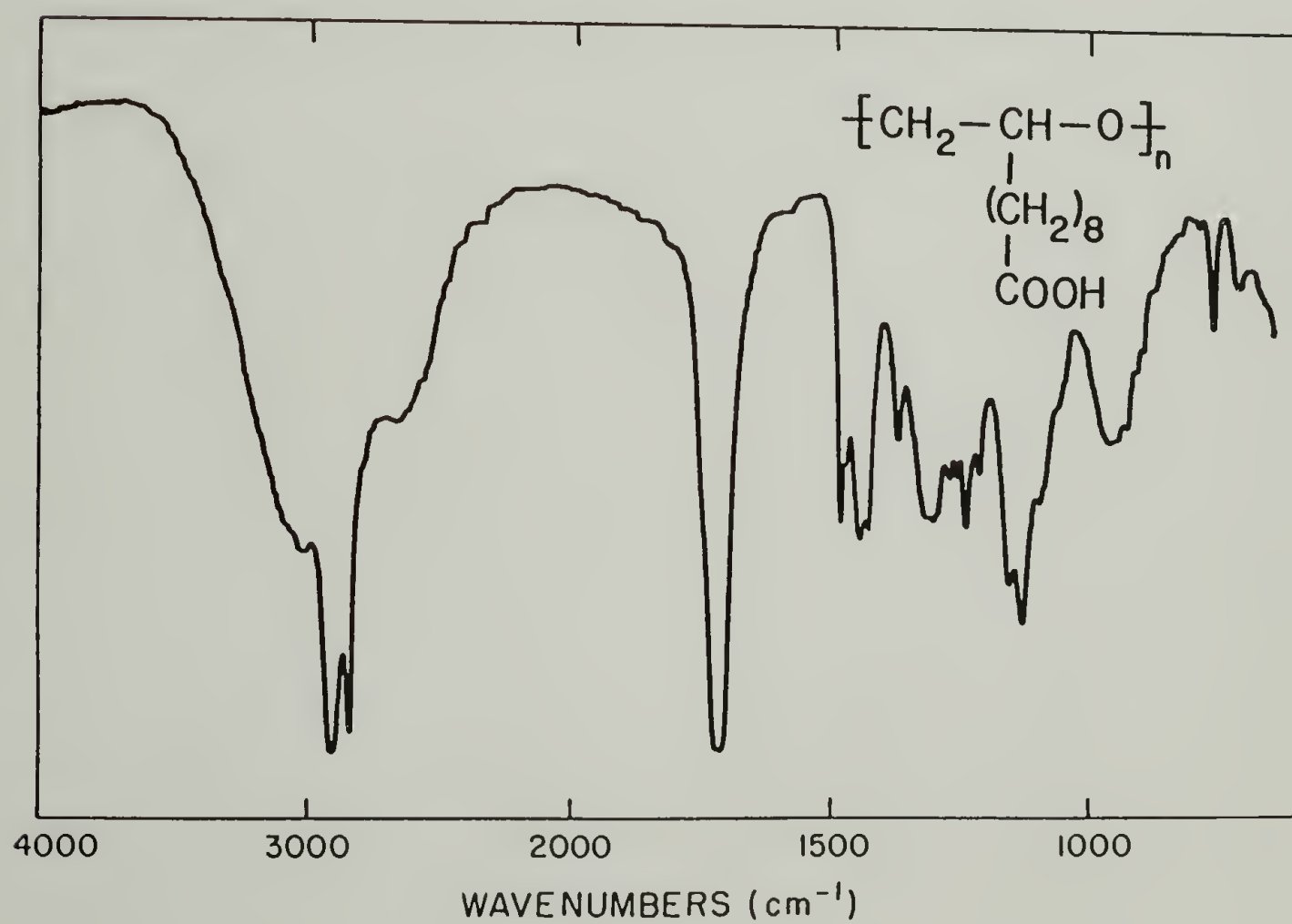
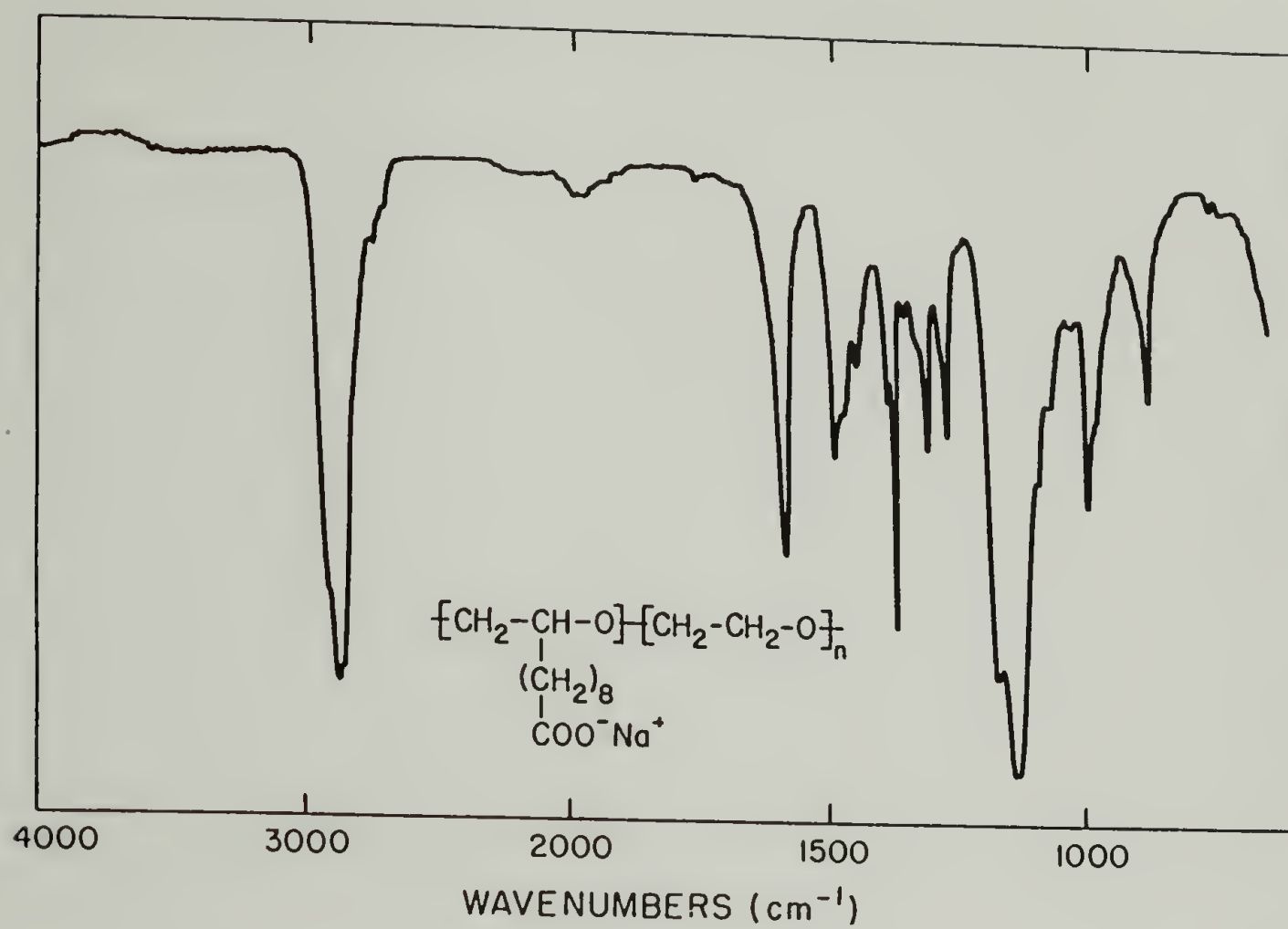


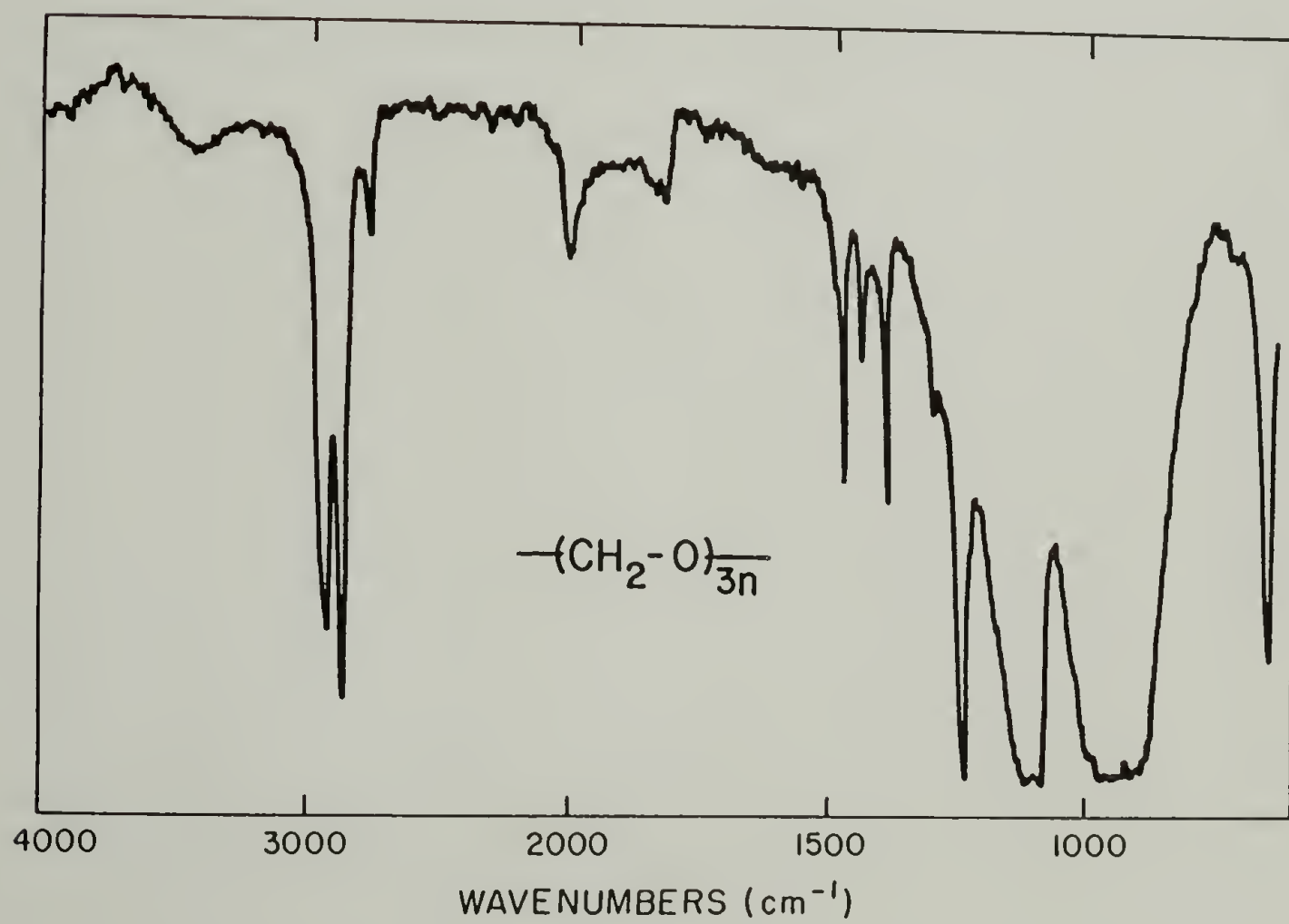
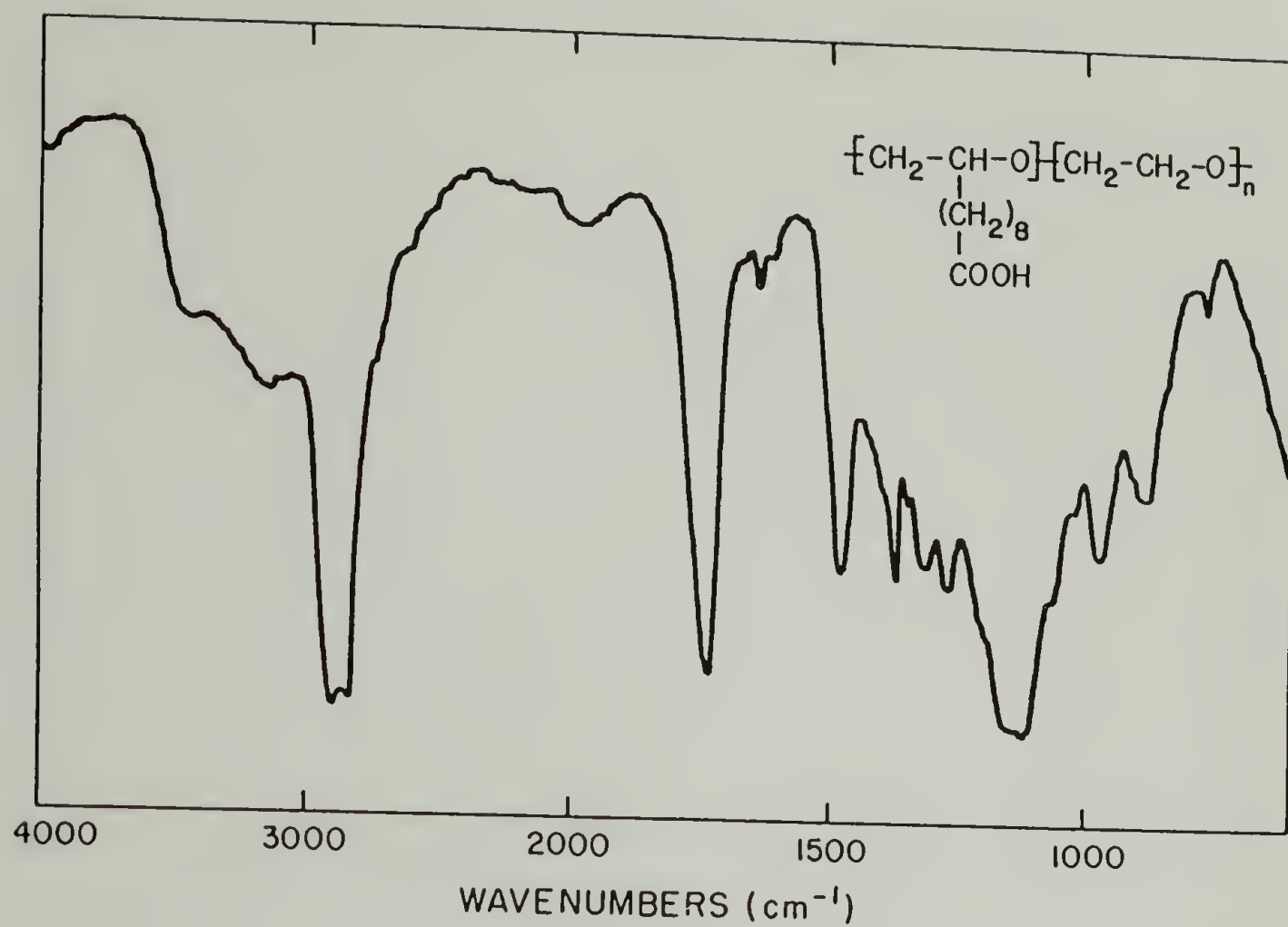


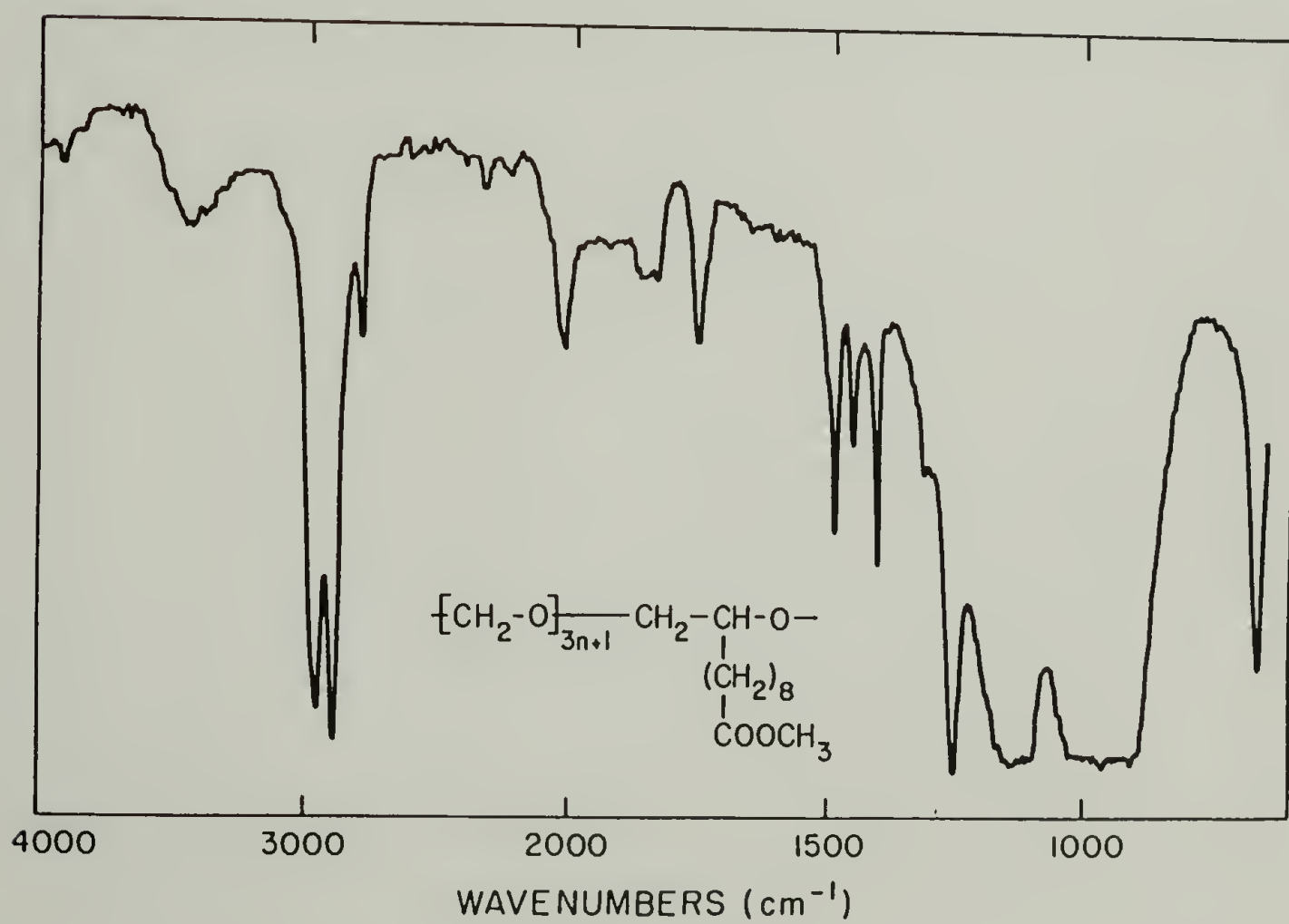
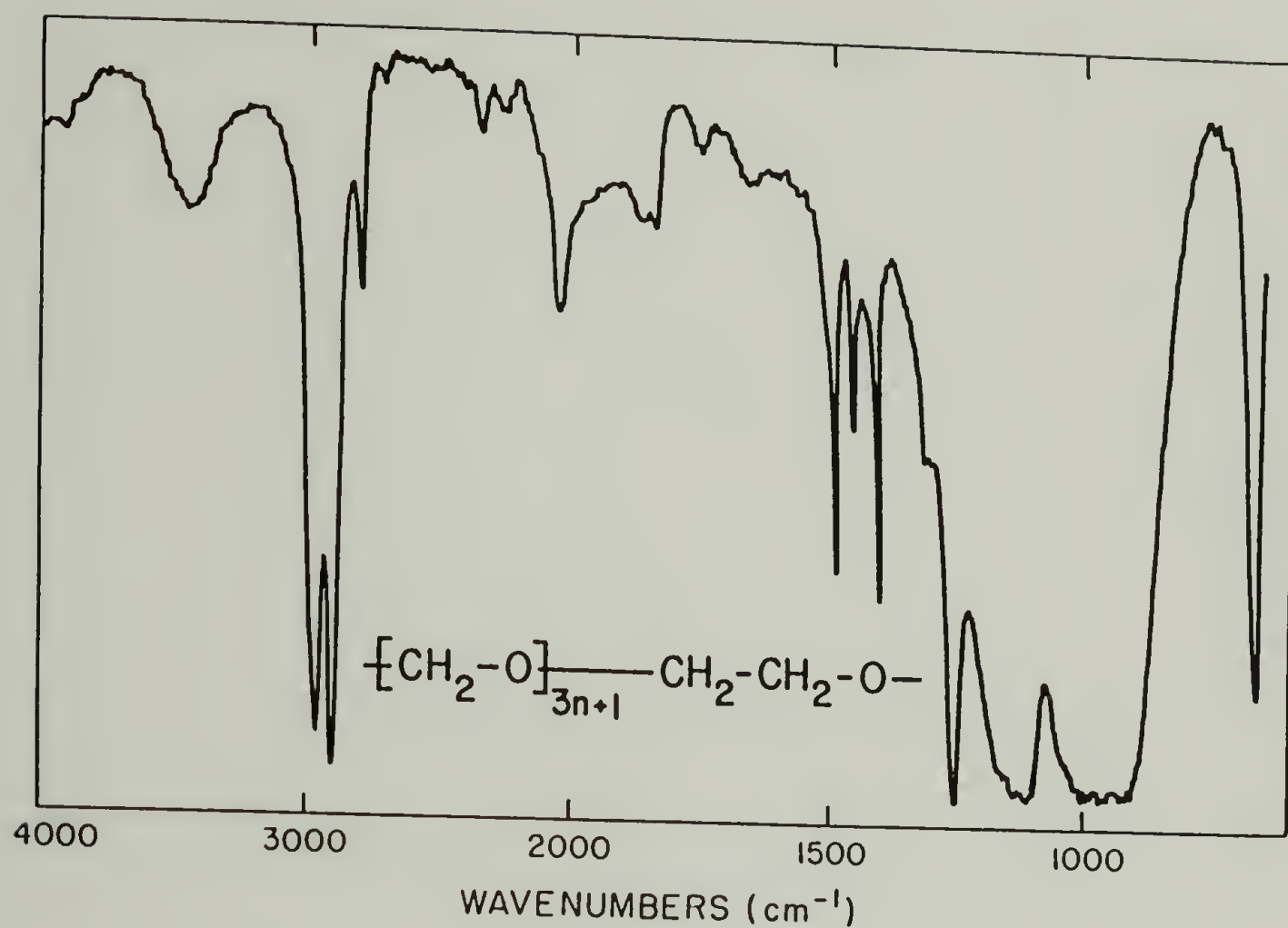


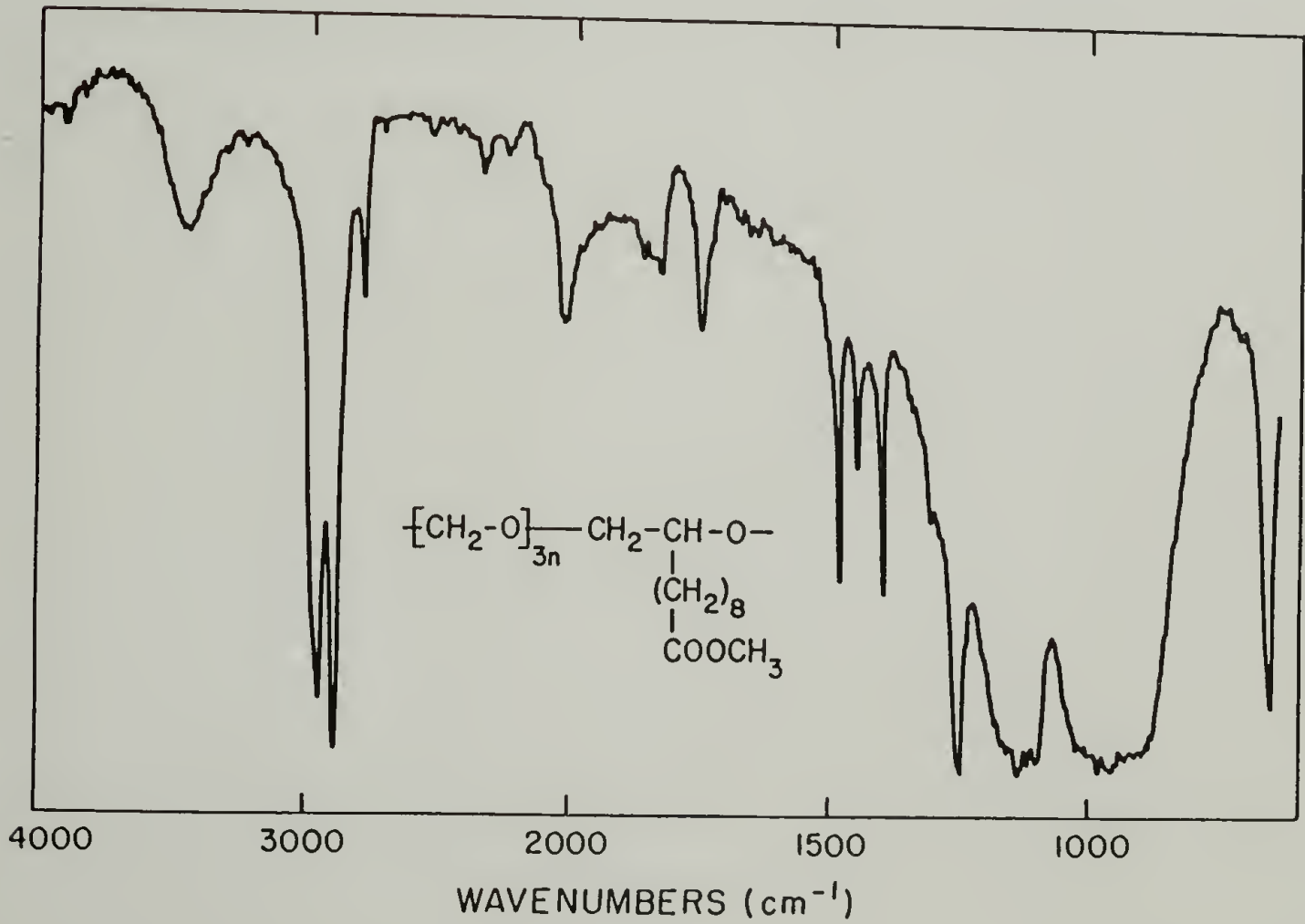
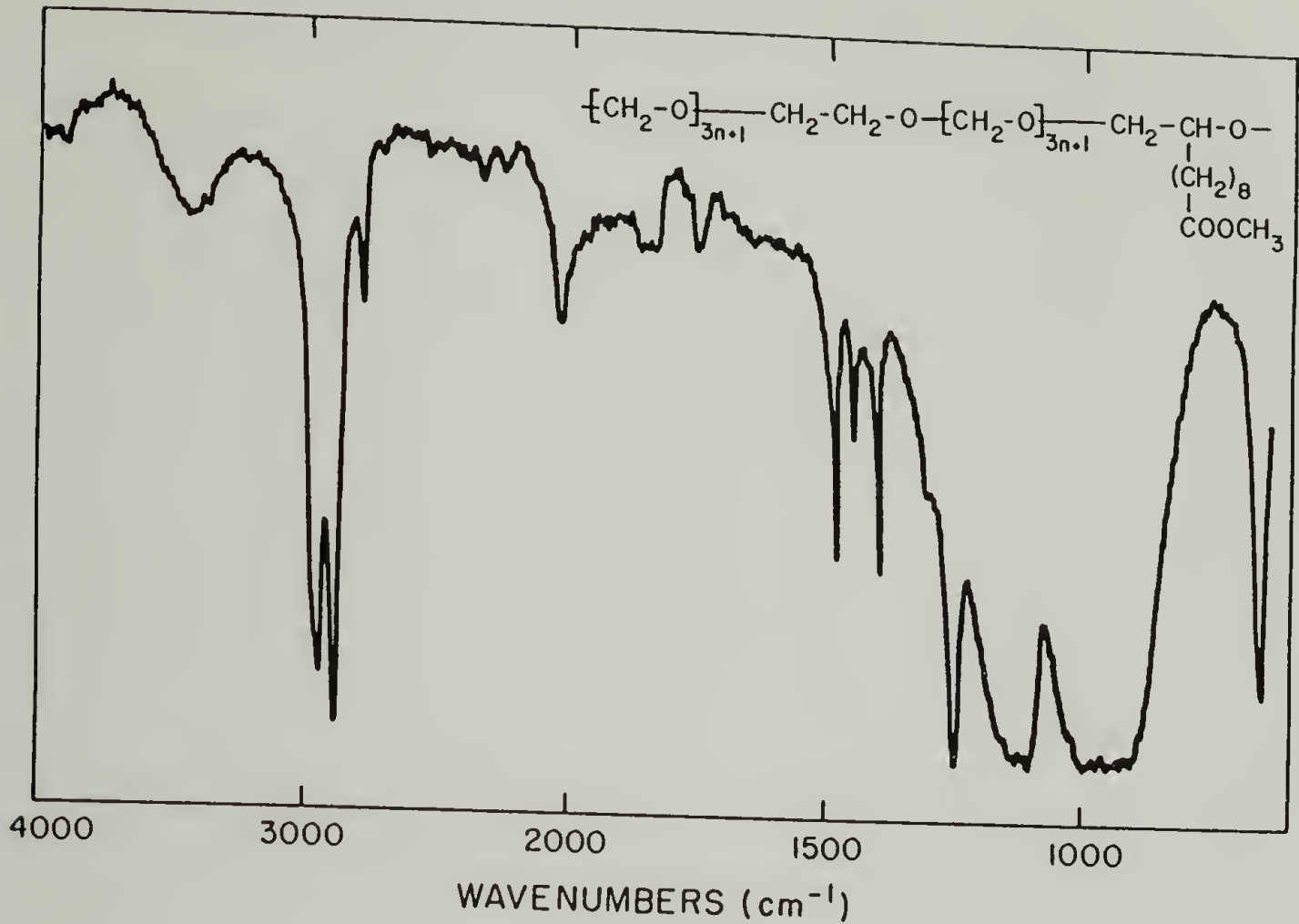


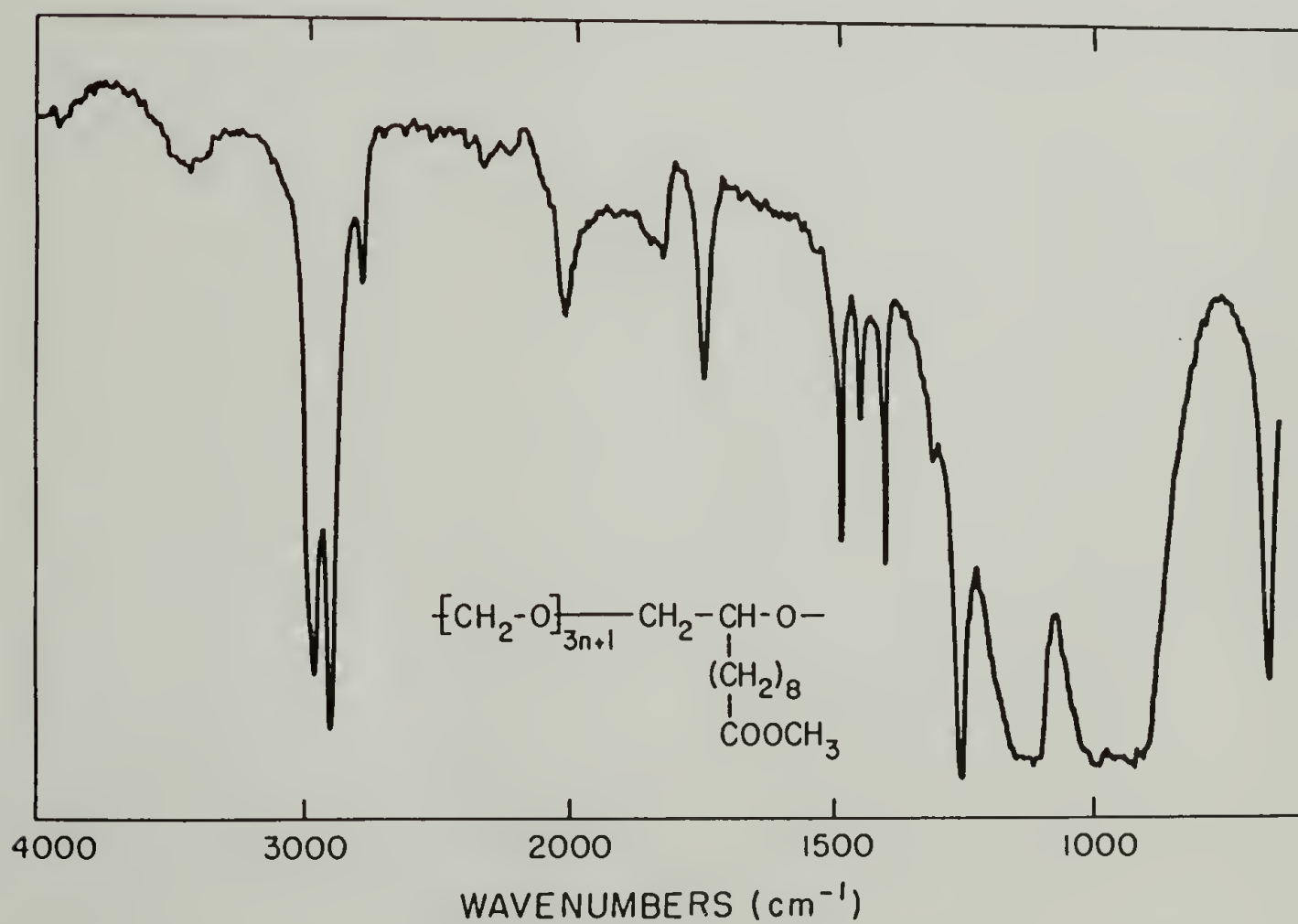
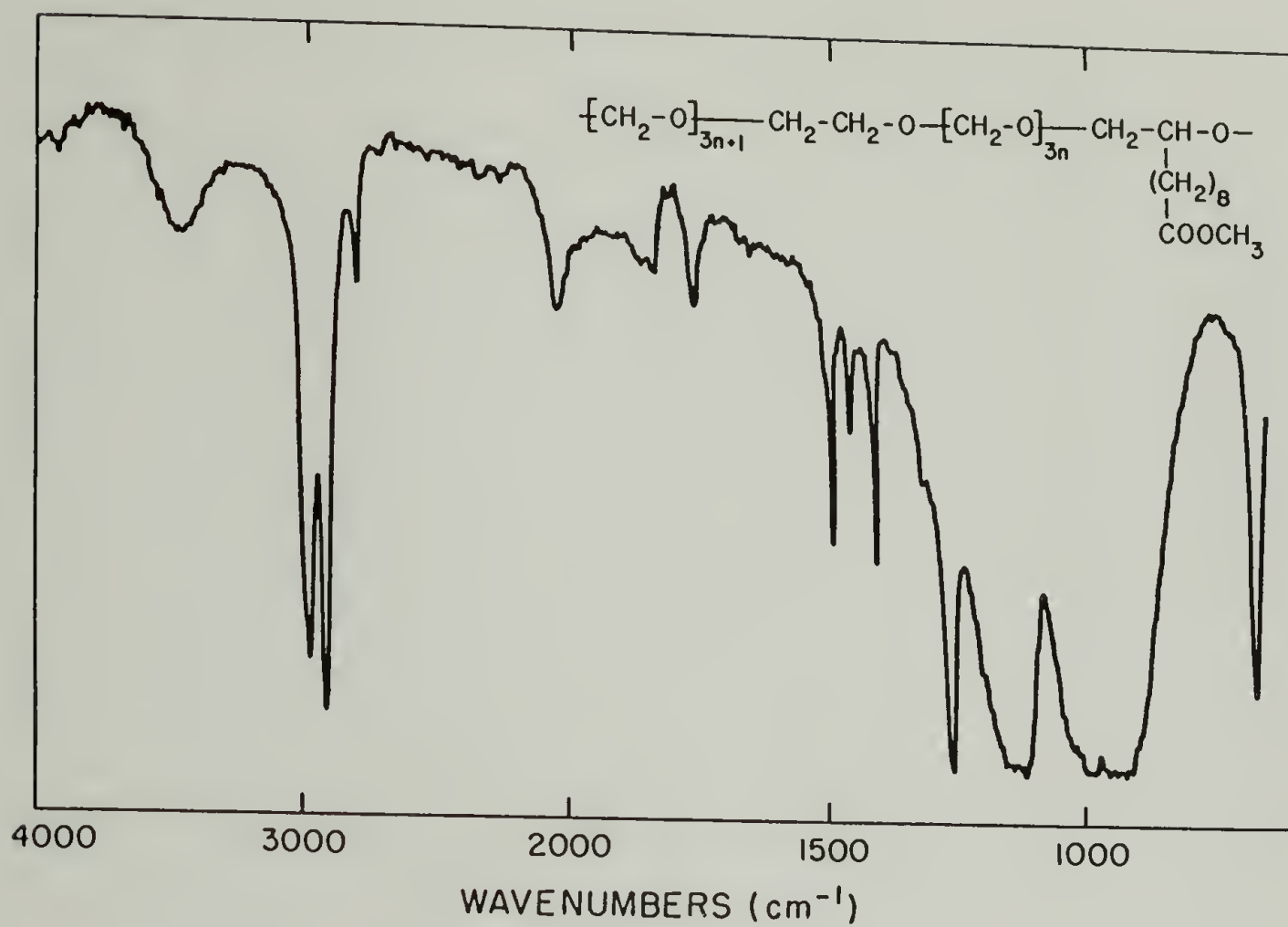


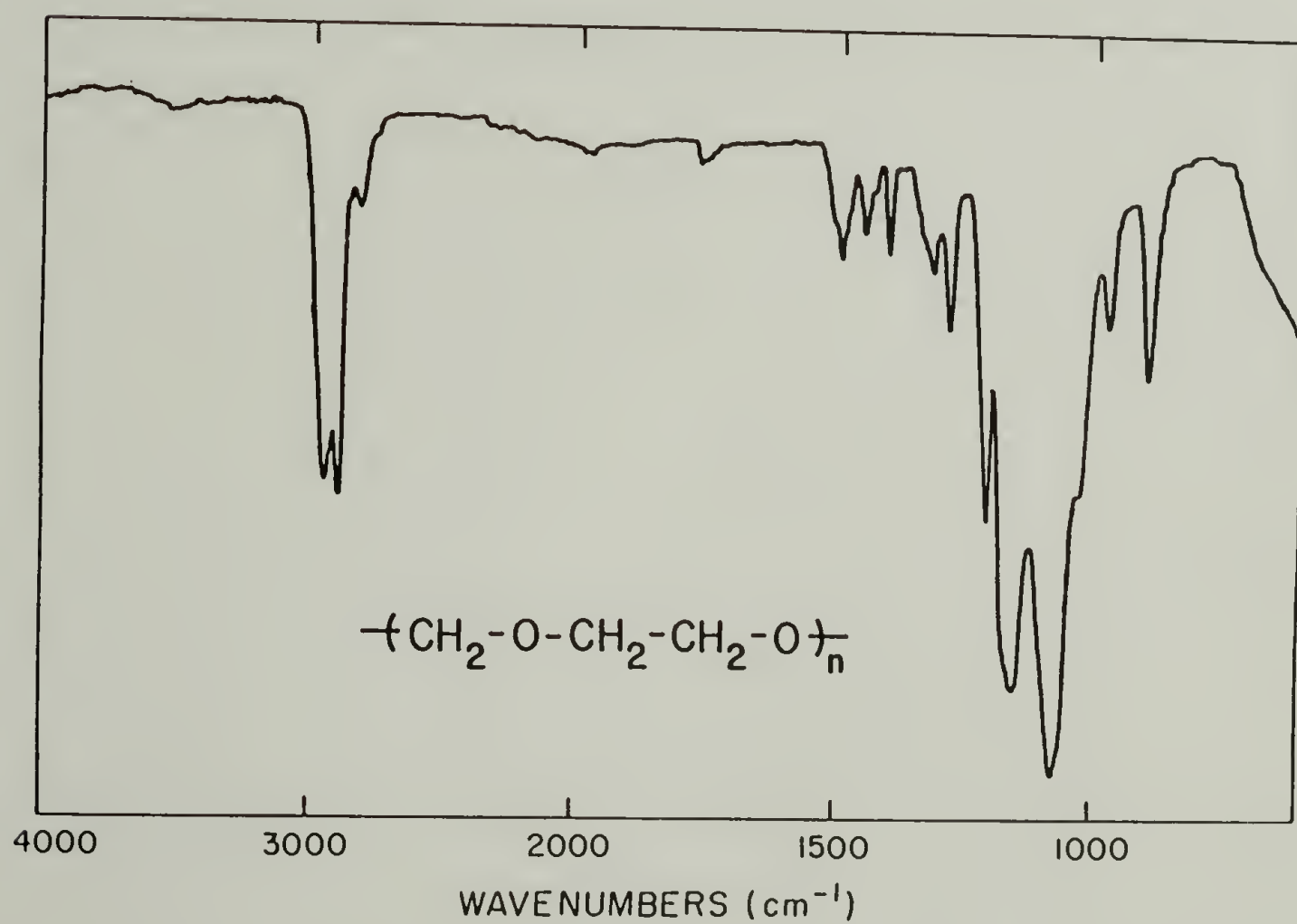
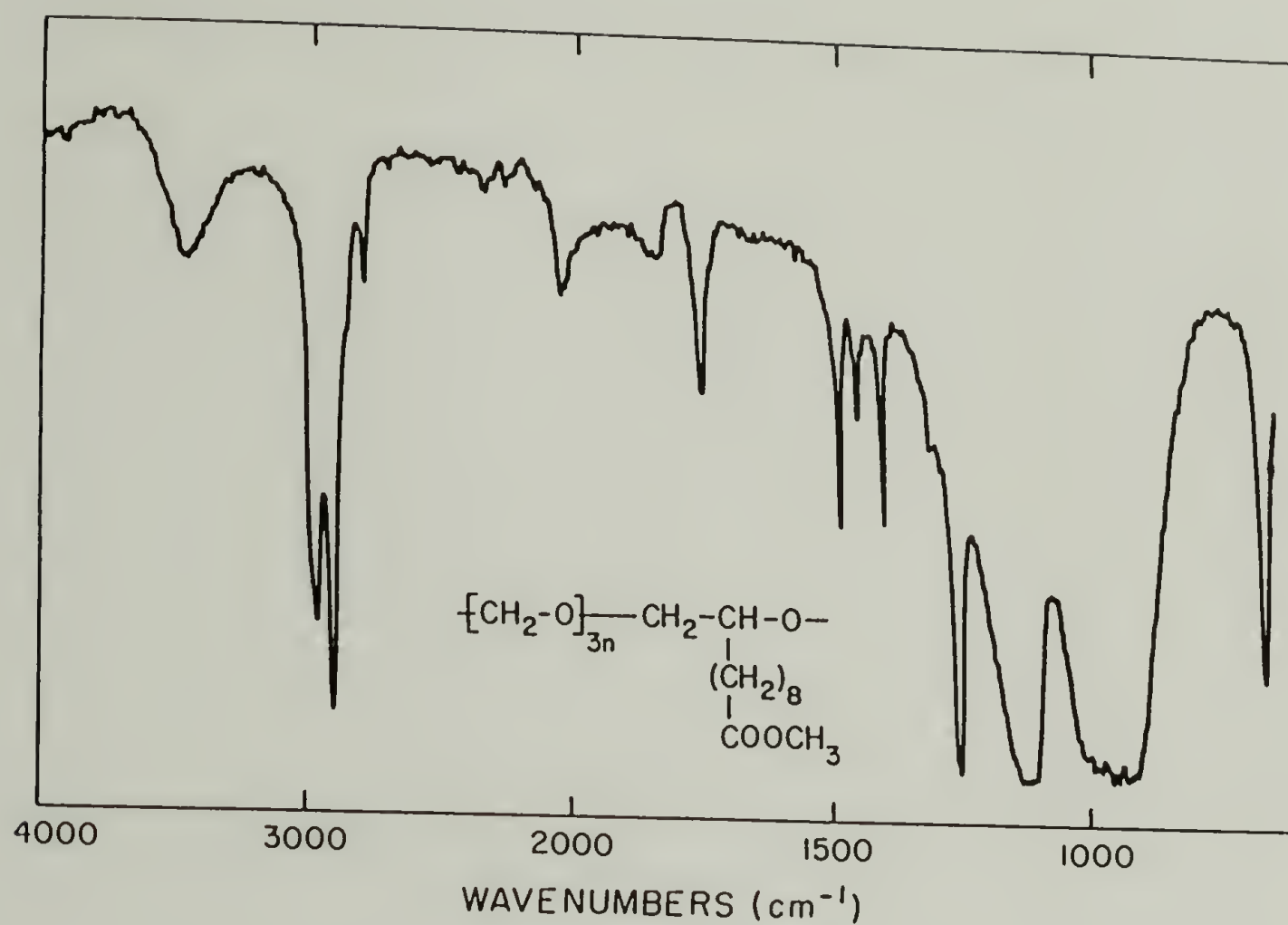




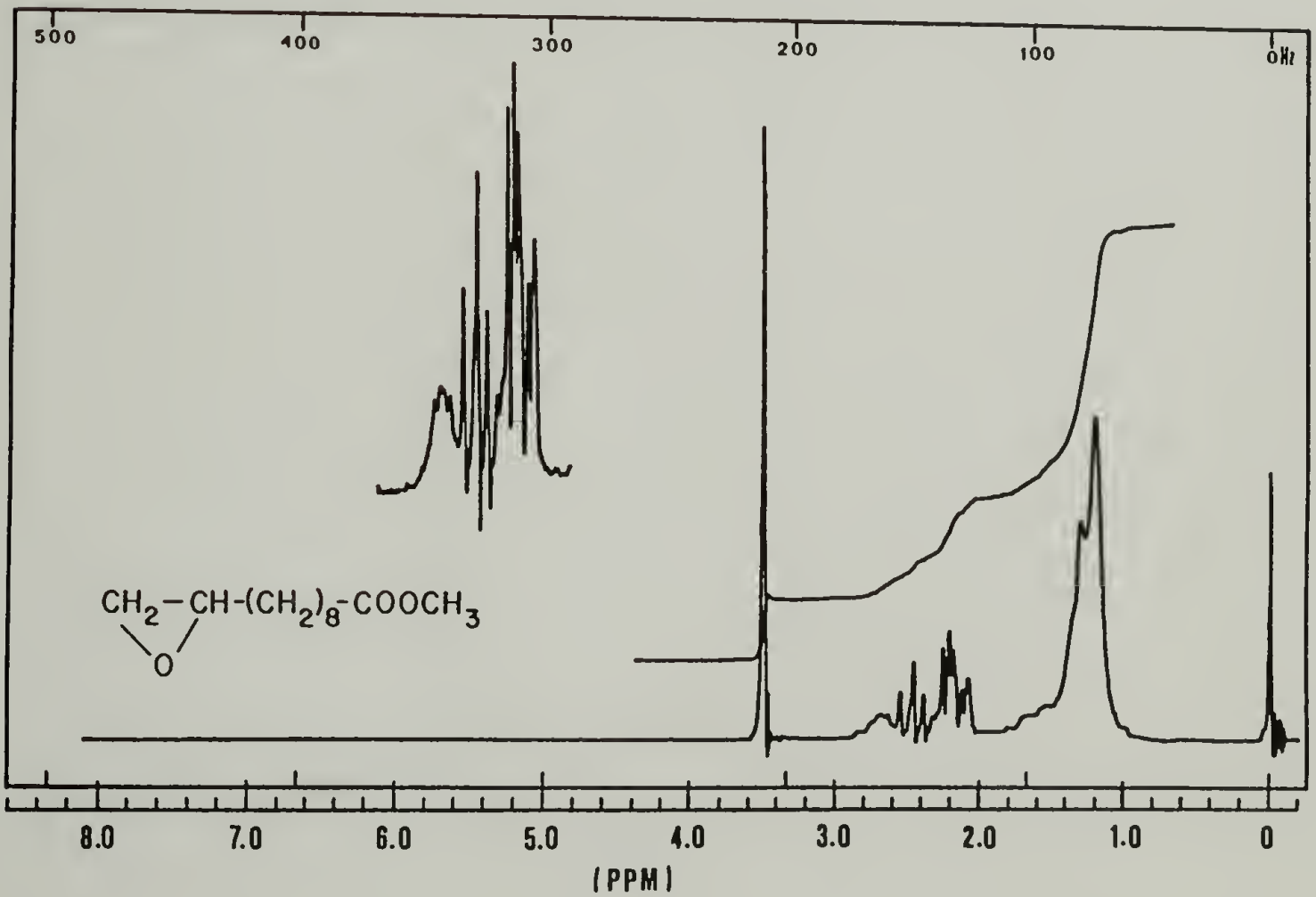
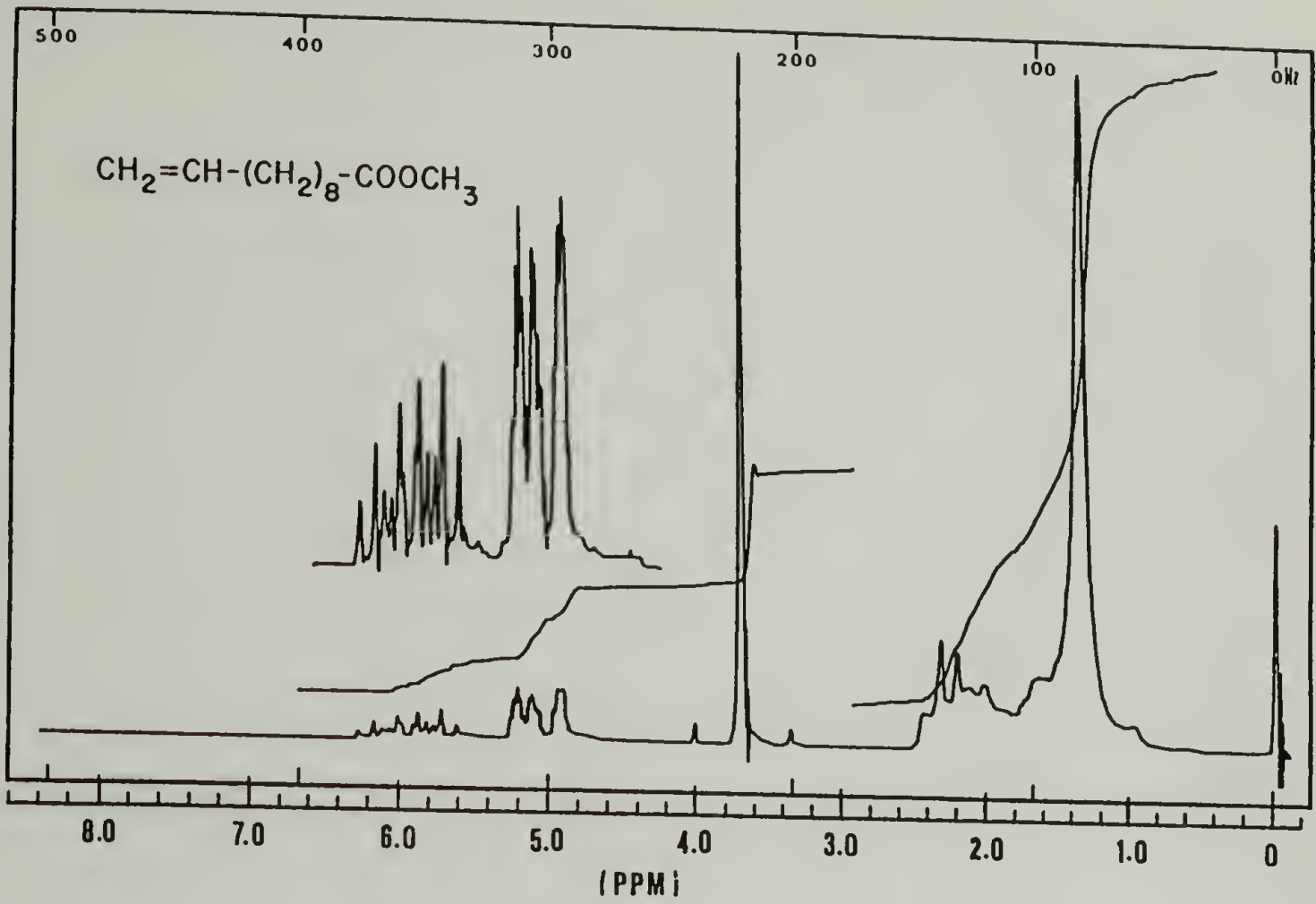


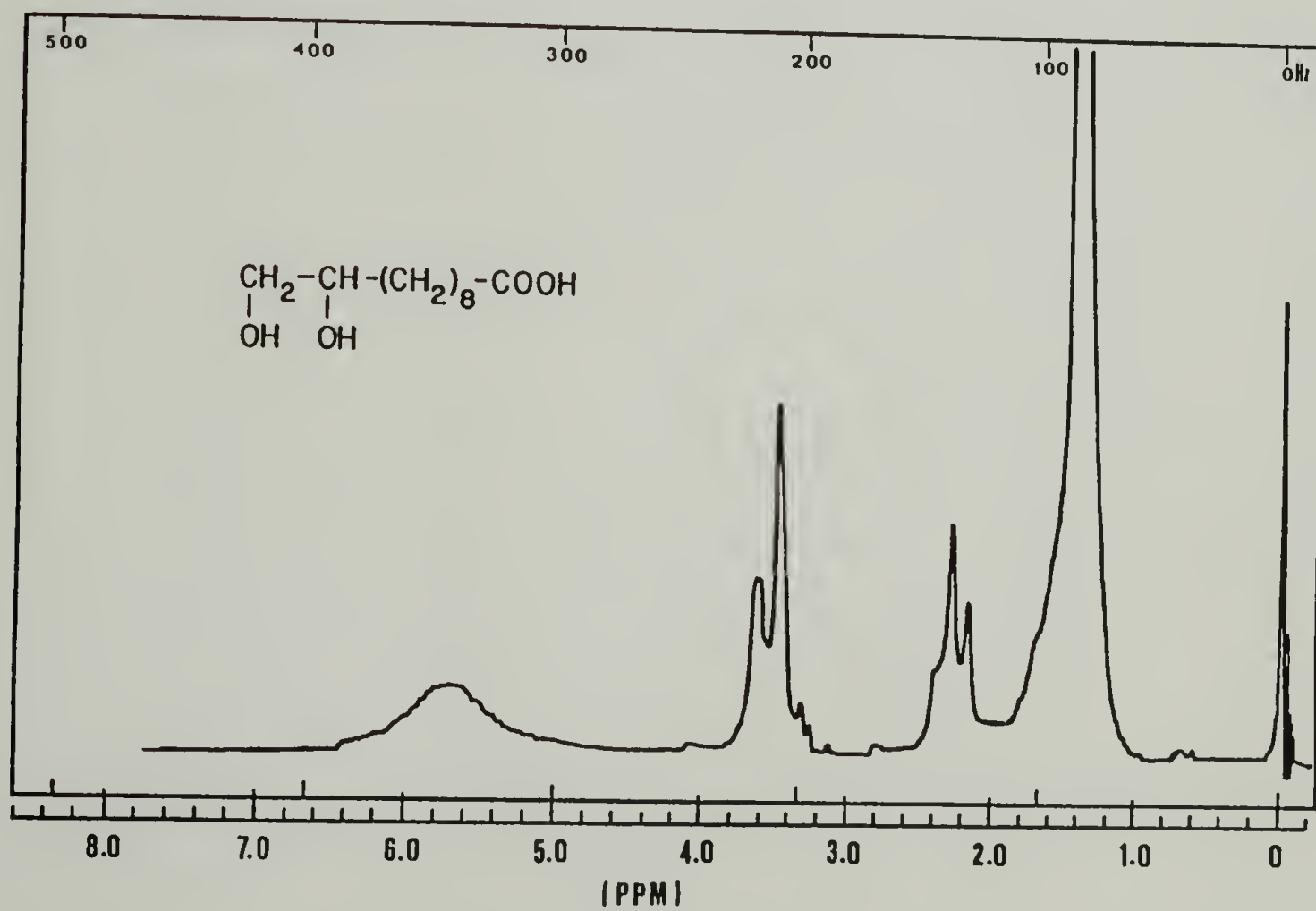
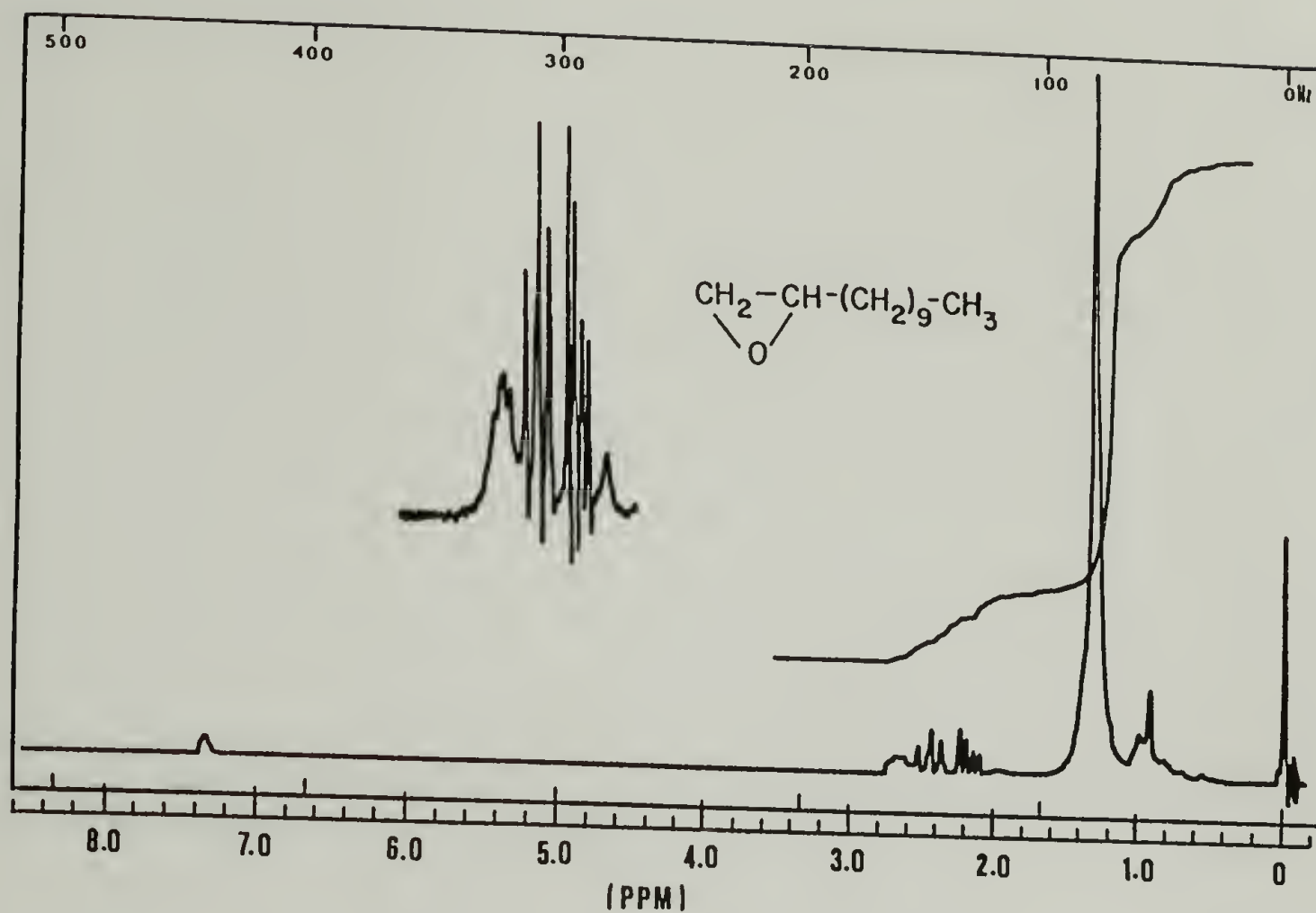


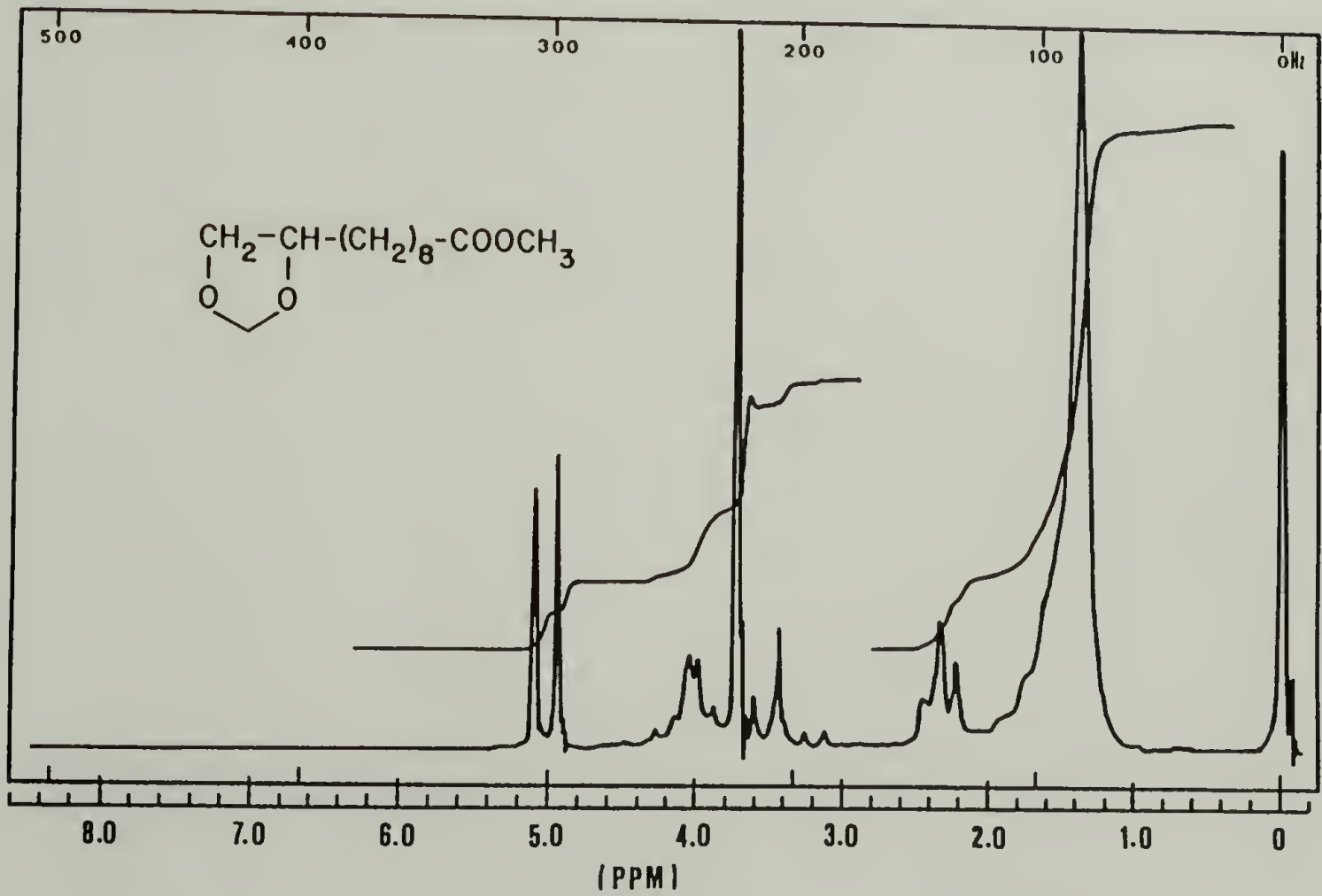
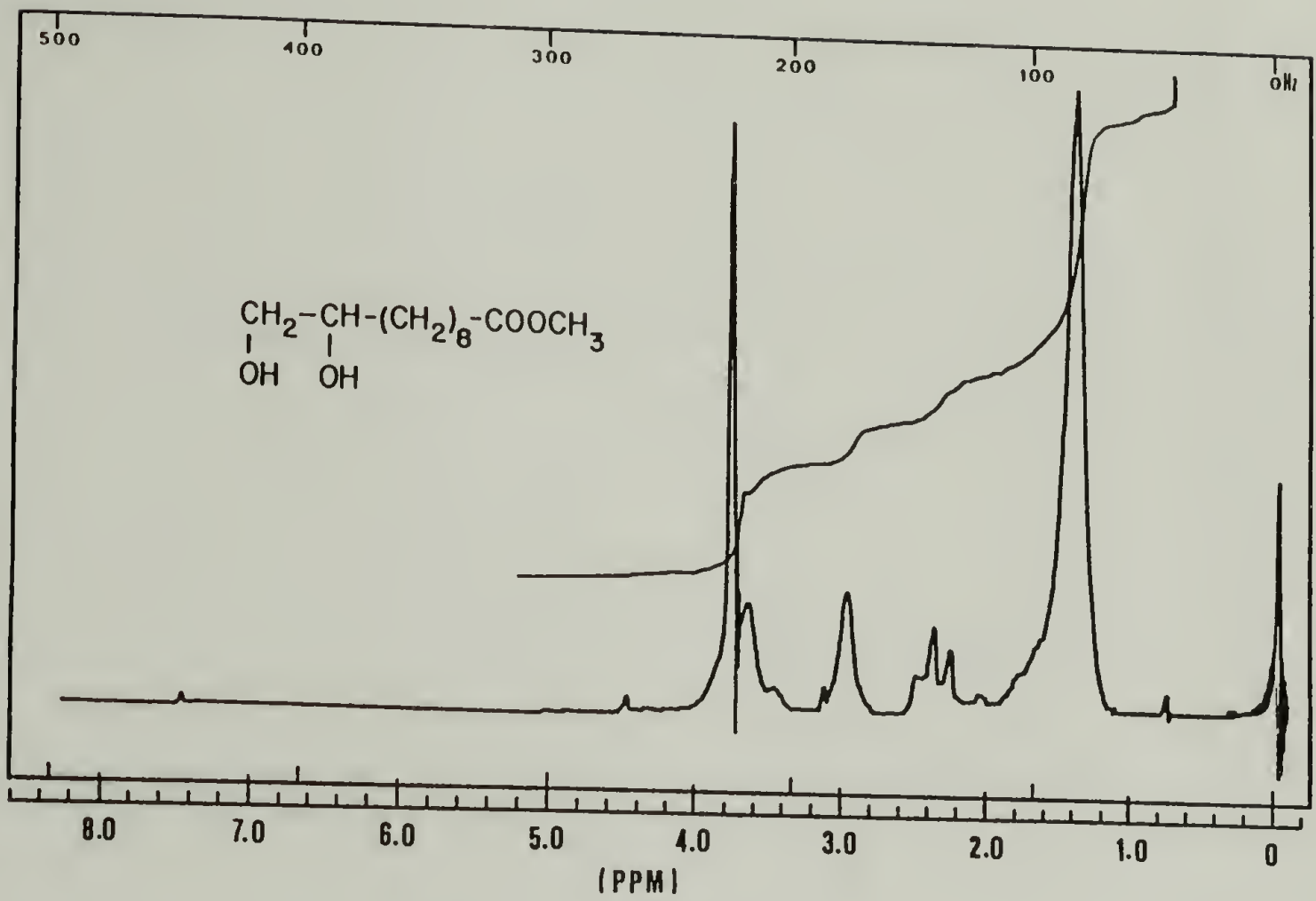




A P P E N D I X B
PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA







A P P E N D I X C
 ^{13}C NUCLEAR MAGNETIC RESONANCE SPECTRA

